

Integrating DFT Calculations and Experimental Approaches for the Design of Dynamic Covalent Networks

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Declaration

The work contained within this thesis is my own, except where acknowledged as part of the following collaborations: The simulation of the effect of MeOH concentration on the effective rate coefficient for dioxaborinane exchange in CHAPTER 2 (I) and the simulation used to calculate the rate coefficients from the quantitative HSQC experiments in CHAPTER 4 (II) were performed by Dr. Nicholas Ballard.

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List of Acronyms

CANs	Covalent Adaptable Networks
DFT	Density Functional Theory
NGP	Neighboring Group Participation
HSQC	Heteronuclear Single Quantum Coherence
NMR	Nuclear magnetic resonance
πCAPs	π -conjugated aromatic polymers
PMMA	Polymethyl Methacrylate
CAGR	Compound annual growth rate
GDP	Gross domestic product
PET	Polyethylene terephthalate
HDPE	High-density polyethylene
PVC	Polyvinyl chloride
LDPE	Low-density polyethylene
PP	Polypropylene
PS	Polystyrene
WLF	Williams-Landel-Ferry
T_g	Glass transition temperature
T_v	Topology freezing transition temperature
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
Zn(OAc)₂	Zinc(II) acetate
PPh₃	Triphenylphosphine
pTsOH	p-Toluene Sulfonic Acid
DBTL	Dibutyltin dilaurate
UV	Ultraviolet radiation

PDMS	Polydimethylsiloxane
BDE	Bond dissociation energies
TS	Transition State
INT	Intermediate
DMSO	Dimethyl sulfoxide
MeOH	Methanol
CDCl₃	Deuterated chloroform
HEMA	2-hydroxyethyl methacrylate
PBA	Poly(butyl acrylate)
DMTA	Dynamic-Mechanical Thermal Analysis
DCM	Dichloromethane
DSC	Differential scanning calorimetry
TGA	Thermogravimetric Analysis
MPa	Megapascal
DMSO-d⁶	Deuterated DMSO
FT-IR	Fourier transform-infrared
ωB97XD	Hybrid exchange-correlation functional (used in DFT)
ZPVE	Zero-point vibrational energy
THF	Tetrahydrofuran
TLC	Thin layer chromatography
MgSO₄	Magnesium sulfate
OFETs	Organic field-effect transistors
LEDs	Light-emitting diodes
HOMO	Highest occupied molecular orbital
LUMO	Lowest occupied molecular orbital
Mes	2,4,6-trimethylphenyl

Tip	2,4,6-triisopropylphenyl
Mes*	2,4,6-tri-tert-butylphenyl
FMes	2,4,6-tris(trifluoromethyl)phenyl
FLPs	Frustrated Lewis pairs
PAHs	Polycyclic aromatic hydrocarbons
HA	Hydride affinity
HMQC	Heteronuclear Multiple Quantum Coherence
GPC	Gel permeation chromatography
CIE 1931	Commission Internationale de l'Éclairage 1931
TD-DFT	Time Dependent Density Functional Theory
n-BuLi	n-Butyllithium
NBS	N-Bromosuccinimide
RDS	Rate Determining Step
Ea	Activation energy
EtOAc	Ethyl acetate
AEMMA	2-(Methacryloyloxy) ethyl acetoacetate

Abstract

Vitrimer materials, positioned as a bridge between thermoplastics and thermosets, offer potential solutions for addressing the end-of-life management of thermosets. However, further research is required to fine-tune their kinetics, preventing issues such as creep or extended reprocessing times. This thesis explores the integration of theoretical calculations, specifically using Density Functional Theory (DFT), with experimental work to investigate vitrimer materials. DFT serves as a preliminary screening tool, enabling rapid evaluation of numerous possibilities. The experimental studies are then guided by the insights gained from these computational analyses. Given the broad applicability of DFT calculations, this combined approach is applied across three experimental chapters, each focusing on different aspects of vitrimer development.

Chapter 1 offers an in-depth examination of the environmental challenges associated with traditional polymers and introduces innovations aimed at enhancing plastic recyclability and reducing waste. A key strategy highlighted is the development of Covalent Adaptable Networks (CANs) and vitrimers, which leverage dynamic covalent bonds to allow polymers to retain their material properties while being reprocessed or recycled through bond rearrangement. The chapter places emphasis on the different strategies used to tune the reprocessability of vitrimer materials, in particular focusing on the internal catalyst approach. In vitrimers, internal catalysis involves incorporating catalytic functionalities directly into the polymer matrix, which helps to mitigate problems like catalyst leaching or loss of activity, characteristic of the external catalyst approach. This approach ensures continuous catalytic performance throughout the polymer network, enabling efficient bond exchange during recycling or reprocessing without the need for external catalysts.

Chapter 2 delves into the dynamics of boronic ester-containing vitrimers, integrating experimental results with computational (DFT) analyses. The study examines two primary mechanisms for boronic ester exchange metathesis: a direct, uncatalyzed metathesis reaction and a nucleophile-mediated exchange process. The addition of nucleophiles, such as methanol or water, is found to significantly accelerate the dynamic exchange, underscoring the role of internal catalysis in enhancing vitrimer reprocessability and performance. The chapter also details the preparation and characterization of dynamic polymer networks containing boronic esters, exploring their mechanical and thermal properties. The findings confirm that nucleophile-assisted mechanisms lower the activation energy for bond exchange, thereby improving the reprocessing and self-healing abilities of these materials.

In **Chapter 3**, the Lewis acidity of boron in π -conjugated aromatic polymers (π CAPs) is investigated. The study focuses on synthesizing a copolymer composed of 9,9-silafluorene and 9,9-dioctylfluorene units. This copolymer displays deep blue fluorescence, with a high quantum yield and excellent thermal stability. A major innovation is the incorporation of a boron-containing scaffold, specifically 9-bromo-9-borafluorene, into the polymer through a silicon-boron exchange reaction, marking the first application of this technique in polymeric systems. This approach enhances the copolymer's optical properties and presents new opportunities for developing dynamic networks based on Lewis pair interactions. The research combines computational (DFT) and experimental analyses of the copolymer's optical and thermal properties, as well as the interaction energies with various Lewis bases, to identify those capable of facilitating dynamic interactions with the boron scaffold, for potential use in dynamic networks.

In **Chapter 4**, the development of vinylogous urethanes as promising materials for vitrimer systems is examined. The study investigates the dynamic exchange mechanisms of vinylogous urethanes using a combinatorial approach, integrating quantum chemical calculations (DFT) with experimental kinetic analyses. The research focuses on the effects of internal catalysis and neighboring group participation (NGP) on transamination kinetics to improve reshaping capabilities. Quantum chemical calculations were used to model the exchange reactions, and the predictions were validated through high-sensitivity HSQC (Heteronuclear Single Quantum Coherence) NMR. Four vitrimer materials were synthesized and characterized, confirming a strong correlation between computational predictions and observed material behavior. This combined computational-experimental approach provides an efficient screening method for optimizing dynamic covalent networks, advancing the development of next-generation vitrimers with enhanced processability and performance.

Finally, **Chapter 5** presents a summary of the key conclusions drawn from each chapter of the thesis.

Resumen

Los materiales vitriméricos, que se posicionan como un enlace innovador entre los materiales termoplásticos y los termoestables, ofrecen soluciones prometedoras para abordar la gestión del fin de vida útil de los materiales termoestables. Sin embargo, es necesario profundizar en su estudio para optimizar la cinética de estos materiales y así evitar problemas como la deformación por fluencia o los tiempos de reprocesamiento prolongados. Esta tesis explora la integración de cálculos teóricos mediante la Teoría del Funcional de la Densidad (DFT) con trabajos experimentales para investigar las propiedades y aplicaciones de los materiales vitriméricos. Los resultados de los cálculos DFT se emplean como una herramienta preliminar de evaluación, permitiendo una rápida evaluación de las distintas posibilidades. Los estudios experimentales se guían a partir de los conocimientos obtenidos en los análisis computacionales. Debido a la versatilidad de los cálculos DFT, este enfoque combinado se aplica a lo largo de tres capítulos experimentales, cada uno enfocado en diferentes aspectos del desarrollo de vitrímeros.

En el **Capítulo 1** se realiza un análisis exhaustivo de los desafíos ambientales asociados con los polímeros tradicionales e introduce innovaciones destinadas a mejorar la reciclabilidad de los plásticos y reducir los residuos. Entre las estrategias destacadas se encuentra el desarrollo de Redes Covalentes Adaptables (CANs, por sus siglas en inglés) y vitrímeros, que emplean enlaces covalentes dinámicos para que los polímeros conserven sus propiedades durante el reprocesamiento y el reciclaje mediante el reordenamiento de los enlaces. El capítulo pone especial énfasis en el enfoque de catalizador interno, que aborda las limitaciones de la reprocesabilidad y la eficiencia del reciclaje. En los vitrímeros, la catálisis interna consiste en incorporar funcionalidades

catalíticas directamente en la matriz polimérica, lo que ayuda a mitigar problemas como la lixiviación del catalizador o la disminución de su actividad. Este enfoque asegura una acción catalítica continua en toda la red polimérica, facilitando el intercambio eficiente de enlaces durante el reciclaje o reprocesamiento sin necesidad de catalizadores externos.

El **Capítulo 2** profundiza en la dinámica de vitrímeros que contienen ésteres borónicos, combinando los resultados experimentales con análisis computacionales basados en la Teoría del Funcional de la Densidad (DFT). El estudio explora dos mecanismos principales para el intercambio de ésteres borónicos por metátesis: una reacción directa sin catalizador y un proceso de intercambio mediado por nucleófilos. Los resultados muestran que la introducción de nucleófilos, como metanol o agua, acelera considerablemente el intercambio dinámico, destacando el papel de la catálisis interna en la mejora de la reprocesabilidad y el rendimiento de los vitrímeros. Además, el capítulo describe en detalle la preparación y caracterización de redes poliméricas dinámicas que contienen ésteres borónicos, explorando sus propiedades mecánicas y térmicas. Los hallazgos confirman que los mecanismos asistidos por nucleófilos reducen la energía de activación para el intercambio de enlaces, optimizando así las capacidades de reprocesamiento y autorreparación de estos materiales.

En el **Capítulo 3**, se profundiza en la acidez de Lewis del boro en polímeros aromáticos π -conjugados (π CAPs). El estudio se centra en la síntesis de un copolímero, denominado Y1, compuesto por unidades de 9,9-silafluoreno y 9,9-dioctilfluoreno. Este copolímero presenta fluorescencia azul profunda, con un alto rendimiento cuántico y excelente estabilidad térmica. Una innovación importante es la incorporación de un esqueleto que contiene boro,

específicamente el 9-bromo-9-borafluoreno, en el polímero mediante una reacción de intercambio silicio-boro, siendo esta la primera aplicación de dicha técnica en sistemas poliméricos. Este método mejora las propiedades ópticas del copolímero y abre nuevas oportunidades para el desarrollo de redes dinámicas basadas en interacciones de pares de Lewis. La investigación combina análisis computacionales y experimentales de las propiedades ópticas y térmicas del copolímero, además de estudiar sus energías de interacción con varias bases de Lewis, para identificar aquellas capaces de establecer interacciones dinámicas con el esqueleto de boro, con vistas a su aplicación en redes dinámicas.

En el **Capítulo 4**, se investiga el desarrollo de uretanos vinílogos como materiales prometedores para materiales vitriméricos. El estudio investiga los mecanismos de intercambio dinámico de los uretanos vinílogos mediante un enfoque combinatorio que integra cálculos computacionales (DFT) con análisis cinéticos experimentales. La investigación se centra en los efectos de la catálisis interna y la participación del grupo vecino (NGP, por sus siglas en inglés) en la cinética de la transaminación, con el objetivo de mejorar las capacidades de remodelado. Se utilizaron los cálculos químico cuánticos para modelizar las reacciones de intercambio, y las predicciones obtenidas se validaron a través de espectroscopía HSQC (Heteronuclear Single Quantum Coherence) de alta sensibilidad. Se sintetizaron y caracterizaron cuatro materiales vitriméricos, confirmando una fuerte correlación entre las predicciones computacionales y el comportamiento observado en los materiales. Este enfoque combinado, que integra métodos computacionales y experimentales, proporciona un método eficiente de cribado para optimizar redes covalentes dinámicas, avanzando en el desarrollo de vitrímeros de nueva generación con mejores capacidades de procesabilidad y rendimiento.

Finalmente, el **Capítulo 5** presenta un resumen de las conclusiones clave derivadas de cada capítulo de la tesis.

Chapter 1

Introduction and objectives

1.1 History of Plastics

In recent years, there has been a swift rise in global awareness regarding the environmental issues linked to plastics. A broad consensus has emerged on the harmful impact of plastic pollution, particularly on marine ecosystems, the widespread infiltration of microplastics into various ecosystems, and the inability of current recycling systems to cope with the growing amounts of plastic waste.^{1,2} To understand how we reached the current state of plastic use and its impact on society, we must first examine the origins of plastics and their rise to prominence. The first architect of polymers was nature. Today, we distinguish between natural polymers, which have existed for millennia, and synthetic polymers, consciously produced by humans for roughly 150 years. Natural polymers, such as cellulose,³ the most abundant organic material on Earth, and lignin, play essential roles in the structure of plants and trees,⁴ determining the rigidity or flexibility of plant matter, with lignin contributing to rigidity and cellulose to flexibility. Other examples of natural polymers include DNA and proteins.

As humanity began to understand the potential of polymers, early industrial efforts focused on modifying naturally occurring polymers to create new materials. These early materials, known as semi-synthetic polymers, were derived from cellulose. Some of the first examples include nitrocellulose (1845),⁵ celluloid (1860),⁶ and cellulose acetate (1865).⁷ These early polymers already demonstrated the versatility that has made plastics so successful and widespread. For instance, nitrocellulose found applications in products ranging from rockets and propellants to printing inks, leather finishes, and even nail polish.^{5,8} Cellulose acetate gained popularity for its use in products such as Ray-Ban sunglasses, famously worn in *The Blues Brothers*, and in cigarette filters. The

success and adaptability of these early semi-synthetic polymers paved the way for the development of the vast array of synthetic plastics we use today. The first fully synthetic polymer was Bakelite, created in 1907. It was used in a variety of applications, such as rotary phones, radios, and pool balls. The use of Bakelite for pool balls highlights the broader societal importance of plastics. Prior to Bakelite, pool balls were made from ivory, harvested from elephant tusks, leading to the widespread killing of elephants. This raises an ethical question: is it better to deplete wildlife or synthesize a material by combining phenol, formaldehyde, and wood to create Bakelite?

It wasn't until the 1920s that humanity began to fully comprehend the nature of polymers, largely thanks to Hermann Staudinger, who first hypothesized the existence of macromolecules.⁹ Following this breakthrough, polymer research and development surged from 1920 to 1950. Several landmark discoveries emerged during this period: PMMA, commonly known as Plexiglas, was developed in 1928;¹⁰ and between 1935 and 1937, the aliphatic polyamide Nylon 6,6 became the first synthetic fiber. Nylon was developed as a substitute for natural silk, which was in short supply due to Japan restricting exports in the lead-up to World War II. According to a popular but unverified legend, the name Nylon stood for "Now You Lose Old Nippon," as it was a critical material for parachutes during the war when the Japanese government decided to stop the export of silk. Another pivotal invention was polyethylene in 1953, which is today the most widely produced and sold plastic in the world.¹¹ These discoveries, combined with the sense that the true potential of polymers was only beginning to be realized, led to a perception in the 1960s that plastics were the material of the future. Many materials traditionally used before the advent of synthetic polymers, such as metals and alloys, inorganic materials, wood, leather, glass,

paper and cellulose derivatives, were poised to be replaced by plastic in a wide range of applications.

Why was plastic considered so promising? As previously mentioned, its remarkable success stems from its unmatched versatility. Plastics exhibit a wide range of properties due to the chemical diversity of polymers, allowing for the creation of new materials or the fine-tuning of existing ones. This can be achieved through blending different polymers, synthesizing copolymers, or incorporating additives into the base polymer formulation.¹² These strategies unlock an immense potential for material customization. Plastics can be tailored to meet specific needs, whether they are lightweight, impact-resistant, serve as thermal and electrical insulators, are rigid or flexible, transparent, or easily moldable, surpassing the adaptability of any material that existed prior to plastic. This versatility made plastic a dominant material in the post-World War II era, becoming intrinsically linked with the rise of consumerism.

A notable example is Nylon, which represents an early instance of planned obsolescence. Planned obsolescence refers to a strategy used by manufacturers where products are deliberately designed with a limited lifespan or functionality, encouraging consumers to replace or upgrade them sooner than necessary. This tactic often involves making products that become outdated, non-functional, or less desirable after a certain period, even though they could theoretically last longer with better design or materials. In this particular case, after the Allies won the war, DuPont, the American company that developed Nylon 6,6, began producing women's stockings from the material. However, Nylon's durability, sufficient to support the weight of a military parachutist, proved excessive for use in stockings. To cater to market demands and increase profitability, DuPont deliberately reduced Nylon's molecular weight, creating a less durable, lower-

cost material that wore out more quickly.^{13–16} This marked one of the earliest instances where consumer demand directly influenced the engineered properties of a product, reflecting the growing impact of consumerism on material science.¹⁶

Nowadays, thanks to its incredible versatility, the worldwide production of plastics reached a staggering 400 Mt in 2022, with a growth rate of approximately 5% annually. Global production of plastics rose from 2 million tonnes in 1950 to 400 million tonnes in 2022, with a compound annual growth rate (CAGR) of 8.4%, significantly outpacing global GDP growth.¹⁷ Notably, the only significant slowdowns in this otherwise relentless growth occurred during major global crises: the 1973 oil crisis, the fall of the Berlin Wall in 1989, and the financial crises of 2007-2008. Only during these periods of systemic collapse plastic production experienced temporary setbacks.¹⁷

1.2 The problem of plastic pollution and its demonization

As of 2015, 6.3 billion tonnes of plastic waste had been generated, with only about 9% recycled, 12% incinerated, and the remaining 79% ending up in landfills or the natural environment.¹⁸ Consequently, recent years have seen the rise of movements advocating for a plastic-free lifestyle. In these movements there is a growing narrative that demonizes plastic, promoting the idea that eliminating it would help mitigate climate change and reduce environmental pollution. However, the ubiquity and utility of plastic make its complete removal from modern life nearly impossible. Without it, we would lose crucial elements like the transport system, communication devices, electrical insulation, biomedical equipment, and sports gear. Moreover, replacing plastic with alternative materials could lead to higher pollution levels, as these alternatives may be less efficient and environmentally friendly than plastic.

In the automotive sector, for example, increasing the use of plastic helps reduce a car's weight, enhancing fuel efficiency and lowering CO₂ emissions.¹⁹ Between 2014 and 2020, the average plastic content in cars was set to increase from 200 kg to nearly 350 kg.²⁰ This trend, known as "Metal Replacement," highlights plastic's advantage over metals due to its lighter weight, reduced transport emissions, and lower environmental impact during production. Another area where plastic faces heavy criticism is packaging, which accounts for around 40% of total plastic production. In reality, single-use packaging plays a crucial role in preserving food quality.²¹ For instance, plastic-wrapped broccoli can extend its shelf life from 5 to 20 days, preventing spoilage and reducing resource waste. The packaging controls oxygen and CO₂ levels, slowing down the vegetable's metabolism and delaying its decay. The misconception that discarding food waste is harmless overlooks the resource-intensive processes involved in food production, such as water, fertilizer, energy, and fuel for transport. Properly used plastic packaging thus helps reduce overall pollution by preserving food and minimizing waste.

Bioplastics are often promoted as an alternative, but as of now, they account for only a tiny fraction of plastic production (~0.6-0.7%). While bioplastics are derived from biomass and may be biodegradable or compostable, they face significant challenges, including high costs, inferior mechanical properties, and complex end-of-life management.²² Furthermore, their water affinity, a trait necessary for biodegradability, makes them unsuitable for packaging foods that need protection from moisture.²³ As research in bioplastics continues, developing materials with better properties remains a long-term goal. Another potential solution to plastic waste, offering a more immediate impact, is recycling. While not all plastics are recyclable, materials like PET have a well-established recycling chain, allowing their transformation into fibers or reuse in

manufacturing new bottles (up to 30%). Other plastics like polyolefins, polyethylene, and polypropylene are more challenging to recycle but can be repurposed for energy recovery in industries like cement production.²⁴

1.3 Challenges in Plastic Recycling

Plastic recycling faces significant challenges due to the complex nature of plastics, contamination, and both economic and technological limitations. Different types of plastics—like PET, HDPE, PVC, LDPE, PP, and PS—have distinct properties, making it difficult to process them together.^{24,25} Contamination from food, oils, and other substances further degrades recycled material quality, increasing costs. Additionally, additives in plastics complicate recycling, and composite materials are often impossible to separate.^{26,27} Plastics also degrade in quality during recycling (downcycling), leading to a limited lifespan for recycled products.^{28,29} Economically, virgin plastic is usually cheaper to produce than recycled plastic, especially when oil prices are low, reducing demand for recycled materials.^{30,31} The recycling process also depends on consumer participation, but improper sorting contaminates recycling streams, making operations less efficient.³²

Lastly, as will be discussed in more detail in the next section, existing recycling technologies are focused on thermoplastics, leaving thermosets and elastomers unrecyclable through traditional methods. Addressing these issues may require innovations in sorting technology and the development of new, more recyclable polymers. Figure 1.1 provides an overview of current plastic waste treatment methods and potential future innovations from ongoing research.

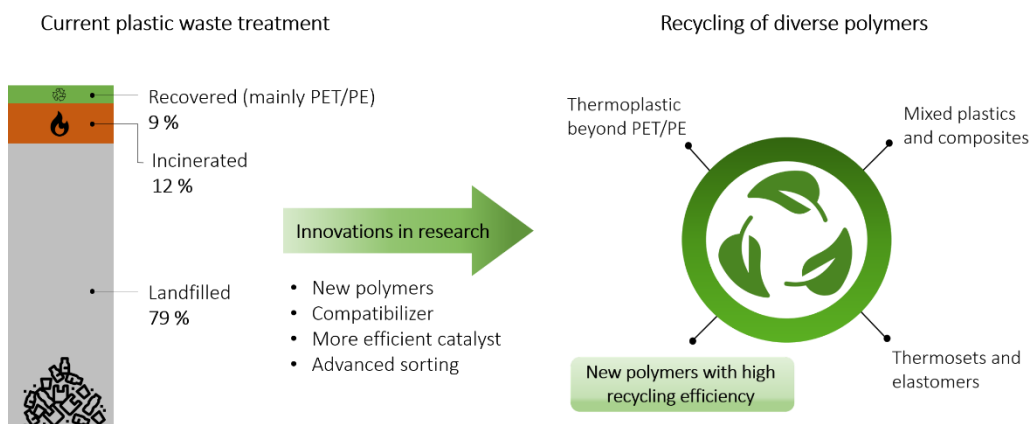


Figure 1.1: Current plastic waste treatment and possible research advances leading to a more sustainable recycling of diverse polymers.

1.4 From thermoplastic and thermosets to CANs and Vitrimers

Plastic materials can be divided into two different categories: thermoplastic and thermosets.³³ In the first category, polymer materials possess viscoelastic properties arising from their chain entanglements, providing strength and durability to objects. The benefit of this class of materials is that moderate heating can often be enough to make polymer chains flow and rearrange their position, allowing for typical plastic processing and, in principle, easy recycling (thermoplastic behavior).³⁴ The clear disadvantage lies in the polymer degradation during recycling, especially regarding mechanical performance and chemical resistance. This intrinsic behavior is one of the reasons why recycled plastics are often only usable as 'downgraded' materials for low-end applications.³⁵ The second category, thermosets, are born from the idea of increasing robustness and resistance against mechanical stress or chemicals by integration of all chains into a covalent network. However, this characteristic leads to major end-of-life management issues. This is because their permanent covalent network also makes them rather rigid, and covalent cross-links prevent the mobility of chains. Because of that, once synthesized, a thermoset will keep

its initial shape, and become intractable as a raw material, preventing them from being recyclable.³⁶

In recent years, attention in the polymer science community has been increasingly turned towards the unrecyclable thermoset class of polymeric materials, not only as a problem, but also as an opportunity. The clear scientific challenge now consists in developing robust polymer networks, with a high degree of cross-linking, providing enduring material properties, which can also overcome the inherent non-recyclability due to the total lack of relative chain mobility. The most straightforward chemical strategy to transform a cross-linked polymer network into a more recyclable material is by introducing dynamic covalent bonds into it. If enough of such chemically reactive bonds are introduced, one arrives at the concept of a covalent adaptable network (CAN), introduced into the polymer field by Bowman and others.^{37–39} Such shape-shifting networks can rearrange their connectivity in response to an external stimulus, with individual dynamic and reversible chemical bond exchange reactions mediating a molecular network rearrangement process.⁴⁰ Figure 1.2 depicts the three classes of polymers, their properties, and end-of-life scenarios.

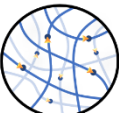
CLASS of POLYMER		PROPERTIES	END OF LIFE SCENARIO
CLASSICAL THERMOSETS		 Mechanical properties  Chemical resistance  Reprocessability	 
THERMOPLASTICS		 Mechanical properties  Chemical resistance  Reprocessability	   
DYNAMIC THERMOSETS CANs	  Dynamic bond	 Mechanical properties  Chemical resistance  Reprocessability	   
 Mechanical recycling  Chemical recycling  Landfill  Incineration			

Figure 1.2: Different classes of polymers with their properties and end-of-life scenario: (i) classical thermosets, (ii) thermoplastics, and (iii) dynamic thermosets (CANs).

Covalent adaptable networks (CANs) can be classified into two main categories based on their exchange mechanism: dissociative and associative.⁴¹ The first category, dissociative CANs, involves a cross-link exchange mechanism where chemical bonds are broken, after the application of a trigger such as UV light or heat and then reformed at a different location within the polymer network in the absence of the trigger. This dissociative mechanism typically results in a temporary loss of network connectivity, allowing for rapid topological rearrangements, stress relaxation, and flow (Fig. 1.3, upper panel).

An example of a dissociative CAN system is the reversible Diels–Alder reaction between furans and maleimides, which is widely used in organic polymer networks.⁴² The Diels–Alder reaction is mildly exothermic, releasing 5–10 kcal/mol of energy, and becomes reversible when heated. As a result, the bond-breaking and reforming rates increase, leading to a net dissociation of bonds as the equilibrium shifts towards the endothermic side. The temporary reduction

in cross-links causes a significant drop in viscosity, similar to the behavior observed in thermoplastics. Upon cooling, the cross-links are restored to their original state, preserving the thermosetting properties of the material, such as stiffness and insolubility.

The second category of CANs relies on associative exchange mechanisms, where the original covalent bond is only broken after a new bond is formed. Unlike dissociative CANs, these networks maintain a fixed cross-link density, ensuring that the polymer does not depolymerize when heated. This creates networks that are both permanent and dynamic (Fig. 1.3, lower panel). The first reported associative CANs emerged in 2005 and utilized photo-mediated free radical addition-fragmentation chain transfer reactions with allyl sulfide moieties.^{43,44} Later developments introduced alternative radical generators, such as trithiocarbonates,^{45–47} to achieve similar exchange mechanisms in CANs. Although these systems demonstrated promising stress-relaxation and flow properties, their adaptability was limited due to termination reactions inherent to the radical nature of the process, which ultimately restricted their dynamic lifetime.

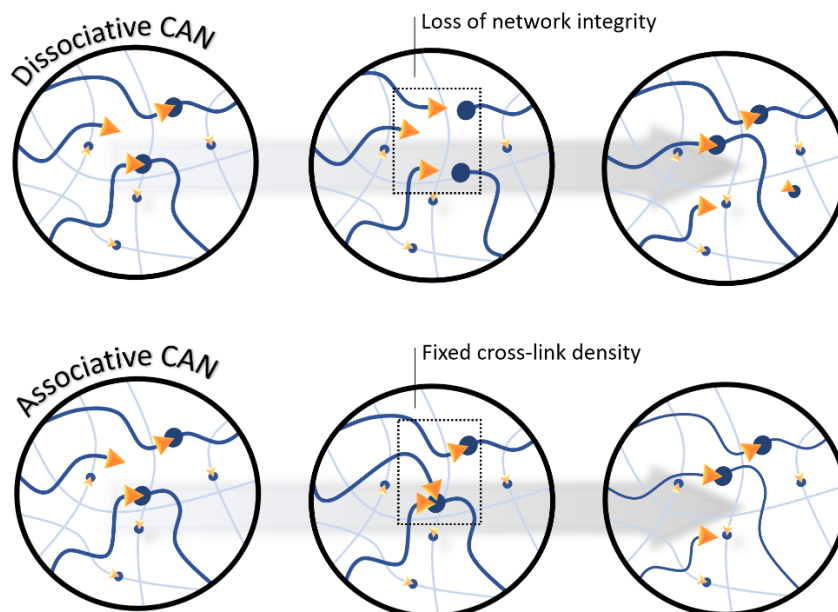


Figure 1.3: Schematic description of dissociative CANs (upper panel) characterized by a loss of network integrity when the exchange reactions are happening and associative CANs (lower panel) characterized by a fixed cross-link density throughout the whole exchange process.

In summary, dissociative CANs enable fast reprocessing by reducing network connectivity through reversible bond dissociation, while associative CANs maintain network integrity during thermal treatment by allowing controlled bond exchange without depolymerization. As a result, the classical distinctions between thermoplastic and thermoset polymers have been increasingly blurred due to recent advancements in polymer chemistry.

1.5 The concept of vitrimers

Building upon the concept of "constant connectivity", Leibler and colleagues designed polymer networks that maintained permanent chemical connectivity while still allowing macromolecular rearrangements, fundamentally changing the landscape of polymer classification. To realize this concept, they extended the realm of associative CANs by adding a suitable transesterification catalyst to epoxy/acid or epoxy/anhydride polyesters-based networks.⁴⁸ This mechanism

involves the formation of a new network bond before releasing the original one, through a thermally triggered catalytic transesterification reaction, ensuring that there is no intermediate loss of connectivity. This approach led to the development of polymer networks that showed a gradual viscosity decrease upon heating, a similar behavior to vitreous silica,⁴⁹ which had never been observed in organic polymer materials. Because of that, to describe this new class of polymers, Leibler and his co-workers coined the term “vitrimers”.

Unlike dissociative covalent adaptable networks (CANs) and thermoplastic polymers, which undergo a more abrupt transition from a solid to a liquid state as described by the Williams–Landel–Ferry (WLF) model, vitrimers exhibit a more gradual change in viscosity, distinguishing them from these other material classes.⁵⁰ The viscoelastic behavior of vitrimers is governed by two transition temperatures. The first is the glass transition temperature (T_g), which marks the transition from the glassy to the rubbery state of the polymer network, associated with the onset of long-range molecular motion. The second transition temperature, referred to as the topology freezing transition temperature (T_v), refers to the temperature at which the network of dynamic covalent bonds within the material “freezes” or becomes kinetically inactive. Below the T_v , the exchange reactions among bonds slow down significantly, effectively stopping any topological rearrangements within the polymer network. As a result, the vitrimer behaves more like a traditional thermoset polymer, with a fixed network structure and minimal flow or reconfiguration. Above the T_v , the dynamic bond exchange processes are activated, allowing for bond reshuffling, which enables the network to rearrange while maintaining covalent connectivity. This transition allows vitrimers to exhibit malleable properties similar to thermoplastics, making it possible to reshape, repair, or recycle the material without degrading its mechanical properties.³⁵

To elucidate the roles of the glass transition temperature (T_g) and the topology freezing transition temperature (T_v), two scenarios can be examined. In the first scenario, the vitrimer system has a T_g lower than the T_v . As the material is heated from below T_g to a temperature between T_g and T_v , it undergoes a transition from a glassy solid to a rubbery state, where it behaves like an elastomer due to the slow kinetics of the exchange reaction. Further heating accelerates the exchange reaction, and the material transitions into a viscoelastic liquid, with its flow behavior determined by cross-link exchange kinetics and an Arrhenius-like reduction in viscosity.

In the second scenario, the material features an intrinsically fast exchange reaction but exists within a rigid polymer matrix with a T_g higher than the anticipated T_v . Here, the network remains static below T_g due to restricted segmental motion, preventing any exchange reactions and preserving the network topology. When heated above T_g , segmental motion and exchange reactions are progressively activated. Initially, the viscosity follows the Williams-Landel-Ferry (WLF) behavior, but with continued heating, it shifts into a regime where viscosity is controlled by exchange reaction kinetics, governed by an Arrhenius-like mechanism.³⁵

The design of vitrimer materials must carefully consider both T_g and T_v , which can be modulated by factors such as cross-link density, the intrinsic rigidity of monomers, exchange reaction kinetics (e.g., catalyst concentration), and the density of exchangeable bonds. For most applications, vitrimers should behave like classical thermosetting polymers within a practical temperature range, avoiding significant creep. However, at elevated temperatures, network reorganization becomes significant, enabling controlled macroscopic flow without structural damage. This thermal processability can even repair defects,

similar to the reprocessing observed in traditional materials like metals and glass.

1.5.1. Vitrimer chemistries

Since the discovery of vitrimer materials in 2011, numerous variations and alternative chemistries capable of inducing their unique thermal behavior have been explored. These chemistries, responsible for vitrimeric behavior, can be categorized based on the types of covalent bonds involved in exchange reactions, as outlined in Table 1.1. Among the various chemistries, the most significant and well-developed include: (i) transesterification reactions, (ii) transamination of vinylogous urethanes, (iii) boronic ester exchange, (iv) disulfide exchange chemistry, (v) siloxane-silanol exchange, (vi) olefin metathesis, and (vii) imine exchange chemistry.

1.5.2. Catalyzed carboxylate transesterification

One of the earliest and most extensively studied vitrimer systems is based on transesterification reactions. In these systems, ester groups undergo exchange with hydroxyl groups, facilitated by a catalyst. Notably, at room temperature, the catalyzed transesterification reaction proceeds at an insignificant rate, allowing soft epoxy/acid networks with glass transition temperatures (T_g) below room temperature to behave similarly to conventional elastomers, exhibiting no creep. However, upon heating, these exchange reactions become active, enabling the rearrangement of the network structure.

The catalyst plays a critical role in controlling the kinetics of these exchange reactions. In the first vitrimer system developed by Leibler and colleagues,⁴⁸ polyester networks were catalyzed by zinc compounds or organocatalysts (Fig. 1.4). Adjusting the type and concentration of the catalyst provides control over the material's relaxation times, making this chemistry highly versatile and

adaptable across various polymer systems. For instance, activation energies for catalysts such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), zinc(II) acetate ($\text{Zn}(\text{OAc})_2$), and triphenylphosphine (PPh_3) are approximately 106 kJ/mol and 43 kJ/mol, respectively.³⁵

In summary, transesterification-based vitrimers, especially epoxy-based variants, are notable for their readily available monomers and straightforward synthesis, making them highly scalable and suitable for industrial applications. However, challenges related to long-term stability may arise, particularly in humid environments due to ester hydrolysis. Additionally, the high catalyst concentrations required for rapid processing can introduce issues such as catalyst insolubility, aging, and leaching, potentially affecting the material's performance over time.⁵¹

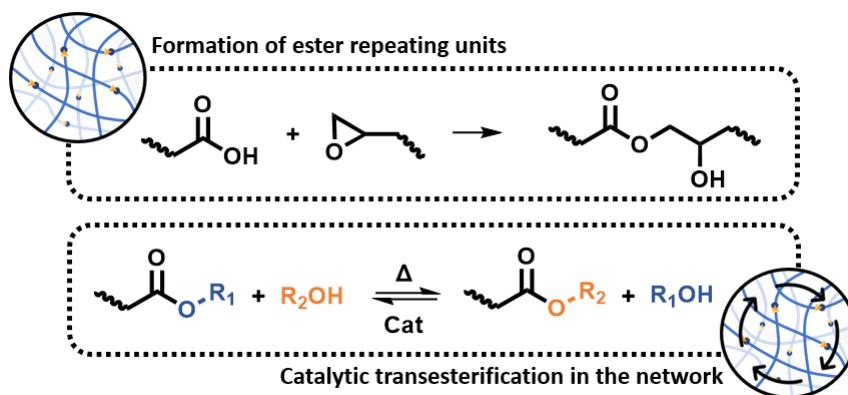


Figure 1.4: Upper panel: the reaction between epoxides and carboxylic acids yields a repeating unit that incorporates both ester and hydroxyl functional groups — Lower panel: the catalytic transesterification reaction that takes place at elevated temperatures.

Table 1.1: Overview of the exchange chemistries utilized in vitrimers

Name	Reaction
Transesterification	$\sim\text{C}(=\text{O})\text{O}-\text{R}_1 + \text{R}_2\text{OH} \rightleftharpoons \sim\text{C}(=\text{O})\text{O}-\text{R}_2 + \text{R}_1\text{OH}$
Transamination of vinylogous urethanes	$\text{R}-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{NH}-\text{R}_1 + \text{H}_2\text{N}-\text{R}_2 \rightleftharpoons \text{R}-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{NH}-\text{R}_2 + \text{H}_2\text{N}-\text{R}_1$
Siloxane/silanol	$\text{Si}^1-\text{O}-\text{Si}^2 + \text{Si}^3-\text{O}^-\text{X}^+ \rightleftharpoons \text{Si}^1-\text{O}-\text{Si}^3 + \text{Si}^2-\text{O}^-\text{X}^+$
Olefin metathesis	$\text{R}_1-\text{CH}=\text{CH}-\text{R}_2 + \text{R}_3-\text{CH}=\text{CH}-\text{R}_4 \rightleftharpoons \text{R}_1-\text{CH}=\text{CH}-\text{R}_3 + \text{R}_2-\text{CH}=\text{CH}-\text{R}_4$
Disulfide exchange	$\text{R}_1-\text{S}-\text{S}-\text{R}_2 + \text{R}_3-\text{S}-\text{S}-\text{R}_4 \rightleftharpoons \text{R}_1-\text{S}-\text{S}-\text{R}_3 + \text{R}_2-\text{S}-\text{S}-\text{R}_4$
Transalkylation of triazolium salts	$\text{R}_1-\text{N} \begin{array}{c} \text{R}_2 \\ \diagup \\ \text{N}=\text{N}^+-\text{C}^--\text{R}_3 \\ \diagdown \\ \text{X}^- \end{array} + \text{R}_5-\text{N} \begin{array}{c} \text{R}_4 \\ \diagup \\ \text{N}=\text{N} \\ \diagdown \\ \text{N}^+-\text{C}^--\text{R}_3 \\ \diagdown \\ \text{X}^- \end{array} \rightleftharpoons \text{R}_1-\text{N} \begin{array}{c} \text{R}_2 \\ \diagup \\ \text{N}=\text{N} \\ \diagdown \\ \text{N}^+-\text{C}^--\text{R}_3 \\ \diagdown \\ \text{X}^- \end{array} + \text{R}_5-\text{N} \begin{array}{c} \text{R}_4 \\ \diagup \\ \text{N}=\text{N}^+-\text{C}^--\text{R}_3 \\ \diagdown \\ \text{X}^- \end{array}$
Transesterification of boronic esters	$\text{R}_1-\text{B} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \begin{array}{c} \text{R}_2 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_3 \end{array} + \begin{array}{c} \text{HO} \quad \text{R}_2 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{HO} \quad \text{R}_3 \end{array} \rightleftharpoons \text{R}_1-\text{B} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \begin{array}{c} \text{R}_2 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_3 \end{array} + \begin{array}{c} \text{HO} \quad \text{R}_2 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{HO} \quad \text{R}_3 \end{array}$
Transcarbamoylation polyhydroxyurethanes	$\sim\text{N}(\text{X})\text{C}(=\text{O})\text{O}-\text{R}_1 + \text{R}_2-\text{OH} \rightleftharpoons \sim\text{N}(\text{X})\text{C}(=\text{O})\text{O}-\text{R}_2 + \text{R}_1-\text{OH}$
Oxime Metathesis	$\text{R}_1-\text{O}-\text{N}=\text{C}(\text{R}_2)-\text{R}_3 + \text{R}_4-\text{N}=\text{C}(\text{R}_5)-\text{O}-\text{R}_6 \rightleftharpoons \text{R}_1-\text{O}-\text{N}=\text{C}(\text{R}_5)-\text{R}_6 + \text{R}_4-\text{N}=\text{C}(\text{R}_2)-\text{O}-\text{R}_3$
Boronic ester metathesis	$\text{R}_1-\text{B} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \begin{array}{c} \text{R}_2 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_3 \end{array} + \text{R}_4-\text{B} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \begin{array}{c} \text{R}_5 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_6 \end{array} \rightleftharpoons \text{R}_1-\text{B} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \begin{array}{c} \text{R}_5 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_6 \end{array} + \text{R}_4-\text{B} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \begin{array}{c} \text{R}_2 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_3 \end{array}$
Transimination	$\text{R}_1-\text{N}=\text{C}(\text{R}_2)-\text{R}_3 + \text{H}_2\text{N}-\text{R}_4 \rightleftharpoons \text{R}_4-\text{N}=\text{C}(\text{R}_2)-\text{R}_3 + \text{R}_1-\text{NH}_2$
Imine metathesis	$\text{R}_1-\text{N}=\text{C}(\text{R}_2)-\text{R}_3 + \text{R}_4-\text{N}=\text{C}(\text{R}_5)-\text{R}_6 \rightleftharpoons \text{R}_1-\text{N}=\text{C}(\text{R}_5)-\text{R}_6 + \text{R}_4-\text{N}=\text{C}(\text{R}_2)-\text{R}_3$

1.5.3. Vinylogous urethane transamination

Vinylogous urethanes represent another type of vitrimer chemistry where exchange reactions occur without the need for a catalyst. The exchange mechanism in these materials occurs via the transamination of vinylogous urethane bonds, where a free amine will undergo a nucleophilic attack on the vinylogous urethane backbone, leading to bond reformation without breaking the overall network structure. The reaction is temperature-dependent, with negligible activity at room temperature and significant activity at temperatures above 100–120 °C.⁵² This behavior allows the material to be processed and re-shaped under heat but remain stable and rigid under normal conditions, with no creep at room temperature.

Although vinylogous urethane vitrimers are typically catalyst-free at higher temperatures, the use of catalysts can influence the reaction kinetics significantly. For example, Brønsted or Lewis acids such as p-toluene sulfonic acid (pTsOH) or dibutyltin dilaurate (DBTL) can accelerate the transamination reactions, reducing the relaxation time and facilitating faster processing. Conversely, the addition of bases like triazabicyclodecene (TBD) can inhibit the reaction by reducing the availability of protonated intermediates required for the reaction to proceed. These catalysts affect the activation energy of the system, with acid catalysts lowering it and bases increasing it, thereby providing control over the material's viscoelastic properties.⁵³

Both experimentally⁵³ and theoretically⁵⁴ it was proven that there exists two main mechanisms for the transamination of the vinylogous urethanes: (i) a neutral/acidic one and (ii) a basic one (Fig. 1.5). In the first one, in the presence of acidic conditions the transamination mechanism goes through an iminium intermediate, resulting in a lower activation energy, while the basic mechanism

will go through a direct conjugated addition and a non-stabilized zwitter-ionic intermediate, resulting in a higher activation energy. It was proven that in neutral or acidic conditions the exchange mechanism is the same, since the activation energy is very similar but nonetheless the reaction rate in the presence of a protic acid is much faster compared to the neutral counterpart. Denissen *et al.*⁵³ explained this as a consequence of the higher concentration of active protonated species (iminium intermediate) compared to the reference material.

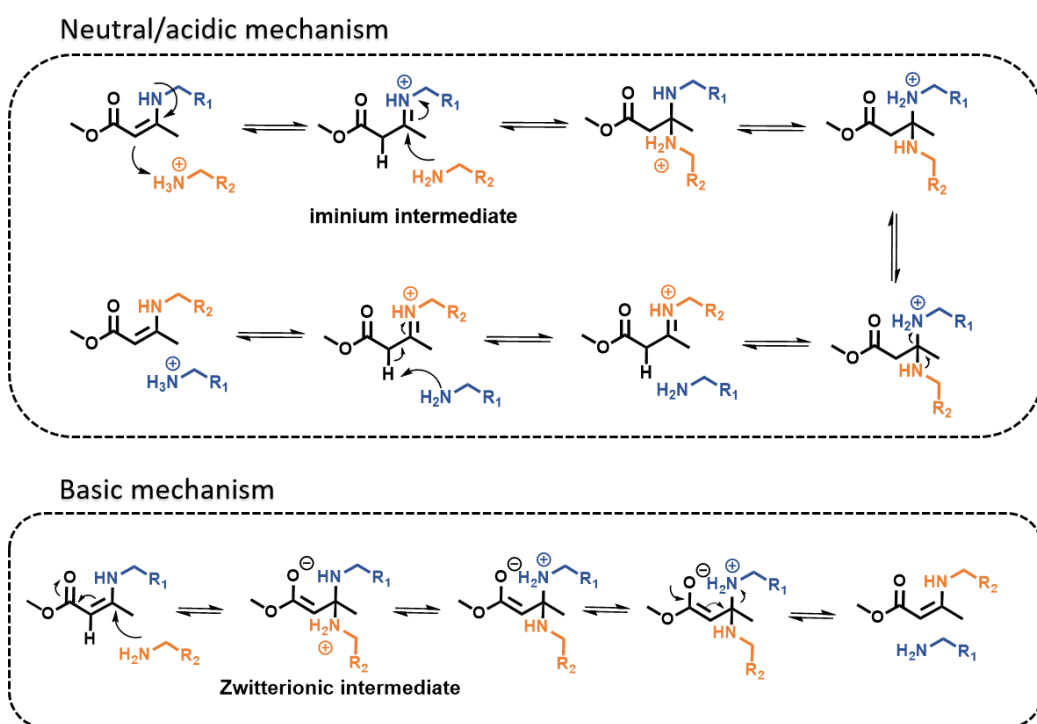


Figure 1.5: Mechanisms for the transamination of vinylogous urethanes under neutral/acidic conditions (upper panel) and basic conditions (lower panel).

1.5.4. Disulfide chemistry

The disulfide exchange is characterized by the dynamic nature of sulfur-sulfur linkages, where disulfides undergo reversible processes through different mechanisms.^{55–59} The exchange is sensitive to various factors, including external stimuli (like heat or UV irradiation), catalytic conditions, and the chemical nature

of the disulfides. One of the simplest mechanisms is the reduction of a disulfide bond into two thiols, which can then be oxidized back to reform the disulfide bond (Fig. 1.6, left panel). This process generally follows a dissociative pathway and is reversible.⁶⁰ Alternatively, under UV light, heat, or shear, disulfide bonds may be homolytically cleaved to form thiyl radicals (Fig. 1.6, center panel). This homolytic cleavage is also dissociative but offers a more direct pathway, as it involves reversible radical formation.^{61–63} An associative exchange mechanism can occur through a nucleophilic substitution, where free thiols or thiyl radicals participate in an addition-elimination process, resulting in the cleavage and reformation of disulfide bonds (Fig. 1.6, right panel). This mechanism is often seen in base-catalyzed conditions, as explored in certain dynamic networks that function similarly to vitrimers.^{64,65}

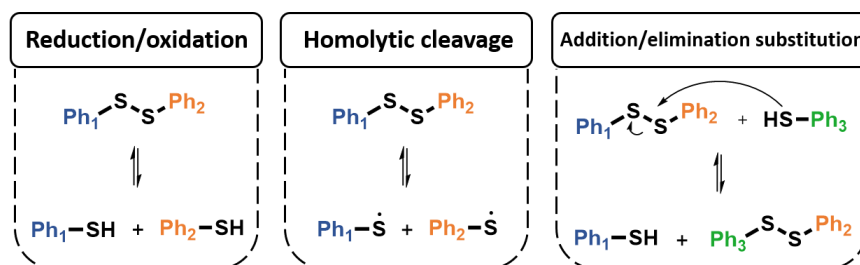


Figure 1.6: Possible disulfide exchange mechanisms: (i) reduction-oxidation (left panel); (ii) homolytic cleavage triggered by UV light or heat (center panel) and (iii) addition/elimination substitution via a nucleophilic attack (right panel).

Recent developments, such as those by Goossens,⁵⁸ Klumperman,⁶⁴ and Odriozola,^{55,56} have demonstrated how these dynamic disulfide exchange reactions can be incorporated into self-healing and reprocessable polymer networks. For instance, the use of aromatic disulfides in poly(urea-urethane) elastomers has been shown to achieve self-healing at room temperature without catalysts or external stimuli due to the inherent reactivity of the disulfide bonds. This efficient exchange is aided by the formation of hydrogen bonds among polymer chains, enhancing the material's self-healing capabilities.

Additionally, at the beginning, disulfide exchange reactions were proposed to proceed via different mechanisms, such as a [2+2] metathesis^{55,56} or a radical-mediated [2+1] mechanism,⁶⁶ depending on the structure of the disulfides involved. However, recent studies have proven, both experimentally and theoretically, that the self-healing process in disulfide-based systems follows the [2+1] radical-mediated mechanism rather than the [2+2] metathesis.^{67,68}

The interplay between disulfide bond exchange and the viscoelastic properties of these networks can also add complexity. For instance, while disulfide exchange allows rapid bond reformation at room temperature, the presence of hydrogen bonds may restrict network flow, leading to a combination of solid-like and elastic behaviors.^{69,70} These processes are nuanced and depend heavily on the precise conditions and substitution patterns of the disulfide bonds, making the disulfide exchange a versatile and valuable reaction in polymer chemistry and materials science.⁶⁷

1.5.5. Boronic esters chemistry

Healable or reprocessable polymer materials containing dynamic boronic esters have gained interest due to their high thermal stability, oxygen tolerance, and tunable dynamic properties without a catalyst.^{71,72} The formation of boronic esters from boronic acids and diols is straightforward, with a favorable equilibrium process, especially when the product is insoluble in the reaction solvent. The formation is entropically driven by the loss of two water molecules. Boronates are characterized by very strong boron-oxygen bonds thanks to the π -back bonding character between the unoccupied boron p-orbital and the oxygen lone pair.⁷³ However, due to boron's empty p-orbital and the consequent electrophilic nature of it, these molecules are vulnerable to

nucleophilic attacks, leading to the formation of tetrahedral intermediates with such molecules.

The stability of boronic ester can be increased using bulky diols, enhancing boronate stability, particularly in six-membered rings, which provide better B-O conjugation than five-membered rings.⁷⁴ Consequently, boronic esters vulnerable to water attack, like acyclic or small cyclic boronates, may hydrolyze, while six-membered dioxaboranines from bulky diols remain stable. This difference is evident in storage practices: five-membered dioxaborolanes require dry, inert conditions, whereas six-membered dioxaboranines are stable in regular storage.⁷⁵ The dynamicity of boronic ester bonds arises from three primary exchange mechanisms: (a) hydrolysis to boronic acid (Figure 1.7, upper panel), (b) transesterification with a diol (Figure 1.7, center panel), and (c) metathesis with another boronate (Figure 1.7, lower panel). Exploiting the first two reaction mechanisms, boron-containing polymers have been used in pH-responsive materials that could be used in smart drug delivery, self-healing or shape memory hydrogels.^{76–80}

However, using the metathesis mechanism, the introduction of boronic esters in vitrimer materials is possible and has opened new avenues for creating dynamic polymer networks with desirable properties such as self-healing, recyclability, and thermal stability. For example, Huang et al.⁸¹ incorporated boronic ester linkages into elastomers to create a vitrimer network with mechanical robustness, shape memory, self-healing, and recyclability properties. The material was designed by crosslinking epoxidized natural rubber with silica nanoparticles through boronic ester bonds, allowing the network to be remodeled through dissociation or metathesis without a catalyst. This vitrimer demonstrated re-processability through hot pressing or dissolution, maintaining

its structural integrity and enabling the fabrication of self-healing flexible electronic devices.

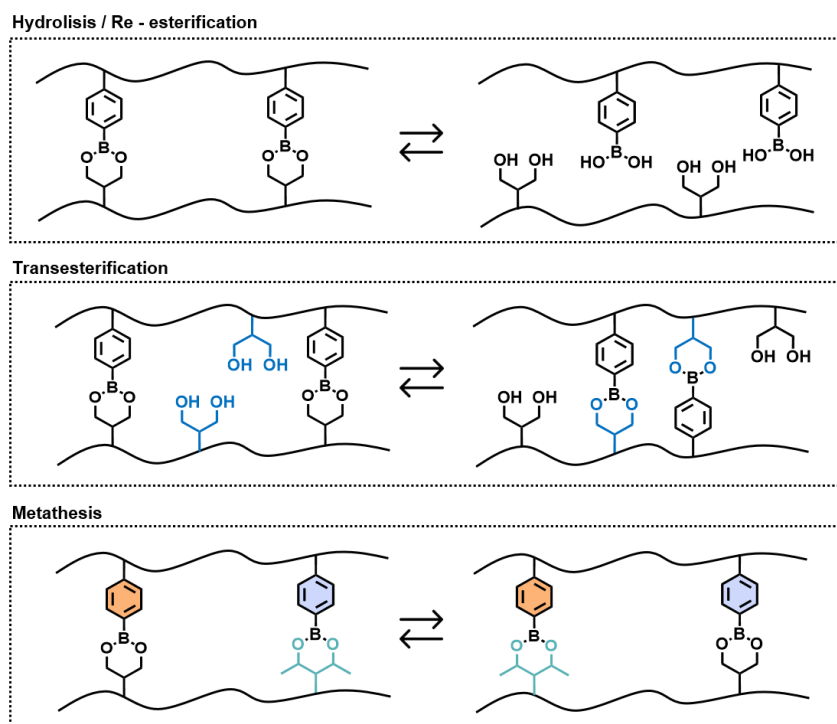


Figure 1.7: Three different exchange mechanisms of boronic esters: (i) hydrolysis/re-esterification when H_2O is added to or removed from the system (upper panel); (ii) transesterification in the presence of an excess of diol moieties (center panel); and (iii) metathesis, which involves the heat-induced exchange of two boronic esters (lower panel).

Zych et al.⁸² focused on a sustainable approach by producing a biobased, biodegradable boronic ester vitrimer from epoxidized soybean oil acrylate. The dynamic nature of boronic ester cross-links allowed the vitrimer to be reprocessed multiple times without compromising mechanical properties. The material could also self-repair abrasions and biodegrade, addressing environmental concerns associated with plastic waste. This highlights the versatility of boronic ester vitrimers in achieving self-healing and environmentally friendly materials. Zeng et al.⁸³ synthesized rosin-based epoxy vitrimers using boronic ester bonds, aiming to improve mechanical properties

while maintaining dynamic behavior. The vitrimer network, derived from rosin, exhibited features such as welding, reprocessing, and shape memory. Due to the dynamic transesterification of boronic ester bonds, the material could be reshaped, recycled, and self-healed, highlighting the multifunctionality achievable through boronic ester-based vitrimers.

1.5.6. Other types of vitrimer chemistries

Other types of chemistry used in vitrimer materials are described shortly here. Siloxane-silanol exchange reactions involve the rearrangement of siloxane bonds in the presence of a silanolate anion (Figure 1.8, panel c). This dynamic covalent chemistry has been applied to polydimethylsiloxane (PDMS) networks, enabling stress relaxation and self-healing behavior.⁸⁴ However, the tendency of siloxanes to undergo degradation through cyclization and hydrolysis can limit their stability.

Olefin metathesis, typically mediated by Grubbs catalysts, involves the exchange of alkene bonds in polymer networks (Fig. 1.8, panel a).^{85,86} This reaction allows network rearrangement at moderate temperatures, making it suitable for creating reprocessable elastomers. However, the sensitivity of the metathesis catalysts and the need for a post-polymerization step to introduce the catalyst into the polymer matrix can complicate the processing of these materials.

Imine bonds are dynamic covalent linkages that can undergo reversible formation and exchange, either through dissociative hydrolysis^{87,88} or associative reactions, such as amine exchange⁸⁹ or imine metathesis (Fig. 1.8, panel b).⁹⁰ In vitrimeric materials, imine exchange reactions enable stress relaxation and re-processability at relatively low temperatures. However, these networks are sensitive to moisture, which can limit their long-term mechanical performance.

Another recent vitrimer system, reported by Drockenmuller and co-workers,⁹¹ involves transalkylation reactions of triazolium salts (Fig. 1.8, panel d). This chemistry has been explored in polyionic networks, where the exchange between triazoles and alkyl halide chains enables stress relaxation and flow. These systems show promising mechanical properties, though scalability and cost remain challenges due to the need for hazardous reagents.

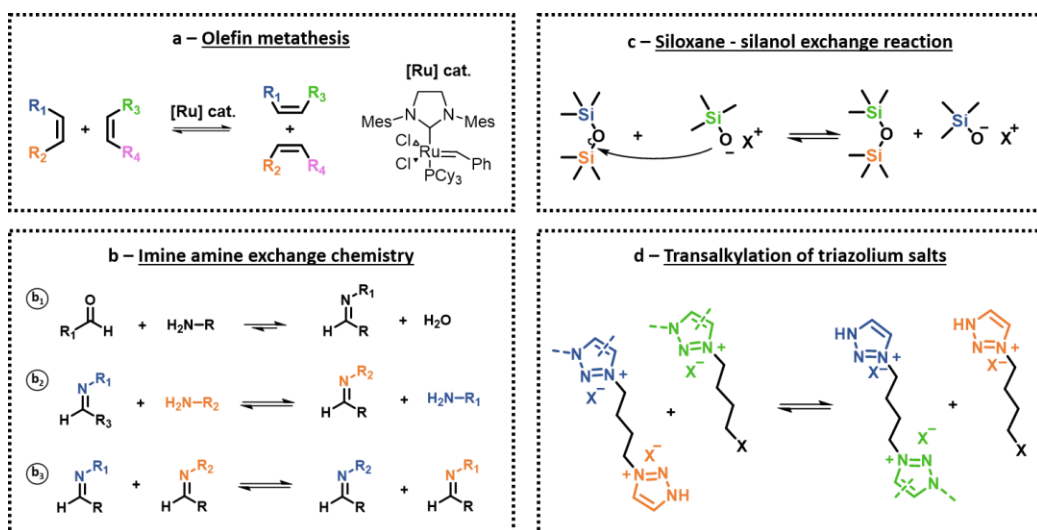


Figure 1.8: Other vitrimer chemistries: (a) olefin metathesis, typically mediated by a Grubbs catalyst; (b) imine-amine exchange chemistry; (c) siloxane-silanol exchange; and (d) transalkylation of triazolium salts.

1.6 External catalyst approach to tune the reprocessability of vitrimers

The challenges in vitrimer chemistry mainly derive from limitations in controlling the exchange kinetics of dynamic covalent bonds. Slow exchange rates can hinder processing, while overly rapid kinetics may lead to undesirable creep at room temperature. As such, a major focus in vitrimer research is developing strategies to achieve precise kinetic control over bond exchanges, both at the molecular level and within the final material.

One prominent strategy to enhance control over vitrimer properties is the use of external catalysts. In these cases, the catalysts are simply blended into the polymer network to modulate the rate of exchange reactions. They offer flexibility in adjusting the reaction rates and enable the processing of vitrimers at desired temperatures. The type and concentration of these catalysts are crucial in determining the activation energy of the exchange processes and the resultant viscoelastic properties. For instance, weaker catalysts can maintain stability under normal conditions while allowing bond exchanges at processing temperatures.

1.6.1. External catalyst approach in transesterification-based vitrimers

To give an example of external catalysis, zinc acetate ($\text{Zn}(\text{OAc})_2$), TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), $\text{P}(\text{Ph})_3$ and different Brønsted acids have been demonstrated to influence the activation energy in polyester-based vitrimers.⁴⁸ TBD and $\text{P}(\text{Ph})_3$ both increased the transesterification reaction rate, leading to faster stress relaxation time. TBD acts as a strong organic base, leading to efficient exchange kinetics even at relatively low temperature, which is particularly beneficial for applications requiring room temperature malleability, while $\text{P}(\text{Ph})_3$ contributes to the transesterification process by enhancing the nucleophilicity of reacting centers, thereby facilitating the exchange of ester bonds.

Zinc acetate also plays a multifaceted role as a Lewis acid catalyst in these types of vitrimer materials. When used as an external catalyst, the Zn^{2+} ions coordinate with ester carbonyl groups and hydroxyl moieties, enhancing the transesterification process through multiple mechanisms. The Zn^{2+} ions shift the alcohol/alkoxide equilibrium towards the nucleophilic alkoxide form, increase the electrophilicity of the carbonyl carbon, and bring reacting centers into close

proximity, which collectively accelerate the exchange reactions. The concentration of $\text{Zn}(\text{OAc})_2$ directly impacts the network dynamics, with higher concentrations promoting faster stress relaxation. The activation energy associated with $\text{Zn}(\text{OAc})_2$ -catalyzed exchanges is around 90 kJ/mol, showing an efficient transesterification process at elevated temperatures. Comparative studies show that $\text{Zn}(\text{OAc})_2$ yields distinct viscoelastic properties compared to $\text{P}(\text{Ph})_3$, resulting in different creep behavior and stress recovery.⁹²

Bates et al.⁹³ explored the effect of Brønsted acids as catalysts in transesterification-based vitrimers, revealing a correlation between acid strength (pKa) and the exchange kinetics. Stronger Brønsted acids significantly accelerate the transesterification reactions at lower temperatures, providing faster relaxation times compared to Lewis acids like $\text{Zn}(\text{OAc})_2$. The activation energies for Brønsted acid-catalyzed exchanges range from 49 to 67 kJ/mol, and the relaxation times are tunable through the choice of acid, allowing control over the vitrimer's reprocessing and mechanical properties.

1.6.2. External catalyst approach in vinylogous urethane vitrimer materials

This external catalyst approach has also been applied to vinylogous urethane chemistries. Denissen et al.⁵³ demonstrated that the viscoelastic properties of vinylogous urethane vitrimers can be finely tuned by incorporating small amounts of additives such as TBD, pTsoH, or dibutyltin dilaurate (DBTL). Brønsted and Lewis acids were found to significantly accelerate the dynamic bond exchange reactions, thereby reducing relaxation times and enabling faster reprocessing. Conversely, bases inhibited the exchange, offering control over the rate of stress relaxation and preventing creep at service temperatures. The addition of each catalyst led to distinct activation energies, suggesting different

exchange mechanisms. Without a catalyst or in the presence of a Brønsted acid, the amine exchange follows a "protic pathway" with an iminium intermediate and an enthalpic barrier of around 75 kJ/mol. However, strong bases inhibited this pathway, revealing a slower Michael-type direct amine addition mechanism, characterized by neutral, unstable zwitterionic intermediates and a higher energy barrier of 100-140 kJ/mol.

1.6.3. Drawbacks of the external catalyst methodology

While often beneficial for controlling exchange rates, the use of external catalysts can also introduce challenges: one of the most notable is achieving a balance between promoting rapid exchange reactions for efficient processability and maintaining a high enough energy barrier to prevent creep and undesired flow at service temperatures. An overly effective catalyst can result in excessive bond exchange, leading to instability and compromised mechanical integrity of the material under normal use conditions.³⁵ Furthermore, external catalysts often suffer from compatibility and stability issues within the polymer matrix. As they are not covalently bound, these catalysts may leach out over time, reducing their effectiveness and causing potential degradation of the material's properties.^{94,95} Their mobility within the matrix can also affect reaction kinetics unpredictably, leading to inconsistencies in material behavior. Additionally, the chemical nature of the catalyst, whether Brønsted or Lewis acid or base, plays a crucial role in determining the activation energies and exchange mechanisms, which can complicate the design of vitrimer systems for specific applications. Lastly, the fine-tuning of catalyst concentration and type requires careful consideration to avoid side reactions and to maintain a balance between fast exchange rates and thermal stability (Fig. 1.9, left panel). This often involves a trade-off between achieving efficient processing temperatures and preserving the desired mechanical properties during the material's application.⁹⁶ Therefore,

while external catalysts are effective in enhancing vitrimer reactivity, they are not the definitive solution to vitrimer's challenges.

1.7 Internal catalyst as a possible alternative methodology

An alternative strategy to address the challenge of introducing external catalysts into a polymer network is the integration of internal catalysts or neighboring group participation (NGP) within the vitrimer structure. Internal catalysis involves introducing catalytic functionalities directly into the polymer matrix, often as part of the network itself. This ensures a more homogeneous distribution of catalytic activity and prevents issues like catalyst leaching or degradation over time (Fig. 1.9, right panel). Neighboring group participation (NGP) is a more specific form of internal catalysis, where a functional group in close proximity to the reaction site accelerates the exchange process in different ways.

The main distinction between internal catalysis and NGP lies in their mechanisms. In NGP, the accelerating group is covalently bonded close to the reaction centre during the exchange process. This close proximity allows the neighboring group to directly interact with the reactive intermediate, stabilizing it and facilitating the bond exchange process. NGP can change the reaction mechanism by creating a more favorable transition state or intermediate, often by forming a new covalent bond during the exchange reaction. Internal catalysis, on the other side, refers to non-covalent interactions, such as electrostatic interactions, steric effects, or weak bonding interactions that occur between the reactive site and functional groups within the polymer matrix. These effects act over a longer range than NGP and can still enhance reaction rates by stabilizing intermediates or making certain reactive sites more accessible. Regarding the most important types of chemistries previously discussed, as (i)

transesterification (ii) boronic ester exchange (iii) vinylogous urethanes and (iv) disulfide exchange chemistry, it has been reported that internal catalysts can modify the reaction kinetic and make processing of the polymer network an easier task.^{72,97–101}

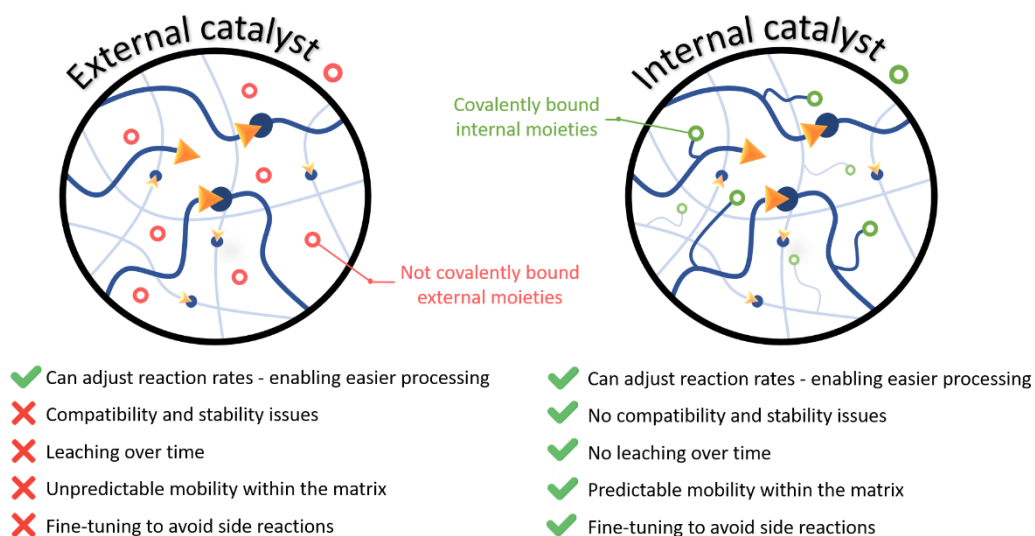


Figure 1.9: Schematic representations of external catalysis (left panel) and internal catalysis (right panel), highlighting their respective pros and cons.

1.7.1. Internal catalysis for transesterification: from small molecules to vitrimer materials

Various activating groups have been reported to significantly influence the reactivity of different dynamic covalent bonds. Inspired by organic chemistry, multiple different functionalizations can be performed on dynamic covalent bonds of interest. For example, when considering transesterification, an ortho-positioned hydroxymethyl group on phenyl esters accelerates transesterification via cyclization, forming a transient lactone through a dissociative mechanism.¹⁰² Translating these concepts to vitrimer materials, it was found that phthalate monoesters exhibit enhanced transesterification, akin to the behavior of o-hydroxymethyl phenyl esters, as shown by Du Prez et al.⁹⁷ The neighboring

carboxylic acid can attack the ester carbonyl, forming a cyclic anhydride and releasing alcohol (Fig. 1.10, upper panel). This effect was further amplified by incorporating a β -amino diol with a dianhydride to form polymer networks (Fig. 1.10, center panel). The enhancing role of β -amines in ester hydrolysis has been documented since 1962, where the presence of a tertiary amine at the β -position of hydroxyl groups provides dual activation: the neighboring group participation of the $-\text{COOH}$ and internal catalysis by the tertiary amine.¹⁰³ This dual activation led to a significant reduction in stress relaxation times, by a factor of 500 compared to networks lacking amines.⁹⁸ A similar effect was observed with 2,5-bis(methoxycarbonyl)benzenesulfonic acid, a benzoester containing an ortho-sulfonic acid moiety, which displayed an even faster stress relaxation compared to its carboxylic acid analogs (Fig.1.10, panel below).⁹⁹

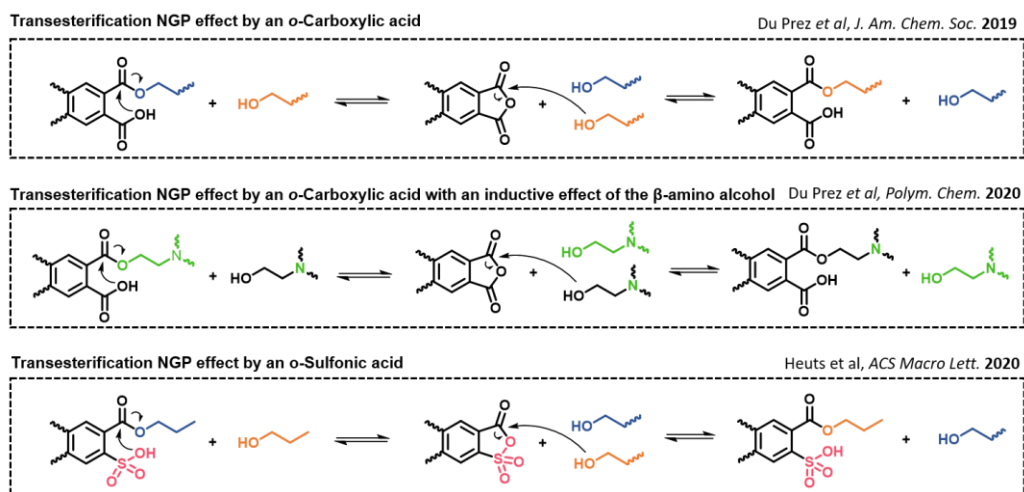


Figure 1.10: Examples of NGP in the transesterification of ortho-functionalized aromatic monoesters: (i) transesterification NGP effect facilitated by an ortho-carboxylic acid; (ii) transesterification NGP effect facilitated by an ortho-carboxylic acid with an inductive effect from the β -amino alcohol; and (iii) transesterification NGP effect facilitated by an ortho-sulfonic acid.

Considering another important class of dynamic covalent mechanism, the transesterification of boronic esters was investigated in the presence of neighboring groups such as oxygen, sulfur, or fluorine, showing that no

functionalization enhanced transesterification. However, nitrogen-containing groups were found to significantly accelerate both esterification and transesterification rates.⁷² Aminomethyl-substituted arylboronic acids are esterified several magnitudes faster than their non-substituted counterparts, as the amino group, whether in ortho or para positions, lowers the pKa and facilitates ester formation through electronic effects and the formation of B–N dative bonds.¹⁰⁴ Such accelerating effects are also observed when nitrogen-containing activating groups are integrated into vitrimers, dramatically reducing stress-relaxation times. For example, Guan and co-workers demonstrated NGP by introducing ortho-amino substituents in boronic esters, acting as proximal bases for faster proton transfer and potentially forming five-membered ring intermediates, significantly accelerating transesterification (Fig.1.11).⁷²

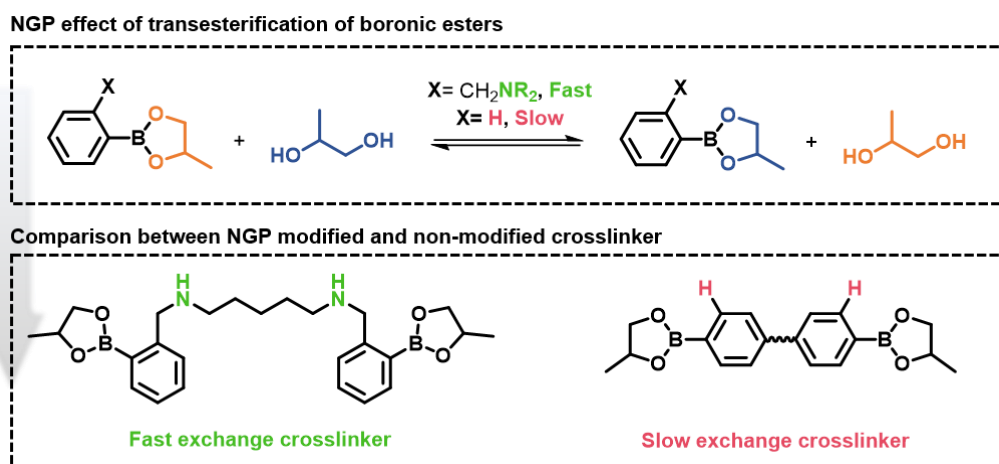


Figure 1.11: NGP effect on the transesterification of boronic esters: ortho-amino substituents in boronic esters act as proximal bases, facilitating faster proton transfer and significantly accelerating transesterification (upper panel). The synthesis of an amino-modified crosslinker leads to faster exchange rates (lower panel).

