

Supporting Information for

Molecular-Pump-Enabled Synthesis of a Daisy Chain Polymer

Kang Cai,^{†#} Yi Shi,^{†#} Guo-Wei Zhuang,[&] Long Zhang,[†] Yunyan Qiu,[†] Dengke Shen,[†] Hongliang Chen,[†] Yang Jiao,[†] Huang Wu,[†] Chuyang Cheng,[‡] J. Fraser Stoddart^{†‡§*}

[†]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States*

[&]*Department of Chemistry, Fudan University, Shanghai 200433, China*

[‡]*Department of Chemistry, Sichuan University, Chengdu, China*

[‡]*Institute for Molecular Design and Synthesis, Tianjin University, 92 Weijin Road, Tianjin 300072, China*

[§]*School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia*

*E-mail: stoddart@northwestern.edu

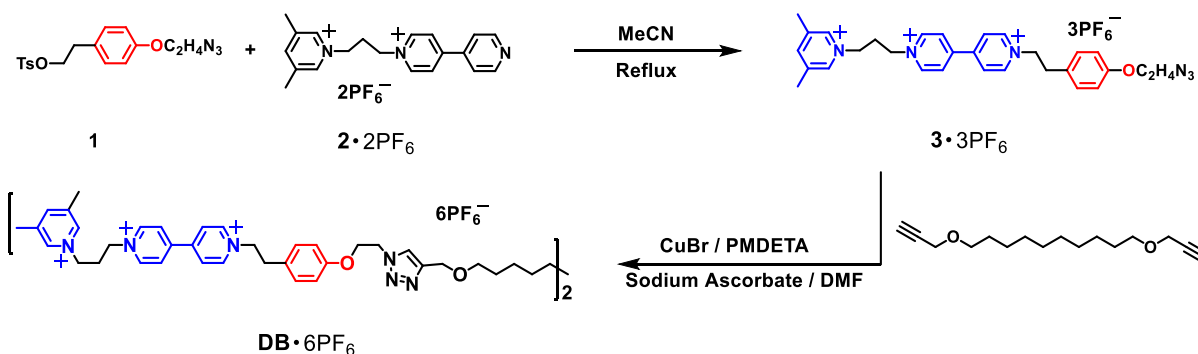
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Section A. General Methods

All reagents were purchased from commercial suppliers and used without further purification. Compounds **2**•2PF₆^{S1}, **CBPQT**•4PF₆^{S2}, **CBPQT-CC**•4PF₆^{S3}, 1,10-bis(prop-2-yn-1-yloxy)decane^{S4} were prepared according to literature procedures. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (E Merck). Reverse-phase column chromatography (RediSep Rf Gold® Reversed-Phase C18), was carried out using CombiFlash® Automation Systems (Teledyne ISCO). UV/Vis Spectra were recorded at room temperature on a Shimadzu UV-3600 spectrophotometer. Nuclear magnetic resonance (NMR) spectra are recorded on Agilent DD2 500 spectrometers, with working frequencies of 500 MHz for ¹H and 125 MHz for ¹³C nuclei, respectively. Variable temperature ¹H NMR and diffusion ordered NMR spectra were recorded using an Agilent DD2 spectrometer with a 600 MHz working frequency for ¹H nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CD₃CN: δ_H = 1.94 ppm and δ_C = 118.26 ppm for ¹³CN). High-resolution mass spectra (HR-ESI) were measured on a Finnigan LCQ iontrap mass spectrometer.

Section B. Synthetic Protocols

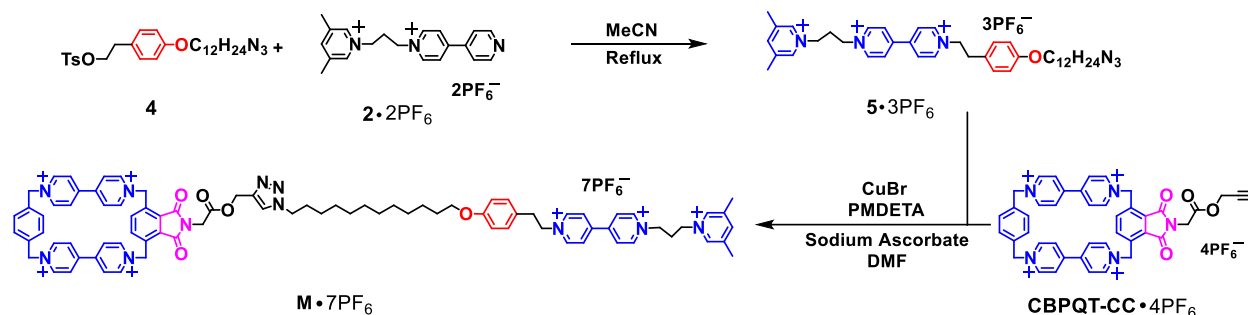


3•3PF₆: Compound **1** (180 mg, 0.50 mmol) and **2**•2PF₆^{S1} (446 mg, 0.75 mmol) were dissolved in MeCN (10 mL) in a 50-mL round-bottomed flask and stirred under reflux for 48 h. After the solvents were removed *in vacuo*, the crude product was purified using reverse-phase flash chromatography (C₁₈: H₂O/MeCN 0.1% TFA 0-100%), followed using anion exchange from TFA⁻ to PF₆⁻ by treating the aqueous fractions with an excess of NH₄PF₆, resulting in a white precipitate

which was collected by centrifugation and washed with H₂O several times before being dried *in vacuo* to afford **3**•3PF₆ as an off-white solid (327 mg, 71%). ¹H NMR (500 MHz, CD₃CN, 298 K): δ 8.92 (d, *J* = 8 Hz, 2H), 8.75 (d, *J* = 8 Hz, 2H), 8.43 (d, *J* = 8 Hz, 2H), 8.40 (s, 2H), 8.34 (d, *J* = 8 Hz, 2H), 8.23 (s, 1H), 7.12 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 8 Hz, 2H), 4.86 (t, *J* = 7 Hz, 2H), 4.72 (t, *J* = 8 Hz, 2H), 4.58 (t, *J* = 8 Hz, 2H), 4.16 (t, *J* = 5 Hz, 2H), 3.62 (t, *J* = 5 Hz, 2H), 3.31 (t, *J* = 7 Hz, 2H), 2.67 (quint, *J* = 8 Hz, 2H), 2.53 (s, 6H). ¹³C NMR (125 MHz, CD₃CN, 298 K): δ 158.8, 148.2, 146.7, 146.5, 142.4, 140.4, 131.1, 128.8, 128.4, 127.9, 116.0, 68.0, 64.2, 59.2, 58.6, 51.0, 36.9, 32.6, 18.3. ESI-HRMS for **3**•3PF₆; Calcd for C₃₀H₃₅F₁₈N₆OP₃: *m/z* = 785.2150 [*M* – PF₆]⁺; found: 785.2158.

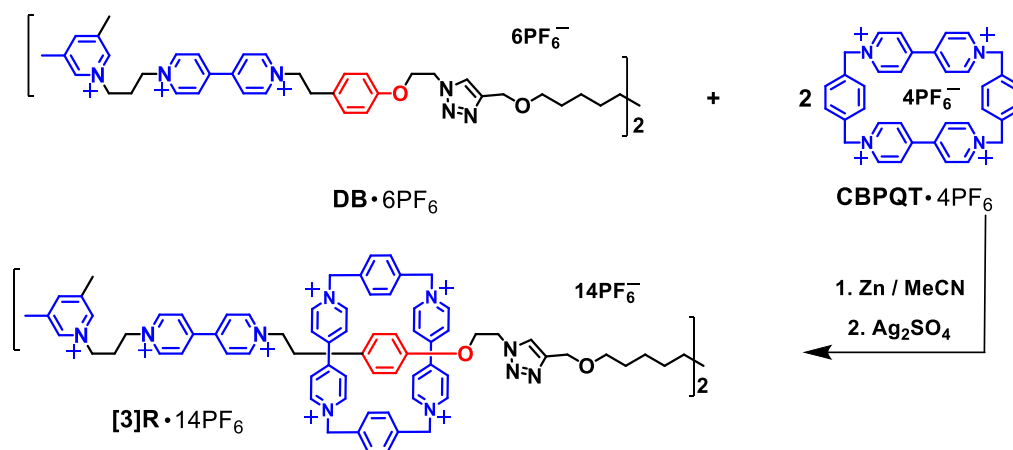
DB•6PF₆: **3**•3PF₆ (200 mg, 0.21 mmol), 1,10-bis(prop-2-yn-1-yloxy)decane^{S4} (25 mg, 0.60 mmol), Cu(MeCN)₄PF₆ (7.5 mg, 0.020 mmol), sodium ascorbate (4.0 mg, 0.020 mmol), and *N,N,N',N'',N'''*-pentamethyldiethyl-enetriamine (PMDETA) (3.5 mg, 0.020 mmol) were dissolved in DMF (6 mL) in a 20-mL vial. The solution was stirred at room temp under a N₂ atmosphere for 24 h. Excess of TBACl was added to the solution and the solids were collected by filtration. The crude product was purified by reverse-phase flash chromatography (C₁₈: H₂O/MeCN 0.1% TFA 0-100%), followed by anion exchange from TFA[–] to PF₆[–] by treating the aqueous fractions with an excess of NH₄PF₆, resulting in a white precipitate which was collected by centrifugation and washed with H₂O several times before being dried *in vacuo* to afford **DB**•6PF₆ as an off-white solid (176 mg, 82%). ¹H NMR (500 MHz, CD₃CN, 298 K): δ 8.93 (d, *J* = 8 Hz, 4H), 8.75 (d, *J* = 8 Hz, 4H), 8.45 (d, *J* = 8 Hz, 4H), 8.40 (s, 4H), 8.34 (d, *J* = 8 Hz, 4H), 8.23 (s, 2H), 7.85 (s, 2H), 7.10 (d, *J* = 8 Hz, 4H), 6.86 (d, *J* = 8 Hz, 4H), 4.85 (t, *J* = 8 Hz, 4H), 4.75-4.72 (m, 4H), 4.58 (t, *J* = 8 Hz, 4H), 4.53 (s, 4H), 4.39 (t, *J* = 5 Hz, 4H), 3.48 (t, *J* = 5 Hz, 4H), 3.28 (t, *J* = 7 Hz, 4H),

