An interdigitated functionally rigid [2]rotaxane†

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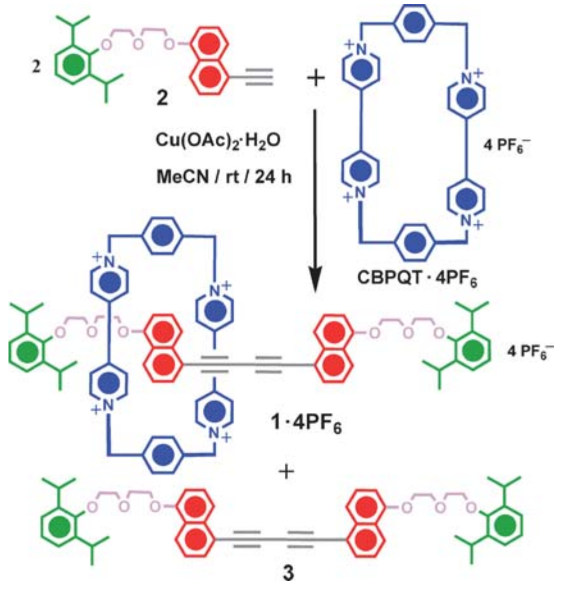
The synthesis of a functionally rigid [2]rotaxane incorporating π-electron rich 1,5-disubstituted naphthalene (NP) ring systems, encircled by the π-electron deficient tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), is described; in the solid state, the molecules of this donor–acceptor [2]rotaxane line themselves up in parallel π–π stacks of alternating NP ring systems and bipyridinium units, affording an interdigitated superstructure.

The absence of covalent bonds between the components of mechanically interlocked molecules known as *rotaxanes* makes this class of compounds potentially applicable as switchable components in functioning molecular devices.[1] In order to understand (and, in the future, predict) the related mechanical motions of the components in rotaxanes in a device context, it is advantageous to operate with rigid systems that have a decreased number of degrees of freedom.[2] With this notion in mind, we have developed[3] recently a functionally rigid and degenerate molecular shuttle[4] **1**·4PF$_6$ (Scheme 1), in which the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}), travels back and forth between two identical naphthalene-based stations (NP) located on the dumbbell component. The study of degenerate functionally rigid dynamic [2]rotaxanes, such as **1**·4PF$_6$, may provide valuable information in the design, synthesis, and characterization of more complex molecular shuttles and switches. Specifically, the dynamic properties that rigid linkers and recognition stations exhibit may be studied with more detail in degenerate model systems as the one described herein. Using dynamic ^{1}H NMR spectroscopy, we calculated the barrier to be 9.6 kcal mol^{-1} for the movement of the CBPQT^{4+} ring along the rigid butadiyne spacer between the two NP stations.[3] Herein, we complement these initial studies with (a) a crystallographic analysis of the solid-state structures of **1**·4PF$_6$ and its dumbbell component **3**, and (b) an improved template-directed[5] synthesis of **1**·4PF$_6$ using the threading approach and Cu^{2+}-mediated Eglinton[6] coupling of two half dumbbells *via* their terminal alkyne functions.

Combining equimolar amounts of **2**[3] and **CBPQT**·4PF$_6$[7] in MeCN produced the red [2]pseudorotaxane [**2** ⊂ **CBPQT**]·4PF$_6$. Treatment of this mixture with 6 equiv. of Cu(OAc)$_2$·H$_2$O at 25 °C for 24 h, followed by column chromatography (SiO$_2$: 1% solution of NH$_4$PF$_6$ in Me$_2$CO), afforded the functionally rigid [2]rotaxane **1**·4PF$_6$ as a red solid in 18% yield—a sizable improvement over the 8% yield previously[3] reported. However, the free dumbbell **3** was isolated as the major product (60%) of the coupling reaction.



Scheme 1 Synthesis of functionally rigid [2]rotaxane **1**·4PF$_6$.

In order to explain the reasons leading to the isolation of a high proportion of undesired free dumbbell **3**, we estimated the binding constant of the [2]pseudorotaxane [**2** ⊂ **CBPQT**]·4PF$_6$ using ^{1}H NMR spectroscopy by successive dilutions of an equimolar solution and found it to be ~15 M^{-1} in MeCN at 298 K. At the specific coupling reaction initial concentrations (12 mM) in MeCN at 298 K, we calculated that only ~14% of [**2** ⊂ **CBPQT**]·4PF$_6$ is formed. This is consistent with the high yield of **3** and the low yield of **1**·4PF$_6$.

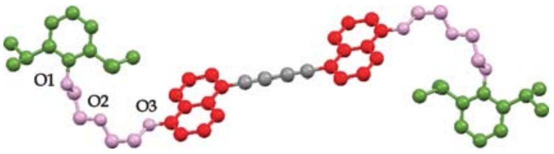


Fig. 1 A ball-and-stick representation of the solid-state structure of **3**. Colours are as used in Scheme 1.

