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Centrosymmetric and Non-centrosymmetric Packing of Aligned Molecular Fibers in the Solid State Self Assemblies of Cyclodextrin-based Rotaxanes

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Two [2]-rotaxanes each comprising α-cyclodextrin as the rotor, and with either 3,3′-difluoro- or 3,3′-dichlorostilbene as the axle and trinitrophenylamino substituents as the blocking groups at the 4- and 4′-positions, were prepared and their structures analyzed in solution and the solid state using ^{1}H NMR spectroscopy and X-ray crystallography, respectively. With each rotaxane, in solution the stilbene rotates freely within the cyclodextrin annulus. In the solid state the 3,3′-dichlorostilbene-based rotaxane adopts two very similar conformations, each having the chlorines in the *anti,anti*-orientation. By comparison, the 3,3′-difluorostilbene-based rotaxane adopts *anti,anti*-, *anti,syn*- and *syn,syn*-orientations of the substituents. The crystal packing of each rotaxane displays aligned molecular fibers, which are centrosymmetrically orientated in the case of the difluoride due to the head-to-head/tail-to-tail alignment of the cyclodextrins. By contrast, all of the cyclodextrins in the dichloride are aligned head-to-tail along a single axis to give a polar, non-centrosymmetric crystal.

Keywords: Rotaxanes; Cyclodextrins; Crystallography; NMR spectroscopy; Self assembly

INTRODUCTION

Rotaxanes consist of macrocycles encompassing axles that are capped with blocking groups to prevent the components from dissociating [1,2]. Cyclodextrin-based rotaxanes have been prepared and used as molecular shuttles and photochemical and mechanical devices [3–32]. Our interest in this area has been mainly focused on α-cyclodextrin-based rotaxanes with stilbenes as the axles and trinitrophenyl blocking groups, as the basis of molecular machines and new materials [25–29]. In particular, we recently reported the synthesis of the rotaxanes **1** and **2** and studies of their solution and solid state structures [29]. In the solid state self assemblies the dumbbells of these species form aligned molecular fibers separated by the cyclodextrins. These resemble the insulated molecular wires with reduced interstrand interactions reported by Anderson et al. [30–32], in their studies of rotaxanes and polyrotaxanes. In those cases the structures are associated with unusual physical, electronic and photochemical properties.

In order to better understand the cooperative molecular recognition events that result in the ordered networks seen in the solid state structures of the rotaxanes **1** and **2**, we have now prepared and studied the corresponding difluoride **3** and dichloride **4**. Each of these retains the molecular fiber structural motif observed with the rotaxanes **1** and **2** but whereas the crystal packing of the rotaxanes **1**–**3** is centrosymmetric, that of the dichloride **4** is non-centrosymmetric with all of the cyclodextrins aligned head-to-tail along a single axis. Non-centrosymmetric crystals are of considerable interest due to their potential for application, for example in optics and optoelectronics [33–38].

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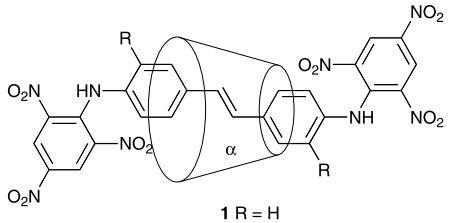
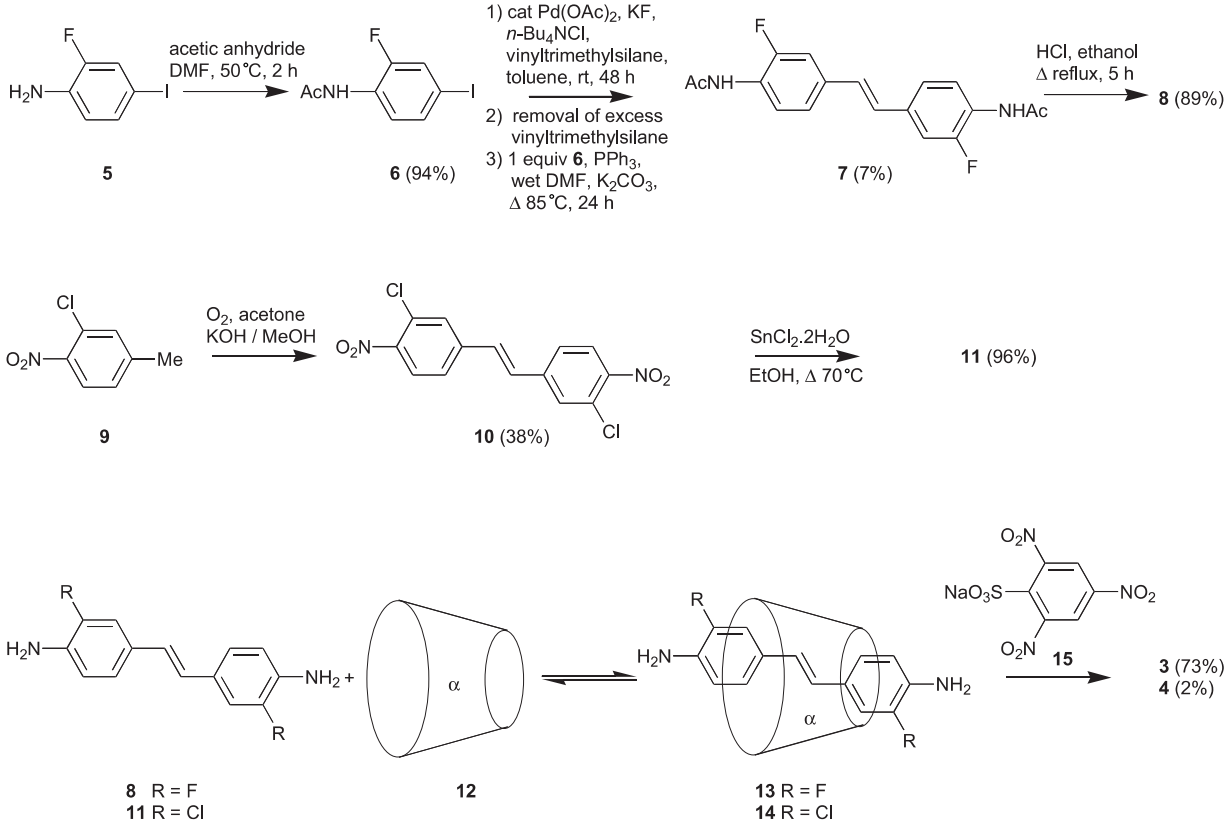


