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

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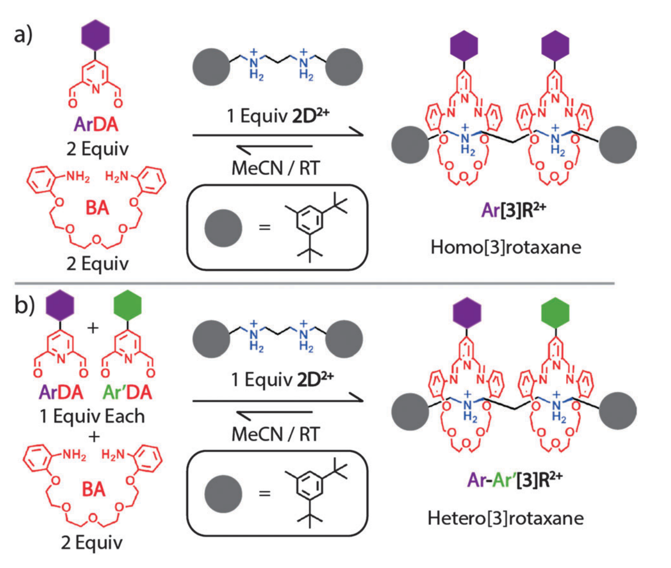
Eleanor A. Wilson, Nicolaas A. Vermeulen, Paul R. McGonigal, Alyssa-Jennifer Avestro, Amy A. Sarjeant, Charlotte L. Stern and J. Fraser Stoddart*

Acid-catalysed scrambling of the mechanically interlocked components between two different homo[3]rotaxanes, constituted of dumbbells containing two secondary dialkylammonium ion recognition sites encircled by 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 molecules,[1] 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 chemistry[2] (DCC) provides the platform from which it is possible to start meeting these two criteria. One[3] of the most efficient ways of synthesising a [2]rotaxane is to template[4] the clipping[5] 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 ($-NH_2^+-$) 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 synthesis[4] of multiply interlocked rotaxanes,[6] as well as to the use of other diformyl derivatives.[5] Recently, we have reported[7] the dynamic assembly of two series of oligorotaxanes in which repeating $-NH_2^+-$ cationic centres are separated along the rod sections of dumbbells by either (i) paraxylylene[8,9] ($-CH_2C_6H_4CH_2-$) or (ii) tris-methylene[10] ($-CH_2CH_2CH_2-$) spacers. In the case of the latter, the spacing of approximately 3.5 Å between the recognition sites within the ($-CH_2NH_2^+CH_2CH_2-$) repeating unit allowing for the incorporation of π–π stacking interactions between the aromatic residues on contiguous rings, leading to positive cooperativity being observed[9] 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 interactions[11] 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 synthesis[4] (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 (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



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

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA. E-mail: stoddart@northwestern.edu; Fax: +1 847 491 1009; Tel: +1 847 491 3793

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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 for the D and A rings, respectively. The phenyl-substituted pyridine dialdehyde (**HDA**) was also available (ESI†) for comparison studies. The three homo[3]rotaxanes $\mathbf{H[3]R^{2+}}$, $\mathbf{M[3]R^{2+}}$ and $\mathbf{F[3]R^{2+}}$ were prepared (Scheme 1a) using standard procedures, starting from **HDA**, **MDA**, and **FDA** (all 2 equiv.), respectively, the dumbbell $\mathbf{2D^{2+}}$ (1 equiv.) and bis(2-aminophenyl)tetraethylene glycol (**BA**, 2 equiv.) in CD_3CN (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, $\mathbf{H[3]R^{2+}}$, $\mathbf{M[3]R^{2+}}$ and $\mathbf{F[3]R^{2+}}$, 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 NH_2^+ protons from δ 7.0 to 9.5 ppm, indicating their encirclement by the crown ether rings. Single crystals of $\mathbf{M[3]R}\cdot 2PF_6$ and $\mathbf{F[3]R}\cdot 2PF_6$, suitable for X-ray analysis, were grown by diffusing iPr_2O into MeCN solutions. The solid-state structures[13] (Fig. 1) of both homo[3]rotaxanes show aromatic π–π stacking interactions between the two rings with average centroid-to-plane distances between the two pyridine units of 3.4 and 3.5 Å, respectively, for $\mathbf{M[3]R^{2+}}$ and $\mathbf{F[3]R^{2+}}$. The ^1H NMR spectroscopic data (ESI†) reveals that an attempt to prepare the hetero[3]rotaxane $\mathbf{M{-}F[3]R^{2+}}$ in CD_3CN (8.0 mM) from $\mathbf{2D^{2+}}$ (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, ESI†) of a catalytic amount of HPF_6. 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.

