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PAPER

A neutral redox-switchable [2]rotaxane†

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A limited range of redox-active, rotaxane-based, molecular switches exist, despite numerous potential applications for them as components of nanoscale devices. We have designed and synthesised a neutral, redox-active [2]rotaxane, which incorporates an electron-deficient pyromellitic diimide (PmI)-containing ring encircling two electron-rich recognition sites in the form of dioxynaphthalene (DNP) and tetrathiafulvalene (TTF) units positioned along the rod section of its dumbbell component. Molecular modeling using MacroModel guided the design of the mechanically interlocked molecular switch. The binding affinities in CH_2Cl_2 at 298 K between the free ring and two electron-rich guests—one ($K_a = 5.8 \times 10^2$ M^{-1}) containing a DNP unit and the other ($K_a = 6.3 \times 10^3$ M^{-1}) containing a TTF unit—are strong: the one order of magnitude difference in their affinities favouring the TTF unit suggested to us the feasibility of integrating these three building blocks into a bistable [2]rotaxane switch. The [2]rotaxane was obtained in 34% yield by relying on neutral donor–acceptor templation and a double copper-catalysed azide–alkyne cycloaddition (CuAAC). Cyclic voltammetry (CV) and spectroelectrochemistry (SEC) were employed to stimulate and observe switching by this neutral bistable rotaxane in solution at 298 K, while ^{1}H NMR spectroscopy was enlisted to investigate switching upon chemical oxidation. The neutral [2]rotaxane is a chemically robust and functional switch with potential for applications in device settings.

Introduction

During the past 15 years, switchable, mechanically interlocked molecules,[1] most notably bistable rotaxanes and catenanes, have been developed and incorporated into a range of different devices, including property-actuated and switching surfaces,[2] molecular switch tunnel junctions in molecular electronic devices,[3] and mechanised mesoporous silica nanoparticles[4] for drug delivery. The versatility and usefulness of these bistable mechanically interlocked molecules can be attributed to their unique architectures and characteristics, not to mention the fact that they respond to a wide variety of stimuli, such as metal ions[5] and light,[6] or changes in solvent,[7] pH,[8] or oxidation state,[9] producing large amplitude co-conformational changes which lead to functionality being expressed in device settings at the nanoscale level.

Scanning tunneling microscopy (STM) has become a powerful tool for investigating the mechanical[10] and electronic[11] properties of single molecules. More specifically, molecular switches are a source of fundamental interest and practical importance on account of the fact that they initiate, at the molecular scale, mechanical motions such as rotation and translocation. Such switches have already been studied on metallic surfaces, yet most of them have been photoactive and photochromic molecules, such as azobenzene and spirophane derivatives.[12] These photo-responsive molecules exhibit complex switching mechanisms that are often quenched on surfaces and so do not perform efficiently. By comparison, redox-responsive bistable [2]rotaxanes are of considerable potential importance, simply because their switching modes can be easily and precisely controlled, and—by employing electrochemical energy inputs—the production of waste products can be avoided.

Much early and subsequent work on redox-controlled rotaxanes features the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene)[13] ($CBPQT^{4+}$), which possesses a broad utility and extensive history that is largely a consequence of its affinity and discrimination for binding to TTF and dioxynaphthalene (DNP) units in bistable catenanes and rotaxanes.

Examples of these bistable molecules which have been probed on surfaces[14] under room temperature conditions by STM have exhibited switching thereupon. Not all such molecules, however, deposited on surfaces exhibit the expected switching behaviour.

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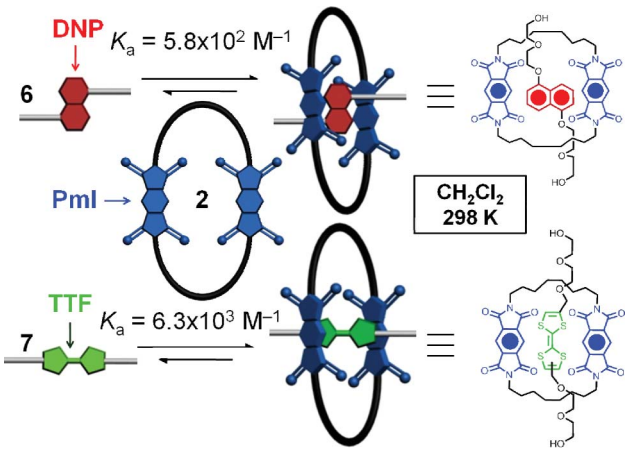


Fig. 1 Graphical representations of the PmI-containing macrocycle **2**, and the two guests, **6** and **7**—1,5-dioxynaphthalene and tetrathiafulvalene derivatives, respectively—and their corresponding complexes and structural formulae. The order of magnitude difference in their association constants, K_a, between **2** and the two guests, **6** and **7** forms the basis for the design of a redox-active bistable neutral [2]rotaxane.

One approach[15] to enhancing the occurrence of this phenomenon of surface switching is to perform low temperature experiments in the range 7–100 K under ultra-high vacuum (10^{-10} mbar), thus limiting the thermal unrest and diffusion of the molecules on the surface.

