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Self-assembling cyclobis(paraquat-4,4'-biphenylene)

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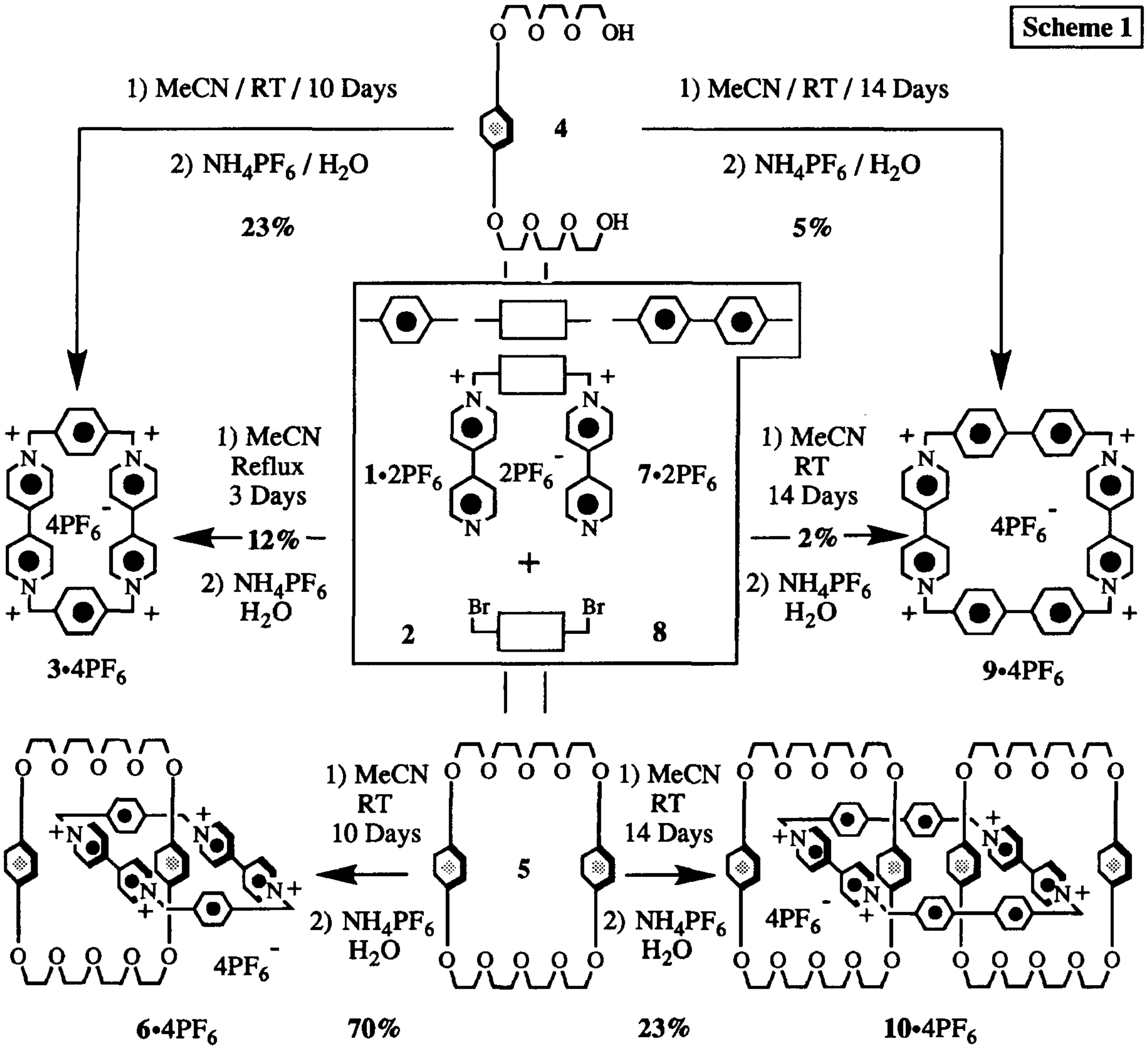
Abstract - The template-directed syntheses of the bipyridinium-based cyclophanes cyclobis(paraquat-*p*-phenylene) and cyclobis(paraquat-4,4'-biphenylene) can be achieved by employing π-electron rich hydroquinone-based and ferrocene-based templates. By employing macrocyclic hydroquinone-based polyether templates, [2]catenanes and [3]catenanes, in which the bipyridinium-based cyclophane is mechanically-interlocked with the macrocyclic template(s), can be self-assembled in solution. The introduction of ester functions within these polyether chains of the macrocyclic templates provides the possibility of *degrading* the catenated structure *via* ester hydrolysis, thus, releasing the tetracationic cyclophane originally trapped within the catenane. The use of ferrocene-based templates provides a more efficient way to synthesise the bipyridinium-based cyclophane incorporating bitolyl spacers. In particular, the use of a 1,1'-disubstituted polyether ferrocene derivative provides the possibility of obtaining the tetracationic cyclophane, cyclobis(paraquat-4,4'-biphenylene) — accessible only in very low yields, without the use of a template — on a preparative scale.

