

the magnetization curve (Figure 4) is in agreement with the magnetic coupling scheme proposed above, that is, antiferromagnetic coupling between $S=1$ and $S=2$ leads to a triplet ground spin state with $g=2.2$. These features rule out the possibility of magnetic ordering through spin canting or a helical ferromagnet. Further magnetic properties of this unique homometallic system are under investigation.

Experimental Section

1: In a typical synthesis, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was heated with $\text{Na}_2(\text{fum})$ (1 mmol) in water (15 mL) at 170°C for 24 h in a teflon-lined steel vessel. Overnight cooling of the vessel results in a microcrystalline green solid along with single crystals (65% yield) suitable for X-ray diffraction. Elemental analysis (%): calcd (found): C 17.57 (17.66), H 3.29 (3.38).

Received: October 2, 2001 [Z18010]

Revised: February 12, 2002

- [1] a) M. Ohba, N. Usuki, N. Fukita, H. Okawa, *Angew. Chem.* **1999**, *111*, 1911; *Angew. Chem. Int. Ed.* **1999**, *38*, 1795; b) X. Hao, Y. Wei, S. Zhang, *Chem. Commun.* **2000**, 2271; c) P. S. Mukherjee, S. Dalai, G. Mostafa, E. Zangrando, T. H. Lu, G. Rogez, T. Mallah, N. R. Chaudhuri, *Chem. Commun.* **2001**, 1346.
- [2] a) O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**, chap. 11; b) P. Day, *J. Chem. Soc. Dalton Trans.* **1997**, 701.
- [3] Crystal data: $\text{C}_8\text{H}_{18}\text{Ni}_3\text{O}_{16}$ (**1**) $M_r=546.35$, monoclinic, space group $P2_1/c$, $a=6.558(3)$, $b=8.128(3)$, $c=15.506(4)$ Å, $\beta=96.36(3)^\circ$, $V=821.4(5)$ Å³, $Z=2$, $\rho_{\text{calcd}}=2.209$ g cm⁻³, $\mu=3.490$ mm⁻¹ ($\text{MoK}\alpha$), $F(000)=556$. θ range for data collection $4.01\text{--}30.15^\circ$, final $R=0.0508$, $wR2=0.1383$, $S=1.141$ for 146 parameters and 3606 reflections, 2216 unique [$R(\text{int})=0.0455$], of which 1866 with $I>2\sigma(I)$, max. positive and negative peaks in ΔF map 0.906 and -0.926 e Å⁻³. The data set was collected on a Nonius DIP-1030H system equipped with $\text{MoK}\alpha$ radiation ($\lambda=0.71073$ Å) at room temperature. A total of 30 frames were collected, each with a rotation of 6° about φ and an exposure time of 12 min over a half of reciprocal space; the detector is 80 mm from the crystal. Data reduction and cell refinement was carried out using the program MOSFLM.^[8] The structure was solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 using SHELX 97^[9] to SHELX 86. All the calculations were performed using the WinGX System (Ver. 1.64).^[10] CCDC 171598 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).
- [4] a) S. Lai, T. Lin, Y. Chen, C. Wang, G. Lee, M. Yang, M. Leung, S. Peng, *J. Am. Chem. Soc.* **1999**, *121*, 250; b) S. Peng, C. Wang, Y. Jang, Y. Chen, F. Li, C. Mau, M. Leung, *J. Magn. Magn. Mater.* **2000**, *80*, 209; c) S. Lai, C. Wang, Y. Chen, C. Lee, Y. Liu, S. Peng, *J. Chin. Chem. Soc.* **1997**, *46*, 477.
- [5] M. R. Bond, R. D. Willett, *Acta Crystallogr. Sect. C* **1993**, *49*, 861.
- [6] Magnetization and variable-temperature (1.9–300 K) magnetic susceptibility measurements (dc and ac) on polycrystalline samples of **1** were carried out with a SQUID magnetometer (Quantum Design) operating at different magnetic fields. Experimental susceptibilities were corrected for diamagnetism (-270×10^{-6} cm³ mol⁻¹), temperature-independent paramagnetism ($+100 \times 10^{-6}$ cm³ mol⁻¹ per Ni atom), and the magnetization of the sample holder.
- [7] a) S. Rauba, E. Ressouche, L. P. Regnault, M. Drillon, *J. Magn. Magn. Mater.* **1996**, *163*, 365; b) M. Kurmoo, P. Day, D. Derory, C. Estournes, R. Poinso, M. J. Stead, C. J. Kepert, *J. Solid State Chem.* **1999**, *145*, 452.
- [8] W. Kabsch, *J. Appl. Crystallogr.* **1993**, *21*, 67.
- [9] G. M. Sheldrick, *SHELXS-97, Programs for Crystal Structure Analysis* (Release 97-2), University of Göttingen, Göttingen (Germany), 1997.
- [10] L. J. Farrugia, *WinGX—A Windows Program for Crystal Structure Analysis*, University of Glasgow, Glasgow, **1998**.

