Molecular Devices

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Foldamer-Tuned Switching Kinetics and Metastability of [2]Rotaxanes**

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Molecular switches and devices based on rotaxanes have been the topic of extensive investigations in supramolecular chemistry.[1,2] In particular, bistable [2]rotaxanes consisting of a linear component incorporaing electron-rich tetrathiafulvalene (TTF) and 1,5-dioxynathpthalene (DNP) binding sites encircled by a cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) ring have been investigated as devices for high-density molecular memories.[3] One issue associated with this type of devices is the short lifetime of the metastable state co-conformation (MSCC), which arises from the quick relaxation of these systems to the ground-state co-conformation (GSCC).[4] Introducing a bulky or electrostatic barrier between the TTF and DNP units can slow down the back shuttling of the $CBPQT^{4+}$ ring from the DNP unit to the neutral TTF unit and generate long-lived MSCC even after removal of the bias by rapid reduction of the pre-oxidized TTF unit.[5] However, it is still desirable to develop novel strategies for the control of the interconversion between the GSCC and the MSCC in a modular manner.

Herein, we describe that hydrogen-bonding-mediated arylamide foldamers can be utilized to effectively tune this interconversion.[6] Foldamers are synthetic oligomers with folded structures stabilized by intramolecular noncovalent forces.[7] The folded states have apparent sizes larger than those of the extended ones. We conjectured that, if the apparent diameter of the extended state of a foldamer is smaller than the internal diameter of a macrocycle while the diameter of its folded state is larger, it would allow the macrocycle to slip over the extended state. However, the process should be slower than that over a similar but flexible molecule, because it needs to, at least partially, break the noncovalent bonds existing in the folded state.[8] Since the length of foldamers can be readily modulated by simply changing the number of their repeating units, foldamer segments could be developed as modular stoppers or spaces for regulating the dynamic behavior of pseudorotaxanes or rotaxanes.

Pseudorotaxanes **1a** and **1b** were first prepared as pure species from dumbbells **2a** and **2b** and $CBPQT^{4+}(PF_6^-)_4$ as models to investigate the extrusion kinetics of the $CBPQT^{4+}$ ring over the foldamer segment of the dumbbells (Figure 1).[9,10] The 2-methoxy-1,3-benzamide-based foldamers were chosen because their intramolecular N–H···O=C hydrogen bonding works in solvents of varying polarity and short oligomers can cause large conformational change upon unfolding.[11,12] The large Fréchet-type **G-3** dendron provides them with good solubility in both less polar and polar solvents.[13] The ^{1}H NMR spectrum of complex **1b** in [D_3]acetonitrile and [D_6]DMSO displayed one set of signals. After standing for 15 minutes, the resonances of the free **2b** and $CBPQT^{4+}(PF_6^-)_4$ appeared and those of the complex diminished, which reached equilibrium after approximately five hours. The ^{1}H NMR spectrum of **1a** in both solvents recorded upon dissolution already exhibited the signals of both free and complexed **2a** and $CBPQT(PF_6)_4$. Based on the relative intensity of the pyridinium β-H signals of the free and complexed $CBPQT^{4+}$ ring, we determined the association constants (K_a values) of **1a** and **1b** as complexes to be 752 and 868 M^{-1}, respectively, in acetonitrile and 157 and 152 M^{-1}, respectively, in DMSO. These values are higher than those reported for the pseudorotaxane formed by the TTF itself and the $CBPQT^{4+}$ ring,[9a] which might be attributed to the formation of the intermolecular C–H···O hydrogen bonds between the pyridinium protons and the neighboring ether oxygen atoms. The fact that the values in acetonitrile were higher than those in more polar DMSO also suggests that DMSO inhibited the above C–H···O hydrogen bonds more efficiently than it strengthened the TTF–bipyridinium donor–acceptor interaction.

