Chem. Mater. **1999,** *11,* 684−690

Self-Assembly of Hydrogen-Bonded Polymeric Rods Based on the Cyanuric Acid·Melamine Lattice

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Received July 29, 1998. Revised Manuscript Received December 28, 1998

This paper describes the self-assembly of hydrogen-bonded polymeric rods based on the lattice of cyanuric acid and melamine (CA·M). Data from ^{1}H NMR spectroscopy, IR spectroscopy, gel permeation chromatography (GPC), and transmission electron microscopy (TEM) are interpreted as indicating that the self-assembly of a bisisocyanuric acid (bisCA) and a bismelamine (bisM) formed polymeric nanorods $[(\text{bisCA})_n(\text{bisM})_n]$ composed of parallel CA·M rosettes. The TEM results suggest that these rods aggregate as bundles. The length of the bundles ranged from 100 to 1500 nm, and their diameter was in the range from 15 to 500 nm.

Introduction

In developing methodologies to prepare supramolecular structures using self-assembly,[1,2] we have prepared a series of soluble, structurally well-defined aggregates based on the isocyanuric acid and melamine (CA·M) lattice (molecular weight range 1.5−6.4 kDa). These compounds show high stabilities in aprotic organic solvents.[3,4] The objective of the work reported here was to demonstrate that the CA·M lattice can also be used to make extended, "polymeric" structures—here, rod structures with high molecular weight—using the same strategy but with components different from those employed with the soluble aggregates.[5]

In this paper we describe a strategy based on self-assembly for making structures that we infer, based on spectroscopic data, to be extended rod structures. Nanorod and nanotube structures have attracted some attention in the past decade for their potential as structures with interesting properties of conductivity, catalysis, and ion transport,[6] and Ghadiri,[7] Lehn,[8] Kunitake,[9] and others[10,11] have prepared nanorod or nanotube materials by self-assembly. Here we report that the self-assembly of bisCA (**1**, **2**, **3**) and bisM (**5**, **6**) forms nanorod materials $[(\text{bisCA})_n(\text{bisM})_n]$ in organic solvents such as CHCl$_3$ and methylcyclohexane and that these rods aggregate into mesoscopic aggregates of rod structures; these structures ultimately form transparent gels in organic solvents. These large aggregates are stable and can be characterized by ^{1}H NMR spectroscopy, IR spectroscopy, gel permeation chromatography (GPC), and transmission electron microscopy (TEM).[12] The work of Lehn,[8] and Kunitake[9] is similar in concept, and our structures add to the understanding of this interesting class of material.

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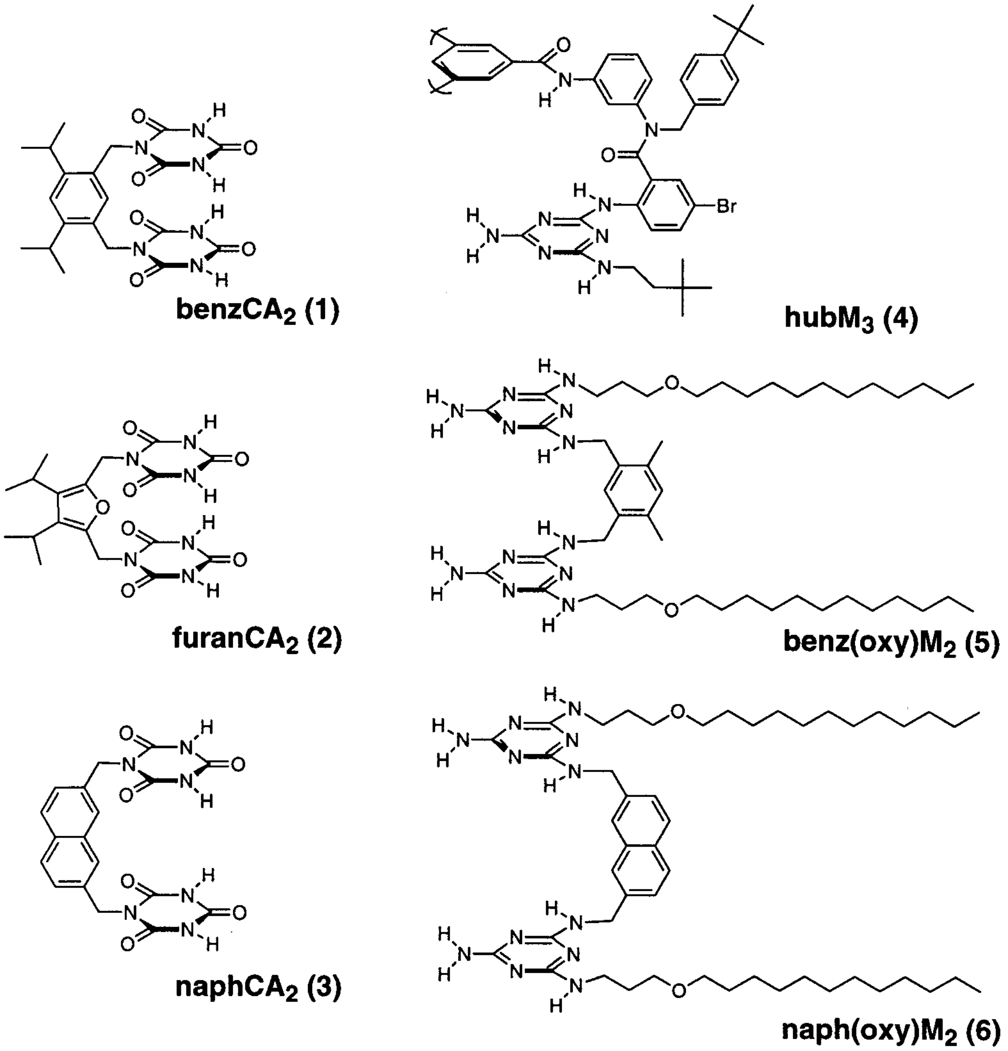
10.1021/cm980540j CCC: $18.00