2.70 (quint, $J = 8$ Hz, 4H), 2.53 (s, 12H), 1.56-1.53 (m, 4H), 1.30-1.28 (m, 12H). ^{13}C NMR (125 MHz, CD_3CN , 298 K) δ 158.5, 151.3, 150.7, 148.2, 146.7, 146.5, 145.8, 142.4, 140.4, 131.1, 129.0, 128.4, 128.0, 127.9, 124.9, 124.8, 116.0, 71.0, 67.4, 64.5, 64.4, 64.1, 59.2, 58.6, 50.3, 36.8, 33.5, 32.6, 30.3, 30.2, 30.2, 30.2, 30.1, 30.0, 26.8, 26.6, 24.2, 20.2, 18.3, 13.7. ESI-HRMS for **DB**•6PF₆; Calcd for $\text{C}_{76}\text{H}_{96}\text{F}_{36}\text{N}_{12}\text{O}_4\text{P}_6$: $m/z = 910.3117$ [$M - 2\text{PF}_6$]²⁺; found: 910.3130.



5•3PF₆: Compound **4** (250 mg, 0.50 mmol) and 2•2PF₆^{S1} (446 mg, 0.75 mmol) were dissolved in MeCN (10 mL) in a 50-mL round-bottomed flask and stirred under reflux for 48 h. After the solvents were removed *in vacuo*, the crude product was purified using reverse-phase flash chromatography (C₁₈: H₂O/MeCN 0.1% TFA 0-100%), followed by anion exchange from TFA⁻ to PF₆⁻ by treating the aqueous fractions with an excess of NH₄PF₆, resulting in a white precipitate which was collected by centrifugation and washed with H₂O several times before being dried *in vacuo* to afford **5•3PF₆** as an off-white solid (385 mg, 71.9%). ^1H NMR (500 MHz, CD_3CN , 298 K): δ 8.92 (d, $J = 8$ Hz, 2H), 8.75 (d, $J = 8$ Hz, 2H), 8.44 (d, $J = 8$ Hz, 2H), 8.40 (s, 2H), 8.34 (d, $J = 8$ Hz, 2H), 8.23 (s, 1H), 7.10 (d, $J = 8$ Hz, 2H), 6.88 (d, $J = 8$ Hz, 2H), 4.85 (t, $J = 7$ Hz, 2H), 4.73 (t, $J = 8$ Hz, 2H), 4.58 (t, $J = 8$ Hz, 2H), 3.96 (t, $J = 5$ Hz, 2H), 3.32-3.28 (m, 4H), 2.69 (quint, $J = 8$ Hz, 2H), 2.53 (s, 6H), 1.75 (quint, $J = 8$ Hz, 2H), 1.62-1.58 (m, 2H), 1.37-0.98 (m, 16H). ^{13}C NMR (125 MHz, CD_3CN , 298 K): δ 159.6, 151.4, 150.7, 148.2, 146.7, 146.5, 142.4, 140.4, 131.0, 128.4, 127.9, 127.9, 118.2, 115.8, 68.8, 64.2, 59.2, 58.6, 52.1, 36.9, 32.5, 30.19, 30.18, 30.15, 30.11, 30.0, 29.9, 29.7, 29.4, 27.3, 26.6, 24.2, 20.2, 18.3, 13.7. ESI-HRMS for **5•3PF₆**; Calcd for $\text{C}_{40}\text{H}_{55}\text{F}_{18}\text{N}_6\text{OP}_3$: $m/z = 925.3715$ [$M - \text{PF}_6$]⁺; found: 925.3729.

M•7PF₆: **5•3PF₆** (106 mg, 0.10 mmol), **CBPQT-CC•4PF₆^{S4}** (127 mg, 0.10 mmol), Cu(MeCN)₄PF₆ (3.8 mg, 0.010 mmol), sodium ascorbate (2.0 mg, 0.010 mmol), and PMDETA (1.8 mg, 0.010 mmol) were dissolved in DMF (5 mL) in a 20-mL vial. The solution was stirred at room temp under N₂ atmosphere for 24 h. Excess of TBACl was added to the solution, and then the solids were collected by filtration. The crude product was purified by reverse-phase flash chromatography (C₁₈: H₂O/MeCN 0.1% TFA 0-100%), followed by anion exchange from TFA⁻ to PF₆⁻ by treating the aqueous fractions with an excess of NH₄PF₆, resulting in a white precipitate which was collected by centrifugation and washed with H₂O several times before being dried *in vacuo* to afford **M•7PF₆** as an off-white solid (189 mg, 81.2%). ¹H NMR (500 MHz, CD₃CN, 298 K): δ 8.94 (d, *J* = 7 Hz, 2H), 8.89 (d, *J* = 7 Hz, 8H), 8.79 (d, *J* = 8 Hz, 2H), 8.44 (d, *J* = 6 Hz, 2H), 8.41 (s, 2H), 8.36 (d, *J* = 8 Hz, 4H), 8.23 (s, 2H), 8.20 (d, *J* = 6 Hz, 4H), 8.14 (d, *J* = 7 Hz, 4H), 8.10 (s, 2H), 7.87 (s, 1H), 7.51 (s, 4H), 7.12 (d, *J* = 9 Hz, 4H), 6.89 (d, *J* = 9 Hz, 4H), 6.21 (s, 4H), 5.77 (s, 4H), 5.28 (s, 2H), 4.84 (t, *J* = 8 Hz, 2H), 4.73 (t, *J* = 8 Hz, 2H), 4.58 (t, *J* = 8 Hz, 2H), 4.29 (t, *J* = 8 Hz, 2H), 4.32 (s, 2H), 3.96 (t, *J* = 7 Hz, 2H), 3.29 (t, *J* = 7 Hz, 2H), 2.69 (quint, *J* = 8 Hz, 2H), 2.53 (s, 6H), 1.91 (quint, *J* = 8 Hz, 2H), 1.76 (quint, *J* = 8 Hz, 2H), 1.46 (quint, *J* = 8 Hz, 2H), 1.35-1.32 (m, 14H), . ¹³C NMR (125 MHz, CD₃CN, 298 K) δ 167.9, 167.6, 159.6, 151.4, 150.7, 148.2, 146.9, 146.7, 146.5, 146.0, 142.5, 142.4, 140.4, 138.6, 136.9, 134.3, 131.5, 131.04, 130.99, 128.4, 128.4, 128.01, 127.96, 127.9, 125.4, 118.2, 118.0, 115.8, 68.9, 65.5, 64.1, 60.2, 59.6, 59.2, 58.6, 50.9, 40.0, 36.9, 32.6, 30.9, 30.3, 30.3, 30.2, 30.1, 30.0, 29.7, 27.1, 26.7, 18.3. ESI-HRMS for **M•7PF₆**; Calcd for C₈₃H₉₀F₄₂N₁₁O₅P₇: *m/z* = 1022.7662 [*M* - 2PF₆]²⁺; found: 1022.7672.



[3]R•14PF₆: **DB•6PF₆** (11 mg, 0.10 mmol) and **CBPQT•4PF₆**^{S2} (33 mg, 0.30 mmol) were dissolved in MeCN (0.40 mL) in a N₂-filled glovebox. Excess of Zn dust was added to the solution, and the resulting mixture were stirred at room temp for 10 min. After removing the Zn dust by filtration, excess of Ag₂SO₄ was added to the deep purple solution under stirring to produce a yellow colored solution. Excess of TBACl was added to the solution, and then the solids were collected by filtration. The crude product was purified by reverse-phase flash chromatography (C₁₈: H₂O/MeCN 0.1% TFA 0-100%), followed by anion exchange from TFA⁻ to PF₆⁻ by treating the aqueous fractions with an excess of NH₄PF₆, resulting in a white precipitate which was collected by centrifugation and washed with H₂O several times before being dried *in vacuo* to afford **[3]R•14PF₆** as an light yellow solid (16 mg, 74%). ¹H NMR (500 MHz, CD₃CN, 298 K): δ 9.22 (d, *J* = 7 Hz, 2H), 9.10 (d, *J* = 7 Hz, 2H), 8.96 (d, *J* = 7 Hz, 8H), 8.66 (d, *J* = 7 Hz, 2H), 8.60 (d, *J* = 7 Hz, 2H), 8.43 (s, 2H), 8.25 (s, 1H), 8.12 (s, 1H), 7.90 (d, *J* = 7 Hz, 2H), 7.87 (s, 8H), 5.84-5.77 (m, 8H), 5.07 (d, *J* = 8 Hz, 2H), 4.83 (s, 2H), 4.74 (t, *J* = 5 Hz, 2H), 4.67-4.60 (m, 4H), 4.75 (t, *J* = 7 Hz, 2H), 3.36 (t, *J* = 5 Hz, 2H), 2.95-2.91 (m, 2H), 2.77-2.72 (m, 2H), 2.71 (d, *J* = 8 Hz, 2H), 2.55 (s, 6H), 1.69 (quint, *J* = 8 Hz, 2H), 1.37-1.30 (m, 6H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ 154.9, 151.1, 151.0, 147.9, 147.6, 146.4, 146.2, 145.9, 145.7, 145.5, 142.1, 140.1, 137.7, 131.3, 130.1, 128.3, 128.0, 127.9, 127.9, 127.2, 127.0, 125.7, 112.5, 71.9, 65.8, 65.5, 64.2, 62.2, 50.0, 58.3, 49.7, 35.0, 32.2, 30.1, 30.0, 26.5, 18.0. ESI-HRMS for **[3]R•14PF₆**; Calcd for C₁₄₈H₁₆₀F₈₄N₂₀O₄P₁₄: *m/z* = 1291.9658 [*M* - 3PF₆]³⁺; found: 1291.9674.

