

A chemical-responsive bis(*m*-phenylene)-32-crown-10/2,7-diazapyrenium salt [2]pseudorotaxane

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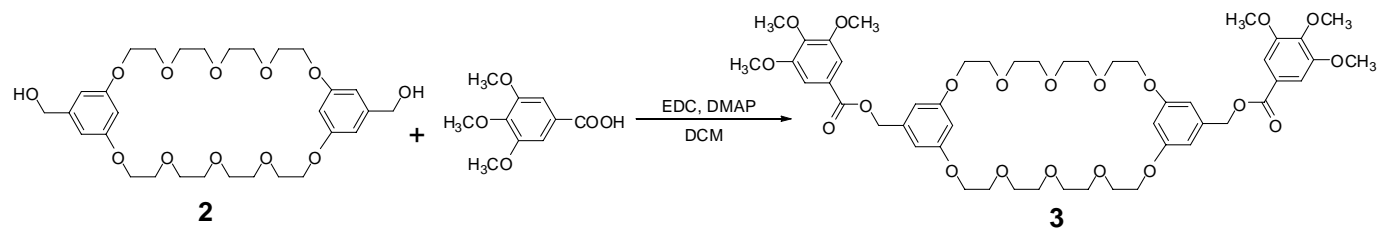
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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. BMP32C10 (**1**),^{S1} BMP32C10 diol (**2**),^{S1} guests **4**,^{S2} **5**,^{S3} **6**,^{S4} and **7**^{S5} were synthesized according to the published literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. The crystals data were collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra. The crystal structures were solved by SHELXS-97^{S6} and refined by SHELXL-97.^{S7}

2. Synthesis of compound 3



A solution of **2** (1.19 g, 2.0 mmol), 3,4,5-trimethoxybenzoic acid (1.70 g, 8.0 mmol) and 4-dimethylaminopyridine (DMAP) (250 mg, 2.0 mmol) in dichloromethane (80 mL) was stirred for 10 minutes at 0 °C. To this solution was added EDC (770 mg, 4.0 mmol). The reaction mixture was stirred for 24 h at room temperature, filtered, and concentrated to give a crude, which was purified by flash column chromatography (methanol/dichloromethane, 1:100 *v/v*) to afford **3** as a white solid (1.81 g, 92%). Mp: 113.2–114.0 °C. The ¹H NMR spectrum of **3** is shown in Figure S1. ¹H NMR (400 MHz, CDCl₃, room temperature) δ (ppm): 7.30 (s, 4H), 6.55 (s, 4H), 6.43 (s, 2H), 5.23 (s, 4H), 4.01–4.09 (m, 8H), 3.89 (s, 6H), 3.88 (s, 12H), 3.77–3.85 (m, 8H), 3.61–3.72 (m, 16H). The ¹³C NMR spectrum of **3** is shown in Figure S2. ¹³C NMR (125 MHz, CDCl₃, room temperature) δ (ppm): 29.68, 56.27, 60.91, 66.60, 67.56, 69.62, 70.86, 101.04, 106.92, 125.04, 138.23, 142.29, 152.93, 160.08, and 165.99. LRESIMS is shown in Figure S3: *m/z* 1002.9 [M + H₃O]⁺, 1007.8 [M + Na]⁺, and 1023.4 [M + K]⁺. HRESIMS: *m/z* calcd for [M + Na]⁺ C₄₂H₅₀N₂O₁₄Na, 1007.3889; found 1007.3855, error –3.4 ppm.

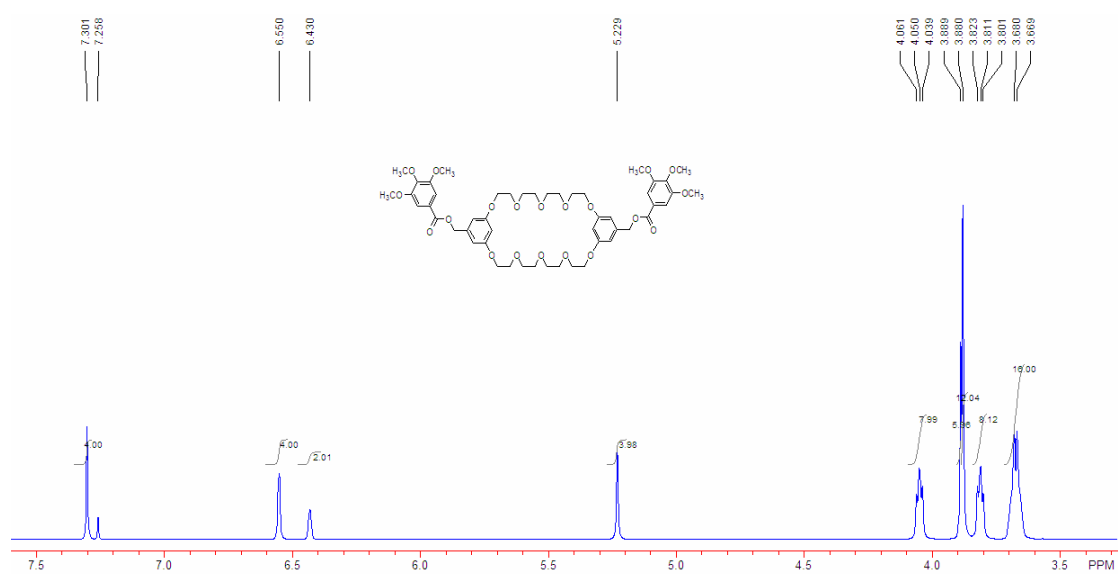


Fig. S1. ¹H NMR spectrum (400 MHz, CDCl₃, room temperature) of **3**.

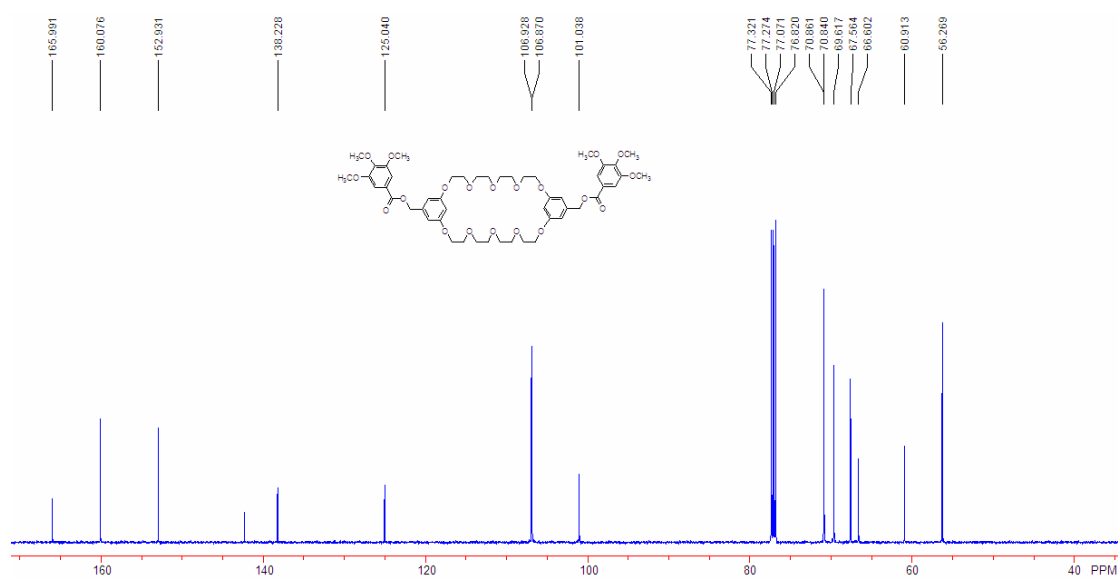


Fig. S2. ¹³C NMR spectrum (125 MHz, CDCl₃, room temperature) of **3**.

