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Degenerate [2]Rotaxanes with Electrostatic Barriers

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† *These authors contributed equally to this work.*

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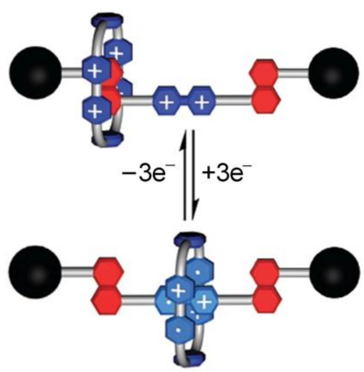


Upon reduction, the one-electron reduced bipyridinium radical cation on the dumbbell components of the degenerate [2]rotaxanes serves as an additional recognition site for the two-electron reduced cyclobis(paraquat-*p*-phenylene) diradical cationic ring components. The ring components in the molecular shuttles can be switched between the three recognition sites – two 1,5-dioxynaphthalene units and one-electron reduced bipyridinium radical cation – under the redox control.

Abstract: A synthetic approach to the preparation of [2]rotaxanes (**1–5**•$6PF_6$) incorporating bispyridinium derivatives and two 1,5-dioxynaphthalene (DNP) units situated in the rod portions of their dumbbell components that are encircled by a single cyclobis(paraquat-*p*-phenylene) tetracationic ($CBPQT^{4+}$) ring, has been developed. Since the π-electron-deficient bispyridinium units are introduced into the dumbbell components of the [2]rotaxanes **1–5**•$6PF_6$, there are Coulombic charge–charge repulsions between these dicationic units and the $CBPQT^{4+}$ ring in the [2]rotaxanes. Thus, the $CBPQT^{4+}$ rings in the degenerate [2]rotaxanes exhibit slow shuttling between two DNP recognition sites on the ^{1}H NMR time-scale on account of the electrostatic barrier posed by the bispyridinium units, as demonstrated by variable-temperature ^{1}H NMR spectroscopy. The electrochemical experiments carried out on the [2]rotaxanes **1**•$6PF_6$ and **2**•$6PF_6$ indicate that the one-electron reduced bipyridinium radical cation in the dumbbell components of the [2]rotaxanes serves as an additional recognition site for the two-electron reduced $CBPQT^{2(\bullet+)}$ diradical cationic ring. Under the appropriate circumstances, the ring components in the degenerate rotaxanes **1**•$6PF_6$ and **2**•$6PF_6$ can shuttle along the recognition sites – two DNP units and one-electron reduced bipyridinium radical cation – under the redox control.

Introduction

Molecular switches and machines[1–3] incorporating donor–acceptor [2]catenanes[1a–e] and [2]rotaxanes[1a–e] have been the focal points of extensive experimental investigations in solution[1a,1c–e] as well as in solid-state devices.[1b,3a,3e] In particular, switchable [2]rotaxanes, containing π-electron-rich tetrathiafulvalene (TTF) and/or 1,5-dioxynaphthalene (DNP) recognition sites, located in the rod portions of their dumbbell components and encircled by a single cyclobis(paraquat-*p*-phenylene)

(CBPQT^{4+}) ring, have been investigated[3a,3b,3e] as one of the leading candidates for expressing relative intramolecular translation motion[1m] of its dumbbell and ring components.

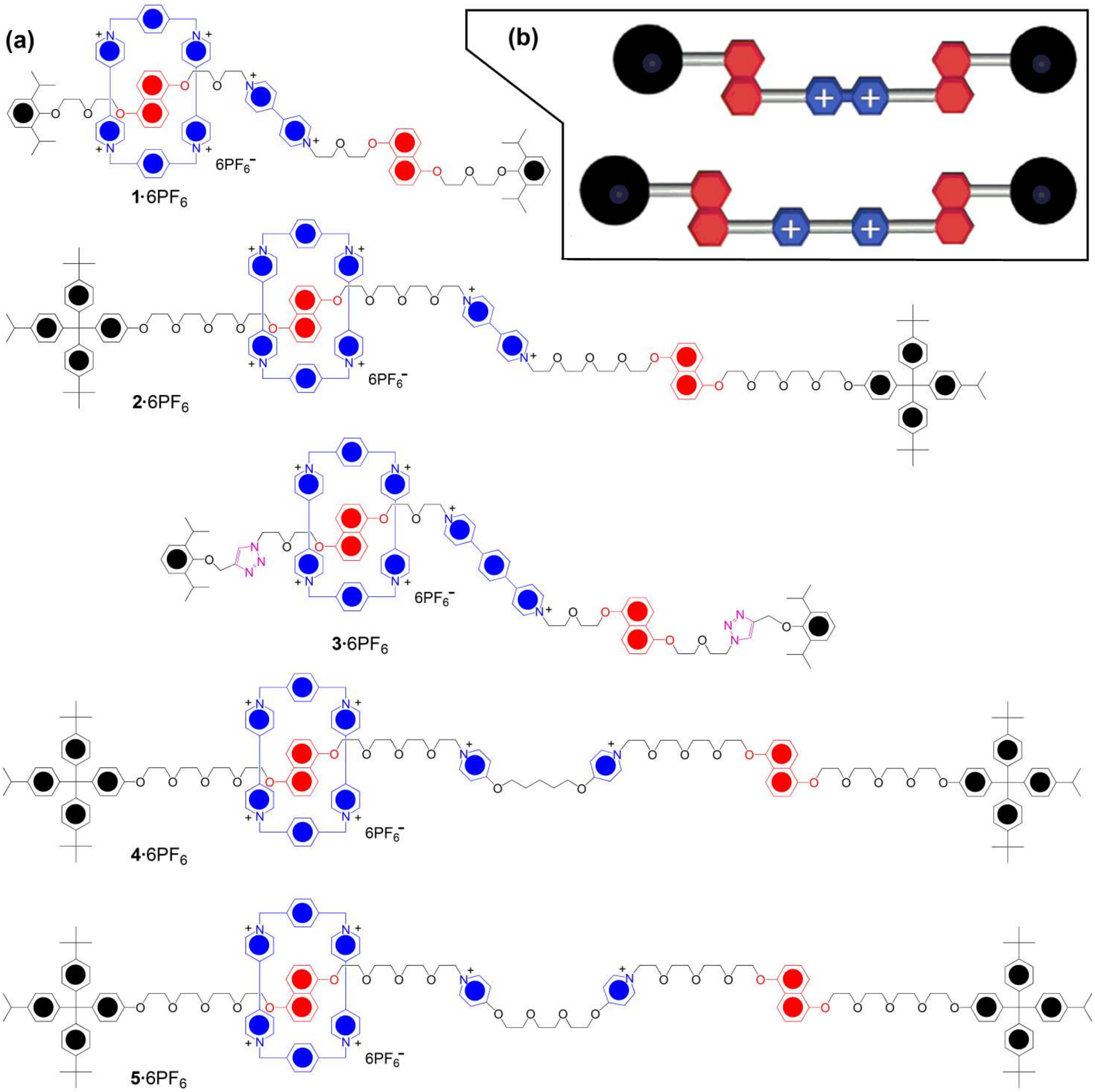


Fig. 1 (a) Structural formulae for the five degenerate [2]rotaxanes **1–5**•6PF$_6$. (b) The two different kinds of dumbbell components present in these five degenerate [2]rotaxanes. In one set (**1–3**•6PF$_6$) of rotaxanes, the two positive charges are part of a conjugate aromatic system, while, in the other set (**4**•6PF$_6$ and **5**•6PF$_6$), the charges are associated with separate aromatic systems.

The constitution of the spacers between the recognition sites on the dumbbell components of the degenerate [2]rotaxanes is an important factor in governing the movement of the $CBPQT^{4+}$ ring. Previously, we investigated the switching behaviour of the $CBPQT^{4+}$ ring in degenerate [2]rotaxanes with spacers such as polyethylene glycol chains,[4] terphenyl units,[5] rigid arylmethyl and butadiynyl rods,[6] and azobenzene units.[7] In the case of degenerate [2]rotaxanes[4c,6c,6d,7] containing two equivalent recognition sites – e.g., two DNP units – the $CBPQT^{4+}$ ring shuttles back and forth between the two sites usually under the influence of heat. In a few instances,[7] the rate of shuttling has been controlled by means of light when, for example, azobenzene units are the spacers. In the case of bistable [2]rotaxanes,[4,5] like those mentioned above, the $CBPQT^{4+}$ ring can be induced to move between TTF and DNP units by means of chemical[5] or electrochemical[4,5] stimuli. The bistability of the switchable [2]rotaxanes relies (Fig. 2) on the ability of the $CBPQT^{4+}$ ring to encircle much more strongly the TTF unit in the so-called ground state co-conformation (GSCC) than it does the considerably less π-electron rich DNP unit in the metastable state co-conformation (MSCC) in the dumbbell components. Switching is achieved by the reversible oxidation of the TTF unit, firstly to the radical cation[4d,4e,8] ($TTF^{+\bullet}$) and then to its dication (TTF^{2+}), thus producing Coulombic charge-charge repulsion between the oxidised $TTF^{+\bullet}$ or TTF^{2+} species and the $CBPQT^{4+}$ ring, leading to the movement of the $CBPQT^{4+}$ ring to the DNP unit. After the reduction of the $TTF^{+\bullet}$ radical cation or TTF^{2+} dication to their neutral form, the MSCC becomes populated, and the $CBPQT^{4+}$ ring begins to migrate back onto the TTF recognition unit. The barrier to this relaxation process ($\Delta G^{\ddagger}$) is 3 kcal mol^{-1} higher[10b] in the presence of the bipyridinium unit ($BIPY^{2+}$).