Section C. NMR Spectroscopy

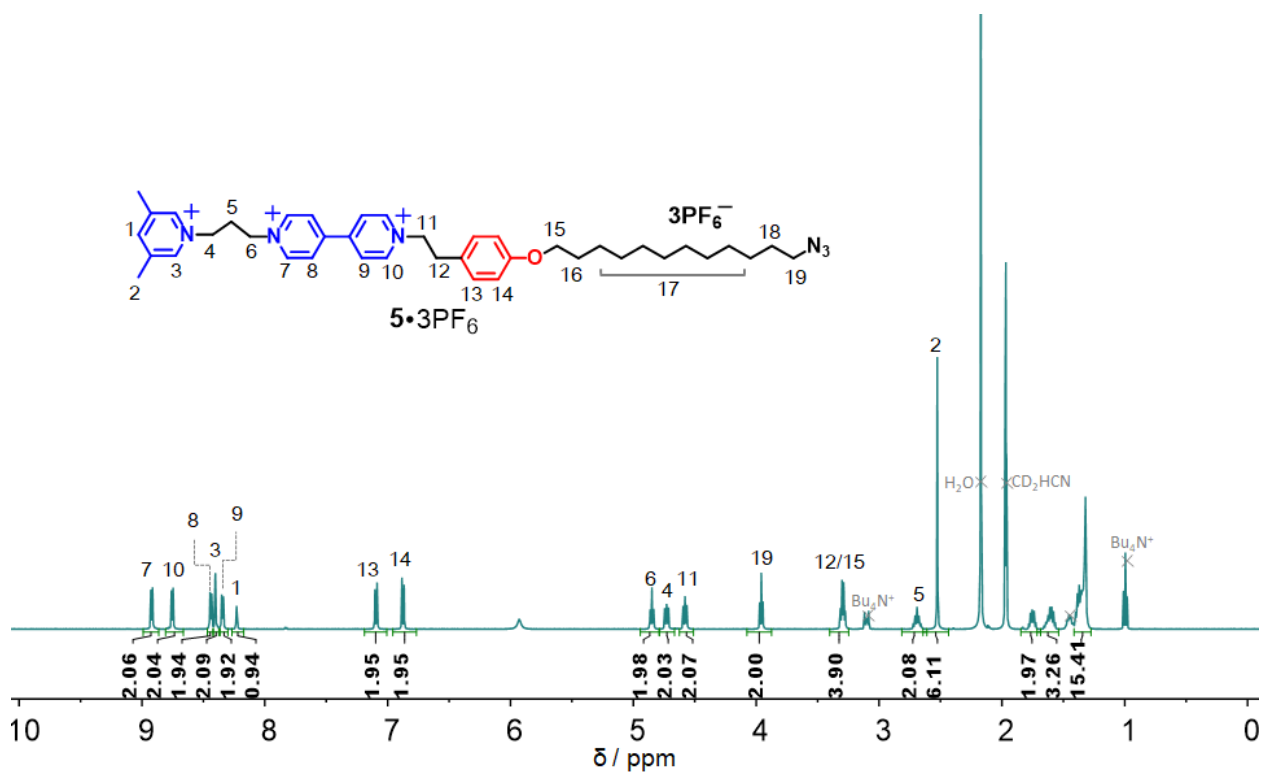


Figure S1. ^1H NMR Spectrum (500 MHz / CD_3CN / 298 K) of **5•3PF₆**

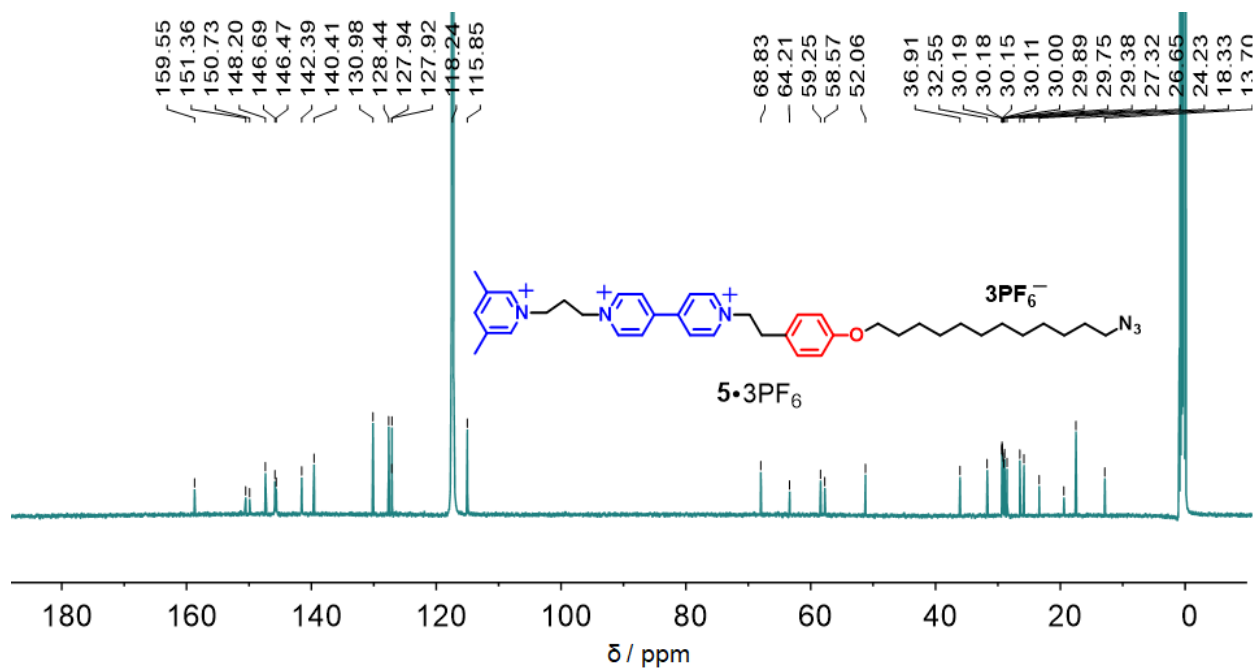


Figure S2. ^{13}C NMR Spectrum (125 MHz / CD_3CN / 298 K) of **5•3PF₆**

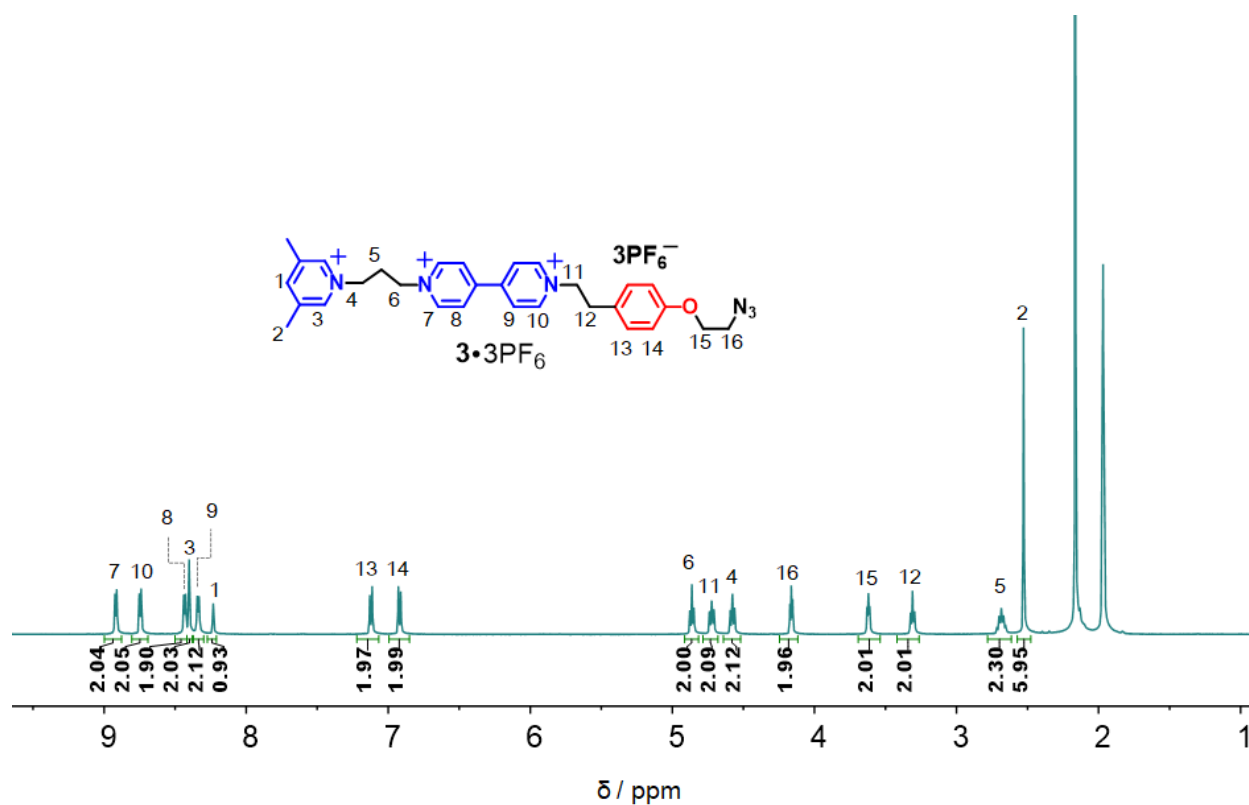


Figure S3. ^1H NMR Spectrum (500 MHz / CD_3CN / 298 K) of $3\cdot 3\text{PF}_6$

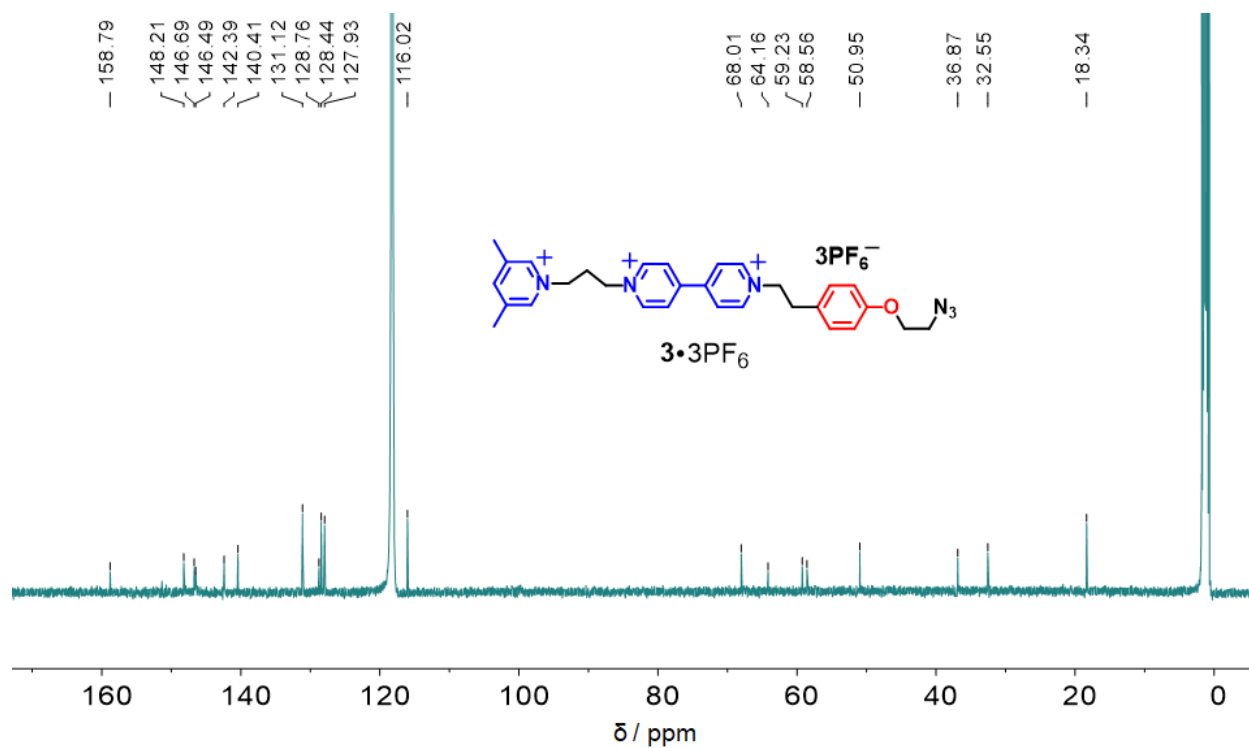


Figure S4. ^{13}C NMR Spectrum (125 MHz / CD_3CN / 298 K) of $3\cdot 3\text{PF}_6$

