

Manipulation of Ordered Nanostructures of Protonated Polyoxometalate through Covalently Bonded Modification

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Dedicated to Professor Gerhard Wegner on the occasion of his 70th birthday

Polyoxometalates (POMs) are a unique class of metal–oxygen clusters (metal = Mo^{VI}, W^{VI}, V^{IV,V}, etc.) with an unmatched range of structural architectures and attractive functionalities that give rise to a variety of applications in diverse fields, such as analytical chemistry, catalysis, materials science, and medicine.^[1] Nevertheless, the relatively poor compatibility of POMs with other materials and their relatively poor processability as inorganic crystalline materials hinder the further engineering of conventional POMs into novel materials with ordered structures to optimize their specified functionalities. In previous decades, therefore, much effort has been directed towards modification through covalent linkages of organic motifs onto POMs.^[2] It has been demonstrated that organically modified POM-based hybrid materials not only combine the advantages of organic molecules and inorganic clusters, but also result in a significant synergistic effect through the construction of POM-containing nanostructures.^[3] Therefore, exploration of new covalently modified hybrids has great significance with some potentially attractive functions, such as proton conduction, electron transfer, and framework materials.

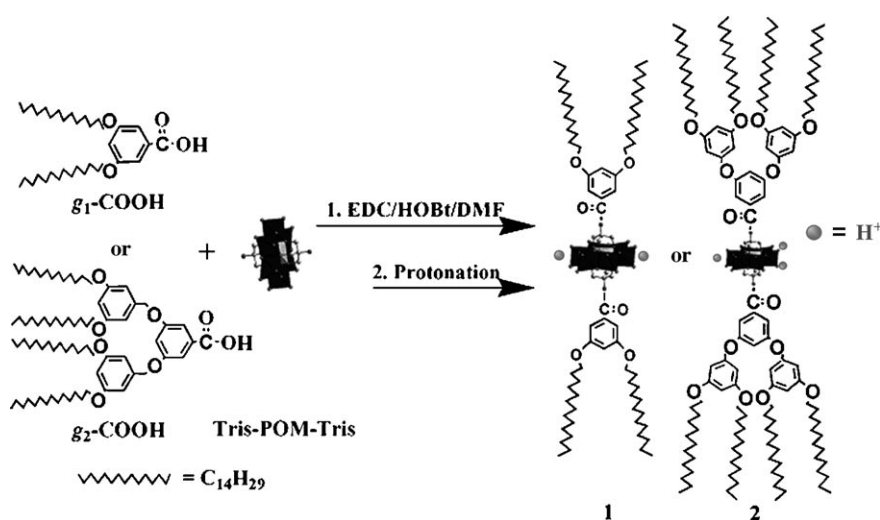
To further facilitate POM applications in hybrid materials, it is important to attach appropriate organic motifs to POMs to constitute and manipulate POM-containing ordered nanostructures in the solid state. Dendrimers and monodendrons are a class of the most influential motifs widely employed in the construction of diverse nanostructures that are

able to be programmatically manipulated by controlling their unique molecular architectures.^[4] In past decades, some dendrons have been employed in the fabrication of some POM-containing hybrids with diverse nanostructures.^[5] The significance of these studies is to demonstrate the correlation between supramolecular structures and properties. However, so far there are only two examples of covalently connected dendron–POM hybrids.^[6] Herein, we report the novel design and synthesis of a new type of dendron–POM–dendron hybrid in which the POMs are directly covalently linked with two low-generation dendrons. By controlling molecular structure of the hybrids by linking different generation dendrons to the POMs, we can construct and manipulate highly ordered layer or cylinder structures that contain the protonated POMs in bulk samples.

