T. W. Bruice, *J. Biol. Chem.* **1997**, *272*, 626–638; c) S. P. Ho, Y. Bao, T. Lesher, R. Malhotra, L. Y. Ma, S. J. Jluharty, R. R. Sakai, *Nat. Biotechnol.* **1998**, *16*, 59–63; d) Y. Matsuda, K. Kamiya, K. Uchida, *Anal. Chim. Acta* **1998**, *365*, 55–58.

[4] a) N. Milner, K. U. Mir, E. M. Southern, *Nat. Biotechnol.* **1997**, *15*, 537–541; b) M. Sohail, S. Akhtar, E. M. Southern, *RNA* **1999**, *5*, 646–655.

[5] T. Tuschl, C. Gohlke, T. M. Jovin, E. Westhof, F. Eckstein, *Science* **1994**, *266*, 785–788.

[6] D. L. Sokol, X. Zhang, P. Lu, A. M. Gewirtz, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 11538–11543.

[7] a) K. Ebata, M. Masuko, H. Ohtani, M. Kashiwasake-Jibu, *Photochem. Photobiol.* **1995**, *62*, 836–839; b) F. D. Lewis, Y. Zhang, R. L. Letsinger, *J. Am. Chem. Soc.* **1997**, *119*, 5451–5452; c) K. Yamana, M. Takei, H. Nakano, *Tetrahedron Lett.* **1997**, *38*, 6051–6054; d) P. L. Paris, J. M. Langenhan, E. T. Kool, *Nucleic Acids Res.* **1998**, *26*, 3789–3793; e) M Masuko, H. Ohtani, K. Ebata, A. Shimadzu, *Nucleic Acids Res.* **1998**, *26*, 5409–5416; f) E. Kostenko, M. Dobrikov, D. Pyshnyi, V. Petyuk, N. Komaruva, V. Vlassov, M. Zenkova, *Nucleic Acids Res.* **2001**, *29*, 3611–3620.

[8] a) K. Yamana, Y. Ohashi, K. Nunota, M. Kitamura, H. Nakano, O Sangen, T. Shimidzu, *Tetrahedron Lett.* **1991**, *32*, 6347–6350; b) K. Yamana, R. Iwase, S. Furutani, H. Tsuchida, H. Zako, T. Yamaoka, A. Murakami, *Nucleic Acids Res.* **1999**, *27*, 2387–2392; c) K. Yamana, H. Zako, K. Asazuma, R. Iwase, H, Nakano, A. Murakami, *Angew. Chem.* **2001**, *113*, 1138–1140; *Angew. Chem. Int. Ed.* **2001**, *40*, 1104–1106.

[9] a) H. F. Noller, *Annu. Rev. Biochem.* **1984**, *53*, 119–162; b) K. H. Johnson, D. M. Gray, *Biopolymers* **1991**, *31*, 385–395; c) M. Szymanski, M. Z. Barciszewska, V. A. Erdmann, J. Barciszewski, *Nucleic Acids Res.* **2002**, *30*, 176–178.

[10] P. C. Bevilacqua, R. Kierzek, K. A. Johnson, D. H. Turner, *Science* **1992**, *258*, 1355–1358.

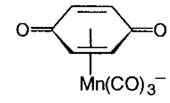
[11] C. C. Correll, B. Freeborn, P. B. Moore, T. A. Steitz, *Cell* **1997**, *91*, 705–712.

[12] N. Ban, P. Nissen, J. Hansen, P. B. Moore, T. A. Steitz, *Science* **2000**, *289*, 905–920.

Self-Assembly Using Organometalloligands as Spacers in the Controlled Formation of Isomeric 1D and 2D Supramolecular Quinonoid Networks[**]

Moonhyun Oh, Gene B. Carpenter, and
Dwight A. Sweigart*

Metal-coordination-directed self-assembly of polymers and discrete nanostructures is a very active research area.[1] The construction of predictable architectures having useful electronic, catalytic, or host–guest properties is the driving force behind this work. To date, the vast majority of reported compounds have metal centers connected by simple organic molecules that serve as multifunctional ligands or spacers.[1] We recently demonstrated, however, that the π-bonded organometallic complex ion [(η^4-benzoquinone)Mn(CO)$_3$]$^-$ (**1**) can serve as a bifunctional ligand ("organometalloligand") by coordinating through the quinone oxygen atoms in the presence of divalent transition-metal ions.[2a] M^{2+} ions (M = Mn, Cd, Zn) and **1** were found to self-assemble into crystalline organometallic quinonoid polymers, whose dimensionality and geometry can be controlled by the choice of added metal ion.



