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Molecular Fibers and Wires in Solid-State and Solution Self-Assemblies of Cyclodextrin [2]Rotaxanes

Subashani Maniam,[†] Marta M. Cieslinski,[†] Stephen F. Lincoln,[‡] Hideki Onagi,[†] Peter J. Steel,[§] Anthony C. Willis,[†] and Christopher J. Easton*[,†,⊥]

Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia, School of Chemistry and Physics, University of Adelaide, Adelaide SA 5005, Australia, Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand, and ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Australia

easton@rsc.anu.edu.au

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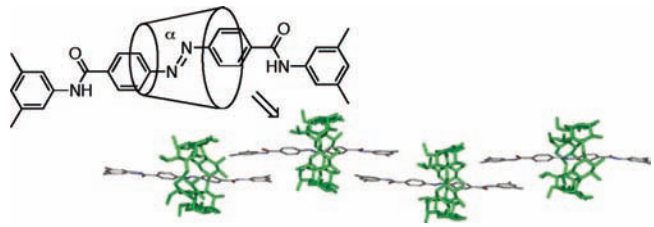
ABSTRACT



Cyclodextrin [2]rotaxanes have been prepared by coupling dimethylanilines with dicarboxylic acids using DMT-MM, in aqueous solutions of α-cyclodextrin, and the example illustrated shows unusual fluorescence emission and other spectroscopic behavior characteristic of the formation of molecular wires in solution, similar to the fibers observed in the solid state.

Rotaxanes are supramolecular species consisting of macrocycles encompassing axles that are bonded to bulky blocking groups in order to prevent the macrocycles and axles from dissociating.[1] Cyclodextrins are well-suited for use as the macrocycles in rotaxane synthesis since, in aqueous solution, they readily form host−guest complexes with hydrophobic species that can be exploited as the axles.[2−5] Accordingly, a range of cyclodextrin-based rotaxanes have been prepared and used as molecular shuttles and other devices.[4−16] Previously, we had prepared the cyclodextrin [2]rotaxanes **1a**−**d** and found, by X-ray crystallographic analysis, that they all form remarkably similar networks of aligned molecular fibers in the solid state.[6,7] Analogous strands were found by the Anderson group[8,9] with the two cyclodextrin [2]rotaxanes that they have

[†] Australian National University.
[‡] University of Adelaide.
[§] University of Canterbury.
[⊥] ARC Centre of Excellence for Free Radical Chemistry and Biotechnology.

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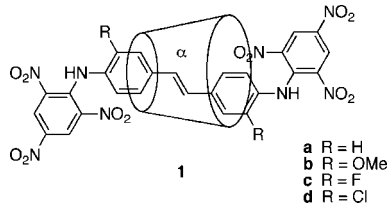

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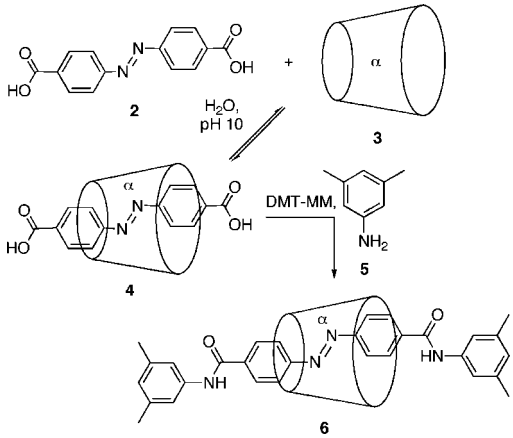
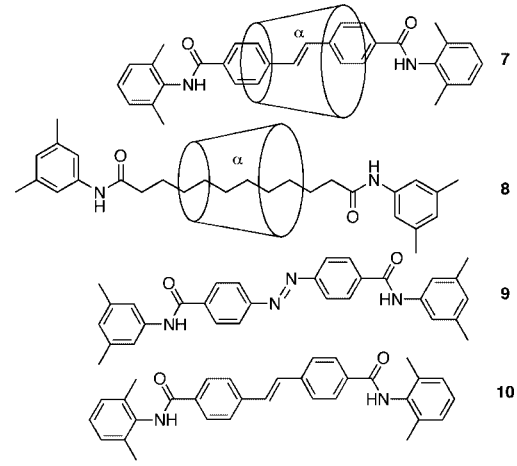
crystallographically characterized. While the trinitrophenyl groups of the rotaxanes **1a**−**d** are twisted at an angle of approximately 90° to the stilbene units, the blocking groups in Anderson's rotaxanes are coplanar and conjugated with those axles, with $\pi-\pi$ stacking arrangements between the blocking groups of the type that are thought to be important in the semiconductivity of insulated molecular wires of related conjugated polyrotaxanes.[5] Here we report the synthesis of a new group of rotaxanes, by coupling dimethylanilines with dicarboxylic acids in aqueous solutions of α-cyclodextrin **3**, using the water-soluble and compatible reagent 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM).[17,18] Through the choice of either 2,6- or 3,5-dimethylaniline **5** as the blocking reagent, this approach allows us to manipulate the extent of conjugation of the blocking groups with the axles, as well as the formation of molecular fibers through solid-state self-assembly of the rotaxanes. Analogous behavior is observed in solution, where spontaneous self-assembly of the rotaxane **6** leads to the formation of molecular fibers similar to those observed in the solid-state. The unusual fluorescence emission and other spectroscopic evidence characteristic of this aggregation in solution reflects intermolecular electronic interactions, which demonstrate, for the first time, that the fibers are clearly behaving as molecular wires.

