

ACCOUNTS of CHEMICAL RESEARCH®

JANUARY 2004

Registered in U.S. Patent and Trademark Office; Copyright 2004 by the American Chemical Society

Supramolecular Metal–Organometallic Coordination Networks Based on Quinonoid π -Complexes

MOONHYUN OH, GENE B. CARPENTER, AND
DWIGHT A. SWEIGART*Department of Chemistry, Brown University,
Providence, Rhode Island 02912

Received June 23, 2003

ABSTRACT

The use of organometallic π -complexes in the coordination-directed self-assembly of polymeric structures is a new area with many potential applications. Supramolecular metal–organometallic coordination networks (MOMNs), which are described herein, consist of metal ion or metal cluster nodes connected by bifunctional “organometallogligands” that serve as spacers. The organometallogligand utilized in this work is the stable anionic complex (η^4 -benzoquinone) $\text{Mn}(\text{CO})_3^-$ (*p*-QMTC), which binds through both quinone oxygen atoms to generate MOMNs having both backbone and pendant metal sites. In many cases the MOMNs are obtained as neutral and thermally stable solids, with molecular structures that depend on the geometrical and electronic requirements of the metal nodes, the solvent, and the presence of organic spacers. Redox-active quinone-based organometallic π -complexes permit the construction of an impressive range of coordination network architectures and hold much promise for the development of functional materials.

Introduction

Self-assembly of modular components into supramolecular nanostructures is the basis for one of the most active and important areas of chemical research.¹ The intermodular molecular recognition events implicit in the formation of nanostructure architectures can range from

weak to fairly strong, the most common of these interactions being hydrogen-bonding, π – π stacking, and metal–ligand bond formation. The use of transition metals in coordination-directed self-assembly has been an especially active area. The resultant metal–organic coordination networks (MONs) can be finite (triangles, squares, etc.)² or infinite (polymeric).^{3–5} Figure 1 provides a representation of a one-dimensional polymeric MON consisting of metal nodes connected by bifunctional organic ligand spacers or linkers. Of course, this pattern can be extended to two and three dimensions. The nodes in most MONs are single metal ions, and the spacers are simple multifunctional organic ligands, usually with pyridine or carboxylate donor sites. However, more complex multimetallic units, termed secondary building units (SBUs), can also function as nodes. Good examples of these are provided by the porous networks obtained by linking together metal carboxylate clusters.⁶

The driving force behind work with coordination networks is the desire to fabricate materials that have applications in areas such as catalysis, guest–host chemistry, optics, and magnetics. A large number of transition metal-based MONs have been reported, and the emphasis is now focused on the synthesis of *functional* networks. In turn, this requires the ability to control or predict the network architectures that obtain from the self-assembly process. Thus, *rational design* is a central, if elusive, goal

* Corresponding author.

Gene B. Carpenter received a B.A. degree from the University of Louisville and a Ph.D. from Harvard University. He was an NRC Postdoctoral Fellow at California Institute of Technology before joining the faculty of Brown University in 1949, where he has remained except for sabbatical leaves at Leeds, Groningen, Zagreb, Göttingen, Canterbury (New Zealand), and Oak Ridge National Laboratory. He has been Professor Emeritus of Chemistry since 1988, but continues to be active in the X-ray crystallography of small molecules, especially organometallic compounds.

Dwight A. Sweigart did undergraduate, graduate, and postdoctoral work at Franklin & Marshall College, Northwestern University, and Oxford University, respectively. He joined the faculty of Brown University in 1980. His research has centered on organometallic and metalloporphyrin chemistry, with an emphasis on electrochemistry, chemical dynamics, bond activations, and supramolecular coordination networks. Prof. Sweigart has been an associate editor of *Organometallics* since 1997.

Moonhyun Oh received B.S. and M.S. degrees in chemistry from Sogang University in 1995 and 1997. He earned a Ph.D. in inorganic chemistry in 2003 from Brown University, where he worked with D. A. Sweigart on the self-assembly of supramolecular metal–organometallic coordination networks. Dr. Oh currently has a postdoctoral appointment with C. A. Mirkin at Northwestern University.

in this area of supramolecular chemistry. The difficulty in predicting structure (hence function) can often be traced to the existence of supramolecular isomers⁴ and the simultaneous presence of two or more interpenetrating networks in the solid.

In the context of coordination networks, we reasoned that the role of the spacer or linker could be provided not only by organic ligands to generate MONs, but also by appropriate *organometallic* π -complexes that have the ability to function as multifunctional ligands (“organometallogligands”) to afford metal–organometallic coordination networks (MOMNs). Figure 1 illustrates the essential difference between the two types of networks for a one-dimensional system. The unique aspect of the MOMN

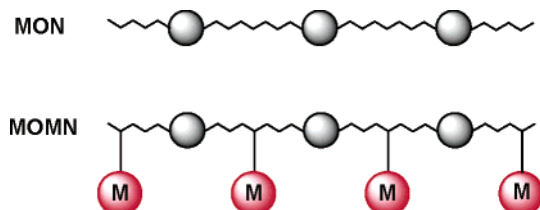


FIGURE 1. One-dimensional coordination networks consisting of metal nodes (in gray) connected by organic spacers to give MONs, or connected by organometallic spacers to give MOMNs.

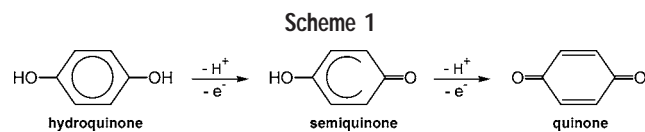
motif is the presence of metals at both backbone and pendant sites. Organometallic networks based on hydrogen-bonding interactions are well known,⁷ as are polymers containing organometallic fragments in the main propagation chain (e.g., polymetalloenes and polyacetylenes).⁸ These systems, however, are fundamentally different from the supramolecular organometallic *coordination* networks (MOMNs) formed by the self-assembly of metal–ligand bonds as described herein.

The utilization of organometallic spacers in coordination networks may lead to interesting and significant applications. From the start, it is obvious that MOMNs offer the possibility of metal–metal interactions not available in corresponding MONs, and this may well be reflected in the magnetic and electronic properties of the former. More generally, the use of organometallogligands in principle allows for the incorporation of a wide variety of spacer types that have no organic analogue, and this may offer novel applications in catalysis and guest–host chemistry. We anticipate that the synthesis of MOMNs will generally require the direct reaction of intact organometallogligand spacers, and will not normally be available by “coordinating” metal fragments to the organic spacers in MONs. Furthermore, the results presented herein with quinonoid systems suggests that MOMN syntheses may be subject to rational design and control to a significant extent (vide infra). Thus, we conclude that MOMNs are a general class of materials that clearly merit development and careful investigation.

Quinonoid π -Complexes

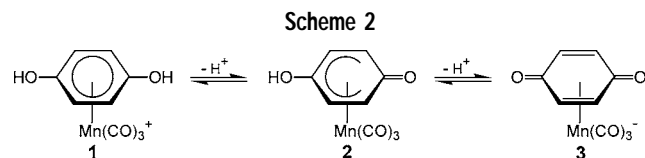
The ability to coordinate a metal to the π -system in hydroquinone and related molecules constitutes the basis

for our work in developing MOMNs. Substituted hydroquinones are fundamentally important in mediating reversible electron and proton transfers in biological systems, as indicated in Scheme 1.⁹ One would anticipate

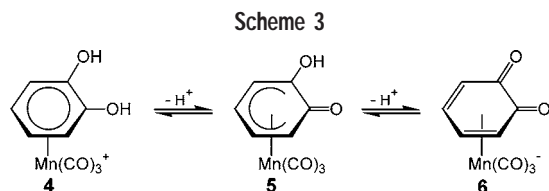


that the attachment of a metal fragment to the π -system would significantly influence the proton and electron transfers occurring in the formation of the semiquinone and quinone oxidation products. It is well known¹⁰ that the members of this series generally σ -bond to metals through the oxygen atoms rather than through the carbocyclic π -system, and, correspondingly, there are only a couple of examples of π -bonded hydroquinone complexes.^{11,12} In 1996, we reported¹² that manganese tricarbonyl transfer reagents of the type (η^6 -naphthalene) $Mn(CO)_3^+$ afford a facile, high-yield route to the *thermally stable* π -complex (η^6 -hydroquinone) $Mn(CO)_3^+$ (**1**), as well as the *o*-hydroquinone (catechol) and *m*-hydroquinone (resorcinol) analogues. It was felt necessary to verify the proposed η^6 -structure for **1** by X-ray diffraction, but repeated attempts to grow X-ray-quality crystals of **[1]BF₄** were initially unsuccessful. However, an acetone solution of **[1]BF₄**, containing a small amount of HBF₄ to suppress proton dissociation (vide infra), deposited high-quality crystals over a period of months at -20 °C. X-ray analysis verified the proposed η^6 -bonding and further disclosed that the anion in the crystal was not BF₄⁻, but rather SiF₆²⁻. The change in anion had resulted from the action of HBF₄ on the glass container to afford a continuous supply of SiF₆²⁻ anions at very low concentration, a condition required for crystal growth because **[1]₂SiF₆** is virtually insoluble in acetone. Four of the six F atoms in each SiF₆²⁻ were found to be strongly hydrogen bonded to the hydroquinone –OH groups, thus accounting for the insolubility.