Display Report

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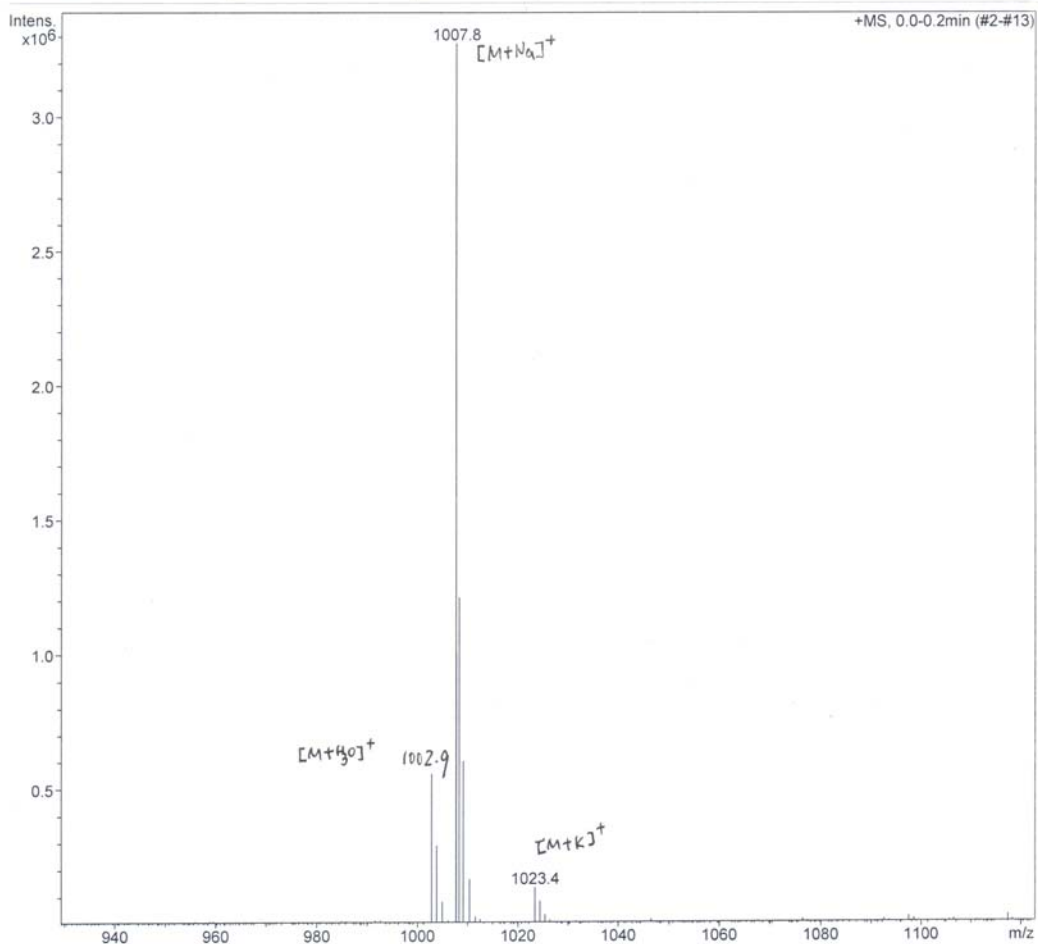
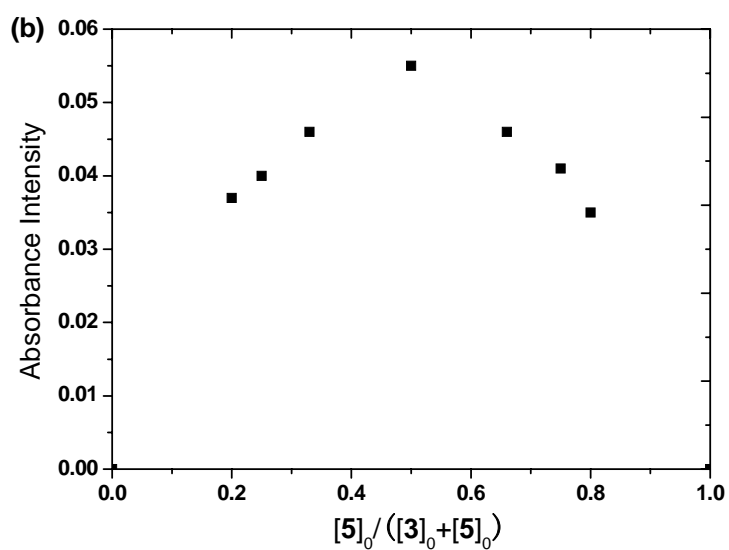
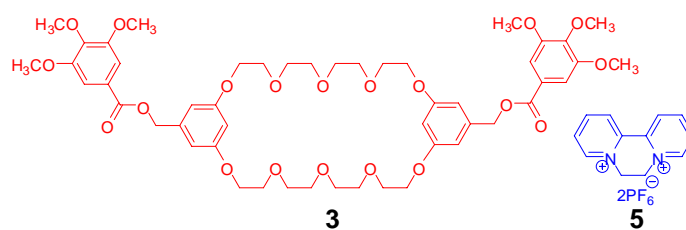
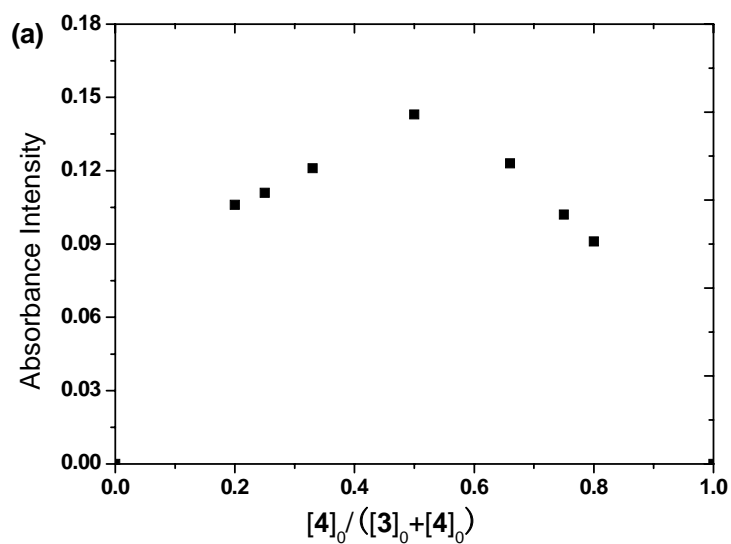
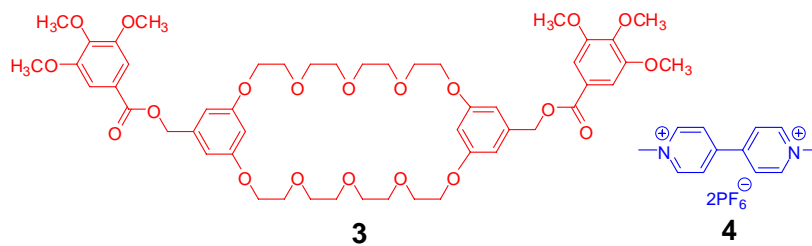