1 R = H
2 R = OMe
3 R = F
4 R = Cl

RESULTS AND DISCUSSION

The rotaxane **3** was prepared as outlined in Scheme 1. The procedure used to prepare the stilbene precursors to the rotaxanes **1** and **2** involved treatment of nitrotoluenes with oxygen under strongly basic conditions. When the same approach was attempted with 3-fluoro-4-nitrotoluene to prepare 3,3′-difluoro-4,4′-dinitrostilbene, instead 3,3′-dihydroxy-4,4′-dinitrostilbene was obtained. Therefore the alternative approach reported by Jeffery and Ferber [39] was adopted. Accordingly, 2-fluoro-4-iodoaniline (**5**) was converted to the corresponding acetamide **6**, which underwent a two-step palladium-catalyzed condensation with vinlyltrimethylsilane to give the stilbene **7**. Hydrolysis then afforded the diaminostilbene **8**. The stilbene **8** was stirred with α-cyclodextrin (**12**) for 16 h in aqueous buffer at room temperature and pH 10, to allow the stilbene **8** to dissolve and the inclusion complex **13** to form. Sodium 2,4,6-trinitrobenzene-1-sulfonate (TNBS) (**15**) was then added and the mixture was stirred for an additional 4 h. The crude product mixture was subjected to a Diaion HP-20 column and then HPLC to give the rotaxane **3** as an orange powder in 73% yield. TLC of this material revealed a single component, showing the characteristic ultraviolet absorbance of the dumbbell-like axle, and pink coloration of a cyclodextrin on exposure to acidic naphthalene-1,3-diol [25–28]. The deprotonated molecular ion of the product **3** was seen at m/z 1639 by ESI-MS operated in the negative ion mode.

The rotaxane **4** was prepared using a method similar to that used to obtain the rotaxane **3** (Scheme 1). The stilbene **11** was obtained as reported, by oxidative dimerization of 3-chloro-4-nitrotoluene (**9**), followed by reduction of the dinitrostilbene **10** [40]. Due to the low solubility of this material, sonication was used to suspend and dissolve it in solution with α-cyclodextrin (**12**). The crude product was subjected to a Diaion HP-20 column and then HPLC to give the rotaxane **4** as an orange powder, but in only 2% yield. The deprotonated molecular ion of the product **4** was seen at m/z 1671 by ESI-MS operated in the negative ion mode. Despite repeated attempts the yield was not improved. This poor



SCHEME 1

yield is probably a result of the low thermodynamic stability of the inclusion complex **14** due to the relatively large size of the chloro substituents. By comparison, the yields of the rotaxanes **1** and **3** were 79% [29] and 73%, respectively, while that of the dimethoxide **2** was 27% [29].

The ^{1}H NMR spectrum of the rotaxane **3** revealed the proton resonances of the cyclodextrin, the stilbene and the blocking groups. The cyclodextrin proton resonances for each glucopyranose unit are equivalent indicating symmetry of the cyclodextrin and therefore free rotation of the axle within the cavity on the NMR time-scale.

2D NMR techniques (ROESY, COSY and TOCSY) were employed for the assignment of the proton resonances of the rotaxane **3**, which were then used to analyze the conformation. Figure 1a is a portion of the ROESY spectrum showing cross-peaks between cyclodextrin and stilbene proton resonances. The cyclodextrin is centered on the stilbene as the axle protons designated A-H2-H6 and H8 show strong interactions with the cyclodextrin protons CD-H3, H5 and H6 whereas protons A-H7 and H1 found on the ends of the stilbene only show weak interactions with CD-H6 and H3, respectively.