Scheme 1. Synthesis of the Rotaxane **6**



The rotaxane **6** was prepared as outlined in Scheme 1.[19] The dicarboxylic acid **2** was stirred at room temperature for 2 h with α-cyclodextrin **3** (8 equiv) in carbonate buffer at pH 10 to allow the corresponding inclusion complex **4** to form. DMT-MM (4 equiv) and 3,5-dimethylaniline **5** (4 equiv) were then added, and the mixture was stirred for a further 10 h before the product **6** was isolated in 27% yield through chromatography on a Diaion HP-20 column. Similar methods were used to prepare the rotaxanes **7**[19] and **8**[19] in yields of 25% and 5%, respectively. For comparison, the diamides **9** and **10** corresponding to the dumbbells of the rotaxanes **6** and **7** were also synthesized.[19]



Attempts to obtain crystals of the rotaxane **8** and the diamide **10** appropriate for X-ray analysis were not successful, but suitable samples were obtained in the cases of the rotaxanes **6** and **7**, and the diamide **9**, through slow evaporation of methanol/water solvent over a period of several weeks for the former pair, and by recrystallization from pyridine with the latter material (see the Supporting Information). In the solid state, the diamide **9** forms a complex lattice of molecules displaying a variety of interactions and oriented on several different axes (Figure 1a). By contrast, the dumbbells of the rotaxane **6** assemble as molecular fibers, linearly aligned along a single axis and insulated by the cyclodextrins, and they only come into contact with adjacent dumbbells through their blocking groups (Figure 1b). The blocking groups are π-π-stacked with the rings coplanar and their mean planes separated by a distance of 3.461 Å. Their relative alignment is characteristic of the most common type of $\pi-\pi$ stacking, with the centroid of one ring lying over one carbon of the other (Figure 2).[20–22] The blocking groups of the dumbbells are almost coplanar with the axles, so there is extended conjugation along the length of each fiber.

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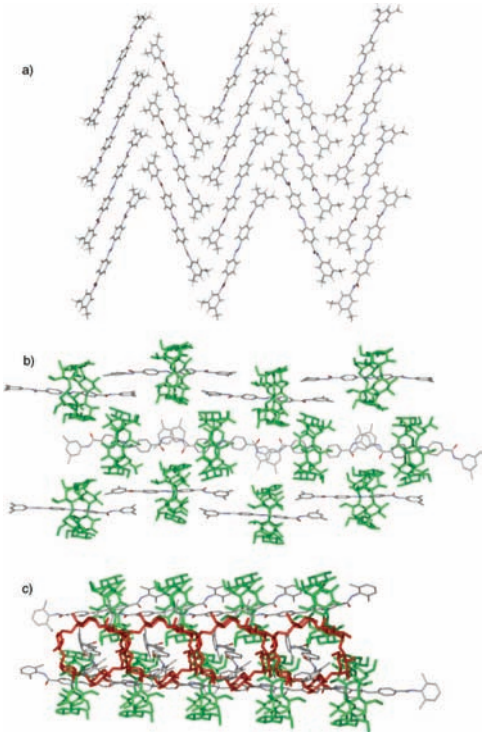

Figure 1. Solid-state structures of (a) the diamide **9**, (b) the rotaxane **6** with the cyclodextrins (green) aligned along a single axis, and (c) the rotaxane **7** with the cyclodextrins oriented in one direction (green) interspersed by others aligned at right angles (red).

