An approach to insulated molecular wires: synthesis of water-soluble conjugated rotaxanes

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Hydrophobic self-assembly has been used to direct the synthesis of conjugated [2] and [3]rotaxanes (20 and 21) in aqueous solution, by Glaser coupling a water-soluble alkyne 3 in the presence of a cyclophane 6. No rotaxanes were formed when cyclodextrins were used instead of the cyclophane. NMR and electrospray mass spectrometry were used to probe the binding properties of the stopper unit 3. NMR ring current shifts and NOEs show that the cyclophane 6 binds mainly to the terminal phenylene unit of 3. In solution cyclodextrins bind less strongly than the cyclophane, whereas in the gas-phase cyclodextrins bind more strongly. The water-soluble rotaxanes are fully characterised by electrospray mass spectrometry, NMR and UV–VIS emission/absorption. Both rotaxanes tend to fragment, by unthreading and by dumbbell-cleavage, during electrospray ionisation, particularly at high cone voltages. The insulation of the conjugated dumbbell inside the [3]rotaxane results in increased fluorescence efficiency. Time-resolved fluorescence measurements show that these rotaxanes decompose during photolysis to give products with longer fluorescence lifetimes; the rate of this photodecomposition is slower for the [3]rotaxane than for the naked dumbbell. The extension of this synthetic approach to larger polyrotaxanes was explored by coupling alkyne 3 and diethynylbenzene 2 in the presence of cyclophane 6; this gives some longer [2] and [3]rotaxanes but higher polyrotaxanes are not formed.

Introduction

Organic molecules with long conjugated π systems can be regarded as 'molecular wires'[1] because they have mobile electrons. These conjugated polymers have many potential applications; in non-linear optics, in organic electroluminescent display devices, and as organic semiconductors,[2] but the small HOMO–LUMO energy gaps responsible for their special electronic properties often lead to chemical reactivity and instability, which can limit their usefulness. We are interested in insulating molecular wires from their neighbours and from the external environment.[3] This idea has been explored by others in a variety of ways, for example, molecular wires have been insulated by threading them through zeolite frameworks,[4] and using ligand shells.[5]

Our approach to the insulation of molecular wires is to thread a series of insulating molecular beads onto a conjugated backbone to form a molecular necklace. The addition of large bulky end-groups, or stoppers, to prevent the insulators from unthreading, yields a polyrotaxane.†[6] Others have pursued related methodologies.[8] Our synthetic strategy is outlined in Fig. 1. The three key steps are: 1. *Threading*: The monomer unit which will form the conjugated backbone threads inside the insulating molecular bead, to form a pseudorotaxane.

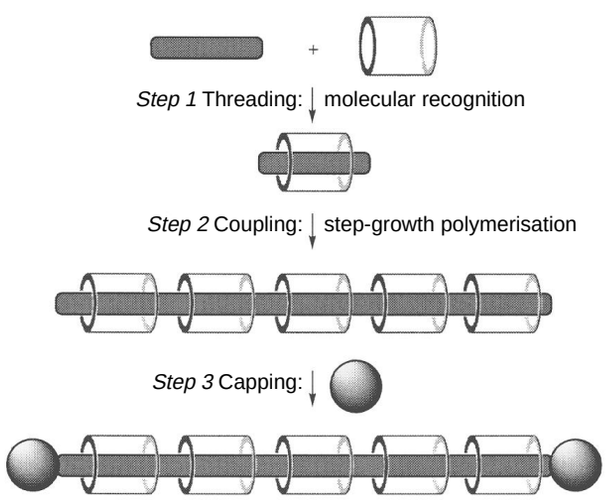


Fig. 1

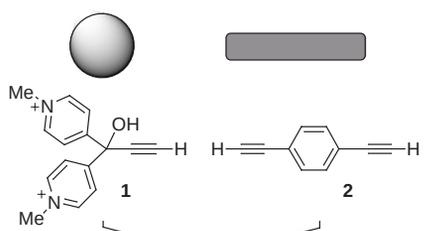
2. *Coupling*: The threaded monomer units are coupled to yield a pseudopolyrotaxane. 3. *Capping*: The insulating beads are prevented from falling off by bulky stopper units, thus forming a polyrotaxane.

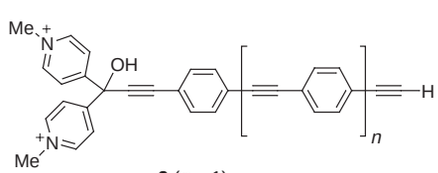
We cannot rely on statistical threading because most insulating macrocycles cannot be used as solvents[6a,b] so molecular recognition and non-covalent binding are needed in the first step. The hydrophobic effect[9] is an appealing way to promote

† Rotaxanes[7a] were first prepared using solid phase synthesis by I. T. Harrison and S. Harrison,[7b] and using directed synthesis by G. Schill and H. Zollenkopf.[7c] Many rotaxanes have been prepared recently,[7d–n] and earlier work has been reviewed.[7e,o,p]

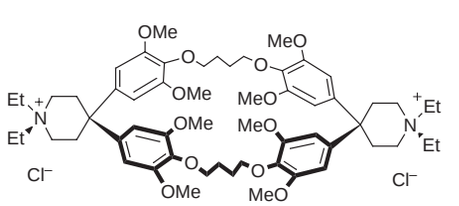
threading because it does not require a special recognition site to be built into the monomer; it will suffice that the monomer is hydrophobic, which is generally true of all the monomers used to make conjugated polymers. The insulating unit needs a hydrophobic interior, to accommodate the guest, and a hydrophilic exterior to render it water-soluble. There are several well documented amphiphilic macrocycles such as cyclophanes[9a–d,10] and the cyclodextrins[11] which bind hydrophobic guests in water. The hydrophobic effect has already been employed to promote rotaxane formation.[7q–y]

If we use the hydrophobic effect to drive threading, then coupling and capping must also be carried out in water. Several reactions can be used to form a conjugated backbone under aqueous conditions; these include Suzuki coupling,[12] Glaser coupling,[13] Heck coupling[14] and azo-coupling.[7y] In this work we have focused on Glaser coupling; the copper mediated oxidative coupling of terminal acetylenes. Glaser coupling can be carried out efficiently in water[13] and has been used to prepare polymers.[15]

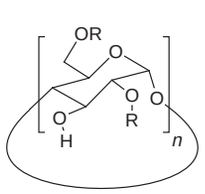




3 (*n* = 1)
4 (*n* = 0)
5 (*n* = 3)



cyclophane **6**



α-CD **7** (R = H, *n* = 6)
β-CD **8** (R = H, *n* = 7)
DM-β-CD **9** (R = Me, *n* = 7)

Scheme 1 Cartoons translated

The molecular components used in this work are introduced in Scheme 1, which translates the cartoons of Fig. 1. The monomer unit is 1,4-diethynylbenzene **2**; hydrophobic, *para*-disubstituted phenylene units of this type are known to bind inside β-cyclodextrin (β-CD, **8**) and 2,6-di-*O*-methyl-β-cyclodextrin[16] (DM-β-CD, **9**) and cyclophane **6** in aqueous solution.[9a,10b] The cyclodextrins are appealing insulating units because of their availability, however cyclophanes such as **6** have greater solubility in water and bind more strongly to hydrophobic guests. We chose to work with **6** because Diederich and co-workers have shown that cyclophanes of this type, with $O(CH_2)_4O$ links, bind benzene derivatives more strongly than those with shorter $O(CH_2)_3O$ links.[9a,10b] The eight methoxy groups result in a high critical micelle concentration[9a] and the diethylammonium groups confer high water-solubility on the chloride salt. The stopper **1** is simply a water-soluble bulky terminal alkyne. Initially, in an attempt to prepare readily characterisable materials, we decided to combine the monomer unit **2** and the bulky stopper **1** to generate stoppers **3**, **4** and **5**, to test whether we could generate rotaxanes with α-, β- and DM-β-CD **7**, **8** and **9** and cyclophane **6**, during a simple one step Glaser coupling.

Conjugated pseudorotaxanes have been reported,[17a,b] including a polymetallorotaxane,[8a] and attempts to form rotaxanes between the conjugated polymer poly para phenylene vinylene (PPV) and crown ethers,[8b] but this is the first example of the synthesis of rotaxanes with conjugated backbones where specific binding sites have not been built into the backbone and rotaxane formation is directed by the hydrophobic effect; some of the work has already been presented in a communication.[7x]