1

Herein, we report that the organometalloligand [(η^4-benzoquinone)Mn(CO)$_3$]$^-$ reacts with Mn^{2+} ions to form two isomeric coordination networks. Figure 1 illustrates the two architectures possible when **1** links to the Mn^{2+} centers. Either a 2D pseudoplanar quinonoid array (Figure 1 a) or 1D "string" arrays (Figure 1 b) can be formed. A representation of these two networks with {Mn(CO)$_3$} moieties attached to the constituent quinone molecules is also given in Figure 1. One would expect that bifunctional spacer molecules could be used to join together the planes in Figure 1 a, or the strings in Figure 1 b. Indeed, we recently demonstrated that **1**, Mn^{2+} ions, and 4,4′-bipyridine self-assemble in dimethyl sulfoxide (DMSO) to afford a polymer (**2**), which contains a 2D planar network linked by bipyridine spacers.[2a] We now report that self-assembly of the same components, but with the Mn^{2+} ions maintained at a very low concentration, results in the formation of the isomeric polymer **3**, consisting of the 1D strings linked by bipyridine spacers. It is noteworthy that polymers **2** and **3** both contain rectangular grid networks. Typically, the isomer distribution found in supramolecular

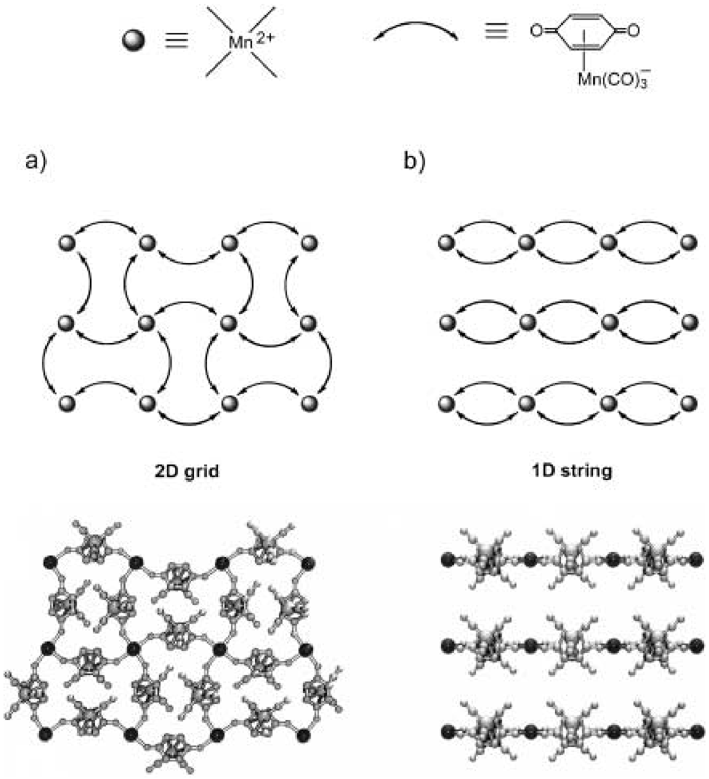


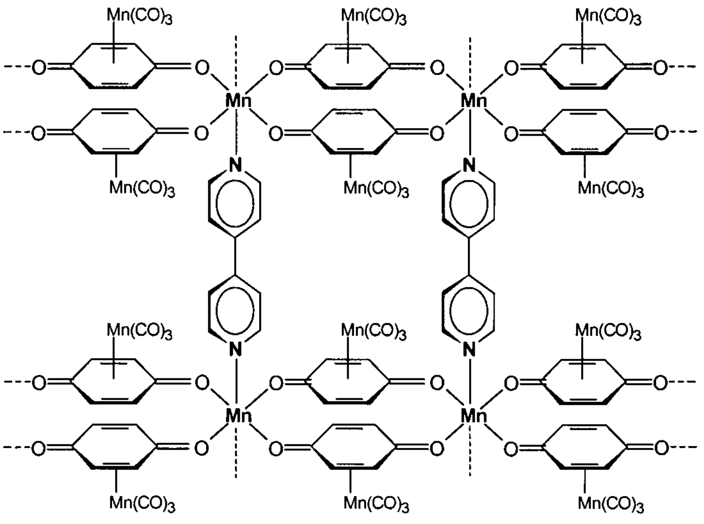
Figure 1. Representation of the self-assembly of Mn^{2+} ions with the η^4-quinone complex **1** to form neutral a) 2D grid and b) 1D string networks.

