# Metal-Mediated Self-Assembly of π-Bonded Benzoquinone Complexes into Polymers with Tunable Geometries**

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Self-assembly of two or more components into supramolecular nanostructures, networks, and polymers has been used to generate materials that have many potential applications in magnetics, optics, molecular recognition, catalysis, sensing, separations, and general host–guest interactions.[1–14] The recognition process implicit in the formation of such materials is most commonly based on hydrogen bonding, π–π stacking, or metal–ligand interactions. The use of transition metals in coordination-directed self-assembly of polymers and nanostructures has become a particularly fruitful area of investigation.

Herein we report that hydroquinone ($H_2Q$), which is the key building block in many biological proton–electron transfer reactions,[15] can be induced to self-assemble into one-, two-, and three-dimensional polymers by suitable interaction
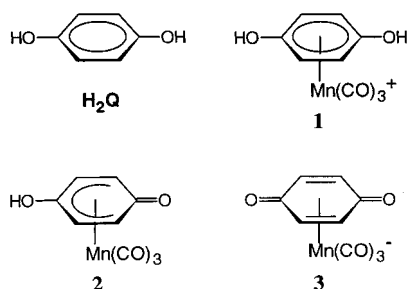
with transition metal ions. The type of polymer obtained appears to be readily controllable. The key step is initial coordination of the transition metal fragment $Mn(CO)_3^+$ to the π system in $H_2Q$, which facilitates proton loss from the OH groups. Subsequent σ complexation of the oxygen atoms to added metal ions is propagated in one, two, or three dimensions in a manner that depends on the geometrical requirements of the metal ion and on the presence of added ligands that function as "spacers".

While there are many examples of metal coordination through σ bonding from the oxygen atoms in hydroquinone, as well as in the isomeric resorcinol and catechol molecules,[16–18] metal complexation to the π network is rare.[19–21] However, $\eta^6$ coordination of the $Mn(CO)_3^+$ moiety to afford complex **1** was found to be facile, and to result in greatly increased acidity of the OH groups, so that even a base as mild as $Et_3N$ effects reversible deprotonation of **1** in DMSO to give $\eta^5$-semi-

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quinone (**2**) and $\eta^4$-quinone (**3**) complexes.[20] As shown herein, the oxygen atoms in **3**, generated from **1** or **2**, readily σ bind to metal ions. With divalent metal ions, the charges balance to neutral with each metal being bound to four quinoid oxygen atoms in a polymeric array. For example, when **2** was allowed to stand in DMSO at either $25\,^\circ$C or $70\,^\circ$C in the presence of ambient light, the one-dimensional (linear) polymer **4** was formed in good yield. In the absence of light,



**4**
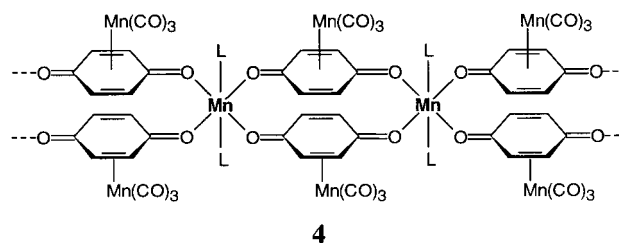
no reaction occurred, which suggests that the $Mn^{II}$ bridging ions in **4** originate from a photodissociation process. The need for light could be circumvented by merely adding $Mn^{II}$ directly to **1** or **2** in the form of the acetate, $Mn(OAc)_2$, which automatically provides the base necessary to deprotonate the OH groups.