Fig. S3. Electrospray ionization mass spectrum of **3**.

3. Job plots of 3→4, 3→5, 3→6, and 3→7 based on UV-vis spectroscopy data in acetone



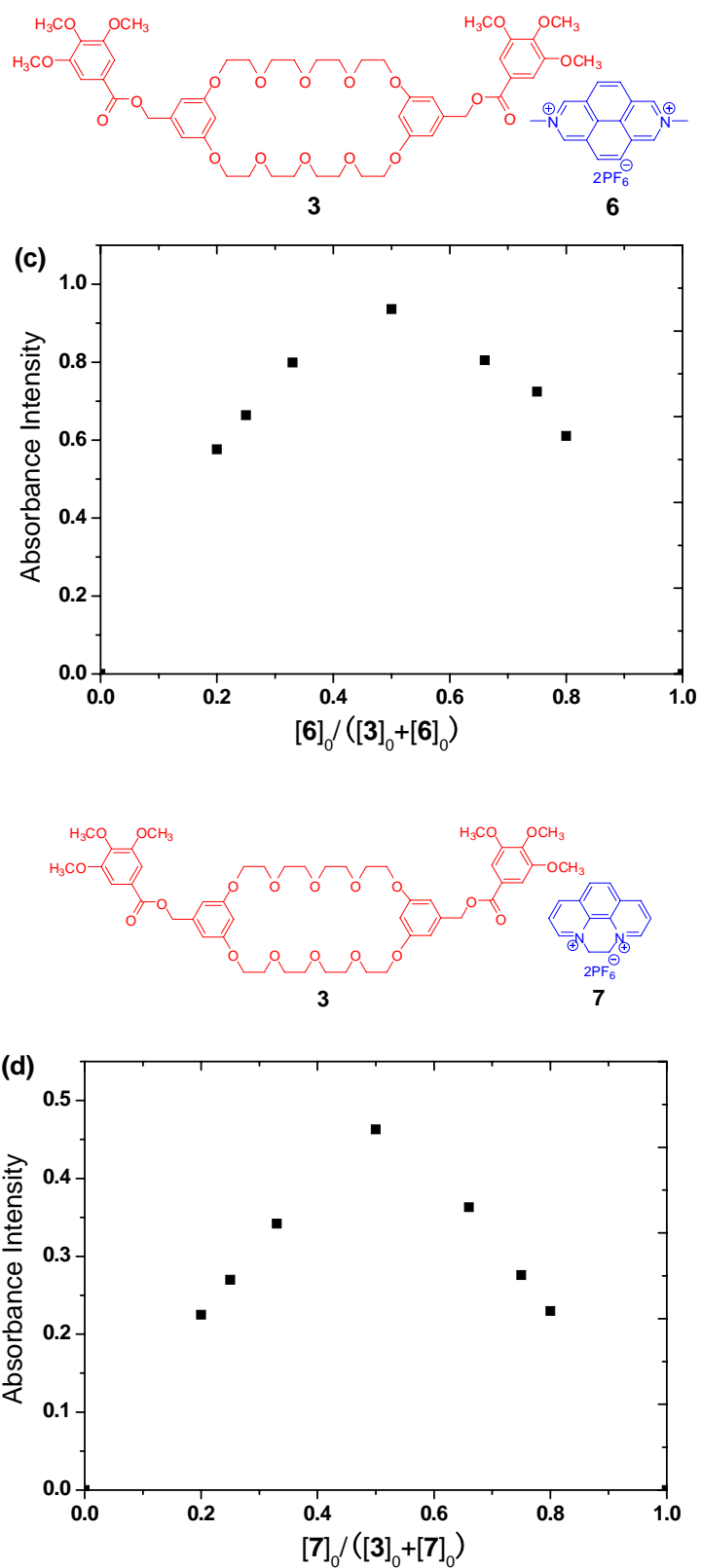


Fig. S4. Job plots showing the 1:1 stoichiometries of the complexes between **3** and **4** (a), **3** and **5** (b), **3** and **6** (c), and **3** and **7** (d) in acetone: (a) $[3]_0 + [4]_0 = 1.00$ mM; (b) $[3]_0 + [5]_0 = 1.00$ mM; (c) $[3]_0 + [6]_0 = 1.00$ mM; (d) $[3]_0 + [7]_0 = 1.00$ mM. $[3]_0$, $[4]_0$, $[5]_0$, $[6]_0$, and $[7]_0$ are the initial concentrations of **3**, **4**, **5**, **6**, and **7**, respectively.