One limitation of this technique is the need to sublime molecules onto a surface after preparation of the substrate. Generally, neutral molecules are less prone to decomposition by heating and easier to sublime than charged ones: also, they come without the added complication of associated counterions.[16] We propose, therefore, to synthesise a neutral bistable rotaxane for probing by STM experiments in order to demonstrate more effectively the possibility of having redox-induced switching on surfaces. Neutral, electron-deficient rings,[17] including those containing pyromellitic diimide (PmI)[18] have been synthesised previously and investigated with a variety of potential applications in mind. There are, however, only a few examples of neutral electrochemically switchable [2]rotaxanes.[5b,9b,9c,19] One example,[9b] designed and synthesised by the Leigh group in Edinburgh, features a hydrogen bonding motif. In this [2]rotaxane, the position occupied by a tetraamide-containing ring can be switched from a succinamide station to a naphthlimide (NpI) one by a one-electron reduction of the NpI. Another example[5b,9c] resulting from a collaboration between our research group, while at the University of California, Los Angeles (UCLA) and the Sanders group in Cambridge, incorporates electron-deficient PmI and NpI stations in the dumbbell component of a [2]rotaxane: the ring component in this case was the π-electron donating 1,5-dinaphtho[38]crown-10 which can be switched from encircling the NpI to encircling the PmI station as a result of a one-electron reduction of the NpI station. A yet more recent example[19] of a neutral, electrochemically switchable [2]rotaxane incorporates TTF as the primary binding station, triazole as the secondary binding station and α-cyclodextrin as the ring component: the latter moves from the TTF station to the triazole on the oxidation of the former.

Herein, we report the synthesis of a neutral PmI-containing ring **2** (Fig. 1) and show that it is chemically robust‡ and binds DNP and TTF units in neutral molecules with high affinities. We have incorporated (Scheme 1) this new π-electron poor ring into a redox-active, bistable [2]rotaxane **1** comprised of a dumbbell component containing TTF and DNP units and investigated the switching behaviour of **1** in solution using cyclic voltammetry (CV), spectroelectrochemistry (SEC) at room temperature, as well as NMR spectroscopy.

Experimental section

General methods

All of the reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without further purification. Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} (E. Merck). Preparative thin layer chromatography was initiated on 20 cm × 20 cm silica gel 60 plates with a thickness of 2 mm (Analtech, 02015). Column chromatography was carried out on silica gel 60 F (Merck 9385, 40–63 μm). NMR Spectra were recorded on Bruker Avance 500 and 600 spectrometers with working frequencies of 500 and 600 MHz for ^{1}H nuclei and 125 and 150 MHz for ^{13}C nuclei, respectively. Chemical shifts are reported in parts per million relative to the signals corresponding to the residual non-deuterated solvents. All of the ^{13}C spectra were recorded with simultaneous decoupling of proton nuclei. Electrospray ionisation (ESI) mass spectrometry (MS) was carried out using an Agilent 6210 LC-TOF high-resolution (HR) mass spectrometer. Cyclic voltammetry (CV) experiments were performed on a Princeton Applied Research 263 A multipurpose instrument interfaced to a PC using a glassy carbon working electrode (0.071 cm^2, Cypress Systems). The electrode surface was polished routinely with a 0.05 μm^2 alumina/water slurry on a felt surface immediately before use. The counter electrode was a Pt coil, and the reference electrode was a saturated calomel electrode. The concentrations of the samples were 1 mM in 0.1 M electrolyte solution ($TBAPF_6$ in Me_2CO or CH_2Cl_2). Spectroelectrochemistry (SEC) experiments were carried out using a custom built optically-transparent thin-layer (OTTLE) cell with a 2 mm pathlength, using a Pt mesh working electrode, a Pt wire as the counter electrode and a Ag wire as a pseudoreference electrode. UV/Vis absorption spectra were recorded on a Varian Cary 300 spectrophotometer. Molecular modeling was performed using MacroModel (version 9.8; Schrödinger, LLC: Portland, OR, 2010).

Ring 2

A solution of 1,8-diaminooctane (1.74 g, 8.00 mmol) in DMF (330 mL) was prepared. A separate solution of 1,2,4,5-benzenetetracarboxylic anhydride (1.15 g, 8.00 mmol) and glacial acetic acid (30 mL) in DMF (300 mL) was also prepared. Both solutions were added simultaneously in 50 mL portions by slow syringe-pump addition to 500 mL of vigorously stirred DMF at

‡ The bistable [2]rotaxane described herein incorporates the same stations (DNP and TTF) in its dumbbell component that have often been used with $CBPQT^{4+}$ as the ring component. The neutrality of the present system could, we speculate, give rise to favourable switching properties in a device setting, while the chemical robustness of the components should allow for flexibility during synthesis and subsequent device fabrication.