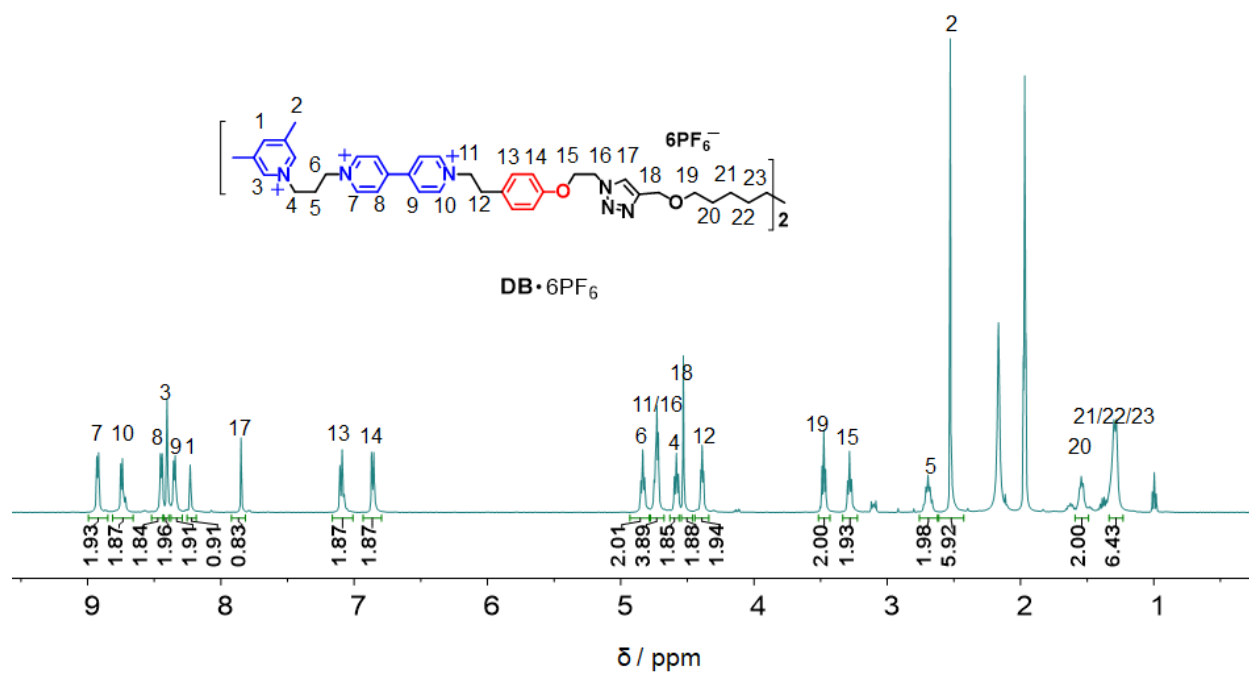


Figure S5. ¹H NMR Spectrum (500 MHz / CD₃CN / 298 K) of **DB•6PF₆**

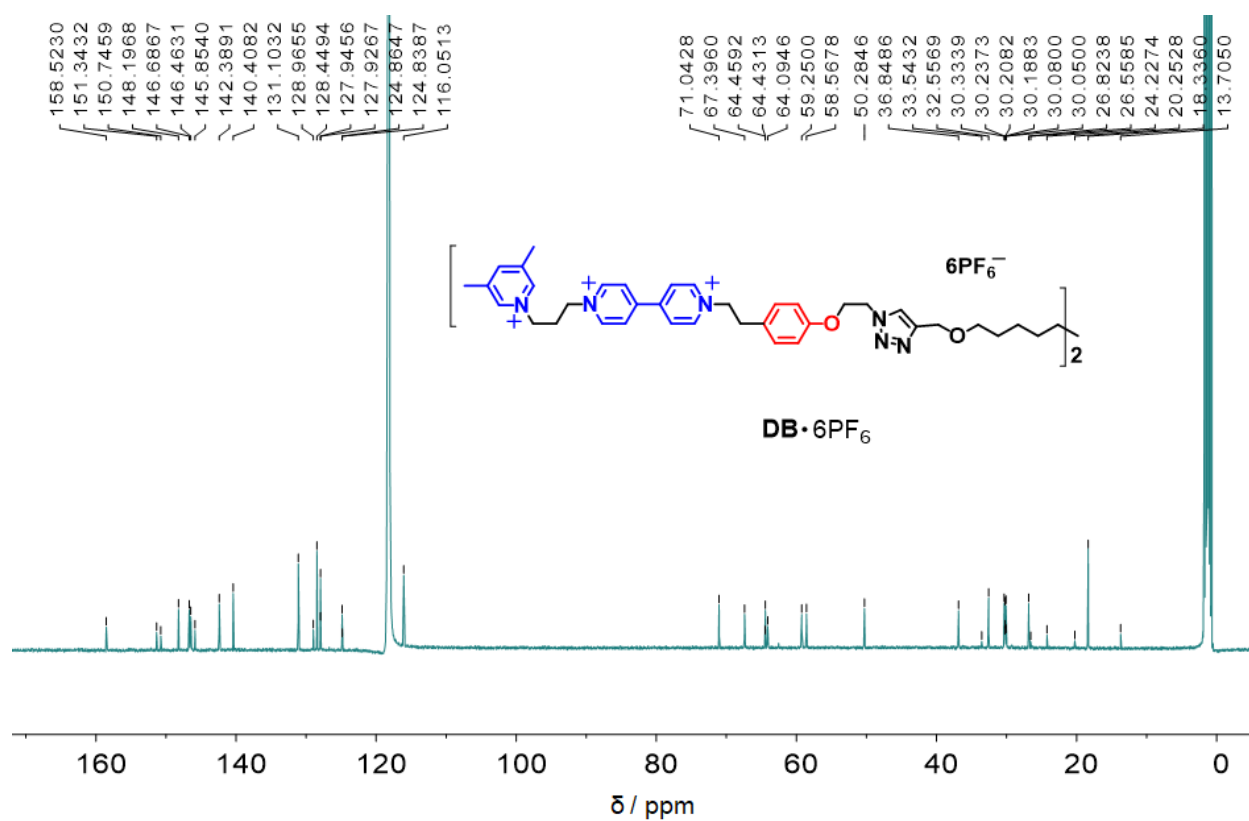


Figure S6. ¹³C NMR Spectrum (125 MHz / CD₃CN / 298 K) of **DB•6PF₆**

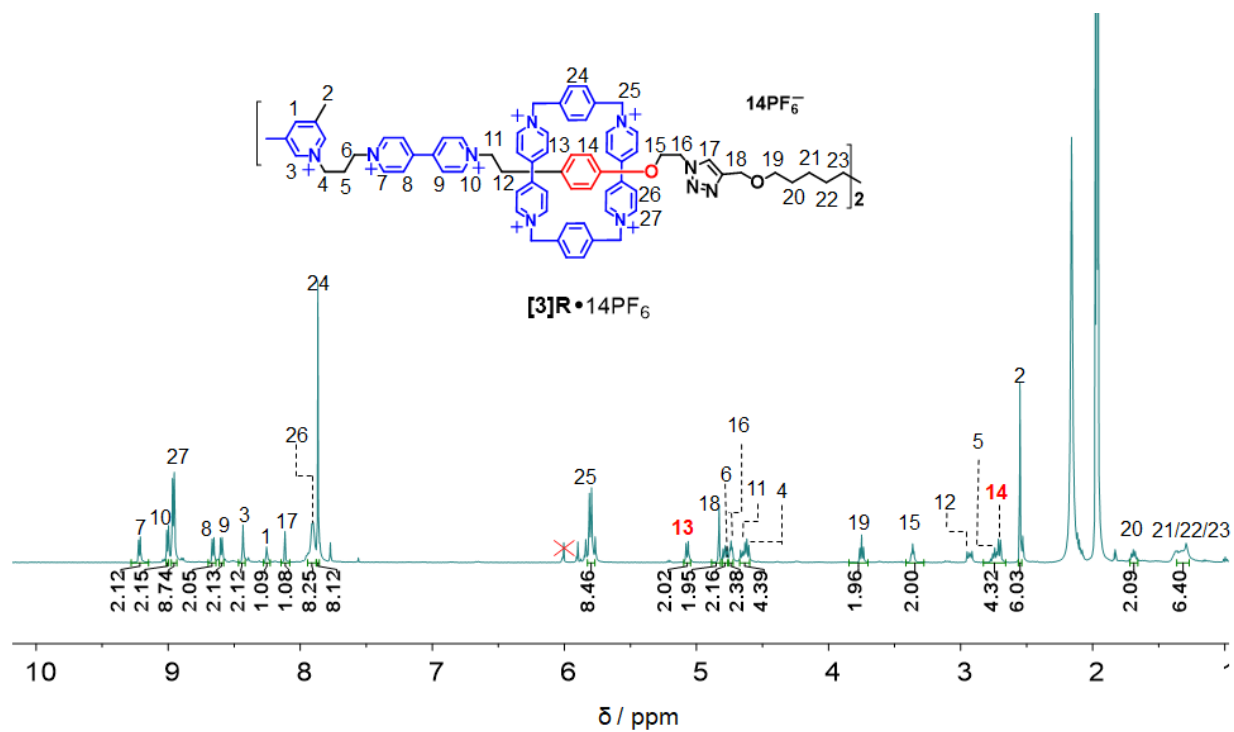


Figure S7. 1H NMR Spectrum (500 MHz / CD_3CN / 298 K) of $[3]R \cdot 14PF_6$