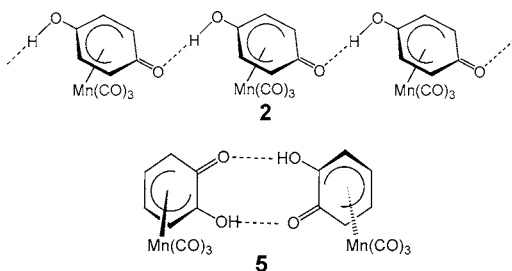
The key to the utility of **1** in the construction of MOMNs is the electrophilic activation provided by the metal fragment, which results in facile reversible deprotonation of the –OH groups to afford the η^5 -semiquinone and η^4 -quinone complexes according to Scheme 2. An



additional factor that turns out to be important is the -1 charge on the η^4 -quinone complex **3** (vide infra). Although the sequence **1** \leftrightarrow **2** \leftrightarrow **3** in Scheme 2 can be viewed as simple deprotonations, the analogy to the proton and electron transfers occurring with free quinones is evident if it is considered that each proton loss is accompanied by electron transfer to the metal, which acts as an internal oxidizing agent or electron sink. Similar reasoning holds

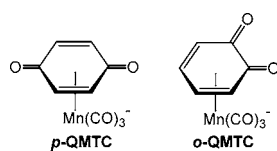


for the catechol analogues shown in Scheme 3. The neutral η^5 -semiquinone complex **2** was found to exist in linear polymeric arrays with the structure dictated by strong intermolecular hydrogen bonding.¹³ By comparison, and as expected, the catechol analogue **5** exists as discrete hydrogen-bonded dimers. The hydrogen-bonding interactions were shown from X-ray structural data to be very strong, e.g., the O...O donor–acceptor distance in **2** is just 2.47 Å. Furthermore, ¹H and ¹³C NMR spectra indicated that the hydrogen-bonding in **2** and **5** is not only strong but also dynamic so that, for example, all four ring hydrogens in **2** are equivalent on the NMR time scale.

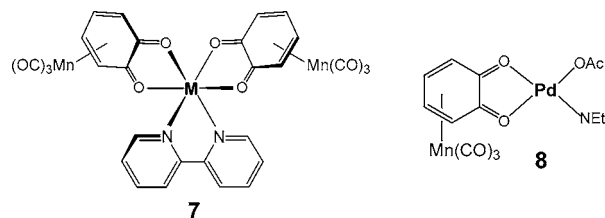


o-Quinonoid Organometallogligands

The anionic *p*- and *o*-quinone manganese tricarbonyl complexes **3** and **6**, obtained from double deprotonation of the corresponding hydroquinone and catechol complexes, can function as bifunctional ligands (“organometallogligands”) in the presence of appropriate metal ions by σ -bonding through the oxygen atoms. These organometallogligands we call *p*-QMTC and *o*-QMTC, respectively.



The chelating ligand *o*-QMTC readily reacts with divalent metal ions to afford neutral monomeric complexes such as $M(o\text{-QMTC})_2(L_2)$ ($M = \text{Mn, Cd, Co}$; $L_2 = \text{phen, 2,2'}$ -bipy, 2 py). Complexes containing deprotonated catechol σ -bonded to metals via the oxygens have long been known¹⁰ to exhibit redox tautomerization due to facile electron transfer between the metal and the catecholate ligand. In effect, this means that the ligand system can easily shuttle between catecholate, semiquinone, or quinone formulations, which is the reason that quinone-type ligands are described as “non-innocent”. There is good evidence that such tautomerization is enhanced in complexes $M(o\text{-QMTC})_2(L_2)$ (e.g., **7**), with the $\text{Mn}(\text{CO})_3$ moiety acting as an electron sink in response to variations in electron density accompanying changes in metal oxidation state or in ligand L_2 .¹⁴ This facile electron-transfer behavior



shown by π -bonded quinone complexes could have novel applications in catalysis, particularly when the substrate binds directly to the σ -bonded metal and thus experiences the self-adjusting electronic environment. To this end, we prepared and characterized the Pd(II) complex **8**, which features two weakly held monodentate ligands and an electron-density-modulating quinone complex.¹⁴ It is anticipated that the dynamic electronic environment at the palladium could self-optimize during the catalytic steps due to the combined influence of the quinone ligand and the redox-active $\text{Mn}(\text{CO})_3$ moiety. In view of the prominence of palladium in catalysis, such an application of quinonoid organometallogligands could have considerable utility.

Complex **7** ($M = \text{Mn, Co, Cd}$) was found¹⁵ to crystallize in an interesting two-dimensional network featuring two types of π - π stacking interactions (Figure 2). The bipyridine ligands in **7** interdigitate via π - π stacking to generate one-dimensional arrays, which self-assemble into a two-dimensional structure via additional pairwise π -stacking interactions involving one-half of the coordinated benzoquinone ligands. One can view the overall structure as consisting of pairwise units shown in Figure 2, which subsequently undergo interdigitation via the bipyridines to generate the observed architecture. A consequence of

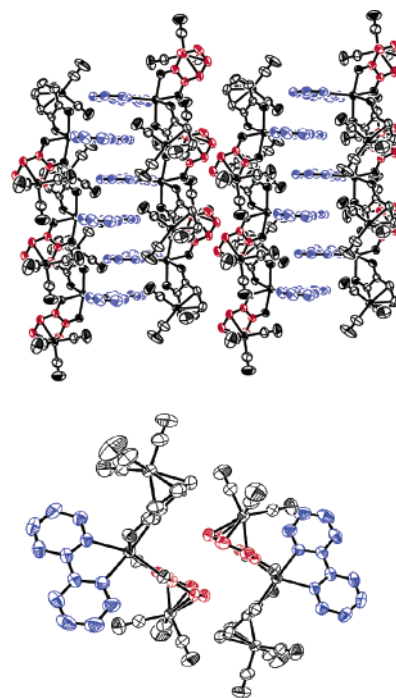
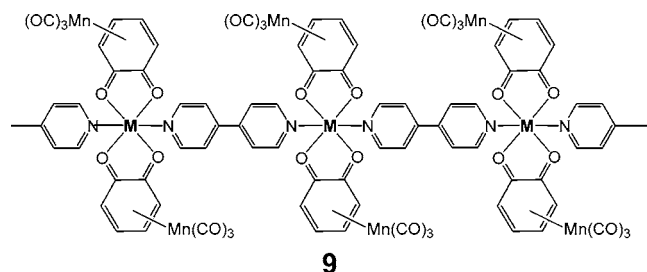


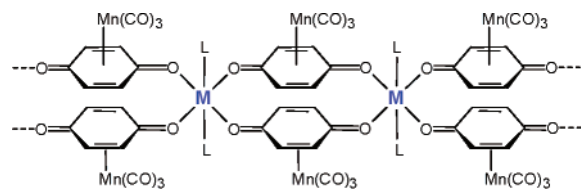
FIGURE 2. Two ORTEP views of $\text{Co}(o\text{-QMTC})_2(4,4'\text{-bipy})$. The interdigitated bipyridine ligands are in blue, and the quinone ligands participating in π -interactions are in red. (Top) Full 2D structure; (bottom) a single pairwise interaction.

