A cyclodextrin-insulated anthracene rotaxane with enhanced fluorescence and photostability†

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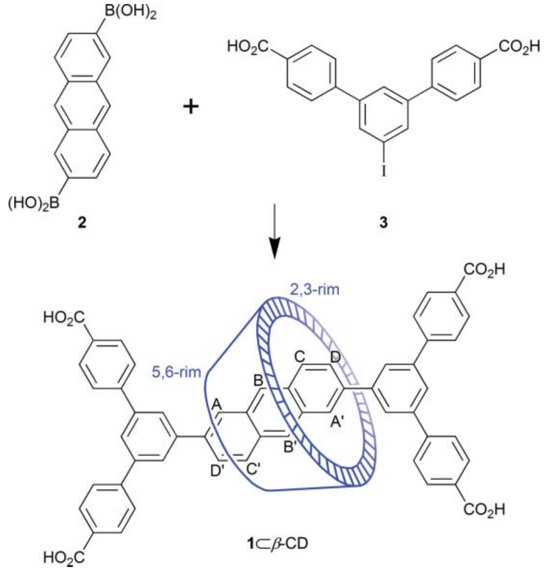
A β-cyclodextrin anthracene rotaxane was synthesized and found to be significantly more resistant to fluorescence quenching and photobleaching than the uninsulated anthracene derivative.

Linear acenes are polycyclic aromatic molecules that have applications as organic materials for field-effect transistors[1–7] and light emitting diodes (LEDs).[8] These compounds are difficult to work with due to their insolubility and instability, both of which become worse with increasing length.[9] We propose a supramolecular strategy to stabilize linear acenes by insulating the reactive central aromatic rings inside cyclodextrin macrocycles. This approach should be applicable to the isolation of much longer linear acene derivatives than have been synthesized to date.[10] The cyclodextrin insulation should also prevent intermolecular fluorescence quenching of linear acenes in the solid-state, which is desirable for organic LED applications.[11] Previously it has been shown that molecular insulation can enhance the chemical stability and photophysical properties of dyes and conducting polymers.[12–20] Synthesis of cyclodextrin insulated structures can be readily accomplished by capping the ends of a threaded complex with bulky groups to form a rotaxane.[21–24] As a first step towards the encapsulation of longer linear acenes, we chose to study an anthracene rotaxane since it could be readily synthesized and anthracenes have application as blue-emitting materials.[25–28] Here we describe the synthesis and characterization of β-cyclodextrin anthracene rotaxane **1**⊂β-CD, which was found to be resistant to fluorescence quenching and photobleaching.

Anthracene rotaxane **1**⊂β-CD was synthesized by the reaction of anthracenediboronic acid **2** with iodoterphenylenedicarboxylic acid **3**[29] in the presence of β-cyclodextrin under aqueous Suzuki coupling conditions and was isolated in 4% yield (15% conversion estimated from HPLC of the crude) (Scheme 1).[30,31] The iodoterphenylenedicarboxylic acid **3** capping group was synthesized according to the reported procedure.[32] When the reaction was run in the presence of α-cyclodextrin only uninsulated dumbbell **1** was obtained. The γ-cyclodextrin rotaxane was also synthesized (15% conversion estimated from HPLC of the crude) although it could only be isolated in a very low yield (>1%) and all studies were therefore conducted on the β-cyclodextrin rotaxane **1**⊂β-CD.



Scheme 1 Synthesis of rotaxane **1**⊂β-CD proceeded in the presence of β-cyclodextrin, potassium carbonate, palladium(II) acetate, and trisodium triphenylphosphine-3,3′,3″-trisulfonate (TPPTS) in water–DMSO (9 : 1) at 45 °C. Dumbbell **1** was isolated in a separate reaction under the same conditions except in the absence of β-cyclodextrin and TPPTS.

The structure of β-cyclodextrin rotaxane **1**⊂β-CD was assigned based on ESI mass spectrometry and NMR spectroscopy. Splitting of the anthracene aromatic peaks in the ^{1}H NMR spectrum of **1**⊂β-CD revealed the influence of the asymmetric cyclodextrin. The close proximity of the cyclodextrin to the anthracene was confirmed from the 2D NOESY spectra that showed multiple through-space contacts between the anthracene and the β-cyclodextrin. The pattern of NOEs is consistent with a molecular model of rotaxane **1**⊂β-CD in which the cyclodextrin is positioned around the anthracene moiety (Fig. 1).[33] The anthracene hydrogens labelled A′ and C showed NOEs to H3 of the wider 2,3-rim of the β-cyclodextrin, while the hydrogens labelled A and D′ showed NOEs to H5 and H6 of the narrower 5,6-rim. The central hydrogens of the anthracene labelled B and B′ showed NOEs to H3, H5, and H6 of both rims of the β-cyclodextrin.