INTRODUCTION

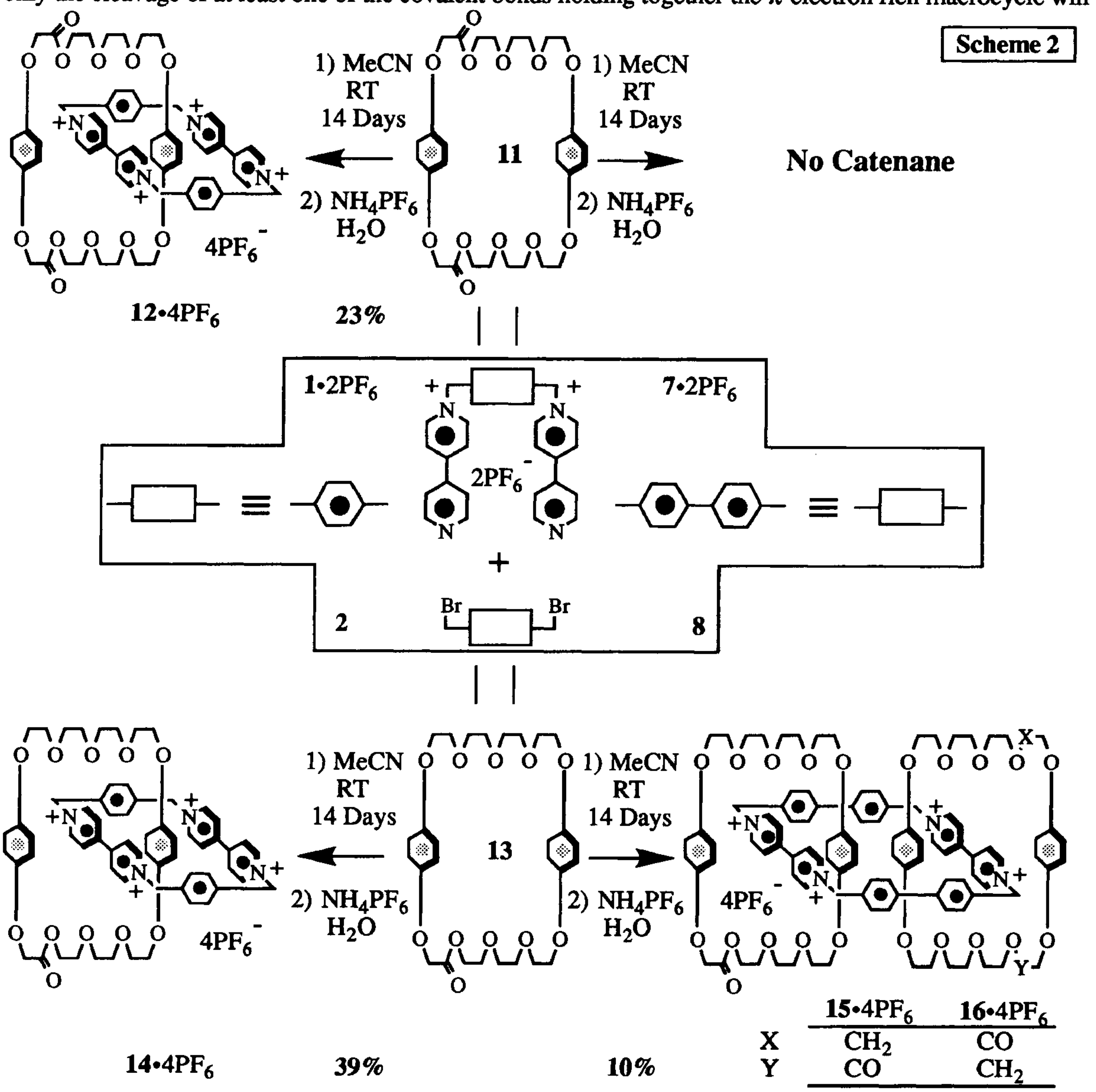
Self-assembly processes (1-3) are based upon the attainment of high complementarity between simple modular components which serve as subunits. Weak noncovalent bonding interactions bring the subunits together, affording an initial superstructure in a so-called nucleation step. By a series of cooperative noncovalent bonding interactions, the initial superstructure evolves into the final thermodynamically-stable supramolecular architecture which can be *captured* by the formation of covalent bonds, sometimes in kinetically-controlled processes. Remarkable efficiency overall, a high degree of control, and error checking and recovery are ensured throughout the process. These features suggest the use (4, 5) of self-assembly processes as a viable alternative to the traditional synthetic methodologies for the generation of wholly-synthetic systems that are rather intricate. Recently, we have developed (6, 7) a synthetic approach to self-assemble interlocked molecular compounds, such as catenanes and rotaxanes, as well as supramolecular arrays, such as pseudorotaxanes. The methodology relies upon the complementarity that exists between π-electron deficient bipyridinium-based macrocyclic components and π-electron rich hydroquinone-based acyclic and cyclic polyethers. In their early stages, self-assembly processes are driven by noncovalent bonding interactions, such as (i) π-π stacking (8, 9) between the π-electron deficient bipyridinium units and the π-electron rich hydroquinone residues, (ii) hydrogen bonding (10, 11) between the polyether oxygen atoms and the hydrogen atoms in the α-positions with respect to the nitrogen atoms of the bipyridinium units, as well as (iii) edge-to-face T-type interactions (12, 13) between the hydrogen atoms of the hydroquinone residues and the π-clouds of the aromatic spacers incorporated within the tetracationic cyclophanes. The template-directed syntheses of cyclobis(paraquat-4,4'-biphenylene) — a *molecular square* (14-16) — has been achieved by self-assembling the bipyridinium-based cyclophane — the host at the end of the process — around preformed π-electron rich component(s) — the guest in the beginning.