4. Electrospray ionization mass spectra of host **3** with guests **4**, **5**, **6**, and **7** in acetone

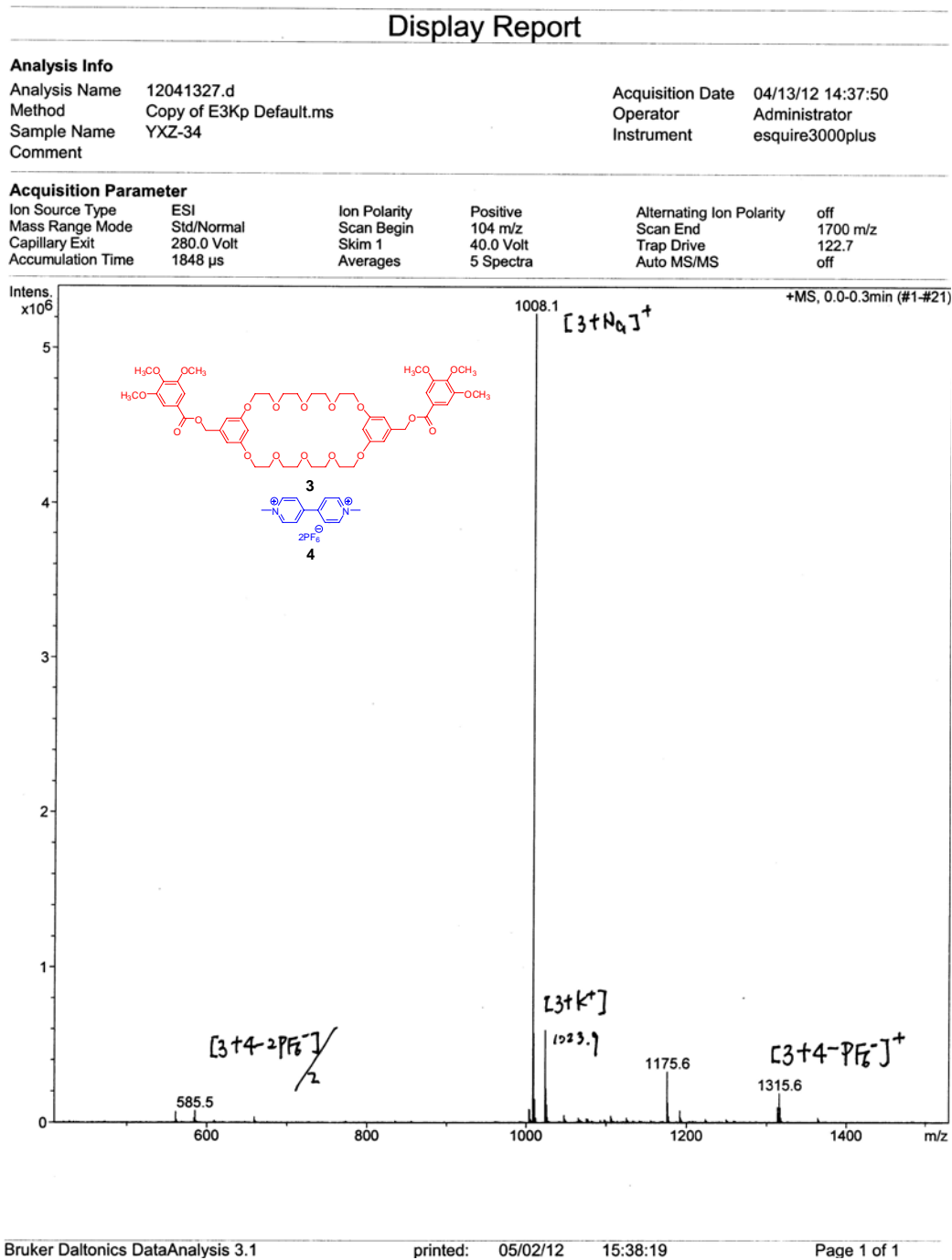


Fig. S5. The positive electrospray ionization mass spectrum of an equimolar mixture of **3** and **4** in acetone. Mass fragments at m/z 1315.6 for $[\mathbf{3} \supset \mathbf{4} - \text{PF}_6]^+$ and m/z 585.5 for $[\mathbf{3} \supset \mathbf{4} - 2\text{PF}_6]^{2+}$ confirmed the 1:1 complexation stoichiometry between **3** and **4**.

Display Report

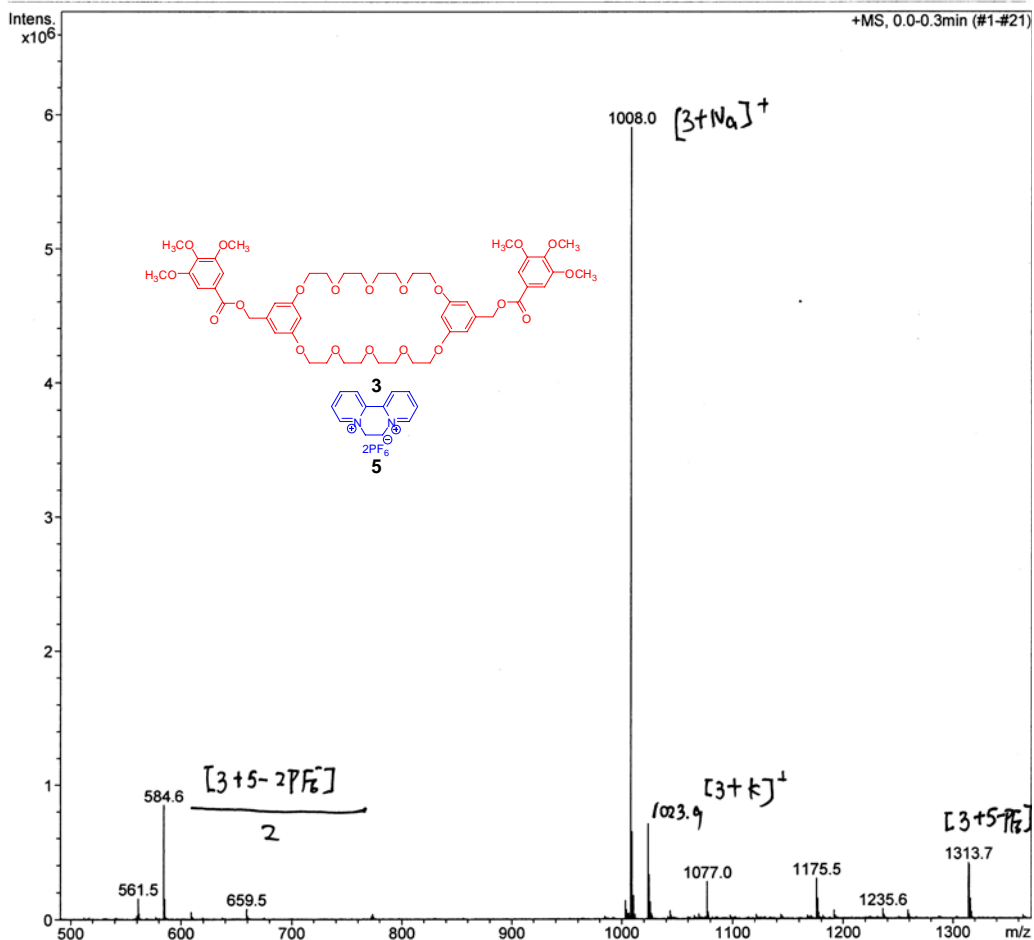
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Fig. S6. The positive electrospray ionization mass spectrum of an equimolar mixture of **3** and **5** in acetone. Mass fragments at m/z 1313.7 for [3 \rightarrow 5 - PF₆]⁺ and m/z 584.6 for [3 \rightarrow 5 - 2PF₆]²⁺ confirmed the 1:1 complexation stoichiometry between **3** and **5**.

