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Formation of a hetero[3]rotaxane by a dynamic component-swapping strategy

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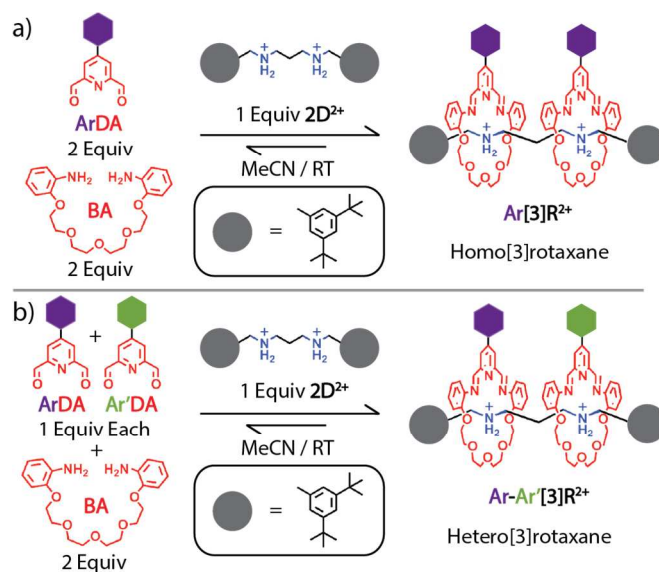
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Acid-catalysed scrambling of the mechanically interlocked components between two different homo[3]rotaxanes, constituted of dumbbells containing two secondary dialkylammonium ion recognition sites for two [24]crown-8 rings, each containing a couple of imine bonds, affords a statistical mixture of a hetero[3]rotaxane along with the two homo[3]rotaxanes, indicating that neither selectivity nor cooperativity is operating during the assembly process.

If mechanically interlocked molecules¹, such as rotaxanes, are going to find applications outside the sanctuary of the research laboratory, then their preparation has to begin with inexpensive starting materials and their production has to be highly efficient. Dynamic covalent chemistry² (DCC) provides the platform from which it is possible to start meeting these two criteria. One³ of the most efficient ways of synthesising a [2]rotaxane is to template⁴ the clipping⁵ of a [24]crown-8 ring, formed from the reversible condensation of 2,6-pyridine dicarboxaldehyde and tetraethylene glycol bis(2-aminophenyl)ether, around a secondary dialkylammonium ion ($-\text{NH}_2^+$) positioned in the middle of a preformed dumbbell. The reaction, which is all but complete (quantitative) in acetonitrile at room temperature inside five minutes, has been extended to the template-directed synthesis⁴ of multiply interlocked rotaxanes⁶, as well as to the use of other diformyl derivatives.⁵ Recently, we have reported⁷ the dynamic assembly of two series of oligorotaxanes in which repeating $-\text{NH}_2^+$ -cationic centres are separated along the rod sections of dumbbells by either (i) paraxylylene^{8,9} ($-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2-$) or (ii) trimethylene¹⁰ ($-\text{CH}_2\text{CH}_2\text{CH}_2-$) spacers. In the case of the latter, the spacing of approximately 3.5 Å between the recognition sites within the ($-\text{CH}_2\text{NH}_2^+\text{CH}_2\text{CH}_2-$) repeating unit allowing for the incorporation of π - π stacking interactions between the aromatic residues on contiguous rings, leading to positive cooperativity being observed⁹ in [n]rotaxanes where $n = 4$ and 5 and most

likely in the higher homologues where $n = 8, 12, 16$ and 20. The ordered cofacial arrangement of the rings along the dumbbells as a result of cumulative π - π stacking interactions¹¹ has, not only allowed us to observe emergent rigid-rod properties, but has also presented us with the opportunity to investigate π -orbital communication along the length of appropriately designed oligorotaxanes.¹² Here, we describe (i) the template-directed synthesis⁴ (Scheme 1) and characterisation, both (ii) in solution and (iii) in the solid state, of two homo[3]rotaxanes — one carrying aromatic donors (D) and the other acceptors (A) on their two ring components — which were then employed successfully



Scheme 1 a) Template-directed synthesis of $\text{Ar}[3]\text{R}^{2+}$ by the direct mixing of 2D^{2+} with ArDA (purple) and BA . b) Proposed assembly of $\text{Ar-Ar}'[3]\text{R}^{2+}$ by the direct mixing of 2D^{2+} with ArDA (purple) and $\text{Ar}'\text{DA}$ (green), and BA .