Scheme 1. Components of Self-assembled Supramolecular Structures Based on the CA·M Lattice



Results and Discussion

Synthesis. *NaphCA$_2$ (3).* Scheme 2 outlines the synthesis of **3**. We chose the commercially available 2,7-dimethylnaphathalene (**7**) as a starting material. The bromination of **7** with NBS formed compound **8** in 98% yield. The reaction of **8** with NaN_3 proceeded smoothly in the presence of (n-Bu)$_4$NI in DMF to form bisazide **9**. The reduction of the bisazide **9** with PPh_3/H_2O formed diamine **10** in quantitative yield. The reaction of **10** with nitrobiuret yielded compound **11**. Further reaction of **11** with diethyl carbonate produced naphCA$_2$ (**3**). This compound is not soluble in most nonpolar solvents, but slightly soluble in methanol and very soluble in DMF. Purification of **3** was achieved by recrystallization from a solution in methanol.

Benz(oxy)M$_2$ (5) and Naph(oxy)M$_2$ (6). Scheme 3 outlines the synthesis of **5**. One chlorine substituent on cyanuric chloride was displaced by 3-lauryloxypropyl-1-amine, and the subsequent reaction of this compound, **12**, with diamine **13** formed compound **14**. The reaction of **14** with ammonium hydroxide gave bismelamine **5** in 64% combined yield based on cyanuric chloride. Naph(oxy)M$_2$ (**6**) was prepared from cyanuric chloride and diamine **10** in 76% yield by using the same procedure.

Preparation and Characterization of Self-Assembled Nanorods (bisCA)$_n$(bisM)$_n$. *Preparation.* Scheme 4 outlines the preparation of self-assembled nanorods from bisCA (**1**, **2**, **3**) and bisM (**5**, **6**). A 1:1 mixture of the bisCA and bisM components was dissolved in a mixture of chloroform and methanol by sonication or brief heating. After removal of the solvent, the resulting white powder material was dissolved in chloroform by sonication. The viscosity of the solution (concentration $10^{-5}-10^{-3}$ M) increased with time, and a transparent gel formed in 2−3 h. Six types of rod samples were obtained; these materials had the following empirical formulas: (naphCA$_2$)$_n$(benz(oxy)M$_2$)$_n$ (**16**), (naphCA$_2$)$_n$(naph(oxy)M$_2$)$_n$ (**17**), (benzCA$_2$)$_n$(benz(oxy)M$_2$)$_n$ (**18**), (benzCA$_2$)$_n$(naph(oxy)M$_2$)$_n$ (**19**), (furanCA$_2$)$_n$(benz(oxy)M$_2$)$_n$ (**20**), and (furanCA$_2$)$_n$(naph(oxy)M$_2$)$_n$ (**21**).[13] The formation of gels suggested that materials with high molecular weight formed from the self-assembly of the two components (bisCA and bisM).

^{1}H NMR Spectroscopy. We recorded the ^{1}H NMR spectra for all six rod materials immediately after a 1:1 mixture of bisCA and bisM had been dissolved in chloroform; only very broad peaks were observed. Broad peaks located between 13 and 16 ppm, which we ascribe to the imide protons of bisCA, suggest the formation of hydrogen bonds between bisCA and bisM.[14] These peaks

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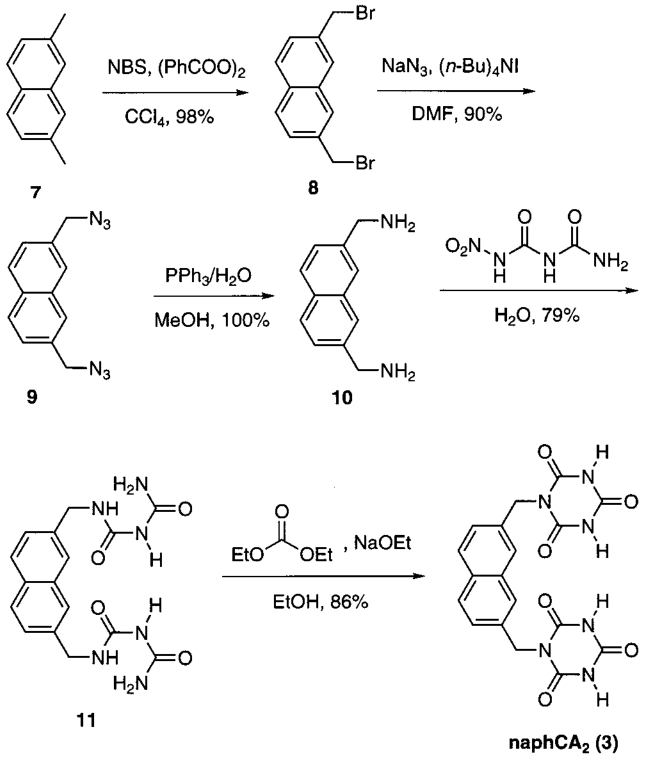
[13] The numbers **16**, **17**, **18**, **19**, **20**, and **21** refer to mixtures of extended polymeric structures.

Scheme 2. Synthesis of NaphCA$_2$ (3)



became too broad to be observed after a few hours, suggesting further growth of the rods and the formation of rod bundles.