Arene – Perfluoroarene Interactions as Physical Cross-Links for Hydrogel Formation**

Andreas F. M. Kilbinger and Robert H. Grubbs*

In 1960 Patrick and Prosser discovered that hexafluorobenzene (HFB, m.p. = 5.0°C) and benzene (m.p. = 5.4°C), both liquids at room temperature, form a 1:1 solid complex with a melting point of 23.7°C when mixed together.^[1] Extensive X-ray crystallographic studies by Dahl showed that a wide variety of aromatics^[2] form such 1:1 cocrystals with HFB, all showing alternating columnar face-to-face stacking. The packing behavior was explained theoretically to arise from electrostatic interactions between the two partners with the quadrupolar moment of HFB being complementary to that of benzene or its hydrocarbon derivatives.^[3, 4] The binding energy between the two aromatic rings (benzene – HFB) was computed to be 3.7 kcal mol⁻¹.^[5] Similar stacking motifs have been observed for several other cocrystals of perfluorinated aromatic compounds with their non-fluorinated analogues.^[6–8] Crystal structures of 1:1 complexes between perfluoroarenes and arenes of mismatched geometry have also been reported.^[9–14] Because the geometric arrangement in the solid state is to some extent predictable, fluorinated compounds have been prepared with the aim of engineering their geometric orientation in the crystal.^[15–17]

We were particularly interested in using perfluoroarene – arene interactions to aggregate polymers in solution. While a number of noncovalent interactions are well investigated in polymeric systems,^[18–20] no case has been reported where perfluoroarene – arene interactions were employed. Our idea was to modify either end of the polymer chain with aromatic groups in the hope that they would form alternating stacks in the presence of a perfluorinated additive in solution. Association by the end groups would increase the molecular weight, this could easily be shown by an increase of viscosity. Naphthalene as the aromatic group at the polymer chain end in combination with the perfluorinated additive octafluoronaphthalene (OFN) seemed a good candidate. The stacking behavior of naphthalene with OFN in the solid state is well known, the 1:1 complex between naphthalene and OFN shows an increased melting temperature of around $45\text{--}50^\circ\text{C}$ with respect to either stacking partner and many naphthalene derivatives are commercially available or synthetically accessible in few reaction steps.

Initial experiments with nonpolar polymers, such as poly(norbornene), poly(cyclooctadiene), and others prepared by ring-opening metathesis polymerization (ROMP), with naph-

[*] Prof. Dr. R. H. Grubbs, Dr. A. F. M. Kilbinger
California Institute of Technology
Division of Chemistry and Chemical Engineering
Mail code 164-30, Pasadena, CA 91125 (USA)
Fax: (+1) 626-5649297
E-mail: rhg@caltech.edu

[**] We thank the Office of Naval Research for funding this work. AFMK thanks the Humboldt-Foundation for a Feodor-Lynen Fellowship. We thank Rob Lammertink for help with the rheology measurements.

Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.

thalene end groups were unsuccessful. As these materials were only soluble in nonpolar solvents, solvation of the naphthalene end groups as well as the perfluorinated additive probably prevented stacking in solution. To gain access to solutions of more polar solvents and to make use of solvophobic effects, we chose to modify poly(ethylene glycol)s (PEGs) with aromatic groups (Figure 1). PEGs are

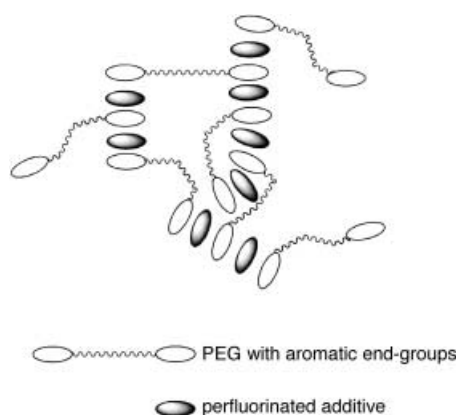
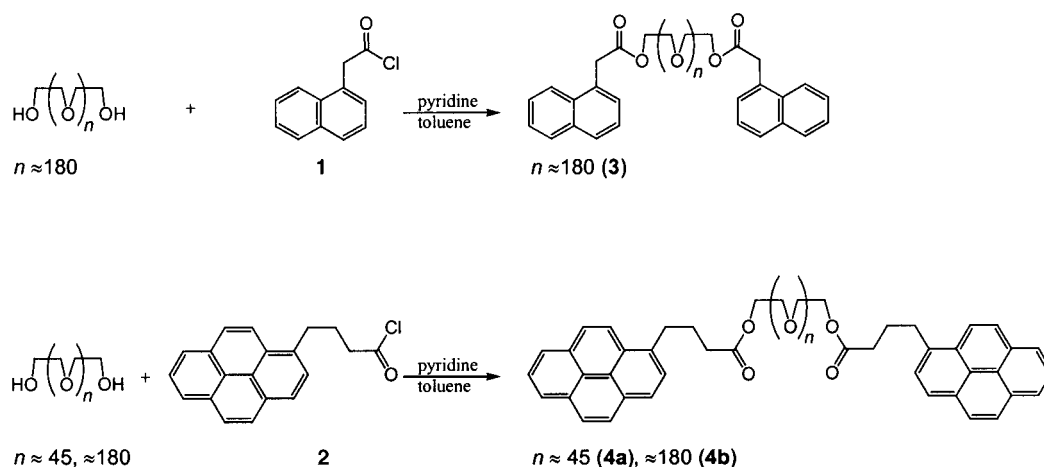


Figure 1. Graphical representation showing PEG chains with aromatic end groups and a possible way of aggregation by face-to-face stacks in the presence of a perfluorinated additive. It is not clear however, what the exact structures of the aggregates are.

soluble in a wide variety of solvents, including organic solvents of low polarity, such as dichloromethane or toluene, as well as in methanol or water. 1-Naphthyl acetoxy chloride (**1**) was used to end cap commercially available PEG ($M_n = 8000$) as the diester **3** (Scheme 1, top). While **3** shows good solubility in common organic solvents, such as chloroform, dichloromethane, or methanol, addition of OFN resulted in clear solutions without any increase of viscosity. OFN added to aqueous solutions of **3** did not dissolve upon heating or sonication and the resulting heterogeneous mixture did not exhibit any increased viscosity. Dissolving OFN in the melt of **3** followed by addition of water also resulted in a heterogeneous mixture of both solid OFN and dissolved polymer and no viscosity increase.

Of all the other stacking partners for OFN (m.p. = 87 °C) reported, pyrene (m.p. = 149 °C) is the one with the highest increase in melting temperature for the 1:1 complex (m.p. = 255,^[21] 248–250^[14]) compared to the individual stacking partners. We therefore changed our strategy and used 1-pyrene butyryl chloride (**2**) to end cap PEGs ($M_n = 2000$ and $M_n = 8000$) as the diesters **4a** and **4b** (Scheme 1, bottom). Both materials show good solubility in organic solvents and water. Dissolving OFN (2 equiv) in the melt of **4a** (1 equiv), letting it solidify, and adding water to the binary mixture, resulted in a slight swelling of the material but the amount of water retained in the material appeared to be low. On the other hand, a material prepared from **4b** and OFN (1:2), formed viscous liquids exhibiting higher viscosities than **4b** in water in the absence of OFN. It is possible that because of the higher concentration of end groups in **4a** than **4b** a cross-linked network was formed which only allowed small amounts of water to be incorporated into the network structure. By increasing the molecular weight of the PEG in **4b** the concentration of end-groups was effectively reduced which lead to a material that dramatically changed viscosity depending on the presence of the perfluorinated additive, OFN.