In addition to the traditional TTF and/or DNP recognition sites for the $CBPQT^{4+}$ ring in the [2]rotaxanes, of particular interest is the introduction of potential electrostatic barriers – that is, positively charged entities – which would potentially curtail the translational motion undergone by the $CBPQT^{4+}$ ring. In order to investigate the influence of placing "speed bumps" in the shape of positively charged entities between two DNP units in degenerate molecular shuttles, the [2]rotaxanes **1–5**•$6PF_6$ (Fig. 1) have been synthesised (Schemes 1, 2 and 3). In **1**•$6PF_6$ and **2**•$6PF_6$, the speed bumps are $BIPY^{2+}$ units. In **3**•$6PF_6$, the speed bump is a 1,4-bis(pyridinium)benzene[9] unit. In the case of **4**•$6PF_6$ and **5**•$6PF_6$, the conjugation between the two pyridinium rings is broken by spacers containing saturated chains of atoms. All of the five molecular shuttles have been investigated by variable temperature (dynamic) ^1H NMR spectroscopy: they all exhibit slow shuttling on the ^1H NMR time-scale, at least up to +70 °C in CD_3CN solutions.

Recently, we introduced[10] $BIPY^{2+}$ units into the dumbbell components of the $CBPQT^{4+}$ ring-containing [2]rotaxanes and demonstrated[10] that the one-electron reduced radical cation ($BIPY^{\bullet+}$) serves as an additional recognition site for the two-electron reduced $CBPQT^{2(\bullet+)}$ ring. Electrochemical experiments carried out on **1**•$6PF_6$ and **2**•$6PF_6$ indicate that the $BIPY^{\bullet+}$ radical cation does act as an additional recognition site for the $CBPQT^{2(\bullet+)}$ ring. Thus, ring shuttling can be induced by reduction in the case of **1**•$6PF_6$ and **2**•$6PF_6$. This paper describes how speed bumps can be introduced into molecular shuttles and how, in some instances, they can be modified by replacing the spacers. Establishing this kind of control in the switching of bistable [2]rotaxanes could have important consequences for the development of molecular flash memory using molecules of this kind.

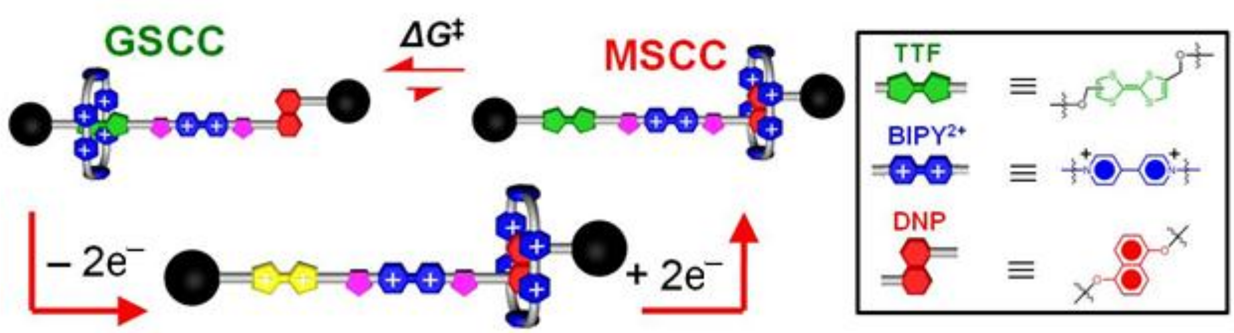
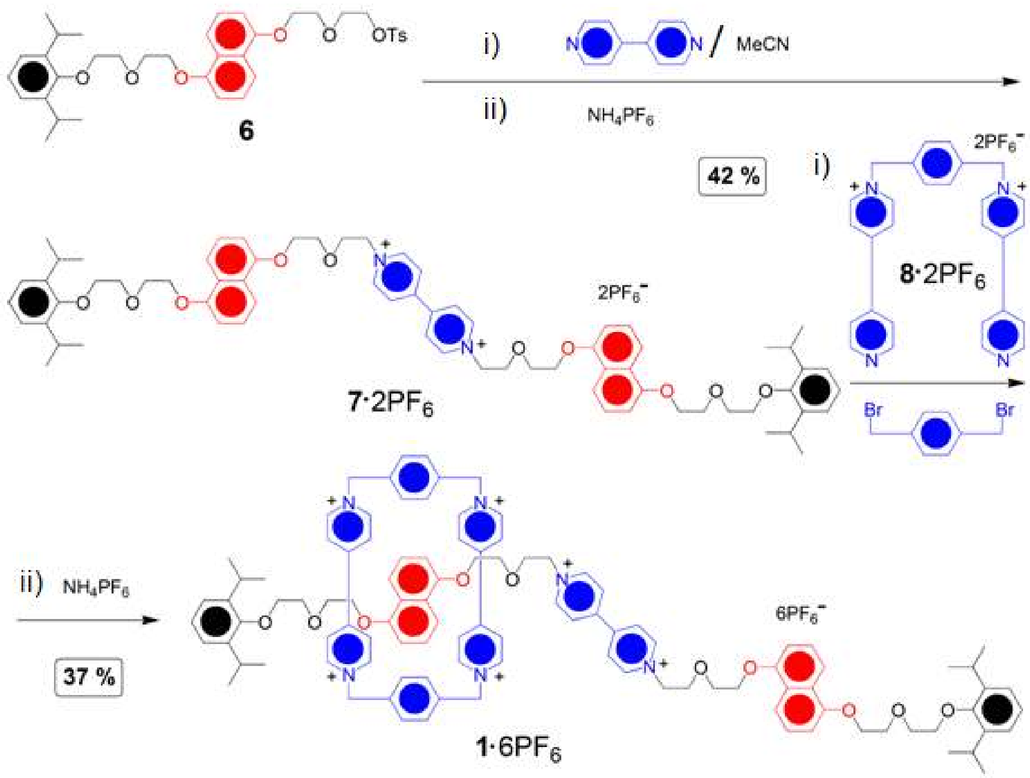


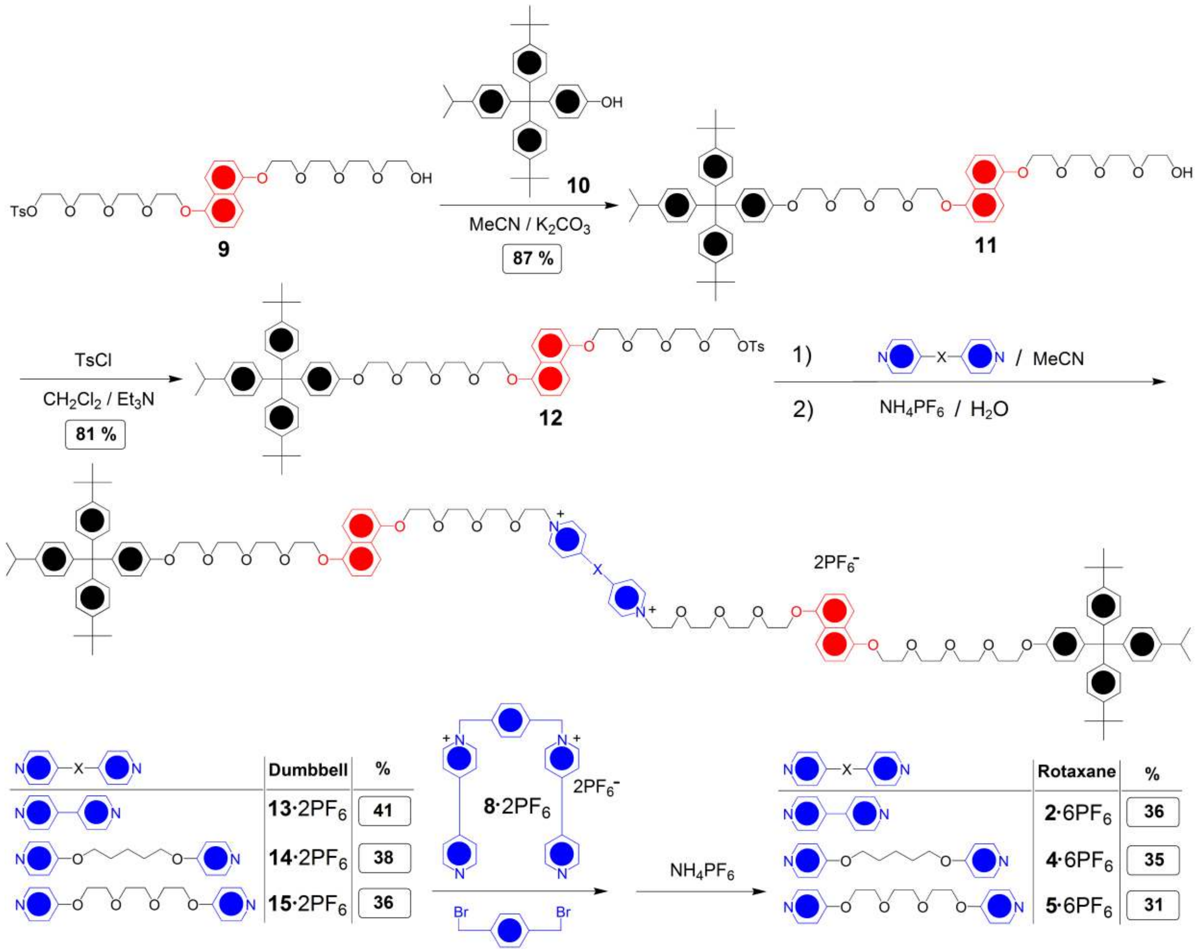
Fig. 2. Graphical representation of a rotaxane undergoing redox stimulated switching employing TTF and DNP recognition units, with a bipyridinium unit ($BIPY^{2+}$) in the middle of the dumbbell component as a "speed bump". The GSCC and the MSCC represent the ground state co-conformation and the metastable state co-conformation, respectively.