The X-ray structure of **4** is shown in Figure 1a.[22] The bridging manganese metal is octahedral, with two axial DMSO ligands (L). The benzoquinone unit in **4** adopts a
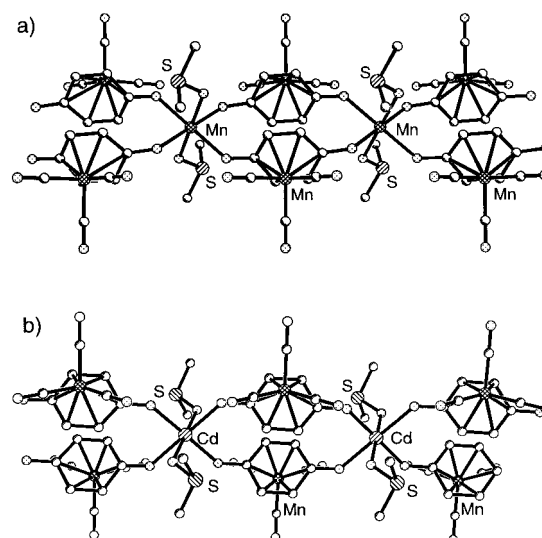


Figure 1. X-ray structure of benzoquinone polymers a) **4** and b) **5**.

boat conformation with the phenolic carbon atoms bent out of the diene plane by about 12°, which results in these carbon atoms being only weakly bonded to the $Mn(CO)_3$ unit. In contrast, the quinoid diene carbon atoms are strongly bonded to the $Mn(CO)_3$, so that the overall structure is best described as an $\eta^4$-quinone. The bridging benzoquinone rings in **4**, which are roughly eclipsed, are separated by a perpendicular distance of 3.30 Å. Measurement of the magnetic susceptability of polymer **4** at 298 K gave $\mu_{eff} = 5.9\,\mu_B$ per monomer unit, as would be expected for a high-spin $Mn^{II}$ bridge.

Examination of the structure of **4** suggests two obvious ways in which the magnetic, optical, and structural properties could be tuned: 1) replacement of the axial ligand L and 2) replacement of the bridging metal. It was found that substitution of the axial DMSO ligands in **4** by pyridine (py) was readily achieved by performing the polymerization in DMSO containing an excess of free pyridine. An X-ray study of the product confirmed that it consists of polymeric structure **4** with L = py. Similarly, performing the polymerization of **3** with Cd(OAc)$_2$ instead of Mn(OAc)$_2$ led to the clean formation of **5**, which is essentially identical to **4** in which octahedral Cd$^{II}$ substitutes for octahedral Mn$^{II}$. The X-ray structure of **5** is shown in Figure 1b.[22] Preliminary experiments indicated that other divalent metal ions that prefer octahedral coordination, for example, Co$^{II}$ and Ni$^{II}$, form analogous polymers.

