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Hindered fluorescence quenching in an insulated molecular wire †

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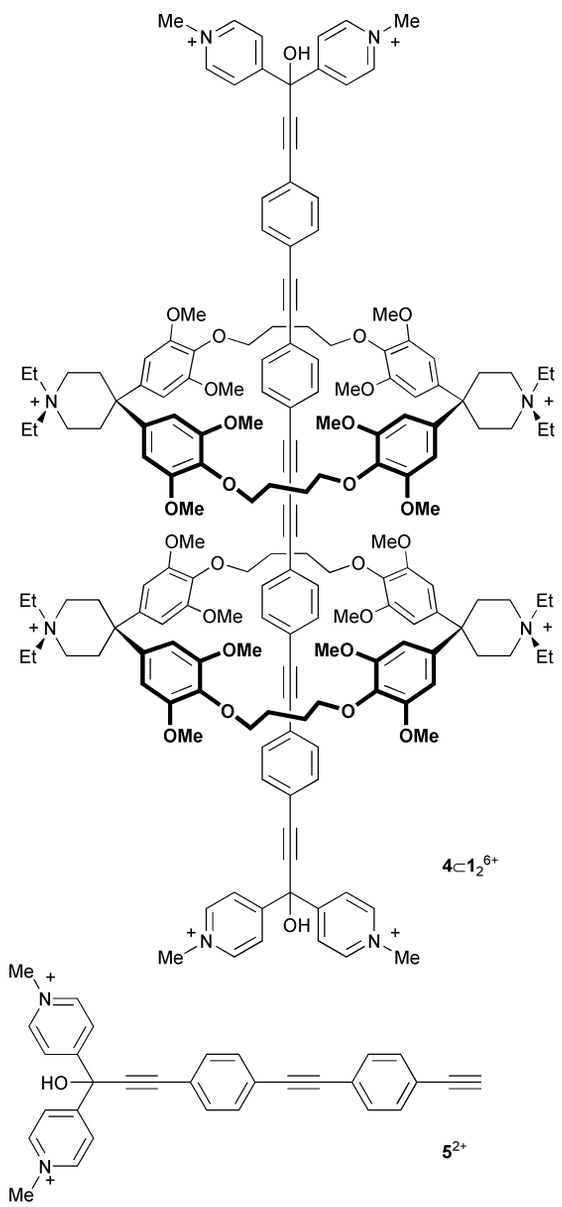
Received 12th June 2003, Accepted 18th August 2003
First published as an Advance Article on the web 29th August 2003

A [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ consisting of an anionic phenylene ethynylene dumbbell $\mathbf{2}^{4-}$ threaded through two cationic cyclophanes $\mathbf{1}^{2+}$ has been prepared using aqueous Glaser coupling. Stern–Volmer analysis of the fluorescence quenching using three different electron-acceptors (methyl viologen $\mathbf{13}^{2+}$, dipropyl-4,4′-bipyridinium disulfonate **14** and anthraquinone-2,6-disulfonate $\mathbf{15}^{2-}$) shows that the threaded cyclophanes inhibit electron-transfer from the excited state of the dumbbell by steric shielding, and by electrostatic shielding in the case of methyl viologen.

Introduction

Long conjugated π-systems have many useful optical and electronic properties.[1] We are interested in developing supramolecular strategies for controlling the behaviour of these materials; one such approach is to encapsulate the π-system by threading it through one or more cylindrical macrocycles to form a rotaxane. Recently we have shown that this type of encapsulation can lead to enhanced chemical stability,[2] photostability,[2–6] redox-reversibility,[5] fluorescence efficiency[3,4,6–9] and electroluminescence efficiency.[9] Here we demonstrate that rotaxane-encapsulation can block quenching of an excited state, by hindering photo-induced electron-transfer. Similar effects have previously been reported in a biacetyl hemicarcerplex[10] and in some cyclodextrin complexes.[11]

As part of this work we prepared a new neutral [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ consisting of two cationic Diederich-type cyclophanes[12] $\mathbf{1}^{2+}$ threaded on a conjugated anionic core $\mathbf{2}^{4-}$, and compared its fluorescence behaviour with the isomeric unthreaded dumbbell-cyclophane salt $\mathbf{2}\cdot\mathbf{1}_2$. The key step in this synthesis is the aqueous Glaser coupling of the cyclophane salt of an anionic alkyne $\mathbf{3}\cdot\mathbf{1}$ (Schemes 1 and 2). This synthesis is analogous to that of our previous cyclophane [3]rotaxane $\mathbf{4}\subset\mathbf{1}_2$, except in that case the precursor alkyne $\mathbf{5}^{2+}$ is cationic rather than anionic, so that Coulombic repulsion between the rotaxane components mitigates against the threading process.[3] Our previous [3]rotaxane $\mathbf{4}\subset\mathbf{1}_2$ also displays poor stability in solution, probably due to the sensitivity of the pyridinium groups to nucleophilic attack. [3]Rotaxane $\mathbf{2}\subset\mathbf{1}_2$ was designed to explore the consequences of attractive Coulombic interactions between the rotaxane components, and to gain access to a more stable fluorescent rotaxane.



