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Tube-like Nanostructures Composed of Networks of Complementary Hydrogen Bonds[1]

Nobuo Kimizuka,* Takayoshi Kawasaki, Kiyoko Hirata, and Toyoki Kunitake

Department of Chemical Science and Technology
Faculty of Engineering, Kyushu University
Higashi-ku, Fukuoka 812, Japan

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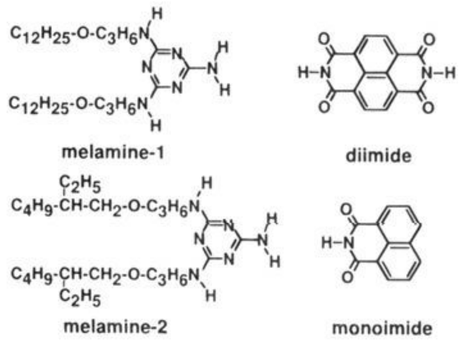
Construction of well-defined hydrogen-bond-mediated supramolecular architectures is currently a topic of intense investigations. These architectures may be soluble oligomers,[2] liquid crystals,[3] surface monolayers,[4] crystalline organic solids,[5] or hollow tubular aggregates.[6] Lacking among them are independent mesoscopic assemblies similar to tobacco mosaic virus and nucleosome.[7] These biological assemblies are characterized by accumulated noncovalent interactions and by their amphiphilic feature. In the present study, we prepared amphiphilic supramolecular architectures that are dispersible in organic media by employing a hydrogen-bond-mediated aromatic sheet as the strongly interacting (solvophobic) unit and alkyl chains as the solvophilic unit.

Chart 1



Dialkylated melamines which contain unbranched alkyl chains (**Melamine-1**)[8] or branched alkyl chains (**melamine-2**) were chosen as one of the components (Chart 1). 1,8:4,5-Naphthalenebis(dicarboximide) ("**diimide**"; Tokyo Kasei) is the other component and was purified by passage through a column of activated aluminum oxide (Merck, aluminum oxide 90, neutral) with dimethyl sulfoxide as eluent. Hydrogen-bonded complexes, **melamine-1/diimide** and **melamine-2/diimide**, were prepared by mixing equimolar amounts of diimide in dimethyl sulfoxide (1 mM) and **melamine-1** or **melamine-2** in ethanol (1 mM) and solvent evaporation. IR spectra (KBr) of the resultant orange-colored powders contained a group of the C=O stretching bands at 1719 and 1685 cm^{-1} which was altered from those observed for diimide alone (1701 and 1680 cm^{-1}). In addition, the triazine ring vibration observed at 812 cm^{-1} for **melamine-1** and **melamine-2** alone was weakened significantly in the equimolar powders. These IR spectral changes are similar to those observed for the hydrogen-bonded pairs of **melamine-1** and isocyanuric acid derivatives[8] and indicate that complementary hydrogen bonds are formed among the mixed components. The powdery complexes were sonicated (Branson Sonifier Model 185, sonic power 45 W, 1 min) in methylcyclohexane to give transparent dispersions (5 × 10^{-5} M). These dispersions are stable for more than 3 months. As diimide alone cannot be dispersed in methylcyclohexane, the observed solubility is endowed by its complexation with complementary solvophilic units, **melamine-1** or **melamine-2**.

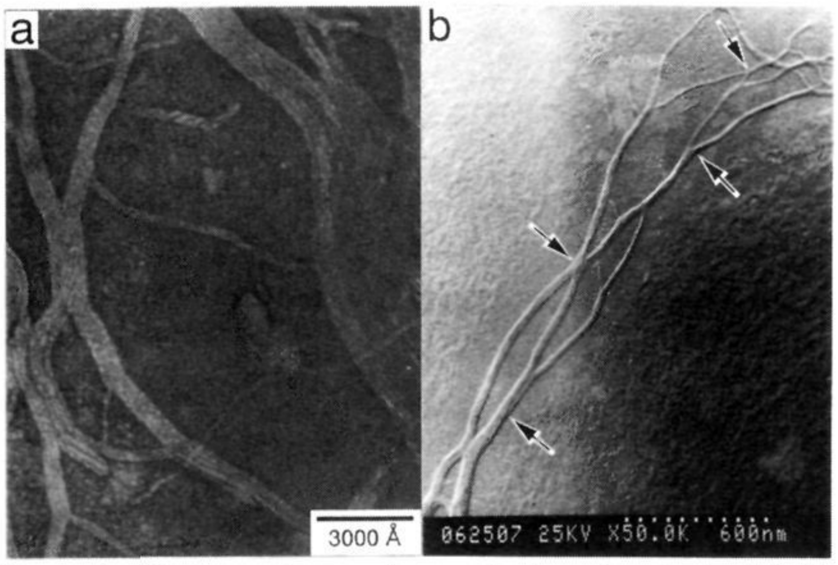


Figure 1. Electron microscopic examination of melamine/diimide complexes. (a) Transmission electron micrograph of melamine-1/diimide complex. The sample was poststained with uranyl acetate. (b) Scanning electron micrograph of melamine-2/diimide complex. The sample was coated with Pt (ca. 10 Å).

