Self-Assembly of Metal-Organometallic Coordination Networks

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

Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

Summary: A range of neutral metal-organometallic coordination networks (MOMNs) containing both backbone and pendant metal sites have been synthesized and characterized. These materials consist of metal ions or metal ion clusters as nodes that are linked by the bifunctional "organometalloligand" (η^4-benzoquinone)$Mn(CO)_3^-$, which binds through the quinone oxygen atoms. The resulting MOMNs can be rationally designed to a significant extent based upon a knowledge of the electronic and geometrical requirements of the metal ion nodes, the solvent, organometalloligand substituents, and the presence or absence of organic spacers. An impressive range of architectures have been accessed in this manner, suggesting that the use of π-organometallics in coordination directed self-assembly holds much promise.

Keywords: coordination networks; organometallics; quinone complexes; self-assembly; supramolecular structures

Introduction

Supramolecular chemistry involves the study of finite and infinite (polymeric) nanostructures consisting of self-assembled modular units.[1] Implicit in the formation of well defined nanostructures is the ability of the modular components to participate in highly efficient molecular recognition events. These involve a variety of possible intermodular interactions, ranging in energy from very weak to fairly strong, with the most common ones being hydrogen-bonding and metal-ligand bond formation. The driving force behind such work is the desire to fabricate new functional solids that have applications in areas such as magnetics, optics, molecular recognition, sensing, catalysis, separations, guest-host chemistry, etc.

Metal-coordination-directed formation of metal-organic or "coordination" supramolecular networks (MONs) have received much recent attention. Both discrete (finite)[2] and infinite[3-5] MONs have been investigated. The nodes in the majority of infinite MONs reported are metal ions, which are bonded to relatively simple multifunctional organic ligands that serve as spacers

© 2003 WILEY-VCH Verlag GmbH & KGaA, Weinheim CCC 1022-1360/00/$ 17,50+.50/0

within the network. In more complex systems, in particular ones that most frequently afford porous structures, the nodes consist of metal carboxylate clusters as secondary building units (SBUs).[6] MON coordination polymers hold much promise, albeit this is tempered somewhat by a generally poor ability to predict structure (and hence function). Difficulty in predicting structure is often due to the existence of supramolecular isomers of similar energies. Even when a particular structural architecture can be pre-designed with some confidence, the product often consists of several interpenetrating networks. Overall, there is a need to develop a better understanding of the factors controlling structure, so that resources can be invested in making new materials with desired properties.

Herein we are concerned with MONs of a special type, namely, metal-*organometallic* coordination networks (MOMNs). The essential difference between MONs and MOMNs is illustrated in Figure 1. In the former, the spacer molecules connecting the metal nodes consist of simple organic ligands, whereas in the latter the spacers consist of *organometallic* π*-complexes* that function as "organometalloligands".

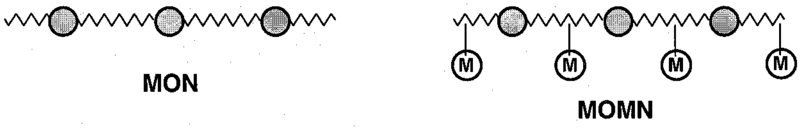
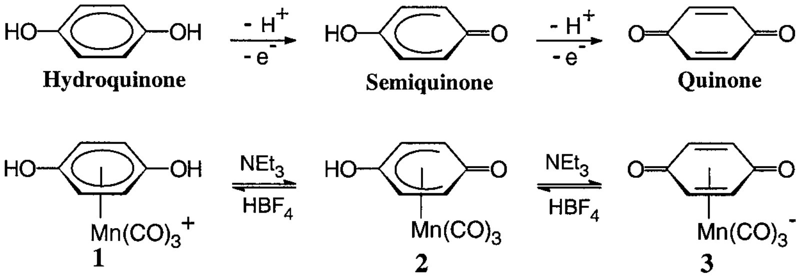


Figure 1. One-dimensional coordination networks with organic and organometallic spacers.