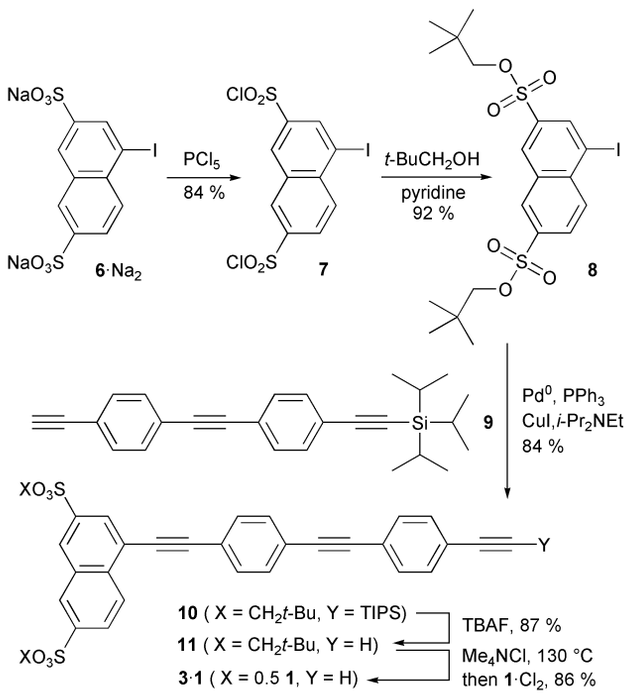
Results and discussion

Synthesis

The alkyne stopper $\mathbf{3}^{2-}$ was prepared as shown in Scheme 1. Initially we attempted to minimise protecting group manipulation by reacting iodonaphthalene $\mathbf{6}\cdot Na_2$ (prepared by the Sandmeyer reaction)[8b] directly with phenylene ethynylene **9**.[13] This chemistry proved troublesome because the polarity of the intermediates makes them difficult to purify. Use of the organic-soluble tetraphenylphosphonium salt $\mathbf{6}\cdot(PPh_4)_2$ did not solve this problem. The neopentyl sulfonate **8** proved much more amenable; these protecting groups were removed in the last step using tetramethylammonium chloride.[14] When $\mathbf{3}^{2-}$ was

† This is one of a number of contributions from the current members of the Dyson Perrins Laboratory to mark the end of almost 90 years of organic chemistry research in that building, as all its current academic staff move across South Parks Road to a new purpose-built laboratory.

DOI: 10.1039/b306727k

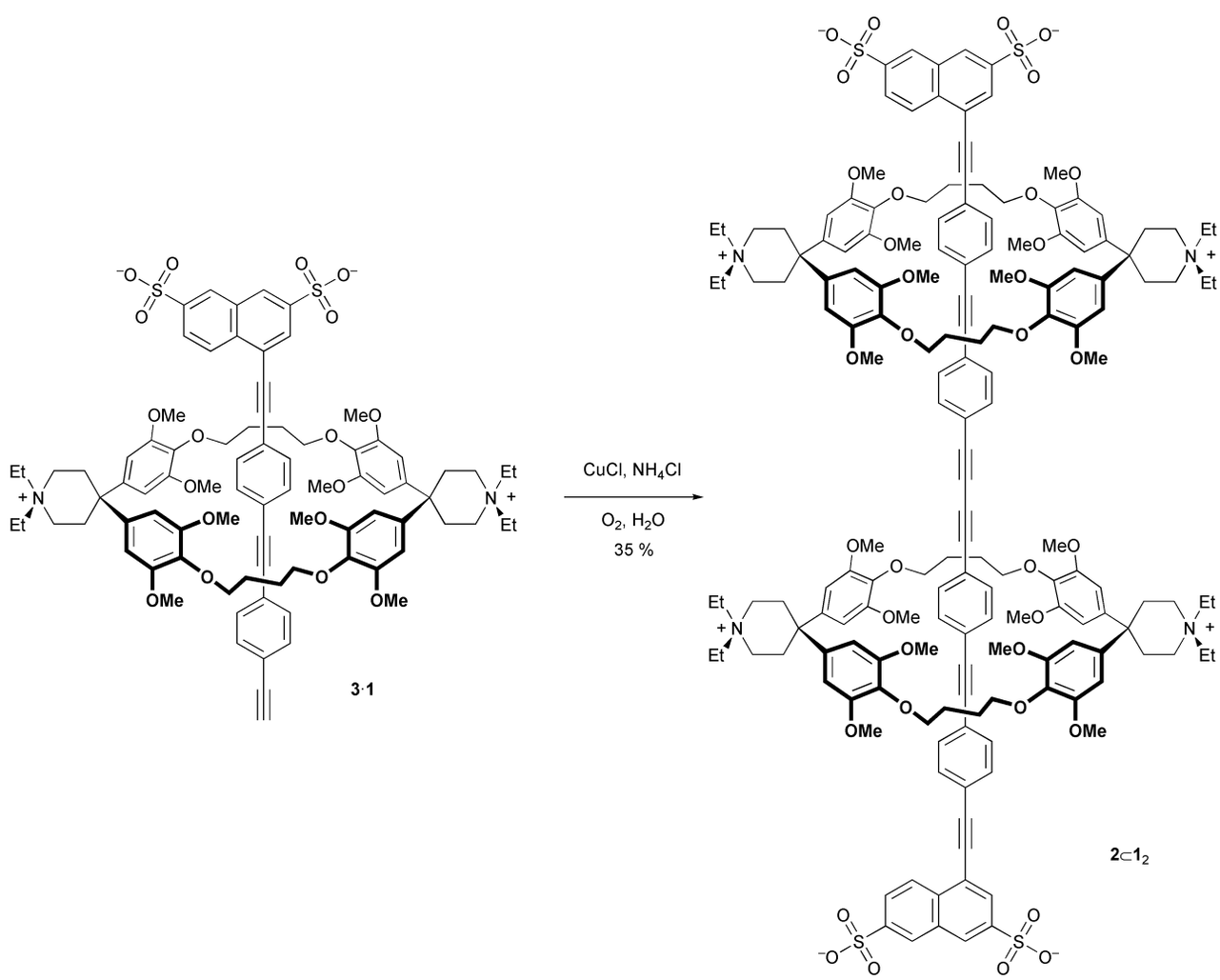


Scheme 1 Synthesis of alkyne–cyclophane complex salt **3·1**.