Similar to that of the rotaxane **3**, the ^{1}H NMR spectrum of the rotaxane **4** reveals only one set of glucopyranose resonances indicating free rotation of the cyclodextrin around the stilbene axle. From the ROESY spectrum (Figure 1b) the conformation can be determined. The cyclodextrin is centered over the stilbene as indicated by the intense cross peaks between the resonances of the axle protons designated A-H2-H6 and H8 and those of the cyclodextrin protons CD-H3, H5 and H6. It is apparent that the stilbene is 'tilted', rotating at an angle to the C_6-axis of the cyclodextrin. This is shown by, for example, the stronger interaction of CD-H5 and H6 with AH2 than H3. Presumably this is a result of the bulk of the chlorines which forces them away from the sides of the cyclodextrin and pushes proton A-H2 further into the cyclodextrin cavity than A-H3.

To extend the study of the effect of various halogens, the synthesis of brominated analogues of the rotaxanes **3** and **4** was attempted. Based on the poor yield of the rotaxane **4** it was believed that the corresponding dibromide would not form, due to the greater bulk of bromine relative to chlorine. Instead, post-assembly rotaxane modification was attempted. Electrophilic aromatic bromination using pyridinium dichlorobromate [41] was envisaged as a way to introduce bromine at the 3- and 3′-positions of the stilbene of the rotaxane **1**, based on the chemistry explored by Dumanski et al. [42] However, such reactions yielded complex mixtures of products. When components were separated and analyzed using ^{1}H NMR spectroscopy, in most cases there was no evidence of olefinic proton resonances, indicating that addition had occurred across the double bond. One of the components was tentatively assigned as compound **16** based on 2D NMR spectroscopy and mass spectrometric studies.

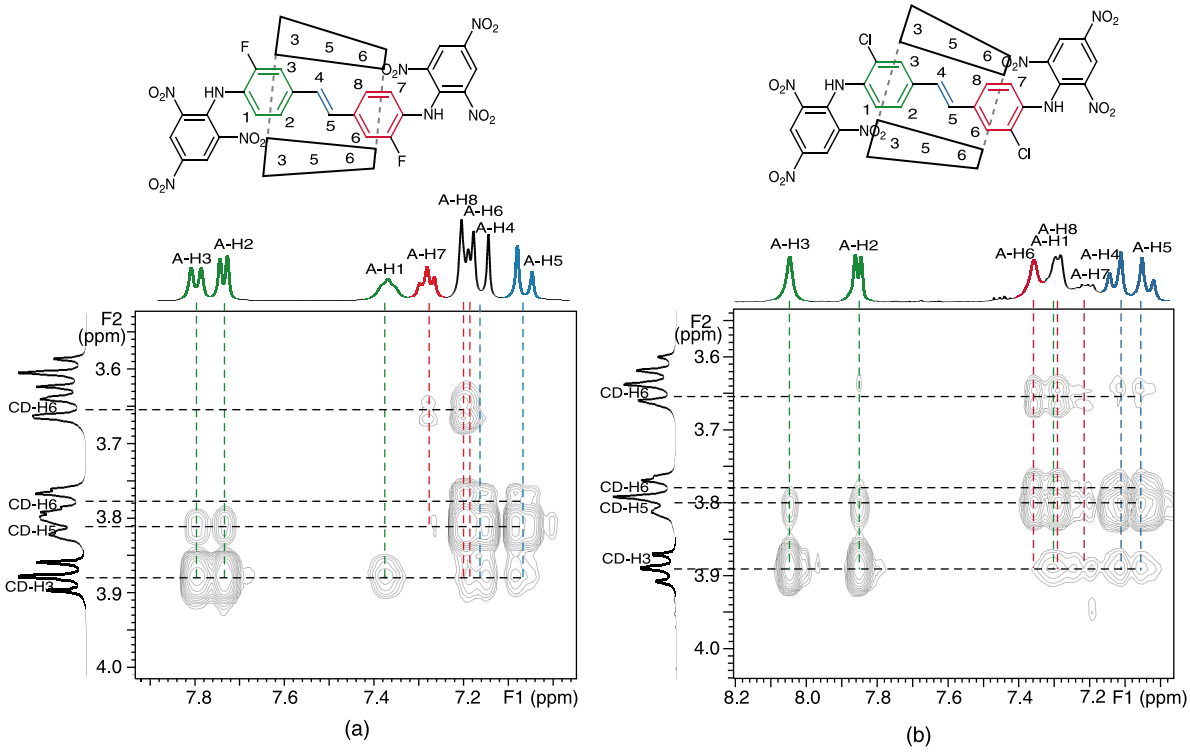
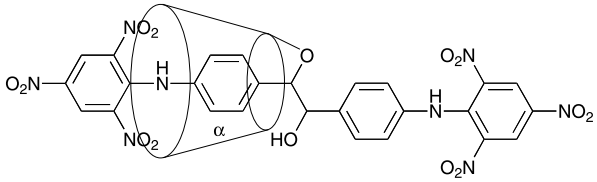


FIGURE 1 Sections of the 500 MHz ROESY spectra of (a) the difluoro rotaxane **3**, and (b) the dichloride **4** in methanol-d_4 at 25°C showing the region where cross-peaks between cyclodextrin and axle proton resonances are found.