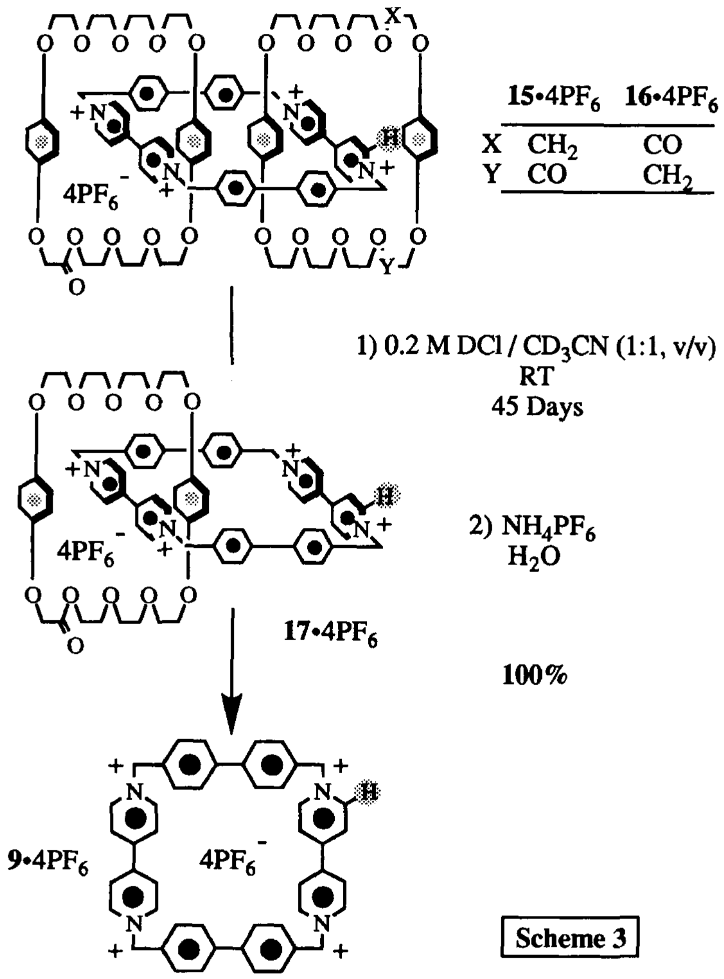
HYDROQUINONE-BASED GUESTS AS TEMPLATES

The bipyridinium-based cyclophane, cyclobis(paraquat-*p*-phenylene) **3**•4PF$_6$, can be obtained (17, 18) (Scheme 1) in a yield of 12% by reaction of the dication **1**•2PF$_6$ with the dibromide **2** in an acetonitrile solution heated under reflux during 3 days. A more efficient template-directed synthesis (19-22) of the π-electron deficient cyclophane **3**•4PF$_6$ can be effected by employing a π-electron rich species, such as the hydroquinone-based polyether **4**. Reaction (Scheme 1) of the dication **1**•2PF$_6$ with the dibromide **2** in acetonitrile at room temperature during 10 days in the presence of the hydroquinone-based polyether **4** affords (18) the tetracationic cyclophane **3**•4PF$_6$ in almost double (23%) yield. When the reaction is repeated (Scheme 1) in the presence of the macrocyclic hydroquinone-based template **5**, under otherwise identical conditions, the [2]catenane **6**•4PF$_6$ self-assembles (18, 23) in the amazing yield of 70%. When the acyclic template **4** is employed, a pseudorotaxane-like complex is generated in solution after the



macrocyclisation of 3•4PF$_6$. Decomplexation of the supramolecular species, which releases the template **4** unchanged and the *free* cyclophane 3•4PF$_6$, can be achieved by chromatographic means or by continuous liquid-liquid extraction of an aqueous solution of the pseudorotaxane with chloroform. When the more effective macrocyclic polyether **5** is employed as the template, the tetracationic cyclophane self-assembles around one of the two hydroquinone recognition sites incorporated within the π-electron rich macrocyclic component **5**, affording a mechanically-interlocked structure in the shape of the [2]catenane **6**•4PF$_6$. As a result of mechanical interlocking, the tetracationic cyclophane is trapped within the catenated structure and only the cleavage of at least one of the covalent bonds holding together the π-electron rich macrocycle will afford the *free* cyclophane 3•4PF$_6$ after the *degradation* of the macrocyclic component of the [2]catenane **6**•4PF$_6$. In the absence of a template, the cyclophane cyclobis(paraquat-4,4'-biphenylene) **9**•4PF$_6$, incorporating the longer bitolyl spacers between the bipyridinium units can only be obtained (Scheme 1) in the very low yield of 2% by reacting (24) the dicationic derivative **7**•2PF$_6$ with the dibromide **8** in acetonitrile at room temperature over 14 days. By performing the reaction in the presence of the hydroquinone-based acyclic template **4**, under otherwise identical conditions, the tetracationic cyclophane


Scheme 2



Scheme 3

$9{\cdot}4PF_6$ can be self-assembled (Scheme 1) in the slightly better yield of 5%. When the macrocyclic hydroquinone-based template **5** is employed, the tetracationic cyclophane self-assembles (Scheme 1) around the two hydroquinone recognition sites, affording (24, 25) the [3]catenane **10**•$4PF_6$ in a yield of 23%. Clearly, the π-electron rich macrocycle **5** is a much more effective template than the acyclic polyether **4** for the self-assembly of the bipyridinium-based cyclophane **9**•$4PF_6$. However, when **5** is employed, the resulting tetracationic cyclophane is trapped within the catenated structure of **10**•$4PF_6$. In order to release the tetracationic component from the [3]catenane **10**•$4PF_6$, *degradation* of the catenated structure was attempted through cleavage of the polyether chains of the π-electron rich components. Unfortunately, the conditions required for the cleavage of the ether bonds are too severe in relation to the bipyridinium-based cyclophane and result in the cleavage of both the π-electron rich and π-electron deficient components of the [3]catenane **10**•$4PF_6$. Thus, we synthesised (26) π-electron rich hydroquinone-based macrocyclic templates **11** and **13** incorporating ester linkages along the polyether chains. The ester bonds can be hydrolysed under mild acidic conditions affording a *safe* method for cleaving the π-electron rich macrocycles within the catenated structures. In order to test the ability of the macrocycles **11** and **13** to template the macrocyclisation of bipyridinium-based cyclophanes, the dication **1**•$2PF_6$ was reacted with the dibromide **2** in acetonitrile at room temperature during 14 days in the presence of **11** and then of **13**. Indeed, the [2]catenane **12**•$4PF_6$ and **14**•$4PF_6$ incorporating macrocyclic lactones as their π-electron rich components were self-assembled (26) (Scheme 2) in yields of 23 and 39%, respectively. When the dication **7**•$2PF_6$ incorporating the bitolyl spacer was reacted (Scheme 2) with the dibromide **8** in acetonitrile during 14 days in the presence of the macrocycle **11**, no catenated products were detected (26). However, by employing the macrocycle **13** under otherwise identical conditions, a 1:1 mixture of the two topologically stereoisomeric [3]catenanes **15**•$4PF_6$ and **16**•$4PF_6$ was obtained in an overall yield of 10%. When the mixture of the two topologically stereoisomeric [3]catenanes **15**•$4PF_6$ and **16**•$4PF_6$ was subjected (Scheme 3) to hydrolysis in a mixture of 0.2 M DCl and CD_3CN at room temperature during 45 days, the tetracationic cyclophane **9**•$4PF_6$ was obtained (26) in a quantitative yield after counterion exchange. The degradation process was followed by ^{1}H-NMR spectroscopy. The partial