The kinetics of extrusion of the $CBPQT^{4+}$ ring from the linear components of pseudorotaxanes **1a** and **1b** was then investigated using the TTF-$CBPQT^{4+}$ charge-transfer (CT) absorption, centered at about 805 nm in the UV/Vis spectra, as the probe. By monitoring the decrease of this CT absorption with time, we obtained the rate constants (k_{off}) of extrusion in eight solvents of low and high polarity by

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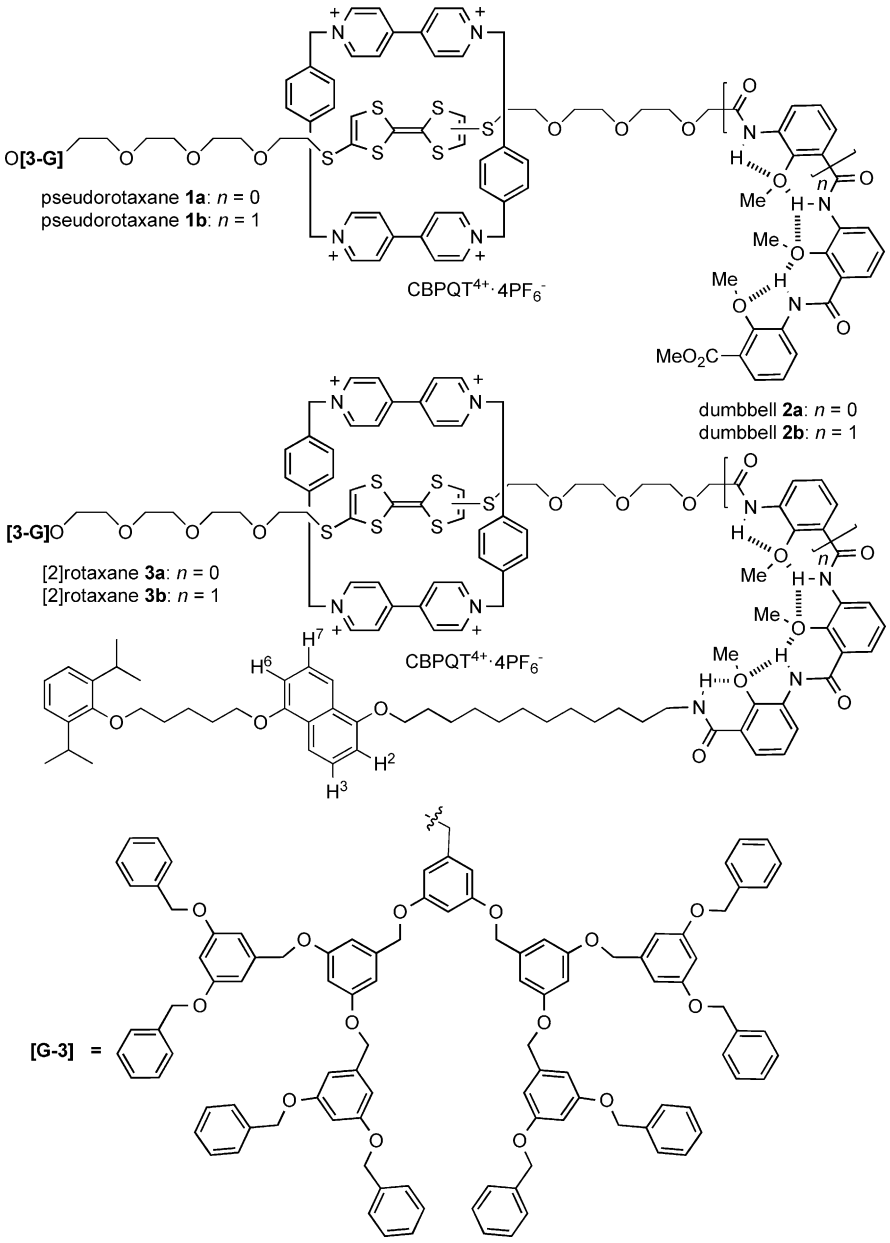