110 °C. Each 50 mL portion was added over 1 h, with the addition of each reagent solution in its entirety requiring approximately 6.5 h. The DMF was evaporated, and the remaining light brown solid was suspended in CH_2Cl_2 (2 × 250 mL), sonicated, and filtered through a plug of Celite. After solvent removal, the crude residue was dissolved in a minimum amount of a 75 : 25 mixture of CH_2Cl_2 and hexafluoroisopropanol and purified by preparative thin layer chromatography (SiO_2; CH_2Cl_2:PhMe:*i*PrOH, 78.5 : 20 : 1.5) to give **2** as a white solid (157 mg, 6%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.05 (s, 4 H), 3.72 (t, J = 6.0 Hz, 8 H), 1.68–1.63 (m, 8 H), 1.33–1.30 (m, 8 H), 1.24–1.20 (m, 8 H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 166.6, 137.3, 117.7, 38.6, 28.4, 28.3, 25.9 ppm; HRMS (ESI): m/z calcd for $C_{36}H_{36}N_4O_8$: 652.2433; found: 653.2601 $[M + H]^+$.

Stopper precursor 4

4-(Bis(4-*tert*-butylphenyl)(4-ethyl-phenyl)methyl)phenol[20] (2.33 g, 4.61 mmol), K_2CO_3 (1.91 g, 13.8 mmol), 18-crown-6 (121 mg, 0.461 mmol), and propargyl bromide (1.65 g of an 80 wt% solution in PhMe, 13.8 mmol) were stirred in MeCN (47 mL) under reflux for 15 h. The solvent was evaporated, and the residue was suspended in CH_2Cl_2 (200 mL) and extracted with H_2O (3 × 200 mL) and brine (200 mL). The organic layer was dried (Na_2SO_4). The solution was evaporated onto silica gel, loaded onto a silica gel column, and then subjected to chromatography using 9 : 1 hexanes : EtOAc as eluent to obtain **4** (1.96 g, 83%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.2 (d, J = 8.5 Hz, 6 H), 7.17–7.08 (m, 8 H), 6.88–6.85 (d, J = 9.0 Hz, 2 H), 4.68 (d, J = 2.5 Hz, 2 H), 2.64 (q, J = 7.5 Hz, 2 H), 2.54 (t, J = 2.5, 1 H), 1.33 (s, 18 H), 1.25 (t, J = 7.5 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.5, 148.4, 144.5, 144.1, 141.5, 140.5, 132.3, 131.1, 130.7, 126.7, 124.1, 113.3, 78.8, 75.4, 63.2, 55.8, 34.3, 31.4, 28.3, 15.4 ppm; HRMS (APPI): m/z calcd for $C_{38}H_{42}O$: 514.3236; found: 514.3237 M^+.

Dumbbell 5

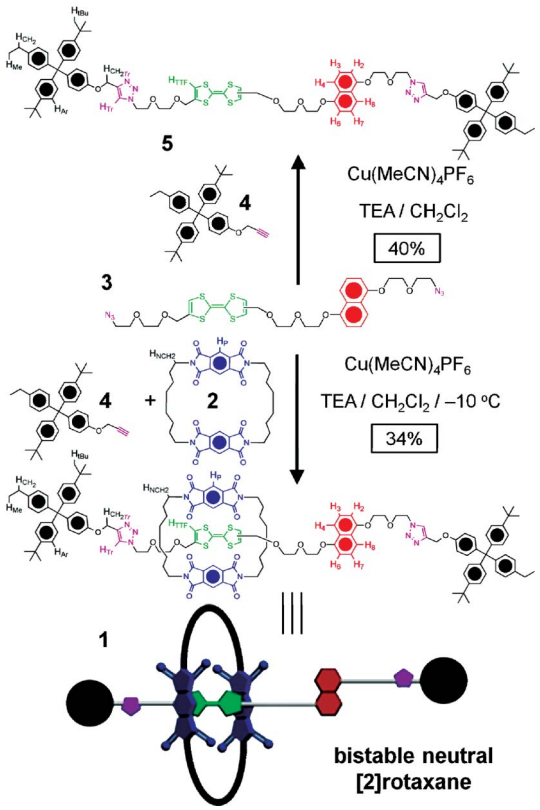
The TTF/DNP–containing diazide **3**[9d] (87.1 mg, 0.119 mmol), the stopper precursor **4** (129 mg, 0.238 mmol), and $Cu(MeCN)_4PF_6$ (44.4 mg, 0.119 mmol) were dissolved in CH_2Cl_2 (5 mL) and stirred at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and extracted with a concentrated aqueous EDTA solution (3 × 30 mL, pH 8), H_2O (1 × 30 mL) and brine (1 × 30 mL). The organic layer was dried (Na_2SO_4). After removal of solvent, the crude residue was dissolved in a minimum amount of CH_2Cl_2 and purified by preparative thin layer chromatography (SiO_2; CH_2Cl_2 : *i*PrOH, 98 : 2) to give **5** as a yellow solid (84 mg, 40%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.82–7.77 (m, 4 H), 7.32–7.27 (m, 2 H), 7.26 (d, J = 8.5 Hz, 8 H), 7.16–7.7.12 (m, 16 H), 6.86 (d, J = 9 Hz, 2 H), 6.81 (d, J = 7.5 Hz, 2 H), 6.78 (d, J = 9 Hz, 2 H), 6.17 (d, J = 3.5 Hz, 1 H), 6.12 (d, J = 13.5, 1 H), 5.12 (d, J = 6.0 Hz, 2 H), 4.95 (d, J = 3.0 Hz, 2 H), 4.24 (m, 6 H), 4.19 (d, J = 4.0 Hz, 2 H), 3.99 (t, J = 5. 0 Hz, 2 H), 3.94–3.91 (m, 4 H), 3.86–3.83 (m, 2 H), 3.74–3.71 (m, 2 H), 3.62–3.61 (m, 2 H), 3.60–3.57 (m, 2 H), 3.54–3.50 (m, 2 H), 2.61 (q, J = 7.5 Hz, 4 H), 1.29 (s, 36 H), 1.21 (t, J = 7.5 Hz, 6 H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 156.7, 156.6, 154.8, 154.6, 148.8, 145.2, 144.8, 144.1, 142.0, 140.5, 140.4, 135.0 (×2), 134.9, 134.8, 132.4, 132.3, 131.1. 130.8, 129.4, 128.6, 127.1, 127.0, 125.8, 125.6, 124.5, 124.5 (×2), 116.9, 116.8, 116.6 (×2), 114.9, 114.5, 113.8 (×2), 111.1, 110.5, 106.1, 106.0, 71.3, 70.8, 70.2 (×2), 70.1, 69.9, 69.8, 69.6, 68.5 (×2), 68.4, 68.1, 63.6, 62.2, 62.0, 50.8, 50.7, 34.6, 31.5, 31.4, 28.6, 25.6, 15.6 ppm; HRMS (ESI): m/z calcd for $C_{36}H_{36}N_4O_8$: 1748.8000; found: 1748.8004 $[M]^+$.