The polymerization of the quinone complex **3** in the presence of a bridging metal that prefers tetrahedral rather than octahedral geometry would be expected to afford a nonlinear polymer structurally quite different from **4**. This possibility was explored using Zn$^{II}$, and the result was the three-dimensional polymer **6**. The X-ray structure of **6** (Figure 2) indeed features a bridging zinc ion that is tetrahe-
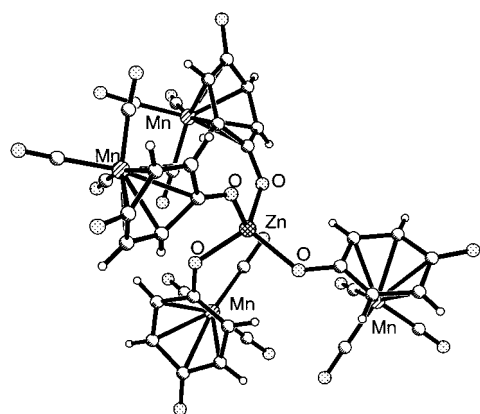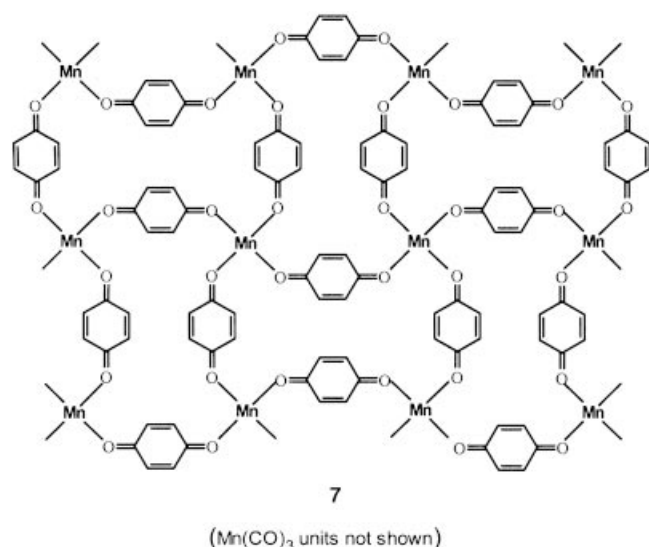
drally coordinated to the quinoid oxygen atoms. The solid-state structure in this case consists of two interpenetrating three-dimensional polymeric networks, as illustrated by the blue and yellow colors in Figure 3a. The polymer crystallizes in a chiral tetragonal space group and the crystals appear to be racemic twins. The chiral nature of the structure is seen in Figure 3b by noting the spiraling around a fourfold screw axis, with the two network spirals threaded together. The basic topology can also be described as two interpenetrating diamondoid networks.
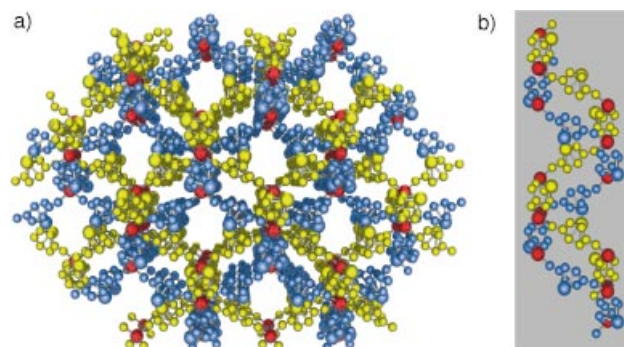


Figure 3. Structure of zinc polymer **6** showing a) the interpenetrating networks in blue and yellow with the zinc atoms shown in red and b) a portion of the structure along the crystallographic *c* axis showing how the spiral arrangements are threaded together. The CO ligands are omitted for clarity.

An attempt was made to synthesize polymer **4** with 4,4′-bipyridine (4,4′-bipy) as the axial ligand. The expectation was that 4,4′-bipy would serve as a bifunctional spacer[23] and join together the linear polymer units in **4**. However, when complex **1** or **2** was combined with Mn(OAc)$_2$ and excess 4,4′-bipy in DMSO, polymerization did not afford a linear product. Rather, two-dimensional pseudo-planar networks joined by 4,4′-bipy spacers were produced (**7**). A comparison of line drawings for **4** and **7** illustrates the different ways in which the quinone molecules **3** are linked to produce one-



Figure 2. X-ray structure of zinc polymer **6**.



**7**

(Mn(CO)$_3$ units not shown)



**7**
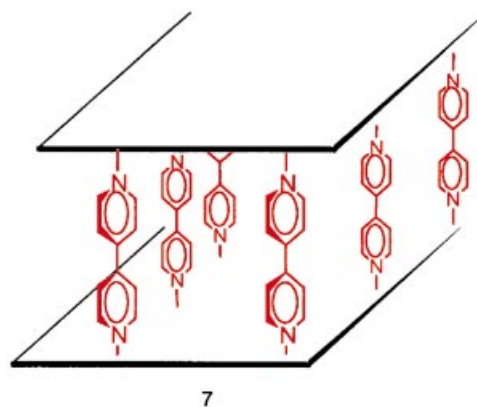
dimensional and two-dimensional structures, respectively. The X-ray structure of **7** was determined and is shown in Figure 4.[22] An intriguing feature of **7** is the presence of rectangular channels or pores that are bounded by the bipyridine spacers and the pseudo-planar quinoid networks. The channels, clearly visible in Figure 4, have a cross section or "opening" of about $12 \times 6$ Å. The longitudinal axis of each channel is propagated in the unit cell *b* direction with a repeat distance of 12.3 Å, thus generating an array of molecular boxes. In the crystalline polymer, the channels are filled with two disordered DMSO solvent molecules per molecular box.
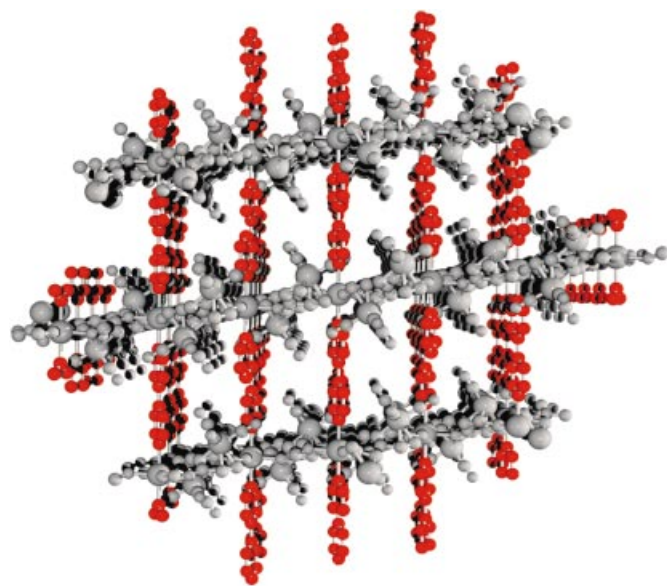