the quinone–quinone stacking is the presence of two types of $\text{Mn}(\text{CO})_3$ moieties, one bonded to a π -stacked quinone and one not so bonded. Coordination networks (MOMNs) based on $\text{M}(o\text{-QMTC})_2$ units can be made by using linear bifunctional spacers such as 4,4'-bipyridine (e.g., polymer **9**).¹⁴



p-Quinonoid Metal–Organometallic Coordination Networks

Simple One-Dimensional MOMNs. We realized in 2000 that the *p*-benzoquinone complex *p*-QMTC could serve as a bifunctional organometallic ligand in the presence of appropriate metal ions by σ -bonding through both oxygen atoms.¹⁶ The 180° disposition of the oxygen donors meant that polymers were more likely to be formed than were simple discrete molecules. Additionally, the negative charge on the *p*-QMTC ligand could be utilized to balance the positive charge of the metal ions used as nodes, thus resulting in the formation of *neutral* coordination networks. The consequent absence of counterions to clog pores and channels could be a distinct advantage. The key to the synthesis of MOMNs having *p*-QMTC spacers was finding the right conditions for the self-assembly process to occur before precipitation of oligomers. Warm DMSO proved to be an excellent medium for the high-yield synthesis of *crystalline* polymers. It turned out to be



especially convenient to start with the η^5 -semiquinone complex **2** dissolved in DMSO and then add a DMSO solution of a divalent metal acetate. It was found¹⁶ that the acetate anion serves as a base to deprotonate the semiquinone complex and generate the desired *p*-QMTC anion in situ. Subsequently, coordination of the oxygen atoms in *p*-QMTC to the added metal ions resulted in the growth of 1D “string” MOMNs (**10**, $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cd}$). These materials are neutral polymers that feature octahedral nodes bonded to four *p*-QMTC spacers and two additional axial ligands. The solvent DMSO functions as the axial ligands unless another ligand, e.g., pyridine, is present. As a typical example, the structure of MOMN $[\text{Cd}(\text{p-QMTC})_2(\text{DMSO})_2]_\infty$ is illustrated in Figure 3. Interestingly, the quinone rings that bridge each pair of nodes

are partially eclipsed, with a separation of only 3.3 Å, indicative of significant π – π stabilization. The nodes are separated by ca. 9 Å. The organometallic ligand in **10** adopts a 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 $\text{Mn}(\text{CO})_3$ unit. In contrast, the quinonoid diene carbon atoms are strongly bonded to the $\text{Mn}(\text{CO})_3$, so that the overall structure is best described as an η^4 -quinone.

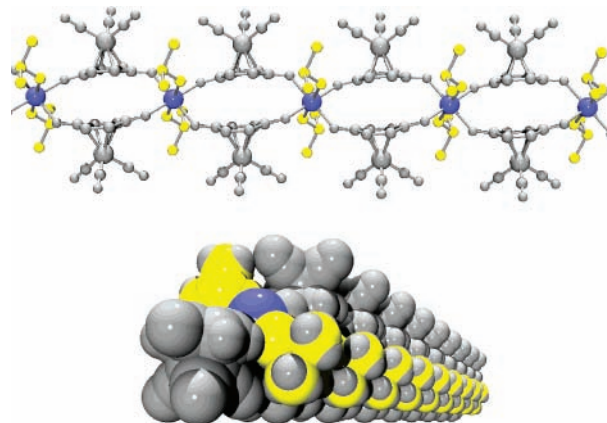


FIGURE 3. Structure and packing diagram for linear 1D MOMN $[\text{Cd}(\text{p-QMTC})_2(\text{DMSO})_2]_\infty$. The cadmium nodes are blue, and the axial DMSO ligands are shown in yellow.

Since the initial synthesis of 1D quinonoid MOMNs, we have found that the *p*-QMTC organometallic ligand can be used for the synthesis of a quite extraordinary array of one-, two-, and three-dimensional polymers. As illustrated in the discussions below, the exact architecture obtained depends on the geometrical requirements of the added metal ion, on the solvent, and on the presence of added organic ligands that function as additional spacers. It was found that in many cases it is possible to predesign a desired structure. This is a significant feature of our work, since the ability to predict and/or control structure has been a major goal in supramolecular chemistry, with the ultimate objective being the rational synthesis of materials having predesigned structures.

An examination of the structure of **10** suggests two obvious ways in which the chemical and physical properties can be tuned: (1) replacement of the bridging metal and (2) replacement of the axial ligand. Additionally, solvent changes and the presence of substituents on the *p*-QMTC spacer are other variables. Dealing first with axial ligand variation, it was found that the 1D strings in **10** could be linked together by having 4,4'-bipyridine present in the reaction mixture.¹⁷ The resulting neutral 2D systems (**11**) were structurally characterized for $\text{M} = \text{Mn}$ and Ni . Figure 4 shows the structural details. The rectangular grids in **11** have dimensions of approximately 10 Å × 12 Å and contain one molecule of DMSO within each rectangular box, with two additional DMSO molecules per box being located between adjacent 2D layers in the solid. Suspending **11** in CD_2Cl_2 at room temperature for 2 h resulted in the complete and quantitative loss of all three DMSO

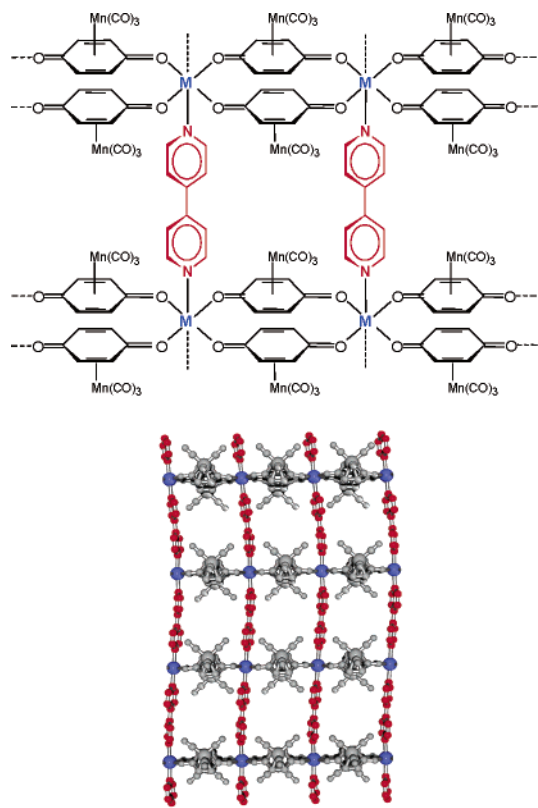


FIGURE 4. Structure of one layer of 2D MOMN $[M(p\text{-QMTC})_2(4,4'\text{-bipy})]_\infty$ (**11**, $M = \text{Mn, Ni}$). DMSO guest molecules are not shown.

molecules. Significantly, X-ray diffraction indicated that this process occurs without affecting the crystallinity of **11**.¹⁷

Supramolecular Isomers. The existence of isomeric supramolecular motifs may occur for kinetic or thermodynamic reasons.⁴ Several similar-energy isomers may exist that do not easily interconvert, so the one formed is dictated by mechanistic (kinetic) factors. Often, the available pathways are dictated by the presence of guest molecules that serve as templates for self-assembly. Alternatively, other factors may dictate which isomer prevails. An excellent illustration of this is provided by the self-assembly of *p*-QMTC and metal ions in the presence of 4,4'-bipyridine. It was pointed out above that the 2D MOMN **11** is readily formed by using 4,4'-bipy to “tie” together the 1D string arrays (**10**). A consideration of the bond lengths and angles in the 1D strings indicates that an energetically reasonable alternative is the 2D “grid” motif pictured in Figure 5. Just as the 1D string combines with a bifunctional organic spacer to afford a 2D MOMN, the 2D grid should combine to give an analogous 3D MOMN. It was found¹⁷ that the prevailing quinonoid network (1D string or 2D grid) could be *predetermined* by controlling the metal ion concentration. Thus, the former is favored at low metal ion concentrations, while higher concentrations favor the 2D grid quinonoid network. Mechanistically, it seems likely that the 2D grid predominates at higher concentrations because the *p*-QMTC binding sites are trapped before assembly into the 1D string can occur. It is therefore concluded that the

