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Counterion-Induced Translational Isomerism in a Bistable [2]Rotaxane

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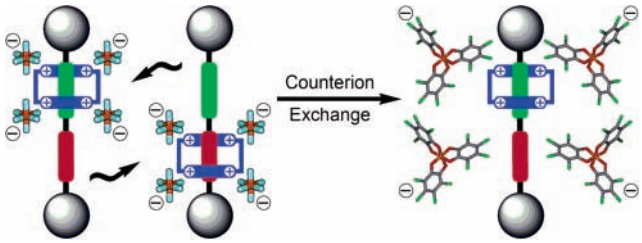
ABSTRACT



Translational isomerization can be induced by changing the anions associated with a bistable rotaxane in which the tetracationic cyclophane (blue box), cyclobis(paraquat-*p*-phenylene), encircles a dumbbell component containing bispyrrolotetrathiafulvalene (green) and a dioxynaphthalene (red) recognition sites. The rotaxane was isolated as both its hexafluorophosphate and tris(tetrachlorobenzenediolato)phosphate(v) (TRISPHAT$^-$) salts. Photophysical measurements and NMR spectroscopy carried out in acetone (CD_3COCD_3) and acetonitrile (CD_3CN) solutions reveal that the much larger TRISPHAT$^-$ anion favors predominantly the encirclement of the green site by the blue box.

[2]Rotaxanes, comprised of a dumbbell component containing 1,5-dioxynaphthalene (DNP) and tetrathiafulvalene (TTF) recognition sites for the ring component, cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$), have been shown[1] to display bistability that is electrochemically controllable insofar as the occupation of the two sites by the $CBPQT^{4+}$ ring can be dictated by the oxidation state of the TTF site, i.e., when it is neutral, it is encircled by the ring, and when it is oxidized, the ring moves to the DNP site. In solution, comprehensive photophysical, electrochemical, and ^{1}H NMR spectroscopic studies have provided[2] a detailed picture of this redox-activated shuttling process in terms of its kinetics and thermodynamics. In addition, recent electrochemical investigations on a bistable rotaxane, self-assembled to a gold electrode, have established[3] that this switching process is conserved in molecular monolayers in a "half-device". A similar electrochemical mechanism is believed[4] to be responsible for the bistability observed in crossbar memory devices in which Langmuir−Blodgett monolayers of am-

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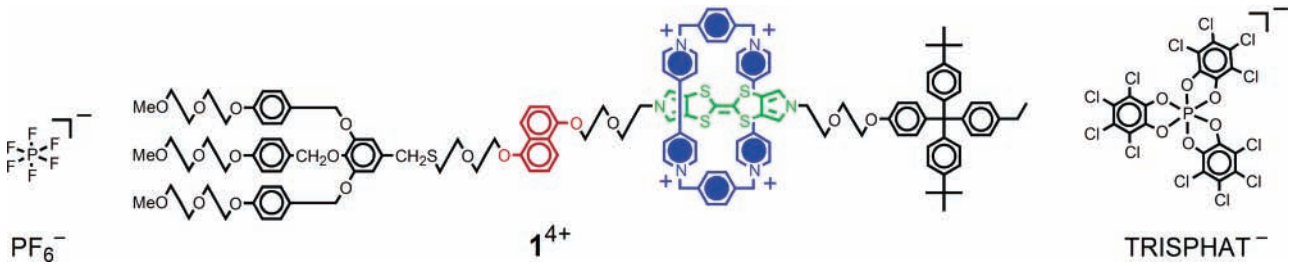

Figure 1. Structural formulas of the green translational isomer of the bistable [2]rotaxane $\mathbf{1}^{4+}$ with the anions PF_6^- and $TRISPHAT^-$ displayed on either side.

phiphilic bistable rotaxanes are sandwiched between two electrodes, one Si or C and the other Ti/Al, in "full devices". In all these rotaxanes, the four positive charges associated with the $CBPQT^{4+}$ ring component are balanced by four hexaflourophosphate (PF_6^-) counterions. Recent studies[5] carried out on Langmuir layers of these rotaxanes, as their PF_6^- salts, suggest that the structures of the monolayers are strongly influenced by interactions between the $CBPQT^{4+}$ ring and its counterions with the water surface. Almost no attention, however, has been paid to the role of the counterions, even although it is very likely that they play an important role, not only in influencing the packing structure of the Langmuir monolayers but also because they may perturb the electron-accepting properties and, hence, shuttling dynamics of the $CBPQT^{4+}$ ring component, particularly in apolar solutions and in solid-state devices where electrostatic attraction and repulsion between the charged moieties are more significant because they are much less shielded by solvent molecules.