16

The solid state structures of the rotaxanes **3** and **4** were examined using X-ray crystallography. Crystals of each of the rotaxanes **3** and **4** were grown by slow evaporation of methanol-d_4/D_2O solvent over a period of several weeks. In each case the asymmetric unit of the unit cell contains two independent molecules of the rotaxane **3** or **4** together with numerous solvent molecules. When there are substituents on the 3- and 3′-positions of a stilbene, three low-energy rotamers are possible, as shown in Figure 2 [43–46]. Both of the independent molecules of the dichloride **4** show the *anti,anti*-conformation. One of those in the asymmetric unit of the difluoride **3** shows disorder between the *anti,syn*- and *syn,syn*-conformations, while the other has the *anti,anti*-orientation. It could be that the *anti,anti*-conformation is favored for the dichloride **4** because this has the 3,3′-substituents furthest apart, as required for the accommodation within the cyclodextrin, which has an annular depth of approximately 8 Å [47].

The conformations adopted by the dumbbells of the rotaxanes **1**–**4** are all very similar in the respect that the trinitrophenyl groups are twisted at an angle to the pseudo-planar stilbene moieties (Figure 3). In principle, these groups can be *anti* or *syn* with respect to the double bond. In practice, the alignment in the rotaxane **3** was found to be *anti*, as observed for the rotaxanes **1** and **2**, but for the rotaxane **4** the trinitrophenyl groups adopt the *syn* conformation. It is likely that the chlorines of the rotaxane **4** are too bulky to allow the crystallization of the trinitrophenyl groups in the same way as for the other rotaxanes **1**–**3**.

Despite the different conformation of the blocking groups in the dichloride **4**, the crystal packing of all four rotaxanes **1**–**4** reveals strikingly similar molecular fibers, where the structural motif appears to be dominated by the intermolecular interactions between the trinitrophenyl substituents (Figure 4).

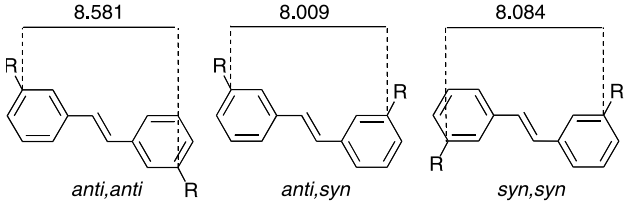


FIGURE 2 Possible rotamers of a 3,3′-disubstituted stilbene showing the average distances between the 3- and 3′-carbons as measured in the crystal structures of the rotaxanes **1**–**4**.

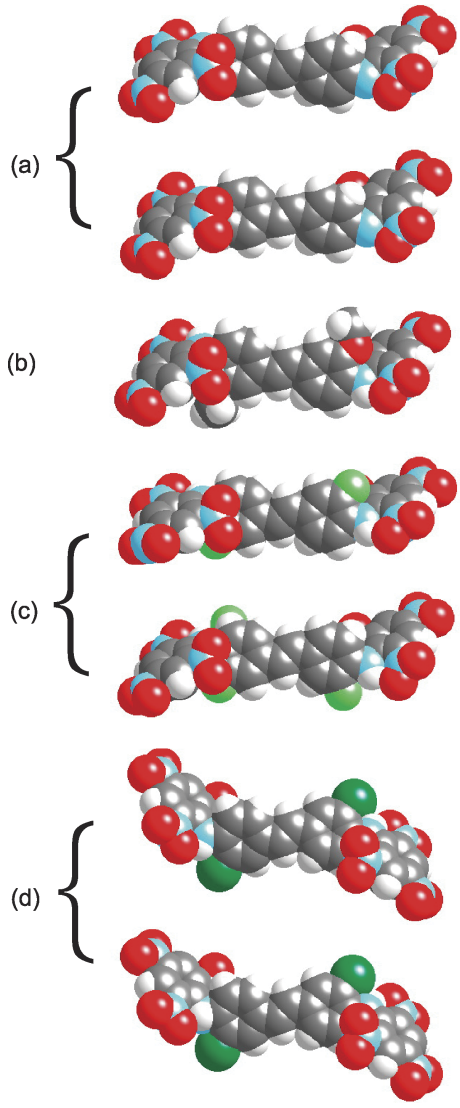


FIGURE 3 Conformations of the dumbbells in the crystals of (a) the rotaxane **1**, (b) the dimethoxide **2**, (c) the difluoride **3**, and (d) the dichloride **4**, showing the alignment of the trinitrophenyl groups. The atoms are shown with their van der Waals radii where grey = carbon, red = oxygen, white = hydrogen, blue = nitrogen, light green = fluorine and dark green = chlorine.

In each case the fibers are aligned along a single axis with the dumbbells insulated by the cyclodextrins. In the absence of the cyclodextrin, the molecule corresponding to the dumbbell of the rotaxane **1** also forms similar fibers in the crystal structure but these are neither all aligned nor insulated [29].