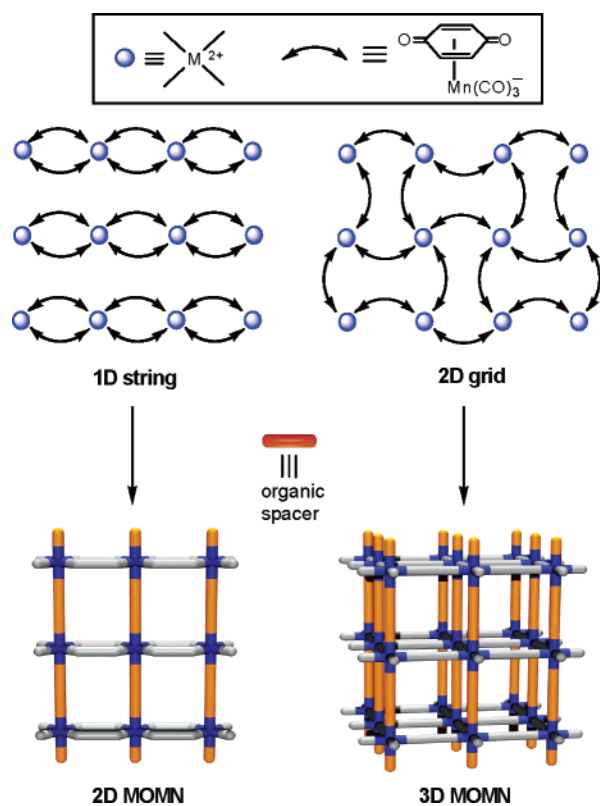


FIGURE 5. Assembly of metal ion nodes and *p*-QMTC spacers into 1D string or 2D grid quinonoid networks, which then combine with a bifunctional organic spacer to afford 2D or 3D MOMNs, respectively.

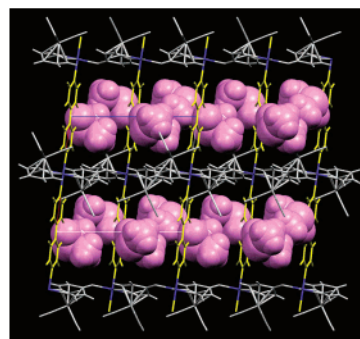
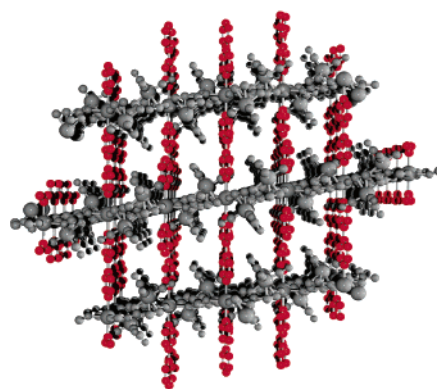


FIGURE 6. (Top) Structure of MOMN **12**, consisting of 2D grid quinonoid planes linked by bipyridine spacers (red). (Bottom) Nanoporous channels in **12** filled with two DMSO molecules per molecular box, as illustrated.

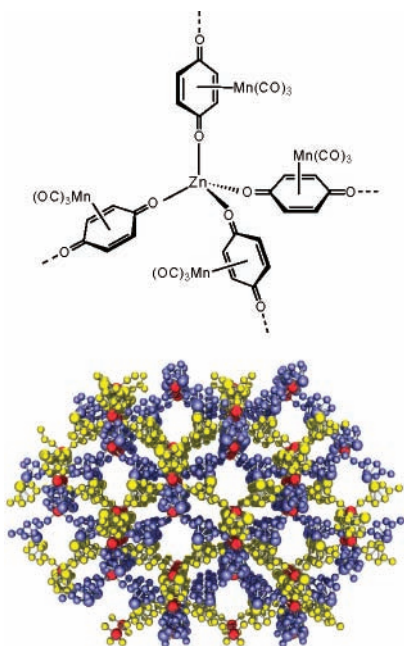


FIGURE 7. Structure of MOMN **13**, consisting of tetrahedral Zn(II) nodes (red) and two interpenetrating diamondoid quinonoid networks (blue, yellow).

isomer distribution is dictated not by the usual templating with a guest, but by variation of metal node concentration.

When 4,4'-bipyridine is present under conditions that promote the quinonoid 2D grid network, subsequent linking of the planes occurs to afford the 3D MOMN $[M(p\text{-QMTC})_2(4,4'\text{-bipy})]_\infty$ (**12**). This interesting polymer contains rectangular pores of dimension ca. $6 \text{ \AA} \times 12 \text{ \AA}$, as shown in Figure 6. The rectangular channels are filled with solvent, such that there are two DMSO molecules per

molecular “box”. MOMN **12**, which was structurally characterized by X-ray diffraction for $M = \text{Mn}$ and Co , is thermally stable at room temperature.¹⁶ By variation of the bifunctional spacer, the quinonoid networks in this material could provide the basis for the synthesis of polymers with pores that offer variable sizes and variable chemical environments for potential guests. The attachment of a redox switch to the spacer may provide a way for addressing the redox-active quinonoid planes.

Tetrahedral Systems. The self-assembly of $p\text{-QMTC}$ in the presence of a bridging metal that prefers tetrahedral rather than octahedral geometry would be expected to afford a MOMN different from any of those described above. This possibility was explored using Zn(II) in DMSO, which produced a MOMN with the formula $[\text{Zn}(p\text{-QMTC})_2]_\infty$ (**13**). As illustrated in Figure 7, the geometry around the zinc node is indeed tetrahedral. Polymer **13** is a dense material consisting of two interpenetrating diamondoid networks, with no solvent incorporated.¹⁶

In the reaction of $p\text{-QMTC}$ with Mn^{2+} and Co^{2+} , it was found that changing from DMSO to the less coordinating solvent, MeOH, leads to the formation of 3D diamondoid structures in which the metal ion nodes adopt tetrahedral rather than octahedral coordination.¹⁸ The polymers $[\text{Co}(p\text{-QMTC})_2]_\infty$ and $[\text{Mn}(p\text{-QMTC})_2]_\infty$ obtained from MeOH possess structures that are virtually identical to that found for $[\text{Zn}(p\text{-QMTC})_2]_\infty$. For Mn^{2+} and Co^{2+} , it is concluded that switching the solvent from DMSO to MeOH results in a fundamental change in polymer architecture that is triggered by a change from octahedral to tetrahedral coordination at the divalent metal ion node. This change in geometry, which is likely due to the generally weaker coordinating ability of MeOH compared to DMSO, is

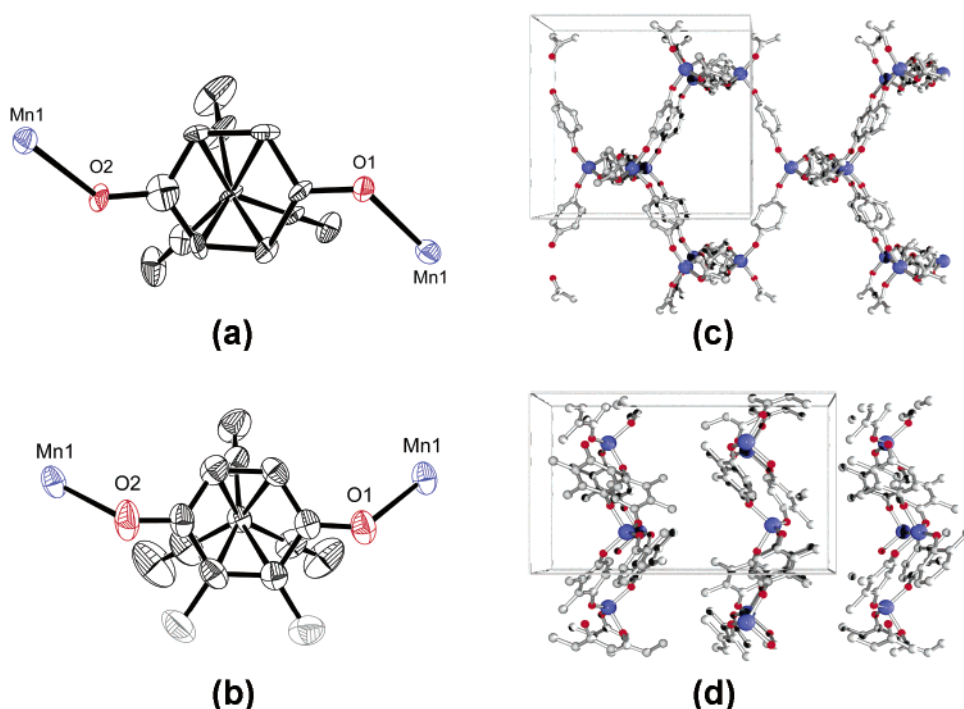


FIGURE 8. Bonding of the quinone oxygens to tetrahedral Mn(II) nodes in (a) $[\text{Mn}(p\text{-QMTC})_2]_\infty$ and (b) $[\text{Mn}(2,3\text{-Me}_2\text{QMTC})_2]_\infty$. The change in lone pair bonding from trans to cis is accompanied by a structural change in the MOMNs from (c) 3D diamondoid to (d) 2D rhombohedral.

