Molecular Devices

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Photoinduced Memory Effect in a Redox Controllable Bistable Mechanical Molecular Switch**

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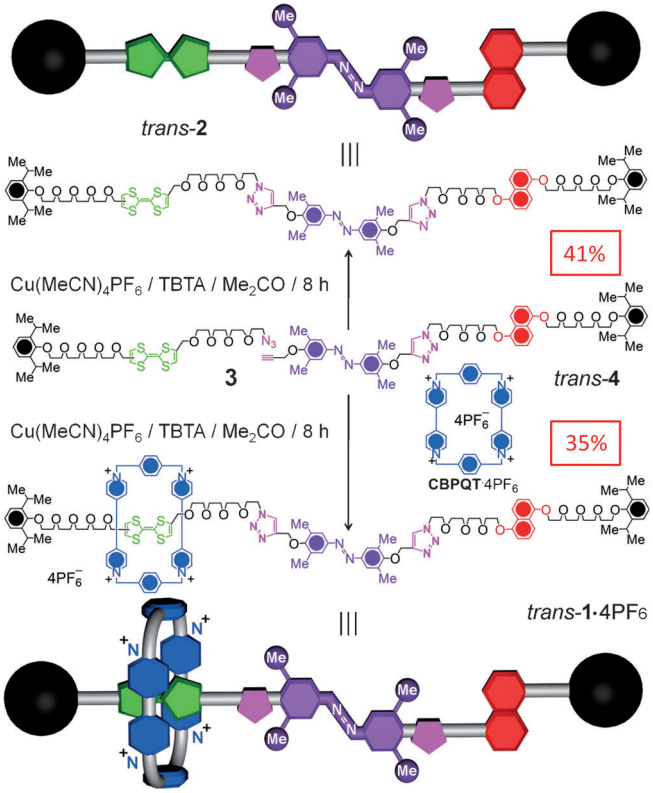
Mechanically interlocked molecules[1] (MIMs) in the form of multi- and bistable rotaxanes in which the ring component can be switched between different co-conformations in response to external stimuli, constitute an artificial molecular switch.[2] They are of importance when it comes to the development of integrated systems and devices,[3] such as responsive surfaces,[4] molecule-based muscles and actuators,[1d,5] nanovalves for controlled drug delivery,[6] and molecular electronic devices[7] (MEDs).

Although the operation of bistable molecular switches is based on classical switching processes between thermodynamically stable states, it has become clear that the fulfillment of useful functions will only become possible if the rates of the mechanical movement between such states can also be controlled. This approach was used[8] recently to implement ratchet-type mechanisms[9] which are essential ingredients for the construction of molecular motors,[10] and is of considerable relevance for the development of sequential logic devices such as flip-flops and memories.[11] For all these purposes, the ability to be able to adjust the shuttling kinetics[12] by modulating the corresponding energy barriers through external stimuli in a convenient, efficient, and reversible manner[13] is a goal which still poses a considerable challenge to chemists.

Herein, we discuss the performance of a molecular switch in the form of a bistable [2]rotaxane (Scheme 1), which 1) undergoes relative mechanical movements of its ring and dumbbell components under redox control and thus can be switched between two states thermodynamically, and wherein 2) the energy barriers between these two states can be controlled kinetically by photochemical means.



Scheme 1. Synthesis of [2]rotaxane *trans*-**1**·4 PF_6 and the corresponding dumbbell *trans*-**2**.

The design of [2]rotaxane $\mathbf{1}^{4+}$ (Scheme 1) is based on a well-studied architecture[7b,14] in which the ring component is cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) and the dumbbell component is comprised of 1) a tetrathiafulvalene (TTF)