Figure 4. Structure of polymer **7** with the bridging bipyridine ligands shown in red. Each rectangular "box" contains two DMSO molecules (not shown).

The nanoporous polymer **7** appears to be of indefinite thermal stability at room temperature. It is likely that the manganese ion bridging the quinone centers in **7** can be substituted for a variety of metals. The quinoid networks in this material could provide the foundation for the synthesis of polymers with tunable pore size by variation of the bifunctional spacer, which may also allow control of the chemical environment in the nanopores. The attachment of a redox switch to the spacer may permit individual quinoid network planes to be differentially addressed and activated.[24]

In conclusion, we have shown that $\pi$ complexation to benzoquinone activates the molecule to metal-mediated polymerization. The resulting materials can be predesigned to have one-, two-, or three-dimensional quinoid structures. Applications of these materials in electrocatalysis are being investigated, as well as possible extension to *ortho-* and *meta*-quinones. The chemistry described herein may also be applicable to the stabilization and utilization of quinone methides, which are reactive species important in biochemical and natural products chemistry, and believed to occur as intermediates in the reactions of some antitumor drugs.[25–27]

## Experimental Section

Synthesis of polymers **4**–**7**: The semiquinone complex **2** (100 mg, 0.40 mmol) and Mn(OAc)$_2$·tetrahydrate (49 mg, 0.20 mmol) were combined in DMSO (10 mL) under N$_2$ at room temperature. The reaction mixture was stirred in the absence of light for 24 h. The crystalline polymer **4** that had precipitated over this period was filtered and washed with acetone and diethyl ether to afford a yield of 86%. The cadmium analogue **5** was obtained in 70% yield by the same procedure except that Cd(OAc)$_2$ replaced the Mn(OAc)$_2$. The zinc polymer **6** was synthesized in 60% yield by combining **2**, Zn(ClO$_4$)$_2$, and NEt$_3$ (molar ratio 1:0.6:1) in DMSO and heating to 70°C for 10 days. The synthesis of **7** was achieved in 78% yield by combining **1** or **2** with Mn(OAc)$_2$ and excess 4,4′-bipyridine in DMSO (70°C, 13 h). Finally, it may be noted that the manganese polymer **4** was also obtained in good yield (73%) by exposing a DMSO solution of **2** to room light for several days.