Rotaxane 1

The TTF/DNP–containing diazide **3** (59.5 mg, 0.0814 mmol), the macrocycle **2**, the alkyne-functionalized stopper **4** and TEA (1.1 µl, 0.00814 mmol) were dissolved in CH_2Cl_2 (8 mL) at room temperature. The temperature was lowered to –10 °C in a salty ice–water bath and stirred for 15 min. at which time $Cu(MeCN)_4PF_6$ (37.3 mg, 0.0814 mmol) was added. The solution was stirred at –10 °C for another 4 h, warmed to room temperature, diluted with CH_2Cl_2 (30 mL), and extracted with a concentrated aqueous EDTA solution (3 × 30 mL, pH 8), H_2O (1 × 30 mL), and brine (1 × 30 mL). The organic layer was dried (Na_2SO_4). After solvent removal, the crude residue was purified by preparative thin layer chromatography (SiO_2; CH_2Cl_2 : *i*PrOH, 98 : 2) to give **1** as a green solid (60 mg, 34%). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.90–7.88 (m, 2 H), 7.84–7.76 (m, 2 H), 7.61 (br s, 4 H), 7.43–7.30 (m, 2 H), 7.26 (d, J = 7.5 Hz, 8 H), 7.17–7.11 (m, 12 H), 7.10–7.16 (m, 4 H), 7.04–6.95 (m, 3 H), 6.89–6.77 (m, 5 H), 6.62–6.52 (m, 2 H), 6.02 (d, J = 16.1 Hz, 1 H), 5.93 (d, J = 8.16 Hz, 1 H), 5.13 (d, J = 8.1 Hz, 2 H), 5.02 (s, 2 H), 4.67–4.54 (m, 4 H), 4.30–3.20 (m, 4 H), 4.15 (s, 3 H), 4.11 (s, 1 H), 4.05–3.98 (m, 4 H), 3.96–3.89 (m, 4 H), 3.85–3.81 (m, 2 H), 3.69 (br s, 2 H), 3.65–3.56 (m, 12 H), 2.62 (m, 4 H), 1.69–1.60 (m, 8 H), 1.38 (br s, 8 H), 1.36–1.26 (m, 44 H), 1.25–1.18 (m, 6 H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ = 166.5, 166.4, 156.0 (×2), 153.7 (×2), 153.5, 153.4, 148.1, 144.5, 144.1, 143.4, 141.3, 139.8, 135.6, 134.7, 134.5, 134.4, 134.3, 131.7. 131.6, 130.4, 130.1, 126.6, 124.0, 116.5, 116.3, 115.3, 115.1, 113.2, 113.1 (×2), 105.2, 105.1, 105.0, 70.2, 69.5, 69.4 (×3), 69.2 (×2), 67.5, 67.4, 67.3, 67.2, 67.1, 62.9, 61.5, 61.3, 50.1 (×2), 38.1, 38.0, 33.9, 30.8, 28.5 (×2), 27.9, 26.0 (×2), 23.5, 19.4, 15.0, 13.0; HRMS (ESI): m/z calcd for $C_{36}H_{36}N_4O_8$: 2401.0532; found: 2401.0524 M^+.

