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Quantifying the working stroke of tetrathiafulvalene-based electrochemically-driven linear motor-molecules

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ELECTRONIC SUPPLEMENTARY INFORMATION

(25 Pages)

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Introduction

In this supplement, we describe the experimental procedures for the synthesis of the [2]rotaxane **5**•4PF_6, together with its spectrometric, spectroscopic, and electrochemical characterization. We also provide more details on the derivations of the kinetic and thermodynamic data obtained for the deslipping of the $CBPQT^{4+}$ ring in $\mathbf{5}^{4+}$, $\mathbf{5}^{5+}$, and $\mathbf{5}^{6+}$.

Experimental Details for the Synthesis of the [2]Rotaxane

General methods: Chemicals were purchased from Aldrich Chemicals and were used as received, unless indicated otherwise. 2-{4-(2-Cyanoethylthio)-5-ethylthio-1,3-dithiole-2-yliden}-5-tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole [1] (**1**), (methoxyethoxy)ethyl iodide, [2] 3,5-di-*t*-butyl-benzylbromid,[3] and 1,1″-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridin-1-ium) bis(hexafluoro-phosphate)[4] were all prepared according to literature procedures. Solvents were dried according to literature procedures.[5] All reactions were carried out under an anhydrous argon atmosphere. High pressure experiments were carried out in a teflon-tube on a Psika high pressure apparatus. Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). The plates were inspected under UV light and, if required, developed in I_2 vapor. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature at 400 MHz and 100 MHz, respectively, on a Bruker ARX400 spectrometer using residual solvent as the internal standard. All chemical shifts are quoted on a δ scale, and all coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used in listing the NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, and bs = broad singlet, and m = multiplet. Samples were prepared using $CDCl_3$, CD_3SOCD_3, or CD_3COCD_3 or purchased from Cambridge Isotope

Labs. Low resolution electrospray ionization mass spectra (ESI-MS) were obtained from a from a Sciex API III+_+ triple quadrupole mass spectrometer, while high resolution matrix-assisted laser-desorption/ionization mass spectrometry (MALDI–MS) and ESI spectra were collected with an IonSpec Ultima 7T FTMS instrument. Elemental analyses were performed by Quantitative Technologies, Inc. UV-Vis spectra were recorded on a Cary 100 Bio Spectrophotometer at room temperature.

Compound 2. A solution of compound **1** (0.52 g, 0.96 mmol) in anhydrous THF (75 mL) was degassed (Ar, 10 min) before a solution of $CsOH{\bullet}H_2O$ (0.16 g, 0.96 mmol) in anhydrous MeOH (10 mL) was added dropwise to the yellow solution via a syringe over a period of 1 h at room temperature. (Methoxyethoxy)ethyl iodide (0.24 g, 1.06 mmol) was added in one portion and the reaction mixture was subsequently stirred for 4 h at room temperature. The solvent was evaporated and the resulting yellow residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 100 mL) and dried ($MgSO_4$). Removal of the solvent gave a red oil, which was purified by column chromatography (SiO_2: CH_2Cl_2/EtOAc 19:1). The broad orange band ($R_f = 0.3$) was collected and concentrated to give 0.49 g (87%) of the title compound **2** as a yellow foam. Data for **2**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30 (t, $J = 7.3$ Hz, 3H, SCH_2CH_3), 2.40 (s, 3H, Ar-CH_3), 2.84 (q, $J = 7.3$ Hz, 2H, SCH_2CH_3), 3.00 (t, $J = 6.8$ Hz, 2H, SCH_2CH_2O), 3.37 (s, 3H, OCH_3), 3.52–3.54 (m, 2H, CH_2O), 3.60–3.68 (m, 4H, 2 × CH_2O), 6.93 (s, 2H, pyrrol-*H*), 7.29 (d, $J = 7.5$ Hz, 2H, Ar-*H*), 7.73 (d, $J = 7.5$ Hz, 2H, Ar-*H*); ^{13}C NMR (CD_3SOCD_3, 100 MHz) δ 15.3, 21.4, 30.1, 35.4, 58.4, 69.5, 69.8, 71.5, 112.8, 113.1 (two lines overlapping), 117.8, 126.3, 126.9, 127.2, 127.2, 127.2, 130.8, 134.8, 146.2; MS(MALDI) *m/z* 593 (M^+ + 2, 10), 592 (M^+ + 1, 5), 591 (M^+, 30), 527 (5), 437 (M^+ – Ts, 100), HiRes-FT-MALDI-MS *m/z* 590.9823 (calcd for $C_{22}H_{25}NO_4S_7^+$ 590.9796).

Compound 3. Compound **2** (0.48 g, 0.81 mmol) was dissolved in anhydrous THF/MeOH (1:1 v/v, 150 mL) and degassed (Ar, 10 min) before a freshly prepared solution of NaOMe (0.66 g,

12.2 mmol) was added in one portion. The yellow solution was heated under reflux for 30 min before being cooled to room temperature, whereupon the solvent was evaporated affording a slightly red oil. The residue was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 100 mL) and dried ($MgSO_4$). Concentration gave a yellow oil, which was subjected to column chromatography (SiO_2: CH_2Cl_2/EtOAc 9:1). The orange band ($R_f = 0.4$) was collected and concentrated to provide 0.33 g (93%) of the title compound **3** as an orange oil. Data for **3**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, J = 7.3 Hz, 3H, SCH_2CH_3), 2.85 (q, J = 7.3 Hz, 2H, SCH_2CH_3), 3.02 (t, J = 6.8 Hz, 2H, SCH_2CH_2O), 3.38 (s, 3H, OCH_3), 3.53–3.56 (m, 2H, CH_2O), 3.62–3.70 (m, 4H, 2 × CH_2O), 6.61 (d, J = 1.3 Hz, 2H, pyrrol-*H*), 8.22 (bs, 1H, N*H*); ^{13}C NMR (CD_3SOCD_3, 100 MHz) δ 15.3, 30.0, 35.3, 58.4, 69.5, 69.8, 71.5, 107.6, 111.1 (two lines overlapping), 117.3 (two lines overlapping), 122.0, 126.8, 127.5. MS(MALDI) *m/z* 439 (M^+ + 2, 15), 438 (M^+ + 1, 20), 437 (M^+, 80), 334 (20), 306 (35), 248 (100). Anal. Calcd for $C_{15}H_{19}NO_2S_6$: C, 41.16; H, 4.38; N, 3.20. Found: C, 41.53; H, 4.47; N, 3.05.

Dumbbell 4. Compound **3** (0.11 g, 0.26 mmol) was dissolved in anhydrous DMF (15 mL) and degassed (Ar, 10 min) before NaH (0.028 g, 1.22 mmol) was added followed by addition of 3,5-di-*t*-butyl-benzylbromid (0.072 g, 0.25 mmol). The reaction mixture was stirred for 1 h at room temperature, causing the initially yellow solution to become more orange. H_2O (50 mL) was added dropwise until no more gas evolution was observed and the mixture extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated affording a yellow oil, which was purified by column chromatography (SiO_2: CH_2Cl_2/EtOAc 9:1). The yellow band ($R_f = 0.8$) was collected and the solvent evaporated, providing 0.15 g (92%) of the title compound **4** as a yellow oil. Data for **4**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (1.30 s, 18H, 2 × $C(CH_3)_3$), 1.31 (t, J = 7.3 Hz, 3H, SCH_2CH_3), 2.85 (q, J = 7.3 Hz, 2H, SCH_2CH_3), 3.02 (t, J = 6.9 Hz, 2H, SCH_2CH_2O), 3.38 (s, 3H, OCH_3), 3.53–3.55 (m, 2H, CH_2O), 3.62–3.64 (m, 2H, CH_2O), 3.68 (t, J = 6.9 Hz, 2H,

C*H*$_2$O), 4.96 (s, 2H, Ar-C*H*$_2$), 6.49 (s, 2H, pyrrole-*H*), 7.00 (d, *J* = 1.7 Hz, 2H, 2 × Ar-*H*), 7.37 (t, 1H, *J* = 1.7 Hz, Ar-*H*); MS(MALDI) *m/z* 639 (M^+, 20), 508 (35), 503 (30), 444 (30), 344 (100). Anal. Calcd for $C_{30}H_{41}NO_2S_6$: C, 56.30; H, 6.46; N, 2.19. Found: C, 56.14; H, 6.83; N, 2.06.