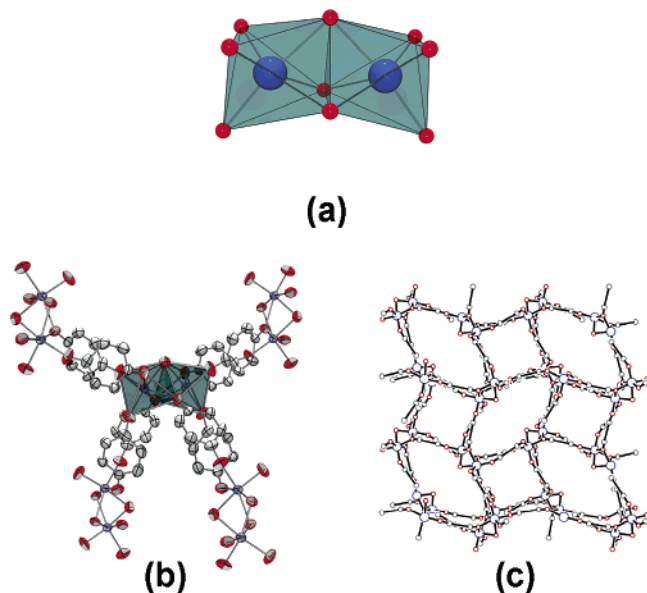


FIGURE 9. (a) Cartoon of the dimanganese SBU in MOMN $[\text{Mn}_2-(p\text{-QMTC})_4(\text{DMSO})]_\infty$. (b) The tetrahedral disposition of the SBUs. (c) The overall diamondoid architecture.

suggestive of a potentially useful methodology for controlling and predicting coordination network architecture. In contrast to the behavior seen with Mn^{2+} and Co^{2+} , the MOMN obtained with Zn^{2+} has the tetrahedral diamondoid structure whether the solvent is MeOH or DMSO. This fact reflects the greater tendency for Zn^{2+} to assume a tetrahedral geometry.

The benzoquinone rings in $[\text{M}(p\text{-QMTC})_2]_\infty$ ($\text{M} = \text{Mn}, \text{Co}, \text{Zn}$) adopt a slightly bowed conformation, with the oxygen atoms being bent about 10° out of the carbocyclic diene plane. Figure 8 gives a view normal to one of the quinone rings in $[\text{Mn}(p\text{-QMTC})_2]_\infty$. An essentially identical picture holds for the cobalt and zinc analogues. It may be seen in Figure 8a that the bonding from the benzoquinone to the metal nodes occurs in a trans manner from the oxygen lone pairs, so the lone pairs appear to be stereochemically active. In contrast, crystal structure analysis of coordination polymers $[\text{M}(2,3\text{-Me}_2\text{QMTC})_2]_\infty$ ($\text{M} = \text{Mn}, \text{Zn}$) grown in MeOH or EtOH solvent revealed that it is the lone pairs projecting away from the methyls that bind to the nodes, resulting in the cis arrangement illustrated in Figure 8b.¹⁸ Presumably, this bonding pattern is dictated by the steric requirements of the methyl substituents on the benzoquinone ring. The stereochemical switch from the trans to cis results in a concomitant change in the polymer architecture from a two-fold interpenetrated 3D diamondoid structure to a non-interpenetrated ruffled 2D rhombohedral grid (Figure 8). In spite of the trans-to-cis and diamondoid-to-rhomboidal structural changes, the metal nodes in $[\text{M}(2,3\text{-Me}_2\text{QMTC})_2]_\infty$ remain tetrahedrally bonded to the quinone oxygens, as typified by Figure 7.

Thus, it is concluded that a change in solvent and/or introduction of substituents on the carbocyclic ring in *p*-QMTC can have a profound effect on the architecture of the resulting coordination network. Significantly, these effects are predictable and may, therefore, find general

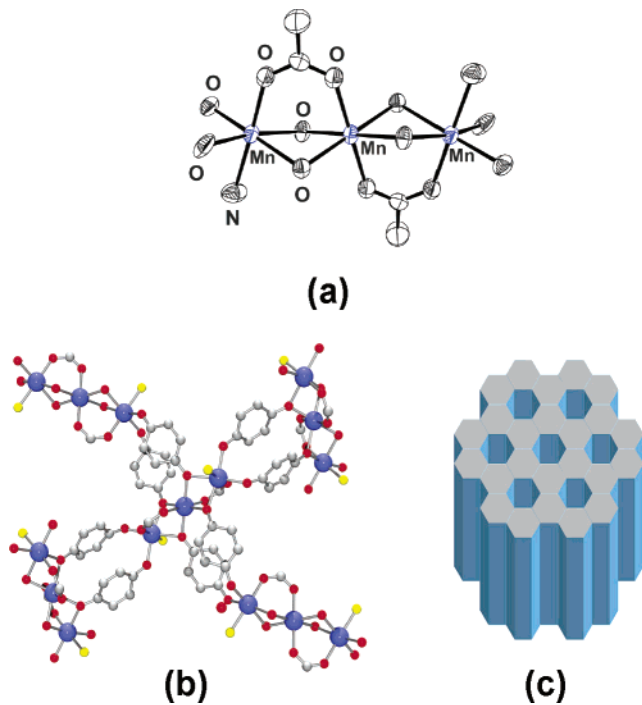


FIGURE 10. (a) ORTEP of the trimanganese SBU in MOMN 14. (b) The connectivity of the SBUs. (c) The overall honeycomb motif.

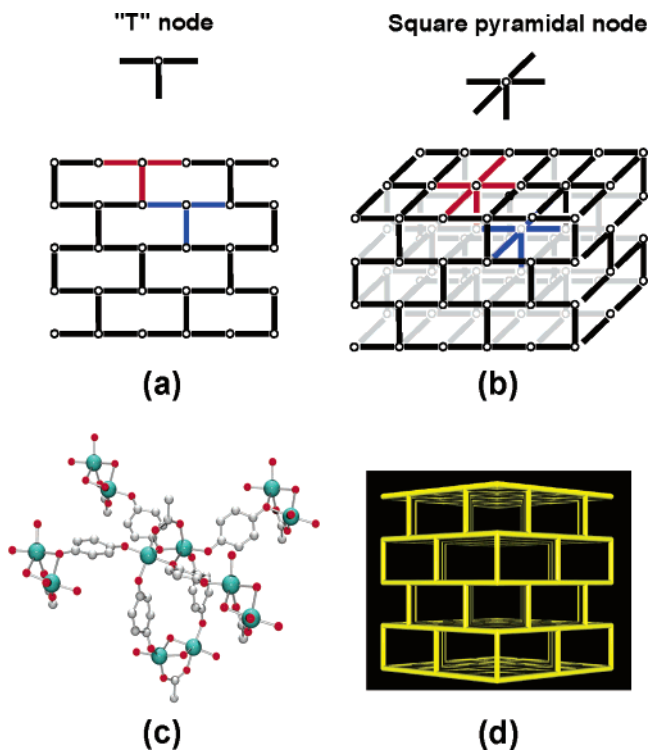


FIGURE 11. (a) Schematic representation of a 2D brick wall motif formed from T-shaped nodes. Changing the T-nodes to ones with square pyramidal connectivity generates a 3D brick structure (b). The reaction of copper acetate and *p*-QMTC produces MOMN 15, which has dicopper SBUs that link in a square pyramidal fashion (c) to generate the 3D brick structure (d).

utility in the controlled synthesis (rational design) of supramolecular coordination networks.

