Supporting Information

Cation-Modulated Rotary Speed in a Light-Driven Crown Ether-Functionalized Molecular Motor

Ruth Dorel, Carla Miró, Yuchen Wei, Sander J. Wezenberg, and Ben L. Feringa*

Center for Systems Chemistry, Stratingh Institute for Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

b.l.feringa@rug.nl

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1. General information

All reagents were purchased from commercial sources and used as received without further purification. Dry solvents were obtained from a MBraun solvent purification system. Column chromatography was performed on silica gel (Merck type 9385 230-400 mesh) or on a Revelers X2 Flash Chromatography system; TLC: silica gel 60, Merck, 0.25 mm. High Resolution Mass spectra (HRMS) were recorded on an LTQ Orbitrap XL. NMR spectra were obtained using a Varian Mercury Plus (1H: 400 MHz, 13C: 100 MHz), a Varian Unity Plus (1H: 500 MHz, 13C: 125 MHz) or a Bruker Innova (1H: 600 MHz, 13C: 151 MHz) in CDCl3, or CD3CN in the case of complexation studies. Chemical shifts are reported in δ units (ppm) relative to the residual deuterated solvent signal of CDCl3 (1H NMR, δ 7.26 ppm; 13C NMR, δ 77.23 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets of doublets), dtd (doublet of triplets of doublets), ddt (doublet of doublets of triplets), td (triplet of doublets), and m (multiplet). UV-vis absorption spectra were measured on a Jasco V-630 or a Hewlett-Packard 8453 spectrometer. Acetonitrile used for spectroscopic studies was of spectroscopic grade (UVASOL Merck) and was degassed prior to the spectroscopic measurements. Irradiations were performed using a spectroline ENB-280C/FE lamp (λ max = 312 nm).

2. Experimental procedures

9-Oxo-9H-thioxanthene-4,5-diyI diacetate (7). AcCl (1.4 mL, 20.47 mmol) was slowly added to a mixture of diol 6 (1.00 g, 4.09 mmol), DMAP (50 mg, 0.41 mmol), and Et3N (5.7 mL, 40.94 mmol) in anhydrous CH2Cl2 (50 mL) at 0 °C under N2 atmosphere. The reaction mixture was allowed to reach rt, stirred for 1 h, and then quenched by the addition of an aqueous solution of HCl (10% v/v, 40 mL). The aqueous phase was extracted with CH2Cl2 (40 mL) and the combined organic layers were dried over MgSO4, filtered, and concentrated under reduced pressure. Purification by column chromatography (pentane:CH2Cl2 3:7) afforded the product as a white solid (1.22 g, 3.72 mmol, 91%).

M.p. = 248-250 °C. 1H NMR (400 MHz, CDCl3) δ 8.51 (dt, J = 7.7, 1.4 Hz, 2H), 7.57 – 7.47 (m, 4H), 2.47 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 168.2, 145.9, 144.0, 130.2, 129.5, 127.3, 126.3, 126.0, 20.8. HRMS (ESI+) m/z calc. for C17H13O5S [M+H]+: 329.0478. Found: 329.0482.

Prepared according to: D. J. van Dijken, J. Chen, M. C. A. Stuart, L. Hou, B. L. Feringa, J. Am. Chem. Soc. 2016, 138, 660–669.
9-Thioxo-9\textit{H}-thioxanthene-4,5-diyl diacetate (8). Lawesson’s reagent (2.29 g, 5.68 mmol) was added to a solution of ketone 7 (933 mg, 2.84 mmol) in anhydrous toluene (120 mL) and the mixture was stirred at 90 °C for 2 h, then cooled down to rt and the volatiles were removed under reduced pressure. Purification by column chromatography (pentane:CH₂Cl₂ 1:1 to 2:8) afforded the product as a green solid, which was directly taken to the next step (966 mg, 2.80 mmol, 99%).

\textbf{M.p.} = 232-234 °C. $^1$H NMR (600 MHz, CDCl₃) δ 8.82 (dd, $J = 8.0, 1.7$ Hz, 2H), 7.49 – 7.44 (m, 4H), 2.47 (s, 6H). $^{13}$C NMR (151 MHz, CDCl₃) δ 210.7, 168.2, 146.0, 138.8, 130.5, 126.6, 125.1, 124.5, 20.8. HRMS could not be obtained due to the oxidation of 8 to the corresponding ketone under the measurement conditions.