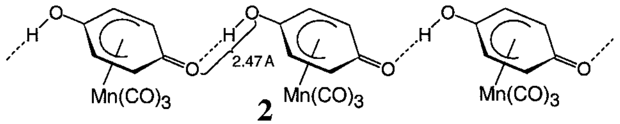
It can be seen that MOMNs may exhibit metal-metal interactions not available in corresponding MONs. Of equal significance is the fact that organometalloligands offer the opportunity to incorporate truly novel types of spacers, especially ones with pendant metal atoms, into coordination networks. We anticipate that MOMNs would most generally be synthesized directly from intact "organometalloligand" spacers, and not by "coordinating" metal fragments to the organic spacers in intact MONs. Overall, it seems that the possibility of constructing novel metal-organometallic coordination networks that have interesting magnetic, electronic and catalytic properties is good.

Substituted hydroquinones are of fundamental importance in mediating electron and proton transfers in biological reactions. Our work with organometallic coordination networks is related to the reversible reactions of hydroquinone to afford semiquinone and quinone oxidation products, as indicated in Scheme 1. The members of this series have a propensity[7] to σ-bond to metals through the oxygen atoms rather than to π-bond through the carbocyclic ring. There are, however, several examples[8,9] of stable complexes containing a hydroquinone *π-bonded* to a transition metal, suggesting that in general such species can be sufficiently stable for isolation and utulization. One would may anticipate that the attachment of a metal fragment to the π-system would facilitate proton and, perhaps, electron transfer.

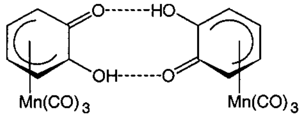
Scheme 1



By using (η^6-naphthalene)$Mn(CO)_3^+$ as a manganese tricarbonyl transfer reagent (MTT), we prepared in high yield the thermally stable π-complex (η^6-hydroquinone)$Mn(CO)_3^+$ (**1**), as well as the catechol and resorcinol analogues.[9] The key to the utility of **1** in the construction of MOMNs is the great ease with which the -OH protons are removed to give η^5-semiquinoine and η^4-quinone complexes according to Scheme 1. Although the sequence **1** $\leftrightarrow$ **2** $\leftrightarrow$ **3** in Scheme 1 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. The neutral η^5-semiquinone complex **2** was structurally characterized and found[10] to exist in linear polymeric arrays with the structure dictated by strong intermolecular hydrogen bonding.[11] By comparison, and as might be expected, the catechol analogue exists as discrete hydrogen bonded dimers.

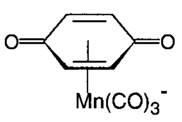


2

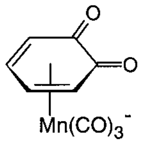


Quinone Organometalloligands

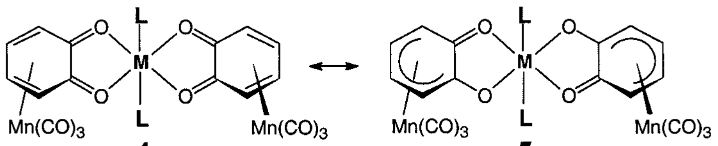
The anionic *para-* and *ortho-*benzoquinone manganese tricarbonyl complexes obtained from double deprotonation of the corresponding hydroquinone and catechol can function as bifunctional ligands ("organometalloligands") in the presence of appropriate metal ions by σ-bonding through the oxygen atoms. These ligands are called *p*-QMTC and *o*-QMTC, respectively. The chemistry of the former is described in some detail in the next section, while that of the latter is briefly summarized in this section. The ligand *o*-QMTC readily reacts with divalent metal ions to afford monomeric complexes **4** (M = Mn, Cd, Co; L = neutral ligand). Complexes containing deprotonated catechol sigma-bonded to metals via the oxygens have long been known[7,12] to exhibit redox or valence tautomerization due to facile electron transfer between the metal and the catechol ligand. There is evidence that this effect is enhanced in the π-bonded complex **4**, with the $Mn(CO)_3$ moiety acting as an electron sink. The particular tautomer that prevails - the η^4-quinone (**4**), η^5-semiquinone (**5**), or even the η^6-catecholate - appears to be a sensitive function of the axial ligand L. This conclusion is based on ν_{CO} bands that are *unusually* dependent on the electron donating properties of the axial ligand. It is possible that the facile electron transfer behavior shown by π-bonded quinone complexes such as **4** may have useful applications in catalysis. This would be especially true when the substrate(s) can partake of the self-adjusting electronic environment by binding directly to the σ-bonded metal.



