lengths are expected to be 56 and 27 nm for PAC-1 and PAC-2, respectively, which correspond approximately to the actual average PAC lengths adsorbed in the presence of alkanes. Therefore, we suggest that the length distribution of PACs in solution is preserved upon co-adsorption of PAC and alkanes. Apparently, PACs and alkanes co-assemble at the interface without interfacial reorganization.

In summary, almost perfectly straight and epitaxially oriented chains of metallosupramolecular coordination-polyelectrolyte–amphiphile complexes formed from rigid ditopic metal ion receptors are self-assembled on the basal plane of graphite by using long chain alkanes as an orienting template layer. Through a sequence of molecular recognition steps comprising metal ion coordination, electrostatic interactions, and amphiphile self-assembly the adsorption of nanoscopic assemblies can be performed at an interface in a predictable manner. Controlling the correlation of position and orientation is of paramount importance for encoding new properties and functions. On-going research in our laboratories indicates that this approach is of general utility. The modularity of this approach provides an entry to encode the value-adding physicochemical properties of metallosupramolecular devices into nanoscopic architectures that can be addressed and manipulated individually by scanning probe techniques.

**Experimental Section**

Ligands 1, 2, and 3 were prepared according to literature procedures. The assembly of MEPE and PAC was carried out according to previously published procedures. Alkanes (C10H22, C12H26, C14H30, Aldrich) were used as received. Solutions of neat PACs (1.3·10⁻³ g·L⁻¹) or mixtures of PAC (1.3·10⁻³ g·L⁻¹) with C12H26, C14H30, C16H34 (1.3·10⁻² g·L⁻¹) were spin-coated onto the basal plane of highly oriented pyrolytic graphite (HOPG, Advanced Ceramics Co., USA, quality ZYH at 40 rps). The coated graphite samples were dried for 10 min at 40°C before SFM investigations were carried out with a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in the tapping mode. An E-scanner over a range of scan lengths from 5 to 0.3 nm, and commercial Si cantilevers (length 125 μm and width 30 μm) with spring constants between 17 and 64 N·m⁻¹ were used.

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**Communications**


[(C6H16N2)[Cr(HPO3)F3]: The First Organically Templated Fluorochromium(III) Phosphite]**

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In recent years the search for new open-framework materials with transition metal elements has become the focus of much interest due to the potential application of these materials as absorbents, ion exchangers, solid-state electrolytes, and catalysts in heterogeneous catalysis. Such applications are not possible with main group systems of the periodical table, but examples dealing with chromium have not been reported. The pattern of behavior of these kinds of compounds is underpinned by the strength of the P–O

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bond, which is broadly comparable with that of Si–O and Al–O bonds. Therefore, the relative stabilities within this family of M-P-O materials are probably determined by the M–O bond strengths. However, less work has been carried out on the anionic part of the inorganic network. The possibility of incorporating the pyramidal (HPO₃)²⁻ hydrogen phosphite group into extended structures templated by inorganic alkaline earth cations was explored a few years ago.[3] Recently we prepared several phosphite compounds templated by alkylamine molecules,[4] which incorporate 3d transition metal cations.

At a first glance it appears that the Cr³⁺-P-O system would surely show excellent kinetic and thermodynamic stability, given the large ligand field stabilization energy of the octahedrally coordinated Cr³⁺ cation. However, the particular behavior of Cr³⁺ in solution, with many condensation steps between the octahedra, can make the attainment of Cr³⁺ phosphate systems difficult.[5] Recently, a chromium(II) dicarboxylate compound exhibiting a microporous structure was formed.[6] To date, neither inorganic–organic hybrid phosphate nor phosphite materials containing the Cr³⁺ cation have been reported. Here we describe the synthesis and crystal structure of (C₂H₈N₂)[Cr(HPO₃)F₃], the first organically templated M-P-O compound containing Cr³⁺.