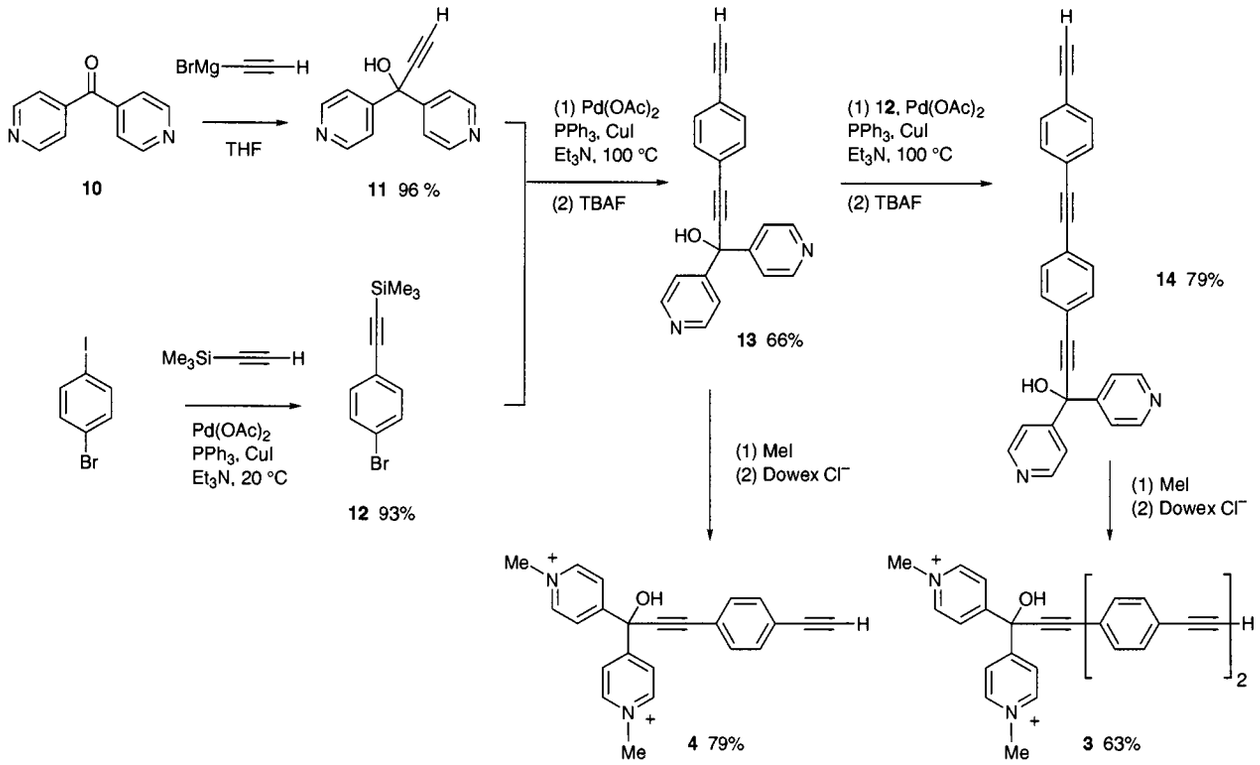
Results and discussion

Synthesis of the stoppers 3 and 4

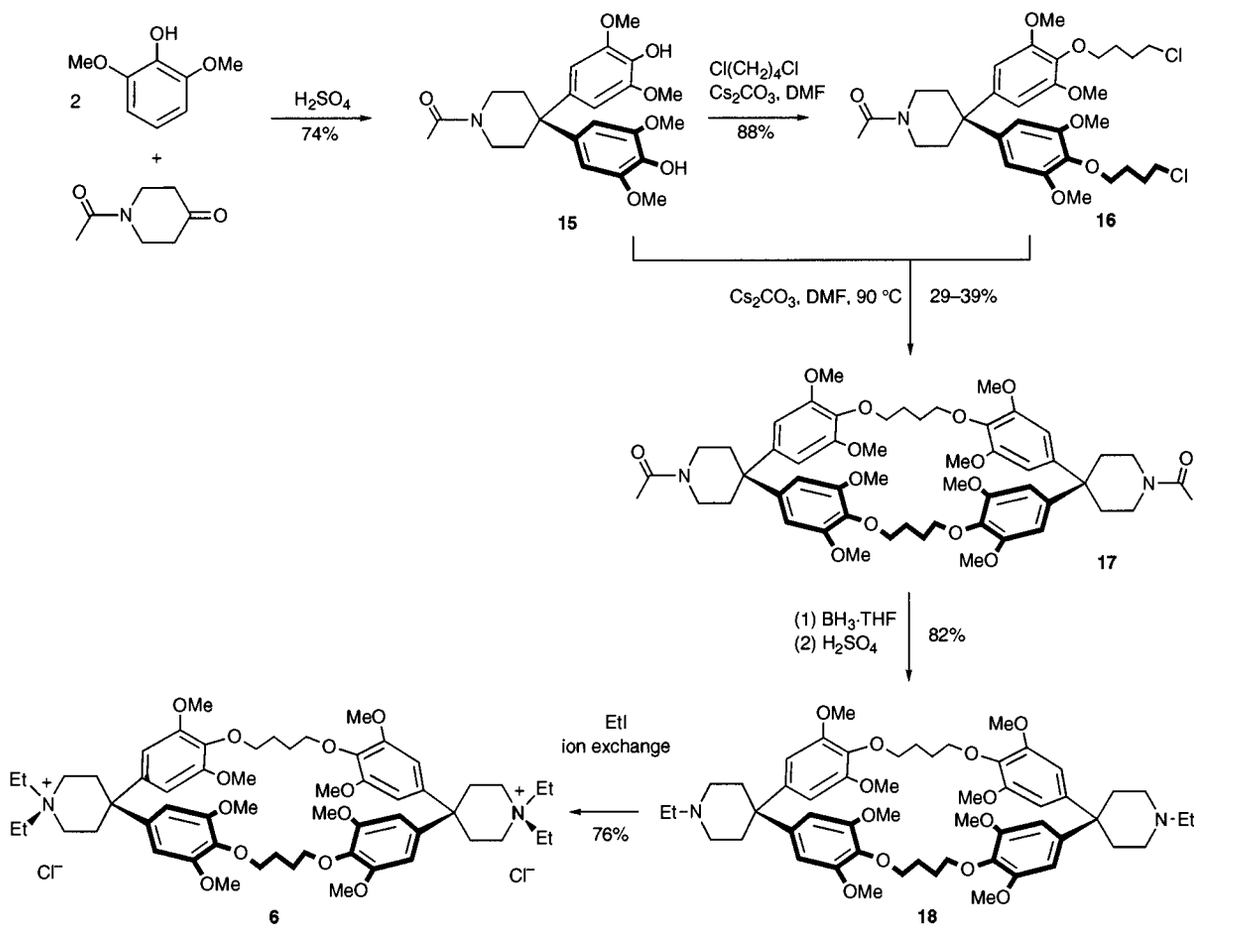
The stopper **3** was synthesised from di-4-pyridylmethanone **10**[18] (Scheme 2) by the addition of ethynylmagnesium bromide and then two successive cycles of Heck–Sonogashira coupling[19] with 1-bromo-4-trimethylsilylethynylbenzene **12**[20] followed by protodesilylation with tetrabutylammonium fluoride (TBAF). **14** was rendered water-soluble by N-methylation of the pyridyl nitrogens using methyl iodide;[18] the iodide anions were then ion exchanged for chloride. A shorter stopper **4**, having only a single phenyleneethynylene unit, was also prepared by methylation of **13**, and a very long stopper **5** was prepared from **14**, by two more cycles of Heck–Sonogashira coupling with 1-bromo-4-trimethylsilylethynylbenzene **12** and protodesilylation, followed by quaternisation and ion exchange.

Synthesis of macrocyclic receptors: cyclophane 6 and DM-β-CD 9

Cyclophane **6** is a slightly modified version of a cyclophane first synthesised by Diederich and co-workers,[9a,10b] and was prepared using chemistry developed by Diederich outlined in Scheme 3.[21] The cleft **15**,[10a] synthesised by the acid promoted condensation of 2,6-dimethoxyphenol and *N*-acetyl-4-piperidone, was alkylated with 1,4-dichlorobutane to yield the dichloride **16**. A 1 : 1 mixture of the dichloride **16** and the bisphenol **15** clefts was then cyclised under dilute conditions to yield 29–39% of the bisamide cyclophane **17**. Rigorous purification of **15** and **16** enabled us to routinely obtain higher yields in this cyclisation than those reported by Diederich.[10b] Recently Diederich and co-workers reported the synthesis of a similar cyclophane where the cyclisation reaction was templated by the addition of *p*-xylene; this resulted in an increase in yield from 20% to 40%.[10c] The amide cyclophane was then reduced to the corresponding amine **18** with borane in THF followed by acid hydrolysis, and finally, quaternisation of the amine **18** was achieved with ethyl iodide in chloroform.[21] The iodide counter anions were exchanged for chloride to yield cyclophane **6** using DOWEX ion exchange resin.



Scheme 2



Scheme 3

Pure α- and β-cyclodextrins (**7** and **8**) are available commercially, whereas commercially available DM-β-CD **9** is a complex mixture of cyclodextrins with varying degrees of methylation. Two procedures have been reported for preparing pure DM-β-CD, from β-CD by methylation, protection, chromatographic separation and deprotection;[16] we prepared pure DM-β-CD by both routes and find that of Takeo most convenient.[16b]

Table 1 Summary of binding constants measured for longer stopper **3** and shorter stopper **4** with several macrocycles. $\Delta\delta_{sat}$ indicates the limiting change in the mean chemical shift of the phenylene protons for **3**, or the mean chemical shift of the phenylene protons furthest away from the N-methylated pyridines for **4**, on binding.

	K/mol^{-1} dm^3 ($\Delta\delta_{sat}$/ppm)	
	[**4**]	[**3**]
Cyclophane **6**	$(1.1 \pm 0.1) \times 10^3$ (1.63)	$(43 \pm 2) \times 10^3$ (1.92)
β-CD **8**	$(2.3 \pm 0.1) \times 10^3$ (0.053)	$(6.5 \pm 0.2) \times 10^3$ (0.062)
α-CD **7**	$(1.3 \pm 0.1) \times 10^3$ (0.240)	$(6.1 \pm 2.4) \times 10^3$ (0.170)
DM-β-CD **9**	$(4.3 \pm 1.0) \times 10^3$ (0.1)	$(27 \pm 8) \times 10^3$ (0.057)
		$(5.3 \pm 0.5) \times 10^3$ (−0.106)

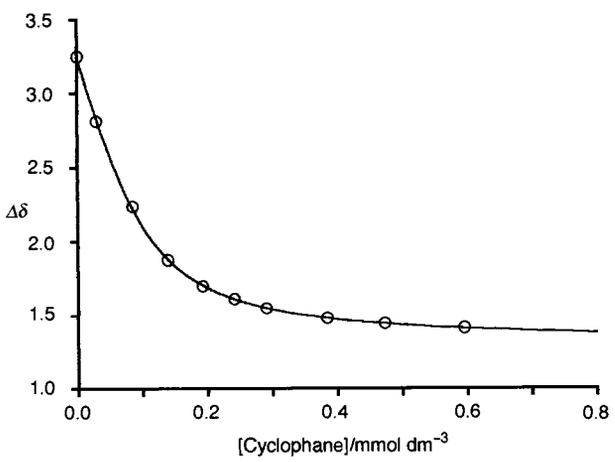


Fig. 2 ^{1}H NMR titration curve for the binding of cyclophane **6** to longer stopper **3**. $\Delta\delta$ is $(\delta_F + \delta_G)/2 - \delta$(pyridinium methyl). The curve represents the calculated isotherm for 1 : 1 binding and the open circles are experimental values.

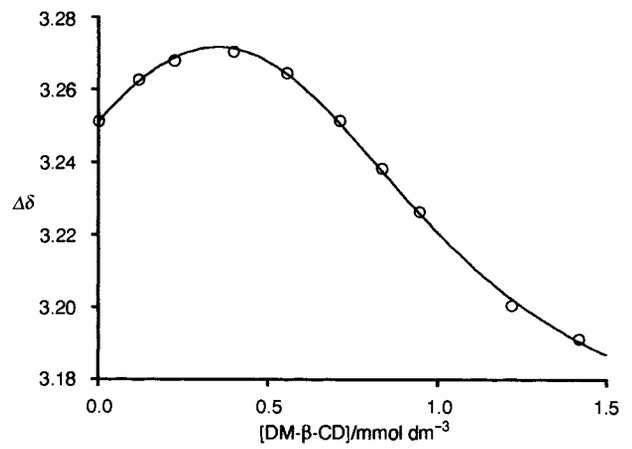


Fig. 3 ^{1}H NMR titration curve for the binding of DM-β-CD **9** to longer stopper **3**. $\Delta\delta$ is $(\delta_F + \delta_G)/2 - \delta$(pyridinium methyl). The curve represents the calculated isotherm for two site binding and the open circles are experimental values.

^{1}H NMR Binding studies

The affinities of stoppers **3** and **4** for the cyclophane **6**, α- and β-cyclodextrins, **7** and **8**, and DM-β-CD **9** were investigated by ^{1}H NMR in D_2O at 298 K. Titrations were carried out at constant stopper concentration (0.8–0.1 mmol dm^{-3}); changes in the chemical shifts of the stopper protons were monitored with respect to increasing macrocycle concentration. All titrations were carried out at least twice. The results are summarised in Table 1. ^{1}H NMR Dilution experiments showed that none of the compounds aggregate significantly in the concentration regime used for these titrations; the critical aggregation concentrations (CAC)[9a] of **3**·Cl_2 and **6**·Cl_2 are 1 mmol dm^{-3} and 2 mmol dm^{-3} respectively. Fig. 2 shows a typical binding curve for cyclophane **6** and longer stopper **3**. All titrations gave simple 1 : 1 curves, except that of the longer stopper **3** and DM-β-CD **9**, which is biphasic (Fig. 3) indicating that up to two DM-β-CD **9** molecules can bind onto the longer stopper **3**. The data fit the calculated curve for two-site binding‡ with $K_1 = 2.7 \times 10^4$ mol^{-1} dm^3 and $K_2 = 5.3 \times 10^3$ mol^{-1} dm^3; the ratio K_1/K_2 is 5.2 which is close to the statistical value of 4, indicating that the sites behave almost independently.

The strongest hydrophobic binding was observed between the cyclophane **6** and longer stopper **3**. This may seem surprising since both species are positively charged: stronger association would be expected between neutral or oppositely charged species, but the cyclophane has a more hydrophobic cavity than the cyclodextrins. Titrations at 298, 323 and 348 K gave a linear van't Hoff plot with ΔH and $(T\Delta S)_{298}$ of 12 kcal mol^{-1} and 6 kcal mol^{-1} respectively, showing that the hydrophobic binding is enthalpically driven as is normal in well defined assemblies of this type.[9a,i] The 1 : 1 stoichiometry of the complex was confirmed by Job plot analysis,[9a,22] as illustrated in Fig. 4. The **3**·$\mathbf{6}_2$ complex is much less stable than the **3**·$\mathbf{9}_2$ complex, whereas the **3**·**6** complex is more stable than the **3**·**9** complex. This reversal in stability order between the 1 : 1 and 2 : 1 complexes is probably due to coulombic repulsion between the positively charged components.

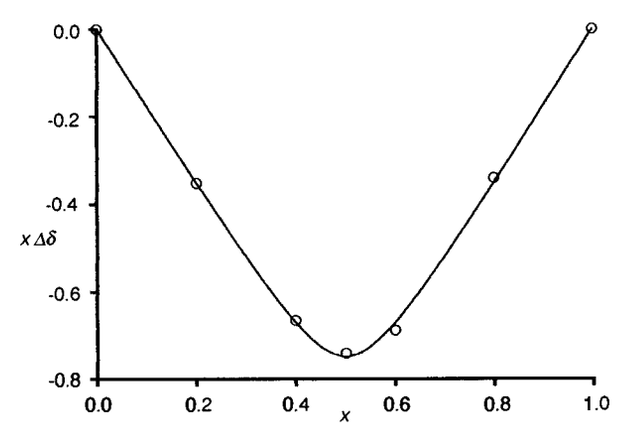
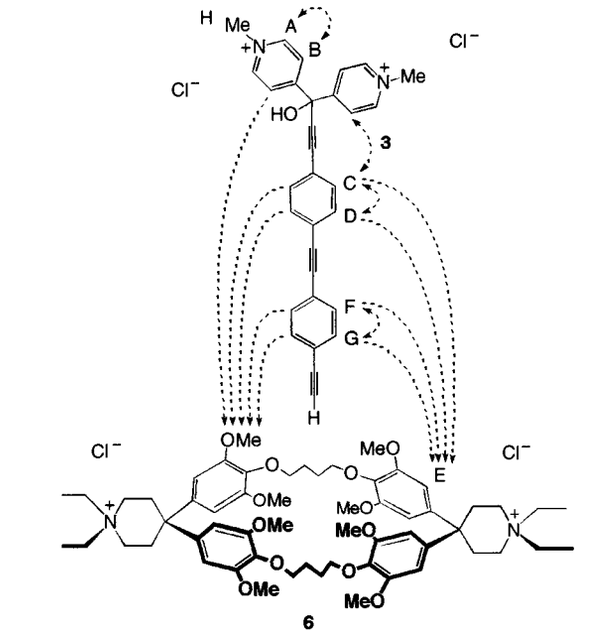


Fig. 4 Job plot for the longer stopper **3** binding cyclophane **6**. $\Delta\delta$ is $(\delta_F + \delta_G)/2 - \delta$(pyridinium methyl). X is the mole-fraction [**3**]/([**3**] + [**6**]); the total concentration ([**3**] + [**6**]) was maintained at 1.0 mmol dm^{-3}. The curve is the calculated 1 : 1 binding isotherm and the open circles are experimental points.