---

[*] Prof. D. A. Sweigart, M. Oh, Prof. G. B. Carpenter
Department of Chemistry
Brown University
Providence, RI 02912 (USA)
Fax: (+1) 401-863-3756
E-mail: Dwight_Sweigart@Brown.edu

[**] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

0044-8249/02/4119-3650 $ 20.00+.50/0



3

structures is dictated by the presence of guest molecules that serve as templates for self-assembly.[1e,3] In our studies, however, the isomer formed is determined not by guest molecules but rather by the concentration of the metal ion that coordinates to the organometalloligand and the bipyridine spacers.

When **1** and 4,4′-bipyridine react in DMSO in air at 70 °C for two days in ambient room light, there is a slow photogeneration of Mn^{2+} ions and concomitant formation of polymer **3**. In contrast, when several equivalents of Mn(OAc)$_2$ are present in the reaction mixture, polymer **2**, which contain a 2D pseudoplanar quinonoid network, is formed exclusively. In reactions with lower Mn^{2+} concentrations, the 1D string analogue **3** appears, and becomes dominant when no Mn(OAc)$_2$ is added at the commencement of the reaction. Table 1 lists the distribution of polymers **2** and **3** as a function of the amount of added Mn(OAc)$_2$.[4] An examination of the disposition of the organometalloligand spacers in Figure 1 suggests that the quinone oxygen donors are more likely to be "trapped" in a 2D planar network where there is an abundance of available Mn^{2+} ions. Formation of the 1D string architecture would be more likely when the concentration of Mn^{2+} ions is maintained at a low level. Support for this hypothesis was obtained by treating **1** with excess Mn(OAc)$_2$ in dimethylacetamide (DMA), from which crystalline polymer [{(η^4-benzoquinone)Mn(CO)$_3$}$_2$Mn(dma)$_2$]$_n$ (**4**) was obtained (reaction in DMSO did not afford suitable crystals). The crystal structure of **4** (Figure 2) verified the anticipated 2D quinonoid network with each Mn^{2+} ion possessing two axial DMA ligands.

Table 1. Distribution of polymeric isomers **2** and **3** in the self-assembly of **1**, 4,4′-bipyridine, and Mn^{2+} ions as a function of the number of added equivalents of Mn(OAc)$_2$.[a]

Equivalents of Mn(OAc)$_2$	Products
8	**2** only
2	**2** only
0.5	**2** (major) and **3**
0.25	**2** and **3** (major)
0	**3** only

[a] In the presence of 1.0 equiv of **1** and 20 equiv of 4,4′-bipyridine in DMSO at 70 °C.

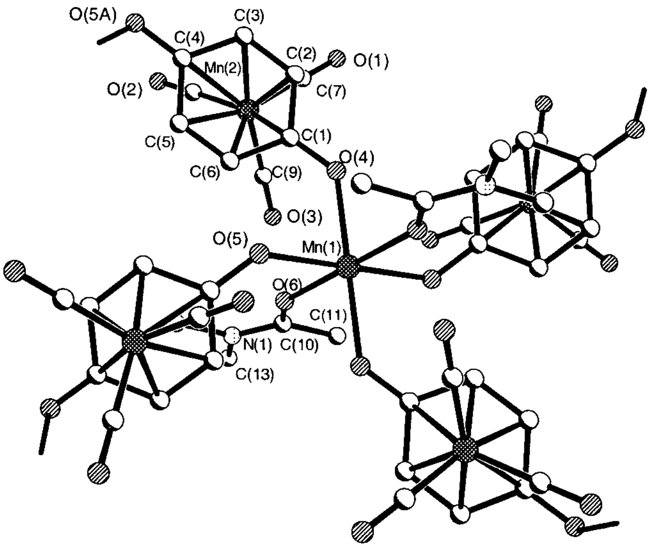


Figure 2. Crystal structure of polymer **4**, [{(η^4-benzoquinone)Mn(CO)$_3$}$_2$Mn(dma)$_2$]$_n$.