***p*-QMTC**

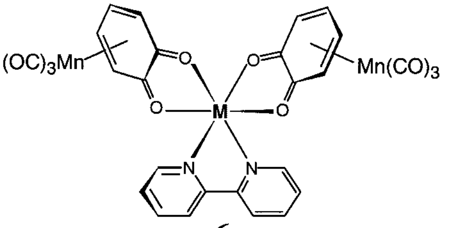


***o*-QMTC**

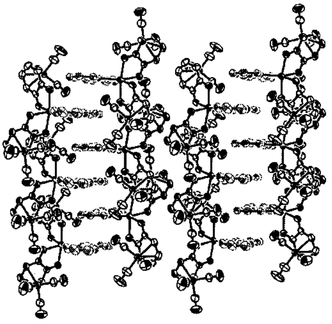


4 **5**

Coordination networks can be made from **4** by using organic spacers as axial ligands, but this chemistry is yet to be developed. The reaction of *o*-QMTC with divalent metal ions in the presence of 2,2-bipyridine affords stable complexes M(*o*-QMTC)$_2$(L-L) (M = Mn, Co, Cd). In the solid state these complexes self-assemble into two-dimensional supramolecular networks, the structure of which are determined by π-π stacking and interdigitation of the bipyridine ligands and by a pairwise π-π stacking of one of the two *o*-benzoquinone ligands in each monomeric unit to generate dimeric units.[13]

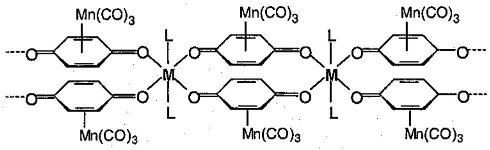


6

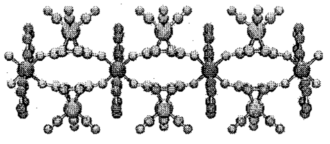


Quinonoid Metal-Organometallic Coordination Networks

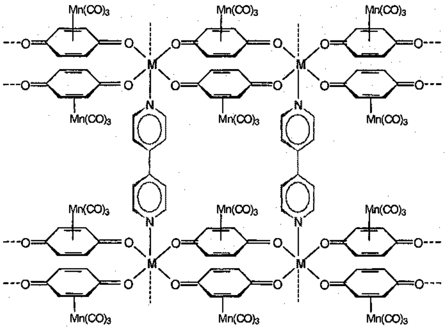
The geometry of the *p*-QMTC complex suggests that it could function as a spacer in the formation of coordnation networks. Indeed, it was found[14] that *p*-QMTC readily binds to metal ions through the oxygen atoms. The key to the synthesis of MOMNs having *p*-QMTC spacers was finding the right solvent and temperature conditions for the self-assembly process to occur without premature precipitation of oligomers. Warm DMSO turned out to be an excellent medium for the high yield synthesis of *crystalline* polymers. Initially, it was found[14] that *p*-QMTC combined with the metal cations to form the 1-dimensional "string" MOMN **7** (M = Mn, Co, Ni, Cd). The crystal structure of the neutral Co quinonoid polymer with pyridine axial ligands is illustrated. It was subsequently found that the *p*-QMTC organometalloligand can be used for the synthesis of an diverse array of 1- 2- and 3-dimensional polymers, with exact architecture obtained depending on the geometrical requirements of the added metal ion, the solvent, and on the presence of added organic ligands that function as additional spacers.