assuming first-order kinetics. The data and the associated change of free energy are listed in Table 1. Compared with those of **1a** in the same solvents, the k_{off} values of **1b** decreased by 5 to 37 times. This observation indicated that all the hydrogen-bonded arylamide units in the foldamer segments contributed to delaying the extrusion of $CBPQT^{4+}$. The largest k_{off} value was displayed by **1a** in DMF, which corresponded to a half-life of 301 s, while the slowest one was displayed by **1b** in chloroform, corresponding to a half-life of 67 days, with a difference of 19167 times. Thus, by choosing discrete foldamer segments and media, we could control the passing of the $CBPQT^{4+}$ ring from the foldamer segments in a remarkably long span of time. It has been established that the donor–acceptor interactions between TTF and bipyridinium units become weakened in less polar solvents owing to the decreased strength of the π-stacking interaction.[14] The decomplexation of **1a** and **1b** was substantially slower in less polar solvents than in polar solvents, suggesting that the increase of the free energy of the CT state from a polar solvent to a less polar solvent was considerably smaller than the increase of the free energy of activation for the extrusion of the $CBPQT^{4+}$ ring over the foldamer segment caused by the enhancement of their intramolecular hydrogen bonds in less polar solvent.

Cyclic voltammetry (CV) measurements were carried out to investigate the redox properties of the TTF unit in pseudorotaxanes **1a** and **1b** in less polar chloroform and polar aceto-

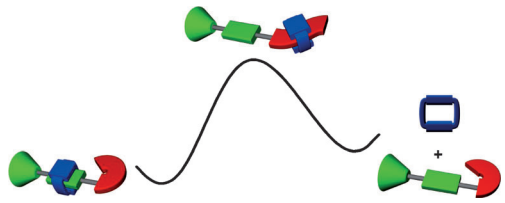

Figure 1. Schematic representation of the foldamer-modulated extrusion (pseudorotaxane decomplexation) or slippage (pseudorotaxane formation) of the $CBPQT^{4+}$ ring (blue) from or onto a TTF-containing thread (green). The foldamer segment (red) in its folded state has a large apparent size and must unfold into an extended conformation to allow the $CBPQT^{4+}$ ring to pass.

Table 1: The kinetic data for the extrusion of the $CBPQT^{4+}$ ring over the foldamer segments in pseudorotaxanes **1a** and **1b** at 25 °C in different solvents.

		1a		**1b**	
Solvent	ε[a]	k_{off} [s^{-1}]	$\Delta G^{\neq}$ [kJ mol^{-1}]	k_{off} [s^{-1}]	$\Delta G^{\neq}$ [kJ mol^{-1}]
DMSO	47.2	1.0×10^{-3}	90	1.1×10^{-4}	96
DMF	36.7	2.3×10^{-3}	88	4.7×10^{-4}	92
MeCN	38.3	5.2×10^{-4}	92	4.0×10^{-5}	98
PhCN	25.7	2.8×10^{-4}	93	2.0×10^{-5}	100
acetone	21.0	8.4×10^{-4}	91	1.3×10^{-4}	95
$Cl(CH_2)_2Cl$	10.4	7.5×10^{-6}	102	2.0×10^{-7}	111
THF	7.5	2.6×10^{-4}	94	8.3×10^{-6}	102
chloroform	4.8	1.9×10^{-6}	106	1.2×10^{-7}	113

[a] Dielectric constant of the solvent.

