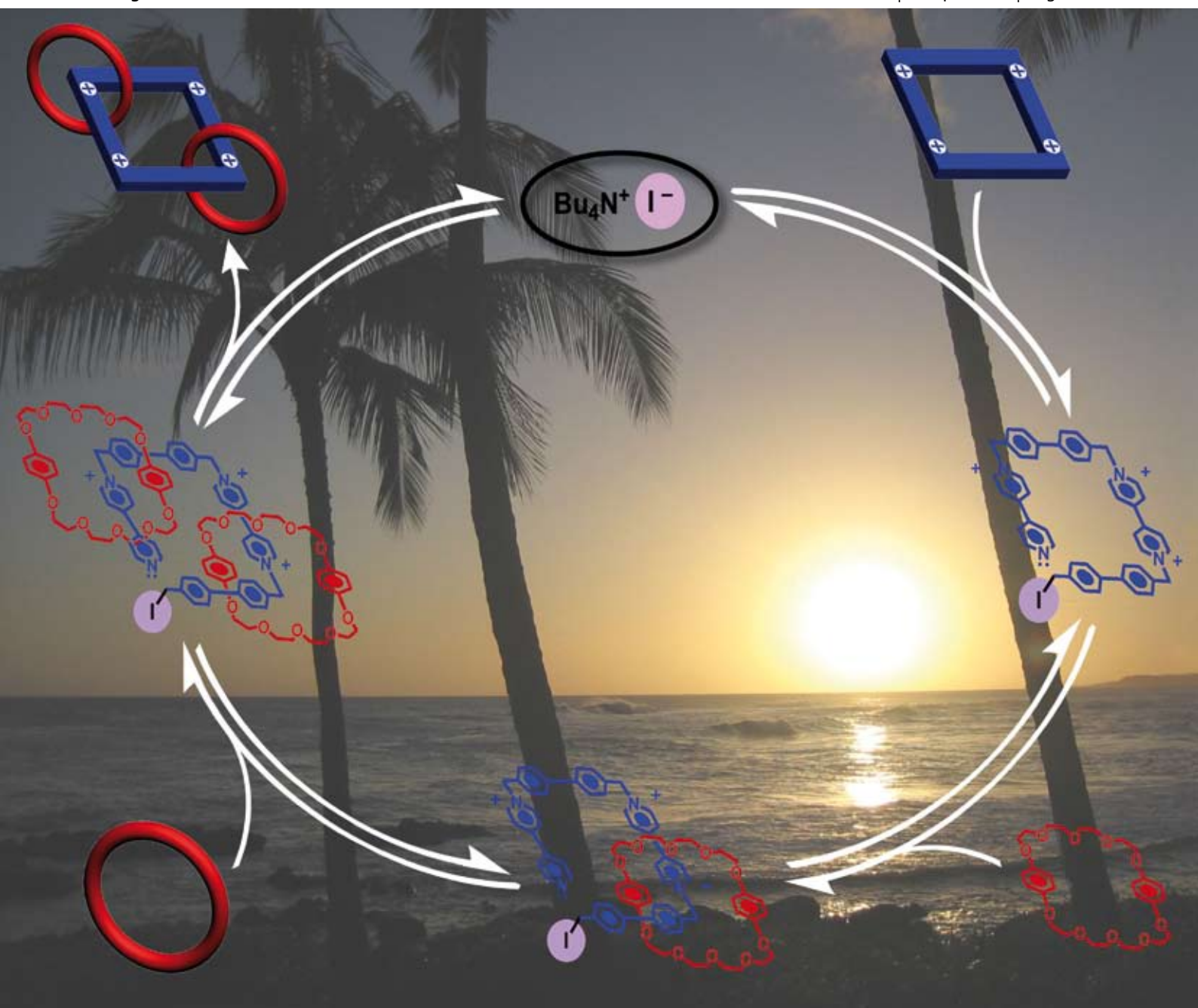


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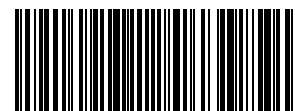
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FEATURE ARTICLE

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Iodide-catalysed self-assembly of donor–acceptor [3]catenanes

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Charged donor–acceptor [3]catenanes comprising the π -accepting cyclobis(paraquat-4,4'-biphenylene) and π -donating aromatic crown ether macrocycles have been prepared in high yields using thermodynamically controlled dynamic nucleophilic substitution.