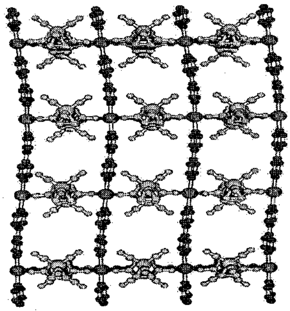
1-Dimensional MOMN 7



M = cobalt and L = pyridine



2-Dimensional MOMN 8



M = Mn(II) or Ni(II)

For example, replacement of the unidentate axial ligand in **7** with 4,4'-bipyridine generates the 2-D polymer **8**. The rectangular grids in **8** are filled with solvent DMSO, which can be easily removed thermally *without* losing crystallinity.[15] Isomeric with the 1-D string motif formed by combination of metal ion nodes and *p*-QMTC spacers is the 2-D grid structure shown in Figure. 2. It was found[15] that the prevailing isomer, 1-D or 2-D can be *predetermined* by controlling the metal ion concentration. At higher concentrations, the 2-D pseudo-planar quinonoid network is favored because *p*-QMTC binding sites are "trapped" before assembly to the 1-D string can occur. When 4,4'-bipyridine is present, the 2-D grids then link together to generate 3-D MOMNs (**9**) containing rectangular pores (12 x 6 Å) filled with DMSO solvent. Polymerization of *p*-QMTC in the presence of a bridging metal that prefers tetrahedral rather than octahedral geometry would be expected to give a nonlinear product quite different from **7-9**. This possibility was explored using Zn(II), and the result obtained from DMSO solvent was the 3-D polymer **10.** The geometry around the zinc is indeed tetrahedral and the solid state structure consists of two interpenetrating diamondoid networks, as illustrated in Figure 3.[14]

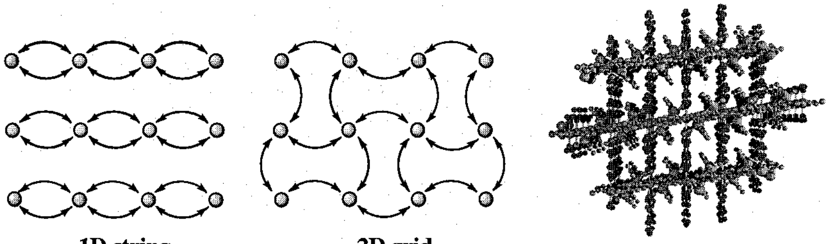
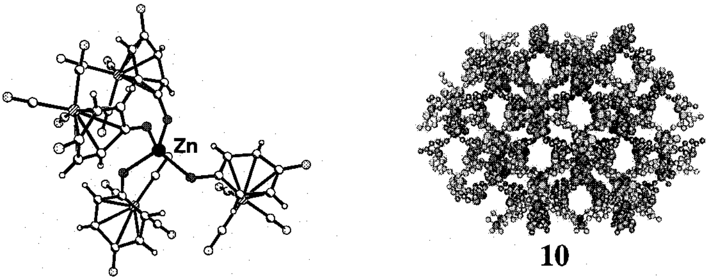

1D string **2D grid** **9**

Figure 2. Supramolecular isomers with *p*-QMTC spacers (double headed arrows).



10

Figure 3. Diamondoid MOMN **10** with tetrahedral Zn(II) nodes.

In the reaction of *p*-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 3-D diamondoid structures in which the metal ion nodes adopt tetrahedral rather than octahedral[16] coordination. The polymers $[Co(QMTC)_2]_\infty$ and $[Mn(QMTC)_2]_\infty$, obtained from MeOH solvent, possess overall structures virtually identical to that found for $[Zn(QMTC)_2]_\infty$ shown in Figure 3. It is concluded that with Mn^{2+} and Co^{2+}, switching the solvent from DMSO to MeOH results in a fundamental change in 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, suggests that solvent variation may be generally useful for controlling coordination network architecture. The introduction of methyl groups at the 2- and 3-positions of the benzoquinone ring was found to greatly influence the manner in which the quinone oxygen lone pairs bind to the metal nodes. Crystal structures of coordination polymers $[M(2,3\text{-}Me_2QMTC)_2]_\infty$ ($M = Mn^{2+}$, Zn^{2+}) 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 4.[16] Presumably, this bonding pattern is dictated by the steric requirements of the methyl groups. The stereochemical switch from the *trans* to *cis* results in a concomitant change in the polymer architecture from a two-fold interpenetrated 3-D diamondoid structure to a noninterpenetrated ruffled 2-D rhombohedral grid. In spite of the *trans* to *cis* and diamondoid to rhombohedral structural changes, the metal nodes in $[M(2,3\text{-}Me_2QMTC)_2]_\infty$ remain tetrahedrally bonded to the quinone oxygens.