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Slow evaporation of a CH_2Cl_2–C_6H_{14}–$i\mathrm{Pr}_2O$ solution of **3** yielded single crystals suitable for X-ray crystallography.‡ In the solid state, **3** adopts (Fig. 1) a centrosymmetric conformation. The total length of the molecule is 31.0 Å and the distance covered by the butadiyne unit as the spacer between two NP units is 3.8 Å, with an S-shaped fully rigid NP–butadiyne–NP unit in which stabilization within and beyond the molecule is achieved by (a) intramolecular [C–H···O] interactions[8] between the oxygen atoms (O2) in the di(ethylene glycol) chains and the protons on the isopropyl groups associated with the stoppers, and (b) intermolecular [C–H···O] interactions between the oxygen atoms (O1) in the di(ethylene glycol) chains and the protons (see ESI†) on the NP unit in the neighboring molecule.

Red-colored single crystals of **1**·4PF$_6$, suitable for X-ray crystallographic analysis,‡ were obtained upon slow vapor diffusion of iPr$_2$O into an MeCN–Me$_2$CO solution of **1**·4PF$_6$. The solid-state structure (Fig. 2) of **1**$^{4+}$ confirms that the CBPQT^{4+} ring encircles one of the two NP units on the rod section of the dumbbell and establishes that the compound is a [2]rotaxane, not a [3]rotaxane! The functionally rigid [2]rotaxane is stabilized by a combination of (a) [C–H···O] interactions[8] between the oxygen atoms (O5 and O6) in the dumbbell and an α-bipyridinium (BIPY^{2+}) proton and a proton on the *p*-xylylene link in the CBPQT^{4+} ring, (b) [C–H···π] interactions[9] between the two *peri* protons (H_{64} and H_{67}, see ESI†) of the NP units and the two *p*-xylylene links, and (c) π–π stacking interactions[10] between the NP and BIPY^{2+} units (see ESI†). Interestingly, the environments of the two half dumbbells are significantly different. The side of the half dumbbell with the encircled CBPQT^{4+} ring is folded to stabilize the [2]rotaxane formation through the [C–H···O] interactions, while the side without the CBPQT^{4+} ring is fully extended, resulting in different lengths of half dumbbells of 15.3 Å when the NP unit is encircled by the CBPQT^{4+} ring and 17.4 Å when the NP unit is free.

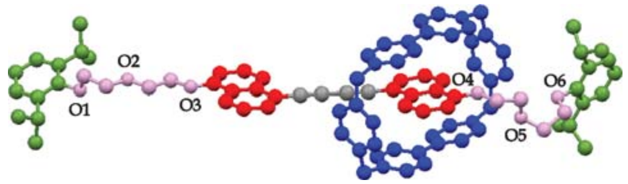

Fig. 2 A ball-and-stick representation of the solid-state structure of **1**$^{4+}$. Colours are as used in Scheme 1.

Fig. 3 illustrates the superstructure (packing diagram) for **1**$^{4+}$. Parallel π–π stacks (shaded pink) of alternating NP and BIPY^{2+} units are aligned along the *b*-axis in the crystal wherein four half molecules occupy the unit cell. The distances associated with the intercomponent (intramolecular) and intermolecular π–π stacking interactions between the alternating mean planes of the encircled and free NP ring systems in the dumbbells and the centroids of the BIPY^{2+} units span the range from 3.26 to 3.44 Å.

We have never ceased to be amazed at how a solid-state structure or superstructure can open up a new vista in supramolecular chemistry and beyond. The solid-state superstructure illustrated in Fig. 3 has been interpreted in a graphical form in Fig. 4. This representation suggests that, if we were to use stoppers which could be linked covalently to each other, perhaps in the solid state itself employing photochemical dimerization[11] of olefinic units attached to the stoppers, we could produce the prototypes of two-dimensional actuators based on extended donor–acceptor stacks constructed of interacting molecular shuttles.

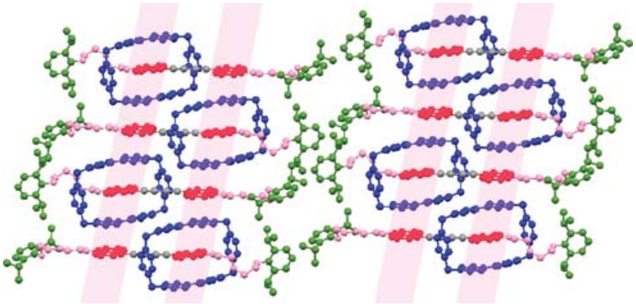

Fig. 3 A ball-and-stick representation of the interdigitated superstructure (packing diagram) of **1**$^{4+}$. Colours are as used in Scheme 1. The pale pink stripes highlight π–π stacks involving the NP ring systems in the dumbbells and the BIPY^{2+} units of the CBPQT^{4+} ring as the [2]rotaxane molecules line up to form parallel donor–acceptor arrays.