Of the available POM clusters, the distinctive tetrabutylammonium (TBA) salt of the Mn-Anderson POM anion {MnMo₆O₁₈[(OCH₂)₃CNH₂]₂}³⁻ (Tris-POM-Tris)^[7] was selected as the starting inorganic building block. Importantly, the amine groups on the both sides of the cluster can be used for further organic modification. Meanwhile, the first- and second-generation dendrons of poly(benzyl ether) (PBE; *g*₁-COOH and *g*₂-COOH in Scheme 1), which contain a carboxyl group at their focal point and two or four 14-carbon alkyl groups on the periphery, were selected as the organic building blocks because their different shapes allow self-organization into diverse ordered structures.^[8] To create the target hybrid molecules, the dendrons were covalently linked to Tris-POM-Tris by amidation between amine and carboxyl groups. The reaction was performed at room temperature for two weeks in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl)/1-hydroxybenzotriazole (HOBt) in *N,N*-dimethylformamide (DMF).^[9] After careful purification by repeated precipitation, newly formed hybrids *g*₁-PBE-TBA₃POM-*g*₁-PBE and *g*₂-PBE-TBA₃POM-*g*₂-PBE were immediately treated by exchanging TBA for protons in DMF^[6a,10] to finally give

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Scheme 1. Synthetic routes and chemical structures of **1** (g_1 -PBE-TBAH₂POM- g_1 -PBE) and **2** (g_2 -PBE-H₃POM- g_2 -PBE).

g_1 -PBE-TBAH₂POM- g_1 -PBE (compound **1**) and g_2 -PBE-H₃POM- g_2 -PBE (compound **2**). Therefore, by forming covalent amide bonds and cation exchange from TBAs to protons we have successfully synthesized the novel dendron-POM-dendron hybrid molecules (**1** and **2**), in which the POMs were covalently modified by dendrons; moreover, the functionalized POMs were neutralized by two protons and one TBA for **1** or three protons for **2**. This is an interesting class of POM-containing hybrids with a combination of direct covalent modification and electrostatic interactions. Note that the protonated POMs in the hybrids are known for their acidic properties due to the presence of the protons, and the increase in proton number may greatly improve the proton conductivity of the hybrids.^[11] Scheme 1 summarizes the synthetic approach and chemical structures of the two hybrid molecules.

¹H NMR spectroscopy, FT-IR spectroscopy, ESI-MS, and EDX have been employed for a full characterization of the hybrids (see Figures S3–S20 in the Supporting Information for details). After the amidation reaction, the N–H stretching band (Figure 1A), C=O stretching band (Figure 1B), and C–N stretching band (Figure 1C) of the hybrids all have obvious shifts compared with the original materials. The FT-IR spectra in Figure 2D highlight the important characteristic bands at $\tilde{\nu}$ = 940, 923, 904, 666, and 561 cm⁻¹ for the Mn-Anderson POM clusters before and after amidation (see dashed lines).^[6,2c] These FT-IR spectra clearly demonstrate the formation of OC–NH linkages between the amine groups in Tris-POM-Tris and the carboxyl groups in the dendrons. The ESI-MS spectra of compounds **1** (Figure 1E) and **2** (Figure 1F) show signals centered at m/z 1107 and 1162, respectively. The signal of **1** can be assigned to cluster anion $[M-3\text{TBA}+\text{H}]^{2+}$ ($[\text{C}_{78}\text{H}_{137}\text{MnMo}_6\text{N}_2\text{O}_{30}]^{2-}$, calcd m/z : 1107), whereas the signal of **2** was assigned as $[M-3\text{H}]^{3-}$ ($[\text{C}_{162}\text{H}_{272}\text{MnMo}_6\text{N}_2\text{O}_{38}]^{3-}$, calcd m/z : 1162). These results combined with the ¹H NMR spectroscopy data provide de-

finite proof for the successful covalent attachment of the PBE dendrons onto Tris-POM-Tris clusters, the protonation of the hybrids and the preservation of the structural integrity of the POM cluster during the process. Furthermore, the ESI-MS spectra in the range of m/z 400 to 4000 provide evidence to indicate the purity of the two compounds (see Figures S11 and S13 in the Supporting Information).

The ordered supramolecular structures in the solid samples of the two hybrids were mainly studied by means of small-angle X-ray scattering (SAXS).

