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LETTERS

A stopperless tetrathiafulvalene based [2]pseudorotaxane molecular shuttle

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Abstract—The first stopperless TTF containing molecular shuttle is described.

An important recent development in supramolecular chemistry has been the construction of molecular machines.[1] Molecular shuttles based upon [2]rotaxanes are an important representative class. These mechanically linked molecules display switching properties resulting from the relative positioning of a macrocyclic 'wheel' component over recognition 'stations' situated along a dumbbell shaped 'axle.' To prevent the wheel from becoming detached from the axle, the latter must be terminated by bulky stoppers (Fig. 1a).[2] [2]Pseudorotaxane based shuttle-like systems have also been described; however, the shuttling process in supramolecules of this type has been restricted to threading/dethreading of the axle and wheel components under chemical, photochemical and electrochemical control (Fig. 1b).[1,3] The majority of [2]rotaxane based molecular shuttles have traditionally been fabricated from π-rich polyhydroquinol containing axles and π-deficient macrocyclic wheels based upon cyclobis-(paraquat-*p*-phenylene) **3**. More recently, the reversible multi-stage redox properties and good electron donor properties[4] of tetrathiafulvalene (TTF) have been used to create donor–acceptor based [2]rotaxanes, in which this electron rich unit forms multiple stations along the axle for the cyclic acceptor **3**.[5] Remarkably, analogous [2]pseudorotaxane molecular shuttles, which involve the shuttling of macrocyclic wheels between multiple TTF units situated along the axle, have not been described (Fig. 1c). Here, we exploit for the first time the effective binding properties between the TTF unit and acceptor **3**, to fabricate the first TTF containing [2]pseudorotaxane based molecular shuttle.[6]

In order to produce a TTF containing axle suitable for a [2]pseudorotaxane molecular shuttle, we opted for a structure based upon **2**.[†] In this system, the axle is

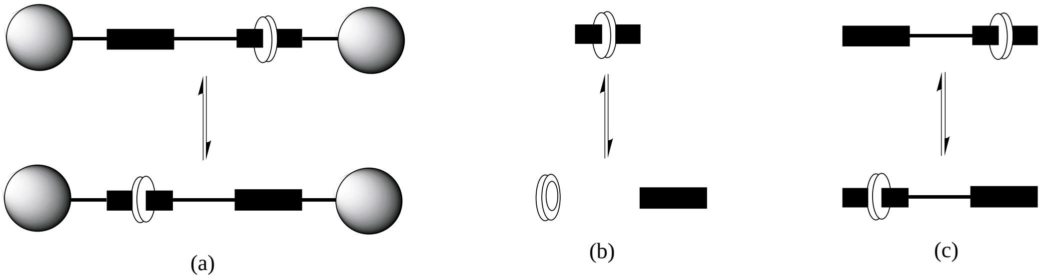

Figure 1. Rotaxane and pseudorotaxane molecular shuttles.

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[†] *Selected data for* **2**: mp 154–156°C. Analysis found: C, 48.90; H, 2.60%; required for $C_{28}H_{18}O_5S_8$: C, 48.70; H, 2.60%; *m*/*z* (DCI) 691 (M^+); δ_H [$(CD_3)_2CO$] 8.04 (4H, d, $J=9.0$ Hz), 7.17 (4H, d, $J=9.0$ Hz), 6.80 (2H, s), 6.59 (4H, s), 5.13 (4H, s).