To show unambiguously that the viscosity increase was induced by the presence of the perfluorinated additive, we measured relative viscosities of aqueous **4b** solutions in the presence (**4b**:OFN = 1:2) and in the absence of OFN at various concentrations (Figure 2). The viscosity of **4b**/OFN is greatly enhanced compared to that of pure **4b** solutions. To ensure that the phenomenon was not the result of a non-specific interaction between the pyrene end groups and OFN, non-fluorinated naphthalene was added to aqueous **4b** solutions. In this case, a heterogeneous mixture was formed and no viscosity increase could be observed. To exclude covalent cross-linking, a sample of **4b** was examined by gel permeation chromatography (GPC) before and after aggregation with OFN. Both samples eluted at the same retention time and covalent cross-linking could be excluded. Aqueous solutions of **4b** and OFN (**4b**:OFN = 1:2) show a decrease in viscosity with increasing temperature (Figure 3) up to about 40 °C where a plateau of constant viscosity is reached. The process is reversible upon cooling. To demonstrate the magnitude of viscosity reached at high concentrations of **4b**



Scheme 1. Synthesis of end-capped PEGs.

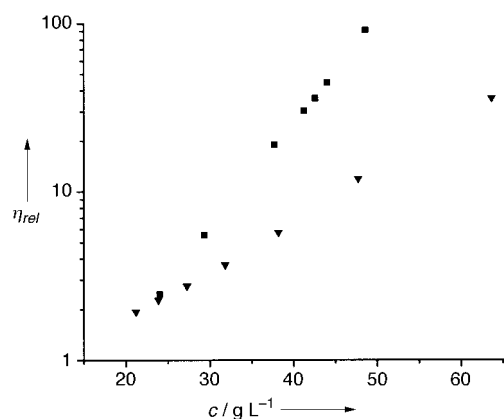


Figure 2. Relative viscosity of **4b** in water (21 °C) at various concentrations. ■: in the presence of two equivalents of OFN, ▼: in the absence of OFN.

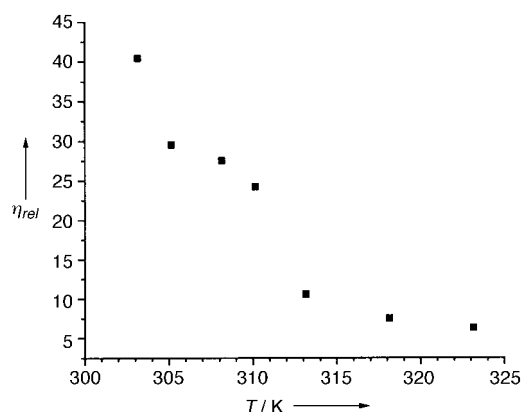


Figure 3. Temperature dependence of the relative viscosity of **4b** ($c = 46.2 \text{ g L}^{-1}$) and 2 mol equivalents of OFN in water.

and OFN (**4b**:OFN = 1:2), zero shear rate viscosities were measured on a rheometer (Figure 4). Very high viscosities were measured in this experiment, clearly showing that a polymer of high molecular weight was formed. The proposed mechanism of aggregation through alternating stacks of aromatic groups favors branched or networked structures

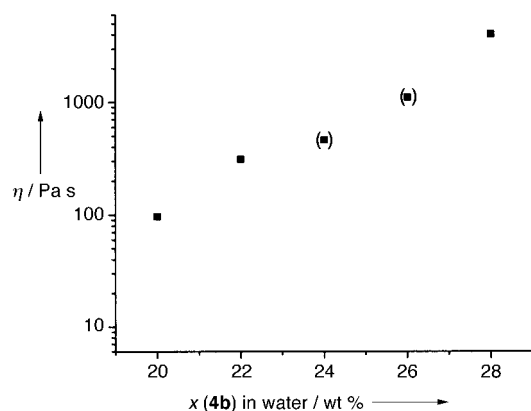


Figure 4. Zero shear rate viscosities of **4b** and 2 mol equivalents of OFN in water (25 °C) at various weight percentages. No steady state was reached during the measurement of 24% and 26% **4b** in water; the data points were extrapolated from the measured data (shown in parenthesis).

over linear ones. However, the physical criterion of network formation, the gel point, could not be observed in our measurements.