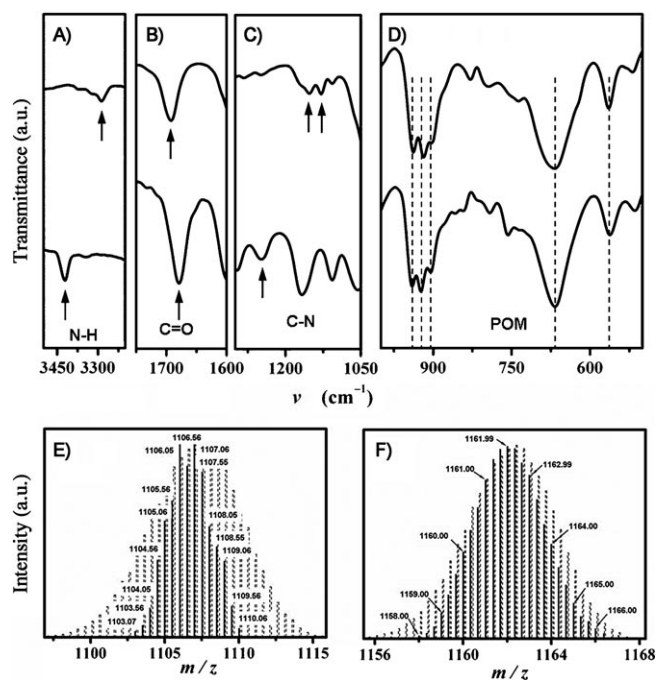


Figure 1. A–D) FT-IR and E,F) ESI-MS spectra demonstrating the successful preparation of **1** and **2**. A) N–H stretching band shift; top: **1**, bottom: Tris-POM-Tris cluster. B) C=O stretching band shift; top: **1**, bottom: g_1 dendron. C) C–N stretching band shift; top: **1**, bottom: Tris-POM-Tris cluster. D) Tris-POM-Tris characteristic peaks; top: **1**, bottom: Tris-POM-Tris cluster. In the ESI-MS spectra the black lines show the actual spectra and the dashed bar graphs are the predicted envelopes.

Figure 2 shows the plots of logarithmic scattering intensity ($\ln I$) versus scattering vector (q ; $q = 4\pi \sin\theta/\lambda$, in which 2θ is the scattering angle and $\lambda = 0.154$ nm is the wavelength of the radiation). The SAXS data provide evidence to show ordered self-assembled hybrid structures.^[12] In Figure 2A, we can clearly see two scattering peaks, indicated by the arrows, at $q_1 = 1.54$ nm⁻¹ and $q_2 = 3.13$ nm⁻¹, respectively, for **1**. The