We have prepared the tris(tetrachlorobenzenediolato)-phosphate(v) ($TRISPHAT^-$) salt of the amphiphilic bistable [2]rotaxane $\mathbf{1}^{4+}$ and compared (Figure 1) its solution-state properties with those of its corresponding PF_6^- salt. Lacour's $TRISPHAT^-$ anion[6] was chosen on account of its considerable size,[7] low polarity,[8] and redox stability.[9] The tetracationic $\mathbf{1}^{4+}$ resembles many of the redox-switchable bistable [2]rotaxanes previously investigated both in solution and in crossbar devices.[1−5] However, $\mathbf{1}^{4+}$ differs from its predecessors in having a symmetric bispyrrolo-TTF (BPTTF) recognition site instead of the previously used monopyrrolo-TTF[1c,e,4] or simple TTF[1d,g,3] sites.

$\mathbf{1}\cdot 4PF_6$ was synthesized by conventional methods, and its $TRISPHAT^-$ salt was produced by mixing $\mathbf{1}\cdot 4PF_6$ with an excess of racemic morpholinium·TRISPHAT[6a] in $CHCl_3$. The more water-soluble PF_6^- anions and morpholinium cations were removed by washing the organic phase with H_2O. Excess of morpholinium·TRISPHAT was removed subsequently by reprecipitating the product from Me_2CO/Et_2O to afford $\mathbf{1}\cdot 4TRISPHAT$ in 72% yield. See Supporting Information for more details on the syntheses of this rotaxane and its spectrometric and spectroscopic characterization. The electrospray mass spectrum (ES-MS) of the [2]rotaxane $\mathbf{1}\cdot 4TRISPHAT$ shows peaks at *m*/*z* 1992, 1072, and 612 corresponding, respectively, to the doubly positively charged $[M - 2TRISPHAT]^{2+}$, the triply positively charged $[M - 3TRISPHAT]^{3+}$, and quadruply positively charged $[M - 4TRISPHAT]^{4+}$ ions. A comparison of the ^{31}P NMR spectra, both recorded in CD_3COCD_3, of $\mathbf{1}\cdot 4PF_6$ and $\mathbf{1}\cdot 4TRISPHAT$ revealed the complete disappearance of the resonance centered on −144.2 ppm associated with the PF_6^- anions and the appearance of a signal resonating at −80.7 ppm, which is characteristic of the $TRISPHAT^-$ anion.[6a] The ^{19}F NMR spectrum of $\mathbf{1}\cdot 4PF_6$ and $\mathbf{1}\cdot 4TRISPHAT$, also recorded in CD_3COCD_3, showed one intense doublet for the PF_6^- ion resonating at −72.5 ppm, whereas no resonances were observed in the ^{19}F NMR spectrum of $\mathbf{1}\cdot 4TRISPHAT$. These observations are clear indications that all four PF_6^- anions have been exchanged by four $TRISPHAT^-$ anions.

In Me_2CO solution, $\mathbf{1}\cdot 4PF_6$ exists as an approximately 1:1 mixture of the two possible translation isomers[10] where the $CBPQT^{4+}$ ring is located around the DNP recognition site in one isomer and around the BPTTF site in the other one. These two translation isomers give raise to characteristic charge transfer (CT) absorption bands centered on 550 nm (red) and 825 nm (green), respectively, in the visible spectrum. Similar equimolar proportions of translational isomers have been observed[1c,e] previously in bistable [2]rotaxanes containing monopyrrolo-TTF units, while bistable [2]rotaxanes containing simpler TTF units usually exist[1d,f,g] almost exclusively as the green isomer. The apparently less favorable

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(7) Molecular modeling of the PF_6^- and $TRISPHAT^-$ anions indicates that they have diameters of ca. 4 and 14 Å, respectively, at least when the ions are approximated to spheres. For crystal structures of $TRISPHAT^-$ salts, see ref 6a and: Lacour, J.; Bernardinelli, G.; Russell, V.; Dance, I. *CrystEngCommun*. **2002**, *4*, 165−170.

