tively, were prepared, giving correspondingly amplified ellipsometric thickness and absorbance. Respective emission decays were identical to those of the unquenched and quenched bilayer structures discussed above.

In summary, we have reported the synthesis, film-forming properties, and photophysical data on **1** and **2**. The films are stable to hot solvents and may be built up repetitively with reproducible thickness per layer and fluorescence behavior. Thus, we introduce a photocharge-generating element to a material class where nonlinear optical, rectifying, and insulating components could also be present at arbitrary positions. Work is in progress to observe and measure lifetimes of the photoinduced charge separated species directly, and to explore the electrical and optical properties of multiple-component superlattices prepared by Zr phosphonate deposition.

Supplementary Material Available: Synthetic schemes for **1** and **2** (2 pages). Ordering information is given on any current masthead page.

Figure 1. Perspective view of a molecule of **2** as it exists in **3**. Intramolecular distances and angles are within expected ranges.[6,7]

Supramolecular Chemistry of [Mn(CO)$_3$(μ_3-OH)]$_4$: Assembly of a Cubic Hydrogen-Bonded Diamondoid Network with 1,2-Diaminoethane

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Predictable self-organization of molecules into one-, two-, or three-dimensional hydrogen-bonded architectures is an area of supramolecular chemistry that is of great current interest.[1] Such research is particularly relevant in the context of solid-state chemistry since rational design, i.e., crystal engineering, of solids has important ramifications for the development of new materials with unusual physical properties.[2] An aspect of this chemistry that is particularly pleasing from an aesthetic perspective and has a number of potential applications, particularly in the area of host–guest chemistry, concerns the construction of three-dimensional hydrogen-bonded diamondoid open networks. The concept was delineated by Ermer in 1988, who demonstrated that if tetrafunctionalized organics with approximate tetrahedral symmetry have the capability to associate via hydrogen bonds, then diamondoid networks may result.[3] Unfortunately, the relative sizes of the cavities formed by adamantane-1,3,5,7-tetracarboxylic acid and 3,3-bis(carboxymethyl)glutaric acid ("methanetetraacetic acid") facilitate interpenetration of five[3a] and three[3b] networks, respectively, thereby precluding formation of internal chambers. However, Ermer subsequently demonstrated that enclathration
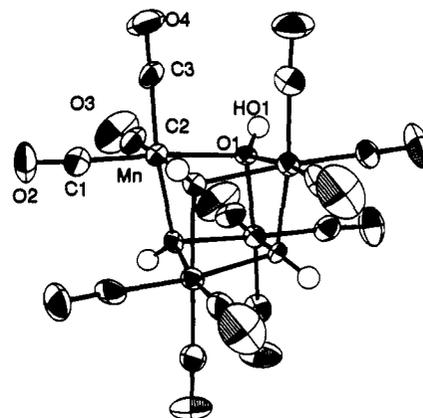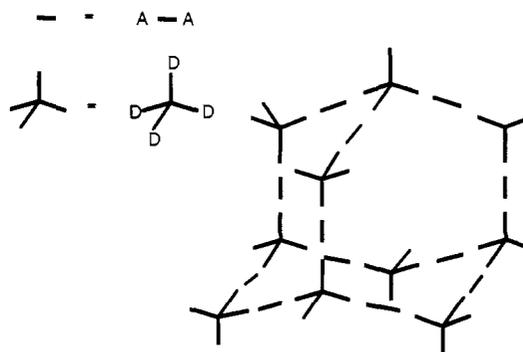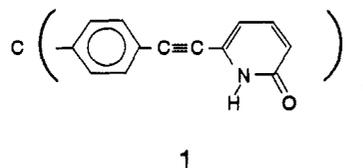
Chart I

can be attained with double-diamond 2,6-dimethylidene-adamantane-1,3,5,7-dicarboxylic acid networks,[4] and in a significant development, Wuest recently demonstrated that tecton **1** can self-assemble to form a diamondoid network that does not

1

interpenetrate and is capable of enclathration.[5] In this communication we develop the theme further by outlining an alternate approach to assembly of diamondoid networks: assembly of a rigid tetrafunctional hydrogen-bond donor with complementary difunctional hydrogen-bond-acceptor molecules (Chart I).