The crystal structure of **3** is shown in Figure 3 and a representation of one layer of the polymeric assembly is provided in Figure 4. The organometalloligand in **3** adopts a boat conformation with the quinone carbon atoms bent out of the plane of the diene by 13°, so that the overall structure is best described as an η^4-quinone. The rectangular grids in **3** have dimensions of approximately 10 × 12 Å. The pseudoplanar layers stack through noncovalent interactions to form the 3D material. As may be seen in Figure 5, the rectangular boxes in one layer are overlaid by {Mn(CO)$_3$} moieties in the next layer, so that the crystal does not contain open channels. Two DMSO molecules per box are located between adjacent

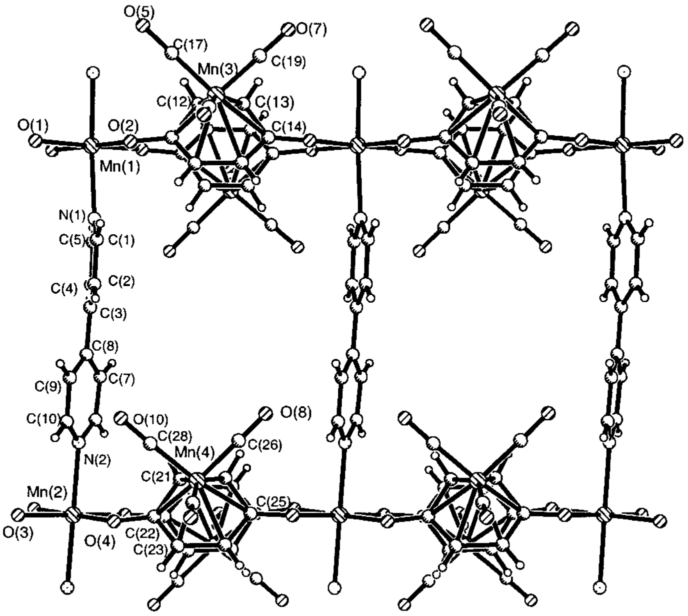


Figure 3. Crystal structure of polymer **3**, [{(η^4-benzoquinone)Mn(CO)$_3$}$_2$Mn(4,4′-bipyridine)]$_n$.

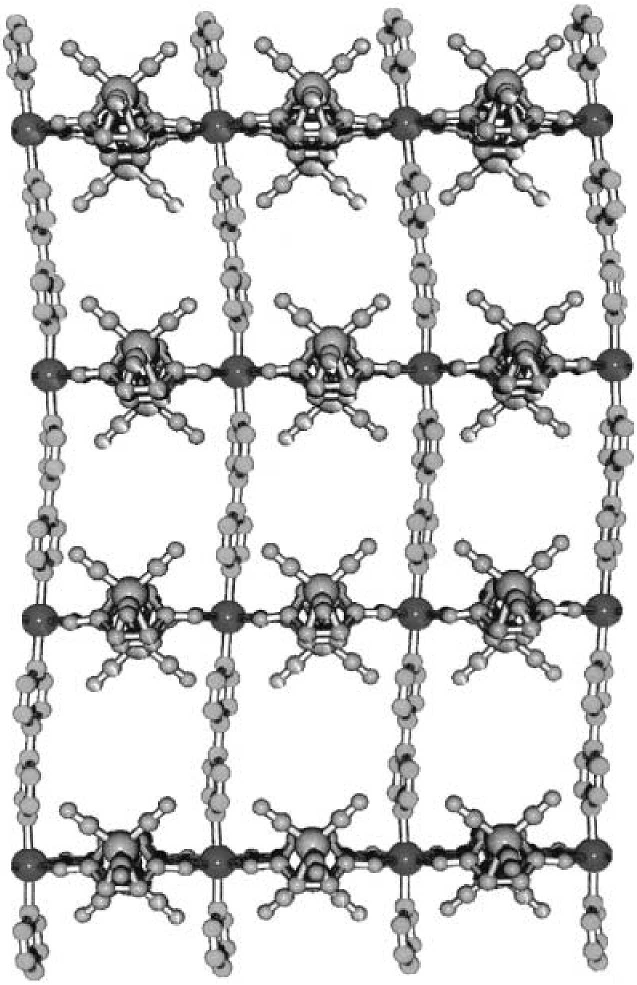


Figure 4. Representation of one layer of polymer **3**.