Overall the crystal packing of the rotaxanes **1** and **3** is pseudo-centrosymmetric with the cyclodextrins orientated in a head-to-head/tail-to-tail fashion along the aligned molecular fibers (Figures 4a and 4c). Consequently these crystals are non-polar. In contrast, the cyclodextrins of the rotaxanes **2** and **4** are faithfully aligned head-to-tail along the individual molecular fibers. In the case of the dimethoxide **2** the cyclodextrins of adjacent fibers are orientated in opposite directions (Figure 4b) and so the crystal is

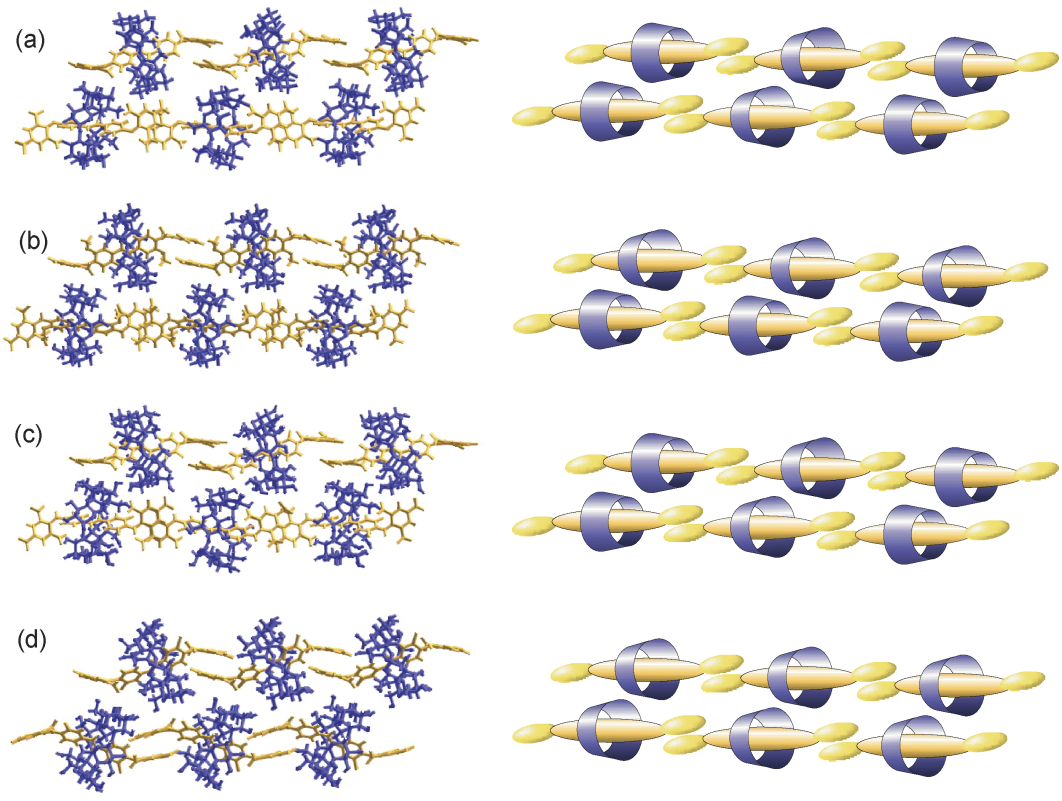


FIGURE 4 Crystal packing (left) and schematic representation of the alignment of the cyclodextrins (right) of two adjacent molecular fibers in (a) the rotaxane **1**, (b) the dimethoxide **2**, (c) the difluoride **3**, and (d) the dichloride **4**. In the truncated cone used to represent the cyclodextrins the wide (head) and narrow (tail) ends correspond to the rims of secondary and primary hydroxyl groups, respectively.

also non-polar and pseudo-centrosymmetric around a 2-fold axis. Conversely, all the cyclodextrins of the rotaxane **4**, including those in adjacent fibers, are aligned head-to-tail along a single axis (Figure 4d) and so the packing in the assembly is non-centrosymmetric and the crystal is polar.

In conclusion, ^{1}H NMR studies of the rotaxanes **1**–**4** have been used to establish that in each case the cyclodextrin is located around the stilbene moiety, which rotates freely within the cyclodextrin annulus on the NMR time scale. The solid state assemblies of all four rotaxanes **1**–**4** show aligned molecular fibers of the dumbbells insulated by the cyclodextrins, in which the interactions between the trinitrophenyl groups form a common structural motif. Interestingly, there are three different modes of alignment of the cyclodextrins in these fibers. While two of these represent centrosymmetric arrangements (for the rotaxanes **1**–**3**), the rotaxane **4** forms non-centrosymmetric and therefore polar crystals.

EXPERIMENTAL

General

NMR spectra were recorded using either a Varian Mercury 300 spectrometer, operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C or a Varian Inova 500 spectrometer, operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. ROESY experiments were performed with a mixing time of 200 to 280 ms on the Inova 500 spectrometer. Mass spectra were obtained using either a VG Quattro II triple quadrupole mass spectrometer operating in either negative or positive modes for electrospray ionization mass spectrometry (ESI-MS) or a VG AutoSpec M series sector instrument for electron impact mass spectrometry (EI-MS). Elemental analyses were performed by the Australian National University Microanalytical Services Unit. Melting points were measured on a Reichert hot-stage microscope apparatus and are uncorrected.