The analysis of aromatic disulfides focused on elucidating bond dissociation energies (BDE) to understand their influence on exchange rates. Considering that the presence of nitrogen in activating groups, such as tertiary amines, significantly influences the reactivity of disulfides¹⁰⁰, aromatic sulfenamide-

derived disulfides have a lower bond dissociation energy (BDE) of approximately 35 kcal/mol compared to their nitrogen-free analogs (around 50 kcal/mol). This reduction in BDE facilitates radical generation, enhancing the exchange reaction and enabling self-healing in some catalyst-free aromatic disulfide-based materials (Fig. 1.12).¹⁰⁵ Also, aromatic disulfides functionalized with 4-hydroxyphenyl groups exhibit even faster radical formation than their 4-aminophenyl analogs, although this effect is not yet fully understood.⁶⁸

Generally, computational studies on disulfide bond dissociation energies show that electron-donating groups decrease the BDE, while electron-withdrawing groups increase it. For example, the BDE of unsubstituted aromatic disulfides is approximately 48 kcal/mol. A sulfonic acid substituent increases this to 55.6 kcal/mol, while an amino substituent decreases it to 41.3 kcal/mol. A trisubstituted bis(2,4,6-triaminephenyl) disulfide reduces the BDE further to 30.1 kcal/mol. Additionally, dendralene and thiuram disulfides exhibit low BDEs, which makes them suitable for self-healing at room temperature and positions them as promising alternatives to aryl disulfides.⁶⁷

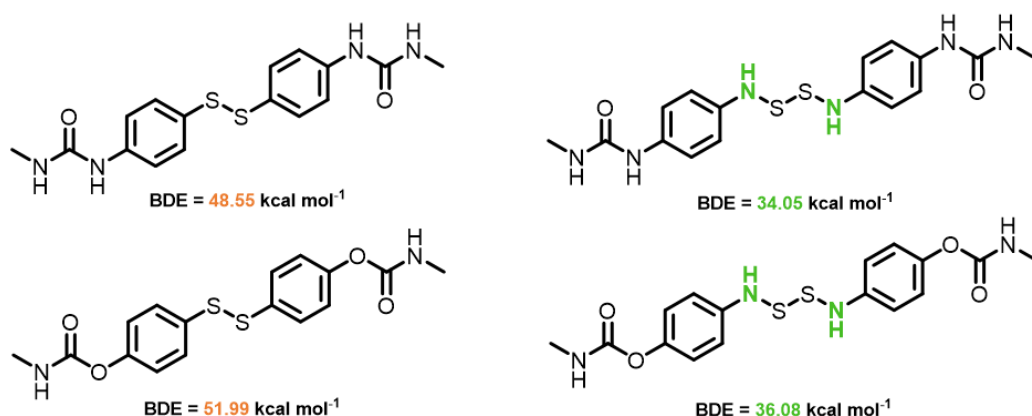


Figure 1.12: Bond dissociation energies (BDE) of various functionalized aromatic disulfides, illustrating how the presence of a neighboring amino group decreases bond strength.

Lastly, a recent study demonstrated internal catalysis in vinylogous urethane-crosslinked epoxy-amine materials through the presence of free-hydroxyl moieties in the material (Fig. 1.13).¹⁰¹ Two synthesis methods were compared: a one-pot process where all reactants were mixed together, resulting in water being trapped in the material, and a two-step process where the amines and bisacetoacetate reacted first, allowing the water to be removed before adding the epoxy resin. At 160 °C, relaxation times were 3.5 s for the one-pot material and 5.5 s for the two-step material, indicating similar performance between the two approaches. These relaxation times are significantly shorter than the 25.5 s observed in similar vinylogous urethane vitrimers without epoxy, suggesting that internal catalysis from hydroxyl groups may play a role in accelerating the exchange reaction.¹⁰¹ To support this, model studies on small molecules showed that the transamination of a vinylogous urethane compound was faster in the presence of hydroxyl-containing solvents like 2-hexanol, confirming the catalytic effect of hydroxyl moieties.¹⁰¹

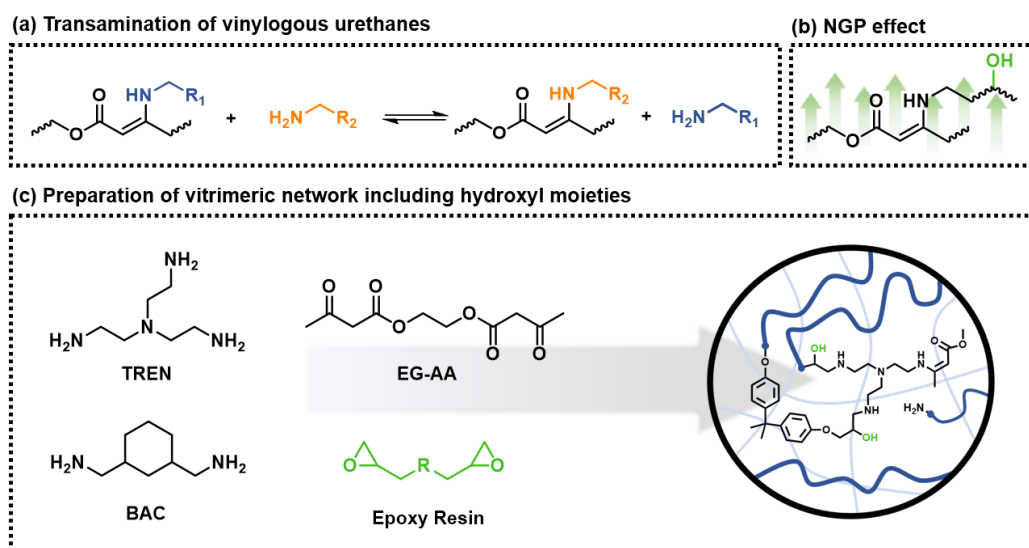


Figure 1.13: (a) Transamination scheme of vinylogous urethanes. (b) The presence of a pending hydroxyl moiety accelerates exchange reactions due to an NGP effect. (c) Preparation of a

vinyllogous urethane-crosslinked epoxy–amine material, where dangling hydroxyl groups act as internal catalysts.

1.8 Objectives

While internal catalysts and neighboring group participation (NGP) have been shown to effectively control vitrimer dynamics, minor changes in polymer design or reaction conditions can have unpredictable effects on exchange mechanisms. Furthermore, the vast range of potential modifications for NGP/internal catalysis across different chemistries presents a significant challenge, particularly when relying on the conventional "trial and error" approach, which can hinder the rapid development of industrially scalable vitrimers.

This thesis aims to leverage quantum chemical calculations, specifically Density Functional Theory (DFT), to understand exchange mechanisms and rapidly screen potential NGP/internal catalysis across various vitrimer chemistries. A precise understanding of the exchange mechanism, particularly identifying the rate-determining step, is crucial for tuning the kinetics of dynamic bonds. In this context, theoretical calculations can provide a detailed framework for predicting which functional groups or structural modifications will most effectively alter the exchange kinetics. Since computational analysis is generally more time-efficient than extensive experimental trials, this methodology allows for the exploration of numerous possibilities and helps narrow down the best candidates. With robust theoretical predictions, the subsequent experimental work can then be more targeted and efficient, accelerating the development and optimization of vitrimer materials (Fig. 1.14).

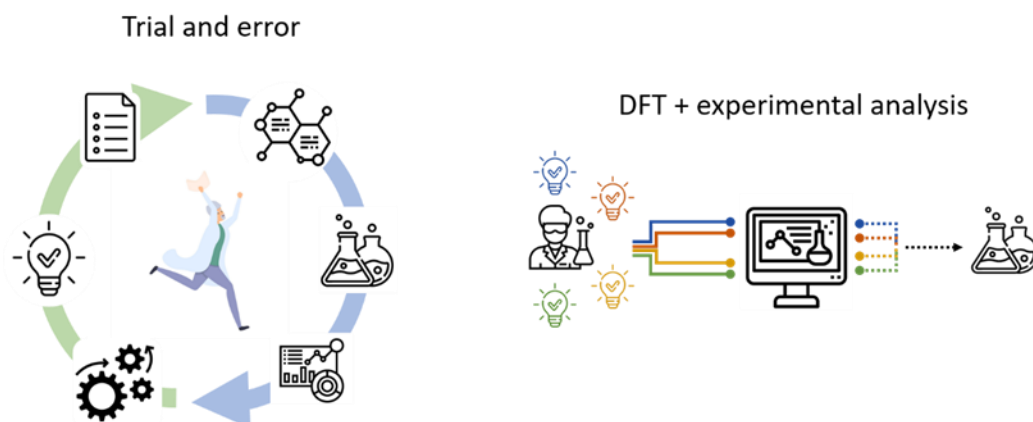


Figure 1.14: Schematic representation of two potential approaches: the left panel depicts the trial and error method, whereas the right panel illustrates the approach employed in this study: a fusion of DFT studies alongside combinatorial chemistry.

In the **second Chapter**, the dynamics of boronic ester-containing vitrimers using a combined experimental and computational approach, integrating Density Functional Theory (DFT) analyses are explored. The study focuses on two exchange mechanisms for boronic ester metathesis: a direct, uncatalyzed reaction and a nucleophile-mediated process. Quantum chemical calculations are employed to analyze the metathesis of dioxaborolanes, predicting two distinct pathways depending on the presence of nucleophiles like water or methanol. The introduction of nucleophiles is found to significantly accelerate the exchange, highlighting their role in lowering activation energy and enhancing vitrimer reprocessability and self-healing abilities. This chapter also covers the synthesis and characterization of dynamic polymer networks with boronic esters, linking the nucleophile-assisted mechanism to improved mechanical and thermal properties. Additionally, the research demonstrates how the incorporation of nucleophilic comonomers into dioxaborinane-based vitrimers facilitates stress relaxation, underscoring the value of theoretical predictions in optimizing vitrimer design with tunable properties.

The **third Chapter** extends the study of boron chemistry, focusing on exploiting the Lewis acidity of boron to introduce a novel dynamic exchange mechanism, based on Lewis Pairs, in π -conjugated aromatic polymers (π CAPs). In this work, a 9-bromo-9-borafluorene scaffold is incorporated into a copolymer composed of 9,9-silafluorene and 9,9-dioctylfluorene units through a silicon-boron (Si-B) exchange reaction, marking its first application in polymer systems. The resulting copolymer, Y1, exhibits deep blue fluorescence, high quantum yield, and excellent thermal stability, making it suitable for optoelectronic applications. The integration of the borafluorene scaffold, without bulky substituents, offers an innovative pathway to tune both optical and electronic properties of the polymer. DFT calculations were employed to explore the electronic structure and assess how the boron-containing unit affects optical properties and band gaps. These insights, combined with experimental analyses, reveal the potential for developing dynamic networks, where interaction energies with various Lewis bases can be harnessed to trigger reversible processes within the polymer backbone.

The **fourth Chapter** delves into the development of vinylogous urethanes as advanced materials for vitrimer applications, employing a combined computational and experimental approach. The study focuses on optimizing dynamic exchange mechanisms in these polymers by exploring the role of internal catalysis and neighboring group participation (NGP) in enhancing transamination kinetics. DFT calculations modeled various amines to predict their impact on exchange reactions, which were validated using high-sensitivity HSQC (Heteronuclear Single Quantum Coherence) NMR experiments. This approach allows for the precise identification of promising candidates for rapid material development, moving beyond traditional trial-and-error methods. The research synthesizes and characterizes multiple vinylogous urethane-based

vitrimers, demonstrating that computational predictions align closely with experimental results. This efficient screening method highlights how NGP and internal catalysis can significantly improve exchange kinetics, enabling faster reprocessing at elevated temperatures and better dimensional stability under service conditions. The integration of theory and experiment not only accelerates the design of dynamic covalent networks but also advances the development of next-generation vitrimers with enhanced processability and performance.

In the **last chapter**, the conclusions of each part of this thesis are commented.

References:

- (1) Ellen MacArthur Foundation and McKinsey & Company. The New Plastics Economy: Rethinking the Future of Plastics. *World Economic Forum*. 2016.
- (2) Nielsen, T. D.; Hasselbalch, J.; Holmberg, K.; Stripple, J. Politics and the Plastic Crisis: A Review throughout the Plastic Life Cycle. *WIREs Energy & Environment* **2020**, 9 (1), e360. <https://doi.org/10.1002/wene.360>.
- (3) Kumar Gupta, P.; Sai Raghunath, S.; Venkatesh Prasanna, D.; Venkat, P.; Shree, V.; Chithananthan, C.; Choudhary, S.; Surender, K.; Geetha, K. An Update on Overview of Cellulose, Its Structure and Applications. In *Cellulose*; Rodríguez Pascual, A., E. Eugenio Martín, M., Eds.; IntechOpen, 2019. <https://doi.org/10.5772/intechopen.84727>.
- (4) Vanholme, R.; Demedts, B.; Morreel, K.; Ralph, J.; Boerjan, W. Lignin Biosynthesis and Structure. *Plant Physiology* **2010**, 153 (3), 895–905. <https://doi.org/10.1104/pp.110.155119>.
- (5) Morris, E.; Pulham, C. R.; Morrison, C. A. Structure and Properties of Nitrocellulose: Approaching 200 Years of Research. *RSC Adv.* **2023**, 13 (46), 32321–32333. <https://doi.org/10.1039/D3RA05457H>.
- (6) Garnett, H. Molecular Dimensions of Celluloid. *Nature* **1925**, 115 (2880), 51–51. <https://doi.org/10.1038/115051d0>.
- (7) Puls, J.; Wilson, S. A.; Hölter, D. Degradation of Cellulose Acetate-Based Materials: A Review. *J Polym Environ* **2011**, 19 (1), 152–165. <https://doi.org/10.1007/s10924-010-0258-0>.
- (8) Fiume, M. M.; Bergfeld, W. F.; Belsito, D. V.; Hill, R. A.; Klaassen, C. D.; Liebler, D. C.; Marks, J. G.; Shank, R. C.; Slaga, T. J.; Snyder, P. W.; Andersen, F. A. Safety Assessment of Nitrocellulose and Collodion as Used in Cosmetics. *Int J Toxicol* **2016**, 35 (1_suppl), 50S-59S. <https://doi.org/10.1177/1091581816651607>.
- (9) Staudinger, H. Über Polymerisation. *Ber. dtsch. Chem. Ges. A/B* **1920**, 53 (6), 1073–1085. <https://doi.org/10.1002/cber.19200530627>.
- (10) Ali, U.; Karim, K. J. Bt. A.; Buang, N. A. A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). *Polymer Reviews* **2015**, 55 (4), 678–705. <https://doi.org/10.1080/15583724.2015.1031377>.
- (11) Matthies, P.; Seydl, W. F. History and Development of Nylon 6. In *High Performance Polymers: Their Origin and Development*; Seymour, R. B., Kirshenbaum, G. S., Eds.; Springer Netherlands: Dordrecht, 1986; pp 39–53. https://doi.org/10.1007/978-94-011-7073-4_4.
- (12) Geyer, R. A Brief History of Plastics. In *Mare Plasticum - The Plastic Sea*; Streit-Bianchi, M., Cimadevila, M., Trettnak, W., Eds.; Springer International Publishing: Cham, 2020; pp 31–47. https://doi.org/10.1007/978-3-030-38945-1_2.
- (13) Planned Obsolescence, 2009. <https://www.economist.com/news/2009/03/23/planned-obsolescence>.
- (14) Sims, A. Designed to Fail: A Short History of Planned Obsolescence.

-
- (15) *Handbook of Research on Entrepreneurship Development and Opportunities in Circular Economy*; Baporikar, N., Ed.; Ordóñez De Pablos, P., Series Ed.; Advances in Business Strategy and Competitive Advantage; IGI Global, 2020. <https://doi.org/10.4018/978-1-7998-5116-5>.
- (16) Rivera, J. L.; Lallmahomed, A. Environmental Implications of Planned Obsolescence and Product Lifetime: A Literature Review. *International Journal of Sustainable Engineering* **2016**, 9 (2), 119–129. <https://doi.org/10.1080/19397038.2015.1099757>.
- (17) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, 3 (7), e1700782. <https://doi.org/10.1126/sciadv.1700782>.
- (18) Rhodes, C. J. Plastic Pollution and Potential Solutions. *Science Progress* **2018**, 101 (3), 207–260. <https://doi.org/10.3184/003685018X15294876706211>.
- (19) Jambor, A.; Beyer, M. New Cars — New Materials. *Materials & Design* **1997**, 18 (4–6), 203–209. [https://doi.org/10.1016/S0261-3069\(97\)00049-6](https://doi.org/10.1016/S0261-3069(97)00049-6).
- (20) Malveda, M. Average Vehicle Could Incorporate 350 Kg of Plastics by 2020, 2016.
- (21) Kan, M.; Miller, S. A. Environmental Impacts of Plastic Packaging of Food Products. *Resources, Conservation and Recycling* **2022**, 180, 106156. <https://doi.org/10.1016/j.resconrec.2022.106156>.
- (22) Lackner, M. Bioplastics. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Kirk-Othmer, Ed.; Wiley, 2015; pp 1–41. <https://doi.org/10.1002/0471238961.koe00006>.
- (23) Peelman, N.; Ragaert, P.; De Meulenaer, B.; Adons, D.; Peeters, R.; Cardon, L.; Van Impe, F.; Devlieghere, F. Application of Bioplastics for Food Packaging. *Trends in Food Science & Technology* **2013**, 32 (2), 128–141. <https://doi.org/10.1016/j.tifs.2013.06.003>.
- (24) Vogt, B. D.; Stokes, K. K.; Kumar, S. K. Why Is Recycling of Postconsumer Plastics so Challenging? *ACS Appl. Polym. Mater.* **2021**, 3 (9), 4325–4346. <https://doi.org/10.1021/acsapm.1c00648>.
- (25) He, H.; Reynolds, C. J.; Hadjikakou, M.; Holyoak, N.; Boland, J. Quantification of Indirect Waste Generation and Treatment Arising from Australian Household Consumption: A Waste Input-Output Analysis. *Journal of Cleaner Production* **2020**, 258, 120935. <https://doi.org/10.1016/j.jclepro.2020.120935>.
- (26) Schyns, Z. O. G.; Shaver, M. P. Mechanical Recycling of Packaging Plastics: A Review. *Macromol. Rapid Commun.* **2021**, 42 (3), 2000415. <https://doi.org/10.1002/marc.202000415>.
- (27) Eriksen, M. K.; Christiansen, J. D.; Daugaard, A. E.; Astrup, T. F. Closing the Loop for PET, PE and PP Waste from Households: Influence of Material Properties and Product Design for Plastic Recycling. *Waste Management* **2019**, 96, 75–85. <https://doi.org/10.1016/j.wasman.2019.07.005>.
- (28) Korley, L. T. J.; Epps, T. H.; Helms, B. A.; Ryan, A. J. Toward Polymer Upcycling—Adding Value and Tackling Circularity. *Science* **2021**, 373 (6550), 66–69. <https://doi.org/10.1126/science.abg4503>.

-
- (29) Helbig, C.; Huether, J.; Joachimsthaler, C.; Lehmann, C.; Raatz, S.; Thorenz, A.; Faulstich, M.; Tuma, A. A Terminology for Downcycling. *J of Industrial Ecology* **2022**, 26 (4), 1164–1174. <https://doi.org/10.1111/jiec.13289>.
- (30) Stubbins, A.; Law, K. L.; Muñoz, S. E.; Bianchi, T. S.; Zhu, L. Plastics in the Earth System. *Science* **2021**, 373 (6550), 51–55. <https://doi.org/10.1126/science.abb0354>.
- (31) Jefferson, M. Whither Plastics?—Petrochemicals, Plastics and Sustainability in a Garbage-Riddled World. *Energy Research & Social Science* **2019**, 56, 101229. <https://doi.org/10.1016/j.erss.2019.101229>.
- (32) Arli, D.; Badejo, A.; Carlini, J.; France, C.; Jebarajakirthy, C.; Knox, K.; Pentecost, R.; Perkins, H.; Thaichon, P.; Sarker, T.; Wright, O. Predicting Intention to Recycle on the Basis of the Theory of Planned Behaviour. *J of Philanthropy and Mktg* **2020**, 25 (2), e1653. <https://doi.org/10.1002/nvsm.1653>.
- (33) Bîrcă, A.; Gherasim, O.; Grumezescu, V.; Grumezescu, A. M. Introduction in Thermoplastic and Thermosetting Polymers. In *Materials for Biomedical Engineering*; Elsevier, 2019; pp 1–28. <https://doi.org/10.1016/B978-0-12-816874-5.00001-3>.
- (34) Garcia, J. M.; Robertson, M. L. The Future of Plastics Recycling. *Science* **2017**, 358 (6365), 870–872. <https://doi.org/10.1126/science.aag0324>.
- (35) Denissen, W.; Winne, J. M.; Du Prez, F. E. Vitrimers: Permanent Organic Networks with Glass-like Fluidity. *Chem. Sci.* **2016**, 7 (1), 30–38. <https://doi.org/10.1039/C5SC02223A>.
- (36) Massy, J. Thermoplastic and Thermosetting Polymers. In *A Little Book about BIG Chemistry*; SpringerBriefs in Materials; Springer International Publishing: Cham, 2017; pp 19–26. https://doi.org/10.1007/978-3-319-54831-9_5.
- (37) Bowman, C. N.; Kloxin, C. J. Covalent Adaptable Networks: Reversible Bond Structures Incorporated in Polymer Networks. *Angew Chem Int Ed* **2012**, 51 (18), 4272–4274. <https://doi.org/10.1002/anie.201200708>.
- (38) Kloxin, C. J.; Bowman, C. N. Covalent Adaptable Networks: Smart, Reconfigurable and Responsive Network Systems. *Chem. Soc. Rev.* **2013**, 42 (17), 7161–7173. <https://doi.org/10.1039/C3CS60046G>.
- (39) Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. Covalent Adaptable Networks (CANs): A Unique Paradigm in Cross-Linked Polymers. *Macromolecules* **2010**, 43 (6), 2643–2653. <https://doi.org/10.1021/ma902596s>.
- (40) Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. Using the Dynamic Bond to Access Macroscopically Responsive Structurally Dynamic Polymers. *Nature Mater* **2011**, 10 (1), 14–27. <https://doi.org/10.1038/nmat2891>.
- (41) Podgórski, M.; Fairbanks, B. D.; Kirkpatrick, B. E.; McBride, M.; Martinez, A.; Dobson, A.; Bongiardina, N. J.; Bowman, C. N. Toward Stimuli-Responsive Dynamic Thermosets through Continuous Development and Improvements in Covalent Adaptable Networks (CANs). *Adv. Mater.* **2020**, 32 (20), 1906876. <https://doi.org/10.1002/adma.201906876>.

-
- (42) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A Thermally Re-Mendable Cross-Linked Polymeric Material. *Science* **2002**, 295 (5560), 1698–1702. <https://doi.org/10.1126/science.1065879>.
- (43) Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N. Photoinduced Plasticity in Cross-Linked Polymers. *Science* **2005**, 308 (5728), 1615–1617. <https://doi.org/10.1126/science.1110505>.
- (44) Kloxin, C. J.; Scott, T. F.; Park, H. Y.; Bowman, C. N. Mechanophotopatterning on a Photoresponsive Elastomer. *Advanced Materials* **2011**, 23 (17), 1977–1981. <https://doi.org/10.1002/adma.201100323>.
- (45) Nicolaÿ, R.; Kamada, J.; Van Wassen, A.; Matyjaszewski, K. Responsive Gels Based on a Dynamic Covalent Trithiocarbonate Cross-Linker. *Macromolecules* **2010**, 43 (9), 4355–4361. <https://doi.org/10.1021/ma100378r>.
- (46) Amamoto, Y.; Kamada, J.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. Repeatable Photoinduced Self-Healing of Covalently Cross-Linked Polymers through Reshuffling of Trithiocarbonate Units. *Angew Chem Int Ed* **2011**, 50 (7), 1660–1663. <https://doi.org/10.1002/anie.201003888>.
- (47) Amamoto, Y.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. Self-Healing of Covalently Cross-Linked Polymers by Reshuffling Thiuram Disulfide Moieties in Air under Visible Light. *Advanced Materials* **2012**, 24 (29), 3975–3980. <https://doi.org/10.1002/adma.201201928>.
- (48) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, 334 (6058), 965–968. <https://doi.org/10.1126/science.1212648>.
- (49) Angell, C. A. Formation of Glasses from Liquids and Biopolymers. *Science* **1995**, 267 (5206), 1924–1935. <https://doi.org/10.1126/science.267.5206.1924>.
- (50) Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L. Metal-Catalyzed Transesterification for Healing and Assembling of Thermosets. *J. Am. Chem. Soc.* **2012**, 134 (18), 7664–7667. <https://doi.org/10.1021/ja302894k>.
- (51) Montarnal, D. Use of Reversible Covalent and Non-Covalent Bonds in New Recyclable and Reprocessable Polymer Materials, Université Pierre et Marie Curie - Paris VI, 2011. <https://pastel.hal.science/pastel-00694348>.
- (52) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, 25 (16), 2451–2457. <https://doi.org/10.1002/adfm.201404553>.
- (53) Denissen, W.; Driesbeke, M.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Chemical Control of the Viscoelastic Properties of Vinylogous Urethane Vitrimers. *Nat Commun* **2017**, 8 (1), 14857. <https://doi.org/10.1038/ncomms14857>.
- (54) Hamzehlou, S.; Ruipérez, F. Computational Study of the Transamination Reaction in Vinylogous Acyls: Paving the Way to Design Vitrimers with Controlled Exchange Kinetics. *Journal of Polymer Science* **2022**, 60 (13), 1988–1999. <https://doi.org/10.1002/pol.20220099>.
- (55) Martin, R.; Rekondo, A.; Ruiz De Luzuriaga, A.; Cabañero, G.; Grande, H. J.; Odriozola, I. The Processability of a Poly(Urea-Urethane) Elastomer Reversibly

- Crosslinked with Aromatic Disulfide Bridges. *J. Mater. Chem. A* **2014**, 2 (16), 5710. <https://doi.org/10.1039/c3ta14927g>.
- (56) Rekondo, A.; Martin, R.; Ruiz De Luzuriaga, A.; Cabañero, G.; Grande, H. J.; Odriozola, I. Catalyst-Free Room-Temperature Self-Healing Elastomers Based on Aromatic Disulfide Metathesis. *Mater. Horiz.* **2014**, 1 (2), 237–240. <https://doi.org/10.1039/C3MH00061C>.
- (57) Lafont, U.; Van Zeijl, H.; Van Der Zwaag, S. Influence of Cross-Linkers on the Cohesive and Adhesive Self-Healing Ability of Polysulfide-Based Thermosets. *ACS Appl. Mater. Interfaces* **2012**, 4 (11), 6280–6288. <https://doi.org/10.1021/am301879z>.
- (58) Canadell, J.; Goossens, H.; Klumperman, B. Self-Healing Materials Based on Disulfide Links. *Macromolecules* **2011**, 44 (8), 2536–2541. <https://doi.org/10.1021/ma2001492>.
- (59) Tesoro, G. C.; Sastri, V. Reversible Crosslinking in Epoxy Resins. I. Feasibility Studies. *J. of Applied Polymer Sci* **1990**, 39 (7), 1425–1437. <https://doi.org/10.1002/app.1990.070390702>.
- (60) Tsarevsky, N. V.; Matyjaszewski, K. Reversible Redox Cleavage/Coupling of Polystyrene with Disulfide or Thiol Groups Prepared by Atom Transfer Radical Polymerization. *Macromolecules* **2002**, 35 (24), 9009–9014. <https://doi.org/10.1021/ma021061f>.
- (61) Tobolsky, A. V.; MacKnight, W. J.; Takahashi, M. Relaxation of Disulfide and Tetrasulfide Polymers. *J. Phys. Chem.* **1964**, 68 (4), 787–790. <https://doi.org/10.1021/j100786a013>.
- (62) Rajan, V. V.; Dierkes, W. K.; Joseph, R.; Noordermeer, J. W. M. Science and Technology of Rubber Reclamation with Special Attention to NR-Based Waste Latex Products. *Progress in Polymer Science* **2006**, 31 (9), 811–834. <https://doi.org/10.1016/j.progpolymsci.2006.08.003>.
- (63) Michal, B. T.; Jaye, C. A.; Spencer, E. J.; Rowan, S. J. Inherently Photohealable and Thermal Shape-Memory Polydisulfide Networks. *ACS Macro Lett.* **2013**, 2 (8), 694–699. <https://doi.org/10.1021/mz400318m>.
- (64) Pepels, M.; Filot, I.; Klumperman, B.; Goossens, H. Self-Healing Systems Based on Disulfide–Thiol Exchange Reactions. *Polym. Chem.* **2013**, 4 (18), 4955. <https://doi.org/10.1039/c3py00087g>.
- (65) Lei, Z. Q.; Xiang, H. P.; Yuan, Y. J.; Rong, M. Z.; Zhang, M. Q. Room-Temperature Self-Healable and Remoldable Cross-Linked Polymer Based on the Dynamic Exchange of Disulfide Bonds. *Chem. Mater.* **2014**, 26 (6), 2038–2046. <https://doi.org/10.1021/cm4040616>.
- (66) Fernandes, P. A.; Ramos, M. J. Theoretical Insights into the Mechanism for Thiol/Disulfide Exchange. *Chemistry A European J* **2004**, 10 (1), 257–266. <https://doi.org/10.1002/chem.200305343>.
- (67) Matxain, J. M.; Asua, J. M.; Ruipérez, F. Design of New Disulfide-Based Organic Compounds for the Improvement of Self-Healing Materials. *Phys. Chem. Chem. Phys.* **2016**, 18 (3), 1758–1770. <https://doi.org/10.1039/C5CP06660C>.

- (68) Nevejans, S.; Ballard, N.; Miranda, J. I.; Reck, B.; Asua, J. M. The Underlying Mechanisms for Self-Healing of Poly(Disulfide)s. *Phys. Chem. Chem. Phys.* **2016**, *18* (39), 27577–27583. <https://doi.org/10.1039/C6CP04028D>.
- (69) Formoso, E.; Asua, J. M.; Matxain, J. M.; Ruipérez, F. The Role of Non-Covalent Interactions in the Self-Healing Mechanism of Disulfide-Based Polymers. *Phys. Chem. Chem. Phys.* **2017**, *19* (28), 18461–18470. <https://doi.org/10.1039/C7CP03570E>.
- (70) Irigoyen, M.; Matxain, J. M.; Ruipérez, F. Effect of Molecular Structure in the Chain Mobility of Dichalcogenide-Based Polymers with Self-Healing Capacity. *Polymers* **2019**, *11* (12), 1960. <https://doi.org/10.3390/polym11121960>.
- (71) Zhang, X.; Wang, S.; Jiang, Z.; Li, Y.; Jing, X. Boronic Ester Based Vitrimers with Enhanced Stability via Internal Boron–Nitrogen Coordination. *J. Am. Chem. Soc.* **2020**, *142* (52), 21852–21860. <https://doi.org/10.1021/jacs.0c10244>.
- (72) Cromwell, O. R.; Chung, J.; Guan, Z. Malleable and Self-Healing Covalent Polymer Networks through Tunable Dynamic Boronic Ester Bonds. *J. Am. Chem. Soc.* **2015**, *137* (20), 6492–6495. <https://doi.org/10.1021/jacs.5b03551>.
- (73) Winne, J. M.; Leibler, L.; Du Prez, F. E. Dynamic Covalent Chemistry in Polymer Networks: A Mechanistic Perspective. *Polym. Chem.* **2019**, *10* (45), 6091–6108. <https://doi.org/10.1039/C9PY01260E>.
- (74) HALL, D. G. *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*; John Wiley & Sons, 2006.
- (75) Röttger, M.; Domenech, T.; Van Der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L. High-Performance Vitrimers from Commodity Thermoplastics through Dioxaborolane Metathesis. *Science* **2017**, *356* (6333), 62–65. <https://doi.org/10.1126/science.aah5281>.
- (76) Jäkle, F. Advances in the Synthesis of Organoborane Polymers for Optical, Electronic, and Sensory Applications. *Chem. Rev.* **2010**, *110* (7), 3985–4022. <https://doi.org/10.1021/cr100026f>.
- (77) Guan, Y.; Zhang, Y. Boronic Acid-Containing Hydrogels: Synthesis and Their Applications. *Chem. Soc. Rev.* **2013**, *42* (20), 8106. <https://doi.org/10.1039/c3cs60152h>.
- (78) Matsumoto, A.; Kataoka, K.; Miyahara, Y. New Directions in the Design of Phenylboronate-Functionalized Polymers for Diagnostic and Therapeutic Applications. *Polym J* **2014**, *46* (8), 483–491. <https://doi.org/10.1038/pj.2014.42>.
- (79) Li, D.; Chen, Y.; Liu, Z. Boronate Affinity Materials for Separation and Molecular Recognition: Structure, Properties and Applications. *Chem. Soc. Rev.* **2015**, *44* (22), 8097–8123. <https://doi.org/10.1039/C5CS00013K>.
- (80) Brooks, W. L. A.; Sumerlin, B. S. Synthesis and Applications of Boronic Acid-Containing Polymers: From Materials to Medicine. *Chem. Rev.* **2016**, *116* (3), 1375–1397. <https://doi.org/10.1021/acs.chemrev.5b00300>.
- (81) Huang, L.; Yang, Y.; Niu, Z.; Wu, R.; Fan, W.; Dai, Q.; He, J.; Bai, C. Boronic Ester Bonds Crosslinked Vitrimer Elastomers with Mechanical Robustness, Shape Memory, Self-Healing and Recyclability Properties. *Composites Science and*

- Technology* **2022**, *228*, 109621.
<https://doi.org/10.1016/j.compscitech.2022.109621>.
- (82) Zych, A.; Tellers, J.; Bertolacci, L.; Ceseracciu, L.; Marini, L.; Mancini, G.; Athanassiou, A. Biobased, Biodegradable, Self-Healing Boronic Ester Vitrimers from Epoxidized Soybean Oil Acrylate. *ACS Appl. Polym. Mater.* **2021**, *3* (2), 1135–1144. <https://doi.org/10.1021/acsapm.0c01335>.
- (83) Zeng, Y.; Li, J.; Liu, S.; Yang, B. Rosin-Based Epoxy Vitrimers with Dynamic Boronic Ester Bonds. *Polymers* **2021**, *13* (19), 3386. <https://doi.org/10.3390/polym13193386>.
- (84) Zheng, P.; McCarthy, T. J. A Surprise from 1954: Siloxane Equilibration Is a Simple, Robust, and Obvious Polymer Self-Healing Mechanism. *J. Am. Chem. Soc.* **2012**, *134* (4), 2024–2027. <https://doi.org/10.1021/ja2113257>.
- (85) Lu, Y.-X.; Tournilhac, F.; Leibler, L.; Guan, Z. Making Insoluble Polymer Networks Malleable via Olefin Metathesis. *J. Am. Chem. Soc.* **2012**, *134* (20), 8424–8427. <https://doi.org/10.1021/ja303356z>.
- (86) Lu, Y.-X.; Guan, Z. Olefin Metathesis for Effective Polymer Healing via Dynamic Exchange of Strong Carbon–Carbon Double Bonds. *J. Am. Chem. Soc.* **2012**, *134* (34), 14226–14231. <https://doi.org/10.1021/ja306287s>.
- (87) Deng, G.; Li, F.; Yu, H.; Liu, F.; Liu, C.; Sun, W.; Jiang, H.; Chen, Y. Dynamic Hydrogels with an Environmental Adaptive Self-Healing Ability and Dual Responsive Sol–Gel Transitions. *ACS Macro Lett.* **2012**, *1* (2), 275–279. <https://doi.org/10.1021/mz200195n>.
- (88) Deng, G.; Tang, C.; Li, F.; Jiang, H.; Chen, Y. Covalent Cross-Linked Polymer Gels with Reversible Sol–Gel Transition and Self-Healing Properties. *Macromolecules* **2010**, *43* (3), 1191–1194. <https://doi.org/10.1021/ma9022197>.
- (89) Ciaccia, M.; Cacciapaglia, R.; Mencarelli, P.; Mandolini, L.; Di Stefano, S. Fast Transimination in Organic Solvents in the Absence of Proton and Metal Catalysts. A Key to Imine Metathesis Catalyzed by Primary Amines under Mild Conditions. *Chem. Sci.* **2013**, *4* (5), 2253. <https://doi.org/10.1039/c3sc50277e>.
- (90) Belowich, M. E.; Stoddart, J. F. Dynamic Imine Chemistry. *Chem. Soc. Rev.* **2012**, *41* (6), 2003. <https://doi.org/10.1039/c2cs15305j>.
- (91) Obadia, M. M.; Mudraboyina, B. P.; Serghei, A.; Montarnal, D.; Drockenmüller, E. Reprocessing and Recycling of Highly Cross-Linked Ion-Conducting Networks through Transalkylation Exchanges of C–N Bonds. *J. Am. Chem. Soc.* **2015**, *137* (18), 6078–6083. <https://doi.org/10.1021/jacs.5b02653>.
- (92) Capelot, M.; Unterlass, M. M.; Tournilhac, F.; Leibler, L. Catalytic Control of the Vitremer Glass Transition. *ACS Macro Lett.* **2012**, *1* (7), 789–792. <https://doi.org/10.1021/mz300239f>.
- (93) Self, J. L.; Dolinski, N. D.; Zayas, M. S.; Read De Alaniz, J.; Bates, C. M. Brønsted-Acid-Catalyzed Exchange in Polyester Dynamic Covalent Networks. *ACS Macro Lett.* **2018**, *7* (7), 817–821. <https://doi.org/10.1021/acsmacrolett.8b00370>.
- (94) Yang, X.; Guo, L.; Xu, X.; Shang, S.; Liu, H. A Fully Bio-Based Epoxy Vitremer: Self-Healing, Triple-Shape Memory and Reprocessing Triggered by Dynamic

- Covalent Bond Exchange. *Materials & Design* **2020**, *186*, 108248. <https://doi.org/10.1016/j.matdes.2019.108248>.
- (95) Han, J.; Liu, T.; Hao, C.; Zhang, S.; Guo, B.; Zhang, J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules* **2018**, *51* (17), 6789–6799. <https://doi.org/10.1021/acs.macromol.8b01424>.
- (96) Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: Directing Chemical Reactivity to Control Material Properties. *Chem. Sci.* **2020**, *11* (19), 4855–4870. <https://doi.org/10.1039/D0SC01069C>.
- (97) Delahaye, M.; Winne, J. M.; Du Prez, F. E. Internal Catalysis in Covalent Adaptable Networks: Phthalate Monoester Transesterification As a Versatile Dynamic Cross-Linking Chemistry. *J. Am. Chem. Soc.* **2019**, *141* (38), 15277–15287. <https://doi.org/10.1021/jacs.9b07269>.
- (98) Delahaye, M.; Tanini, F.; Holloway, J. O.; Winne, J. M.; Du Prez, F. E. Double Neighbouring Group Participation for Ultrafast Exchange in Phthalate Monoester Networks. *Polym. Chem.* **2020**, *11* (32), 5207–5215. <https://doi.org/10.1039/D0PY00681E>.
- (99) Zhang, H.; Majumdar, S.; Van Benthem, R. A. T. M.; Sijbesma, R. P.; Heuts, J. P. A. Intramolecularly Catalyzed Dynamic Polyester Networks Using Neighboring Carboxylic and Sulfonic Acid Groups. *ACS Macro Lett.* **2020**, *9* (2), 272–277. <https://doi.org/10.1021/acsmacrolett.9b01023>.
- (100) Azcune, I.; Odriozola, I. Aromatic Disulfide Crosslinks in Polymer Systems: Self-Healing, Reprocessability, Recyclability and More. *European Polymer Journal* **2016**, *84*, 147–160. <https://doi.org/10.1016/j.eurpolymj.2016.09.023>.
- (101) Spiesschaert, Y.; Guerre, M.; De Baere, I.; Van Paepegem, W.; Winne, J. M.; Du Prez, F. E. Dynamic Curing Agents for Amine-Hardened Epoxy Vitrimers with Short (Re)Processing Times. *Macromolecules* **2020**, *53* (7), 2485–2495. <https://doi.org/10.1021/acs.macromol.9b02526>.
- (102) Fife, T. H.; Benjamin, B. M. General Base Catalyzed Intramolecular Transesterification. *J. Am. Chem. Soc.* **1973**, *95* (6), 2059–2061. <https://doi.org/10.1021/ja00787a082>.
- (103) Shafer, J. A.; Morawetz, H. Hydrolysis of an Ester with a Neighboring Carboxyl and a Quaternary Ammonium Group¹. *J. Org. Chem.* **1962**, *27* (6), 2269–2270. <https://doi.org/10.1021/jo01053a542>.
- (104) Wulff, G.; Lauer, M.; Böhnke, H. Rapid Proton Transfer as Cause of an Unusually Large Neighboring Group Effect. *Angew. Chem. Int. Ed. Engl.* **1984**, *23* (9), 741–742. <https://doi.org/10.1002/anie.198407411>.
- (105) Ruipérez, F.; Galdeano, M.; Gimenez, E.; Matxain, J. M. Sulfenamides as Building Blocks for Efficient Disulfide-Based Self-Healing Materials. A Quantum Chemical Study. *ChemistryOpen* **2018**, *7* (3), 248–255. <https://doi.org/10.1002/open.201800003>.

Chapter 2

A combined theoretical and experimental study of metathesis and nucleophile-mediated exchange mechanisms in boronic ester-containing vitrimers

2.1 Introduction

The first application of the combined approach involving theoretical calculations (DFT) and experimental analysis was directed toward understanding the mechanisms underlying boronic ester exchange, specifically metathesis. Although metathesis is a known reaction in the literature, its detailed mechanistic steps remained elusive until this combined methodology was employed. As previously mentioned in the introduction, although various exchange reactions have been shown to generate CANs,¹⁻⁵ boronic esters have garnered significant attention due to their excellent thermal stability, oxygen tolerance, easily tunable dynamic nature without a catalyst, and broad compatibility with functional groups.⁶ The preparation of boronic esters from boronic acid and diols is straightforward, as the process is an equilibrium, and the forward reaction is rapid and particularly favored when the boronic ester product is insoluble in the reaction solvent.⁷ Boronates are characterized by the formation of strong boron-oxygen bonds, attributed to π -back bonding between the unoccupied p-orbital of boron and the lone pair on oxygen.⁸ However, the intrinsic electrophilic nature of boron, due to its empty p-orbital, makes these compounds susceptible to nucleophilic attacks, which can result in the formation of tetrahedral intermediates.

The stability of boronic esters can be enhanced through the use of bulky diols, particularly in six-membered ring systems, where better B-O conjugation is achieved compared to five-membered rings.⁹ As a result, boronic esters prone to hydrolysis, such as acyclic or small cyclic boronates, may degrade in the presence of water. In contrast, six-membered dioxaborinanes formed from bulky diols exhibit greater stability. This contrast is evident in storage requirements: five-membered dioxaborolanes necessitate dry, inert conditions, while six-membered

dioxaborinanes, like the ones used in this chapter, remain stable under standard storage conditions.¹⁰

The dynamic nature of boronic ester bonds is governed by three main exchange mechanisms outlined in Figure 2.1: (a) hydrolysis to boronic acid, (b) transesterification with a diol, and (c) metathesis with another boronate. By leveraging the first two reaction mechanisms, boron-containing polymers have been extensively utilized in pH-responsive materials, which hold potential for smart drug delivery, self-healing systems, or shape memory hydrogels.^{11–16}

A pioneering study on the synthesis of self-healing polymers containing boronic ester bonds, conducted by the Lavigne group in 2005,¹⁴ reported the development of poly(dioxaborolane) in linear polymer form. The authors selected monomers to minimize cross-linking by reducing the occurrence of unbound hydroxyl groups, while enhancing solubility. To assess the material's self-repair capabilities, the polymer was first degraded by hydrolysis in a water-saturated organic solvent. Re-assembly was achieved by removing the solvent under reduced pressure, followed by storing the resulting residue under vacuum. The degree of polymer degradation varied, and self-repair was carried out under mild conditions, restoring the polymer to a length comparable to the original. Remarkably, the material demonstrated self-healing properties without the need for an external catalyst, relying solely on the presence of excess diols, which facilitated transesterification in the solid state.

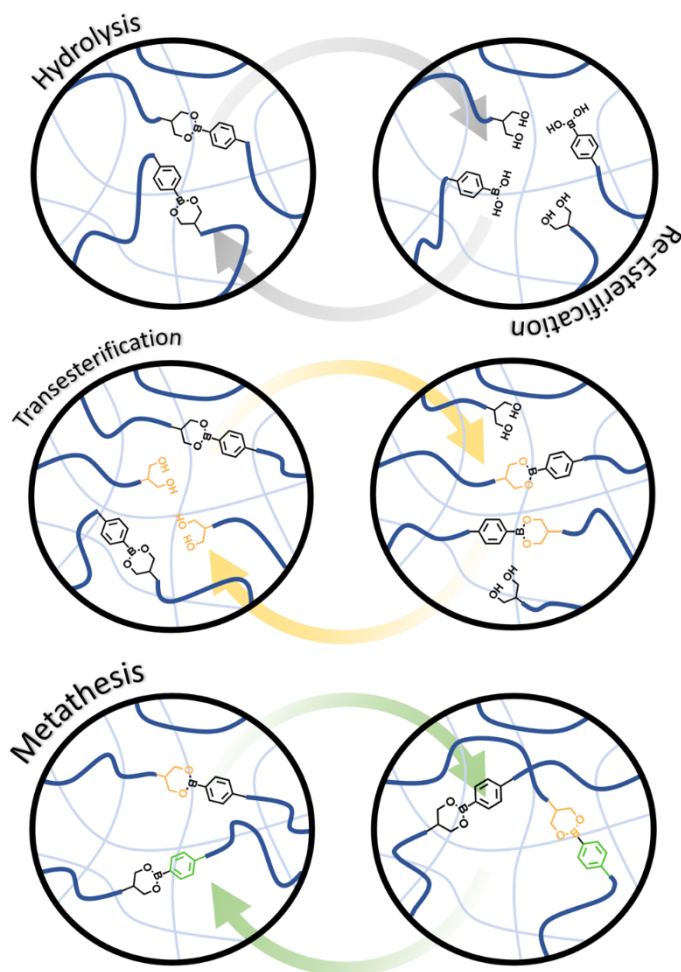


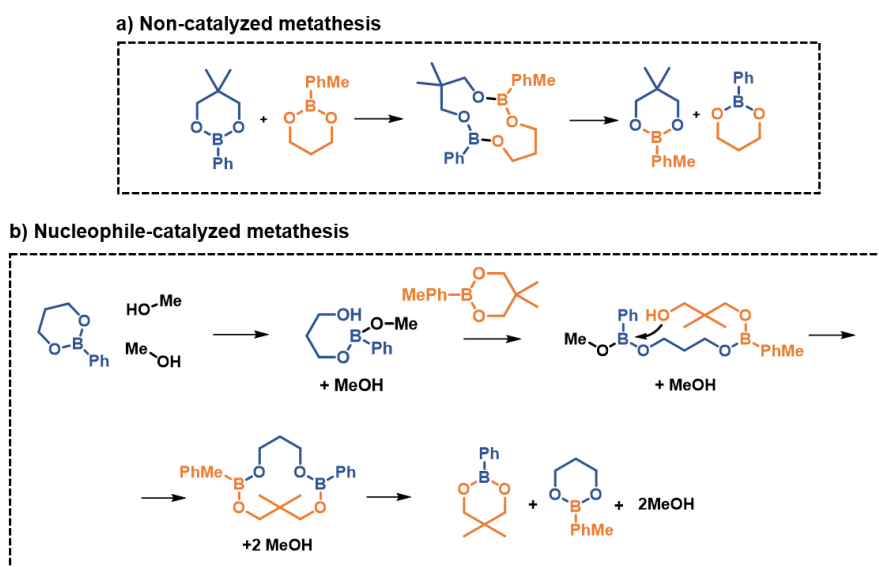
Figure 2.1: Different exchange mechanisms of boronic esters in polymer networks: (a) hydrolysis/re-esterification (upper panel); (b) transesterification (middle panel); and (c) metathesis (lower panel).

The first study demonstrating that three-dimensional (3D) bulk polymer materials containing boronic ester bonds could self-heal at room temperature was conducted by Sumerlin et al. in 2015.¹⁷ The authors synthesized a cross-linked polymer network incorporating boronic esters using photo-initiated radical thiol-ene click chemistry. In this system, self-healing occurred through the hydrolysis and subsequent re-esterification of the boronic esters within the polymer matrix. The authors proposed that hydrolysis of surface-exposed boronic esters could be triggered by deliberately wetting the damaged area,

enabling boronic ester exchange and facilitating the formation of covalent bridges across the damaged interface to restore the material's integrity. To address the limitations related to creep and stress relaxation observed in their earlier work, the Sumerlin group conducted a study in 2018 that explored both hydrolysis/re-esterification and transesterification mechanisms of boronic esters simultaneously, while introducing irreversible cross-links to enhance structural stability. Transesterification was investigated by varying the concentration of excess free diols, and experiments were performed in environments with different humidity levels to assess the self-healing behavior via hydrolysis/re-esterification. This study revealed which exchange mechanism predominated under different conditions, depending on humidity and the amount of free diols present. By leveraging both exchange reactions, the authors were able to design a material that exhibited both dynamic self-healing properties and enhanced stability, with the self-healing rate being tunable by adjusting the humidity and free diol content.¹⁸

More recently, metathesis-like reactions of boronic esters have been employed in the development of various dynamic networks, ranging from durable, self-healing elastomers to vitrimers.^{19–22} In the context of metathesis reactions and their application in vitrimer systems, the underlying mechanism remains poorly understood, and only a limited number of studies are available. Röttger et al.¹⁰ reported the synthesis of a vitrimer material where the dynamic exchange was proposed to occur via metathesis of dioxaborolanes (five-membered boronic esters) without the need for any catalyst, at temperatures as low as 60 °C. The authors speculated that the reaction could proceed either through a direct pathway or via successive transesterification of dioxaborolanes with undetectable traces of diols. In a review on dynamic covalent chemistry, Winne

et al.⁸ suggested that the metathesis reaction likely involves a multistep process initiated by the formation of a zwitterionic adduct. However, the existence of a genuine metathesis reaction is yet to be confirmed. Recently, Brunet et al.²³ investigated the dynamic exchange in styrenic-based polymers containing pinacol boronate ester groups. Based on experimental analysis and DFT calculations, they concluded that the most likely mechanism involved a nucleophilic ring-opening step to accelerate the exchange process, making metathesis improbable. Supporting the ring-opening mechanism, Yang et al.²⁴ demonstrated that free alcohol groups enhance the exchange rate of six-membered phenyl boronic esters. The two possible mechanisms for the exchange process are illustrated in Scheme 2.1



Scheme 2.1: Illustration of the main steps of the two metathesis mechanisms of dioxaborinanes: (a) direct uncatalyzed metathesis and (b) nucleophile-mediated metathesis.

Although various mechanisms have been proposed for the exchange reactions of boronic esters, a comprehensive mechanistic study has yet to be conducted. Given the importance of fully understanding these mechanisms for controlling the kinetics of dynamic bonds, this chapter combines quantum chemical

calculations with experimental model studies to elucidate the metathesis mechanism of boronates, both in the presence and absence of a nucleophilic mediator. The focus is placed on dioxaborinanes (six-membered ring boronic esters) due to their increased stability in aqueous environments. A detailed computational analysis is presented to explore potential mechanistic pathways involved in boronic ester exchange, followed by a comparative kinetic evaluation of the two pathways, including an assessment of the potential impact of hydrolysis on the reaction.

2.2 Results and Discussion

2.2.1 Density Functional Theory (DFT) Results

Nucleophile-mediated Exchange Reaction Mechanism

As a first step towards understanding the mechanism of exchange in boronic esters, the mechanistic pathway of the nucleophile-mediated exchange of boronic esters was investigated using DFT calculations. The model reaction considered the exchange between **B1** and **B2** with methanol serving as the nucleophilic mediator. Figure 2.2 displays the calculated potential energy surface, while the detailed molecular structures of all intermediates and transition states are provided in Figure 2.3 and Figure 2.4.

The theoretical calculations show that the mechanism begins with the nucleophilic attack of a MeOH molecule on the boron atom (TS1, 15.74 kcal/mol). This is followed by a hydrogen transfer from the methanol oxygen to one of the dioxaborinane oxygens, assisted by a second MeOH molecule (TS2, 20.96 kcal/mol), resulting in the formation of a zwitterionic species. This species undergoes a ring opening to form an acyclic intermediate with a free hydroxyl group (INT2, 14.74 kcal/mol). The free hydroxyl group, acting as a nucleophile, can then attack a second dioxaborinane molecule (TS3, 26.97 kcal/mol). A

hydrogen transfer between oxygens, again assisted by a MeOH molecule, occurs through a transition state similar to TS2 (TS4, 30.83 kcal/mol). The generated zwitterionic species undergoes ring-opening, leading to an intermediate with another free hydroxyl group (INT4, 25.12 kcal/mol). This hydroxyl can perform an intramolecular nucleophilic attack on the boron atom of the first boronic ester (TS5, 34.27 kcal/mol), forming a zwitterionic cyclic dimer of dioxaborinanes (INT5, 31.08 kcal/mol).

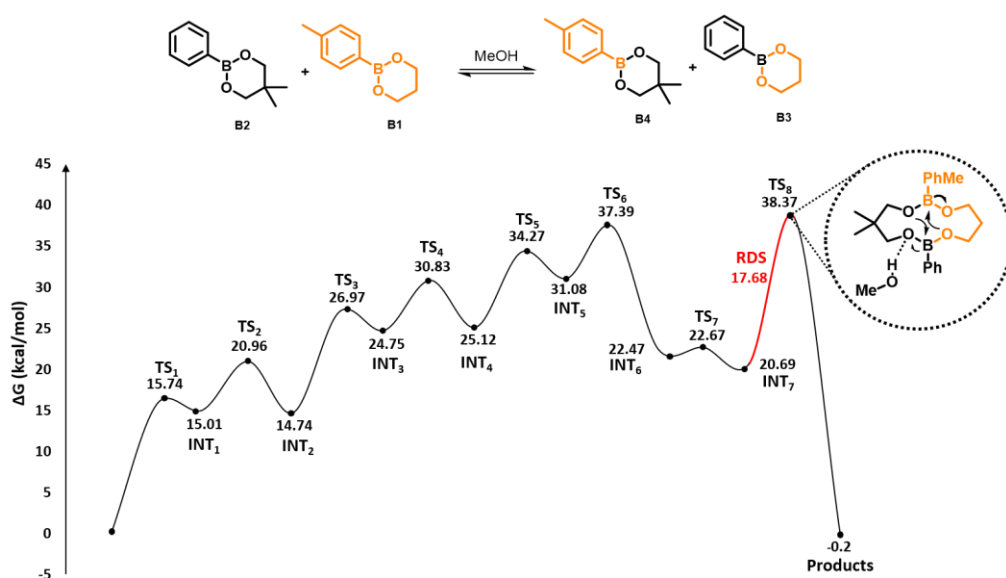


Figure 2.2: Potential energy surface of the MeOH-mediated exchange of dioxaborinanes. Gibbs free energies (ΔG) in kcal mol⁻¹. The red line indicates the rate-determining step (RDS) of the reaction with the value in kcal mol⁻¹.

Subsequently, a hydrogen transfer from the positively charged oxygen to the oxygen of the pendant methoxy group in the first dioxaborinane occurs (TS6, 37.99 kcal/mol), and the resulting methanol group departs (TS7, 22.67 kcal/mol), yielding a neutral cyclic dimer (INT7, 20.69 kcal/mol) and regenerating the methanol. The final step involves an intramolecular metathesis of the cyclic dimer, where two oxygen atoms simultaneously attack the boron atoms, forming

two new dioxaborinanes. This is the rate-limiting step, with an energy barrier of 17.68 kcal/mol.

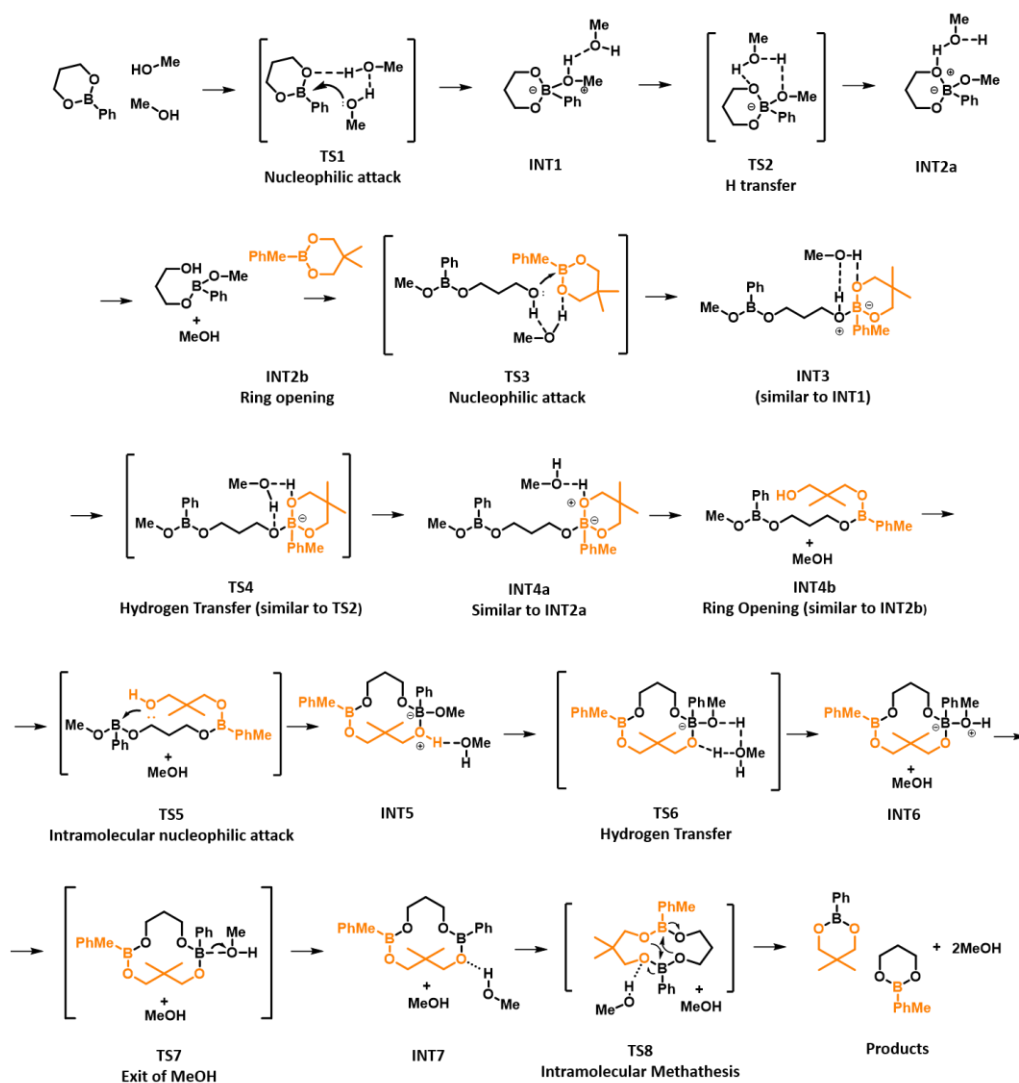


Figure 2.3: Molecular structures of all intermediates and transition states scheme of the exchange mechanism of the metathesis reaction catalyzed by MeOH.

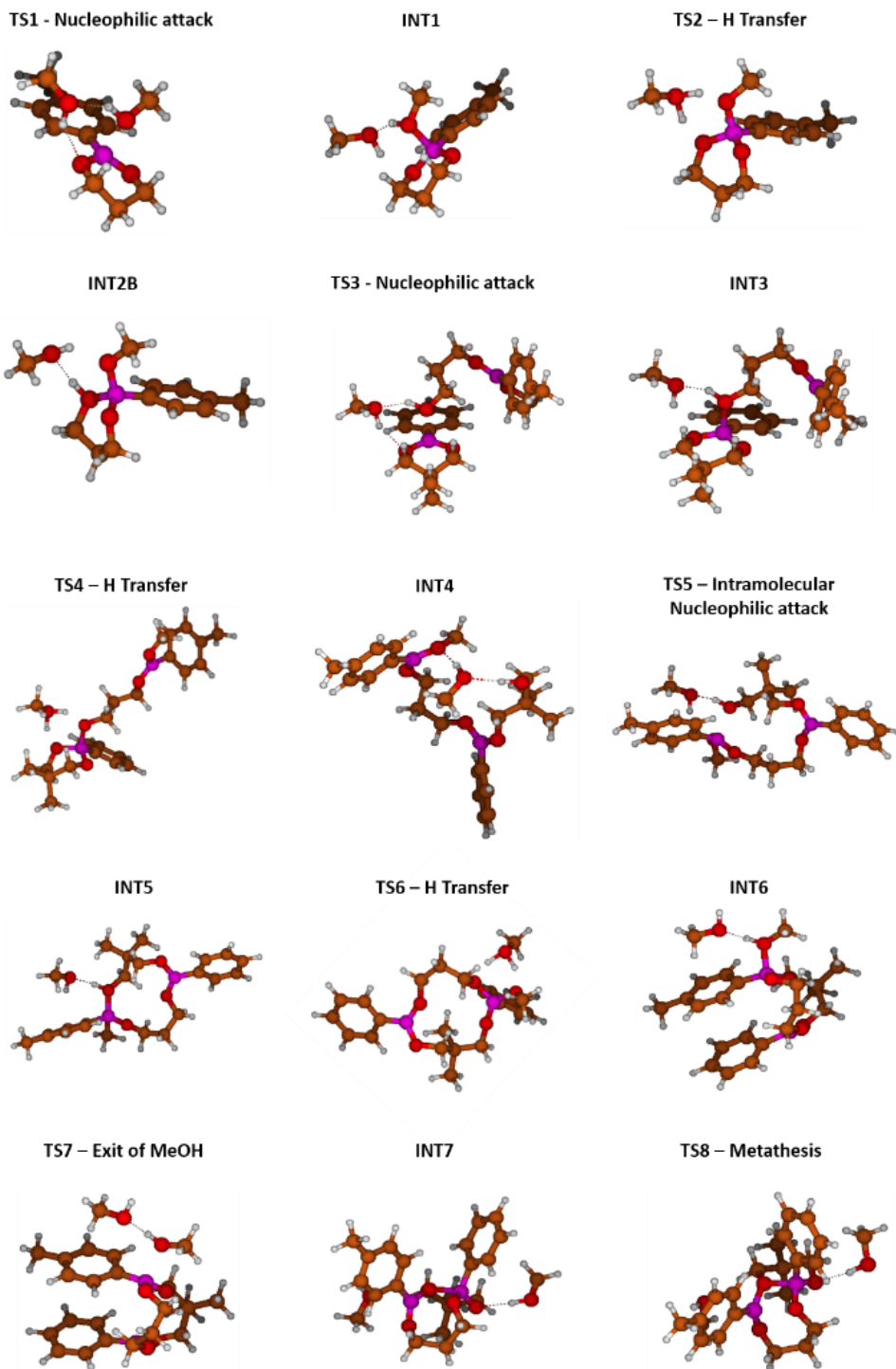


Figure 2.4: DFT-optimised transition states and intermediate structures for the MeOH-catalyzed metathesis exchange of dioxaboronanes. Color code: orange, carbon; white, hydrogen; red, oxygen; purple, boron.

Direct Metathesis Mechanism Exchange

In the nucleophile-assisted mechanism discussed above, methanol plays a crucial role in facilitating the exchange of dioxaborinanes. However, since the last rate-limiting step is an intramolecular metathesis, it is plausible that a non-catalyzed pathway could also occur, in which two dioxaborinane monomers undergo metathesis, as previously hypothesized in the literature.^{8,10} To investigate this, DFT calculations were used to examine the possibility of a direct metathesis pathway. Figure 2.5 shows the calculated potential energy surface for this process, and the molecular structures of all intermediates and transition states plus the DFT optimized structures are provided in Figure 2.6 and Figure 2.7.

When two dioxaborinanes approach, the oxygens can initiate a nucleophilic attack on the boron atoms in a [2+2] cycloaddition reaction (TS1, 29.15 kcal/mol), forming a four-membered cyclic structure that subsequently opens to create a macrocyclic dimer of the two original boronic esters (INT1, 17.58 kcal/mol). This step is the rate-limiting stage of the reaction, with an energy barrier of 29.15 kcal/mol. An intramolecular metathesis then occurs (TS2, 32.58 kcal/mol), resulting in the formation of two new dioxaborinane molecules. These two exchange mechanisms highlight that the reaction can proceed via different pathways, each with distinct energy barriers. Although the MeOH-mediated exchange is more complex and involves multiple steps, the rate-limiting step has a relatively low energy barrier of 17.68 kcal/mol. In contrast, the direct metathesis pathway consists of just two steps, but the rate-limiting step involves a significantly higher barrier (29.15 kcal/mol). Therefore, the presence of methanol (or another nucleophile) in the reaction mixture is expected to facilitate the boronic ester exchange.

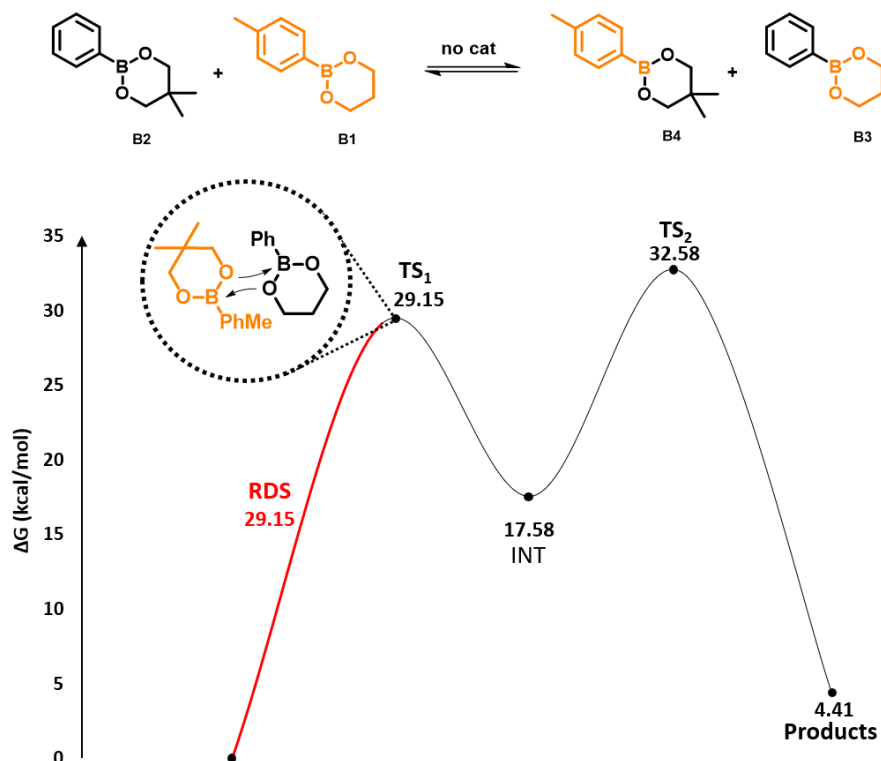


Figure 2.5: Potential energy surface of the direct metathesis reaction of dioxaborinanes. Gibbs free energies (ΔG) in kcal mol⁻¹. The red line indicates the rate-determining step (RDS) with the value in kcal mol⁻¹.

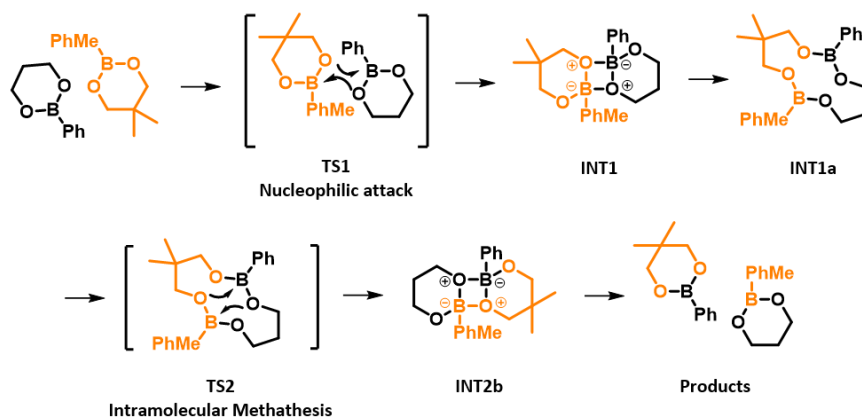
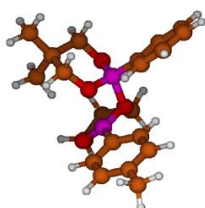
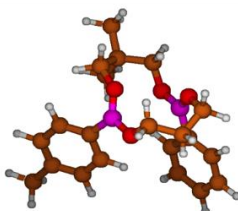


Figure 2.6: Molecular structures of all intermediates and transition states scheme of the exchange mechanism of the non-catalyzed metathesis reaction.

TS1 - Nucleophilic attack



INT1



TS2 – Intramolecular metathesis

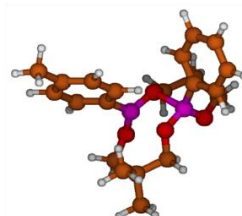


Figure 2.7: DFT-optimised transition states and intermediate structures for the direct metathesis exchange of dioxaborinanes. Color code: orange, carbon; white, hydrogen; red, oxygen; purple, boron.

2.2.2 Model studies

To assess whether the effects predicted by the quantum chemical calculations manifest in experimental differences in exchange dynamics, several exchange experiments were conducted using small molecules as model compounds. Previous studies have suggested that adventitious nucleophiles may play a significant role, even when none are intentionally added.²⁵ Therefore, we first examined the stability of the dioxaborinanes used in this study by adding water and MeOH to **B4** at 60°C for 4 hours (Scheme 2.2). These tests were performed in DMSO to avoid solubility issues when using water. The aromatic peaks at 7.60 ppm for the boronic ester and 7.70 ppm for the hydrolyzed product were integrated to determine the relative percentages of the two components in the mixture. The NMR spectra are provided in Figures S2.18-S2.30 for reference.



Scheme 2.2: Hydrolysis or MeOH-nucleophilic attack to dioxaborinane **B4** to give product **BH1**.

Dioxaborinane **B4** displayed high stability in the presence of MeOH. When 0.1 and 0.2 molar equivalents of MeOH were added to the boronic ester in deuterated DMSO and heated at 60°C for 4 hours, only 1% of the boronic ester underwent alcoholysis to form product BH1 (see Figures S2.19-S2.20 for the corresponding NMR spectra). Similarly, with 0.5 or 1 equivalent of MeOH, only 3% BH1 formed after 4 hours (see Figures S2.21-S2.22 for NMR spectra). Even at higher MeOH concentrations, the extent of hydrolysis remained low, with only 8% of the material hydrolyzed after adding 5 molar equivalents of MeOH (see Figure S2.24 for the NMR spectra). Since one possible exchange mechanism involves hydrolysis to boronic acid followed by re-esterification (see Figure 2.1), we also tested water as a nucleophile. Once again, **B4** showed high stability against hydrolysis. Notably, the six-membered dioxaborinanes used here are significantly more stable than the dioxaborolanes employed in many earlier studies, where complete hydrolysis occurs even with small amounts of water.¹⁸ Compared to MeOH, water led to more hydrolysis: with 0.1 and 0.2 equivalents, 2% and 3% of the boronic ester, respectively, were hydrolyzed to BH1. However, with water as the nucleophile, the extent of hydrolysis increased substantially at higher molar equivalents, reaching 28% with 5 molar equivalents (Table 2.1 and Figure S2.25-S2.30).

Table 2.1: MeOH/hydrolytic stability of dioxaborinane **B4**. Different equivalents (0.10, 0.20, 0.50, 1, 2.5, 5) of the two nucleophiles were added and the percentage of the hydrolysed/BH1 product is shown.