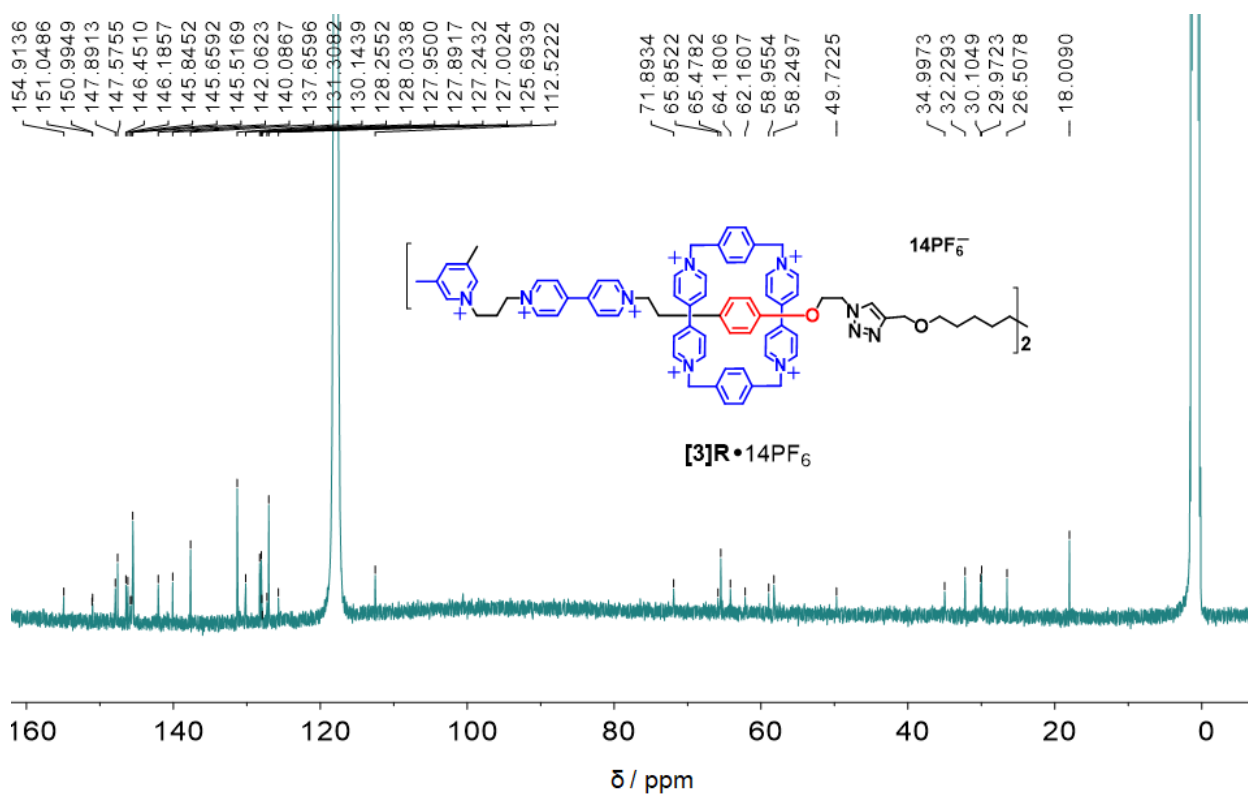


Figure S8. ^{13}C NMR Spectrum (125 MHz / CD_3CN / 298 K) of $[3]R \cdot 14PF_6$

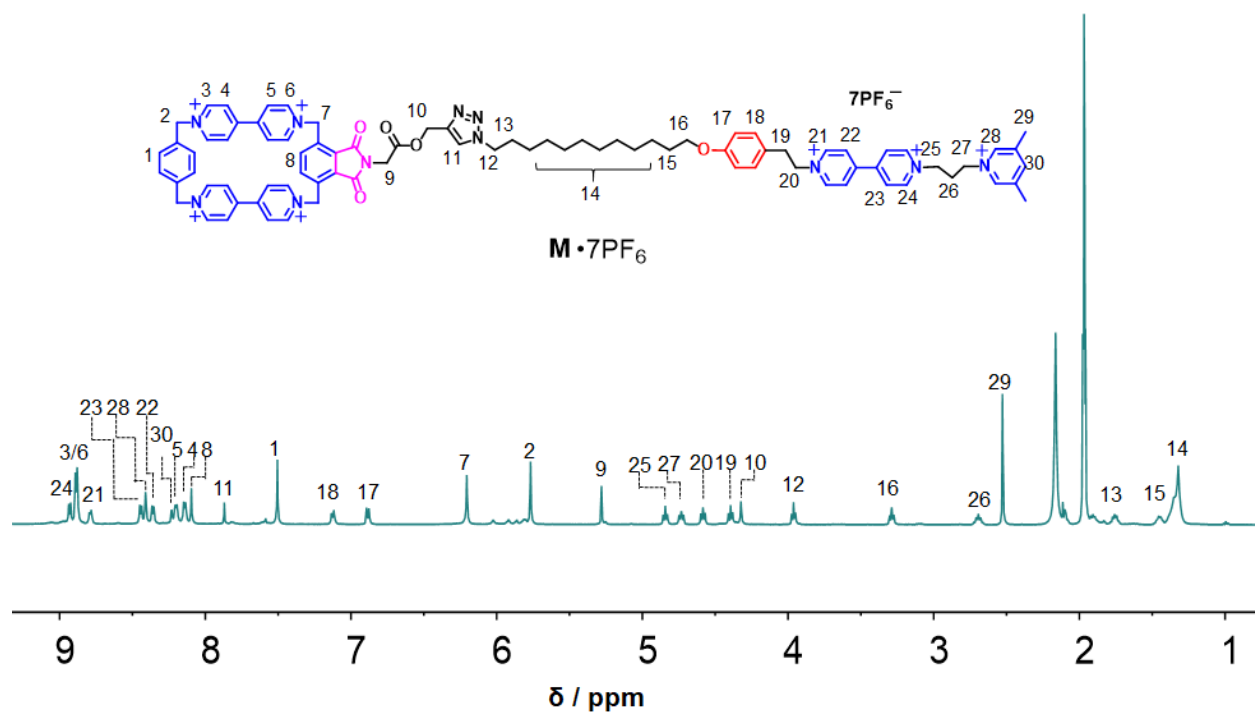


Figure S9. ^1H NMR Spectrum (500 MHz / CD_3CN / 298 K) of $\mathbf{M} \cdot 7\text{PF}_6$

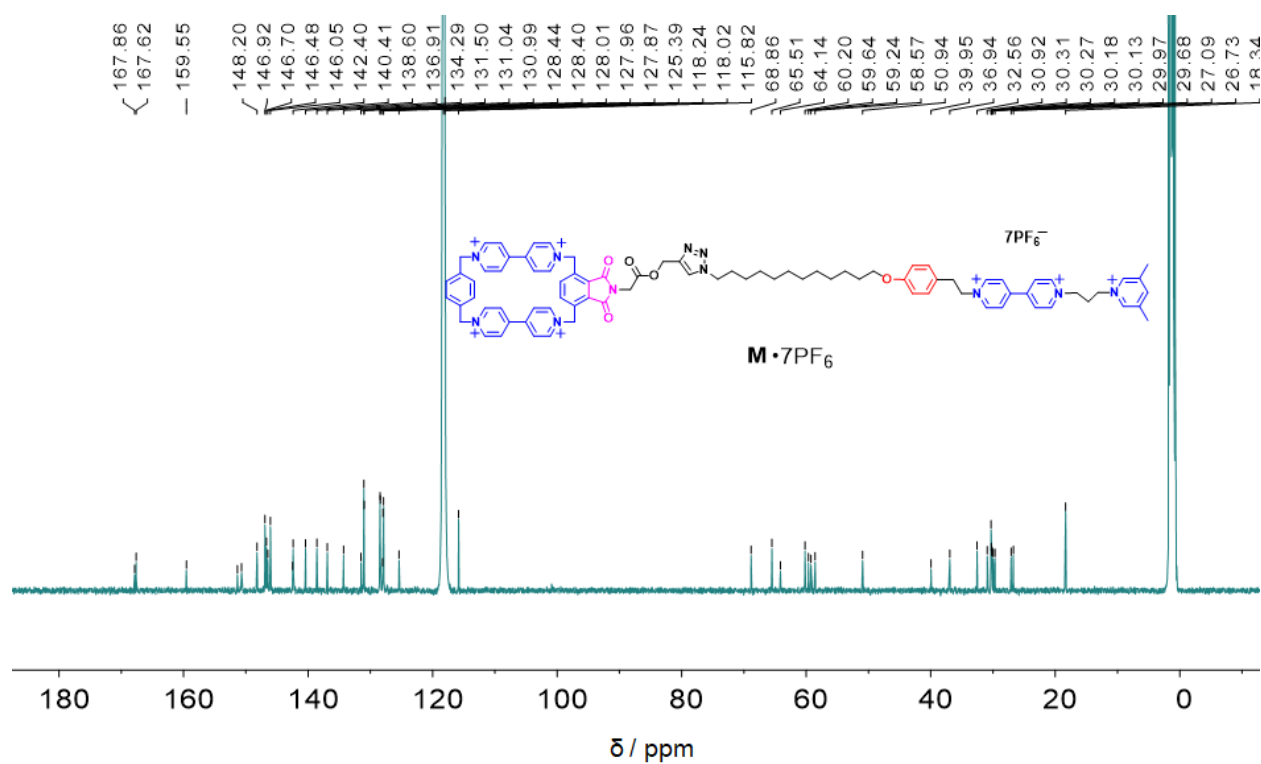