Print Date: 20 Apr 2012 22:16:44

Spectrum 1A Plot - 2012-4-20 22:16

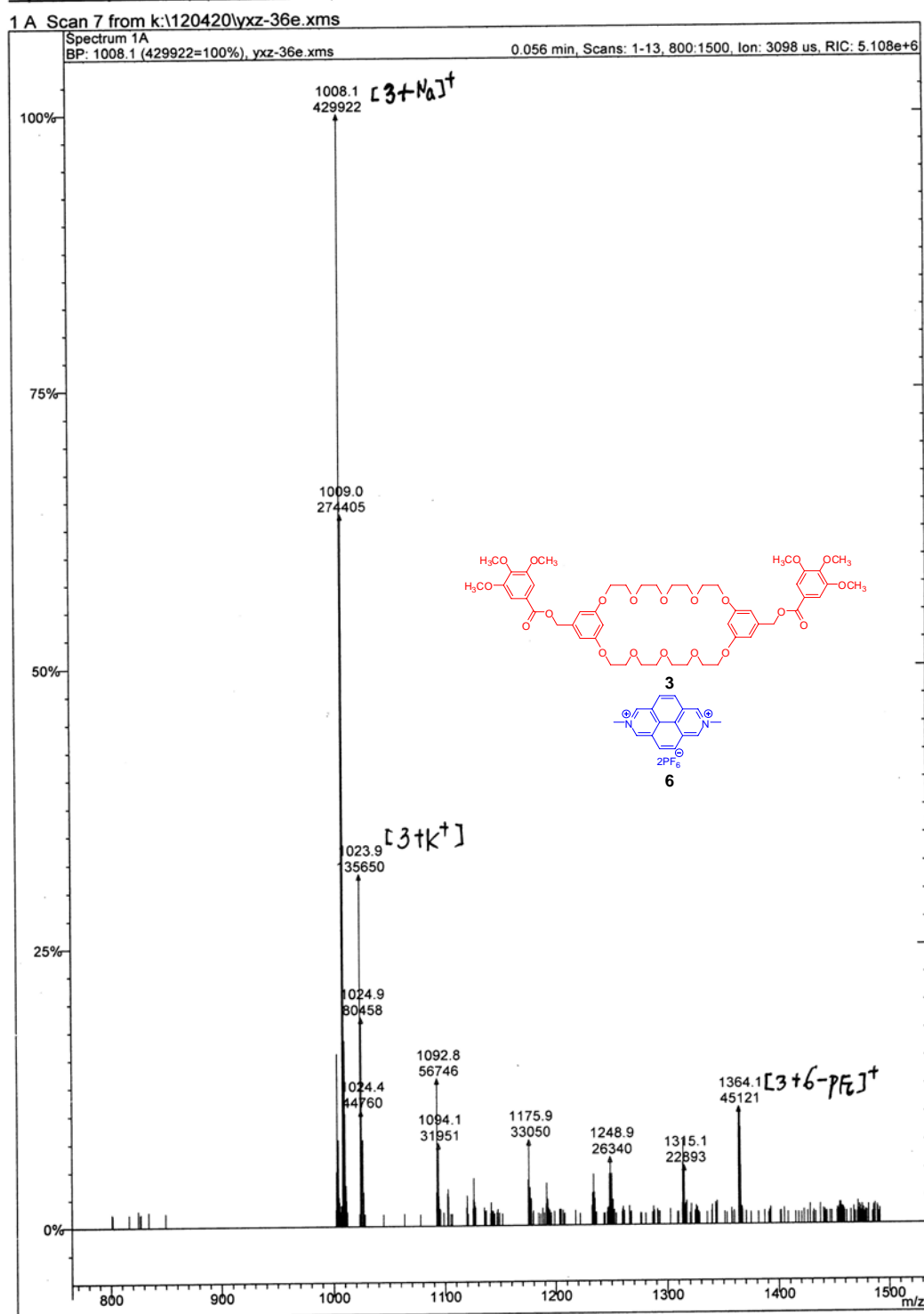


Fig. S7. The positive electrospray ionization mass spectrum of an equimolar mixture of **3** and **6** in acetone. A mass fragment at m/z 1364.1 for $[3+6 - PF_6]^+$ confirmed the 1:1 complexation stoichiometry between **3** and **6**.

Display Report

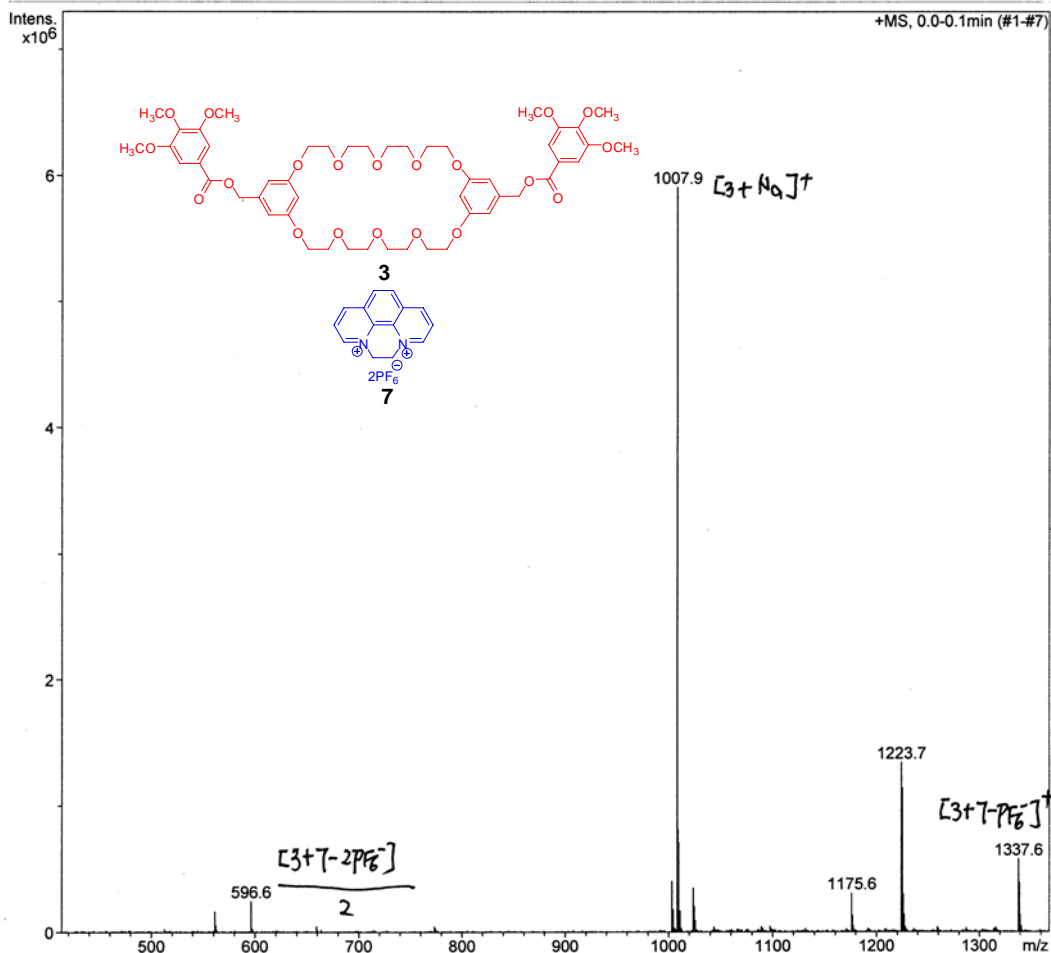
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Bruker Daltonics DataAnalysis 3.1

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Fig. S8. The positive electrospray ionization mass spectrum of an equimolar mixture of **3** and **7** in acetone. Mass fragments at m/z 1337.6 for $[3\supset 7 - \text{PF}_6]^+$ and m/z 596.6 for $[3\supset 7 - 2\text{PF}_6]^{2+}$ confirmed the 1:1 complexation stoichiometry between **3** and **7**.