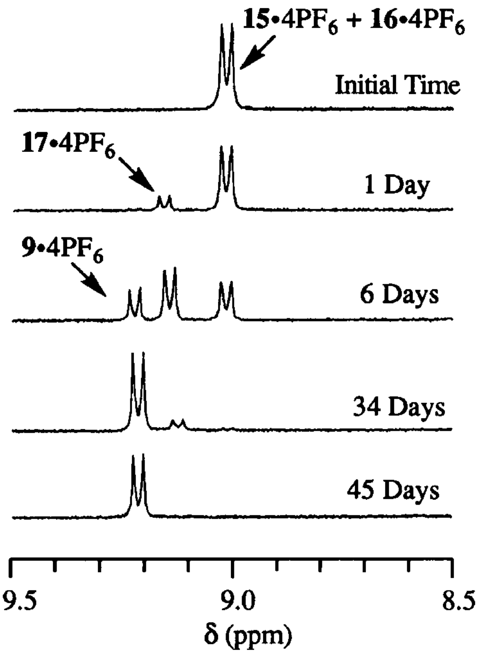
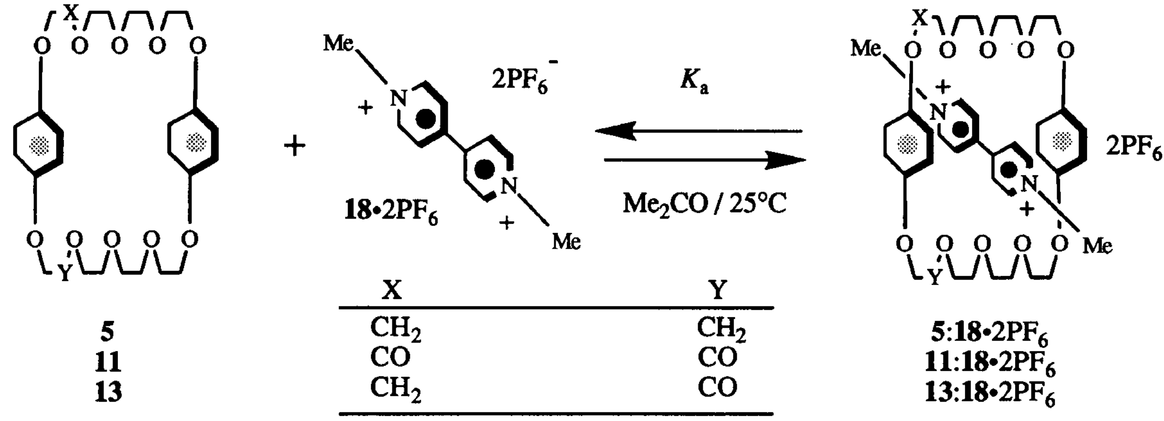


Fig. 1 Partial ^1H-NMR spectra recorded in 0.2 M DCl / CD_3CN at room temperature illustrating the formation of the *free* cyclophane $9 \bullet 4PF_6$ from the isomeric [3]catenanes $15 \bullet 4PF_6$ and $16 \bullet 4PF_6$ after the hydrolysis of the π-electron rich macrocyclic lactones incorporated within their catenated structures.

^1H-NMR spectra, showing the resonances corresponding to the hydrogen atoms in the α-positions with respect to the nitrogen atoms of the bipyridinium units within the species involved in the process — namely, the [3]catenanes **15**•4PF$_6$ and **16**•4PF$_6$, the [2]catenane **17**•4PF$_6$ and the cyclophane **9**•4PF$_6$— are shown in Fig. 1. The ^1H-NMR spectrum recorded at the beginning of the reaction shows only one doublet in the region between δ 8.5 and 9.5 corresponding to the [3]catenanes **15**•4PF$_6$ and **16**•4PF$_6$. After one day, a second doublet, corresponding to the [2]catenane **17**•4PF$_6$ is evident at lower fields. After six days, a third doublet corresponding to the *free* cyclophane **9**•4PF$_6$ starts to appear at even lower fields. The ^1H-NMR spectrum recorded after forty-five days shows — in the region between δ 8.5 and 9.5 — only the resonances corresponding to the *free* cyclophane **9**•4PF$_6$, thus demonstrating the completion of the hydrolysis. On going from the π-electron rich macrocycle **5** to the macrocycles **13** and **11** incorporating, respectively, one and two ester functions along the polyether chains, the yields for the self-assembly of the corresponding [2]catenanes decreased from 70 to 39 and 23%. Similarly, the yields for the self-assembly of the [3]catenanes decreased from 23 to 10 and 0%, respectively, when the macrocycles **5**, **13** and **11** were employed in separate experiments as the templating species. Thus, as a result of the introduction of one and subsequently two ester functions along the polyether chains of the π-electron rich macrocycle, the templating ability is dramatically reduced. In order to investigate further the influence on the self-assembly processes of the presence of ester functions along the polyether chains of the templates, the complexation (Fig. 2) of paraquat **18**•2PF$_6$ by the π-electron rich macrocycles **5**, **11** and **13** was investigated. By employing the titration methodology, and measuring spectrophotometrically, the change in the intensity of the charge transfer band arising from the π-π



	X	Y
5	CH_2	CH_2
11	CO	CO
13	CH_2	CO

Fig. 2 Complexation of paraquat $18 \bullet 2PF_6$ by the π-electron rich macrocycles **5**, **11**, and **13**.

