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Solid-state structures and superstructures of two charged donor-acceptor rotaxanes

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Since the first report\(^1\) of the synthesis of cyclobis(paraquat-p-phenylene) (CBPQT\(^{4+}\)) in 1988, CBPQT\(^{4+}\) ring-containing catenanes and rotaxanes have attracted\(^2\) the attention of chemists, physicists, materials scientists and engineers, on account of the fact that these mechanically interlocked molecules can be harnessed in molecular muscle-activated cantilevers,\(^3\) macroscopic sol-gel and liquid-crystalline switches,\(^4\) molecular electronic devices,\(^5\) mechanized mesoporous silica nanoparticles,\(^6\) and metal-organic frameworks.\(^7\) In particular, bistable [2]rotaxanes have commonly consisted of \(\pi\)-electron-rich tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) units located in the rod portions of their dumbbell components encircled by single CBPQT\(^{4+}\) rings. The geometries and switching characteristics of these bistable [2]rotaxanes have been investigated\(^8\) in solution in order to obtain an understanding of the intramolecular interactions between the ring and dumbbell components. It is also instructive, however, to obtain solid-state structures of these [2]rotaxanes in order to understand their switching properties. A systematic search (Fig. 1) of the literature has revealed a total of 91 crystal structures of cyclophane-based donor-acceptor catenanes already reported\(^9\) by ourselves and others to date. By contrast, as a result of the difficulties encountered during attempts to crystallize cyclophane-based donor-acceptor [2]rotaxanes, there are only 15 of their solid-state structures reported in literature. Bistable [2]rotaxanes have been synthesized which incorporate DNP, TTF, and HQ (hydroquinone) units along with the CBPQT\(^{4+}\) ring and stoppers such as monoaza-18-crown-6,\(^10\) triisopropylsilane,\(^11\) \((1R,2S,5R)-\)menthyl groups,\(^12\) 2,6-diisopropylbenzene,\(^13\) 3,5-di(tert-butyl)benzene,\(^14\) adamantane,\(^15\) anthracene,\(^16\) and ferrocene.\(^16\) Herein, we report the preparation and characterization, by single crystal X-ray crystallography, of two donor-acceptor [2]rotaxanes 1R•4PF\(_6\) and 2R•4PF\(_6\) and one [2]pseudorotaxane [D⊂CBPQT]•4PF\(_6\).

The preparation of the [2]rotaxanes 1R•4PF\(_6\) and 2R•4PF\(_6\), and the [2]pseudorotaxane [D⊂CBPQT]•4PF\(_6\) is presented in the Supplementary Data (SD). The dumbbell compounds were prepared from the appropriate ditosylated DNP diethylene glycol derivatives\(^17\) and 4-[4-isopropylphenyl bis-(4-tert-butylphenyl)methyl]phenol,\(^18\) 2,6-diisopropylphenol, or thymol. The [2]rotaxanes 1R•4PF\(_6\) and 2R•4PF\(_6\), and the [2]pseudorotaxane [D⊂CBPQT]•4PF\(_6\) were obtained subsequently by a template-directed synthetic approach from their corresponding dumbbell...
compound, 1,1’-[1,4-phenylenebis(methylene)]bis-4,4’-bipyridinium bis(hexafluorophosphate), and 1,4-bis(bromomethyl benzene) in DMF under 10 kbar pressure at room temperature for 3 days. The two [2]rotaxanes and one [2]pseudorotaxane were isolated as analytically pure solids in yields ranging from 57% to 66%, after SiO$_2$ column chromatography with Me$_2$CO / NH$_4$PF$_6$ (100:1 v/w) as eluent. Although [D<sub>c</sub>CBPQT]4PF$_6$ is a [2]pseudorotaxane, it is very stable during the processes involved in its preparation and characterization. The [2]rotaxanes 1R•4PF$_6$ and 2R•4PF$_6$ and the [2]pseudorotaxane [D<sub>c</sub>CBPQT]4PF$_6$ were characterized by NMR spectroscopy, electrospray ionization mass spectrometry, and X-ray crystallography.

The UV-Vis spectra of the [2]rotaxanes and the [2]pseudorotaxane, recorded in MeCN, show charge transfer (CT) absorption bands in the 450–600 nm region, an observation which indicates that the CBPQT$^{4+}$ rings in 1R•4PF$_6$, 2R•4PF$_6$, and [D<sub>c</sub>CBPQT]4PF$_6$ encircle the DNP units as shown above. In the $^1$H NMR spectra of 1R•4PF$_6$, 2R•4PF$_6$, and [D<sub>c</sub>CBPQT]4PF$_6$ recorded in CD$_2$CN at 298 K, the resonances of the DNP units experience large upfield shifts, on account of the shielding effect of the encircling CBPQT$^{4+}$ ring, to ca. 2.3 (H$_{4a}$), 5.9 (H$_{1c}$), and 6.2 (H$_{2c}$) ppm as compared with those for the same protons in the corresponding dumbbell compounds where the resonances appear in the region $\delta$ = 7–8 ppm.

Slow vapor diffusion of Pr$_2$O into MeCN solutions of 1R•4PF$_6$, 2R•4PF$_6$, and [D<sub>c</sub>CBPQT]4PF$_6$ for 2–4 days afforded single crystals suitable for X-ray crystallographic analysis. The crystals had a cuboidal shape and were relatively large, attaining up to several millimeters in length (Fig. 2).