5. Determination of association constants of complexes **3**⇌**4**, **3**⇌**5**, **3**⇌**6**, and **3**⇌**7** in acetone

The association constants (K_a) of complexes **3**⇌**4**, **3**⇌**5**, **3**⇌**6**, and **3**⇌**7** were determined by probing the charge-transfer bands of the complexes by UV-vis spectroscopy and employing a titration method. Progressive addition of an acetone solution with high guest concentration and low host concentration to an acetone solution with the same host concentration resulted in an increase of the intensity of the charge-transfer band of the complex. Treatment of the collected absorbance data with a non-linear curve-fitting program afforded the corresponding association constants (K_a): $1.67 \times 10^2 \text{ M}^{-1}$ for **3**⇌**4**, 63.6 M^{-1} for **3**⇌**5**, $2.17 \times 10^3 \text{ M}^{-1}$ for **3**⇌**6**, and $3.91 \times 10^2 \text{ M}^{-1}$ for **3**⇌**7**.

The non-linear curve-fitting was based on the equation:

$$A = (A_\infty/[H]_0) (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5([G]_0^2 + (2[G]_0(1/K_a - [H]_0) + (1/K_a + [H]_0)^2)^{0.5})) \quad (\text{Eq. S1})$$

Where A is the absorption intensity of the charge-transfer band at $[G]_0$, A_∞ is the absorption intensity of the charge-transfer band when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of the guest.

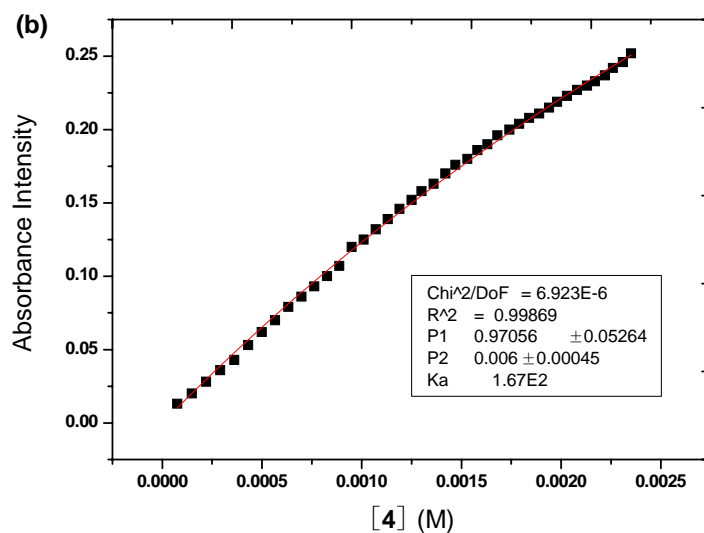
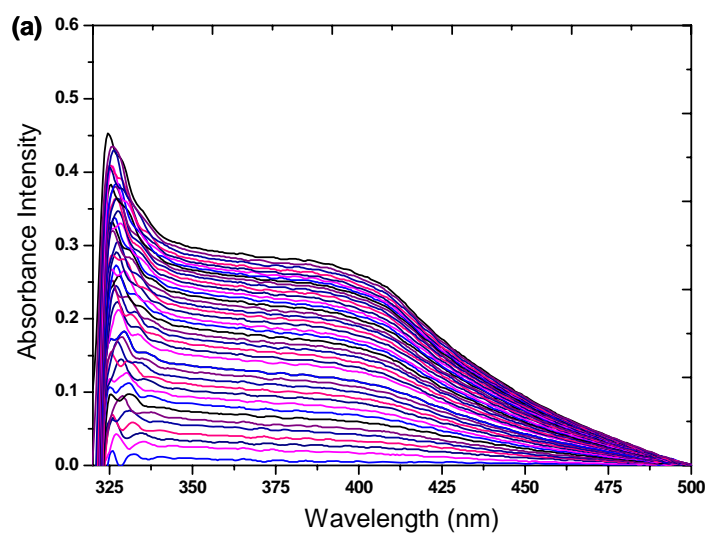
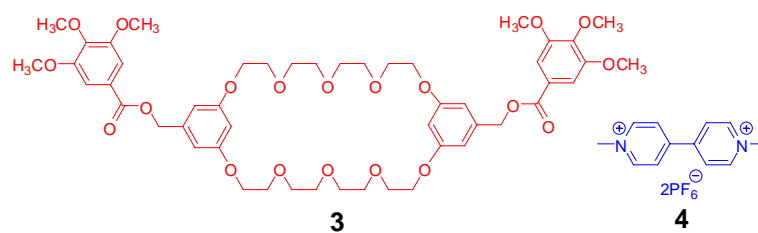


Fig. S9. (a) The absorption spectral changes of **3** (1.00 mM) upon addition of **4** and (b) the absorbance intensity changes at $\lambda = 403$ nm upon addition of **4** (from 0 to 2.35 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