Results and discussion

Prior to setting out to synthesize the bistable [2]rotaxane, we turned our attention towards modeling of the PmI-containing ring in order to provide insight into its potential to behave as a host as well as to accommodate the size of the stoppers needed to construct a [2]rotaxane. In the event, modeling studies using MacroModel led to the design of the ring **2**. Complementary steric fits with TTF and DNP guests were predicted for a ring, namely **2**, having oligomethylene linkers containing eight methylene groups between the two PmI moieties. Not only were similar PmI-containing rings with longer linkers expected to be too large for optimum binding, but they were also deemed too large to form rotaxanes incorporating the commonly used tetraarylmethane stoppers: pseudorotaxanes would be formed, rather than mechanically interlocked molecules, simply because large rings would slip over the tetraarylmethane stoppers. Rings with *para*-xylylene linkers, such as those present in $CBPQT^{4+}$, were also examined but afforded cavities that were too small to accommodate the TTF and DNP units in the rod section of the dumbbell. Also, without additional solubilizing groups such rigid cyclophanes would most likely be insoluble in most organic solvents because of their propensity to self-aggregate.



Scheme 1 Template-directed synthesis (arrow pointing down) of the bistable neutral [2]rotaxane **1** composed of the redox-active TTF and DNP recognition units along with a PmI-containing ring component. The synthesis (arrow pointing up) of the free dumbbell **5**.

The ring **2** was synthesised by relying on a one-step procedure already described in the literature by Lehn and coworkers[21] to prepare a similar NpI-containing ring. Briefly, DMF solutions of (i) pyromellitic dianhydride and acetic acid along with (ii) 1,8-octanediamine were added during 6.5 h employing a double syringe-pump addition to 500 mL of hot (110 °C) and vigorously stirred solvent. The pure ring **2** was isolated after preparative TLC as a white solid in 6% yield after work-up.

The binding of two guests—2,2′-[1,5-naphthalenediyl-bis(oxy-2,1-ethanediyloxy)]bisethanol[22] (**6**) and 2-[2-[[2-[4-[[2-(2-hydroxyethoxy)ethoxy]methyl]-1,3-dithiol-2-ylidene]-1,3-dithiol-4-yl]methoxy]ethoxy]ethanol[23] (**7**)—was measured by titration using UV/Vis spectroscopy in CH_2Cl_2. Binding studies in the more commonly used MeCN or Me_2CO were not possible because **2** is insoluble in these solvents. The association constants in CH_2Cl_2 (K_a values) were found (Fig. 1) to be 5.8×10^2 M^{-1} and 6.3×10^3 M^{-1} for **6** and **7**, forming yellow and green coloured solutions, respectively. This one order of magnitude difference in binding affinity suggested the feasibility of designing a rotaxane switch with TTF and DNP stations in which the ring would encircle§ the TTF station in the ground-state preferentially.[24]

§ For comparison, the association constants for complexes of $CBPQT^{4+}$ with **6** and **7** are 3.8×10^5 M^{-1} and 3.6×10^4 M^{-1}, respectively, albeit in MeCN. This difference of approximately one order of magnitude manifests itself in the ground state of analogous rotaxanes as a 9 : 1 distribution of $CBPQT^{4+}$ between TTF and DNP recognition sites, respectively. See ref. 24.