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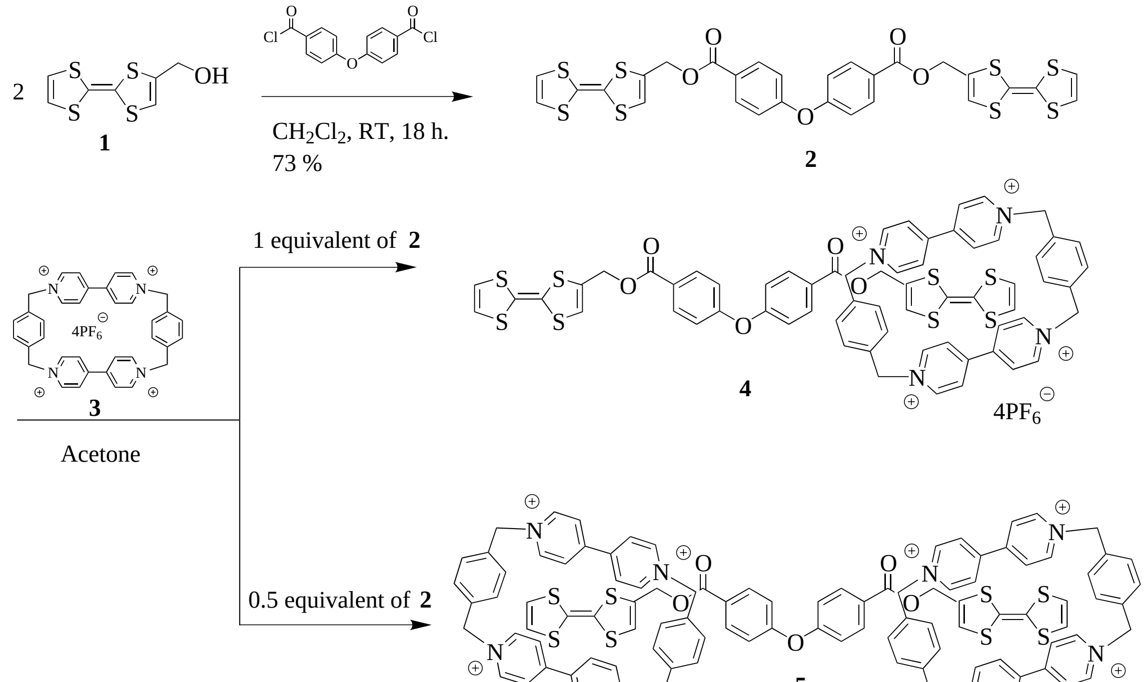
terminated by two TTF units that are linked by an electron rich bisphenylether moiety. This linker was included to help coax the macrocycle **3** to shuttle intramolecularly between the two TTF units, thereby discouraging the dethreading of **3** from **2**. The axle was synthesised by reacting alcohol **1** with half an equivalent of 4,4′-oxybis(benzenecarbonyl chloride) in CH_2Cl_2 at room temperature for 18 h, and the resulting mixture was purified using column chromatography (silica gel, CH_2Cl_2/acetone 50:50 v/v) to afford **2** in 73% yield (Scheme 1). The [2]pseudorotaxane **4**[‡] was prepared by mixing **2** with an equimolar proportion of **3** in acetone, which resulted in the immediate formation of an emerald green-coloured solution as a result of the appearance of a charge-transfer (C-T) band in the visible region of the spectra centred at around 854 nm. FAB mass spectral analysis revealed peaks at *m*/*z* 1645 and 1500 corresponding to $(M-PF_6)^+$ and $(M-2PF_6)^{2+}$, resulting from the loss of one and two PF_6^- counterions, respectively, from **4**. The association constant (K_a), obtained using the dilution method in acetone, for **4** was found to be 3300 M^{-1}, corresponding to a free energy of complexation of 4.73 kcal mol^{-1}.

^1H NMR spectroscopic data performed at ambient temperature on complex **4** clearly suggest the [2]pseudorotaxane to be an inclusion complex, with a TTF unit inserted into the cavity of cyclophane **3**. Both of the TTF units of axle **2** appear to be ‘occupied’ by the macrocyclic guest **3** with 1:1 stoichiometry, indicating a rapid shuttling of **3** back and forth along **2** on the NMR timescale. There are no signals in the spectrum arising from an unoccupied TTF unit, thereby arguing against a dethreading of the wheel from the axle.[2] The changes in the chemical shifts are in accordance with those reported for the complex of TTF and **3**,[7] indicating a similar binding geometry for underivatised TTF to that of the substituted TTF derivative of the axle. The displacements, Δδ, in the ^1H NMR spectra of **4** are collated in Table 1. The largest changes in chemical shift are experienced by the C_6H_4 of the cyclophane, the 4′,5′-TTF protons and the phenyl ether protons. The upfield shift of the TTF protons indicates a complex in which the TTF ring system is approximately coplanar with the bipyridinium (bipy) aromatic rings. Larger chemical shift displacements occur for the TTF protons



Scheme 1.

Table 1. Chemical shift displacements Δδ (ppm) for **4** at 20°C in the 400 MHz NMR resonances of guest **3** with host **2** after their admixture in CD_3COCD_3

Unit	αC**H**(Ph)	βC**H**(bipy)	C_6**H_4**	NC**H_2**	4-TTF	4′,5′-TTF	TTF C**H_2**	αC**H**(Ph)	βC**H**(Ph)
3	+0.07	−0.09	+0.17	−0.03	–	–	–	–	–
2	–	–	–	–	−0.08	−0.12	+0.03	+0.15	+0.11

[‡] *Selected data for [2]pseudorotaxane* ***4***: *m*/*z* (FAB) 1645 $(M-PF_6)$; δ_H $[(CD_3)_2CO]$ 9.50 (8H, s), 8.50 (8H, s), 8.24 (4H, d, *J*=8.4 Hz), 7.92 (8H, s), 7.23 (4H, d, *J*=8.8 Hz), 6.72 (2H, s), 6.46 (4H, s), 6.11 (8H, s), 5.17 (4H, s).