Mechanically interlocked and topologically non-trivial molecules, known as catenanes, have attracted considerable attention as synthetic targets¹ and—more recently—as proposed and realised components of functioning molecular devices, such as switches,² unidirectional motors,³ and electronic displays.⁴ Traditional catenane syntheses—dominated by kinetically controlled reactions—often employ noncovalent bonding interactions to organise the precursors into an arrangement optimal for the catenation.⁵ Kinetic control comes with the caveat of irreversibility—that is, if starting materials “misreact” and form undesired side-products, they are effectively wasted. On the other hand, formation of catenanes under thermodynamically controlled conditions⁶ appears advantageous as (1) the inherent thermodynamic stabilisation of the catenane *versus* its constituent rings, brought about by the favourable noncovalent bonding interactions, strongly favours the catenane in the equilibrium mixture, and (2) the portion of the starting materials that initially undergoes side reactions is repeatedly recycled until equilibrium is established.

We have recently disclosed⁷ the thermodynamically controlled preparation of donor–acceptor [2]catenanes based on crown ether π -donor rings and cyclobis(paraquat-*p*-phenylene) (1^{4+} , Fig. 1) as the π -acceptor ring. In this communication, we report the extension of the above protocol to the larger [3]catenanes—a first step towards the application of this methodology to the template-directed synthesis⁸ of the elusive donor–acceptor polycatenanes.

Cyclobis(paraquat-*p*-phenylene)⁹ (1^{4+}) is a tetracationic cyclophane capable of binding electron-rich arenes—exclusively with 1 : 1 stoichiometries—within its electron-poor cavity. Formation of higher donor–acceptor [*n*]catenanes necessitates larger π -accepting rings, such as cyclobis(paraquat-4,4'-biphenylene)¹⁰ (2^{4+}). Its extended cavity allows the formation of 1 : 2 complexes with electron-rich arenes, and, consequently, the construction¹¹ of [3]catenanes. The presence of reactive benzylic positions in both 1^{4+} and 2^{4+} makes the two tetracationic cyclophanes analogous in their reactivities

and so we set out to explore the accuracy of this analogy by pursuing the thermodynamically controlled assembly of [3]catenanes from 2^{4+} .

More specifically, we envisioned that the formation of [3]catenanes from 2^{4+} would proceed by the mechanism proposed in Scheme 1. Tetrabutylammonium iodide (TBAI) would act initially as a nucleophile, opening up the tetracationic cyclophane 2^{4+} into the π -accepting tricationic species 3^{3+} . Coordination of 3^{3+} with a crown ether, such as **4**, would provide the intermediate [2]pseudorotaxane [**3** \subset **4**]³⁺; subsequent coordination of an additional molecule of **4** would give rise¹² to [3]pseudorotaxane [**3** \subset **4**]³⁺. Finally, reverse nucleophilic attack of pyridyl nitrogen onto the benzylic position in [**3** \subset **4**]³⁺ would create the [3]catenane 5^{4+} , regenerating the catalyst, the iodide ion, in the process.

Experiments have proven this hypothesis to be correct. Exposure of **2**·4PF₆ to two equivalents of bisparaphenylene[34]crown-10 (**4a**)¹³ and TBAI (30 mol%) in acetonitrile-*d*₃ (CD₃CN) for 72 h at 80 °C resulted in a deep red solution.¹⁴ After purification by preparative thin layer chromatography (TLC), the [3]catenane **5a**·4PF₆ (ref. 11) was obtained in 84% yield, as a red solid. An analogous experiment, beginning with **2** and dinaphtho[38]crown-10¹⁵ (**4b**) afforded the purple [3]catenane¹¹ **5b**·4PF₆ in 91% yield. Because of the (co-)conformational processes that occur in **5a**·4PF₆ and **5b**·4PF₆, their room-temperature ¹H NMR spectra are broadened and not easy to interpret, a situation that prevented us from monitoring the reaction progress directly. Nevertheless, after isolation, both catenanes were unambiguously characterised by the comparison of their ESI MS and low-temperature (−70 °C) ¹H NMR spectra with the previously reported spectra.

In conclusion, we have shown that the thermodynamically controlled syntheses of [3]catenanes proceeds in yields that are comparable⁷ with those obtained in the preparation of their smaller congeners. This undiminished efficiency, using thermodynamically controlled conditions for the preparation of