3-Methyl-2,3-dihydro-1\textit{H}-dispiro[phenanthrene-4,2'-thiirane-3',9''-thioxanthene]-4'',5''-diyl diacetate (10). A solution of PhI(OTf)$_2$ (748.3 mg, 0.74 mmol) in anhydrous DMF (20 mL) precooled to -50 °C was added to a solution of hydrazone 4² (390 mg, 1.74 mmol) in anhydrous DMF (100 mL) at -50 °C under N₂ atmosphere and the resulting mixture was stirred at that temperature for 30 s. A solution of thioketone 8 (600 mg, 1.74 mmol) in anhydrous DMF (100 mL) precooled to -50 °C was subsequently added and the reaction was stirred for 16 h while allowed to reach rt. After dilution with EtOAc (150 mL) the mixture was washed with water (2x100 mL) and brine (100 mL) and then dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by column chromatography (pentane:EtOAc 9:1 to 85:15) afforded the product as a pale yellow solid (112 mg, 0.21 mmol, yield = 28%). Flushing of the column with CH₂Cl₂ allowed the recovery of unreacted starting thioketone 8 (419 mg, 1.22 mmol, 70%).

\textbf{M.p.} = 203-205 °C. $^1$H NMR (600 MHz, CDCl₃) δ 9.21 (d, $J = 8.9$ Hz, 1H), 7.89 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.56 (d, $J = 8.3$ Hz, 1H), 7.43 (ddd, $J = 8.6, 6.7, 1.5$ Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 1H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.30 (ddd, $J = 7.9, 6.7, 1.1$ Hz, 1H), 7.14 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.10 (dd, $J = 8.1, 1.2$ Hz, 1H), 6.98 (d, $J = 8.2$ Hz, 1H), 6.53 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.34 (t, $J = 8.0$ Hz, 1H), 3.47 (ddd, $J$

\[\text{Prepared according to: N. Komura, E. M. Geertsema, M. B. van Gelder, A. Meetsma, B. L. Feringa, }\textit{J. Am. Chem. Soc.} \textbf{2002}, \textit{124}, 5037–5051.\]
= 16.4, 8.8, 7.4 Hz, 1H), 2.58 (ddd, \( J = 16.3, 6.6, 4.6 \text{ Hz}, 1H \)), 2.40 (s, 3H), 2.29 (s, 3H), 1.97 (dtd, \( J = 13.7, 6.9, 4.4 \text{ Hz}, 1H \)), 1.82 (dtd, \( J = 12.7, 7.7, 4.6 \text{ Hz}, 1H \)), 1.10 (d, \( J = 6.9 \text{ Hz}, 3H \)), 1.06 (dtd, \( J = 9.2, 6.6, 3.4 \text{ Hz}, 1H \)).

**\(^{13}C\) NMR** (151 MHz, CDCl\(_3\)) \( \delta 168.5, 168.2, 146.6, 145.7, 141.2, 135.0, 134.2, 134.0, 128.4, 128.1, 128.0, 127.8, 127.4, 127.4, 126.3, 126.0, 125.1, 124.5, 123.9, 123.7, 121.2, 120.3, 66.7, 61.4, 37.4, 28.7, 28.6, 22.3, 20.7, 20.6. **HRMS** (ESI+) \( m/z \) calc. for C\(_{32}\)H\(_{26}\)O\(_2\)S\(_2\)Na [M+Na]\(^+\): 561.1165. Found: 561.1161.

**9-(3-Methyl-2,3-dihydrophenanthren-4(1H)-ylidene)-9H-thioxanthene-4,5-diol (11).** A solution of episulfide 10 (180 mg, 0.34 mmol) and HMPT (0.18 mL, 1.01 mmol) in anhydrous toluene (34 mL) was heated at 80 °C for 16 h. After cooling to rt the mixture was diluted with EtOAc (25 mL), washed with an aqueous solution of HCl (10% v/v, 50 mL), dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The resulting crude was directly dissolved in MeOH:CH\(_2\)Cl\(_2\) 2:1 (30 mL) and treated with solid NaOH (40 mg, 1.01 mmol). After stirring at rt for 1 h an aqueous solution of HCl (10% v/v, 40 mL) was added and the product was extracted with EtOAc (2x30 mL). The combined organic layers were dried over MgSO\(_4\), filtered and concentrated under reduced pressure. Purification by column chromatography (pentane:EtOAc 8:2 to 1:1) afforded the product as a white solid (105 mg, 0.25 mmol, 73% over 2 steps).