TABLE. Association constants (K_a) and binding energies ($\Delta G°$) for the complexation of paraquat **18**•2PF$_6$ by the π-electron rich macrocycles **5**, **11**, and **13** and for the complexation of ferrocene **19** and the 1,1'-disubstituted ferrocene derivative **20** by the π-electron deficient cyclophane **9**•4PF$_6$

Complex	λ^a (nm)	K_a (M^{-1})	$\Delta G°$ (kcal mol^{-1})
5:**18**•2PF$_6$	436	730^b	-3.9
11:**18**•2PF$_6$	417	5^b	-1.0
13:**18**•2PF$_6$	427	73^b	-2.5
9:**19**•4PF$_6$	—	80^c	-2.0
9:**20**•4PF$_6$	—	1600^c	-4.4

[a] Wavelength corresponding to the maximum of the charge-transfer band of the complexes. [b] The association constants for the complexation of paraquat **18**•2PF$_6$ by the π-electron rich macrocycles **5**, **11** and **13** were determined in Me$_2$CO at 25°C by UV-Vis spectroscopy employing the titration methodology. [c] The association constants for the complexation of ferrocene **19** and the 1,1'-disubstituted ferrocene derivative **20** by the π-electron deficient cyclophane **9**•4PF$_6$ were determined in CD$_3$CN at 25°C by ^{1}H-NMR spectroscopy employing the titration methodology.

interactions between the π-electron rich hydroquinone rings incorporated within the host and the bipyridinium unit of the guest, the association constants (K_a) and the binding energies ($\Delta G°$) for the complexes **5**:**18**•2PF$_6$, **11**:**18**•2PF$_6$ and **13**:**18**•2PF$_6$ were evaluated. The K_a and $\Delta G°$ values are listed in the Table. The association constant for the complex **5**:**18**•2PF$_6$ is estimated (27) to be 730 M^{-1}. As a result of the introduction sequentially of one and then two ester functions along the polyether chains of the host, the K_a values decrease (26) to 73 and 5 M^{-1} for the complexes **13**:**18**•2PF$_6$ and **11**:**18**•2PF$_6$, respectively. Plots of the percentage yields for the self-assembly of both the [2]catenanes and the [3]catenanes against the binding energies for the complexation of paraquat **18**•2PF$_6$ by the macrocycles **5**, **11** and **13** are represented in Fig. 3. An approximately linear relationship is observed in both cases, emphasising that the dramatic decrease in the efficiency of the self-assembly processes upon the introduction of one and subsequently two ester functions along the polyether chains of the π-electron rich component is associated intimately with the extent of the

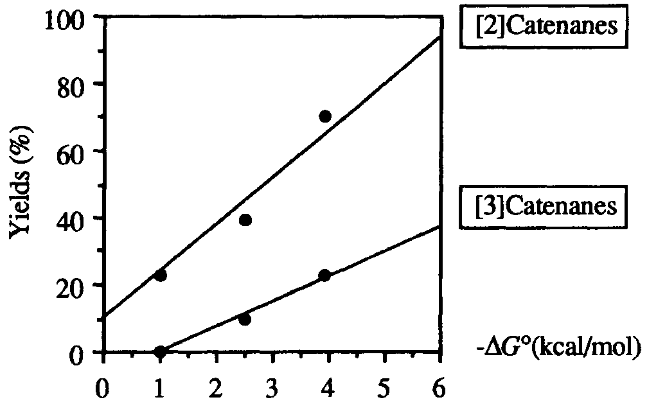
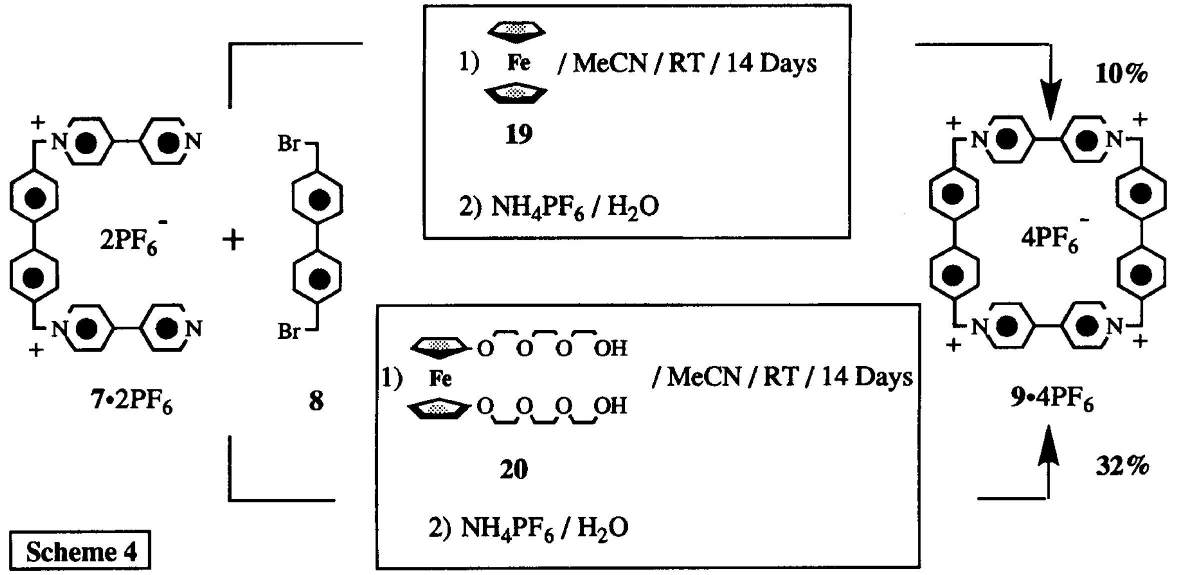


Fig. 3 Correlation between the percentage yields of the [2]catenanes and the [3]catenanes and the binding energies for the complexation of paraquat **18**•2PF$_6$ by the π-electron rich macrocycles **5**, **11** and **13**.

molecular recognition between the self-assembling components.