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(iv) in an acid-catalysed, thermodynamically controlled scrambling of the D and A rings to afford a hetero[3]rotaxane in a statistical mixture with the two parent homo[3]rotaxanes, which (v) offers advantages over simply mixing (Scheme 1b) stoichiometric amounts of the acyclic rotaxane precursors with a view to forming a hetero[3]rotaxane directly.

The 4-methoxyphenyl- (**MDA**) and 3,5-difluorophenyl- (**FDA**) substituted pyridine dialdehydes were chosen (ESI[†]) as precursors of the D and A rings, respectively. The phenyl-substituted pyridine dialdehyde (**HDA**) was also available (ESI[†]) for comparison studies. The three homo[3]rotaxanes **H[3]R²⁺**, **M[3]R²⁺** and **F[3]R²⁺** were prepared (Scheme 1a) using standard procedures, starting from **HDA**, **MDA**, and **FDA** (all 2 equiv), respectively, the dumbbell **2D²⁺** (1 equiv) and bis(2-aminophenyl)tetraethylene glycol (**BA**, 2 equiv) in CD₃CN (8.0 mM) at room temperature. The crude ¹H NMR spectra of the reaction mixtures, recorded after 5 min, revealed near-quantitative conversion of the starting materials to the respective homo[3]rotaxanes, **H[3]R²⁺**, **M[3]R²⁺** and **F[3]R²⁺**, as evidenced by (i) the complete consumption of **BA** and the disappearance of the aldehyde resonance at *ca.* 10.2 ppm and (ii) the shift of the broad signal for the NH₂⁺ protons from δ 7.0 to 9.5 ppm, indicating their encirclement by the crown ether rings. Single crystals of **M[3]R•2PF₆** and **F[3]R•2PF₆**, suitable for X-ray analysis, were grown by diffusing *i*Pr₂O into MeCN solutions. The solid-state structures¹³ (Fig. 1) of both homo[3]rotaxanes show

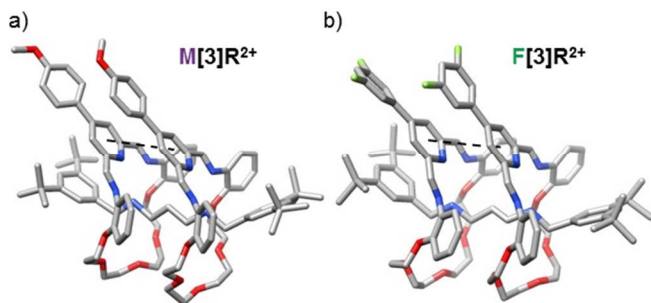


Fig. 1 Tubular representations of the solid-state structures of a) **M[3]R²⁺** and b) **F[3]R²⁺** showing the centroid-to-centroid distances of 4.6 and 3.8 Å, respectively, between the pyridyl units.