Results and discussion



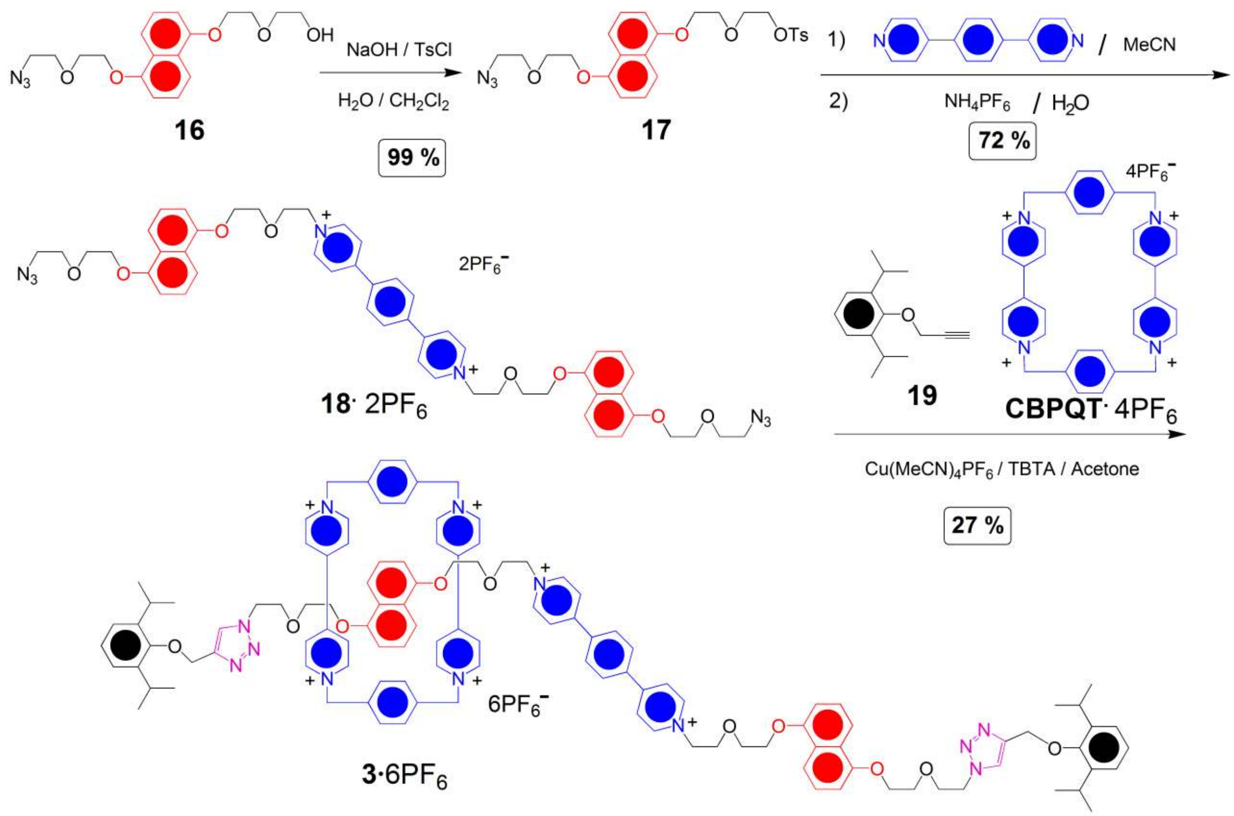
Scheme 1 The synthesis of the [2]rotaxane **1**•6PF$_6$

The synthesis of the [2]rotaxane **1**•6PF$_6$ is summarised in Scheme 1. Reaction of the tosylated half dumbbell[10] **6** with 4,4′-bipyridine afforded the dumbbell **7**•2PF$_6$ after counterion exchange. The [2]rotaxane **1**•6PF$_6$ was obtained from **7**•2PF$_6$, the **8**•2PF$_6$ salt,[11] and 1,4-bis(bromomethylbenzene) using a template-directed protocol[12] in DMF under 10 kbar pressure at room temperature for 3 days. After the reaction was complete, the crude mixture was purified by preparative TLC on silica gel using Me$_2$CO / NH$_4$PF$_6$ (100/1 v/w) as the mobile phase to afford **1**•6PF$_6$ in an overall yield of 37 %. The syntheses of the [2]rotaxanes **2**•6PF$_6$,**4**•6PF$_6$ and **5**•6PF$_6$ are summarised in Scheme 2.



Scheme 2 The syntheses of the [2]rotaxanes **2**•$6PF_6$–**4**•$6PF_6$

In a manner reminiscent of the synthesis of the [2]rotaxane **1**•$6PF_6$, the dumbbell compounds **13**•$2PF_6$–**15**•$2PF_6$ were obtained from the tosylated half dumbbell **12** by reaction, in turn, with 4,4′-bipyridine, 1,5-bis(pyridinyloxy)pentane, and 1,2-bis(2-(pyridinyloxy)ethoxy)ethane. The [2]rotaxanes **2**•$6PF_6$,**4**•$6PF_6$ and **5**•$6PF_6$ were prepared from corresponding dumbbells by means of a templation protocol,[12] similar to that employed in the synthesis of **1**•$6PF_6$, in yields ranging from 30 % to 40 %. The synthesis of the [2]rotaxane **3**•$6PF_6$ is summarised in Scheme 3. In contrast with the synthetic strategies associated with the clipping methodology[13], a strategy of threading-followed-by-stoppering[14] was utilised in the synthesis of the [2]rotaxane **3**•$6PF_6$. Reaction (Scheme 3) of the azide derivative **16** with 1,4-bis(4-pyridyl)benzene afforded the dumbbell **17**•$2PF_6$ after counterion exchange. The [2]rotaxane **3**•6PF_6 was isolated in 27% yield, following the reaction of **17**•2PF_6 with the alkyne derivative **18** in Me_2CO using the copper(I)-catalyzed azide-alkyne cycloaddition in the presence of **CBPQT**•4PF_6 salt. The [2]rotaxanes **1−5**•6PF_6 were all fully characterized by ^{1}H and ^{13}C NMR spectroscopies and by electrospray ionization mass spectrometry.



Scheme 3 The syntheses of the [2]rotaxanes **3**•6PF_6

In the ^{1}H NMR spectra of these five [2]rotaxanes recorded in CD_3CN at 298 K, the protons of the DNP units and stoppers resonate as two sets of peaks, demonstrating that the $CBPQT^{4+}$ rings in the [2]rotaxanes encircle one of the two equivalent DNP units in their dumbbell components, i.e., the $CBPQT^{4+}$ ring is not shuttling rapidly between the two DNP units on the ^{1}H NMR time-scale. As a result of this slow shuttling on the ^{1}H NMR time-scale, two sets of the resonances are observed for the DNP protons for all five [2]rotaxanes − one DNP unit that is "free" and one that is encircled by the $CBPQT^{4+}$ ring. This fact is further substantiated from the observation that the set of resonances corresponding to the protons of the free DNP units have very similar δ values to those recorded for the DNP protons in their corresponding dumbbell compounds. The resonances for the protons on the other DNP units encircled by the $CBPQT^{4+}$ ring experience large upfield shifts that can be observed at ca. δ = 2.3, 5.9, and 6.2 ppm as a result of [π···π] stacking interactions with the encircling $CBPQT^{4+}$ ring.

A series of variable-temperature (VT) ^{1}H NMR spectroscopic experiments have been performed in CD_3CN or d_7-DMF in order to investigate[6d,7] the shuttling behaviour of the $CBPQT^{4+}$ rings in the degenerate [2]rotaxanes. We did not observe any substantial changes in the ^{1}H NMR spectra of **1–5**•$6PF_6$ in the temperature range 233–343 K, indicating that the $CBPQT^{4+}$ rings are not shuttling rapidly back and forth between the two DNP units on the ^{1}H NMR time-scale in this temperature