To support our assumption, that **4b** associates through alternating stacks of pyrene end groups and OFN in solution, OFN was titrated into a solution of **4b** in water and the fluorescence intensity of the band for monomeric pyrene emission ($\lambda = 377 \text{ nm}$) and the excimer band emission ($\lambda = 480 \text{ nm}$) was plotted against the ratio of OFN to polymer (Figure 5). The intensity of excimer emission decreases with

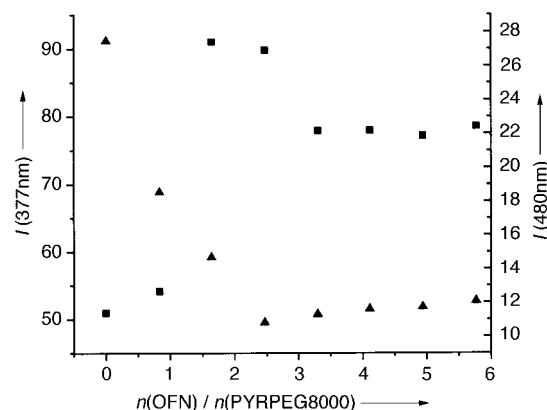


Figure 5. Titration of OFN into a solution of **4b** in water (4 g L^{-1}). The fluorescence intensity at $\lambda = 377 \text{ nm}$ (■; monomer emission) and $\lambda = 480 \text{ nm}$ (▲; excimer emission) are plotted against equivalents of OFN added to the solution.

increasing OFN concentration to reach a plateau at a ratio of approximately two equivalents of OFN per polymer chain while the monomer emission increases and reaches a maximum at the same OFN to polymer ratio. Maitra and D'Souza investigated the binding of OFN to molecular tweezers constructed from pyrene-substituted bile acids.^[22, 23] In their study, an OFN molecule binds between two pyrene moieties of the molecular tweezers which causes the fluorescence emission of monomeric pyrene to increase. However, no decrease of the intramolecular pyrene excimer emission was reported.

If the pyrene end groups of polymer **4b** stacked in an alternating fashion with OFN in solution, the spatial separation of the pyrene units from one another would hinder excimer formation of a photoexcited pyrene unit and hence give rise to an increase of monomeric pyrene emission together with a decrease of excimer emission. At a ratio of two OFN molecules per polymer chain or, in other words one OFN molecule per pyrene end group the system is saturated causing the excimer emission to reach a constant level and the monomer emission to peak.

We have demonstrated that arene–perfluoroarene interactions can act as supramolecular synthons for aggregation not only in the solid state but also in solution. The effect could only be observed in aqueous solutions presumably because of the hydrophobic effect. Nonetheless, it was shown that a specific interaction between the pyrene end groups of the PEG and OFN was responsible for the aggregation phenomenon. Dramatic viscosity changes in the presence of the

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.

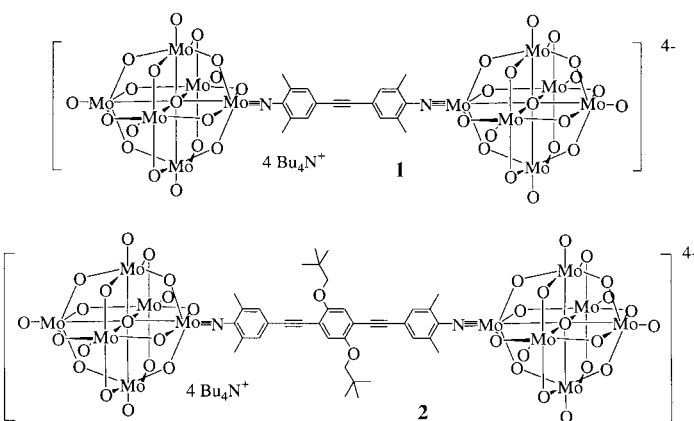
Received: December 21, 2001 [Z18428]