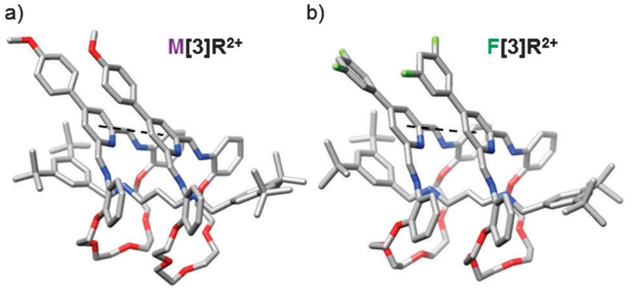


Fig. 1 Tubular representations of the solid-state structures of (a) $\mathbf{M[3]R^{2+}}$ and (b) $\mathbf{F[3]R^{2+}}$ showing the centroid-to-centroid distances of 4.6 and 3.8 Å, respectively, between the pyridyl units.

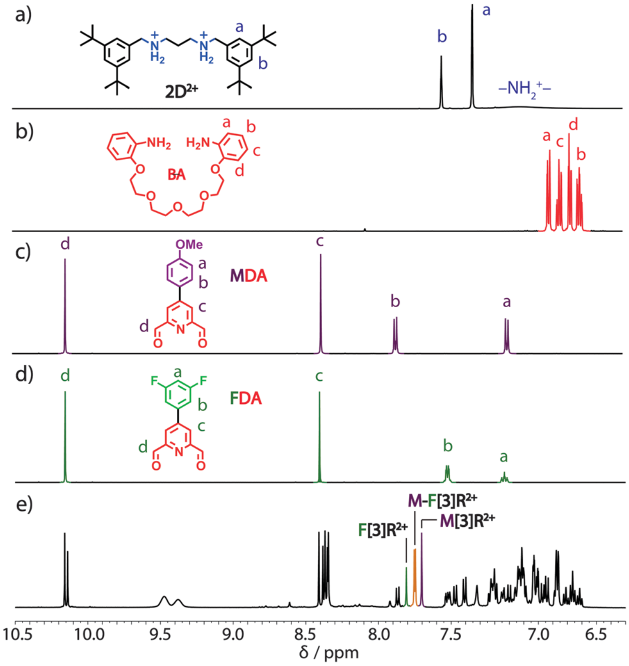
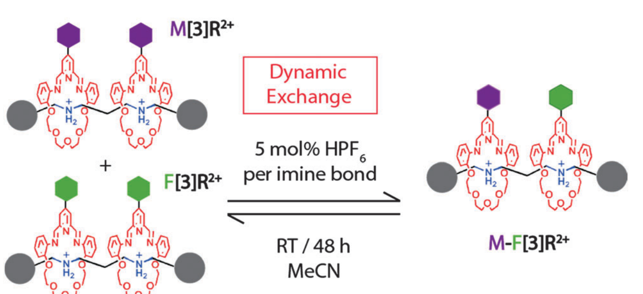


Fig. 2 Partial ^1H NMR spectra (500 MHz, CD_3CN, 298 K) of (a) $\mathbf{2D^{2+}}$ (b) **BA** (c) **MDA** and (d) **FDA**. (e) Products of the direct mixing of 2 equiv. of **BA** with 1 equiv. each of $\mathbf{2D^{2+}}$, **MDA** and **FDA** in CD_3CN at 298 K at 3.0 mM.

