

The Self Assembly of [2]- and [3]-Rotaxanes by Slippage

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Both a [2]- and a [3]-rotaxane have been synthesised in good yield by slippage at 55 °C in acetonitrile of bisparaphenylene-34-crown-10 over size-complementary stoppers on a dumbbell-shaped molecule containing two 4,4'-bipyridinium recognition sites.

The formation of large and structured molecular assemblies and supramolecular arrays by self-assembly—a paradigm that has been exploited to the point of perfection by Nature—has become^{1–3} a source of inspiration to synthetic chemists intent upon the construction of unnatural products.⁴ The rapid development of supramolecular chemistry⁵ during the last two decades has provided the climate for the utilisation of the noncovalent bond in template-directed syntheses.⁶ Catenanes and rotaxanes^{7–10} may be regarded¹¹ as model compounds for larger and more complicated molecular assemblies and supramolecular arrays.

In the previous communication,¹² an alternative approach to the traditional *threading*^{1,11,13–15} and/or *clipping*^{1,11,16–18} procedures employed to construct rotaxanes was described: it was *slippage*.¹⁹ This approach to rotaxane formation is based upon the size-complementarity between the macrocyclic polyether, bisparaphenylene-34-crown-10 (BPP34C10) containing two π -electron rich recognition sites and the stoppers comprised of suitably substituted tris(aryl) methyl groups, on a dumbbell-shaped molecule incorporating a 4,4'-bipyridinium dication as the matching π -electron deficient binding site. The slippage method has proved to be successful¹² in the thermally promoted self-assembly of a number of room temperature stable [2]rotaxanes containing *one* 4,4'-bipyridinium dication in the dumbbell encircled by *one* BPP34C10 ring. It follows that, by employing larger dumbbells with *n* dicationic binding sites in slippage experiments, it should be

possible to self-assemble, thermally, [*n*]rotaxanes, along with the corresponding [*n* – 1], [*n* – 2], *etc.* rotaxanes. Here, we describe (i) the syntheses of a [3]rotaxane 3·4PF₆ and the intermediate [2]rotaxane 2·4PF₆ from the dumbbell-shaped compound 1·4PF₆ and (ii) the characterisation[†] of the two

[†] 1·4PF₆: m.p. 280–285 °C decomp. C₁₁₆H₁₂₂N₄O₆P₄F₂₄ requires [M]⁺ 2246. Found (positive-ion FABMS) [M – PF₆]⁺ 2101. ¹H NMR: δ (300 MHz, CD₃CN): 8.93 (4H, d, *J* 6.5 Hz), 8.91 (4H, d, *J* 6.5 Hz), 8.36 (4H, d, *J* 6.5 Hz), 8.32 (4H, d, *J* 6.5 Hz), 7.58 (4H, s), 7.45 (4H, d, *J* 8.5 Hz), 7.09–7.35 (30H, m), 7.03 (4H, d, *J* 8.5 Hz), 6.10 (4H, d, *J* 9 Hz), 5.83 (4H, s), 5.73 (4H, s), 4.11–4.16 (4H, m), 4.05–4.10 (4H, m), 3.78–3.88 (8H, m), 1.28 (36H, s). ¹³C NMR: δ (CD₃CN, 75 MHz): 161.5, 157.9, 151.8, 149.8, 148.7, 147.6, 146.8, 146.5, 145.6, 140.8, 135.5, 133.0, 132.5, 131.8, 131.6, 131.5, 128.7, 128.5, 127.0, 125.7, 125.5, 116.7, 114.6, 70.7, 70.4, 68.9, 68.6, 65.6, 65.2, 64.6, 35.1, 31.8.

2·4PF₆: m.p. 140–145 °C decomp. C₁₄₄H₁₆₂N₄O₁₆P₄F₂₄ requires [M]⁺ 2782. Found (positive ion FABMS) [M – PF₆]⁺ 2638. ¹H NMR: δ (300 MHz, CD₃CN): 8.93 (4H, d, *J* 6.5 Hz), 8.87 (4H, d, *J* 6.5 Hz), 8.07 (4H, d, *J* 6.5 Hz), 8.01 (4H, d, *J* 6.5 Hz), 7.71 (4H, s), 7.53 (4H, d, *J* 8.5 Hz), 7.02–7.33 (34H, m), 6.79 (4H, d, *J* 9 Hz), 5.98 (8H, s), 5.87 (4H, s), 5.75 (4H, s), 4.11–4.17 (4H, m), 4.04–4.10 (4H, m), 3.78–3.86 (8H, m), 3.69 (16H, bs), 3.60–3.66 (8H, m), 3.48–3.54 (8H, m), 1.28 (36H, s). ¹³C NMR: δ (CD₃CN, 75 MHz): 161.2, 157.7, 153.1, 149.6, 148.6, 147.5, 146.8, 146.6, 146.3, 145.4, 140.6, 135.7, 132.8, 132.5, 131.6, 131.5, 131.3, 128.6, 127.4, 127.2, 126.8, 125.5, 116.6, 115.7, 114.4, 71.4, 71.2, 70.7, 70.5, 70.3, 68.8, 68.5, 68.4, 65.2, 64.9, 64.4, 35.0, 31.6.