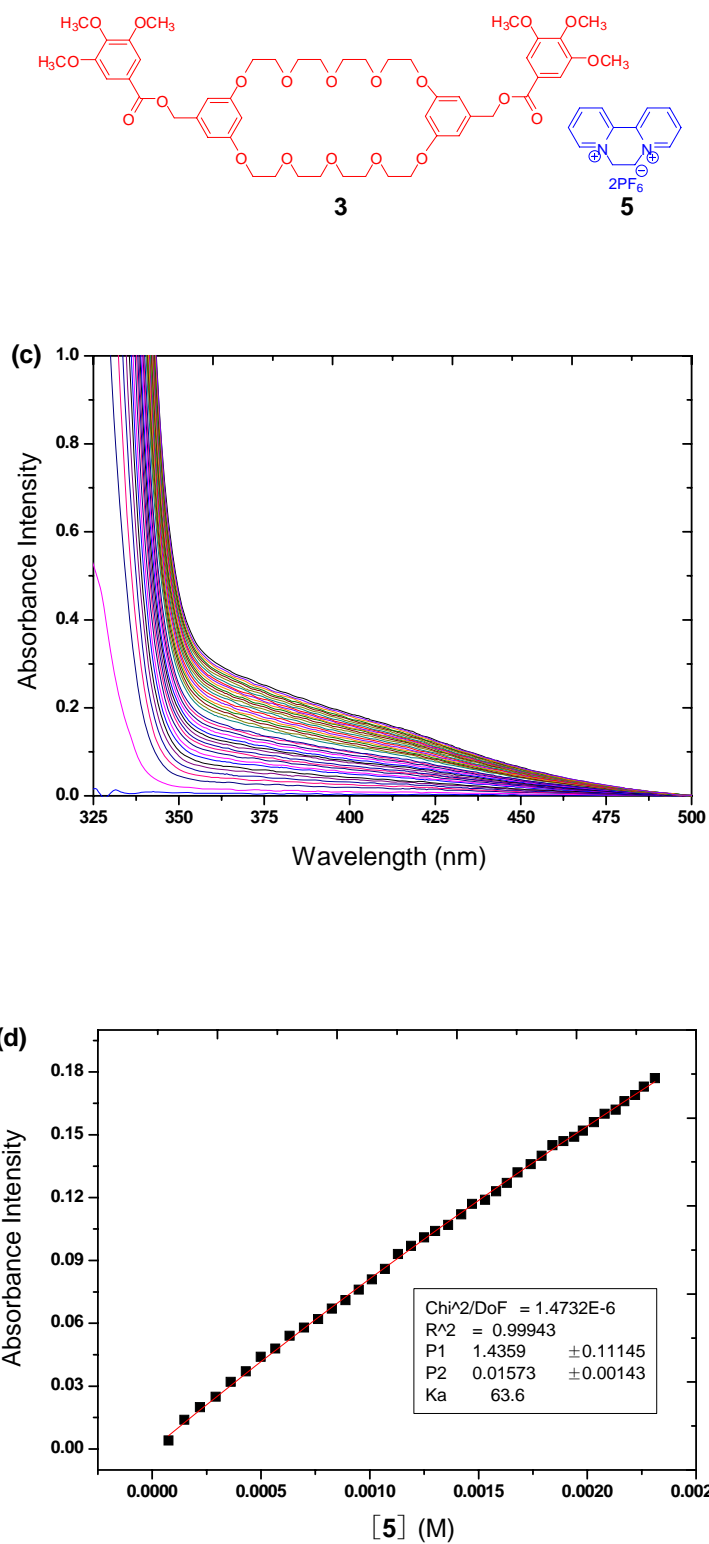


Fig. S10. (c) The absorption spectral changes of **3** (1.00 mM) upon addition of **5** and (d) the absorbance intensity changes at $\lambda = 403$ nm upon addition of **5** (from 0 to 2.31 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

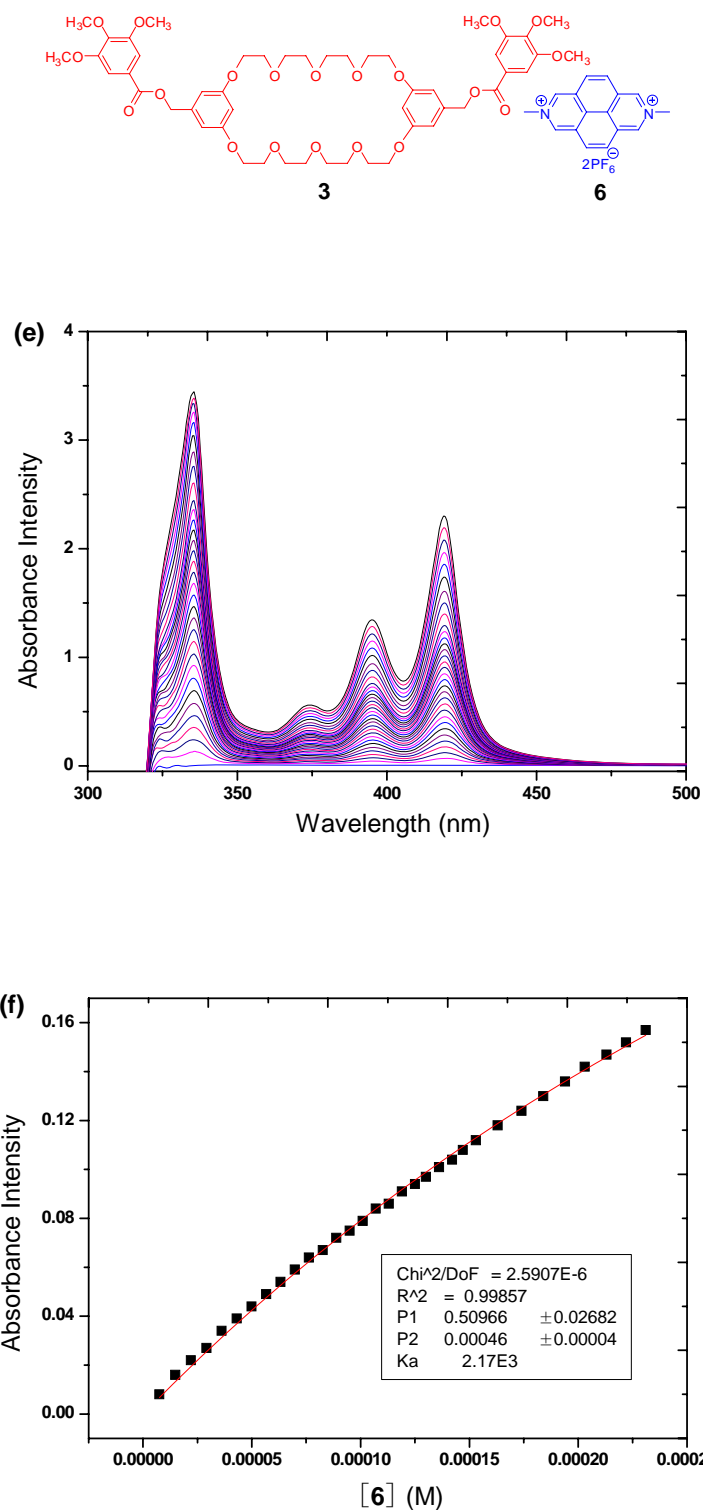


Fig. S11. (e) The absorption spectral changes of **3** (0.10 mM) upon addition of **6** and (f) the absorbance intensity changes at $\lambda = 440$ nm upon addition of **6** (from 0 to 0.23 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

