perfluorinated additive OFN, as well as evidence from fluorescence measurements, show that the supramolecular synthon pyrene–OFN can be used for the association of PEGs in aqueous solution.

Experimental Section

Detailed information on synthesis and characterization is published as Supporting Information.

3–4b: Poly(ethylene glycol) (4 mmol) was melted in a flask and stirred under high vacuum. Toluene (100 mL) and **1** or **2** (12 mmol) were added to the polymer and the mixture heated until a clear solution was obtained. Pyridine (1 mL) was added slowly dropwise to the solution followed by stirring at 80 °C for 12 h. The reaction mixture was cooled to RT, the precipitated pyridinium hydrochloride removed by filtration through Celite (Aldrich) and the toluene solution added dropwise to diethyl ether (1 L). The polymer precipitate was collected by filtration, dried under high vacuum, redissolved in a small amount of dichloromethane and reprecipitated into diethyl ether. After recovering the product by filtration the polymer was dried under high vacuum for 24 h.

General procedure for the preparation of gels: **4b** (1 equiv) was melted at approximately 60 °C and OFN (2 equiv) dissolved in the melt. The melt was cooled to RT where it solidified. A mixture of deionized water and the desired amount of the solid mixture were sealed in a glass vial and heated in a steam bath under stirring for about 10 min until a homogeneous mixture was obtained. Upon cooling to RT a clear yellow gel or viscous liquid was formed.

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Hybrid Molecular Dumbbells: Bridging Polyoxometalate Clusters with an Organic π-Conjugated Rod**

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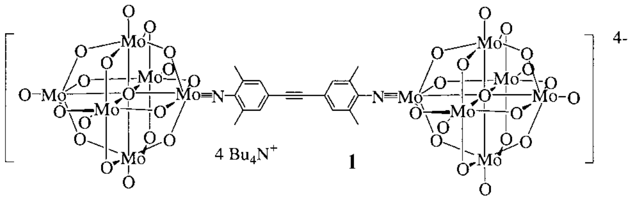
We report the facile synthesis of novel hybrid molecular dumbbells in which two polyoxometalate (POM) clusters are covalently bridged by a rigid, π-conjugated organic rod of controllable length. Hybrid materials based on covalently linked POMs and organic species have been extensively studied in recent years.[1–3] The motivation lies not only in the combinations of "value-adding properties",[4] but also in introducing possible synergistic effects. Among the many organic derivatives of POMs, organoimido derivatives have attracted particular interest because the organic π electrons may extend their conjugation to the inorganic framework and thus dramatically modify the redox properties of the cluster.[4, 5] Moreover, organoimido derivatives of POMs with a remote functionality may be utilized to construct covalently linked POM networks. Here we show that functionalized POM clusters can indeed be utilized to conveniently and efficiently construct POM networks.[3a] Specifically, we report the synthesis of two novel hybrid dumbbells **1** and **2**, in which two POM cages are linked through an extended π-conjugated organic bridge.[5c, 6]



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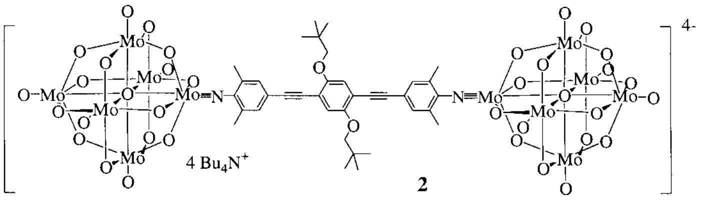

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The hybrid dumbbells were synthesized by the Pd-catalyzed Sonogashira coupling reaction.[7,8] As shown in Scheme 1, direct coupling of the iodo-functionalized hexamolybdate

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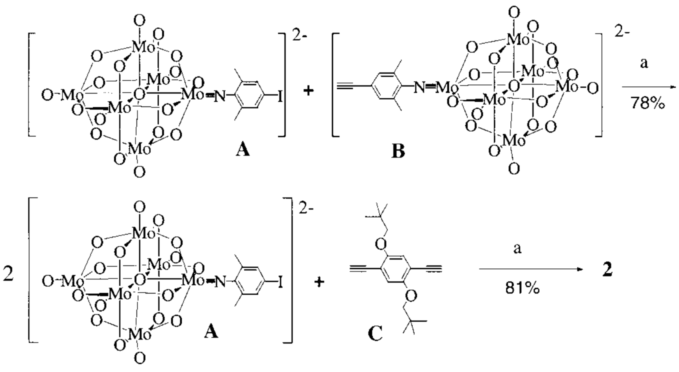

Scheme 1. Syntheses of hybrid molecular dumbbells. The countercation is tetrabutylammonium. a) $[PdCl_2(PPh_3)_2]$, CuI, K_2CO_3, Et_3N, CH_3CN, RT.