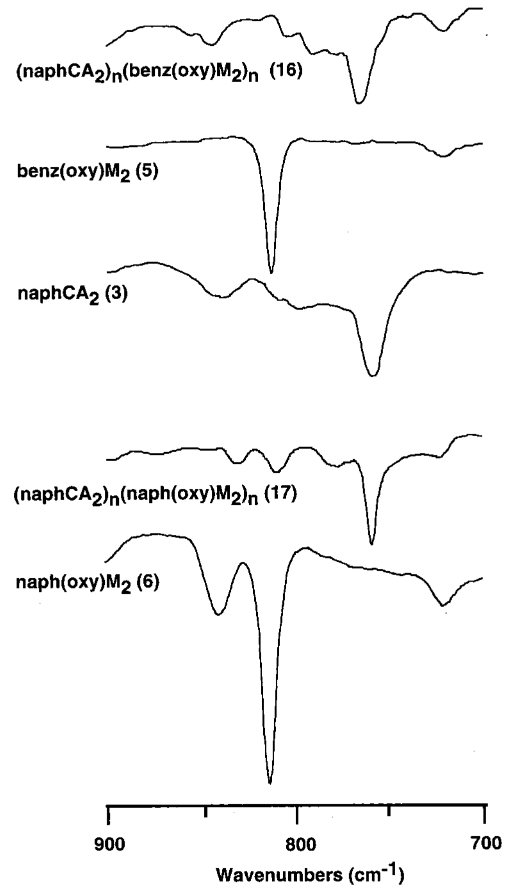


Figure 1. The FT-IR spectra (700−900 cm^{-1}) of components **3**, **5**, **6**, and their self-assembled aggregates **16** and **17**: samples were made as thin films on a KBr plate (**5**, **6**, **16**, and **17**) or as a KBr pellet (**3**).

FT-IR Spectroscopy. We recorded the IR spectra of gel samples (as a thin film on a KBr plate) and their components (either as a KBr pellet or a thin film coated on a KBr plate). Significant changes in the spectra were observed on going from the components to the rod. Figure 1 shows selected region (700−900 cm^{-1}) of the IR spectra for gel samples (**16**, **17**) and their components (bisCA **3**, bisM **5** and **6**). The changes on the triazine ring vibration at 813 cm^{-1} for bisM (**5** and **6**) are diagnostic: these peaks are sharp and strong for bisM alone, but they are significantly weakened for the rod samples (**16** and **17**).[15] These spectral changes strongly suggest that the hydrogen bonds holding the CA·M rosettes form efficiently. Similar changes were observed earlier by Kunitake and co-workers for their bilayer membranes and nanotubes based on CA·M-like networks.[9,15b]

Gel Permeation Chromatography. The gel sample was diluted with chloroform to give a solution (~10^{-5} M in the components), and this solution was analyzed by GPC. Figure 2 shows the GPC chromatograms of a small aggregate **15** and gel samples **16** and **17**. Aggregate **15** is a 2 + 3 hydrogen-bonded aggregate from hubM$_3$ (**4**) and naphCA$_2$ (**3**); its molecular weight is 5417. The GPC chromatogram of **15** (Figure 2a) was used as a marker of molecular weight.[16] Parts b and c of Figure 2 show the GPC chromatograms of gel sample **16** and **17**. The short retention times for these rods suggest that the molecular weight is high for whatever form of the sample is present in the GPC (we presume single rods or aggregates).[17] The peak observed for **17** in the GPC trace is quite symmetrical and sharp; this observation suggests that the self-assembled rods are stable, and the molecular weight distribution indicates few low molecular weight compounds. We believe that the molecular weight was controlled by the ratio of the two components and the impurities present in the mixture.[18] Because the column was not calibrated (and because it is not clear what compound to use for such calibration), we cannot estimate a molecular weight for the species present in these peaks.

Transmission Electron Microscopy. We obtained structural information about these aggregates in the solid state using transmission electron microscopy.[7,9,19] Fig-

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[14] Similar features in ^{1}H NMR spectra have been observed in related CA·M-based self-assembled structures: Simanek, E. E.; Wazeer, M. I. M.; Mathias, J. P.; Whitesides, G. M. *J. Org. Chem.* **1994**, *59*, 4904. Chin, N. D.; Simanek, E. E.; Li, X.; Wazeer, M. I. M.; Whitesides, G. M. *J. Org. Chem.* **1997**, *62*, 1891. Simanek, E. E.; Qiao, S.; Choi, I. S.; Whitesides, G. M. *J. Org. Chem.* **1997**, *62*, 2619.

[15] Such phenomena are not without precedent in somewhat related systems: (a) Padgett, W. M., II; Hamner, W. F. *J. Am. Chem. Soc.* **1958**, *80*, 803. (b) Kimizuka, N.; Kawasaki, T.; Kunitake, T. *J. Am. Chem. Soc.* **1993**, *115*, 4387.