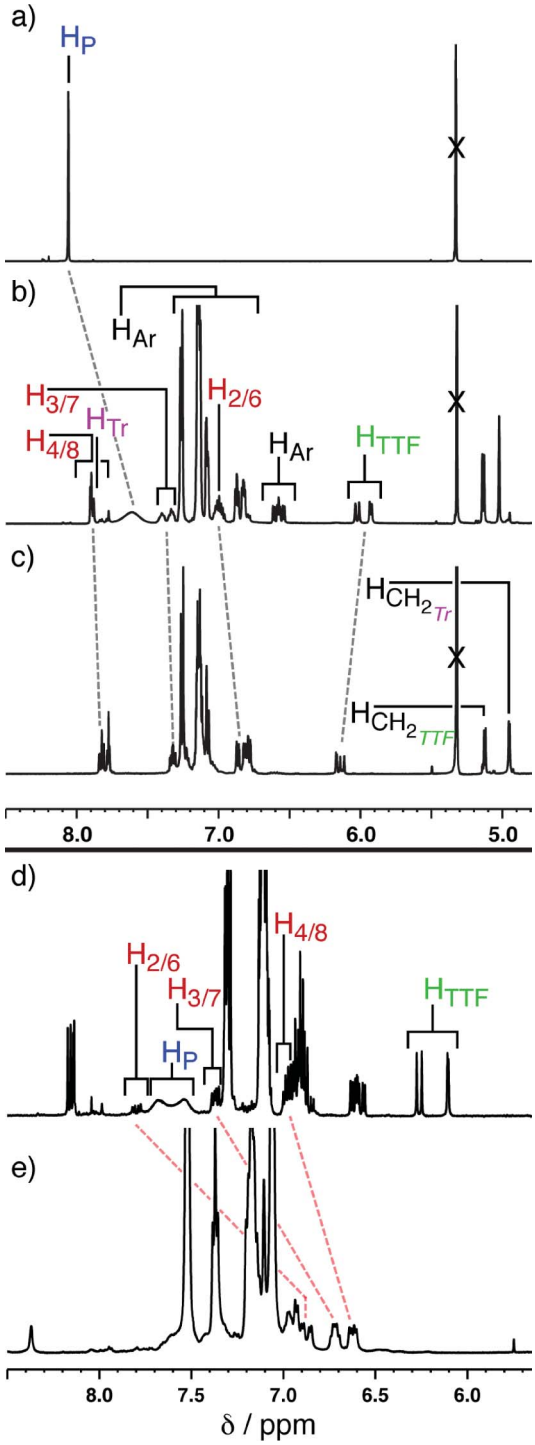


Fig. 2 ^1H NMR spectra (600 MHz, CD_2Cl_2, room temperature) of (a) the ring **2**, (b) the neutral, bistable [2]rotaxane **1**, (c) the free dumbbell **5**, and the [2]rotaxane **1** (d) in CD_3COCD_3 at 233 K and (e) in CD_3COCD_3 at 233 K, following the addition of 3 equiv of tris-4-bromophenyliminium hexachloroantimonate. Gray dashed lines (top) indicate key chemical shift changes observed in the rotaxane with reference to the ring on its own and the free dumbbell. Red dashed lines (bottom) show the key chemical shift changes observed for protons on the DNP unit when the ring component moves away from the TTF unit upon its oxidation to encircle the DNP unit. Proton annotations can be found in Scheme 1.

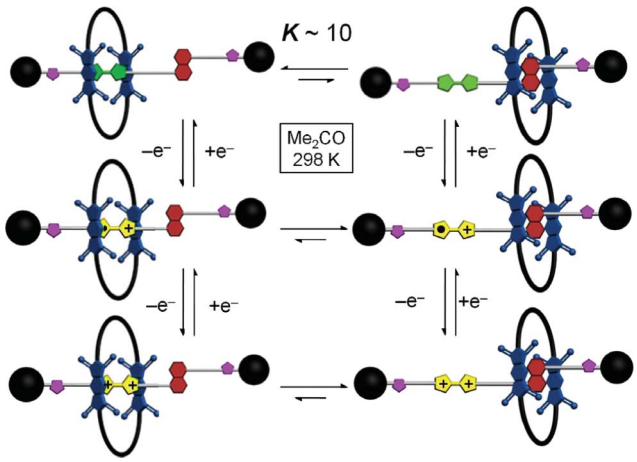


Fig. 3 Proposed mechanism of redox-stimulated switching for the neutral bistable [2]rotaxane **1**. In the ground state, at which point the TTF station is in its neutral form, the PmI-containing ring distributes itself between the TTF and DNP stations in an approximately 10 : 1 ratio. Oxidation of the TTF to first of all its radical cation form, and then to its dication results in translation of the macrocycle onto the DNP station. Re-reduction of the TTF dication back to its neutral form restores the initial ground state.

The bistable [2]rotaxane **1** was synthesised employing a template-directed protocol as outlined in Scheme 1. The known diazide **3** was prepared in 11 steps from commercially available compounds as previously reported.[9d] It was added to the ring **2**, NEt_3 and the propargyl ether **4** in CH_2Cl_2 solution. After cooling the solution down to −10 °C to promote pseudorotaxane formation, $Cu(MeCN)_4PF_6$ was added to initiate[25] a double copper-catalysed azide–alkyne (CuAAC) cycloaddition to form¶ the bistable [2]rotaxane **1** as a dark green solid in 34% yield.

^{1}H NMR spectroscopic analysis, in CD_2Cl_2 at room temperature, was employed to characterise the newly formed neutral bistable [2]rotaxane **1**. In order to assign the ^{1}H NMR spectrum (Fig. 2a–c) of **1** fully, the spectra of the dumbbell **5** and the ring **2**, also acquired in CD_2Cl_2 at room temperature, were used as comparative leads. Of particular interest is the line-broadening and upfield chemical shift ($\Delta\delta = 0.5$ ppm) observed for the resonance associated with the four aromatic PmI protons (H_P) contained in the macrocycle. Variable temperature ^{1}H NMR experiments were performed in order to investigate‖ this line-broadening (see ESI also†). Additionally, the ~0.2 ppm upfield shift of the resonances associated with the TTF olefinic protons (H_{TTF}) is consistent with previously reported[9c] donor–acceptor charge transfer (CT) complexes including TTF. Spectroscopic analyses were also aided (see ESI) by multidimensional ^{1}H–^{1}H correlation spectroscopy (COSY).