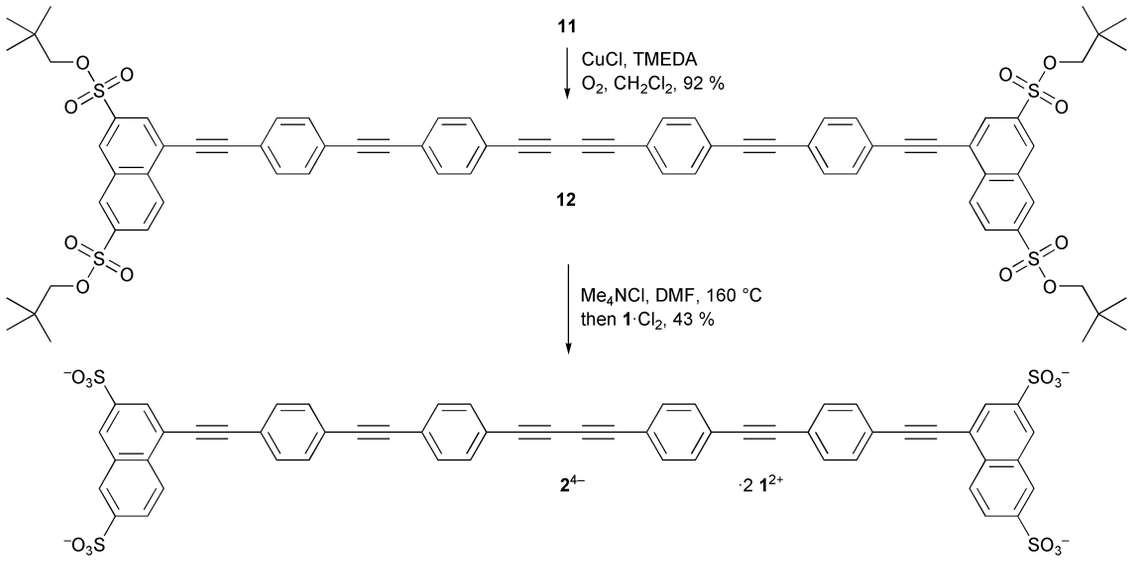
isolated as the tetramethylammonium salt, the yield of this deprotection step was only 40% because **3**·$(NMe_4)_2$ is difficult to isolate, but treatment of the crude product with **1**·Cl_2 enabled the cyclophane salt of the alkyne **3·1** to be isolated in 86% yield.

The affinity of this anionic alkyne $\mathbf{3}^{2-}$ with the cationic cyclophane $\mathbf{1}^{2+}$ was tested in water at 298 K by UV titration, using **3**·$(NMe_4)_2$ and **1**·Cl_2. A combination of strong hydrophobic binding and strong electrostatic attraction make the $\mathbf{3}^{2-}\cdot\mathbf{1}^{2+}$ complex extremely stable; it has a stability constant of $4.5 \pm 0.5 \times 10^6$ M^{-1}, which is two orders of magnitude greater than that of the $\mathbf{5}^{2+}\cdot\mathbf{1}^{2+}$ complex ($4.3 \pm 0.2 \times 10^4$ M^{-1}).[3] However the neutrality of $\mathbf{3}^{2-}\cdot\mathbf{1}^{2+}$ results in poor solubility in water, whereas $\mathbf{5}^{2+}\cdot\mathbf{1}^{2+}\cdot(Cl^-)_4$ is extremely water-soluble. ^{1}H NMR experiments indicated that the stability constant of **3·1** in d_4-methanol is *ca.* 5×10^3 M^{-1} and that the complex is largely dissociated in d_6-DMSO, so the [3]rotaxane was prepared by oxidatively coupling an aqueous suspension of **3·1**. ^{1}H NMR analysis of the crude reaction mixture showed that it consists of 53% [3]rotaxane **2**⊂$\mathbf{1}_2$, 32% [2]rotaxane **2**⊂**1** and 14% dumbbell **1**. The very high stability of the **3·1** complex does not translate into a high yield of the [3]rotaxane because the low solubility of this 1 : 1 complex results in coupling at high dilution. The [3]rotaxane was isolated from the reaction mixture in 35% yield using size exclusion chromatography and recrystallisation. This yield is only marginally better than that of our previous [3]rotaxane **4**⊂$\mathbf{1}_2$ (isolated yield 30%). Unfortunately we were unable to isolate pure samples of the [2]rotaxane **2**⊂**1** and dumbbell **1** from the reaction mixture. The unthreaded dumbbell-cyclophane salt $\mathbf{2}\cdot\mathbf{1}_2$ was prepared *via* Glaser coupling of the neopentyl protected stopper **11** as shown in Scheme 3.

The structure of the [3]rotaxane **2**⊂$\mathbf{1}_2$ was confirmed by ^{1}H NMR, ^{13}C NMR and electrospray mass spectrometry (ES MS). Initial attempts at recording the ES MS of **2**⊂$\mathbf{1}_2$ were unsuccessful, but addition of diethylamine led to the appearance of peaks at *m/z* 756.3, 1008.1 and 1511.6 corresponding to M^{4+},



Scheme 2 Synthesis of [3]rotaxane **2**⊂$\mathbf{1}_2$.



Scheme 3 Synthesis of the dumbbell salt $\mathbf{2{\cdot}1}_2$.

M^{3+} and M^{2+}. The ^{1}H NMR spectra of the isomers $\mathbf{2}\subset\mathbf{1}_2$ and $\mathbf{2{\cdot}1}_2$ are compared in Fig. 1. These spectra were fully assigned using 2D NMR techniques. The strong up-field shift in H_f, H_g, H_h and H_i in the rotaxane demonstrates that these *para*-phenylene units reside inside the cavity of the cyclophane, and the greatest shifts at protons H_f and H_g shows that the cyclophanes sit near the ends of the dumbbell. This is confirmed by NOE measurements. For example irradiation of the cyclophane aromatic resonance, or the cyclophane methoxy resonance, results in NOEs to H_g, H_f, H_h, H_i, H_c and H_d, with much the strongest NOEs to H_g and H_f in both cases. This conformation contrasts with that in $\mathbf{4}\subset\mathbf{1}_2$, where the cyclophanes sit near the centre of the dumbbell,[3] reflecting the different electrostatic interaction with the end groups.

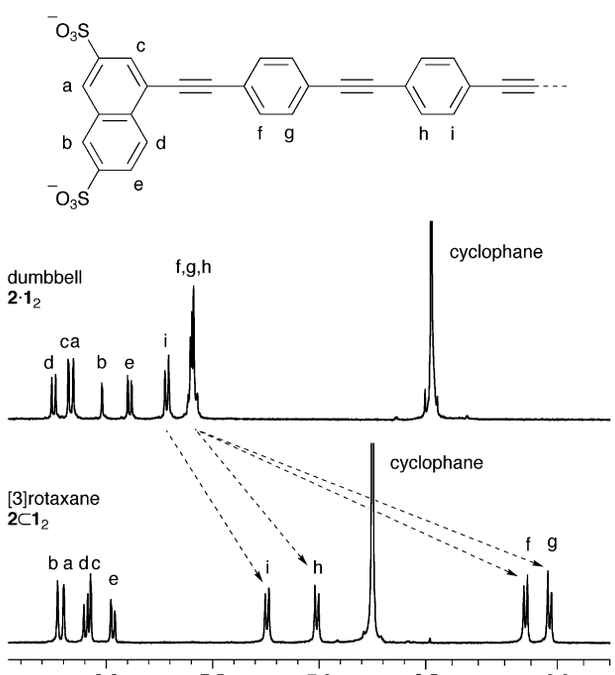


Fig. 1 Aromatic regions of the ^{1}H NMR spectra of [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ and dumbbell $\mathbf{2{\cdot}1}_2$ (d_6-DMSO, 500 MHz).