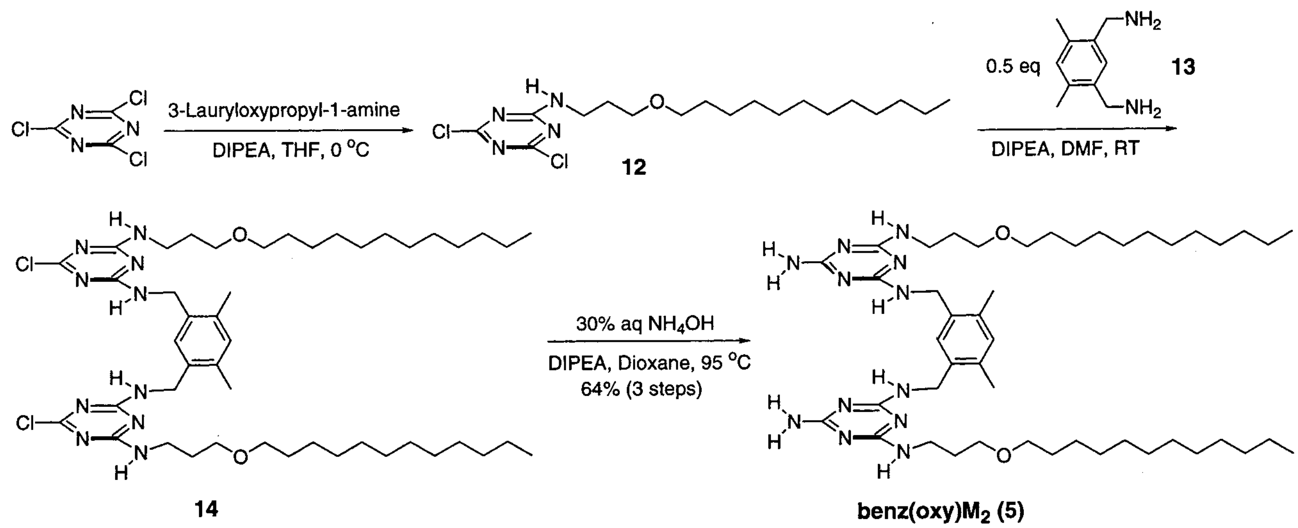
[16] Aggregate **15** is a new 2 + 3 aggregate from hubM$_3$ and NaphCA$_2$, and this aggregate was characterized by ^{1}H NMR spectroscopy. For other 2 + 3 hydrogen-bonded aggregates, see ref 5.

[17] Mathias, J. P.; Simanek, E. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4326.

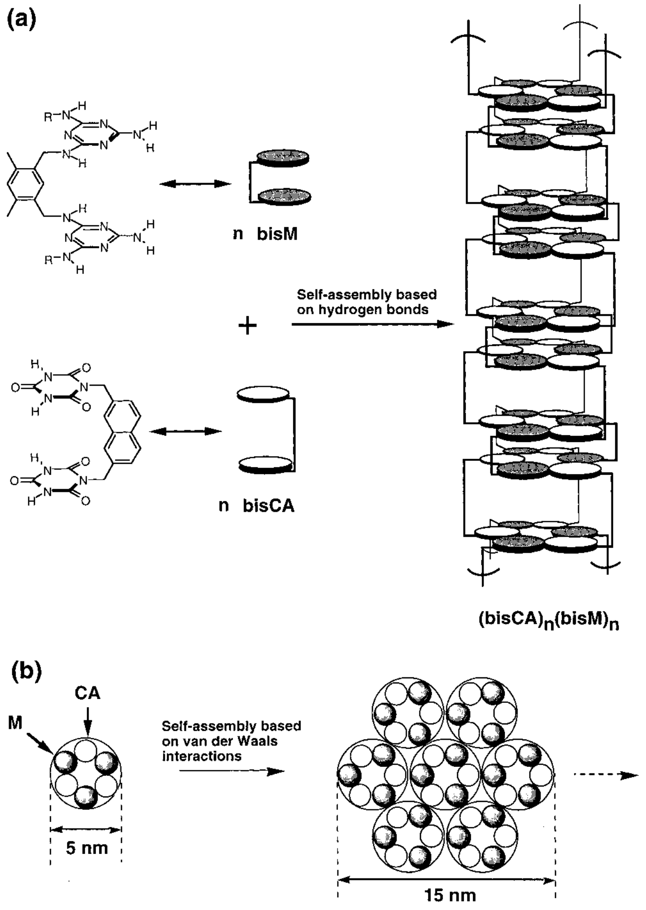
[18] The control of the molecular weight of these self-assembled rods is similar to that observed for the conventional two-component condensation polymerization; the ratio of the two components and impurities control the molecular weight of the polymer. See Billmeyer, F. W., Jr. *Textbook of Polymer Science*; John Wiley and Sons: New York, 1984.

[19] Williams, D. B.; Carter, C. B. *Transmission Electron Microscopy*; Plenum Press: New York, 1996.

Scheme 3. Synthesis of Benz(oxy)M_2 (5)



Scheme 4. Proposed Processes for the Self-Assembly of BisM (bismelamines) and BisCA (bisisocyanurates) to Give Polymeric Nanorods: (a) Self-Assembly of a Single Rod Based on Hydrogen Bonds and (b) Self-Assembly of Bundles of Rods Based on van der Waals Interactions $R = (CH)_2O(CH_2)_{11}CH_3$



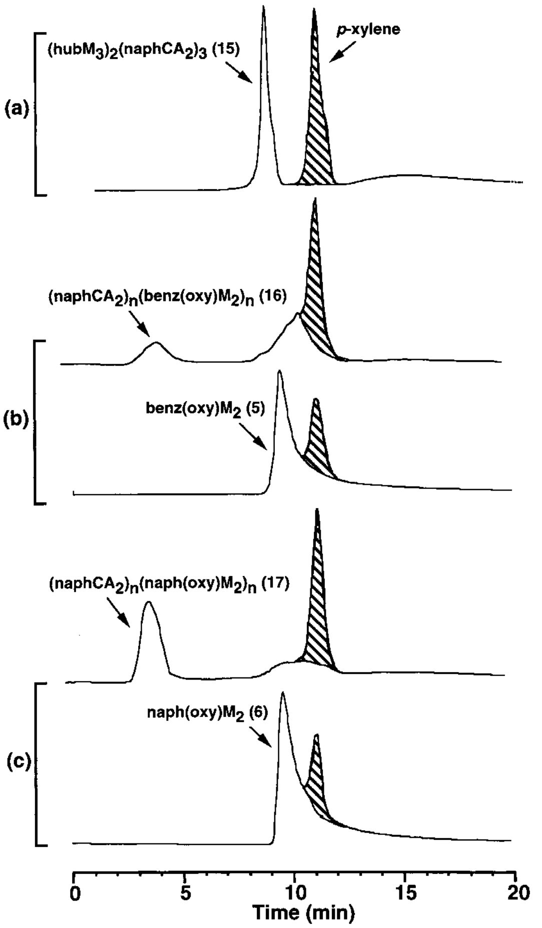


Figure 2. Gel permeation chromatograms of **5**, **6**, **15**, **16**, and **17**. Methylene chloride was used as an eluent and *p*-xylene was used as an internal standard. The injection volume was 20 μL, and the concentrations for these samples were in the range from 10 μM to 1 mM in the components.