The proposed mechanism (Fig. 3) for switching in **1** is based on data obtained from a series of electrochemical experiments. In the first instance, evidence for switching in the bistable [2]rotaxane **1** at room temperature was obtained from CV which was carried out initially in argon-purged CH_2Cl_2. Slow electron-transfer kinetics in this nonpolar solvent result in quasi-reversible processes (see ESI†) which manifest themselves as peak broadening and flattening in the voltammograms as the scan rate is increased.[26] Experiments performed in Me_2CO produced** results that are easier to interpret. CV Experiments on 1.0 mM of the dumbbell **5** in Me_2CO in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) at 200 mV s^{-1} revealed (Fig. 4), as expected, two one-electron oxidation processes—one at +0.46 and the other at +0.80 V. The CV of the bistable [2]rotaxane **1** under the same conditions also revealed two reversible one-electron oxidations, in this case at +0.53 and +0.80 V. The most significant difference between the CVs of **1** and **5** is a shift in the first oxidation potential.†† The fact that the first oxidation potential of **1** is 60 mV more positive than the first one for **5** is consistent‡‡ with a situation

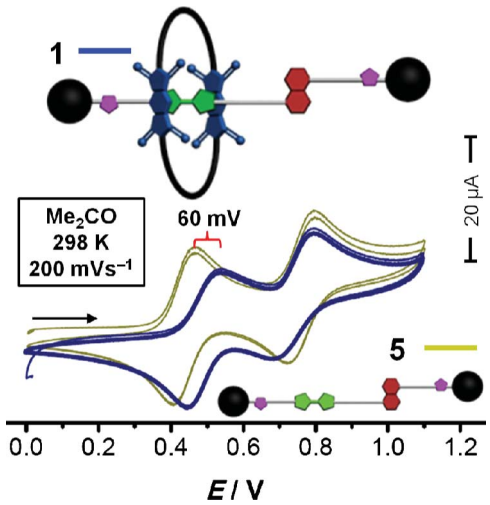


Fig. 4 CVs of the [2]rotaxane **1** (blue traces, first and second scans) and its corresponding dumbbell **5** (gold traces, first and second scans). Experiments were carried out with 1.0 mM concentrations of sample in argon-purged Me_2CO containing 0.1 M $TBAPF_6$. Note the 60 mV shift of the first oxidation potential of the TTF unit in **1** compared to the dumbbell **5**.

¶ The corresponding dumbbell **5**, lacking the ring component, was also synthesised. This application of "click" chemistry had been employed previously by us in the synthesis of a bistable [2]rotaxane incorporating TTF, DNP, and $CBPQT^{4+}$. See ref. 9d.

‖ This line broadening is associated with a rotary movement (see ESI) of the PmI subunits in the ring component. At lower temperatures, the single broad resonance associated with the PmI protons separates into two singlets with a difference in frequency $\Delta\nu$ of 222 Hz in the slow exchange limit. Employing the expression $k_c = (\pi\Delta\nu)/2^{1/2}$, we have calculated the rate of exchange k_c to be 491 s^{-1} at the coalescence temperature T_c of 293 K. By using the Eyring equation, $\Delta G_c^{\ddagger} = RT_c\ln(k_c h/k_B T_c)$, in which R is the gas constant, h is Planck's constant, and k_B is Boltzmann's constant, this rate constant (k_c) corresponds to a $\Delta G_c^{\ddagger}$ of 13.5 kcal mol^{-1} at T_c.

** The shapes of the CV curves were maintained at faster scan rates; only a small increase (~30 mV) between the anodic and cathodic peak separations was observed, indicating near reversibility.

†† No peaks corresponding to a first oxidation of "free TTF" were observed during second scans of the [2]rotaxane at any scan rate, nor after oxidising the [2]rotaxane for 10 s at +1.1 V just before the run. As a result, the relaxation of any putative metastable state—in which the ring encircles DNP in a neutral rotaxane—could not be measured. In other words, the [2]rotaxane always appeared to be at equilibrium at every point in the scan of the CV.

‡‡ No resonances were observed in the ^{1}H NMR spectrum of **1** for the co-conformation in which the PmI-containing ring component encircles the DNP unit. The fact that this minor co-conformation constitutes at equilibrium only one part in 10 approximately, alongside the major co-conformation in which the ring encircles the TTF unit, makes it nigh

where the ring encircles the TTF station with respect to the DNP one in an approximately 10 : 1 ratio. The observation that the second oxidation potentials in the case of both **1** and **5** are the same is consistent with the ring in the bistable [2]rotaxane having moved away from the $TTF^{\bullet+}$ radical cation onto the DNP station before the second oxidation: in other words, the second oxidation experienced by both **1** and **5** appears to be of a "free", *i.e.*, an unencircled $TTF^{\bullet+}$ radical cation. Squarewave differential pulse voltammetry (DPV) confirms (see ESI) the results from the CV experiments and is consistent with the proposed mechanism illustrated in Fig. 3.

We have also performed spectroelectrochemistry (SEC) at room temperature in order to investigate the switching behaviour of the bistable [2]rotaxane in even more detail. When neutral (E = 0 V), the absorption spectrum of **1** displays a charge transfer (CT) band at 606 nm, resulting from the ring encircling the TTF in the ground state of the molecule. Application of a potential of +700 mV to **1** resulted (Fig. 5a) in the growth of two broad bands with absorption maxima centred at 456 and 611 nm, indicative of $TTF^{\bullet+}$ radical cation formation. By comparison, when the dumbbell **5** was subjected to a potential of +500 mV, two relatively sharp bands characteristic of the $TTF^{\bullet+}$ radical cation appear (see ESI†) with the absorption maxima centred on 451 and 598 nm. We hypothesise that the relative broadness of the bands in the spectrum of $\mathbf{1}^{\bullet+}$ may be a consequence of the ring, when it encircles the DNP station, giving rise to a relatively broad CT band in the 400–700 nm region.