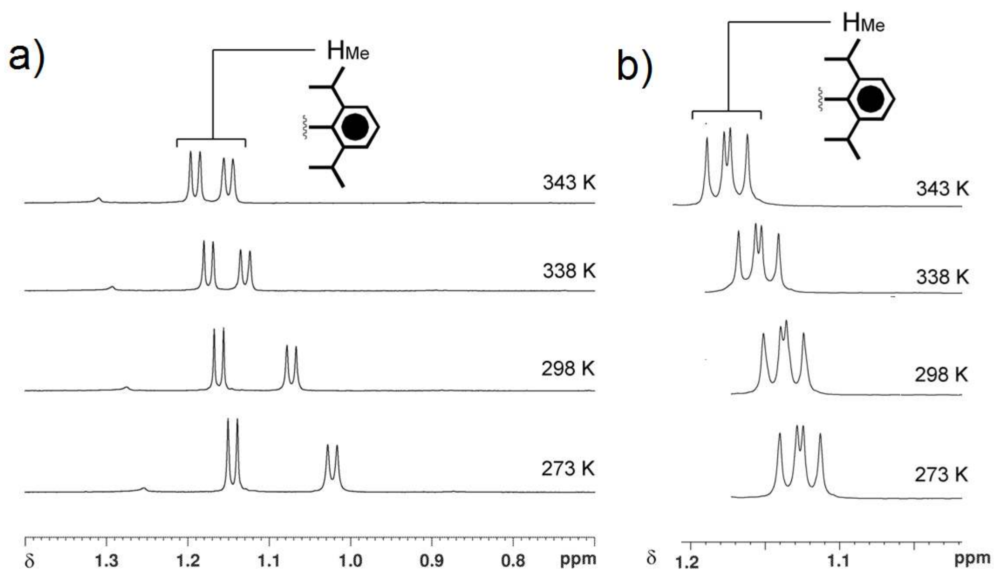


Fig. 3 Partial ^{1}H NMR spectra of the [2]rotaxane a) **1**•$6PF_6$ and b) **3**•$6PF_6$ recorded in CD_3CN at different temperatures showing the signals for the probe protons (H_{Me}) in the form of the methyl groups on the 2,6-diisopropylphenyl stoppers. No coalescence could be observed.

range. Two examples are presented in Fig. 3 which illustrates the partial VT ^{1}H NMR spectra of the degenerate [2]rotaxane **1**•$6PF_6$ and **3**•$6PF_6$ recorded in CD_3CN in the temperature range 233−343 K. The methyl protons (H_{Me}) on the 2,6-diisopropylphenyl stoppers, which can be employed in order to probe the shuttling process, feature two doublets at 273 K. While the two doublets in each case undergo temperature-dependent shifts, they were not observed to coalesce. These observations indicate that the shuttling of the $CBPQT^{4+}$ ring in the case of all five [2]rotaxanes is slow on the ^1H NMR time-scale, even at 343 K.

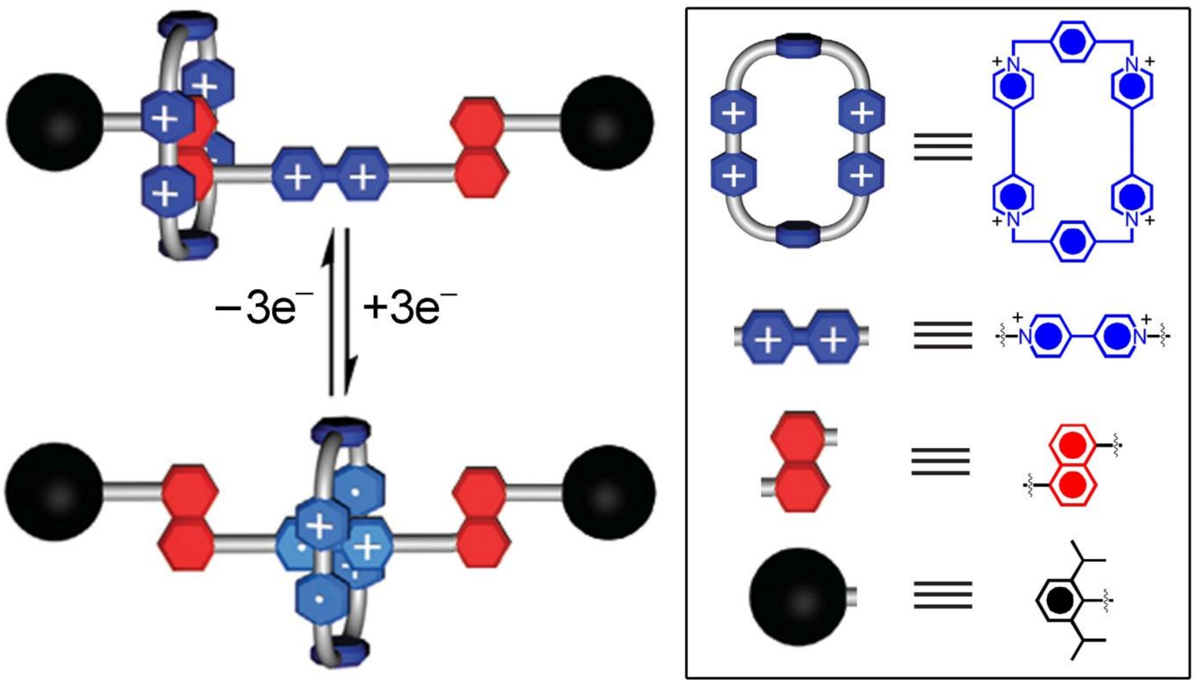


Fig. 4 Schematic of the switching of the $CBPQT^{4+}$ ring in the [2]rotaxane **1**•$6PF_6$ or **2**•$6PF_6$ upon redox control

The location of the $BIPY^{2+}$ unit in the [2]rotaxanes **1**•$6PF_6$ and **2**•$6PF_6$ allows for a reduction-based switching process to occur which also eradicates the electrostatic barrier to shuttling of the ring between the two DNP units in the degenerate [2]rotaxane **1**•$6PF_6$ and **2**•$6PF_6$. We have shown recently[10b] that, upon a two-electron reduction of the $CBPQT^{4+}$ ring to its diradical dication $CBPQT^{2(\bullet+)}$ and a one-electron reduction of the $BIPY^{2+}$ unit − located in either the dumbbell component of a rotaxane or in the thread component of a pseudorotaxane − to its radical cation

BIPY$^{\bullet+}$, encirclement of the ring around the dumbbell or thread occurs as a result of radical-pairing interactions (Fig. 4). These interactions have been characterized by cyclic voltammetry (CV) which provides evidence for the bistability of the [2]rotaxanes **1**•$6PF_6$ and **2**•$6PF_6$ under the influence of reductive potentials.

The [2]rotaxane **1**•$6PF_6$ displays the characteristic CV behaviour observed previously[10] for the reduction-induced switching of the CBPQT^{4+} ring in relation to the BIPY^{2+} unit in its dumbbell component. The first feature of significance in the CV (Fig. 5) is a three-electron reduction process at −0.29 V, the potential at which two electrons are gained by the CBPQT^{4+} ring component while the third electron is taken up by the BIPY^{2+} unit in the dumbbell component. The three-electron reduction results in the encirclement of the CBPQT$^{2(\bullet+)}$ diradical cationic ring component around the BIPY$^{\bullet+}$ radical cationic unit in the dumbbell component. In the radical pairing interactions

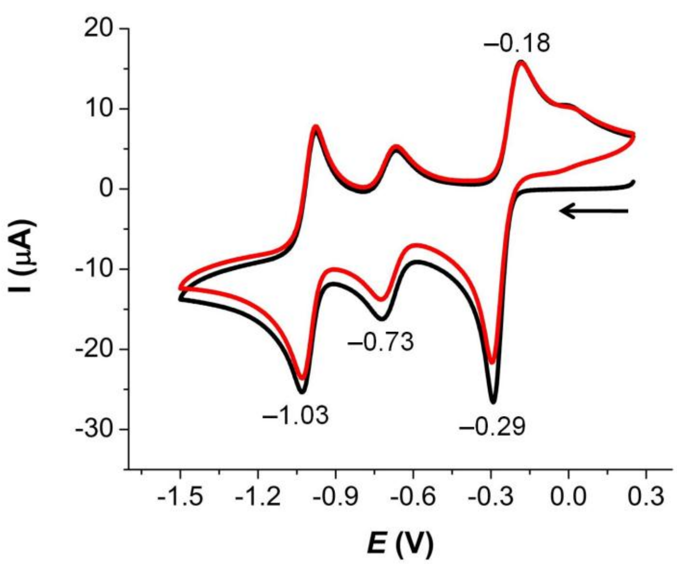


Fig. 5 The first (black) and second (red) scans arising from the CV of the [2]rotaxane **1**•$6PF_6$ in the reduction region.

which are driving this intramolecular reaction to occur, one of the BIPY$^{\bullet+}$ radical cations on the

$CBPQT^{2(\bullet+)}$ ring is engaged intimately with $BIPY^{\bullet+}$ present in the dumbbell component. This biased interaction results in the splitting of the second reduction cycle of the ring component into two one-electron processes at peak potentials of –0.73 and –1.03 V, the more negative of which is coupled to the second reduction of the BIPY unit in the dumbbell component. The return scan shows (Fig. 5) that these two redox processes are completely reversible. Re-oxidation of the trisradical species shows one broad anodic process at –0.18 V (200 mV s^{-1} scan rate) corresponding to a potential that is considerably more positive than would be expected for a totally reversible process with respect to the initial three-electron reduction, an observation which reflects the highly stabilizing interactions that result as a consequence of a $BIPY^{\bullet+}$ radical cation in the dumbbell component that is encircled by a $CBPQT^{2(\bullet+)}$ ring. The **2**•$6PF_6$ also exhibited similar bistability and switching behaviour when investigated by CV. It follows that the two [2]rotaxanes **1**•$6PF_6$ and **2**•$6PF_6$, where bipyridinium radical cations can be generated in conjugated systems such that electron-delocalization can occur, may also be regarded as the precursors to tristable [2]rotaxanes when one of the two DNP units is replaced, for example, by a TTF unit.