Figure S10. ^{13}C NMR Spectrum (125 MHz / CD_3CN / 298 K) of $\mathbf{M} \cdot 7\text{PF}_6$

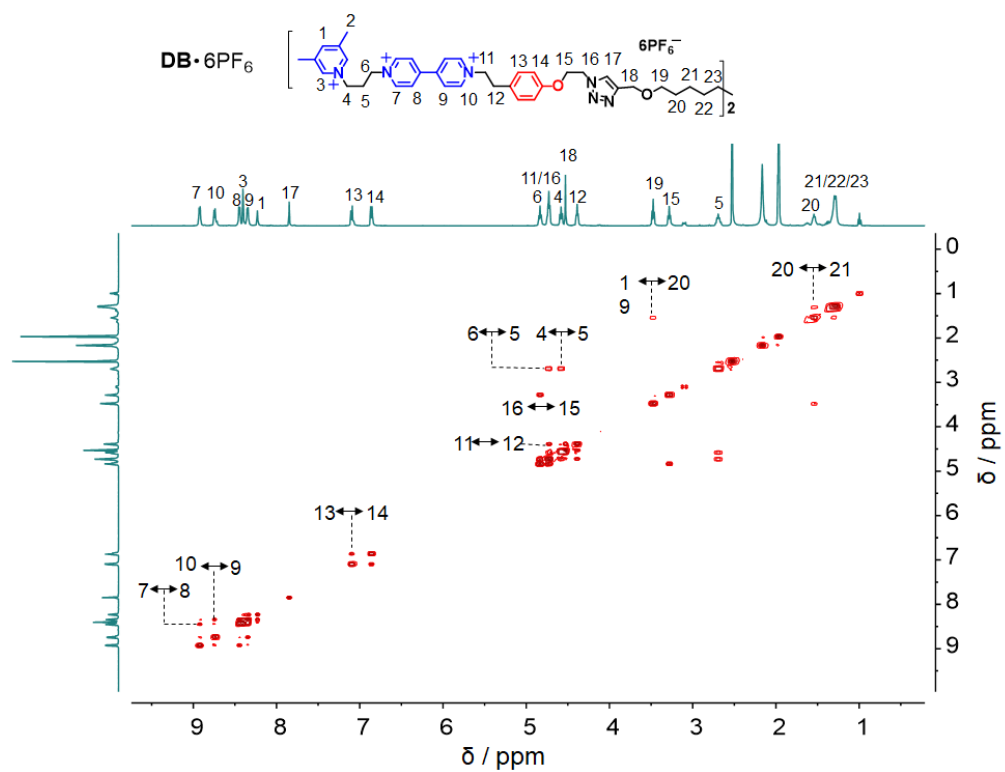


Figure S11. ^1H - ^1H COSY NMR Spectrum (500 MHz / CD_3CN / 298 K) of **DB•6PF₆**

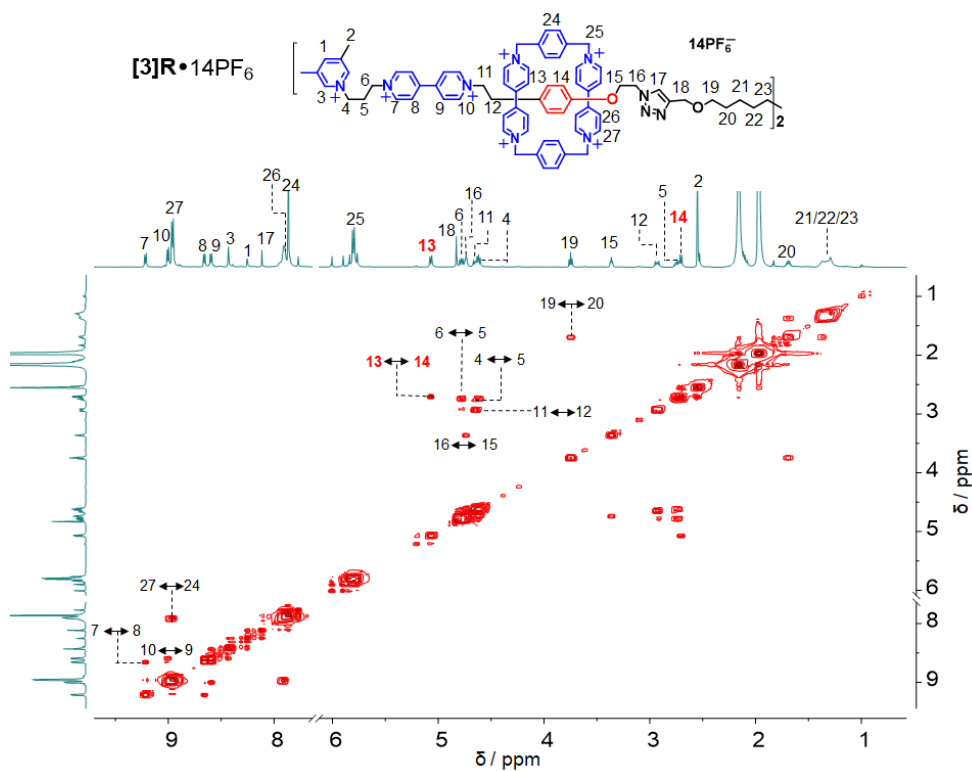


Figure S12. ^1H - ^1H COSY NMR Spectrum (500 MHz / CD_3CN / 298 K) of **[3]R•14PF₆**