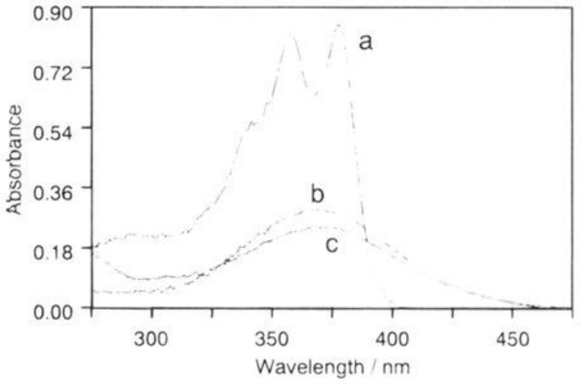


Figure 2. UV−vis absorption spectra of the diimide moiety; [Diimide] = 2.5 × 10^{-5} M, 25 °C. (a) Diimide alone dissolved in DMSO. (b) The equimolar melamine-1/diimide complex dispersed in methylcyclohexane. (c) The equimolar melamine-2/diimide complex dispersed in methylcyclohexane.

Figure 1 displays transmission and scanning electron micrographs. In the TEM picture, bundles of 100-Å-wide strands are abundantly present and some of the bundles are separated into individual strands. A similar morphology was found for the **melamine-2/diimide** complex. In the SEM observation, the overall morphology is identical to that of the TEM picture. As indicated by the arrow, multiple strands are twisted into helical bundles. This twisting was recognized also in a preliminary AFM observation.

Figure 2 compares UV−vis spectra of **diimide** in dimethyl sulfoxide and in the equimolar complexes dispersed in methylcyclohexane. **Diimide** alone possesses a structured absorption with maxima at 357 and 368 nm, but the equimolar complexes displayed broad absorption peaks centered at 370 nm with significant decreases in absorption intensity. Similar hypo-

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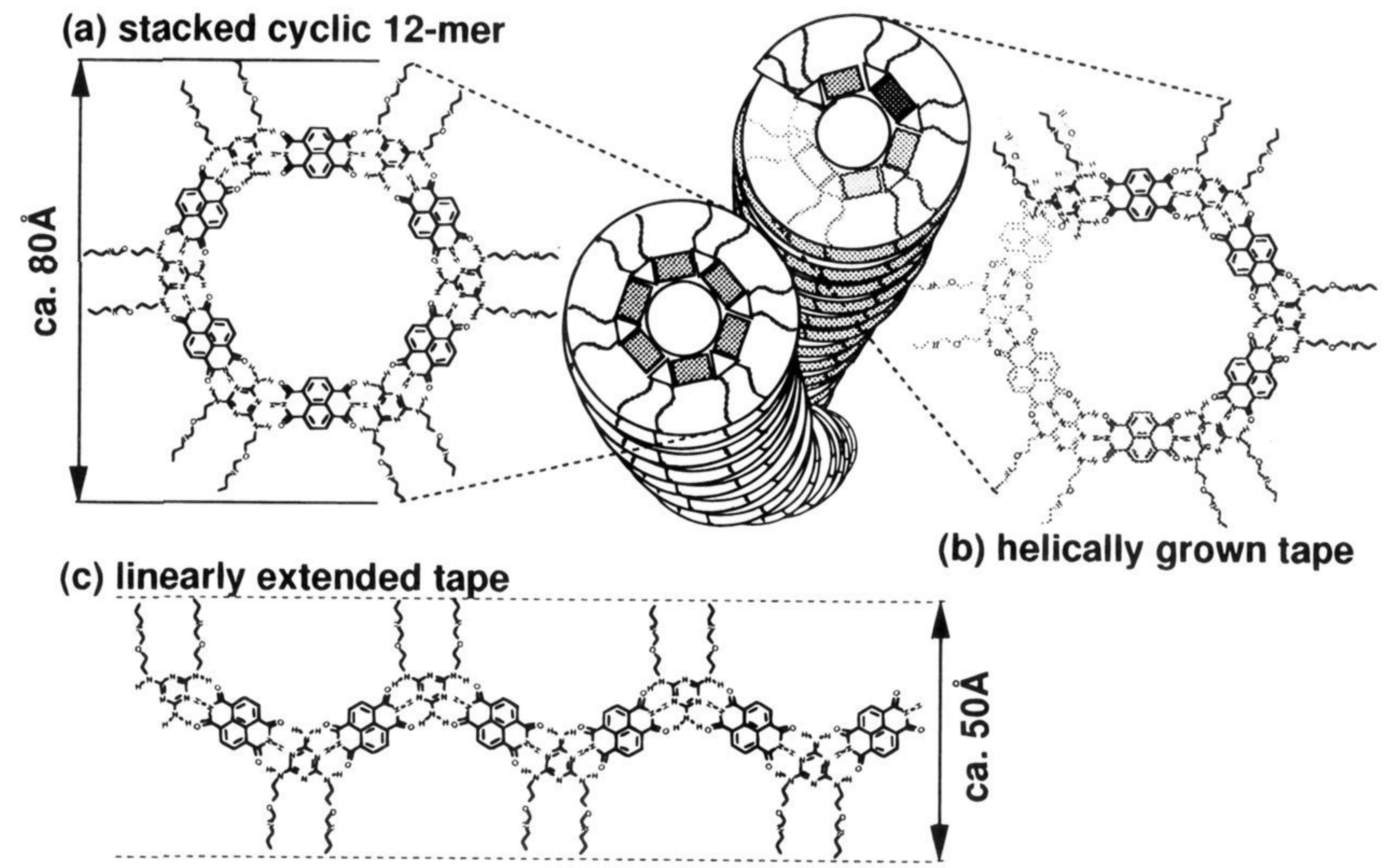