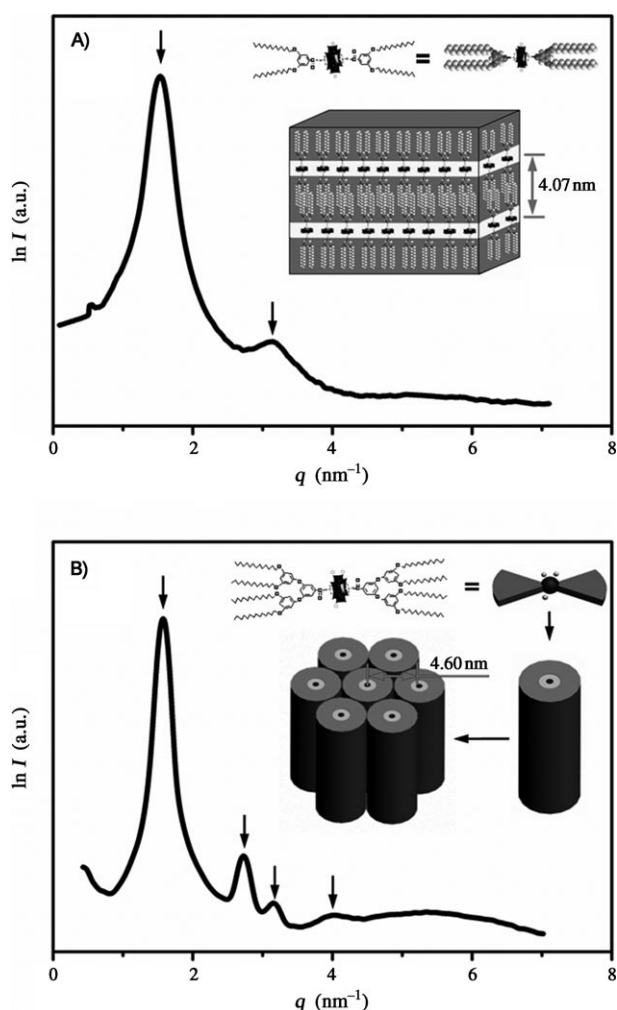


Figure 2. SAXS diffractograms of A) **1** and B) **2**. Insets: The suggested layer and hexagonal-packed cylinder structures.

ratio of $q_1/q_2=1:2$ and the first peak position at $q_1=1.54\text{ nm}^{-1}$ suggests a layer structure with a long period of 4.08 nm. Figure 2B shows the SAXS data of **2**. Four scattering peaks are indicated at $q_1=1.58\text{ nm}^{-1}$, $q_2=2.72\text{ nm}^{-1}$, $q_3=3.16\text{ nm}^{-1}$, and $q_4=3.99\text{ nm}^{-1}$, respectively. Clearly, the ratio of $q_1/q_2/q_3/q_4=1:\sqrt{3}:2:\sqrt{7}$ is clear-cut evidence for the formation of a well-organized hexagonal-packed cylinder structure with an intercolumnar distance of $d=4\pi/\sqrt{3}q_1=4.60\text{ nm}$. It is worth noting that the supramolecular structures of the protonated dendron-POM-dendron hybrids (**1** and **2**) are quite different from the complete TBA-encapsulated hybrids (g_1 -PBE-TBA₃POM- g_1 -PBE and g_2 -PBE-TBA₃POM- g_2 -PBE), which have also been carefully investigated (see Figures S21–S23 in the Supporting Information for details). This difference reflects the effect of protonated POM clusters on the supramolecular nanostructures.

Herein we used the ChemDraw software (MM2 force field) to carry out a simple estimation of the sizes of the two dendrons and the Diamond software to calculate the POM diameter from the reported crystallographic data.^[13] The results are shown in Figure S26 in the Supporting Information.

The POM diameter (about 0.75 nm) is similar to the width of the g_1 -dendron molecule but smaller than that of the g_2 -dendron molecule. The differences between the crystal structure of pristine Tris-POM-Tris^[7] and the supramolecular structures of the TBA-encapsulated or protonated dendron-POM-dendron hybrids indicate that the dendrons play an important role in manipulating the nanoassembly of the hybrid molecules. Nevertheless, the hydrophilic protonated POM clusters will greatly affect the ability of the hybrid molecules to self-assemble into ordered nanostructures, which has been demonstrated by the obvious differences between the supramolecular structures of TBA-encapsulated and protonated hybrids. The insets in Figure 2 present the ideal supramolecular structures of the two hybrid compounds, suggested after consideration of the molecular structures of the hybrids. For compound **1**, the layer structure is composed of alternating protonated POM layers and organic layers, whereas in **2** the highly ordered protonated POM cylinders are surrounded by organic layers of dendrons. The interesting regular structures have long-range order in the solid state and this kind of highly ordered supramolecular structure is relatively rare in bulk samples of POM-based organic–inorganic hybrids. Most importantly, the ordered POM layers or cylinders are protonated, so the compounds could be employed as solid proton conductors.

In summary, we have successfully designed and synthesized novel dendron-POM-dendron hybrids in which first- and second-generation dendrons have been directly covalently bonded to an organically modified Mn-Anderson POM. Exchanging the TBA with protons results in the formation of new POM-containing nanoassemblies in which the POMs are covalently functionalized by dendrons and partially or completely enclosed by protons. These hybrids can self-assemble into highly ordered layers or hexagonally packed cylinders in the bulk sample. The most important finding is that we have actually obtained one-dimensional protonated POM cylinders or two-dimensional protonated POM layers in an organic matrix by manipulating the molecular shape of the dendrons. This investigation could open a new avenue for the future fabrication of novel solid proton conductors with highly ordered structures.