Systems with Secondary Building Units. The work described above involved MOMNs with nodes consisting

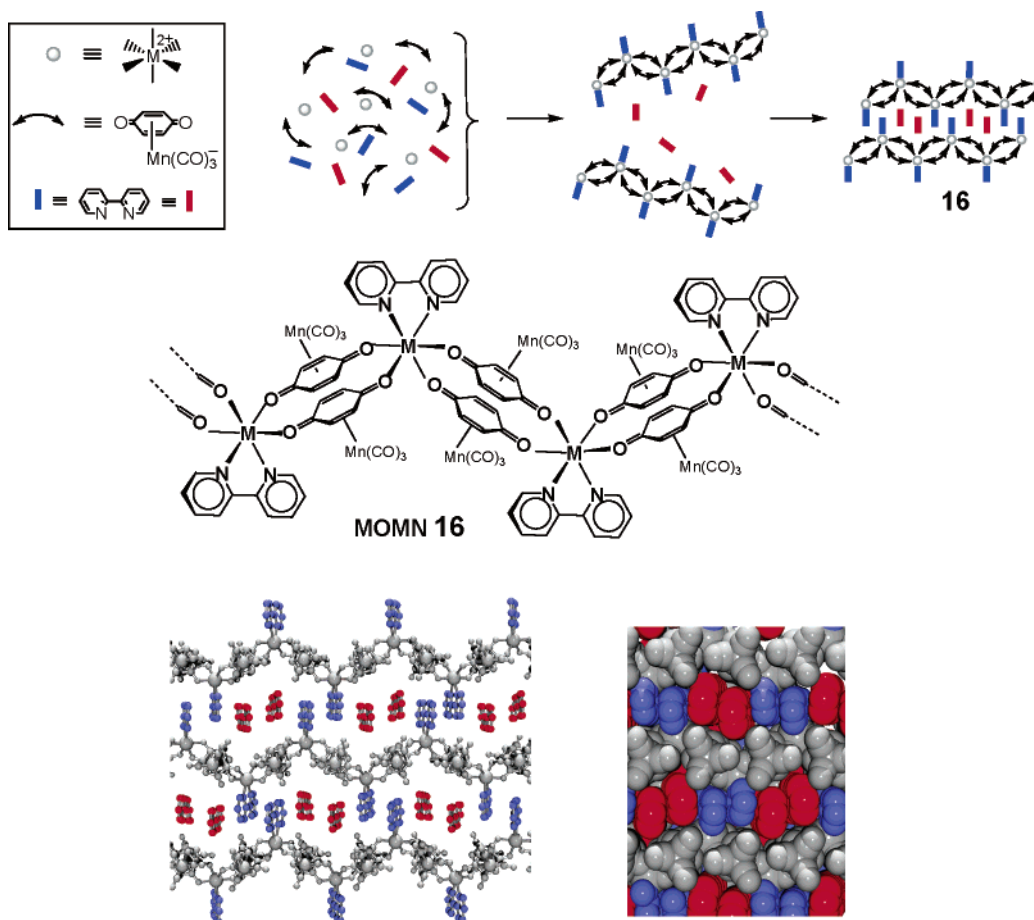


FIGURE 12. Self-assembly of *p*-QMTC and 2,2'-bipyridine into 1D networks that interdigitate via π – π stacking (blue) to generate MOMN 16, having " π -pockets" that bind free 2,2'-bipyridine (red).

of a single metal center. The use of *multimetallic* nodes offers the possibility of exciting new architectures, particularly high-porosity ones that may find applications in guest–host chemistry. In the realm of MON chemistry, nodes consisting of metal carboxylate clusters that function as "secondary building units" (SBUs) have been utilized in the construction of remarkably porous networks.⁶ We have recently found that under certain experimental conditions quinonoid MOMNs with organometallic SBUs can be synthesized. Thus, combining *p*-QMTC with Mn²⁺ in 1:1 DMSO–MeOH resulted in the slow generation of MOMN [Mn₂(*p*-QMTC)₄(DMSO)]_∞, which has the structure shown in Figure 9.¹⁹ The novel feature of the structure is the presence of dimanganese clusters that are held in place by quinone molecules that bridge the two metals from the same oxygen (Figure 9a). There is also a bridging DMSO ligand. The resultant network consists of organometallic clusters that interconnect via *p*-QMTC pairwise spacers. The basic SBU assembly possesses four-fold tetrahedral connectivity to adjacent SBUs to generate the 3D diamondoid network illustrated in Figure 9. The dimanganese SBU contains two slightly distorted octahedra of oxygen atoms around each Mn center with one triangular face shared. There are two types of *p*-QMTC spacers, one connecting to two Mn sites and another that connects to three Mn sites.

The reaction of *p*-QMTC and Mn²⁺ in methanol containing the organic spacer 4,4'-trimethylenedipyridine (tmbipy) gave MOMN 14, illustrated in Figure 10.¹⁴ In this case, the SBU consists of trimetallic units held together by both *p*-QMTC and acetate anions. Each metal in the trimanganese cluster has octahedral coordination, and the SBUs possess the four-fold connectivity shown in Figure 10b. The tmbipy molecule was found to act as a unidentate ligand, with the uncoordinated end of the molecule flexible (disordered). The resultant structure features a 3D honeycomb motif. The aim behind this work is the synthesis of materials with flexible pores that can self-adjust to accommodate available guests.

The reaction of *p*-QMTC and Cu(OAc)₂ in MeOH led to a fascinating result.²⁰ The MOMN generated (15) was found to possess a *three-dimensional* "brick wall" structure, which to our knowledge is an architecture unprecedented in the study of coordination polymers. Figure 11 illustrates how a 3D brick wall can be generated starting with T-shaped nodes that are connected in a linear fashion. The familiar 2D brick wall²¹ shown in Figure 11a is one of several observed motifs derivable from T-shaped nodes.⁴ Extension of the brick wall from 2D to 3D, as shown in Figure 11b, involves converting the T-shaped nodes to square pyramidal nodes possessing five-fold connectivity. MOMN 15 formed from *p*-QMTC and Cu-

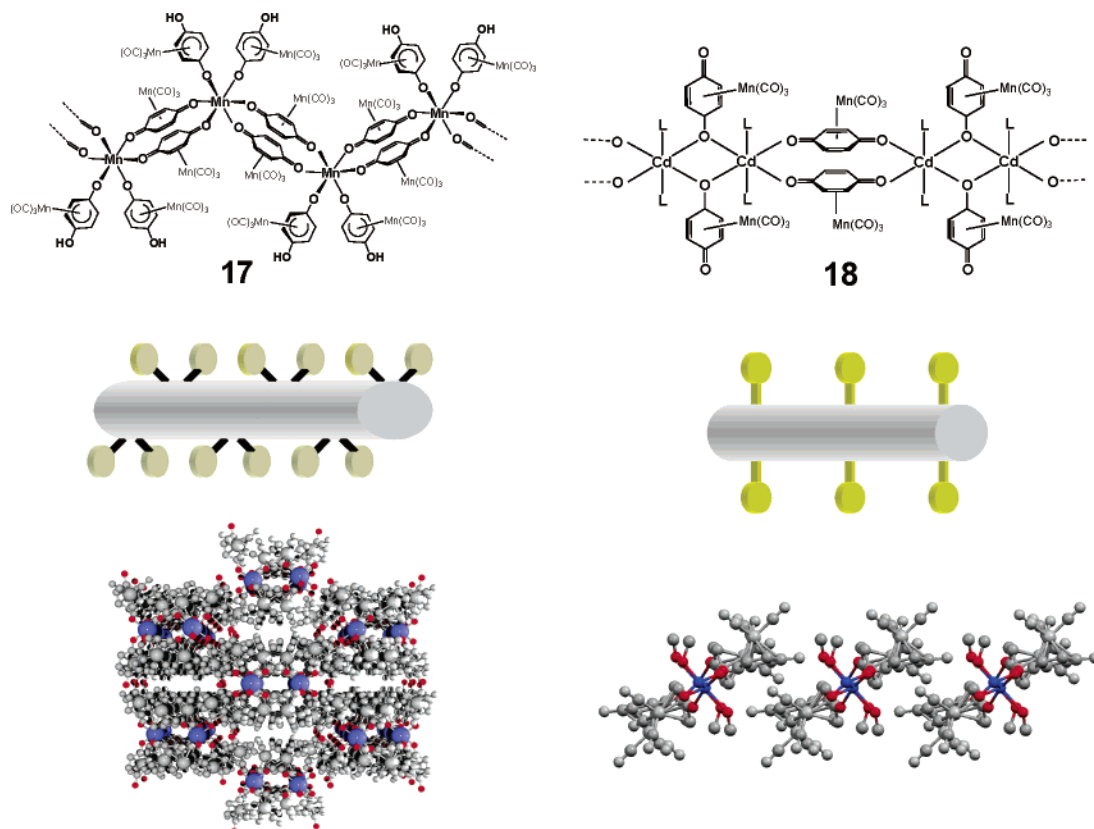


FIGURE 13. Structure of two 1D MOMNs that contain semiquinone (**17**) and quinone (**18**) “antennae” protruding from the network backbone. The antennae engage in interstrand π – π stacking in the solid state.