**M.p.** = 237-239 °C. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta 7.69 (d, J = 8.2 \text{ Hz}, 1H), 7.63 (d, J = 8.2 \text{ Hz}, 1H), 7.57 (d, J = 8.5 \text{ Hz}, 1H), 7.36 (d, J = 8.2 \text{ Hz}, 1H), 7.29 (t, J = 7.9 \text{ Hz}, 1H), 7.24 (d, J = 7.7 \text{ Hz}, 1H), 7.16 (t, J = 7.5 \text{ Hz}, 1H), 7.05 (t, J = 7.6 \text{ Hz}, 1H), 6.90 (d, J = 7.8 \text{ Hz}, 1H), 6.38 (t, J = 8.1 \text{ Hz}, 1H), 6.32 (t, J = 7.7 \text{ Hz}, 1H), 5.88 (d, J = 7.4 \text{ Hz}, 1H), 5.53 (s, 1H), 5.29 (s, 1H), 4.02 – 3.90 (m, 1H), 3.09 – 2.91 (m, 2H), 2.63 – 2.52 (m, 1H), 1.54 – 1.43 (m, 1H), 0.69 (d, J = 6.9 \text{ Hz}, 3H). \(^{13}C\) NMR (151 MHz, CDCl\(_3\)) \( \delta 152.9, 151.9, 141.9, 139.9, 139.6, 138.6, 133.5, 132.0, 131.8, 130.1, 128.0, 127.5, 127.4, 127.0, 125.5, 125.2, 125.0, 124.3, 121.3, 121.2, 120.8, 119.4, 113.3, 112.4, 31.3, 30.6, 29.0, 21.8. **HRMS** (ESI+) \( m/z \) calc. for C\(_{32}\)H\(_{28}\)O\(_2\)S [M+H]\(^+\): 423.1435. Found: 423.1413.
1\(^{9}\)-(3-Methyl-2,3-dihydrophenanthren-4(1\(H\))-ylidene)-1\(^{9}\)\(H\)-2,5,8,11,14-pentaoxa-1(4,5)thioxanthenacyclotetradecaphane (2). K\(_2\)CO\(_3\) (355 mg, 1.09 mmol) and solution of ((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzensulfonate)\(^3\) (122 mg, 0.24 mmol) in MeCN (2 mL) were added to a solution of 11 (92 mg, 0.22 mmol) in MeCN (20 mL) at rt and the resulting mixture was stirred under reflux overnight. After cooling to rt the volatiles were removed under reduced pressure and the crude product was suspended in CH\(_2\)Cl\(_2\) (30 mL) and washed with aqueous HCl (10\% v/v, 30 mL). The organic layer was dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. Purification by column chromatography (CH\(_2\)Cl\(_2\):MeOH 1:0 to 99:1) and trituration of the resulting foam with pentane gave a yellowish solid, which was washed with MeOH to afford the product as a white solid (64 mg, 0.11 mmol, 50\%).

M.p. = 182-184 \(^\circ\)C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.69 (d, \(J = 8.2\) Hz, 1H), 7.64 (d, \(J = 8.1\) Hz, 1H), 7.49 (d, \(J = 8.5\) Hz, 1H), 7.37 (d, \(J = 8.2\) Hz, 1H), 7.31 (t, \(J = 7.9\) Hz, 1H), 7.27 (d, \(J = 7.7\) Hz, 1H), 7.16 (t, \(J = 7.4\) Hz, 1H), 7.02 (t, \(J = 7.6\) Hz, 1H), 6.82 (dd, \(J = 7.9\), 1.2 Hz, 1H), 6.36 – 6.29 (m, 2H), 5.93 (d, \(J = 7.1\) Hz, 1H), 4.32 – 4.25 (m, 2H), 4.15 – 3.87 (m, 15H), 3.11 – 3.01 (m, 1H), 3.00 – 2.93 (m, 1H), 2.63 – 2.54 (m, 1H), 1.48 (td, \(J = 11.8\), 11.4, 4.5 Hz, 1H), 0.62 (d, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 155.4, 154.7, 139.3, 138.6, 138.5, 137.1, 134.2, 131.9, 131.3, 130.1, 127.3, 127.1, 126.1, 125.5, 125.4, 125.2, 125.1, 125.0, 124.1, 123.9, 121.5, 121.0, 108.7, 108.6, 71.5, 71.3, 70.5, 70.3, 69.3, 69.2, 69.1, 69.0, 30.9, 30.7, 29.1, 21.8. HRMS (ESI+) \(m/\)z calc. for C\(_{36}\)H\(_{17}\)O\(_5\)S [M+H]\(^+\): 581.2356. Found: 581.2387.