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unit and a 1,5-dioxynaphthalene (DNP) unit as the primary and secondary π-electron-donating recognition sites, respectively, for the π-electron-deficient $CBPQT^{4+}$ ring, and 2) a photoactive 3,5,3′,5′-tetramethylazobenzene (TMeAB) unit, which can be switched between its *cis* and *trans* configurations reversibly and efficiently by photochemical stimuli, located in between the TTF and DNP units. Since the TTF unit is more π-electron-rich than the DNP one, the $CBPQT^{4+}$ ring prefers to reside on the TTF unit rather than on the DNP unit in the ground state co-conformation (GSCC) of $\mathbf{1}^{4+}$. Upon chemical or electrochemical oxidation of the TTF unit to its radical cation ($TTF^{\bullet+}$) form, the $CBPQT^{4+}$ ring shuttles to the DNP recognition site on account of the Coulombic repulsion between the ring and the oxidized TTF unit, namely the $TTF^{\bullet+}$ radical cation. Upon reduction of the $TTF^{\bullet+}$ unit to its neutral state, the $CBPQT^{4+}$ ring resides on the DNP recognition site (metastable state co-conformation, MSCC) for some time before its relaxation to the GSCC is complete. The lifetime of the MSCC can be controlled (Figure 1) by isomerization of the TMeAB unit from its *trans* to *cis* configuration, a process which brings about a large geometrical change capable of affecting substantially the free-energy barrier for the shuttling of the $CBPQT^{4+}$ ring along the dumbbell component,[15] given that a *cis* azobenzene unit poses a much larger steric hindrance to the shuttling of the ring than does a *trans* azobenzene unit.

The template-directed strategy, which was employed in the synthesis of *trans*-$\mathbf{1}\cdot 4PF_6$, is outlined in Scheme 1 and described in detail in the Supporting Information. The TTF derivative **3** bearing an azide, and the azobenzene derivative *trans*-**4**, incorporating a DNP unit and a terminal alkyne were obtained in relatively high yields in three and one steps, respectively. The [2]rotaxane *trans*-$\mathbf{1}\cdot 4PF_6$ was isolated in 35% yield, following the reaction of **3** with *trans*-**4** in Me_2CO using a copper(I)-catalyzed azide–alkyne cycloaddition[16] (CuAAC) in the presence of $CBPQT\cdot 4PF_6$, while relying upon a threading-followed-by-stoppering approach to form the [2]rotaxane. The resulting [2]rotaxane was characterized by NMR spectroscopy and mass spectrometry (see the Supporting Information). The ^{1}H NMR spectrum of *trans*-$\mathbf{1}\cdot 4PF_6$ in CD_3CN shows that the $CBPQT^{4+}$ ring prefers to reside on the TTF unit opposed to the DNP one in an approximately 9:1 ratio. The simple dumbbell *trans*-**2** was obtained under similar experimental conditions in 41% yield.

The redox- and light-induced switching (Figure 2) of $\mathbf{1}^{4+}$ and its corresponding dumbbell **2** (see the Supporting Information) were performed in MeCN at room temperature and monitored by both steady-state and time-resolved UV/Vis absorption spectroscopies. The most remarkable features in the absorption spectrum of *trans*-$\mathbf{1}^{4+}$ (Figure 2a, black trace) are 1) an intense band with a maximum intensity at 281 nm, arising from the π–π* band of the bipyridinium dicationic ($BIPY^{2+}$) units of the $CBPQT^{4+}$ ring, 2) the two sharp DNP absorption peaks at 313 and 326 nm, 3) shoulders at 350 and 440 nm which correspond to the π–π* and n–π* bands of the TMeAB unit,

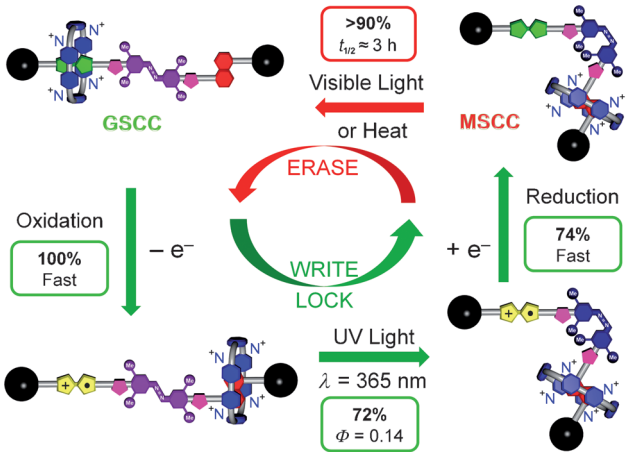

Figure 1. Chemically and photochemically triggered memory switching cycle of the [2]rotaxane $\mathbf{1}^{4+}$.