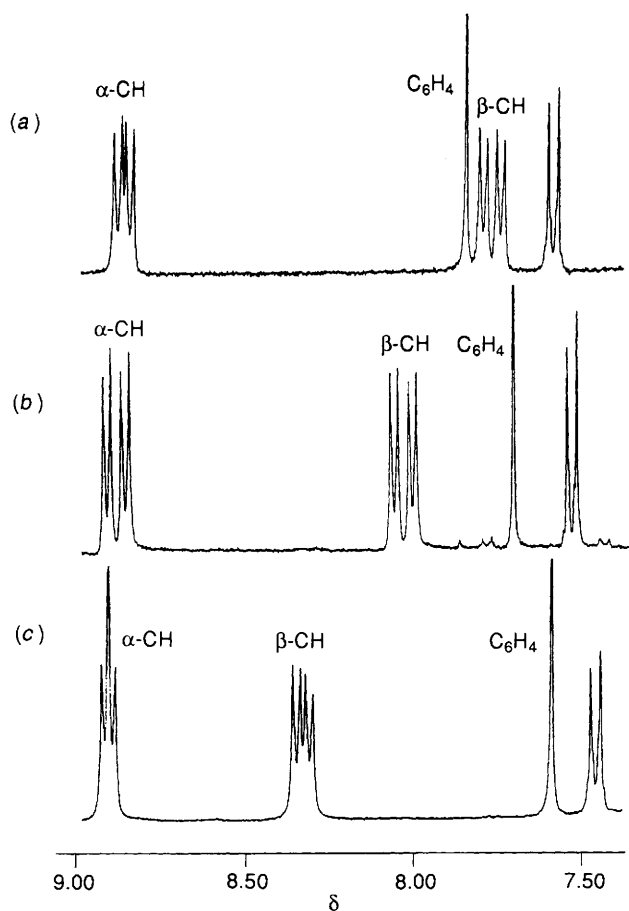


Fig. 1 Partial 300 MHz ^1H NMR spectra of (a) $3\cdot 4\text{PF}_6$, (b) $2\cdot 4\text{PF}_6$ and (c) $1\cdot 4\text{PF}_6$. The labels $\alpha\text{-CH}$ and $\beta\text{-CH}$ refer to protons α and β to nitrogen in 4,4'-bipyridinium units within $1\cdot 4\text{PF}_6$, $2\cdot 4\text{PF}_6$, and $3\cdot 4\text{PF}_6$. The label C_6H_4 refers to the *p*-xylyl residue which connects the 4,4'-bipyridinium dication in $1\cdot 4\text{PF}_6$, $2\cdot 4\text{PF}_6$, and $3\cdot 4\text{PF}_6$.

rotaxanes by fast atom bombardment mass spectrometry (FABMS) and ^1H NMR spectroscopy.

The dumbbell-shaped compound $1\cdot 4\text{PF}_6$ was prepared (Scheme 1) in 44% yield from reaction of 1,1'-[1,4-phenylenebis(methylene)]bis-4-pyridylpyridinium bis(hexafluorophosphate)¹¹ with 2.5 equiv. of the appropriate benzylic halide¹² in refluxing acetonitrile for 3 days. Heating $1\cdot 4\text{PF}_6$ with 4.0 equiv. of BPP34C10 in acetonitrile solution at 55 °C for 10 days led to the isolation (see below) of the [2]rotaxane $2\cdot 4\text{PF}_6$ and the [3]rotaxane $3\cdot 4\text{PF}_6$ in 31 and 8% yield, respectively. The proportions of the rotaxanes obtained can be varied and the efficiency of the slippage process influenced by increasing the concentration of the BPP34C10 present in the reaction mixture. Thus, the yields of $2\cdot 4\text{PF}_6$ and $3\cdot 4\text{PF}_6$ were 20 and 55%, respectively, when 10 equiv. of the crown ether were employed under the same conditions. At room temperature,