ure 3 shows transmission electron micrographs of **16** (Figure 3a) and **17** (Figure 3b). The specimens were prepared from gel samples. These TEM pictures show that the diameter of these rods is in the range of 15–500 nm. We estimate the diameter of a single rod with fully extended alkyl chains to be 5 nm. The majority of the rods observed are in the form of bundles with diameters ranging from 15 nm (a possible seven-rod bundle) to very large bundles (diameter 500 nm) (see Scheme 4b). The length of these rods ranged from 100 nm (about 200 stacked CA·M rosettes) to 1500 nm (about 3000 stacked CA·M rosettes). We presume that these microcrystalline structures (rod bundles) formed from further aggregation of polymeric rods by the

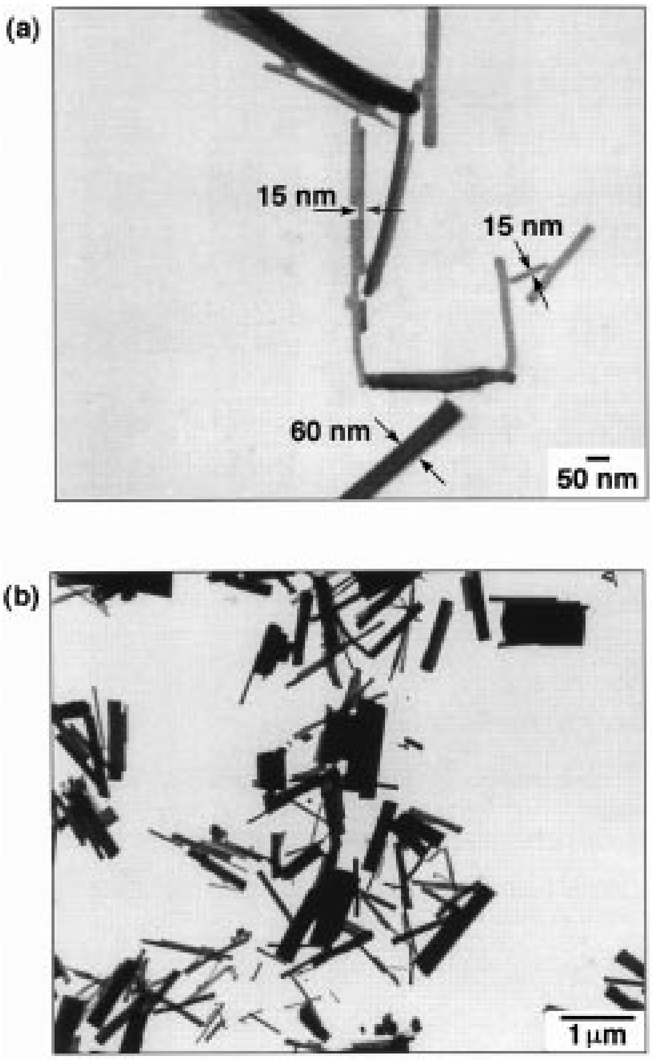


Figure 3. Transmission electron micrographs of self-assembled rods: (a) **16** and (b) **17**. The solvent was chloroform.

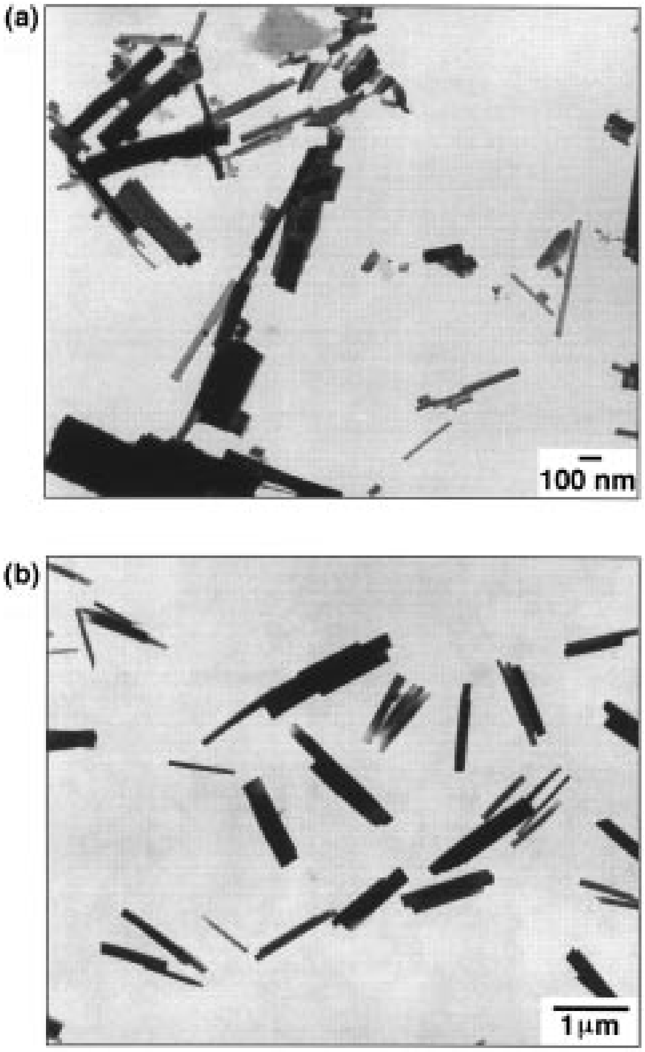


Figure 4. Solvent effect: transmission electron micrograph of **20** precipitated from (a) chloroform and (b) methylcyclohexane.