(8) Lacour, J.; Barchéchath, S.; Jodry, J. J.; Ginglinger, C. *Tetrahedron Lett.* **1998**, *39*, 567−570.

(9) If $\mathbf{1}\cdot 4TRISPHAT$ is going to be used in a redox-switchable context, as in crossbar devices, for example, it is important that the $TRISPHAT^-$ anions do not undergo redox chemistry within the potential range where the bistable [2]rotaxane $\mathbf{1}^{4+}$ switches. We therefore investigated the redox chemistry of $Me_4N\cdot TRISPHAT$ in MeCN solution by cyclic voltammetry and found that this salt is not redox active in the range from −2 to +1.7 V vs SCE using ferrocene/ferrocenium as the internal standard.

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binding between the monopyrrolo-TTF units[1e] and the CBPQT^{4+} ring has been ascribed to less efficient [C−H···O] interactions between the ethyleneglycol linkers in the dumbbells and the CBPQT^{4+} ring, caused by the extended nature of the TTF derivative, rather than by its π-electron donor strength, which is almost similar to that of the simpler TTF unit. In agreement with this interpretation, the green isomer of **1**·4PF$_6$ becomes favored at higher temperatures in polar solvents, where intramolecular [C−H···O] interactions stabilizing the red isomer become less important.

Exchanging the counterions of **1**$^{4+}$ from PF$_6^-$ to TRISPHAT$^-$ in a separating funnel (Figure 2) changes the

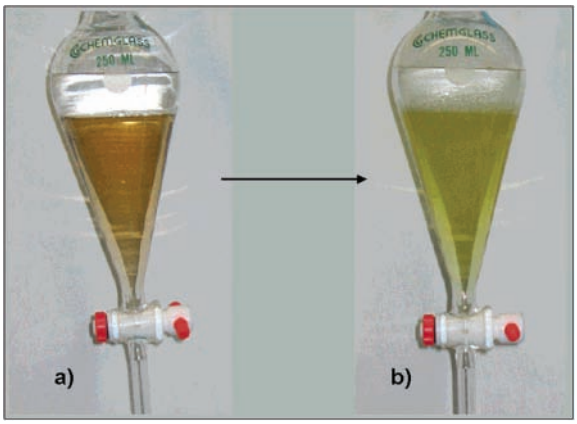

Figure 2. Photograph showing the color change accompanying counterion exchange. In funnel a, the lower reddish $CHCl_3$ phase contains **1**$^{4+}$, PF$_6^-$, morpholinium, and TRISPHAT$^-$ ions and is topped with a carefully added H_2O phase. In funnel b, we see the result of shaking the separation funnel and allowing the phases to separate: now the morpholinium and PF$_6^-$ ions are in the H_2O phase, leaving **1**$^{4+}$ with the TRISPHAT$^-$ ions in the now greenish $CHCl_3$ phase.

proportion of translational isomers in favor of the green isomer, a phenomenon that can be observed directly by the naked eye. The exact ratios of translation isomers can easily be determined from the ^{1}H NMR spectra recorded for **1**·4PF$_6$ and **1**·4TRISPHAT, respectively, since several of the protons in the dumbbell component give rise to two sets of signals, one for each of the two translation isomers. From integration of the resonances associated with the benzylic protons in the hydrophilic stopper, the isomer distributions for **1**·4PF$_6$ and **1**·4TRISPHAT were determined at 295 K in CD_3COCD_3 and CD_3CN solutions. In CD_3COCD_3, **1**·4PF$_6$ was found (Figure 3) to contain 45% of the red translation isomer, while **1**·4TRISPHAT featured less than 5% of this isomer. These observations can be accounted for by the fact that the counterions must be closely associated with the tetracationic rotaxane and must have a profound influence upon the noncovalent bonding interactions that occur between the different portions of the latter. In more polar solvents, where the ions will be better solvated, such effects are expected to be less significant. Hence in CD_3CN, a much smaller change in the isomer ratio, from 25 to 15% of the red translational