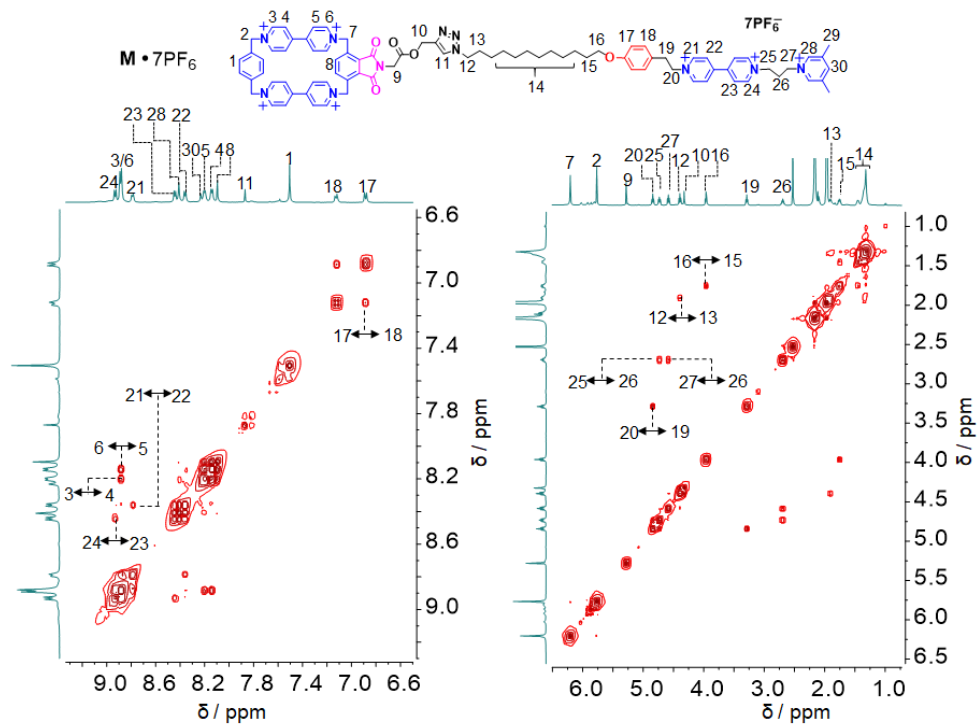


Figure S13. ^1H - ^1H COSY NMR Spectrum (500 MHz / CD_3CN / 298 K) of **M**• 7PF_6

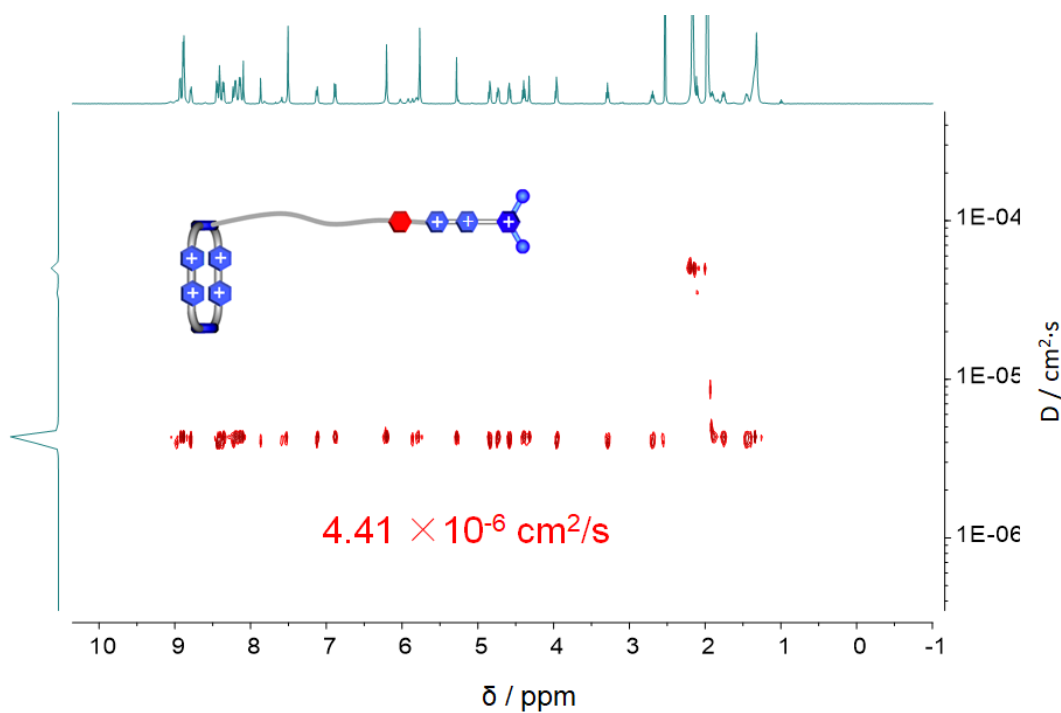


Figure S14. Diffusion ordered NMR Spectrum (600 MHz / CD_3CN / 298 K) of **M**• 7PF_6

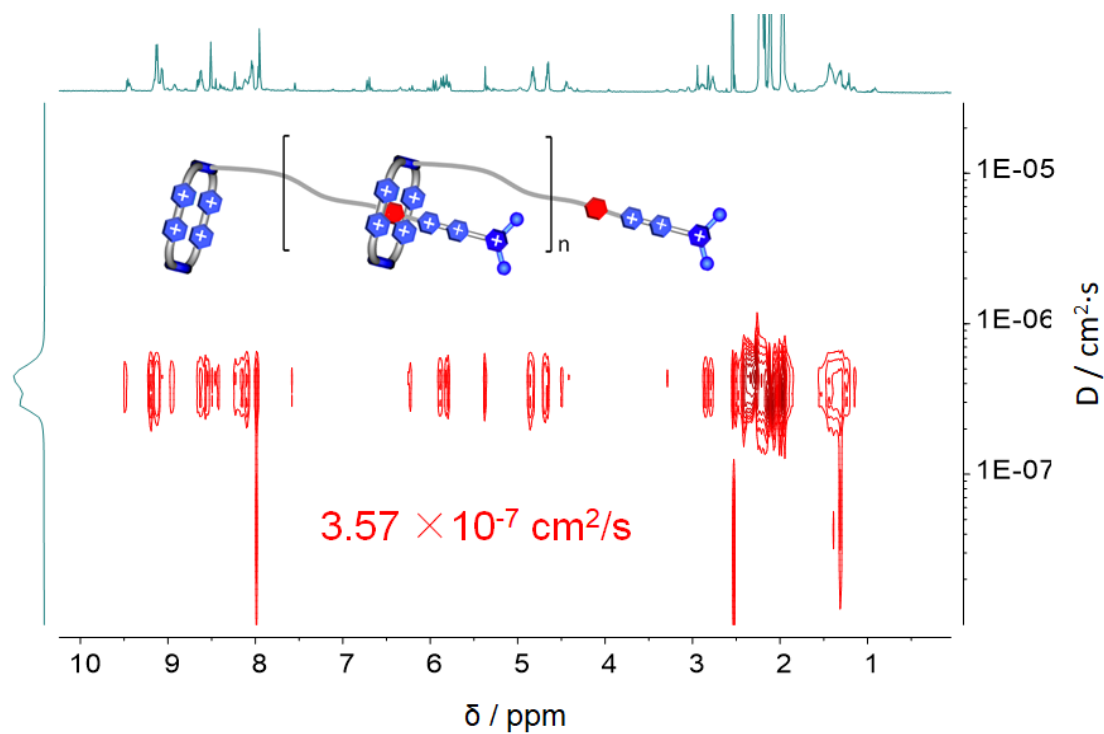


Figure S15. Diffusion ordered NMR Spectrum (600 MHz / CD_3CN / 298 K) of the daisy chain polymer