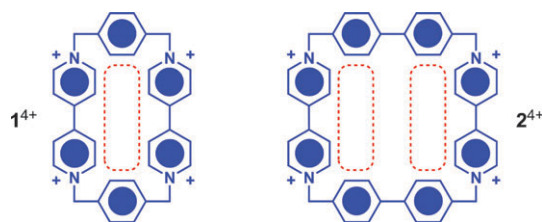
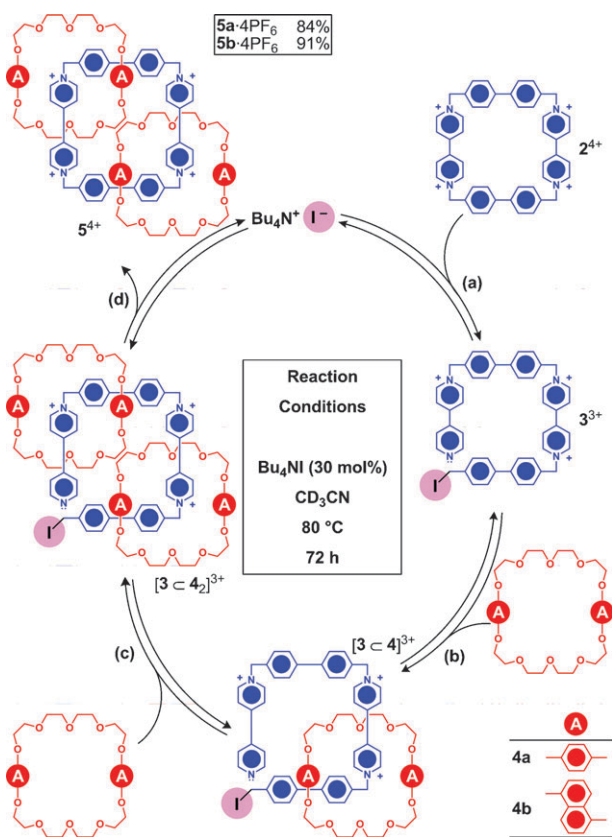


Fig. 1 Tetracationic cyclophanes used in the construction of donor–acceptor catenanes: cyclobis(paraquat-*p*-phenylene) (1^{4+}) and cyclobis(paraquat-4,4'-biphenylene) (2^{4+}). Red dashed rectangles indicate approximate binding sites for electron-rich arenes.

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Scheme 1 The proposed mechanism of the formation of [3]catenanes from 2^{4+} : (a) initial nucleophilic attack of iodide opens up 2^{4+} to give 3^{3+} ; (b) and (c) coordination of 3^{3+} with one and two molecules of **4**, respectively, gives first [2]pseudorotaxane [**3** < **4**] $^{3+}$ and then [3]pseudorotaxane [**3** < **4**₂] $^{3+}$; (d) reverse nucleophilic attack occurs in [**3** < **4**₂] $^{3+}$ expelling the iodide catalyst and finally forming the catenane 5^{4+} .

[3]catenanes, makes dynamic nucleophilic substitution a promising synthetic method for accessing polycatenanes of the donor-acceptor type, starting from cyclobis(paraquat-4,4'-biphenylene) and larger crown ether rings.

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 - The [2]pseudorotaxane [**3** < **4**] $^{3+}$ could, in principle, also undergo the reverse nucleophilic closure to give a [2]catenane. Nucleophilic opening of such a species back to [**3** < **4**] $^{3+}$ would then be followed by coordination of another molecule of **4** to give [**3** < **4**] $^{3+}$. Thermodynamic control of the reaction, however, makes this mechanistic intricacy synthetically inconsequential, since the [3]catenane remains more stable than the sum of a [2]catenane and an isolated crown ether.
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 - Experimental part.** All reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without purification. Compounds **2-4PF₆** (ref. 10), **4a** (ref. 13) and **4b** (ref. 15) were prepared according to literature procedures. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). Preparative thin layer chromatography (prep TLC) was performed on glass plates with a 2 mm thick layer of silica gel 60 F (E. Merck). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 (¹H: 500 MHz) spectrometer at 298 K and 203 K. Electrospray ionisation mass spectra were obtained on a Finnigan LCQ ion trap mass spectrometer. **Preparation of 5a-4PF₆**. TBAI (4.4 mg, 0.012 mmol) was added to a mixture of **4a** (43.0 mg, 0.08 mmol) and **2**.

4PF₆ (50.0 mg, 0.04 mmol) in CD₃CN (2 mL). The solution was held at 80 °C for 72 h, during which time deep red coloration developed. Purification by preparative TLC (eluent: MeOH–MeNO₂–NH₄PF₆ = 7 : 2 : 1) afforded **5a**·4PF₆ (78.0 mg, 84%). Its spectral data were identical to those reported in the literature (ref. 11). **Preparation of 5b**·4PF₆. TBAI (4.4 mg, 0.012 mol) was added to a mixture of **4b** (51.0 mg, 0.08 mmol) and **2**·4PF₆ (50.0 mg, 0.04 mmol) in CD₃CN (2 mL).

The mixture was then held at 80 °C for 72 h after which time a vivid purple solution was seen. Purification by prep TLC (eluent: MeOH–MeNO₂–NH₄PF₆ = 7 : 2 : 1) afforded **5b**·4PF₆ (92.0 mg, 91%). Its spectral data were identical to those reported in the literature (ref. 11).

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