attractive van der Waals interactions between the lauryloxypropyl chains on adjacent rods. The rectangular shape of the crystal suggests that crystal growth was most rapid along the rod axis. We are not able to draw any inferences about the mechanisms of growth of the crystals, and we do not know if they form by aggregation of soluble rods, by addition of monomer units, or both. The square ends suggest annealing to minimize the surface area and interfacial free energy of these faces. This annealing might also involve dissociation of monomers or aggregates. We were unable to observe any single rods or bundles (that is, structures with a diameter less than 15 nm). These rods are straight (as shown in the micrographs), probably because the linkers in the bisM and bisCA components are rigid. This type of structure is in contrast with the curved structures of bilayers and tubes obtained by Kunitake and co-workers[9] and strongly supports our assumption that these rods are formed from stacked CA·M rosettes; other forms of aggregates between bisCA and bisM would yield structures with different sizes and shapes.

Solvent Effects. The nature of the solvent affected the size and morphology of the aggregates. For instance, when chloroform was removed from a gel sample of (furanCA_2)$_n$(benz(oxy)M_2)$_n$ (**20**) and methylcyclohexane was added to the resulting white powder, a new transparent gel was obtained. TEM (Figure 4b) shows the formation of remarkably uniform structures. Although we have not established the nature of this morphological change of crystals of rod bundles, the formation of uniform structures in methylcyclohexane is notable. When methanol was used as the solvent for gel sample **20**, we did not observe rods but did observe large (90 nm) fibers (Figure 5). We observed the same structure (fibers) when water was used. We presume that methanol or water disrupts the hydrogen bonding within the CA·M lattice and generates this less ordered fiber structure: we observed a mixture of rectangular crystalline structures and fiber structures when we took TEM micrographs immediately after the addition of methanol to the white powder (Figure 5b).

The Lauryloxypropyl Group on bisM Is Important for the Formation of High Molecular Weight Rods and Rod Bundles. In a previous report, we have shown that the assembly of a bismelamine presenting 4-*tert*-butylaniline substituents and benzCA_2 (**1**) formed a mixture of aggregates as a white powder.[17] We failed to obtain gels when an equimolar mixture of these two components was dissolved in chloroform. We also failed to obtain gels with a bismelamine presenting octadecylamine substituents. The complex ^{1}H NMR spectrum

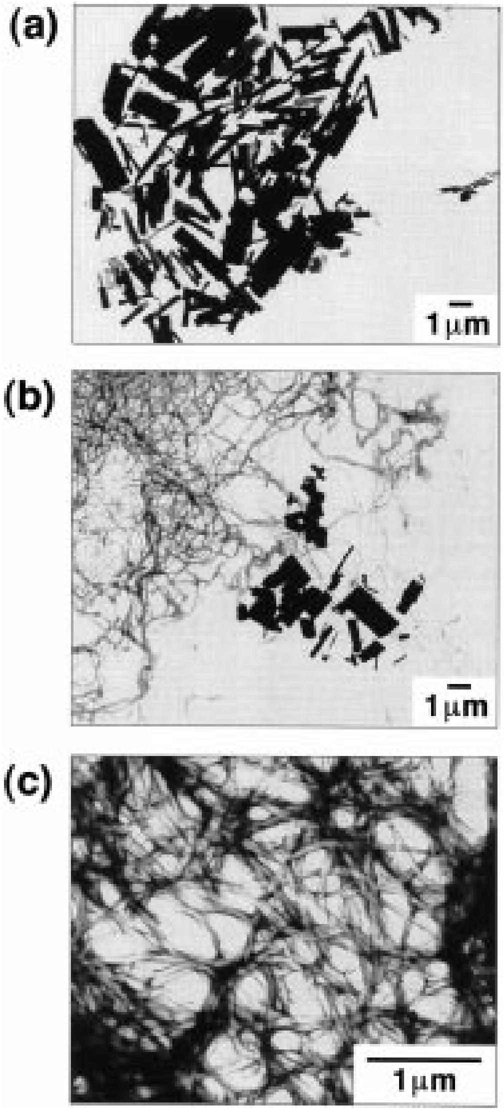


Figure 5. Solvent effect: transmission electron micrograph of a mixture of furanCA$_2$ (**3**) and benz(oxy)M$_2$ (**5**) (a) precipitated from chloroform; (b) taken right after the addition of methanol; and (c) precipitated from methanol.

suggested that the composition and the structure of this mixture were complicated, and we presume that it was a mixture of small oligomers. In this research, with the lauryloxypropyl groups on the bismelamines, we were able to prepare transparent gels with high stability. Kunitake and co-workers have also shown previously that introduction of an ether linkage to the alkyl side chains is an important factor in improving the solubility of aggregates and in generating ordered, stable assemblies.[15b,20]

Conclusions

We have demonstrated a strategy for making high molecular weight materials from small subunits by self-assembly. Related efforts by Lehn, Kunitake, Ghadiri, and Atwood have led to results that are similar to those reported here.[2,7,9] This preparation offers, however, several interesting features: parallel stacks of hydrogen-bonded rosettes; high viscosity in aprotic solvents; and a significant effect of solvent on morphology. The assembly of bisCA with bisM affords high molecular weight rods, which tend to form large rod bundles. BisCA and bisM are easy to synthesize and it may be possible to assemble functional materials by attaching functional groups to these components.