[2]Rotaxane 5•4PF$_6$. A solution of the dumbbell **4** (0.30 g, 0.47 mmol), 1,1′′-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridin-1-ium) bis(hexafluorophosphate) (0.97 g, 1.37 mmol), and 1,4-bis(bromomethyl)benzene (0.36 g, 1.36 mmol) in anhydrous DMF (12 mL) was transferred to a teflon-tube and subjected to 10 kbar of pressure at room temperature for 3 d. The green solution was directly subjected to column chromatography (SiO_2) and unreacted dumbbell was eluted with Me_2CO, whereupon the eluent was changed to Me_2CO/NH_4PF_6 (1.0 g NH_4PF_6 in 100 mL Me_2CO) and the green band was collected. Most of the solvent was removed in vacuo ($T < 30$ °C), followed by addition of H_2O (100 mL). The resulting green precipitate was collected by filtration, washed with H_2O (2 × 20 mL) and Et_2O (2 × 30 mL) and dried in vacuo over P_2O_5, affording 0.17 g (20%) of the title compound **5**•4PF$_6$ as a green solid. Data for **5**•4PF$_6$. ^{1}H NMR (CD_3COCD_3) δ 1.40 (s, 18H, 2 × C(C*H*$_3$)$_3$), 1.51 (t, *J* = 7.4 Hz, 2H, SCH$_2$C*H*$_3$), 3.14 (q, *J* = 7.4 Hz, 2H, SC*H*$_2$CH$_3$), 3.31 (t, *J* = 6.3 Hz, 2H, SC*H*$_2$CH$_2$O), 3.35 (s, 3H, C*H*$_3$O), 3.68–3.70 (m, 2H, C*H*$_2$O), 3.84–3.86 (m, 2H, C*H*$_2$O), 3.91 (s, *J* = 6.3 Hz, 2H, C*H*$_2$O), 5.33 (s, 2H, Ar-C*H*$_2$), 6.10 (bs, 8H, 4 × $^+$NC*H*$_2$), 6.97 (AB q, *J* = 2.0 Hz, 2H, pyrrol-*H*), 7.37 (d, *J* = 1.6 Hz, 2H, 2 × Ar-*H*), 7.57 (t, *J* = 1.6 Hz, 1H, Ar-*H*), 8.09 (bs, 8H, 8 × xylyl-*H*), 8.18 (bs, 4H, 4 × β-H), 8.61 (bs, 4H, 4 × β-H), 9.46 (bs, 4H, 4 × α-H), 9.63 (bs, 4H, 4 × α-H); MS(ESI) *m/z* 1595.4 (100, $[M - 1PF_6]^+$), 1015.2 (15), 724.9 (15, $[M - 2PF_6]^{2+}$); UV-Vis (MeCN, 298 K): λ_{max} = 764 nm (ε = 1870 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{66}H_{72}F_{24}N_5O_2P_4S_6$: C, 45.54; H, 4.23; N, 4.02. Found: C, 45.08; H, 4.24; N, 3.74.

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Spectroscopic Characterization of 5•4PF$_6$

A full ^{1}H NMR spectrum (400 MHz) of the highly constrained [2]rotaxane **5**•4PF$_6$ recorded in CD_3COCD_3 at room temperature is shown in Figure S1.

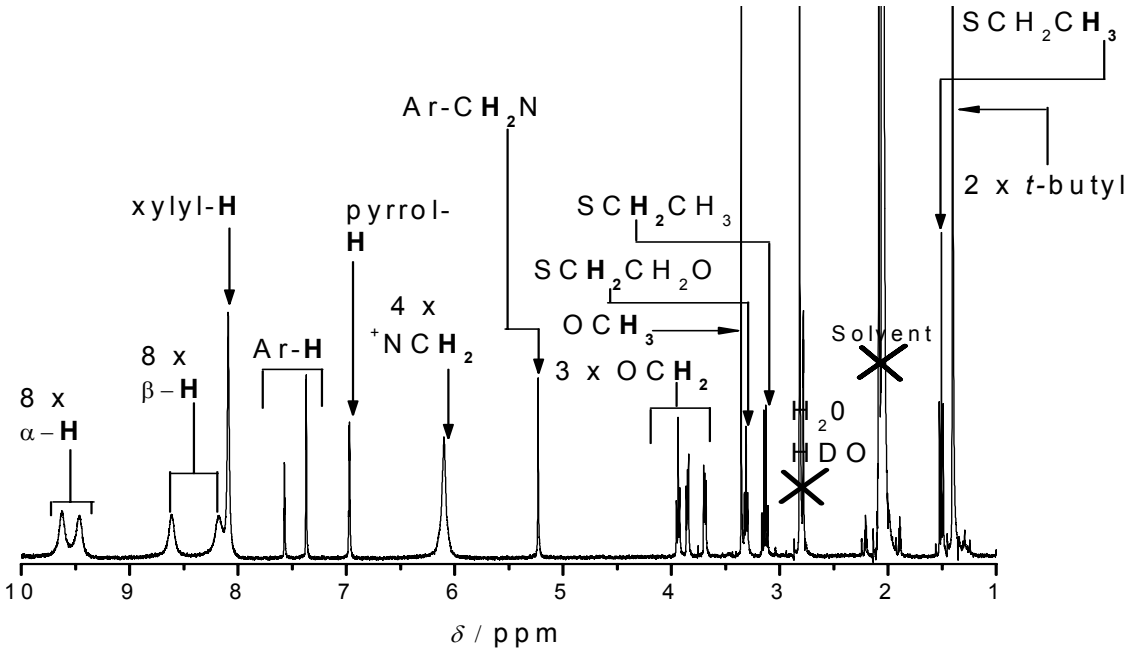

Figure S1. ^{1}H NMR spectrum (400 MHz) of **5**•4PF$_6$ in recorded in CD_3COCD_3 at room temperature.

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Electrochemical Characterization

General methods: Electrochemical experiments were carried out in Argon purged MeCN solutions at room temperature, with a Princeton Applied Research 263A Multipurpose instrument interfaced to a pc. Cyclic voltammetric experiments were performed using a glassy carbon working electrode. The counter electrode was a Pt wire and the reference electrode a Standard Calomel electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) was added as the supporting electrolyte. The cyclic voltammograms were obtained at a scan rate of 200 mV s^{-1}.

The cyclic voltammograms (CVs) of the dumbbell compound **4** and the highly constrained [2]rotaxane **5**•$4PF_6$ recorded in MeCN at room temperature is shovn in Figure S2 and S3.

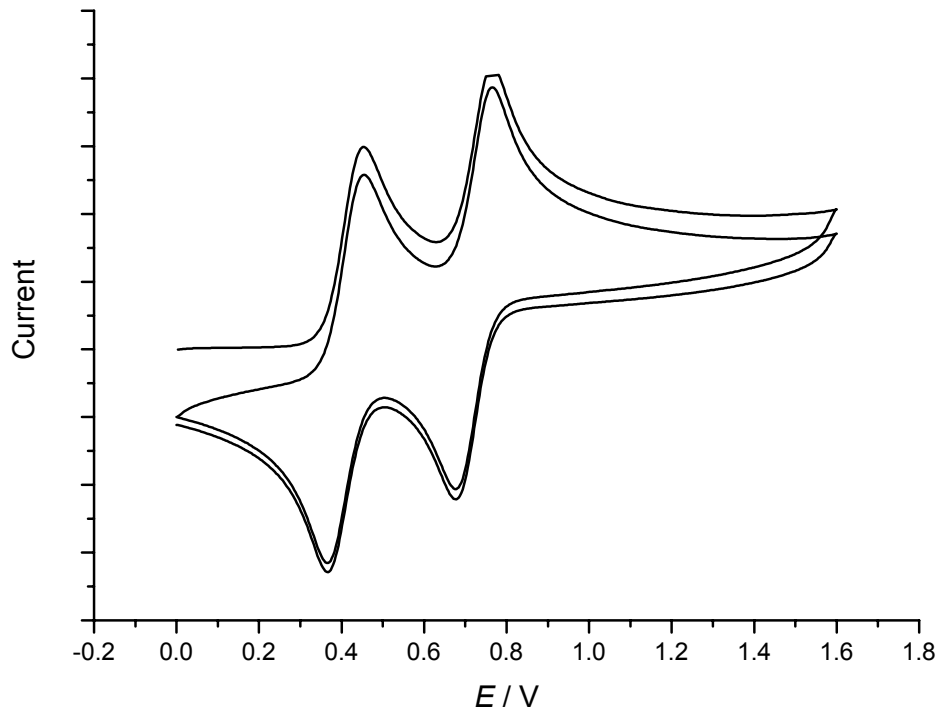

Figure S2. A CV of the dumbbell compound **4** against a Standard Calomel Electrode recorded in MeCN at room temperature.