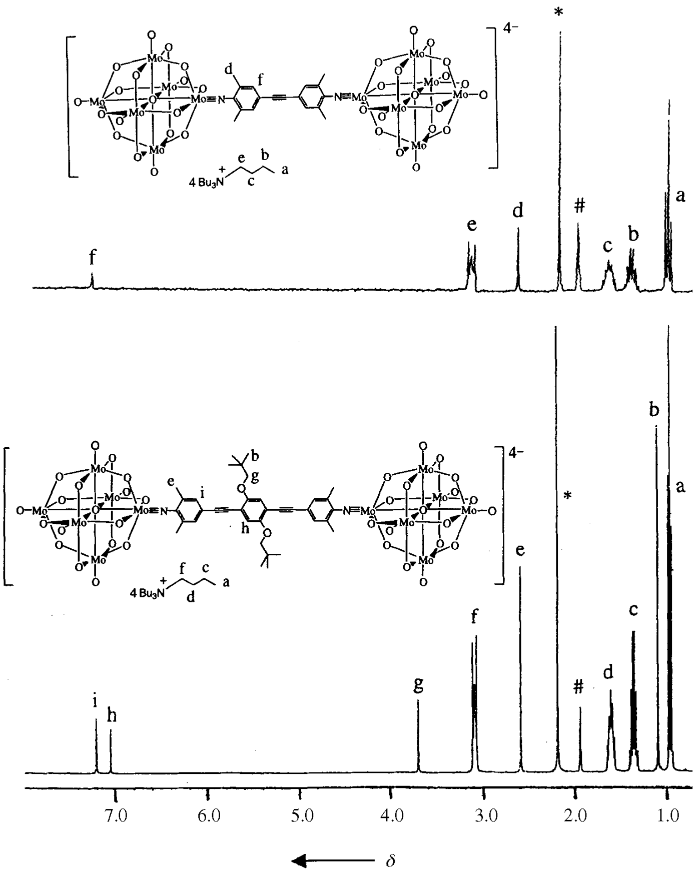

Figure 1. ^1H NMR spectra of **1** and **2**. The peaks marked with * and # correspond to the protons of acetone and acetonitrile, respectively.

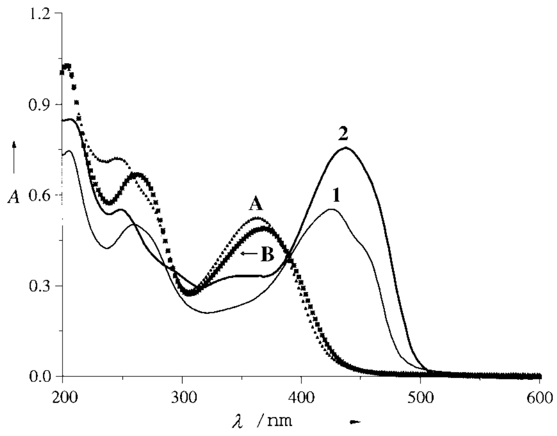

Figure 2. UV/Vis absorption spectra of **1**, **2**, **A**, and **B** in acetronitrile.

anion **A** and the ethynyl-substituted analogue **B**, both synthesized by using an approach developed in our laboratory,[9] gave hybrid **1** in greater than 78% yield of isolated, pure, crystalline product. Hybrid **2**, which has a longer bridge, was prepared by coupling of 2,5-bis(2,2-dimethylpropoxy)-1,4-diethynylbenzene and 2 equiv of **A**. Both reactions proceeded smoothly at room temperature and were completed in less than one hour. Analytically pure products can be obtained by simple recrystallization.

Hybrid **2** shows excellent solubility in common organic solvents such as acetone, acetonitrile, dichloromethane, and chloroform, but hybrid **1** is only slightly soluble in these solvents. Their ^1H NMR spectra (in CD_3CN) are shown in Figure 1. The spectrum of **1** is nearly identical to that of **B** except for the absence of the signal for the ethynyl proton at $\delta = 3.65$. The signals for the aromatic and methyl protons appear as singlets at $\delta = 7.22$ and 2.59, respectively. The remaining peaks correspond to the protons of the tetrabutylammonium cation. The spectrum of **2** has, in addition to the peaks found in **1**, three additional signals at $\delta = 7.06$, 3.71, and 1.09. These three singlets correspond to the aromatic protons on the central phenyl ring, the methylene protons linked to the oxygen atom, and the benzyl methyl protons, respectively. Both spectra show clearly resolved signals, all of which can be unambiguously assigned (see Figure 1 for complete assignment).