MeOH/H ₂ O eq	% Alcoholysis	% Hydrolysis
0.10	≤1%	2%
0.20	1%	3%
0.50	3%	6%
1	3%	7%
2.5	3%	17%
5	3%	28%

After completing the stability experiments, a series of kinetic measurements of boronic ester exchange were conducted in the absence of nucleophile, as well as with the addition of MeOH and H₂O at varying molar percentages at 60°C in CDCl₃. The total concentration of dioxaborinanes was kept at 0.5 mol L⁻¹ in all cases. At regular intervals, small volumes of the reaction mixture were sampled for ¹H NMR analysis in CDCl₃. The methylene signals (–OCH₂–) at 3.80 ppm for **B4** and 3.82 ppm for **B3** were integrated to calculate the relative percentages of the four components in the reaction mixture. The corresponding NMR spectra are provided in the experimental section (Figures S2.9-S2.17). Figure 2.8 illustrates the evolution of the reaction mixture over time for the different reactions. When **B2** and **B1** were left in solution without a catalyst at 60°C, the exchange process was slow, and after 4 hours the ratio of starting reagent **B2** to metathesis product **B4** was just 9/1. In contrast, under the same conditions in bulk, the reaction between the two dioxaborinanes reached near equilibrium after 4 hours, with a **B2/B4** ratio of 6.1/3.9. The relatively faster exchange in bulk is due to the higher concentration of reactants, yet it also demonstrates that exchange occurs even without an intentionally added mediator, further supporting the hypothesis of a metathesis reaction.

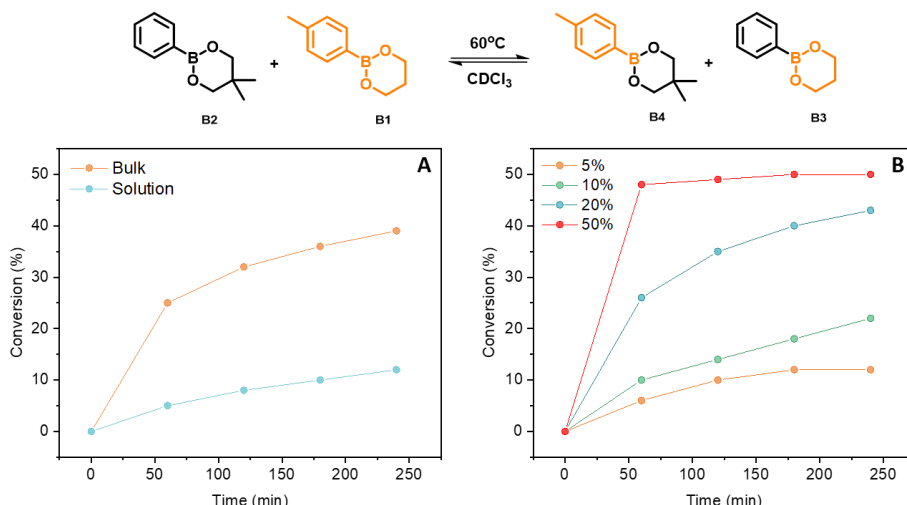


Figure 2.8: Experimental kinetics of the reaction between dioxaborinane B2 and B1 at 60 °C for 4 hours (Panel above). Kinetics of B2 + B1 without catalyst in solution (CDCl_3) and in bulk (graph A). Kinetics of B2 + B1 in solution with 5, 10, 20, and 50 mol% of MeOH with respect to the dioxaborinanes (graph B).

For the reactions in solution with varying amounts of MeOH as a nucleophilic catalyst, higher MeOH concentrations clearly accelerated the exchange dynamics. As shown in Figure 2.8, graph B, when 5% or 10% MeOH was added, the exchange rate was not significantly different from the uncatalyzed reaction. However, when the MeOH concentration was increased to 20% and 50% molar, the rate increased markedly. This behavior can be attributed to the role of MeOH, which in larger quantities facilitates the opening of the dioxaborinane cycle. To quantify this effect, the effective rate coefficient for the exchange reaction was determined from the kinetic plots, assuming identical rate coefficients for the forward and reverse reactions. As shown in Figure 2.9, while the effective rate coefficient increases with MeOH concentration, it decreases to a non-zero value as the MeOH concentration is reduced, suggesting a significant contribution from the direct metathesis pathway. In addition to using MeOH, we also tested water as a nucleophile by adding 50% water relative to dioxaborinanes, resulting in a water-saturated reaction mixture (see Figure

S2.31). Similar to methanol, the reaction rate was substantially faster than in experiments without any added nucleophile. The combination of kinetic results and DFT calculations allows us to draw conclusions about the exchange pathways in boronic esters. Based on the minimal alcoholysis reported in Table 2.1, even at relatively high alcohol concentrations, and the high exchange rate observed at zero or low alcohol concentrations in Figure 2.8, it seems the direct metathesis pathway identified in the DFT calculations plays a significant role.

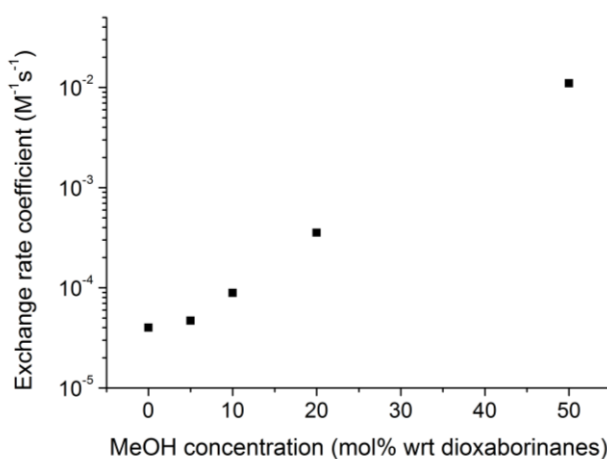


Figure 2.9: Effect of concentration of MeOH on the effective rate coefficient of exchange of dioxaborinanes. The effective rate coefficients are obtained from the kinetic data shown in Figure 2.8 (graph B) by fitting the value of the rate coefficient, k_{ex} , to the rate equation $[B3] = \frac{[B3]_0}{2} + \frac{[B3]_0}{2} e^{-2[B3]_0 k_{ex} t}$ derived by assuming reversible exchange between [B3] and [B4] to give [B1] and [B2] occur with identical rate coefficients for the forward and backward reactions.

In the presence of MeOH, the substantial increase in the exchange rate indicates that the nucleophile-mediated pathway becomes more prominent. However, it is important to note that due to the very different hydrolytic stabilities of dioxaborolanes and dioxaborinanes, these conclusions for dioxaborinanes may not hold when changing the boronic ester structure. In the case of dioxaborolanes, even small amounts of water can lead to significant hydrolysis, thereby promoting the ring-opening mechanisms proposed by Raynaud et al.²³

2.2.3 Preparation and characterization of dynamic networks

As a demonstration of the nucleophile-mediated mechanism in vitrimer-type materials, a thermoset network containing pendant alcohol groups and a dioxaborinane-based crosslinker were prepared. To create this network, a new dioxaborinane-based crosslinker (**B6**) was synthesized and photopolymerized using butyl acrylate and 2-hydroxyethyl methacrylate (HEMA) as monomers. It was hypothesized that HEMA would act as an accelerator through its nucleophilic alcohol group. Additionally, a commercial dimethacrylate crosslinker, ethylene glycol dimethacrylate (**M1**), was used to prepare non-dynamic control materials. The crosslinker was introduced at 3 mol% relative to BA in the monomer feed, and a series of PBA + pHEMA networks were prepared with 0, 0.6, and 1.5 mol% HEMA, relative to the main monomer in the formulation (see Figure 2.10). After photopolymerization, the vitrimers were obtained as free-standing films.

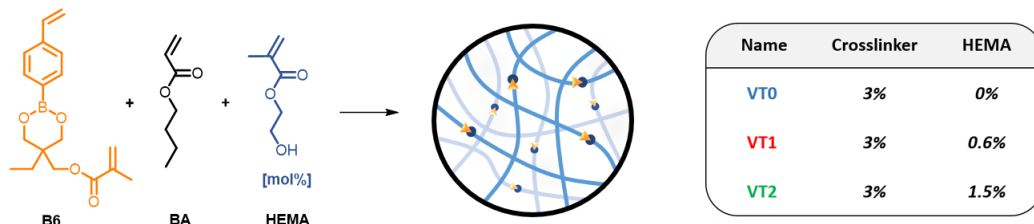


Figure 2.10 Synthetic procedure to prepare vitrimer materials VT0, VT1, and VT2 based on dioxaborinane crosslinker B6, butyl acrylate, and HEMA (left panel). Variation of mol% of HEMA, compared to the moles of butyl acrylate for samples VT0, VT1, and VT2.

2.2.4 Characterization of the materials

The cross-linked nature of the vitrimers was confirmed through swelling measurements and DMTA analysis. Swelling tests in DCM showed that the vitrimers had similar swelling behavior to the control sample, indicating that the crosslinked networks were structurally comparable in all cases. The T_g was measured by DSC, revealing that all samples had a T_g around -41°C , with no

significant change due to the incorporation of HEMA (Figure 2.11 and Figure S2.42).



Figure 2.11: Picture representing pristine VT2 (left) and the swollen in CH₂Cl₂ counterpart (left panel) and swelling ratio and T_g data for each formulation of vitrimer VT0, VT1 and VT2 and control crosslinked network blank.

All samples exhibited a single glass transition in the DMTA, above which the modulus remained constant, as expected for a crosslinked material (see Figure 2.12). Thermal properties were assessed by TGA, showing that all networks were thermally stable up to 310°C under a nitrogen atmosphere, with temperatures for 5% weight loss exceeding 335°C (see Figure S2.32). These values were considerably higher than the temperatures needed for dioxaborinane metathesis, as shown in Figure 2.8.

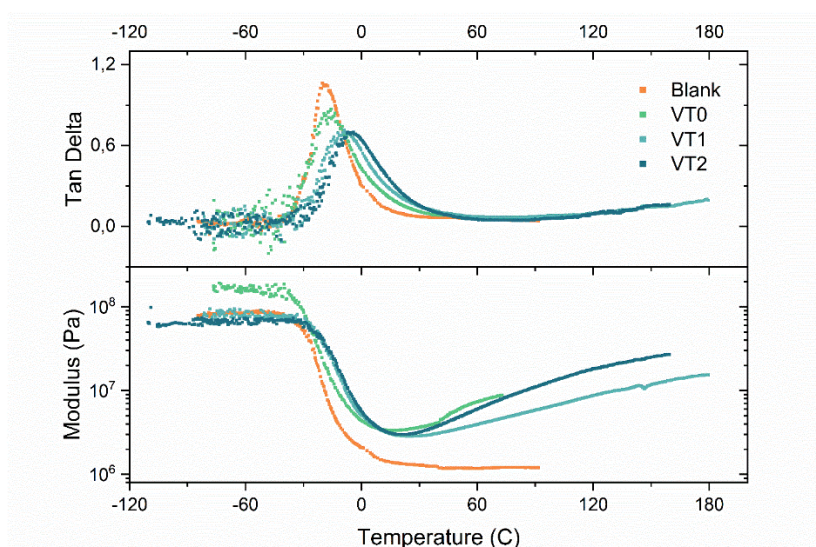


Figure 2.12: Comparison of storage modulus and tan delta of control crosslinked network blank and vitrimer networks VT0, VT1 and VT2 as function of temperature. Note that the increase of

the modulus above the T_g in the case of VT0, VT1 and VT2 is an artifact of the measurement due to the adhesion of the sample to the probe.

2.2.5 Rheological properties

To confirm that the material dynamics were accelerated by the catalytic hydroxyl groups, stress relaxation measurements of the dynamic vitrimer networks were conducted at various temperatures (see Figure 2.13). A representative measurement at 160°C, comparing the blank sample and those containing the dynamic crosslinker with or without HEMA, is shown in Figure 2.14. It is evident that all vitrimer networks with the boronic ester crosslinker exhibit stress relaxation, with samples containing higher concentrations of HEMA displaying significantly reduced relaxation times. In contrast, the control sample, as expected for a non-dynamic crosslinked material, showed no stress relaxation.

The characteristic relaxation times for the different samples were obtained by fitting the stress relaxation data to a stretched exponential across all temperatures. The Arrhenius plot of the relaxation times at different temperatures is shown in Figure 2.14. Two key observations can be made. First, there is a significant reduction in relaxation time at a given temperature. This decrease is particularly notable given the relatively low concentrations of HEMA in the formulations. Additionally, the faster stress relaxation was evident at low frequencies in frequency sweep experiments, where vitrimer sample VT2 reached a G', G'' crossover point (see Figures S2.33-S2.36). Second, there is a notable reduction in activation energy when HEMA is incorporated into the copolymer. These findings are consistent with DFT studies, which indicate a lower energy barrier for the rate-determining step in the MeOH-mediated mechanism compared to the direct metathesis pathway.

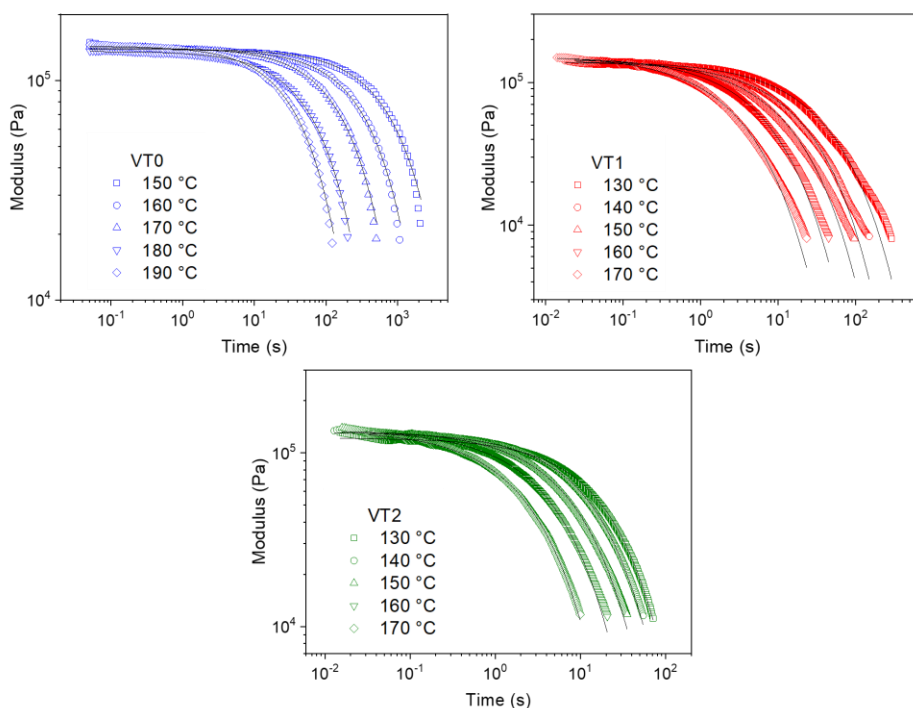


Figure 2.13: Stress relaxation measurements of network VT0, VT1 and VT2 carried out at various temperatures. The full lines correspond to fits of the data to a stretched exponential of the form $\sigma(t) = \sigma_0 e^{-\left(\frac{t}{\tau}\right)^\beta}$.

As illustrated in Figure 2.14, the activation energies align closely with the calculated rate-determining step. Specifically, VT0 exhibits an E_a of 126.5 kJ/mol (approximately 30 kcal/mol), closely matching the calculated metathesis barrier of 29.15 kcal/mol. Similarly, VT2 shows an E_a of 79.6 kJ/mol (about 19 kcal/mol), aligning well with the calculated RDS barrier for the MeOH-catalyzed reaction at 17.68 kcal/mol. This behavior is consistent with the model studies, where the addition of MeOH increased the reaction rate. Furthermore, the stress relaxation observed in vitrimer sample VT0 provides additional evidence of the metathesis mechanism occurring in the absence of a catalyst.

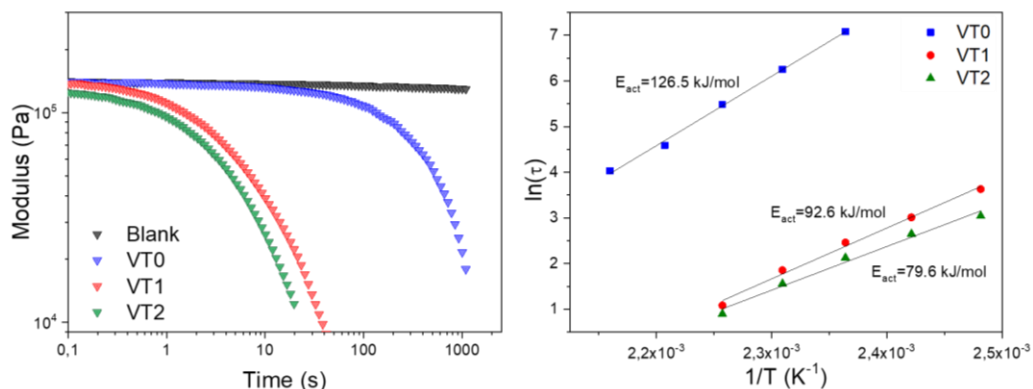


Figure 2.14: Stress relaxation analysis of control crosslinked network “blank”, vitrimer VT0, VT1, and VT2 at 160 °C as function of time (left panel) and Arrhenius plot of relaxation times for vitrimer VT0, VT1, and VT2 to give the activation energy for bond exchange (right panel).

2.2.6 Thermal healing and reprocessing

To evaluate the reprocessing ability of the vitrimer networks based on dioxaborinanes, the prepared samples were cut into several pieces and hot-pressed for 10 minutes at 150°C under 8 MPa. The networks containing boronic esters were successfully reprocessed, with intact specimens fully recovered (see Figure 2.15 and Figure S2.37). In contrast, applying the same processing protocol (150°C) to the control networks resulted in samples of very poor quality, too weak for characterization (see Figure S2.38). Frequency sweep and stress relaxation measurements on the reprocessed samples revealed no significant changes in their mechanical properties (see Figure 2.15 and Figures S2.39-S2.41).

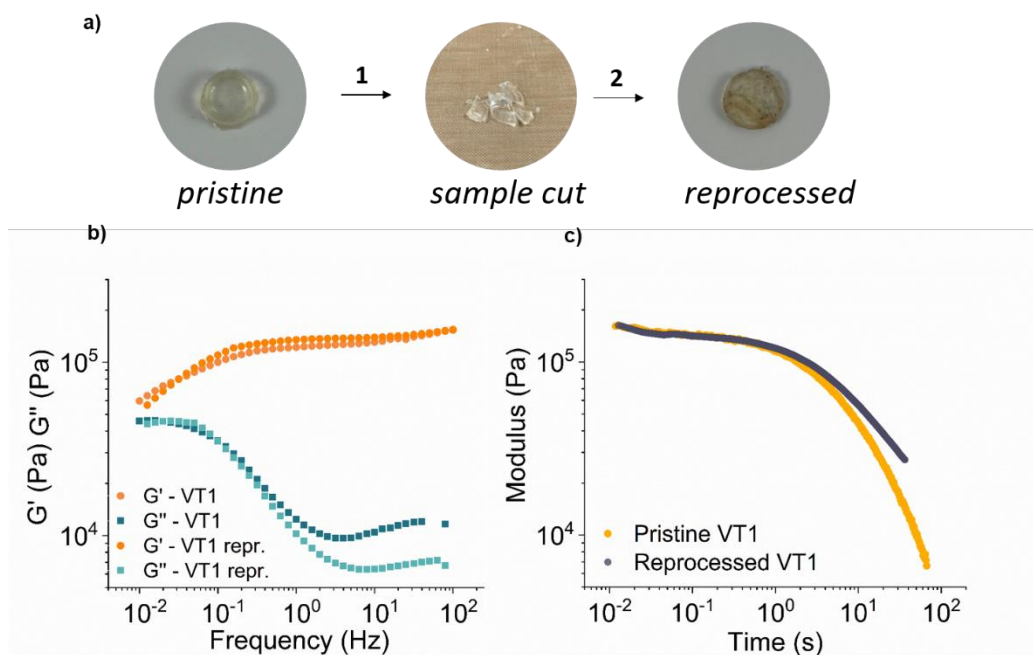


Figure 2.15: (a) Reprocessing of vitrimer network VT1: step 1 consists in cutting in small pieces the pristine vitrimer material. Step 2 refers to the thermal reprocessing at 150 °C for 10 minutes to give the reprocessed material. (b) Storage and loss modulus of pristine and reprocessed VT1. (c) Stress relaxation behavior of pristine and reprocessed VT1.

2.3 Conclusions

In this chapter, computational and experimental approaches were combined to investigate the mechanism of bond exchange in boronic ester-containing polymer networks, particularly focusing on vitrimers. Quantum chemical calculations, specifically density functional theory (DFT), revealed two distinct mechanistic pathways for the exchange reaction: a direct metathesis pathway occurring in the absence of a nucleophilic species, and a nucleophile-mediated pathway that significantly accelerates the rate of exchange. Experimental evidence supported these findings, demonstrating that the presence of nucleophiles, such as water or methanol, dramatically enhances the bond exchange rate in small molecule systems, such as dioxaborinanes. This accelerated exchange was further validated in vitrimer materials synthesized

with dioxaborinane-based crosslinkers and a hydroxyl-functional monomer acting as an internal catalyst. The inclusion of nucleophile-containing comonomers enabled a substantial reduction in stress relaxation times in vitrimers, highlighting how the mechanistic insights from this study can be leveraged to optimize the rheological properties and performance of vitrimer materials.

2.4 Experimental section

2.4.1 Materials

4-Methyl phenyl boronic acid, phenylboronic acid, 4-vinyl phenyl boronic acid, 2,2-dimethyl-1,3-propanediol and 1,3-propanediol were purchased from TCI and used without further purification. Butyl acrylate, (2-hydroxyethyl) methacrylate, triethylamine, methacryloyl chloride, trimethylol propane, sodium sulfate and the solvents dry THF and CH_2Cl_2 , were purchased from Sigma Aldrich and used without further purification. Deuterated solvents were purchased from Sigma Aldrich and were dried over molecular sieves.

2.4.2 Characterization

^1H and ^{13}C NMR spectra were recorded at ambient temperature, using deuterated chloroform (CDCl_3) or deuterated DMSO (DMSO-d_6) with a 300 MHz Bruker Avance III.

Fourier transform-infrared (FT-IR) spectra were recorded using a Nicolet 6700 FTIR with an ATR accessory (MKII Golden Gate) from SPECAC with a diamond crystal. The measurements were recorded using 16 scans and a resolution of 8 cm^{-1} .

Thermogravimetric analysis (TGA) was performed in a TGA 8000 from PerkinElmer under a nitrogen atmosphere from 30 to 900 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C min}^{-1}$.

Differential Scanning Calorimetry was performed on a TA Instruments DSC 250 calibrated with indium, and the curves were analyzed using the Trios software. The sample was first equilibrated at -85°C followed by a 1-minute isothermal step. A heating ramp of 20 $^\circ\text{C/min}$ was then performed until 100 $^\circ\text{C}$. The sample was then kept at 100 $^\circ\text{C}$ for 1 minute before being cooled down with a cooling rate of 50 $^\circ\text{C/min}$ until -85°C . A second heating ramp was then performed with

the same parameters as the first one. Tgs were measured as the inflection point of the first DSC scan.

Dynamic Mechanical Thermal Analysis (DMTA) was performed in compression mode using a Triton 2000 DMA (Triton Technology). The experiments were carried out using circular samples with a diameter of 8 mm at a frequency of 1 Hz. The chosen temperature range was from -80 °C to 150 °C at a heating rate of 4 °C min⁻¹.

Samples were reprocessed in Collin P200E compression molding machine under the following conditions: (1) preheating the mold for 5 min at 150 °C; (2) heating the sample at 150 °C for 10 min at 300 bar of pressure and finally (3) cooling the sample.

Rheological experiments were performed using the ARES-G2 rheometer from TA Instruments. Frequency sweeps were performed in shear geometry with 8 mm diameter plates under linear viscoelastic conditions, in which the storage modulus and the loss modulus of the samples were determined. Confirmation that the measurements were recorded within the linear viscoelastic regime was obtained through strain sweeps at a frequency of 1 Hz. Stress relaxation measurements were performed to obtain the relaxation modulus ($G(t)$) in shear using plates with 8 mm of diameter under linear viscoelastic conditions. The samples had a thickness between 0.6 mm and 1 mm.

To measure the degree of swelling a piece (7mm in diameter and 1 mm in thickness) of the polymerized material was immersed in 2 mL of dry CH₂Cl₂ overnight at room temperature. The swollen sample was weighed and the swelling ratio was obtained following the equation written below:

$$\text{Swelling ratio} = (M_s - M_d)/M_d$$

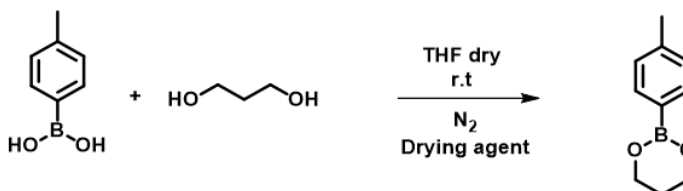
Where M_d and M_s , denote the mass of the pristine dry sample and the swollen sample respectively.

2.4.3 Computational Methodology

All geometry optimizations were executed within density functional theory (DFT) using the ω B97XD²⁸ functional combined with the 6–31+G(d)²⁹ basis set for all atoms. Frequency calculations were carried out at the same level of theory to validate that the optimized structures were minima or transition states on the potential energy surfaces. These frequencies were then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal corrections to the enthalpy (H) and Gibbs free energy (G), at $T = 298.15$ K, in the harmonic oscillator approximation. To refine the electronic energies, single-point calculations using the 6–311++G(2df,2p) basis set³⁰ were performed on the optimized structures. All the calculations were performed with the Gaussian 16 suite of programs.³¹ The molecular models used in the simulations for the boronic ester compounds are depicted in Scheme 1.1.

2.4.4 Synthetic Procedures:

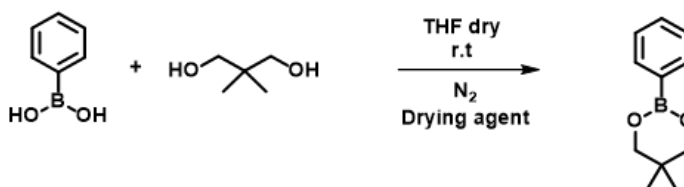
Synthesis of 2-(4-methylphenyl)-1,3,2-dioxaborinane (**B1**):



Scheme S2.1: Synthesis of 2-(4-methylphenyl)-1,3,2-dioxaborinane (**B1**)

The synthesis of dioxaborinanes used as model compounds was achieved following a general procedure based on previously published work.³² As a representative procedure, in the synthesis of **B1**, 4-Methyl phenyl boronic acid (1.65 g, 12 mmol), 1,3-propanediol (0.78 mL, 11 mmol) and sodium sulfate were added in 30 mL of dry THF in a 100 mL round bottom flask under nitrogen atmosphere. The reaction was stirred overnight at room temperature and the formation of the boronic ester was checked with thin layer chromatography (TLC). Sodium sulfate was then filtered off using a porous funnel, with celite and sodium sulfate and the solvent was removed in vacuo. Hexane was then added and the solution was filtered with the same conditions (Celite and sodium sulfate) and the solvent was removed in vacuo yielding the desired product without the need of further purification. The product was obtained as a yellowish liquid. Yield: 90%, 1.85g. ^1H NMR (300 MHz, Chloroform- d) δ 7.75 – 7.63 (m, 2H), 7.18 (dp, J = 7.1, 0.8 Hz, 2H), 4.23 – 4.13 (m, 4H), 2.38 (s, 3H), 2.14 – 2.00 (m, 2H). Spectroscopic data is in agreement with previously reported literature.²⁵

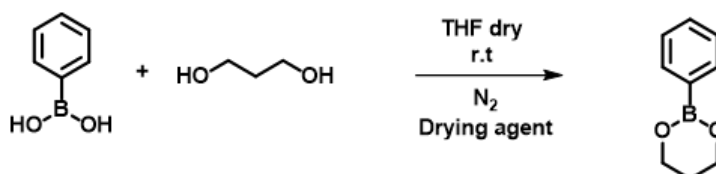
Synthesis of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**B2**):



Scheme S2.2: Synthesis of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**B2**)

The synthesis of **B2** was achieved using the general protocol reported for **B1** using phenyl boronic acid (3 g, 24 mmol) and 2,2-dimethyl-1,3-propanediol (2.39 g, 23 mmol). The product was obtained as a white solid. Yield: 95%, 4.25g. ¹H NMR (300 MHz, Chloroform-d) δ 7.89 – 7.32 (m, 5H), 3.80 (s, 4H), 1.05 (s, 6H). Spectroscopic data is in agreement with previously reported literature.²⁴

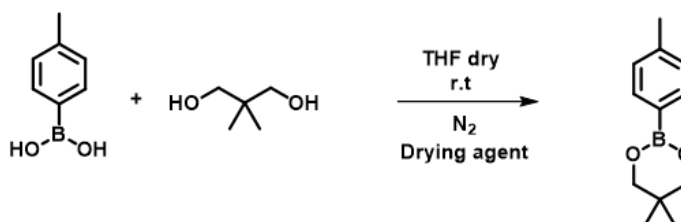
Synthesis of 2-Phenyl-1,3,2-dioxaborinane (**B3**):



Scheme S2.3: Synthesis of 2-Phenyl-1,3,2-dioxaborinane (**B3**)

The synthesis of **B3** was achieved using the general protocol reported for **B1** using phenyl boronic acid (3 g, 24 mmol) and 1,3-propanediol (2.39g, 23 mmol). The product was obtained as a yellowish liquid. Yield: 81.5%, 2.65g. ¹H NMR (300 MHz, Chloroform-d) δ 7.88 – 7.74 (m, 2H), 7.53 – 7.33 (m, 3H), 4.27 – 4.11 (m, 4H), 2.17 – 1.96 (m, 2H). Spectroscopic data is in agreement with previously reported literature.³³

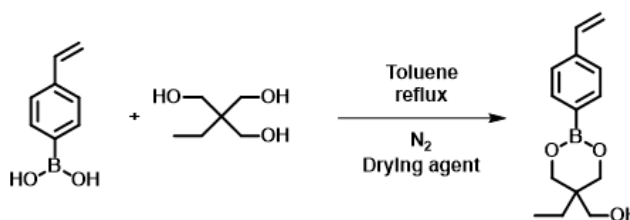
Synthesis of 5,5-dimethyl-2-(4-methylphenyl)-1,3,2-dioxaborinane (**B4**):



Scheme S2.4: Synthesis of 5,5-dimethyl-2-(4-methylphenyl)-1,3,2-dioxaborinane (**B4**)

The synthesis of **B4** was achieved using the general protocol reported for **B1** using 4-methyl phenyl boronic acid (1 g, 7.3 mmol) and 2,2-dimethyl-1,3-propanediol (0.76 mL, 7.3 mmol). The product was obtained as a white solid. Yield : 95%, 1.42g. ^1H NMR (300 MHz, Chloroform- d) δ 7.76 – 7.67 (m, 2H), 7.20 (dtd, $J = 7.8, 1.4, 0.7$ Hz, 2H), 3.79 (s, 4H), 2.39 (s, 3H), 1.05 (s, 6H). Spectroscopic data is in agreement with previously reported literature.²⁴

Synthesis of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methanol (**B5**):

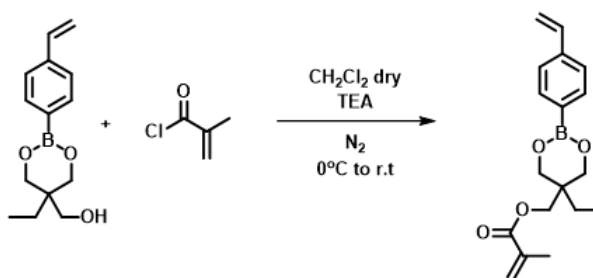


Scheme S2.5: Synthesis of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methanol (**B5**)

The synthesis of **B5** was based on procedures published by Yang *et al.*²⁴ Vinyl phenyl boronic acid (1g, 6.75 mmol), trimethylol propane (0.99 g, 7.40 mmol) and sodium sulfate were added in 30 mL of dry toluene in a 100 mL round bottom flask under nitrogen atmosphere. The reaction was stirred overnight at reflux and the formation of the boronic ester was checked with thin layer chromatography (TLC). The reaction solution was filtered and evaporated to remove toluene under reduced pressure, affording a yellow powder. Yield: 91%, 1.51g. ^1H NMR

(300 MHz, Chloroform- d) δ 7.87 – 7.68 (m, 1H), 7.50 – 7.35 (m, 1H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.82 (dd, J = 17.6, 1.0 Hz, 1H), 5.30 (dd, J = 10.9, 1.0 Hz, 1H), 1.48 (q, J = 7.6 Hz, 2H), 0.95 (t, J = 7.6 Hz, 2H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 139.17, 136.65, 133.85, 128.88, 128.19, 125.33, 115.06, 66.31, 22.59, 7.17.

Synthesis of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methyl methacrylate (**B6**):

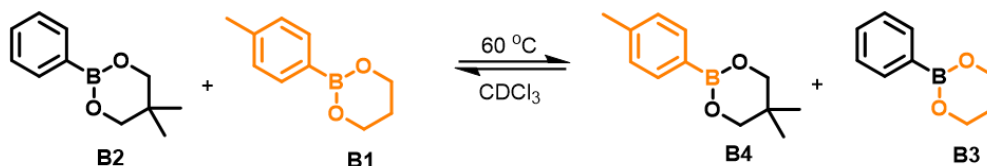


Scheme S2.6: Synthesis of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methyl methacrylate (**B6**)

Boronic ester **B6** (1.67g, 6.78 mmol) was dissolved in anhydrous DCM (20 mL), followed by addition of 1.14 mL of TEA (8.13 mmol). After cooling to 0°C in a water/ice bath, 0.79 mL (8.13 mmol) of methacryloyl chloride in 10 mL dry DCM was added dropwise within 30 minutes. Then, the reaction mixture was warmed to room temperature, stirred overnight, and filtered. The filtrate was concentrated on a rotary evaporator and diluted by ethyl acetate, and washed with brine three times. After drying over MgSO_4 , the organic solution was concentrated and purified by silica flash column chromatography using hexane and ethyl acetate (v/v = 85/15) as the eluent. **B6** was obtained as yellow oil. Yield: 91%, 1.27g. ^1H NMR (300 MHz, Chloroform- d) δ 7.83 – 7.67 (m, 1H), 7.41 (d, J = 8.0 Hz, 1H), 6.75 (dd, J = 17.5, 10.8 Hz, 1H), 6.13 (t, J = 1.3 Hz, 0H), 5.82 (dd, J = 17.6, 0.9 Hz, 0H), 5.61 (p, J = 1.6 Hz, 0H), 5.30 (dd, J = 10.8, 0.9 Hz, 0H), 4.19 (s, 1H), 4.12 – 4.03 (m, 1H), 3.98 – 3.91 (m, 1H), 1.97 (d, J = 1.3 Hz, 1H), 1.56 – 1.46

(m, 1H), 0.93 (dt, $J = 10.7, 7.6$ Hz, 2H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 166.28, 138.91, 136.69, 133.87, 126.15, 125.33, 65.94, 63.26, 37.52, 23.16, 17.90, 7.11.

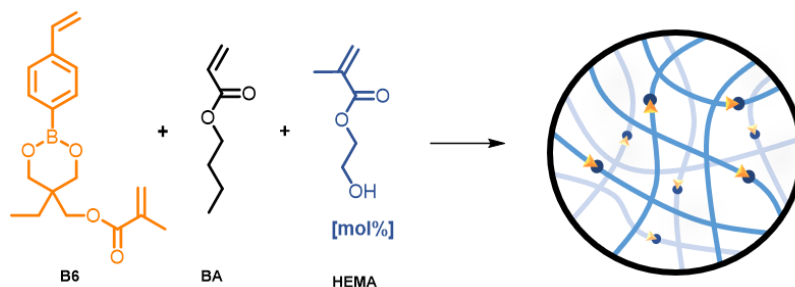
2.4.5 Metathesis kinetics of model compounds



Scheme S2.7: Exchange reaction between **B2** and **B1**

All the compounds used in the model reactions were dried in a vacuum oven overnight prior to use and were handled under ambient conditions. The metathesis kinetics experiments between equal molar amounts of **B1** and **B2** were performed in CDCl_3 at 60°C with a total concentration of 0.5 M (*i.e.* $[\text{B1}] + [\text{B2}] = 0.5$ M). Different solutions with the addition of 5, 10, 20, 50 mol% of MeOH and 50 mol% of H_2O based on the concentration of boronic ester as nucleophiles were prepared, and the kinetics of metathesis were evaluated. In the case of reaction with added water, the solubility limit of water in CDCl_3 is exceeded and these reactions are therefore carried out under saturated conditions. At determined intervals, a small amount of the reaction mixture was taken out to perform ^1H NMR. The characteristic signals of the methylene $-\text{OCH}_2-$ at 3.80 ppm for **B2** and 3.82 ppm for **B4** were integrated to determine the relative amount of the four components in the reaction mixture. The NMR spectra are shown in Figure S2.9-S2.17.

2.4.6 Preparation of crosslinked networks



Scheme S2.8: Preparation of crosslinked networks

A series of crosslinked networks were prepared starting from **B6** by photopolymerization using butyl acrylate and Darocure 1175 (1 wt%) as the photoinitiator. In all networks 3 mol% of B6 with respect to butyl acrylate was used as crosslinker. Different molar percentages of 2-hydroxyethyl methacrylate (HEMA, 20% – 50%) with respect to the crosslinker moles were added to evaluate the effects of the presence of free hydroxyl groups on exchange kinetics. The solutions were poured into silicone molds and UV-irradiated three times in a Light Curing Systems UVC-5 (Dymax) with a lamp intensity of $400 \text{ mW} \cdot \text{cm}^{-2}$ for 10 minutes. After a solid material was obtained, the samples were peeled off and stored at room temperature.

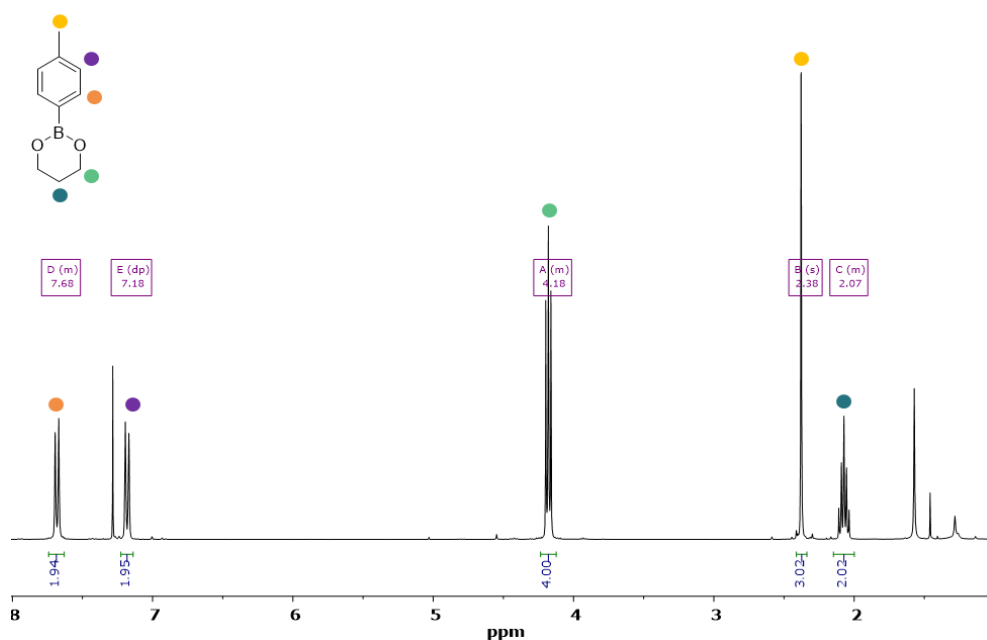


Figure S2.1: ¹H NMR of 2-(4-methylphenyl)-1,3,2-dioxaborinane (B1) in CDCl₃.

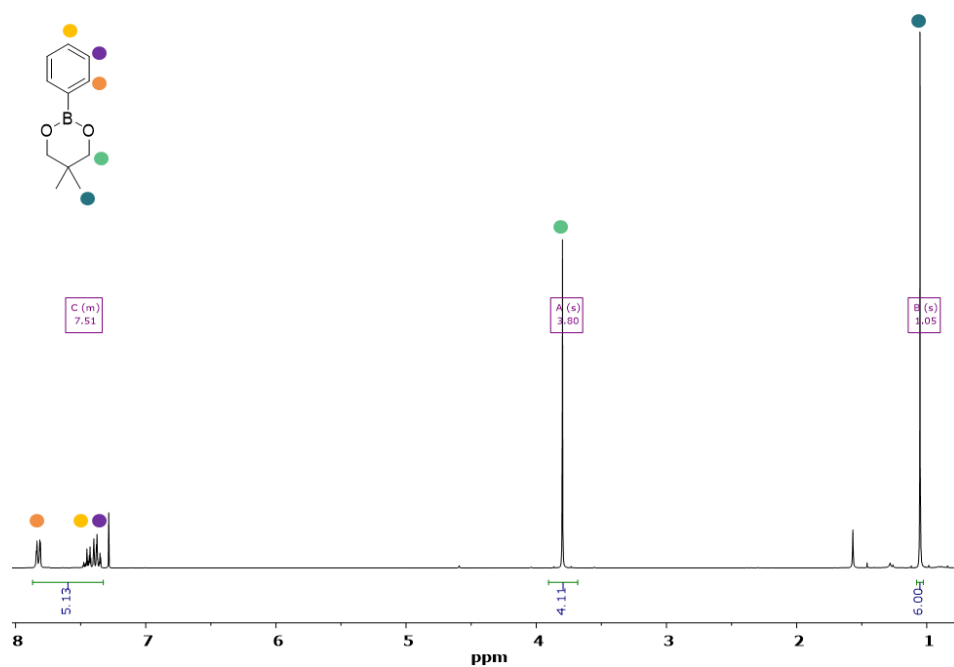
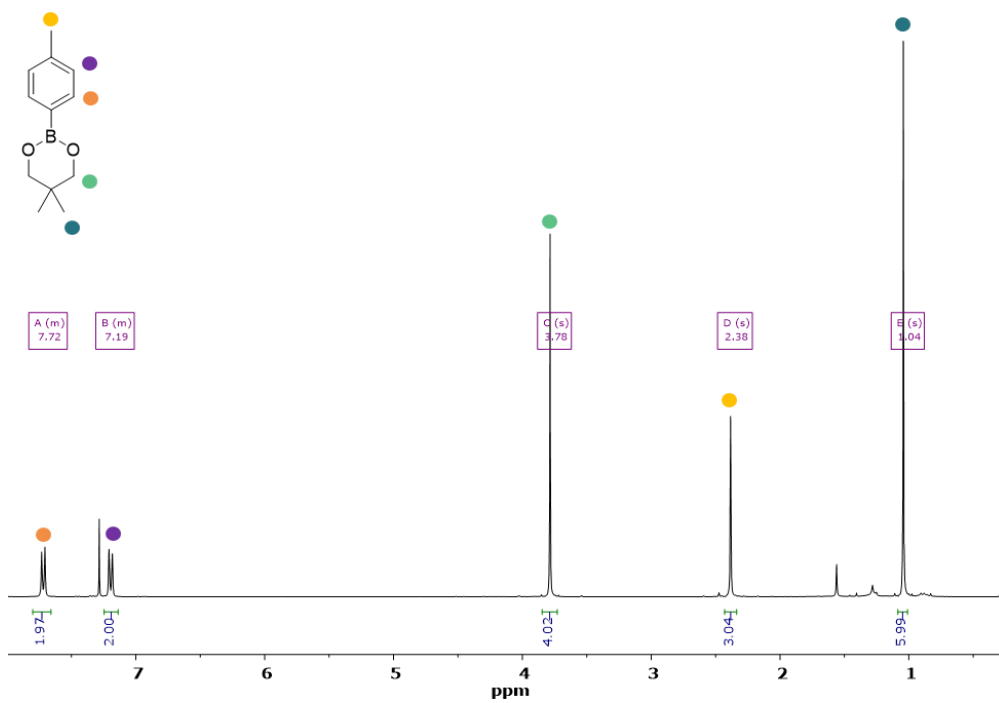
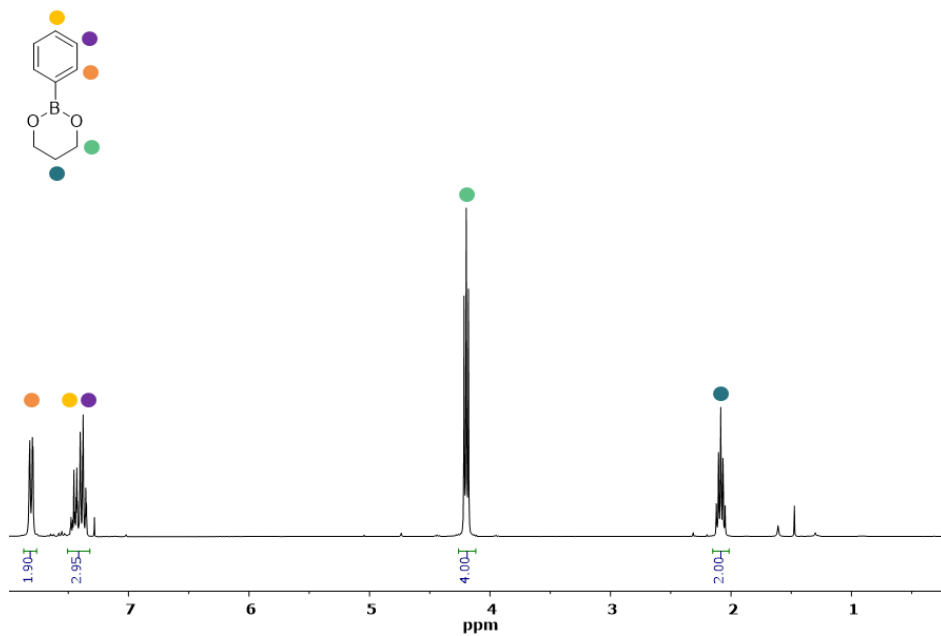


Figure S2.2: ¹H NMR of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (B2) in CDCl₃.



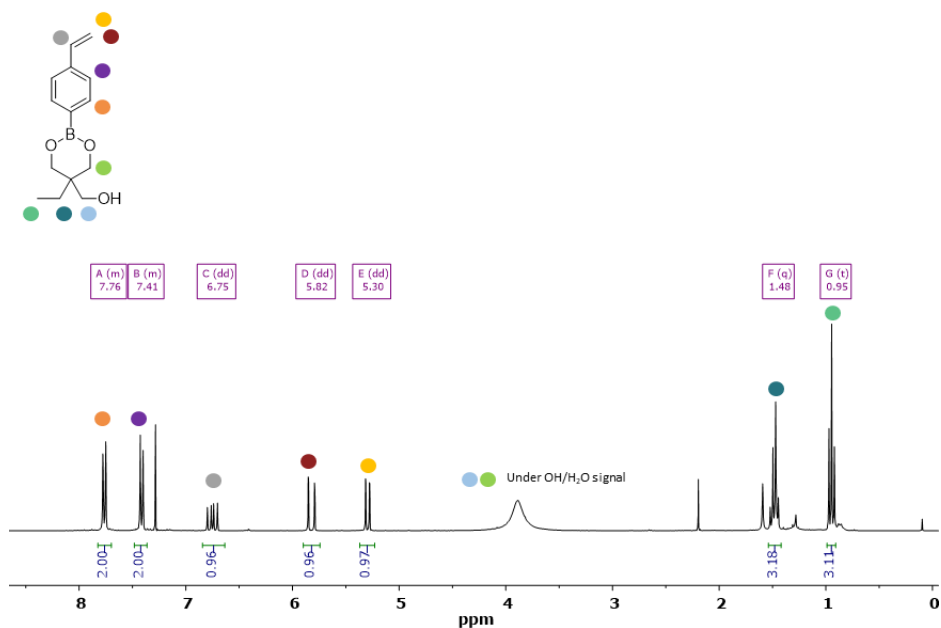


Figure S2.5: ¹H NMR of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methanol (B5) in CDCl₃

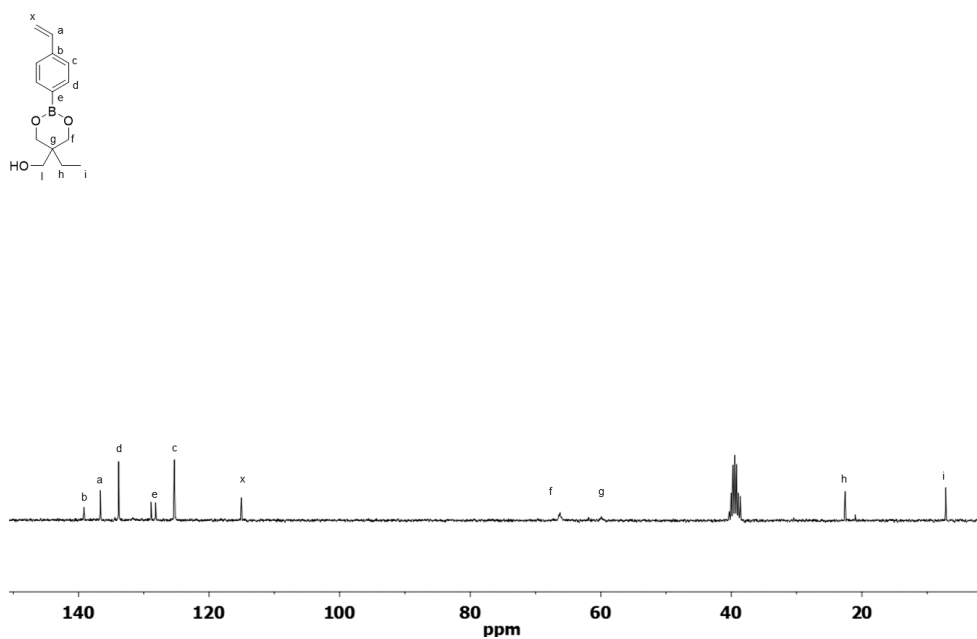


Figure S2.6: ¹³C NMR of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methanol (B5) in DMSO-d₆

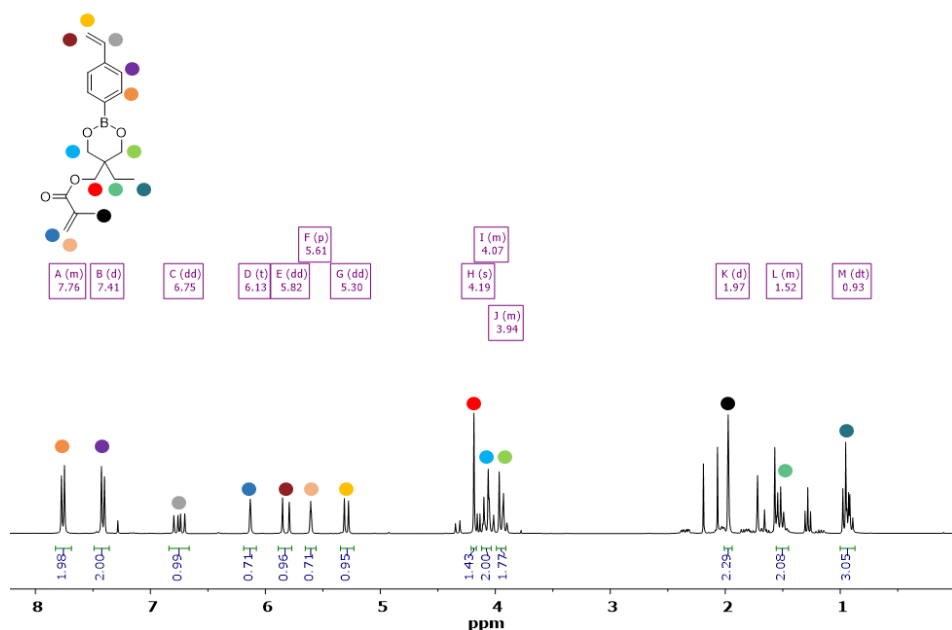


Figure S2.7: ^1H NMR of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methyl methacrylate (B6) in CDCl_3

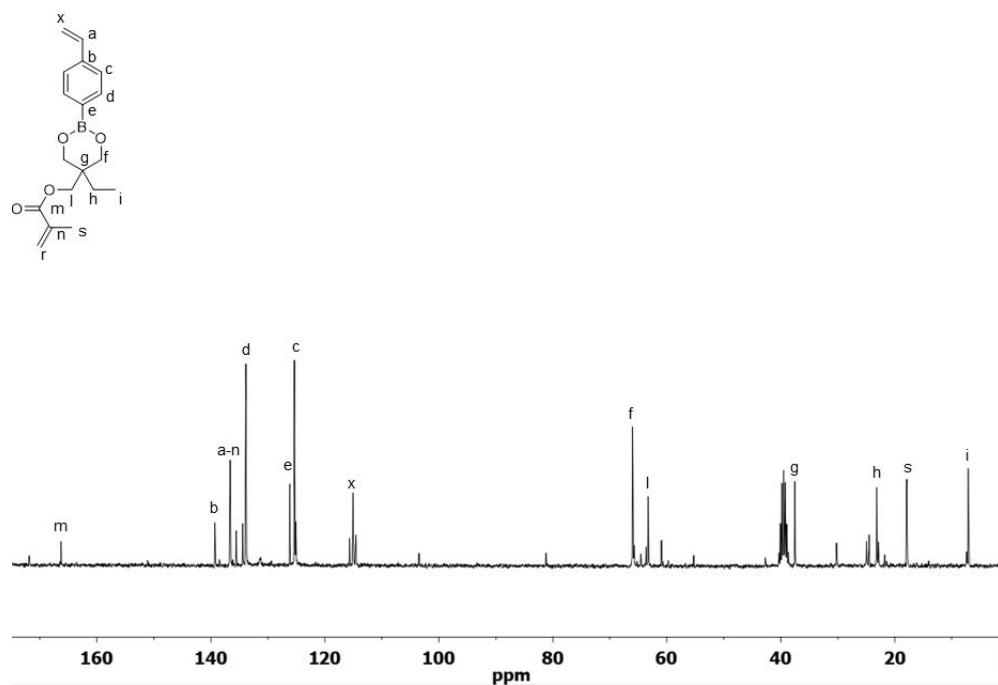


Figure S2.8: ^{13}C NMR of (5-ethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinan-5-yl)methyl methacrylate (B6) in DMSO-d_6

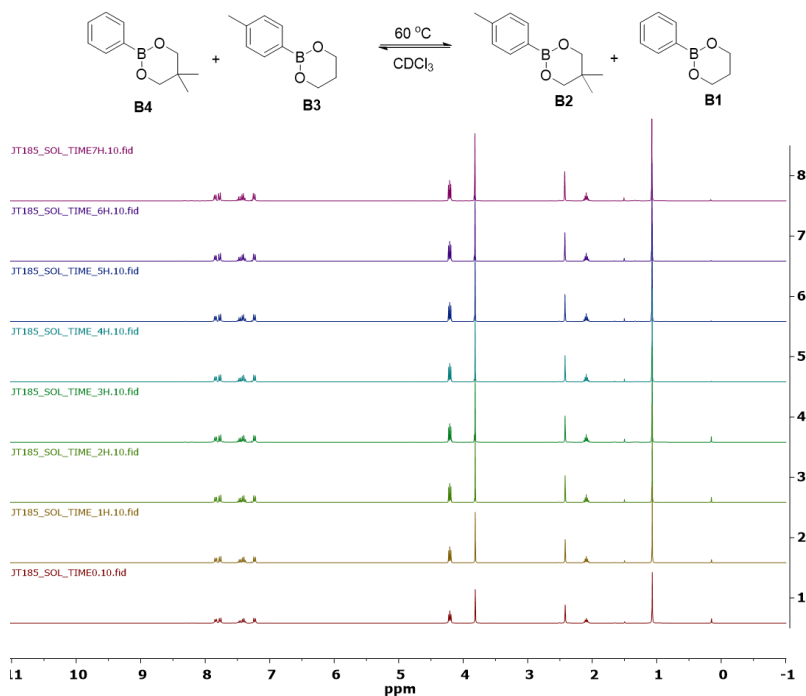


Fig. S2.9: Time-dependent ^1H NMR spectra of the reaction mixture of B4 and B3 in CDCl_3 at 60°C

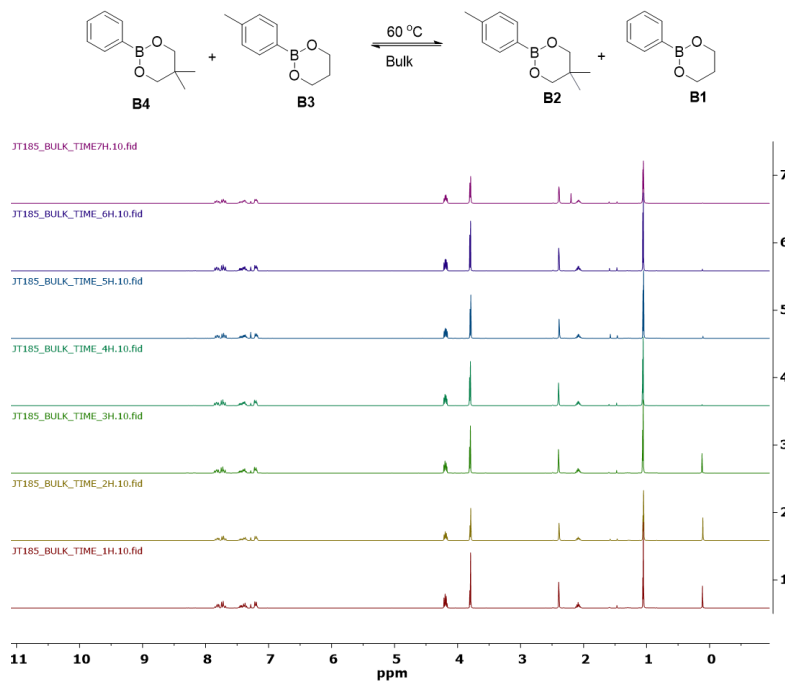


Fig. S2.10: Time-dependent ^1H NMR spectra of the reaction mixture of B4 and B3 in bulk at 60°C

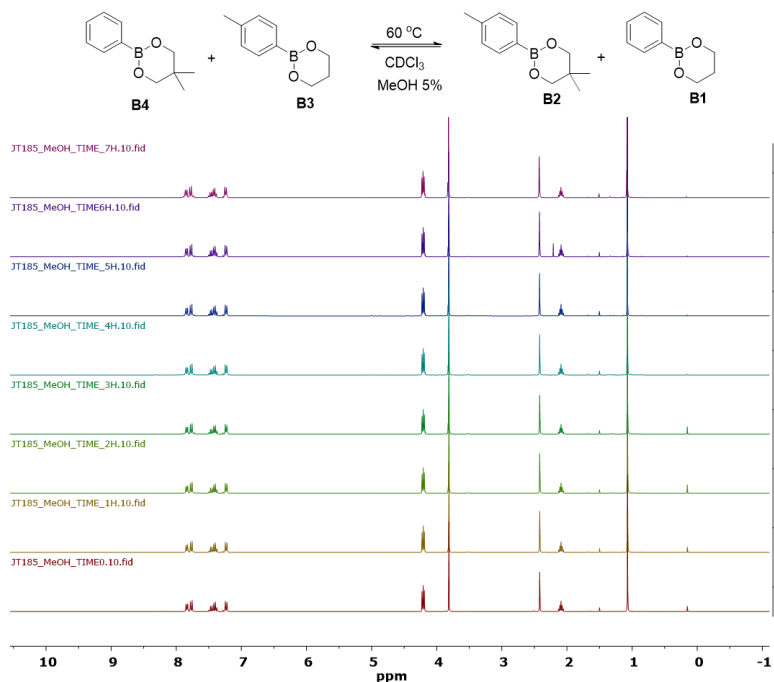


Fig. S2.11: Time-dependent ¹H NMR spectra of the reaction mixture of B4 and B3 with 5 mol% of MeOH in CDCl₃ at 60 °C

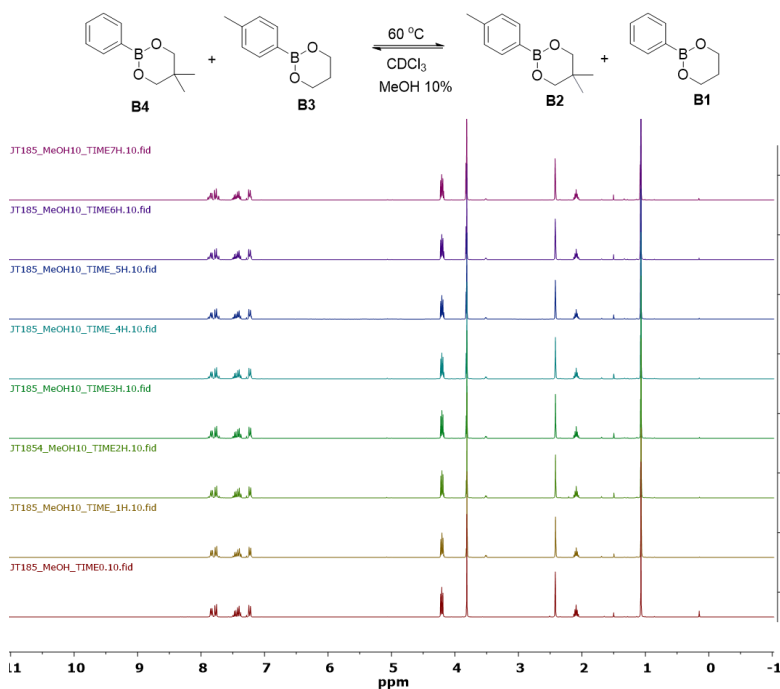


Fig. S2.12: Time-dependent ¹H NMR spectra of the reaction mixture of B4 and B3 with 10 mol% of MeOH in CDCl₃ at 60 °C

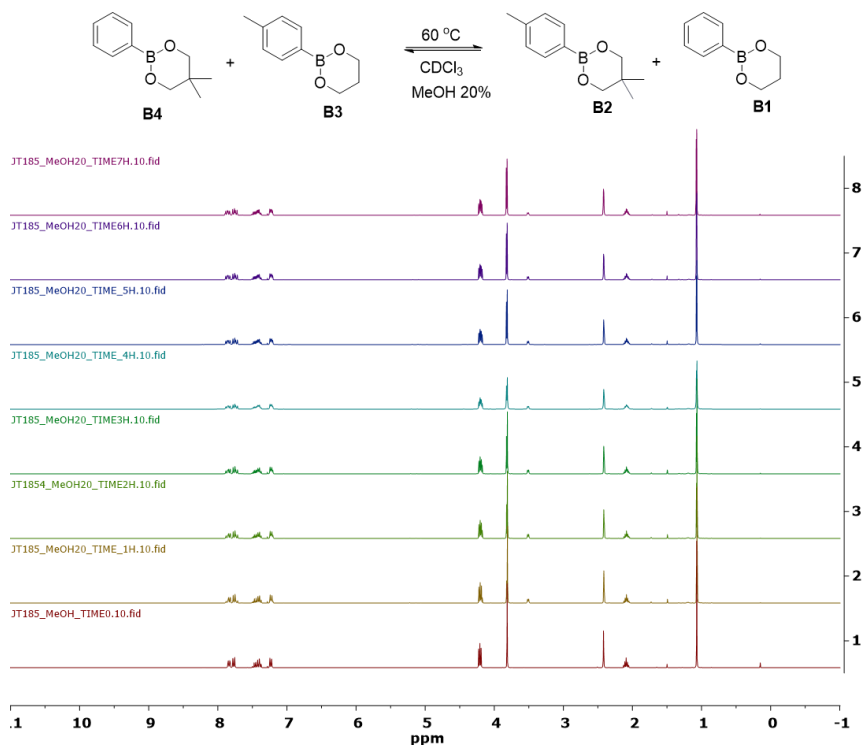


Fig. S2.13: Time-dependent ¹H NMR spectra of the reaction mixture of **B4** and **B3** with 20 mol% of MeOH in CDCl₃ at 60 °C

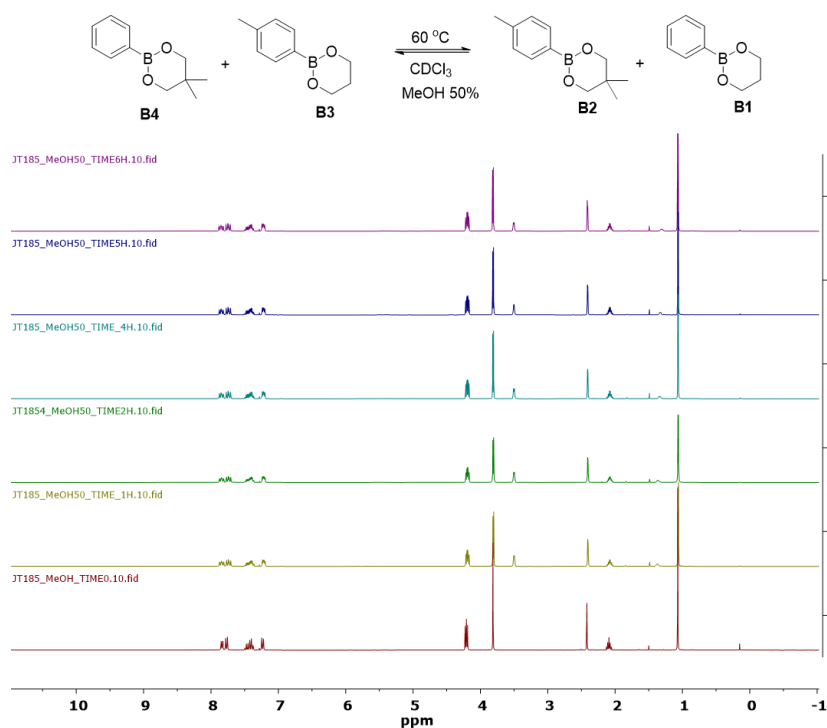


Fig. S2.14: Time-dependent ^1H NMR spectra of the reaction mixture of B4 and B3 with 50 mol% of MeOH in CDCl_3 at 60°C

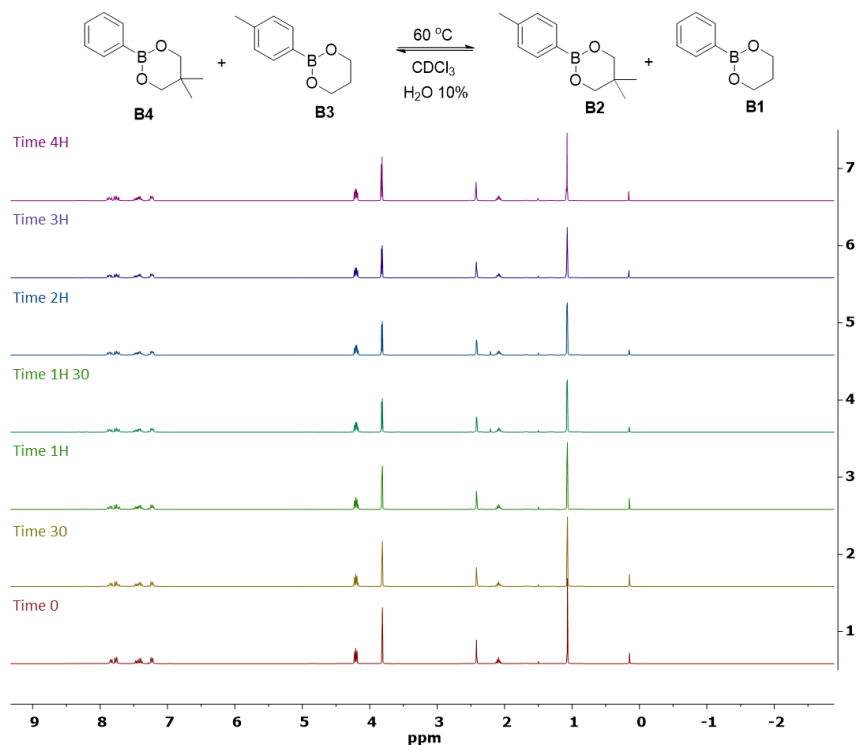


Fig. S2.15: Time-dependent ^1H NMR spectra of the reaction mixture of B4 and B3 with 10 mol% of H_2O in CDCl_3 at 60°C

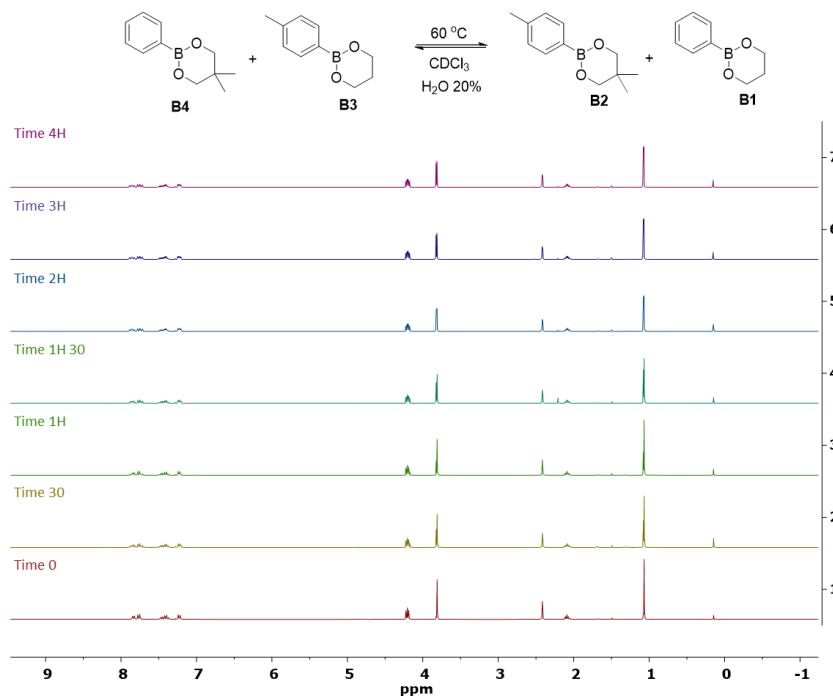


Fig. S2.16: Time-dependent ¹H NMR spectra of the reaction mixture of B4 and B3 with 20 mol% of H₂O in CDCl₃ at 60 °C

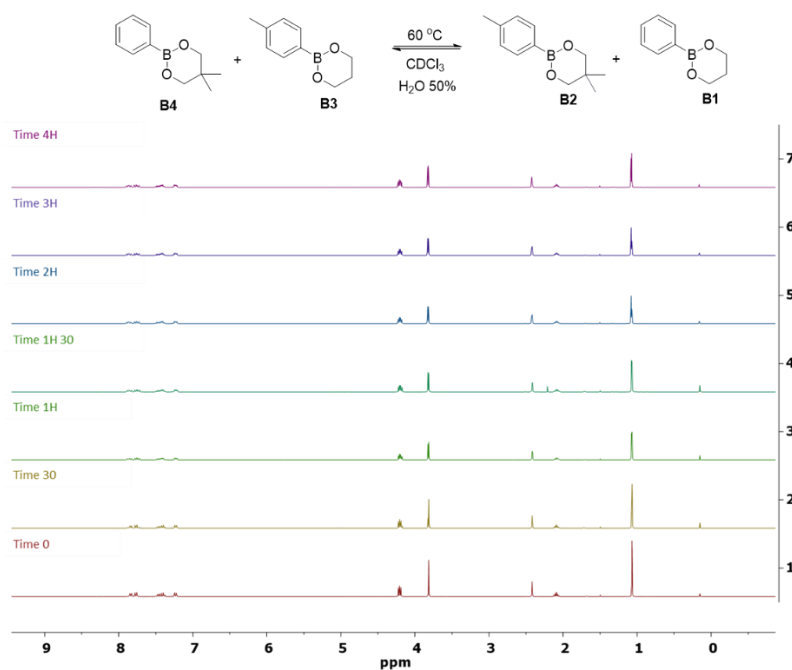


Fig. S2.17: Time-dependent ¹H NMR spectra of the reaction mixture of B4 and B3 with 50 mol% of H₂O in CDCl₃ at 60 °C

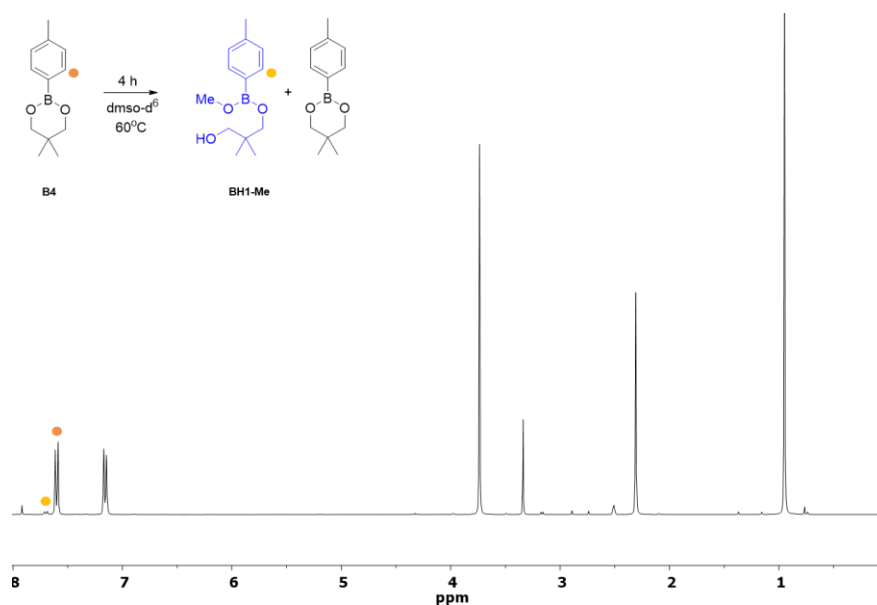


Fig. S2.18: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d₆ at 60°C.