With the rotaxane **7**, coplanarity of each blocking group with the axle is prevented by nonbonding steric interactions between the amide oxygen and the methyl substituents at the 2- and 6-positions of the blocking group (Figure 3). This stops conjugation through the dumbbell. The out-of-plane amide moiety also precludes the extent of overlap of adjacent blocking groups required for $\pi-\pi$-stacking of the type seen with the rotaxane **6** (Figure 2). Other interactions between the blocking groups can be envisaged, including that actually observed, but then there is less overlap of adjacent dumbbells. As a consequence, the cyclodextrins are forced too far apart for a close-packed arrangement along one axis and, instead, the cyclodextrins oriented in one direction are interspersed by others aligned at right angles (Figure 1c).

Thus, as is illustrated in Figure 1, this study shows that for the alignment of the rotaxanes into fibers along a single axis, of the type described here for the rotaxane **6** and reported earlier

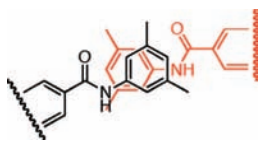

Figure 2. Schematic representation of $\pi-\pi$ stacking between blocking groups observed in the solid-state structure of the rotaxane **6**.

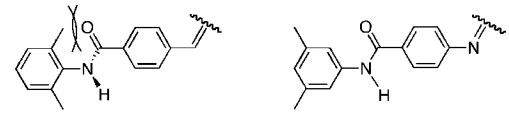

Figure 3. Illustration of steric interactions preventing coplanarity of the blocking groups with the axle in the rotaxane **7** (left) and their absence in the rotaxane **6** (right).

for the trinitrophenyl-capped rotaxanes **1a**−**d**,[6,7] the length required to accommodate each successive dumbbell in the fiber is twice the depth of the cyclodextrin, and the extent of overlap of adjacent blocking groups must correspond to this. Further, the choice of either 2,6- or 3,5-dimethylaniline **5** as the blocking reagent can be used to manipulate this overlap and therefore to control both the formation of axially aligned and separated molecular fibers of the axles through self-assembly of rotaxanes as well as the extent of conjugation of the axles with the blocking groups.

In solution, ultraviolet−visible spectra of the rotaxane **6** in either methanol or DMSO obey Beer's law; that is, there is a direct correlation between the concentration of the rotaxane **6** and the absorbance of the solution, with λ_{max} 350 nm in each solvent and ϵ_{max} 32000 and 28000 in methanol and DMSO, respectively (Figures 4a,b). By contrast, solutions in water show substantial deviations from this correlation, particularly at concentrations of the rotaxane **6** above 10 μM (Figure 4c). For example, at 350 nm, the absorbance of a 100 μM solution is less than 5 times that of a 10 μM one, instead of the typical 10. At the higher concentrations and as the deviations become greater, the spectra also exhibit an absorbance of increasing intensity around 430 nm, ranging up to 600 nm, and excitation of these solutions at 480 nm results in fluorescence emission at 520 nm (Figure 5). The absorbance at 350 nm is characteristic of an azobenzene, while those at higher wavelengths, and the deviations as well as the fluorescence behavior referred to above, are typical of aggregation through $\pi-\pi$-stacking.[20,23–28] In the absence of aggregation, the azobenzene chromophore is generally nonfluorescent in solution at room temperature, because radiative deactivation of photoexcited azobenzenes is not competitive with their photoisomerization.[29–31]

The ultraviolet−visible and fluorescence spectra show that the aggregates form at concentrations above about 15 μM. The structure of the rotaxane **6** limits the possible modes of aggregation. The cyclodextrin insulates the axle, so only the blocking groups are accessible for $\pi-\pi$-interactions. These must

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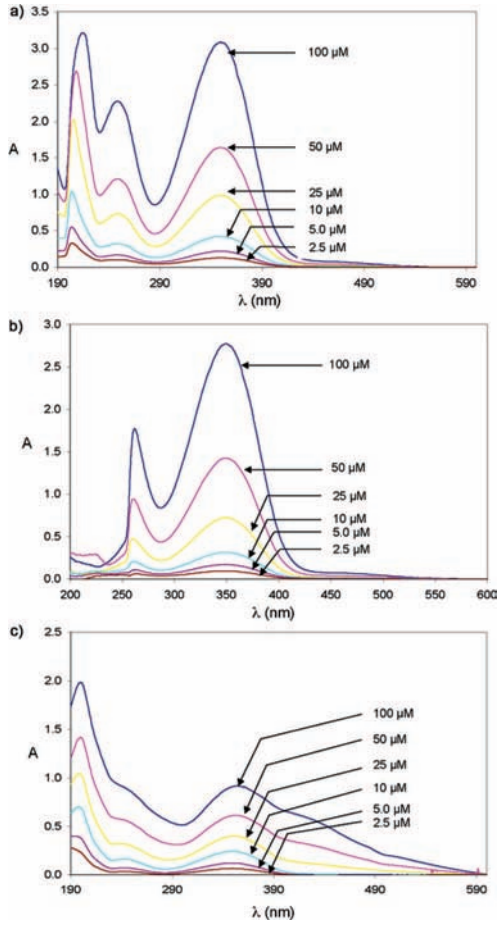