We have also investigated the reduction properties of the degenerate [2]rotaxanes **4**•$6PF_6$ and **5**•$6PF_6$ under the same conditions as for **1**•$6PF_6$ and **2**•$6PF_6$ and did not observe any interactions between the $CBPQT^{2(\bullet+)}$ diradical cationic ring and the flexible spacers containing two pyridinium units in their dumbbell components. Consequently, the $CBPQT^{4+}$ ring cannot be induced to shuttle electrochemically between the two degenerate DNP units in the dumbbell component of **4**•$6PF_6$ and **5**•$6PF_6$. The reason for the inability to undergo well-defined switching upon reduction no doubt resides in the fact that the two pyridinium units are not conjugated and so cannot generate radical cations for binding with the $CBPQT^{2(\bullet+)}$ diradical cationic ring. In the case of the [2]rotaxane **3**•$6PF_6$, we are currently investigating its electrochemical behaviour, which is revealing interesting preliminary results – likely as a consequence of the aromatic conjugation between the two pyridinium units.

Conclusions

In degenerate donor-acceptor rotaxanes inserting positively charged entities which can be reduced readily leads to electrostatic barriers to the shuttling of a cyclobis(paraquat-*p*-phenylene) ring. When, however, the positive charge is associated with a conjugated bipyridinium ring, or its higher homologues, then reduction to form radical cations leads to a dramatic stabilisation when interacting with the ring also in a partially reduced form. This interaction, not only removes the electrostatic barrier to shuttling, but also renders the [2]rotaxanes bistable. Investigation of the potential for the 1,4-bis(pyridinium)benzene unit in the degenerate [2]rotaxane **3**•6PF_6 to serve as a recognition site for a $CBPQT^{4+}$ ring is still under investigation at the time. These redox-active bistable molecules involving direct and reversible control on oxidation, could come into their own as an attractive means of developing the next generation of molecular electronic devices.

Experimental

General

All reagents were purchased from Aldrich and were used without further purification. The starting materials **5**,[10] **7**•2PF_6,[11] **8**,[15] **9**,[16] **16**,[15] 1,4-bis(4-pyridyl)benzene[17] and **CBQPT**•4PF_6[18] were prepared according to literature procedures. Deuterated solvents (Cambridge Isotope Laboratories) for nuclear magnetic resonance (NMR) spectroscopic analyses were used as received. NMR Spectra were recorded on a Bruker Avance 500 MHz or 600 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from the Me_4Si resonance which was used as the internal standard when recording ^1H NMR spectra. High resolution mass spectra were measured on an Applied Biosystems Voyager DE-PRO MALDI TOF mass spectrometer or a Micromass Q-TOF Ultima electrospray ionization mass spectrometer. The reported molecular mass (m/z) values were the most abundant monoisotopic mass. UV-Vis spectra were recorded at room temperature on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Electrochemical experiments were carried out at 298 K in Ar-purged MeCN, with a multipurpose instrument with a Gamry Multipurpose instrument (Reference 600) interfaced to a PC. Cyclic voltammetry (CV) experiments were performed using a glassy carbon working electrode (0.071 cm^2, Cypress system). Its surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was an Ag/AgCl electrode. The concentration of the sample and supporting electrolyte tetrabutylammonium hexafluorophosphate (TBA•PF_6) were 1.0×10^{-3} mol L^{-1} and 0.1 mol L^{-1}, respectively.

Syntheses

7•2PF_6: A mixture of **6** (65.0 g, 0.10 mmol) and 4,4′-bipyridine (6.3 mg, 0.04 mmol) in anhydrous DMF (5.0 mL) was transferred to a teflon tube and subjected to 10 kbar pressure at room temperature for 4 d. The purple solution was subjected directly to column chromatography (SiO_2) and unreacted starting materials were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO / NH_4PF_6 (100:1 v/w) and the purple band was collected. Most of the solvent was removed in vacuo, followed by addition of H_2O (15 mL). The resulting precipitate was collected by filtration, affording the dumbbell **7**•2PF_6 (24.2 mg, 42 %). ^{1}H NMR (500 MHz, $(CD_3)_2CO$, TMS): δ = 1.14–1.15 (d, 24H, J = 7.0 Hz), 3.35–3.37 (m, 4H), 3.66–3.79 (m, 20H), 4.47–4.51 (m, 12H), 6.89−6.91 (d, 4H, J = 7.6 Hz), 7.07−7.10 (d, 6H), 7.43−7.45 (d, 4H, J = 7.6 Hz), 7.89−7.90 (d, 4H, J = 7.6 Hz), 8.12−8.14 (d, 4H, J = 7.8 Hz), 9.09−9.11 ppm (d, 4H, J = 7.8 Hz). ^{13}C NMR (125 MHz, $(CD_3)_2CO$, TMS): δ = 23.5, 28.4, 68.4, 69.9, 70.5, 108.1, 115.8, 121.7, 123.6, 124.3, 126.2, 128.6, 142.0, 144.8, 148.7, 150.8, 154.3 ppm. HRMS: calcd for $C_{70}H_{86}F_6N_2O_{10}P$ $[M - PF_6]^+$ m/z = 1259.5924, found m/z = 1259.5914; calcd for $C_{70}H_{86}N_2O_{10}$ $[M - 2PF_6]^{2+}$ m/z = 557.3141, found m/z = 557.3179.

1•6PF_6: The dumbbell compound **7**•2PF_6 (70.2 mg, 0.05 mmol), **8**•2PF_6 (28.2 mg, 0.04 mmol), and 1,4-bis(bromomethylbenzene) (10.5 mg, 0.04 mmol) were dissolved in anhydrous DMF (8 mL). The reaction mixture was subjected to 10 kbar pressure at room temperature for 3 d. After the solvent had been removed in vacuo, the purple solid was dissolved in Me_2CO and the [2]rotaxane **1**•6PF_6 was isolated by means of preparative TLC using Me_2CO / NH_4PF_6 (100:1 v/w) as the mobile phase. The product was recovered from the silica gel by washing with an excess of eluent. The solution was concentrated to a minimum volume and the product was precipitated from the solution by addition of H_2O (12 mL). The resulting precipitate was collected by filtration, affording the pure [2]rotaxane **1**•6PF_6 (37.1 mg, 37 %). ^{1}H NMR (500 MHz, CD_3CN, TMS): δ = 1.07–1.08 (d, 12H, J = 6.8 Hz), 1.16–1.17 (d, 12H, J = 6.8 Hz), 2.31–2.33 (m, 2H), 3.21–3.23 (m, 2H), 3.32–3.34 (m, 2H), 3.59–3.89 (m, 20H), 4.32–4.47 (m, 12H), 5.68–5.74 (m, 8H), 5.86–5.88 (m, 2H), 6.21–6.23 (m, 2H), 6.86−6.88 (d, 2H, J = 8.0 Hz), 7.03−7.16 (m, 14H), 7.44−7.46 (d, 2H, J = 8.0 Hz), 7.77−7.79 (d, 2H, J = 8.0 Hz), 7.88−7.92 (m, 8H), 8.08−8.14 (m, 4H), 8.89−8.91 (d, 2H, J = 7.0 Hz), 8.94−8.96 (d, 2H, J = 7.0 Hz), 9.06−9.11 ppm (m, 8H). ^{13}C NMR (125 MHz, CD_3CN, TMS): δ = 23.4, 28.6, 62.4, 68.7, 69.5, 70.7, 108.2, 115.7, 121.2, 121.7, 123.4, 124.6, 126.2, 127.5, 128.8, 134.7, 142.1, 144.9, 148.6, 150.8, 154.4 ppm. HRMS: calcd for $C_{106}H_{118}F_{30}N_6O_{10}P_5$ $[M - PF_6]^+$ m/z = 2359.7118, found m/z = 2359.7467; calcd for $C_{106}H_{118}F_{24}N_6O_{10}P_4$ $[M - 2PF_6]^{2+}$ m/z = 1107.3739, found m/z = 1107. 4133.

1,2-Bis(2-(pyridinyloxy)ethoxy)ethane: A mixture of 4-chloropyridine (2.5 g, 22.0 mmol), 2-[2-(2-chloroethoxy)ethoxy]ethanol (1.5 g, 10.0 mmol), and NaH (1.0 g, 40.0 mmol) in dry DMF (80 mL) was stirred for 2 d at 80 °C under an atmosphere of Ar. After the solvent had been removed under reduced pressure, the residue was triturated with CH_2Cl_2 and the precipitated salts were removed by filtration. The filtrate was concentrated under reduced pressure to yield a crude product, which was subjected to column chromatography (SiO_2, EtOAc) to give 1,2-bis(2-(pyridinyloxy)ethoxy)ethane (0.9 g, 31 %). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ = 3.53−3.55 (m, 4H, OCH_2), 3.77−3.80 (m, 4H, OCH_2), 4.27−4.29 (m, 4H, OCH_2), 7.07−7.09 (d, 4H, Ar-H), 8.41−8.43 ppm (d, 4H, Ar-H). ^{13}C NMR (125 MHz, CD_2Cl_2, TMS): δ = 69.1, 70.3, 110.2, 150.8, 161.7 ppm. MS: calcd for $C_{16}H_{21}N_2O_4$ $[M + H]^+$ m/z = 305.150, found m/z = 305.173.