The reflectance diffuse spectrum of (C₂H₈N₂)[Cr(HPO₃)F₃] is characteristic of Cr³⁺ with octahedral coordination.[7] The values of the Dq and Racah parameters are Dq = 1535 cm⁻¹, B = 720 cm⁻¹, and C = 3280 cm⁻¹. The B parameter is approximately 75% of that corresponding to the Cr³⁺ ion (918 cm⁻¹), which indicates the existence of significant covalent character in the Cr-O bonds.

The molar magnetic susceptibility χₐ increases with decreasing temperature in the range studied (Figure 3). The thermal evolution of χₐ shows the Curie–Weiss law at temperatures above 10 K, with Cₐ = 1.88 cm³ K mol⁻¹ and θ = −5.4 K. The value for χₐT decreases from 1.84 cm³ K mol⁻¹ at 300 K to 0.88 cm³ K mol⁻¹ at 5.0 K, indicating the existence of antiferromagnetic interactions.

**Experimental Section**

(C₂H₈N₂)[Cr(HPO₃)F₃]: A mixture of Cr(NO₃)₃·9H₂O (1.00 g, 2.51 mmol), H₃PO₃ (1.23 g, 15.00 mmol), HF (1.0 mL, 27.59 mmol), and ethylenediamine (up to pH 2.0) in 20 mL of water/ethanol (1/1) was stirred until homogeneous, and sealed in a PTFE-lined (PTFE = poly(tetrafluoroethylene-
measured reflections (2.70 Å).

Elemental analysis was calculated for C₂H₁₁CrF₃N₂O₃P: C 9.5, H 4.3, N 11.1, P 12.2, Cr 20.5, F 22.5; found: C 9.3, H 4.1, N 10.8, P 12.0, Cr 20.1, F 22.0. The IR spectrum does not show any bands above 3500 cm⁻¹, in accordance with the absence of (OH) groups. A density of 2.111(1) g·cm⁻³ was measured by CHCl₃/CH₂Cl₂.

Physical measurements: The diffuse reflectance spectrum was recorded at room temperature on a Cary 2415 spectrometer from 210–2000 nm. Magnetic measurements on powdered samples were performed at temperatures between 5.0–300 K, using a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field was 1.703 mm, and the data were collected on a BRUKER SMART-APEX CCD automated diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, Ψ = 100 K). Of 4588 measured reflections, 2.70° ≤ 2θ ≤ 28.45°, 1176 were independent (Rint = 0.0521) and 1100 observed (I > 2σ(I)). An absorption correction based on symmetry-equivalent reflections was applied using SADABS. The structure was solved by direct methods (SHELXS 97) and refined by the full-matrix least-squares method based on F², using the SHELXL 97 computer program belonging to the WINGX V1.63.02 software package.

All non-hydrogen atoms were assigned anisotropic thermal parameters. The atomic coordinates of the hydrogen atoms of the ethylenediammonium cations were geometrically calculated for C for 5d, and then the mixture was slowly cooled to room temperature. The pH value did not show any appreciable change during the hydrothermal reaction. Small, well-formed, green single crystals were formed. Elemental analysis calculated for C₂H₁₁CrF₃N₂O₃P: C 9.5, H 4.3, N 11.1, P 12.2, Cr 20.5, F 22.5; found: C 9.3, H 4.1, N 10.8, P 12.0, Cr 20.1, F 22.0. The IR spectrum does not show any bands above 3500 cm⁻¹, in accordance with the absence of (OH) groups. A density of 2.111(1) g·cm⁻³ was measured by CHCl₃/CH₂Cl₂.

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All non-hydrogen atoms were assigned anisotropic thermal parameters. The atomic coordinates of the hydrogen atoms of the phosphite anions were calculated from difference Fourier maps, the structure was solved by direct methods (SHELXS 97) and refined by the full-matrix least-squares method based on F², using the SHELXL 97 program belonging to the WINGX V1.63.02 software package.

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