The absorption and fluorescence spectra of [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ and dumbbell-cyclophane salt $\mathbf{2{\cdot}1}_2$ in aqueous solution are compared in Fig. 2. There is a slight blue-shift in both the absorption (rotaxane λ_{max} = 369 nm; dumbbell λ_{max} = 372 nm)

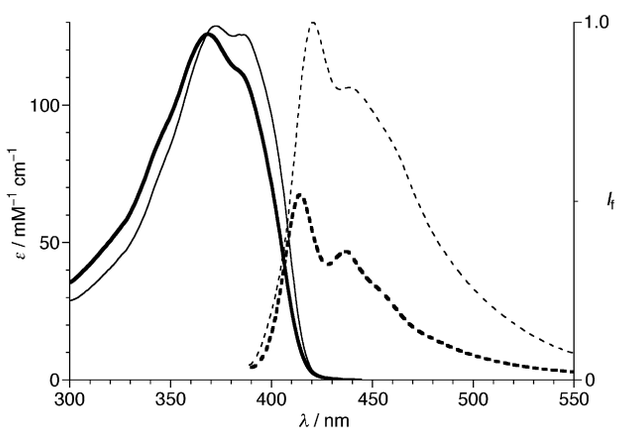


Fig. 2 UV absorption and emission spectra of [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ (bold) and dumbbell $\mathbf{2{\cdot}1}_2$ (plain) in water. I_f is emission intensity (arbitrary units). Both emission spectra were recorded at a concentration of 4×10^{-8} M with excitation at 370 nm.

and the emission (rotaxane λ_{max} = 414 nm; dumbbell λ_{max} = 420 nm) of the rotaxane. The fluorescence quantum yield of the rotaxane (Φ_0 = 0.06) is lower than that of the dumbbell (Φ_0 = 0.15). Macrocyclic encapsulation generally enhances the fluorescence efficiency, but a few examples of rotaxane-encapsulated dyes and macrocyclic inclusion complexes with reduced fluorescence quantum yields have been reported.[4,15] The similarity between the absorption and emission spectra of $\mathbf{2}\subset\mathbf{1}_2$ and $\mathbf{2{\cdot}1}_2$ indicates that there is little interaction between the encapsulated π-system and the cyclophane, in both the ground state and the excited state, but there is evidently sufficient interaction to facilitate nonradiative decay in the rotaxane.

Fluorescence quenching experiments

Electron-acceptors such as methyl viologen $\mathbf{13}^{2+}$ (also known as paraquat) quench the fluorescence of many organic chromophores by accepting an electron from the excited state of the π-system.[16,17] We explored the fluorescence quenching of [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ and dumbbell-cyclophane salt $\mathbf{2{\cdot}1}_2$ to test whether the presence of the threaded cyclophane hinders photo-induced electron-transfer to an added electron-acceptor.

We selected three different quenchers to probe the Coulombic and steric shielding effect of the cyclophane: dication $\mathbf{13}^{2+}$, neutral viologen $\mathbf{14}$[18] and sulfonated anthraquinone dianion $\mathbf{15}^{2-}$ (Fig. 3). When each acceptor was titrated into an aqueous solution of the rotaxane or dumbbell, the shape of the

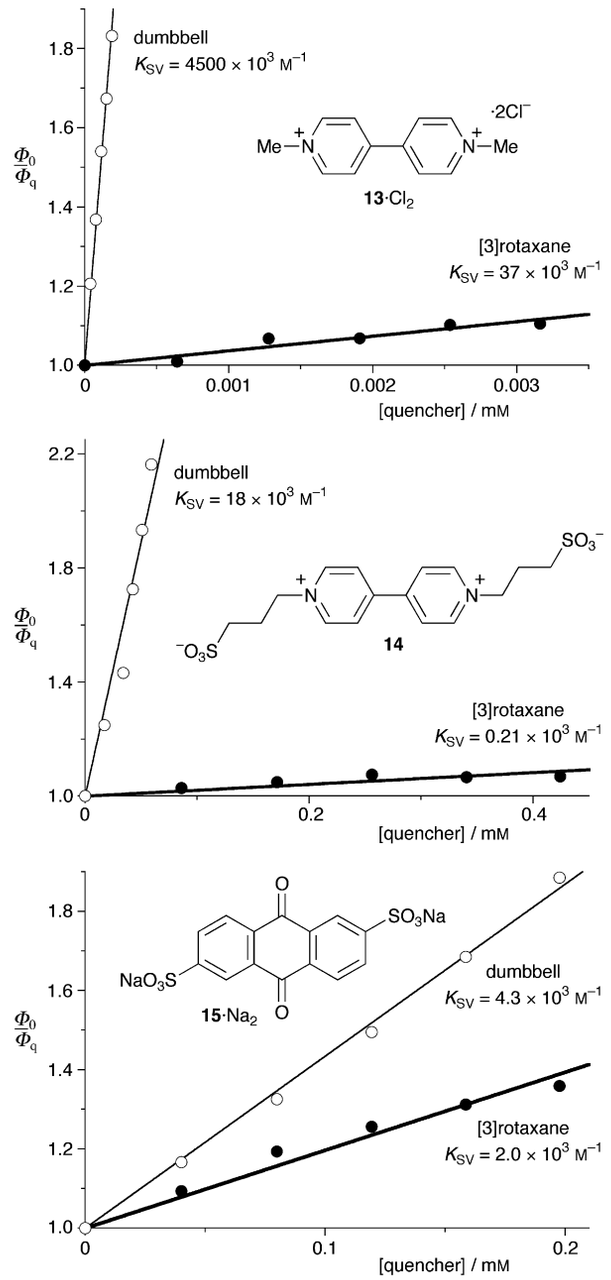


Fig. 3 Stern–Volmer data for titration of [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ and dumbbell $\mathbf{2}\cdot\mathbf{1}_2$ with quenchers $\mathbf{13}\cdot Cl_2$, **14** and $\mathbf{15}\cdot Na_2$ in water at 298 K. The concentration of $\mathbf{2}\subset\mathbf{1}_2$ and $\mathbf{2}\cdot\mathbf{1}_2$ is 4×10^{-8} M. Error limits in K_{SV} are *ca.* ± 10%.