1,5-Bis(pyridinyloxy)pentane: A mixture of 4-chloropyridine (2.5 g, 22.0 mmol), 1,5-pentanediol (1.0 g, 10.0 mmol), and NaH (1.0 g, 40.0 mmol) in dry DMF (80 mL) was stirred for 2 d at 80 °C under an atmosphere of Ar. After the solvent had been removed under reduced pressure, the residue was triturated with CH_2Cl_2 and the precipitated salts were removed by filtration. The filtrate was concentrated under reduced pressure to yield a crude product, which was subjected to column chromatography (SiO_2, CH_2Cl_2) to give 1,5-bis(pyridinyloxy)pentane (1.0 g, 39 %). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ = 1.59−1.61 (m, 2H, CH_2), 1.76−1.78 (m, 4H, CH_2), 4.05−4.07 (m, 4H, CH_2), 7.08−7.10 (d, 4H, Ar-H), 8.42−8.44 ppm (d, 4H, Ar-H). ^{13}C NMR (125 MHz, CD_2Cl_2, TMS): δ = 22.5, 30.2, 68.9, 110.1, 150.7, 161.5 ppm. MS: calcd for $C_{15}H_{19}N_2O_2$ $[M + H]^+$ m/z = 259.145, found m/z = 259.157.

11: A mixture of **9** (2.0 g, 3.0 mmol), **10** (1.5 g, 3.0 mmol), K_2CO_3 (0.8 g, 6.0 mmol), LiBr (17.2 mg, 0.2 mmol), and [18]crown-6 (26.4 mg, 0.1 mmol) in anhydrous MeCN (80 mL) was heated under reflux for 16 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with MeCN. The combined organic solution was concentrated and the residue was purified by column chromatography (SiO_2, EtOAc : MeOH = 98:2) to give compound **11** (2.6 g, 87 %). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ = 1.22−1.24 (d, 6H, J = 8.0 Hz), 1.33 (s, 18H), 2.86−2.87 (m, 1H), 3.48−3.56 (m, 20H), 3.79−3.81 (m, 6H), 4.33−4.35 (m, 6H), 6.75−6.77 (d, 2H, J = 8.2 Hz), 6.82−6.83 (d, 2H, J = 7.8 Hz), 7.08−7.18 (m, 10H), 7.28−7.30 (d, 4H), 7.45−7.47 (d, 2H, J = 7.8 Hz), 7.88−7.90 ppm (d, 2H, J = 7.8 Hz). ^{13}C NMR (125 MHz, CD_2Cl_2, TMS): δ = 23.6, 31.5, 33.9, 34.7, 61.7, 64.6, 69.4, 70.8, 108.2, 115.3, 116.1, 125.7, 126.8, 128.0, 128.9, 139.9, 145.2, 146.4, 149.5, 154.3, 156.5 ppm. MS: calcd for $C_{62}H_{81}O_{10}$ $[M + H]^+$ m/z = 985.583, found m/z = 985.598.

12: A solution of TsCl (1.0 g, 5.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of **11** (3.9 g, 4.0 mmol), Et_3N (1 mL), and DMAP (12.5 mg, 0.1 mmol) in CH_2Cl_2 (100 mL) at 0 °C under an atmosphere of Ar. The mixture was warmed up to room temperature while stirring for 16 h. After the precipitated salts were filtered off and the solvent had been evaporated under reduced pressure, the residue was purified by column chromatography (SiO_2, EtOAc) to give compound **12** (3.7 g, 81 %). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ = 1.21−1.23 (d, 6H, J = 7.8 Hz), 1.34 (s, 18H), 2.33 (s, 3H), 2.86−2.87 (m, 1H), 3.51−3.57 (m, 18H), 3.76−3.82 (m, 8H), 4.32−4.35 (m, 6H), 6.80−6.82 (d, 2H, J = 8.0 Hz), 6.83−6.84 (d, 2H, J = 8.0 Hz), 7.10−7.18 (m, 10H), 7.35−7.37 (d, 2H, J = 7.5 Hz), 7.46−7.47 (d, 2H, J = 8.0 Hz), 7.76−7.78 (d, 2H, J = 8.2 Hz), 7.88−7.90 (d, 2H, J = 8.0 Hz), 7.29−7.31 ppm (d, 4H). ^{13}C NMR (125 MHz, CD_2Cl_2, TMS): δ = 21.5, 23.6, 31.4, 33.7, 34.3, 64.5, 68.1, 69.6, 70.5, 108.0, 115.4, 116.2, 125.6, 126.9, 128.2, 129.1, 130.7, 139.5, 144.2, 145.1, 146.2, 149.3, 154.5, 156.7 ppm. MS: calcd for $C_{69}H_{87}O_{12}S$ $[M + H]^+$ m/z = 1139.592, found m/z = 1139.607.

13•2PF$_6$: A mixture of **12** (0.11 g, 0.10 mmol) and 4,4′-bipyridine (6.3 mg, 0.04 mmol) in anhydrous DMF (5.0 mL) was transferred to a teflon tube and subjected to 10 kbar pressure at room temperature for 4 d. The purple solution was directly subjected to column chromatography (SiO_2) and the unreacted starting materials were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO / NH_4PF_6 (100:1 v/w) and the purple band was collected. Most of the solvent was removed in vacuo, followed by addition of H_2O (15 mL). The resulting precipitate was collected by filtration, affording the dumbbell **13•2PF$_6$** (39.1 mg, 41 %). ^{1}H NMR (500 MHz, $(CD_3)_2CO$, TMS): δ = 1.18−1.20 (d, 12H, J = 6.9 Hz), 1.31 (s, 36H), 2.83−2.85 (m, 2H), 3.58−3.66 (m, 12H), 3.70−3.72 (m, 4H), 3.73−3.80 (m, 16H), 3.82−3.84 (m, 4H), 3.93−3.96 (m, 8H), 4.03−4.04 (m, 4H), 4.09−4.12 (m, 4H), 4.18−4.21 (m, 8H), 4.76−4.78 (m, 4H), 6.73−6.78 (m, 8H), 7.05−7.12 (m, 20H), 7.29−7.31 (m, 8H), 7.41−7.43 (d, 4H, J = 8.4 Hz), 7.94−7.95 (d, 4H, J = 6.8 Hz), 8.13−8.15 (d, 4H, J = 8.4 Hz), 9.03−9.04 ppm (d, 4H, J = 6.8 Hz). ^{13}C NMR (500 MHz, $(CD_3)_2CO$, TMS): δ = 23.3, 30.6, 33.2, 33.8, 53.1, 63.9, 69.2, 70.0, 70.4, 106.6, 113.8, 115.0, 121.6, 125.4, 126.1, 127.9, 128.7, 139.4, 144.6, 145.5, 145.9, 148.4, 150.6, 153.7, 156.7 ppm. HRMS: calcd for $C_{134}H_{166}N_2O_{18}$ $[M-2PF_6]^{2+}$ m/z = 1045.6068, found m/z = 1046.0909.

14•2PF$_6$: A mixture of **12** (0.11 g, 0.10 mmol) and 1,5-bis(pyridinyloxy)pentane (10.3 mg, 0.04 mmol) in anhydrous DMF (5.0 mL) was transferred to a teflon tube and subjected to 10 kbar pressure at room temperature for 4 d. The purple solution was subjected directly to column chromatography (SiO_2) and the unreacted starting materials were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO / NH_4PF_6 (100:1 v/w) and the purple band was collected. Most of the solvent was removed in vacuo, followed by addition of H_2O (15 mL). The resulting precipitate was collected by filtration, affording the dumbbell **14•2PF$_6$** (37.7 mg, 38 %). ^{1}H NMR (500 MHz,

$(CD_3)_2CO$, TMS): δ = 1.18−1.21 (d, 12H), 1.65−1.73 (m, 6H), 1.32 (s, 36H), 2.82−2.84 (m, 2H), 3.58−3.65 (m, 12H), 3.70−3.73 (m, 4H), 3.74−3.81 (m, 16H), 3.82−3.85 (m, 4H), 3.92−3.96 (m, 8H), 4.03−4.07 (m, 8H), 4.10−4.13 (m, 4H), 4.18−4.22 (m, 8H), 4.75−4.78 (m, 4H), 6.74−6.78 (m, 8H), 7.06−7.14 (m, 24H), 7.28−7.32 (m, 8H), 7.42−7.44 (d, 4H, J = 8.4 Hz), 8.13−8.15 (d, 4H, J = 8.4 Hz), 8.85−8.87 ppm (d, 4H, J = 7.0 Hz). ^{13}C NMR (500 MHz, $(CD_3)_2CO$, TMS): δ = 22.7, 23.4, 30.3, 33.0, 33.7, 53.2, 63.9, 68.6, 69.3, 70.1, 70.6, 100.4, 106.8, 113.8, 115.5, 125.1, 126.3, 127.9, 128.9, 139.5, 144.8, 145.7, 148.6, 150.3, 153.4, 156.5, 161.5 ppm. HRMS: calcd for $C_{139}H_{176}N_2O_{20}$ $[M{-}2PF_6]^{2+}$ m/z = 1096.6408, found m/z = 1096.6402.