Application of a +1200 mV potential to a solution of the bistable [2]rotaxane **1** resulted (Fig. 5b) in decreases in the intensities of the two bands at 456 and 611 nm. Similarly, application of +1000 mV to a solution of the dumbbell **5** resulted (see ESI) in decreases in the intensities of the two relatively sharp bands at 451 and 598 nm. In both cases these decreases are characteristic of the generation of the TTF^{2+} dication. However, in the case of the bistable rotaxane **1**, the band observed at 450 nm is different in both shape and intensity. This difference is once again believed to arise from the relatively intense CT band caused by the donor–acceptor interactions between the ring and the DNP station. These results from the SEC experiments provide yet further evidence for the mechanism (Fig. 3) where the translational motion of the ring in the bistable [2]rotaxane **1** from the TTF station to the DNP one occurs after the first oxidation of the TTF unit.

The switching behaviour of **1** was also investigated (Fig. 2d–e) by ^{1}H NMR spectroscopy in CD_3COCD_3 solution at 233 K. The outcome of these experiments supported the results obtained from the electro- and spectroelectrochemical studies. Chemical oxidation of the TTF unit to its TTF^{2+} dication in **1** resulted in upfield shifts of the resonances associated with the protons of the DNP unit, a change in spectroscopic behavior which indicates that the translation of the ring away from the TTF^{2+} dication and onto the DNP unit had occurred. A visual colour change from green to yellow was evident following oxidation, an observation which is qualitatively consistent with the results obtained from SEC and the titration experiments.

impossible to be able to detect signals for the minor co-conformation. The situation is exacerbated on account of the complexity of the ^{1}H NMR spectrum caused by, for example, the slow *cis–trans* isomerism on the ^{1}H NMR timescale of the TTF unit producing a doubling up of signals for the minor co-conformation.

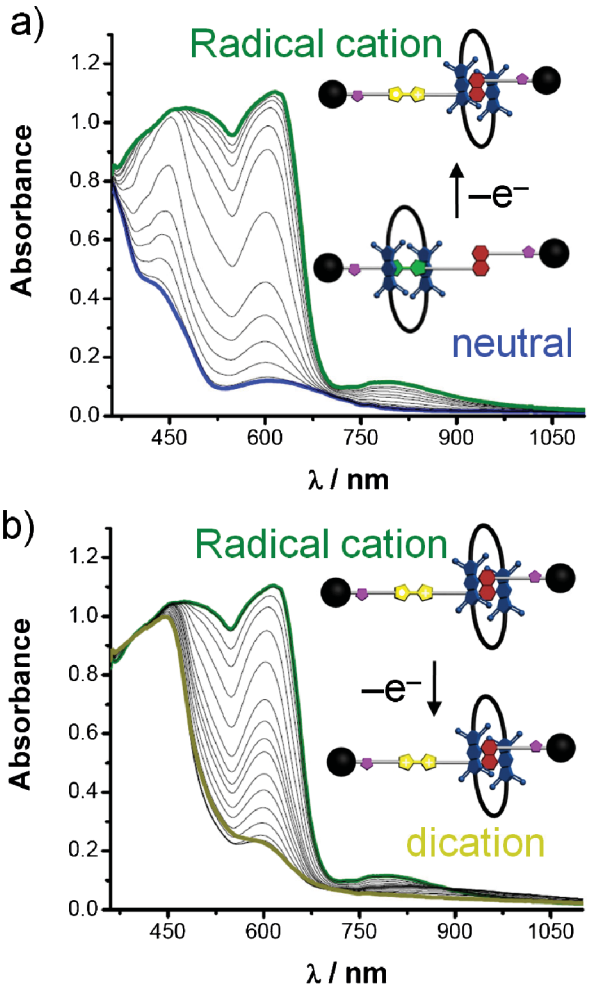


Fig. 5 SEC Experiments of 1.0 mM solutions of rotaxane **1** in argon-purged CH_2Cl_2 containing 0.1 M $TBAPF_6$ taken at different applied oxidation potentials. (a) Resulting spectra of **1** after applying a potential of +700 mV. (b) Resulting spectra of **1** after applying a voltage of +1200 mV immediately following the initial +700 mV potential.

Conclusions

We have designed and incorporated a neutral, electron-deficient, PmI-containing ring into a bistable [2]rotaxane and characterised its switching behaviour by CV, SEC and ^{1}H NMR spectroscopy following both electrochemical and chemical oxidation. These experiments provide firm evidence for switching on oxidation at room temperature and are consistent with a qualitative colour change from green to yellow when the bistable [2]rotaxane is oxidised chemically. The neutral molecules constituting this molecular switch will now be investigated by STM under high vacuum conditions at low temperatures on a metal surface. These experiments await the preparation of more of the [2]rotaxane, an objective predicated upon achieving a more efficient synthesis of the ring.

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