Mesoscopic Supramolecular Assembly of a 'Janus' Molecule and a Melamine Derivative *via* Complementary Hydrogen Bonds

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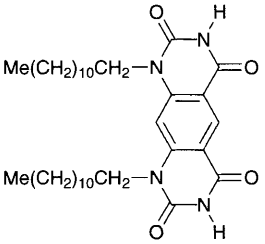
Irregular rods with a minimum diameter of *ca.* 150 Å and lengths of several tens of μm were formed in methylcyclohexane from complementary hydrogen-bond pairs of an alkylalanate-derivatized melamine and a 'Janus' molecule; circular dichroism with exciton coupling was induced for the 'Janus' chromophore *via* hydrogen bonds, probably due to the structural regularity of the molecular assembly.

Biological systems present numerous mesoscopic molecular assemblies as exemplified by tobacco mosaic virus and nucleosome. The exquisite biological superstructures have inspired construction of artificial counterparts by molecular recognition-directed self-assembly.[1–4] These artificial systems are usually obtained as organic solids, liquid crystals or oligomeric assemblies in aprotic media. Steric crowding among complementary subunits has been used as a means for selective assembly of one of several possible aggregate structures.[2] However, this approach is not necessarily suitable for producing soluble mesoscopic superstructures that have dimensions in the range of nano- to micro-metre scales.

Hydrogen-bonded amphiphilic complexes represent a key strategy to generate mesoscopic self-assemblies in aqueous media.[5–7] This concept has been extended to an 'amphiphilic' combination of dialkylated melamine and naphthalenebis(dicarboximide) which produced a tube-like superstructure in organic media.[8] Following the principle of double-faced Janus molecules† as components for self-assembly,[9] the new complementary units of $2C_{12}$-Janus **1** and Mela(-L-ala-Ole)$_2$ **2** were synthesized and their assembling characteristics were invesitigated.‡ The Janus components presents two hydrogen-bonding faces in the chromophore, while the melamine counterpart possesses flexible oleyl chains as solvophilic unit.[10] A transparent dispersion was obtainable from an equimolar mixture of **1** and **2** in methylcyclohexane (*ca.* 0.1 mmol dm^{-3}) by ultrasonication. **1** alone could not be dispersed in methylcyclohexane. IR spectra (KBr) of the dispersion after solvent removal contained a considerably weakened triazine ring vibration at 810 cm^{-1} relative to that of **2** alone at 816 cm^{-1}. This IR spectral change has been typically observed for complementary hydrogen-bonded pairs of melamine derivatives.[5–8]

Fig. 1 displays a transmission electron micrograph of **1**·**2** stained with bis(pivaroyl) lead. Twisted flexible ropes made of *ca.* 150 Å-wide strands are observed. CD spectra of **1**·**2** and **2** alone in methylcyclohexane are shown in Fig. 2. The CD intensity is weak for chiral **2** alone in the range 220–400 nm : $[\theta]_{226} = -1.8 \times 10^3$ ° cm^2 dmol^{-1}. In contrast, the equimolar complex showed exciton coupled extrema at 220 nm ([θ] = -8.6×10^4 ° cm^2 dmol^{-1}) and 253 nm ([θ = 6.6×10^4 ° cm^2 dmol^{-1}), together with a negative peak at 335 nm. These CD bands arise from the Janus chromophore in the complex, which possesses an absorption maximum at 263 nm. It is clear that the exciton interaction among Janus chromophores exists as a result of their regular stacking in the chiral environment of hydrogen-bonded **2**, even at a remarkably low concentration (*ca.* 1 × 10^{-5} mol dm^{-3}). Chirality transmission *via* complementary hydrogen bonds has been noted for an aqueous bilayer system.[7]



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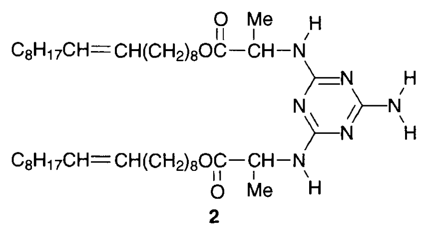

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The formation of complementary hydrogen-bond networks as probed by IR spectroscopy may be compatible either with a