layers, with a third DMSO molecule situated within each box (Figure 5). Suspending **3** in CD_2Cl_2 at room temperature for 2 h resulted in the complete and quantitative loss of all three DMSO molecules (Figure 6). Significantly, an X-ray rotation photograph taken after removal of DMSO indicated that this process occurs without affecting the crystallinity.

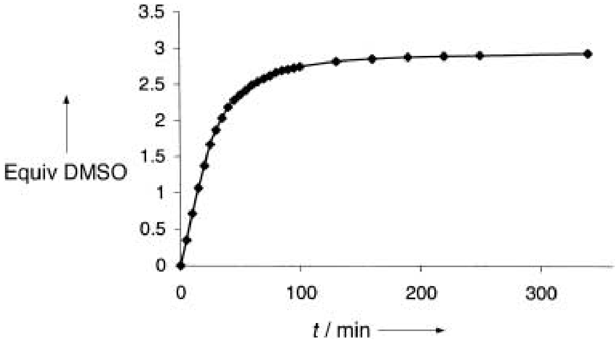


Figure 6. Equivalents of DMSO displaced at room temperature from polymer **3**·3DMSO when suspended in CD_2Cl_2.

In conclusion, we have demonstrated the selective polymerization of π-bonded quinone complexes to afford 1D and 2D networks which can be subsequently linked by bipyridine spacers to generate isomeric polymers containing rectangular grids.[5] This chemistry constitutes a rare example of the use of a π-bonded organometallic complex to function as a spacer (organometalloligand) in the coordination-directed self-assembly of a supramolecular structure. It is reasonable to suppose that organometalloligand spacers may find general application in supramolecular chemistry. They offer the possibility of novel structural features, as well as novel applications based on through-bond metal–metal interactions between organometallic and inorganic metal centers.

Experimental Section

Syntheses of polymers **3** and **4**: The complex [(η^5-1,4-semiquinone)Mn(CO)$_3$][2b] (12 mg, 0.048 mmol) and excess 4,4′-bipyridine (10 equiv) were combined in DMSO (0.5 mL) at 70 °C in ambient room light. The bipyridine rapidly converted the manganese complex into the quinone complex **1**. After 2 days, crystals of polymer **3** suitable for X-ray studies were obtained in 77 % yield. IR (KBr): $\tilde{\nu}_{CO} = 2027$ (s), 1960 (s), 1929 (s), 1603 (w), 1567 (s), 1521 (s) cm^{-1}; elemental analysis calcd (%) for **3**·3DMSO, $C_{34}H_{34}Mn_3N_2O_{13}S_3$: C 43.46, H 3.65, N 2.98, S 10.24; found: C 43.09, H 3.56, N 2.88, S 10.01. Polymer **4** was synthesized by combining [(η^5-1,4-semiquinone)Mn(CO)$_3$] (12 mg, 0.048 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (2 equiv) in dimethylacetamide (DMA, 0.5 mL) at 70 °C. After 2 days, crystals of **4** suitable for X-ray studies were obtained in 75 % yield. IR (KBr): $\tilde{\nu}_{CO} = 2026$ (s), 1949 (s), 1929 (s), 1558 (s), 1510 (s) cm^{-1}.