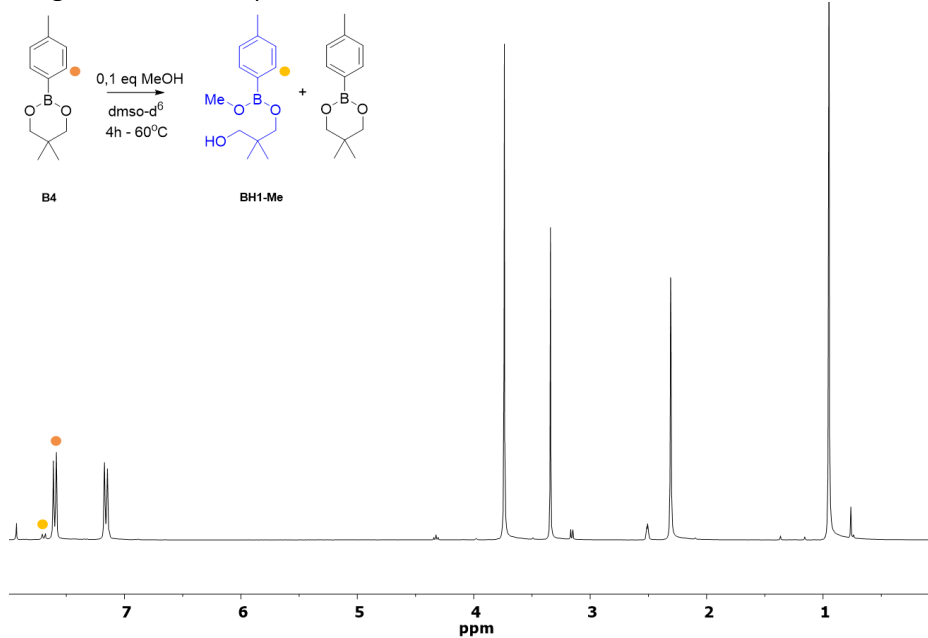


Fig. S2.19: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO -d₆ at 60°C with 0.1 equivalent of MeOH.

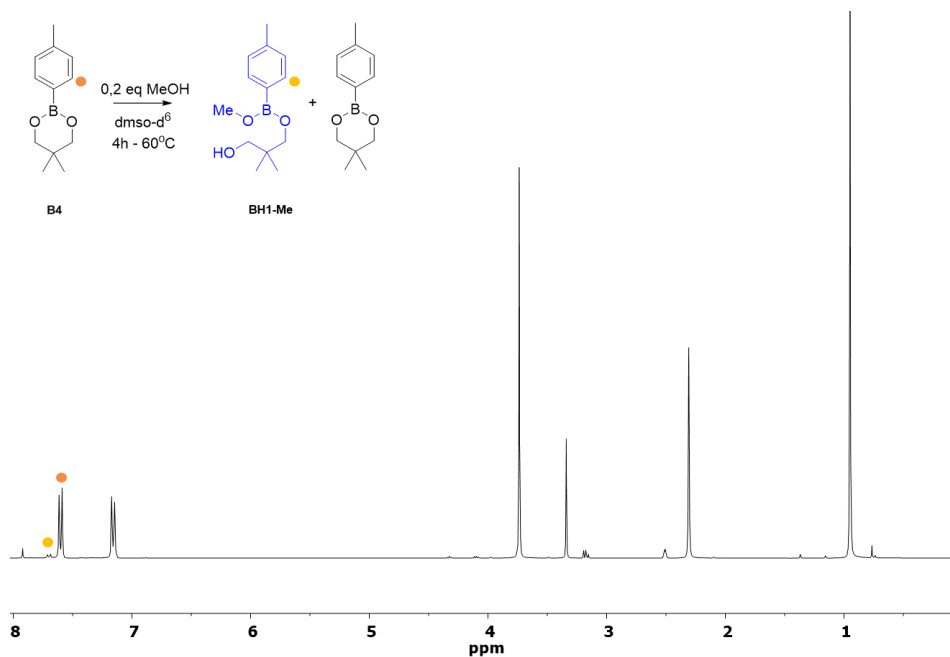


Fig. S2.20: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d₆ at 60°C with 0.2 equivalents of MeOH.

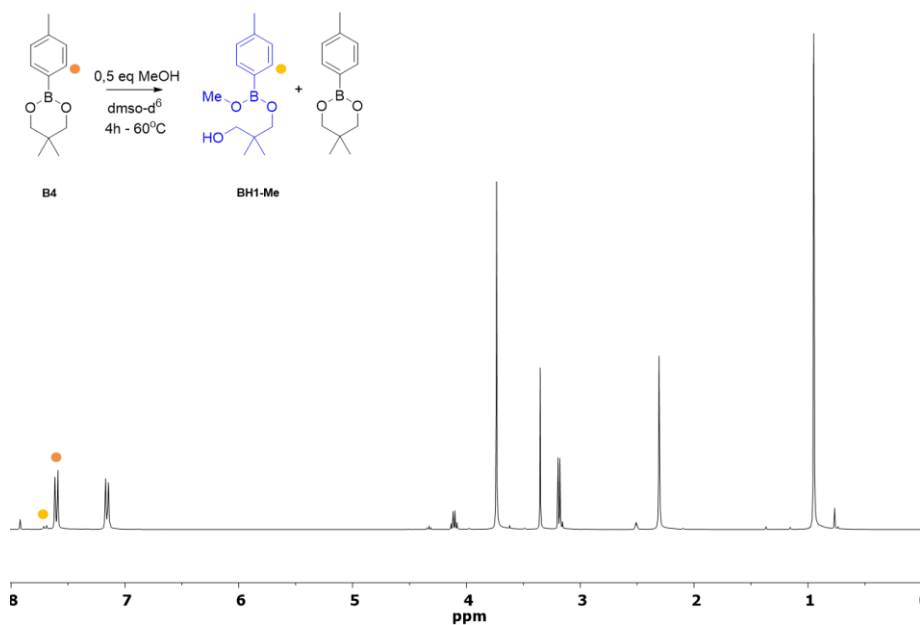


Fig. S2.21: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d₆ at 60°C with 0.5 equivalents of MeOH.

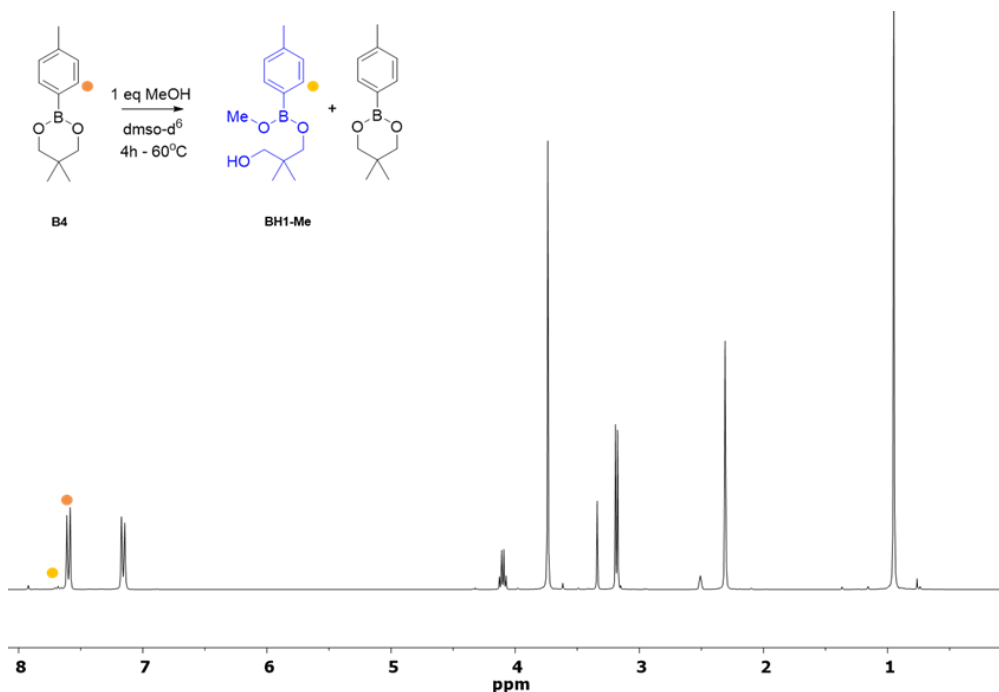


Fig. S2.22: ^1H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d_6 at 60°C with 1 equivalent of MeOH.

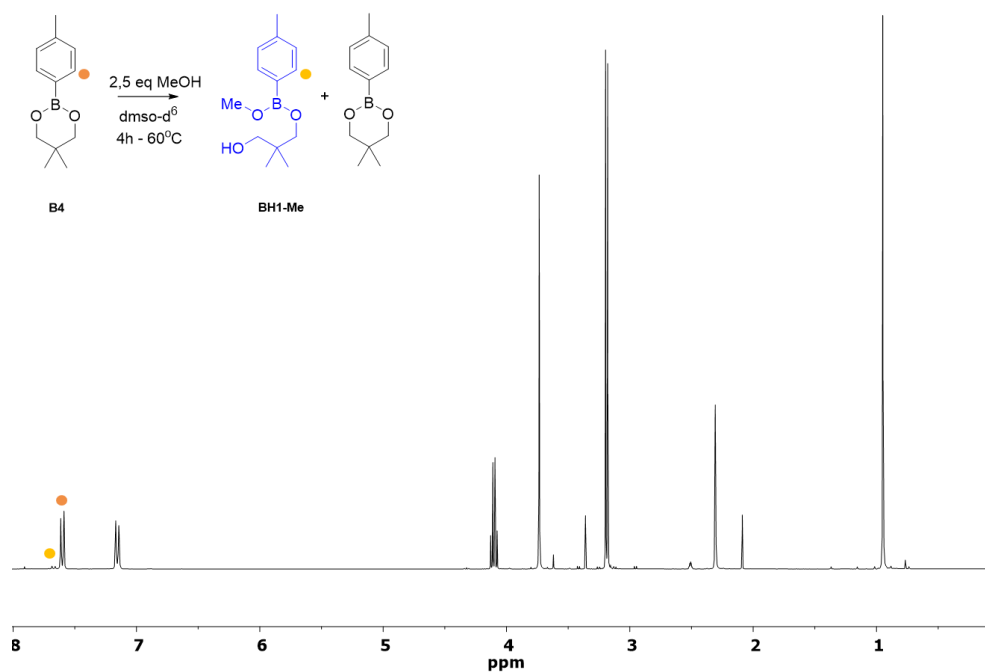


Fig. S2.23: ^1H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d_6 at 60°C with 2.5 equivalents of MeOH.

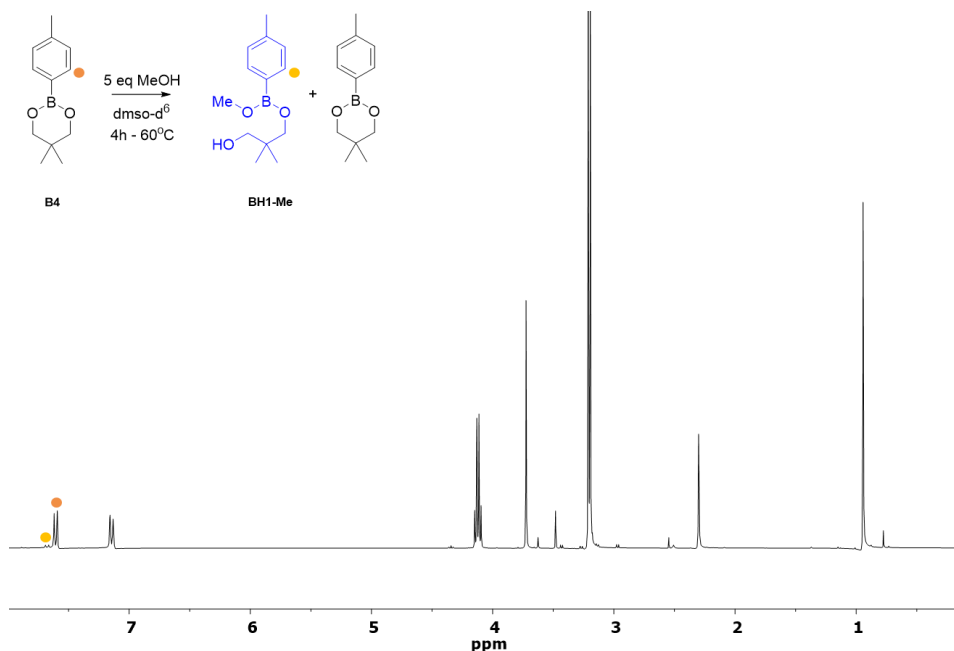


Fig. S2.24: ^1H NMR spectra of dioxaborinane **B4** after 4 hours in DMSO-d^6 at 60°C with 5 equivalents of MeOH.

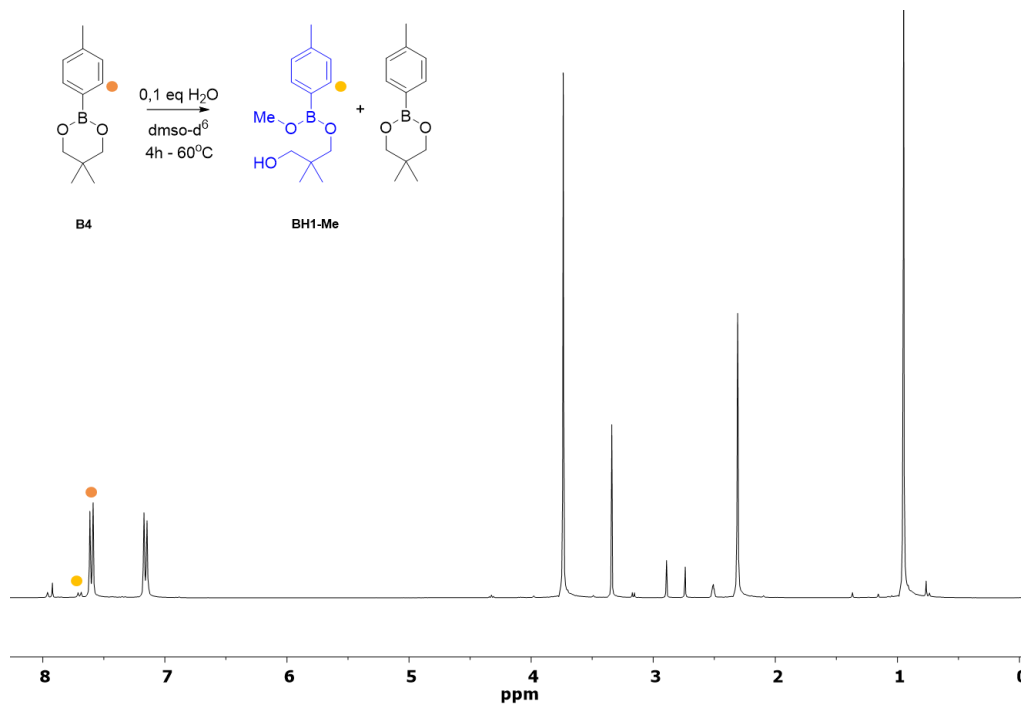


Fig. S2.25: ^1H NMR spectra of dioxaborinane **B4** after 4 hours in DMSO-d^6 at 60°C with 0.1 equivalents of H_2O .

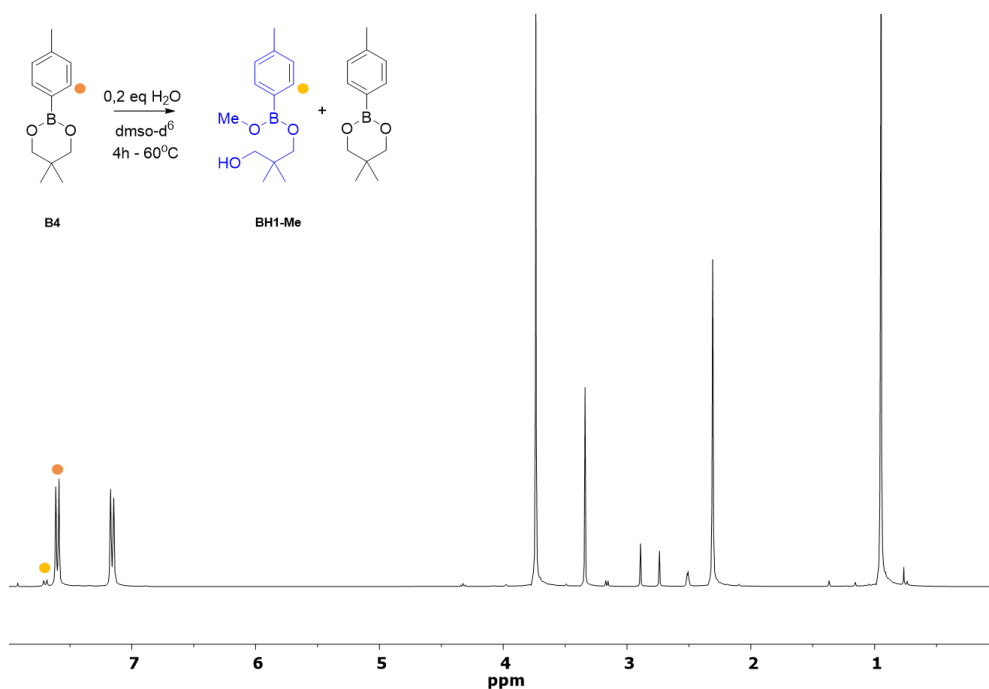


Fig. S2.26: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d₆ at 60°C with 0.2 equivalents of H₂O.

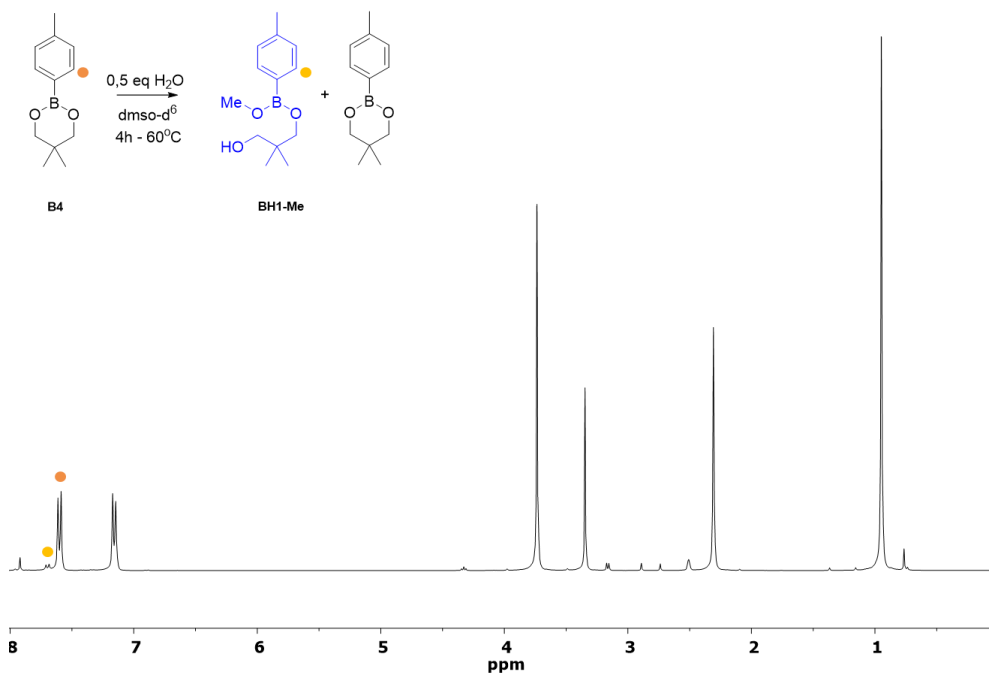


Fig. S2.27: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d₆ at 60°C with 0.5 equivalents of H₂O.

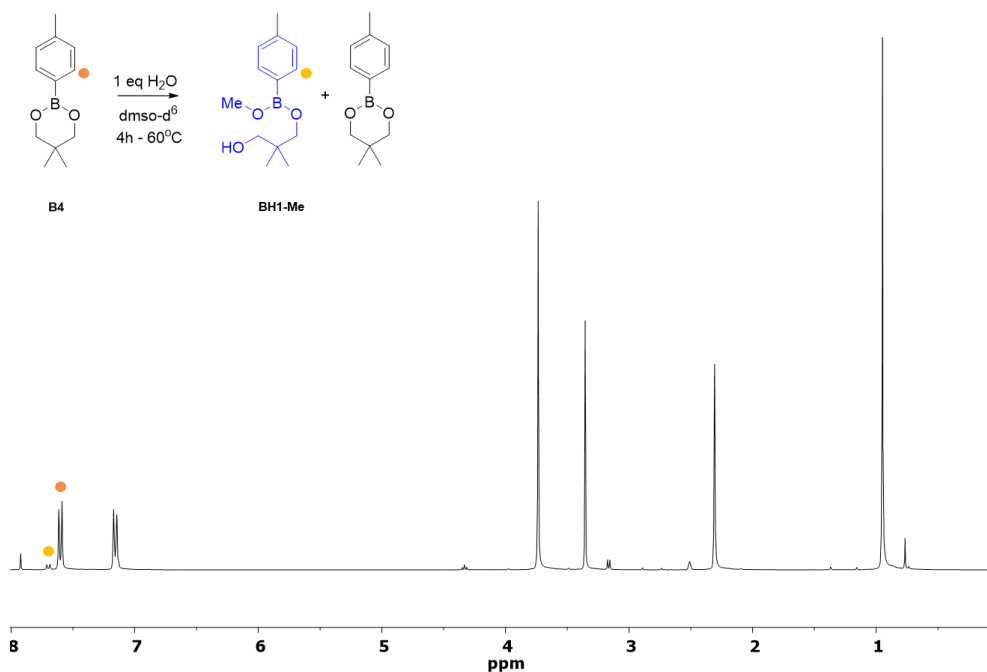


Fig. S2.28: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d⁶ at 60°C with 1 equivalent of H₂O.

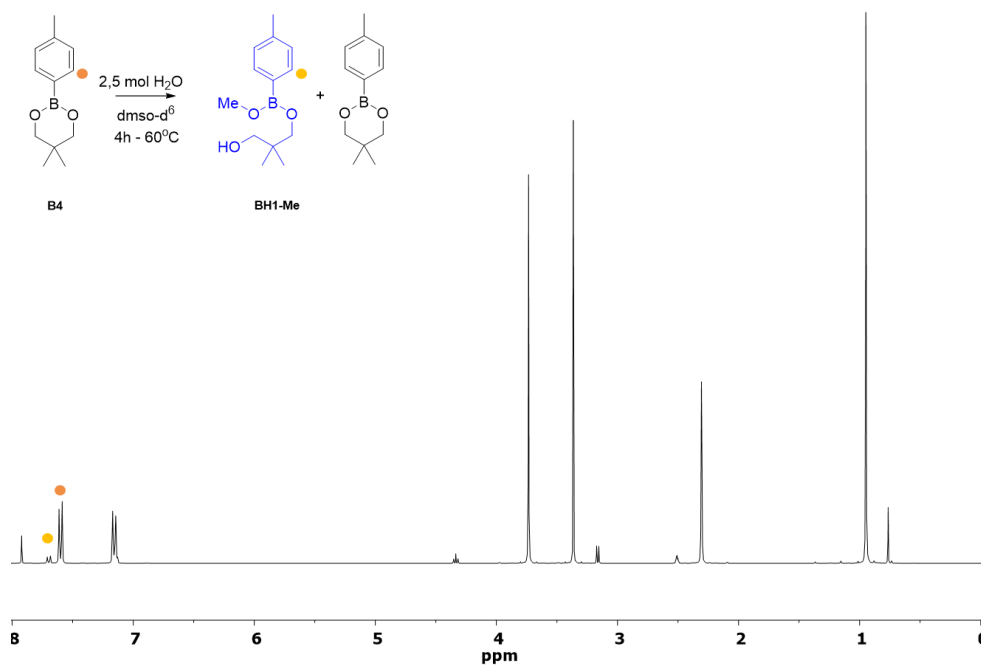


Fig. S2.29: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d⁶ at 60°C with 2.5 equivalents of H₂O.

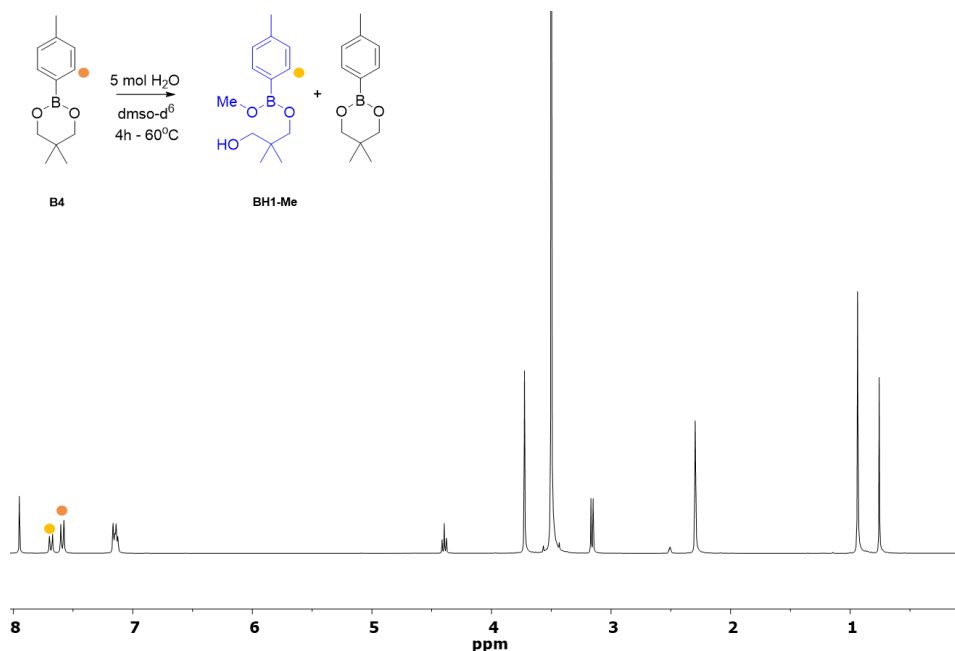


Fig. S2.30: ¹H NMR spectra of dioxaborinane B4 after 4 hours in DMSO-d₆ at 60°C with 5 equivalents of H₂O.

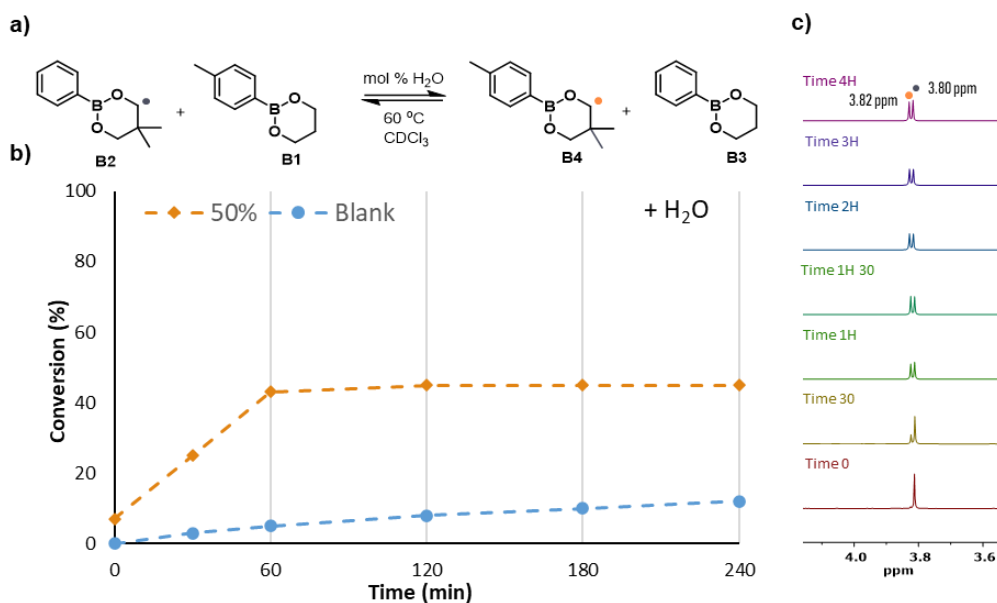


Fig. S2.31: Experimental kinetics between dioxaborinane B2 and B1 with H₂O as accelerator at 60°C. (a) Left panel b: kinetics of B2 + B1 in solution with H₂O. Right panel c: time-dependent ¹H-NMR spectra of the reaction.

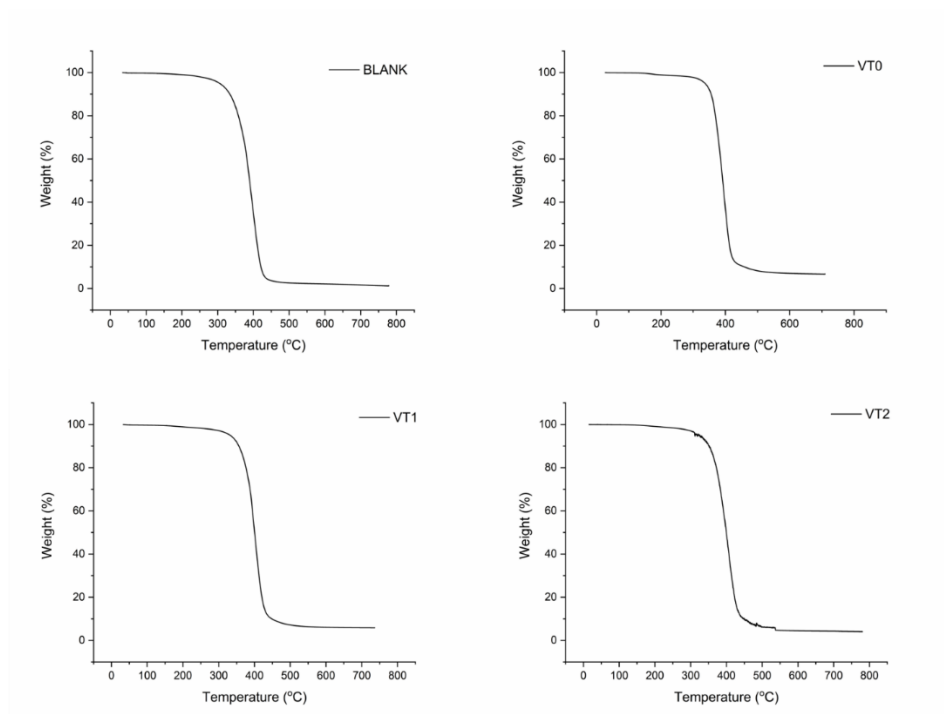


Fig. S2.32: Thermal gravimetric analyses of the vitrimer networks VT0, VT1 and VT2 and blank crosslinked network carried out under nitrogen atmosphere.

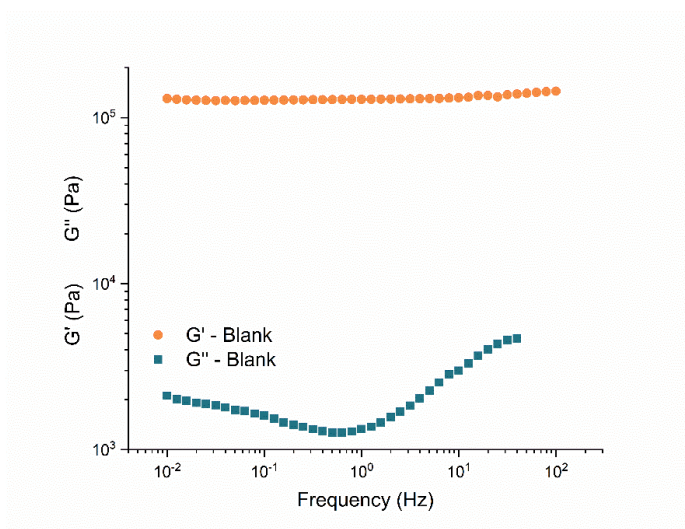


Fig. S2.33: Storage modulus and loss modulus of "blank" crosslinked network at 160 °C as a function of frequency.

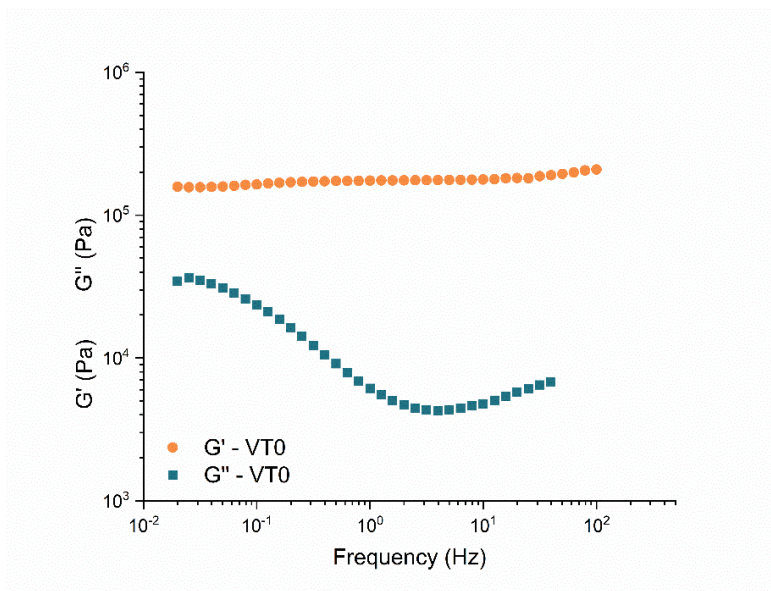


Fig. S2.34: Storage modulus and loss modulus of vitrimer VT0 at 160 °C as a function of frequency.

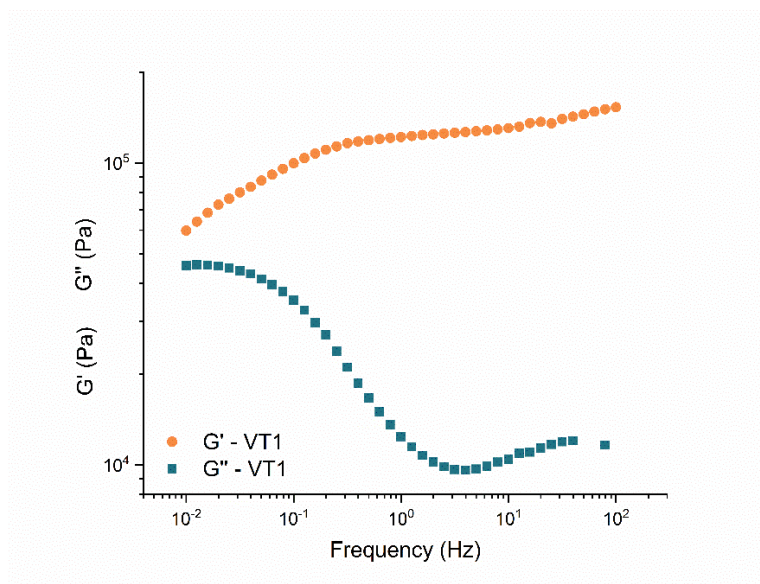


Fig. S2.35: Storage modulus and loss modulus of vitrimer VT1 at 160 °C as a function of frequency.

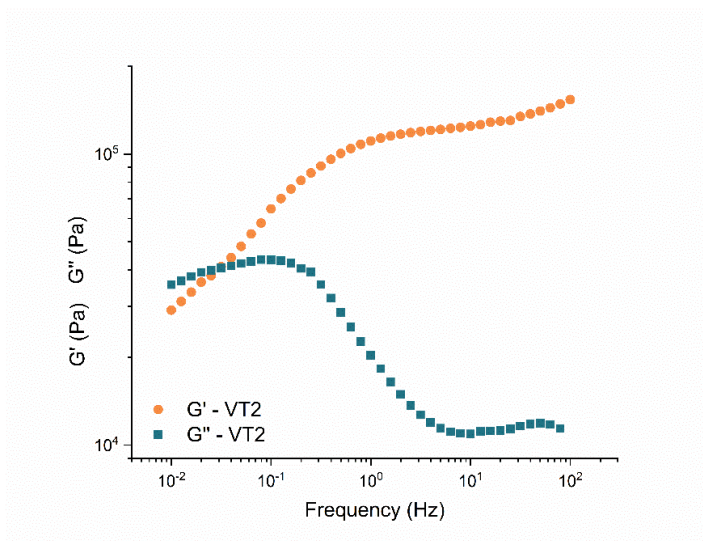


Fig. S2.36: Storage modulus and loss modulus of vitrimer VT2 at 160 °C as a function of frequency.

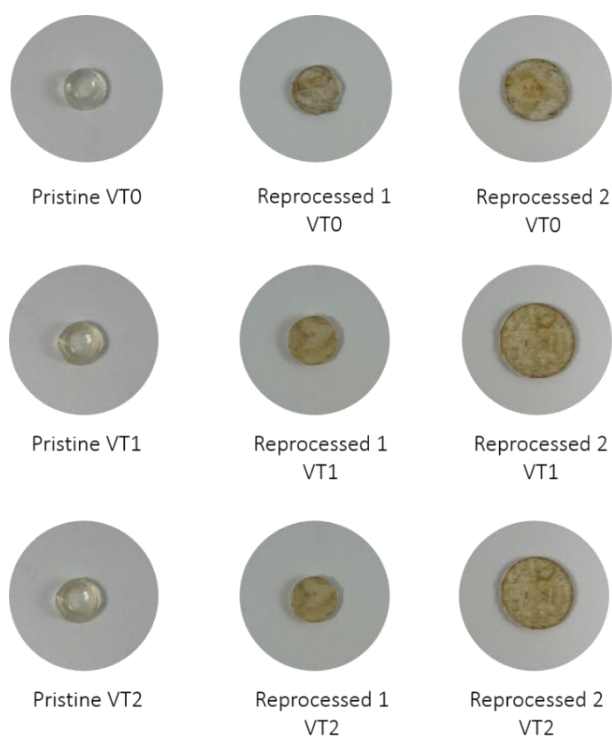


Fig. S2.37: Picture representing pristine VT0 and the reprocessed counterparts (above), pristine VT1 and the reprocessed counterparts (centre), and pristine VT2 and the reprocessed counterparts (below).



Fig. S2.38: Picture representing reprocessing trial of control crosslinked network “blank”.

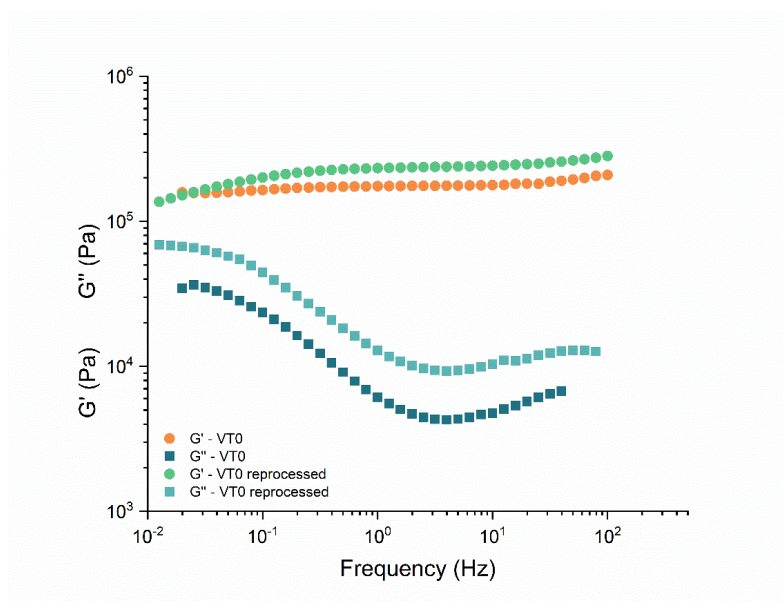


Fig. S2.39: Storage modulus and loss modulus of pristine and reprocessed vitrimer VT0 at 160 °C as a function of frequency.

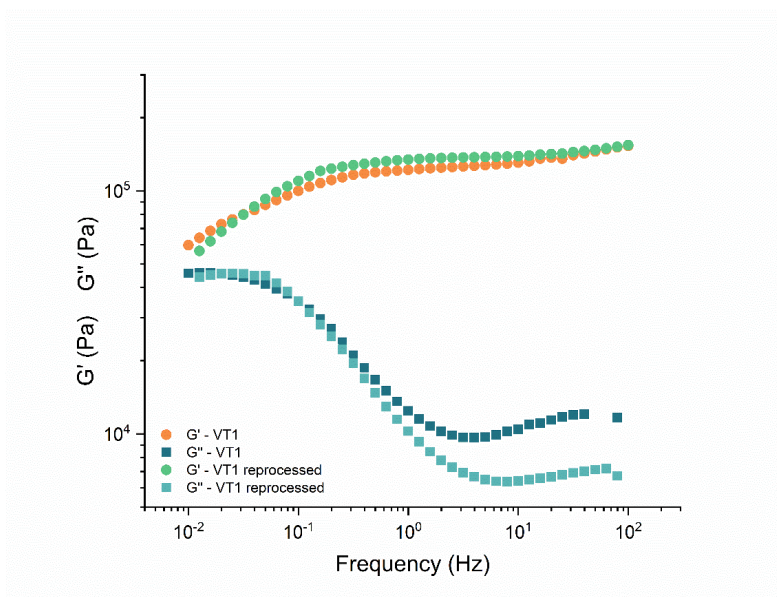


Fig. S2.40: Storage modulus and loss modulus of pristine and reprocessed vitrimer VT1 at 160 °C as a function of frequency.

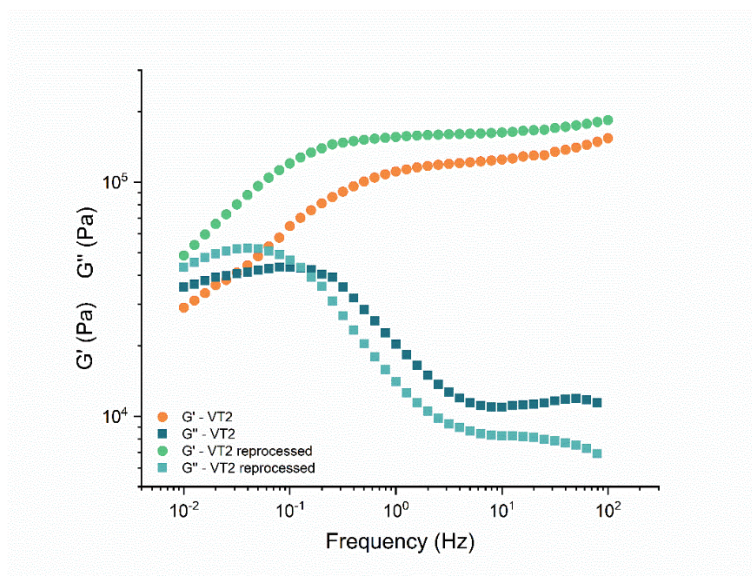


Fig. S2.41: Storage modulus and loss modulus of pristine and reprocessed vitrimer VT2 at 160 °C as a function of frequency.

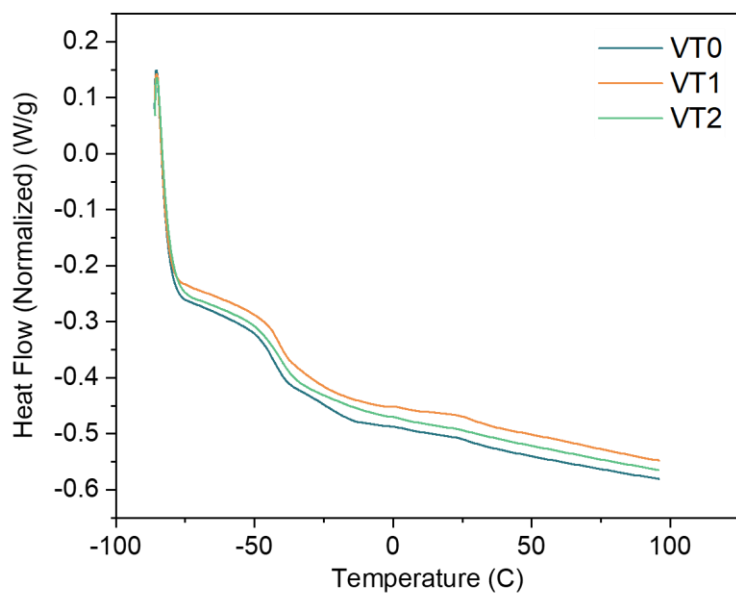


Figure S2.42: DSC analysis of the vitrimer materials VT0, VT1 and VT2

References:

1. Rowan SJ, Cantrill SJ, Cousins GRL, Sanders JKM, Stoddart JF. Dynamic Covalent Chemistry. *Angew Chem Int Ed*. 2002;41(6):898-952. doi:10.1002/1521-3773(20020315)41:6<898::AID-ANIE898>3.0.CO;2-E
2. Adzima BJ, Aguirre HA, Kloxin CJ, Scott TF, Bowman CN. Rheological and Chemical Analysis of Reverse Gelation in a Covalently Cross-Linked Diels–Alder Polymer Network. *Macromolecules*. 2008;41(23):9112-9117. doi:10.1021/ma801863d
3. Zou W, Dong J, Luo Y, Zhao Q, Xie T. Dynamic Covalent Polymer Networks: from Old Chemistry to Modern Day Innovations. *Adv Mater*. 2017;29(14):1606100. doi:10.1002/adma.201606100
4. Huang S, Kong X, Xiong Y, et al. An overview of dynamic covalent bonds in polymer material and their applications. *European Polymer Journal*. 2020;141:110094. doi:10.1016/j.eurpolymj.2020.110094
5. Zhang ZP, Rong MZ, Zhang MQ. Polymer engineering based on reversible covalent chemistry: A promising innovative pathway towards new materials and new functionalities. *Progress in Polymer Science*. 2018;80:39-93. doi:10.1016/j.progpolymsci.2018.03.002
6. Brooks WLA, Sumerlin BS. Synthesis and Applications of Boronic Acid-Containing Polymers: From Materials to Medicine. *Chem Rev*. 2016;116(3):1375-1397. doi:10.1021/acs.chemrev.5b00300
7. Gosecki M, Gosecka M. Boronic Acid Esters and Anhydrates as Dynamic Cross-Links in Vitrimers. *Polymers*. 2022;14(4):842. doi:10.3390/polym14040842
8. Winne JM, Leibler L, Du Prez FE. Dynamic covalent chemistry in polymer networks: a mechanistic perspective. *Polym Chem*. 2019;10(45):6091-6108. doi:10.1039/C9PY01260E
9. HALL DG. *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*. John Wiley & Sons; 2006.
10. Röttger M, Domenech T, Van Der Weegen R, Breuillac A, Nicolaÿ R, Leibler L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science*. 2017;356(6333):62-65. doi:10.1126/science.aah5281
11. Bapat AP, Roy D, Ray JG, Savin DA, Sumerlin BS. Dynamic-Covalent Macromolecular Stars with Boronic Ester Linkages. *J Am Chem Soc*. 2011;133(49):19832-19838. doi:10.1021/ja207005z

12. Jäkle F. Advances in the Synthesis of Organoborane Polymers for Optical, Electronic, and Sensory Applications. *Chem Rev.* 2010;110(7):3985-4022. doi:10.1021/cr100026f
13. Fujita N, Shinkai S, James TD. Boronic Acids in Molecular Self-Assembly. *Chem Asian J.* 2008;3(7):1076-1091. doi:10.1002/asia.200800069
14. Niu W, O'Sullivan C, Rambo BM, Smith MD, Lavigne JJ. Self-repairing polymers: poly(dioxaborolane)s containing trigonal planar boron. *Chem Commun.* 2005;(34):4342. doi:10.1039/b504634c
15. James TD, Sandanayake KRAS, Shinkai S. Saccharide Sensing with Molecular Receptors Based on Boronic Acid. *Angew Chem Int Ed Engl.* 1996;35(17):1910-1922. doi:10.1002/anie.199619101
16. He L, Fullenkamp DE, Rivera JG, Messersmith PB. pH responsive self-healing hydrogels formed by boronate–catechol complexation. *Chem Commun.* 2011;47(26):7497. doi:10.1039/c1cc11928a
17. Cash JJ, Kubo T, Bapat AP, Sumerlin BS. Room-Temperature Self-Healing Polymers Based on Dynamic-Covalent Boronic Esters. *Macromolecules.* 2015;48(7):2098-2106. doi:10.1021/acs.macromol.5b00210
18. Cash JJ, Kubo T, Dobbins DJ, Sumerlin BS. Maximizing the symbiosis of static and dynamic bonds in self-healing boronic ester networks. *Polym Chem.* 2018;9(15):2011-2020. doi:10.1039/C8PY00123E
19. Caffy F, Nicolaÿ R. Transformation of polyethylene into a vitrimer by nitroxide radical coupling of a bis-dioxaborolane. *Polym Chem.* 2019;10(23):3107-3115. doi:10.1039/C9PY00253G
20. Chen Y, Tang Z, Liu Y, Wu S, Guo B. Mechanically Robust, Self-Healable, and Reprocessable Elastomers Enabled by Dynamic Dual Cross-Links. *Macromolecules.* 2019;52(10):3805-3812. doi:10.1021/acs.macromol.9b00419
21. Chen Y, Tang Z, Zhang X, Liu Y, Wu S, Guo B. Covalently Cross-Linked Elastomers with Self-Healing and Malleable Abilities Enabled by Boronic Ester Bonds. *ACS Appl Mater Interfaces.* 2018;10(28):24224-24231. doi:10.1021/acsami.8b09863
22. Breuillac A, Kassalias A, Nicolaÿ R. Polybutadiene Vitrimers Based on Dioxaborolane Chemistry and Dual Networks with Static and Dynamic Cross-links. *Macromolecules.* 2019;52(18):7102-7113. doi:10.1021/acs.macromol.9b01288

23. Brunet J, Collas F, Humbert M, et al. High Glass-Transition Temperature Polymer Networks Harnessing the Dynamic Ring Opening of Pinacol Boronates. *Angew Chem Int Ed*. 2019;58(35):12216-12222. doi:10.1002/anie.201904559
24. Yang Y, Du FS, Li ZC. Thermally healable and reprocessable polymethacrylate networks based on diol-mediated metathesis of 6-membered boronic esters. *Polym Chem*. 2020;11(11):1860-1870. doi:10.1039/C9PY01546A
25. Dastbaravardeh N, Schnürch M, Mihovilovic MD. Ruthenium(0)-Catalyzed sp^3 C–H Bond Arylation of Benzylic Amines Using Arylboronates. *Org Lett*. 2012;14(7):1930-1933. doi:10.1021/ol300627p
26. Schoonbrood HAS, Van Den Reijen B, De Kock JBL, Manders BG, Van Herk AM, German AL. Pulsed laser terpolymerization of styrene, methyl methacrylate and methyl acrylate. *Macromol Rapid Commun*. 1995;16(2):119-124. doi:10.1002/marc.1995.030160204
27. Kazemi N, Duever TA, Penlidis A. Demystifying the estimation of reactivity ratios for terpolymerization systems. *AIChE Journal*. 2014;60(5):1752-1766. doi:10.1002/aic.14439
28. Chai JD, Head-Gordon M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys Chem Chem Phys*. 2008;10(44):6615. doi:10.1039/b810189b
29. Krishnan R, Binkley JS, Seeger R, Pople JA. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *The Journal of Chemical Physics*. 1980;72(1):650-654. doi:10.1063/1.438955
30. Hehre WJ, Ditchfield R, Pople JA. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *The Journal of Chemical Physics*. 1972;56(5):2257-2261. doi:10.1063/1.1677527
31. Frisch MJ, Trucks GW, Schlegel GE, et al. Gaussian 16 Revision C.01, gaussian Inc, Wallingford CT2016.
32. Siopa F, Ramis Cladera VA, Afonso CAM, Oble J, Poli G. Ruthenium-Catalyzed C–H Arylation and Alkenylation of Furfural Imines with Boronates: Ruthenium-Catalyzed C–H Arylation and Alkenylation of Furfural Imines with Boronates. *Eur J Org Chem*. 2018;2018(44):6101-6106. doi:10.1002/ejoc.201800767
33. Tailor SB, Manzotti M, Smith GJ, Davis SA, Bedford RB. Cobalt-Catalyzed Coupling of Aryl Chlorides with Aryl Boron Esters Activated by Alkoxides. *ACS Catal*. 2021;11(7):3856-3866. doi:10.1021/acscatal.0c05557

Chapter 3

Introduction of a 9-Bromo-9-Borafluorene scaffold into deep blue emitting π -conjugated polymers

3.1 Introduction

Following the study of the metathesis of the boronic esters, this chapter extends the study of boron chemistry, focusing on exploiting the Lewis acidity of boron to introduce a novel dynamic exchange mechanism, based on Lewis Pairs, in π -conjugated aromatic polymers (π CAPs). Over recent decades, these polymers have emerged as one of the fastest-growing areas in materials science, driven by their potential applications in various domains such as sensory materials,^{1–3} transistors,⁴ display technology,^{5,6} and solar cells.^{7–9}

Specifically, an area where significant research efforts have been focused is the functionalization of organic conjugated polymers with main group elements.^{10–12} For example, recent research has extensively explored the incorporation of silicon, particularly in the form of silafluorene units, into π -conjugated systems, with a focus on investigating their optical properties.¹³ The integration of these compounds into polyfluorenes has enabled the development of high-efficiency, spectrum-stable blue light-emitting polymers.^{14,15} Additionally, due to their efficient and stable blue electroluminescence, these materials have found use in a variety of applications, including novel classes of high-energy gap light-emitting polymers,¹⁶ copolymers with potential as blue OLED emissive materials, and organic field-effect transistors (OFETs).¹⁷ Another main group element that has garnered significant attention for its incorporation into π -conjugated polymers is boron.¹⁸ These materials, known as p - π^* conjugated polymers, arise from the interaction between the boron p -orbital, which is inherently electron-deficient and a strong π -acceptor, and the adjacent π^* -orbital.^{19,20} They represent an appealing class of novel materials with a wide range of potential applications, including light-emitting diodes (LEDs), non-linear optical materials, and sensors for detecting small Lewis bases.^{21–24}

However, the introduction of tricoordinate boron-containing scaffolds into conjugated polymers while maintaining precise control over the polymer's molecular weight remains challenging.^{3,25} The presence of the empty p-orbital tends to make boranes prone to react with Lewis bases, which can lead to hydrolytic or oxidative degradation.²² Consequently, electron-deficient yet robust conjugated polymers with tricoordinate boron in the main chain remain rare. Recent advancements have reported various synthetic methods to incorporate tricoordinate organoborane moieties into conjugated polymers, including (i) hydroboration, (ii) Si/B or Sn/B exchange protocols, and (iii) direct polymerization of suitable organoboron building blocks (Figure 3.1, panel a, b, and c). Hydroboration was first introduced by the pioneering work of Chujo and co-workers and is a versatile synthetic method for incorporating tricoordinate boron into π -conjugated polymers.^{26–28} Si/B or Sn/B exchanges, explored mainly by Jakle and co-workers, introduce tricoordinate boron as a linker between monomeric units or as a pendant group in the polymer chain.^{2,29–32} Direct polymerization of suitable organoboron building blocks involves adding bulky substituents to protect the tricoordinate boron from Lewis bases but also enables its integration within polycyclic aromatic hydrocarbons (PAHs) in the π -conjugated polymer system.^{33–35} 9-Borafluorene, an organoboron scaffold of particular interest due to its significantly reduced HOMO and LUMO levels upon polymerization, was synthesized into its corresponding homopolymer via Yamamoto coupling. This was achieved by shielding the tricoordinate boron with a bulky substituent (Figure 3.1, panel d).³⁶

Due to stability issues, tricoordinate boranes typically require bulky aryl substituents for kinetic protection: less bulky triarylboranes decompose through hydrolysis, necessitating the use of stabilizing groups like 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tip), 2,4,6-tri-tert-butylphenyl (Mes*), and

2,4,6-tris(trifluoromethyl)phenyl (^FMes).³ These bulky groups, while enhancing chemical stability, reduce atom economy and hinder strong intermolecular interactions, which is unfavorable for developing high electron mobility n-type semiconductors.^{37–39} They might also inhibit strong interactions when using boron as a Lewis acid for potential Lewis pair interactions in a dynamic network resulting in frustrated Lewis pairs (FLPs).^{34,40,41} Introducing tricoordinate boron atoms without bulky substituents into polymers is challenging due to their poor stability,²² with only a few examples in the literature, primarily as linkers in π -conjugated copolymers.^{2,28} Notably, doped polycyclic aromatic hydrocarbons (PAHs) comprising tricoordinate boron without bulky substituents have not yet been incorporated into polymers. Doping standard PAHs with boron introduces a vacant orbital that can modify the HOMO-LUMO energy gaps, enhancing their potential utility in various electronic devices and transforming them into Lewis acids.^{42,43} The introduction of a new tricoordinate boron-doped (PAH) into a polymer, where boron is not shielded by bulky substituents, paves the way for potential new applications and chemistries, including post-functionalization and the development of novel Lewis acids.⁴⁴

This study aims to synthesize and characterize a π -conjugated copolymer by incorporating 9-bromo-9-borafluorene into a polymer framework of 9,9-silafluorene and 9,9-dioctylfluorene through a Si-B exchange reaction (Figure 3.1, panel e). A comprehensive computational analysis is undertaken to explore the optical properties of the copolymer, including HOMO and LUMO energy levels and involved electronic transitions. The study also seeks to characterize the interaction energies between 9-bromo-9-borafluorene and various Lewis bases, examining these interactions as a potential platform for developing dynamic networks. Experimentally, 4,4'-bipyridine is employed to test the feasibility of establishing Lewis pair interactions in this boron-containing polymer, with the

broader objective of creating materials with tunable optical, electronic, and dynamic properties, opening new pathways in the design of responsive and functional polymers.

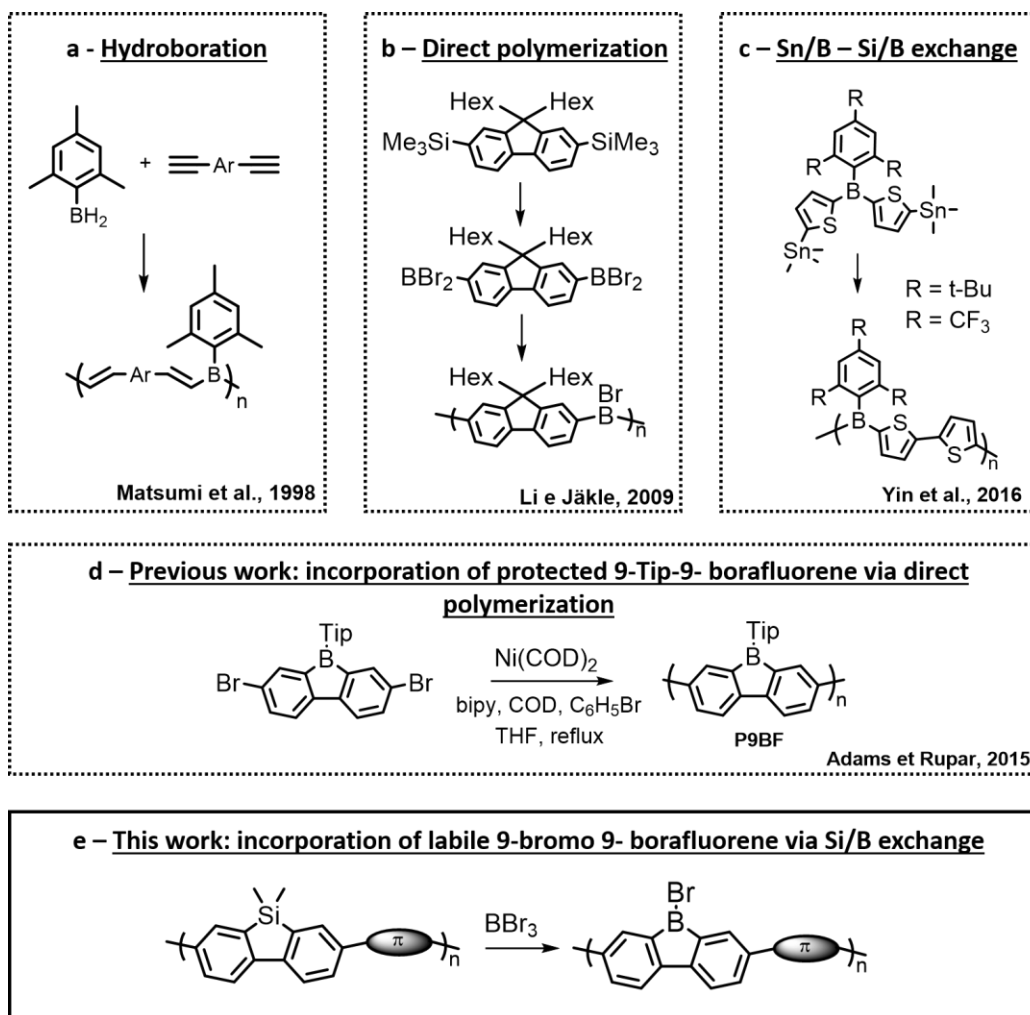


Figure 3.1: Different methodologies to introduce a tricoordinate organoborane into conjugated polymers: hydroboration (panel a),²⁶ Si/B or Sn/B exchange (panel b),² and direct polymerization of suitable organoboron scaffolds (panel c).²² Previous work by Adam et Ruper et al.³⁶ on the direct incorporation of a sterically hindered and protected 9-Tip-9-borafluorene via direct polymerization (panel d). This work, incorporation of labile 9-bromo-9-borafluorene via Si/B exchange in a deep blue emitting copolymer (panel e).

3.2 Results and Discussion

The direct incorporation of an organoboron scaffold, where boron is bonded to a small, non-bulky substituent, into a polymer via polymerization is challenging due to stability issues. To address this problem, the incorporation of a labile boron-doped polycyclic aromatic hydrocarbon (PAH) into a macromolecule using the Si-B exchange reaction was proposed.⁴⁵ The Si-B exchange was chosen over the Sn-B exchange due to the stability of silicon precursors under polymerization conditions. After various potential organoboron moieties were analyzed for incorporation into a polymer chain, and suitable starting silicon building blocks were identified through a retrosynthetic approach, 9-borofluorene (**B1**) and borolo[3,2-b:4,5-b']dithiophene (**B2**) were determined to be the most promising candidates (Fig. 3.2).

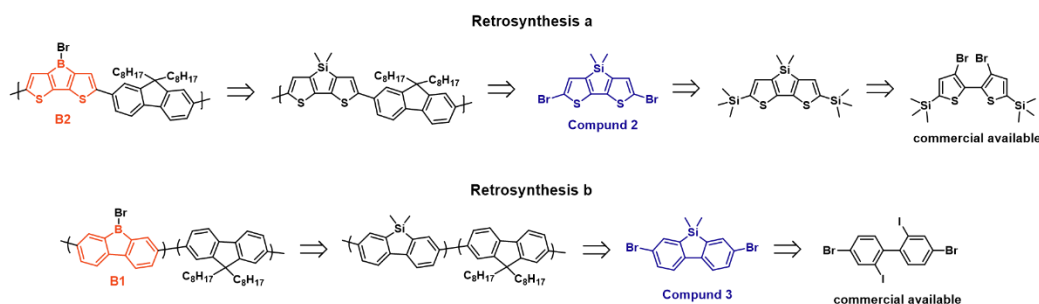


Figure 3.2: Retrosynthetic approaches (a) and (b) for the synthesis of boron-doped polycyclic aromatic hydrocarbons used in polymers.

3.2.1 Evaluation of Lewis Acidity and Lewis Pairs Binding Energy

The first aim of this study was to assess the Lewis acidity of these two boron-containing scaffold compounds and compare their properties with those of previously utilized boron Lewis acids such as 2-phenyl-1,3,2-benzodioxaborole (**BCat**) and phenyldi-2-thienylborane (**BTh₂**), which have been used in dynamic networks, in a study by Vidal *et al.*⁴⁶ This evaluation was conducted to determine

the suitability of the new boron scaffolds as dynamic crosslinking points, based on their Lewis acidity. For comparison, 5-phenyl-5H-dibenzoborole (**Ph-B1**) and 4-phenyl-4H-borolo[3,2-b:4,5-b']dithiophene (**Ph-B2**) were selected. Initially, **B1** was hypothesized to be a significantly stronger Lewis acid than the other scaffolds due to the absence of electron-donating groups near the boron atom. Conversely, **B2** was expected to exhibit Lewis acidity similar to that of **BTh₂** because of the presence of adjacent thiophene moieties. The acidity of the scaffolds was evaluated by computing the hydride affinity (HA) as the enthalpy change (ΔH) and the data is presented in Fig. 3.3.

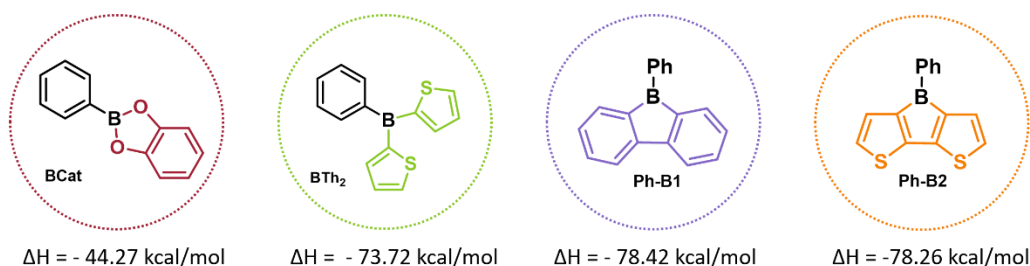


Figure 3.3: Hydride affinity values of different boronic structures: From left, in order, 2-phenyl-1,3,2-benzodioxaborole (BCat), phenyldi-2-thienylborane (BTh₂), 5-phenyl-5H-dibenzoborole (Ph-B1) and 4-phenyl-borolo[3,2-b:4,5-b']dithiophene (Ph-B2). The values were calculated using quantum theoretical calculations (DFT) following the reaction $(R)_3B + H^- \rightarrow (R)_3BH^-$.

The hydride affinity of BCat, calculated as ΔH , is -44.27 kcal/mol, while BTh₂ is -73.72 kcal/mol. Surprisingly, the hydride affinity of Ph-B1 is very similar to that of BTh₂, being -78.42 kcal/mol, suggesting similar Lewis strength for the two. Moreover, the hydride affinity of Ph-B2, which was expected to be weaker than that of Ph-B1, is almost identical to the latter, with a ΔH of -78.26 kcal/mol. Considering that in the article of Vidal *et al.*,⁴⁶ the authors successfully prepared dynamic bonds with BTh₂, this preliminary assessment supports the potential introduction of B1 or B2 scaffolds into polymers as dynamic crosslinking points. Following this assessment, the subsequent step involved determining the Lewis acidity of diverse 9-borafluorene (B1) and borolo[3,2-b:4,5-b']dithiophene (B2)

derivatives that can be incorporated into a polymer. An extensive analysis of the hydride affinity for various substituents, including Br, Cl, F, OH, and O-Me, was conducted (Fig. 3.4, left panel, Fig S3.17).

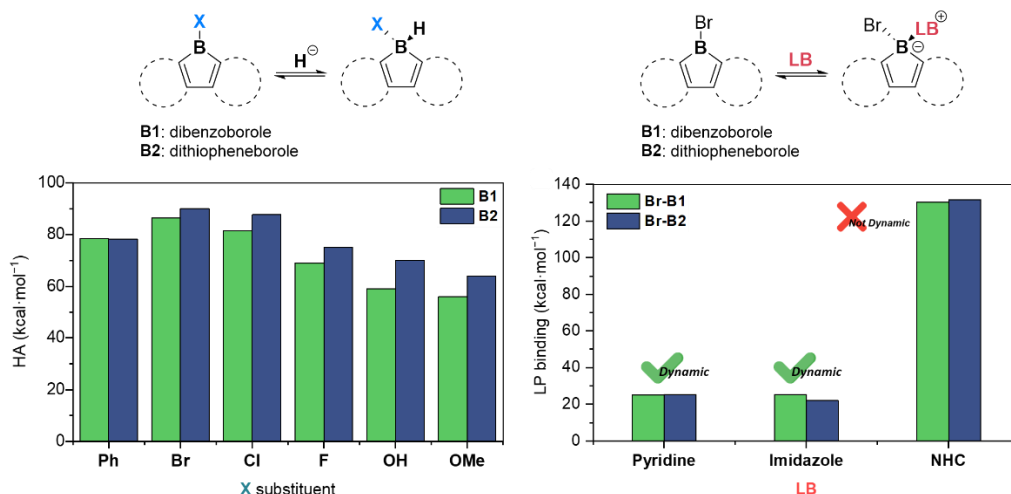


Figure 3.4: Hydride affinity model reactions and values as ΔH (in kcal/mol) of B1 and B2 derivatives (X = -Ph, -Br, -Cl, -F, -OH, -OMe) (left panel). Binding energies model reactions and values of Lewis Pairs between 9-bromo-borabluorene (Br-B1) and 4-bromo-4H-borolo[3,2-b:4,5-b']dithiophene (Br-B2), and Lewis bases pyridine, imidazole and NHC (right panel).

The data reveal a clear trend in the hydride affinities of the B1 scaffolds. Halogen substituents, such as bromine (Br) and chlorine (Cl), increase the absolute value of the hydride affinity, indicating an enhancement in Lewis acidity due to their electron-withdrawing properties. Fluorine (F) deviates from this trend, showing a slightly lower value than the reference phenyl (Ph) group, likely due to partial π -donation from fluorine's p orbital to boron's empty p orbital. In contrast, substituents like hydroxyl (OH) and methoxy (OMe) decrease the absolute value of the hydride affinity. This reduction is attributed to the electron-donating nature of oxygen atoms, which can partially occupy the empty boron orbital via π -donation to the boron's 2p orbital,⁴⁶ thus reducing the overall Lewis acidity. The hydride affinity values for B2 derivatives follow a similar trend. Generally, these values are higher than those of the B1 scaffold, indicating stronger interactions and greater Lewis acidity. In summary, theoretical calculations, in

agreement with previously reported literature,⁴⁷ indicate that halogen derivatives should be utilized when stronger interactions are desired, whereas oxygen derivatives are more suitable for weaker interactions.

Hydride affinities were calculated to estimate Lewis acidity in terms of electron deficiency, as hydrides are small and can effectively approach the boron center even in the presence of bulky substituents. However, for dynamic polymers incorporating these types of boronic scaffolds, larger Lewis bases will be used, and their interactions will be influenced by steric hindrance, leading to decreased interaction strength. Additional density functional theory (DFT) calculations were conducted using pyridine, 1-methylimidazole, and 1,3-di(methyl)imidazole-2-ylidene (NHC) as potential Lewis bases to address the interaction strength between these Lewis bases and the two selected boronic scaffolds, B1 (Figure 3.5, left panel) and B2 (Figure 3.5, right panel).

The results indicated in Figure 3.5, show that the ΔH values of the two boronic scaffolds, with different substituents, are very similar and demonstrate that pyridine and imidazole, being weaker Lewis bases compared to carbene, form weaker interactions that are suitable for dynamic materials. In contrast, carbene forms a stronger interaction, which inhibits dynamicity. Based on previously reported reactions, boron is commonly introduced into similar scaffolds using BBr_3 , making this derivative particularly relevant to this study (Fig. 3.4, right panel). The theoretical results indicate that either pyridine-based or imidazole-based Lewis bases yield dynamic interactions with the bromine-boron derivatives studied; consequently it was concluded that incorporating 9-bromo-9-borafluorene (Br-B1) and 4-bromo-4H-borolo[3,2-b:4,5-b']dithiophene (Br-B2) into a polymer matrix can facilitate the development of dynamic networks or sensor materials (Fig. 3.4, right panel).