fluorescence spectrum was unaffected, but the intensity of the emission decreased, as shown by the Stern–Volmer plots of Φ_0/Φ_q *vs.* acceptor concentration in Fig. 3 (Φ_q is the fluorescence quantum yield in the presence of quencher).[16] The Stern–Volmer constants, K_{SV}, shown on Fig. 3 were obtained from the straight line fits according to equation (1),

$$\Phi_0/\Phi_q = 1 + K_{SV}[Q] \qquad (1)$$

where [Q] is the concentration of quencher.

The data in Fig. 3 show that all three electron-acceptors quench the fluorescence of the dumbbell much more than that of the rotaxane. The difference is greatest with the cationic quencher $\mathbf{13}^{2+}$ and smallest with the anionic quencher $\mathbf{15}^{2-}$, illustrating the electrostatic shielding effect of the cyclophane, but the fact that the quenching efficiencies are not reversed by changing the charge on the quencher shows that there is a significant steric shielding effect. There are two possible mechanisms for this type of fluorescence quenching:[16] static quenching, in which the electron-acceptor is already associated with the chromophore before excitation, and dynamic quenching, in which electron-acceptors approach the excited state of the chromophore by diffusion. Further experiments will be required to determine the dominant mechanism in these systems. However the extremely high sensitivity of the unthreaded dumbbell $\mathbf{2}^{4-}$ to methyl viologen $\mathbf{13}^{2+}$ ($K_{SV} = 4.5 \times 10^6$ M^{-1}) indicates that $\mathbf{2}^{4-}$ probably aggregates in the presence of $\mathbf{13}^{2+}$ even under the very dilute conditions of this experiment ([$\mathbf{2}^{4-}$] = 4×10^{-8} M), leading to static quenching.[19] Dynamic quenching is more likely with the neutral and anionic electron-acceptors, **14** and $\mathbf{15}^{2-}$.

Conclusions

The high affinity of $\mathbf{3}^{2-}$ for cyclophane $\mathbf{1}^{2+}$ ($K = 4.5 \pm 0.5 \times 10^6$ M^{-1}) illustrates the importance of electrostatic interactions in molecular recognition, even in water. However there is a penalty for charge-compensation: the **3·1** complex has poor solubility in water, resulting in a modest yield of the [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$. Electrostatic interactions in the [3]rotaxane $\mathbf{2}\subset\mathbf{1}_2$ shift the cyclophane units towards the ends of the dumbbell, in contrast to the conformation adopted by [3]rotaxane $\mathbf{4}\subset\mathbf{1}_2$. Stern–Volmer titrations show that the presence of the threaded cyclophanes inhibits fluorescence quenching in $\mathbf{2}\subset\mathbf{1}_2$, by sterically hindering the approach of the quencher, and also by electrostatic repulsion in the case of cationic quenchers. The fluorescence of the unthreaded dumbbell $\mathbf{2}^{4-}$ is remarkably sensitive to quenching by methyl viologen $\mathbf{13}^{2+}$ ($K_{SV} = 4.5 \times 10^6$ M^{-1}) suggesting that non-polymeric chromophores of this type could be utilised in sensor applications.[17,19] These results also suggest that it might be possible to use a threaded macrocycle to hinder electron–hole recombination in a photovoltaic device.

Experimental

1-Iodonaphthalene-3,6-disulfonylchloride 7

1-Iodonaphthalene-3,6-disulfonic acid disodium salt $\mathbf{6}\cdot Na_2$ (3.0 g, 6.5 mmol) and phosphorus pentachloride (8.2 g, 39 mmol) were heated with stirring at 110 °C for 1 h. The mixture was then heated at 110 °C under reduced pressure (0.1 mmHg) to distil off $POCl_3$ and excess PCl_5. The residue was dissolved in chloroform (100 ml) and washed with water (4 × 100 ml). The organic layer was dried over magnesium sulfate, filtered and evaporated to yield **7** as a pale grey solid (2.49 g, 84%); mp 145–146 °C; δ_H (500 MHz, $CDCl_3$) 8.80 (s, 1H), 8.79 (s, 1H), 8.76 (d, ^4J 2 Hz, 1H), 8.52 (d, ^3J 9 Hz, 1H), 8.35 (dd, ^3J 9 Hz, ^4J 2 Hz, 1H); δ_C (125.7 MHz, $CDCl_3$) 144.35, 143.80, 139.42, 136.21, 135.62, 130.96, 130.71, 127.39, 101.18; λ_{max} ($CHCl_3$) 316 nm (logε 3.75); *m*/*z* (CI/NH_3) 449.8 (M^+, $C_{10}H_5Cl_2IO_4S_2$ requires 449.8).

1-Iodonaphthalene-3,6-dineopentylsulfonate 8

1-Iodonaphthalene-3,6-disulfonylchloride **7** (1.0 g, 2.2 mmol), neopentyl alcohol (0.39 g, 4.4 mmol) and pyridine (6 ml) were stirred at −10 °C for 18 h. HCl (50 ml, 2 M aq.) was added and the product extracted with chloroform (2 × 50 ml). The combined organic layers were dried ($MgSO_4$) and the product was recrystallised from CH_2Cl_2/hexane to yield **8** as a white solid (1.16 g, 94%); mp 151–152 °C; δ_H (500 MHz, $CDCl_3$) 8.62 (d, ^4J 2 Hz, 1H), 8.60 (d, ^4J 2 Hz, 1H), 8.57 (d, ^4J 2 Hz, 1H), 8.39 (d, ^3J 9 Hz, 1H), 8.13 (dd, ^3J 9 Hz, ^4J 2 Hz, 1H), 3.80 (s, 2H), 3.78 (s, 2H), 0.95 (s, 9H), 0.93 (s, 9H); δ_C (125.7 MHz, $CDCl_3$) 138.28, 136.80, 136.37, 136.14, 134.59, 131.30, 131.26, 131.10, 127.75, 100.60, 80.78, 80.61, 32.05, 31.99, 26.20; λ_{max} ($CHCl_3$) 336 nm (logε 3.31); *m*/*z* (FAB+) 554.0 (M^+, $C_{20}H_{27}IO_6S_2$ requires 554.0).