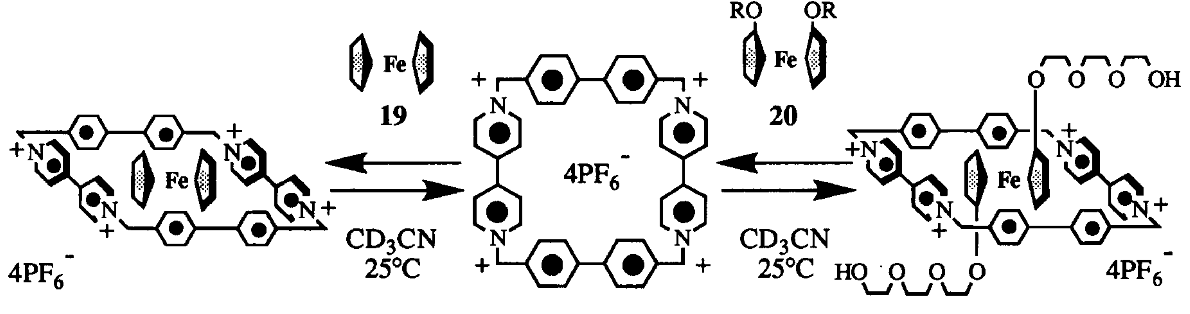
FERROCENE-BASED GUESTS AS TEMPLATES

The tetracationic cyclophane, cyclobis(paraquat-4,4'-biphenylene) **9**•$4PF_6$, can be obtained only in very low yields with or without acyclic hydroquinone-based templates. The use of the macrocyclic hydroquinone-based template **13** incorporating one ester function along one of the two polyether chains provides the possibility of isolating quantitatively the *free* cyclophane **9**•$4PF_6$, after the ***degradation*** by acid-catalysed hydrolysis of [3]catenanes **15**•$4PF_6$ and **16**•$4PF_6$. However, the syntheses of **13** and the corresponding [3]catenanes are in themselves time-consuming and low yielding processes. In order to gain access to the cyclophane **9**•$4PF_6$ on a preparative scale, a simpler and readily-available template had to be identified and employed. The X-ray crystal structure of the [3]catenane **10**•$4PF_6$ shows (24, 25) that the mean planes of the two π-electron rich hydroquinone rings inserted inside the cavity of the tetracationic cyclophane are separated by a distance of 3.63 Å. By contrast, the two π-electron rich cyclopentadienyl rings of ferrocene **19** are characterised (28) by an interplanar distance of 3.32 Å. Furthermore, many examples of charge transfer complexes between ferrocene-based derivatives and π-electron deficient compounds have been reported (29-32) in the literature. Therefore, we reasoned that ferrocene **19** and, even more so, a 1,1'-disubstituted ferrocene derivative, such as **20**, should possess the stereoelectronic requirements to template the macrocyclisation of the bipyridinium-based cyclophane **9**•$4PF_6$. Reaction (Scheme 4) of the dication **7**•$4PF_6$ with the dibromide **8** in acetonitrile at room temperature during 14 days in the presence of ferrocene **19** affords (26, 33) the cyclophane **9**•$4PF_6$ in a yield of 10%. When the 1,1'-disubstituted ferrocene-based derivative **20** was employed as the template, under otherwise identical conditions, the cyclophane **9**•$4PF_6$ was isolated in a yield of 32%. As a result of the second-sphere coordination (34, 35) established by π-π stacking interactions between the π-electron rich cyclopentadienyl rings of the transition metal complexes and the π-electron deficient bipyridinium units as well as, in the case of **20**, by hydrogen bonding interactions between the polyether oxygen atoms and the hydrogen atoms in the α-position with respect to the nitrogen atoms in the bipyridinium units, the tetracationic cyclophane **9**•$4PF_6$ — the host — is self-assembled around the ferrocene residue of either **19** or **20** — the guest — affording a pseudorotaxane-like 1:1 complex. Column chromatography on silica gel promotes decomplexation of the 1:1 complexes yielding the *free* cyclophane as well as generating the unchanged



Scheme 4

template: the latter can be recycled. The association constants for the complexation (Fig. 4) of ferrocene **19** and the 1,1'-ferrocene derivative **20** by the bipyridinium-based cyclophane **9**•4PF$_6$ were evaluated (26, 33) by ^{1}H-NMR spectroscopy employing the titration methodology and are listed in the Table. The association constant for the 1:1 complex **9**:**19**•4PF$_6$ corresponds to 80 M^{-1}, whilst, when the 1,1'-disubstituted ferrocene derivative **20** bearing two polyether chains is employed as the guest, the association constant for the corresponding 1:1 complex rises to 1600 M^{-1}. The dramatic increase in the binding energy on going from **19** to **20** is presumably a result of the additional hydrogen bonding interactions between the polyether oxygen atoms of **20** and the acidic protons of the bipyridinium units incorporated within **9**•4PF$_6$. The formation of a 1:1 complex between the cyclophane **9**•4PF$_6$ and **20** was confirmed (26, 33) by both ^{1}H-NMR spectroscopy and FAB mass spectrometry. Upon mixing equimolar amounts of the host **9**•4PF$_6$ with the guest **20**, a deep green colour develops immediately, presumably as a result of a charge transfer interaction occurring between the cyclopentadienyl rings of the guest and the bipyridinium units present in the host. The resonances corresponding to the cyclopentadienyl rings protons in the ^{1}H-NMR spectrum of **9**:**20**•4PF$_6$ in CD$_3$CN are shifted upfield by *ca.* 1.5 ppm at room temperature. The FAB mass spectrum of **9**:**20**•4PF$_6$ shows a peak at *m/z* 1735 corresponding to the sum of the molecular weights of host and guest along with additional peaks at *m/z* 1589, 1443 and 1298 for the loss of one, two and three hexafluorophosphate counterions, respectively, from the pseudorotaxane.