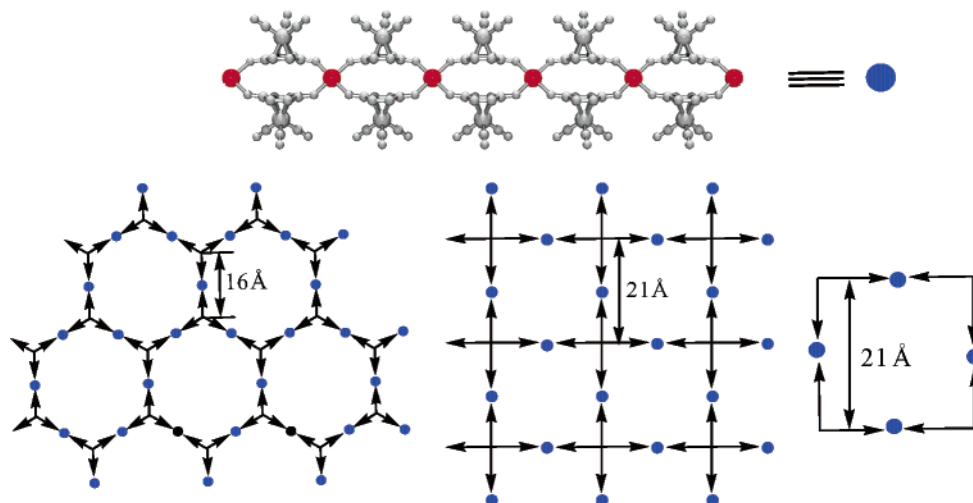


FIGURE 14. Hypothetical highly porous MOMNs consisting of quinonoid 1D string polymers as infinite SBUs and appropriate organic spacers.

(OAc)₂ consists of bimetallic nodes (SBUs) of formula $\text{Cu}_2(\mu\text{-CH}_3\text{CO}_2)^{3+}$, which are linked via linear *p*-QMTC spacers in the requisite square pyramidal geometry (Figure 11c). The resultant 3D structure, which has the molecular formula $[\text{Cu}_2(\textit{p}\text{-QMTC})_3(\mu\text{-CH}_3\text{CO}_2)]_\infty$, constitutes the previously unknown extended (3D) brick wall architecture illustrated in Figure 11d.

Novel Functional MOMN Systems. Using *p*-QMTC, several MOMNs were prepared and characterized that offer opportunities for further elaboration through the binding of suitable substrates to special sites in the polymer. For this reason, we term these *functional* MO-

MNs. In the reaction of *p*-QMTC and M^{2+} ($\text{M} = \text{Cd}, \text{Mn}$) in the presence of 2,2′-bipyridine, both nitrogens of the organic spacer are constrained to bind to the same metal node, and this led to formation of the 1D “zigzag” polymer **16** by the self-assembly process shown at the top of Figure 12.¹⁴ The crystal structures of the zigzag MOMNs revealed that the individual 1D polymer units interdigitate via π – π stacking of the 2,2′-bipyridine ligands. While π – π stacking is a well-known phenomenon,²² the structure of **16** is particularly interesting for two reasons. First, the interstrand metal nodes are linked via π – π stacking of the bipyridine rings, and this is likely to influence the tem-

perature at which magnetic ordering occurs in paramagnetic nodes (e.g., Mn^{2+}).²³ The second interesting feature of the π -stacked polymer is the inclusion of two “free” bipyridine molecules between each pair of coordinated bipyridines, resulting in a continuous π -stacking along the entire length of the polymer. It is possible that the “ π -pocket” in this or related MOMNs can be used to bind π -molecules of appropriate size other than free bipyridine, thereby offering potential applications.

When $\text{Mn}(\text{NO}_3)_2$ in MeOH was reacted with the η^5 -semiquinone complex **2**, a 1D zigzag polymer was generated that contains two semiquinone organometallogands bound in a cis manner to each Mn^{2+} node.¹⁴ The resultant MOMN **17** contains semiquinone moieties protruding from the central core, rather like antennae, that can be used for interstrand π - π stacking or binding to external electrophilic sites. As can be seen in Figure 13, the semiquinone “antennae” in each 1D unit of **17** π - π stacks with four other 1D units to form the motif shown at the bottom of the figure. It seems likely that the external semiquinone functionalities in **17** could be deprotonated and used for binding to metal acceptor sites. The equally interesting MOMN **18**, containing dicadmium SBUs with protruding quinone moieties, was formed from **2** and $\text{Cd}(\text{NO}_3)_2$ in MeOH. In this case, the quinone antennae repeat every 12 Å along the polymer chain (Figure 13). In the solid state, the protruding quinones in **18** π - π stack such that each 1D network interacts with two others.

Conclusions and Future Directions

The use of organometallics in coordination-directed self-assembly holds much promise for the synthesis of functional materials with useful applications. We have demonstrated the construction of supramolecular metal–organometallic networks (MOMNs) using π -bonded quinonoid complexes of manganese as “organometallogands”. Preliminary results indicate that the redox-active quinone-based complexes permit the construction of an impressive range of architectures. Further, it appears that the available architectures can be *rationally designed* on the basis of the coordination number, oxidation state, and geometrical requirements of the metallic nodes that link the organometallogands. The quinonoid coordination polymers may have novel applications that depend on anticipated facile electron-transfer behavior. For example, 3D networks such as MOMN **12** are being investigated as templates for nanowire construction. Extension of the quinonoid chemistry to include trivalent and tetravalent metal nodes like Fe(III) and Th(IV) may produce architectures with unusual porosities. Related to this is the exciting possibility of using 1D quinonoid strings such as **10** as infinite SBUs²⁴ in the synthesis of highly porous materials. With organic spacers of appropriate geometry, the large channel polymers shown in Figure 14 are predicted. In the absence of interpenetration, the dimensions indicated are inferred. Finally, it should be noted that the principles delineated in this report concerning the construction of MOMNs are very general and should be applicable to many types of organometallic systems.

In this context, the prospects for the utilization of organometallics in the construction of novel and useful supramolecular coordination networks are bright indeed.²⁵

Acknowledgment is made to donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (CHE-0308640) for support of this research.