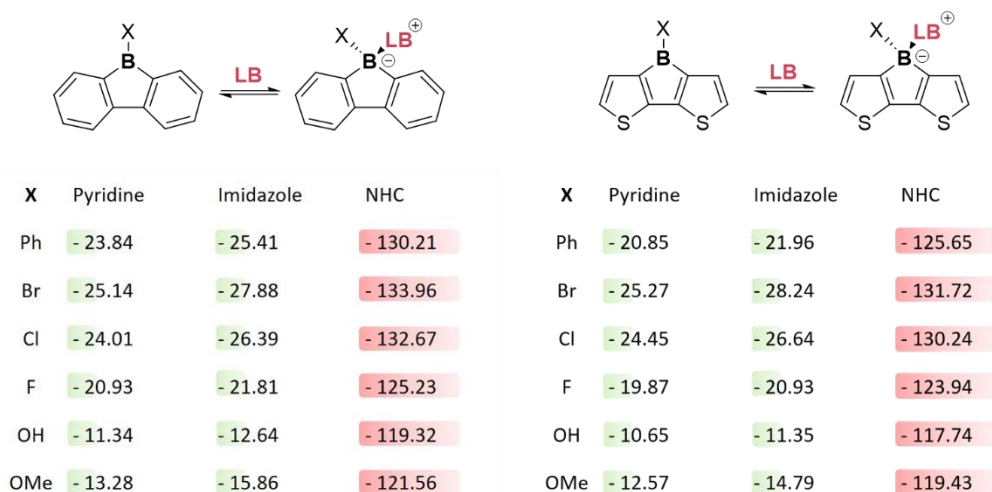


Figure 3.5: Evaluation of Lewis pairs interaction strength between B1 derivatives (left panel) and B2 derivatives (right panel), and different Lewis bases (pyridine, 1-methylimidazole and 1,3-dimethylimidazole-2-ylidene) (left panel).

3.2.2 Synthesis of Si-cycle monomers

The selection of these two boronic scaffolds, B1 and B2, is based on two key factors: the feasibility of synthesizing their silacyclic precursors (Fig. 3.2) and their classification as doped polycyclic aromatic hydrocarbons (PAHs). Doping standard PAHs with boron introduces a vacant orbital that can modify the HOMO-LUMO energy gaps, enhancing their potential utility in various electronic devices and transforming them into Lewis acids.^{42,43} Furthermore, the differing structures 9-borabfluorene (B1) and borolo[3,2-b:4,5-b']dithiophene (B2) are expected to influence the energy gaps and Lewis acidity, when introduced in a material, in distinct ways, leading to varied properties.

As noted in the introduction, silacyclic precursors are of great interest in π -conjugated polymeric systems. Incorporating silicon heterocycles into polyfluorene copolymers has yielded a versatile class of polymers for optoelectronic applications, including lasers, solar cells, transistors, and OLEDs.^{48–51}

2,6-Dibromo-4,4-dimethyl-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (compound **2** in Fig. 3.2) has not been reported in the literature and was

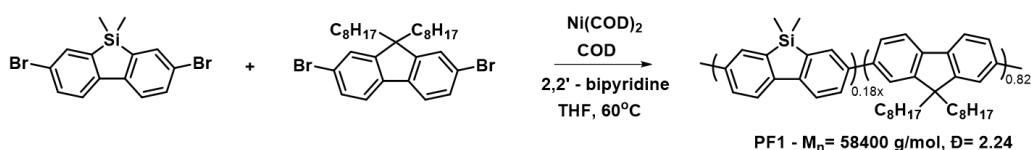
synthesized using a two-step approach, requiring purification through column chromatography at each step, resulting in a final yield of 27%. In contrast, 2,7-Dibromo-9,9-dimethyl-9*H*-9-silafluorene (compound **3** shown in Fig. 3.2), was synthesized using a one-step approach, also requiring purification via column chromatography, with an 84% final yield.⁵²

3.2.3 Synthesis of copolymer PF1 and introduction of Br-B1

Given the similar theoretical results for the B1 and B2 scaffolds and the greater challenges in synthesizing the Si-precursor of the latter, the focus was placed on incorporating 9-Bromo-borafluorene (Br-B1) into a polymer chain. The synthetic approach to copolymer **PF1** is outlined in Scheme 3.1. A 2:8 molar equivalent ratio of 2,7-dibromo-9,9-dimethyl-9*H*-9-silafluorene and 2,7-dibromo-9,9-dioctylfluorene was subjected to copolymerization via Yamamoto-type aryl coupling to obtain copolymer PF1. This material was chosen not only as a starting point for the Si-B exchange but also because, as said previously, literature reports indicate that combining these two monomers in this specific ratio can produce high-efficiency spectrum-stable blue light-emitting polymers with a range of promising applications.¹⁴ Envisioning the copolymer as a platform for a dynamic network, we aimed to introduce a number of crosslinking points between 1 and 10%. Anticipating a lower silicon-boron exchange yield compared to the reported reaction for small molecules,⁴⁵ due to the steric hindrance presented by macromolecules, we selected a 2:8 molar ratio between the two comonomers.

After precipitation, twice from methanol and then from hexane, copolymer PF1 was obtained in 75% yield. The number-average molecular weight (M_n) of PF1 was determined to be 58400 g/mol, and the weight-average molecular weight (M_w) was 131000 g/mol, with a dispersity ($\mathcal{D}$) of 2.24; as determined by gel

chromatography against polystyrene standards using THF/ CHCl_3 as eluent. The thermal stability of PF1, analyzed via thermal gravimetric analysis, shows that the copolymer has remarkable stability, reaching temperatures of over 435°C , very similar to the one reported for the homopolymer of 9,9-dihexyl-2,7-dibenzosilole (P27SiF) (436°C).¹⁶

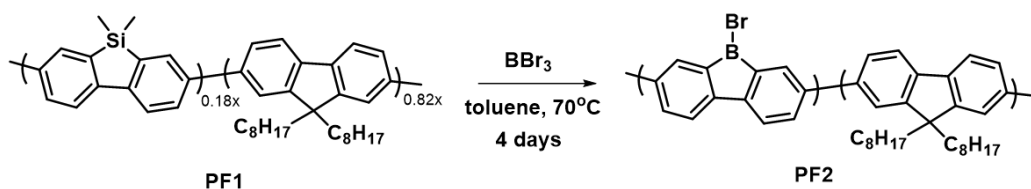


Scheme 3.1: Model reaction of Yamamoto coupling copolymerization for the synthesis of copolymer PF1.

The introduction of 9,9-dimethyl-9H-9-silafluorene into the polymer chain was confirmed with ^1H - ^{29}Si HMQC (Heteronuclear Multiple Quantum Coherence), which shows two 2D NMR correlations: one correlating with the aliphatic region and one with the aromatic region. The correlation with the aliphatic region relates to the protons of the two methyl groups connected to the Si atom, while the correlation with the aromatic region can be explained by the interaction between the Si atom and the protons of the adjacent benzyl groups. Comparing the ^1H - ^{29}Si HMQC of **PF1** with the ^1H - ^{29}Si HMQC of the monomer 2,7-dibromo-9,9-dimethyl-9H-9-silafluorene, a shift in the Si 2D NMR correlation can be noted. The signals present in the HMQC of the monomer are located at $^1\text{H} = 0.46$ ppm and $^{29}\text{Si} = 1.66$ ppm in the aliphatic region and at $^1\text{H} = 7.74$ ppm and $^{29}\text{Si} = 1.66$ ppm in the aromatic region. In contrast, the signals of the HMQC of the PF1 copolymer are located at $^1\text{H} = 0.61$ ppm and $^{29}\text{Si} = 0.93$ ppm in the aliphatic region and at $^1\text{H} = 7.98$ ppm and $^{29}\text{Si} = 1.66$ ppm in the aromatic region. Moreover, analysis of the ^1H -NMR of copolymer PF1 indicates that the

incorporation of 2,7-dibromo-9,9-dimethyl-9H-9-silafluorene constitutes 18% of the entire polymer chain. (Fig S3.7-S3.9).

The initial objective was to incorporate the Br-B1 unit in a 9,9-dioctylfluorene polymer, for which starting from the Si-cycle precursor was deemed the most viable option. 9-Borafluorenes bonded to halogens are generally not stable to air and moisture, and thus may not withstand the polymerization reaction. By following and adapting a procedure reported by Wakamiya et al.,⁴⁵ the introduction of the Br-B1 moiety into the copolymer through a post-polymerization reaction was successfully performed, as shown in Scheme 3.2. After precipitation into anhydrous hexane copolymer, PF2 was obtained as a brownish solid in a 73% yield. The molecular weight of PF2 was analyzed using GPC, resulting in an M_n of 76400 g/mol with a dispersity ($\mathcal{D}$) of 2.01 as determined by gel chromatography against polystyrene standards using THF/ CHCl_3 as eluent. In the ^{11}B -NMR spectrum of PF2, a distinct peak around $\delta = 57$ ppm is observed, consistent with previously reported Br-B1 monomer.⁵³ Furthermore, a comparison of the ^1H -NMR spectra of PF2 and PF1 reveals a decrease in the integration of the methyls peak of the 9,9-dimethyl-9H-9-silafluorene, indicating that the total introduction of Br-B1 into the copolymer accounts for 9.5%. Consequently, the reaction yield is approximately 53%, lower than previously reported similar reactions.^{51,66} Additionally, TGA analysis indicates that PF2 remains stable until 431 °C, showing very similar thermal stability compared to PF1. (Fig. S3.10-S3.15)



Scheme 3.2: Model reaction to introduce Br-B1, through a Si-B exchange, into copolymer PF1.

3.2.4 Optical spectroscopic characterization of copolymer PF1 and copolymer PF2

The emission–absorption spectra were analyzed in two different solvents, DCM and toluene, to investigate any solvent effects on the optical spectroscopic data. When dissolved in DCM, PF1 exhibits an absorption peak at 388 nm and, when excited at 390 nm, shows one main emission peak at 416 nm, a secondary shoulder at 439 nm, and a minor shoulder around 475 nm (Fig. 3.6, left panel). The Stokes shift in this case is minimal, accounting for a total of 28 cm^{-1} . This is consistent with the rigidity of the fluorophore structure.^{2,54}

In toluene (Fig. S3.12), PF1 displays almost identical optical behavior compared to DCM. The absorption peak occurs at approximately 386 nm, indicating a slight hypsochromic shift relative to the DCM solution. Upon excitation at 390 nm, PF1 shows one main emission peak at 416 nm, a secondary shoulder at 439 nm, and a minor shoulder around 475 nm, displaying identical emission behavior compared to the DCM solution. Here, the Stokes shift of 30 cm^{-1} is still very small, again reflecting the rigidity of the structure.

The emission behavior of PF1 is remarkably similar to that of poly(9,9-dioctylfluorene), which suggests that the extent of the π -conjugation within PF1 is comparable to the one in PF0, as previously reported in the literature for polydibenzosilole and copolymers of poly(dibenzosilole-alt-fluorene).^{16,55} Moreover, as reported by Chan et al.¹⁶, the homopolymer of 9,9-dimethyl-9H-silafluorene, called poly(9,9-dihexyl-2,7-dibenzosilole), exhibits almost identical optical properties to poly(9,9-dioctylfluorene). Considering that the doping moiety introduced does not exhibit different optical behavior from poly(9,9-dioctylfluorene), it is reasonable to conclude that its introduction, even more in a minor quantity, into a copolymer primarily characterized by 9,9-dioctyl-9H-

fluorene will not significantly modify the optical properties derived from this latter monomer.

When analyzing the emission of PF1, it was noticed that the copolymer exhibits a blue fluorescence, as shown in Fig. 3.6, in the center panel. Interested by the brightness and clarity of its emission, PF1 was also characterized using the CIE 1931 coordinates (Commission Internationale de l'Éclairage 1931).⁵⁶ These coordinates are a standardized way to quantify and represent colors based on human vision. This system defines color in terms of three coordinates, X, Y, and Z, which describe a color's chromaticity (hue and saturation) and brightness (luminance). The location of the coordinates in the CIE diagram also provides information about color purity. Colors closer to the edges of the diagram are more saturated, while those closer to the center are less pure, appearing more whitish. When calculating the CIE 1931 coordinates, considering that the s-RGB standard for blue is ($X=0.15$, $Y=0.06$),⁵⁷ a deep blue emission of the polymer was observed, with CIE coordinates $X = 0.15$ and $Y = 0.04$. Deep blue emission is usually centered around 400-450 nm and it's characterized, on the CIE 1931 chromaticity diagram, by y values < 0.15 along with an $(x+y)$ value < 0.30 , aligning with the blue corner of the diagram, indicating a pure blue with minimal green or red.⁵⁸ Moreover, the quantum yield of PF1 was analyzed and resulted very high, at $\Phi = 93.9\%$.

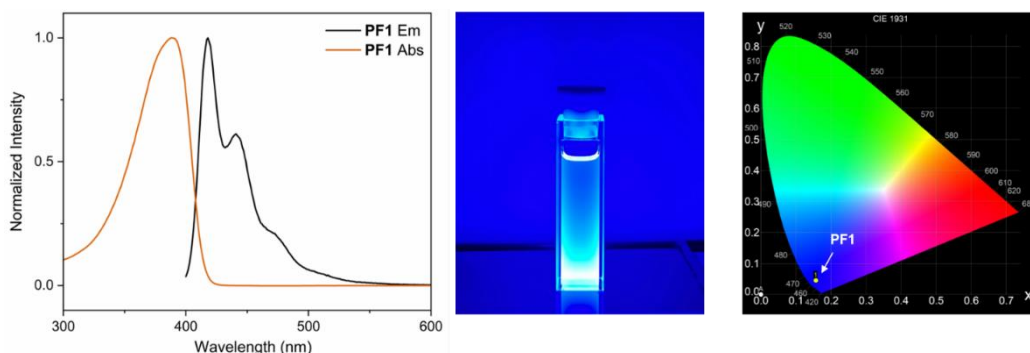


Figure 3.6: Optical spectroscopic data of PF1 in DCM (left panel). The absorption peak is at 388 nm, and the emission peaks are at 416 nm, 439 nm, and 475 nm when excited at 390 nm. The Stokes shift is 28 nm. Deep blue emission of PF1 in DCM solution (center panel) with its CIE 1931 coordinates ($X = 0.15$ and $Y = 0.04$) (right panel).

When comparing these coordinates with those of the homopolymer of 9,9-dioctyl-9H-fluorene, known as poly(9,9-dioctylfluorene) or PF0 ($X=0.19$, $Y=0.19$), it was observed that the introduction of 9,9-dimethyl-9H-silafluorene into the polymer chain at the used molar ratio notably shifts the emission to a deeper blue. As previously reported in literature, this blue shift arises from the participation of both 9,9-dioctyl-9H-fluorene and 9,9-dimethyl-9H-silafluorene comonomers in the π -conjugation along the polymer backbone.¹⁴ This participation forms a uniform band structure by mixing the electronic states of the two monomer units, and since the homopolymer of silafluorene has a wider bandgap than polyfluorene (PFO), the introduction of silafluorenes will increase the bandgaps of the copolymer, leading to a blue-shift.⁵⁹ Other similar polymers or copolymers containing 9,9-Dimethyl-9H-silafluorene structures exhibit comparable absorption-emission behavior to PF1 but show less pronounced deep blue-shifted CIE coordinates. For instance, Chan et al.¹⁶ prepared a homopolymer of 9,9-Dimethyl-9H-silafluorene (P27SiF) which, in film form, demonstrates optical properties similar to PF0, with CIE coordinates of $X = 0.15$ and $Y = 0.11$. Wang et al.¹⁴ reported various copolymers of 3,6-silafluorene and 9,9-dioctyl-9H-fluorene, all with higher CIE coordinates values compared to PF1.

An interesting study by Wang et al.⁶⁰ involved the insertion of bulky aryl substituents instead of alkyl side chains bonded to the silicon atom, aiming to suppress the typical interchain stacking observed with C-Si bonds as opposed to C-C bonds.⁶¹ This suppression of aggregation resulted in the poly(9,9-dialkoxypheyl-2,7-silafluorene) (PSF) exhibiting CIE coordinates of $X = 0.17$ and $Y = 0.13$. Additionally, Xu et al.⁵⁷ introduced a perpendicular arrangement between two spiro-linked dibenzosilole units, resulting in a deep-blue emitting poly(2,3,6,7-tetraoctyl-2,7-spirosilabifluorene) (PSSiBF) with CIE coordinates of $X = 0.16$ and $Y = 0.06$. However, copolymer PF1, prepared by incorporating 9,9-dimethyl-9H-silafluorene into a polyfluorene copolymer at a 2:8 molar ratio, exhibits a deeper blue emission compared to all these reported examples in the literature (Fig. 3.7).

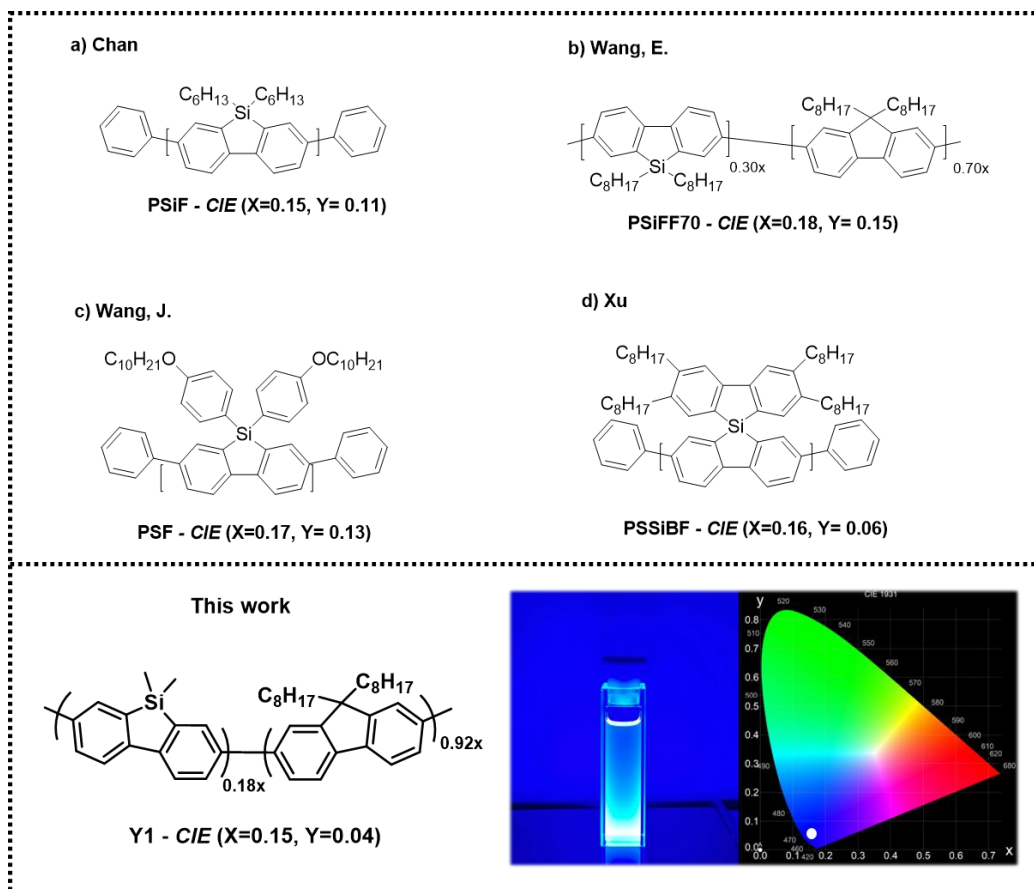


Figure 3.7: Previously reported silicon-containing copolymers with deep-blue emission with their reported CIE coordinates (left panel) compared to PF1 blue emission in DCM and CIE coordinates (right panel). PSiF, Chan, et al.¹⁶ – PSiFF70, Wang, E. et al.¹⁴ – PSF, Wang, J. et al.⁶⁰ and PSSiB1, Xu et al.⁵⁷

The emission behavior of PF1 was also analyzed in its solid state. As shown in Fig. 3.8, in the solid state, PF1 displays an initial emission peak at 442 nm, followed by a maximum emission peak at 462 nm, another peak at 493 nm, and a small shoulder at 536 nm. These values are slightly red-shifted compared to the emission in solution. Intermolecular interactions, such as π - π stacking, may be favored, and slight peak shifts were observed. The quantum yield of PF1 in the solid state is 26.5%; a decrease in the quantum yield from the solution to the solid state suggests that the alignment of the polymer chains leads to a certain extent of luminescence quenching, as already reported in the literature.⁵⁴

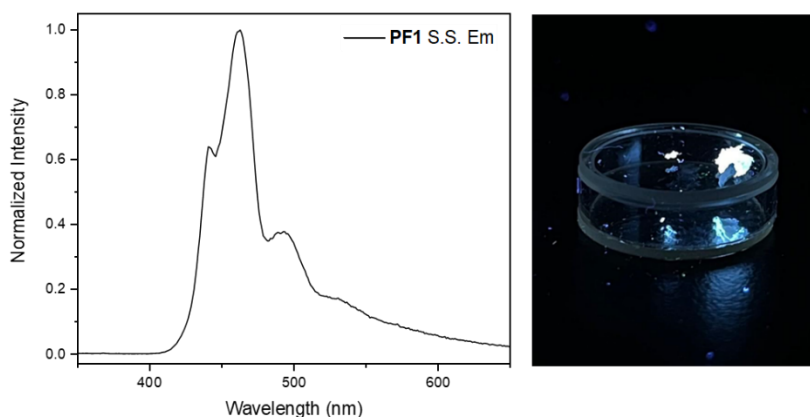


Figure 3.8: Optical spectroscopic data of PF1 in solid state. The emission peaks are at 462 nm, 493 nm, and 563 nm when excited at 300 nm. $\Phi = 26.5\%$.

The optical spectroscopic data of PF2 closely resemble those of PF1 (Fig. S3.16). The boron-doped copolymer exhibits an absorption peak at 377 nm and, when excited at 380 nm, displays a main emission peak at 415 nm, accompanied by another peak at 439 nm and a small shoulder at 475 nm. Considering that the introduction of boron is expected to decrease the energy gap between the HOMO and LUMO due to an increase in π -conjugation, the hypsochromic shift of the absorption peak of PF2 compared to PF1 is unexpected.

TDDFT calculations on oligomers containing 5 repeating units were conducted to clarify the origins of the photophysical characteristics. For the PF0 and PF1 oligomers, both HOMOs and LUMOs are fully delocalized along the polymer chain, with no contribution from the silicon atom in PF1 (Fig 3.9 and Fig 3.10).

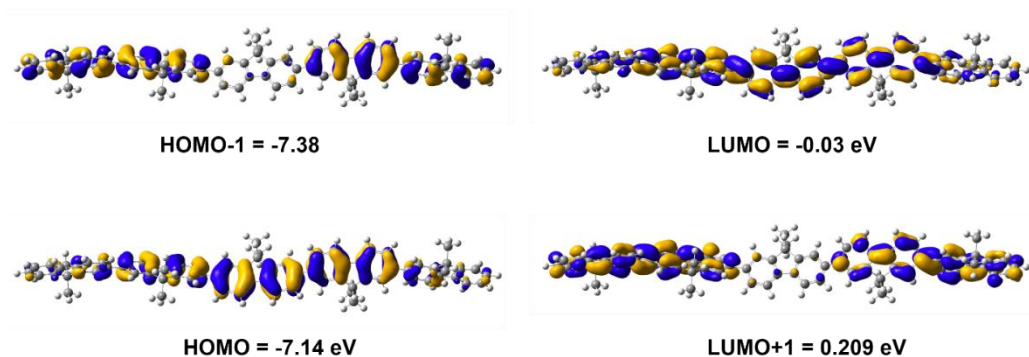


Figure 3.9: Orbital representations for 5 repeating unit oligomer of PF0 of HOMO-1, HOMO, LUMO and LUMO+1 with their corresponding energy values.

In both cases, the high degree of HOMO and LUMO delocalization along the polymer chain indicates that absorption is primarily due to the (HOMO $\rightarrow$ LUMO) π - π^* transition.

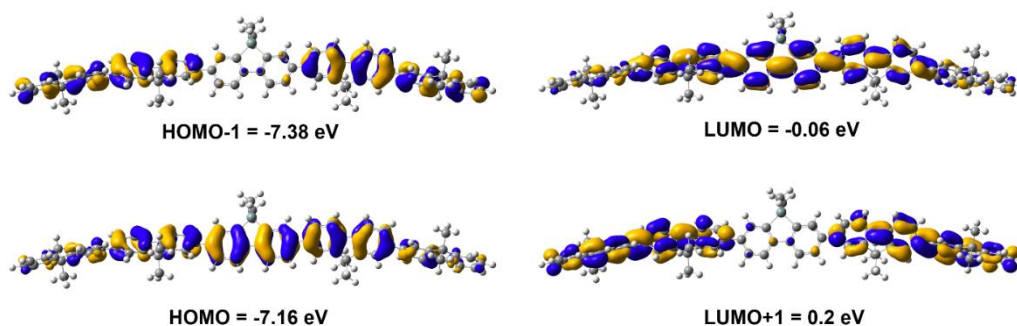


Figure 3.10: Orbital representations for 5 repeating unit oligomer of PF1 of HOMO-1, HOMO, LUMO and LUMO+1 with their corresponding energy values.

In **PF2**, however, while the HOMO remains delocalized along the chain, the LUMO does not. Interestingly, the LUMO+1 in PF2 shows delocalization along the chain, similar to the HOMO (Fig. 3.11). TD-DFT calculations reveal that the most favorable absorption, indicated by a higher oscillator strength (Table S3.4), occurs not between the HOMO and LUMO, but rather between the HOMO and LUMO+1. This transition corresponds to a higher energy and, consequently, a shorter wavelength (Fig. 3.12).

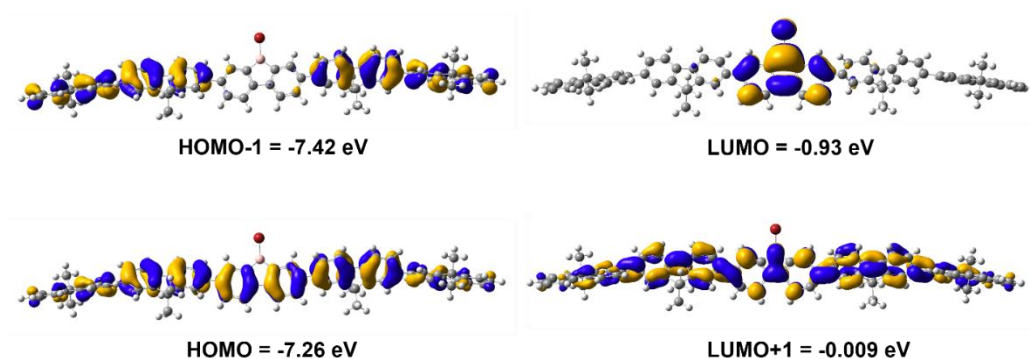


Figure 3.11: Orbital representations for 5 repeating unit oligomer PF2 of HOMO-1, HOMO, LUMO and LUMO+1 with their corresponding energy values.

This phenomenon is explained by examining the HOMO, LUMO, and LUMO+1 orbitals of PF2. Since the LUMO+1 is more delocalized along the polymer chain than the LUMO, it likely achieves better overlap with the HOMO, which, in conjugated polymers, promotes stronger electron-electron interactions, making transitions to these orbitals more probable. Furthermore, the symmetry and orientation of the LUMO+1 in PF2 complement the shape of the HOMO, increasing the transition probability and leading to a higher oscillator strength.

Moreover, given that the introduction of B1-Br into the polymer is minimal, accounting for just 9.5% of the total, it is understandable that the modified copolymer does not undergo significant changes in its optical properties. The fluorescence decay histogram of PF1 in solution yields $\tau = 0.52$ ns, which fits reasonably well with a monoexponential function ($\chi^2 = 1.06$).

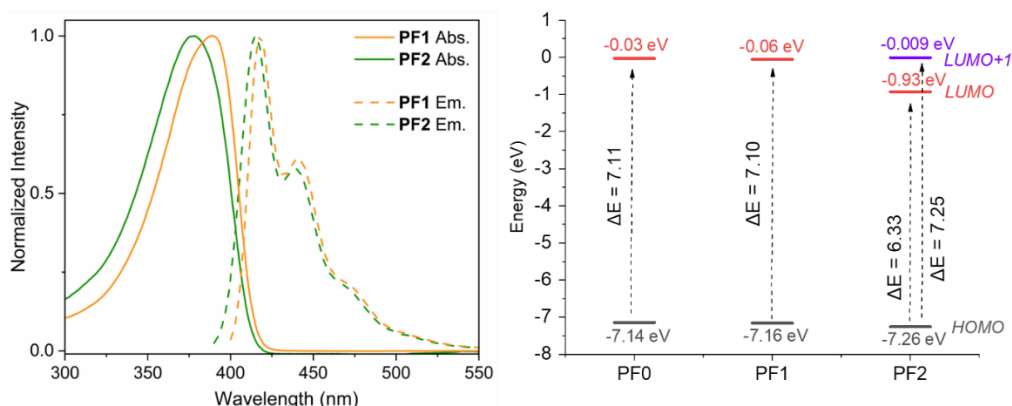
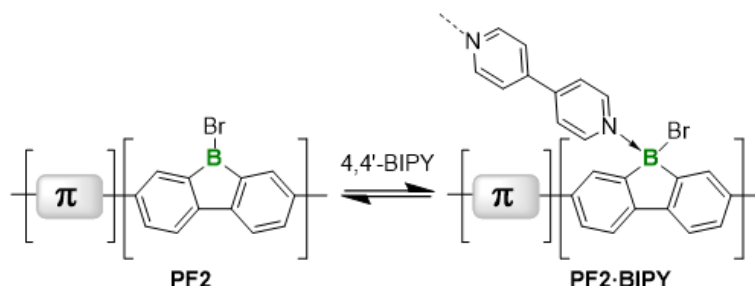


Figure 3.12: UV-vis absorption and fluorescence spectra of silole and borole polyfluorenes PF1 and PF2 in DCM solution. (left panel). Plots of Kohn-Sham orbital and electronic transitions for PFO, PF1, and PF2 (geometry optimized at the WB97XD/6-31+G(d) level and TD-DFT calculation carried out at the WB97XD/6-31+G(d) level) (right panel).

3.2.5 Lewis Pairs Coordination

To assess whether the introduction of a Lewis base would coordinate with the Br-B1 moieties introduced in the copolymers, the reaction scheme displayed in Scheme 3.3 was analyzed via ^{11}B -NMR.



Scheme 3.3: Model reaction used to follow, via ^{11}B -NMR, the coordination of 4,4'-bipyridine to PF2.

The goal was to observe, after the addition of an excess of 4,4'-bipyridine, a shift of the peak corresponding to the Br-B1 from the tricoordinate state (between 30 ppm and 60 ppm) to the tetracoordinate state (-5 ppm to 15 ppm). Using, as a substrate, the PF2 copolymer, after the addition of 2 molar equivalents of 4,4'-bipyridine compared to the 9-Bromo-borofluorene's moles inserted in PF2, we

observed the complete disappearance of the previously identified Br-B1's peak at 57.06 ppm and the appearance of a new peak at 4.64 ppm, which is consistent with a tetracoordinate Br-B1 (Fig. 3.13).^{53,62,63}

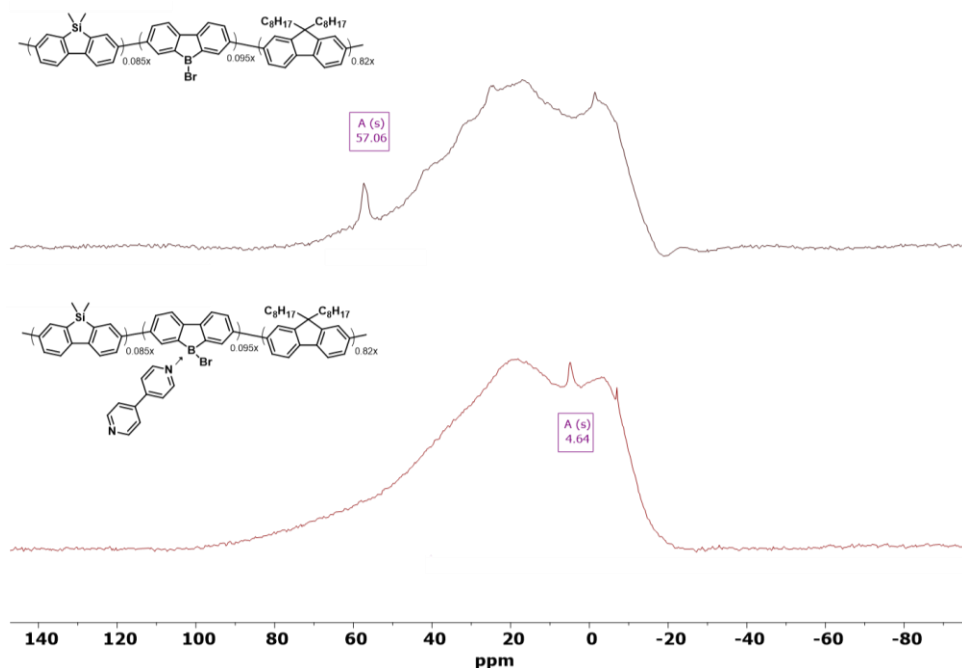


Figure 3.13: ^{11}B -NMR of PF2 (panel above) and PF2-BIPY (below). A shift in the boron peak can be noted, from 57.11 ppm for the tricoordinate boron to 4.88 ppm for the tetracoordinate one.

These results confirm that the introduction of a Lewis base, such as 4,4'-bipyridine, can effectively coordinate with the 9-Bromo-borfluorene moieties in the copolymers. This coordination leads to a significant change in their coordination state, as evidenced by ^{11}B -NMR spectroscopy. The theoretical calculations that were performed in advance indicate that this type of interaction has an enthalpy change (ΔH) of approximately -25 kcal/mol, which allows for dynamic bonding. This dynamic coordination is crucial for applications where reversible bonding is required and can pave the way to a new class of dynamic networks.

3.3 Conclusions

In conclusion, a novel high molecular-weight copolymer composed of 9,9-silafluorene and 9,9-dioctylfluorene units in a 1:5 ratio was successfully synthesized via Yamamoto coupling. This copolymer exhibits deep blue emission with CIE coordinates ($X = 0.15$ and $Y = 0.04$), and has a high quantum yield ($\Phi = 93.9\%$). With thermal stability reaching nearly 440°C , this copolymer shows great potential for application in blue organic light-emitting diodes (OLEDs), a field that has seen considerable efforts from both academia and industry globally. Additionally, this polymer was employed as a platform for the first-time introduction of 9-bromo-9-borafluorene into a π -conjugated system through a silicon-boron exchange. The incorporation of the tricoordinate boron scaffold was confirmed by ^{11}B -NMR. DFT calculations were conducted to analyze the optical properties and explore the potential use of the boron-containing polymer as a platform for future dynamic networks leveraging the Lewis acidity of the tricoordinate boron moiety. These findings confirm that incorporating two main group elements into a π -conjugated system allows for the creation of materials with potential for diverse applications, with tuning yielding different end uses.

3.4 Experimental section

3.4.1 General Procedures

All air- and moisture-sensitive reactions were carried out under an inert atmosphere of argon using standard Schlenk techniques or in an MBRAUN LABmaster glovebox equipped with a -36 °C freezer. Reaction solvents including toluene, hexanes, diethyl ether, and tetrahydrofuran (THF) were purified by distillation over Na/benzophenone. Dichloromethane (DCM) and chlorobenzene were purified via distillation over CaH₂. Deuterated solvents were purchased from Cambridge Isotope Laboratories and distilled over Na/benzophenone (C₆D₆) or CaH₂ (CD₃CN, o-DCB-d₄). All glassware used for reactions was oven-dried overnight at 190 °C.

The NMR spectra were collected on Bruker Advance III 400 MHz, and Bruker Advance III 600 MHz. Proton and carbon signals are reported in ppm and referenced to residual solvent peaks of the deuterated solvent (¹H: CDCl₃ δ 7.26, C₆D₆ δ 7.16; CD₃CN δ 1.94; o-DCB-d₄ δ 7.19, 6.93; ¹³C: CDCl₃ δ 77.16, C₆D₆ δ 128.06; CD₃CN δ 118.7, 1.4). Abbreviations are as follows; s = singlet, d = doublet, t = triplet, hept = heptet, dt = doublet of triplets, m = multiplet, br = broad. All boron signals are reported in ppm and were referenced to an external standard, B₁₃·Et₂O (¹¹B: δ = 0.00). Due to the use of a borosilicate NMR probe, there is a broad signal observed from -25 to 50 ppm.

UV-vis data were collected on a Cary 60 UV-vis spectrometer and samples were prepared in 1 cm square quartz cuvettes. Fluorescence data were collected on an Edinburgh Instruments FS5 spectrofluorometer equipped with a double monochromator for excitation and emission. Absolute fluorescence quantum yields were determined using a Hamamatsu C11347-11 Quantaaurus-QY Absolute PL Quantum Yield Spectrometer. Samples were prepared inside the glovebox in 1 cm square quartz cuvettes with Teflon screw caps (solutions). Solutions were

prepared in DCM and data were collected with absorbance values below 0.1. Fluorescence lifetimes were recorded using a time-correlated single photon counting (TCSPC) method using an Edinburgh Instruments FS5 spectrofluorometer equipped with a double monochromator for excitation and emission. Measurements were made in the right-angle geometry mode, and the emission was collected through a polarizer set to the magic angle. The excitation source was a 337.5 nm excitation LED lamp. The instrument response function (IRF) was measured for solution samples using a Ludox® solution in deionized water. The quality of all decay fits was judged to be satisfactory, based on the calculated values of the reduced χ^2 (0.8-1.2) and Durbin Watson parameters and visual inspection of the weighted residuals.

Thermogravimetric analysis (TGA) was performed in a TGA 8000 from PerkinElmer under a nitrogen atmosphere from 30 to 900 °C at a heating rate of 10 °C min⁻¹. Polymer samples were analyzed in THF using an Agilent 1260 Infinity GPC system with variable wavelength diode array (254, 450, and 530 nm) and refractive index detectors. The instrument was calibrated with narrow-dispersity polystyrene standards between 1.7 and 3150 kg mol⁻¹.

Compounds **1** and **3** were prepared according to literature procedures.^{52,64} All other chemicals were purchased from Millipore Sigma or Ambeed and used as received.

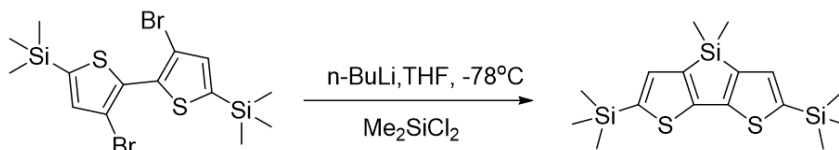
3.4.2 Computational Methodology

All geometry optimizations were executed within density functional theory (DFT) using the ω B97XD⁶⁵ functional combined with the 6-31+G(d)⁶⁶ basis set for all atoms. Frequency calculations were carried out at the same level of theory to validate that the optimized structures were minima or transition states on the potential energy surfaces. These frequencies were then used to evaluate the

zero-point vibrational energy (ZPVE) and the thermal corrections to the enthalpy (H) and Gibbs free energy (G), at $T = 298.15$ K, in the harmonic oscillator approximation. To refine the electronic energies, single-point calculations using the 6-311++G(2df,2p) basis set⁶⁷ were performed on the optimized structures. Time-dependent density functional theory (TDDFT)⁶⁸ calculations have been performed using the WB97XD functional together with the 6-31+G(d) basis set. All the calculations were performed with the Gaussian 16 suite of programs.⁶⁹

3.4.3 Synthetic Procedures:

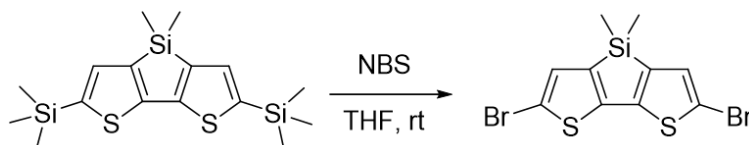
Synthesis of 4,4-Dimethyl-2,6-bis(trimethylsilyl)-4H-silolo[3,2-b:4,5-b']dithiophene (**1**)



Scheme S3.1: Synthesis of 4,4-Dimethyl-2,6-bis(trimethylsilyl)-4H-silolo[3,2-b:4,5-b']dithiophene (**1**).

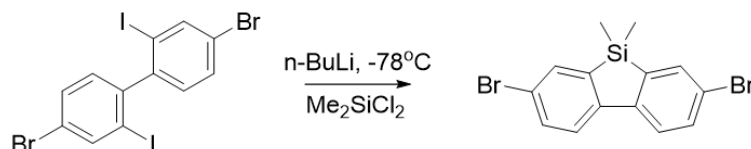
Compound **1** was prepared by a modified protocol according to a literature procedure published by Matsumoto et al.⁶⁴ To a cold ($-78\text{ }^{\circ}\text{C}$) solution of 3,3'-dibromo-5,5'-trimethylsilyl-2,2'-bithiophene (1.0 g, 2.1 mmol) in THF (10 mL), *n*-BuLi (1.6 M in hexane, 2.8 mL, 4.5 mmol) was added dropwise. After the reaction mixture was stirred for 1 h, dichlorodimethylsilane (0.30 g, 280 μL , 2.4 mmol) was added to the solution at $-78\text{ }^{\circ}\text{C}$. After warming to room temperature, the mixture was stirred for 8 h. The solution was diluted in chloroform, washed with brine, and dried over MgSO_4 . After the solvent was removed, the crude mixture was purified by silica gel column chromatography using hexane, $R_f=0.79$. Recrystallization from methanol/chloroform gave a white solid (510 mg) in 61% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (s, 2H), 0.41 (s, 6H), 0.33 (s, 18H).

Synthesis of 2,6-Dibromo-4,4-dimethyl-4H-silolo[3,2-b:4,5-b']dithiophene (**2**)

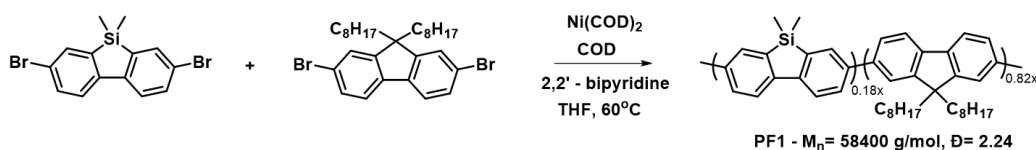


Scheme S3.2 Synthesis of 2,6-Dibromo-4,4-dimethyl-4H-silolo[3,2-b:4,5-b']dithiophene (**2**).

4,4-Dimethyl-2,6-bis(trimethylsilyl)-4H-silolo[3,2-b:4,5-b']dithiophene (170 mg, 0.458 mmol, 1 eq) was dissolved into THF and NBS (178 mg, 1 mmol, 2.2 eq) was added in one portion. The solution mixture was stirred at room temperature overnight and then extracted by diethyl ether. The organic phase was washed with brine and dried over MgSO_4 . After the solvent was removed, the residue was purified by silica gel chromatography using hexane as eluent, $R_f = 0.82$, and gave 80 mg (45%) yield, as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.02 (s, 1H), 0.40 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.87, 142.11, 131.97, 111.74, -3.58.

Synthesis of 2,7-Dibromo-9,9-dimethyl-9H-9-silafluorene (**3**)**Scheme S3.3:** Synthesis of 2,7-Dibromo-9,9-dimethyl-9H-9-silafluorene (**3**).

Compound **3** was prepared according to a literature procedure.⁵² Under an inert atmosphere 4,4'-dibromo-2,2'-diiodo-1,1'-biphenyl (4 g, 7.1 mmol) and 30 ml of dry THF were put into a flask and cooled down to -78°C by a liquid nitrogen-acetone bath. Then, 6.2 mL of n-butyllithium solution in hexane (2.5 mol/L) was added dropwise, and the reactant was stirred for another hour at that temperature. Subsequently, 2g of dichlorodimethylsilane (15.6 mmol) was added in one portion, the cooling bath was removed and the reaction mixture was stirred for 12 hours at ambient temperature. The reaction mixture was poured into water and extracted by ethyl ether several times. The volatiles were removed under vacuum. The residue was purified by silica gel chromatography using hexane as eluent, $R_f = 0.76$, and gave 2.2 g of 2,7-Dibromo-9,9-dimethyl-9H-9-silafluorene (yield 84%) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.75 – 7.53 (m, 1H), 0.46 (s, 1H).

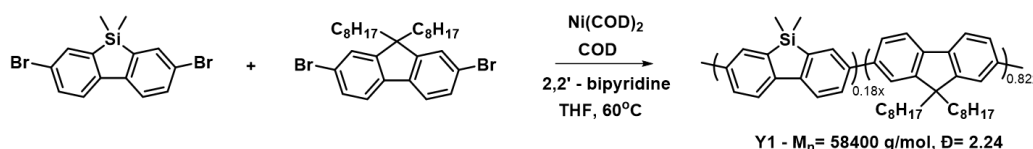
Synthesis of Copolymer **PF1****Scheme S3.4:** Yamamoto coupling for the synthesis of copolymer **PF1**.

2,7-Dibromo-9,9-dimethyl-9H-9-silafluorene (20 mg, 0.054 mmol), 2,7-dibromo-9,9-dioctylfluorene (199 mg, 0.21 mmol), 2,2'-bipyridine (84 mg, 0.54 mmol, 2.0

eq) were charged into a flame-dried Schlenk flask with a screw cap. In a glovebox, the mixture was dissolved in 24 mL of anhydrous THF and $\text{Ni}(\text{COD})_2$ (0.12 g, 0.44 mmol, 2.5 eq) and 1,5-cyclooctadiene (0.029 g, 0.27 mmol, 1.5 eq) were added. The mixture was taken outside the box and heated to 60 °C with stirring for 8 hours, then allowed to cool down to room temperature and poured into an acidic methanol solution. The collected precipitate was redissolved in THF and precipitated again in methanol. Finally, the collected solid was redissolved in THF and precipitated in hexanes. The product was obtained as a white solid that was dried for 18 hours under a high vacuum. Yield: 71 mg (75%). TGA: $T_d^5 = 439^\circ\text{C}$. GPC (THF, 1 mL min⁻¹): $M_n = 58470$, $M_w = 131290$, $\bar{D} = 2.24$. UV-Vis (DCM): $\lambda_{\text{abs}} (\epsilon) = 388 \text{ nm}$; fluorescence (THF, $\lambda_{\text{exc}} = 390 \text{ nm}$): $\lambda_{\text{Fl}} = 416 \text{ nm}$, 439 nm and 475 nm. $\Phi = 93.9 \%$. CIE coordinates ($X = 0.15$ $y = 0.04$). Lifetime $\tau = 0.49 \text{ ns}$, $\chi^2 = 1.25$.

^1H NMR (400 MHz, CDCl_3) δ 8.08 – 7.47 (m, 3H), 1.16 (s, 24H), 0.84 (t, $J = 7.0 \text{ Hz}$, 5H), 0.61 (t, $J = 5.5 \text{ Hz}$, 1H). ^1H - ^{29}Si HMQC ($^1\text{H} = 0.61$, $^{29}\text{Si} = 0.63$) – ($^1\text{H} = 7.74$, $^{29}\text{Si} = 0.63$).

Synthesis of boron-doped copolymer **PF2**



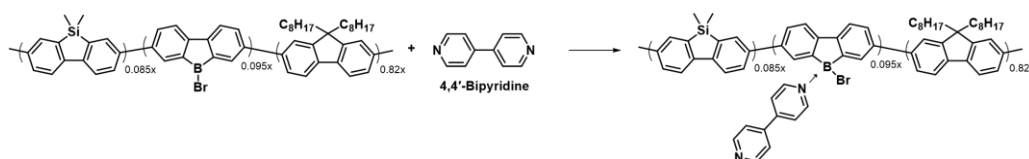
Scheme S3.5: Synthesis of boron-doped copolymer **PF2**.

The synthesis of copolymer **PF2** was adapted from a literature procedure by Wakamiya et al.⁴⁵

PF1 (100mg, 0.2 mmol, ~ 0.035 mmol of 9,9-Dimethyl-silafuorene) was added into a flame-dried pressure Schlenk tube with a screw cap. In a glovebox, 5 mL of anhydrous toluene was added and the mixture was stirred until **PF1** was

completely dissolved. Consequently, neat BBr_3 (3 mol eq. compared to 9,9-Dimethyl-silafluorene's, 0.1 mmol, 26 mg, 10 μL) was added into the Schlenk tube and the reaction mixture was stirred at 70 °C for 4 days. The solution, in a glovebox, was allowed to cool down to room temperature, and the solvent with BBr_3 was removed under high vacuum. Consequently, the residue was precipitated into anhydrous hexane to give a brownish solid. Yield: 74 mg (73%). ^1H NMR (500 MHz, C_6D_6) δ 8.18 – 7.21 (m, 6H), 1.38 – 0.96 (m, 18H), 0.87 (t, J = 7.2 Hz, 16H), 0.52 (s, 1H). $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_6D_6) δ = 57. UV-Vis (DCM): λ_{abs} (ϵ) = 377 nm; fluorescence (THF, λ_{exc} = 380 nm): λ_{Fl} = 416 nm, 439 nm and 475 nm. Φ = 93.9 %. Lifetime τ = 0.49 ns, χ^2 = 1.25.

Coordination of PF2 $\leftarrow$ 4,4'-Bipyridine



Scheme S3.6: Coordination scheme of PF2 with 4,4'-Bipyridine.

To a suspension of **PF2** (100 mg, 0.2 mmol) in anhydrous toluene (5 mL), a solution of 4,4'-Bipyridine in toluene (6mg, 0.05 mmol, 2eq compared to 9-Bromo-borafluorene's mmol) in anhydrous toluene (1 mL) was added dropwise. The reaction was stirred at room for 4 hours before the toluene was removed under vacuum. The crude solid was washed with hexanes to give a brownish solid as the final product. $^{11}\text{B}\{^1\text{H}\}$ NMR (192 MHz, C_6D_6) δ = 4.88.

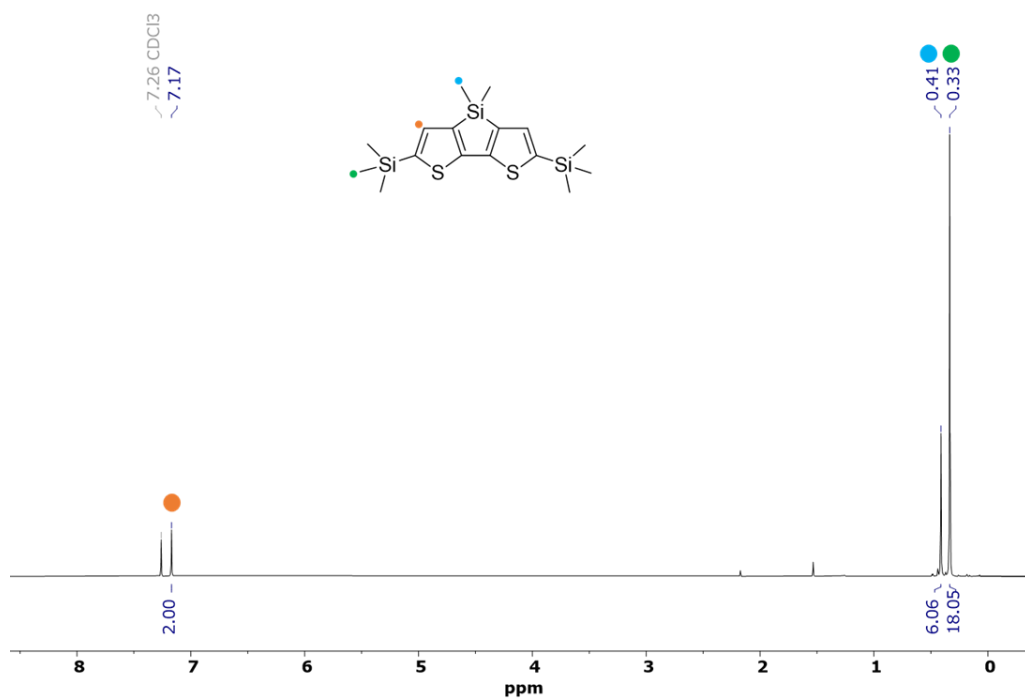


Figure S3.1: ^1H -NMR (600 MHz, C_6D_6) spectrum of **1**.

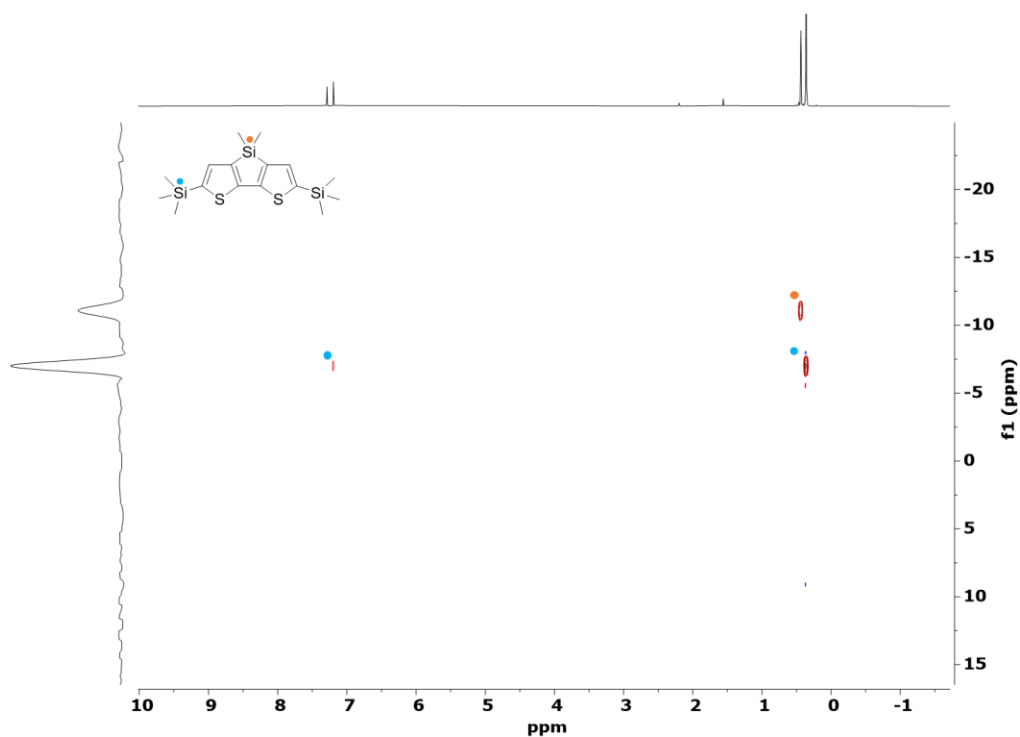
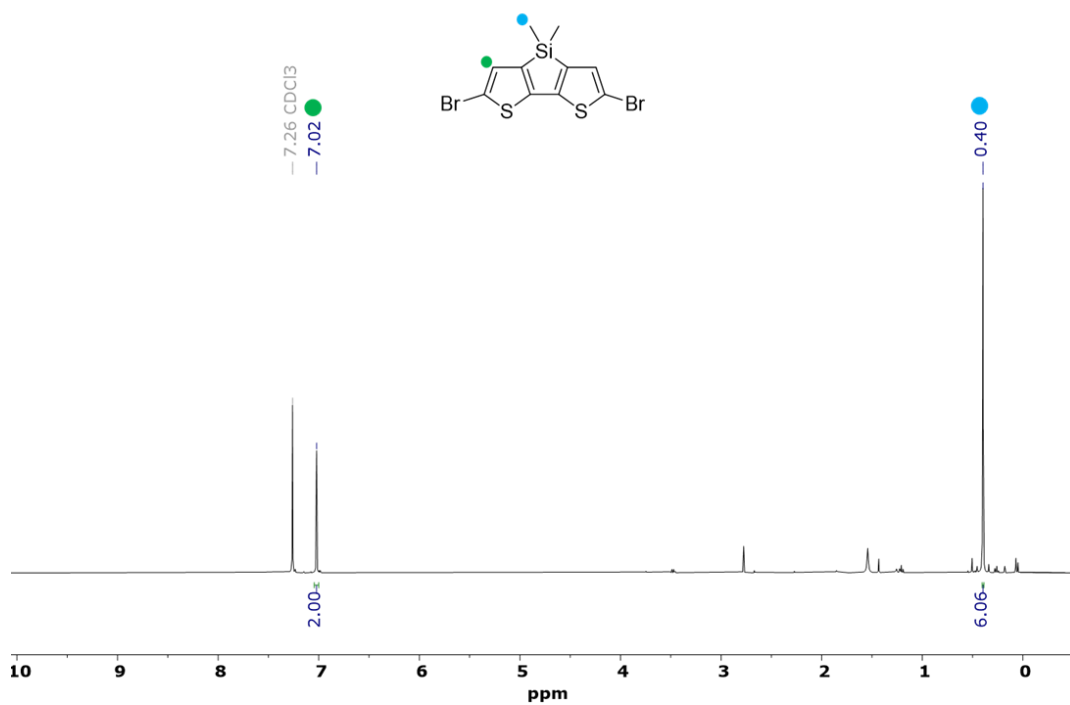
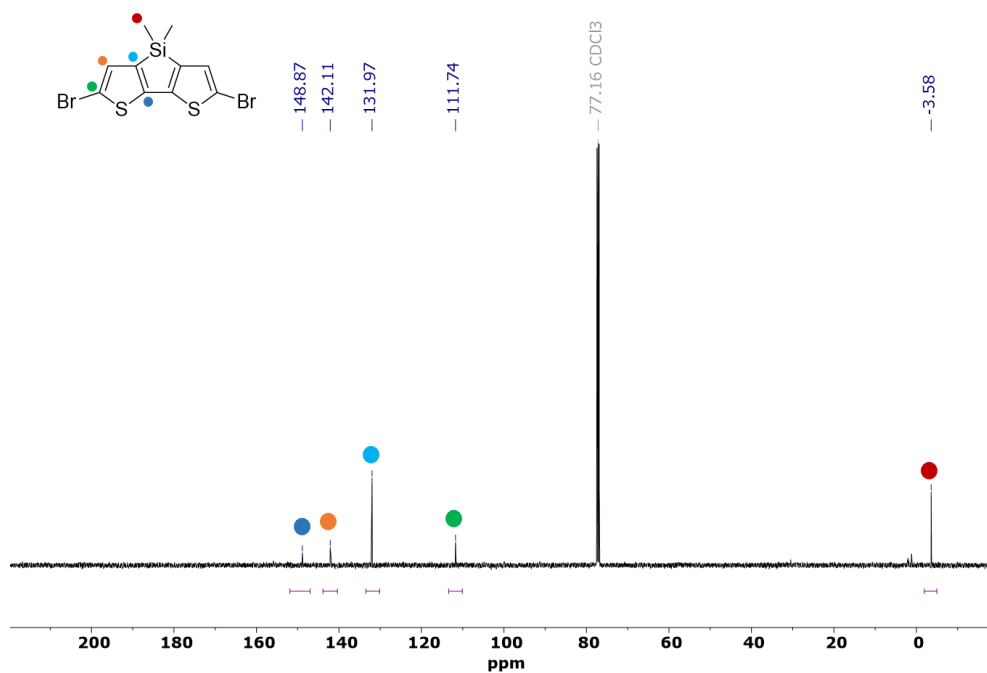


Figure S3.2: ^1H - ^{29}Si HMQC (600 MHz, C_6D_6) spectrum of **1**.

Figure S3.3: $^1\text{H-NMR}$ (600 MHz, C_6D_6) spectrum of **2**.Figure S3.4: $^{13}\text{C-NMR}$ (600 MHz, C_6D_6) spectrum of **2**.

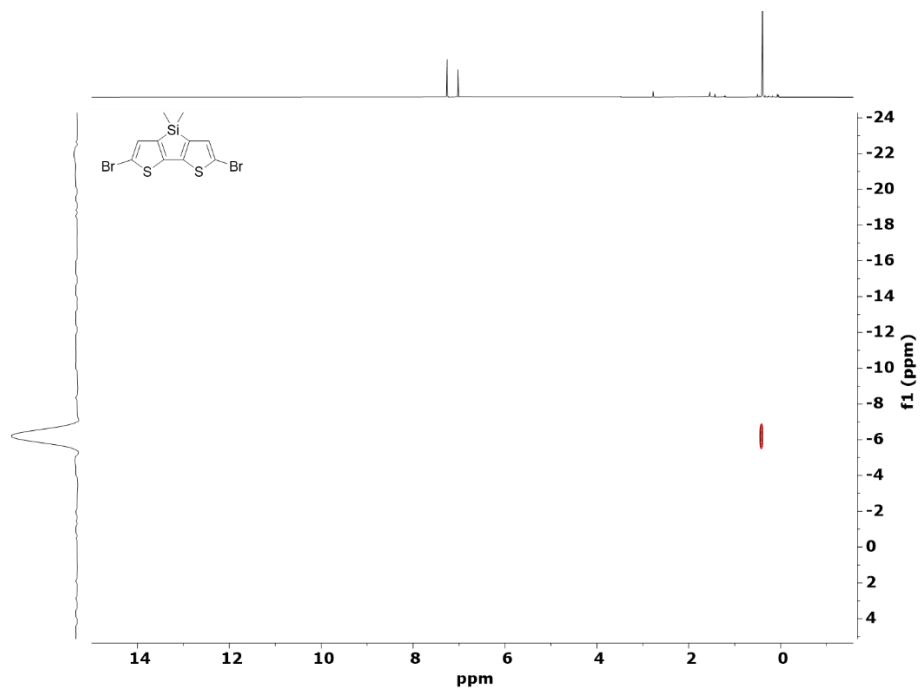


Figure S3.5: ^1H - ^{29}Si HMQC (600 MHz, C_6D_6) spectrum of **2**.

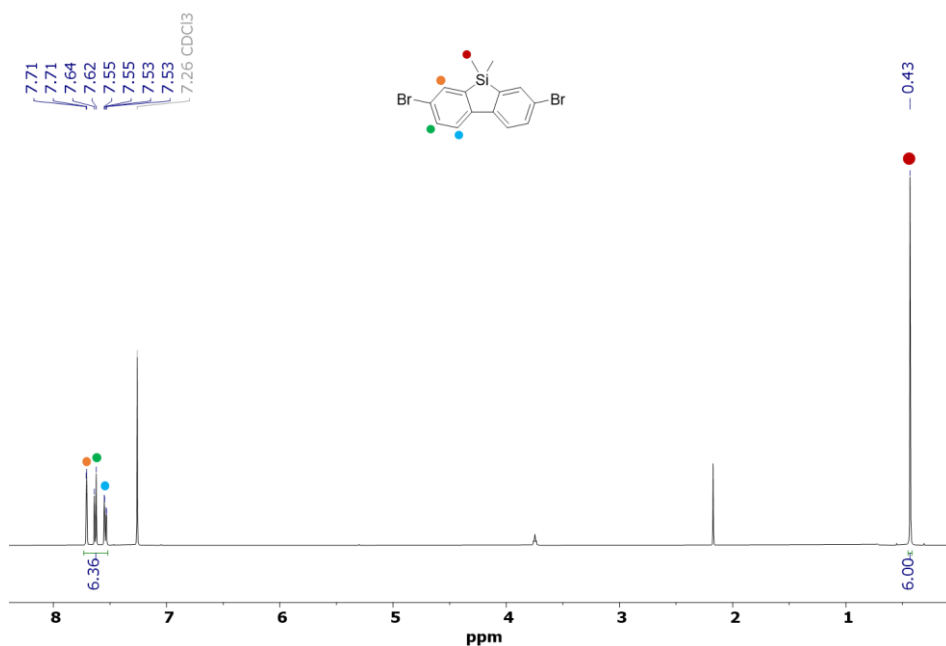


Figure S3.6: ^1H -NMR (600 MHz, C_6D_6) spectrum of **3**

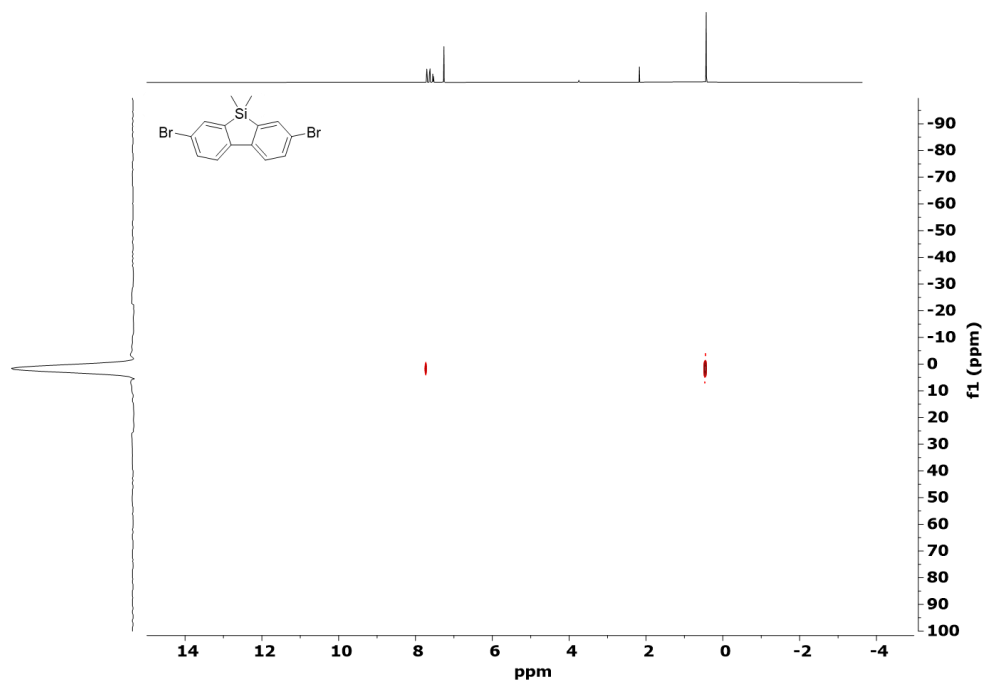


Figure S3.7: ^1H - ^{29}Si HMQC (600 MHz, C_6D_6) spectrum of **3**. The Si signals present are located at $^1\text{H} = 0,46$ ppm $^{29}\text{Si} = 1,66$ ppm for the aliphatic one and at $^1\text{H} = 7,74$ ppm $^{29}\text{Si} = 1,66$ ppm for the aromatic one.

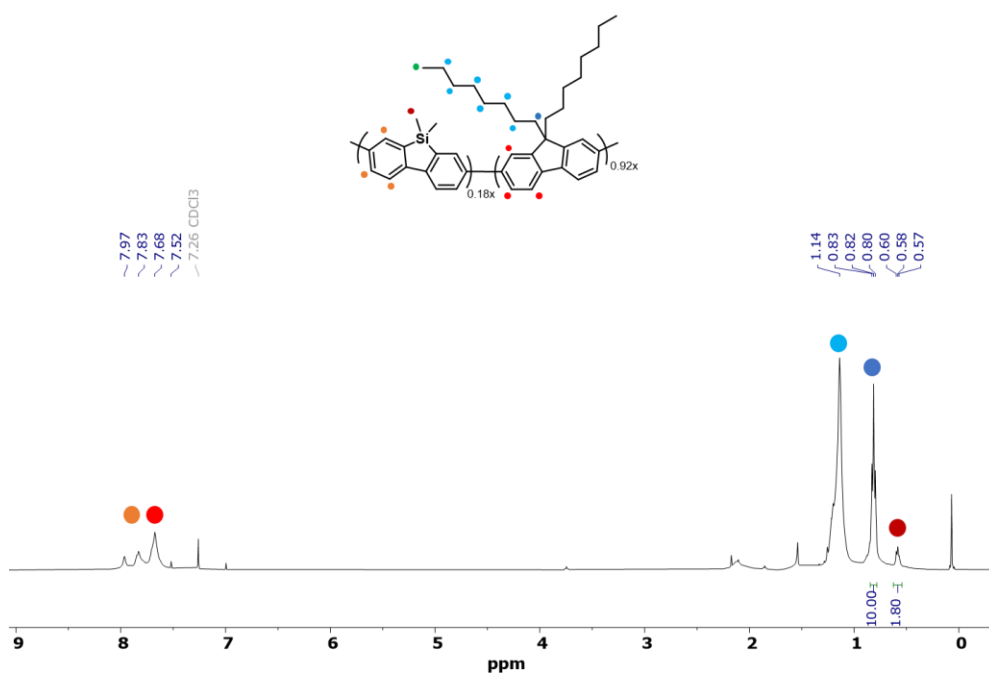


Figure S3.8: ^1H -NMR (600 MHz, C_6D_6) spectrum of copolymer PF1.

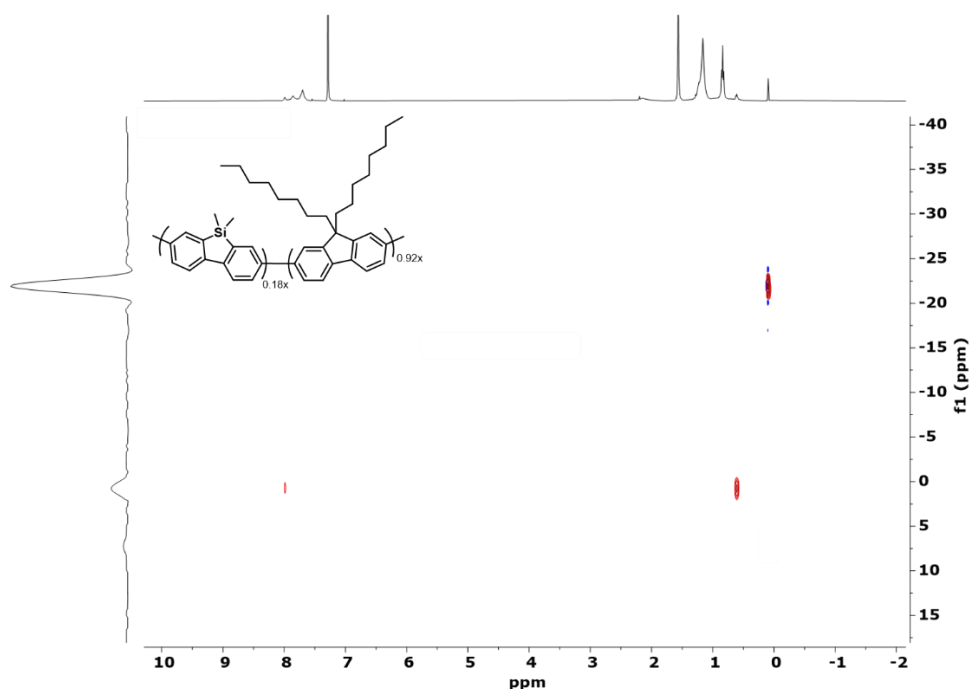


Figure S3.9: ^1H - ^{29}Si HMQC (600 MHz, C_6D_6) spectrum of copolymer PF1. Si signals of PF1 copolymer are located at $^1\text{H} = 0,61$ ppm $^{29}\text{Si} = 0,93$ ppm for the aliphatic one and at $^1\text{H} = 7,98$ ppm $^{29}\text{Si} = 1,66$ ppm for the aromatic one. Si signal present at $^1\text{H} = 0.09$ - $^{29}\text{Si} = -21.93$ ppm corresponds to silicon grease.

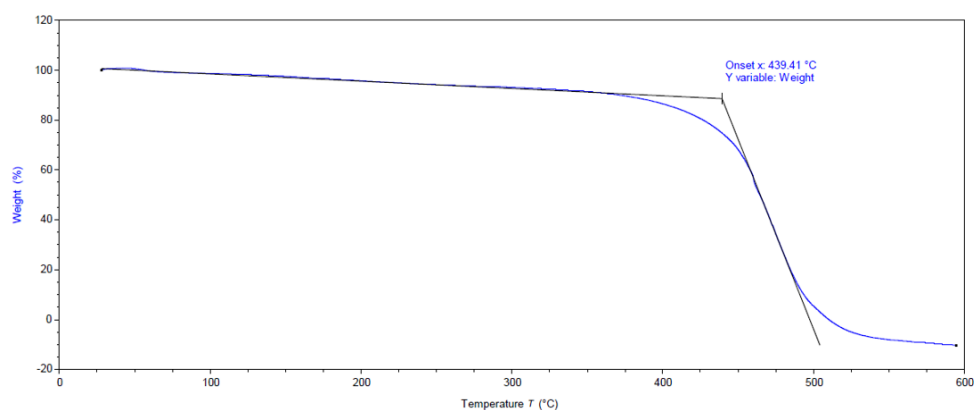


Figure S3.10: Thermal Gravimetric Analysis of PF1 in N_2 .