All four macrocycles bind the shorter stopper **4** more weakly than the longer stopper **3** (Table 1) because of its smaller hydrophobic surface; this is particularly marked with cyclophane **6**, presumably because there is only one phenyl ring in **4** on which the cyclophane **6** can reside, forcing the positive

‡ The binding isotherm was analysed by simulation using a Simplex–Newton–Raphson algorithm which solved the following cubic equation $K_1K_2L^3 + (K_1 + 2K_1K_2M_{tot} - K_1K_2L_{tot})L^2 + L(1 + K_1M_{tot} - K_1L_{tot}) - L_{tot} = 0$ where L = [unbound DM-β-CD], M_{tot} = [total longer stopper], L_{tot} = [total DM-β-CD], K_1 and K_2 are the macroscopic binding constants.



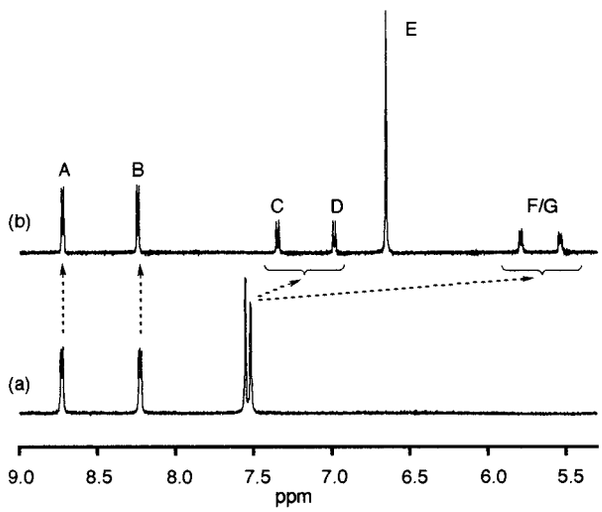


Fig. 5 (a) Shows the ^{1}H NMR spectrum of the aromatic region for longer stopper **3** (2 mmol dm^{-3} in D_2O), (b) shows the ^{1}H NMR spectrum of the aromatic region of a mixture of longer stopper **3** (2 mmol dm^{-3}) and cyclophane **6** (3 mmol dm^{-3}). Significant cyclophane ring-current induced chemical shift changes for the phenylene protons C, D, F and G of the longer stopper **3** are observed.

charges of the stopper **4** and macrocycle into closer proximity. Thus cyclophane **6** binds **4** more weakly than any of the cyclodextrins, whereas it binds **3** most strongly. It is interesting that α-CD **7** binds both stoppers fairly strongly, despite being too narrow to bind directly over a *para*-phenylene unit.

Some structural information about the complexes with cyclophane **6** can be deduced from the ring current induced chemical shift changes that occur as the stopper threads through the cyclophane, see Fig. 5. The stopper phenylene protons are shifted upfield as they experience the ring current from the aromatic rings of the cyclophane. In the case of longer stopper **3**, complexation is accompanied by large upfield shifts in the ^{1}H NMR signals of the aromatic protons of the two phenyl groups ($\Delta\delta_{sat} = 0.13$, 0.49, 1.72 and 2.04 ppm for H_C, H_D, H_F and H_G). These assignments were made using 1D gradient ROESY[23a] experiments on a mixture of **3** and **6** in D_2O (2 mmol dm^{-3} longer stopper and 3 mmol dm^{-3} cyclophane) which revealed the NOEs summarised in Fig. 5. The greater complexation-induced shifts at $H_{F/G}$ suggest that the time averaged position of the cyclophane is nearer the terminal phenylene units, as expected due to charge : charge repulsion,

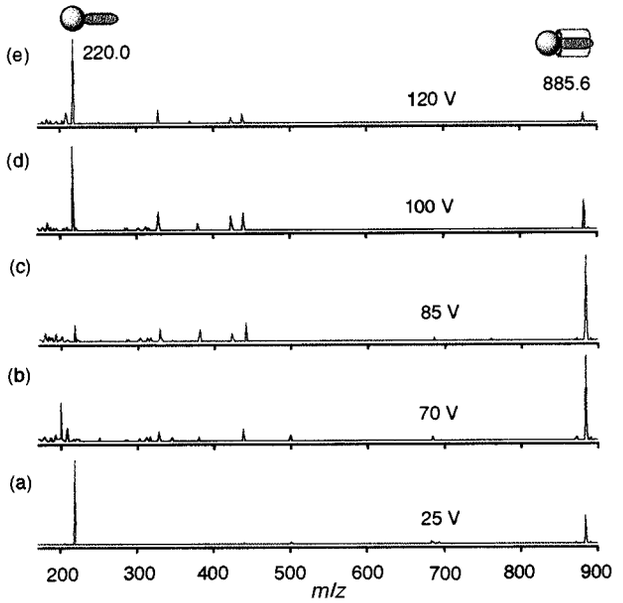


Fig. 6 ESI mass spectra for a 1 : 1 mixture of longer stopper **3** (chloride salt) and DM-β-CD **9**, spraying from water. Cone voltages are indicated above the spectra.

and as implied by the weaker binding constant for **6**. A similar situation is observed in the [3]rotaxane, as discussed later.

Mass spectrometric binding studies on longer stopper 3

Association between the longer stopper **3** and the macrocycles was also investigated in the gas phase, by positive ion electrospray ionisation mass spectrometry (ESI$^+$ MS).[24] Using a 1 : 1 mixture of macrocycle and stopper chloride salt, cyclodextrin complexes were only observed when water was used as the spraying solvent and when the spraying tip was cooled to near room temperature (normally the tip is at *ca.* 50 °C). All three cyclodextrins exhibited peaks due to 1 : 1 complexes with **3**; the adduct peak is most intense with DM-β-CD **9**. The intensities of the adduct peaks diminish as the cone voltage is increased and the spectra of all three cyclodextrin complexes exhibited the evolution with increasing cone voltage illustrated for DM-β-CD in Fig. 6. As the cone voltage was increased above 25 V the intensity of the molecular ion due to free **3** declined relative to that of the complex, a characteristic fragmentation pattern developed, see Fig. 6a, b and c. At cone voltages above 85 V the complex began to decompose and the molecular ion corresponding to free **3** reappeared in the spectrum, see Fig. 6d and e. Formation of the complex appears to protect **3** from fragmentation during electrospray evaporation. Experiments with cyclophane **6** were unable to detect any association in the gas phase; presumably complex formation is inhibited by the charge : charge repulsion, which becomes particularly destabilising when the aqueous environment is stripped away.

Synthesis of rotaxanes

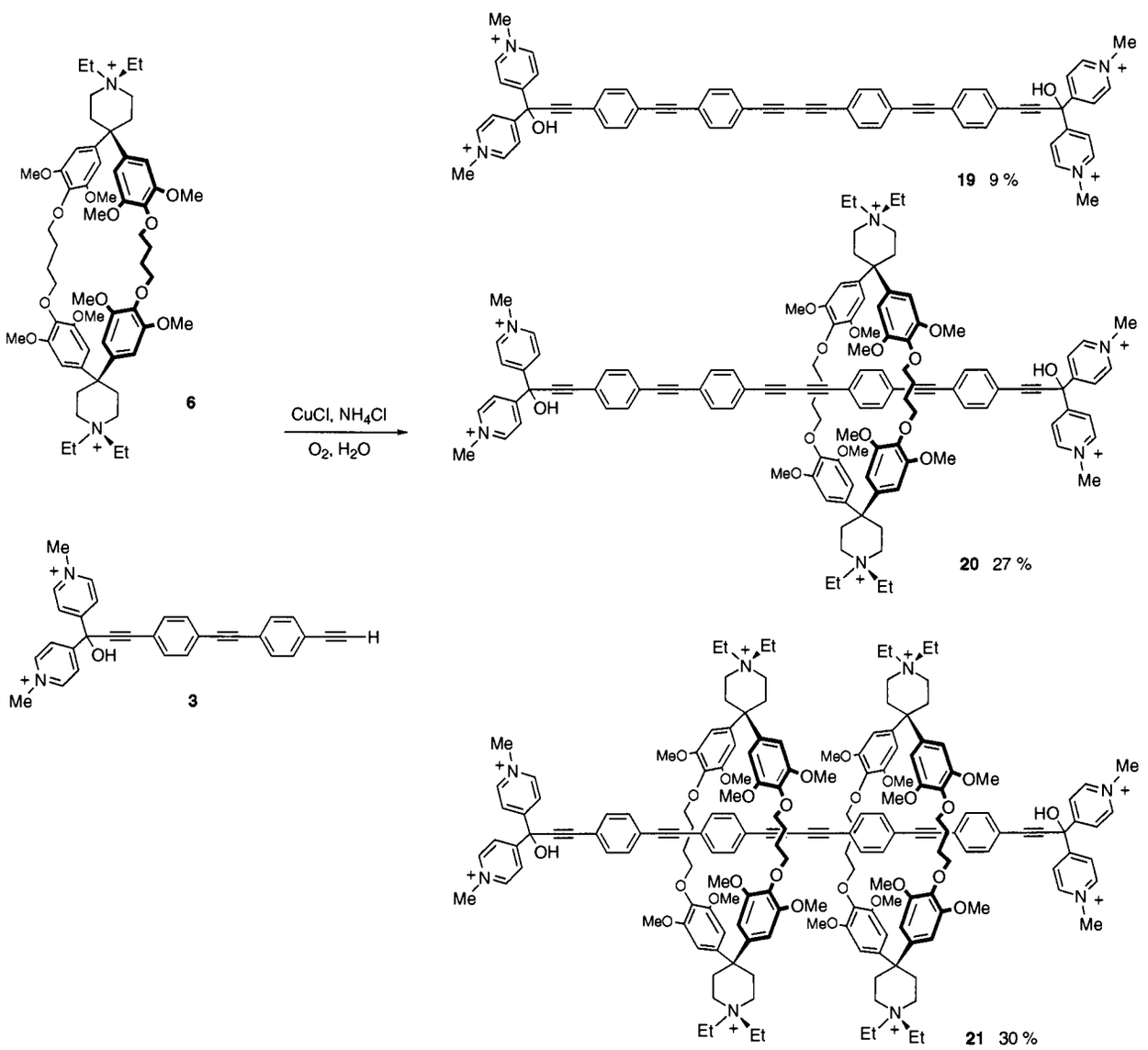
Glaser coupling of the longer stopper **3** was carried out using excess aqueous ammonium chloride (6 mol dm^{-3}) and copper(I) chloride (2 mol dm^{-3}) under an atmosphere of oxygen. These reaction conditions are derived from those of Armitage, Jones and Whiting;[13] these workers used alkyne concentrations of 0.6–0.3 mol dm^{-3}, but we found that the reaction proceeds well at alkyne concentrations of down to 0.003 mol dm^{-3}. The dumbbell **19**, corresponding to dimerisation, was observed by thin layer chromatography of the reaction mixture on silica, eluting with a mixture of methanol, aqueous ammonium chloride (2 mol dm^{-3}) and nitromethane[25] (5 : 3 : 2); **19** runs about twice as slowly as **3** because it has twice the charge. The dumbbell **19** was isolated from the reaction mixture by the addition of hydrochloric acid (2 mol dm^{-3}), which dissolves the

copper(II) hydroxide that forms over the course of the reaction, followed by ammonium hexafluorophosphate to precipitate **19** as its hexafluorophosphate salt. The precipitate was collected *via* filtration, washed with water and recrystallised from methanol–acetone with layered addition of diethyl ether. The shorter stopper **4** also coupled cleanly under these conditions.

The coupling procedure outlined above was carried out with both **3** and **4** in the presence of α, β and DM-β-cyclodextrins (**7**, **8** and **9**) and cyclophane **6**. Rotaxane formation was observed for only one of these eight combinations: that of the longer stopper **3** and cyclophane **6** (Scheme 4). DM-β-CD **9**, which forms the next strongest complex with stopper **3** did not form any rotaxanes. A likely explanation for this is that the cyclodextrin cavity is blocked by complexation of copper cations under the reaction conditions.[26]

The concentrations of cyclophane **6** and longer stopper **3** during coupling were varied as indicated in Table 2. The yields of [3]rotaxane **21**, [2]rotaxane **20** and dumbbell **19** were determined by integration of ^{1}H NMR spectra of crude reaction mixtures. In Fig. 7 the yields are compared for various concentrations of cyclophane for an initial stopper concentration of 12 mmol dm^{-3}. At stopper concentrations of less than 3 mmol dm^{-3} the reaction failed to reach completion after 48 h and no further reaction occurred with longer reaction times. Interestingly the percentage of cyclophane **6** incorporated into rotaxanes was never greater than 56%. This may suggest that the strength of interaction between the cyclophane **6** and the longer stopper **3** is reduced by the presence of the coupling reagent or it may be due to the kinetically slower coupling of the complexed stopper. From the association constant of 4.3×10^4 mol^{-1} dm^3 we would expect 92% of the cyclophane **6** to be bound to longer stopper **3** at the concentration used in run 6 (3 mmol dm^{-3}). Increasing the cyclophane **6** concentration (for example runs 1–3) does not lead to a significant increase in the proportion of cyclophane incorporated; it may be that some of the cyclophane precipitates under the reaction conditions, as the salt of a chlorocuprate anion.