References

- (1) (a) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995. (b) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, 2000.
- (2) (a) Philp, D.; Stoddart, J. F. Self-assembly in Natural and Unnatural Systems. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154–1196. (b) Holliday, B. J.; Mirkin, C. A. Strategies for the Construction of Supramolecular Compounds through Coordination Chemistry. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043. (c) Fujita, M. Molecular Paneling Through Metal-Directed Self-Assembly. *Struct. Bonding* **2000**, *96*, 177–201. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. Self-Assembly of Discrete Cyclic Nanostructures Mediated by Transition Metals. *Chem. Rev.* **2000**, *100*, 853–908.
- (3) (a) Robson, R. A net-based approach to coordination polymers. *J. Chem. Soc., Dalton Trans.* **2000**, 3735–3744. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Acc. Chem. Res.* **2001**, *34*, 319–330. (c) Desiraju, G. R. Chemistry beyond the molecule. *Nature* **2001**, *412*, 397–400. (d) Evans, O. R.; Lin, W. Crystal Engineering of NLO Materials Based on Metal-Organic Coordination Networks. *Acc. Chem. Res.* **2002**, *35*, 511–522.
- (4) Moulton, B.; Zaworotko, M. J. From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids. *Chem. Rev.* **2001**, *101*, 1629–1658.
- (5) (a) Biradha, K.; Fujita, M. A Springlike 3D-Coordination Network That Shrinks or Swells in a Crystal-to-Crystal Manner upon Guest Removal or Readsorption. *Angew. Chem., Int. Ed.* **2002**, *41*, 3392–3395. (b) Saalfrank, R. W.; Maid, H.; Hampel, F.; Peters, K. 1D- and 2D-Coordination Polymers from Self-Complementary Building Blocks: Co-Crystallization of (P)- and (M)-Single-Stranded Diastereomers. *Eur. J. Inorg. Chem.* **1999**, 1859–1867.
- (6) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O’Keeffe, M.; Yaghi, O. M. Interwoven Metal-Organic Framework on a Periodic Minimal Surface with Extra-Large Pores. *Science* **2001**, *291*, 1021–1023.
- (7) (a) Braga, D.; Grepioni, F.; Desiraju, G. R. Crystal Engineering and Organometallic Architecture. *Chem. Rev.* **1998**, *98*, 1375–1406. (b) Fraser, C. A. S.; Jenkins, H. A.; Jennings, M. C.; Puddephatt, R. J. Organoplatinum(IV) Complexes with Hydrogen Bonds: From Monomers to Polymers. *Organometallics* **2000**, *19*, 1635–1642. (c) Steiner, T. The Hydrogen Bond in the Solid State. *Angew. Chem., Int. Ed.* **2002**, *41*, 48–76.
- (8) Nguyen, P.; Gomez-Eliphe, P.; Manners, I. Organometallic Polymers with Transition Metals in the Main Chain. *Chem. Rev.* **1999**, *99*, 1515–1548.
- (9) Lenaz, G., Ed. *Coenzyme Q: Biochemistry, Bioenergetics and Clinical Applications of Ubiquinone*; Wiley: New York, 1985.
- (10) (a) Pierpont, C. G. Studies on charge distribution and valence tautomerism in transition metal complexes of catecholate and zsemiquinonate ligands. *Coord. Chem. Rev.* **2001**, *216*, 99–125. (b) Attica, A. S.; Pierpont, C. G. New Semiquinone/Catecholate Complexes That Exhibit Valence Tautomerism. *Inorg. Chem.* **1998**, *37*, 3051–3056.
- (11) (a) Huang, Y.-S.; Sabo-Etienne, S.; He, X.-D.; Chaudret, B. Reactions of Quinones and Quinoid Molecules with the Cp^*Ru^+ Fragment. Electron Redistribution and Transposition Reactions. *Organometallics* **1992**, *11*, 3031–3035. (b) Le Bras, J.; Amouri, H.; Vaissermann, J. *p*-, *o*- η^4 -Benzoquinone and the Related η^6 -Hydroquinone, η^6 -Catechol Complexes of Pentamethylcyclopentadienyliridium: Synthesis, Structures and Reactivity. *Organometallics* **1998**, *17*, 1116–1121. (c) Amouri, H.; Le Bras, J. Taming Reactive Phenol Tautomers and *o*-Quinone Methides with Transition Metals: A Structure–Reactivity Relationship. *Acc. Chem. Res.* **2002**, *35*, 501–510.
- (12) Sun, S.; Carpenter, G. B.; Sweigart, D. A η^6 -Hydroquinone and catechol complexes of manganese tricarbonyl. Molecular structure of $[(\eta^6\text{-hydroquinone})\text{Mn}(\text{CO})_3]_2\text{SiF}_6$. *J. Organomet. Chem.* **1996**, *512*, 257–259.

- (13) Oh, M.; Carpenter, G. B.; Sweigart, D. A. η^5 -Semiquinone and η^4 -Quinone Complexes of Manganese Tricarbonyl. Intermolecular Hydrogen bonding in the Solid State and in Solution. *Organometallics* **2002**, *21*, 1290–1295.
- (14) Oh, M.; Carpenter, G. B.; Sweigart, D. A. Unpublished results.
- (15) Oh, M.; Carpenter, G. B.; Sweigart, D. A. The η^4 -*o*-Benzoquinone Manganese Tricarbonyl Anion (*o*-QMTC) as an Organometallogand in the Formation of $M(o\text{-QMTC})_2(L-L)$ Complexes ($M = \text{Mn, Co, Cd}$; $L-L = \text{bipy, phen}$): Generation of Neutral 2-D Networks Containing Two Types of π - π Stacking. *Organometallics* **2003**, *22*, 1437–1442.
- (16) Oh, M.; Carpenter, G. B.; Sweigart, D. A. Metal-Mediated Self-Assembly of π -Bonded Benzoquinone Complexes into Polymers with Tunable Geometries. *Angew. Chem., Int. Ed.* **2001**, *40*, 3191–3194.
- (17) Oh, M.; Carpenter, G. B.; Sweigart, D. A. Self-Assembly Using Organometallogands as Spacers in the Controlled Formation of Isomeric 1D and 2D Supramolecular Quinonoid Networks. *Angew. Chem., Int. Ed.* **2002**, *41*, 3650–3653.
- (18) Oh, M.; Carpenter, G. B.; Sweigart, D. A. Toward the Rational Design of Supramolecular Coordination Polymers. The Effect of Solvent and Substituent Changes on the Structure of Self-Assembled Metal–Organometallic Networks. *Organometallics* **2003**, *22*, 2364–2366.
- (19) Oh, M.; Carpenter, G. B.; Sweigart, D. A. A coordination network containing metal–organometallic secondary building units based on π -bonded benzoquinone complexes. *Chem. Commun.* **2002**, 2168–2169.
- (20) Oh, M.; Carpenter, G. B.; Sweigart, D. A. A Novel 3D Brick-Wall Coordination Network Based on Nodes with Square-Pyramidal Connectivity. *Angew. Chem., Int. Ed.* **2003**, *42*, 2025.
- (21) (a) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. Interpenetrating Molecular Ladders and Bricks. *J. Am. Chem. Soc.* **1995**, *117*, 7287–7288. (b) Choi, H. J.; Suh, M. P. Self-Assembly of Molecular Brick Wall and Molecular Honeycomb from Nickel(II) Macrocycle and 1,3,5-Benzenetricarboxylate: Guest-Dependent Host Structures. *J. Am. Chem. Soc.* **1998**, *120*, 10622–10628.
- (22) (a) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. Aromatic Interactions. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651–669. (b) Roessky, H. W.; Andruh, M. The interplay of coordinative, hydrogen bonding and π - π stacking interactions in sustaining supramolecular solid-state architectures. A study case of bis(4-pyridyl)- and bis(4-pyridyl-*N*-oxide) tectons. *Coord. Chem. Rev.* **2003**, *236*, 91–119.
- (23) (a) Kahn, O. Chemistry and Physics of Supramolecular magnetic Materials. *Acc. Chem. Res.* **2000**, *33*, 647–657. (b) Barthelet, K.; Marrot, J.; Riou, D.; Ferey, G. A Breathing Hybrid Organic–Inorganic Solid with Very Large Pores and High Magnetic Characteristics. *Angew. Chem., Int. Ed.* **2002**, *41*, 281–284. (c) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin, V. Coexistence of ferromagnetism and metallic conductivity in a molecule-based layered compound. *Nature* **2000**, *408*, 447–449.
- (24) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. Infinite Secondary Building Units and Forbidden Catenation in Metal–Organic Frameworks. *Angew. Chem., Int. Ed.* **2002**, *41*, 284–287.
- (25) Several very interesting MONs incorporating quinones have recently been reported. Wolczanski et al. prepared σ -bonded quinonoid polymers via the alcoholysis reaction of hydroquinone with precursor $M(IV)$ alkoxides ($M = \text{Ti, V, Zr}$).²⁶ Due to the oxophilic nature of the metals involved, these unique MONs contain strong covalent $M-O$ bonds, as opposed to the more standard weaker dative $M-O$ bonds present in most MONs. Also of note is a recent report by Kitagawa et al. of a MON containing a pendant benzoquinone π -bonded to a dicopper(I) SBU.²⁷
- (26) (a) Vaid, T. P.; Tanski, J. M.; Pette, J. M.; Lobkovsky, E. B.; Wolczanski, P. T. Covalent Three-Dimensional Titanium(IV)-Aryloxide Networks. *Inorg. Chem.* **1999**, *38*, 3394–3405. (b) Tanski, J. M.; Vaid, T. P.; Lobkovsky, E. B.; Wolczanski, P. T. Covalent Metal–Organic Networks: Pyridines Induce 2-Dimensional Oligomerization of $(\mu\text{-OC}_6\text{H}_4\text{O})_2\text{Mpy}_2$ ($M = \text{Ti, V, Zr}$). *Inorg. Chem.* **2000**, *39*, 4756–4765.
- (27) Masaoka, S.; Akiyama, G.; Horike, S.; Kitagawa, S.; Ida, T.; Endo, K. Novel Cu(I) Dinuclear Complexes Containing μ_2 - η^2 , η^2 -Type Benzoquinone Ligand. *J. Am. Chem. Soc.* **2003**, *125*, 1152–1153.

AR030175O