$3\cdot 4\text{PF}_6$: m.p. 150–153 °C decomp. $\text{C}_{172}\text{H}_{202}\text{N}_4\text{O}_{26}\text{P}_4\text{F}_{24}$ requires $[M]^+$ 3318. Found (positive ion FABMS) $[M - 2\text{PF}_6]^+$ 3028. ^1H NMR δ (CD_3CN , 400 MHz): 8.90 (4H, d, J 6.5 Hz), 8.86 (4H, d, J 6.5 Hz), 7.86 (4H, s), 7.81 (4H, d, J 6.5 Hz), 7.76 (4H, d, J 6.5 Hz), 7.60 (4H, d, J 8.5 Hz), 7.03–7.33 (34H, m), 6.78 (4H, d, J 9 Hz), 5.97 (16H, s), 5.96 (4H, s), 5.81 (4H, s), 4.11–4.17 (4H, m), 4.04–4.10 (4H, m), 3.77–3.86 (8H, m), 3.68 (32H, bs), 3.61–3.67 (16H, m), 3.47–3.55 (16H, m), 1.28 (36H, s). ^{13}C NMR: δ (CD_3CN , 75 MHz): 161.2, 157.7, 153.0, 149.6, 148.6, 147.4, 146.8, 146.6, 146.3, 145.4, 140.6, 135.8, 132.8, 132.6, 131.8, 131.6, 131.3, 128.6, 126.8, 126.2, 126.0, 125.5, 116.4, 115.7, 114.4, 71.4, 71.2, 70.7, 70.5, 70.3, 68.8, 68.5, 68.4, 65.0, 64.7, 64.4, 35.0, 31.6.

Table 1 Kinetic and thermodynamic parameters for the degenerate site exchange process occurring in $2\cdot 4\text{PF}_6$

Probe protons	$\Delta\nu/\text{Hz}$	k_c/s^{-1a}	T_c/K^b	$\Delta G^\ddagger/\text{kcal mol}^{-1c}$
$\alpha\text{-CH}$	152	337.6	214.6	9.9
$\beta\text{-CH}$	112	248.8	214.6	10.0

^a Calculated from the approximate expression, $k_c = \pi(\Delta\nu)/2^{1/2}$.

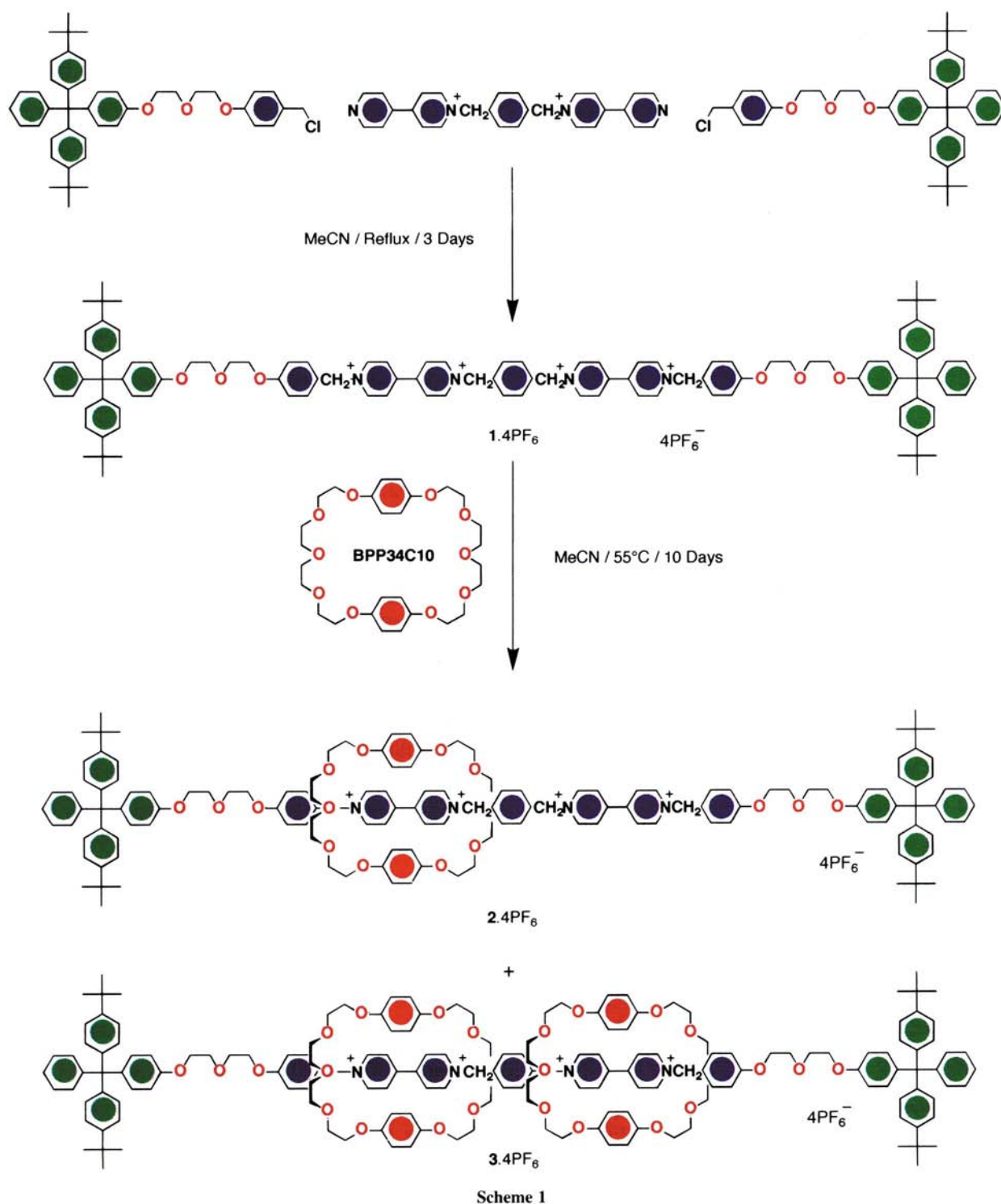
^b Temperature of the spectrometer probe at coalescence measured using an electronic thermometer. ^c Calculated using the Eyring equation.