For large scale preparations of the [2] and [3]rotaxanes (**20** and **21**) a 1:1 mixture of cyclophane **6** and longer stopper **3** (both 3 mmol dm^{-3}) was used. These were the most efficient conditions requiring the least cyclophane **6**, even though a slightly higher yield of rotaxanes was achieved when a five-fold excess of cyclophane was used. The pure rotaxanes were isolated by chromatography. Isolated yields of rotaxanes reflected well the yields determined from integration of ^{1}H NMR spectra of the crude reaction mixtures. Yields of dumbbell **19** were lower than expected, presumably because the hexafluorophosphate salt is more soluble in water than the corresponding salts of the rotaxanes so that the two precipitation steps during work-up and purification are less efficient. The chloride salts of the rotaxanes and dumbbell were readily



Scheme 4

prepared by ion exchange chromatography. Both rotaxanes were fully characterised by ^{1}H and ^{13}C NMR, mass spectrometry and elemental analysis.

Electrospray ionisation mass spectrometry of rotaxanes[27]

ESI^{+} MS of the dumbbell **19**, [2]rotaxane **20** and [3]rotaxane **21** were recorded for both chloride salts and hexafluorophosphate salts, using solvent mixtures ranging from pure water to pure acetonitrile, with a range of cone voltages. The molecular ions observed in some of these spectra are summarised in Table 3. All three compounds give the expected polycations, $\mathbf{19}^{4+}$, $\mathbf{20}^{6+}$ and $\mathbf{21}^{8+}$, under at least some conditions, but ion-cluster and fragment peaks are also observed. For example the ESI^{+} mass spectrum of the [3]rotaxane **21** in acetonitrile with 15 V cone voltage, in Fig. 8, exhibits peaks due to $\mathbf{21}^{8+}$, $[\mathbf{21} - H]^{7+}$ and $[\mathbf{21} - 2H]^{6+}$. The assignment of these peaks is confirmed by high resolution spectra, such as that for $\mathbf{21}^{8+}$ in Fig. 9.[28] Deprotonated species, analogous to $[\mathbf{21} - H]^{7+}$ and $[\mathbf{21} - 2H]^{6+}$, are seen to a lesser extent with the [2]rotaxane **20** and they are never observed with the dumbbell **19**, which must reflect the increase in gas-phase acidity of the dumbbell hydroxy groups caused by the electric field from one or two positively charged cyclophanes.

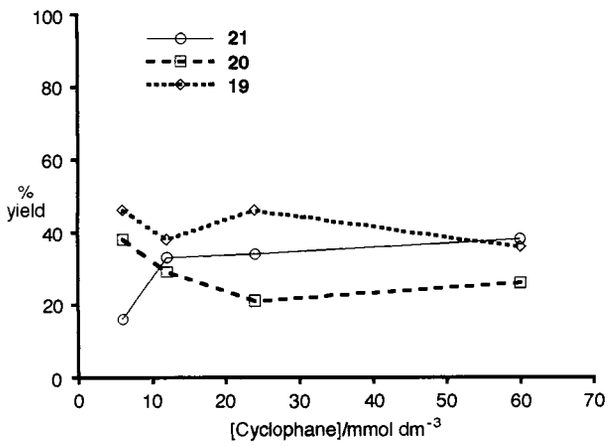


Fig. 7 Comparison of the yields of dumbbell **19**, [2]rotaxane **20** and [3]rotaxane obtained when longer stopper **3** was coupled at various cyclophane **6** concentrations. All experiments were carried out at [**3**] = 12 mmol dm^{-3}.

Both rotaxanes tend to unthread during electrospray ionisation, particularly at higher cone voltages. For example the ESI^{+} MS of the [3]rotaxane **21** in acetonitrile with 30 V cone voltage, exhibits peaks due to the [2]rotaxane $\mathbf{20}^{6+}$ and dumbbell $\mathbf{19}^{4+}$, but these peaks are not observed at 15 V. A strong peak is also seen for cyclophane $\mathbf{6}^{2+}$; this may be produced by dumbbell-cleavage as well as unthreading, because it is observed even at low cone voltage, as in Fig. 8. The [3]rotaxane fragments more readily than the [2]rotaxane, and yet the [2]rotaxane $\mathbf{20}^{6+}$ only appears as minor peaks in spectra of the [3]rotaxane, which also implies that fragmentation occurs by dumbbell-cleavage as well as unthreading. At high cone voltages cyclophane $\mathbf{6}^{2+}$

Table 2 Concentrations of longer stopper **3** and cyclophane **6** used during rotaxane synthesis optimisation. Yields for **19**, **20** and **21** were calculated by integration of the ^{1}H NMR [1:1 CD_3OD:$(CD_3)_2CO$] spectra of crude reaction mixtures.

Run	[**6**]/mmol dm^{-3}	[**3**]/mmol dm^{-3}	Yield **21** (%) [3]rotaxane	Yield **20** (%) [2]rotaxane	Yield **19** (%) dumbbell	**6** incorporated (%)
1	6	12	16	38	46	35
2	12	12	33	29	38	48
3	24	12	34	21	46	45
4	60	12	38	26	36	51
5	120	12		incomplete reaction		
6	3	3	32	39	29	52
7	15	3	40	32	27	56
8	1	1		incomplete reaction		
9	5	1		incomplete reaction		

Table 3 Summary of the data obtained from ESI^{+} MS of **19**, **20** and **21**. CV indicates that these *m/z* values were observed for some of the cone voltages but not all.

Compound	Solvent	**6** cyclophane	**19** dumbbell	**20** [2]rotaxane	**21** [3]rotaxane
19·Cl_4	H_2O	—	M^{4+}	—	—
19·$(PF_6)_4$	H_2O–MeCN (9:1)	—	M^{4+} $[M + PF_6]^{3+}$ $[M + 2PF_6]^{2+}$	—	—
19·$(PF_6)_4$	MeCN	—	M^{4+}	—	—
20·Cl_6	H_2O	M^{2+}	M^{4+}	M^{6+} $[M - H]^{5+}$ $[M - 2H]^{4+}$	—
20·$(PF_6)_6$	H_2O–MeCN (97:3)	M^{2+}	M^{4+}	M^{6+} $[M + PF_6]^{5+}$ $[M + 2PF_6]^{4+}$ $[M + 3PF_6]^{3+}$	—
20·$(PF_6)_6$	MeCN	M^{2+}	M^{4+} (CV ≥ 40 V)	M^{6+} $[M + PF_6]^{5+}$ $[M - H]^{5+}$	—
21·Cl_8	H_2O	M^{2+}	—	—	—
21·$(PF_6)_8$	H_2O–MeCN (97:3)	M^{2+}	M^{4+}	M^{6+}	M^{8+} $[M + PF_6]^{7+}$ $[M + 2PF_6]^{6+}$ $[M + 3PF_6]^{5+}$ $[M + 4PF_6]^{4+}$
21·$(PF_6)_8$	MeCN	M^{2+}	M^{4+} (CV ≥ 20 V)	M^{6+} (CV ≥ 20 V)	M^{8+} $[M - H]^{7+}$ $[M - 2H]^{6+}$

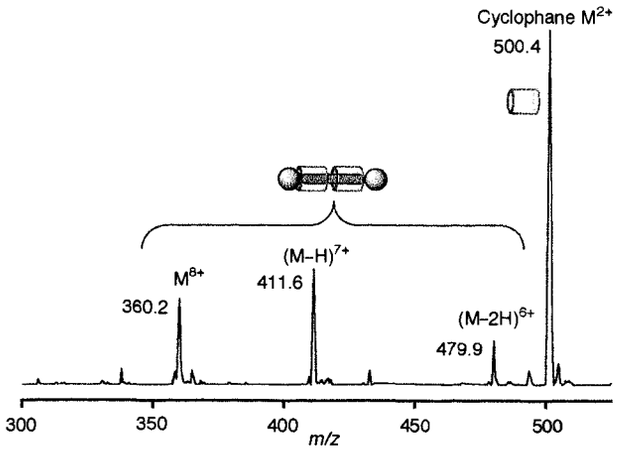


Fig. 8 ESI^+ mass spectrum for [3]rotaxane·$8PF_6^-$ **21** spraying from acetonitrile with 15 V cone voltage

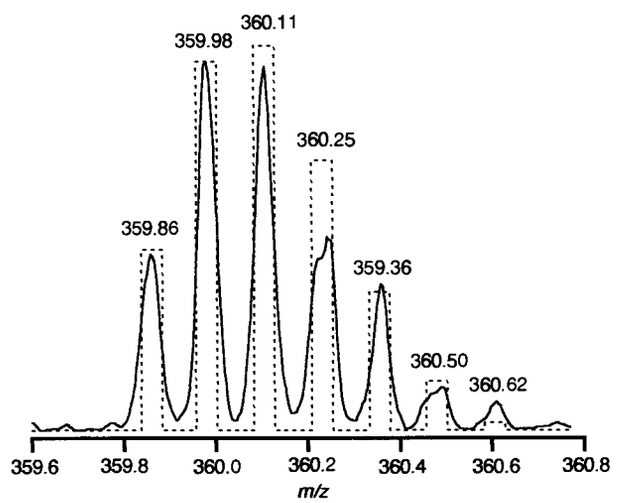


Fig. 9 High resolution ESI MS of the M^{8+} peak for [3]rotaxane **21**. Dashed lines represent the calculated isotope pattern.

becomes the dominant peak, for both rotaxanes under all solvent conditions. Unthreading occurs more readily when spraying from water, or aqueous acetonitrile, than when using pure acetonitrile. Unthreading is not observed in aqueous solution, by ^1H NMR, even up to 100 °C, so its occurrence during electrospray ionisation must be due to the greater repulsion between the cationic components in the gas phase.

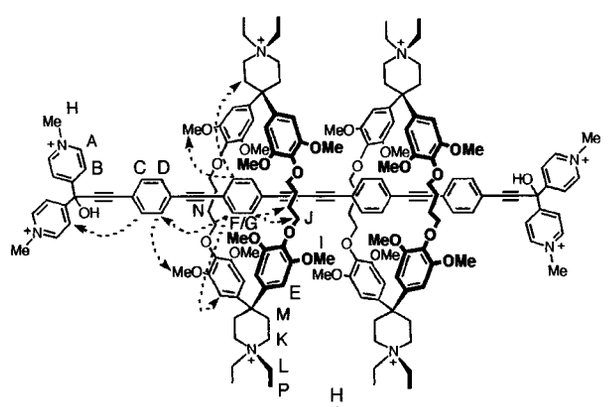
The ESI^+ MS of hexafluorophosphate salts sprayed from 3–10% acetonitrile in water all show ion-cluster patterns. For example the [3]rotaxane **21** gives peaks due to $(\mathbf{21} + n\ PF_6)^{(8-n)+}$, where $n = 0$–4 (these assignments were confirmed by high resolution analysis). This behaviour is not exhibited by the chloride salts and it occurs much less in pure acetonitrile. It can be attributed to the lipophilicity of the PF_6^- anion, which also causes the lower solubility of the hexafluorophosphate salts in water. The formation of ion-clusters appears to suppress formation of deprotonated molecular ions, by reducing the electric field effect of the cyclophanes.

^1H NMR of the rotaxanes

The ^1H NMR spectrum of the [3]rotaxane **21** chloride salt in D_2O was fully assigned by NOESY and COSY experiments. Many NOEs were observed within the dumbbell, within the cyclophane **6** and between the two components (Table 4); some of these are illustrated in Fig. 10. All NOEs were negative except for those from the pyridinium methyl, H_H, and between H_A and H_B which were all positive, indicating that the pyridinium end groups are most mobile; ROESY[23a] spectra

Table 4 NOEs observed for the chloride salt of [3]rotoxane **21** dissolved in D_2O. NOEs marked 'S' were observed during standard 2D NOESY experiments; NOEs marked 'W' were only observed during gradient assisted 1D NOESY experiments.