Thin layer chromatography (TLC) was performed on aluminum-backed 0.2 mm thick silica gel 60 F254 plates as supplied by Merck Chemical Company. The running solvent was 5:4:3 *n*-butanol:ethanol:water, by volume [25–28]. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with an acidic solution of naphthalene-1,3-diol (0.1% weight to volume) in ethanol:water:H_2SO_4 (200:157:43, by volume) followed by heating [25–28]. The R_f values are reported relative to that of α-cyclodextrin (**12**). Flash chromatography was performed using analytical grade solvents and silica gel 60 (0.040–0.0063 mm) as supplied by Merck Chemical Company. Semi-preparative high performance

liquid chromatography (HPLC) was performed using a Waters Alliance Separation Module 2690 with a Waters 996 photodiode array detector. The Waters Millenium 3.2 operating system was used to control the instrument.

α-Cyclodextrin (**12**) was the generous gift of Nihon Shokuhin Kako Company, Japan, in 99.1% purity and dried in vacuo over P_2O_5 to a constant weight before use. 2,4,6-Trinitrobenzene-1-sulfonic acid sodium salt dihydrate (TNBS) was purchased from Tokyo Kasei. Diaion HP-20 resin was purchased from Supelco, PA. 2-Fluoro-4-iodoaniline (**5**) was obtained from Apollo Scientific Limited. Other starting materials and reagents were obtained from the Sigma–Aldrich, Merck and Lancaster Chemical Companies and were used as supplied.

N-(2-Fluoro-4-iodophenyl)acetamide (6)

2-Fluoro-4-iodoaniline (**5**) (0.50 mg, 2.11 mmol) was dissolved in DMF (5 cm^3). Acetic anhydride (2 cm^3, 21.2 mmol) was added and the mixture was heated at 50°C for 2 h. The solution was then cooled to room temperature and 1 N HCl (40 cm^3) was added. EtOAc (4 × 50 cm^3) was used to extract the product from the aqueous solution. The combined organic extracts were washed with water (3 × 40 cm^3) and dried using $MgSO_4$. The solvent was removed under reduced pressure to yield the title compound **6** (554 mg, 94%) as a light purple solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.80 (1H, br s, NH), 7.73 (1H, apparent t, J = 8.4 Hz, ArH), 7.66 (1H, dd, J = 10.2 and 1.8 Hz, ArH), 7.50 (1H, ddd, J = 8.4, 1.8 and 0.9 Hz, ArH), 2.07 (3H, s, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.8, 153.1 (d), 133.2, 126.4, 125.4, 124.1, 87.0, 23.5; m/z (EI-MS): 279 ($M^{\cdot+}$, 70%), 137 (100). Anal. Calcd for C_8H_7FINO: C, 34.43; H, 2.53; N, 5.02%. Found: C, 34.56; H, 2.57; N, 5.13%.

(E)-3,3′-Difluoro-4,4′-diacetamidostilbene (7)

Potassium fluoride (156 mg, 2.78 mmol) and n-Bu_4NBr (578 mg, 1.79 mmol) were suspended in toluene (5 cm^3) and *N*-(2-fluoro-4-iodophenyl)acetamide (**6**) (250 mg, 0.90 mmol), $Pd(OAc)_2$ (20 mg, 89 μmol) and vinyltrimethylsilane (1 cm^3, 6.82 mmol) were added. The mixture was stirred vigorously at room temperature, under a nitrogen atmosphere, for 40 h. Wet DMF (4 cm^3) and PPh_3 (47 mg, 0.18 mmol) were then added and the excess vinyltrimethylsilane was removed under reduced pressure. After the addition of K_2CO_3 (310 mg, 2.24 mmol) and a further equivalent of *N*-(2-fluoro-4-iodophenyl)acetamide (**6**) (250 mg, 0.9 mmol) stirring was continued at 85°C for 24 h. EtOAc (100 cm^3) was then added to the cooled solution and the mixture was filtered through Celite. The organic phase was washed with water and brine (2 × 50 cm^3 each), and dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to flash chromatography on silica gel or HPLC to give the title compound **7** (20 mg, 7%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.78 (2H, s, NH), 7.93 (2H, apparent t, J = 8.5 Hz, ArH), 7.50 (2H, dd, J = 12.0 and 1.5 Hz, ArH), 7.33 (2H, apparent d, J = 8.5 Hz, ArH), 7.20 (2H, s, olefinic), 2.11 (6H, s, 2 × CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.5, 153.3 (d), 133.9, 127.2, 123.5, 122.6, 125.5, 112.4, 23.4; m/z (+ve ESI-MS): 353 ([M + Na]$^+$).

(E)-3,3′-Difluoro-4,4′-diaminostilbene (8)

(*E*)-3,3′-Difluoro-4,4′-diacetamidostilbene (**7**) (6 mg, 0.18 μmol) was dissolved in ethanol (20 cm^3). Concentrated hydrochloric acid (5 cm^3) was added and the solution was heated at reflux for 5 h. The mixture was then cooled, water was added and the pH was made basic (pH > 8) with sodium bicarbonate. The solution was extracted with EtOAc (5 × 40 cm^3) and the extracts were combined and concentrated to give an orange solid, which was subjected to HPLC to give the title compound **8** (4 mg, 89%) as a white powder. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.23 (2H, d, J = 12.9 Hz, ArH), 7.07 (2H, d, J = 8.4 Hz, ArH), 6.85 (2H, s, olefinic), 6.78 (2H, apparent t, J = 8.4 Hz, ArH); ^{13}C NMR (125 MHz, DMSO-d_6): δ 151.2 (d), 134.3, 127.4, 124.8, 123.1, 116.9, 112.1.