A molecule which possesses S_4 symmetry and the requisite four H-bond donors[6] is the cubane-like cluster [Mn(CO)$_3$(μ_3-OH)]$_4$, **2**, which can be synthesized quantitatively in one step from Mn$_2$(CO)$_{10}$.[7] Reaction of **2** with excess 1,2-diaminoethane, en, in toluene immediately affords a yellow-orange precipitate, which may be recrystallized from CHCl$_3$/CH$_3$CN to afford cocrystals of composition **2·2en**, **3**.[8] X-ray crystallographic analysis[9] reveals

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(3) (a) Ermer, O. *J. Am. Chem. Soc.* 1988, *110*, 3747. (b) Ermer, O.; Eling, A. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 829.

(4) Ermer, O.; Lindenberg, L. *Helv. Chim. Acta* 1991, *74*, 825.

(5) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* 1991, *113*, 4696.

(6) **2** is able to form isolable 1:4 adducts with H-bond acceptors as diverse in nature as water and triphenylphosphine oxide: Clerk, M. D.; Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *Supramol. Chem.* 1992, *1*, 7.

(7) Clerk, M. D.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* 1991, 1607.

(8) In a typical reaction, a recrystallized yield of **3** of 80% is afforded. IR (KBr, cm^{-1}): ν_{CO} 2011 s, 1916 s; $\nu_{NH,OH}$ 3375 bs. Anal. Found: (calcd) C, 26.12 (25.84); H, 2.68 (2.69); N, 7.26 (7.53).
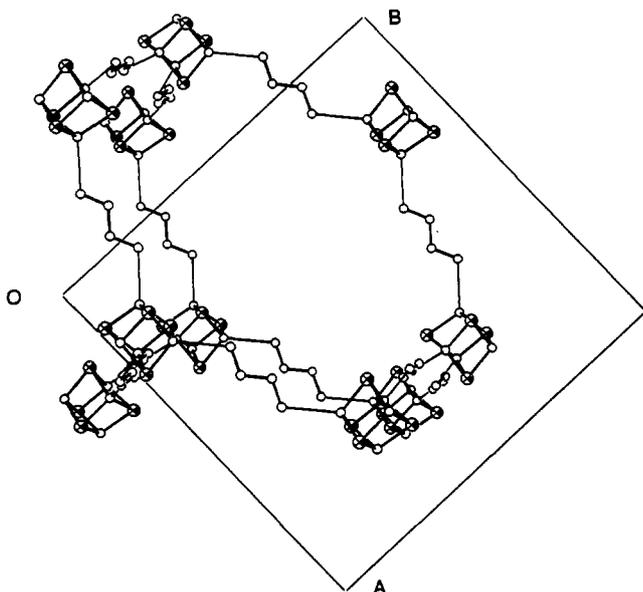
Figure 2. Perspective view of the tertiary structure of **3** viewed down the *c*-axis. For the sake of clarity, an adamantane-like unit of only one of the three networks is illustrated and all hydrogen atoms and carbonyl ligands are omitted.

that **3** exists in the solid state as an undistorted triple diamondoid network of **2** linked by en bridges. O···N and O–H···N distances of 2.774 (8) and 1.94 (6) Å, respectively, O–H···N angles of 165 (5)°, and IR spectroscopy[8] confirm the presence of hydrogen bonds. The O–H···en···H–O linkages therefore serve the same geometric function as C–C bonds in diamond but can be much more readily disassembled and reassembled. The rigid tetrahedral geometry of **2**, which is illustrated in Figure 1, is reinforced crystallographically since **2** lies around a 4̄ position. The adamantane-like architecture of one of the independent diamondoid networks of **3** is illustrated in Figure 2.