Experimental Section

Compound 1 (g_1 -PBE-TBAH₂POM- g_1 -PBE): The first-generation dendron (0.35 g, 0.64 mmol) and Tris-POM-Tris (0.60 g, 0.32 mmol) were dissolved in DMF (10 mL) and CH₂Cl₂ (5 mL). EDC·HCl (0.32 g, 1.89 mmol) and HOBt (0.23 g, 1.89 mmol) were added and the reaction was kept at 40 °C for 14 d. A white precipitate was filtered off and the filtrate was evaporated. The orange product was dissolved in DMF (5 mL) and added dropwise to H₂O (100 mL). Collection of the light orange solid afforded pure g_1 -PBE-TBA₃POM- g_1 -PBE (yield: 353 mg, 0.120 mmol, 38%). The powder (150 mg, 0.051 mmol) was dissolved in DMF (15 mL) and stirred for 48 h with cation-exchange resin (300 mL; Amberlite IR120H). The resin was then filtered off and the solvent was dried under vacuum to give a yellow-orange solid (yield: 105 mg, 0.043 mmol, 85%). ¹H NMR (400 MHz, [D₆]DMSO): $\delta=0.86$ (t, $J=6.4\text{ Hz}$, 12H; CH₃), 0.94 (t, $J=7.2\text{ Hz}$, 12H; TBA), 1.25 (m, 88H; CH₂+

TBA), 1.41 (m, 8H; CH₂), 1.58 (m, 8H; TBA), 1.70 (m, 8H; CH₂), 3.17 (m, 8H; TBA), 3.99 (t, *J* = 6.6 Hz, 8H; CH₂), 6.52 (s, 2H; CH), 6.90 ppm (s, 4H; CH); FT-IR (KBr pellet): $\tilde{\nu}$ = 3421 (m), 2956 (s), 2925 (s), 2853 (s), 1679 (s), 1592(s), 1508 (s), 1469 (s), 1344 (m), 1328 (m), 1297 (m), 1248 (w), 1167 (m), 1106 (m), 1055 (m), 1033 (m), 940 (s), 923 (s), 904 (m), 667 (s), 561 cm⁻¹ (w); ESI-MS (eV): *m/z* calcd for [C₇₈H₁₃₇MnMo₆N₂O₃₀]²⁺: 1107 [M-TBA-H]²⁺; found: 1107.

Compound 2 (g₂-PBE-H₃POM-g₂-PBE): The synthesis route for g₂-PBE-TBA₃POM-g₂-PBE is similar to that of g₁-PBE-TBA₃POM-g₁-PBE (yield: 485 mg, 0.114 mmol, 36%). The protonation process of compound **2** is similar to that of **1** (yield: 104 mg, 0.030 mmol, 84%). ¹H NMR (400 MHz, [D₆]DMSO): δ = 0.84 (t, *J* = 7.2 Hz, 24H; CH₃), 1.23 (m, 196H; CH₂), 1.67 (m, 8H; CH₂), 3.92 (t, *J* = 6.6 Hz, 16H; CH₂), 5.03 (s, 8H; CH₂), 6.37 (s, 4H; CH), 6.57 (s, 8H; CH), 6.64 (s, 2H; CH), 6.69 ppm (s, 4H; CH); FT-IR (KBr pellet): $\tilde{\nu}$ = 3340 (m), 2922 (s), 2852 (s), 1656 (m), 1597 (s), 1527 (m), 1460 (s), 1372 (m), 1344 (m), 1298 (m), 1260 (w), 1164 (s), 1101 (w), 1051 (m), 947 (m), 927 (m), 904 (m), 669 (s), 569 cm⁻¹ (w). ESI-MS (eV): *m/z* calcd for [C₁₆₂H₂₇₂MnMo₆N₂O₃₈]³⁺: 1162 [M-3H]³⁺; found: 1162.

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