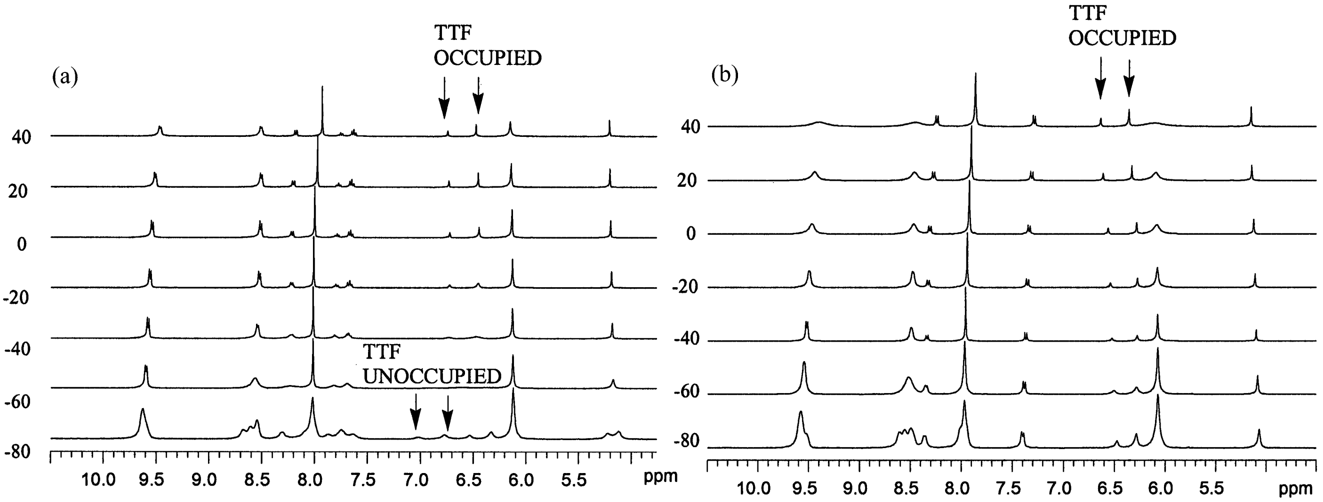


Figure 2. Variable temperature ^{1}H NMR (400 MHz) data for pseudorotaxanes **4** (a) and **5** (b) recorded at +40 to −80°C in CD_3COCD_3.

of **2** than for the biphenyl ether protons, implying that complexation is more associated with a TTF unit. However, the phenyl ether protons are shifted downfield indicating that this unit is located close to the edge of the bipy units, and outside the cavity.

[2]Pseudorotaxane **4** displayed the temperature-dependent behaviour expected of a molecular shuttle.[2] The variable temperature (VT) ^{1}H NMR spectra are provided in Fig. 2. Upon cooling a sample of **4**, the signals corresponding to **2** broaden. At −80°C, these signals split into two sets of signals of equal intensity, arising from the occupied and unoccupied TTF moieties of **2**. Therefore, the data are consistent with the macrocycle becoming 'frozen' around one of the TTF units at low temperature. We have also obtained VT ^{1}H NMR data for [3]pseudorotaxane **5**, produced by adding two molar equivalents of **3** to **2**. In this system, the shuttling of **3** along axle **2** is prevented by Coulombic repulsion between the two macrocycles. As a result, any observed shuttling phenomena would be restricted to threading/dethreading processes. At ambient temperatures the NMR spectrum of **5** clearly show both of the TTF units being occupied by two molecules of **3**. Reducing the temperature to −80°C, the NMR spectrum is consistent with TTF stations remaining occupied, thereby suggesting the association constants between the components of **4** and **5** are sufficiently strong to discourage dethreading, even when intracomplex Coulombic repulsion is introduced into the pseudorotaxane.

We have modelled the [2]pseudorotaxane **4** using procedures previously described.[6a] The energy minimised structure is shown in Fig. 3, and clearly predicts that one of the TTF moieties of **2** is deeply inserted into the cavity of **3** which further supports the NMR and the UV–vis data described above. Furthermore, it is apparent from the modelled structure that the phenyl ether ring of **2** is in close proximity to the C_6H_4 ring of cyclophane **3**, thereby accounting for the large changes in chemical shift observed for these moieties in the NMR spectrum of **4**.

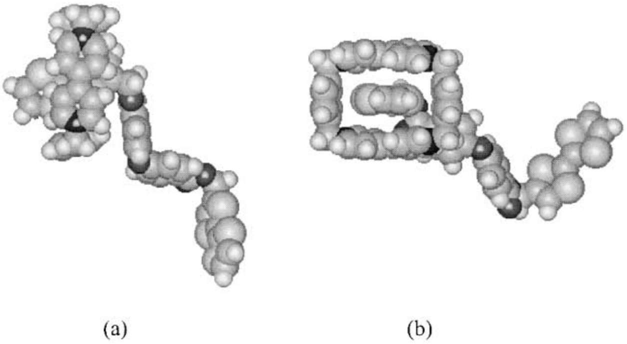


Figure 3. Energy minimised structure of the [2]pseudorotaxane molecular shuttle **4** [(a) plan view, (b) side view].

In conclusion, we have produced the first TTF based [2]pseudorotaxane molecular shuttle, by exploiting the ability of the TTF units to form effective inclusion complexes with **3**. We are in the process of synthesising axle units containing TTF moieties with disparate ionisation potentials to furnish electrochemically addressable shuttles, and this will be reported in due course.

Acknowledgements

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