respectively, and 4) a broad and relatively weak band with $\lambda_{max} = 850$ nm, which arises from a charge-transfer (CT) interaction from the TTF unit on the dumbbell component to the $BIPY^{2+}$ units of the $CBPQT^{4+}$ ring.[7b,14] The absorption changes (Figure 2a) show that the addition of 1.0 equiv of $Fe(ClO_4)_3$ to *trans*-$\mathbf{1}^{4+}$ causes the one-electron oxidation of its TTF unit, generating *trans*-$\mathbf{1}^{5+}$ quantitatively. As expected, the TTF-$CBPQT^{4+}$ CT absorption band centered at 850 nm disappears and, furthermore, the sharp DNP-based peaks are no longer present, an observation which indicates that the $CBPQT^{4+}$ ring shuttles from the TTF to the DNP recognition site upon mono-oxidation of the former, in line with similar

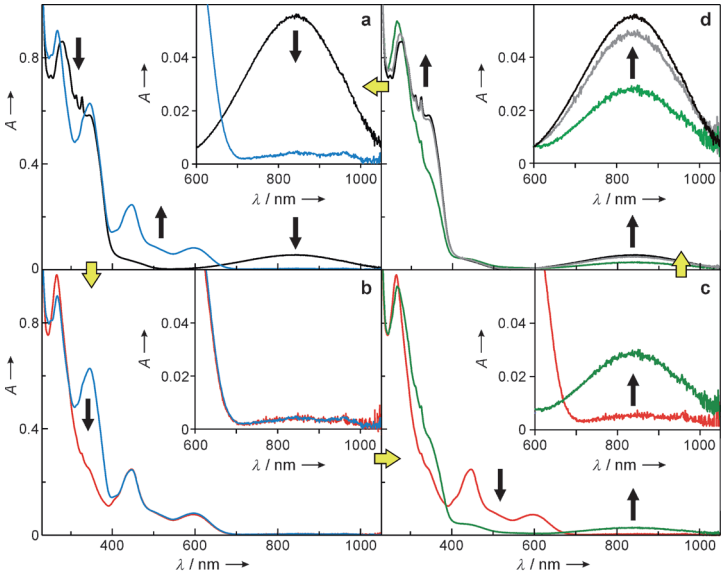

Figure 2. Changes in the absorption spectrum observed in MeCN at 295 K for a 19 μM solution of *trans*-$\mathbf{1}^{4+}$ (black trace) resulting from the following sequence of operations: a) oxidation with up to 1 equiv of $Fe(ClO_4)_3$ to obtain *trans*-$\mathbf{1}^{5+}$ (blue trace); b) exhaustive irradiation at 365 nm to obtain *cis*-$\mathbf{1}^{5+}$ (red trace); c) reduction with 1 equiv of $Me_{10}Fc$ to obtain *cis*-$\mathbf{1}^{4+}$ (green trace); d) equilibration in the dark to obtain *trans*-$\mathbf{1}^{4+}$ (grey trace). The absorption bands of the $Me_{10}Fc^+$ cation, generated in the reaction between $\mathbf{1}^{5+}$ and $Me_{10}Fc$, were arithmetically subtracted from the spectra shown as green and grey traces.

systems.[7b,14] The addition of 1.0 equiv of decamethylferrocene ($Me_{10}Fc$) affords the fast and quantitative reduction of *trans*-$\mathbf{1}^{5+}$ back to *trans*-$\mathbf{1}^{4+}$, leading to the repositioning of the $CBPQT^{4+}$ ring onto the TTF recognition site (see the Supporting Information).

Irradiation of *trans*-$\mathbf{1}^{4+}$ at 365 nm causes the *trans–cis* photoisomerization of the TMeAB unit (see the Supporting Information) with a quantum yield of 0.14, in agreement with those measured for **2** and a TMeAB model. This photoreaction affects neither the CT band centered at 850 nm, nor the DNP sharp features at around 320 nm. All these observations indicate that 1) the presence of the $CBPQT^{4+}$ ring does not influence the isomerization of the TMeAB gate, and 2) the *trans–cis* conversion of the latter unit does not have an impact on the distribution of the $CBPQT^{4+}$ ring between the TTF and DNP recognition sites. The first-order rate constant for the thermal *cis–trans* back transformation of the TMeAB unit of $\mathbf{1}^{4+}$ is $7.5\times10^{-6}\ s^{-1}$.