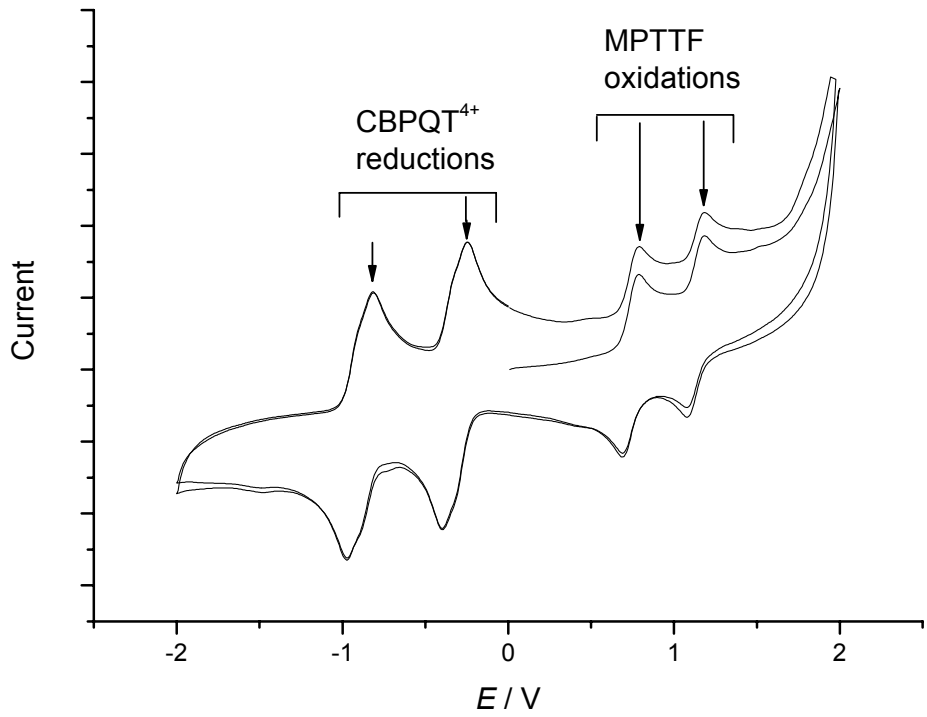

Figure S3. A CV of the [2]rotaxane **5**•4PF$_6$ against a Standard Calomel Electrode recorded in MeCN at room temperature.

The half-wave potentials obtained from the CVs in Figure S2 and S3 are listed in Table S1.

Table S1. Summary of the electrochemical data for **4** and **5**•4PF$_6$.

	$E_{1/2}^1$ (MPTTF)	$E_{1/2}^2$ (MPTTF)	$E_{1/2}^1$ (CBPQT^{4+})	$E_{1/2}^2$ (CBPQT^{4+})
4	+411 mV	+720 mV	–	–
5•4PF$_6$	+736 mV	+1128 mV	–320 mV	–893 mV
ΔE½	+325 mV	+408 mV	–	–

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Absorption Spectroscopy

General methods: Absorption spectra were recorded on a Cary 100 Bio Spectrophotometer at room temperature.

The titrational addition of 1.0 equiv of $Fe(ClO_4)_3$ to a solution of the dumbbell compound **4** in MeCN at room temperature results (Figure S4) in the formation of three absorption bands centered on 287 nm, 432, and 760 nm, respectively.

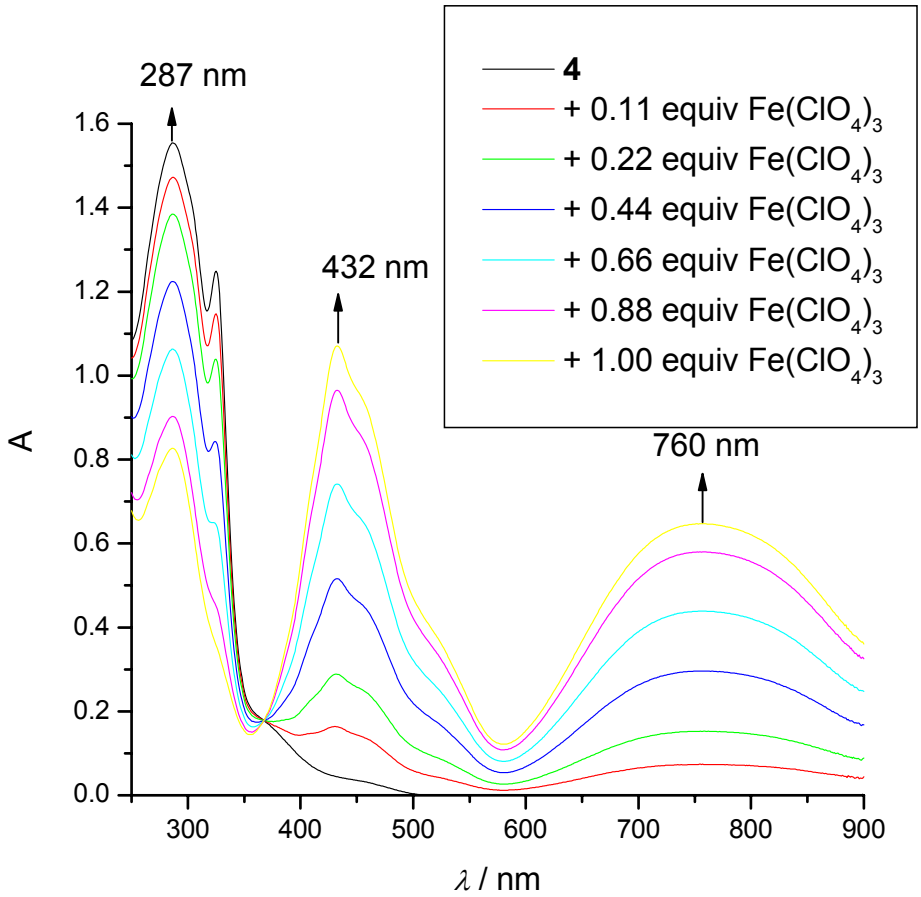

Figure S4. Addition of 1.0 equiv of $Fe(ClO_4)_3$ to a solution of **4** in MeCN at room temperature.

The titration of the dumbbell compound **4** in MeCN at room temperature with an additional 1.1 equiv of $Fe(ClO_4)_3$ to a total of 2.1 equiv $Fe(ClO_4)_3$ results in the disappearance (Figure S5) of the 432 nm and 760 nm band, respectively, and the appearance of a 625 nm absorption band.