The crystal structure of the [2]rotaxane 1R•4PF$_6$ is monoclinic and belongs to the space group $P2_1/c$. It reveals that the dumbbell component is threaded centrosymmetrically through the middle of the CBPQT$^{4+}$ ring, the DNP unit on the dumbbell component being located inside the CBPQT$^{4+}$ ring with interplanar separations of ca. 3.5 Å between the average mean planes of the $\pi$-donor and $\pi$-acceptors. The DNP unit on the dumbbell component has an *anti* geometry associated with the conformation of the diethyleneglycol chains. In addition to the [1$\pi$-1$\pi$] stacking interactions between the electron-rich DNP unit and the electron-deficient bipyridinium units on the CBPQT$^{4+}$ ring, there are (1) T-type edge-to-face interactions between the H$_{4a}$ protons of the DNP unit on the dumbbell component and the $p$-xylyl residues of the CBPQT$^{4+}$ ring and (2) [C–H–O] hydrogen bonds between the oxygen atoms of the diethyleneglycol chains on the dumbbell component and (i) the bipyridinium H$_{1c}$, (ii) the $p$-xylyl H$_{6}$ and (iii) the methyl H$_{5}$ protons of the CBPQT$^{4+}$ ring. The PF$_6^-$ counterions do not participate in hydrogen bond interactions with either the dumbbell component or the CBPQT$^{4+}$ ring directly.

In the case of the [2]rotaxane 2R•4PF$_6$, which carries smaller stoppers on its dumbbell component, its crystal structure (Fig. 3 and Fig. S2 in the SD) changes to being triclinic and belongs to the space group $P1$. The crystal structure reveals an elegant structural arrangement wherein the 2,6-diisopropylphenyl-terminated dumbbell component is threaded centrosymmetrically through the middle of the CBPQT$^{4+}$ ring, the axis of the DNP unit being inclined by approximate 45° to the plane of the CBPQT$^{4+}$ ring. The DNP unit on the dumbbell component has an *anti* geometry associated with the conformation of the diethyleneglycol chains. The DNP unit is located inside the CBPQT$^{4+}$ ring with interplanar separations of ca. 3.5 Å between the $\pi$-donor and $\pi$-acceptors. In addition to the [1$\pi$-1$\pi$] stacking interaction between the electron-rich DNP unit and the electron-deficient bipyridinium units on the CBPQT$^{4+}$ ring, there are once again (1) T-type edge-to-face interactions between the H$_{4a}$

Figure 2. Photographs (a and b) of the single crystals grown by vapor diffusion of Pr$_2$O into a solution of 2R•4PF$_6$ in MeCN at room temperature.

Figure 3. Ball-and-stick representations of the crystal structures of the [2]rotaxanes 1R$^{4+}$ and 2R$^{4+}$. Hydrogen atoms, solvent molecules, and counterions are omitted for the sake of clarity. The DNP unit is colored red, the CBPQT$^{4+}$ ring blue, and the remainder gray.
protons of the DNP unit on the dumbbell component and the p-xylxy residues of the CBPQT$^\text{4+}$ ring. (2) $[\text{C}^\cdots\text{H}^\cdots\text{O}]$ interactions between the oxygen atoms of the diethyleneglycol chains on the dumbbell component and (i) the bipyridinium $D_{\text{pp}}$ and (ii) the methylene $H_{\text{p}}$ protons of the CBPQT$^\text{4+}$ ring. (3) $[\text{C}^\cdots\text{H}^\cdots\text{N}]$ hydrogen bonds between the nitrogen atoms of the solvent (MeCN) and the bipyridinium $H_{\text{p}}$ protons on the CBPQT$^\text{4+}$ ring, and (4) $[\text{C}^\cdots\text{H}^\cdots\text{F}]$ hydrogen bonds between the fluorine atoms of three $\text{PF}_{\text{e}}$ counterions and (i) the bipyridinium $H_{\text{pp}}$, (ii) the p-xylxy $H_{\alpha}$, (iii) the methylene $H_{\delta}$ and (iv) the diethyleneglycol protons.

In the packing of $1\text{R}^\text{2}+\text{PF}_{\text{e}}$ and $2\text{R}^\text{2}+\text{PF}_{\text{e}}$, the $2$[rotaxanes are connected by intermolecular $[\pi\cdots\pi]$ stacking interactions aided and abetted by a hydrogen bonding network associated with intervening $\text{PF}_{\text{e}}$ counterions and solvent molecules. The $2$[rotaxane $1\text{R}^\text{2}+\text{PF}_{\text{e}}$ assumes a cluster-like packing mode (Fig. 4a), while $2\text{R}^\text{2}+\text{PF}_{\text{e}}$ adopts a sheet-like packing mode (Fig. 4b).

In analogy with the $2$[rotaxane $2\text{R}^\text{2}+\text{PF}_{\text{e}}$, the $2$[pseudorotaxane adopts a sheet-like packing mode.

![Figure 4. Packing superstructures of the $2$[rotaxanes $1\text{R}^\text{2}+\text{PF}_{\text{e}}$ (a) and $2\text{R}^\text{2}+\text{PF}_{\text{e}}$ (b). Hydrogen atoms are omitted for the sake of clarity.](image)](image)

In summary, two $2$[rotaxanes and one $2$[pseudorotaxane have been prepared and their solid-state (super)structures have been obtained. Close examination of these (super)structures indicates that the geometries of the $2$[rotaxanes and $2$[pseudorotaxane in the solid state are stabilized, not only by the $[\pi\cdots\pi]$, $[\text{C}^\cdots\text{H}^\cdots\pi]$, and $[\text{C}^\cdots\text{H}^\cdots\text{O}]$ interactions between the dumbbells and the CBPQT$^\text{4+}$ rings, but also by the participation of solvent molecules and counterions in hydrogen bonding. Yet again, the importance of counterions in dictating the solid-state superstructures of rotaxanes and pseudorotaxanes is clearly evident.

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Supplementary Data

Supplementary data (detailed synthetic procedures, characterization, crystal figures) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.XXX.

References and notes