15•2PF_6: A mixture of **12** (0.11 g, 0.10 mmol) and 1,2-bis(2-(pyridinyloxy)ethoxy)ethane (12.2 mg, 0.04 mmol) in anhydrous DMF (5.0 mL) was transferred to a teflon tube and subjected to 10 kbar pressure at room temperature for 4 d. The purple solution was subjected directly to column chromatography (SiO_2) and the unreacted starting materials were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO / NH_4PF_6 (100:1 v/w) and the purple band was collected. Most of the solvent was removed in vacuo, followed by addition of H_2O (15 mL). The resulting precipitate was collected by filtration, affording the dumbbell **15**•2PF_6 (36.4 mg, 36 %). ^{1}H NMR (500 MHz, $(CD_3)_2CO$, TMS): δ = 1.19−1.21 (d, 12H, J = 6.8 Hz), 1.30 (s, 36H), 2.84−2.85 (m, 2H), 3.58−3.65 (m, 16H), 3.71−3.74 (m, 4H), 3.72−3.81 (m, 20H), 3.81−3.84 (m, 4H), 3.92−3.96 (m, 8H), 4.03−4.05 (m, 4H), 4.08−4.13 (m, 4H), 4.21−4.32 (m, 12H), 4.73−4.75 (m, 4H), 6.74−6.80 (m, 8H), 7.08−7.13 (m, 24H), 7.29−7.32 (m, 8H), 7.41−7.43 (d, 4H, J = 8.4 Hz), 8.15−8.17 (d, 4H, J = 8.4 Hz), 8.89−8.91 ppm (d, 4H, J = 7.0 Hz). ^{13}C NMR (500 MHz, $(CD_3)_2CO$, TMS): δ = 23.0, 30.5, 33.7, 34.2, 53.4, 64.1, 69.5, 70.1, 70.8, 100.2, 106.4, 113.8, 115.3, 125.7, 126.2, 127.9, 128.8, 140.3, 144.4, 145.8, 148.7, 150.2, 153.8, 156.5, 161.6 ppm. HRMS: calcd for $C_{140}H_{178}N_2O_{22}$ $[M{-}2PF_6]^{2+}$ m/z = 1119.6436, found m/z = 1119.6588.

2•6PF_6: The dumbbell compound **13**•2PF_6 (119.1 mg, 0.05 mmol), **8**•2PF_6 (28.2 mg, 0.04 mmol), and 1,4-bis(bromomethylbenzene) (10.5 mg, 0.04 mmol) were dissolved in anhydrous DMF (8 mL). The reaction mixture was subjected to 10 kbar pressure at room temperature for 3 d. After the solvent had been removed in vacuo, the purple solid was dissolved in Me_2CO and the [2]rotaxane **2**•6PF_6 was isolated by means of preparative TLC using Me_2CO / NH_4PF_6 (100:1 v/w) as the mobile phase. The product was recovered from the silica gel by washing with an excess of eluent. The solution was concentrated to a minimum volume and the product was precipitated from the solution by addition of H_2O (12 mL). The resulting precipitate was collected by filtration, affording the pure [2]rotaxane **2**•6PF_6 (50.1 mg, 36 %). ^{1}H NMR (500 MHz, CD_3CN, TMS): δ = 1.10−1.11 (d, 6H, J = 7.0 Hz), 1.18−1.20 (d, 6H, J = 7.0 Hz), 1.28 (s, 18H), 1.30 (s, 18H), 2.57−2.59 (m, 2H), 2.86−2.89 (m, 2H), 3.60−3.67 (m, 12H), 3.71−3.78 (m, 20H), 3.89−3.95 (m, 12H), 4.04−4.06 (m, 4H), 4.20−4.25 (m, 8H), 4.36−4.38 (m, 4H), 4.73−4.76 (m, 4H), 5.69−5.74 (q, 8H, J = 8.0 Hz), 5.95−5.97 (m, 2H), 6.31−6.34 (m, 2H), 6.69−6.72 (d, 2H, J = 8.6 Hz), 6.83−6.86 (m, 4H), 7.05−7.19 (m, 28H), 7.32−7.36 (m, 10H), 7.73−7.75 (d, 2H, J = 8.6 Hz), 7.99−8.02 (m, 8H), 8.11−8.15 (m, 4H), 8.89−9.01 ppm (m, 12H). ^{13}C NMR (500 MHz, CD_3CN, TMS): δ = 23.6, 30.4, 33.3, 33.9, 53.2, 62.2, 64.0, 69.2, 70.1, 70.5, 106.6, 113.7, 115.3, 120.9, 121.6, 125.5, 126.3, 127.3, 128.0, 128.8, 134.6, 139.6, 144.1, 144.7, 145.3, 145.8, 148.6, 150.1, 150.7, 153.5, 156.8 ppm. HRMS: calcd for $C_{170}H_{198}F_{24}N_6O_{18}P_4$ $[M - 2PF_6]^{2+}$ m/z = 1595.6665, found m/z = 1596.2242; calcd for $C_{170}H_{198}F_{18}N_6O_{18}P_3$ $[M - 3PF_6]^{3+}$ m/z = 1015.4563, found m/z = 1015.9544.

4•6PF_6: The dumbbell compound **14**•2PF_6 (124.2 mg, 0.05 mmol), **8**•2PF_6 (28.2 mg, 0.04 mmol), and 1,4-bis(bromomethylbenzene) (10.5 mg, 0.04 mmol) were dissolved in anhydrous DMF (8 mL). The reaction mixture was subjected to 10 kbar pressure at room temperature for 3 d. After the solvent had been removed in vacuo, the purple solid was dissolved in Me_2CO and the [2]rotaxane **4**•$6PF_6$ was isolated by means of preparative TLC using Me_2CO / NH_4PF_6 (100:1 v/w) as the mobile phase. The product was recovered from the silica gel by washing with an excess of eluent. The solution was concentrated to a minimum volume and the product was precipitated from the solution by addition of H_2O (12 mL). The resulting precipitate was collected by filtration, affording the pure [2]rotaxane **4**•$6PF_6$ (50.2 mg, 35 %). ^{1}H NMR (500 MHz, CD_3CN, TMS): δ = 1.12−1.13 (d, 6H, J = 4.6 Hz), 1.19−1.21 (d, 6H, J = 4.6 Hz), 1.27 (s, 18H), 1.31 (s, 18H), 1.64−1.76 (m, 6H), 2.58−2.60 (m, 2H), 2.85−2.88 (m, 2H), 3.61−3.67 (m, 12H), 3.72−3.79 (m, 20H), 3.88−3.95 (m, 12H), 4.04−4.08 (m, 8H), 4.21−4.25 (m, 8H), 4.36−4.39 (m, 4H), 4.74−4.76 (m, 4H), 5.69−5.75 (q, 8H, J = 8.6 Hz), 5.95−5.97 (m, 2H), 6.32−6.34 (m, 2H), 6.70−6.73 (d, 2H, J = 8.2 Hz), 6.83−6.86 (m, 4H), 7.03−7.10 (m, 12H), 7.12−7.19 (m, 20H), 7.33−7.37 (m, 10H), 7.74−7.76 (d, 2H, J = 8.2 Hz), 7.98−8.02 (m, 8H), 8.89−9.01 ppm (m, 12H). ^{13}C NMR (500 MHz, CD_3CN, TMS): δ = 22.5, 23.7, 30.1, 33.4, 33.8, 53.1, 62.3, 63.8, 68.8, 69.5, 70.4, 70.9, 100.3, 106.6, 113.7, 115.3, 121.7, 125.4, 126.6, 127.4, 127.9, 128.7, 134.7, 139.2, 144.2, 144.9, 145.5, 148.3, 150.7, 153.6, 156.3, 161.8 ppm. HRMS: calcd for $C_{175}H_{208}F_{24}N_6O_{20}P_4$ $[M - 2PF_6]^{2+}$ m/z = 1646.7006, found m/z = 1646.7394; calcd for $C_{175}H_{208}F_{18}N_6O_{20}P_3$ $[M - 3PF_6]^{3+}$ m/z = 1049.4790, found m/z = 1049.5258.

5•$6PF_6$: The dumbbell compound **15**•$2PF_6$ (126.5 mg, 0.05 mmol), **8**•$2PF_6$ (28.2 mg, 0.04 mmol), and 1,4-bis(bromomethylbenzene) (10.5 mg, 0.04 mmol) were dissolved in anhydrous DMF (8 mL). The reaction mixture was subjected to 10 kbar pressure at room temperature for 3 d. After the solvent had been removed in vacuo, the purple solid was dissolved in Me_2CO and the [2]rotaxane **5**•$6PF_6$ was isolated by means of preparative TLC using Me_2CO / NH_4PF_6 (100:1 v/w) as the mobile phase. The product was recovered from the silica gel by washing with an excess of eluent. The solution was concentrated to a minimum volume and the product was precipitated from the solution by addition of H_2O (12 mL). The resulting precipitate was collected by filtration, affording the pure [2]rotaxane **5**•6PF_6 (45.0 mg, 31 %). ^1H NMR (500 MHz, CD_3CN, TMS): δ = 1.12−1.14 (d, 6H, J = 4.2 Hz), 1.18−1.20 (d, 6H, J = 4.2 Hz), 1.27 (s, 18H), 1.32 (s, 18H), 2.58−2.60 (m, 2H), 2.86−2.88 (m, 2H), 3.58−3.66 (m, 16H), 3.74−3.81 (m, 24H), 3.87−3.95 (m, 12H), 4.04−4.08 (m, 4H), 4.22−4.25 (m, 8H), 4.30−4.38 (m, 8H), 4.74−4.77 (m, 4H), 5.70−5.75 (q, 8H, J = 8.4 Hz), 5.96−5.98 (m, 2H), 6.32−6.34 (m, 2H), 6.71−6.73 (d, 2H, J = 8.6 Hz), 6.84−6.86 (m, 4H), 7.03−7.11 (m, 12H), 7.13−7.20 (m, 20H), 7.34−7.38 (m, 10H), 7.74−7.76 (d, 2H, J = 8.6 Hz), 7.97−8.02 (m, 8H), 8.89−9.02 ppm (m, 12H). ^{13}C NMR (500 MHz, CD_3CN, TMS): δ = 23.1, 30.6, 33.5, 34.7, 53.3, 61.8, 64.4, 69.9, 70.3, 71.1, 100.5, 106.1, 113.6, 115.7, 121.6, 125.4, 126.6, 127.1, 127.8, 128.4, 134.7, 140.6, 144.5, 145.3, 148.2, 150.4, 153.6, 156.8, 161.2 ppm. HRMS: calcd for $C_{176}H_{210}F_{24}N_6O_{22}P_4$ $[M - 2PF_6]^{2+}$ m/z = 1669.7033, found m/z = 1669.7159; calcd for $C_{176}H_{210}F_{18}N_6O_{22}P_3$ $[M - 3PF_6]^{3+}$ m/z = 1064.8141, found m/z = 1064.8356.