We have performed in situ oxidation/photoirradiation/reduction/thermal reset experiments to explore the possibility of trapping the shuttle in the MSCC by photochemically closing the azobenzene gate when the $CBPQT^{4+}$ ring resides on the DNP secondary recognition site. Specifically, we anticipated that 1) chemical oxidation causes the shuttling of the $CBPQT^{4+}$ ring from the $TTF^{\bullet+}$ to the DNP recognition site, 2) light irradiation converts the TMeAB unit from a *trans* to a *cis* configuration (gate closed), 3) successive chemical reduction regenerates the neutral TTF unit with the $CBPQT^{4+}$ ring still residing on the DNP unit, and 4) thermal *cis–trans* isomerization opens the gate and allows the repositioning of the $CBPQT^{4+}$ ring onto the TTF primary recognition site, thereby affording (Figure 1) full reset of the system.

The results of such a "write-lock-erase" experiment are summarized in Figure 2. The addition of 1 equiv of Fe^{3+} ions to *trans*-$\mathbf{1}^{4+}$ yields *trans*-$\mathbf{1}^{5+}$ quantitatively, leading (Figure 2a) to the shuttling of the $CBPQT^{4+}$ ring from the $TTF^{\bullet+}$ onto the DNP recognition site. Exhaustive irradiation of this solution at 365 nm causes (Figure 2b) the *trans–cis* isomerization of the TMeAB unit; at the photostationary state we estimate that the azobenzene gate has been closed in 72% of the rotaxane molecules. Following the successive addition of 1 equiv of $Me_{10}Fc$ to reduce *cis*-$\mathbf{1}^{5+}$ back (Figure 2c) to *cis*-$\mathbf{1}^{4+}$, an analysis of the absorption bands shows that about 53% of the $CBPQT^{4+}$ rings remain trapped on the DNP recognition site, while 47% of the rings have shuttled back to the regenerated neutral TTF site. Such a partial trapping is a result of the fact that 1) the *trans–cis* photoisomerization is incomplete (the ring can freely shuttle back to the TTF recognition site in 28% of the rotaxane molecules), and 2) some *cis–trans* thermal isomerization can occur while the chemical reduction is being performed.[17] The initial absorption spectrum of *trans*-$\mathbf{1}^{4+}$ is regenerated (Figure 2d) after 30 h in the dark. Specifically, the TTF-$CBPQT^{4+}$ CT band at 850 nm, the DNP features at around 320 nm, and the π–π^* band of the *trans*-TMeAB unit at 350 nm gain almost completely their original intensities, indicating that 2) the azobenzene gate has opened, and 2) the $CBPQT^{4+}$ ring has migrated back to its starting position, namely the TTF unit.

The time analysis of the spectral changes in Figure 2d provides information about the effectiveness of the kinetic trapping exerted by the *cis*-TMeAB gate. The rate constants for the recovery of the *trans*-TMeAB absorption ($5.7\times10^{-5}\ s^{-1}$, Figure 3a) and the TTF-$CBPQT^{4+}$ CT band ($9.3\times10^{-5}\ s^{-1}$, Figure 3b) are comparable. This observation indicates that in *cis*-$\mathbf{1}^{4+}$ the $CBPQT^{4+}$ ring cannot move from the DNP to the TTF site over the *cis*-TMeAB unit, and the relaxation rate from the MSCC to the GSCC is determined by the rate of the thermal opening of the gate. It is also interesting to note that the rate of thermal conversion of the azobenzene gate from its *cis* to *trans* configuration depends on the position of the $CBPQT^{4+}$ ring on the dumbbell. In fact, the *trans*-TMeAB isomer is regenerated with $k=7.5\times10^{-6}\ s^{-1}$ when the $CBPQT^{4+}$ ring surrounds the TTF recognition site (see the Supporting Information), whereas $k=5.7\times10^{-5}\ s^{-1}$—that is, almost one order of magnitude faster—when the ring is located on the DNP recognition site (Figure 3a).