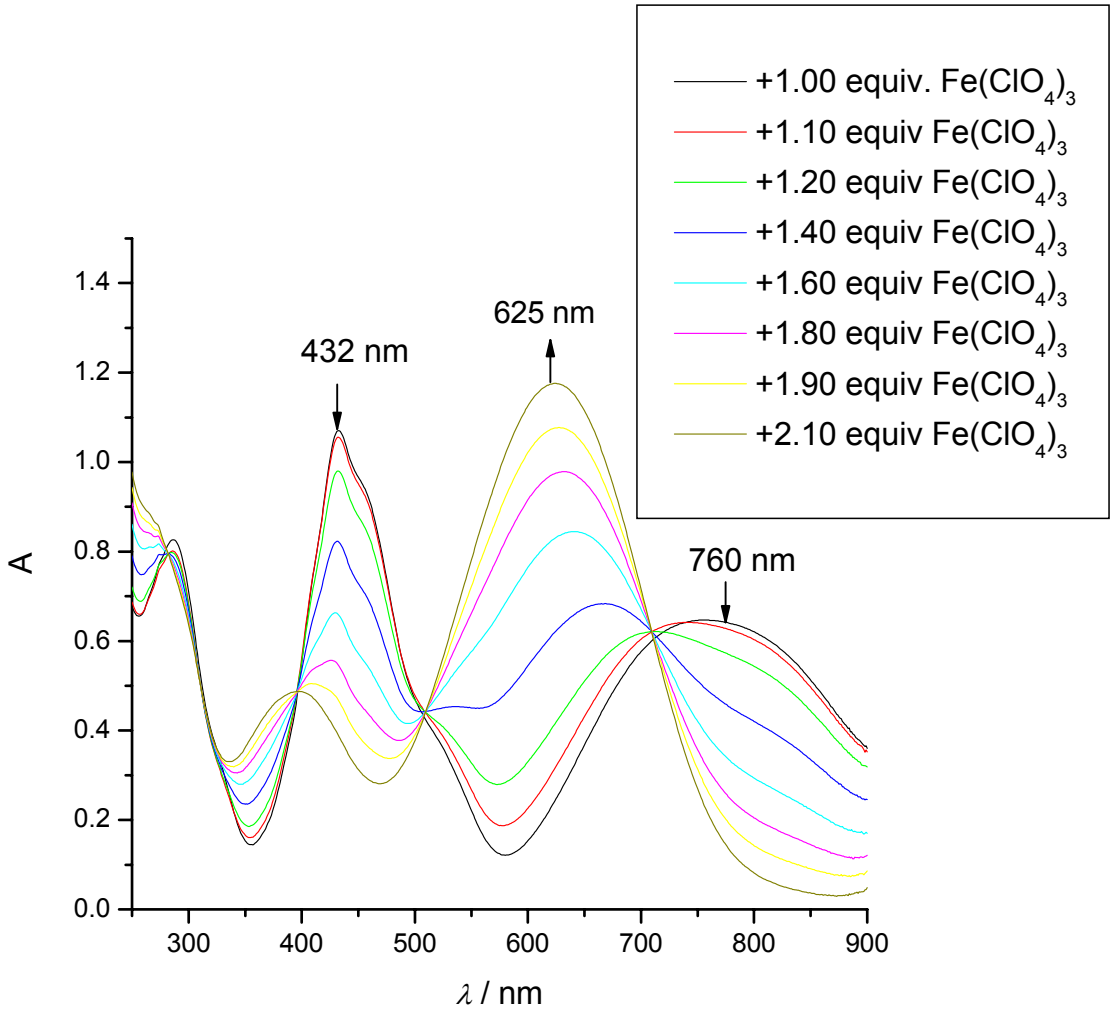

Figure S5. Addition of a total of 2.1 equiv of $Fe(ClO_4)_3$ to a solution of **4** in MeCN at room temperature.

The titrational addition of 1.25 equiv of $Fe(ClO_4)_3$ to a solution of **5**•$4PF_6$ in MeCN at room temperature results (Figure S6) in the formation of two absorption bands centered on 465 nm and 880 nm, respectively.

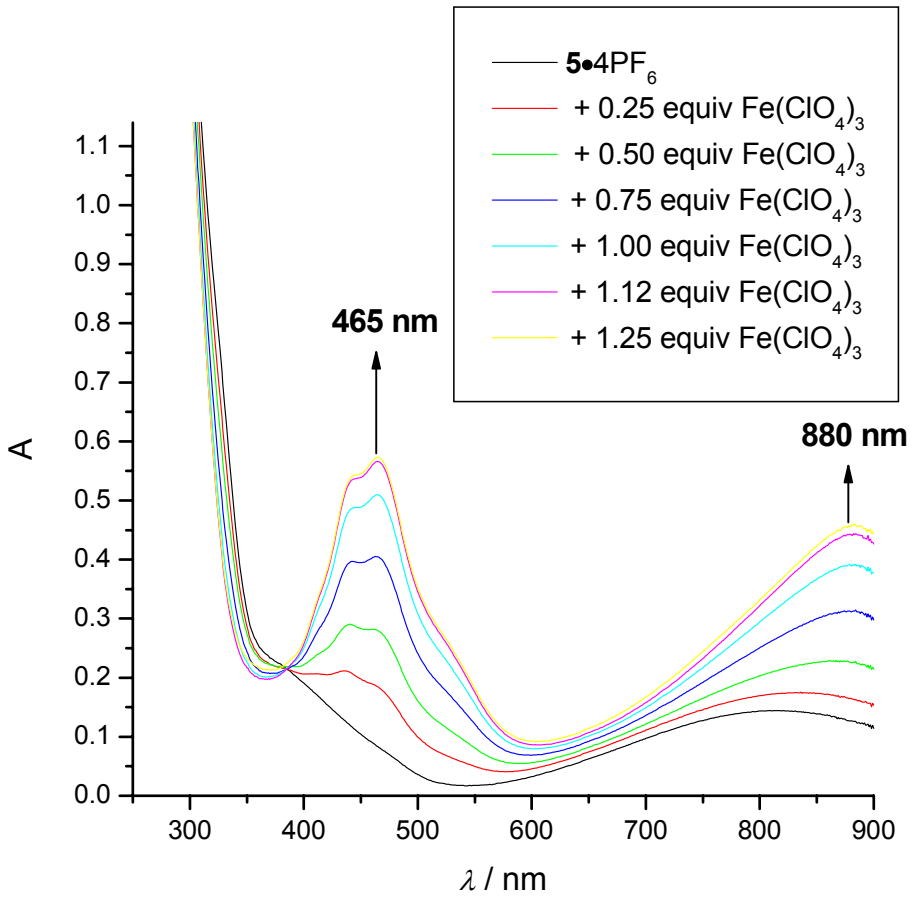

Figure S6. Addition of 1.25 equiv of $Fe(ClO_4)_3$ to a solution of **5**•$4PF_6$ in MeCN at room temperature.

The addition of 2.5 equiv of $(FeClO_4)_3$ to a solution of **5**•$4PF_6$ in MeCN at room temperature results in the disappearance (Figur S7) of the 465 nm absorption band and within minutes formation of a broad absorption centered on 625 nm. This absorption is characteristic for the doubly-oxidized uncomplexed MPTTF unit $\mathbf{4}^{2+}$.

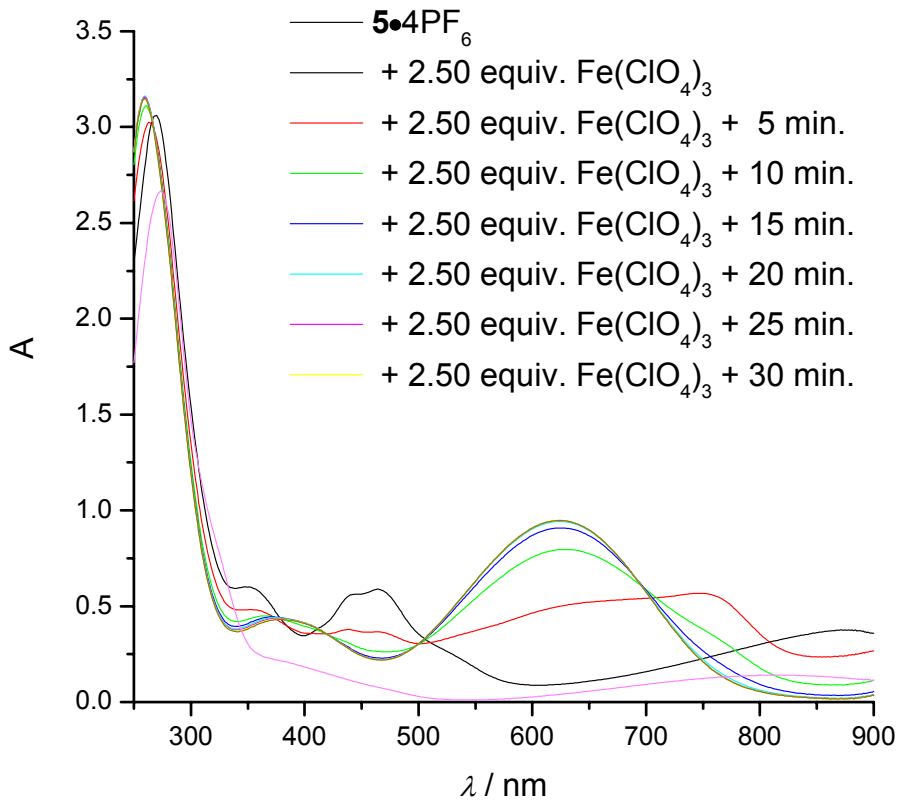

Figure S7. Addition of 2.5 equiv of $(FeClO_4)_3$ to a solution of **5**•$4PF_6$ in MeCN at room temperature.