- [1] C. R. Patrick, G. S. Prosser, *Nature* **1960**, 187, 1021.
- [2] T. Dahl, *Acta Chem. Scand. Ser. A* **1988**, 42, 1.
- [3] J. H. Williams, *Acc. Chem. Res.* **1993**, 26, 593.
- [4] C. A. Hunter, *Angew. Chem.* **1993**, 105, 1653; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1584.
- [5] A. P. West, S. Mecozzi, D. A. Dougherty, *J. Phys. Org. Chem.* **1997**, 10, 347.
- [6] J. Potenza, D. Mastropaolo, *Acta Crystallogr.* **1975**, 31, 2527.
- [7] D. G. Naai, *Acta Crystallogr. Sect. B* **1979**, 35, 2765.
- [8] V. B. Smith, A. G. Massey, *Tetrahedron* **1969**, 25, 5495.
- [9] U. H. F. Bunz, V. Enkelmann, *Chem. Eur. J.* **1999**, 5, 263.
- [10] A. S. Batsanov, J. A. K. Howard, T. B. Marder, E. G. Robins, *Acta Crystallogr. Sect. C* **2001**, 57, 1303.
- [11] A. S. Batsanov, J. C. Collings, J. A. K. Howard, T. B. Marder, *Acta Crystallogr. Sect. E* **2001**, 57, o950.
- [12] A. S. Batsanov, J. C. Collings, J. A. K. Howard, T. B. Marder, D. F. Perepichka, *Acta Crystallogr. Sect. C* **2001**, 57, 1306.
- [13] J. C. Collings, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Acta Crystallogr. Sect. C* **2001**, 57, 870.
- [14] J. C. Collings, K. P. Roscoe, R. L. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard, T. B. Marder, *New J. Chem.* **2001**, 25, 1410.
- [15] G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty, R. H. Grubbs, *Angew. Chem.* **1997**, 109, 290; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 248.
- [16] G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, 120, 3641.
- [17] W. J. Feast, P. W. Lovenich, H. Puschmann, C. Taliani, *Chem. Commun.* **2001**, 505.
- [18] L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, 101, 4071.
- [19] See for example G. Tae, J. A. Kornfield, J. A. Hubbell, D. Johannsmann, T. E. Hogen-Esch, *Macromolecules* **2001**, 34, 6409, and references therein.
- [20] See for example S. B. Kennedy, E. R. deAzevedo, W. A. Petka, T. P. Russell, D. A. Tirrell, M. Hong, *Macromolecules* **2001**, 34, 8675, and references therein.
- [21] S. Miyagishi, A. Isomi, M. Iwata, T. Asakawa, M. Nishida, *Bull. Chem. Soc. Jpn.* **1985**, 58, 3643.
- [22] L. J. D'Souza, U. Maitra, *J. Org. Chem.* **1996**, 61, 9494.
- [23] U. Maitra, L. J. D'souza, *J. Chem. Soc. Chem. Commun.* **1994**, 2793.

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

Meng Lu, Yongge Wei, Bubin Xu, Calida Fung-Chi Cheung, Zhonghua Peng,* and Douglas R. Powell

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]



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

[*] Prof. Z. Peng, M. Lu, Dr. Y. Wei, B. Xu, C. F.-C. Cheung
Department of Chemistry
University of Missouri – Kansas City
Kansas City, MO 64110 (USA)
Fax: (+1) 816-235-5502
E-mail: pengz@umkc.edu

Dr. D. R. Powell
Department of Chemistry
University of Kansas
Lawrence, KS 66045 (USA)

[**] This work is supported by Research Corporation, National Science Foundation (DMR 0134032) and the Office of Naval Research. Acknowledgement is also made to the Donors of Petroleum Research Fund, administered by the American Chemical Society, for the support of this work.