Characterization of polymers **4**–**7**: For **4**: IR (DMSO): $\tilde{v}_{CO} = 1997$ (s), 1915 (s) cm$^{-1}$; IR (KBr): $\tilde{v}_{CO} = 2021$ (s), 1945 (s), 1566 (s), 1521 (s), 1016 (m) cm$^{-1}$; elemental analysis calcd (%) for C$_{18}$H$_8$Mn$_3$O$_{10}$·(DMSO)$_2$: C 37.46, H 2.86, S 9.09; found: C 37.60, H 2.74, S 8.92. For **5**: IR (DMSO): $\tilde{v}_{CO} = 1997$ (s), 1918 (s) cm$^{-1}$; IR (KBr): $\tilde{v}_{CO} = 2020$ (s), 1948 (s), 1559 (s), 1519 (s), 1010 (m) cm$^{-1}$; $^1$H NMR ([D$_6$]DMSO): $\delta = 4.83$ (br, 4H); elemental analysis calcd (%) for C$_{18}$H$_8$Mn$_2$CdO$_{10}$·(DMSO)$_2$: C 34.64, H 2.64, S 8.41; found: C 34.22, H 2.34, S 7.15. For **6**: IR (DMSO): $\tilde{v}_{CO} = 1997$ (s), 1917 (s) cm$^{-1}$; IR (KBr): $\tilde{v}_{CO} = 2024$ (s), 1945 (s), 1559 (s), 1513 (s) cm$^{-1}$; $^1$H NMR ([D$_6$]DMSO): $\delta = 4.78$ (br, 4H); elemental analysis calcd (%) for C$_{18}$H$_8$Mn$_2$ZnO$_{10}$: C 38.64, H 1.44; found: C 37.45, H 1.37. For **7**·2 DMSO: IR (DMSO): $\tilde{v}_{CO} = 1998$ (s), 1918 (s) cm$^{-1}$; IR (KBr): $\tilde{v}_{CO} = 2021$ (s), 1957 (s), 1931 (s), 1603 (w), 1566 (s), 1520 (s), 1058 (m) cm$^{-1}$; elemental analysis calcd (%) for C$_{32}$H$_{28}$Mn$_3$N$_2$O$_{12}$S$_2$: C 44.61, H 3.28, N 3.25, S 7.44; found: C 43.73, H 2.98, N 2.84, S 7.42.

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[22] X-ray structural analysis of **4**–**7**. Crystals of **4**–**7** suitable for X-ray studies were grown from DMSO solutions. In all cases, X-ray data collection with Mo$_{K\alpha}$ radiation was carried out at 298 K using a Siemens P4 diffractometer equipped with a CCD area detector.

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# A Large Dendritic Multiporphyrin Array as a Mimic of the Bacterial Light-Harvesting Antenna Complex: Molecular Design of an Efficient Energy Funnel for Visible Photons**

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Photosynthesis is triggered by the absorption of a photon by the light-harvesting antenna system, which has a large absorption cross-section. This process is followed by a rapid and efficient transfer of the excitation energy to the reaction center, where conversion of solar energy into chemical potentials in the form of a charge-separated state takes place.[1, 2] To mimic the natural photosynthetic systems, artificial light-harvesting antennae consisting of many porphyrin units linked through covalent[3] and noncovalent[4] bonds have been synthesized which can provide a large absorption cross-section to capture dilute photons. However, utilization of the light energy requires further molecular design to realize a long-range vectorial transfer of the excitation energy to a designated point. An efficient cooperation of chromophore units is essential if this is to be achieved. Such a molecular design could be inspired by the successful crystal-structure analysis of the light-harvesting antenna complex (LH2) from purple photosynthetic bacterium *Rhodopseudomonas acidophila* strain 10050, where highly efficient light-driven energy migration and transfer are realized by the wheel-like arrays of a large number of bacteriochlorophyll *a* (Bchl *a*) units.[5]

Recently, dendritic architectures have attracted attention as potential scaffolds for the incorporation of many light-absorbing units to enable the efficient capturing of photons.[6] Herein we report on a designed large multiporphyrin array $(7P_{Zn})_4P_{FB}$[7] consisting of four dendritic wedges of a zinc porphyrin heptamer $(7P_{Zn})$ as the energy-donating units which are anchored by a focal free-base porphyrin unit $(P_{FB})$ which functions as the energy acceptor. This star-shaped dendritic macromolecule is intended to mimic the unique morphology of the wheel-like chromophore array in LH2, and is expected to operate as an efficient energy funnel for visible

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