Mixing $\mathbf{M[3]R}\cdot 2PF_6$ and $\mathbf{F[3]R}\cdot 2PF_6$ in a 1 : 1 molar ratio in CD_3CN (3.0 mM) at room temperature[14] in the presence of HPF_6 (5 mol% per imine bond) facilitates slow imine exchange over 48 h and leads (Scheme 2) to the formation of the hetero[3]rotaxane $\mathbf{M{-}F[3]R}\cdot 2PF_6$. This strategy resulted in exchange to form $\mathbf{M{-}F[3]R^{2+}}$ in equilibrium with $\mathbf{M[3]R^{2+}}$ and $\mathbf{F[3]R^{2+}}$, 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 $\mathbf{M[3]R^{2+}}$, $\mathbf{F[3]R^{2+}}$ and $\mathbf{M{-}F[3]R^{2+}}$, 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 $\mathbf{H[3]R}\cdot 2PF_6$ and $\mathbf{M[3]R}\cdot$



Scheme 2 Dynamic component-swapping strategy. The acid-catalysed equilibration of the two homo[3]rotaxanes $\mathbf{M[3]R^{2+}}$ and $\mathbf{F[3]R^{2+}}$ gives rise to hetero[3]rotaxane $\mathbf{M{-}F[3]R^{2+}}$.

$2PF_6$ to give **H–M[3]R**·$2PF_6$, and **H[3]R**·$2PF_6$ and **F[3]R**·$2PF_6$ to give **H–F[3]R**·$2PF_6$. See Fig. S31 and S32 in the ESI.† The ^{1}H NMR spectrum (Fig. 3b) of the equilibrated mixture obtained by this approach revealed two sets of signals associated with **M[3]R^{2+}** and **F[3]R^{2+}**, in addition to the emergence of an additional set of resonances arising from **M–F[3]R^{2+}**. In particular, in the region of chemical shift from 7.5 to 8.0 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]R^{2+}**, **M–F[3]R^{2+}** (middle two resonances) and **F[3]R^{2+}**, respectively. The two peaks at 7.75 and 7.76 ppm, which occur approximately half way between those of **M[3]R^{2+}** and **F[3]R^{2+}**, can be assigned to **M–F[3]R^{2+}**. Moreover, the fact that the ratio of **M[3]R^{2+}**, **M–F[3]R^{2+}** and **F[3]R^{2+}** 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 reduced,[3] locking the rings into place around the dumbbells and allowing the products to be isolated. Addition of a methanolic solution of $NaBH_4$ to the crude rotaxane mixture in CH_2Cl_2 at room temperature, followed by 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**·$2PF_6$ and its d_5-phenyl analogue **D[3]R**·$2PF_6$ with a catalytic amount of HPF_6 (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]R^{2+}**, **H–D[3]R^{2+}** and **D[3]R^{2+}**, respectively. See Fig. S33 in the ESI.† In light of the outcome

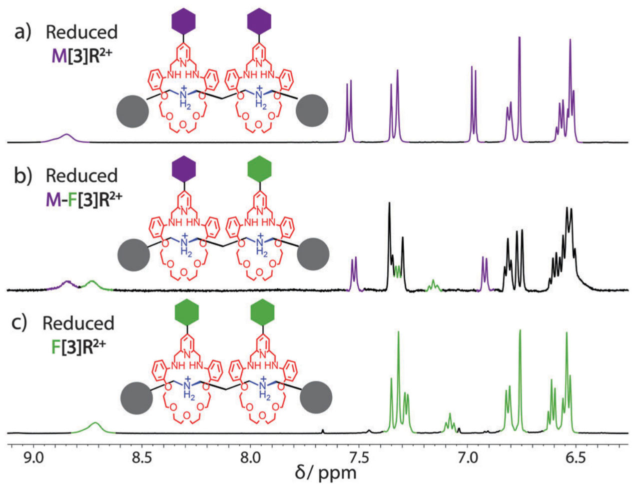


Fig. 4 Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of (a) reduced **M[3]R^{2+}**, (b) reduced **M–F[3]R^{2+}** (notable components of M and F rings are highlighted in purple and green, respectively), and (c) reduced **F[3]R^{2+}**.