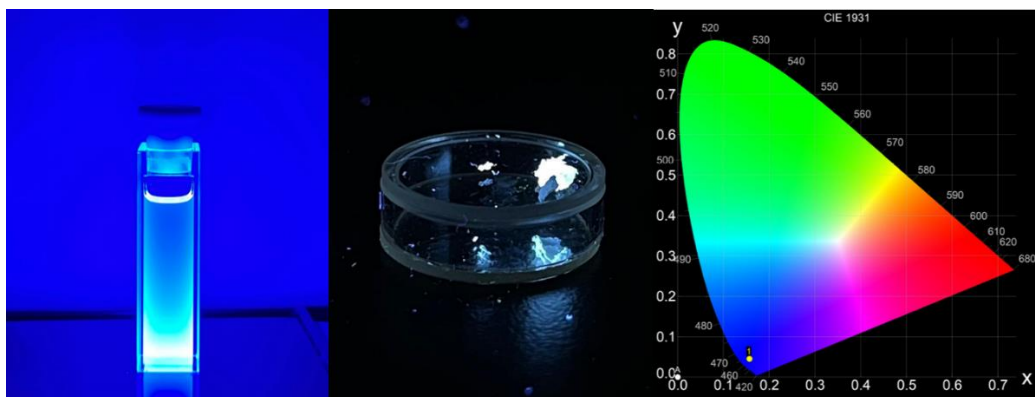


Figure S3.11: PF1 copolymer deep blue fluorescent emission in DCM solution (left panel), in solid state (middle panel) and CIE coordinates (X=0.15, Y=0.04) (right panel).

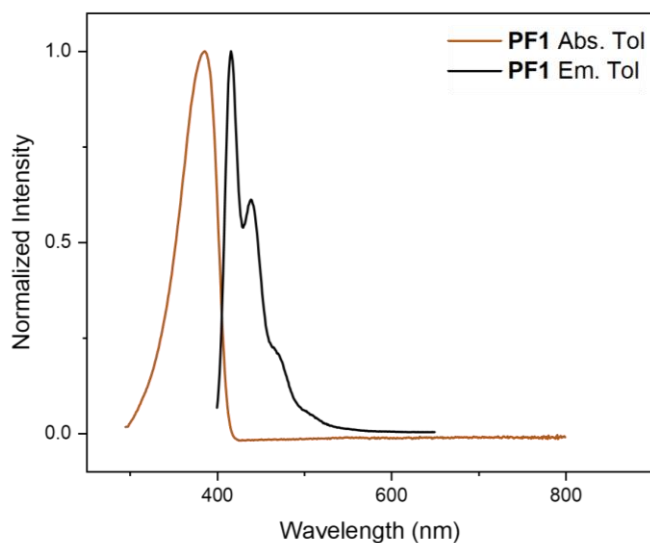


Figure S3.12: Optical spectroscopic data of PF1 in toluene. The absorption peak is at 386 nm, and the emission peaks are at 416 nm, 439 nm, and 475 nm when excited at 390 nm. The Stokes shift is 30 cm⁻¹.

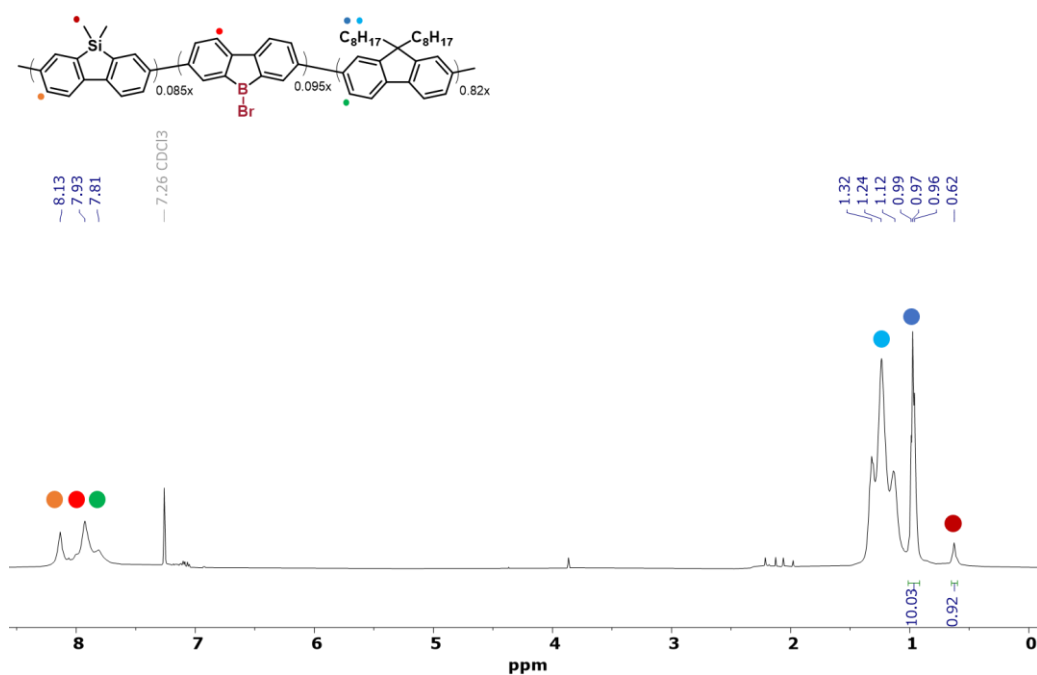


Figure S3.13: $^1\text{H-NMR}$ (600 MHz, C_6D_6) spectrum of copolymer PF1.

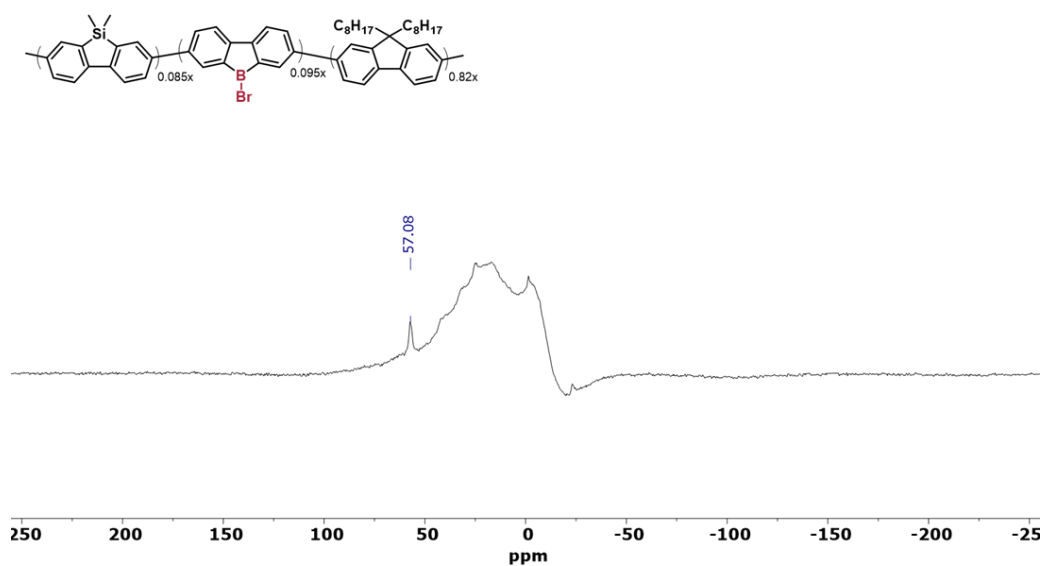


Figure S3.14: $^{11}\text{B-NMR}$ (600 MHz, C_6D_6) of PF2 copolymer.

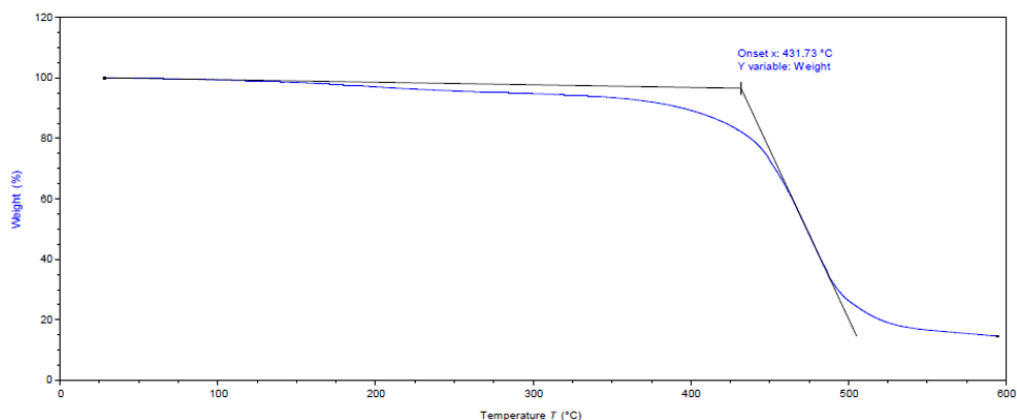


Figure S3.15: Thermal Gravimetric Analysis of PF2 in N₂.

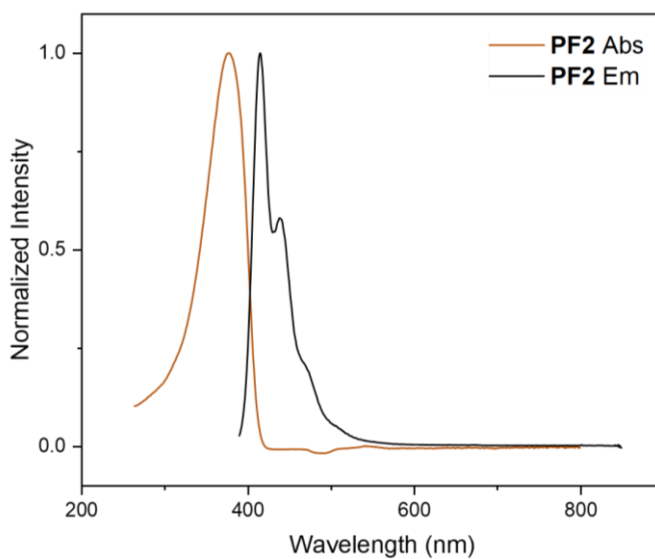
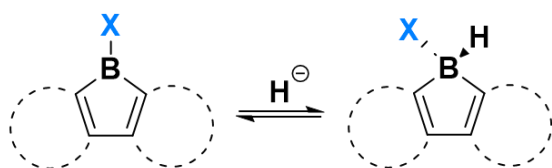


Figure S3.16: Optical spectroscopic data of PF2 in DCM. The absorption peak is at 377 nm, and the emission peaks are at 415 nm, 439 nm, and 475 nm when excited at 380 nm. The Stokes shift is 38 cm⁻¹.



Bf: dibenzoborole
Bt: dithiopheneborole

X	Bf	Bt
Ph	-78.42	-78.26
Br	-69.00	-76.07
Cl	-81.56	-87.67
F	-86.38	-90.15
OH	-56.43	-64.12
OMe	-59.06	-70.09

Figure S3.17: Hydride Affinity values as ΔH in kcal/mol of Bf and Bt derivatives (-Ph, -Br, -Cl, -F, -OH, -OMe).

Table S3.1: HOMO, LUMO, and energy bandgap values in eV for PF0, PF1, and PF2

Molecule	HOMO-1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)	Energy Gap (H-> L) (eV)
PF0	-7.38	-7.14	-0.03	0.209	7.11
PF1	-7.38	-7.16	-0.06	0.2	7.10
PF2	-7.42	-7.26	-0.93	-0.009	6.33

Table S3.2: Results from TDDFT calculations on **PFO** oligomer

λ (nm)	Oscillator strength f	Assignment (%)
377	3.4021	H-1 $\rightarrow$ L+1 (3.29) H $\rightarrow$ L (45.59)
345	0.0014	H-1 $\rightarrow$ L (24.79) H $\rightarrow$ L+1 (23.51)
335	0.0001	H-1 $\rightarrow$ L (23.08) H $\rightarrow$ L+1 (24.33)
320	0.6949	H-2 $\rightarrow$ L (2.89) H-1 $\rightarrow$ L+1 (39.84) H $\rightarrow$ L (2.49) H $\rightarrow$ L+2 (3.44)
315	0.0010	H-2 $\rightarrow$ L (22.14) H-1 $\rightarrow$ L+1 (5.06) H $\rightarrow$ L (1.60) H $\rightarrow$ L+2 (19.08)
310	0.0651	H-2 $\rightarrow$ L (22.14) H-1 $\rightarrow$ L+1 (5.06) H $\rightarrow$ L (1.60) H $\rightarrow$ L+2 (19.08)
298	0.0051	H-2 $\rightarrow$ L+1 (1.06) H-1 $\rightarrow$ L+2 (26.41) H-1 $\rightarrow$ L+4 (1.49) H $\rightarrow$ L+3 (14.39)
296	0.0014	H-3 $\rightarrow$ L (5.34) H-2 $\rightarrow$ L+1 (36.56) H $\rightarrow$ L+3 (3.23)

λ (nm)	Oscillator strength f	Assignment (%)
294	0.0001	H-13 $\rightarrow$ L+1 (1.62) H-2 $\rightarrow$ L+4 (4.94) H-1 $\rightarrow$ L+5 (6.49) H $\rightarrow$ L+8 (3.18)
293	0.0021	H-14 $\rightarrow$ L (3.55) H-1 $\rightarrow$ L+6 (12.06)
290	0.0001	H-2 $\rightarrow$ L+8 (1.29) H-1 $\rightarrow$ L+9 (21.64) H $\rightarrow$ L+6 (5.31)
286.9	0.0006	H-4 $\rightarrow$ L+7 (5.44) H-1 $\rightarrow$ L+8 (12.36)
286.6	0.0021	H-5 $\rightarrow$ L+8 (2.98) H-1 $\rightarrow$ L+5 (23.77)
282	0.0026	H-2 $\rightarrow$ L+9 (3.99) H-1 $\rightarrow$ L+8 (4.26)
275.6	0.1757	H-3 $\rightarrow$ L (16.31) H $\rightarrow$ L+5 (1.23)
275.3	0.2155	H-8 $\rightarrow$ L+1 (5.66)
274.	0.0009	H-9 $\rightarrow$ L+2 (4.12)

Table S3.3: Results from TDDFT calculations on **PF1** oligomer

λ (nm)	Oscillator strength f	Assignment (%)	λ (nm)	Oscillator strength f	Assignment (%)	λ (nm)	Oscillator strength f	Assignment (%)				
379	3.2176	H-1 $\rightarrow$ L+1 (2.98) H $\rightarrow$ L (45.77)	295	0.0006	H-12 $\rightarrow$ L (1.93) H-2 $\rightarrow$ L+1 (9.10) H-1 $\rightarrow$ L+3 (4.51) H-1 $\rightarrow$ L+6 (5.25) H $\rightarrow$ L+5 (10.88) H $\rightarrow$ L+7 (8.15) H $\rightarrow$ L+9 (2.93)	282	0.0001	H-3 $\rightarrow$ L (4.01) H-2 $\rightarrow$ L+5 (1.35) H-2 $\rightarrow$ L+9 (1.47) H-1 $\rightarrow$ L+6 (4.33) H-1 $\rightarrow$ L+8 (3.12) H-1 $\rightarrow$ L+10 (2.48) H $\rightarrow$ L+5 (11.94) H $\rightarrow$ L+9 (14.45)				
346	0.0319	H-1 $\rightarrow$ L (33.60) H $\rightarrow$ L+1 (14.59)			294			0.0019	H-13 $\rightarrow$ L (2.49) H-12 $\rightarrow$ L+1 (1.70) H-1 $\rightarrow$ L+5 (4.24) H-1 $\rightarrow$ L+7 (4.91) H-1 $\rightarrow$ L+9 (2.19) H $\rightarrow$ L+6 (25.21) H $\rightarrow$ L+8 (3.61) H $\rightarrow$ L+10 (1.68)	281	0.0516	H-4 $\rightarrow$ L (13.68) H-3 $\rightarrow$ L+1 (14.20) H-2 $\rightarrow$ L+3 (7.02) H-1 $\rightarrow$ L+5 (3.05) H-1 $\rightarrow$ L+9 (1.82) H $\rightarrow$ L+6 (1.03) H $\rightarrow$ L+10 (4.86)
336	0.0029	H-1 $\rightarrow$ L (14.40) H-1 $\rightarrow$ L+2 (1.62) H $\rightarrow$ L+1 (32.76)							292			0.0004
323	0.6613	H-2 $\rightarrow$ L (1.10) H-2 $\rightarrow$ L+4 (1.07) H-1 $\rightarrow$ L+1 (21.73) H $\rightarrow$ L+2 (18.18) H $\rightarrow$ L+4 (5.73)	287	0.0001		H-3 $\rightarrow$ L (8.57) H-2 $\rightarrow$ L+9 (1.05) H-1 $\rightarrow$ L+4 (10.00) H-1 $\rightarrow$ L+8 (6.87) H $\rightarrow$ L+5 (4.33) H $\rightarrow$ L+7 (10.57)	275					
317	0.1393	H-2 $\rightarrow$ L (7.71) H-1 $\rightarrow$ L+1 (17.19) H $\rightarrow$ L (1.29) H $\rightarrow$ L+2 (12.40) H $\rightarrow$ L+4 (7.82)			286	0.0006		H-10 $\rightarrow$ L+2 (1.69) H-9 $\rightarrow$ L (1.25) H-2 $\rightarrow$ L+3 (1.04) H-2 $\rightarrow$ L+8 (2.42) H-1 $\rightarrow$ L+5 (4.75) H-1 $\rightarrow$ L+7 (6.70) H-1 $\rightarrow$ L+9 (4.91) H $\rightarrow$ L+6 (1.52) H $\rightarrow$ L+8 (17.83)		274	0.0024	
315	0.0456	H-2 $\rightarrow$ L (32.80) H-1 $\rightarrow$ L+1 (4.11) H $\rightarrow$ L (1.16) H $\rightarrow$ L+4 (7.69)						285	0.0003			H-14 $\rightarrow$ L (1.09) H-3 $\rightarrow$ L+3 (1.39) H-1 $\rightarrow$ L+3 (1.15) H-1 $\rightarrow$ L+4 (31.10) H-1 $\rightarrow$ L+8 (2.48) H $\rightarrow$ L+5 (4.53) H $\rightarrow$ L+7 (3.48) H $\rightarrow$ L+12 (1.21)
309	0.0465	H-11 $\rightarrow$ L (1.13) H-2 $\rightarrow$ L (5.93) H-2 $\rightarrow$ L+4 (1.16) H-1 $\rightarrow$ L+1 (2.16) H $\rightarrow$ L+2 (16.56) H $\rightarrow$ L+4 (20.05)										
300	0.0145	H-2 $\rightarrow$ L+1 (2.38) H-1 $\rightarrow$ L+3 (39.75) H $\rightarrow$ L+1 (1.45) H $\rightarrow$ L+5 (3.80)										
297	0.0037	H-3 $\rightarrow$ L (10.29) H-2 $\rightarrow$ L+1 (24.17) H-1 $\rightarrow$ L+6 (1.97) H $\rightarrow$ L+5 (9.45)										

Table S3.4: Results from TDDFT calculations on **PF2** oligomer

λ (nm)	Oscillator strength f	Assignment (%)	λ (nm)	Oscillator strength f	Assignment (%)	λ (nm)	Oscillator strength f	Assignment (%)
526	0.1532	H-2 $\rightarrow$ L (5.53) H $\rightarrow$ L (43.27)	321.95	0.0010	H-12 $\rightarrow$ L (6.26) H-11 $\rightarrow$ L (11.08) H-8 $\rightarrow$ L (5.46) H-7 $\rightarrow$ L (24.73)	307.8	0.0045	H-12 $\rightarrow$ L (18.87) H-10 $\rightarrow$ L (3.71) H-8 $\rightarrow$ L (2.09) H-7 $\rightarrow$ L (10.02) H-6 $\rightarrow$ L (13.18)
456	0.0004	H-3 $\rightarrow$ L (1.28) H-1 $\rightarrow$ L (48.50)	321.92	0.0009	H-12 $\rightarrow$ L (9.29) H-11 $\rightarrow$ L (7.60) H-10 $\rightarrow$ L (1.24) H-8 $\rightarrow$ L (24.32) H-7 $\rightarrow$ L (6.02)	307.2	0.0001	H-11 $\rightarrow$ L (4.49) H-9 $\rightarrow$ L (1.29) H-8 $\rightarrow$ L (2.43) H-6 $\rightarrow$ L (3.49) H-5 $\rightarrow$ L (36.78)
417	0.0345	H-4 $\rightarrow$ L (4.14) H-2 $\rightarrow$ L (38.83) H $\rightarrow$ L (6.53)	315	0.1543	H-13 $\rightarrow$ L (6.50) H-2 $\rightarrow$ L+1 (1.99) H-2 $\rightarrow$ L+4 (1.42) H-1 $\rightarrow$ L+2 (32.06) H $\rightarrow$ L+1 (5.91)	307.1	0.0005	H-12 $\rightarrow$ L (9.41) H-8 $\rightarrow$ L (1.47) H-7 $\rightarrow$ L (4.46) H-6 $\rightarrow$ L (30.88) H-5 $\rightarrow$ L (2.97)
369	0.0011	H-3 $\rightarrow$ L (47.78) H-1 $\rightarrow$ L (1.39)	310	0.0001	H-16 $\rightarrow$ L (42.71) H-14 $\rightarrow$ L (1.46) H-11 $\rightarrow$ L (2.32) H-8 $\rightarrow$ L (1.94)	301	0.1195	H-13 $\rightarrow$ L (9.72) H-3 $\rightarrow$ L+2 (1.34) H-2 $\rightarrow$ L+1 (19.68) H-1 $\rightarrow$ L+5 (1.07) H $\rightarrow$ L+4 (13.87)
367	2.9946	H-1 $\rightarrow$ L+2 (3.89) H $\rightarrow$ L+1 (43.39)	309	0.0054	H-2 $\rightarrow$ L+1 (20.16) H-1 $\rightarrow$ L+5 (1.18) H $\rightarrow$ L+4 (25.85)	300	0.0013	H-14 $\rightarrow$ L (1.10) H-9 $\rightarrow$ L (42.23) H-5 $\rightarrow$ L (2.04) H-1 $\rightarrow$ L+4 (1.73)
350	0.1462	H-13 $\rightarrow$ L (1.89) H-4 $\rightarrow$ L (41.62) H-2 $\rightarrow$ L (5.09)	308	0.0001	H-16 $\rightarrow$ L (4.44) H-11 $\rightarrow$ L (21.74) H-9 $\rightarrow$ L (1.40) H-8 $\rightarrow$ L (11.52) H-6 $\rightarrow$ L (4.27)			
342	0.0090	H-1 $\rightarrow$ L+1 (27.13) H $\rightarrow$ L+2 (21.19)						
331	0.9342	H-13 $\rightarrow$ L (22.76) H-4 $\rightarrow$ L (2.15) H-2 $\rightarrow$ L+1 (4.00) H-1 $\rightarrow$ L+2 (10.95) H $\rightarrow$ L+4 (6.24)						
330	0.0004	H-1 $\rightarrow$ L+1 (20.96) H-1 $\rightarrow$ L+4 (1.52) H $\rightarrow$ L+2 (26.05)						

References

1. Swager TM. The Molecular Wire Approach to Sensory Signal Amplification. *Acc Chem Res.* 1998;31(5):201-207. doi:10.1021/ar9600502
2. Li H, Jäkle F. Universal Scaffold for Fluorescent Conjugated Organoborane Polymers. *Angew Chem.* 2009;121(13):2349-2352. doi:10.1002/ange.200805863
3. Jäkle F. Lewis acidic organoboron polymers. *Coordination Chemistry Reviews.* 2006;250(9-10):1107-1121. doi:10.1016/j.ccr.2006.01.007
4. Sirringhaus H. 25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon. *Advanced Materials.* 2014;26(9):1319-1335. doi:10.1002/adma.201304346
5. Beaujuge PM, Reynolds JR. Color Control in π -Conjugated Organic Polymers for Use in Electrochromic Devices. *Chem Rev.* 2010;110(1):268-320. doi:10.1021/cr900129a
6. Kulkarni AP, Tonzola CJ, Babel A, Jenekhe SA. Electron Transport Materials for Organic Light-Emitting Diodes. *Chem Mater.* 2004;16(23):4556-4573. doi:10.1021/cm049473l
7. Nelson J. Polymer:fullerene bulk heterojunction solar cells. *Materials Today.* 2011;14(10):462-470. doi:10.1016/S1369-7021(11)70210-3
8. Padinger F, Rittberger RS, Sariciftci NS. Effects of Postproduction Treatment on Plastic Solar Cells. *Adv Funct Materials.* 2003;13(1):85-88. doi:10.1002/adfm.200390011
9. Blouin N, Michaud A, Gendron D, et al. Toward a Rational Design of Poly(2,7-Carbazole) Derivatives for Solar Cells. *J Am Chem Soc.* 2008;130(2):732-742. doi:10.1021/ja0771989
10. Rivard E. Tellurophenes and Their Emergence as Building Blocks for Polymeric and Light-emitting Materials. *Chemistry Letters.* 2015;44(6):730-736. doi:10.1246/cl.150119
11. Linshoeft J, Baum EJ, Hussain A, Gates PJ, Näther C, Staubitz A. Highly Tin-Selective Stille Coupling: Synthesis of a Polymer Containing a Stannole in the Main Chain. *Angew Chem Int Ed.* 2014;53(47):12916-12920. doi:10.1002/anie.201407377

12. Fell VHK, Mikosch A, Steppert AK, et al. Synthesis and Optical Characterization of Hybrid Organic–Inorganic Heterofluorene Polymers. *Macromolecules*. 2017;50(6):2338-2343. doi:10.1021/acs.macromol.6b02611
13. Wang E, Li C, Peng J, Cao Y. High-efficiency blue light-emitting polymers based on 3,6-silafluorene and 2,7-silafluorene. *J Polym Sci A Polym Chem*. 2007;45(21):4941-4949. doi:10.1002/pola.22243
14. Wang E, Li C, Mo Y, et al. Poly(3,6-silafluorene-co-2,7-fluorene)-based high-efficiency and color-pure blue light-emitting polymers with extremely narrow band-width and high spectral stability. *J Mater Chem*. 2006;16(42):4133. doi:10.1039/b609250k
15. Kim DY, Cho HN, Kim CY. Blue light emitting polymers. *Progress in Polymer Science*. 2000;25(8):1089-1139. doi:10.1016/S0079-6700(00)00034-4
16. Chan KL, McKiernan MJ, Towns CR, Holmes AB. Poly(2,7-dibenzosilole): A Blue Light Emitting Polymer. *J Am Chem Soc*. 2005;127(21):7662-7663. doi:10.1021/ja0508065
17. Keyworth CW, Chan KL, Labram JG, et al. The tuning of the energy levels of dibenzosilole copolymers and applications in organic electronics. *J Mater Chem*. 2011;21(32):11800. doi:10.1039/c1jm11242b
18. Jäkle F. Advances in the Synthesis of Organoborane Polymers for Optical, Electronic, and Sensory Applications. *Chem Rev*. 2010;110(7):3985-4022. doi:10.1021/cr100026f
19. Yu Y, Dong C, Alahmadi AF, et al. A p - π^* conjugated triarylborane as an alcohol-processable n -type semiconductor for organic optoelectronic devices. *J Mater Chem C*. 2019;7(24):7427-7432. doi:10.1039/C9TC01562K
20. Entwistle CD, Marder TB. Boron Chemistry Lights the Way: Optical Properties of Molecular and Polymeric Systems C.D.E. thanks EPSRC for a postgraduate studentship and Syngenta for a postgraduate scholarship, and T.B.M. thanks the University of Durham for support and Prof. Dr. K. Tamao for a preprint of ref. 32. *Angew Chem Int Ed*. 2002;41(16):2927. doi:10.1002/1521-3773(20020816)41:16<2927::AID-ANIE2927>3.0.CO;2-L
21. Ansorg K, Braunschweig H, Chiu C, et al. The Pentaphenylborole–2,6-Lutidine Adduct: A System with Unusual Thermochromic and Photochromic Properties. *Angew Chem Int Ed*. 2011;50(12):2833-2836. doi:10.1002/anie.201006234
22. Yin X, Guo F, Lalancette RA, Jäkle F. Luminescent Main-Chain Organoborane Polymers: Highly Robust, Electron-Deficient Poly(oligothiophene borane)s via Stille

- Coupling Polymerization. *Macromolecules*. 2016;49(2):537-546. doi:10.1021/acs.macromol.5b02446
23. Hudnall TW, Chiu CW, Gabbai FP. Fluoride Ion Recognition by Chelating and Cationic Boranes. *Acc Chem Res*. 2009;42(2):388-397. doi:10.1021/ar8001816
24. Wade CR, Broomsgrove AEJ, Aldridge S, Gabbai FP. Fluoride Ion Complexation and Sensing Using Organoboron Compounds. *Chem Rev*. 2010;110(7):3958-3984. doi:10.1021/cr900401a
25. Cheng F, Jäkle F. Boron-containing polymers as versatile building blocks for functional nanostructured materials. *Polym Chem*. 2011;2(10):2122. doi:10.1039/c1py00123j
26. Matsumi N, Naka K, Chujo Y. Extension of π -Conjugation Length via the Vacant p-Orbital of the Boron Atom. Synthesis of Novel Electron Deficient π -Conjugated Systems by Hydroboration Polymerization and Their Blue Light Emission. *J Am Chem Soc*. 1998;120(20):5112-5113. doi:10.1021/ja9741943
27. Chujo Y, Morimoto M, Tomita I. Hydroboration Copolymerization of Dienes and Dicyano Compounds with Thexylborane. *Polym J*. 1995;27(1):90-97. doi:10.1295/polymj.27.90
28. Chujo Y, Takizawa N, Sakurai T. Synthesis of poly(organoboron halide)s by hydroboration polymerization between diene and monobromoborane. *J Chem Soc, Chem Commun*. 1994;(2):227. doi:10.1039/c39940000227
29. Li H, Jäkle F. Donor- π -Acceptor Polymer with Alternating Triarylborane and Triphenylamine Moieties. *Macromol Rapid Commun*. 2010;31(9-10):915-920. doi:10.1002/marc.200900932
30. Sundararaman A, Venkatasubbaiah K, Victor M, Zakharov LN, Rheingold AL, Jäkle F. Electronic Communication and Negative Binding Cooperativity in Diborylated Bithiophenes. *J Am Chem Soc*. 2006;128(51):16554-16565. doi:10.1021/ja064396b
31. Parab K, Venkatasubbaiah K, Jäkle F. Luminescent Triarylborane-Functionalized Polystyrene: Synthesis, Photophysical Characterization, and Anion-Binding Studies. *J Am Chem Soc*. 2006;128(39):12879-12885. doi:10.1021/ja063302v
32. Qin Y, Cheng G, Achara O, Parab K, Jäkle F. A New Route to Organoboron Polymers via Highly Selective Polymer Modification Reactions. *Macromolecules*. 2004;37(19):7123-7131. doi:10.1021/ma035880r

-
33. Alahmadi AF, Zuo J, Jäkle F. B-N Lewis pair-fused dipyriddyfluorene copolymers incorporating electron-deficient benzothiadiazole comonomers. *Polym J.* 2023;55(4):433-442. doi:10.1038/s41428-022-00723-y
 34. Adachi Y, Sakabe M, Nomura T, Ohshita J. Conjugated polymers with thiophene-fused thiaborin units and their strong intermolecular interactions. *Polym J.* 2023;55(4):489-496. doi:10.1038/s41428-022-00726-9
 35. Qin Y, Cheng G, Sundararaman A, Jäkle F. Well-Defined Boron-Containing Polymeric Lewis Acids. *J Am Chem Soc.* 2002;124(43):12672-12673. doi:10.1021/ja020773i
 36. Adams IA, Rugar PA. A Poly(9-Borafluorene) Homopolymer: An Electron-Deficient Polyfluorene with "Turn-On" Fluorescence Sensing of NH₃ Vapor. *Macromol Rapid Commun.* 2015;36(14):1336-1340. doi:10.1002/marc.201500107
 37. Ren Y, Jäkle F. Merging thiophene with boron: new building blocks for conjugated materials. *Dalton Trans.* 2016;45(36):13996-14007. doi:10.1039/C6DT02756C
 38. Ji L, Griesbeck S, Marder TB. Recent developments in and perspectives on three-coordinate boron materials: a bright future. *Chem Sci.* 2017;8(2):846-863. doi:10.1039/C6SC04245G
 39. Helten H. Doping the Backbone of π -Conjugated Polymers with Tricoordinate Boron: Synthetic Strategies and Emerging Applications. *Chemistry An Asian Journal.* 2019;14(7):919-935. doi:10.1002/asia.201900016
 40. Wang M, Nudelman F, Matthes RR, Shaver MP. Frustrated Lewis Pair Polymers as Responsive Self-Healing Gels. *J Am Chem Soc.* 2017;139(40):14232-14236. doi:10.1021/jacs.7b07725
 41. Liu R, Wang Y, Yan Q. CO₂-Strengthened Double-Cross-Linked Polymer Gels from Frustrated Lewis Pair Networks. *Macromol Rapid Commun.* 2021;42(6):2000699. doi:10.1002/marc.202000699
 42. Anthony JE. Functionalized Acenes and Heteroacenes for Organic Electronics. *Chem Rev.* 2006;106(12):5028-5048. doi:10.1021/cr050966z
 43. Zhang L, Cao Y, Colella NS, et al. Unconventional, Chemically Stable, and Soluble Two-Dimensional Angular Polycyclic Aromatic Hydrocarbons: From Molecular Design to Device Applications. *Acc Chem Res.* 2015;48(3):500-509. doi:10.1021/ar500278w
 44. Hollister KK, Molino A, Breiner G, et al. Air-Stable Thermoluminescent Carbodicarbene-Borafluorenium Ions. *J Am Chem Soc.* 2022;144(1):590-598. doi:10.1021/jacs.1c11861

45. Wakamiya A, Mishima K, Ekawa K, Yamaguchi S. Kinetically stabilized dibenzoborole as an electron-accepting building unit. *Chem Commun.* 2008;(5):579-581. doi:10.1039/B716107G
46. Vidal F, Gomezcoello J, Lalancette RA, Jäkle F. Lewis Pairs as Highly Tunable Dynamic Cross-Links in Transient Polymer Networks. *J Am Chem Soc.* 2019;141(40):15963-15971. doi:10.1021/jacs.9b07452
47. Plumley JA, Evanseck JD. Periodic Trends and Index of Boron Lewis Acidity. *J Phys Chem A.* 2009;113(20):5985-5992. doi:10.1021/jp811202c
48. Kim Y, Cook S, Choulis SA, Nelson J, Durrant JR, Bradley DDC. Organic Photovoltaic Devices Based on Blends of Regioregular Poly(3-hexylthiophene) and Poly(9,9-dioctylfluorene- co -benzothiadiazole). *Chem Mater.* 2004;16(23):4812-4818. doi:10.1021/cm049585c
49. Tsiminis G, Ruseckas A, Samuel IDW, Turnbull GA. A two-photon pumped polyfluorene laser. *Applied Physics Letters.* 2009;94(25):253304. doi:10.1063/1.3149827
50. Zaumseil J, Donley CL, Kim J -S., Friend RH, Sirringhaus H. Efficient Top-Gate, Ambipolar, Light-Emitting Field-Effect Transistors Based on a Green-Light-Emitting Polyfluorene. *Advanced Materials.* 2006;18(20):2708-2712. doi:10.1002/adma.200601080
51. Geng Y, Chen ACA, Ou JJ, et al. Monodisperse Glassy-Nematic Conjugated Oligomers with Chemically Tunable Polarized Light Emission. *Chem Mater.* 2003;15(23):4352-4360. doi:10.1021/cm034579m
52. Song J, Du C, Li C, Bo Z. Silole-containing polymers for high-efficiency polymer solar cells. *J Polym Sci A Polym Chem.* 2011;49(19):4267-4274. doi:10.1002/pola.24870
53. Su X, Bartholome TA, Tidwell JR, et al. 9-Borafluorenes: Synthesis, Properties, and Reactivity. *Chem Rev.* 2021;121(7):4147-4192. doi:10.1021/acs.chemrev.0c01068
54. Neher D. Polyfluorene Homopolymers: Conjugated Liquid-Crystalline Polymers for Bright Blue Emission and Polarized Electroluminescence. *Macromol Rapid Commun.* 2001;22(17):1365-1385. doi:10.1002/1521-3927(20011101)22:17<1365::AID-MARC1365>3.0.CO;2-B
55. Chan KL, McKiernan MJ, Towns CR, Holmes AB. Enhanced color stability from poly(2,7-dibenzosilole). In: Kafafi ZH, Lane PA, eds. ; 2005:59372A. doi:10.1117/12.646429

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56. Smith T, Guild J. The C.I.E. colorimetric standards and their use. *Trans Opt Soc.* 1931;33(3):73-134. doi:10.1088/1475-4878/33/3/301
57. Xu X, Bai K, Ding J, Wang L. Deep-blue emitting poly(2',3',6',7'-tetraoctyl-2,7-spirosilabifluorene) simultaneously with good color purity and high external quantum efficiency. *Organic Electronics.* 2018;59:77-83. doi:10.1016/j.orgel.2018.04.046
58. Zhu M, Yang C. Blue fluorescent emitters: design tactics and applications in organic light-emitting diodes. *Chem Soc Rev.* 2013;42(12):4963. doi:10.1039/c3cs35440g
59. Klärner G, Davey MH, Chen WD, Scott JC, Miller RD. Colorfast Blue-Light-Emitting Random Copolymers Derived from Di-n-hexylfluorene and Anthracene. *Adv Mater.* 1998;10(13):993-997. doi:10.1002/(SICI)1521-4095(199809)10:13<993::AID-ADMA993>3.0.CO;2-2
60. Wang J, Zhang C qing, Zhong C mei, et al. Highly Efficient and Stable Deep Blue Light Emitting Poly(9,9-dialkoxyphenyl- 2,7-silafluorene): Synthesis and Electroluminescent Properties. *Macromolecules.* 2011;44(1):17-19. doi:10.1021/ma102446b
61. Chen H, Hou J, Hayden AE, Yang H, Houk KN, Yang Y. Silicon Atom Substitution Enhances Interchain Packing in a Thiophene-Based Polymer System. *Advanced Materials.* 2010;22(3):371-375. doi:10.1002/adma.200902469
62. Berger CJ, He G, Merten C, McDonald R, Ferguson MJ, Rivard E. Synthesis and Luminescent Properties of Lewis Base-Appended Borafluorenes. *Inorg Chem.* 2014;53(3):1475-1486. doi:10.1021/ic402408t
63. Narula CK, Noeth H. Contribution to the chemistry of boron. 150. Competition between adduct and cation formation in reactions between diorganylborane derivatives and pyridine or lutidines. *Inorg Chem.* 1985;24(16):2532-2539. doi:10.1021/ic00210a014
64. Matsumoto T, Tanaka K, Chujo Y. High HOMO levels and narrow energy band gaps of dithienogalloles. *RSC Adv.* 2015;5(68):55406-55410. doi:10.1039/C5RA08584E
65. Chai JD, Head-Gordon M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys Chem Chem Phys.* 2008;10(44):6615. doi:10.1039/b810189b
66. Krishnan R, Binkley JS, Seeger R, Pople JA. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *The Journal of Chemical Physics.* 1980;72(1):650-654. doi:10.1063/1.438955

67. Hehre WJ, Ditchfield R, Pople JA. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *The Journal of Chemical Physics*. 1972;56(5):2257-2261. doi:10.1063/1.1677527
68. Runge E, Gross EKV. Density-Functional Theory for Time-Dependent Systems. *Phys Rev Lett*. 1984;52(12):997-1000. doi:10.1103/PhysRevLett.52.997
69. Frisch MJ, Trucks GW, Schlegel GE, et al. Gaussian 16 Revision C.01, gaussian Inc, Wallingford CT2016.

Chapter 4

Dynamic exchange in vinylogous urethanes
- combinatorial approaches for structure -
property relationships

4.1 Introduction

In the previous chapters, theoretical calculations provided crucial insights that guided more efficient experimental efforts. In Chapter 2, the mechanism of exchange in boron-based dynamic polymers was explored using a combination of DFT calculations and experimental validation, facilitating the design of covalent adaptable networks. Through DFT, we rationalized that a nucleophile like methanol (MeOH) could catalyze the exchange reaction, which was later confirmed experimentally in model studies and the material itself. This understanding highlighted how the incorporation of a nucleophilic moiety in a comonomer significantly accelerated stress relaxation, enabling more efficient material performance.

In Chapter 3, DFT served as a screening tool to identify boronic scaffolds for introduction into π -conjugated aromatic polymers (π CAPs) to achieve dynamic interactions with Lewis pairs. Additionally, DFT was instrumental in guiding the design by rationalizing the spectroscopic properties of the synthesized copolymer, ensuring the introduction of boron into the polymer framework would influence its optical behavior and electronic properties. These results underscored the predictive power of DFT in tailoring functional polymers for specific applications. This approach is extended in Chapter 4, focusing on vinylogous urethane-based CANs. DFT calculations were employed to gain a deeper understanding of the exchange reaction pathways, rate-determining steps, and the influence of structural variations on the transamination kinetics of different amines. By leveraging the advantages of DFT, we efficiently identified functional groups and structural modifications that could enhance reaction kinetics, providing a foundation for designing high-performance materials with improved processability and dynamic behavior.

Vinylogous urethanes stand out as a promising solution to the challenge of combining the high-performance characteristics of thermosets with the processability of thermoplastics.¹ What differentiates vinylogous urethanes from other vitrimer systems is their ability to undergo rapid exchange reactions at temperatures above 100°C without the need for external catalysts, while exhibiting a low or negligible exchange rate at room temperature.¹ This feature offers an important balance between ease of processing and maintaining structural integrity at service temperatures.² The catalyst-free nature of vinylogous urethanes, coupled with their dynamic behavior, makes them particularly appealing for advanced applications requiring both durability and the potential for reprocessing or reshaping. However, there is increasing interest to fine-tune the control of the reaction kinetics of these materials. Recent studies have demonstrated that external catalysts such as Toluene Sulfonic Acid and various Lewis and Brønsted acids can significantly enhance the exchange rate.^{3,4} Nevertheless, this approach presents challenges, particularly in minimizing catalyst loadings to avoid long-term degradation of material performance.^{2,5,6}

To address current challenges, this work focuses on fine-tuning the exchange kinetics of vinylogous urethanes through internal catalysis and neighboring group participation (NGP).⁹ By incorporating NGP into their molecular design, the goal is to enhance reshaping capabilities without the need for external catalysts, thus unlocking new functionalities and improving the efficiency and versatility of these materials.⁹ This involves introducing functional groups near exchangeable bonds to accelerate reaction rates via steric or electronic effects.¹⁰ Notable examples include citric acid-based esters, boronic esters, and silyl ethers, which represent an emerging area in vitrimer research.^{7,10–13}

An example of NGP in vinylogous urethanes was reported by Spiesschaert et al. (2020),¹⁴ where a comparison was made between a one-pot and a two-step synthesis for epoxy resins. The one-pot method exhibited faster relaxation times ($\tau = 3.5$ s) compared to the two-step process ($\tau = 5.5$ s), significantly outperforming systems without epoxy ($\tau = 25.5$ s). This suggests that hydroxyl groups formed during the reaction act catalytically to accelerate the exchange process. Supporting studies demonstrated that transamination reactions in vinylogous urethanes occur more rapidly in hydroxyl-containing solvents like 2-hexanol.

To further optimize these materials, this study integrates density functional theory (DFT) with experimental analyses. DFT serves as a rapid screening tool to identify functional groups that can enhance transamination kinetics, allowing for efficient identification of promising amine substrates. Initially, DFT calculations are used to analyze the kinetics of transamination reactions through detailed mechanistic studies, predicting the reactivity of various amines to guide the synthesis of materials with tailored processing and relaxation times

The theoretical predictions are validated through kinetic analyses, including quantitative HSQC NMR studies, to streamline the experimental process and focus efforts on the most promising candidates. By integrating DFT modelling with experimental data, this approach goes beyond traditional trial-and-error methods, targeting the development of vitrimer systems with improved exchange kinetics for efficient processing at elevated temperatures and enhanced dimensional stability during service conditions. This strategy accelerates the discovery of high-performance materials while ensuring both efficiency and precision (Fig. 4.1)

Streamlining process through DFT



Figure 4.1: Schematic representation of the process of streamlining through DFT (Density Functional Theory) through the use of computational modeling to reduce the complexity, time, and resources required in experimental workflows.

4.2 Results and discussion

4.2.1 Computational Results

The initial phase of the study focused on a theoretical analysis of the transamination kinetics between various amines and vinylogous urethanes. An aniline-based vinylogous urethane was used as a reference, and a diverse range of amines was selected to evaluate the impact of structural variations and functional groups on the transamination kinetics. The amines chosen for structural analysis included: (i) benzylamine (BnNH_2), (ii) furfurylamine (FuNH_2), (iii) 2-ethylhexylamine (2-EHA), (iv) butylamine (BuNH_2), and (v) tert-butylamine (tBuNH_2). To assess the effects of functional groups, the selected amines were: (i) 3-methoxypropylamine (3-MET), (ii) 3-aminopropanol (3-APO), (iii) N,N-dimethyl-1,3-diaminopropane (N,N-Diam), and (iv) cysteamine (Cys) (Fig 4.2).

Aniline (PhNH_2) was chosen as the starting vinylogous urethane due to its sterically hindered aromatic amine nature. The reaction of this amine with acetoacetates to form the vinylogous urethane product typically results in lower yields compared to non-sterically hindered amines, which is attributed to its increased bulkiness. This characteristic, along with the observation that all other selected amines—except tert-butylamine (tBuNH_2), which was chosen for comparison with aniline— will react more readily to form the corresponding

vinyllogous urethane product, justified the selection of aniline vinyllogous urethane as the starting, slower, reactant for kinetic studies using DFT.

Benzylamine (BnNH_2) was selected to reduce steric bulk in the proximity of the reactive amino group compared to aniline while maintaining aromatic character due to its phenyl group. Furfurylamine (FuNH_2), another aromatic amine, was chosen for its furan ring, differing in size and aromaticity from benzene. The remaining three amines were aliphatic: 2-ethyl hexylamine (2-EHA), previously used in a study on vinyllogous urethane vitrimers,³ introduces bulkiness due to its ethyl substituent; butylamine (BuNH_2), a straightforward, sterically unhindered aliphatic amine; and tert-butylamine (tBuNH_2), a sterically hindered aliphatic amine. This selection enabled a comprehensive examination of how structural variations among amines affect transamination kinetics.

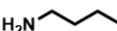
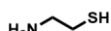
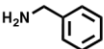
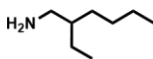
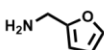
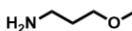
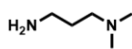
Structural analysis				Functional group analysis	
Name	Mol. Struct.	Name	Mol. Struct.	Name	Mol. Struct.
PhNH_2		BuNH_2		Cys	
BnNH_2		2-EHA		3-APO	
FuNH_2		tBuNH_2		3-MET	
				N,N-Diam	

Figure 4.2: Structures of amines used in the study: amines for structural analysis (left panel) and amines for functional group analysis (right panel).

For the study of the effects of different functional groups on transamination kinetics, 3-aminopropanol (3-APO) and cysteamine (Cys) were selected to investigate whether the presence of hydroxyl and thiol groups, respectively, could increase the transamination reaction rate, as suggested by previous studies on similar structures.^{14,15} Additionally, hydroxyl and thiol groups can

form hydrogen bonds, which can act as catalysts by bringing reactive centers closer together and stabilizing their orientation, thereby facilitating interactions and accelerating the reaction rate.¹⁶ 3-methoxypropylamine (3-MET) was chosen as a comparison to 3-APO to evaluate the kinetic effects of an ether group in contrast with a hydroxyl one. N,N-dimethyl-1,3-diaminopropane (N,N-Diam) was included because tertiary amines in proximity to reactive sites in dynamic covalent networks have been reported to potentially enhance reaction kinetics in dynamic covalent networks.^{17,18}

All the amines used for the structural and functional group analysis are depicted in Fig. 4.2. As reported in the literature, two primary mechanisms for the transamination of vinylogous urethanes exist: (i) a protic mechanism under neutral or acidic conditions, and (ii) an aprotic mechanism under basic conditions or in the presence of a Lewis acid.^{3,19} Since the model studies are to be conducted under neutral or slightly acidic conditions, the analysis centered on the transamination reaction via the protic mechanism (Fig 4.3).

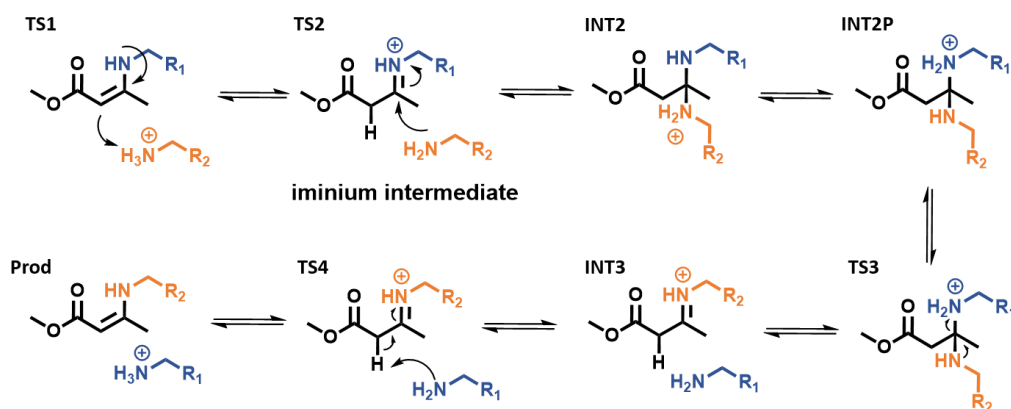


Figure 4.3: Mechanistic pathway for neutral/acidic pathway of the vinylogous urethane transamination.

To examine the impact of structural differences on transamination kinetics, the protic pathway of the selected amines with aniline vinylogous urethane was investigated (Fig. 4.4).

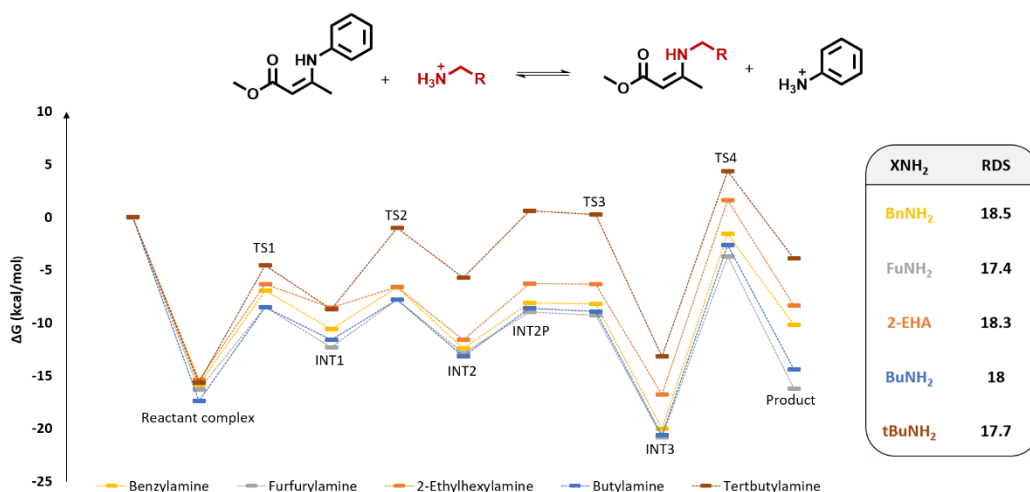


Figure 4.4: Potential energy surface of the protic transamination process following a protic mechanism for VU_PhNH₂ and different structural amines: (i) BnNH₂ (yellow line) (ii) FuNH₂ (grey line) (iii) 2-EHA (orange line) (iv) BuNH₂ (blue line) and (v) tBuNH₂ (brown line) (left panel) and rate-determining step (INT3 → TS4) values for each transamination reaction in kcal/mol (right table).

Analysis of Fig. 4.4 reveals that the rate-determining step in each transamination reaction is the transition from INT3 to TS4 (Fig. 4.5 and Fig. S4.25). This step involves the transfer of a proton from the stable vinylic α -carbon in INT3 to neutral aniline. In INT3, the vinylogous urethane with the newly exchanged furfurylamine adopts a protonated iminium form, while the aniline exits the structure in its neutral form. The stability of INT3 is attributed to its formation in a minimum energy state following TS3, where the vinylogous urethane structure tilts slightly to facilitate the departure of aniline. This stable cis-conformation is further stabilized by hydrogen bonding between the NH group and the carbonyl oxygen. In the subsequent transition state (TS4), aniline abstracts a proton from

the methylene carbon, driving the rearrangement from the iminium to the enamine form (Fig. 4.5 and Fig. S4.28).

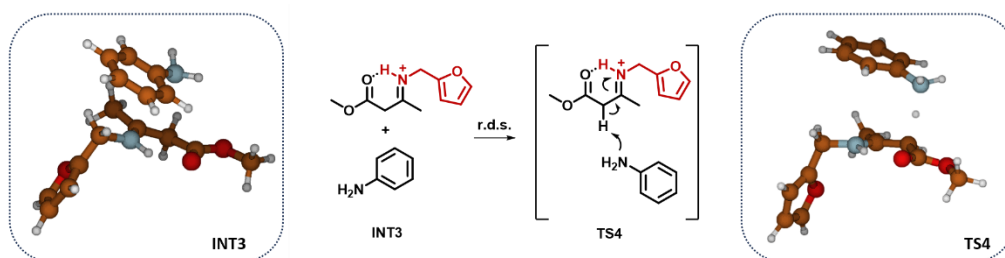


Figure 4.5: The molecular structures of the rate-determining step (from INT3 to TS4) of the transamination reaction between VU_PhNH₂ and furfurylamine are shown.

INT3 is particularly stable for VU_FuNH₂ (-20.81 kcal/mol) and VU_BuNH₂ (-20.67 kcal/mol). In VU_FuNH₂, the cis-conformation is stabilized by hydrogen bonding between the amino group and carbonyl oxygen (N-H...O=C = 1.840 Å) (Fig. S4.29). The furfurylamine moiety is positioned outside the VU plane, opposite the aniline, whose amino group is near the methylene carbon, facilitating proton abstraction (3.178 Å). Similarly, INT3 of VU_BuNH₂ forms a cis isomer with stabilizing H-bonding (1.839 Å), and the butylamine moiety extends partially in-plane with the amino group 3.16 Å from the methylene carbon (Fig. S4.30). The INT3 structure of VU_BnNH₂ (-19.88 kcal/mol) is similar to VU_FuNH₂, featuring a cis-conformation and intramolecular H-bonding (1.830 Å). The benzylamine moiety points opposite to the aniline, with its amino group closer to the methylene carbon (2.943 Å) (Fig. S4.31). VU_2EHA (-16.76 kcal/mol) also exhibits a cis-conformation with stabilizing H-bonding (1.843 Å) and maintains a similar distance between the aniline amino group and the methylene carbon (3.168 Å) (Fig. S4.32). Finally, the INT3 structure of the vinylogous urethane of tert-butylamine is the least stable (-13.18 kcal/mol). Still, it retains a cis-conformation and H-bonding (1.770 Å), with a more distant aniline NH group from the methylene carbon (3.295 Å) (Fig. S4.33).

The primary conclusion from this potential energy surface analysis is that the reaction between aniline vinylogous urethane and tert-butylamine (tBuNH_2) is the least favorable, owing to a more energetically demanding reaction pathway. The bulky structure of tert-butylamine introduces significant steric hindrance near the reactive site, leading to a higher energy pathway and reduced reaction efficiency. This increased activation energy makes its transamination reaction less favorable compared to other amines.

A second important conclusion that can be drawn from these results is that the differences in potential energy surfaces and rate-determining steps (RDS) among the other amines are minimal, with activation energies for the RDS being approximately 18 kcal/mol, varying by no more than 1 kcal/mol. This suggests that, for primary amines such as benzylamine, furfurylamine, 2-ethylhexylamine, and butylamine, steric and electronic differences exert minimal influence on reaction kinetics.

When analyzing the transamination reactions with amines bearing different functional groups, the results are similar to those obtained from the structural study (Fig. 4.6). Given that the same mechanism is studied, it is not surprising that the potential energy surfaces are alike, with the rate-determining step still being the transition from INT3 to TS4, corresponding to the proton transfer. The main difference is that the rate-determining step values for the transamination kinetics of these amines are significantly lower than those of previously studied structural amines, suggesting that exchange reactions are expected to proceed more quickly.

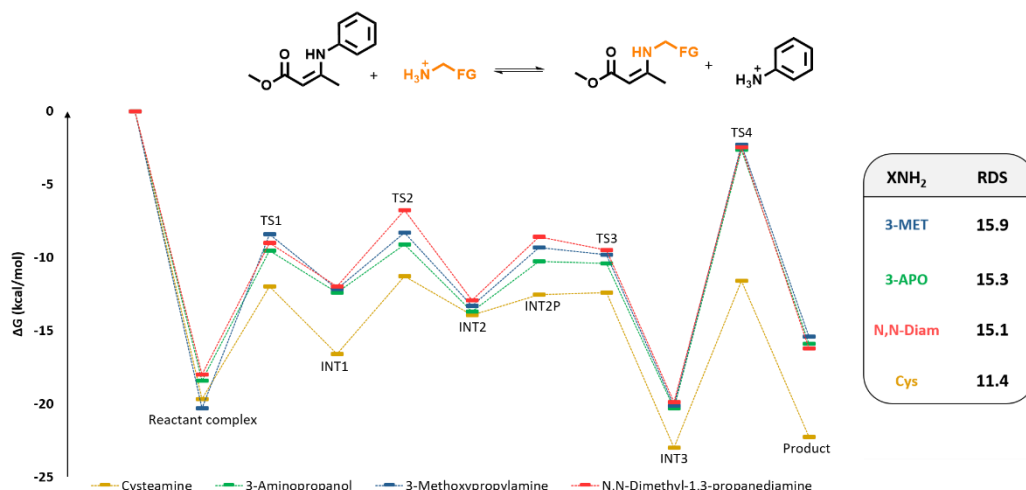


Figure 4.6: Potential energy surface of the protic transamination process following a protic mechanism for VU_PhNH₂ and different amines bearing diverse functional groups: (i) 3-MET (blue line) (ii) 3-APO (green line) (iii) N,N-Diam (red line), and (iv) Cys (yellow line) (left panel) and rate-determining step (INT3 → TS4) values for each transamination reaction in kcal/mol (right table).

It is noteworthy to observe the different conformations of INT3 with various functional groups. In the reaction mechanism with VU_Cys, the INT3 vinylogous urethane is the most stable analyzed (-23 kcal/mol). It adopts a slightly twisted cis-conformation, positioning one of the methylene (-CH₂) hydrogens alpha to the carbonyl at 3.161 Å from the -NH₂ group of the aniline, facilitating the subsequent step (TS4) (Fig. S4.34). Both VU_3-APO (-20.3 kcal/mol) and VU_3-MET (-20.11 kcal/mol) exhibit a planar cis-conformation, with hydrogen bonding between the NH group and the carbonyl oxygen, at 1.835 Å and 1.836 Å respectively, and a similar distance between the NH₂ group of the aniline and the methylene of the vinylogous urethane, at 3.169 Å and 3.168 Å respectively (Fig. S4.35 – S4.36). Notably, the intermediate of the N,N-Diam vinylogous urethane (-19.87 kcal/mol) adopts a twisted conformation where the NH group cannot establish hydrogen bonding with the carbonyl oxygen due to interaction

with the amino group of the aniline, which in turn interacts with the dimethyl-substituted nitrogen group present in the aliphatic chain (Fig. S4.37).

In conclusion, this initial study of the potential energy surface of transamination reactions with different primary amines indicates that modifying the aliphatic or aromatic structure generally does not lead to significant differences in reaction kinetics. However, steric bulk can play a role, as bulkier amines like aniline and tert-butylamine will result in less favorable transamination exchange due to steric hindrance near the reactive site, whereas smaller amines facilitate faster reactions. Additionally, incorporating amines with thiol, hydroxyl, or tertiary amine groups should further enhance the reaction rate, enabling the development of materials with faster dynamic exchanges.

4.2.2 Quantitative HSQC (Heteronuclear single quantum coherence spectroscopy) analysis

In the computational work described in the previous section, 10 different vinylogous urethanes were analyzed. Determining the exchange kinetics for all possible vinylogous urethane/amine pairs individually to validate the computational approach would therefore require a large number of kinetic experiments. To circumvent this, a protocol was developed to simultaneously determine kinetic rate coefficients in a combinatorial pool of vinylogous urethane/amine mixtures.

An experiment was designed where, starting with aniline vinylogous urethane, the previously DFT-studied amines were sequentially added at 4-hour intervals, allowing the exchange reaction to proceed. In each stage, the change in concentration of a given vinylogous urethane species, VU_i , is measured. This experimental value is then compared with values calculated by numerical

integration of Equations 1 and 2 for all amines and vinylogous urethanes present in the system at a given moment:

$$\frac{d[VU_i]}{dt} = \sum_{j=1,2,3\dots} k_{ij}[VU_j][Am_i] - k_{ji}[VU_i][Am_j] \quad \text{Equation 1}$$

$$\frac{d[Am_i]}{dt} = \sum_{j=1,2,3\dots} k_{ji}[VU_i][Am_j] - k_{ij}[VU_j][Am_i] \quad \text{Equation 2}$$

Where k_{xy} is the rate coefficient for amine x with vinylogous urethane y . Equations 1 and 2 are used to set up a system of ordinary differential equations that can be solved numerically such that the individual rate coefficients can be estimated using $[VU]_j$ from the NMR data by minimization of the sum of squares error. By sequential addition of the amines, rate coefficients can be estimated sequentially and fixed for the subsequent additions such that the number of parameters to estimate at each stage is limited. Although this still leads to a relatively large number of parameters to be estimated, it was envisaged that analysis of the obtained rate coefficients would allow a good insight into which amine/VU pairs are most reactive and serve to validate the DFT results.

Two separate experiments were conducted: one for structural analysis and another for functional group analysis. Due to the high number of structures involved in each kinetic study, ^1H -NMR was not feasible because of overlapping signals. As a solution to this problem quantitative ^1H - ^{13}C HSQC NMR with a specified window was employed, a technique previously used by Gasparini et al.²⁰

The first step in applying this methodology involved a characterization of each vinylogous urethane to be included in the combinatorial analysis, ensuring that clear, quantifiable correlations for each component could be established. The analysis of the vinylogous urethane structures is detailed in the Supporting

Information (Fig. S4.4-S4.27). Starting with the structural analysis of amines, the vinylogous urethane derived from aniline was first introduced, followed by sequential additions of BnNH_2 , FuNH_2 , 2-EHA, and BuNH_2 to the reaction mixture at 100°C , each spaced 4 hours apart. tBuNH_2 was excluded due to synthetic challenges associated with its corresponding vinylogous urethane.

As shown in the left panel of Fig. 4.7, the formation of each VU is plotted against reaction time under neutral conditions with the evolution of concentrations estimated from equations 1 and 2 shown as the dashed line. Notably, after the addition of BnNH_2 , the concentration of aniline-derived vinylogous urethane decreases rapidly, and following the subsequent addition of FuNH_2 , it disappears completely in around 500 minutes. This can be attributed to aniline's steric hindrance, which limits its reactivity compared to the less bulky amines, as predicted by DFT calculations. Consequently, with only less sterically congested amines present in the mixture, the aniline-derived vinylogous urethane does not reform.

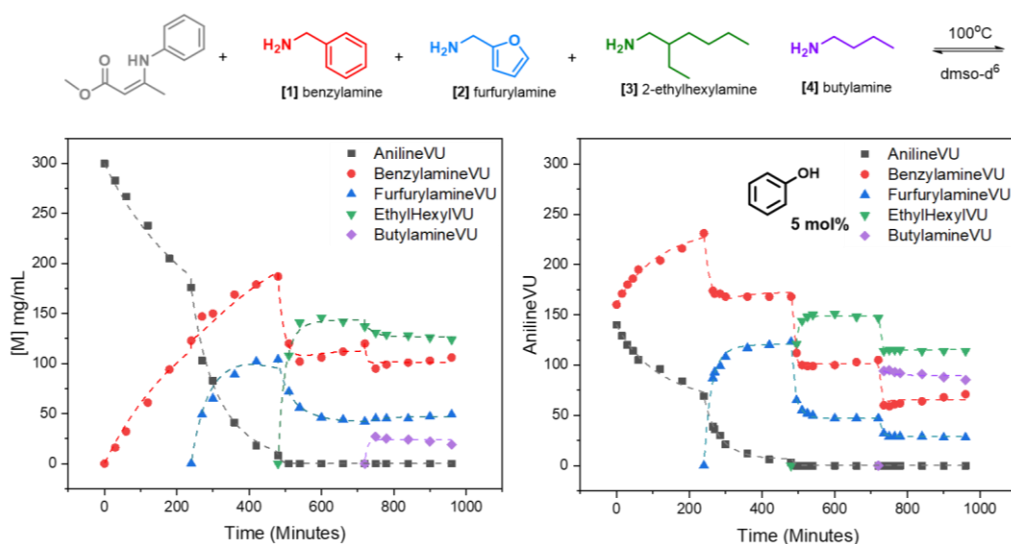


Figure 4.7: Formation, through exchange reactions followed by quantitative ^1H - ^{13}C HSQC NMR, of the vinylogous urethane molecules as a function of time at 100°C analyzing structural amines without catalyst (left panel) and with the addition of 5 mol% of phenol (right panel). Scatter

graphs represent experimental data while dotted lines represent simulated data using the estimated rate coefficients.

The same experiment was conducted by adding 5 mol% per amine addition of phenol as an acidic source. The action of phenol as a catalyst was confirmed by experiments on the transamination reaction between benzylamine vinyllogous urethane and butylamine with the addition of different molar percentages of phenol (Fig S4.38), on the same line as previous literature reports.³ In the right panel of Fig. 4.7, the formation of the diverse vinyllogous urethane in acidic conditions, is plotted against time. As expected, the equilibrium is reached much faster than in the neutral reaction. This is because, as previously reported in literature, in an acidic environment the presence of the iminium species increases, which in turn will increase the exchange rate.^{3,19}

To predict the behavior of the exchanges at each step of the combinatorial study further DFT calculations were carried out, analyzing exclusively the rate-determining step (RDS) of the exchange between every vinyllogous urethane and amine present (Fig. 4.8). Figure 4.8 illustrates a comparison of the relative values obtained from the rate-determining step (RDS) using DFT calculations and the experimentally derived rate coefficients estimated from NMR data. The close alignment observed between the two approaches in the first three steps suggests that DFT provides accurate insights into the exchange process. However, as the analysis progresses to step 4, the reliability of estimating rate coefficients diminishes. This is attributed to the increased complexity, where a larger number of rate coefficients need to be determined based on a limited range of experimental data. Therefore, while the DFT approach remains robust throughout, the effectiveness of the rate coefficient estimation is constrained as the data set becomes more complex. Consequently, in Figure 4.8, the

corresponding table for the rate coefficients is left blank beyond step 3, reflecting these limitations in obtaining reliable estimates.

Step 1	Exchange	RDS (kcal/mol)	k ($M^{-1}s^{-1}$)	k (+) ($M^{-1}s^{-1}$)
	VU_PhNH ₂ + BnNH ₂	15.4	1.4×10^{-4}	6.49×10^{-4}
	VU_BnNH ₂ + PhNH ₂	18.9	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$
Step 2	Exchange	RDS (kcal/mol)	k ($M^{-1}s^{-1}$)	k (+) ($M^{-1}s^{-1}$)
	VU_PhNH ₂ + FuNH ₂	12.1	7.75×10^{-4}	1.29×10^{-3}
	VU_BnNH ₂ + FuNH ₂	17.1	$< 1 \times 10^{-5}$	1×10^{-3}
	VU_FuNH ₂ + PhNH ₂	18.7	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$
	VU_FuNH ₂ + BnNH ₂	12.3	3.21×10^{-4}	2.1×10^{-3}
Step 3	Exchange	RDS (kcal/mol)	k ($M^{-1}s^{-1}$)	k (+) ($M^{-1}s^{-1}$)
	VU_FuNH ₂ + 2-EHA	12.3	9.46×10^{-4}	1.4×10^{-3}
	VU_BnNH ₂ + 2-EHA	10.1	1.66×10^{-3}	7.8×10^{-3}
	VU_2-EHA + BnNH ₂	13.6	9.91×10^{-4}	4.2×10^{-3}
	VU_2-EHA + FuNH ₂	12.9	2.28×10^{-4}	9.22×10^{-5}
Step 4	Exchange	RDS (kcal/mol)	k ($M^{-1}s^{-1}$)	k (+) ($M^{-1}s^{-1}$)
	VU_2-EHA + BuNH ₂	15.6		
	VU_FuNH ₂ + BuNH ₂	16.2		
	VU_BnNH ₂ + BuNH ₂	12.2		
	VU_BuNH ₂ + BnNH ₂	13.2		
	VU_BuNH ₂ + FuNH ₂	12.8		
	VU_BuNH ₂ + 2-EHA	12.9		

Figure 4.8: ΔG values (in kcal/mol) for the rate-determining step (RDS, INT3 $\rightarrow$ TS4) of each exchange reaction occurring at each step of the structural combinatorial analysis between vinylogous urethanes and free amines. The figure also includes estimated rate coefficients for both neutral (k) and protic ($k(+)$) environments.

Building on the earlier observations, a detailed comparison between DFT predictions and the experimentally determined rate coefficients reveals a strong correlation throughout the combinatorial steps. The initial stages of the exchange reactions demonstrate how DFT accurately captures the kinetic trends observed experimentally. For instance, the unfavorable exchange between PhNH₂ and VU_BnNH₂ results in a steady depletion of VU_PhNH₂. This is further validated when FuNH₂ is introduced, where both DFT calculations and

experimental data confirm that the exchange with FuNH_2 is energetically more favorable ($\Delta G = 12.1$ kcal/mol), leading to a shift towards the formation of VU_FuNH_2 . Subsequently, the addition of 2-EHA and BuNH_2 continues to align with DFT predictions, demonstrating the ability to forecast the reaction pathways and the relative reactivity of different amines. Overall, the structural analysis indicates that differences in transamination rates are not affected by variations in the amine structure, except in the specific case of aromatic aniline. While aliphatic amines exhibit similar reaction rates regardless of structural differences, the presence of the aromatic ring in aniline significantly increases the activation energy, making it the sole outlier with slower kinetics.

The same combinatorial analysis methodology was applied to amines bearing diverse functional groups. Starting with the aniline vinylogous urethane in DMSO-d_6 at 100°C , the amines studied through DFT calculations were sequentially added at 4-hour intervals. Cysteine (Cys) was not included in the study due to difficulties encountered in synthesizing the corresponding vinylogous urethane. Before analyzing the combinatorial mixture, single-model transamination reactions were conducted using benzylamine vinylogous urethane (VU_BnNH_2) with 3-MET, 3-APO, and N,N-Diam, as larger differences were anticipated compared to the analysis with structural amines. The rate coefficients for these reactions were determined with just one amine/VU pair (Fig. 4.9).

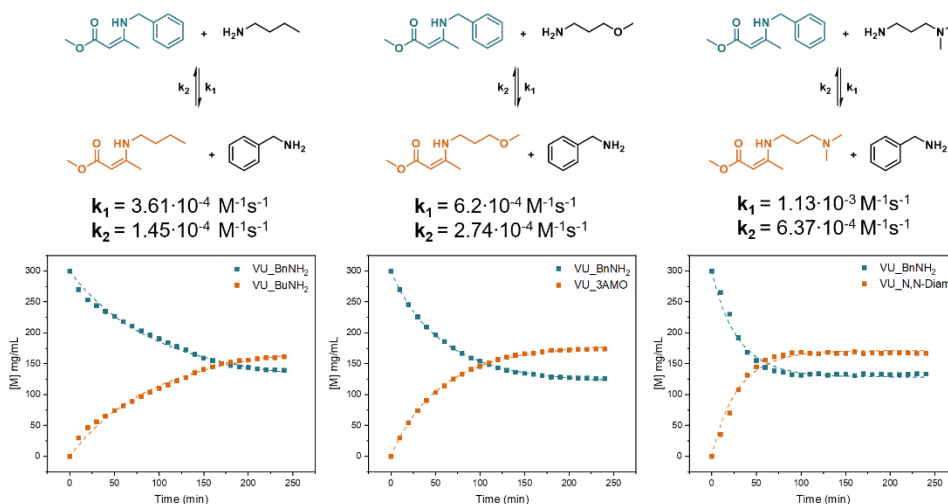


Figure 4.9: Single-model transamination reactions kinetics and equilibrium constants between VU_BnNH₂ and 3-methoxypropylamine (3-MET), (ii) 3-aminopropanol (3-APO), (iii) N,N-dimethyl-1,3-diaminopropane (N,N-Diam).

As demonstrated in Figure 4.9, the presence of different functional groups significantly influences the transamination kinetics of vinylogous urethanes. The results show that the incorporation of a methoxy group accelerates the exchange process, allowing equilibrium to be reached in approximately 100 minutes, as compared to the 175 minutes required for butylamine. The effect is even more pronounced with N,N-dimethyl-1,3-diaminopropane, where the presence of a tertiary amine substantially enhances the reaction rate, reaching equilibrium in just 50 minutes.