Experimental Section

General Procedures. NMR spectra were recorded using the solvents as the internal references. Carbon tetrachloride was distilled and stored over 4A molecular sieves. THF was distilled from sodium benzophenone ketyl. DMF was dried and stored over 4A molecular sieves. Absolute ethanol was used as received.

2,7-Dibromomethylnaphthalene (8). A solution of **7** (1.90 g, 12.16 mmol), NBS (4.90 g, 26.13 mmol), and benzoyl peroxide (20 mg, 0.083 mmol) in carbon tetrachloride (100 mL) was heated at reflux for 10 h under N_2. The solid product was removed by filtration, and the filtrate was concentrated in vacuo. The residue was partitioned between ethyl acetate (100 mL) and water (100 mL). The organic extract was washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The mixture was purified by column chromatography (elution with 50:50 $CHCl_3$/hexane) to give 3.79 g (11.92 mmol, 98%) of the product as a white solid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.83−7.80 (m, 4H), 7.52 (dd, $J = 8.4$ Hz, $J = 1.8$ Hz, 2H), 4.65 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.88, 133.00, 132.72, 128.63, 127.92, 127.54, 33.78; HRMS-EI (M^+) calcd for $C_{12}H_{10}Br_2$ 311.9150, found 311.9157.

2,7-Diazidomethylnaphthalene (9). A mixture of **8** (0.25 g, 0.796 mmol), sodium azide (0.114 g, 1.75 mmol), and tetrabutylamonium iodide (3 mg, 0.0081 mmol) in DMF (20 mL) was heated at 60 °C for 2 h under N_2. The excess of sodium azide was removed by filtration, and the solvent was removed under vacuum. The residue was partitioned between ethyl acetate (30 mL) and water (30 mL). The organic extract was washed with water (30 mL) and brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (elution with 2:98 ethyl acetate/hexane) to give 0.17 g (0.716 mmol, 90%) of the product as a white solid: R_f 0.30 (5:95 ethyl acetate/hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.77 (s, 2H), 7.44 (dd, $J = 8.4$ Hz, $J = 1.7$ Hz, 2H), 4.49 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.66, 133.20, 132.77, 128.71, 127.19, 126.37, 54.97; HRMS (M^+) calcd for $C_{12}H_{10}N_6$ 238.0967, found 238.0973.

2,7-Diaminomethylnaphthalene (10). A mixture of **9** (0.90 g, 3.78 mmol), and water (0.27 g, 15.0 mmol) in THF (15 mL) was placed in a 50-mL round-bottomed flask. Triphenyl phosphine (2.48 g, 9.45 mmol) was added slowly to the reaction mixture with stirring at 0 °C. Gas (N_2) evolution was observed immediately after the addition of triphenyl phosphine. The mixture was stirred at room temperature for 10 h under N_2. A white solid (Ph_3PO) was removed by filtration, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (elution with 2:98 NH_4OH/MeOH) to give 0.71 g (3.76 mmol, 100%) of the product as a light yellow solid: R_f 0.45 (10:90 NH_4OH/MeOH); ^1H NMR (300 MHz, DMSO-d_6) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.73 (s, 2H), 7.43 (d, $J = 8.3$ Hz, 2H), 3.86 (s, 4H), 2.30 (bs, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 141.85, 133.11, 130.84, 130.75, 127.24, 125.45, 124.38, 124.30, 48.82; HRMS-EI (M^+) calcd for $C_{12}H_{14}N_2$ 186.1157, found 186.1149.

Bisbiuret (11). A mixture of **10** (0.40 g, 2.15 mmol) and nitrobiuret (0.70 g, 5.4 mmol) in water (30 mL) was placed in a 100-mL flask and heated at reflux for 2 h. Dioxane (10 mL) was added to the flask and the mixture was heated at reflux for another 10 h. The reaction mixture was cooled to room temperature and concentrated in vacuo. The residue was suspended in water (100 mL), sonicated, and filtered. The white solid material was washed with water (3 × 200 mL) and

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dried in an oven at 110 °C for 2 h, giving 0.61 g (1.70 mmol, 79%) of the product as a white solid: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (s, 2H), 8.04 (s, 2H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.69 (s, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 6.78 (s, 4H), 4.45 (d, $J = 5.9$ Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.71, 154.80, 137.56, 132.92, 131.39, 128.00, 125.68, 125.20, 42.74; HRMS-FAB (M + H$^+$) calcd for $C_{16}H_{18}N_6O_4$ 359.1468, found 359.1464.

NaphCA$_2$ (3). Sodium metal (0.32 g, 14.0 mg-atom) was added in small pieces to a 250-mL flask charged with 150 mL of absolute ethanol at 0 °C under N_2. The mixture was stirred at 0 °C until all the sodium was dissolved, and then 0.50 g (1.40 mmol) of the biuret **11** and 0.66 g (5.6 mmol) of diethyl carbonate were added. The mixture was heated at reflux for 40 h. The solvent was removed in vacuo, and 30 mL of absolute ethanol was added. The precipitated solid material was collected by vacuum filtration, washed with ethanol (200 mL), redissolved in water (15 mL), and filtered to remove the insoluble material. The filtrate was acidified to pH 2 with concentrated HCl solution, and the precipitated product was collected and washed with water (30 mL). The solid was redissolved in 1 N NaOH solution, and 1 N HCl solution was added dropwise until the pH reached 8.5. The yellow solid material was separated by filtration, and the acidity of the filtrate was adjusted to pH 2 with 1 N HCl solution. A white solid material was obtained by filtration. The crude product was preloaded on silica gel and eluted with methanol. The material collected from the column was further purified by recrystallization from methanol to give 0.494 g (1.20 mmol, 86%) of the product as a white solid: ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.88 (s, 4H), 7.81 (s, 2H), 7.68 (s, 2H), 7.39 (s, 2H), 4.97 (s, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 152.80, 152.49, 135.58, 132.57, 131.09, 127.42, 125.43, 125.09, 43.30; HRMS−FAB (M$^+$) calcd for $C_{18}H_{14}N_6O_6$ 410.0975, found 410.0978.