nitrile. In chloroform, for both samples, the first oxidation potential was 0.65 V, which was larger than that of control **2a** (0.53 V), reflecting the decreased electron-donating ability of the complexed TTF unit with respect to the free one. The second oxidation potential was 0.84 V for all the three samples, implying that the formation of radical cation TTF^{+} had forced the $CBPQT^{4+}$ ring of **1a** and **1b** to slip off the TTF unit; hence the $CBPQT^{4+}$ ring did not affect the formation of the TTF^{2+} ion. The electrochemical behavior is different in acetonitrile. Both **1a** and **1b** exhibited only one oxidation process at 0.77 V, while **2a** still gave rise to two peaks at 0.44 and 0.78 V. The voltammogram of **1a** showed an additional weak broad peak at 0.44 V, assignable to the oxidation of the free TTF unit. Such a peak was not observed for **1b**, thus indicating that within the time scale of the measurement, **1a** started to decomplex, while **1b** did not, consistent with the above UV/Vis kinetic experiments, reflecting the higher stability of **1b**.

The redox-activated dynamics of pseudorotaxanes **1a** and **1b** were further investigated using chemical oxidation and reduction methods. Their k_{off} values in both the mono- (TTF^{+}) and dioxidized (TTF^{2+}) states in acetonitrile were determined to be 0.11 and 0.02 s^{-1}, respectively (see the Supporting Information for the method). Since the electrostatic repulsion between dication TTF^{2+} and $CBPQT^{4+}$ should be larger than that between radical cation TTF^{+} and $CBPQT^{4+}$, the fact that both pseudorotaxanes in the two different oxidation states displayed an identical rate of decomplexation suggested that the energy barrier for the extrusion of the $CBPQT^{4+}$ ring from the linear component, after the first oxidation of the TTF unit, was predominantly controlled by its de-slippage over the bulky foldamer segment. This result may be rationalized by considering that the linker between the TTF and foldamer units is long enough to allow the $CBPQT^{4+}$ ring to rapidly escape far away from the oxidized TTF unit. The corresponding charge repulsion decayed exponentially to an insignificant level compared with the energy cost for the $CBPQT^{4+}$ ring slipping over the foldamer segment. On the other hand, the k_{off} values of the mono- and dioxidized **1a** and **1b** in acetonitrile were 212 and 500 times higher than the values of the corresponding un-oxidized samples in the same solvent.

Since the dimeric and trimeric foldamer segments in pseudorotaxanes **1a** and **1b** were capable of providing an energy barrier for the $CBPQT^{4+}$ ring to extrude at a rate of $10^{-3} \approx 10^{-7}$ s^{-1}, we then prepared bistable [2]rotaxanes **3a** and **3b** to study the foldamer-tuned switching of the $CBPQT^{4+}$ ring between the TTF and 1,5-dioxynapthalene (DNP) sites. Since the TTF unit is more electron-rich than the DNP unit, in a two-state model (Figure 2), the equilibrium should be shifted toward the $CBPQT^{4+}$ ring encircling the TTF site to form the GSCC, rather than toward the $CBPQT^{4+}$ ring encircling the DNP site to form the less stable MSCC. The ^{1}H NMR spectra of [2]rotaxanes **3a** and **3b** in [D_3]acetonitrile and [D_6]acetone displayed one set of signals (see the Supporting Information), thus indicating that their $CBPQT^{4+}$ ring predominantly encircled the TTF unit to form the GSCC (Figure 2A).

Considering that the TTF sides of their threads have identical structures, the rate constant of the shuttling of the

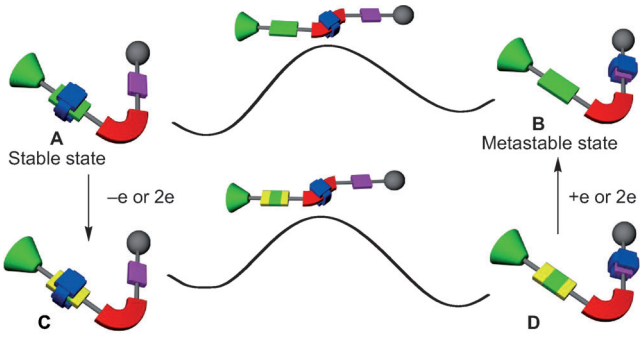

Figure 2. Schematic representation of foldamer-tuned switching of the $CBPQT^{4+}$ ring between the TTF and DNP sites in bistable [2]rotaxanes **3a** and **3b**, with the TTF unit being neutral or oxidized to $TTF^{+\cdot}$ or TTF^{2+}.