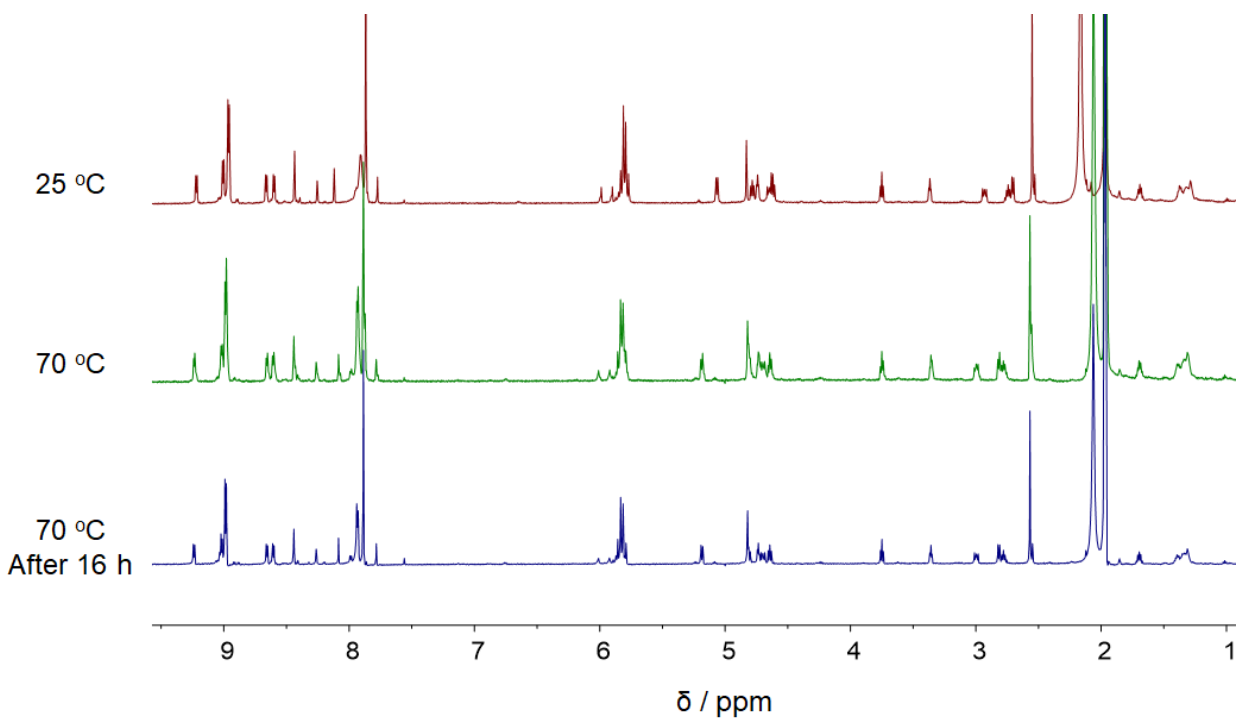


Figure S16. ^1H NMR Spectra (600 MHz / CD_3CN / 298 K) of $[3]\text{R} \cdot 14\text{PF}_6$ at 25 °C (top), 70 °C (middle), and after heating for 16 h at 70 °C (bottom)

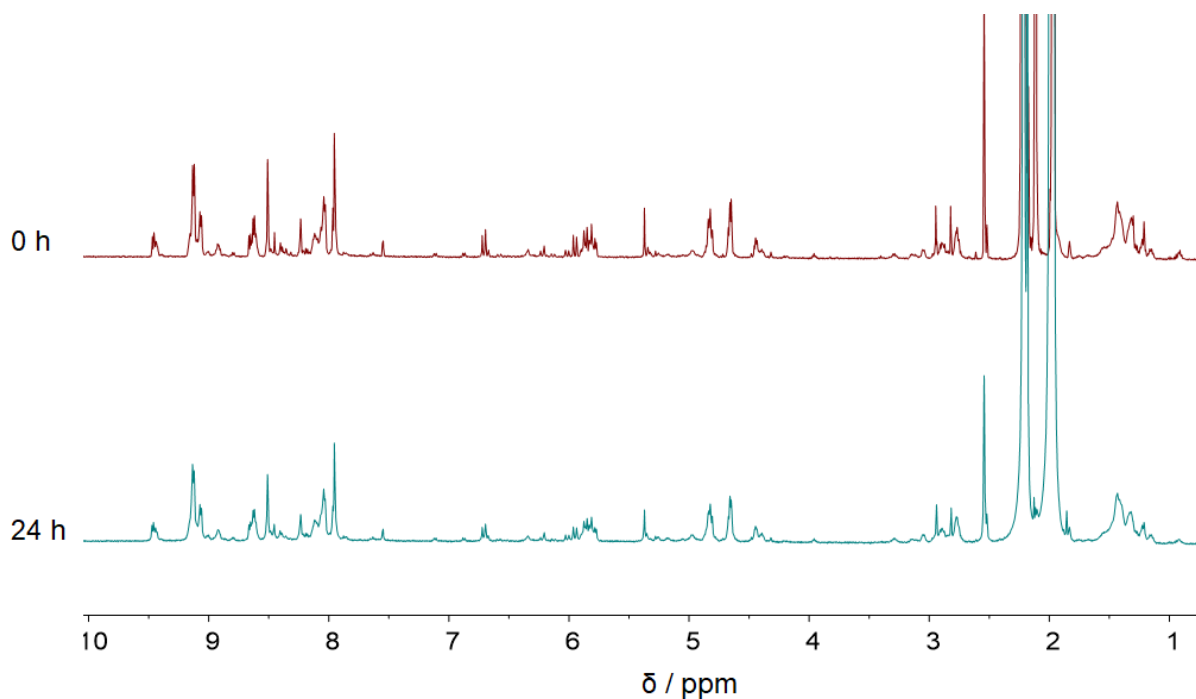


Figure S17. ^1H NMR Spectra (600 MHz / CD_3CN / 298 K) of the daisy chain polymer heating at 70 $^\circ\text{C}$ for 0 h (top) and 24 h (bottom)

Section D. Binding Constant Measurement

The binding constant of $5^{2+} \subset \text{CBPQT}^{2(++)}$ complex was determined by Vis/NIR titration in MeCN following a previously reported^{S5} protocol.

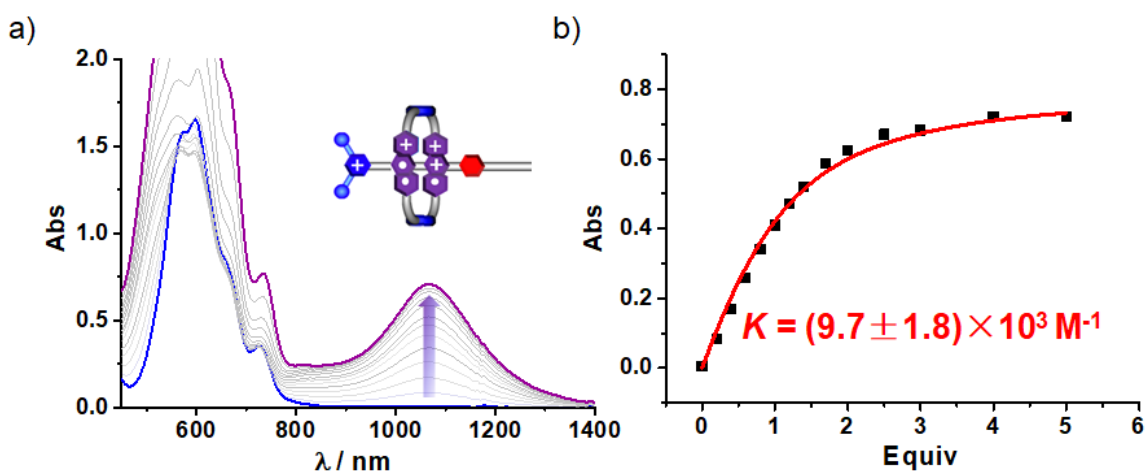


Figure S18. a) Stacked Vis/NIR spectra obtained by titrating 5^{2+} into a solution of $\text{CBPQT}^{2(++)}$ (0.25 mM in MeCN). b) Binding isotherm simulation. Optical length: 2 mm.

Section E. References

- (1) Cheng, C.; McGonigal, P. R.; Liu, W. G.; Li, H.; Vermeulen, N. A.; Ke, C.; Frasconi, M.; Stern, C. L.; Goddard III, W. A.; Stoddart, J. F. Energetically demanding transport in a supramolecular assembly. *J. Am. Chem. Soc.* **2014**, *136*, 14702–14705.
- (2) Asakawa, M.; Dehaen, W.; L'abbé, G.; Menzer, S.; Nouwen, J.; Raymo, F. M.; Stoddart, J. Improved Template-Directed Synthesis of Cyclobis(paraquat-p-phenylene). *J. Org. Chem.* **1996**, *61*, 9591–9595.
- (3) Wang, Y.; Sun, J.; Liu, Z.; Nassar, M. S.; Botros, Y. Y.; Stoddart, J. F. Radically promoted formation of a molecular lasso. *Chem. Sci.* **2017**, *8*, 562–2568.
- (4) Chwalek, M.; Auzély, R.; Fort, S. Synthesis and biological evaluation of multivalent carbohydrate ligands obtained by click assembly of pseudo-rotaxanes. *Org. Biomol. Chem.* **2009**, *7*, 1680–1688.
- (5) Cheng, C.; Cheng, T.; Xiao, H.; Krzyaniak, M. D.; Wang, Y.; McGonigal, P. R.; Frasconi, M.; Barnes, J. C.; Fahrenbach, A. C.; Wasielewski, M. R. Goddard III, W. A. Stoddart, J. F. Influence of constitution and charge on radical pairing interactions in trisradical tricationic complexes. *J. Am. Chem. Soc.* **2016**, *138*, 8288–8300.