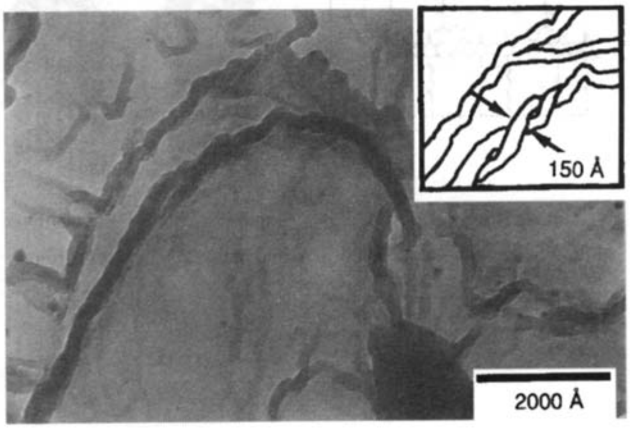


Fig. 1 Electron micrograph of **1**·**2** dispersed in methylcyclohexane (10 mmol dm^{-3}) stained by bis(pivaloyl)lead

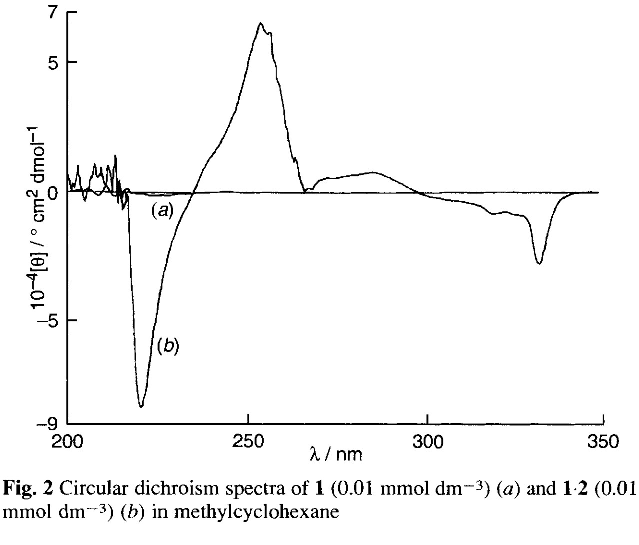
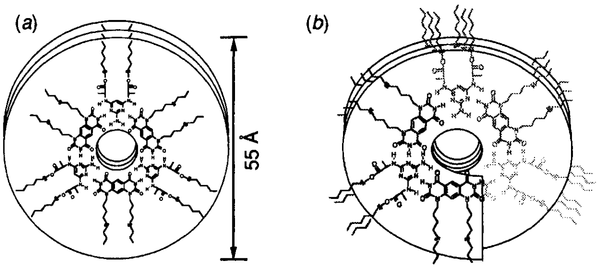
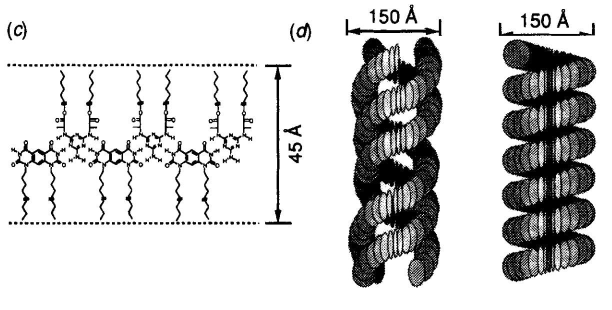


Fig. 2 Circular dichroism spectra of **1** (0.01 mmol dm^{-3}) (*a*) and **1**·**2** (0.01 mmol dm^{-3}) (*b*) in methylcyclohexane

cyclic structure, a helically grown structure, or a linearly extended structure as basic motifs [Fig. 3(*a*)–(*c*)]. Minimum diameters of circular and linear aggregates are estimated to be *ca.* 55 and 45 Å, respectively, from their space-filling molecular models. The observed minimum diameter (150 Å) of the flexible rope-like structure in electron microscopy is larger than those estimated from the simplified models of Fig. 3(*a*)–(*c*), and is indicative of multiple or tubular-helix assemblies of the circular structure as schematically shown in Fig. 3(*d*). Similar multiple helices were formed from *N*-octylgluconamide aggregates.[11] The existence of the circular structure as a basic structural motif is supported by the observation of enhanced exciton coupling that indicates that two neighbouring Janus chromophores exist in a translationally non-equivalent orientation.



stacked cyclic 6-mer helically grown tape



linearly extended tape multiple-helix tubular-helix

Fig. 3 Schematic illustration of possible mesoscopic superstructures

The present results indicate that mesoscopic supramolecular architectures may be generated from Janus components on the basis of complementary hydrogen bonding patterns. Amphiphilic design of the hydrogen bond-mediated network[5–8] is a key strategy to generate soluble supramolecular assemblies that are distinct from conventional molecular solids[1–3] or liquid crystalline systems.[4]

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Footnotes

† Janus is a Roman mythological god with two faces in the front and back of his head. The Janus molecule possesses two hydrogen-bonding faces.

‡ Detailed synthetic procedures of these components will be reported elsewhere.

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