Figure 4. Absorption spectra of the rotaxane **6** in (a) methanol, (b) DMSO, and (c) water at concentrations ranging from 2.5 to 100 μM, recorded at room temperature (see the Supporting Information for corresponding plots of absorbance at 350 nm vs concentration of the rotaxane **6**).

be intermolecular such that the rotaxane **6** is forming fibers. Nevertheless, these $\pi-\pi$-interactions between the blocking groups of adjacent dumbbells affect the spectral characteristics

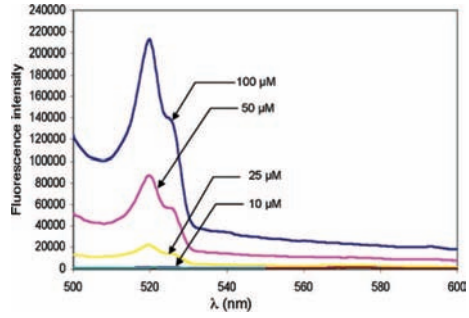

Figure 5. Fluorescence emission spectra of the rotaxane **6** in water at concentrations ranging from 10 to 100 μM, recorded at room temperature (λ_{ex} = 480 nm, see the Supporting Information for the corresponding plot of fluorescence emission intensity vs concentration of the rotaxane **6**).

of the azobenzene moiety, so the axles of the dumbbells must be fully conjugated with the blocking groups. Thus, there are striking similarities between the solution and solid-state self-assemblies of the rotaxane **6**.

The spectra indicate that there is no aggregation of the rotaxane **6** in either methanol or DMSO, presumably because these solvents disrupt $\pi-\pi$-stacking. There was no evidence of abnormal spectroscopic behavior with solutions of either the diamide **9** in DMSO, or the rotaxane **7** in either methanol or water (see the Supporting Information). Due to its low solubility, it was not practical to examine the properties of the diamide **9** in aqueous solution. In regard to the rotaxane **7**, aggregation may still be occurring yet not be reflected in the spectra because of the lack of conjugation of the dumbbell in that case.

The fibrous structure adopted by the dumbbells of the rotaxane **6** in the solid state (Figure 1b) is suggestive of a network of aligned molecular wires. There is extended conjugation along the length of each fiber, comprising $\pi-\pi$-interactions between the blocking groups of sequential dumbbells as well as coplanarity of the blocking groups of the dumbbells with their axles. However, there is no property of the solid that directly reflects this structure or shows behavior characteristic of a wire. By contrast, the spectroscopic evidence of the formation of the molecular fibers of the rotaxane **6** in solution reflects intermolecular electronic interactions along the extensively conjugated system and demonstrates that in this phase the fibers are indeed performing as molecular wires.

In summary, cyclodextrin [2]rotaxanes have been prepared by coupling dimethylanilines with dicarboxylic acids using DMT-MM in aqueous solutions of α-cyclodextrin **3**. The choice of either 2,6- or 3,5-dimethylaniline **5** can be exploited to manipulate both the extent of conjugation of the axles with the blocking groups and the formation of molecular fibers through self-assembly of the rotaxanes in the solid state. There are striking similarities between the solid-state behavior of the rotaxane **6** and that observed in solution, where spontaneous self-assembly leads to the formation of fibers displaying spectroscopic properties characteristic of their performance as molecular wires. Such fibers could possibly form interesting lyotropic liquid crystalline phases.[32]

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Supporting Information Available: Details of the synthesis of compounds **6**−**10**, X-ray crystallographic analysis of compounds **6**, **7**, and **9**, ultraviolet/visible spectroscopy of compounds **7** and **9**, graphs of ultraviolet−visible absorbance and fluorescence emission intensity vs concentration for aqueous solutions of the rotaxane **6**, and ^{1}H and ^{13}C spectra of compounds **6**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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