both rotaxanes are stable compounds. They were isolated by chromatography (SiO_2 : MeOH: CH_2Cl_2 : MeNO₂: 2 mol dm⁻³ NH_4Cl 70: 16: 11: 3) and characterised by FABMS in the first instance. The FABMS[‡] of $2\cdot 4\text{PF}_6$ reveals peaks at m/z 2637, 2492 and 2347 corresponding to the loss of one, two and three hexafluorophosphate counterions, respectively, from the intact [2]rotaxane. In addition, a peak is observed at m/z 2101 corresponding to the loss of the BPP34C10 macrocycle and one counterion from the original [2]rotaxane. The FABMS of $3\cdot 4\text{PF}_6$ reveals a peak at m/z 3028 corresponding to the loss of two hexafluorophosphate counterions from the intact [3]rotaxane. In addition, peaks are also observed at m/z 2637, 2492 and 2347 corresponding to the loss of one, two and three hexafluorophosphate counterions, respectively, from the [2]rotaxane arising from the loss of one of the BPP34C10 macrocycles from the [3]rotaxane.

The ^1H NMR spectrum (Fig. 1) of $3\cdot 4\text{PF}_6$ in CD_3COCD_3 solution at room temperature reveals that the incorporation of two BPP34C10 macrocycles has a profound effect on the resonances for the protons on the dumbbell shaped component of the [3]rotaxane. In addition to small upfield shifts ($\Delta\delta$ -0.03 and -0.05 ppm) of the resonances for the $\alpha\text{-CH}$ protons, there are dramatic upfield shifts ($\Delta\delta$ -0.50 and -0.51 ppm) observed for the $\beta\text{-CH}$ resonances and a dramatic downfield shift ($\Delta\delta$ +0.28 ppm) of the resonance for the central C_6H_4 unit of the dumbbell. By contrast, the chemical shift changes observed for the corresponding resonances in the ^1H NMR spectrum (Fig. 1) of the [2]rotaxane $2\cdot 4\text{PF}_6$ in CD_3COCD_3 solution at room temperature are somewhat smaller. This observation reflects the fact that the one BPP34C10 macrocycle is moving rapidly on the ^1H NMR timescale between the two equivalent 4,4'-bipyridinium dicationic sites within the dumbbell component. On cooling the CD_3COCD_3 solution of the [2]rotaxane $2\cdot 4\text{PF}_6$ down to 198 K, the degenerate site exchange process becomes slow on the ^1H NMR timescale. This behaviour is demonstrated by the appearance of four signals for both the protons α to nitrogen and the protons β to nitrogen in the dumbbell component. The coalescence method²⁰ was used to derive (Table 1) a free energy of activation (ΔG^\ddagger) of ca. 10 kcal mol⁻¹ (1 cal = 4.184 J) for the degenerate site exchange process associated with the molecular shuttling action.

The self-assembly of the [3]rotaxane in good yield by slippage illustrates the potential of this method in the synthesis of oligo- and poly-rotaxanes.²¹ The principle of size-complementarity¹² between the rings and stoppers of [*n*]rotaxanes in combination with stabilising noncovalent bonding interac-

[‡] FABMS was carried out on a Kratos MS80RF mass spectrometer (accelerating voltage, 3 kV; resolution 1000) coupled to a DS90 data system. The atom gun was an adapted saddle field source (Ion Tech Ltd.) operated at ca. 7 keV with a tube current of ca. 2 mA. Krypton was used to provide a primary beam of atoms. The samples were dissolved in a small volume of 3-nitrobenzyl alcohol, which had been previously coated on to a stainless steel probe tip. Spectra were recorded in the positive-ion mode at a scan speed of 30 s per decade.



tions between the dumbbell and ring components opens up yet another avenue for the construction of novel molecular architectures and new advanced materials.

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