$CBPQT^{4+}$ ring in bistable [2]rotaxanes **3a** and **3b** from the GSCC to the MSCC should be comparable to the corresponding k_{off} values of pseudorotaxanes **1a** and **1b** in the same solvent. Upon oxidation of the TTF unit to $TTF^{+\cdot}$ or TTF^{2+}, the $CBPQT^{4+}$ ring of the [2]rotaxanes would be repelled to slip more rapidly over the foldamer segment to encircle the DNP unit (Figure 2C→D), and the shuttling rates should be similar to the rates of decomplexation of the corresponding mono- and dioxidized pseudorotaxanes **1a** and **1b** in the same solvent. Reduction of the $TTF^{+\cdot}$ or TTF^{2+} cation of the preoxidized [2]rotaxanes to TTF would lead to the formation of the MSCC (Figure 2D→B), and the $CBPQT^{4+}$ ring would slip back to the TTF side to form the GSCC (Figure 2B→A). This last process is directly related to the lifetime of the MSCC and is critical for nonvolatile molecular memory with high metastability.

CV measurements on the two bistable [2]rotaxanes were then performed in both acetonitrile and chloroform at varying scan rates to investigate the above processes. For the second scans, for **3a** in acetonitrile (Figure 3), at the slow scan rates of 5 and 10 mV s^{-1}, no peak was displayed at about 0.44 V, which is typically formed by the free TTF and, for bistable [2]rotaxane **3a**, associated with its MSCC. Within the range of scan rates from 25 to 75 mV s^{-1}, this peak was formed and

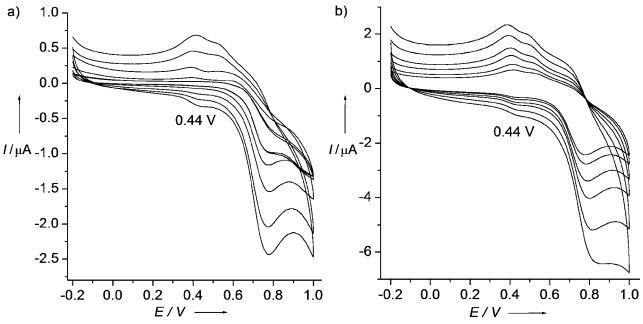

Figure 3. Cyclic voltammagrams of bistable [2]rotaxane **3a** (0.1 mM) in MeCN at 25 °C: a) the first cycle at 5 mV s^{-1} and subsequent cycles at 5, 10, 25, 50, and 75 mV s^{-1}. b) The subsequent cycles at 75, 100, 150, 200, 300, and 400 mV s^{-1}. Pt button and coil and Ag/AgCl electrodes were used as working, counter, and reference electrodes. [nBu$_4$N][PF$_6$] (0.1 M) was used as the electrolyte.

intensified pronouncedly with the increase of the scan rate. This result indicated that even in solution the MSCC of **3a** had a relatively long lifetime at ambient temperature, which is comparable with that observed in the $CBPQT^{4+}$-TTF-DNP-based rotaxanes entrapped in a solid-state polymer.[4c] With further increase of the scan rate from 100 to 400 $mV\,s^{-1}$, this peak still survived, but weakened, which might be attributed to the decreased conversion of C to D (Figure 2) at the rapid scan rates. For **3a** in chloroform and **3b** in both chloroform and acetonitrile, no peaks corresponding to the free TTF unit were observed at different scan rates, which might be rationalized by considering the decreased C→D conversion as well as the increased stability of the GSCC of the [2]rotaxanes.