1-(4-[(4-Triisopropylsilylethynylphenyl)ethynyl]phenylethynyl)-naphthalene-3,6-dineopentylsulfonate 10

A solution of **8** (500 mg, 0.90 mmol), **9** (430 mg, 1.1 mmol), triphenylphosphine (47 mg, 0.18 mmol), CuI (8.6 mg, 0.045 mmol) and tris(dibenzylideneacetone)dipalladium(0) (41 mg, 0.045 mmol) in diisopropylethylamine (2 ml) and toluene (20 ml) was stirred under nitrogen at 60 °C for 2 h. The mixture was cooled, chromatographed (SiO_2, hexane/CH_2Cl_2 2/1) and recrystallised from CH_2Cl_2/hexane to give **10** as a yellow solid (610 mg, 84%); δ_H (500 MHz, $CDCl_3$) 8.67 (d, ^3J 9 Hz, 1H), 8.65 (d, ^4J 2 Hz, 1H), 8.57 (d, ^4J 2 Hz, 1H), 8.30 (d, ^4J 2 Hz, 1H), 8.17 (dd, ^3J 9 Hz, ^4J 2 Hz, 1H), 7.66 (d, ^3J 9 Hz, 2H), 7.60 (d, ^3J 9 Hz, 2H), 7.46–7.49 (m, 4H), 3.83 (s, 2H), 3.79 (s, 2H), 1.15 (s, 21H), 0.96 (s, 9H), 0.94 (s, 9H); δ_C (125.7 MHz, $CDCl_3$) 136.85, 136.18, 135.51, 132.27, 132.09, 132.03, 131.67, 131.22, 131.07, 130.30, 129.77, 128.66, 126.88, 124.55, 124.05, 123.98, 122.82, 121.92, 106.75, 97.68, 93.45, 92.06, 90.75, 86.75, 80.70, 80.56, 32.07, 32.01, 26.26, 26.23, 18.89, 11.54; λ_{max} ($CHCl_3$) 355 (logε 4.76); *m*/*z* (FAB+) 808.5 (M^+, $C_{47}H_{56}O_6S_2Si$ requires 808.3).

1-(4-[(4-Ethynylphenyl)ethynyl]phenylethynyl)naphthalene-3,6-dineopentylsulfonate 11

A solution of **10** (550 mg, 0.680 mmol) in CH_2Cl_2 (30 ml) was treated with TBAF (0.70 ml, 1 M in THF, 0.70 mmol) and stirred for 45 min. The mixture was washed with water (2 × 20 ml), dried ($MgSO_4$) and evaporated to dryness under reduced pressure. The product was purified by chromatography (SiO_2, CH_2Cl_2/hexane 1/1) and recrystallised from CH_2Cl_2/hexane to give **11** as a yellow solid (386 mg, 87 %); δ_H (500 MHz, $CDCl_3$) 8.67 (d, ^3J 9 Hz, 1H), 8.65 (d, ^4J 2 Hz, 1H), 8.57 (s, 1H), 8.31 (d, ^4J 2 Hz, 1H), 8.17 (dd, ^3J 9 Hz, ^4J 2 Hz, 1H), 7.66 (d, ^3J 9 Hz, 2H), 7.60 (d, ^3J 9 Hz, 2H), 7.49–7.52 (m, 4H), 3.82 (s, 2H), 3.79 (s, 2H), 3.20 (s, 1H), 0.96 (s, 9H), 0.94 (s, 9H); δ_C (125.7 MHz, $CDCl_3$) 136.84, 136.12, 135.45, 132.38, 132.09, 132.06, 131.77, 131.18, 131.08, 130.32, 129.78, 128.66, 126.88, 124.41, 123.94, 123.45, 122.57, 122.01, 97.63, 91.73, 90.90, 86.77, 83.37, 80.70, 80.56, 79.44, 32.06, 32.00, 26.23 (2C); λ_{max} ($CHCl_3$) 355 (logε 4.77); *m*/*z* (FAB+) 652.2 (M^+, $C_{38}H_{36}O_6S_2$ requires 652.2).

Protected dumbbell 12

A mixture of **11** (50 mg, 0.077 mmol), copper(I) chloride (456 mg, 4.6 mmol), TMEDA (0.67 ml, 4.5 mmol) and CH_2Cl_2 (10 ml) was vigorously stirred under oxygen for 30 min. The reaction mixture was washed with water (5 × 50 ml) and the product was purified by chromatography (SiO_2, $CHCl_3$) and recrystallised from toluene to give **12** as a yellow solid (46 mg, 92%); δ_H (500 MHz, $CDCl_3$) 8.66 (d, ^3J 9 Hz, 2H), 8.65 (s, 2H), 8.57 (s, 2H), 8.31 (s, 2H), 8.17 (d, ^3J 9 Hz, 2H), 7.67 (d, ^3J 9 Hz, 4H), 7.60 (d, ^3J 9 Hz, 4H), 7.53–7.56 (m, 8H), 3.86 (s, 4H), 3.83 (s, 4H), 0.98 (s, 18H), 0.96 (s, 18H); δ_C (125.7 MHz, $CDCl_3$) 136.92, 136.77, 136.07, 132.78, 132.16, 132.15, 131.97, 131.44, 130.98, 130.27, 129.87, 128.59, 126.95, 124.55, 124.21, 124.02, 122.34, 122.29, 97.69, 91.86, 91.79, 87.02, 82.49, 80.69, 80.54, 76.24, 32.08, 32.03, 26.31 (2C); λ_{max} ($CHCl_3$) 372 (logε 4.99); *m*/*z* (FAB+) 1302.4 (M^+, $C_{76}H_{70}O_{12}S_4$ requires 1302.4).