Figure 3. Schemetic illustration of conceivable supramolecular structures.

chromism is reported for soluble oligomers of complementary hydrogen-bond pairs,[9] and broadening of absorption bands is often associated with stacked aromatic chromophores.[10] Thus, the latter spectral characteristics are attributable to the aromatic stacking of the **diimide** subunit in the mesoscopic strand. Addition of ethanol to a methylcyclohexane dispersion of **melamine-1/diimide** (up to 50 vol %) caused precipitation of the **diimide** component together with appearance of structured absorption of the unstacked **diimide**. This must be related to partial disruption of the hydrogen-bonded aggregate.

The formation of extended hydrogen-bond networks between the melamine and imide moieties as probed by FT-IR spectroscopy requires aggregate geometries that are compatible with either a cyclic structure (Figure 3a), a helically grown structure (Figure 3b), or a linearly extended structure (Figure 3c). In Figure 3a, the tublar structure is generated by columnar stacking of a cyclic heterododecamer of **melamine-1** (or **-2**) and **diimide**. The cyclic unit contains the circular combination of the two components via complementary hydrogen bonds. In Figure 3b, the diimide and melamine components give a helically wound tape that is extended in the normal direction. These structures would possess a diameter of ca. 80 Å, and this is consistent with the electron microscopic observation. In contrast, aromatic stacking of linear tapes of Figure 3c would form a sheet-like structure with a 50-Å width by assuming parallel stacking.

We cannot give a definite supramolecular structure at this stage, but it is clear that the following structural features are responsible for the surprising aggregation stability. First, the extended hydrogen-bond network is indispensable. This is readily confirmed by the absence of observable supramolecular architectures when an equimolar mixture of **melamine-1** and 1,8-naphthalenedicarboximide (**monoimide**) was dispersed in methylcyclohexane. **Monoimide** is not capable of producing the extended network, and the equimolar mixture appears to yield smaller, if any, hydrogen-bonded complexes.[11] Similarly, the 1:2 complex of **melamine-1** and **monoimide** as prepared in ethanol could not be stably dispersed in methylcyclohexane. Second, the regular molecular alignment and the consequent aromatic stacking improve the aggregation stability, as has been found for some hydrogen-bonded complexes.[2,3] This effect is also crucial for aqueous bilayers formed from amphiphilic hydrogen-bond networks.[8] Third, the hydrogen-bonded aromatic moiety is quite solvophobic in nonpolar solvents such as methylcyclohexane. Therefore, impartment of the amphiphilic nature by alkyl substitution is essential for stabilized mesoscopic dispersion. It is noteworthy that these soluble nanostructures are stable at remarkably low concentrations (ca. 2.5×10^{-5} M), which are 2 orders of magnitude lower than those required for the soluble cyclic hydrogen-bonded "rosette" formed from melamine and cyanuric acid derivatives (ca. 4×10^{-3} M).[2c]

It is important to point out the architectural analogy between our mesoscopic structures and tobacco mosaic virus.[12] The fibrous assembly via molecular recognition and the three-dimensional growth via molecular stacking are common features in both systems. The general strategy described in this paper would be extended to the design and synthesis of a wide range of mesoscopic superstructures with specified internal organizations and surface characteristics. Detailed structural analysis of the present mesoscopic superstructure is currently in progress.

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(11) When an ethanolic solution (1 mM, 100 μL) of **monoimide** was injected to methylcyclohexane (final **monoimide** concentration, 2.5×10^{-5} M), a broad absorption peak around 330 nm was observed, indicating the presence of the stacked **monoimide** species. This peak was replaced by a structured monomeric absorption with maxima at 327 and 342 nm upon addition of an equimolar amount of **melamine-1**. Apparently self-aggregated **monoimide** in methylcyclohexane is converted to a molecularly dispersed **melamine-1/monoimide** complex.

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