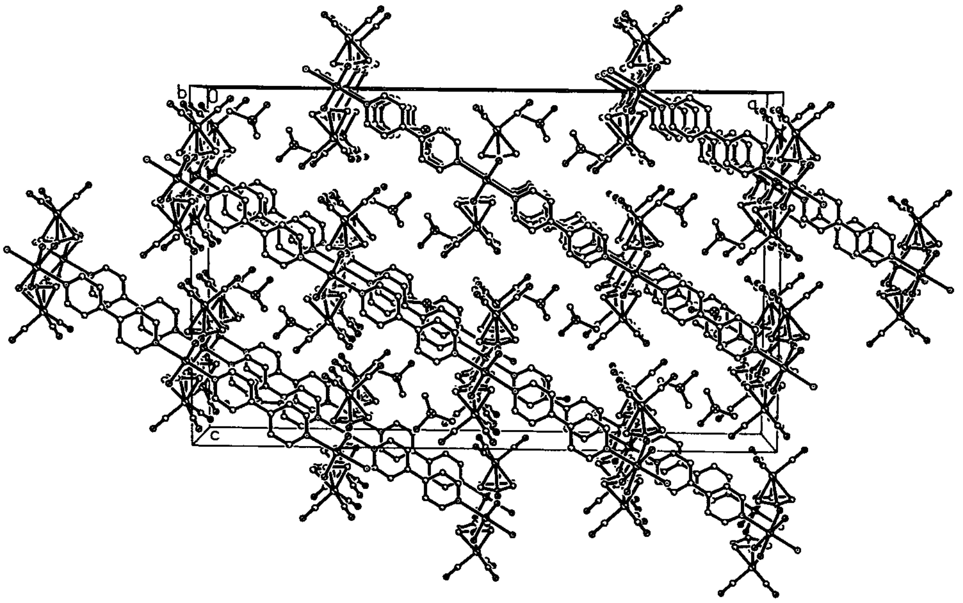


Figure 5. Packing diagram of polymer **3** showing the relative disposition of the layers and the presence of two DMSO molecules located between the layers and a third DMSO molecule located in each rectangular box.

Crystal structures of **3** and **4**: Crystals of **3** suitable for X-ray studies were grown from a solution in DMSO. X-ray data collection with Mo$_{K\alpha}$ radiation was carried out at 298 K by using a Siemens P4 diffractometer equipped with a CCD area-detector. The structure was determined by direct methods and refined on F^2 using SHELXTL version 5. All hydrogen atoms were inserted in ideal positions, riding on their carbon atoms. Crystal data for **3**: $C_{17}H_{17}Mn_{1.5}NO_{6.5}S_{1.5}$, $M_r = 469.82$, monoclinic, space group $C2/c$, $a = 39.700(3)$, $b = 8.3664(6)$, $c = 24.390(2)$ Å, $\beta = 90.128(2)°$, $V = 8101.0(11)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.541$ g cm^{-3}, $\mu = 1.139$ mm^{-1}, $F(000) = 3832$, θ range 1.03–26.40°, 520 variables refined with 8304 independent reflections to final R indices $[I > 2\sigma(I)]$ of $R_1 = 0.0676$ and $wR_2 = 0.1892$, and GOF = 1.025. Crystals of **4** suitable for X-ray studies were grown from a solution in DMA. Crystal data for **4**: $C_{26}H_{26}Mn_3N_2O_{12}$, $M_r = 723.31$, monoclinic, space group $P2_1/c$, $a = 12.939(2)$, $b = 10.0886(15)$, $c = 12.9121(19)$ Å, $\beta = 90.128(2)°$, $V = 1510.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.591$ g cm^{-3}, $\mu = 1.299$ mm^{-1}, $F(000) = 734$, θ range 2.68–26.36°, 206 variables refined with 12734 independent reflections to final R indices $[I > 2\sigma(I)]$ of $R_1 = 0.0570$ and $wR_2 = 0.1397$, and GOF = 0.979. CCDC-182869 and -186586 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).

Received: April 9, 2002
Revised: June 17, 2002 [Z19062]

---

[1] a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; b) R. Robson, *J. Chem. Soc. Dalton Trans.* **2000**, 3735; c) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154; d) B. J. Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 2035; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022; e) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; f) K. Biradha, M. Fujita, *J. Chem. Soc. Dalton Trans.* **2000**, 3805; g) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

[2] a) M. Oh, G. B. Carpenter, D. A. Sweigart, *Angew. Chem.* **2001**, *113*, 3291; *Angew. Chem. Int. Ed.* **2001**, *40*, 3191; b) M. Oh, G. B. Carpenter, D. A. Sweigart, *Organometallics* **2002**, *21*, 1290.