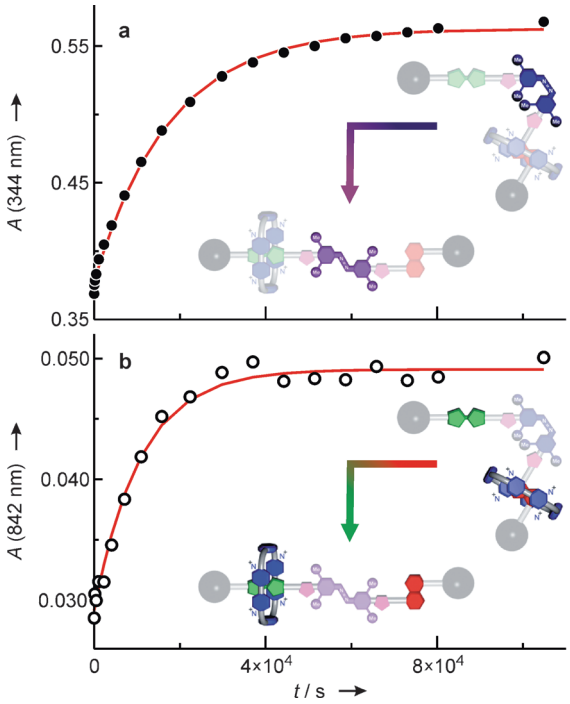

Figure 3. Time-dependent absorption changes (MeCN, 295 K), monitored at a) 344 nm, (*trans*-TMeAB absorption) and b) 842 nm (TTF-$CBPQT^{4+}$ CT absorption), showing the regeneration of *trans*-$\mathbf{1}^{4+}$ from the metastable state *cis*-$\mathbf{1}^{4+}$. The lines represent the data fitting according to a first-order kinetic equation. The corresponding absorption spectra are shown in Figure 2d.

We have inverted the order of the chemical and light inputs and performed the oxidation of the rotaxane after the photochemical closure of the gate to confirm the memory behavior of the rotaxane and investigate the hampering effect of the *cis*-azobenzene gate on the shuttling motion. The results (see the Supporting Information) show that the addition of Fe^{3+} at the photostationary state—containing around 70% *cis*-$\mathbf{1}^{4+}$ and 30% *trans*-$\mathbf{1}^{4+}$—causes the immediate, quantitative oxidation of *trans*-$\mathbf{1}^{4+}$ which is followed by

ring shuttling to the DNP recognition site, whereas *cis*-$\mathbf{1}^{4+}$ is oxidized on a much slower time scale, that is, the reaction is complete after around 10 min.[18] This observation might result from the fact that the movement of the $CBPQT^{4+}$ ring away from the oxidized TTF unit may be hindered kinetically by the presence of the *cis*-TMeAB unit. Indeed, the entrapment of the $CBPQT^{4+}$ ring on the TTF unit by the *cis*-TMeAB unit could thwart the oxidation of the latter for both thermodynamic (increase of the potential for oxidation) and kinetic (molecular encapsulation, electrostatic repulsion between Fe^{3+} and $CBPQT^{4+}$) reasons.[19]

The reluctance of *cis*-$\mathbf{1}^{4+}$ to become oxidized relative to its *trans* counterpart, can be exploited, in principle, to implement a photochemical write–protection mechanism, that is, the light-induced *trans–cis* transformation renders the rotaxane molecules less reactive towards chemical oxidation, thereby hampering data writing.

In summary, we have shown that a [2]rotaxane can operate as a bistable memory element under kinetic control. The data can be written on the rotaxane by an oxidation stimulus, and locked by UV light irradiation. After the writing session, the oxidized species can be reduced back to the original form without losing the written data for a remarkably longer time, compared to most thermodynamically controlled molecular switches, in which the MSCCs have short lifetimes. The data remain stored for a few hours in the dark at room temperature until the thermal opening of the azobenzene gate occurs. Light irradiation, not only locks the data previously recorded by oxidation, but also protects the nonoxidized rotaxanes from accidental writing. These properties have positive implications for the use of such molecules in engineered test devices.[5b,7e] In general, integrated systems in which sophisticated functionalities can be accessed by convenient and reversible processes under mild conditions represent a promising step forward towards real world applications in many fields of nanotechnology.