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Deslipping of the Highly Constrained [2]Rotaxane

The deslipping of $CBPQT^{4+}$ from $\mathbf{5}^{4+}$ has been investigated in CD_3SOCD_3 and PhCN using NMR spectroscopy and absorption spectroscopy, respectively, whereas the deslipping of $CBPQT^{4+}$ from $\mathbf{5}^{5+}$ and $\mathbf{5}^{6+}$ has been carried out in MeCN and probed using absorption spectroscopy.

An ^{1}H NMR spectrum recorded of the reaction mixture after a deslipping process of **5**•$4PF_6$ carried out in CD_3SOCD_3, revealed that it contained free dumbbell **4** and the free CBPQT•$4PF_6$ ring with only minor amounts of decomposition products being observed as illustrated in Figure S8.

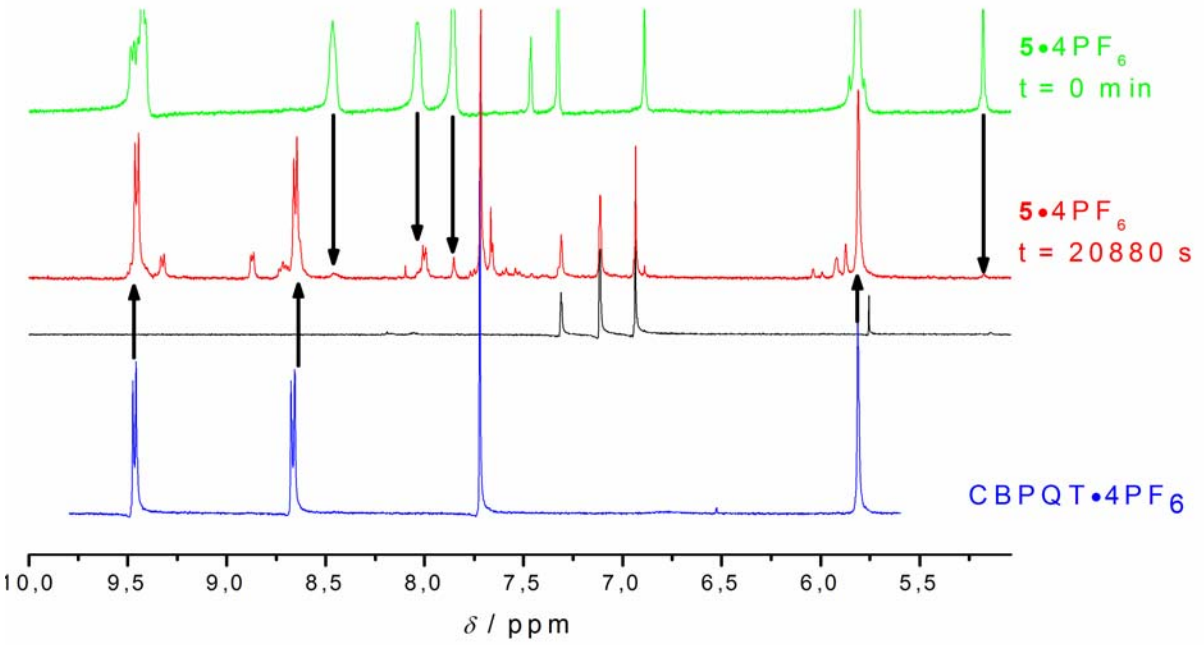

Figure S8. A display of partial ^{1}H NMR spectra (5–10 ppm) of **5**•$4PF_6$ recorded in CD_3SOCD_3 before heating (green spectrum) and after heating (red spectrum) to 397 K for 20880 seconds. The spectra of the free dumbbell **4** (black spectrum) and free $CBPQT^{4+}$ (blue spectrum) is shown as a reference to prove that the prolonged heating predominately results in deslipping of the $CBPQT^{4+}$ ring and consequently the formation of the free dumbbell **4** and free $CBPQT^{4+}$.

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Rate Constant Measurements

The rate constants were measured by absorption spectroscopy. The decrease in a specific band was analyzed according to Equation S1, which facilitated the calculation of the reaction fraction α.

Equation S1. The reaction fraction α can be calculated using the given relationship.

$$\alpha(t) = \frac{A(t) - A(t_\infty)}{A(t_0) - A(t_\infty)}$$

Where $A(t_0)$ is the initial absorbance and $A(t_\infty)$ is the absorbance after infinite reaction time, obtained for fitting of the appropriate functions (based on first order kinetics) to the recorded data points.

Under the assumption of first order kinetics, the rate constant k, can be obtained from the slope of the plot of $\ln(\alpha)$ as a function of the reaction time. The corresponding free energy of activations ($\Delta G^{\ddagger}$) can be calculated using the relationship in Equation S2.

Equation S2. Calculation of $\Delta G^{\ddagger}$.

$$\Delta G^{\ddagger} = -RT \times \ln\left(\frac{kh}{k_B T}\right)$$

Where $R = 8.3145$ J K^{-1} mol; $h = 6.626 \times 10^{-34}$ J s; $k_B = 1.3807 \times 10^{-23}$ J K^{-1}

Deslipping of 5^{4+} (non-oxidized state)

The deslipping of the non-oxidized [2]rotaxane **5**•4PF_6 was monitored in PhCN at various temperatures between 405 K and 447 K using the CT band at 844 nm as a probe. The sample was transferred to a UV-Vis cuvette and heated to the designated temperature for a specified amount of time followed by rapid cooling in an Me_2CO/dry ice bath. The UV-Vis spectrum was then

measured. The rate constant k was determined (Figure S9) to be 3.5×10^{-5} s^{-1} at 405 K corresponding to a $\Delta G^{\ddagger}$ value of 32.3 kcal mol^{-1}.

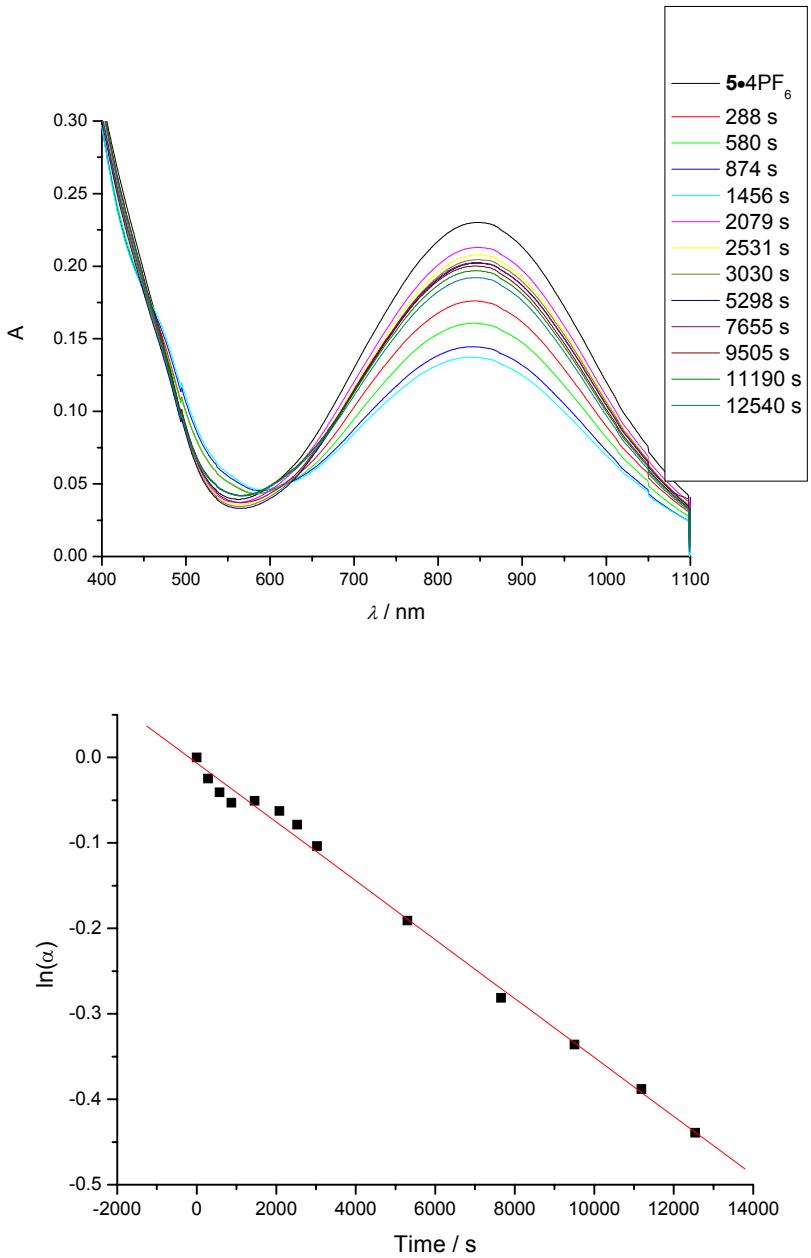

Figure S9. The upper plot show the decrease in the CT band at 844 nm as a solution of **5**•$4PF_6$, in PhCN was heated to 405 K for the time of period specified. The lower plot show the linear relationship between ln(α) and the reaction time and from the slope, a rate constant k of 3.5×10^{-5} s^{-1} was obtained corresponding to a $\Delta G^{\ddagger}$ of 32.3 kcal mol^{-1} at 405 K.