Dumbbell-cyclophane salt 2·1$_2$

A solution of **11** (30 mg, 0.023 mmol) and tetramethylammonium chloride (207 mg, 1.9 mmol) in DMF (5 ml) was heated at 160 °C for 16 h. Water (20 ml) was added, the aqueous phase was washed with CH_2Cl_2 (2 × 25 ml) and evaporated to dryness. The resulting residue was redissolved in water (1 ml) and a solution of cyclophane **1**·Cl_2 (30 mg, 0.028 mmol) in water (1 ml) was added causing a flocculent precipitate. The precipitate was isolated by filtration, washed with water and recrystallised from DMSO/MeOH to give **2·1$_2$** as a yellow solid (30 mg, 43%); δ_H (500 MHz, d_6-DMSO) 8.27 (d, ^3J 9 Hz, 2H), 8.20 (d, ^3J 2 Hz, 2H), 8.18 (s, 2H), 8.05 (d, ^4J 2 Hz, 2H), 7.93 (dd, ^3J 9 Hz, ^4J 2 Hz, 2H), 7.76 (d, ^3J 9 Hz, 4H), 7.67–7.64 (m, 12H), 6.59 (s, 16H), 3.89–3.71 (m, 16H), 3.69 (s, 48H), 3.40 (q, ^3J 7 Hz, 16H), 3.30–3.28 (m, 16H), 2.68–2.65 (m, 16H), 1.72–1.74 (m, 16H), 1.20 (t, ^3J 7 Hz, 24H); λ_{max} ($CHCl_3$) 371 (logε 5.11); *m*/*z* (ES–) 254.8 (M^{4-}, $C_{56}H_{26}O_{12}S_4$ requires 254.5), 340.1 (MH^{3-}, $C_{56}H_{27}O_{12}S_4$ requires 339.7).

1-(4-[(4-Ethynylphenyl)ethynyl]phenylethynyl)naphthalene-3,6-disulfonic acid ditetramethylammonium salt 3·(NMe$_4$)$_2$

A solution of **11** (65 mg, 0.10 mmol), tetramethylammonium chloride (190 mg, 1.7 mmol) and DMF (2 ml) was heated at 160 °C for 16 h. Water (20 ml) was added, the aqueous phase was washed with CH_2Cl_2 (2 × 25 ml) and evaporated to dryness. The product was purified on a Sephadex G25 size exclusion column eluting with water and then recrystallised from DMSO/CH_2Cl_2 to give **3**·(NMe$_4$)$_2$ as a white solid (25 mg, 40%); δ_H (500 MHz, d_6-DMSO) 8.32 (d, ^3J 9 Hz, 1H), 8.21 (s, 1H), 8.19 (s, 1H), 8.00 (d, ^4J 2 Hz, 1H), 7.89 (dd, ^3J 9 Hz, ^4J 2 Hz, 1H), 7.81 (d, ^3J 9 Hz, 2H), 7.67 (d, ^3J 9 Hz, 2H), 7.61 (d, ^3J 9 Hz, 2H), 7.54 (d, ^4J 9 Hz, 2H), 4.40 (s, 1H), 3.09 (s, 24H); δ_C (125.7 MHz, d_6-DMSO) 147.00 (2C), 145.78, 132.09, 132.02, 131.81, 131.73, 131.49, 129.10, 125.96, 125.83, 125.19, 125.15, 122.71, 122.50, 122.30, 122.15, 119.06, 93.74, 90.99, 90.84, 89.17, 83.08, 83.00, 54.37; λ_{max} (H_2O) 339 (logε 4.75); *m*/*z* (ES–) 255.7 (M^{2-}, calc. for $C_{28}H_{14}O_6S_2$ requires 255.0).

This reaction was also carried out using **11** (100 mg, 0.15 mmol) and Me_4NCl (500 mg, 4.5 mol) in DMF (13 ml) at 130 °C for 16 h followed by addition of water. Addition of cyclophane chloride **1**·Cl_2 (150 mg, 0.14 mmol) to the aqueous solution of the crude product resulted in a white precipitate, which was filtered off and dried under vacuum to yield **3·1** (197 mg, 86%).

[3]Rotaxane 2⊂1$_2$

A solution of **3**·(NMe$_4$)$_2$ (43 mg, 0.066 mmol) in water (1 ml) was treated with a solution of cyclophane **1**·Cl_2 (71 mg, 0.066 mmol) in water (1 ml). The resulting precipitate was filtered off, suspended in water (20 ml) and then treated with ammonium chloride (6.3 g, 0.12 mol) and copper(I) chloride (4.0 g, 40 mmol). After stirring for 4 days under O_2 the reaction mixture was treated with HCl (100 ml, 2 M aq.). The precipitate was isolated by centrifugation and dried under high vacuum, then dissolved in hot DMSO (130 °C) and passed through a short Sephadex G25 size exclusion column eluting with DMSO. The fluorescent band was evaporated to dryness. The residue was recrystallised twice from DMSO/MeOH to give **2⊂1$_2$** as a pale yellow solid (35 mg, 35%); δ_H (500 MHz, d_6-DMSO) 8.24 (s, 2H), 8.22 (s, 2H), 8.13 (d, ^3J 9 Hz, 2H), 8.11 (d, ^4J 2 Hz, 2H), 8.01 (dd, ^3J 9 Hz, ^4J 2 Hz, 2H), 7.32 (d, ^3J 9 Hz, 4H), 7.10 (d, ^3J 9 Hz, 4H), 6.86 (s, 16H), 6.18 (d, ^3J 9 Hz, 4H), 6.07 (d, ^3J 9 Hz, 4H), 3.72 (s, 48H), 3.43–3.41 (m, 32H), 3.39–3.31 (m, 16H), 2.90–2.83 (m, 16H), 1.54–1.45 (m, 16H), 1.20 (t, ^3J 7 Hz, 24H); δ_C (125.7 MHz, d_6-DMSO) 152.87, 147.31, 146.12, 139.69, 136.01, 131.71, 131.18, 131.14, 130.63, 130.19, 130.03, 128.74, 125.14, 125.03, 124.56, 123.76, 123.04, 121.40, 120.41, 119.81, 118.48, 104.26, 92.74, 91.17, 89.16, 88.42, 81.79, 74.70, 71.11, 55.91,54.56, ‡54.46, ‡52.71,42.22,28.12, ‡27.41, ‡25.01,6.32; λ_{max} (DMSO) 369 (logε5.10); *m*/*z* (ES+, 1 : 1 MeCN/H_2O, Et_2NH) 756.3 (M^{4+}, $C_{172}H_{194}N_4O_{36}S_4$ requires 756.3), 1008.1 (M^{3+}, $C_{172}H_{194}N_4O_{36}S_4$ requires 1008.1), 1511.6 (M^{2+}, $C_{172}H_{194}N_4O_{36}S_4$ requires 1511.6).