	A	B	C	D	E	F/G	H	I	J	K	L	M	N	P
A		S					S							
B	S		W											
C		W		S	W			S						
D			S		W	W		S						
E						S		S		S		S		S
F/G				W	S			S	S			W	W	
H	S													
I			S	S	S	S			S	S		S	S	
J						S		S					S	
K					S			S				S		S
L												S		S
M					S			S		S	S			S
N								S	S					
P					S					S	S	S		



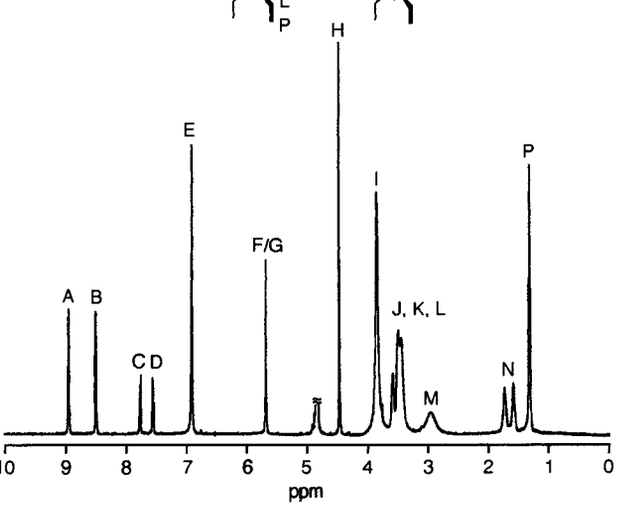


Fig. 10 ^1H NMR spectrum of [3]rotaxane·Cl_8 **21** in D_2O. The dashed arrows represent some of the most diagnostic NOEs. The truncated peak is HOD.

were also recorded but they gave no new information. Weak NOEs (only observed with pulsed field gradient NOESY experiments[23b]) were observed between the β-pyridyl proton H_B and H_C on the dumbbell backbone, and between H_D and $H_{F/G}$; these NOEs unambiguously confirmed that $H_{F/G}$ are the protons at 5.6 ppm. $H_{F/G}$ showed NOEs to many of the cyclophane protons H_E, H_I, H_N, H_J and H_M; both the observation of these NOEs and the large upfield shift of the $H_{F/G}$ resonance ($\Delta\delta = 1.97$ ppm) shows that the cyclophane prefers to reside

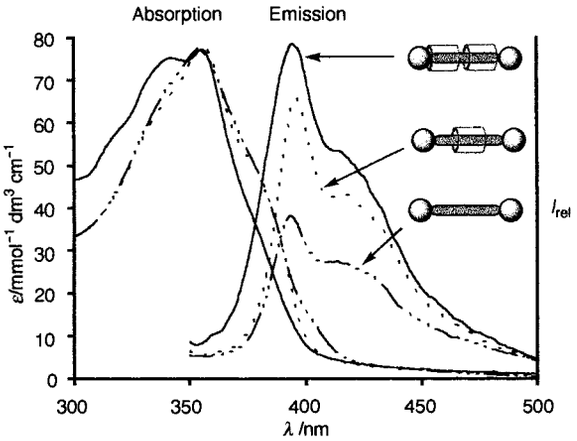


Fig. 11 UV absorption and emission (excitation 300 nm) spectra for dumbbell·Cl_4 **19**, [2]rotaxane·Cl_6 **20** and [3]rotaxane·Cl_8 **21**, in water. All emission spectra were recorded at a concentration of 0.5 μmol dm^{-3}.

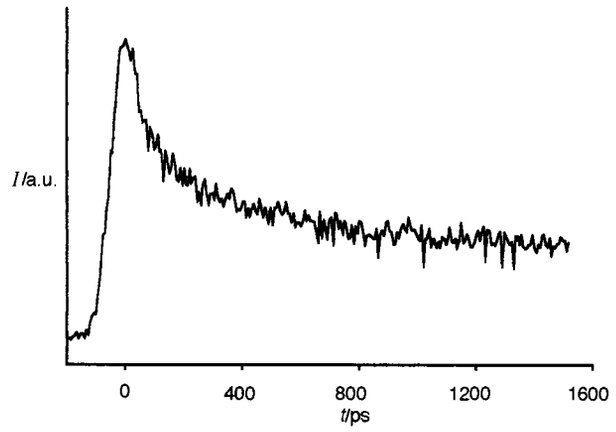


Fig. 12 Emission decay curve for [3]rotaxane·Cl_8 **21** in water at 0.8 μmol dm^{-3} monitoring at 507 nm

on the central phenylene rings, away from the cationic stoppers. The rims of the cyclophane **6** are non-equivalent in the [3]rotaxane **21** so the diastereomeric protons of the methylenes in the $O(CH_2)_4O$ chain, such as H_N, give rise to multiplets. However, the aromatic H_E and the methoxy H_I protons of the cyclophane give rise to singlets at room temperature, showing that the aromatic rings of the cyclophane are rotating fast on the chemical shift time-scale. At 278 K this process is slow and split signals are observed for the resonance H_I. However, in **21**·$(PF_6)_8$ in 1 : 1 CD_3OD : $(CD_3)_2CO$ this cyclophane aryl ring flipping is in fast exchange down to 233 K. ^{1}H NMR spectra of the [2]rotaxane **20** in D_2O show two *para*-phenylene environments and no splitting of the cyclophane signals; broadening occurs on cooling to 278 K but the cyclophane shuttling process along the dumbbell does not enter a slow exchange regime on the ^{1}H NMR time-scale. This behaviour contrasts with that of some of Stoddart's molecular shuttles, which exhibit slow translational isomerism.[25] When CD_3OD is used instead of D_2O for the NMR solvent then fast exchange spectra are observed down to 193 K. In general these cyclophanes are more dynamic in non-aqueous solvents because of diminished hydrophobic binding between the cyclophane and the dumbbell; as in Stoddart's systems, the non-covalent interactions used to direct self-assembly live on in the rotaxane products.

Electronic absorption and emission spectra, and photostability

The absorption and steady-state emission spectra of the dumbbell **19** and [2] and [3]rotaxanes (**20**,**21**) were measured in aqueous solution and are compared in Fig. 11. The absorption spectra in the 300–400 nm region are similar because the cyclophane does not absorb significantly at wavelengths greater than 250 nm. All three compounds show emission at about 400 nm when excited at 300 nm. The quantum efficiencies are as follows: dumbbell **19** 0.19%, [2]rotaxane **20** 0.34% and [3]rotaxane **21** 0.35%. The rotaxanes are about 1.8 times more emissive than the naked dumbbell. This is not surprising because it is known that many cyclodextrin–dye complexes exhibit enhanced fluorescence in aqueous solution.[29] Five-fold fluorescence enhancements are common,[29a–c] and 90-fold enhancements have been reported.[29d]

Preliminary fluorescence measurements[7y] on **19**, **20** and **21** indicated a greater difference in quantum efficiency between the dumbbell and the rotaxanes; when we re-investigated this we found that part of the apparent difference had been due to the lower photostability of the dumbbell.[30] This difference in photostability became obvious during time-resolved fluorescence measurements using an intense laser pulse from a Ti:sapphire laser operating at a repetition rate of 76 MHz at 380 nm (pulse width was 200 fs). The ultrafast time resolved luminescence was measured with a streak camera, giving a temporal resolution of 20 ps.

The natural lifetimes calculated for the dumbbell and rotaxanes, from integrated absorption spectra using the Strickler Berg§[31] equation are all about 5 ns. Therefore, the experimentally measured quantum efficiencies indicate that the fluorescence lifetimes should be about 2 ps, 2 ps and 1 ps for [3]rotaxane **21**, [2]rotaxane **20** and dumbbell **19**. The emission from all three compounds decayed too rapidly to be resolved, in keeping with the predicted lifetimes. However the emissions also exhibit a component which decays on a ns time-scale, as shown on the emission decay curve for [3]rotaxane in Fig. 12. This slow component can be attributed to photochemical decomposition product(s) because it grows at the expense of the rapidly decaying component during irradiation, on a ms time-scale. The slowly decaying component of the emission spectrum also peaks at longer wavelength than that of the pristine compounds. The rate of photodecomposition is faster with dumbbell **19** and [2]rotaxane **20**, than with [3]rotaxane **21**. Time-integrated emission spectra were recorded during irradiation with the Ti:sapphire laser using a CCD camera. They showed decay of the initial emission peak at 400 nm and growth of a new peak at 475 nm which we attribute to photodecomposition product(s). These experiments also showed the faster decay of dumbbell **19** compared with [3]rotaxane **21**, see Figs. 13 and 14. It appears that encapsulation of the conjugated dumbbell inside the cyclophanes, in the [3]rotaxane, reduces the rate of photochemical decomposition. The photophysical behaviour of these systems is currently being investigated in more detail using transient absorption spectroscopy.

Synthesis of longer polyrotaxanes

The incorporation of extra 1,4-diethynylbenzene **2**[20] units into the backbone of the dumbbell was attempted as a step towards the formation of longer sheathed molecular wires. Glaser coupling was carried out on the mixtures of longer stopper **3**, 1,4-diethynylbenzene **2** and cyclophane **6** as outlined in Scheme 5 and Table 5. In each case the longer stopper **3** (3 mmol dm^{-3}) and 1,4-diethynylbenzene **2** (x mmol dm^{-3}) were mixed with cyclophane **6** ($3 + x$ mmol dm^{-3}) in water,

§ We used the approximate form of the Strickler Berg equation for resonant fluorescence, which allows one to estimate the natural life time (τ^0_r) from the peak absorption frequency (ν_{max}), the integrated absorption coefficient ($\mathscr{A} = \int \varepsilon \, d\nu$, where ε is the extinction coefficient, in mol^{-1} dm^3 cm^{-1}, and ν is the frequency in cm^{-1}) and the refractive index of the solvent (n), using the equation $\tau^0_r = 3.471 \times 10^8/(\nu_{max}{}^2 n^2 \mathscr{A}^\circ)$. The ratio of the measured fluorescence lifetime (τ_f) to the natural lifetime (τ^0_r), τ_f/τ^0_r, is the fluorescence quantum yield (Φ_f).

and added to copper(I) chloride and ammonium chloride and stirred at room temperature under oxygen. After 48 h, hydrochloric acid (2 mol dm^{-3}) was added to dissolve the copper(II) hydroxide; some solid material remained which may be polymeric. The organic products were collected by precipitation with ammonium hexafluorophosphate and filtration. The crude reaction mixtures were analysed by ^1H NMR and TLC eluting with aqueous ammonium chloride (2 mol dm^{-3}), methanol and nitromethane (3:5:2); the ^1H NMR spectra were difficult to interpret due to the large number of different species present. TLC showed that all products fell into four main categories: (a) those running closely to unreacted stopper **3**, (b) those close to dumbbell **19**, (c) those close to [2]rotaxane **20** and (d) those close to [3]rotaxane **21**. Since chromatographic mobility under these conditions is dominated by charge, it seems likely that these categories of product correspond to (a) free cyclophane **6** and dicationic stoppers, from incomplete coupling, (b) tetracationic dumbbells, $n = 0$, (c) hexacationic [2]rotaxanes, $n = 1$ and (d) octacationic [3]rotaxanes, $n = 2$ (Scheme 5). No species running more slowly than the [3]rotaxane **21** were observed, suggesting that higher rotaxanes, with $n > 2$, were not formed. ESI^+ MS of the crude reaction mixtures suggested that up to two 1,4-diethynylbenzene units were incorporated into [2] and [3]rotaxanes (**20**, **21**), to give species such as **22–25**. No evidence for [4] or higher rotaxanes was seen in any of the mass spectra using a wide range of conditions.