The relative size and shape of **2**, the length of en, and the interpenetration of the networks do not facilitate enclathration of guest molecules; however, the concept of assembly of complementary molecules to generate diamondoid networks is confirmed. A significant feature of this concept (as opposed to self-assembly of identical molecules) is that judicious choice of the bridging H-bond-acceptor moiety should permit rational design of cavity size without extensive synthetic procedures (i.e., breakage or formation of covalent bonds). As noted previously,[3,4] there are numerous potential applications of diamondoid networks. In addition to those already discussed, we point out that molecules such as **2** may be photoreactive[10] and that **2** is not the only cubane cluster with such geometric features.[11]   The generality of the

(9) Crystals of **3** belong to the noncentrosymmetric cubic space group *I*4̄3*d* (*T*$_d$, No. 220) with *a* = 20.733 (3) Å, *V* = 8912.2 (13) Å³, *D*$_{calcd}$ = 1.66 g cm⁻³, and *Z* = 12. Molecules of **2** lie around a 4̄ position whereas the bridging en molecules lie around 2-fold axes. Full matrix least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters, the μ_3-OH hydrogen atom with an isotropic thermal parameter, and with all other hydrogen atoms fixed in calculated positions, afforded *R* = 0.027 and *R*$_w$ = 0.026. The tertiary structure consists of three independent diamondoid networks based upon molecules of **2** that lie 11.59 Å from each other around corresponding sets of four 4̄ positions (Set 1: $^7/_8$, 0, $^1/_4$; $^5/_8$, 0, $^3/_4$; $^3/_8$, $^1/_2$, $^3/_4$, $^1/_8$, $^1/_2$, $^1/_4$. Set 2: $^1/_4$, $^7/_8$, 0; $^3/_4$, $^5/_8$, 0; $^3/_4$, $^3/_8$, $^1/_2$; $^1/_4$, $^1/_8$, $^1/_2$. Set 3: 0, $^1/_4$, $^7/_8$; 0, $^3/_4$, $^5/_8$; $^1/_2$, $^3/_4$, $^3/_8$; $^1/_2$, $^1/_4$, $^5/_8$). The network illustrated in Figure 2 is based upon set 2.

(10) Mn₄O₄ cubes are considered a model for one of the "S-states" of PS-II, a water oxidation enzyme: Proserpio, D. M.; Hoffmann, R.; Dismukes, G. C. *J. Am. Chem. Soc.* **1992,** *114,* 4364 and references therein.

(11) There are numerous examples of rigid M₄X₄ cubanes spanning a wide range of metals (including main group) and X moieties. **2** has close analogues in [Mo(CO)₂(NO)(μ_3-OH)]₄, which also forms a 1:4 adduct with triphenylphosphine oxide (Albano, V.; Bellon, P.; Ciani, G.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1969,** 1242) and [Re(CO)₃(μ_3-OH)]₄ (Herberhold, M.; Suss, G.; Ellermann, J.; Gabelein, H. *Chem. Ber.* **1978,** *111,* 2931). X could also be an H-bond acceptor, thereby facilitating assembly of diamondoid networks with rigid tetrafunctional H-bond acceptors and simple difunctional H-bond-donor molecules.

(12) A plethora of potential bridging molecules exists. A double diamondoid network is obtained when **2** is cocrystallized with the bulkier but longer hydrogen-bond acceptor 1,2-bis(diphenylphosphinyl)ethane). The two interweaved diamondoid networks are tetragonally distorted, and the phenyl rings are disordered, resulting in an *R* value of 0.11. Space group *P*4₂/*n*, *a* = 14.290 (5) Å, *c* = 18.028 (8) Å, *V* = 3681.4 Å³, *Z* = 2. Full details will be published at a later date.

Trisilaallyl Anion Structures. Is Conjugation Effective?

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To what extent can analogies between carbon and silicon species be applied to the trisilaallyl anion SiH₂SiHSiH₂⁻, **1**? Is the potential resonance energy in **1** sufficient to overcome the inherent nonplanar preferences of the related silicon species? While the methyl anion inversion barrier is only 2.3 kcal/mol at MP2/6-31+G*,[1] the SiH₃⁻ barrier is an order of magnitude higher (25.9 kcal/mol).[2] Unsaturated carbon species are planar, while the silicon analogs are not. The bent structures of disilaethylene[3] and hexasilabenzene[4] are examples.[4e]

The structure and stabilization energy of the allyl anion (**2**) have been determined both experimentally and theoretically,[5] but

(1) See: Salzner, U.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992,** in press and references cited for other values.

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