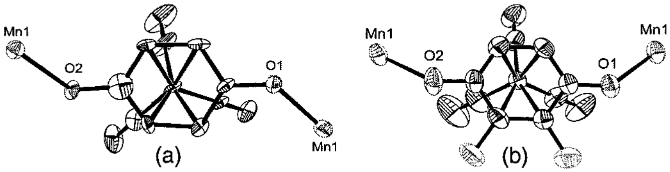
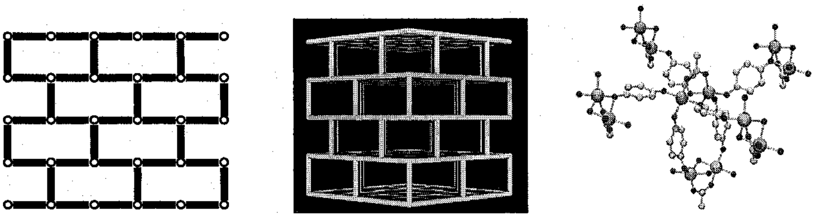


Figure 4. Bonding of the quinone oxygens to Mn(II) nodes in (a) $[Mn(p\text{-}QMTC)_2]_\infty$ and (b) $[Mn(2,3\text{-}Me_2QMTC)_2]_\infty$.

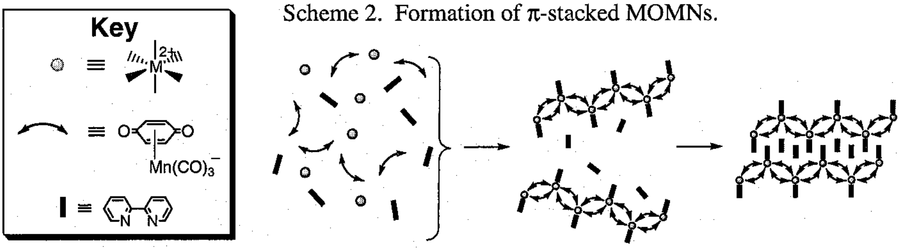
The reaction of *p*-QMTC with Mn^{2+} in a DMSO/MeOH solvent mixture produced a 3-D diamonoid polymer containing dimanganese secondary building units.[17] Mixing *p*-QMTC and $Cu(OAc)_2$ in MeOH generated a MOMN possessing an unprecedented *3-dimensional* "brick wall" structure.[18] Figure 5 illustrates how a 3-D brick wall can be generated starting with "T" shaped nodes that connect to form the familiar 2-D brick wall.[19] Extension of the brick wall from 2-D (Figure 5a) to 3-D (Figure 5b) involves converting the T-shaped node to a square pyramidal node possessing fivefold connectivity. The MOMN formed from *p*-QMTC and $Cu(OAc)_2$ consists of bimetallic SBUs of formula $Cu_2(\mu\text{-}CH_3CO_2)^{3+}$, which are linked via *p*-QMTC spacers with the square pyramidal geometry shown in Figure 5c. The resultant 3-D structure, which has the molecular formula $[Cu_2(p\text{-}QMTC)_3(\mu\text{-}CH_3CO_2)]_\infty$, constitutes a previously unknown extended (3-D) brick wall architecture.



(a) (b) (c)

Figure 5. (a) 2-D and (b) 3-D brick wall motifs and (c) square pyramidal connectivity in MOMN $[Cu_2(QMTC)_3(\mu\text{-}CH_3CO_2)]_\infty$.

When *p*-QMTC and M^{2+} (M = Cd, Mn) were reacted in the presence of 2,2'-bipyridine, a most interesting MOMN was isolated.[20] Because both nitrogens in 2,2'-bipyridine are constrained to bind to the same metal node, two structures can result - a nanotube, which is yet to be observed and a 1-D zigzag polymer (Scheme 2). The crystal structure of the zigzag MOMNs revealed that the individual 1-D polymer units interdigitate via π-π stacking of the 2,2'-bipyridine ligands. While π-π stacking is a well known phenonomen,[21] the structure in Scheme 2 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 temperature at which magnetic ordering occurs when the nodes are paramagnetic (e.g., Mn^{2+}).[22] 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, and thereby have a number of potential applications.