Similar experiments were carried out (Figure S10) at 409, 413, 429, and 447 K and the rate constants k were obtained employing a similar data analysis as described above. The

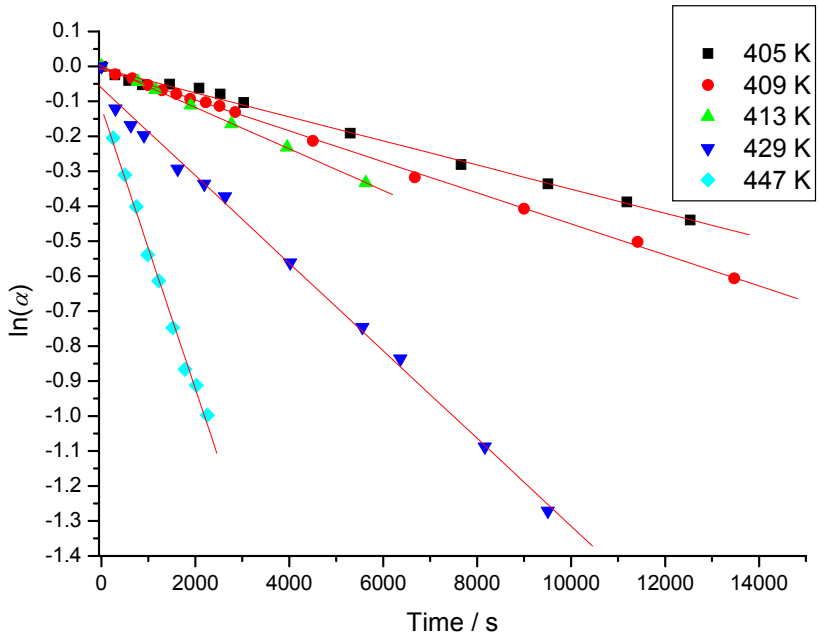

Figure S10. The linear relationship between ln(α) and the reaction time for the deslipping of $\mathbf{5}^{4+}$ determined at 405, 409, 413, 429, and 447 K in PhCN.

corresponding $\Delta G^{\ddagger}$ values were calculated and are listed in Table S2, together with the rate constants.

Table S2. Rate constants and derived $\Delta G^{\ddagger}$ values for the deslipping of $\mathbf{5}^{4+}$ determined by absorption spectroscopy in PhCN at different temperatures using the MPTTF/CBPQT^{4+} CT band as probe.

T / K	k / s^{-1}	$\Delta G^{\ddagger}$ / kcal mol^{-1}
405	3.45×10^{-5}	32.25
409	4.43×10^{-5}	32.37
413	5.93×10^{-5}	32.46
429	1.25×10^{-4}	33.08
447	4.02×10^{-4}	33.50

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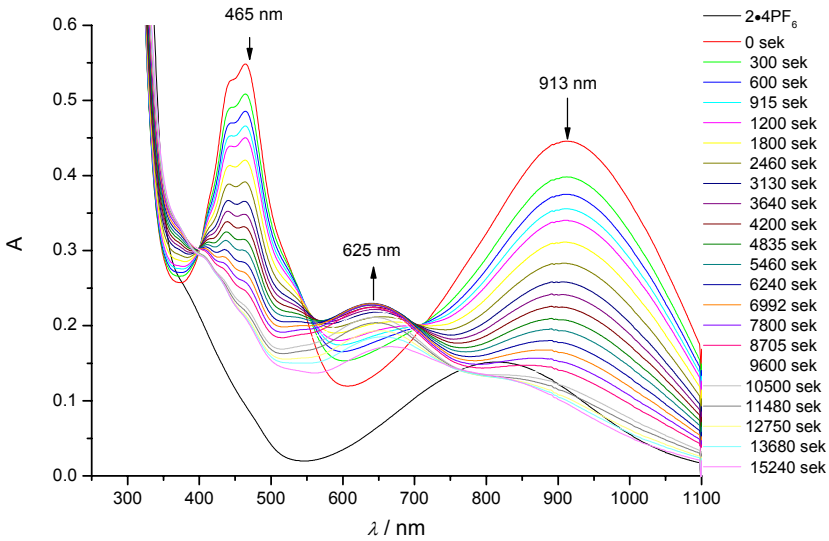
Deslipping of 5^{5+} (mono-oxidized state)

A sample of the highly constrained [2]rotaxane **5**•$4PF_6$, in MeCN was transferred to a UV-Vis Cuvette and heated to 323, followed by addition of 1.0 equiv of $Fe(ClO_4)_3$. The UV-Vis spectrum of the solution was recorded before the addition of $Fe(ClO_4)_3$ and at the specified points after the addition of the oxidant. The addition of the oxidant results in the formation of a well-defined 465 nm absorption band assigned to the MPTTF radical cation located inside the $CBPQT^{4+}$ ring, which then starts to diminish as a function of time as a consequence of the deslipping process. The observed (Figure S11) rate constant of 2.2×10^{-4} s^{-1} is twice the actual deslipping rate constant, as a result of the dismuation reaction (see main text) occurring between $\mathbf{4}^{+}$ and $\mathbf{5}^{5+}$. This means that the deslipping rate constant is 1.1×10^{-5} s^{-1} for $\mathbf{5}^{5+}$ at 323 K.



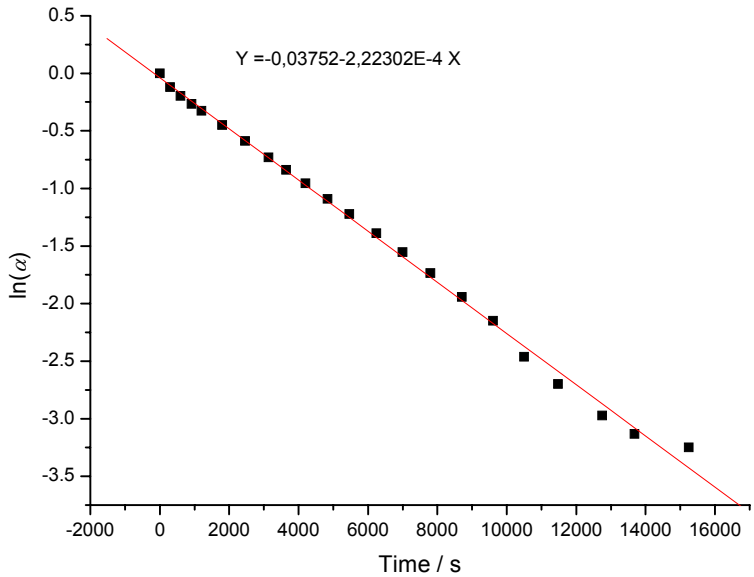


Figure S11. The upper plot illustrate that the addition of 1.0 equiv of $Fe(ClO_4)_3$ to **5**•$4PF_6$ in MeCN heated to 323 K results in the formation of a well defined absorption band centered at 465 nm, much more intense then the original CT band at 812 nm originating from the [2]rotaxane. The decrease in this band was used to determine α. The lower plot shows the linear relationship between ln(α) and the reaction time. The rate constant k for the deslipping of $\mathbf{5}^{5+}$ was determined to be 1.1×10^{-4} s^{-1} corresponding to a $\Delta G^{\ddagger}$ of 24.8 kcal mol^{-1} at 323 K.