[(E)-4,4′-Bis(2,4,6-trinitrophenylamino)-3,3′-difluorostilbene]-[α-cyclodextrin]-[2]-rotaxane (3)

The stilbene **8** (3 mg, 12 μmol) was stirred with α-cyclodextrin **12** (460 mg, 47.3 mmol) in 0.2 M carbonate buffer (pH 10.0, 25 cm^3) at room temperature for 16 h. TNBS **15** (10.5 mg, 30 μmol) was added and stirring was continued for a further 4 h. The reaction mixture was then washed with EtOAc (4 × 25 cm^3) and concentrated to a volume of 50 cm^3. The residue was applied to a Diaion HP-20 column (250 × 15 mm). The column was washed with water until no unreacted α-cyclodextrin **12** was detected by TLC. A methanol/water gradient was then applied. The fractions which contained the rotaxane **3** (50–70% methanol) were combined and the solvent was removed under reduced pressure. The crude product **3** was dissolved in a small amount of water and purified by HPLC. After freeze drying, the title compound **3** (4.5 mg, 73%) was obtained as a red powder. TLC: R_f = 2.00; ^{1}H NMR (500 MHz, methanol-d_4): δ 9.11 (2H, s, trinitrophenyl), 9.08 (2H, s, trinitrophenyl), 7.80 (1H, d, J = 11.5 Hz, A-H3), 7.74 (1H, d, J = 8.0 Hz, A-H2), 7.37 (1H, br A-H1), 7.29 (1H, apparent t, J = 8.0 Hz, A-H7), 7.21–7.15 (3H, m, A-H8, H6 and H4), 7.07 (1H, d, J = 16.5 Hz, A-H5), 4.95 (6H, d, J = 3.5 Hz, CD-H1), 3.88 (6H, apparent t, J = 9.5 Hz, CD-H3), 3.82–3.76 (12H, m, CD-H5 and H6), 3.67–3.59 (12H, m, CD-H4 and H6), 3.46 (6H,

dd, $J = 10.0$ and 3.5 Hz, A-H2); ^{13}C NMR (125 MHz, methanol-d_4): δ 140.5, 140.1, 128.1, 127.9, 125.2, 125.5, 124.4, 116.1, 114.7, 104.3, 83.4, 75.2, 74.0, 61.6. m/z (−ve ESI-MS): 1639 ($[M - H]^-$); HPLC: t_R 9.6 min (Phenomenex Luna, 250 × 10 mm; 26% aq CH_3CN; flow rate: 2.5 $cm^3\,min^{-1}$).

(E)-3,3′-Dichloro-4,4′-dinitrostilbene (10)

3-Chloro-4-nitrotoluene **9** (5.0 g, 29 mmol) was dissolved in acetone (5 cm^3) and the solution was added dropwise to methanolic KOH (33% by weight, 200 cm^3). Oxygen was bubbled through the reaction mixture. The solution was stirred vigorously with ice-bath cooling for 2 h and then for a further 3 h at room temperature. The solution was then poured into 2 dm^3 of water. The resultant precipitate was collected by filtration and recrystallized three times from glacial acetic acid to give the title compound **10** (1.86 g, 38%) as a yellow solid, mp 236–240°C (lit. [9] 284–285°C). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.16 (2H, d, $J = 8.4$ Hz, ArH), 8.04 (2H, d, $J = 1.5$ Hz, ArH), 7.81 (2H, dd, $J = 8.4$ and 1.5 Hz, ArH), 7.65 (2H, s, olefinic); m/z (EI-MS): 338 ($M^{\cdot+}$, 100%), 340 (63), 308 (35), 199 (50), 176 (75).

(E)-3,3′-Dichloro-4,4′-diaminostilbene (11)

(*E*)-3,3′-Dichloro-4,4′-dinitrostilbene (**10**) (200 mg, 0.58 mmol) and $SnCl_2.2H_2O$ (1.33 g, 5.89 mmol) were suspended in ethanol (8 cm^3). The mixture was heated at 70°C for 1 h under nitrogen, then allowed to cool to room temperature and poured onto ice. The pH was made basic (pH > 8) by addition of sodium bicarbonate and then the solution was extracted with EtOAc (4 × 25 cm^3). The combined organic extracts were dried using $MgSO_4$ and concentrated under reduced pressure to give the title compound **11** (158 mg, 96%) as an orange solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.35 (2H, d, $J = 1.8$ Hz, ArH), 7.20 (2H, dd, $J = 8.4$ and 1.8 Hz, ArH), 6.81 (2H, s, olefinic), 6.75 (2H, d, $J = 8.4$, Hz ArH), 5.46 (4H, s, NH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 147.5, 126.8, 126.4, 125.4, 123.8, 117.2, 115.3; m/z (EI-MS): 278 (M^+, 100%), 280 (75).