aromatic π - π stacking interactions between the two rings with averaged centroid-to-plane distances between the two pyridine units of 3.4 and 3.5 Å, respectively, for **M[3]R²⁺** and **F[3]R²⁺**. The ¹H NMR spectroscopic data (ESI[†]) reveals that an attempt to prepare the hetero[3]rotaxane **M-F[3]R²⁺** in CD₃CN (8.0 mM) from **2D²⁺** (1 equiv), **BA** (2 equiv), **MDA** (1 equiv) and **FDA** (1 equiv) resulted in the formation of a complex mixture of products. Product selectivity improved when the reaction was repeated at lower concentration (3.0 mM), as observed by ¹H NMR spectroscopy (Fig 2), as well as in the presence (Fig S21) of a catalytic amount of HPF₆. It became increasingly difficult, however, to control the molar ratios of the starting materials at this lower concentration. More importantly, byproducts were observed, both in solution and in the form of precipitates—presumably kinetically trapped oligomers—resulting in a mass loss of *ca.* 34%. This situation encouraged us to focus on an alternative preparation of the hetero[3]rotaxane by subjecting an equimolar mixture of the two homo[3]rotaxanes to dynamic exchange, exploiting all the attributes of DCC. By adopting this strategy, we impose (i) precise control over the component stoichiometry, (ii) minimize the concentration of free aldehyde and amine intermediates at any giving time, and (iii) avoid the irreversible loss of viable components for hetero[3]rotaxane formation.

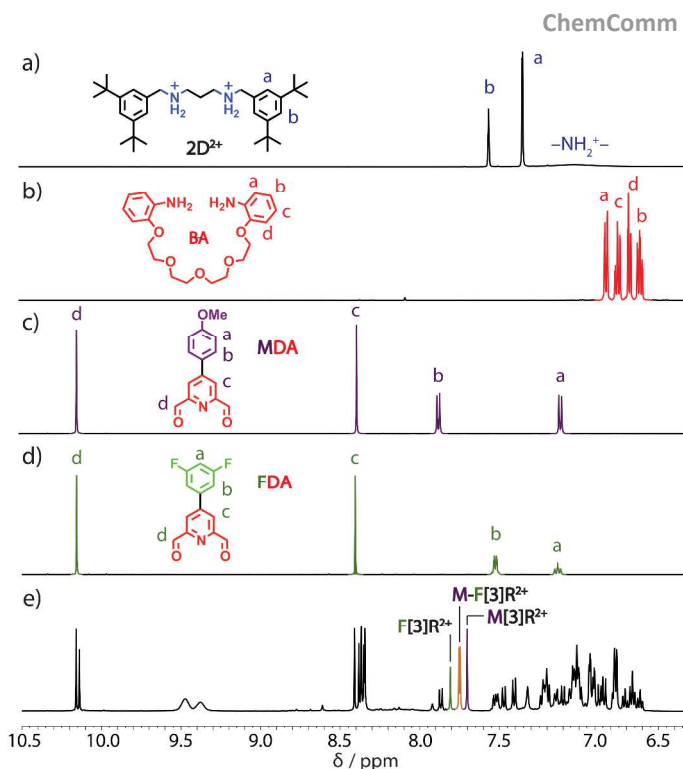
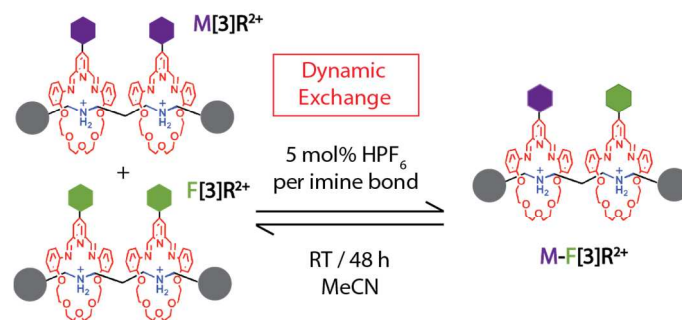


Fig. 2 Partial ¹H NMR spectra (500 MHz, CD₃CN, 298 K) of a) **2D²⁺** b) **BA** c) **MDA** and d) **FDA**. e) Products of the condensation of 2 equiv of **BA** with 1 equiv each of **2D²⁺**, **MDA** and **FDA** in CD₃CN at 298 K at 3.0 mM.