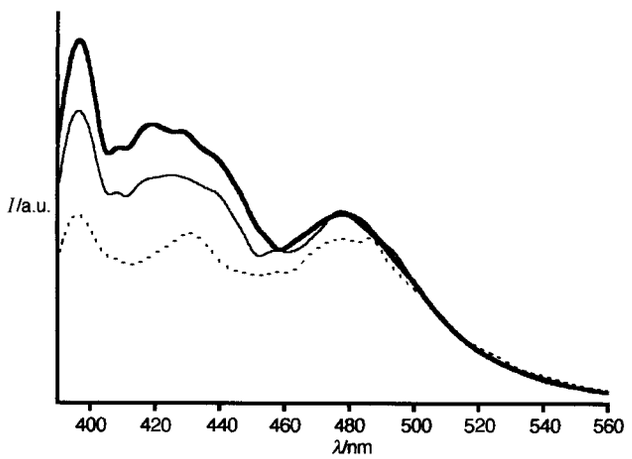


Fig. 13 Emission spectrum of [3]rotaxane·Cl_8 **21** in water at 0.8 μmol dm^{-3} during 75 MHz pulsed laser photolysis after irradiation times of (a) 0.01 s (bold), (b) 0.1 s (plain) and (d) 2 s (dashed)

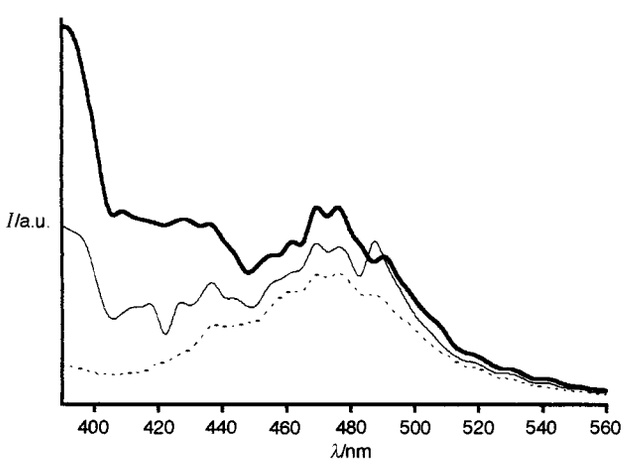


Fig. 14 Emission spectrum of dumbbell·Cl_4 **19** in water 2.2 μmol dm^{-3} during 75 MHz pulsed laser photolysis after irradiation times of (a) 0.01 s (bold), (b) 0.25 s (plain) and (c) 2 s (dashed)

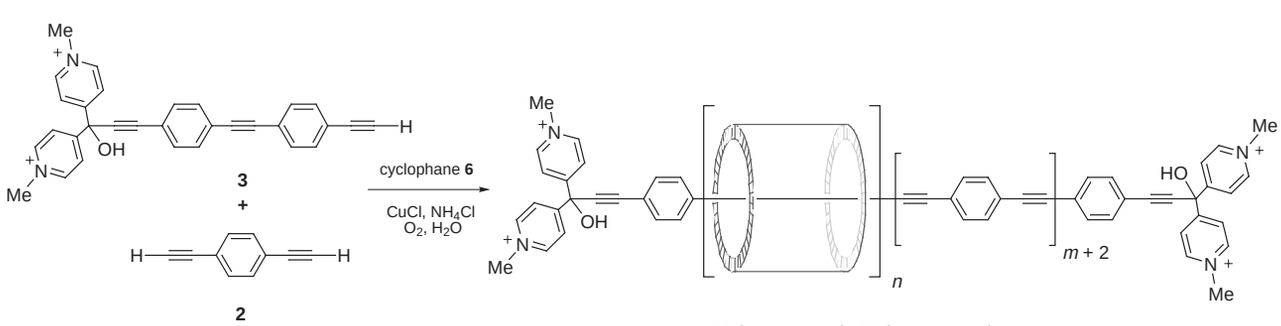
In order to measure the efficiency of incorporation each reaction mixture was chromatographed and the fractions containing material with 8 positive charges analysed by ^1H NMR. [3]Rotaxane with one diethynylbenzene unit incorporated, **24**, proved to be particularly simple to identify. As described earlier the phenylene signals of the [3]rotaxane **21** are shifted upfield by the ring current effects of the cyclophanes and the protons H_F and H_G appear as two doublets at 6.21 and 5.83 ppm when a mixture of $(CD_3)_2CO$ and CD_3OD (1:1) is used as solvent. When a single diethynylbenzene unit has been incorporated into the centre of the [3]rotaxane (to form **24**) then a singlet is added to the shielded pair of doublets and the pattern shown in Fig. 15 is observed. Further incorporation, to give **25**, results in smaller upfield cyclophane induced shifts and hence signals overlap with the cyclophane aromatic region.

The ratio of **24**:**21** (Table 5) reaches a maximum at 19% when the diethynylbenzene:stopper stoichiometry is 1:1; adding more diethynylbenzene **2** reduces the amount of incorporation. The diethynylbenzene **2** may be lost by the formation of oligomers or elongated stoppers which are insoluble under the reaction conditions. This interpretation is supported by the fact that **30** (prepared as in Scheme 6), the 'dimer' of diethynylbenzene,[32] does not dissolve in D_2O in the presence of cyclophane, even on prolonged heating, sonication and stirring; if **30** is formed inside one or two cyclophanes **6**, in aqueous solution, precipitation will be thermodynamically favourable. Unfortunately Glaser coupling is fairly slow, so that **30** will precipitate before further coupling.

The chloride salt of the very long stopper **5** is only slightly water-soluble even in the presence of cyclophane **6** and no reaction was observed when this mixture was submitted to Glaser coupling conditions for 48 h, which may also explain

Table 5 Incorporation of 1,4-diethynylbenzene **2** into [3]rotaxanes. The concentration of longer stopper **3** was 3 mmol dm^{-3} in all coupling reactions.

Run	[**2**]/mmol dm^{-3}	Product ratio **24**/**21**
1	1.5	0.12
2	3	0.19
3	6	0.18
4	9	0.12



22 ($n = 1$, $m = 1$) **23** ($n = 1$, $m = 2$)
24 ($n = 2$, $m = 1$) **25** ($n = 2$, $m = 2$)

Scheme 5

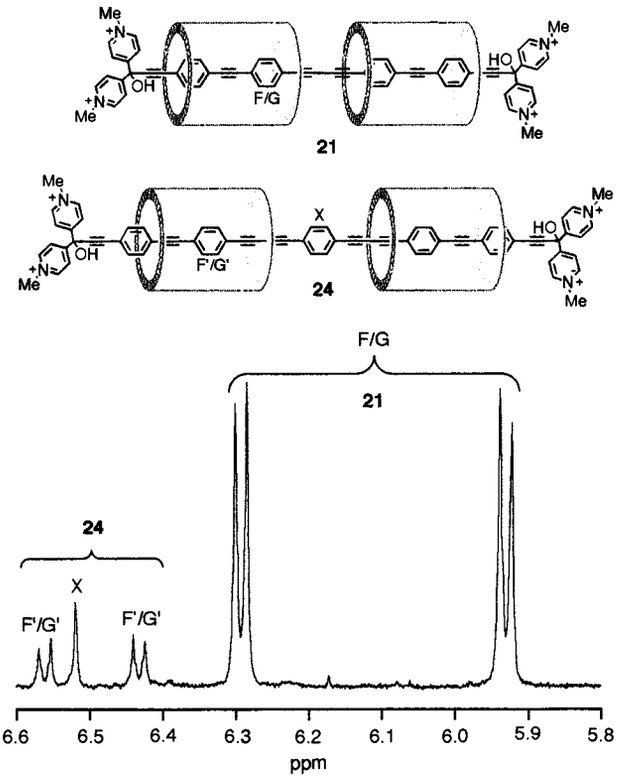
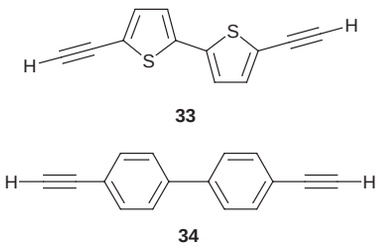


Fig. 15 Part of the ^{1}H NMR spectrum of the [3]rotaxanes fraction from the incorporation experiment using 3 mmol dm^{-3} longer stopper **3** and 3 mmol dm^{-3} diethynyl benzene (entry 2, Table 5). F′/G′ and X are from **24** and F/G from **21**.

why no higher rotaxanes with $n > 2$ were observed in the incorporation reactions (Scheme 5). When one diethynylbenzene unit couples to **3**, it may still be too short to thread onto more than one cyclophane, whereas when two diethynylbenzene units couple to **3**, it probably becomes too insoluble or too strongly aggregated to undergo aqueous Glaser coupling, even in the presence of cyclophane.

We also tested some other diethynyl monomer units, **33**,[15b] **34**[20] and **32**,[33] to see whether any of them would have greater

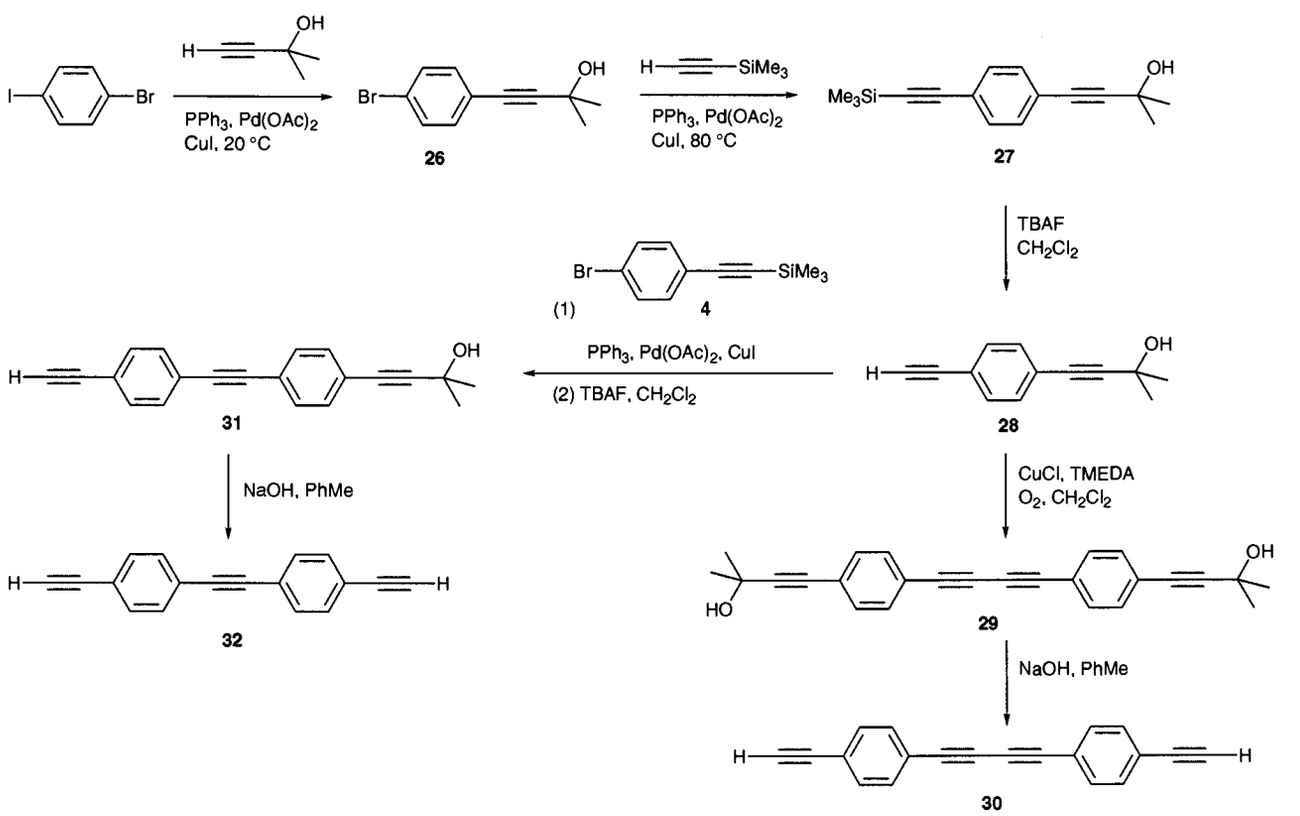


solubility in water in the presence of cyclophane. Only **33** was found to be partially extracted (0.25 equivalents) into D_2O in the presence of one equivalent of cyclophane **6**. An incorporation experiment with **33** was attempted using 3 mmol dm^{-3} longer stopper **3**, 6 mmol dm^{-3} **33** and 9 mmol dm^{-3} cyclophane. ^{1}H NMR and TLC indicated that little or no incorporation had taken place. Once again solubility in water is likely to be the main reason why this incorporation strategy failed.

Conclusions

We have explored the scope and limitations of the approach to insulated molecular wires shown in Fig. 1 using the molecular components of Scheme 1. This is a viable approach to short lengths of 'encapsulated molecular wire', but the slow kinetics of aqueous Glaser coupling and the insolubility of oligomers of 1,4-diethynylbenzene prevent formation of longer polyrotaxanes. In order to extend this approach to prepare longer conjugated polyrotaxanes, it will be necessary to use a faster coupling reaction, or to slow down the rate of unthreading.

We have compared the four different amphiphilic macrocycles, in Scheme 1, as potential insulating units. The



Scheme 6

Diederich-type cyclophane **6** is the only macrocycle which gave successful rotaxane formation, which is probably due to its superior binding properties, and because the cyclodextrins form copper complexes which hinder threading; this is a problem with the Glaser coupling reaction conditions. The charge on the cyclophane gives it excellent water-solubility, but electrostatic repulsion between cationic cyclophanes must mitigate against the formation of polyrotaxanes, as shown by the fact that DM-β-CD, **9**, forms a 2:1 complex with the long stopper **3**, whereas the cyclophane, **6**, only forms a 1:1 complex. The use of neutral or anionic stopper units would probably have given us a more efficient synthesis of a [3]rotaxane, but this would not advance us towards the goal of making long insulated molecular wires.

Most of the compounds prepared during this work are polycationic, which has enabled us to make extensive use of electrospray ionisation mass spectrometry for testing thermodynamic and kinetic stability in the gas phase. There are many correlations between gas-phase and solution-phase behaviour, for example DM-β-CD, **9**, forms more stable complexes than β-CD, **8**, in both regimes, however electrostatic effects are of course much more dominant in the gas-phase. Both the ESI^+ MS cone-voltage experiments on the **3·9** complex and the pulsed photolysis experiments on **19**, **20** and **21**, in water, provide evidence for encapsulation enhanced stability. Our primary motivation for pursuing the synthesis of insulated molecular wires is their promise of enhanced stability.