[3] a) H. Gudbjartson, K. Biradha, K. M. Poirer, M. J. Zaworotko, *J. Am. Chem. Soc.* **1999**, *121*, 2599; b) K. Kasai, M. Aoyagi, M. Fujita, *J. Am. Chem. Soc.* **2000**, *122*, 2140; c) Y. L. Cho, H. Uh, S.-Y. Chang, H.-Y. Chang, M.-G. Choi, I. Shin, K.-S. Jeong, *J. Am. Chem. Soc.* **2001**, *123*, 1258; d) F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *Angew. Chem.* **2001**, *113*, 1577; *Angew. Chem. Int. Ed.* **2001**, *40*, 1529.

[4] Polymers **2** and **3** have distinctly different shapes, and this was used as the basis for determining their relative proportions. Verification of this procedure was obtained by performing unit-cell determinations on both types of crystals in reactions that yielded a mixture of the two products.

[5] a) L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc.* **1998**, *120*, 2676; b) K. D. Benkstein, J. T. Hupp, C. L. Stern, *J. Am. Chem. Soc.* **1998**, *120*, 12982; c) K. D. Benkstein, J. T. Hupp, C. L. Stern, *Angew. Chem.* **2000**, *112*, 3013; *Angew. Chem. Int. Ed.* **2000**, *39*, 2891; d) K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 15.

Reversible Photoinsertion of Ferrocene into a Hydrophobic Semiconductor Surface: A Chemionic Switch[**]

Masahiro Muraoka, Stephen L. Gillett, and Thomas W. Bell[*]

Molecular devices are currently of intense interest,[1] but functional supramolecular devices are shorter term candidates for various applications including signal processing[2] and separation.[3] Control of the self-assembly[4] of photonic, electronic, and ionic supramolecular, or "chemionic",[2a,5] devices remains an important challenge. We have devised a surprisingly simple, self-reversing, photoredox system that functions as a chemionic switch (Figure 1). This bi-stable supramolecular device can be switched "on" by light and "off" by chemical oxidation. Light is an attractive agent for mediating self-assembly, and this has led us to base our chemionic switch on a photoredox reaction driven by an illuminated semiconductor.[6] Electron–hole pairs formed near the surface of the semiconductor by the absorption of

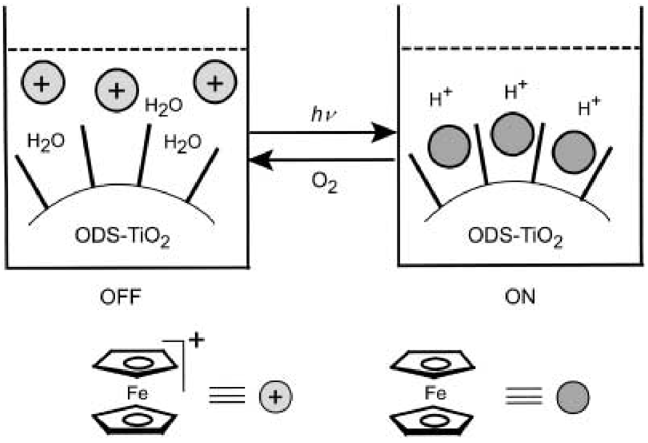


Figure 1. Illustration of the self-reversing chemionic switch. "ODS-TiO_2" describes TiO_2 particles surface-functionalized with octadecyltrichlorosilane (ODS). Holes generated by near-UV illumination oxidize the solvent to generate hydrogen ions, while photogenerated electrons reduce solution ferrocenium (Fc^+) to ferrocene (Fc), which dissolves into the hydrophobic monolayer on the surface of the TiO_2. After storing the sample in the dark for several hours the ferrocene spontaneously reoxidizes by reaction with atmospheric O_2.

---

[*] Prof. T. W. Bell, Dr. M. Muraoka
Department of Chemistry
University of Nevada
Reno, NV 89557 (USA)
Fax: (+1) 775-784-6804
E-mail: twb@unr.edu

Prof. S. L. Gillett
Department of Geological Sciences
University of Nevada
Reno, NV 89557 (USA)

[**] We thank Degussa AG for a gift of P25 TiO_2. We also thank Mario Desilets of the Nevada Bureau of Mines and Geology for X-ray diffraction data.

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