Similar experiments were carried out (Figure S12) at 313, 318, 329, and 335 K and the rate constants k were obtained employing a similar data analysis as described above. The

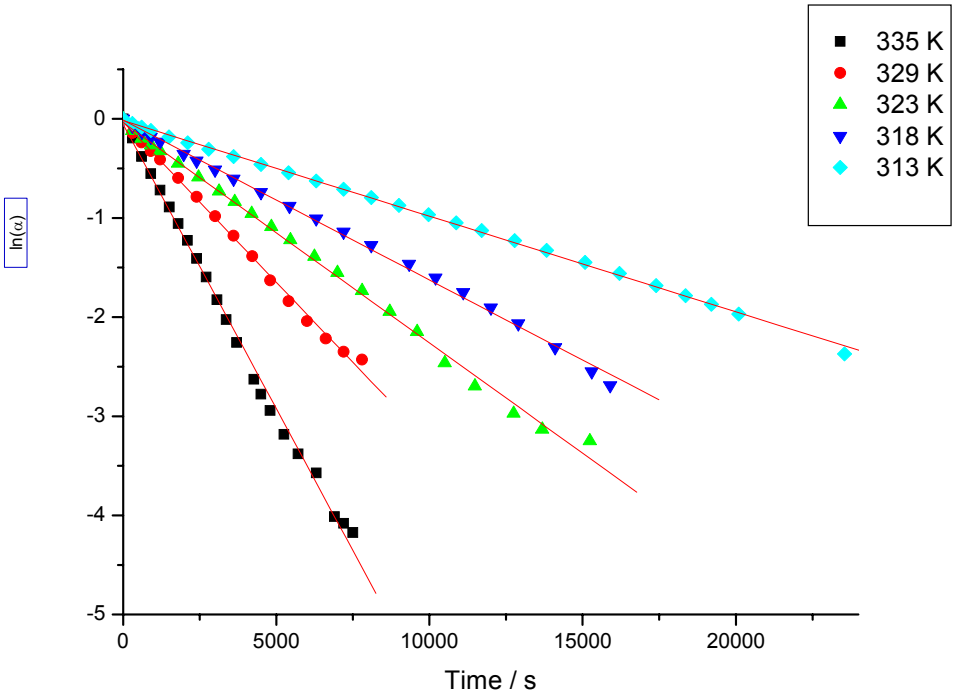


Figure S12. The linear relationship between ln(α) and the reaction time for the deslipping of $\mathbf{5}^{5+}$ determined at 313, 318, 323, 329, and 335 K in MeCN.

corresponding $\Delta G^{\ddagger}$ values were calculated and are listed in Table S3, together with the rate constants.

Table S3. Rate constants and derived $\Delta G^{\ddagger}$ values for the deslipping of $\mathbf{5}^{5+}$ determined by absorption spectroscopy in MeCN at different temperatures using the 465 nm absorption band as probe.

T / K	k / s^{-1}	$\Delta G^{\ddagger}$ / kcal mol^{-1}
313	4.83×10^{-5}	24.56
318	8.05×10^{-5}	24.64
323	1.11×10^{-4}	24.83
329	1.62×10^{-4}	25.05
335	2.87×10^{-4}	25.14

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Deslipping of 5^{6+} (doubly oxidized state)

A sample of the highly constrained [2]rotaxane **5**•$4PF_6$ in MeCN was transferred to a UV-Vis cuvette and cooled to 280 K, followed by addition of excess of $Fe(ClO_4)_3$ to facilitate the formation of $\mathbf{5}^{6+}$. The UV-Vis spectrum of the solution was recorded before the addition of $Fe(ClO_4)_3$ and at the specified points of time after the addition of the oxidant. The addition of the oxidant results in the formation of a broad 750 nm absorption band which can be assigned to the MPTTF dication located inside the $CBPQT^{4+}$ ring, which then starts to diminish as a function of time as the deslipping of the $CBPQT^{4+}$ ring occurs. The rate constant k was determined (Figure S13) to be 16.2×10^{-4} s^{-1} at 280 K corresponding to a $\Delta G^{\ddagger}$ of 20.0 kcal mol^{-1}.

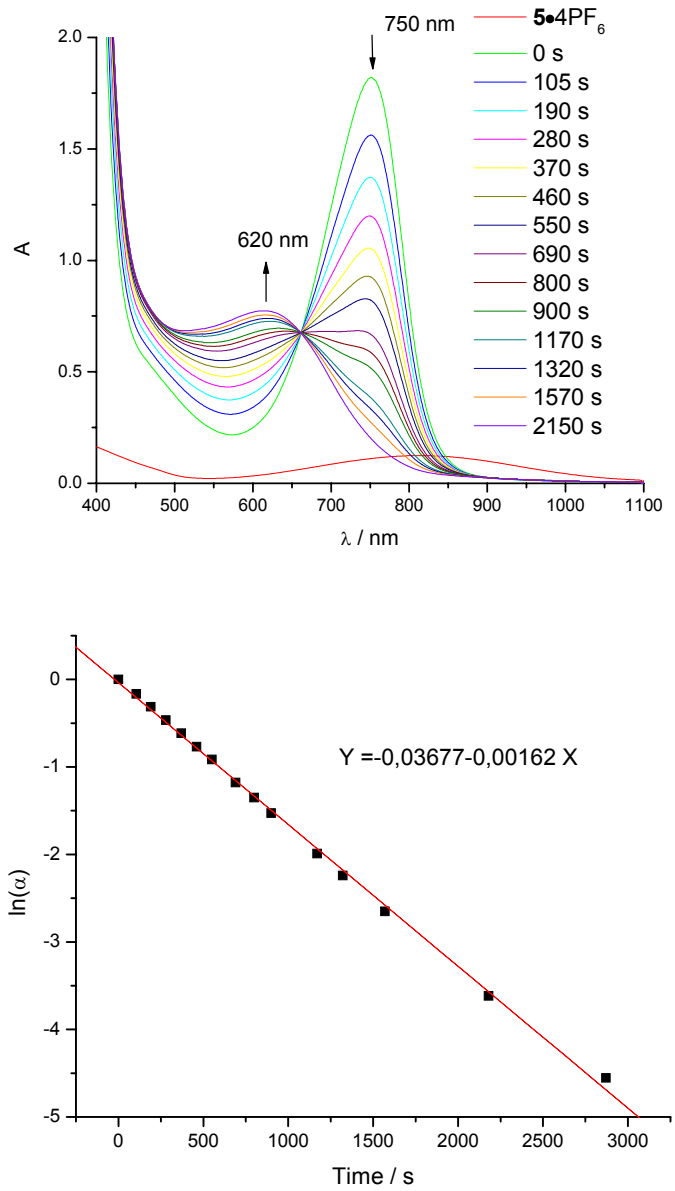

Figure S13. The upper plot illustrate how the addition of excess of $Fe(ClO_4)_3$ to **5**•$4PF_6$, in MeCN cooled to 280 K results in the formation of a broad absorption band centered at 750 nm, much more intense then the original CT band at 812 nm originating from the [2]rotaxane. The decrease in the 750 nm absorption band was used to determine α. The lower plot shows the linear relationship between ln(α) and the reaction time. The rate constant k for the deslipping of $\mathbf{5}^{6+}$ was determined to be 16.2×10^{-4} s^{-1} corresponding to a $\Delta G^{\ddagger}$ of 20.0 kcal mol^{-1} at 280 K.