‡ The ^{13}C NMR resonances of the CH_2 carbons of the cyclophane piperidine ring of [3]rotaxane **2⊂1$_2$** are both split due to the different environments of the inner and outer rims of the cyclophane. One would also expect this type of splitting with **4⊂1$_2$** but in that case it is not resolved.

Fluorescence spectra and Stern–Volmer titrations

Emission spectra were recorded on a Spex Fluoromax-2 fluorimeter with 5 nm bandwidth slits for both excitation and emission. Fluorescence quantum yields were determined relative to 9,10-diphenylanthracene in cyclohexane (Φ = 0.95). Stern–Volmer titrations were carried out by making up a solution of the [3]rotaxane or dumbbell in DMSO with a concentration of 7.8×10^{-6} M (optical density 1.0 at λ_{max} in a 10 mm path length cell) and adding 15 μl of this solution to 3.00 ml of water in a fluorescence cuvette to give a solution with a concentration of 4.0×10^{-8} M. The intensity of the emission at 414 nm was then monitored as 10 μl aliquots of an aqueous solution of the quencher were titrated into the fluorescence cuvette, with excitation at 370 nm.

Acknowledgements

We thank Dr T. D. W. Claridge for his detailed NMR analysis of the [3]rotaxane **2**⊂**1**$_2$, Dr M. Sirish for preparing cyclophane **1**·Cl_2, Dr M. G. Hutchings (DyStar Ltd., Manchester) for generously providing disodium 1-aminonaphthalene-3,6-disulfonate for preparation of **6**·Na_2 and EPSRC for funding.

References

1 *Electronic Materials: The Oligomer Approach*, ed. K. Müllen and G. Wegner, Wiley-VCH, Chichester, 1998.
2 M. R. Craig, M. G. Hutchings, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2001, **40**, 1071.
3 S. Anderson and H. L. Anderson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1956; S. Anderson, R. T. Aplin, T. D. W. Claridge, T. Goodson, A. C. Maciel, G. Rumbles, J. F. Ryan and H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2383.
4 J. E. H. Buston, J. R. Young and H. L. Anderson, *Chem. Commun.*, 2000, 905.
5 J. E. H. Buston, F. Marken and H. L. Anderson, *Chem. Commun.*, 2001, 1046.
6 C. A. Stanier, S. J. Alderman, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2002, **41**, 1769.
7 C. A. Stanier, M. J. O'Connell, W. Clegg and H. L. Anderson, *Chem. Commun.*, 2001, 493; C. A. Stanier, M. J. O'Connell, W. Clegg and H. L. Anderson, *Chem. Commun.*, 2001, 787.
8 (*a*) P. N. Taylor, M. J. O'Connell, L. A. McNeill, M. J. Hall, R. T. Aplin and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2000, **39**, 3456; (*b*) J. J. Michels, M. J. O'Connell, P. N. Taylor, J. S. Wilson, F. Cacialli and H. L. Anderson, *Chem. Eur. J.*, 2003, **9**, in press.
9 F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorì, J. P. Rabe, M. J. O'Connell, P. N. Taylor and H. L. Anderson, *Nature Mater.*, 2002, **1**, 160.
10 A. J. Parola, F. Pina, E. Ferreira, M. Maestri and V. Balzani, *J. Am. Chem. Soc.*, 1996, **118**, 11610.
11 N. J. Turro, J. D. Bolt, Y. Kuroda and I. Tabushi, *Photochem. Photobiol.*, 1982, **35**, 69.
12 F. Diederich, *Cyclophanes*, Royal Society of Chemistry, Cambridge, 1991; F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 362; S. B. Ferguson, E. M. Seward, F. Diederich, E. M. Sanford, A. Chou, P. Inocencio-Szweda and C. B. Knobler, *J. Org. Chem.*, 1988, **53**, 5593.
13 O. Lavastre, L. Ollivier, P. H. Dixneuf and S. Sibandhit, *Tetrahedron*, 1996, **52**, 5495; O. Mongin, C. Papamicaël, N. Hoyler and A. Gossauer, *J. Org. Chem.*, 1998, **63**, 5568.
14 J. C. Roberts, H. Gao, A. Gopalsamy, A. Kongsjahju and R. J. Patch, *Tetrahedron Lett.*, 1997, **38**, 355.
15 B. Sarkar, U. Das, S. Bhattacharyya and S. K. Bose, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1807; I. R. Politzer, K. T. Crago, T. Hampton, J. Joseph, J. H. Boyer and M. Shah, *Chem. Phys. Lett.*, 1989, **159**, 258; W. R. Bergmark, A. Davis, C. York, A. Macintosh and G. Jones, II, *J. Phys. Chem.*, 1990, **94**, 5020.
16 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd edition, Plenum, New York, 1999.
17 T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201; L. Chen, D. W. McBranch, H.-S. Wang, R. Helgeson, F. Wudl and D. G. Whitten, *Proc. Natl. Accad. Sci. U.S.A.*, 1999, **96**, 12287; H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, *J. Am. Chem. Soc.*, 2003, **125**, 3821.
18 I. Willner and W. E. Ford, *J. Heterocycl. Chem.*, 1983, **20**, 113.
19 J. Wang, D. Wang, E. K. Miller, D. Moses, G. C. Bazan and A. J. Heeger, *Macromolecules*, 2000, **33**, 5153; D. Wang, J. Wang, D. Moses, G. C. Bazan and A. J. Heeger, *Langmuir*, 2001, **17**, 1262; R. M. Jones, T. S. Bergstedt, C. T. Buscher, D. McBranch and D. Whitten, *Langmuir*, 2001, **17**, 2568; C. Fan, T. Hirasa, K. W. Plaxco and A. J. Heeger, *Langmuir*, 2003, **19**, 3554.