Building on this initial analysis, a combinatorial experiment was then conducted to further investigate the impact of different amines under various conditions. For the functional group combinatorial analysis, the experiment began with an aniline-derived vinylogous urethane as the starting material. Sequential additions of 3-MET, 3-APO, and finally N,N-diaminopropane (N,N-Diam) were made every 4 hours at 100°C. The left panel of Figure 4.9 shows the formation of each vinylogous urethane (VU) over time under neutral conditions. A notable decline in the concentration of the initial aniline-derived urethane was observed

following the addition of 3-MET, aligning with trends identified in the structural analysis phase. The steric hindrance of PhNH_2 leads to a steady decrease in its concentration throughout the experiment.

In contrast, the right panel of Figure 4.10 illustrates the same experiment conducted with the addition of phenol (5 mol% per amine addition) as an acidic catalyst. The catalytic effect of phenol is clearly evident, significantly accelerating the reaction kinetics. This enhancement is likely due to the increased formation of iminium intermediates, which facilitate the transamination process as discussed previously.³

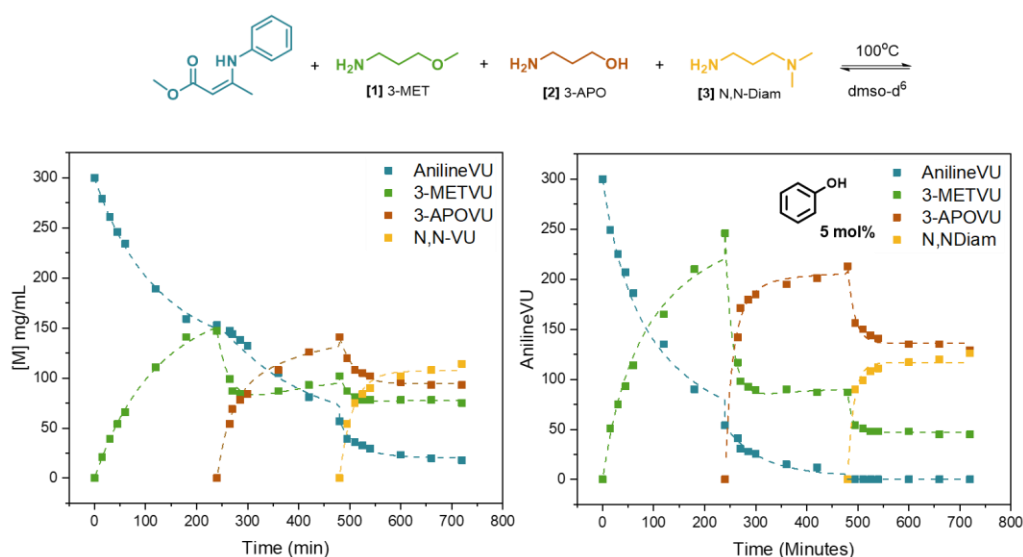


Figure 4.10: Formation, through exchange reactions followed by quantitative ^1H - ^{13}C HSQC NMR, of the vinylogous urethane molecules as a function of time at 100°C analyzing functional group analysis without catalyst (left panel) and with the addition of 5 mol% of phenol (right panel). Scatter graphs represent experimental data while dotted lines represent simulated data using the estimated rate coefficients.

Further DFT calculations, focusing exclusively on the rate-determining step (RDS) for the exchange between each vinylogous urethane and amine pair, were performed to predict the behavior of the exchanges at each step of the combinatorial study and to compare with experimentally determined rate coefficients (Fig. 4.11). These calculations once again demonstrate a good

correlation between theoretical predictions and experimental data, validating the approach used.

In step 1 the initial exchange reactions align with DFT calculations, where less sterically hindered amines like 3-MET facilitate a more favorable exchange with VU_PhNH₂. Theoretical predictions and experimental data both confirm that these reactions are driven by reduced steric hindrance, leading to a faster forward reaction compared to its reverse. The addition of an acidic catalyst further accelerates these exchanges, enhancing reaction rates significantly.

With the addition of 3-APO in the second step, the experiment shows that VU_3APO forms primarily at the expense of VU_3MET, with a lesser impact on VU_PhNH₂. DFT calculations predict this trend, confirming that the exchange between 3-APO and VU_3MET is more favorable than with other urethanes. The introduction of 3-APO results in varied reactivity, where some exchanges proceed efficiently while others are hindered due to higher activation barriers. Acidic conditions once again enhance the reaction rates, though the effects vary depending on the specific exchange.

The final step involves introducing N,N-Dimethyl-1,3-diaminopropane (N,N-Diam), which significantly speeds up the reaction kinetics. The presence of the tertiary amine in N,N-Diam leads to rapid formation of VU_N,N-DIAM, depleting other urethanes, particularly VU_3APO and VU_3MET. DFT calculations align with experimental observations, showing that exchanges involving N,N-Diam are the fastest due to the lower activation energies. The use of an acidic catalyst dramatically boosts the rates even further, indicating that N,N-Diam can efficiently catalyze transamination reactions under both neutral and acidic conditions.

Step 1	Exchange	RDS (kcal/mol)	k ($M^{-1}s^{-1}$)	k (+) ($M^{-1}s^{-1}$)
	VU_PhNH ₂ + 3-MET	15.9	2.81×10^{-4}	6.44×10^{-4}
	VU_3-MET + PhNH ₂	17.7	1.19×10^{-4}	$< 1 \times 10^{-5}$
Step 2	Exchange	RDS (kcal/mol)	k ($M^{-1}s^{-1}$)	k (+) ($M^{-1}s^{-1}$)
	VU_PhNH ₂ + 3-APO	15.4	$< 1 \times 10^{-5}$	7.18×10^{-4}
	VU_3-MET + 3-APO	12.1	1.2×10^{-3}	3×10^{-3}
	VU_3-APO + PhNH ₂	17.2	$< 1 \times 10^{-5}$	$< 1 \times 10^{-5}$
	VU_3-APO + 3-MET	13.1	5.9×10^{-4}	7.3×10^{-4}
Step 3	Exchange	RDS (kcal/mol)	k ($M^{-1}s^{-1}$)	k (+) ($M^{-1}s^{-1}$)
	VU_PhNH ₂ + N,N-DIAM	15.1	1.1×10^{-3}	9.9×10^{-3}
	VU_3-MET + N,N-DIAM	8.1	7.7×10^{-4}	2.9×10^{-3}
	VU_3-APO + N,N-DIAM	7.4	6.6×10^{-4}	1.4×10^{-3}
	VU_N,N-DIAM + PhNH ₂	19.4	1.1×10^{-4}	$< 1 \times 10^{-5}$
	VU_N,N-DIAM + 3-APO	8.2	3.09×10^{-4}	1.7×10^{-3}
	VU_N,N-DIAM + 3-MET	8.7	7.5×10^{-4}	9.6×10^{-4}

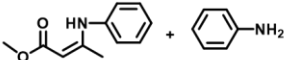
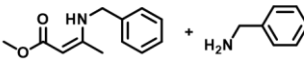
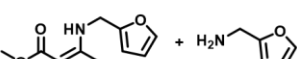
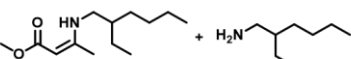
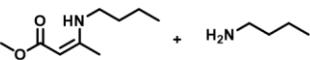
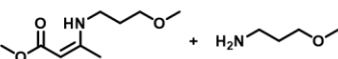
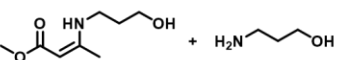
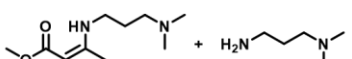
Figure 4.11: ΔG values in kcal/mol of the RDS (INT3 $\rightarrow$ TS4) of every exchange happening at each step of the functional group combinatorial analysis between the vinylogous urethanes and the free amines. The figure also includes estimated rate coefficients for both neutral and protic environments.

In conclusion, this study demonstrates the value of DFT calculations in predicting the behavior of complex systems. By comparing trends observed in DFT predictions with experimental analyses, particularly through quantitative HSQC analysis, we establish a correlation between computational and experimental results. This combined methodology not only validates the reliability of theoretical models but also enables efficient monitoring of the kinetics of intricate systems.

In the final phase of theoretical calculations, the focus was on identifying the rate-determining step (RDS) of the transamination exchange reaction between vinylogous urethane (VU_XNH₂) and the corresponding amine (XNH₂), as detailed in Table 4.1. The data indicate that the exchange involving aniline, as expected, is the least favorable. In contrast, the exchange with benzylamine

exhibits a slightly lower RDS, likely due to reduced steric hindrance around the amino group. For aliphatic amines, including those containing hydroxyl (-OH) or methoxy (-OMe) groups, the RDS consistently falls within the range of 12-13 kcal/mol, showing minimal variation among them, with 3-aminopropanol having the lowest RDS. Notably, N,N-dimethyl-1,3-diaminopropane demonstrates a significantly lower RDS compared to all other calculated exchanges, in agreement with previous DFT calculations and single model studies kinetics (Fig. 4.9).

Table 4.1: Rate-determining step of the exchange reaction between VU_XNH₂ and XNH₂.

Name	Reaction	RDS (kcal/mol)
Aniline		19.74
Benzylamine		15.83
Furfurylamine		12.65
2-Ethylhexylamine		13.35
Butylamine		12.38
3-methoxypropylamine		12.11
3-aminopropanol		11.64
N,N-dimethyl-1,3-diaminopropane		9.87

4.2.3 Synthesis and characterization of dynamic networks

Having established the effects of various amines on model reactions involving low-MW compounds, the influence of different crosslinkers, prepared from amines that would mimic the ones used in the previous experiments, on the viscoelastic behavior of vinylogous urethane-based polymer networks was examined. In the study, various vitrimer dynamic networks were synthesized using different vinylogous urethane cross-linkers.

The cross-linkers were prepared by reacting 2-(Acetoacetoxy)ethyl methacrylate with different diamines at a 1:0.6 molar ratio.^{21,22} This ratio was specifically chosen to produce a divalent vinylogous urethane cross-linker alongside a vinylogous urethane with a free amine group, facilitating the exchange reaction as detailed in the experimental section. The selected diamines were: (i) 1,4-Butanediamine, similar to butylamine; (ii) m-Xylylenediamine, analogous to benzylamine; (ii) 1,4-Butanediamine, similar to butylamine; (iii) Bis(3-aminopropyl)methylamine, resembling N,N-dimethyl-1,3-diaminopropane; and (iv) 4,9-Dioxa-1,12-dodecanediamine, similar to 3-methoxypropylamine (Fig. 4.12).

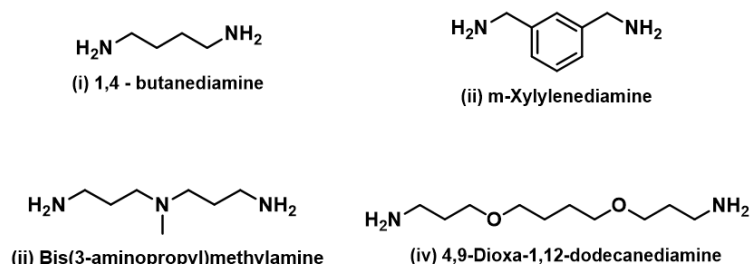


Figure 4.12: Selected diamines for the preparation of the four different materials: (i) 1,4-Butanediamine, similar to butylamine for the preparation of VT1; (ii) m-Xylylenediamine, analogous to benzylamine for the preparation of VT3; (iii) Bis(3-aminopropyl)methylamine, resembling N,N-dimethyl-1,3-diaminopropane for the preparation of VT2; and (iv) 4,9-Dioxa-1,12-dodecanediamine, similar to 3-methoxypropylamine for the preparation of VT4.

After mixing the reactants, the mixture was added as 50% by weight to butyl methacrylate containing a photoinitiator, followed by irradiation to form the vitrimer materials. All the materials were thermally tested with TGA and showed similar behavior with a decomposition temperature of around 250°C (Fig. S4.39-S4.42). The obtained networks were subjected to stress–relaxation experiments, to determine if the predicted behaviors from density functional theory (DFT) calculations and observed kinetics from ^1H - ^{13}C HSQC NMR spectroscopy were consistent in the material network. Relaxation times were calculated by fitting the stress relaxation data to a stretched exponential of the form written below across all measured temperatures (Figure S4.43).

$$\sigma(t) = \sigma_0 e^{-\left(\frac{t}{\tau}\right)^\beta}$$

A representative measurement performed at 120°C, comparing the four different vitrimeric materials prepared, is shown in Fig. 4.13. VT3, which includes *m*-xylylenediamine, is the slowest material with a relaxation time $\tau \sim 142$ seconds. VT1, including 1,4 -butanediamine, shows a relaxation time of $\tau \sim 69$ seconds. The two vitrimeric materials containing functional groups that are expected to catalyze bond exchange, VT4 (containing bis(3-aminopropyl)methylamine) and VT2 (containing *N,N*-dimethyl-1,3-diaminopropane), showed faster relaxation times, of around $\tau \sim 34$ seconds and $\tau \sim 11$ respectively.

The behavior of the prepared materials aligns well with the kinetic studies of the single model transamination reactions, as depicted in Fig. 4.9. In these studies, *N,N*-Diam exhibited the fastest exchange rate, followed by 3-MET, with butylamine showing the slowest exchange rate among the amines. These findings are consistent not only with the experimental analysis but also with the

DFT studies conducted. VT2, the material with the shortest relaxation time, incorporates a vinylogous urethane di-crosslinker containing a tertiary amine.^{11,17,18} As demonstrated in the DFT studies, tertiary amines such as N,N-Diam have a lower rate-determining step compared to the other amines used in the material preparation. Similarly, 3-MET, represented by VT4, which has the second fastest relaxation time, also exhibited the second lowest RDS among the studied amines. In contrast, VT1, representing butylamine, and VT3 representing benzylamine, have a significantly higher energy barrier in the RDS, leading to correspondingly longer relaxation times in the final polymer network due to reduced rates of bond exchange.

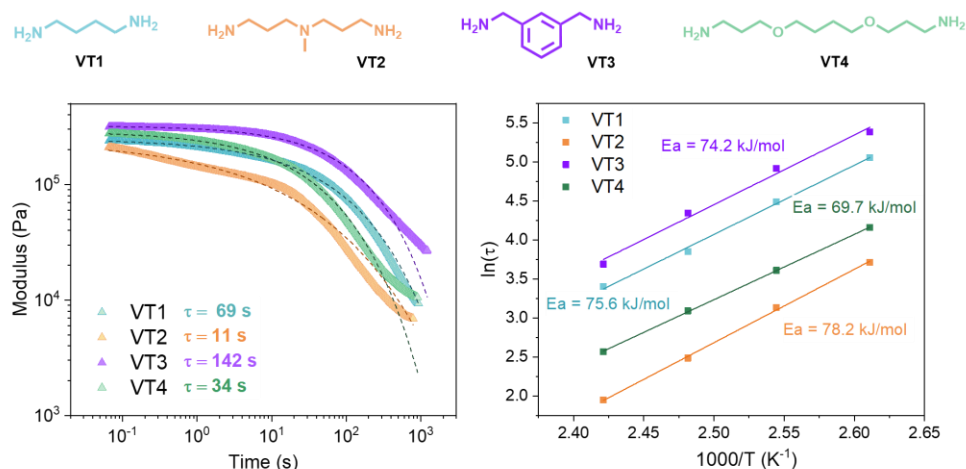


Figure 4.13: Stress Relaxation analysis of VT1, VT2, VT3, and VT4 (left panel) with their relaxation times extracted from the stretched exponential fit. Arrhenius plot of an extended kinetic study of the activation energies of the vitrimeric materials VT1, VT2, VT3, and VT4 (right panel). The diamines used in the synthesis of the crosslinker incorporated into each vitrimeric material are depicted.

When the relaxation times at different temperatures (Fig. S4.43) are examined in an Arrhenius plot, a linear relationship is observed, which is characteristic of vitrimer materials.²³ The calculated activation energies, shown in the right panel of Fig. 4.13, for the four different vitrimer materials are very similar. This similarity can be explained by the fact that unlike in previous studies where the

addition of a catalyst altered the reaction pathway and consequently the activation energy (E_a) of the materials, the reaction pathway involved in the dynamic exchange of the vinylogous urethane is the same for all the materials analyzed: the neutral/acidic pathway.⁹ Furthermore, the activation energies calculated here are in good agreement with those reported in previous studies on vitrimers following the neutral pathway.³

4.3 Conclusions

In conclusion, a combined computational and experimental analysis was conducted to investigate the effects of different amines, varying in structure and functional groups, on the dynamic exchange of vinylogous urethanes. Quantum chemical calculations (DFT) were employed to analyze the potential energy surfaces of various vinylogous urethane-amine exchanges, examining each intermediate and transition state while calculating their rate-determining steps (RDS) to predict their kinetics. These predictions were experimentally validated through combinatorial kinetic analyses, using quantitative HSQC methodology. Four distinct vinylogous urethane vitrimer materials were then prepared, based on two amines from the structural analysis and two from the functional group analysis. The materials were characterized, and stress-relaxation experiments confirmed that the observed behavior in both the DFT calculations and experimental studies was consistent in the vitrimer materials. This study presents an approach for enabling combinatorial analysis of a wide range of compounds, facilitating the rapid prediction of behavior within a chemical library of building blocks, both in single-model reactions and complex multi-component systems. By integrating computational methods with experimental validation, this approach streamlines the identification of promising candidates for targeted synthesis, optimizing reaction conditions and material properties. The

framework allows for efficient exploration of chemical space, accelerating the discovery of new compounds with desirable functionalities while reducing the need for extensive trial-and-error experimentation.

4.4 Experimental section

4.4.1 Materials

Materials: Methyl acetoacetate (99%), benzylamine (99%), aniline ($\geq 99.5\%$), tert-butylamine (98%), furfurylamine ($\geq 99\%$), cyclohexylamine (99%), 2-ethylhexylamine (99%), 3-aminopropanol ($\geq 99\%$), 3-methoxypropylamine (99%) and N,N-Dimethyl-1,3-propanediamine (97%) were purchased from TCI and used without further purification. Butyl methacrylate (99%), butylamine (99.5%), Cysteamine (95%), 2-(Acetoacetoxy)ethyl methacrylate (95%), Sodium Sulfate, MeOH, EtOAc were purchased by Sigma Aldrich and used without further purification. Deuterated solvents were purchased from Sigma Aldrich.

4.4.2 Characterization

^1H and ^{13}C NMR spectra were recorded at ambient temperature, using deuterated chloroform (CDCl_3) or deuterated DMSO (DMSO-d_6) with a 300 MHz Bruker Avance III.

Thermogravimetric analysis (TGA) was performed in a TGA 8000 from PerkinElmer under a nitrogen atmosphere from 30 to 900 °C at a heating rate of 10 °C min⁻¹.

Rheological experiments were performed in the ARES-G2 rheometer from TA Instruments. Frequency sweeps were performed in shear geometry with 8 mm diameter plates under linear viscoelastic conditions, in which the storage modulus and the loss modulus of the samples were determined. Confirmation that the measurements were recorded within the linear viscoelastic regime was

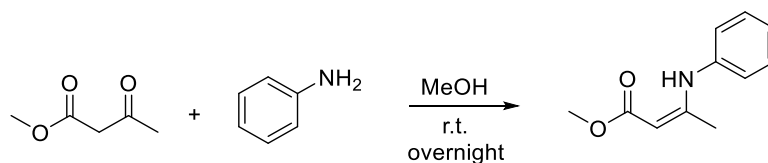
obtained through strain sweeps at a frequency of 1 Hz. Stress relaxation measurements were performed to obtain the relaxation modulus ($G(t)$) in shear using plates with 8 mm of diameter under linear viscoelastic conditions. The samples had a thickness between 0.6 mm and 1 mm.

4.4.3 Computational Methodology

All geometry optimizations were executed within density functional theory (DFT) using the ω B97XD²⁴ functional combined with the 6–31+G(d)²⁵ basis set for all atoms. Frequency calculations were carried out at the same level of theory to validate that the optimized structures were minima or transition states on the potential energy surfaces. These frequencies were then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal corrections to the enthalpy (H) and Gibbs free energy (G), at $T = 298.15$ K, in the harmonic oscillator approximation. To refine the electronic energies, single-point calculations using the 6–311++G(2df,2p) basis set²⁶ were performed on the optimized structures. All the calculations were performed with the Gaussian 16 suite of programs.²⁷

4.4.4 Synthetic Procedures:

Synthesis of Methyl-3-(phenylamino)but-2-enoate (VU_PhNH₂):

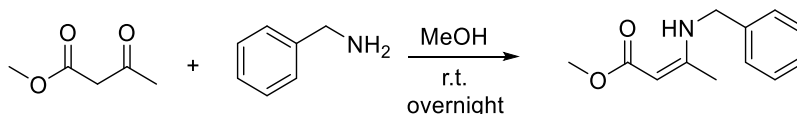


Scheme S4.1: Schematic representation of the synthesis of Methyl-3-(phenylamino)but-2-enoate (VU_PhNH₂).

The synthesis of VU_PhNH₂ was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (5g, 43 mmol) and aniline (8,4g, 90 mmol) were added in 30 mL of MeOH in a 100 mL round bottom flask. The reaction was stirred

overnight at room temperature and the formation of the product was checked with thin-layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO_4 and evaporated, yielding the desired product as a yellowish liquid. The obtained product was purified by flash chromatography using EtOAc/hexane (v/v = 85/15) as the eluent. Yield of methyl-3-(phenylamino)but-2-enoate: 58%, 4.8 g. ^1H NMR (400 MHz, DMSO-d_6) δ 7.59 – 6.95 (m, 5H), 4.71 (d, J = 0.7 Hz, 1H), 3.59 (s, 3H), 2.01 (d, J = 0.6 Hz, 3H).

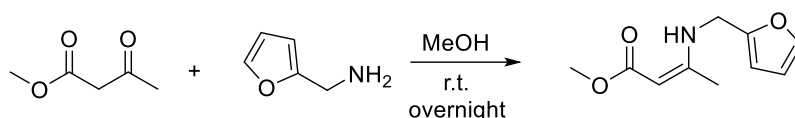
Synthesis of Methyl-3-(benzylamino)but-2-enoate (VU_BnNH₂):



Scheme S4.2: Schematic representation of the synthesis of Methyl-3-(benzylamino)but-2-enoate (VU_BnNH₂).

The synthesis of VU_BnNH₂ was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (2g, 17 mmol) and benzylamine (3.6g, 34 mmol) were added in 20 mL of MeOH in a 100 mL round bottom flask. The reaction was stirred overnight at room temperature and the formation of the product was checked with thin-layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO_4 and evaporated, yielding the desired product as a yellowish liquid. Yield of methyl-3-(benzylamino)but-2-enoate: 98%, 3.40g. ^1H NMR (400 MHz, DMSO-d_6) δ 8.95 – 8.79 (m, 1H), 7.45 – 7.18 (m, 4H), 4.48 – 4.46 (m, 2H), 4.44 (s, 1H), 3.50 (s, 3H), 1.90 (d, J = 0.6 Hz, 3H).

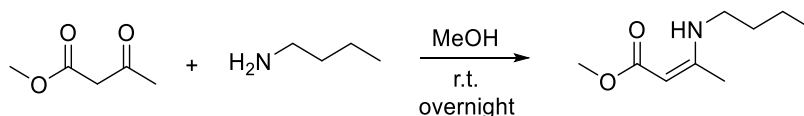
Synthesis of Methyl-3-(furfurylamino)but-2-enoate (VU_FuNH₂):



Scheme S4.3: Schematic representation of the synthesis of Methyl-3-(furfurylamino)but-2-enoate (VU_FuNH₂).

The synthesis of VU_FuNH₂ was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (2g, 17 mmol) and furfurylamine (3.3g, 34 mmol) were added in 20 mL of MeOH in a 100 mL round bottom flask. The reaction was stirred overnight at room temperature and the formation of the product was checked with thin-layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO₄ and evaporated, yielding the desired product as a yellowish liquid. Yield of methyl-3-(furfurylamino)but-2-enoate: 98%, 3.26g. ¹H NMR (400 MHz, DMSO-d₆) δ 8.69 (t, J = 6.2 Hz, 1H), 6.42 (dd, J = 3.2, 1.9 Hz, 1H), 6.30 (dt, J = 3.2, 0.8 Hz, 1H), 4.46 (d, J = 0.7 Hz, 1H), 4.44 (t, J = 0.7 Hz, 2H), 3.48 (s, 3H), 1.97 (d, J = 0.6 Hz, 3H).

Synthesis of Methyl-3-(butylamino)but-2-enoate (VU_BuNH₂):

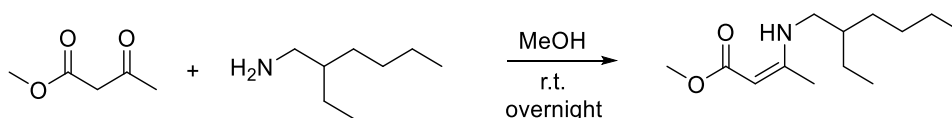


Scheme S4.4: Schematic representation of the synthesis of Methyl-3-(butylamino)but-2-enoate (VU_BuNH₂).

The synthesis of VU_BuNH₂ was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (2g, 17 mmol) and butylamine (2.5g, 34 mmol) were added in 20 mL of MeOH in a 100 mL round bottom flask. The reaction was

stirred overnight at room temperature and the formation of the product was checked with thin-layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO_4 and evaporated, yielding the desired product as a yellowish liquid. Yield of methyl-3-(butylamino)but-2-enoate: 98%, 2.79g. ^1H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 1H), 4.35 (d, $J = 0.6$ Hz, 1H), 3.47 (s, 3H), 3.20 (td, $J = 6.9, 5.8$ Hz, 2H), 1.89 (d, $J = 0.6$ Hz, 3H), 1.53 – 1.40 (m, 2H), 1.41 – 1.26 (m, 2H), 0.95 – 0.85 (m, 3H).

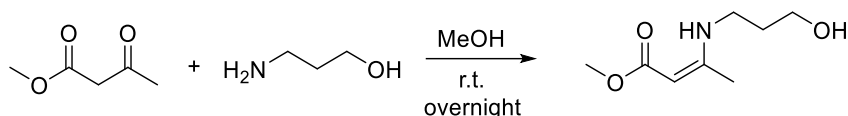
Synthesis of Methyl-3-(2-ethylhexylamino)but-2-enoate (VU_2EHA):



Scheme S4.5: Schematic representation of the synthesis of Methyl-3-(2-ethylhexylamino)but-2-enoate (VU_2EHA).

The synthesis of VU_2EHA was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (2g, 17 mmol) and 2-ethylhexylamine (4.4g, 34 mmol) were added in 20 mL of MeOH in a 100 mL round bottom flask. The reaction was stirred overnight at room temperature and the formation of the product was checked with thin-layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO_4 and evaporated, yielding the desired product as a yellowish liquid. Yield of methyl-3-(2-ethylhexylamino)but-2-enoate: 99%, 3.74g. ^1H NMR (400 MHz, DMSO-d_6) δ 8.60 (t, $J = 5.8$ Hz, 1H), 4.36 (d, $J = 0.7$ Hz, 1H), 3.48 (s, 3H), 3.13 (td, $J = 5.9, 0.8$ Hz, 2H), 1.89 (d, $J = 0.6$ Hz, 4H), 1.39 – 1.19 (m, 13H), 0.92 – 0.79 (m, 7H).

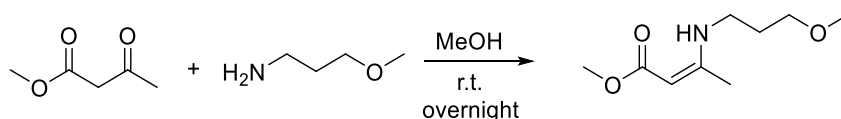
Synthesis of Methyl-3-(3-propanolamino)but-2-enoate (VU_3MET):



Scheme S4.6: Schematic representation of the synthesis of Methyl-3-(3-propanolamino)but-2-enoate (VU_3MET).

The synthesis of VU_3MET was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (2g, 17 mmol) and 3-aminopropanol (2,55g, 34 mmol) were added in 20 mL of MeOH in a 100 mL round bottom flask. The reaction was stirred overnight at room temperature and the formation of the product was checked with thin-layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO₄ and evaporated, yielding the desired product as a yellowish liquid. Yield of methyl-3-(3-aminopropanol)but-2-enoate: 94%, 2,61g. ¹H NMR (300 MHz, CDCl₃) δ 8.54 (s, 1H), 4.43 (s, 1H), 3.71 (t, 1H), 3.59 (s, 5H), 3.33 (t, 1H), 1.92 (s, 5H), 1.86 – 1.71 (m, 1H).

Synthesis of Methyl-3-(3-methoxypropylamino)but-2-enoate (VU_3APO):

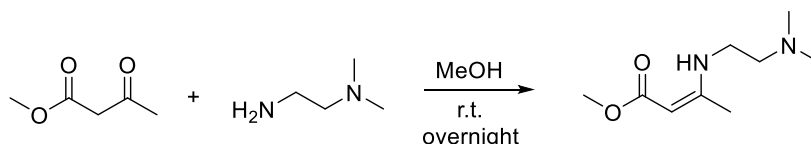


Scheme S4.7: Schematic representation of the synthesis of Methyl-3-(3-methoxypropylamino)but-2-enoate (VU_3APO).

The synthesis of VU_3APO was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (2g, 17 mmol) and 3-methoxypropylamine (3g, 34 mmol) were added in 20 mL of MeOH in a 100 mL round bottom flask. The reaction was stirred overnight at room temperature and the formation of the

product was checked with thin layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO_4 and evaporated, yielding the desired product as a yellowish liquid. Yield of methyl-3-(3-methoxypropylamine)but-2-enoate: 97%, 3,07g. ^1H NMR (300 MHz, DMSO) δ 8.52 (s, 1H), 4.37 (s, 1H), 3.49 (s, 4H), 3.37 (t, 2H), 3.32 – 3.27 (m, 1H), 3.25 (s, 4H), 1.90 (s, 4H), 1.77 – 1.67 (m, 1H).

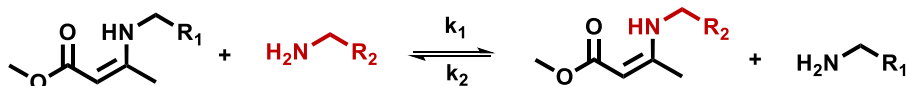
Synthesis of Methyl-3-(N,N-dimethyl-1,3-propanediamino)but-2-enoate (VU_N,NDIAM):



Scheme S4.8: Schematic representation of the synthesis of Methyl-3-(N,N-dimethyl-1,3-propanediamino)but-2-enoate (VU_N,NDIAM).

The synthesis of VU_N,NDIAM was based on procedures published by Denissen *et al.*¹. Methyl acetoacetate (2g, 17 mmol) and N,N-dimethylethylenediamine (3g, 34 mmol) were added in 20 mL of MeOH in a 100 mL round bottom flask. The reaction was stirred overnight at room temperature and the formation of the product was checked with thin layer chromatography (TLC). The solvent was removed in vacuo and the mixture was extracted twice with brine and EtOAc. The combined organic phases were dried with MgSO_4 and evaporated, yielding the desired product as a yellowish liquid. Yield of methyl-3-(N,N-dimethyl-1,3-propanediamino)but-2-enoate: 96%, 3,03g. ^1H NMR (300 MHz, Chloroform- d) δ 8.63 (s, 1H), 4.47 (d, J = 0.7 Hz, 1H), 3.64 (d, J = 1.2 Hz, 3H), 3.31 (td, J = 6.6, 5.6 Hz, 2H), 2.48 (t, J = 6.6 Hz, 2H), 2.28 (s, 6H), 1.94 (d, J = 0.6 Hz, 3H).

4.4.5 Kinetic NMR studies of model compounds



Scheme S4.9: Schematic representation of general reaction for the kinetic NMR studies of model compounds.

All the compounds used in the model reactions were dried in a vacuum oven overnight before use. The kinetic experiments between equal molar amounts of vinyllogous urethane and free amine, corresponding to 1.05 mmol, were performed in a vial filled with 3.5 mL of DMSO- d_6 at 100°C. At determined intervals, a small amount of the reaction mixture was taken out to perform ^1H NMR analysis. The peaks of the methylene $-\text{CH}_2$ in α to the NH group and the peaks of the methyl in β to the NH group were integrated to determine the relative amount of the two components in the reaction mixture.

4.4.6 Quantitative HSQC kinetics of model compounds

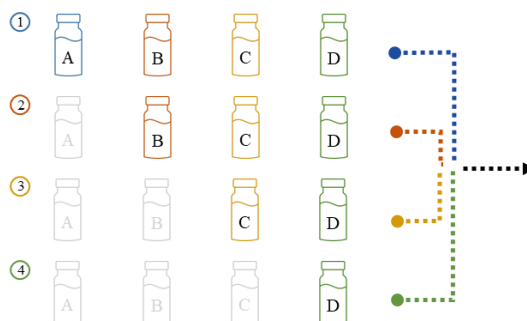


Figure S4.1: Displayed methodology for the quantitative HSQC (Heteronuclear single quantum coherence) spectroscopy analysis.

Before use, all compounds involved in the model reactions were dried overnight in a vacuum oven. Four vials were each filled with 3.5 mL of deuterated DMSO- d_6 , and 1.05 mmol of both the vinyllogous urethane moiety and the free amine were added to each vial. The reaction mixtures were then heated to 100°C for 4

hours. At specific time intervals, aliquots were withdrawn from the reaction mixtures for quantitative HSQC analysis. After the initial 4-hour period, the second free amine was added, and the reaction kinetics were again monitored via quantitative HSQC over an additional 4 hours at 100°C. This procedure was repeated until the entire combinatorial analysis, including all the different free amines, was completed. The peaks of the methylene -CH₂ in α to the NH group and the peaks of the methyl in β to the NH group were carefully integrated to determine the relative amount of the two components in the reaction mixture.

4.4.7 Preparation of crosslinked networks

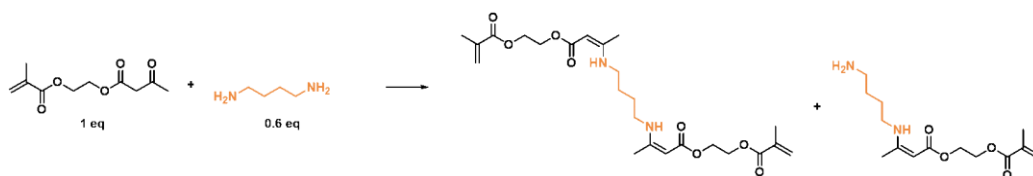


Figure S4.2: Methodology for the preparation of the crosslinkers

A series of crosslinked networks was prepared by photopolymerization, starting with a mixture of 2-(Methacryloyloxy) ethyl acetoacetate and various diamines in a 1:0.6 molar ratio, using butyl methacrylate and Darocure 1175 (1 wt%) as the photoinitiator. The mixture of these two components, whose ratio was chosen to produce a divalent vinylogous urethane cross-linker alongside a vinylogous urethane with a free amine group was added to butyl methacrylate at a concentration of 50 wt%. The selected diamines were: (i) m-Xylylenediamine, (ii) 1,4-butanediamine, (iii) Bis(3-aminopropyl)methylamine, and (iv) 4,9-Dioxa-1,12-dodecanediamine. All vitrimer materials were prepared according to the following procedure:

In a vial, 2g of butyl methacrylate was combined with 1g of the mixture of AEMMA and the diamine selected. Subsequently, ~15 mg of Darocure 1175 was added to the solution, which was then stirred until a homogeneous mixture was obtained. The solution was then dispensed into Teflon molds of various sizes using a Pasteur pipette and subjected to UV irradiation using a Light Curing System UVC-5 (Dymax) with a lamp intensity of $400 \text{ mW}\cdot\text{cm}^{-2}$. After solidification, the samples were peeled from the molds and stored at room temperature.

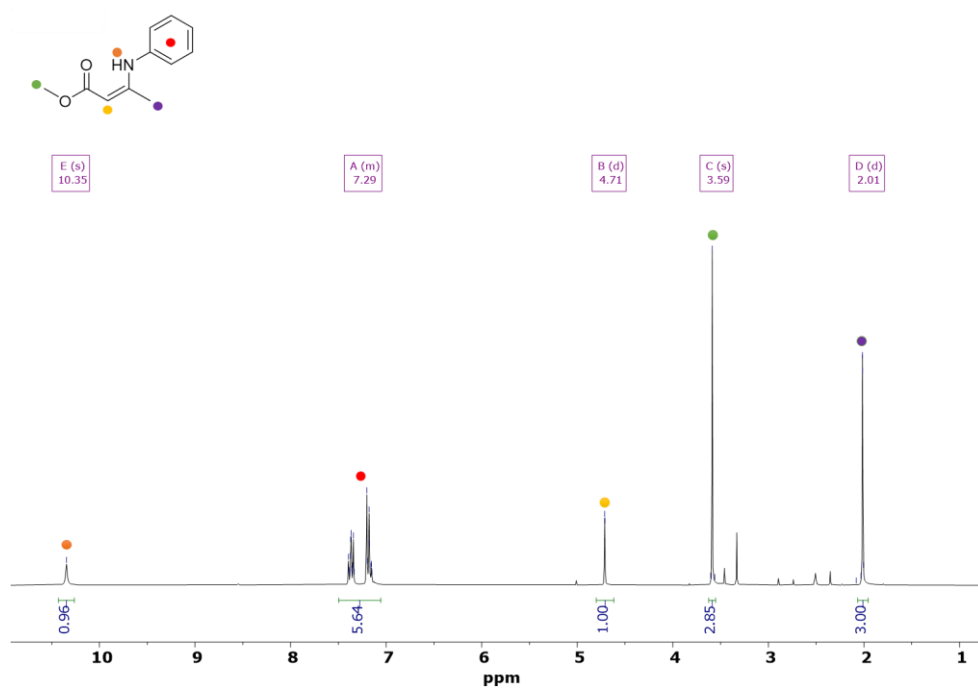


Figure S4.1: ¹H-NMR (400 MHz, dmso-d₆) spectrum of VU_PhNH₂

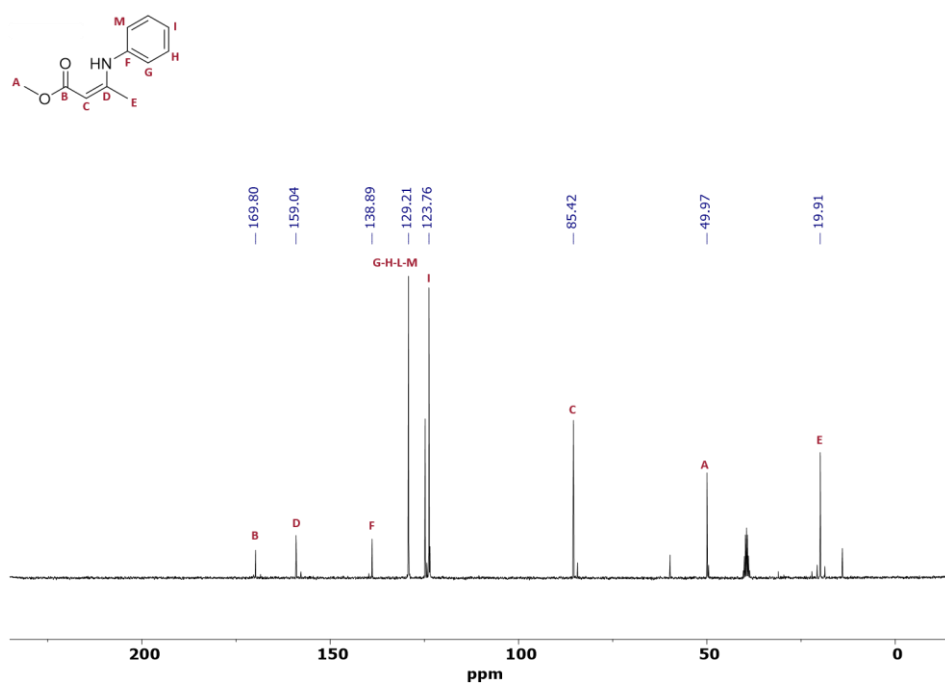


Figure S2.4: ¹³C-NMR (400 MHz, dmso-d₆) spectrum of VU_PhNH₂

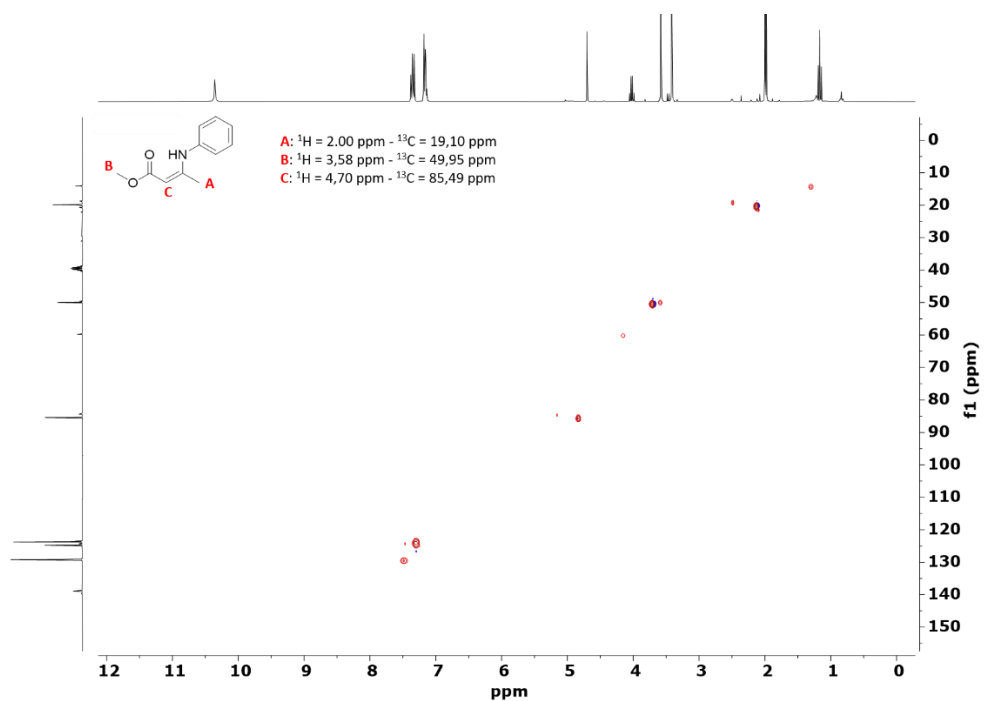


Figure S4.3: HSQC NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_PhNH₂.

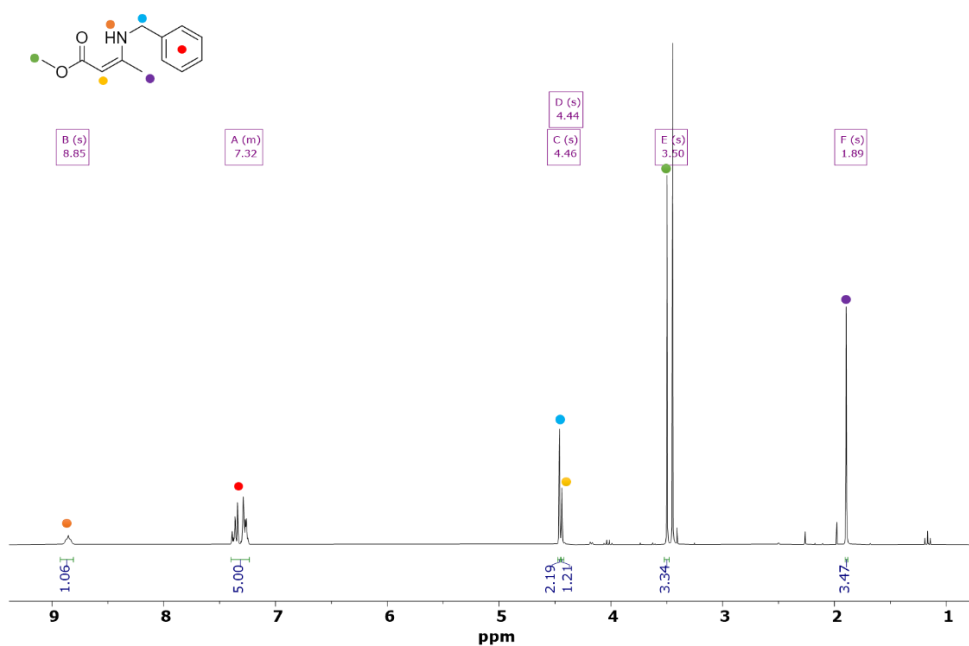


Figure S4.4: ^1H -NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_BnNH₂.

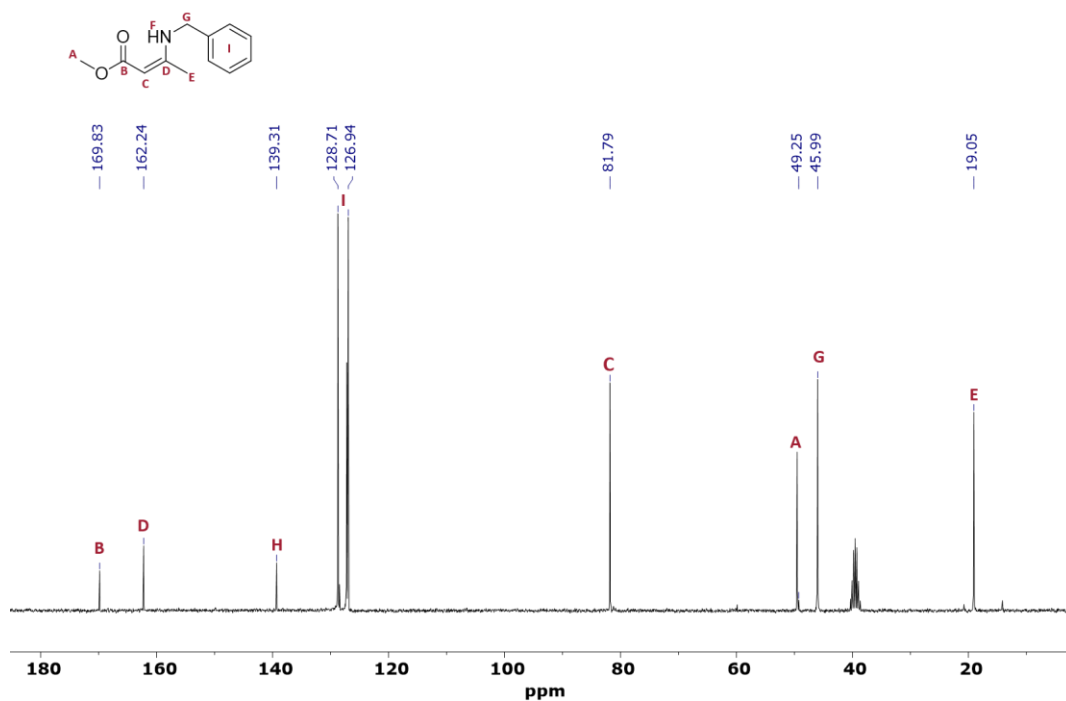


Figure S4.5: ¹³C-NMR (400 MHz, dmsd-d₆) spectrum of VU_BnNH₂.

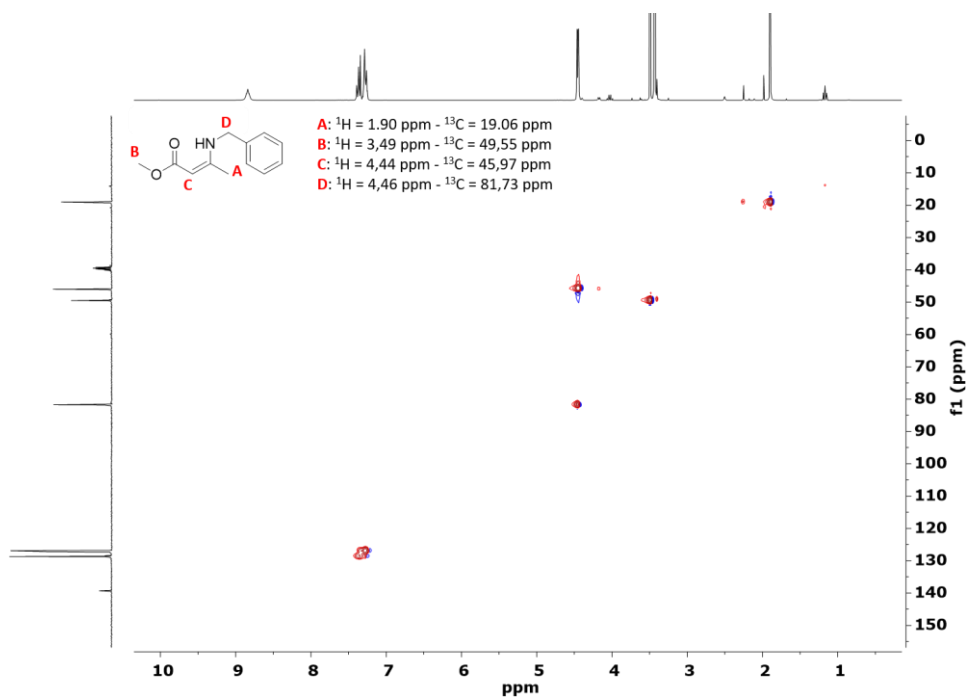


Figure S4.6: HSQC NMR (400 MHz, dmsd-d₆) spectrum of VU_BnNH₂.

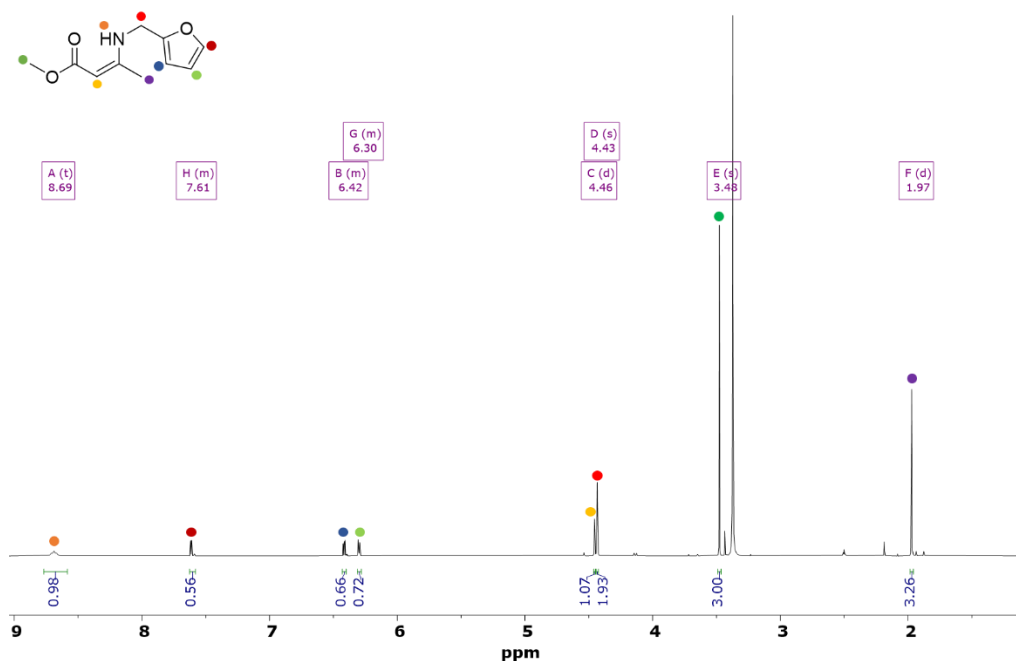


Figure S4.7: ¹H-NMR (400 MHz, dmso-d₆) spectrum of VU_FuNH₂.

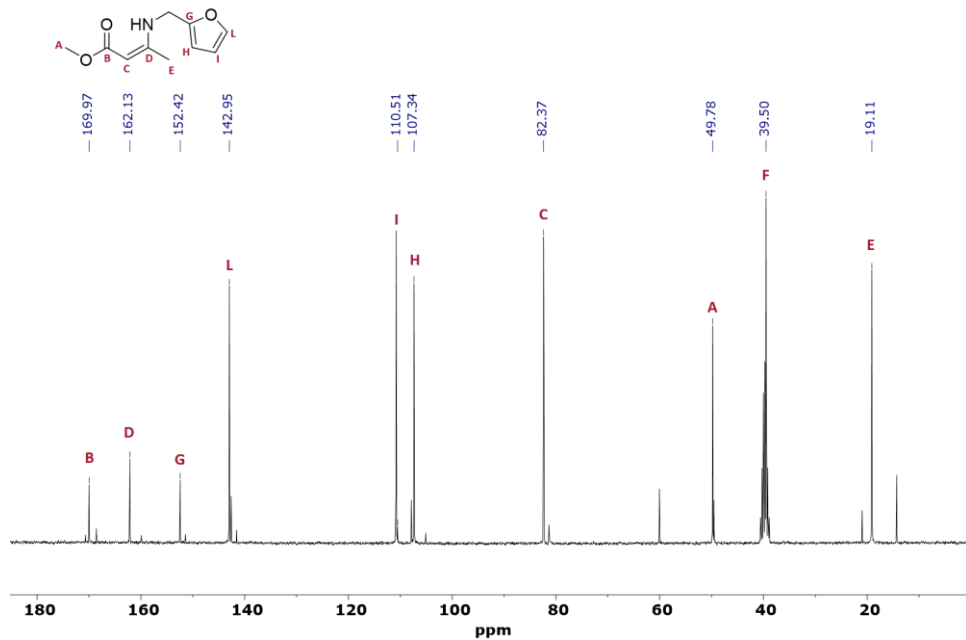


Figure S4.8: ¹³C-NMR (400 MHz, dmso-d₆) spectrum of VU_FuNH₂.

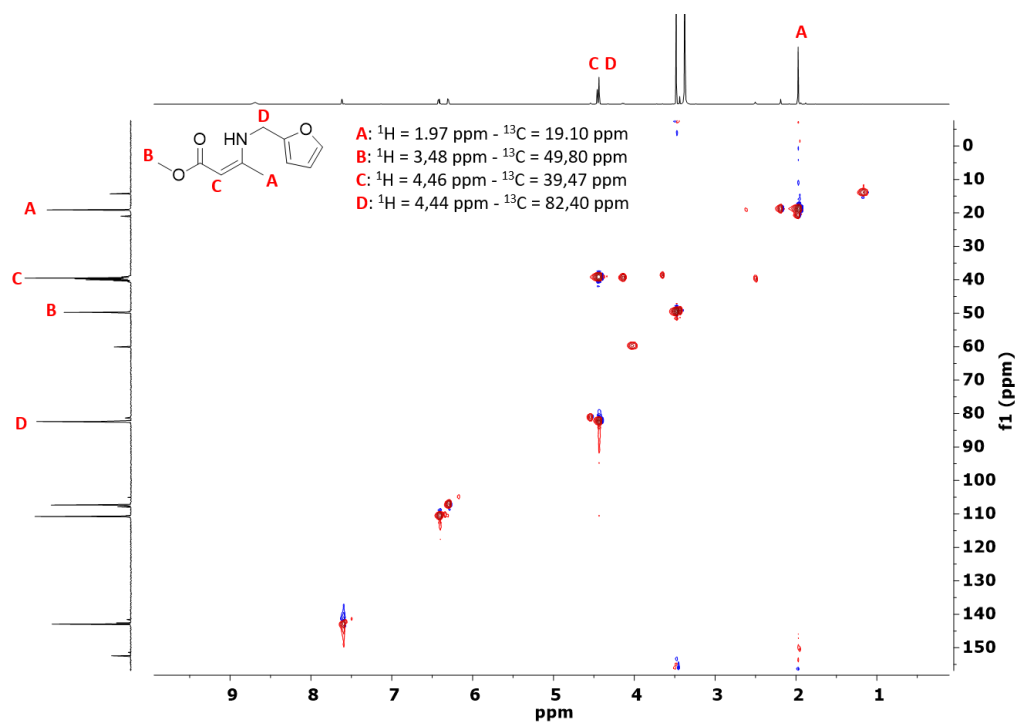


Figure S4.9: HSQC NMR (400 MHz, dmso-d₆) spectrum of VU_FuNH₂.

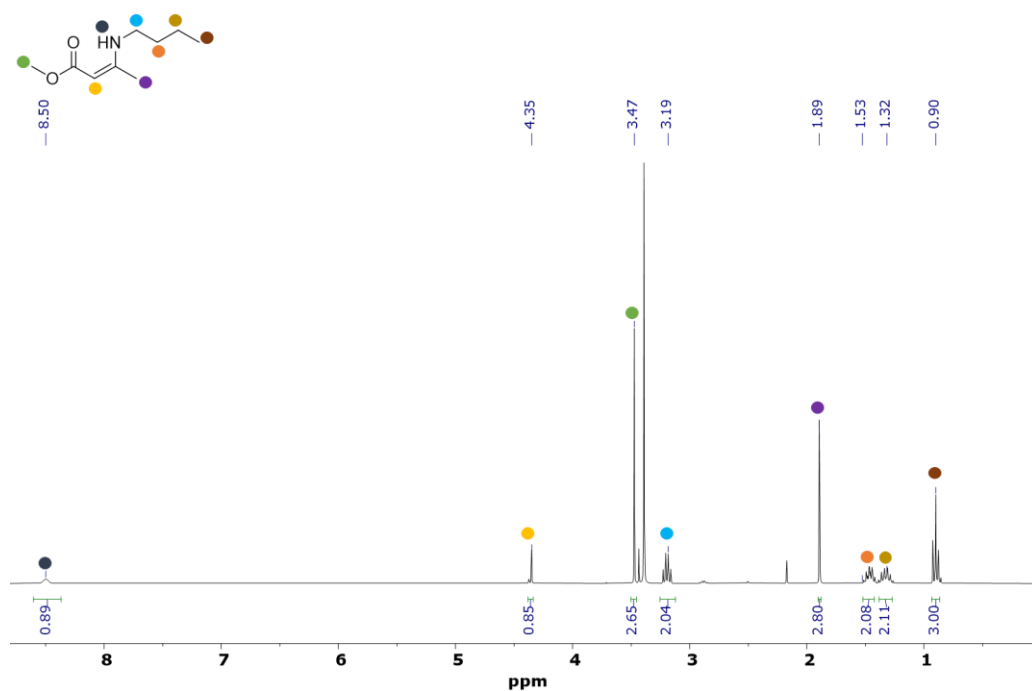


Figure S4.10: ¹H-NMR (400 MHz, dmso-d₆) spectrum of VU_BuNH₂.

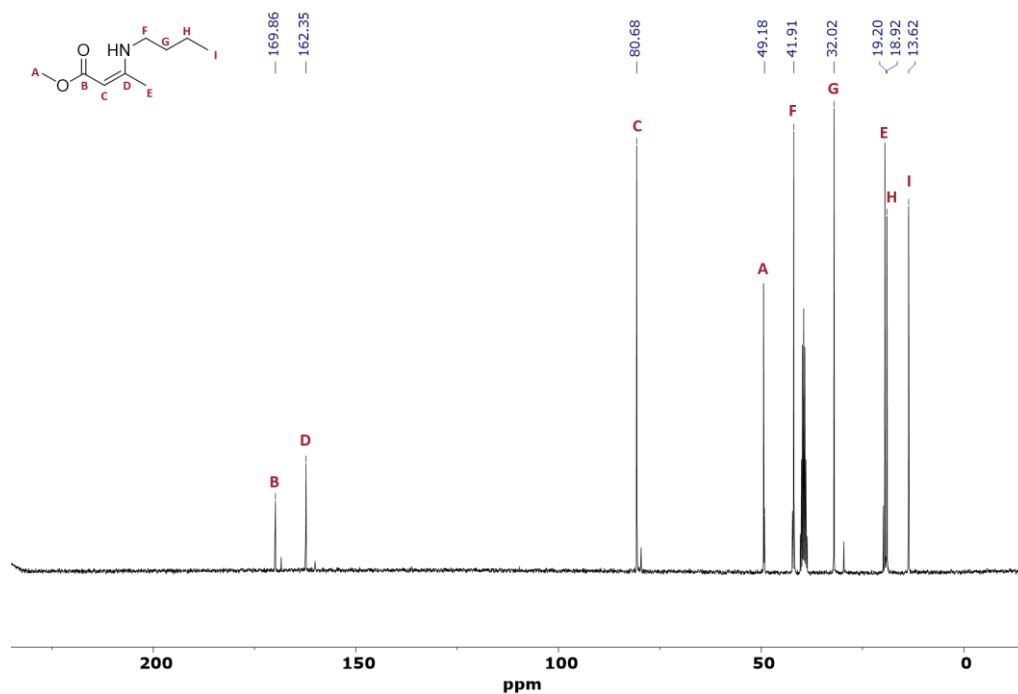


Figure S4.11: ¹³C-NMR (400 MHz, dmsO-d₆) spectrum of VU_BuNH₂.

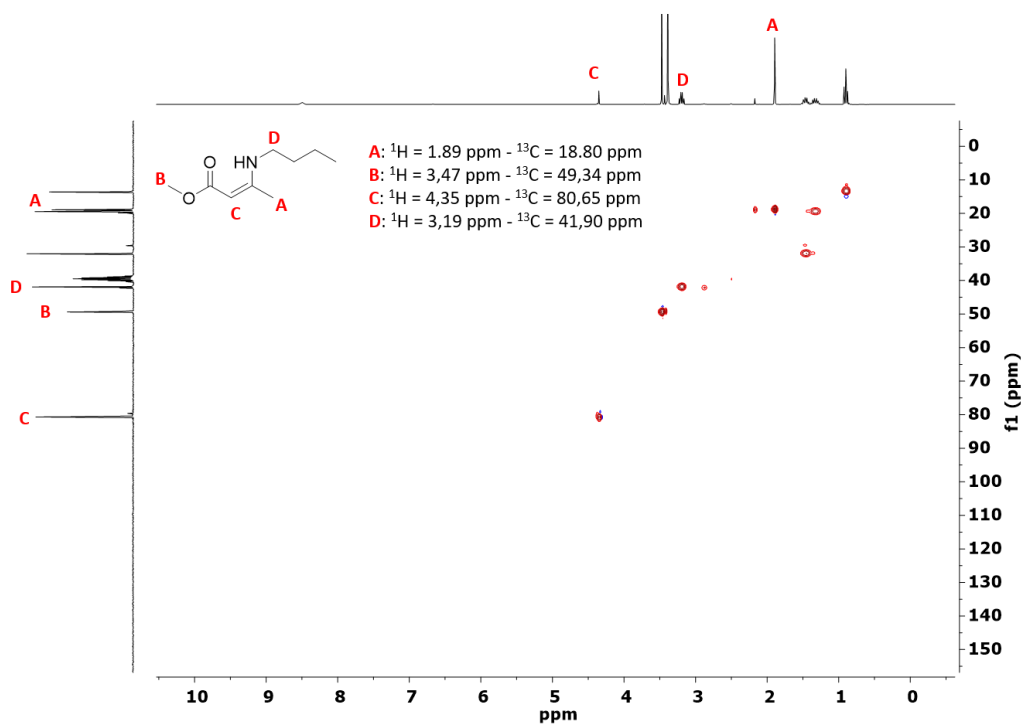


Figure S4.12: HSQC NMR (400 MHz, dmsO-d₆) spectrum of VU_BuNH₂.

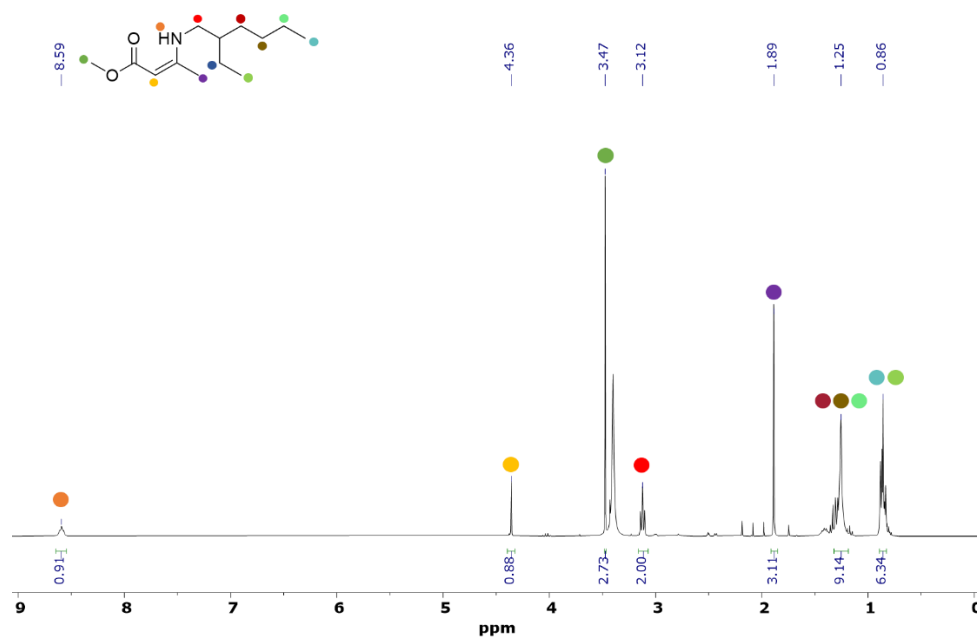


Figure S4.13: ¹H-NMR (400 MHz, dmso-d₆) spectrum of VU_2EHA.

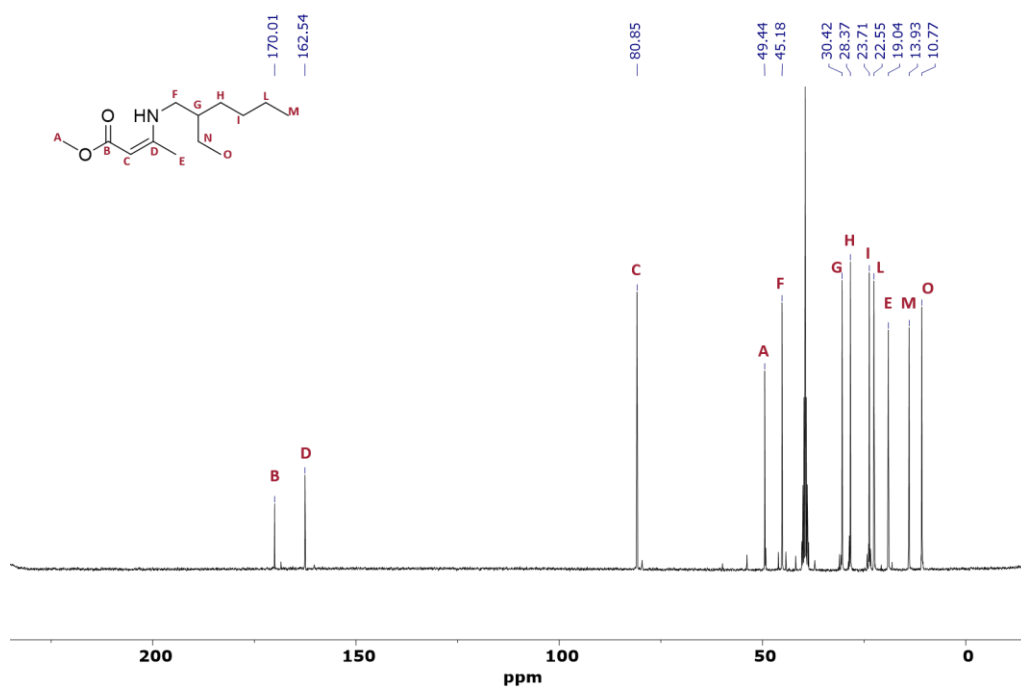


Figure S4.14: ¹³C-NMR (400 MHz, dmso-d₆) spectrum of VU_2EHA.

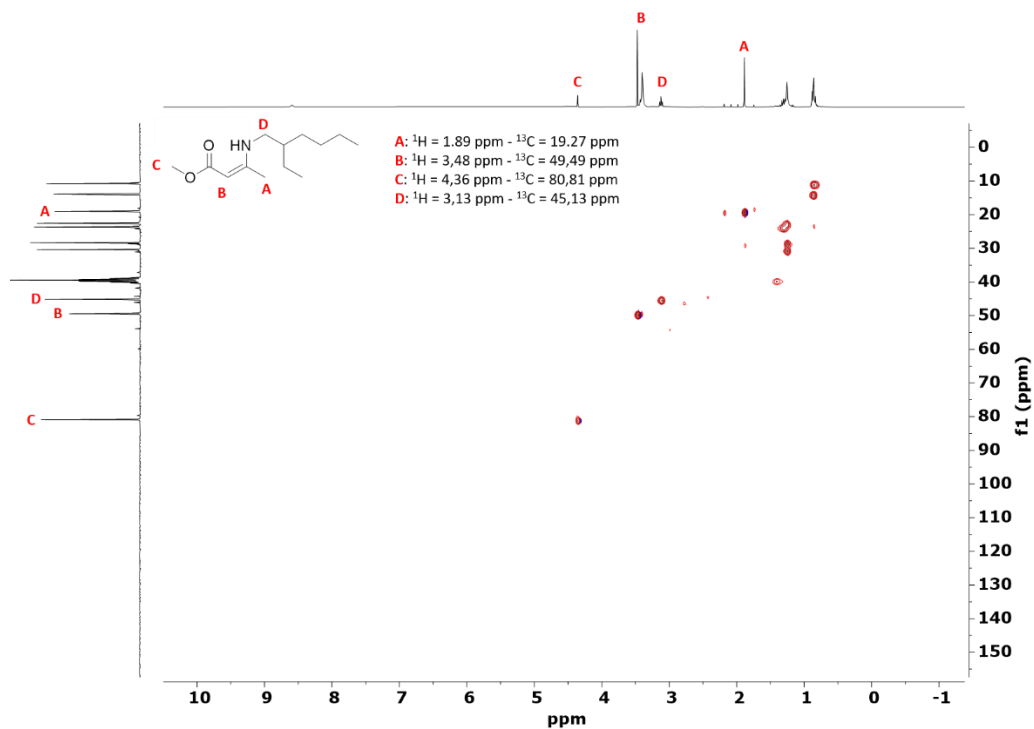


Figure S4.15: HSQC NMR (400 MHz, dmso-d_6) spectrum of VU_2EHA.

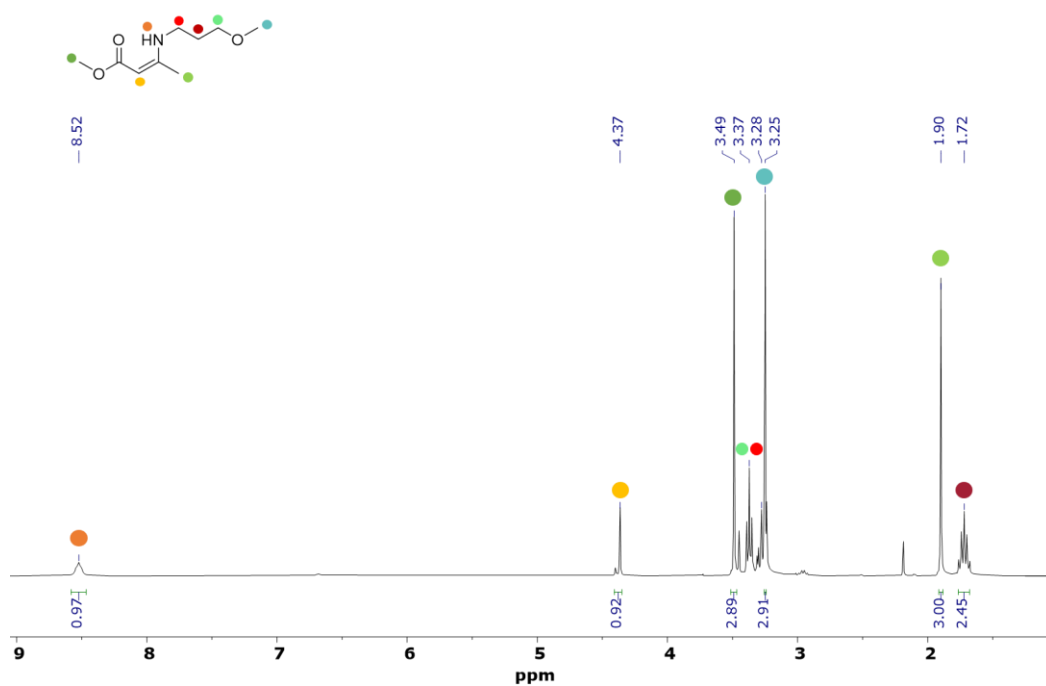


Figure S4.16 : ^1H -NMR (400 MHz, dmso-d_6) spectrum of VU_3MET.