Note: Prior to UV/Vis and \(^1\)H-NMR studies, any possible traces of alkali ions were removed by washing with 2.2.2-cryptand. To do so, compound 2 was dissolved in toluene followed by the addition of distilled water and 2 equivalents of 2.2.2-cryptand. After stirring for 15 min the organic phase was separated, washed with distilled water (x5), and the volatiles were subsequently removed under reduced pressure. Complete removal of the 2.2.2-cryptand was verified by \(^1\)H-NMR.

\(^3\) Prepared according to: K. M. Bonger, R. J. B. H. N. van den Berg, L. H. Heitman, Ad P. Ijzerman, J. Oosterom, C. M. Timmers, H. S. Overkleeft, G. A. van der Marel, Bioorg. Med. Chem. 2007, 15, 4841–4856.
3. NMR Spectra

**Figure S1.** $^1$H NMR spectrum of 7.

**Figure S2.** $^{13}$C NMR spectrum of 7.

S5
Figure S3. $^1$H NMR spectrum of 8.

Figure S4. $^{13}$C NMR spectrum of 8.
Figure S5. $^1$H NMR spectrum of 10.

Figure S6. $^{13}$C NMR spectrum of 10.
Figure S7. $^1$H NMR spectrum of 11.

Figure S8. $^{13}$C NMR spectrum of 11.
Figure S9. $^1$H NMR spectrum of 2.

Figure S10. $^{13}$C NMR spectrum of 2.
4. 2D-NMR of 2: Assignment of $^1$H NMR signals

Figure S11. COSY spectrum of 2.

Figure S12. HSQC spectrum of 2.
Figure S13. HMBC spectrum of 2.

Figure S14. NOESY spectrum of 2.
Figure S15. Assignment of signals in the $^1$H NMR spectrum of 2.
5. UV/Vis spectra: Coordination of cations to 2

![UV/Vis spectra](image)

**Figure S16.** Changes in the UV-Vis spectrum of a solution of motor 2 in CH3CN (c = 3 x 10^{-4} M, 1 mm cuvette) upon addition of 50 equiv of the corresponding salts.

6. NMR Titration Experiments: Binding constants\(^4\)

Titration experiments were carried out in CD3CN at rt monitoring the chemical shift of the methyl group at the stereogenic center. In separate NMR tubes, 0.3 mL of a stock solution of 2 in CD3CN (10^{-3} M) were mixed with the required amount (0, 0.3, 0.6, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0, 9.0, 10.0, 12.0, 15.0, and 20.0 equiv) of a stock solution of the corresponding salt (2·10^{-2} M in CH3CN) and then additional CD3CN was added so that the total volume was kept constant in all the tubes (0.6 mL).

![Titration curve](image)

**Figure S17.** Titration curve for 2 with increasing amounts of NH4PF6.

\( ^4 \) www.supramolecular.org
Figure S18. Titration curve for 2 with increasing amounts of NaPF₆.

Figure S19. Titration curve for 2 with increasing amounts of KPF₆.

Figure S20. Titration curve for 2 with increasing amounts of Ca(OTf)₂.
7. **PSS determination by $^1$H NMR**

Samples of motor 2 + 20 equiv of the corresponding salt were prepared in degassed CD$_3$CN ($c = 5 \times 10^{-4}$ M) and kept under N$_2$. Irradiation was performed with $\lambda_{\text{max}} = 312$ nm light for 6 h at $-40$ °C in an NMR tube, which was subsequently inserted into the NMR probe (precooled to $-30$ °C). The PSS ratios were obtained by integration of the signals corresponding to the methyl group at the stereogenic centre.