Mixing **M[3]R•2PF₆** and **F[3]R•2PF₆** in a 1:1 molar ratio in CD₃CN (3.0 mM) at room temperature¹⁴ in the presence of HPF₆ (5 mol% per imine bond) facilitates slow imine exchange over 48 h and leads (Scheme 2) to the formation of the hetero[3]rotaxane **M-F[3]R•2PF₆**. This strategy resulted in exchange to form **M-F[3]R²⁺** in equilibrium with **M[3]R²⁺** and **F[3]R²⁺**, as indicated by ¹H NMR spectroscopy (Fig. 3) and mass spectrometry where three peaks at *m/z* 821.4757, 827.4466, and 824.4614, corresponding to **M[3]R²⁺**, **F[3]R²⁺** and **M-F[3]R²⁺**, respectively, were identified in the high resolution electrospray ionisation (HR-ESI) mass spectrum. See Fig. S30 in the ESI[†]. Similar results were obtained on mixing **H[3]R•2PF₆** and **M[3]R•2PF₆** to give **H-M[3]R•2PF₆**, and **H[3]R•2PF₆** and **F[3]R•2PF₆** to give **H-F[3]R•2PF₆**. See Figs. S31 and S32 in the ESI[†]. The ¹H NMR spectrum (Fig. 3b) of the equilibrated mixture obtained by this approach revealed two sets of signals associated with **M[3]R²⁺** and **F[3]R²⁺**, in addition to the emergence of an additional set of resonances arising from **M-F[3]R²⁺**. In particular, in the region of chemical shift from 7.5 to 8.0



Scheme 2 Dynamic component-swapping strategy. The acid-catalysed equilibration of the two homo[3]rotaxanes **M[3]R²⁺** and **F[3]R²⁺** gives rise to hetero[3]rotaxane **M-F[3]R²⁺**.

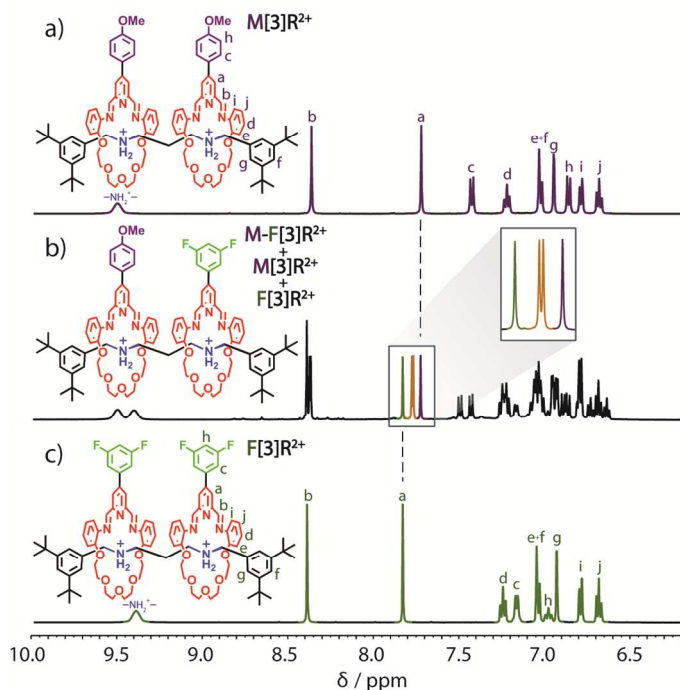


Fig. 3 Partial ¹H NMR spectra (500 MHz, CD₃CN, 298 K) of a) **M[3]R²⁺**, b) an equilibrated mixture of **M[3]R²⁺** and **F[3]R²⁺** by dynamic component-swapping, revealing the presence of **M-F[3]R²⁺** (orange) and c) **F[3]R²⁺**.