Scheme 2. Formation of π-stacked MOMNs.

When Mn^{2+} in MeOH solvent reacts with the η^5-semiquinone complex **2** instead of *p*-QMTC, a 1-D zigzag polymer is generated that contains two semiquinone organometalloligands bound in a *cis* manner to each Mn^{2+} node.[20] The resultant MONN **(11)** 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. An equally interesting MOMN containing dicadmium SBUs with protruding quinone moieties **(12)** is formed from **2** and Cd^{2+} in MeOH.

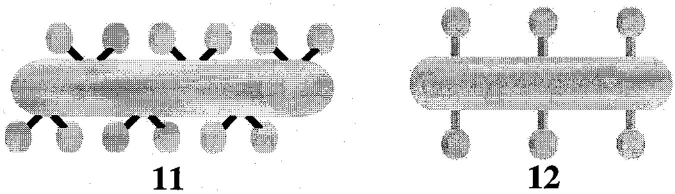


Figure 6. Cartoon representations of $\{Mn(p\text{-QMTC})_2[(\eta^5\text{-semiquinone})Mn(CO)_3]_2\}_\infty$ **(11)** and $[Cd_2(p\text{-QMTC})_4(MeOH)_4]_\infty$ **(12)**.

Conclusion

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 "organometalloligands". 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* based upon the coordination number, oxidation state, and geometrical requirements of the metallic nodes that link the organometalloligands.

Acknowledgment

Acknowledgment is made to donors of the Petroleum Research Fund, administered by the ACS, for support of this research.

[1] J. M. Lehn, "Supramolecular Chemistry: Concepts and Perspectives", VCH, Weinheim, **1995**; J. W. Steed, J. L. Atwood, "Supramolecular Chemistry", Wiley, Chichester, **2000**.

[2] D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed.* **1996**, *35*, 1154; S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022; M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417; L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc. 1998,* **120**, 2676; Y. L. Cho, H. Uh, S.-Y. Chang, H.-Y. Chang, M.-G. Choi, I. Shin and K.-S. Jeong, *J. Am. Chem. Soc.* **2001**, *123*, 1258.

[3] S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460; R. Robson, *J. Chem. Soc., Dalton Trans.* **2000**, 3735; M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319; O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511.

[4] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629.

[5] S. A. Bourne, J. Lu, A. Mondal, B. Moulton, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2001**, *40*, 2111; H. Abourahma, B. Moulton, V. Kravtsov, M. J. Zaworotko, *J. Am. Chem. Soc.* **2002**, *124*, 9990; Y.-B. Dong, R. C. Layland, N. G. Pschirer, M. D. Smith, U. H. F. Bunz, H.-C. zur Loye, *Chem. Mater.* **1999**, *11*, 1413; H. J. Choi, M. P. Suh, *J. Am. Chem. Soc.* **1998**, *120*, 10622; K. Biradha, M. Fujita, *J. Chem. Soc., Dalton Trans.* **2000**, 3805; K. Biradha, M. Fujita, *Angew. Chem. Int. Ed.* **2002**, *41*, 3392; Y. Cui, O. R. Evans, H. L. Ngo, P. S. White and W. Lin, *Angew. Chem. Int. Ed.* **2002**, *41*, 1159; O. R. Evans, W. Lin, *Chem. Mater.* **2001**, *13*, 3009; N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2002**, *41*, 284.

[6] J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239; M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391, B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe, O. M. Yaghi, *Science* **2001**, *291*, 1021.

[7] C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *216*, 99; A. Caneschi, A. Dei, D. Gatteschi, L. Sorace, K. Vostrikova, *Angew. Chem.* **2000**, *39*, 246; C. G. Pierpont, C. W. Langi, *Prog. Inorg. Chem.* **1994**, *41*, 331; C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *216-217*, 99.