Experimental

All chromatography was carried out using Merck Kieselgel 60 μm. Light petroleum refers to the fraction boiling in the range 60–80 °C. α- and β-Cyclodextrins were purchased from Lancaster Synthesis and used without further purification. Deuterochloroform was deacidified before use by standing over anhydrous potassium carbonate for 24 h. Triethylamine, dichloromethane and ethyl iodide were freshly distilled from calcium hydride. THF was distilled from sodium wire and benzophenone. Dimethylformamide was left to stand over barium oxide for 24 h, decanted and then distilled. Nuclear magnetic resonance spectra were recorded on Bruker AM-500, AMX-500 or WH-300, or Varian Gemini 200. *J* Values are given in Hz. Low resolution electrospray ionisation mass spectrometry (ESI MS) was carried out on a Micromass BioQ II atmospheric pressure triple quadrupole spectrometer. High resolution and accurate mass, mass spectra were measured on a Micromass Autospec OA TOF mass spectrometer. The hexafluorophosphate salts (2–5 pmol μl^{-1}) were analysed from acetonitrile and a water:acetonitrile mixture (3–10% MeCN). The chlorides were analysed from aqueous solutions (2–5 pmol μl^{-1}). UV–VIS absorption spectra were recorded using a Perkin-Elmer Lambda 20 instrument. Microanalyses were carried out in the Dyson Perrins Laboratory.

1,1-Di-4-pyridylprop-2-yn-1-ol 11

Ethynylmagnesium bromide (0.5 mol dm^{-3} in THF, 20 cm^3, 10 mmol) was added to di-4-pyridylmethanone **10**[18] (1.8 g, 10 mmol) in THF (100 cm^3) and stirred overnight. The mixture was poured into aqueous ammonium chloride (2 mol dm^{-3}) and the product extracted with chloroform. The pale brown solid was recrystallised from chloroform:methanol (1:1) by layered addition of light petroleum to yield **11** (1.97 g, 96%) as a cream coloured solid (Found: C, 74.1; H, 4.7; N, 13.3. $C_{13}H_{10}N_2O$ requires C, 74.3; H, 4.8; N, 13.3%); δ_H(300 MHz; CD_3OD) 3.51 (1 H, s, C≡C–H), 7.69 (4 H, d, *J* 6.2, β-pyridyl), 8.51 (4 H, d, *J* 6.2, α-pyridyl); *m/z* [ESI^+ MS; MeCN, H_2O (1:1), 1% HCO_2H] 211 (MH^+).

1,1-Di-4-pyridyl-3-(4-ethynylphenyl)prop-2-yn-1-ol 13

1,1-Di-4-pyridylprop-2-yn-1-ol **11** (1.0 g, 4.76 mmol), 1-bromo-4-trimethylsilylethynylbenzene **12**[17] (1.2 g, 4.76 mmol), palladium(II) acetate (21.3 mg, 0.10 mmol), triphenylphosphine (49.9 mg, 0.19 mmol) and copper(I) iodide (5.2 mg, 0.047 mmol) were dissolved in triethylamine (60 cm^3) and the mixture heated to reflux for 4 h. When no starting material was observed by TLC the reaction mixture was poured into water and extracted with chloroform. The resulting pale brown solid was dissolved in a minimum of dichloromethane and treated with TBAF (0.5 cm^3, 5.0 mmol, 1.0 mol dm^{-3} solution in THF); after 10 min the mixture was poured onto a silica column (CH_2Cl_2) and the product eluted with dichloromethane containing 2% methanol. Recrystallisation from dichloromethane:methanol (19:1) by layered addition of light petroleum yielded **13** (1.27 g, 86%) as a pale yellow solid (Found: C, 81.3, H, 4.4; N, 9.0. $C_{21}H_{14}N_2O$ requires C, 81.3; H, 4.6; N, 9.0%); δ_H(200 MHz, $CDCl_3$) 3.22 (1 H, s, C≡C–H), 6.0 (1 H, br s, OH), 7.44 (4 H, ABq, *J* 8.4, phenylene), 7.57 (4 H, d, *J* 6.4, β-pyridyl), 8.54 (4 H, d, *J* 6.4, α-pyridyl); *m/z* [ESI^+ MS; MeCN:H_2O (1:1), 0.2% HCO_2H] 311 (MH^+).

1,1′-Dimethyl-4,4′-[3-(4-ethynylphenyl)-1-hydroxyprop-2-ynylidene]dipyridinium dichloride 4

A solution of methyl iodide (12 cm^3, 0.19 mol) in butan-2-one (12 cm^3) was added dropwise to a refluxing solution of **13** (600 mg, 1.93 mmol) in butan-2-one (60 cm^3). The mixture was left at reflux for 6 h and then to stand overnight. The dark green oil which had formed was separated from the butan-2-one by decantation. The iodide ions were then exchanged for chloride by ion exchange chromatography (DOWEX 1X8 400Cl eluting with 1:1 methanol:water) to yield **4** (500 mg, 79%) as a green glassy solid; δ_H(500 MHz, D_2O) 3.59 (1 H, s, C≡C–H), 4.33 (6 H, s, N^+-Me), 7.54 (4 H, ABq, *J* 8.4, phenylene), 8.34 (4 H, d, *J* 6.8, β-pyridinium), 8.80 (4 H, d, *J* 6.8, α-pyridinium); δ_C(125 MHz, D_2O) 47.9, 71.9, 80.5, 82.8, 86.4, 90.3, 120.4, 123.1, 125.0, 131.8, 132.1, 146.0, 159.1; *m/z* [ESI^+ MS; MeCN:H_2O (1:1)] 170 (M^{2+}).

1,1-Di-4-pyridyl-3-{4-[(4-ethynylphenyl)ethynyl]phenyl}prop-2-yn-1-ol 14

Compound **13** (800 mg, 2.58 mmol), 1-bromo-4-trimethylsilylethynylbenzene **12** (653 mg, 2.58 mmol), palladium(II) acetate (11.6 mg, 2.0 mol%), triphenylphosphine (27 mg, 4.0 mol%), copper(I) iodide (2.8 mg, 1.0 mol%) and triethylamine (60 cm^3) were refluxed for 4 h. The mixture was then poured into water and extracted with chloroform. The resulting yellow foam was dissolved in dichloromethane and treated with TBAF (1.0 cm^3, 1.0 mol dm^{-3} solution in THF). The reaction was left to stir at room temperature for 1 h and then poured onto a silica column (CH_2Cl_2) and the product eluted with chloroform containing 5% methanol. Recrystallisation was carried out from chloroform:methanol (19:1) by layered addition of light petroleum to yield **14** (833 mg, 79%) as a pale yellow solid (Found: C, 85.1; H, 4.1; N, 6.6. $C_{29}H_{18}N_2O$ requires C, 84.9; H, 4.4; N, 6.8%); δ_H(300 MHz; $CDCl_3$) 3.20 (1 H, s, C≡C–H), 3.36 (1 H, br s, OH), 7.49–7.54 (4 H, m, phenylene), 7.58 (4 H, d, *J* 6.1, β-pyridyl), 8.64 (4 H, d, *J* 6.1, α-pyridyl); *m/z* (ESI^+ MS; MeCN) 411 (MH^+).

1,1′-Dimethyl-4,4′-(3-{4-[(4-ethynylphenyl)ethynyl]phenyl}-1-hydroxyprop-2-ynylidene)dipyridinium dichloride 3

A solution of methyl iodide (21.2 cm^3, 0.34 mol) in butan-2-one (100 cm^3) was added dropwise to a refluxing solution of **14** (1.4 g, 3.41 mmol) in butan-2-one (200 cm^3). The mixture was left at reflux for 6 h and stirred overnight. The precipitate was collected and dissolved in water:methanol (1:1) and passed through an ion exchange column (DOWEX 1X8 400Cl). Recrystallisation from methanol by layered addition of diethyl ether yielded the longer stopper **3** dichloride salt (1.1 g, 63%) as a pale brown solid (Found: C, 68.7; H, 4.8; N, 5.2. $C_{31}H_{24}N_2OCl_2 \cdot 1.7H_2O$ requires C, 68.7; H, 4.8; N, 5.2%);

δ_H(300 MHz; D_2O) 3.49 (1 H, s, C≡C–H), 4.24 (6 H, s, H_H), 7.42 (4 H, m, H_F and H_G), 7.48 (4 H, m, H_C and H_D), 8.25 (4 H, d, *J* 6.3, H_B), 8.71 (4 H, d, *J* 6.3, H_A); δ_C(50 MHz; D_2O) 47.9, 71.9, 81.1, 83.0, 87.3, 89.9, 90.7, 91.1, 120.3, 121.7, 122.5, 123.6, 125.2, 131.4, 131.6, 131.9, 132.1, 146.2, 159.1; *m*/*z* (ESI^+ MS; MeCN) 220 (M^{2+}).

1,1″-Diacetyl-8′,12′,16′,18′,27′,31′,35′,37′-octamethoxydispiro-[piperidine-4,13′-1,6,20,25]tetraoxa[6.1.6.1]paracyclophane-32′,4″-piperidine} 17[10b]

Compound **15**[10a] (5.64 g, 13.1 mmol, recrystallised from chloroform light petroleum) and caesium carbonate (22.0 g, 67.5 mmol) were dried at 0.01 mmHg for 1 h. Compound **16**[10b] (7.99 g, 13.1 mmol, previously dried at 0.01 mmHg and 60 °C for 12 h) and DMF (650 ml) were added. The mixture was saturated with nitrogen, and heated to 90 °C for 6 days. The caesium carbonate was removed by filtration through Celite and the DMF by distillation (0.01 mmHg, 45 °C). The resulting yellow oil was dissolved in CH_2Cl_2, washed with HCl aq (10%, 200 cm^3) and dried over magnesium sulfate. The cyclophane was purified by flash column chromatography eluting with CH_2Cl_2. The polarity was gradually increased by the addition of methanol (up to 3%). The cyclophane **17** was then crystallised from dichloromethane by layered addition of diethyl ether to yield a white solid, 4.0 g, 32%, characterisation data as literature.[10b]

8′,12′,16′,18′,27′,31′,35′,37′-Octamethoxy-1,1,1″,1″-tetraethyldispiro{piperidinium-4,13′-[1,6,20,25]tetraoxa[6.1.6.1]paracyclophane-32′,4″-piperidinium} dichloride 6

A solution of **17** (3.00 g, 3.09 mmol) in THF (15 cm^3) was treated with borane–tetrahydrofuran complex (46.4 cm^3, 1.0 mol dm^{-3} in THF, 46 mmol). The mixture was refluxed overnight. Excess borane was quenched with methanol and the solvent removed *in vacuo* before dissolving the residue in ethanol (150 cm^3) and concentrated sulfuric acid (4.5 cm^3); the mixture was refluxed until all the solid had dissolved (24 h). The acid was then neutralised with aqueous sodium hydroxide (1 mol dm^{-3}) and the ethanol removed *in vacuo*. The remaining solid was partitioned between chloroform and aqueous sodium hydroxide and the aqueous layer extracted with chloroform. The solvent was removed and the oil dried at 0.01 mmHg. This material (**18**; 2.4 g, 2.5 mmol; 82%) was used directly in the quaternisation step: it was dissolved in chloroform (360 cm^3, dried and deacidified by standing over sodium carbonate overnight) and treated with anhydrous ethyl iodide (100 cm^3, 1.3 mol) under nitrogen at room temperature in the dark. The progress of the reaction was monitored by TLC and after 3 days no starting material amine remained and a white precipitate had formed. The precipitate was collected *via* filtration and dried *in vacuo*. The iodide salt was dissolved in water : methanol (1 : 1) and passed through the ion exchange column (DOWEX 1X8 400Cl). Recrystallisation was carried out from methanol by layered addition of diethyl ether yielding the chloride salt **6** (2.1 g, 76%) as a white solid (Found: C, 64.4; H, 8.4; N, 2.6. $C_{58}H_{84}N_2O_{12}Cl_2{\cdot}0.5H_2O$ requires C, 64.4; H, 7.9; N, 2.6%); δ_H(300 MHz; D_2O) 1.08 (12 H, t, *J* 7, H_P), 1.46 (8 H, m, H_N), 2.59 (8 H, m, H_M), 3.21 (16 H, m, H_L and H_K), 3.49 (24 H, s, H_I), 3.73 (8 H, M, H_J), 6.47 (8 H, s, H_E); δ_C(125 MHz, D_2O) 6.9, 25.6, 29.1, 44.0, 54.0, 55.7, 56.5, 73.0, 104.4, 134.6, 141.6, 153.6; *m*/*z* [ESI^+ MS; MeCN : H_2O (1 : 1)] 500.7 (M^{2+}).