The electronic properties of the hybrid dumbbells were studied by UV/Vis absorption and fluorescence measurements. As shown in Figure 2, the lowest energy electronic transition exhibits a significant bathochromic shift on going from **A** (362 nm) and **B** (368 nm) to **1** (426 nm) and **2** (438 nm), and this indicates that the Mo–N π electrons are delocalized over the organic conjugated π system. In other words, there is strong electronic interaction between the metal–oxygen cluster and the organic conjugated segment. Static fluorescence studies show that hybrids **1** and **2** show no fluorescence under excitation from 200 to 500 nm. Since oligo(phenylene ethynylene)s are strongly fluorescent molecules,[10] the hexamolybdate cluster clearly acts as a fluorescence quencher, presumably by accepting the excited electrons.

The molecular structure of **1** was determined by single-crystal X-ray diffraction.[11] Compound **1** crystallizes in the monoclinic space group $P2_1/c$. Each cluster anion sits on a crystallographic center of symmetry, so that only one half of an anion is included in the asymmetric unit. As expected, the anion of **1** (Figure 3) is indeed made up of two terminally substituted imidohexamolybdate cages bridged by a *para*-disubstituted, conjugated, rodlike aromatic system. This cluster anion has crystallographically imposed ideal C_i symmetry with the inversion center located at the middle of the C≡C bond. As a result of the slight bending of the Mo-N-C bonds (172.8° bond angle), the hybrid dumbbell adopts a flattened S-shape. The slight bending of the C–C≡C bonds results in a minor vertical displacement of the two parallel

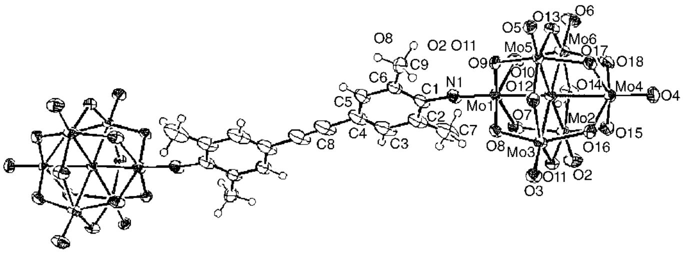

Figure 3. ORTEP plot of the anion of **1** (50% probability thermal ellipsoids for non-hydrogen atoms) showing the atom-labeling scheme for the asymmetric unit. Selected bond lengths [Å] and angles [°]: C1-N1 1.381(4), Mo1-N1 1.744(3), Mo1-O1 2.211(2), Mo2-O2 1.692(3), Mo2-O1 2.330(2), Mo3-O3 1.689(2), Mo3-O1 2.327(2), Mo4-O4 1.687(3), Mo4-O1 2.359(2), Mo5-O5 1.694(2), Mo5-O1 2.331(2), Mo6-O6 1.686(3), Mo6-O14 2.029(3), Mo6-O1 2.350(2); C1-N1-Mo1 172.8(3), N1-Mo1-O7 100.51(14), N1-Mo1-O10 102.87(13), N1-Mo1-O9 103.11(13), N1-Mo1-O8 101.02(12), N1-Mo1-O1 178.28(12).

phenyl rings. The hexamolybdate cages in **1** show features typical of other arylimido derivatives:[5] the Mo≡N bond has substantial triple bond character, as evidenced by its short bond length and near linear Mo-N-C bond angle; the central oxygen atom inside the cluster cage is drawn closer to the imido-bearing Mo atom; the equatorial Mo_4O_4 belt perpendicular to the long axis of the molecule shows regular short–long bond length alternation. Careful comparison of the bond lengths of **1** with those of **A** and **B** reveals some notable differences. In **1**, the bond between the central oxygen atom and the imido-bearing Mo atom and the N–C bond are shorter, while the Mo≡N bond is longer than the corresponding bonds in **A** and **B**. These results indicate stronger π-electron delocalization among the molecular axes, which makes the bond-length alternation less pronounced.

In conclusion, we have demonstrated that functionalized organoimido derivatives of polyoxometalates can be utilized to construct covalently linked POM hybrids. The modular building block approach introduces the advantages of versatility, flexibility, and controllability of organic reactions into the synthesis of covalently linked POM/organic hybrids with predetermined structures. The strong electronic interactions between the POM clusters and the conjugated organic bridge in these hybrid molecular dumbbells makes them an interesting new class of electrically active materials. In addition to molecular dumbbells, many other POM/organic hybrids linked in a variety of geometries can in principle be prepared by similar approaches.