[8] Y.-S. Huang, S. Sabo-Etienne, X.-D. He, B. Chaudret, *Organometallics* **1992**, *11*, 3031; J. Le Bras, H. Amouri, J. Vaissermann, *Organometallics*, **1998**, *17*, 1116; H. Schumann, A. M. Arif, T. G. Richmond, *Polyhedron* **1990**, *9*, 1677; G. Fairhurst, C. White, *J. Chem. Soc., Dalton Trans.* **1979**, 1531; H. Amouri, J. Le Bras, *Acc. Chem. Res.* **2002**, *35*, 501.

[9] S. Sun, G. B. Carpenter, D. A. Sweigart, *J. Organomet. Chem.* **1996**, *512*, 257.

[10] M. Oh, G. B. Carpenter, D. A. Sweigart, *Organometallics* **2002**, *21*, 1290.

[11] Y.-B. Dong, M. D. Smith, R. C. Layland, H.-C. zur Loye, *J. Chem. Soc., Dalton Trans.* **2000**, 775; D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375; D. Braga, F. Grepioni, *Coord. Chem. Rev.* **1999**, *183*, 19; D. Braga, L. Maini, F. Grepioni, C. Elschenbroich, F. Paganelli, O. Schiemann, *Organometallics* **2001**, *20*, 1875; C. A. S. Fraser, H. A. Jenkins, M. C. Jennings, R. J. Puddephatt, *Organometallics* **2000**, *19*, 1635, T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.

[12] A. S. Attia, C. G. Pierpont, *Inorg. Chem.* **1998**, *37*, 3051; O.-S. Jung, D. H. Jo, Y.-A. Lee, Y. S. Sohn, C. G. Pierpont, *Inorg. Chem.* **1998**, *37*, 5875.

[13] M. Oh, G. B. Carpenter, D. A. Sweigart, *Organometallics*, in press.

[14] M. Oh, G. B. Carpenter, D. A. Sweigart, *Angew. Chem. Int. Ed.*, **2001**, *40*, 3191.

[15] M. Oh, G. B. Carpenter, D. A. Sweigart, *Angew. Chem. Int. Ed.*, **2002**, *41*, 3650.

[16] M. Oh, G. B. Carpenter, D. A. Sweigart, *J. Am. Chem. Soc.*, submitted.

[17] M. Oh, G. B. Carpenter, D. A. Sweigart, *Chem. Commun.* **2002**, 2168.

[18] M. Oh, G. B. Carpenter, D. A. Sweigart, *Angew. Chem. Int. Ed.*, in press.

[19] M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, *J. Am. Chem. Soc.* **1998**, *120*, 10622; L. Carlucci,

G. Ciani, D. M. Proserpio, *New J. Chem.* **1998**, 1319; L. Carlucci, G. Ciani, D. M. Proserpio, *J. Chem. Soc., Dalton Trans.* **1999**, 1799. (f) M. Kondo, M. Shimamura, S. Noro, S. Minakoshi, A. Asami, K. Seki, S. Kitagawa, *Chem. Mater.* **2000**, *12*, 1288

[20] M. Oh, G. B. Carpenter, D. A. Sweigart, unpublished results.

[21] O. M. Yaghi, H. Li, T. L. Groy, *Inorg. Chem.* **1997**, *36*, 4292; K. V. Domasevitch, G. D. Enright, B. Moulton, M. J. Zaworotko, *J. Sol. State Chem.* **2000**, *152*, 280; C. A. Hunter, *Chem. Soc. Rev.* **1994**, 101; C. A. Hunter, X.-J. Lu, *J. Mol. Biol.* **1997**, *265*, 603; C. A. Hunter, K. R. Lawson, J. Perkins, C. J. Urch, *J. Chem. Soc., Perkin Trans.2*, **2001**, 651; L. J. Childs, N. W. Alcock, M. J. Hannon, *Angew. Chem. Int. Ed.* **2001**, *40*, 1079; A. Hori, A. Akasaka, K. Biradha, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem. Int. Ed.* **2002**, *41*, 3269.

[22] O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647; K. Barthelet, J. Marrot, D. Riou, G. Ferey, *Angew. Chem. Int. Ed.* **2002**, *41*, 281; E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia, V. Laukhin, *Nature* **2000**, *408*, 447.