The fluorescence behaviour of rotaxane **1**⊂β-CD and dumbbell **1** was then examined. The difference between the fluorescence emissions of the two compounds in solution is perceptible to the naked eye under a 365 nm ultraviolet lamp (Fig. 2). At a concentration of 9 μM in aqueous solution, dumbbell **1** appears light yellow while rotaxane **1**⊂β-CD is an intense blue. The

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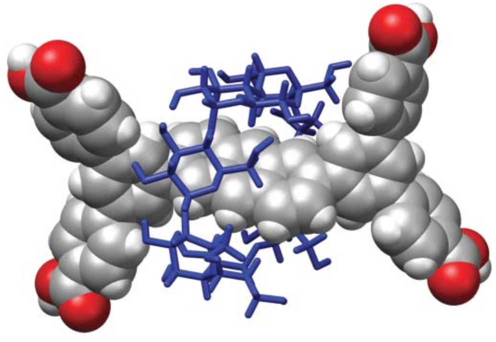


Fig. 1 Calculated model of β-cyclodextrin rotaxane **1**⊂β-CD.[33]

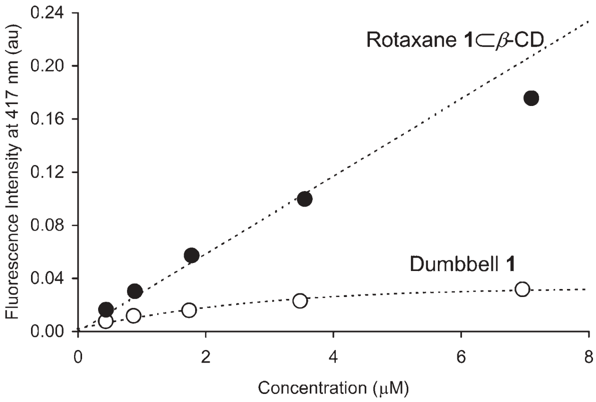


Fig. 3 Fluorescence intensities at 417 nm of rotaxane **1**⊂β-CD and dumbbell **1** excited at 365 nm as a function of concentration. The first four points for rotaxane **1**⊂β-CD were fit to a straight line. A line has been drawn though the points for dumbbell **1** as a guide to the eye.

fluorescence spectrum of rotaxane **1**⊂β-CD consists primarily of two sharp peaks at 417 nm and 440 nm. The shape of the spectrum is independent of concentration while the intensity shows a linear dependence that only deviates significantly at higher concentrations (Fig. 3). In contrast, the fluorescence spectrum of dumbbell **1** showed an additional broad band centered at 550 nm, which grows with increasing concentration. The shorter wavelength bands, at 417 and 440 nm, are reduced in intensity relative to those for rotaxane **1**⊂β-CD and show an asymptotic dependence on concentration.

Based on the concentration dependence of the fluorescence, we hypothesized that the differences were due to aggregation of dumbbell **1**, which is disrupted by the β-cyclodextrin for rotaxane **1**⊂β-CD. Upon scrutinizing the UV absorption spectra of dumbbell **1** over a similar concentration range, a small shift was identified, while none was observed for rotaxane **1**⊂β-CD. At sufficiently dilute concentrations (<0.1 μM), the emission spectra of rotaxane **1**⊂β-CD and dumbbell **1** are superimposable. At these dilute concentrations, the fluorescence quantum yields of rotaxane **1**⊂β-CD (Φ_F = 0.39) and dumbbell **1** (Φ_F = 0.38) are identical within the standard 10% error.

Next we examined the stability of β-cyclodextrin rotaxane **1**⊂β-CD to photobleaching. Photochemical studies of water-soluble anthracenes have shown that their reactivity is influenced by complexation with cyclodextrin.[34–36] The enhanced solution stability of insulated rotaxane **1**⊂β-CD relative to dumbbell **1** was evident even under regular laboratory lighting. The UV absorbance spectrum of dumbbell **1** in aqueous solution was found to undergo a dramatic transformation when left on the bench top for several hours, while the spectrum of rotaxane **1**⊂β-CD under the same conditions remained unchanged for days. To quantify the difference in rates of photobleaching, their degradation was monitored using UV absorbance upon irradiation at 380 nm in pH 11.4 phosphate buffered aqueous solutions at a concentration of of ~7 μM. The spectra of rotaxane **1**⊂β-CD were fit to a pseudo first-order rate model (Fig. 4) to give a half-life of 109 ± 4 min. The spectra of dumbbell **1** fit better to a second-order rate and had a first half-life of 13 ± 0.4 min. The difference in the spectra of the products of irradiation and rates of reaction suggest