Experimental Section

Trans-$\mathbf{1}\cdot 4PF_6$: A solution of **3** (80 mg, 0.1 mmol), *trans*-**4** (104 mg, 0.1 mmol), CBPQT·$4PF_6$ (110 mg, 0.1 mmol), TBTA (9 mg, 0.017 mmol), and $Cu(MeCN)_4PF_6$ (6 mg, 0.017 mmol) in anhydrous Me_2CO (5 mL) was stirred for 8 h at room temperature. The solvent was then evaporated and the resulting green solid was purified by column chromatography (SiO_2: MeOH, then 0.5% NH_4PF_6 in Me_2CO). The green fraction in Me_2CO was collected and concentrated to a very small volume, before the crude product was precipitated by the addition of H_2O. The resulting solid was collected by filtration to afford the [2]rotaxane *trans*-$\mathbf{1}\cdot 4PF_6$ (102 mg, 35%) as a green powder. ^{1}H NMR (500 MHz, CD_3CN, 233 K): $\delta = 9.06$–8.65 (m, 8H), 7.97–7.94 (m, 2H), 7.86 (b, 8H), 7.77 (t, $J = 8.0$ Hz, 2H), 7.64 (b, 8H), 7.52 (b, 4H), 7.34 (t, $J = 8.0$ Hz, 2H), 7.15–7.06 (m, 6H), 6.90 (t, $J = 8.0$ Hz, 2H), 6.26 (t, $J = 8.0$ Hz, 2H), 6.21 (s, 1H), 6.20 (s, 1H), 5.97 (t, $J = 8.0$ Hz, 2H), 5.17–5.62 (m, 8H), 5.01 (s, 4H), 4.58–3.46 (m, 68H), 3.43–3.23 (m, 4H), 2.42 (t, $J = 8.0$ Hz, 2H), 2.27 (s, 6H), 2.24 (s, 6H), 1.21–1.13 ppm (*m*, 24H). ESI-HRMS calcd for $m/z = 1327.5148$ $[M-2PF_6]^{2+}$, found $m/z = 1327.5148$; calcd for $m/z = 836.6903$ $[M-3PF_6]^{3+}$, found $m/z = 836.6982$.

Trans-**2**: A solution of **3** (40 mg, 0.05 mmol), *trans*-**4** (52 mg, 0.05 mmol), TBTA (9 mg, 0.017 mmol), and $Cu(MeCN)_4PF_6$ (6 mg, 0.017 mmol) in anhydrous Me_2CO (5 mL) were stirred for 8 h at room temperature. The solvent was then evaporated and the resulting brown solid was purified by column chromatography (SiO_2: EtOAc) to afford the desired dumbbell *trans*-**2** (38 mg, 41%) as a orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.85$ (d, $J = 4.5$ Hz, 1H), 7.84 (d, $J = 4.5$ Hz, 1H), 7.82 (s, 2H), 7.59 (s, 2H), 7.58 (s, 2H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.09 (b, 6H), 6.80 (t, $J = 7.5$ Hz, 2H), 6.19 (b, 2H), 5.03 (s, 2H), 5.00 (s, 2H), 4.58 (t, $J = 5.0$ Hz, 2H), 4.51 (t, $J = 5.0$ Hz, 2H), 4.28 (t, $J = 5.0$ Hz, 2H), 4.26 (s, 2H), 4.24 (s, 2H), 4.00 (t, $J = 5.0$ Hz, 2H), 3.96 (t, $J = 5.0$ Hz, 2H), 3.91–3.60 (m, 54H), 3.37 (septet, $J = 7.0$ Hz, 2H), 2.38 (s, 6H), 2.37 (s, 6H), 1.21 (d, $J = 7.0$ Hz, 12H), 1.21 ppm (d, $J = 7.0$ Hz, 12H). MS (MALDI-TOF) calcd for $m/z = 1844.844$ $[M]^+$, found $m/z = 1844.848$.

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[17] The thermal *cis–trans* isomerization of the TMeAB unit is accelerated substantially, both in the rotaxane and in the dumbbell component, when the nearby TTF unit is oxidized. Such a relatively fast thermal reset requires that the chemical reduction of *cis*-$\mathbf{1}^{5+}$ is accomplished quickly and efficiently.

[18] It is difficult to establish the position of the $CBPQT^{4+}$ ring after chemical oxidation of *cis*-$\mathbf{1}^{4+}$, particularly since the *cis–trans* thermal isomerization occurs on a time scale comparable with that of the chemical oxidation.

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