9:**19**•4PF$_6$ **9**•4PF$_6$ **9**:**20**•4PF$_6$

Fig. 4 Complexation of ferrocene **19** and the 1,1'-disubstituted ferrocene derivative **20** [R = -(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$OH] by the π-electron deficient cyclophane **9**•4PF$_6$.

CONCLUSIONS AND REFLECTIONS

The self-assembly of the bipyridinium-based cyclophanes **3**•4PF$_6$ and **9**•4PF$_6$ around π-electron rich hydroquinone-based and ferrocene-based templates has been achieved by relying upon noncovalent bonding interactions such as π-π stacking between the complementary aromatic units, CH···O hydrogen bonding and edge-to-face T-type interactions. By employing acyclic templates (Figure 5), pseudorotaxane-like complexes can be self-assembled in solution. Their decomplexation releases the *free* cyclophane and the unchanged template which can be recycled. In particular, the use of a 1,1'-disubstituted ferrocene derivative provides the possibility of obtaining the tetracationic cyclophane, cyclobis(paraquat-4,4'-biphenylene) — accessible only in very low yield without the use of a template — on a preparative scale. When appropriate macrocyclic polyethers are employed as the templates (Figure 5), [2]catenanes and [3]catenanes can be self-assembled in acetonitrile solution at room temperature. Thus, the tetracationic cyclophanes are trapped within the catenated structures as a result of mechanical linkages with the π-electron rich macrocyclic component(s). The introduction of ester functions within the polyether chains of the macrocyclic templates provides a way of generating *degradable* catenanes. Subsequent ester hydrolyses

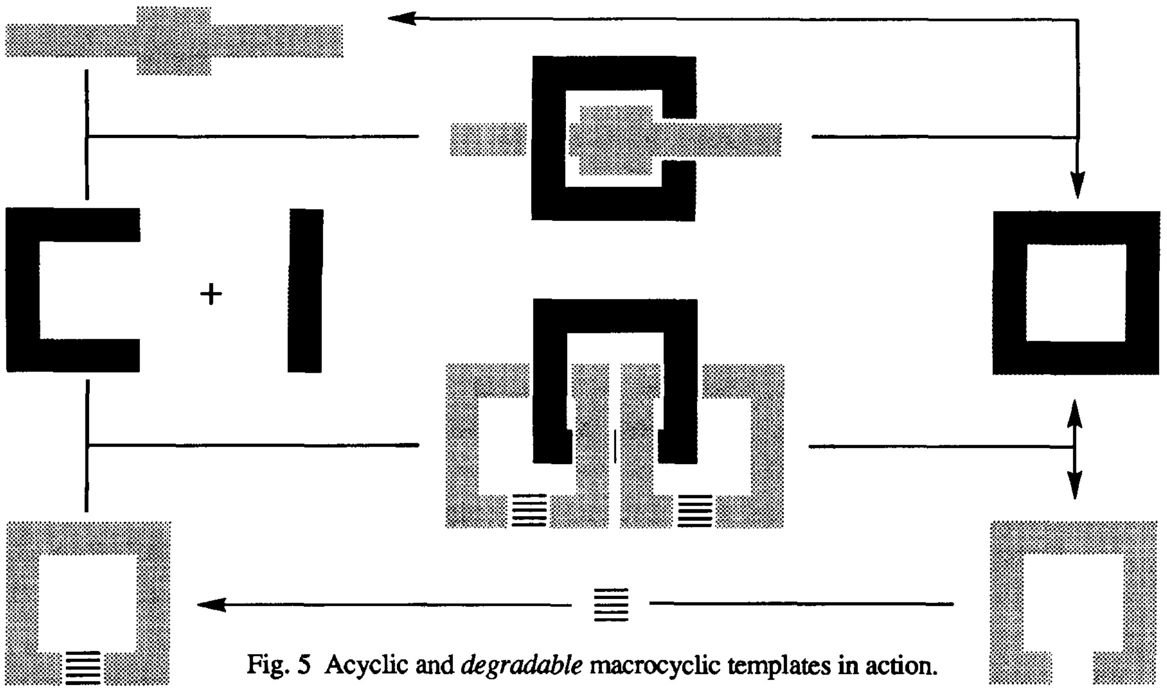


Fig. 5 Acyclic and *degradable* macrocyclic templates in action.

of the macrocyclic lactones incorporated within the catenated structures afford, after the *destruction* of the catenane, the *free* bipyridinium-based component in a quantitative yield. Complex formation between ferrocene-based derivatives and the bipyridinium-based cyclophane $\mathbf{9}\cdot 4\mathrm{PF}_6$ opens up possibilities of generating electrochemically-active (36-39) catenanes, rotaxanes and pseudorotaxanes having potential device-like (40, 41) characteristics.