ppm, four equal intensity signals were observed at 7.70, 7.75, 7.76 and 7.81 ppm for the pyridyl protons present in **M[3]R²⁺**, **M-F[3]R²⁺** (middle two resonances) and **F[3]R²⁺**, respectively. The two peaks at 7.75 and 7.76 ppm, which occur approximately half way between those of **M[3]R²⁺** and **F[3]R²⁺**, can be assigned to **M-F[3]R²⁺**. Moreover, the fact that the ratio of **M[3]R²⁺**, **M-F[3]R²⁺** and **F[3]R²⁺** is 1:2:1, based on the integration of these pyridyl proton resonances, is consistent with statistical scrambling of the rings in a dynamic exchange process. In order to verify the constitution of the hetero[3]rotaxane, all the imine bonds were reduced³, locking the rings into place around the dumbbells and allowing the products to be isolated. Addition of a methanolic solution of NaBH₄ to the crude rotaxane mixture in CH₂Cl₂ at room temperature, followed by

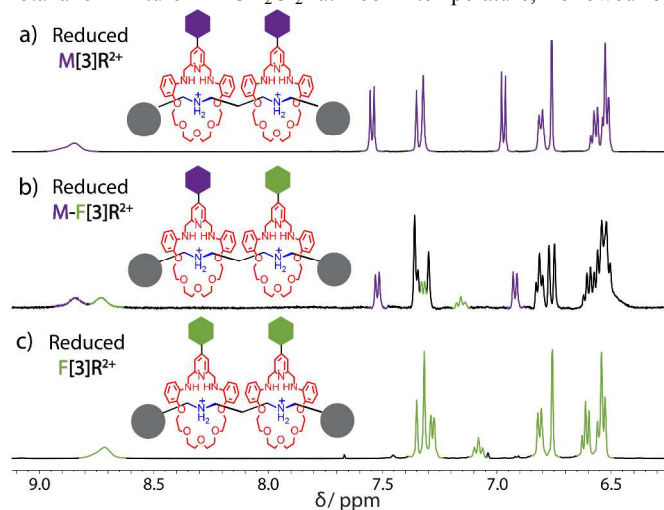


Fig. 4 Partial ¹H NMR spectra (500 MHz, CD₃CN, 298 K) of a) reduced **M[3]R²⁺**, b) reduced **M-F[3]R²⁺** (notable components of **M** and **F** rings are highlighted in purple and green, respectively), and c) reduced **F[3]R²⁺**.

purification by reverse-phase HPLC, resulted (Fig. 4) in the isolation of the reduced products.

In order to establish the statistical generality of the dynamic component-swapping strategy, we treated an equimolar mixture (3.0 mM) of **H[3]R•2PF₆** and its *d*₅-phenyl analogue **D[3]R•2PF₆** with a catalytic amount of HPF₆ (5 mol% per imine bond), only to discover that HR-ESI mass spectrometric analysis of the reaction mixture reveals a 1:2:1 ratio of peaks at *m/z* 791.9658, 794.4820 and 796.9972 for **H[3]R²⁺**, **H-D[3]R²⁺** and **D[3]R²⁺**, respectively. See Fig. S33 in the ESI†. In light of the outcome of this control experiment, it follows that the D and A rings in **M-F[3]R²⁺** are not experiencing any stabilising aromatic π-π stacking interactions, i.e., the rotaxane-to-rotaxane transformation is devoid of cooperativity and selectivity in both a kinetic and thermodynamic sense. It remains to be established if self-sorting, driven by favourable D–A interactions¹¹, occurs as the number of recognition sites and rings increases in extended hetero[n]rotaxanes. Such an outcome would be reminiscent⁹ of the emergence¹⁵ of π-mediated positive cooperativity in the analogous homo[n]rotaxanes.

We have demonstrated a modular synthetic strategy for the formation of mixed ring hetero[3]rotaxanes in a rotaxane-to-rotaxane transformation. The acid-catalysed dynamic component-swapping of two homo[3]rotaxanes, which was exemplified by the formation of four different hetero[3]rotaxanes, could become a versatile technique for the production of hetero[n]rotaxanes¹⁶ containing ordered, mixed ring components. Hetero[3]rotaxanes assembled in this manner may also be looked upon as a new emerging family of molecular torsional balances¹⁷ for investigating π–π stacking interactions between donating and accepting aromatic rings.

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