Experimental Section

1: A mixture of **A** (0.75 g, 0.5 mmol), **B** (0.80 g, 0.5 mmol), $[PdCl_2(PPh_3)_2]$ (10 mg, 0.01 mmol), copper(I) iodide (6 mg, 0.02 mmol), K_2CO_3 (anhydrous, 1.0 g, 7 mmol), triethylamine in acetonitrile (0.5 mL of a 1 M solution, 0.5 mmol), and acetonitrile (20 mL) was stirred at room temperature for about 30 min under nitrogen. The resulting dark red solution was added to CH_2Cl_2 (100 mL), washed twice with brine, and then concentrated to about 30 mL. After the addition of ethyl acetate (100 mL), the solution was left standing without disturbance for about 8 h. The orange precipitate was collected by filtration and washed successively with dichloromethane and acetone. It was further purified by recrystallizing twice from acetone (yield: 1.16 g, 78%). The single crystals used for X-ray diffraction were obtained by diffusion of ethyl acetate into a solution of **1** in DMF. Elemental analysis (%) calcd for $C_{82}H_{160}N_6O_{36}Mo_{12}$: C 33.30, H 5.45, N 2.84; found: C 33.06, H 5.53, N 2.80. ^1H NMR (250 MHz, CD_3CN, 25 °C, TMS): $\delta = 7.22$ (s, ArH, 4 H), 3.09 (t, $J = 8.50$ Hz, NCH_2, 32 H), 2.59 (s, $(Ar)CH_3$, 12 H), 1.60 (q, $J = 7.94$ Hz, CH_2, 32 H), 1.35 (H, $J = 7.25$ Hz, CH_2, 32 H), 0.96 (t, $J = 7.25$Hz, CH_3, 48 H); UV/Vis (MeCN): λ/nm (ε/M^{-1}cm^{-1}) = 206 (1.40×10^5), 260 (9.43×10^4), 426 (1.04×10^5).

2: A mixture of **C** (0.5 mmol), **A** (1.75 g, 1.1 mmol), $[PdCl_2(PPh_3)_2]$ (40 mg, 0.057 mmol), copper(I) iodide (20 mg, 0.1 mmol), triethylamine (1 mL), and acetonitrile (40 mL) was stirred under nitrogen for 1 h at room temperature. The dark red solution was added to CH_2Cl_2 (300 mL) and washed twice with water. The organic layer was collected, and its solvent removed by vacuum evaporation. Acetone (20 mL) was added to the residue. The resulting suspension was filtered through a syringe filter (0.2 μm), and the filtrate was concentrated to ca. 10 mL. The concentrated solution was added slowly to diethyl ether (200 mL). After standing for 10 min, the top layer of solvents was decanted. The oily residue was dried under vacuum overnight to give a dark red powder, which was purified by recrystalizion from acetone/diethyl ether to yield analytically pure product (81%). Elemental analysis (%) calcd for $C_{100}H_{182}N_6O_{38}Mo_{12}$: C 37.21, H 5.68, N 2.60; found: C 37.60, H 5.24, N 2.33. ^1H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 0.96$ (t, $J = 7.25$ Hz, 48 H, CH_3), 1.09 (s, 18 H, CH_3), 1.35 (m, 32 H, CH_2), 1.59 (m, 32 H, CH_2), 2.60 (s, 12 H, $ArCH_3$),3.10 (m, 32 H, NCH_2), 3.71 (s, 4 H, OCH_2), 7.05 (s, 2 H, ArH), 7.21 (s, 4 H, ArH); ^{13}C NMR (400 MHz, CD_3CN, 25 °C): $\delta = 14.2$, 18.8, 20.7, 24.7, 27.2, 33.2, 59.6, 80.4, 89.7, 95.9, 114.9, 123.4, 131.2, 139.7, 154.6, 155.3; UV/Vis (MeCN): λ_{max}/nm (ε/M^{-1}cm^{-1}) = 206 (1.36×10^5), 250 (8.82×10^4), 438 (1.24×10^5).

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[11] Crystal data for **1**: red crystals, $M_r = 2957.44$, monoclinic, $P2_1/c$, $a = 19.9192(10)$, $b = 16.9000(8)$, $c = 16.2697(8)$ Å, $\beta = 102.879(2)°$, $V = 5339.2(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.840$ Mg m^3, $T = 100(2)$ K, $R1 = 0.0427$, $wR2 = 0.1251$, GOF 1.023. CCDC-174671 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).