of this control experiment, it follows that the D and A rings in **M–F[3]R^{2+}** 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 interactions,[11] occurs as the number of recognition sites and rings increases in extended hetero[*n*]rotaxanes. Such an outcome would be reminiscent[9] of the emergence[15] of π-mediated positive cooperativity[16] 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*]rotaxanes[17] 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 balances[18] for investigating π–π stacking interactions between donating and accepting aromatic rings.

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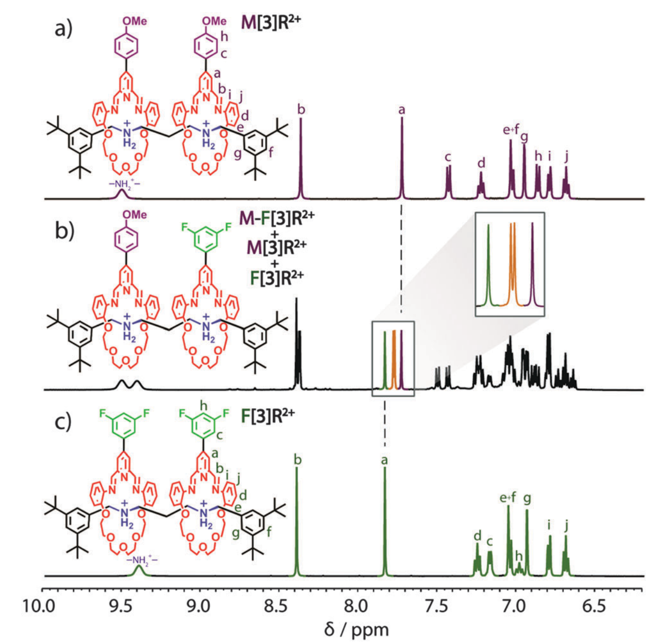

Fig. 3 Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of (a) **M[3]R^{2+}**, (b) an equilibrated mixture of **M[3]R^{2+}** (purple) and **F[3]R^{2+}** (green) by dynamic component-swapping, revealing the presence of **M–F[3]R^{2+}** (orange) and (c) **F[3]R^{2+}**.

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13 Crystal data for **M[3]R**$^{2+}$: $C_{106}H_{136}F_{12}N_9O_{12.5}P_2$, M_W = 2026.227 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 20.542(2) Å, b = 23.791(3) Å, c = 24.599(2) Å, β = 95.326(7)°, V = 10 773(2) Å^3, T = 100(2) K, Z = 4, ρ_{calc} = 1.249 g cm^{-3}, μ(Cu-Kα) = 1.066, F(000) = 4292. Independent measured reflections 20 131. R_1 = 0.1475, wR_2 = 0.4305 for 6275 independent observed reflections [$2\theta \leq 58.93°$, $I > 2\sigma(I)$]. Crystal data for **F[3]R**$^{2+}$: $C_{105}H_{127}F_{16}N_{11}O_{10}P_2$, M_W = 2069.153 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 17.5877(8) Å, b = 18.0515(9) Å, c = 19.1109(9) Å, β = 64.138(2)°, V = 5221.1(4) Å^3, T = 100(2) K, Z = 2, ρ_{calc} = 1.316 g cm^{-3}, μ(Cu-Kα) = 1.157, F(000) = 2176. Independent measured reflections 17 189. R_1 = 0.0922, wR_2 = 0.2715 for 14 403 independent observed reflections [$2\theta \leq 65.203°$, $I > 2\sigma(I)$]. CCDC 999555 (**M[3]R**$^{2+}$) and 999556 (**F[3]R**$^{2+}$) contain the supplementary crystallographic data for this paper.

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