The ^1H NMR spectra in [D_3]acetonitrile showed that adding 2.0 equivalents Magic Blue ($(4\text{-}BrC_6H_4)_4N^+SbCl_6^-$) to the solution of the rotaxanes resulted in the appearance of a new set of signals (see the Supporting Information). For **3a**, the two signals (at 5.78 and 5.89 ppm) of the protons of the TTF unit encapsulated in the $CBPQT^{4+}$ ring disappeared, while the signals of the H2/6 (at 6.16 and 6.20 ppm) and H3/7 (at 5.89 ppm) protons of the DNP unit encapsulated in the $CBPQT^{4+}$ ring emerged (see the structure for numbering).[15] These results supported that the $CBPQT^{4+}$ ring had shuttled from the TTF side to the DNP side. Similar results are also observed for **3b**. In separate UV/Vis experiments, both **3a** and **3b** were oxidized with 2.0 equivalents $Fe(ClO_4)_3$ in acetonitrile to produce the doubly oxidized TTF^{2+} ion. After standing for 50 min, the solutions were quickly treated with an excess of zinc powder to reduce TTF^{2+} ion to TTF. The time-dependent UV/Vis spectra of the solutions were then recorded, which showed that the DNP–$CBPQT^{4+}$ CT absorption at 550 nm gradually decreased in intensity, and the TTF–$CBPQT^{4+}$ CT absorption at 805 nm appeared and increased in intensity (see the Supporting Information). By assuming first-order kinetics, we determined the rate constants of the shuttling of the $CBPQT^{4+}$ ring of **3a** and **3b** from the MSCC to the GSCC to be 1.1×10^{-2} and $7.4\times10^{-4}\ s^{-1}$, respectively, which corresponded to half-lives of 66 and 930 s. Using the same method, the rate constant of the same process of **3a** in chloroform was determined to be $9.9\times10^{-6}\ s^{-1}$, corresponding to a half-life of 19.5 h, 1064 times longer than that in acetonitrile. These rate constants were all higher than the related k_{off} values of pseudorotaxanes **1a** and **1b** (Table 1), which was consistent with the fact that the donor–acceptor interaction between DNP and $CBPQT^{4+}$ is weaker than that between the TTF unit and the $CBPQT^{4+}$ ring. Since the foldamer segments were not symmetric, the energy barrier experienced by the $CBPQT^{4+}$ ring from the two sides might be slightly different, which also contributed to the difference. Remarkably, the solution of the MSCC of **3b** in chloroform, obtained using a similar method, did not exhibit a perceptible TTF–$CBPQT^{4+}$ CT band in the UV/Vis spectrum even after three days, thus indicating that the foldamer segment efficiently blocked the conversion of the MSCC to the GSCC. Because both bistable [2]rotaxanes are soluble in organic solvents of both low and high polarity, the results suggest that, by changing the length of the foldamer segments and the polarity of the media, we are actually capable of controlling the lifetime of the MSCC of the [2]rotaxanes in a wide range of timescale.

In conclusion, we have demonstrated for the first time that hydrogen-bonding-induced arylamide foldamers can serve as a new, deformable moiety in switchable pseudorotaxanes and rotaxanes to modulate the switching kinetics and metastability. The noncovalent nature of the folding conformation in foldamers endows structural flexibility, making them versatile structural units to modulate the mechanical movements of the $CBPQT^{4+}$ ring along the dumbbell component. In bistable [2]rotaxanes where foldamer segments are introduced to bridge a TTF unit and a DNP unit in the dumbbell, the deformable sizes of the foldamers effectively serve as a steric barrier to the relaxation from the MSCC to the GSCC. The lifetime of the post-oxidation MSCC is thus dramatically increased. The generation of the long-lived MSCC in the [2]rotaxanes from minutes to days holds great promise for the application of these mechanically interlocked molecules in nonvolatile molecular memories. Thus, the marriage of deformable foldamers and interlocked molecular switches opens up the possibility of exploring more responsive dynamic molecular materials.

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