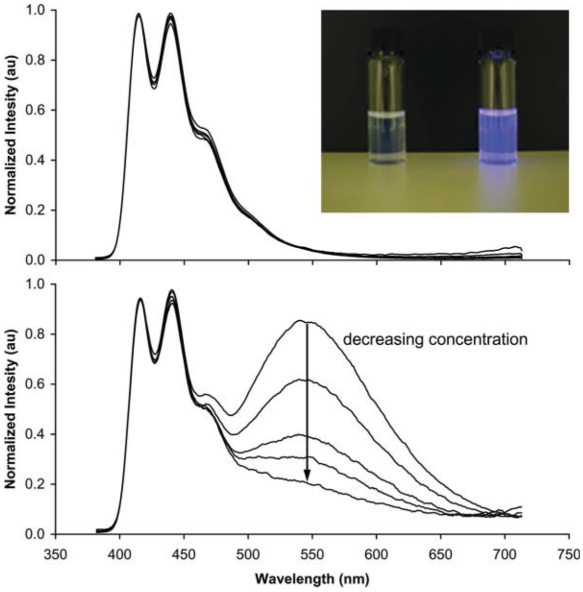


Fig. 2 Fluorescence spectra of rotaxane **1**⊂β-CD (top) and dumbbell **1** (bottom) collected in pH 11.4 phosphate buffered aqueous solution excited at 365 nm. Spectra were collected at *ca.* 7.2, 3.6, 1.8, 0.90, and 0.45 μM and normalized at 417 nm for comparison of peak shape. Inset shows 9 μM solutions of **1** (left) and **1**⊂β-CD (right) under irradiation at 365 nm.

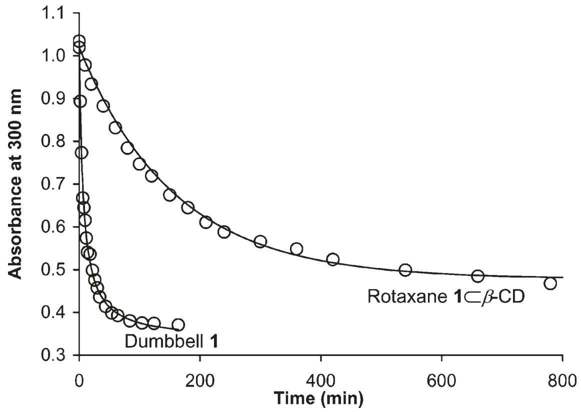
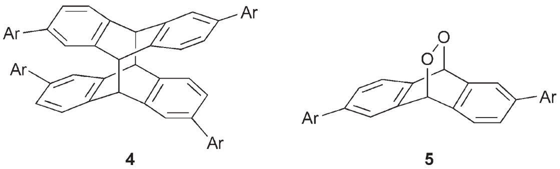


Fig. 4 UV absorbances of rotaxane **1**⊂β-CD and dumbbell **1**, irradiated at 380 nm, as a function of time, with lines corresponding to a first-order and second-order rate equation respectively. Rates were obtained by fitting spectra using SPECFIT/32 3.0.36 (Spectrum Software Associates) software.[37]



4 **5**

Fig. 5 Products formed by photodimerization of dumbbell **1** (left) and photooxidation of rotaxane **1**⊂β-CD (right). Note that only one stereoisomer is represented and that Ar represents the terphenyldicarboxylate end group as in shown in Scheme 1.

that the two compounds undergo photobleaching by different processes.

The products of rotaxane **1**⊂β-CD and dumbbell **1** after irradiation were examined using a tungsten filament light source for 18 h in pH 11.4 phosphate buffered aqueous solution at a concentration of $\sim$1 mM. The ESI mass spectrum of dumbbell **1** after irradiation indicated the formation of dimerized product **4** (Fig. 5). The presence of the cyclodextrin was found to inhibit photodimerization of rotaxane **1**⊂β-CD, which gave the endoperoxide **5**⊂β-CD. Both products are consistent with the known photochemistry of anthracene.[38,39] It is interesting that the rotaxane **1**⊂β-CD is able to react even at a slower rate since there is very little space available in the cavity of the β-cyclodextrin. However, previous studies of cyclodextrin rotaxanes have shown that even tightly insulated stilbenes underwent photohydrolysis, although at a rate five times slower than the analogous uninsulated dumbbells.[40]

In conclusion, we have demonstrated that fluorescence quenching of anthracene can be prevented by cyclodextrin insulation. Insulation of the anthracene in rotaxane **1**⊂β-CD was also found to prevent photodimerization of the dumbbell, which is advantageous for application in solid-state devices. Efforts are currently underway to extend this approach to longer linear acenes, such as pentacene.

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