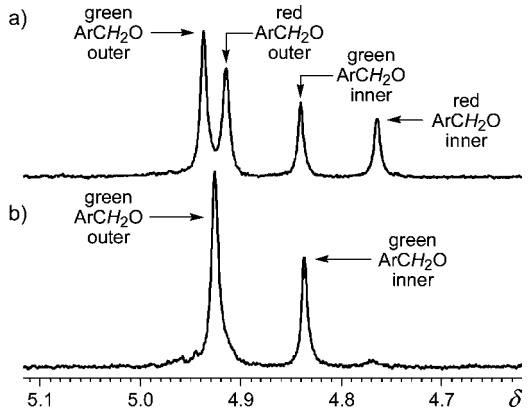

Figure 3. Partial ^{1}H NMR spectra (400 MHz) of **1**·4PF$_6$ (a) and **1**·4TRISPHAT (b) recorded in CD_3COCD_3 at 295 K, showing the signals for the benzylic methylene protons as two singlets in the ratio of 2:1 for each of the two translational isomers.

isomer, was observed on replacing PF$_6^-$ with TRISPHAT$^-$ counterions.

To elucidate the role of the counterions even further, Me_2CO/CD_3COCD_3 solutions of **1**·4PF$_6$ and **1**·4TRISPHAT were titrated with Bu$_4$N·PF$_6$ and Me$_4$N·TRISPHAT, respectively, and both the UV−vis and ^{1}H NMR spectra were monitored. In the case of **1**·4TRISPHAT, addition of PF$_6^-$ ions very rapidly brings the isomer ratio back to that of the pure PF$_6^-$ salt, **1**·4PF$_6$. Already, after addition of only 1 equiv of Bu$_4$N·PF$_6$, giving a 1:1 ratio of PF$_6^-$ to TRISPHAT$^-$ ions in solution, the isomer ratio reaches 80% of the value found for the pure PF$_6^-$ salt. Titration of **1**·4PF$_6$ with Me$_4$N·TRISPHAT shows, on the other hand, that a much larger excess of the TRISPHAT$^-$ ion is required to shift the isomer distribution. The titration curves show (Figure 4) clearly that the CBPQT^{4+} ring has a higher affinity for the PF$_6^-$ ion than for the larger TRISPHAT$^-$ ion.

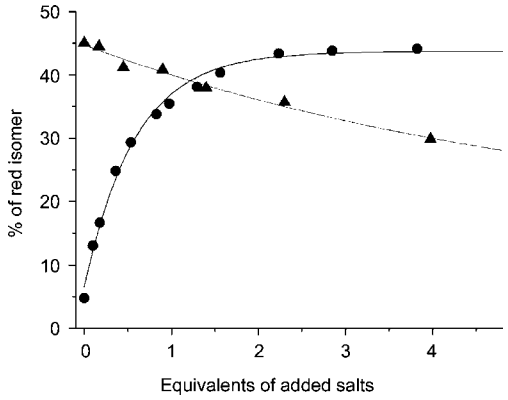

Figure 4. Translation isomer distribution in CD_3COCD_3 at 295 K as a function of added salts determined by ^{1}H NMR spectroscopy. Dots (●) show the titration of **1**·4TRISPHAT by Bu$_4$N·PF$_6$ with a first-order exponential function fitted to the data points. Triangles (▲) show the titration of **1**·4PF$_6$ with Me$_4$N·TRISPHAT with a first-order exponential function fitted to the data points.

UV−vis titrations of more diluted Me_2CO solutions (ca. 10^{-4} M as compared with ca. 10^{-3} M for the ^1H NMR experiments) show similar trends on probing changes in the characteristic CT absorption bands as functions of added PF_6^- or TRISPHAT$^-$ salt. Several possible explanations may be advanced to account for the counterion influence on the translational isomer ratio in $\mathbf{1}^{4+}$. There are at least two effects that favor the green isomer when the counterion is changed from PF_6^- to TRISPHAT$^-$: (1) One effect is an electronic effect caused by the large size of the TRISPHAT$^-$ ion, which increases the average distance between the tetracationic ring and the negative charges of the ions in close ion-pairs, causing the CBPQT^{4+} ring to become a stronger π-electron acceptor and so favor binding to the stronger π-electron donor, i.e., the BPTTF unit. (2) The other effect is a steric effect whereby the larger TRISPHAT$^-$ ions shield the CBPQT^{4+} ring in the close ion-pair, thus disfavoring the [C−H···O] interactions between the ring and the ethylene glycol units when it resides on the DNP unit. The fact that addition of a large excess of PF_6^- ions to $\mathbf{1}\cdot 4PF_6$ does not lead to a pronounced increase in the proportion of the red isomer leads us to exclude mechanisms involving specific interactions between $\mathbf{1}^{4+}$ and the PF_6^- ions favoring this isomer.