In summary, we have adapted the Eglinton coupling protocol, previously utilized[6c,12] in the preparation of donor–acceptor catenanes, to the synthesis of a symmetric donor–acceptor

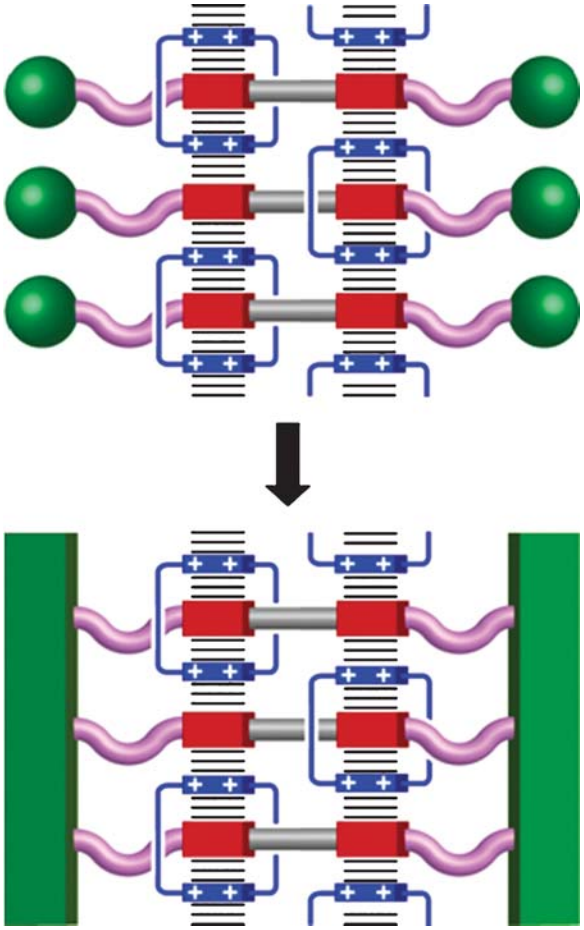

Fig. 4 A graphical representation of how a solid-state (X-ray crystal) superstructure might be transformed by post-covalent assembly into an integrated two-dimensional prototype of a device.

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[2]rotaxane. Characterization of this system by X-ray crystallography revealed a non-centrosymmetric [2]rotaxane formation in the solid state. Interestingly, this functionally rigid [2]rotaxane forms a superstructure wherein parallel π–π stacks of alternating NP ring systems and $BIPY^{2+}$ units line up in a continuous manner. The rigidity of the central linker in the rotaxane molecules is likely the key to this very organized supramolecular assembly in the crystal. This observation could be useful in the design and synthesis of mechanically interlocked molecules, as well as for the development of devices based on more rigid molecular systems.

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Notes and references

‡ Crystal data for **1**·4PF_6: $C_{102}H_{109}F_{24}N_9O_6P_4$, M_r = 2136.86, triclinic, space group $P\bar{1}$, a = 12.7352(2), b = 14.0183(3), c = 31.6155(6) Å, α = 90.064(2)°, β = 99.628(1)°, γ = 110.549(1)°, V = 5199.7(2) Å^3, Z = 2, ρ_{calcd} = 1.365 g cm^{-3}, μ(Cu Kα) = 1.542 mm^{-1}, $2\theta_{max}$ = 122.62°, 67 667 reflections measured and 15 208 were independent (R_{int} = 0.1499), T = 100(2) K, red needle, 0.10 × 0.10 × 0.02 mm, R_1 = 0.0911 [$I > 2\,\sigma(I)$], wR_2 = 0.2640 (all data), GOF = 0.841. The crystal size was very small and diffraction data at high angles are very weak or absent resulting in the higher R_{int} for redundant data. Crystal data for **3**: $C_{56}H_{62}O_6$, M_r = 831.06, monoclinic, space group $P2_1/n$, a = 10.235(3), b = 8.654(2), c = 27.061(7) Å, β = 90.967(3)°, V = 2396.5(11) Å^3, Z = 2, ρ_{calcd} = 1.152 g cm^{-3}, μ(Mo Kα) = 0.073 mm^{-1}, $2\theta_{max}$ = 56.48°, 18 014 reflections measured and 5864 were independent (R_{int} = 0.0445), T = 100(2) K, colorless cut-block, 0.60 × 0.40 × 0.40 mm, R_1 = 0.0457 [$I > 2\,\sigma(I)$], wR_2 = 0.1224 (all data), GOF = 1.056. The data were processed using the program SAINT[13] to give the structure factors. The structures were solved by direct methods and refined by full-matrix least squares against $|F_2|$. Absorption corrections were based on multiple and symmetry-equivalent reflections in the data sets using the SADABS[14] program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL[15] 6.12 program library. CCDC 661695 (**1**·4PF_6), and CCDC 661694 (**3**).†

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