Benz(oxy)M$_2$ (5). A 100-mL, three-necked, round-bottomed flask was charged with cyanuric chloride (360 mg, 1.95 mmol), THF (20 mL), and DIPEA (2 mL), and the solution was cooled to 0 °C under an atmosphere of nitrogen. 3-Lauryloxypropyl-1-amine (480 mg, 1.97 mmol) in THF (10 mL) was added to the solution dropwise over 20 min. After 1 h, the reaction mixture was warmed to room temperature, and bisamine **13** (160 mg, 0.974 mmol) was added. This mixture was stirred at room temperature for 5 h. The reaction mixture was concentrated in vacuo and this material was dissolved in 1,4-dioxane (20 mL) and 30% NH_4OH (16 mL). The solution was sealed in a Parr vessel and heated at 95 °C for 15 h. The mixture was cooled to room temperature, depressurized, and concentrated in vacuo. The residue was partitioned between EtOAc (40 mL) and water (30 mL). The organic extract was washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (elution with 90:10 CH_2Cl_2/MeOH) to afford 522 mg (0.625 mmol, 64%) of the product as a white foam: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.20 (br s, 1 H), 6.86 (br s, 1 H), 6.86−6.50 (br m, 2 H), 6.50−6.24 (br m, 2 H), 6.03−5.84 (br m, 4 H), 4.30 (br s, 4 H), 3.35−3.18 (br m, 12 H), 2.20 (br s, 6 H), 1.66 (br s, 4 H), 1.44 (br s, 4 H), 1.40−1.00 (br s, 36 H), 0.84 (t, $J = 6.9$ Hz, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.76, 166.01, 135.17, 133.36, 131.39, 131.04, 70.07, 68.11, 42.53, 37.67, 31.29, 29.63, 29.23, 29.03, 28.90, 28.70, 25.68, 22.07, 18.23, and 13.91; HRMS-FAB (M + H$^+$) calcd for $C_{46}H_{82}N_{12}O_2$ 835.6762, found 835.6760.

Naph(oxy)M$_2$ (6). A 100-mL, three-necked, round-bottomed flask was charged with cyanuric chloride (180 mg, 0.975 mmol), THF (20 mL), and DIPEA (0.2 mL), and the solution was cooled to 0 °C under an atmosphere of nitrogen. 3-Lauryloxypropyl-1-amine (240 mg, 0.986 mmol) in THF (10 mL) was added to the solution dropwise over 10 min. After 1 h, the reaction mixture was warmed to room temperature and concentrated in vacuo. This material was dissolved in DMF (50 mL), and to the solution were added DIPEA (0.3 mL) and bisamine **10** (90 mg, 0.483 mmol). This mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated in vacuo and the resulting solid was dissolved in 1,4-dioxane (12 mL) and 30% NH_4OH (10 mL). The solution was sealed in a Parr vessel and heated at 95 °C for 30 h. The mixture was cooled to room temperature, depressurized, and concentrated in vacuo. The residue was partitioned between EtOAc (30 mL) and water (20 mL). The organic extract was washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (eluted with 90:10 CH_2Cl_2/MeOH) to afford 314 mg (0.366 mmol, 76%) of the product as a white foam: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.77−7.38 (br m, 6 H), 7.13−6.95 (br m, 2 H), 6.47−6.38 (br m, 2 H), 6.08−5.88 (br m, 4 H), 4.55 (br s, 4 H), 3.35−3.21 (br m, 12 H) 1.67−1.00 (br m, 44 H), 0.83 (t, $J = 6.7$ Hz, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.75, 166.11, 138.64, 132.79, 130.94, 127.31, 125.27, 124.59, 70.11, 68.10, 43.14, 37.41, 31.33, 29.65, 29.27, 29.07, 29.05, 28.93, 28.75, 25.72, 22.11, and 13.94; HRMS-FAB (M + Na$^+$) calcd for $C_{48}H_{80}N_{12}O_2Na$ 857.6605, found 857.6578.

Gel Permeation Chromatography (GPC). Gel permeation chromatography was performed using a Waters 600E HPLC with a Waters 484 UV detector and Waters analytical gel permeation column (Ultra-styragel, 1000 ≈ pore size). Elutions were performed at room temperature using HPLC-grade methylene chloride as the solvent at a flow rate of 1.0 mL/min.

Transmission Electron Microscopy (TEM). A drop of a solution of an aggregate (10^{-3} M) was placed on a carbon foil supported on a copper grid supported by a filter paper. After the solvent was evaporated, the absorbed aggregate film was stained by a drop of a saturated aqueous solution of uranyl acetate. The sample was analyzed on a Philips EM 420 TEM using an accelerating voltage of 120 kV.

Acknowledgment. This work was supported by NSF Grant CHE-91-22331. The NMR facility was supported by NIH Grant 1-510-RR04870-01 and NSF Grant CHE 88-14019. Mass spectra were obtained by Dr. Andrew Tyler. The Mass Spectrometry facility was supported by NSF Grant CHE-90-20043 and the NIH Grant 1 S10 RR06716-01. We thank Dr. Yuan Lu, for his assistance with the TEM work, and Dr. Peter Glink, for stimulating discussion.

CM980540J