6·$(PF_6)_2$

The hexafluorophosphate salt of **6** was prepared in quantitative yield by the addition of aqueous ammonium hexafluorophosphate (0.5 mol dm^{-3}) to the cyclophane chloride salt dissolved in a minimum volume of water. A thick precipitate formed which was collected by filtration and washed with water. δ_H[500 MHz; 1 : 1 CD_3OD : $(CD_3)_2CO$] 1.30 (12 H, t, *J* 7, H_P), 1.75 (8 H, m, H_N), 2.80 (8 H, m, H_M), 3.50 (16 H, m, H_L and H_K), 3.68 (24 H, s, H_I), 3.86 (8 H, m, H_J), 6.64 (8 H, s, H_E); *m*/*z* (ESI^+ MS; MeCN) 500.5 (M^{2+}).

Preparation of dumbbell 19, [2]rotaxane 20 and [3]rotaxane 21.

A solution of **6**·Cl_2 (210 mg, 0.196 mmol) and **3**·Cl_2 (100 mg, 0.196 mmol) in water (15 cm^3) was added to a solution of copper(I) chloride (12.9 g, 0.13 mol) and ammonium chloride (20.9 g, 0.39 mol) in water (50 cm^3) and the mixture was stirred under oxygen for 48 h.[13] The reaction was quenched by the addition of hydrochloric acid (50 cm^3, 2 mol dm^{-3}). NH_4PF_6 was added to the resulting green solution until no further precipitation occurred and the solid product was collected by centrifugation. The crude product mixture was analysed at this stage by ^1H NMR in 1 : 1 CD_3OD : $(CD_3)_2CO$. The three components were separated by flash column chromatography on silica eluting with methanol : aqueous ammonium chloride (2 mol dm^{-3}) : nitromethane[25] (7 : 2 : 1 v/v) for dumbbell **19** and [2]-rotaxane **20**. The polarity was increased to methanol : aqueous ammonium chloride (2 mol dm^{-3}) : nitromethane (5 : 3 : 2 v/v) once the [3]rotaxane **21** started to elute. Each fraction was treated with excess NH_4PF_6 to precipitate the cationic product. Each product was recrystallised from methanol : acetone (1 : 1) by layered addition of diethyl ether, filtered under nitrogen and dried under vacuum to yield [3]rotaxane **21**·$(PF_6)_8$ 120 mg (30%), [2]rotaxane **20**·$(PF_6)_6$ 57 mg (27%) and dumbbell **19**·$(PF_6)_4$ 13 mg (9%).

1,1′,1″,1‴-Tetramethyl-4,4′,4″,4‴-{buta-1,3-diyne-1,4-diyl-bis[4,1-phenylene-2,1-ethynediyl-4,1-phenylene(1-hydroxyprop-2-yn-3-yl-1-ylidene)]}tetrapyridinium tetrakis(hexafluorophosphate) [19·$(PF_6)_4$]. δ_H(300 MHz; CD_3OD) 4.44 (12 H, s, H_H), 7.60–7.72 (16 H, s, H_C, H_D, H_F, and H_G), 8.48 (8 H, d, *J* 6.8, H_B), 8.97 (8 H, d, *J* 6.8, H_A); δ_C[125 MHz; 1 : 1 CD_3OD : $(CD_3)_2CO$] 48,¶ 73.0, 76.1, 82.8, 88.7, 90.8, 92.0[× 2], 121.8, 122.5, 124.9, 125.3, 126.1, 132.68, 132.73, 133.1, 133.5, 147.5, 161.1; *m*/*z* (ESI^+ MS; MeCN) 219.8 (M^{4+}).

8′,12′,16′,18′,27′,31′,35′,37′-Octamethoxy-1,1,1″,1″-tetraethyldispiro{piperidinium-4,13′-[1,6,20,25]tetraoxa[6.1.6.1]-paracyclophane-32′,4″-piperidinium} bis(hexafluorophosphate), rotaxane compound with 1,1′,1″,1‴-tetramethyl-4,4′,4″,4‴-{buta-1,3-diyne-1,4-diylbis[4,1-phenylene-2,1-ethynediyl-4,1-phenylene(1-hydroxyprop-2-yn-3-yl-1-ylidene)]}tetrapyridinium tetrakis(hexafluorophosphate) (1 : 1) [20·$(PF_6)_6$]. (Found: C, 52.7; H, 5.1; N, 3.1. $C_{120}H_{130}N_6O_{14}P_6F_{36}$ requires C, 52.4; H, 4.8; N, 3.1%); δ_H[500 MHz; 1 : 1 CD_3OD : $(CD_3)_2CO$] 1.30 (12 H, t, *J* 7.5, H_P), 1.51–1.59 (8 H, m, H_N), 2.70–3.10 (8 H, m, H_M), 3.34–3.42 (8 H, m, H_J), 3.46–3.57 (16 H, m, H_K and H_L), 3.75 (24 H, s, H_I), 4.48 (12 H, s, H_H), 6.72 (8 H, s, H_F and H_G), 6.86 (8 H, s, H_E), 7.42 (4 H, d, *J* 8.4, H_C), 7.62 (4 H, d, *J* 8.4, H_D), 8.50 (8 H, d, *J* 6.9, H_B), 9.03 (8 H, d, *J* 6.9, H_A); δ_C[125 MHz, 1 : 1 CD_3OD : $(CD_3)_2CO$] 7.3, 26.6, 30,¶ 44.2, 48[× 2],¶ 56.6[× 2], 72.7, 73.1, 76.0, 82.8, 88.8, 90.8, 91.88, 91.93, 104.3, 121.7, 121.9, 124.2, 125.1, 126.1, 132.4, 132.6, 133.2[× 2], 136.9, 142 (br), 147.5, 154.8, 161.1; *m*/*z* (ESI^+ MS; MeCN) 313.4 (M^{6+}), 375.8 [$(M - H)^{5+}$].

8′,12′,16′,18′,27′,31′,35′,37′-Octamethoxy-1,1,1″,1″-tetraethyldispiro{piperidinium-4,13′-[1,6,20,25]tetraoxa[6.1.6.1]-paracyclophane-32′,4″-piperidinium} bis(hexafluorophosphate), rotaxane compound with 1,1′,1″,1‴-tetramethyl-4,4′,4″,4‴-{buta-1,3-diyne-1,4-diylbis[4,1-phenylene-2,1-ethynediyl-4,1-phenylene(1-hydroxyprop-2-yn-3-yl-1-ylidene)]}tetrapyridinium tetrakis(hexafluorophosphate) (2 : 1) [21·$(PF_6)_8$]. (Found: C, 53.2; H, 5.4; N, 2.8. $C_{178}H_{214}N_8O_{26}P_8F_{48}$ requires C, 52.9; H, 5.4; N, 2.8%); δ_H[500 MHz; 1 : 1 CD_3OD : $(CD_3)_2CO$] 1.31 (24 H, t, *J* 7.3, H_P), 1.52–1.61 (16 H, m, H_N), 2.71–3.12 (16 H, m, H_M), 3.35–3.63 (48 H, m, H_J, H_K and H_L), 3.76 (48 H, s, H_I), 4.50 (12 H, s, H_H), 5.83 (4 H, d, *J* 8.0, H_G or H_F), 6.21 (4 H, d, *J* 8.0, H_G or H_F), 6.87 (16 H, s, H_E), 7.03 (4 H, d, *J* 8.4, H_D), 7.47 (4 H,

¶ Signal hidden by the solvent.

d, J 8.4, H_C), 8.50 (8 H, d, J 6.9, H_B), 9.04 (8 H, d, J 6.9, H_A); δ_C[125 MHz, 1:1 CD_3OD:$(CD_3)_2CO$] 7.4, 26.6, 30,¶ 44.1, 48[× 2],¶ 56.6[× 2], 72.6, 73.1, 75.8, 82.6, 88.6, 90.8, 91.6, 91.9, 104.2, 121.2, 121.3, 123.6, 124.9, 126.1, 132.1, 132.5, 132.7, 133.0, 136.9, 142 (br), 147.7, 154.7, 161.0; m/z (ESI^+ MS; MeCN) 360.2 (M^{8+}), 411.5 [$(M - H)^{7+}$], 479.9 [$(M - 2H)^{6+}$].

Conversion of hexafluorophosphate salts into chloride salts

The hexafluorophosphate salt of the rotaxanes or dumbbell was dissolved in a mixture of acetone, water and methanol (1:1:1) and then passed through a DOWEX (1X8 400Cl) column which was pre-washed with the same solvent system. The chloride salts were recrystallised from methanol by layered addition of diethyl ether.

19·Cl$_4$. δ_H(500 MHz; D_2O) 4.42 (12 H, s, H_H), 7.65 (8 H, s, H_F and H_G), 7.68 (8 H, s, H_C and H_D), 8.43 (8 H, d, J 6.8, H_B), 8.89 (8 H, d, J 6.8, H_A); λ_{max}(H_2O)/nm 354 (ε/dm^3 mol^{-1} cm^{-1} 7.7 × 10^4).

20·Cl$_6$. δ_H(500 MHz; D_2O) 1.31 (12 H, t, J 7.0, H_P), 1.60–1.70 (8 H, m, H_N), 2.70–3.10 (8 H, m, H_M), 3.30–3.60 (24 H, m, H_J, H_K and H_L), 3.86 (24 H, s, H_I), 4.46 (12 H, s, H_H), 6.76 (8 H, ABq, J 8.2, H_F and H_G), 6.92 (8 H, s, H_E), 7.67 (8 H, ABq, J 8.4, H_C and H_D), 8.48 (8 H, d, J 6.9, H_B), 8.94 (8 H, d, J 6.9, H_A); λ_{max}(H_2O)/nm 354 (ε/dm^3 mol^{-1} cm^{-1} 7.8 × 10^4).

21·Cl$_8$. δ_H(500 MHz; D_2O) 1.31 (24 H, t, J 6.9, H_P), 1.50–1.80 (16 H, m, H_N), 2.80–3.20 (16 H, m, H_M), 3.43–3.60 (48 H, m, H_J, H_K, and H_L), 3.83 (48 H, s, H_I), 4.46 (12 H, s, H_H), 5.68 (8 H, s, H_F and H_G), 6.90 (16 H, s, H_E), 7.54 (4 H, d, J 8.2, H_D), 7.76 (4 H, d, J 8.2, H_C), 8.48 (8 H, d, J 6.9, H_B), 8.94 (8 H, d, J 6.9, H_A); λ_{max}(H_2O)/nm 356 (ε/dm^3 mol^{-1} cm^{-1} 7.7 × 10^4).

Measurement of binding constants using ^{1}H NMR

^{1}H NMR titrations were carried out at 500 MHz and 298 K. In each titration, the total stopper concentration (0.8–0.1 mmol) was kept constant. The concentrations of macrocycle and stopper were chosen such that during the titrations the percentage of bound stopper was varied between 20 and 80%. The association constants for the 1:1 or 1:2 complexes were extracted from the titration curves using a simplex least-squares curve-fitting process.[34]

Photoluminescence experiments

(i) Steady-state emission. The fluorescence yields of **19·**Cl_4, **20·**Cl_6, and **21·**Cl_8 in water were measured by comparison with anthracene in ethanol (27%)[35] using a SPEX Fluoromax fluorimeter. Excitation was carried out at 300 nm. These quantum yields were independent of concentration for concentrations less than 1 μmol dm^{-3}.

(ii) Time resolved emission. All measurements were carried out in water. The samples were excited by the frequency doubled output (380 nm) of a Ti:sapphire laser operating at a repetition rate of 76 MHz. The pulse width was 200 fs and typically a power of 10 mW was focused on the sample held in a cuvette (1.0 mm width) to a beam waste of 100 μm. Time-integrated spectra were recorded by a CCD camera coupled to a SPEX triplemate spectrometer, and the signal was integrated for successive intervals of 50 ms while the laser was illuminating the sample. Ultrafast time-resolved luminescence was measured with a streak camera system; the overall temporal resolution was 20 ps and the intensity decay could be followed for a maximum of about 2 ns.

Incorporation experiments

Cyclophane **6** (12.5 mg, 1.17 × 10^{-5} mol) and 1,4-diethynylbenzene (1.5 mg, 1.17 × 10^{-5} mol) were dissolved in water (1.0 cm^3) and after heating and sonication allowed to stand overnight. To this solution, longer stopper **3** (3 mg, 5.87 × 10^{-6} mol) and further cyclophane (6.3 mg, 5.87 × 10^{-6} mol) dissolved in water (0.5 cm^3) was added, the resultant solution was added to the copper(I) chloride (396 mg) and ammonium chloride (640 mg) dissolved in water (0.5 cm^3). The mixture was degassed and saturated with oxygen and then left to stir under 1 atm oxygen for 48 h. Work up was carried out as for the rotaxane preparation.

Acknowledgements

This work was supported by the EPSRC. S. A. gratefully acknowledges a Research Fellowship and generous support from Trinity College, Cambridge. T. G. III acknowledges the National Research Council (USA) and the Ford Foundation for a fellowship.

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Paper 8/02680G
Received 8*th April* 1998
Accepted 2*nd June* 1998