**Figure S21.** Aliphatic region of the $^1$H NMR spectra before (top) and after (bottom) irradiation measured at $-30$ °C. a) 2. b) 2 + NH$_4$PF$_6$. c) 2 + KPF$_6$. d) 2 + NaPF$_6$. e) 2 + Ca(OTf)$_2$. 
8. Eyring plots

**Figure S22.** Eyring plot of the THI of 2. A solution of 2 in degassed CH$_3$CN (3·10$^{-4}$ M) in a 1 mm cuvette was irradiated to PSS with 312 nm light. The rate of the thermal relaxation was followed by monitoring the absorbance at 330 nm at 5 different temperatures (5, 10, 15, 20, 25 ºC).

\[
\Delta^\ddagger G (20 \, ^\circ C) = 89.0 \, \text{kJ} \cdot \text{mol}^{-1}
\]
\[
\Delta^\ddagger H^\circ = 74.1 \, \text{kJ} \cdot \text{mol}^{-1}
\]
\[
\Delta^\ddagger S^\circ = -51.1 \, \text{kJ} \cdot \text{mol}^{-1}
\]

**Figure S23.** Eyring plot of the THI of 2-$\text{NH}_4$. A solution of 2 in degassed CH$_3$CN (3·10$^{-4}$ M) + 50 equiv NH$_4$PF$_6$ in a 1 mm cuvette was irradiated to PSS with 312 nm light. The rate of the thermal relaxation was followed by monitoring the absorbance at 330 nm at 5 different temperatures (5, 10, 15, 20, 25 ºC).

\[
\Delta^\ddagger G (20 \, ^\circ C) = 88.8 \, \text{kJ} \cdot \text{mol}^{-1}
\]
\[
\Delta^\ddagger H^\circ = 67.8 \, \text{kJ} \cdot \text{mol}^{-1}
\]
\[
\Delta^\ddagger S^\circ = -71.7 \, \text{kJ} \cdot \text{mol}^{-1}
\]
Figure S24. Eyring plot of the THI of 2-K. A solution of 2 in degassed CH$_3$CN (3·10$^{-4}$ M) + 50 equiv KPF$_6$ in a 1 mm cuvette was irradiated to PSS with 312 nm light. The rate of the thermal relaxation was followed by monitoring the absorbance at 330 nm at 5 different temperatures (5, 10, 15, 20, 25 °C).

\[
\Delta^\ddagger G (20 ^\circ C) = 87.6 \text{ kJ mol}^{-1} \\
\Delta^\ddagger H^\circ = 73.2 \text{ kJ mol}^{-1} \\
\Delta^\ddagger S^\circ = -62.9 \text{ kJ mol}^{-1}
\]

Figure S25. Eyring plot of the THI of 2-Na. A solution of 2 in degassed CH$_3$CN (3·10$^{-4}$ M) + 50 equiv NaPF$_6$ in a 1 mm cuvette was irradiated to PSS with 312 nm light. The rate of the thermal relaxation was followed by monitoring the absorbance at 330 nm at 5 different temperatures (5, 10, 15, 20, 25 °C).

\[
\Delta^\ddagger G (20 ^\circ C) = 88.0 \text{ kJ mol}^{-1} \\
\Delta^\ddagger H^\circ = 69.6 \text{ kJ mol}^{-1} \\
\Delta^\ddagger S^\circ = -49.2 \text{ kJ mol}^{-1}
\]
Figure S26. Eyring plot of the THI of 2-Ca. A solution of 2 in degassed CH₂CN (3·10⁻⁴ M) + 50 equiv Ca(OTf)₂ in a 1 mm cuvette was irradiated to PSS with 312 nm light. The rate of the thermal relaxation was followed by monitoring the absorbance at 330 nm at 5 different temperatures (5, 10, 15, 20, 25 ºC).

Δ‡G (20 ºC) = 87.4 kJ·mol⁻¹
Δ‡H° = 72.6 kJ·mol⁻¹
Δ‡S° = -50.8 kJ·mol⁻¹

Figure S27. Eyring plot of the THI of 2 after cation decomplexation. A solution of 2 in degassed CH₂CN (3·10⁻⁴ M) + Ca(OTf)₂ (20 equiv) + crypt-222 (50 equiv) in a 1 mm cuvette was irradiated to PSS with 312 nm light. The rate of the thermal relaxation was followed by monitoring the absorbance at 330 nm at 5 different temperatures (5, 10, 15, 20, 25 ºC).

Δ‡G (20 ºC) = 89.1 kJ·mol⁻¹
Δ‡H° = 83.7 kJ·mol⁻¹
Δ‡S° = -13.4 kJ·mol⁻¹
9. Reversible coordination of Ca(OTf)$_2$ to 2

![NMR spectra](image)

**Figure S28.** a) $^1$H NMR spectrum of 2 (1.5·10$^{-3}$ M solution in CD$_3$CN); b) $^1$H NMR spectrum after the addition of 20 equiv Ca(OTf)$_2$ to the solution in a); c) $^1$H NMR spectrum after the addition of 50 equiv crypt-222 to the solution in b).