17: A 50% aqueous NaOH solution (8 mL) was added to a solution of compound **16** (360 mg, 1 mmol) in THF (50 mL) at 0 °C. After stirring the mixture for 30 min, *p*-toluene-sulfonylchloride (TsCl) (210 mg, 1.1 mmol) in tetrahydrofuran (THF) (50 mL) was added slowly to the mixture. The solution was stirred for 2 h, and then poured into H_2O. The resulting mixture was extracted with $CHCl_3$ (3 x 20 mL) and the combined organic phases were washed with a saturated aqueous NaCl solution (3 x 100 mL). After drying ($MgSO_4$), the solvent was removed in vacuo to afford the desired product **17** (510 mg, 99%) as a colorless oil, which was used immediately in the next step without further purification.

18•2PF_6: A mixture of **17** (503 mg, 0.98 mmol) and 1,4-bis(4-pyridyl)benzene (57 mg, 0.25 mmol) in anhydrous DMF (5.0 mL) was transferred to a teflon tube and subjected to 10 kbar pressure at room temperature for 4 d. The purple solution was subjected directly to column chromatography (SiO_2) and the unreacted starting materials were eluted with Me_2CO, whereupon the eluent was changed to Me_2CO / NH_4PF_6 (100:1 v/w) and the purple fractions were collected. The solvent was removed in vacuo to a minimal volume, followed by the addition of H_2O (15 mL). The resulting precipitate was collected by filtration, affording the dumbbell **18**•$2PF_6$ (180 mg, 61 %). ^{1}H NMR (500 MHz, CD_3CN): δ = 3.35 (t, 4H, J = 4.5 Hz), 3.69 (t, 4H, J = 5.0 Hz), 3.79 (t, 4H, J = 4.5 Hz), 3.97 (t, 4H, J = 4.0 Hz), 4.05 (t, 4H, J = 5.0 Hz), 4.13 (t, 4H, J = 5.0 Hz), 4.16 (t, 4H, J = 4.0 Hz), 4.75 (t, 4H, J = 5.0 Hz), 6.71 (d, 2H, J = 8.0 Hz), 6.82 (d, 2H, J = 7.5 Hz), 7.26 (t, 2H, J = 8.0 Hz), 7.30 (t, 2H, J = 7.5 Hz), 7.52 (d, 2H, J = 8.5 Hz), 7.54 (s, 4H), 7.66 (d, 2H, J = 8.5 Hz), 7.93 (d, 4H, J = 7.0 Hz), 8.73 ppm(d, 4H, J = 7.0 Hz). ^{13}C NMR (125 MHz, CD_3CN): δ = 50.1, 60.5, 67.2, 67.5, 68.6, 68.9, 69.0, 69.5, 105.2, 105.4, 113.7, 113.8, 124.2, 125.0, 125.1, 125.7, 126.1, 128.3, 135.8, 144.7, 153.6, 153.8, 154.0 ppm. HRMS: calcd for $C_{52}H_{56}F_6N_8O_8P$ $[M - PF_6]^+$ m/z = 1065.3862, found m/z = 1065.3870.

19: A mixture of 2,6-diisopropylphenol (178 mg, 1 mmol), propargyl bromide (130 mg, 1.1 mmol) and potassium carbonate (1.39g, 10 mmol) was suspended in anhydrous DMF (25.0 mL). The mixture was stirred at 80 °C for 16 h. After cooling, the solution was poured into H_2O (200 mL). The resulting mixture was extracted with EtOAc (3 x 20 mL) and the combined organic phases were washed three times with saturated aqueous NaCl solution (3 x 100 mL). After drying ($MgSO_4$), the solvent was removed in vacuo to afford the desired product **19** (210 mg, 99%) as a colorless oil, which was used immediately in the next step without further purification.

3•$6PF_6$: A solution of **18**•$2PF_6$ (32 mg, 0.026 mmol), **19** (80 mg, 0.37 mmol), **CBPQT**·$4PF_6$ (30 mg, 0.027 mmol), TBTA (9 mg,0.017 mmol), and tetrakis(acetonitrile)copper(I) hexafluorophosphate

(6 mg, 0.017 mmol) in anhydrous Me_2CO (5 mL) were stirred for 24 h at room temperature. The solvent was then evaporated and the resulting purple solid was purified by column chromatography [SiO_2: 2M NH_4Cl / MeOH / $MeNO_2$ (12 : 7: 1)], then MeOH, Me_2CO and 2% NH_4PF_6 / Me_2CO, respectively]. The purple fraction in Me_2CO were collected, and concentrated to a minimum volume before the crude product was precipitated by the addition of H_2O. The resulting solid was collected by filtration to afford **3**·$6PF_6$ (20 mg, 27%) as a purple powder. ^1H NMR (500 MHz, CD_3CN): δ = 1.17 (d, 12H, J = 5.5 Hz), 1.18 (d, 12H, J = 5.5 Hz), 2.55 (d, 1H, J = 6.0 Hz), 2.59 (d, 1H, J = 6.0 Hz), 3.35−3.40 (m, 4H), 3.90 (t, 2H, J = 3.5 Hz), 3.98 (t, 2H, J = 3.5 Hz), 4.03 (t, 2H, J = 4.5 Hz), 4.14 (t, 2H, J = 4.0 Hz), 4.20−4.23 (m, 4H), 4.27 (t, 2H, J = 3.0 Hz), 4.30 (t, 2H, J = 4.0 Hz), 4.36−4.41 (m, 6H), 4.49 (t, 2H, J = 4.3 Hz), 4.58 (t, 2H, J = 5.0 Hz), 4.73 (t, 2H, J = 4.0 Hz), 4.81 (s, 2H), 4.87 (t, 2H, J = 4.5 Hz), 4.88 (s, 2H), 5.05 (t, 2H, J = 4.3 Hz), 5.78 (d, 4H, J = 11.5 Hz), 5.86 (d, 4H, J = 11.5 Hz), 6.01 (t, 1H, J = 7.0 Hz), 6.05 (t, 1H, J = 7.0 Hz), 6.31 (d, 1H, J = 6.5 Hz), 6.38 (d, 1H, J = 6.5 Hz), 6.86 (t, 2H, J = 6.5 Hz), 7.09−7.15 (m, 6H), 7.31 (t, 2H, J = 7.0 Hz), 7.37 (d, 8H, J = 5.0 Hz), 7.64 (d, 1H, J = 6.5 Hz), 7.70 (d, 1H, J = 7.0 Hz), 7.84 (d, 2H, J = 7.5 Hz), 7.87 (s, 2H), 7.99 (s, 8H), 8.01 (d, 1H, J = 6.5 Hz), 8.11 (d, 2H, J = 6.5 Hz), 8.12 (s, 1H), 8.49 (d, 2H, J = 6.0 Hz), 8.68 (d, 2H, J = 5.5 Hz), 8.74 (b, 8H), 8.99 (d, 2H, J = 6.0 Hz). ^{13}C NMR (125 MHz, CD_3CN): δ = 23.3, 23.3, 26.5, 26.5, 28.7, 29.9, 50.1, 54.2, 61.0, 67.2, 67.5, 67.7, 67.9, 69.0, 69.3, 69.3, 69.4, 69.5, 69.8, 70.0, 104.5, 105.6, 105.9, 114.1, 124.1, 124.2, 124.3, 124.4, 124.7, 125.0, 125.2, 125.4, 125.6, 126.5, 129.1, 129.1, 131.3, 136.6, 141.6, 141.9, 143.7, 144.6, 145.0, 145.3, 150.9, 152.7, 152.8, 154.0. HRMS: calcd for $C_{118}H_{128}F_{24}N_{12}O_{10}P_4$ $[M - 2PF_6]^{2+}$ m/z = 1226.9238, found m/z = 1226.9281.

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8 UV-Vis Spectroelectrochemical experiments support firmly that the translational movement of the $CBPQT^{4+}$ ring in the bistable [2]rotaxanes occurs after the first one-electron oxidation of the TTF unit on the dumbbell components.

9 In this manuscript, "*bipyridinium*" refers to *N*,*N′*-dialkyl-4,4′-bipyridinium ($BIPY^{2+}$) units in which two pyridinium moieties attached to each other directly without any other connection units (in compound **1**•$6PF_6$ and **2**•$6PF_6$). The term "*bispyridinium*" refers to units in which the two pyridinium moieties are connected indirectly in the 4,4′ positions by either a benzene ring (in compound **3**•$6PF_6$) or a saturated chain (in compound **4**•$6PF_6$ and **5**•$6PF_6$).

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