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REFERENCES

1. J.S. Lindsey, *New J. Chem.*, **15**, 153 (1991).
2. G.M. Whitesides, J. P. Mathias, and C.T. Seto, *Science*, **254**, 1312 (1991).
3. G.M. Whitesides, E.R. Simanek, J.P. Mathias, C.T. Seto, D.N. Chin, M. Mammen, and D.M. Gordon, *Acc. Chem. Res.*, **28**, 37 (1995).
4. J.F. Stoddart, *Host-Guest Molecular Interactions: From Chemistry to Biology*, CIBA Foundation Symposium 158, p. 5, Wiley, Chichester (1991).
5. D.B. Amabilino and J.F. Stoddart, *New Scientist*, 19 February No 1913, 25 (1994).
6. D. Philp and J.F. Stoddart, *Synlett*, 445 (1991).
7. D.B. Amabilino and J.F. Stoddart, *Pure Appl. Chem.*, **65**, 2351 (1993).
8. C.A. Hunter and J.K.M. Sanders, *J. Am. Chem. Soc.*, **112**, 5525 (1990).
9. C.A. Hunter, *Angew. Chem., Int. Ed. Engl.*, **105**, 1653 (1993).
10. M.C. Etter, *Acc. Chem. Res.*, **23**, 120 (1990).
11. G.R. Desiraju, *Acc. Chem. Res.*, **24**, 290 (1991).
12. W.L. Jorgensen and D.L. Severance, *J. Am. Chem. Soc.*, **112**, 4786 (1990).
13. M.J. Zaworotko, *Chem. Soc. Rev.*, **23**, 283 (1994).
14. M. Fujita, Y.J. Kwon, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994).
15. P.J. Stang, D.H. Cao, S. Saito, and A.M. Arif, *J. Am. Chem. Soc.*, **117**, 6273 (1995).

16. C.A. Hunter, *Angew. Chem., Int. Ed. Engl.*, **34**, 1079 (1995).
17. B. Odell, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, and D.J. Williams, *Angew. Chem., Int. Ed. Engl.*, **27**, 1547 (1988).
18. P.L. Anelli, P.R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M.T. Gandolfi, T.T. Goodnow, A.E. Kaifer, D. Philp, M. Pietraskiewicz, L. Prodi, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, C. Vicent, and D. J. Williams, *J. Am. Chem. Soc.*, **114**, 193 (1992).
19. D. H. Busch and N. A. Stephenson, *Coord. Chem. Rev.*, **100**, 119 (1990).
20. D. H. Busch, *J. Incl. Phenom.*, **12**, 389 (1992).
21. S. Anderson, H.L. Anderson, and J.K.M. Sanders, *Acc. Chem. Res.*, **26**, 389 (1993).
22. R. Hoss and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, **33**, 373 (1994).
23. P.R. Ashton, T.T Goodnow, A.E. Kaifer, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, C. Vicent, and D.J. Williams, *Angew. Chem., Int. Ed. Engl.*, **28**, 1396 (1989).
24. D.B. Amabilino, P.R. Ashton, C.L. Brown, E. Córdova, L.A. Godínez, T.T. Goodnow, A.E. Kaifer, S.P. Newton, M. Pietraskiewicz, D. Philp, F.M. Raymo, A.S. Reder, M.T. Rutland, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, and D.J. Williams, *J. Am. Chem. Soc*, **117**, 1271 (1995).
25. P.R. Ashton, C.L. Brown, E.J.T. Chrystal, T.T. Goodnow, A.E. Kaifer, K.P. Parry, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, and D.J. Williams, *Angew. Chem., Int. Ed. Engl.*, **30**, 1039 (1991).
26. M. Asakawa, P.R. Ashton, S. Menzer, F.M. Raymo, J.F. Stoddart, and D.J. Williams, *Chem. Eur. J.*, In preparation.
27. B.L. Allwood, N. Spencer, H. Shahriari-Zavareh, J.F. Stoddart, and D.J. Williams, *J. Chem. Soc., Chem. Commun.*, 1064 (1987).
28. J.D. Dunitz, L.E. Orgel, and A. Rich, *Acta Cryst.*, **9**, 373 (1956).
29. J.S. Miller, J.C. Calabrese, R.L. Harlow, D.A. Dixon, J.H. Zhang, W.M. Reiff, S. Chittipeddi, M.A. Selover, and A.J. Epstein, *J. Am. Chem. Soc.*, **112**, 5946 (1990).
30. D. Stein, H. Sitzmann, and R. Boese, *J. Organomet. Chem.*, **421**, 275 (1991).
31. K.M. Chi, J.C. Calabrese, W.M. Reiff, and J.S. Miller, *Organometallics*, **10**, 688 (1991).
32. A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech, and H. Keller, *Organometallics*, **13**, 1224 (1994).
33. P.R. Ashton, S. Menzer, F.M. Raymo, G. Shimizu, J.F. Stoddart, and D.J. Williams, *Angew. Chem., Int. Ed. Engl.*, Submitted.
34. J.F. Stoddart and R. Zarzycki, *Cation Binding by Macrocycles*, Eds. Y. Inoue and G.W. Gokel, Dekker, New York (1990), pp. 631-699.
35. J.E. Kicham and S.J. Loeb, *Inorg. Chem.*, **33**, 4351 (1994).
36. A. Livoreil, C.O. Dietrich-Buchecker, and J.P. Sauvage, *J. Am. Chem. Soc.*, **116**, 9399 (1994).
37. P.R. Ashton, R. Ballardini, V. Balzani, M.T. Gandolfi, D.J.F. Marquis, L. Pérez-Garcia, L. Prodi, J.F. Stoddart, and M. Venturi, *J. Chem. Soc., Chem. Commun.*, 177 (1994).
38. R.A. Bissell, E. Córdova, A.E. Kaifer, and J.F. Stoddart, *Nature*, **369**, 133 (1994).
39. J.A. Preece and J.F. Stoddart, *Molecular Engineering for Advanced Materials*, Eds. J. Becher, K. Schaumburg, p. 1, Kluwer Academic Publisher, Dordrecht (1995).
40. J.M. Lehn, *Science*, **260**, 1762 (1993).
41. E.C. Constable, *Nature*, **374**, 760 (1995).