[(E)-4,4′-Bis(2,4,6-trinitrophenylamino)-3,3′-dichlorostilbene]-[α-cyclodextrin]-[2]-rotaxane (4)

α-Cyclodextrin **12** (2.5 g, 2.57 mmol) was dissolved in 0.2 M carbonate buffer (pH 10.0, 25 cm^3). The stilbene **11** (100 mg, 0.36 mmol) was added to the solution and the mixture was stirred for 5 h, then it was sonicated for 1 h before the addition of TNBS **15** (278 mg, 0.79 mmol). After 10 h the solution was washed with EtOAc (5 × 25 cm^3) and concentrated to ~10 cm^3 before water (40 cm^3) was added. The solution was applied to a Diaion HP-20 column (250 × 15 mm). The column was washed with water until no unreacted α-cyclodextrin **12** was detected by TLC and then eluted with increasing concentrations of methanol. The fractions containing the desired product (50–70% methanol) were combined and the solvent evaporated. The residual solid was dissolved in 1 cm^3 of water and the solution was subjected to HPLC. The desired fraction was collected and freeze dried to give the title compound **4** (9 mg, 2%) as a red powder. TLC: $R_f = 2.05$; mp 264–270°C (dec); ^{1}H NMR (500 MHz, methanol-d_4): δ 9.10 (4H, br, trinitrophenyl), 8.05 (1H, s, A-H3), 7.85 (1H, d, $J = 8.0$ Hz, A-H2), 7.36 (1H, s, A-H6), 7.29 (2H, m, A-H1 and H8), 7.21 (1H, m, A-H7), 7.13 (1H, d, $J = 16.5$ Hz, A-H4), 7.04 (1H, d, $J = 16.5$ Hz, A-H5), 4.95 (6H, d, $J = 3.0$ Hz, CD-H1), 3.89 (6H, apparent t, $J = 9.0$ Hz, CD-H3), 3.82–3.77 (12H, m, CD-H5 and H6), 3.67–3.61 (12H, m, CD-H4 and H6), 4.46 (6H, dd, $J = 3.0$ and 9.5 Hz, CD-H2); ^{13}C NMR (75 MHz, methanol-d_4): δ 140.5, 139.9, 130.7, 130.5, 130.1, 130.0, 129.1, 128.7, 128.2, 128.2, 127.7, 126.5, 124.4, 123.7, 104.3, 83.4, 75.2, 74.1, 74.0, 61.6; m/z (−ve ESI-MS): 1671 ($[M - H]^-$, 90%), 1673 (100); HPLC: t_R 19.7 min (Phenomenex Luna, 250 × 10 mm; 22% aq CH_3CN; flow rate: 2.5 $cm^3\,min^{-1}$). Anal. Calcd for $C_{62}H_{74}Cl_2N_8O_{42}.9H_2O$: C, 40.55; H, 5.05; N, 6.10%. Found: C, 40.71; H, 4.79; N, 5.74%.

X-ray Crystallography

The crystal data, data collection and refinement parameters are listed below. Measurements were made with a Nonius KappaCCD area detector using Mo Kα ($\lambda = 0.71073$ Å) radiation. The intensities were corrected for Lorentz and polarization effects and for absorption. The structures were solved by direct methods using SHELXM [48] and refined on F^2 using all data by full-matrix least-squares procedures using SHELXL97 [49]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions except for the many water molecules in each structure which were included only as oxygen atoms. In the structure of the rotaxane **3**, the orientations of two of the hydroxymethyl groups of one of the independent cyclodextrin units were disordered over two positions, and there was disorder in the position of one of the fluorine atoms.

Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre (CCDC No 295511 and 295512). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).

Crystal data for the rotaxane ***3***: $C_{62}H_{74}F_2N_8O_{54}$, $M = 1833.3$, monoclinic, $a = 13.4409(4)$, $b = 17.3928(5)$, $c = 34.6908(10)$ Å, $\beta = 94.2146(7)°$, $V = 8087.9(4)$ Å^3, $F(000) = 3808$, $T = 200$ K, space group $P2_1$, $Z = 4$, orange plate, 0.40 × 0.36 ×

$0.08\,mm^3$, $\mu = 0.137\,mm^{-1}$, $D_c = 1.506\,g\,cm^{-3}$, 116052 reflections measured, 28053 unique [$R_{int} = 0.0651$], 2325 parameters, wR_2 (all data) = 0.2032, R_1 [24339 data with $I > 2\sigma(I)$] = 0.0754.

Crystal data for the rotaxane **4**: $C_{62}H_{74}Cl_2N_8O_{52.5}$, $M = 1842.2$, monoclinic, $a = 17.7801(1)$, $b = 16.2393(1)$, $c = 27.3531(2)$ Å, $\beta = 94.2746(4)°$, $V = 7875.9(1)$ Å^3, $F(000) = 3824$, $T = 200\,K$, space group $P2_1$, $Z = 4$, red prism, $0.26 \times 0.24 \times 0.22\,mm^3$, $\mu = 0.202\,mm^{-1}$, $D_c = 1.554\,g\,cm^{-3}$, 201686 reflections measured, 35994 unique [$R_{int} = 0.0450$], 2251 parameters, wR_2 (all data) = 0.1810, R_1 [28985 data with $I > 2\sigma(I)$] = 0.0630.

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