Similar experiments were carried out (Figure S14) at 276, 283, 288, and 291 K and the rate constants k were obtained employing a similar data analysis as described above. The

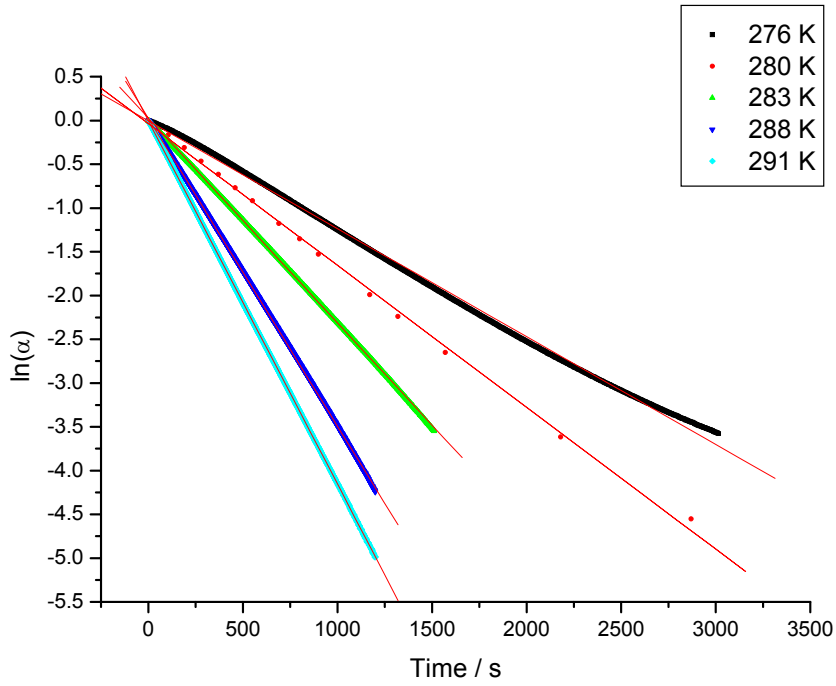

Figure S14. The linear relationship between ln(α) and the reaction time the deslipping of $\mathbf{5}^{6+}$ determined at 276, 280, 283, 289, and 291 K in MeCN.

corresponding $\Delta G^{\ddagger}$ values were calculated and are listed in Table S4, together with the rate constants.

Table S4. Rate constants and derived $\Delta G^{\ddagger}$ values for the deslipping of $\mathbf{5}^{6+}$ determined by absorption spectroscopy in MeCN at different temperatures using the 750 nm absorption band as probe.

T / K	k / s^{-1}	$\Delta G^{\ddagger}$ / kcal mol^{-1}
276	12.3×10^{-4}	19.80
280	16.2×10^{-4}	19.95
283	23.4×10^{-4}	19.96
288	35.2×10^{-4}	20.09
291	41.5×10^{-4}	20.21

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Kinetic Parameters

Since, the $\Delta G^{\ddagger}$ values have been determined at different temperatures the enthalpic ($\Delta H^{\ddagger}$) and entropic ($\Delta S^{\ddagger}$) contributions to the deslipping processes occurring in $\mathbf{5}^{4+}$, $\mathbf{5}^{5+}$, and $\mathbf{5}^{6+}$ can be obtained (Figure S15–S17) from Gibbs Helmholtz plots, i.e., using the relationship $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

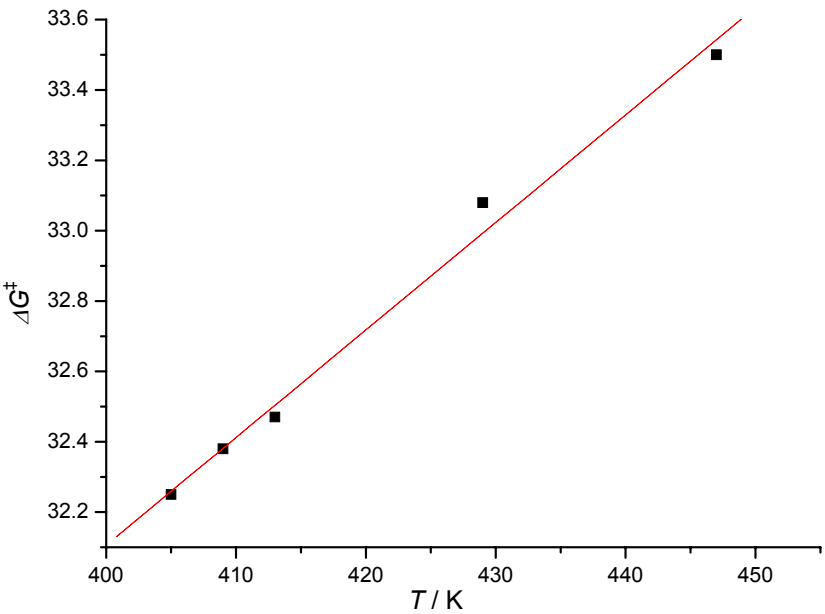

Figure S15. Gibbs-Helmholtz plot depicting the linear relationship between $\Delta G^{\ddagger}$ and the temperature for the deslipping of $\mathbf{5}^{4+}$ in PhCN.

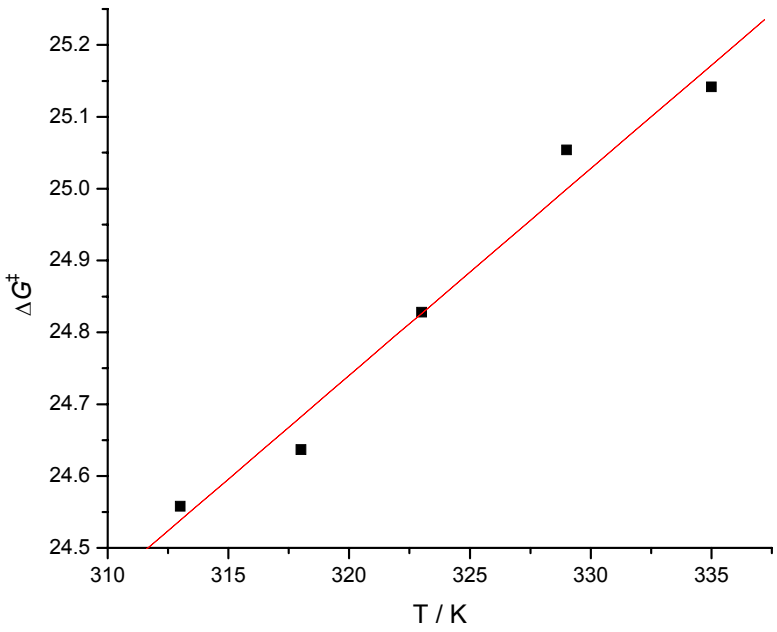

Figure S16. Gibbs-Helmholtz plot depicting the linear relationship between $\Delta G^{\ddagger}$ and the temperature for the deslipping of $\mathbf{5}^{5+}$ in MeCN.

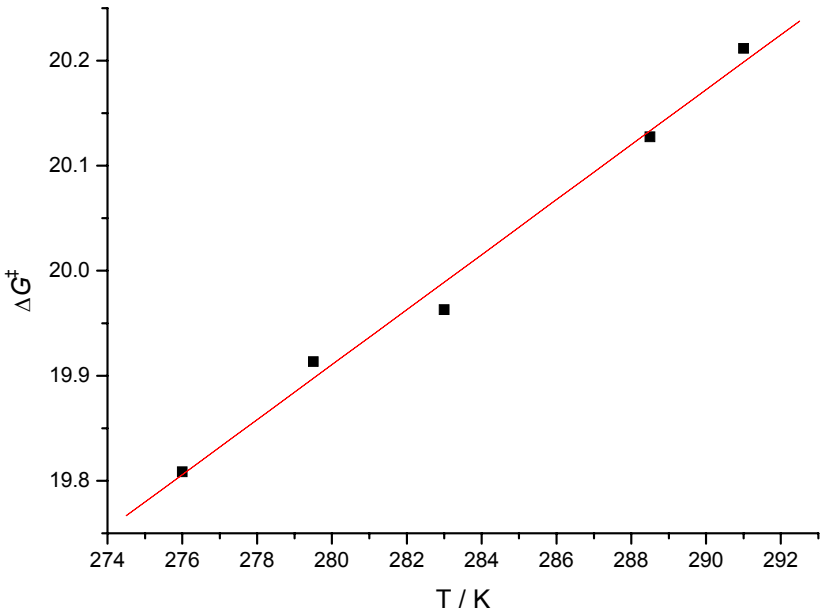

Figure S17. Gibbs-Helmholtz plot depicting the linear relationship between $\Delta G^{\ddagger}$ and the temperature for the deslipping of $\mathbf{5}^{6+}$ in MeCN.

The kinetic parameters obtained from these plots are summarized in Table S5, together with the extrapolated $\Delta G^{\ddagger}$ values at 300 K.

Table S5. Kinetic and thermodynamic parameters for the deslipping of $CBPQT^{4+}$ in $\mathbf{5}^{4+}$, $\mathbf{5}^{5+}$, and $\mathbf{5}^{6+}$.

	Solvent	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ (300 K) / kcal mol^{-1}
$\mathbf{5}^{4+}$	PhCN	19.9	–30.6	29.1
$\mathbf{5}^{5+}$	MeCN	15.5	–28.8	24.2
$\mathbf{5}^{6+}$	MeCN	12.6	–26.2	20.4

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