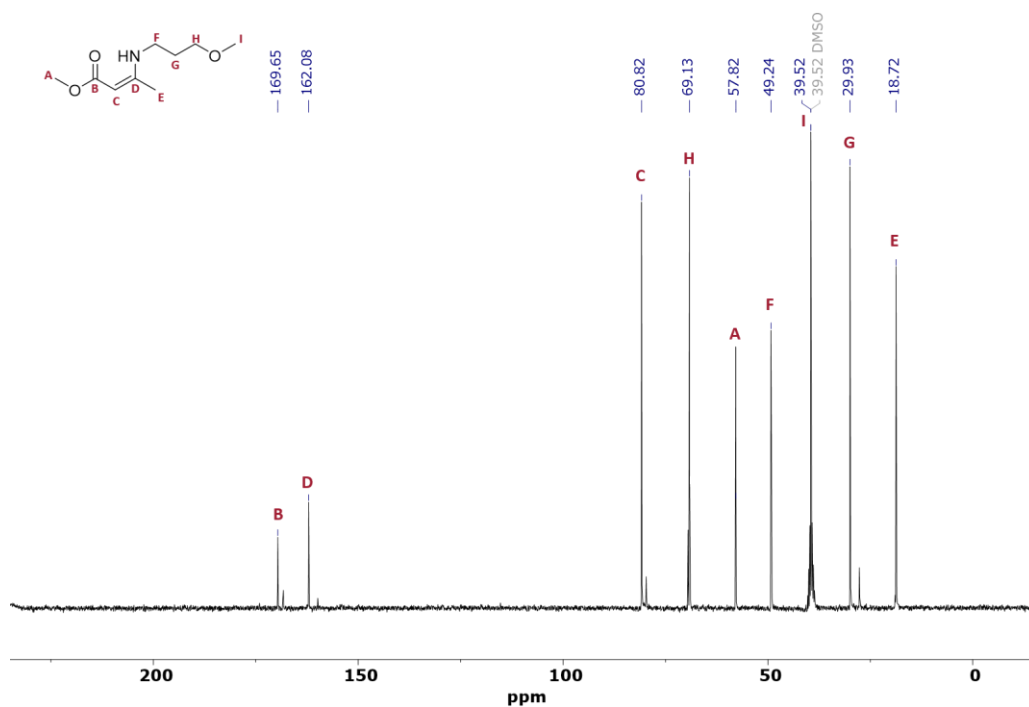


Figure S4.17: ^{13}C -NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_3MET.

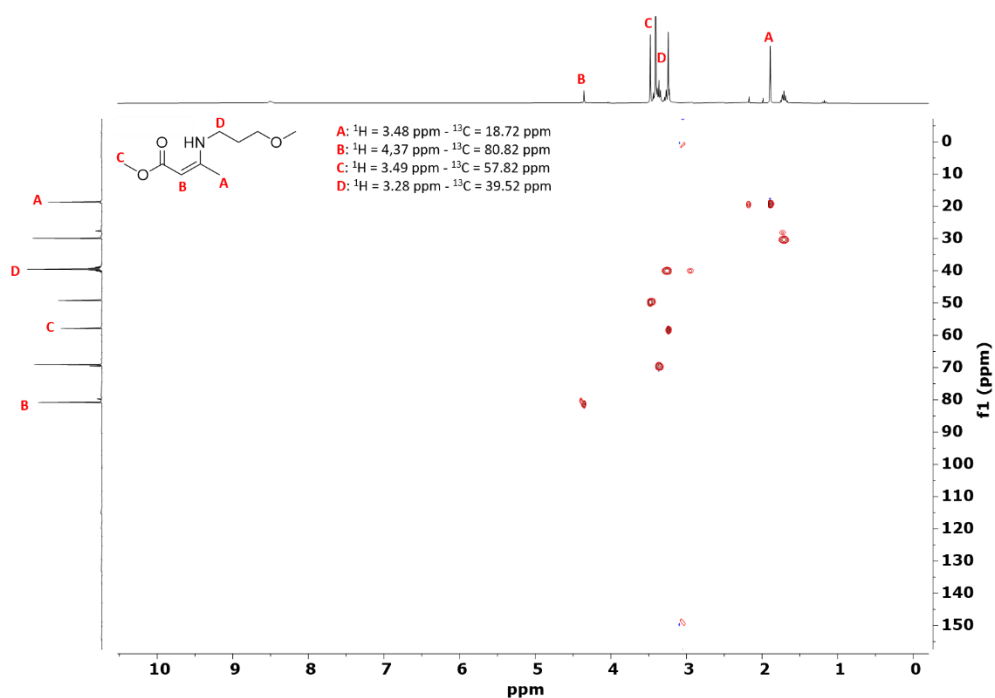


Figure S4.18: HSQC NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_3MET.

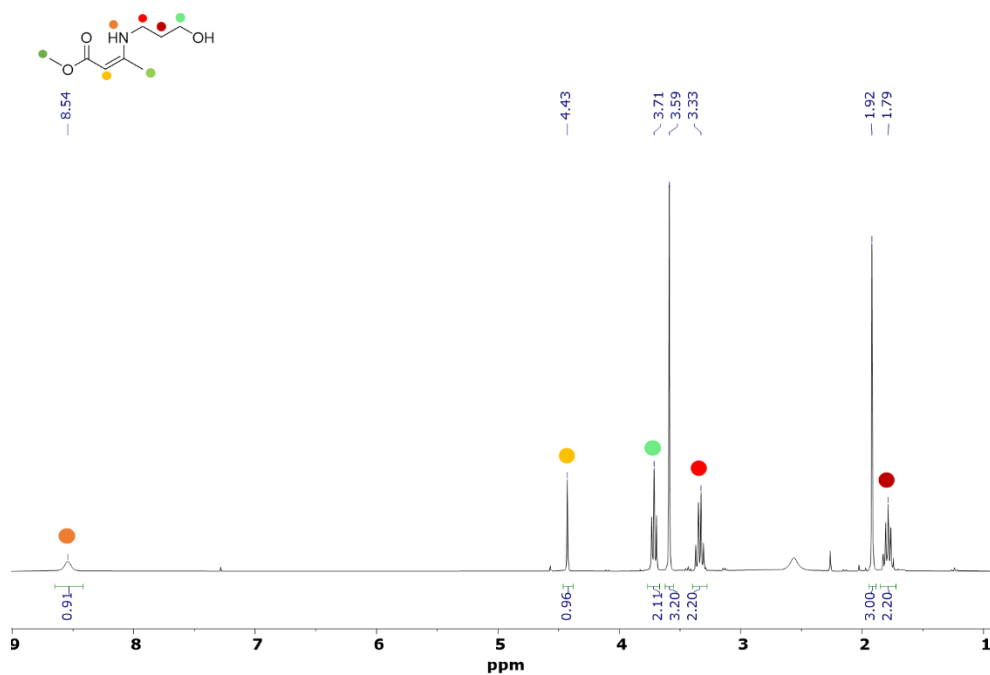


Figure S4.19: $^1\text{H-NMR}$ (400 MHz, dmso-d_6) spectrum of VU_3APO.

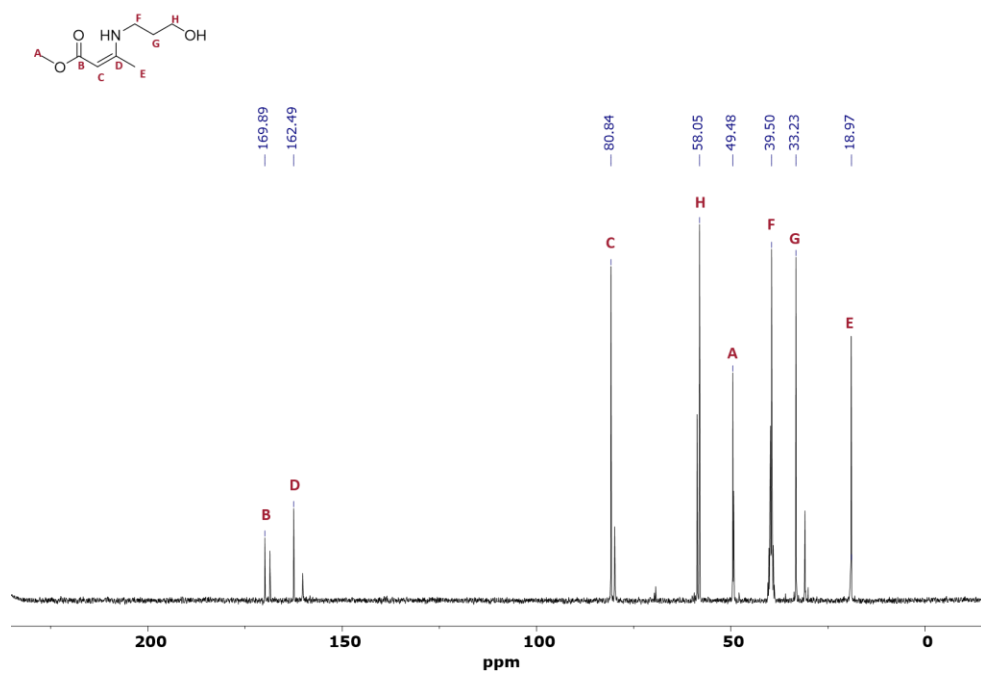


Figure S4.20: $^{13}\text{C-NMR}$ (400 MHz, dmso-d_6) spectrum of VU_3APO.

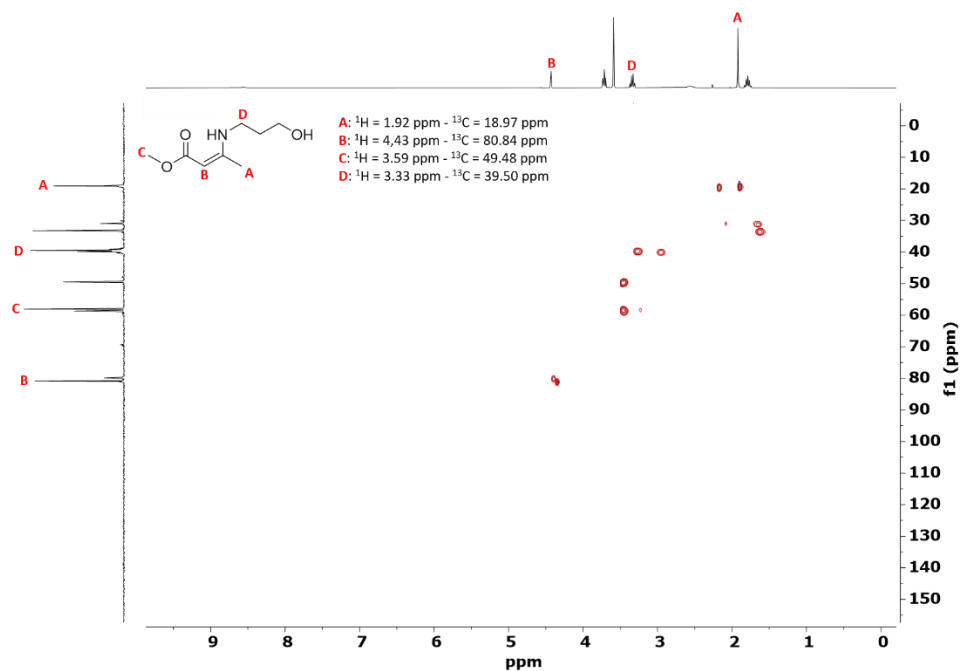


Figure S4.21: HSQC NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_3APO.

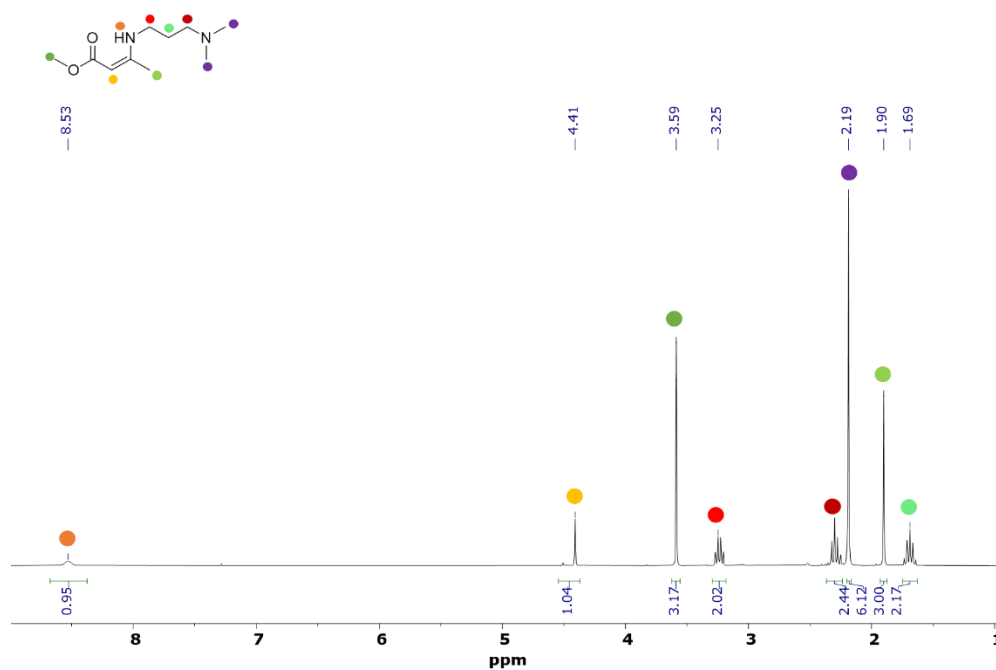


Figure S4.22: ^1H -NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_N,NDIAM.

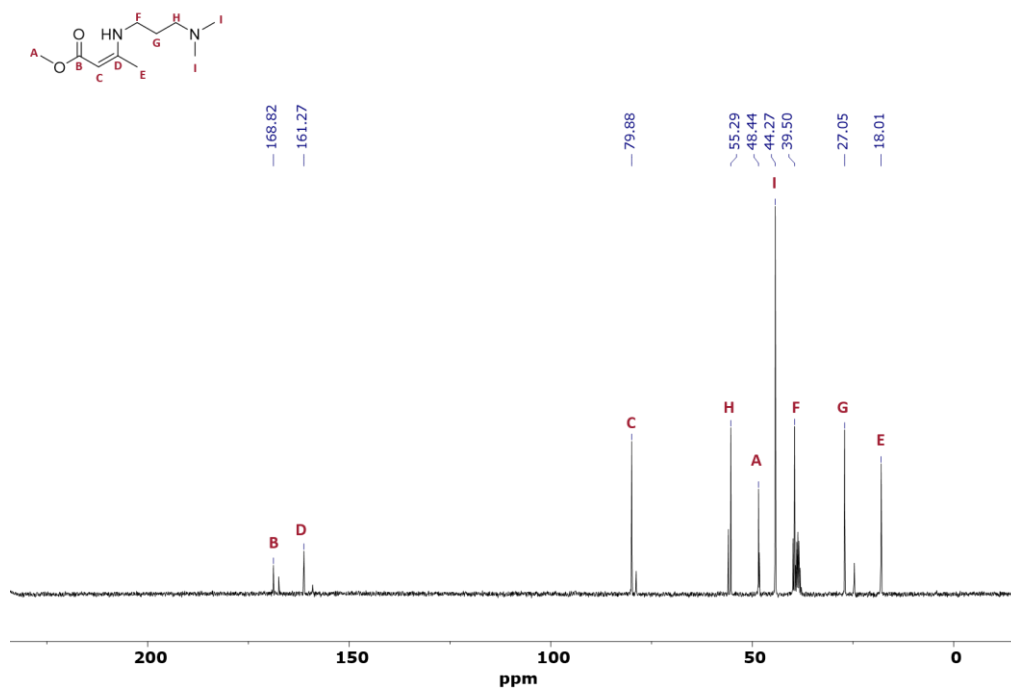


Figure S4.23: ^{13}C -NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_N,NDIAM.

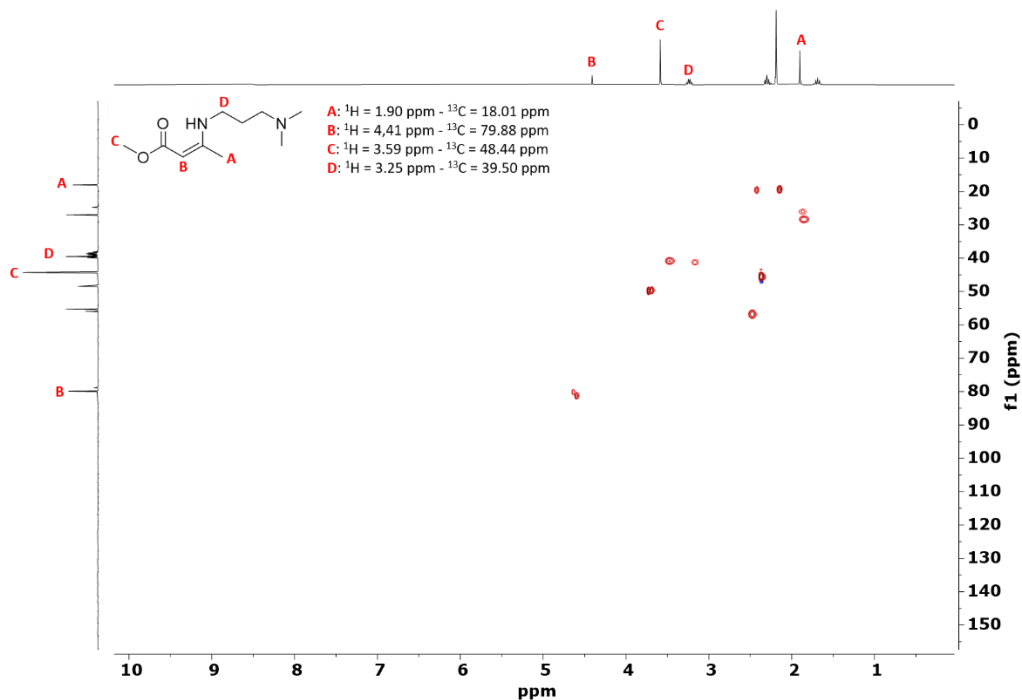


Figure S4.24: HSQC NMR (400 MHz, $\text{dms}\text{-d}_6$) spectrum of VU_N,NDIAM.

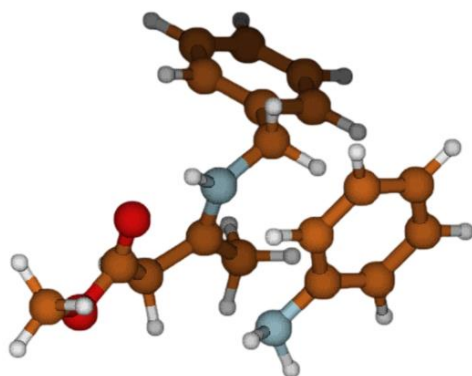


Figure S4.28: Example of INT3 in cis-conformation. This conformation is stabilized by hydrogen bonding between the NH group and the oxygen of the carbonyl group.

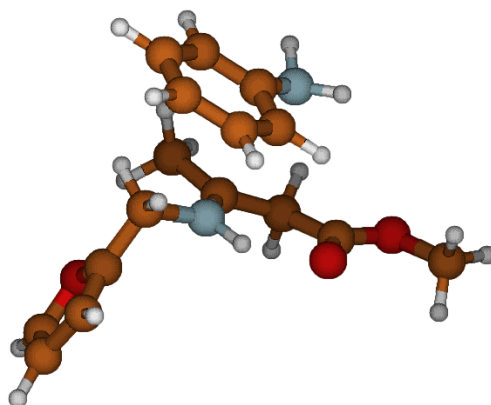


Figure S4.29: INT3 of the exchange between VU_PhNH₂ and FuNH₂. The vinylogous urethane structure is stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.840 Å). The NH group of the aniline is distant 3.178 Å from the methylene carbon of the vinylogous urethane from which it will later subtract the proton (TS4).

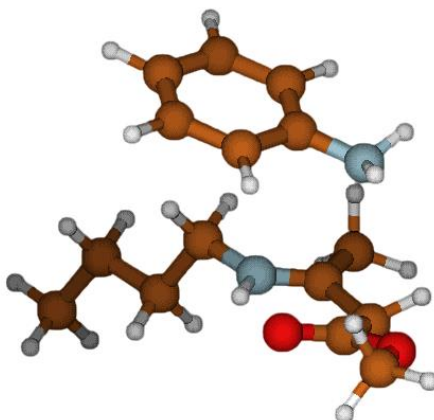


Figure S4.30: INT3 of the exchange between VU_PhNH₂ and BuNH₂. The vinyllogous urethane structure is stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.839 Å). The NH group of the aniline is distant 3.16 Å from the methylene carbon of the vinyllogous urethane from which it will later subtract the proton (TS4).

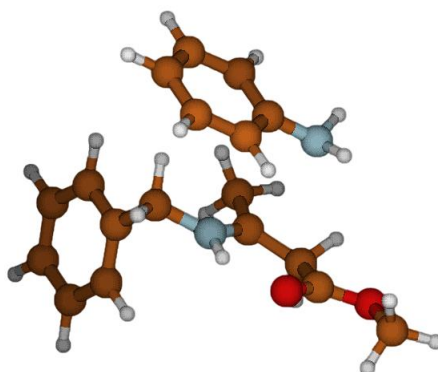


Figure S4.31: INT3 of the exchange between VU_PhNH₂ and BnNH₂. The vinyllogous urethane structure is stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.830 Å). The NH group of the aniline is distant 2.943 Å from the methylene carbon of the vinyllogous urethane from which it will later subtract the proton (TS4).

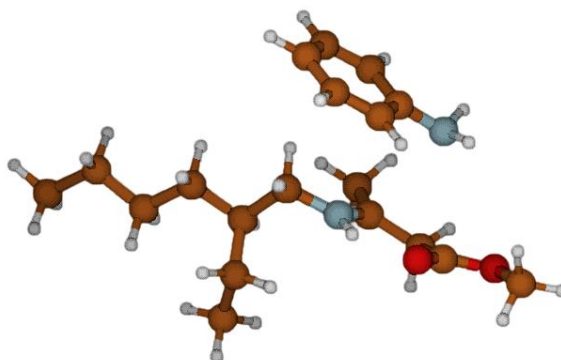


Figure S4.32: INT3 of the exchange between VU_PhNH₂ and 2-EHA. The vinyllogous urethane structure is stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.843 Å). The NH group of the aniline is distant 3.168 Å from the methylene carbon of the vinyllogous urethane from which it will later subtract the proton (TS4).

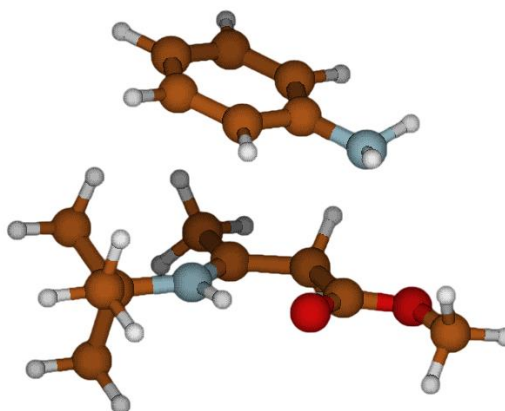


Figure S4.33: INT3 of the exchange between VU_PhNH₂ and tBuNH₂. The vinyllogous urethane structure is in a *cis*-conformation stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.770 Å). However, the NH group of the aniline is distant 3.295 Å from the methylene carbon of the vinyllogous urethane from which it will later subtract the proton (TS4).

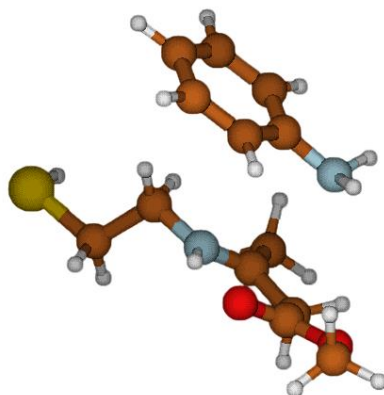


Figure S4.34: INT3 of the exchange between VU_PhNH₂ and Cys. The vinyllogous urethane structure (-23 kcal/mol) is stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.803 Å). The NH group of the aniline is distant 3.161 Å from the methylene carbon of the vinyllogous urethane from which it will later subtract the proton (TS4).

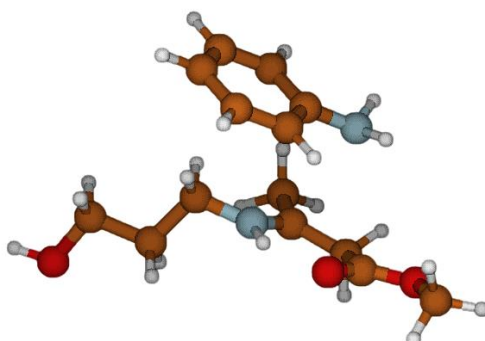


Figure S4.35: INT3 of the exchange between VU_PhNH₂ and 3-APO. The vinyllogous urethane structure (-20.3 kcal/mol) is stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.835 Å). The NH group of the aniline is distant 3.169 Å from the methylene carbon of the vinyllogous urethane from which it will later subtract the proton (TS4).

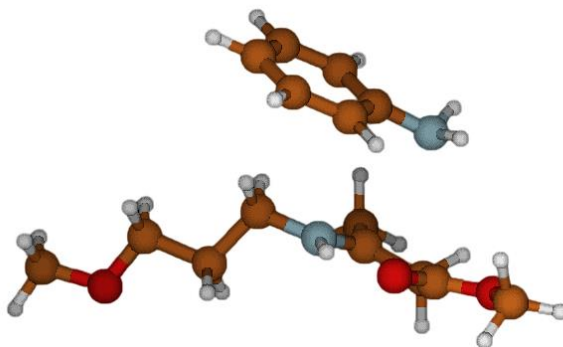


Figure S4.36: INT3 of the exchange between VU_PhNH₂ and 3-MET. The vinyllogous urethane structure (-20.11 kcal/mol) is stabilized by the hydrogen bonding between the NH group and the oxygen of the carbonyl group (1.836 Å). The NH group of the aniline is distant 3.168 Å from the methylene carbon of the vinyllogous urethane from which it will later subtract the proton (TS4).

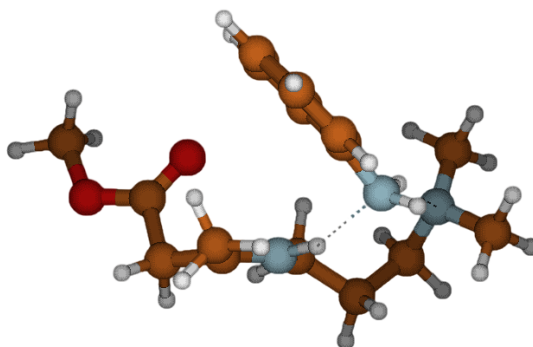


Figure S4.37: INT3 of the exchange between VU_PhNH₂ and N,N-Diam. The vinyllogous urethane structure (-19.87 kcal/mol) adopts a twisted conformation where the NH group cannot establish hydrogen bonding with the carbonyl oxygen due to interaction with the amino group of the aniline, which in turn interacts with the dimethyl-substituted nitrogen group present in the aliphatic chain.

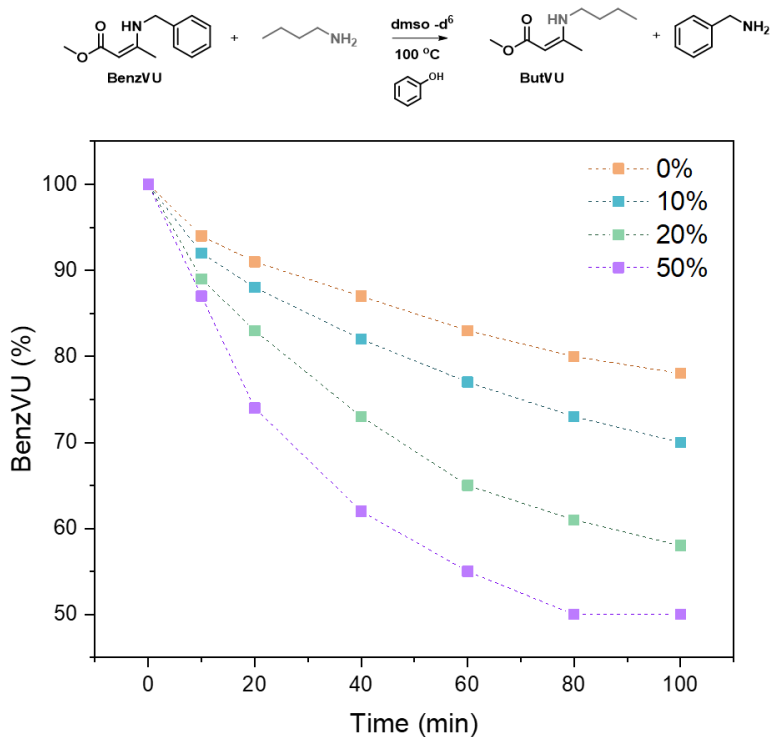


Figure S4.38: Single-model transamination kinetics with different addition of phenol as an acid catalyst. In the graph, is plotted the disappearance rate of BenzVU against time.

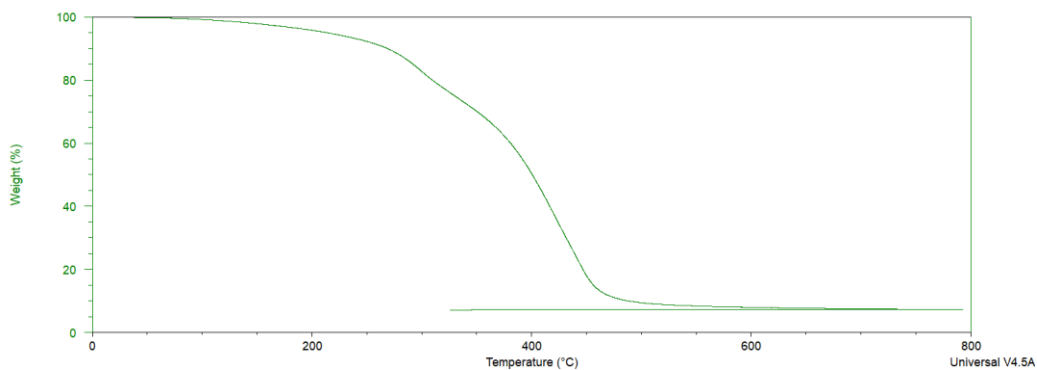


Figure S4.39: Thermal Gravimetric Analysis (TGA) of VT1.

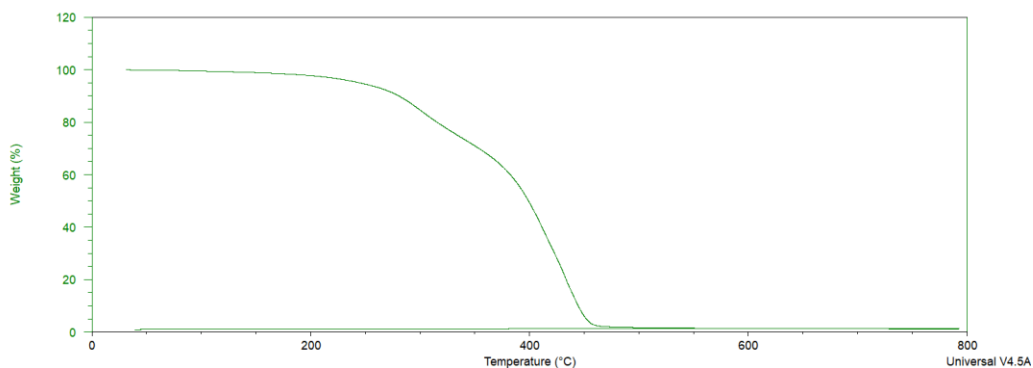


Figure S4.40: Thermal Gravimetric analysis of VT2.

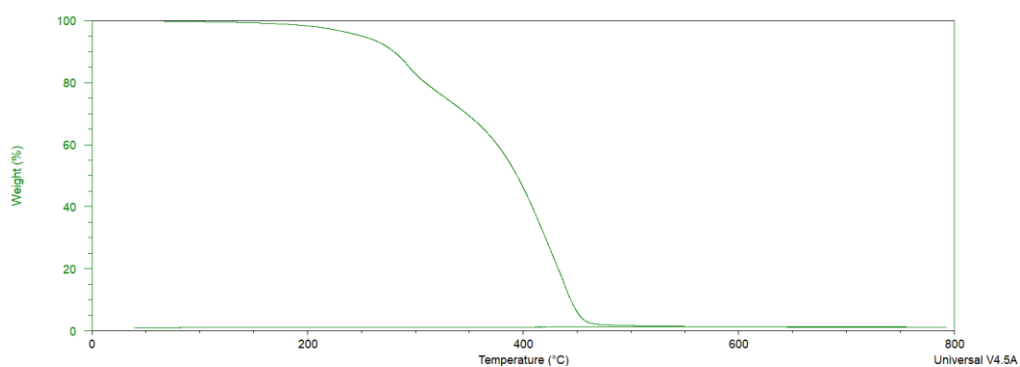


Figure S4.41: Thermal Gravimetric analysis of VT3.

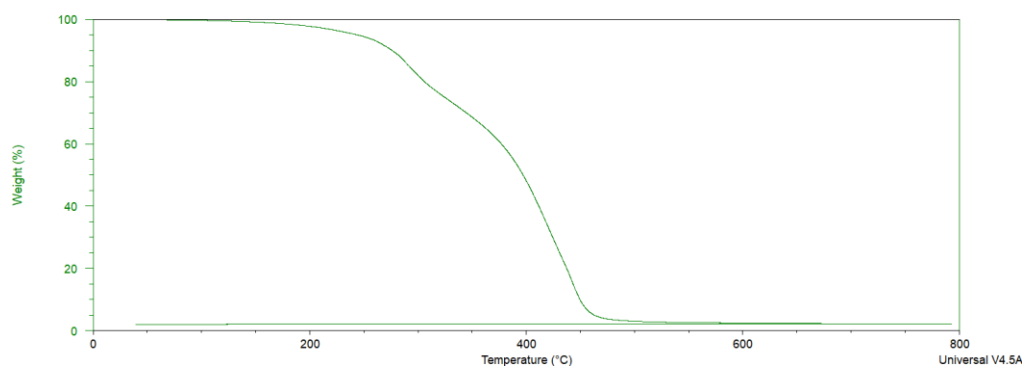


Figure S4.42: Thermal Gravimetric analysis of VT4.

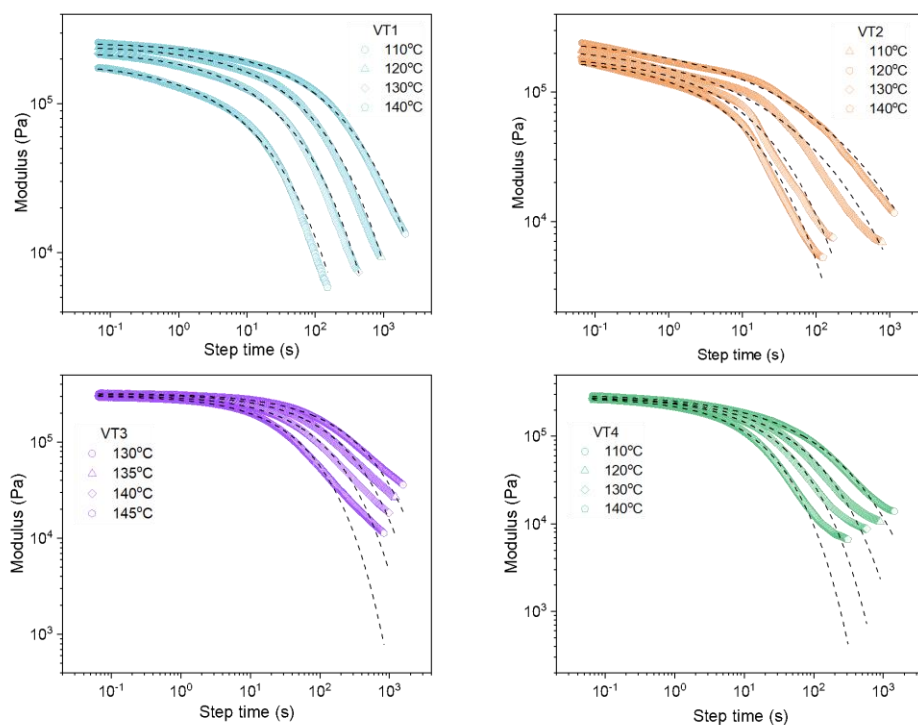


Figure S4.43: Stress relaxation measurements of network VT1, VT2, VT3, and VT4 carried out at various temperatures. The full lines correspond to fits of the data to a stretched exponential of the form $\sigma(t) = \sigma_0 e^{-\left(\frac{t}{\tau}\right)^\beta}$.

References

1. Denissen W, Rivero G, Nicolaÿ R, Leibler L, Winne JM, Du Prez FE. Vinylogous Urethane Vitrimers. *Adv Funct Mater.* 2015;25(16):2451-2457. doi:10.1002/adfm.201404553
2. Van Zee NJ, Nicolaÿ R. Vitrimers: Permanently crosslinked polymers with dynamic network topology. *Progress in Polymer Science.* 2020;104:101233. doi:10.1016/j.progpolymsci.2020.101233
3. Denissen W, Driesbeke M, Nicolaÿ R, Leibler L, Winne JM, Du Prez FE. Chemical control of the viscoelastic properties of vinylogous urethane vitrimers. *Nat Commun.* 2017;8(1):14857. doi:10.1038/ncomms14857
4. Friary RJ, Seidl V, Schwerdt JH, Cohen MP, Hou D, Nafissi M. Intramolecular transaminations of enamines: a synthesis of fused, polycyclic, N-aryl pyridones. *Tetrahedron.* 1993;49(33):7169-7178. doi:10.1016/S0040-4020(01)87196-9
5. Yang Y, Du FS, Li ZC. Thermally healable and reprocessable polymethacrylate networks based on diol-mediated metathesis of 6-membered boronic esters. *Polym Chem.* 2020;11(11):1860-1870. doi:10.1039/C9PY01546A
6. Han J, Liu T, Hao C, Zhang S, Guo B, Zhang J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules.* 2018;51(17):6789-6799. doi:10.1021/acs.macromol.8b01424
7. Delahaye M, Winne JM, Du Prez FE. Internal Catalysis in Covalent Adaptable Networks: Phthalate Monoester Transesterification As a Versatile Dynamic Cross-Linking Chemistry. *J Am Chem Soc.* 2019;141(38):15277-15287. doi:10.1021/jacs.9b07269
8. Van Lijsebetten F, Holloway JO, Winne JM, Du Prez FE. Internal catalysis for dynamic covalent chemistry applications and polymer science. *Chem Soc Rev.* 2020;49(23):8425-8438. doi:10.1039/D0CS00452A
9. Guerre M, Taplan C, Winne JM, Du Prez FE. Vitrimers: directing chemical reactivity to control material properties. *Chem Sci.* 2020;11(19):4855-4870. doi:10.1039/D0SC01069C

10. Altuna FI, Pettarin V, Williams RJJ. Self-healable polymer networks based on the cross-linking of epoxidised soybean oil by an aqueous citric acid solution. *Green Chem.* 2013;15(12):3360. doi:10.1039/c3gc41384e
11. Cromwell OR, Chung J, Guan Z. Malleable and Self-Healing Covalent Polymer Networks through Tunable Dynamic Boronic Ester Bonds. *J Am Chem Soc.* 2015;137(20):6492-6495. doi:10.1021/jacs.5b03551
12. Nishimura Y, Chung J, Muradyan H, Guan Z. Silyl Ether as a Robust and Thermally Stable Dynamic Covalent Motif for Malleable Polymer Design. *J Am Chem Soc.* 2017;139(42):14881-14884. doi:10.1021/jacs.7b08826
13. Zhang H, Majumdar S, Van Benthem RATM, Sijbesma RP, Heuts JPA. Intramolecularly Catalyzed Dynamic Polyester Networks Using Neighboring Carboxylic and Sulfonic Acid Groups. *ACS Macro Lett.* 2020;9(2):272-277. doi:10.1021/acsmacrolett.9b01023
14. Spiesschaert Y, Guerre M, De Baere I, Van Paepegem W, Winne JM, Du Prez FE. Dynamic Curing Agents for Amine-Hardened Epoxy Vitrimers with Short (Re)processing Times. *Macromolecules.* 2020;53(7):2485-2495. doi:10.1021/acs.macromol.9b02526
15. Engelen S, Wróblewska AA, De Bruycker K, et al. Sustainable design of vanillin-based vitrimers using vinylogous urethane chemistry. *Polym Chem.* 2022;13(18):2665-2673. doi:10.1039/D2PY00351A
16. Engelen S, Dolinski ND, Chen C, et al. Vinylogous Urea—Urethane Vitrimers: Accelerating and Inhibiting Network Dynamics through Hydrogen Bonding. *Angew Chem Int Ed.* Published online January 24, 2024:e202318412. doi:10.1002/anie.202318412
17. Altuna FI, Casado U, dell'Erba IE, Luna L, Hoppe CE, Williams RJJ. Epoxy vitrimers incorporating physical crosslinks produced by self-association of alkyl chains. *Polym Chem.* 2020;11(7):1337-1347. doi:10.1039/C9PY01787A
18. Li Y, Liu T, Zhang S, et al. Catalyst-free vitrimer elastomers based on a dimer acid: robust mechanical performance, adaptability and hydrothermal recyclability. *Green Chem.* 2020;22(3):870-881. doi:10.1039/C9GC04080C
19. Hamzehlou S, Ruipérez F. Computational study of the transamination reaction in vinylogous acyls: Paving the way to design vitrimers with

- controlled exchange kinetics. *Journal of Polymer Science*. 2022;60(13):1988-1999. doi:10.1002/pol.20220099
20. Gasparini G, Vitorge B, Scrimin P, Jeannerat D, Prins LJ. Real-time monitoring of a dynamic molecular system using ^1H - ^{13}C HSQC NMR spectroscopy with an optimized ^{13}C window. *Chem Commun*. 2008;(26):3034. doi:10.1039/b803074j
21. Ballester-Bayarri L, Limousin E, Fernández M, Aguirresarobe R, Ballard N. Scalable synthesis of methacrylate-based vitrimer powders by suspension polymerization. *Polym Chem*. 2023;14(14):1656-1664. doi:10.1039/D3PY00128H
22. Lessard JJ, Garcia LF, Easterling CP, et al. Catalyst-Free Vitrimers from Vinyl Polymers. *Macromolecules*. 2019;52(5):2105-2111. doi:10.1021/acs.macromol.8b02477
23. Montarnal D, Capelot M, Tournilhac F, Leibler L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science*. 2011;334(6058):965-968. doi:10.1126/science.1212648
24. Chai JD, Head-Gordon M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys Chem Chem Phys*. 2008;10(44):6615. doi:10.1039/b810189b
25. Krishnan R, Binkley JS, Seeger R, Pople JA. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *The Journal of Chemical Physics*. 1980;72(1):650-654. doi:10.1063/1.438955
26. Hehre WJ, Ditchfield R, Pople JA. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *The Journal of Chemical Physics*. 1972;56(5):2257-2261. doi:10.1063/1.1677527
27. Frisch MJ, Trucks GW, Schlegel GE, et al. Gaussian 16 Revision C.01, gaussian Inc, Wallingford CT2016.

Chapter 5

Conclusion & Perspectives

Conclusion & Perspectives

This thesis has addressed the challenges and innovations in the development of vitrimers, a new type of material that bridges the gap between thermoplastics and thermosets. Through a combination of computational modeling and experimental validation, several promising polymeric systems have been investigated. This research advances the field of sustainable materials while underscoring the critical role of fundamental understanding in designing polymers with high adaptability and self-healing capabilities.

Chapter 1 emphasized the vital role of plastics in modern society due to their versatility and cost-effectiveness. However, their extensive use has led to severe environmental challenges, particularly related to disposal and recycling. To address these issues, Covalent Adaptable Networks (CANs) have been developed. CANs feature dynamic covalent bonds that allow reshaping and self-healing while maintaining material integrity.

Vitrimers are an especially promising class of CANs, combining the strength of thermosets with the recyclability of thermoplastics. Vitrimers utilize dynamic covalent bonding that enables network rearrangement, allowing for reshaping and recycling without the need for complete depolymerization. A critical innovation in vitrimer technology is the use of internal catalysts integrated into the polymer network. Unlike external catalysts, which can leach out or lose activity over time, internal catalysts provide consistent catalytic activity, improving the efficiency of bond exchange during recycling. This approach enhances the material's recyclability and sustainability by

ensuring stable, long-term catalyst functionality. The subsequent experimental chapters further explored these catalytic strategies, aiming to optimize the recyclability and durability of advanced polymers, offering a potential solution to plastic pollution.

Chapter 2 explored the dynamic behavior of boronic ester-based vitrimers, specifically focusing on the metathesis of dioxaborinanes. The study combined computational (DFT) calculations with experimental model studies to analyze two main exchange mechanisms: direct metathesis and nucleophile-mediated exchange. DFT calculations offered insights into these mechanisms by revealing that nucleophile-assisted pathways significantly lower the activation energy for boronic ester bond exchange, a finding corroborated by subsequent experimental models. This alignment between theoretical predictions and experimental evidence highlighted how nucleophiles such as methanol and water catalyze the exchange process, thereby showing promise in enhancing the reprocessing and self-healing capabilities of these polymers.

The study then demonstrated that the relaxation times of prepared crosslinked polymers using a novel dioxaborinanes crosslinker could be effectively tuned by introducing co-monomers capable of acting as internal nucleophiles within the boronic ester network. This internal nucleophilicity promoted a faster exchange between boronic ester bonds through nucleophile-mediated mechanisms, thereby lowering the activation energy required for bond reconfiguration. Furthermore, the chapter showed that the materials could be successfully reprocessed, showcasing their durability and adaptability in real-world

applications. Reprocessing tests involved cutting vitrimer networks into pieces and thermally pressing them at 150°C under pressure, which led to the full recovery of intact materials. Importantly, mechanical properties remained stable across reprocessing cycles, indicating that the dynamic network structure supported repeated re-use without degradation.

Overall, Chapter 2 illustrated how computational and experimental synergies enable the rational design of vitrimers with robust reprocessing capabilities, offering a pathway for optimizing CAN materials with enhanced recyclability and durability. This integration of theory and experiment provides a framework for understanding and controlling dynamic behavior in boronic ester-containing networks, reinforcing their potential as sustainable alternatives in polymer science.

Chapter 3 built upon the prior investigation into boron chemistry, expanding beyond the metathesis of boronic esters to explore the potential of boron-based dynamic interactions. This chapter focused on developing a novel dynamic bonding mechanism that leverages the Lewis acidity of boron. The study specifically examined the formation of Lewis pairs between a boronic scaffold (serving as a Lewis acid) and various Lewis bases within a newly developed class of π -conjugated copolymers.

The core of this chapter was the synthesis and characterization of a π -conjugated copolymer that incorporated tricoordinate boron through a Si-B exchange reaction. The incorporation of unprotected tricoordinate

boron aimed to exploit its Lewis acidity to introduce a dynamic exchange mechanism based on Lewis pairs. The resulting silafluorene-dioctylfluorene copolymer demonstrated deep blue emission with CIE coordinates ($X = 0.15$, $Y = 0.04$) and a high quantum yield of 93.9%, making it a promising candidate for blue organic light-emitting diodes (OLEDs). Additionally, the copolymer exhibited exceptional thermal stability, with a decomposition temperature nearing 440°C.

A significant achievement of this study was the successful introduction of 9-bromo-9-borafluorene into the π -conjugated system. This is the first instance of integrating an unprotected tricoordinate boron scaffold into such a polymer matrix, thereby broadening the material's functional capabilities and paving the way for new applications. The incorporation of the boron moiety was confirmed via ^{11}B -NMR spectroscopy, which verified the structural integrity and precise placement of the tricoordinate boron within the copolymer.

To deepen the understanding of the impact of boron integration, DFT calculations were conducted to analyze the copolymer's optical properties. These computational studies provided insights into its electronic structure and highlighted the potential for developing future dynamic networks that capitalize on the Lewis acidity of tricoordinate boron. Overall, these results demonstrate that strategically incorporating two main group elements into a π -conjugated system can yield materials with versatile applications. This approach underscores how fine-tuning the structural and electronic properties of the copolymer can lead to adaptable materials suitable for advanced technological applications

Chapter 4 presented a study on vinylogous urethane-based vitrimers, emphasizing the dynamic transamination mechanisms that enable these materials' adaptability and reprocessability. A combined approach using DFT calculations and experimental combinatorial model studies enabled a deeper understanding of the relationship between molecular structure and material performance. DFT calculations provided detailed insights into the exchange reaction pathways and rate-determining steps of various amine structures, establishing foundational predictions on how structural variations and functional groups influence exchange kinetics.

The theoretical predictions were then validated through quantitative kinetic experiments using quantitative HSQC NMR, which allowed for the assessment of reaction rates across a range of amine and vinylogous urethane combinations. By systematically adjusting amine structures and analyzing their behavior in model reactions, this study confirmed the predictive accuracy of the DFT models and underscored the value of a combinatorial approach to rapidly screen and optimize dynamic networks. This integrated framework was extended to synthesized vitrimeric materials, where rheological stress-relaxation tests were conducted to observe the relaxation behavior of the polymers under stress. These tests demonstrated a strong alignment between the DFT predictions, combinatorial model findings, and actual stress relaxation properties of the materials. Each vitrimer's relaxation time could be correlated with the computed and experimentally determined kinetics, revealing how molecular-level interactions translate into macroscopic material properties. Overall, this work establishes a robust methodology

for designing vitrimers with tunable exchange dynamics by connecting computational, combinatorial, and material-level analyses. This approach not only accelerates the development of reprocessable polymers but also provides a framework for creating advanced materials with tailored stress relaxation and thermal reprocessing capabilities, paving the way for their use in high-performance, sustainable applications.

To sum up, the findings presented in this thesis represent substantial progress in the design of recyclable and adaptable polymeric materials. By combining computational and experimental methods, this work provides a framework for the rapid screening and optimization of dynamic covalent networks, minimizing the reliance on traditional trial-and-error approaches. This research lays the groundwork for further exploration of dynamic covalent bonds and functional doping in polymers, particularly in achieving a balance between durability and recyclability. Future studies could expand on these findings by investigating additional main group elements, exploring new catalyst-free dynamic chemistries, and scaling up synthesis processes for industrial applications. By focusing on sustainable material design, this thesis contributes to addressing the global plastic waste problem while advancing the functionality and environmental compatibility of next-generation polymers.

Methods

M.1 Computational Methodology

M.1.1 Introduction to Quantum Chemistry

Computational chemistry utilizes quantum mechanical principles to calculate various properties of chemical systems. This approach enables researchers to explore properties that may be experimentally inaccessible, as well as to gain deeper insights into experimental findings. By using quantum mechanical frameworks, it becomes possible to model and interpret the electronic structure, energy states, and interactions within a molecule or material system with considerable accuracy.

M.1.2 The Schrödinger Equation

The foundation of quantum mechanics in chemistry lies in the Schrödinger equation,¹ a fundamental equation describing the evolution of a quantum system's wavefunction, Ψ , under the influence of the total energy operator, or Hamiltonian, $\hat{H}$. The time-dependent Schrödinger equation, given by:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

is a partial differential equation that governs the behavior of quantum systems over time. For a closed system, where energy conservation applies, it is possible to separate the time and spatial components of the wavefunction. This results in the time-independent Schrödinger equation, represented as an eigenvalue equation:

$$\hat{H}(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R})$$

where E is the energy eigenvalue corresponding to the wavefunction $\Psi(\mathbf{r}, \mathbf{R})$ for the spatial coordinates of electrons ($\mathbf{r}$) and nuclei ($\mathbf{R}$).

For a system containing N electrons and M nuclei, the non-relativistic Hamiltonian operator encompasses various energetic contributions: the kinetic energies of both electrons ($\hat{T}_e$), and nuclei ($\hat{T}_n$), the attractive electron-nucleus potential ($\hat{V}_{ne}$), and the repulsive interactions between electrons ($\hat{V}_{ee}$) and between nuclei ($\hat{V}_{nn}$):

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}$$

Expanding each term for clarity:

$$\begin{aligned} \hat{H} = & \sum_{i=1}^N \left[\frac{-\nabla_i^2}{2} + \sum_{A=1}^M \frac{-Z_A}{|\vec{r}_i - \vec{R}_A|} \right] + \sum_{i>j}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{A=1}^M \frac{-\nabla_A^2}{2m_A} \\ & + \sum_{A>B}^M \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \end{aligned}$$

where i and j represent electron indices, and A and B denote nuclei. In this formulation, Z_A and Z_B are the nuclear charges, and m_A is the mass of nucleus A . Solving this equation exactly is only feasible for a one-electron system (such as the hydrogen atom) due to the complexity introduced by the electron-electron interaction term ($|\vec{r}_i - \vec{r}_j|$). Consequently, approximations are essential for systems with more than one electron.

M.1.3 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation² is a pivotal concept in quantum chemistry that leverages the significant mass and velocity differences between electrons and nuclei. This approximation enables the exact wavefunction

$\Psi(\mathbf{r}, \mathbf{R})$, of a molecular system to be expressed as a product of an electronic component and a nuclear component:

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi_{el}(\mathbf{r})\psi_{nuc}(\mathbf{R}).$$

Due to the vastly lower mass of electrons compared to nuclei, electronic motion occurs at speeds several orders of magnitude faster than nuclear motion. Consequently, on the timescale of electronic motion, nuclei can be approximated as stationary, and electrons are assumed to adapt instantaneously to any change in the nuclear configuration. Under this assumption, the nuclei move within a mean-field created by the electrons, and this separation allows for independent treatment of the nuclear and electronic components of the Schrödinger equation.

For electronic calculations, this approximation allows us to disregard the nuclear kinetic energy term, $(\hat{T}_n)$, and treat the nuclear repulsion term, $(\hat{V}_{nn})$, as a constant. Meanwhile, the electron-nucleus interaction, $(\hat{V}_{ne})$ depends parametrically on the fixed nuclear positions. This simplification transforms the molecular Schrödinger equation into an electronic Schrödinger equation, where the electronic wavefunction $\psi_{el}(\mathbf{r})$, depends explicitly only on the electronic coordinates. In this thesis, only the electronic Hamiltonian will be considered, following the Born-Oppenheimer approximation.

M.1.4 Basis Sets

Another key approximation in quantum chemistry is the use of a basis set, which allows an unknown function, such as an atomic orbital, to be expanded in terms of known functions. An atomic orbital (AO) can be represented as a combination of Gaussian and spherical harmonic functions:

$$\phi(\mathbf{r}) = R(r)e^{-\alpha r^2}Y_{lm_l}(\theta, \varphi)$$

where $R(\mathbf{r})$ is the radial function, α is a Gaussian decay parameter, and $Y_{lm_l}(\theta, \varphi)$ is the spherical harmonic. A molecular orbital (MO) can then be described as a linear combination of atomic orbitals (LCAO)³.

A minimal basis set, containing only one basis function per occupied atomic orbital, is termed a *single- ζ* basis set. While this minimal description is computationally efficient, it is often insufficient for accurate molecular orbital representation. The basis set can be refined by splitting it: doubling the basis functions per orbital results in a *double- ζ* quality, while further splittings create *triple- ζ* and *quadruple- ζ* basis sets, providing progressively better approximations. Additional improvements to the basis set include polarization functions, which consist of higher angular momentum functions. These are essential for accurately describing electron correlation and account for the more flexible electron distribution in molecules. For systems with a diffuse electron cloud, such as anions, diffuse functions enhance the representation of the electron density in the outer regions of the molecule. The accuracy of quantum chemical calculations depends on both the theoretical model and the quality of the basis set used. Increasing the number of basis functions improves the fidelity of molecular orbitals and, consequently, the wavefunction. Therefore, a judicious choice of basis set is crucial for achieving reliable computational results.

M.1.5 Quantum Chemical Methods

Quantum chemistry offers two principal families of methods for calculating the properties of chemical systems: (i) wavefunction-based (WF) methods and (ii) density functional theory (DFT)-based methods. Wavefunction-based methods provide a direct, albeit approximate, solution to the Schrödinger equation by constructing and manipulating the electronic wavefunction, while

density functional theory methods determine energy as a functional of electron density rather than the wavefunction.

M.1.6 Wavefunction Theory: The Hartree-Fock Method

Wavefunction-based methods aim to solve the Schrödinger equation to derive the electronic structure and energy for a system with N electrons. The expectation value of the electronic Hamiltonian can be written as:

$$E_{el} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Using the variational principle, the lowest possible energy of the system, E_{el} is obtained by varying the energy with respect to the orbitals. This process, often facilitated by Lagrange's method of undetermined multipliers, ensures that the resulting wavefunction minimizes the system's energy. If a Slater determinant is used as a trial wavefunction, the Hartree-Fock (HF) equations can be derived^{4,5} :

$$\hat{F}\Psi = \varepsilon\Psi$$

In the Hartree-Fock method, the Hamiltonian consists of a one-electron operator $\hat{h}_i$ that describes the kinetic energy of each electron i in the field of the nuclei, as well as a two-electron operator that accounts for electron-electron repulsion. The electron-electron repulsion term includes the Coulomb interaction ($\hat{J}_{ij}$) representing the classical repulsion between electrons, and the exchange interaction ($\hat{K}_{ij}$), which arises due to the antisymmetry requirement of the wavefunction.

The Hartree-Fock method is implemented through an iterative Self-Consistent Field (SCF) procedure. In this approach, an initial approximate Hamiltonian is used to solve the Schrödinger equation, generating a preliminary set of molecular orbitals. These orbitals are then used to construct a new Hamiltonian, yielding a more accurate set of molecular orbitals in each

iteration until convergence is achieved. This SCF process ultimately leads to molecular orbitals that minimize the system's energy. The Hartree-Fock energy can be expressed as:

$$E_{HF} = \sum_{i=1}^N \hat{h}_{ii} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (\hat{J}_{ij} - \hat{K}_{ij})$$

The Hartree-Fock method is the foundation for molecular orbital theory, providing a framework for more sophisticated models. It accurately describes equilibrium geometries and molecular conformations, particularly for systems without transition metals. However, it is less reliable for thermochemical predictions, especially when bond formation or cleavage occurs. This limitation stems from the method's incomplete treatment of electron correlation, which is the interaction between the motions of electrons.

To address electron correlation, various post-Hartree-Fock methods have been developed. Notable approaches include:

1. **Configuration Interaction (CI)**⁶: This method expands the wavefunction by combining ground-state and excited-state configurations, enabling a more flexible description of electronic interactions.
2. **Møller-Plesset Perturbation Theory (MP)**⁷: MP theory improves upon HF by treating electron correlation as a perturbation to the HF wavefunction. MP2, the second-order perturbation, is commonly used for accurate energy calculations.
3. **Coupled-Cluster (CC) Theory**⁸: CC theory provides a highly accurate wavefunction by incorporating single, double, and higher-order excitations through an exponential operator. This approach is highly effective for thermochemical properties and is often considered the "gold standard" in quantum chemistry.

These advanced methods extend the HF framework by introducing multiple Slater determinants, derived from permutations of electron occupancies across all molecular orbitals, to improve the description of electron correlation. Although computationally demanding, these post-Hartree-Fock methods significantly enhance accuracy in predicting reaction thermochemistry and provide a more comprehensive understanding of chemical interactions.

M.1.7 Density Functional Theory

Density Functional Theory (DFT) represents a fundamentally different approach to quantum chemistry by focusing on the electron density (ρ), rather than the many-electron wavefunction Ψ . Unlike wavefunction-based methods, which depend on the $3N$ spatial coordinates of all electrons, DFT relies only on three spatial coordinates, making it a computationally efficient method to include electron correlation.

M.1.8 The Hohenberg-Kohn Theorems

The foundation of DFT rests on two theorems formulated by Hohenberg and Kohn⁹:

1. **First Theorem:** Any observable of a stationary, non-degenerate ground state can, in principle, be exactly determined from the ground-state electron density alone. This implies that the energy and other properties of a system are unique functionals of the ground-state electron density.
2. **Second Theorem:** The exact ground-state electron density can be obtained by minimizing the energy functional for the ground state.

The first theorem establishes that the energy of the ground state, as well as other properties of a system, can be expressed solely in terms of the electron density (ρ):

$$E_0[\rho] = T[\rho] + E_{ee}[\rho] + E_{Ne}[\rho]$$

or, alternatively,

$$E_0[\rho] = F_{HK}[\rho] + E_{Ne}[\rho]$$

where $E_0[\rho]$ represents the ground-state energy as the sum of the kinetic energy $T[\rho]$, electron-electron repulsion energy ($E_{ee}[\rho]$), and nucleus-electron attraction energy ($E_{Ne}[\rho]$). Since both $T[\rho]$ and $E_{ee}[\rho]$ are complex and generally unknown, they are grouped into the Hohenberg-Kohn functional $F_{HK}[\rho]$. The second theorem provides a variational principle for $E(\rho)$, enabling the determination of the optimal electron density (ρ) by minimizing this energy functional.

Despite their foundational importance, the Hohenberg-Kohn theorems do not offer a direct approach for calculating ρ or the energy, as they lack explicit formulas for these calculations. To address this limitation, Kohn and Sham introduced a practical framework for determining the ground-state electron density by using a non-interacting reference system.¹⁰

M.1.9 The Kohn-Sham Approach

The Kohn-Sham method provides a solution by proposing a hypothetical, non-interacting system with the same electron density as the real, interacting system. The Hamiltonian for this non-interacting system is defined as:

$$\hat{H}_S = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N V_S(\mathbf{r}_i)$$

where the first term represents the kinetic energy of the electrons, and the second term, $V_S(\mathbf{r}_i)$, is an effective local potential. In this formulation, since

there is no direct electron-electron interaction, the ground-state wavefunction Ψ can be constructed from spin orbitals (φ_i), similar to the Hartree-Fock method. These orbitals are eigenfunctions of the Kohn-Sham operator ($\hat{h}^{KS}$), given by:

$$\hat{h}^{KS}(i)\varphi(i) = \varepsilon_i\varphi(i)$$

where

$$\hat{h}^{KS}(i) = -\frac{1}{2}\nabla_i^2 - V_S(i)$$

M.1.10 Reformulating the Hohenberg-Kohn Functional

To approximate the energy of a real interacting system, Kohn and Sham modified the Hohenberg-Kohn functional as follows:

$$F_{HK}[\rho] = T_S[\rho] + E_{ee}[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho]$$

In this expression, the electron-electron repulsion term $E_{ee}[\rho]$ is separated into the classical Coulomb interaction $J[\rho]$ and an exchange-correlation energy term ($E_{xc}[\rho]$). The exchange-correlation term encapsulates the non-classical components of the electron-electron interactions, including the residual kinetic energy ($T[\rho] - T_S[\rho]$) and the non-classical part of the electrostatic interactions $E_{ee}[\rho] - J[\rho]$.

M.1.11 Exchange-Correlation Potential

The exchange-correlation potential ($V_{xc}[\rho]$) is derived from the exchange-correlation energy functional $E_{xc}[\rho]$ and is crucial for achieving an accurate description of electron correlation effects in DFT calculations. It is defined as the functional derivative of $E_{xc}[\rho]$:

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

In practice, the exact form of $E_{xc}[\rho]$ is unknown, and various approximations, such as the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA), are used to model this term.

Through these approximations and the Kohn-Sham framework, DFT offers a balance between computational efficiency and accuracy, making it a widely adopted method in quantum chemistry. It provides a cost-effective yet reliable means of including electron correlation, which is particularly advantageous for larger systems where wavefunction-based methods may be computationally prohibitive.

M.1.12 Exchange-Correlation Functionals

The development of accurate exchange-correlation functionals is one of the core challenges in Density Functional Theory (DFT), as these functionals are essential for capturing inter-electronic repulsion, which includes both exchange and correlation components:

$$E_{xc} = E_x + E_c$$

M.1.13 Local Density Approximation (LDA)

The earliest approximation for the exchange-correlation energy, the Local Density Approximation (LDA), treats the electron density as a homogeneous electron gas, assuming each spatial point has a constant density. While computationally efficient, the LDA approach typically overestimates binding energies and underestimates bond lengths. LDA may be effective for systems with slowly varying electron densities but is generally insufficient for most chemical systems where electron density varies significantly.

M.1.14 Generalized Gradient Approximation (GGA)

To improve upon LDA, gradient-corrected functionals, or Generalized Gradient Approximation (GGA) functionals, were introduced. These functionals

incorporate the electron density gradient ($\nabla\rho$) to account for variations in electron density, expressed as:

$$E_{xc}^{GGA}[\rho] = \int \rho \varepsilon_{xc}^{GGA}(\rho, \nabla\rho) d\mathbf{r}$$

An example of a GGA functional is the B88 exchange functional, developed by Becke,¹¹ which includes a parameter fitted to the exact exchange energies of noble gases (He, Ne, Ar, Kr, and Xe). The LYP correlation functional,¹² proposed by Lee, Yang, and Parr, adds further accuracy with four parameters fitted to match the correlation energy of helium. The combination of B88 and LYP is widely used in the BLYP functional.¹³ Other GGA examples include the PBE¹⁴ functional and the BP86 functional, which combines B88 exchange with Perdew's correlation corrections.¹⁵

M.1.15 Meta-GGA and Hybrid Functionals

For even greater accuracy, meta-GGA functionals use higher-order derivatives of the electron density, such as the Laplacian or the local kinetic energy density. Hybrid functionals further improve on GGA by incorporating a portion of exact exchange from Hartree-Fock theory. One commonly used hybrid functional is B3LYP,^{11,12,16} which combines the Local Spin Density Approximation (LSDA), Hartree-Fock exchange, and GGA corrections:

$$E_{XC}^{B3LYP} = (1 - a)E_X^{LSDA} + aE_X^{HF} + b\Delta E_X^B + (1 - c)E_C^{LSDA} + cE_C^{LYP}$$

where the parameters $a = 0.20$, $b = 0.72$ and $c = 0.81$ were optimized based on atomization energies, ionization potentials, proton affinities, and atomic energies from the G1 test set.¹⁷ Another hybrid functional, B3PW91,¹⁸⁻²⁰ combines Becke's three-parameter functional with the PW91 correlation functional, sharing the 20% Hartree-Fock exchange.

The M06-2X functional, developed by Truhlar and Zhao,²¹ takes this approach further by incorporating 51% Hartree-Fock exchange, aiming for greater accuracy in thermochemical and non-covalent interaction calculations:

$$E_{XC}^{M06-2X} = (1 - a)E_X^{M06} + aE_X^{HF} + E_c^{M06}$$

M.1.16 Long-Range Corrected Functionals

A key limitation of conventional functionals is their inability to capture long-range electron-electron interactions accurately, as they rely solely on local quantities like electron density. Savin introduced a long-range exchange correction scheme for LDA functionals in 1996,²² which decomposes the two-electron operator $1/r_{ij}$ into short-range and long-range components using the error function (erf):

$$\frac{1}{r_{ij}} = \frac{1 - \text{erf}(\mu r_{ij})}{r_{ij}} + \frac{\text{erf}(\mu r_{ij})}{r_{ij}}$$

where μ controls the partitioning between short- and long-range parts. This method, however, was initially inapplicable to conventional GGA functionals. In 2001, Iikura, Tsuneda, Yanai, and Hirao addressed this issue with the long-range correction (LC) scheme, designed to reproduce the original GGA exchange functional when $\mu = 0$.²³ Functionals like CAM-B3LYP²⁴ and ω B97X²⁵ are examples of this approach.

M.1.17 Dispersion Corrections

Another significant limitation of semilocal and conventional hybrid functionals is their failure to correctly represent the $-C_6/R^6$ dependence of dispersion interactions, critical for van der Waals complexes and the thermodynamics of large molecules. This issue arises because dispersion energy is inherently a wavefunction-based, long-range electron correlation effect. For instance, in

Møller-Plesset perturbation theory (MP2),⁷ dispersion energy arises from Coulomb and exchange interactions in single-electron transition densities:

$$E_{disp}^{(2)} = - \sum_{ia} \sum_{jb} \frac{(ia|ja)[(ia|jb) - (ib|ja)]}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

where i, j , and a, b represent orbitals on interacting fragments A and B , $(ia|jb)$ is a two-electron integral, and ϵ denotes orbital energies.

To approximate dispersion interactions in DFT, empirical corrections have been developed, recognizing that standard functionals are accurate for short-range interactions but lack the necessary long-range behavior. Dispersion-corrected functionals, such as X3LYP²⁶, TPSS²⁷, and ω B97XD²⁸, introduce terms that smoothly transition between short- and long-range interactions, accounting for dispersion effects more accurately.

References

- (1) Schrödinger, E. *Annalen der Physik* **1926**, *81*, 109.
- (2) Born, M.; Oppenheimer, R. Zur Quantentheorie Der Molekeln. *Annalen der Physik* **1927**, *389* (20), 457–484.
<https://doi.org/10.1002/andp.19273892002>.
- (3) Eschrig, H. *Optimized LCAO Method and the Electronic Structure of Extended Systems*; 1989. <https://doi.org/10.1007/978-3-662-02562-8>.
- (4) Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. *Mathematical Proceedings of the Cambridge Philosophical Society* **1928**, *24* (1), 89–110. <https://doi.org/10.1017/S0305004100011919>.
- (5) Fock, V. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Z. Physik* **1930**, *61* (1), 126–148.
<https://doi.org/10.1007/BF01340294>.
- (6) Kutzelnigg, W. Present and Future Trends in Quantum Chemical Calculations. *Journal of Molecular Structure: THEOCHEM* **1988**, *181* (1), 33–54. [https://doi.org/10.1016/0166-1280\(88\)80028-9](https://doi.org/10.1016/0166-1280(88)80028-9).
- (7) Møller, Chr.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46* (7), 618–622.
<https://doi.org/10.1103/PhysRev.46.618>.
- (8) Bartlett Rodney, J. *Recent Advances In Coupled-Cluster Methods*, Bartlett Rodney J.; World Scientific, 1997.
- (9) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136* (3B), B864–B871.
<https://doi.org/10.1103/PhysRev.136.B864>.
- (10) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140* (4A), A1133–A1138. <https://doi.org/10.1103/PhysRev.140.A1133>.
- (11) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38* (6), 3098–3100.
<https://doi.org/10.1103/PhysRevA.38.3098>.
- (12) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37* (2), 785–789.
<https://doi.org/10.1103/PhysRevB.37.785>.

- (13) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chemical Physics Letters* **1989**, *157* (3), 200–206. [https://doi.org/10.1016/0009-2614\(89\)87234-3](https://doi.org/10.1016/0009-2614(89)87234-3).
- (14) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (15) Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. *Phys. Rev. B* **1986**, *33* (12), 8822–8824. <https://doi.org/10.1103/PhysRevB.33.8822>.
- (16) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* **1980**, *58* (8), 1200–1211. <https://doi.org/10.1139/p80-159>.
- (17) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. Gaussian-1 Theory: A General Procedure for Prediction of Molecular Energies. *J. Chem. Phys.* **1989**, *90* (10), 5622–5629. <https://doi.org/10.1063/1.456415>.
- (18) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652. <https://doi.org/10.1063/1.464913>.
- (19) *Electronic Density Functional Theory: Recent Progress and New Directions*, 1998 edition.; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Springer: New York, 1998.
- (20) Perdew, J. P. *Electronic Structure of Solids*, 1st ed.; Akademie Verlag: Berlin, 1991.
- (21) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor Chem Account* **2008**, *120* (1), 215–241. <https://doi.org/10.1007/s00214-007-0310-x>.
- (22) Seminario, J. M. *Recent Developments and Applications of Modern Density Functional Theory*; Elsevier, 1996.
- (23) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. A Long-Range Correction Scheme for Generalized-Gradient-Approximation Exchange Functionals. *J. Chem. Phys.* **2001**, *115* (8), 3540–3544. <https://doi.org/10.1063/1.1383587>.

- (24) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chemical Physics Letters* **2004**, *393* (1), 51–57. <https://doi.org/10.1016/j.cplett.2004.06.011>.
- (25) Chai, J.-D.; Head-Gordon, M. Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *J. Chem. Phys.* **2008**, *128* (8), 084106. <https://doi.org/10.1063/1.2834918>.
- (26) Xu, X.; Goddard, W. A. The X3LYP Extended Density Functional for Accurate Descriptions of Nonbond Interactions, Spin States, and Thermochemical Properties. *PNAS* **2004**, *101* (9), 2673–2677. <https://doi.org/10.1073/pnas.0308730100>.
- (27) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative Assessment of a New Nonempirical Density Functional: Molecules and Hydrogen-Bonded Complexes. *J. Chem. Phys.* **2003**, *119* (23), 12129–12137. <https://doi.org/10.1063/1.1626543>.
- (28) Chai, J.-D.; Head-Gordon, M. Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *Physical Chemistry Chemical Physics* **2008**, *10* (44), 6615–6620. <https://doi.org/10.1039/B810189B>.