The fact that the nature and size of the counterions have such a profound influence upon the ratio of translational isomers[11−15] in bistable donor−acceptor rotaxanes where a π-accepting tetracationic cyclophane shuttles between two different π-donating recognition sites indicates that even larger counterion effects will be operative in condensed-phase systems, e.g., Langmuir and Langmuir−Blodgett monolayers,[5] when they are employed in device settings.[5,16] This phenomenon is under investigations following the demonstration[17] that the kinetics and the thermodynamics of the switching by amphiphilic bistable rotaxanes vary in a perfectly logical manner on traversing the environment from the solution phase, through polymer matrixes and half-devices into the full devices used in random access memory circuits.[5,16]

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Supporting Information Available: Synthetic schemes and experimental procedures for $\mathbf{1}\cdot PF_6$ and $\mathbf{1}\cdot$TRISPHAT, along with spectroscopic characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Several other examples of translational isomerism, in both bistable catananes and rotaxanes, induced by an environmental change such as solvent and temperature have been reported. See: (a) Ashton, P. R.; Blower, M.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Ballardini, R.; Ciano, M.; Balzani, V.; Gandolfi, M. T.; Prodi, L.; Mclean, C. H. *New. J. Chem.* **1993**, *17*, 689−695. (b) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Menzer, S.; Pérez-García, L.; Prodi, L.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11171−11197. (c) Leigh, D. A.; Moody, K.; Smart, J. P.; Watson, K. J.; Slawin, A. M. Z. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 306−310. (d) Lane, A. S.; Leigh, D. A.; Murphy, A. *J. Am. Chem. Soc.* **1997**, *119*, 11092−11093. (e) Leigh, D. A.; Murphy, A.; Smart, J. P.; Deleuze, M. S.; Zerbetto, F. *J. Am. Chem. Soc.* **1998**, *120*, 6458−6467. (f) See ref 1c. (g) See ref 1e. (h) Bottari, G.; Dehez, F.; Leigh, D. A.; Nash, P. J.; Pérez, E. M.; Wong, J. K. Y.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 5886−5889.

(12) The influence of solvation on the conformational isomerism of calix[4]arene and *p-tert*-butylcalix[4]arene has also been reported. See, for example: (a) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713−1734. (b) Cajan, M.; Lhotak, P.; Lang, J.; Dvorakova, H.; Stibor, I.; Koca, J. *J. Chem. Soc., Perkin Trans. 2* **2002**, *11*, 1922−1929. (c) Alemán, C.; den Otter, W. K.; Tolpekina, T. V.; Briels, W. J. *J. Org. Chem.* **2004**, *69*, 951−958.

(13) It has also been shown that conformational isomerism in cyclohexanones such as 2-*N*,*N*-dimethylaminocyclohexanone is strongly influenced by the polarity of the solvent. The conformational equilibrium between the axial and equatorial conformation of 2-*N*,*N*-dimethylaminocyclohexanone has been investigated, and it was found that the axial conformation was dominant in CD_3SOCD_3 solution whereas the equatorial conformation was the most dominant in more apolar solvents such as $CDCl_3$. See: Freitas, M. P.; Tormena, C. F.; Garcia, J. C.; Rittner, R.; Abraham, R. J.; Basso, E. A.; Santos, F. P.; Cedran, J. C. *J. Phys. Org. Chem.* **2003**, *16*, 833−838.

(14) Only one previous example of anion-induced translational isomerism in a [2]rotaxane has been reported. See: Keaveney, C. M.; Leigh, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 1222−1224.

(15) Very recently, Li^+ ions have been used to control the distribution of translational isomers in a neutral bistable [2]rotaxane. See: Vignon, S. A.; Jarrosson, T.; Iijima, T.; Tseng, H.-R.; Sanders, J. K. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*,. 9884−9885.

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