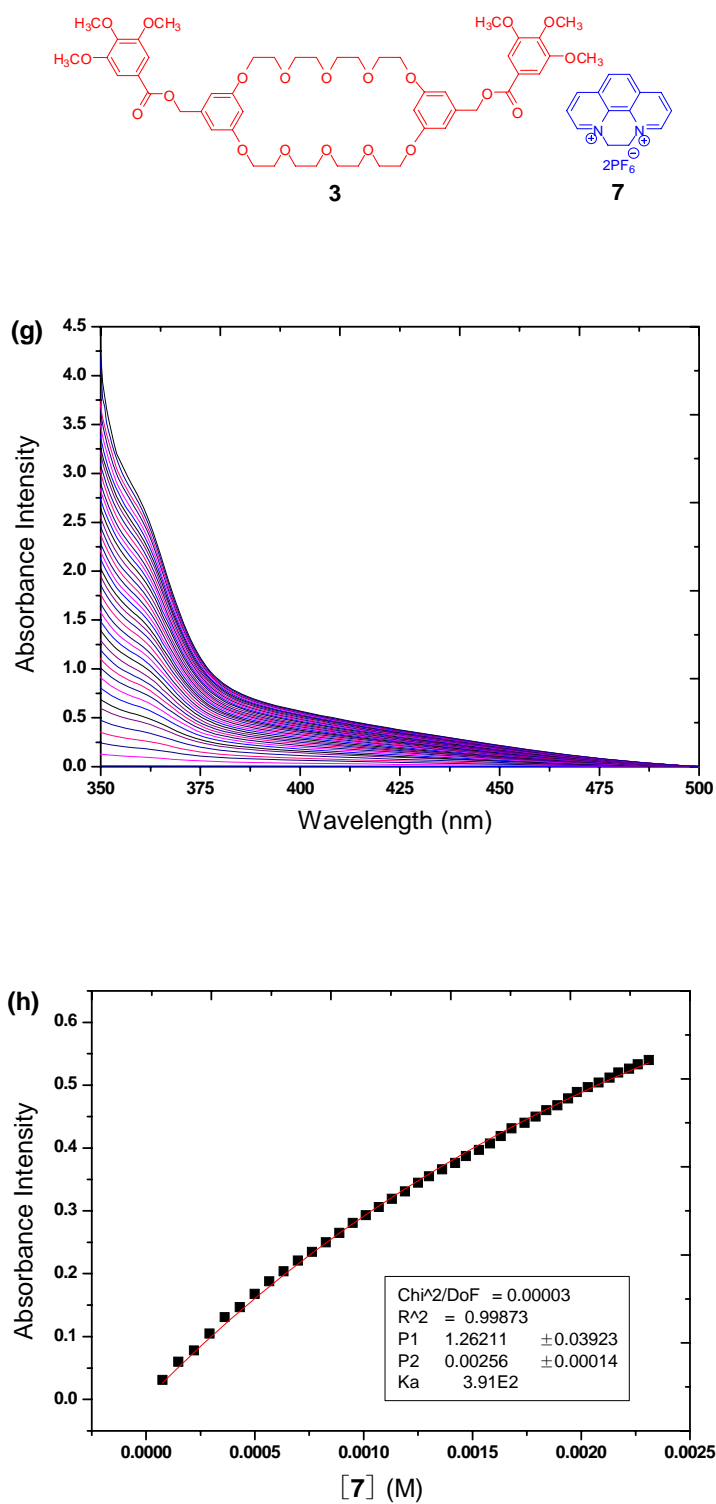


Fig. S12. (g) The absorption spectral changes of **3** (1.00 mM) upon addition of **6** and (h) the absorbance intensity changes at $\lambda = 403$ nm upon addition of **7** (from 0 to 2.31 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

6. Proton NMR spectra of equimolar (2.00 mM) acetone- d_6 solutions of **3** with **5** and **7**

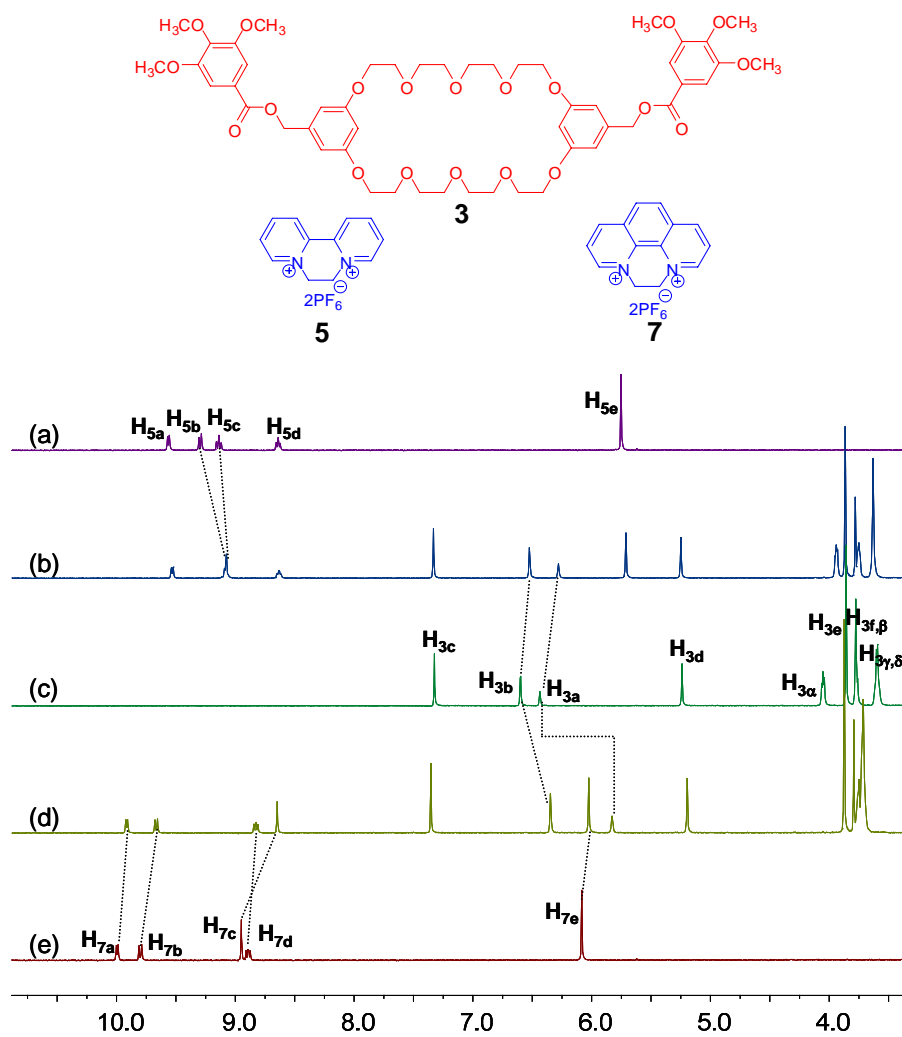


Fig. S13. Partial ^1H NMR spectra (acetone- d_6 , 293 K, 400 MHz) of (a) 1.00 mM **5**; (b) 1.00 mM **3** + 1.00 mM **5**; (c) 1.00 mM **3**; (d) 1.00 mM **3** + 1.00 mM **7**; (e) 1.00 mM **7**.

7. pH-controlled complexation between **3** and **6** based on UV-vis spectroscopy

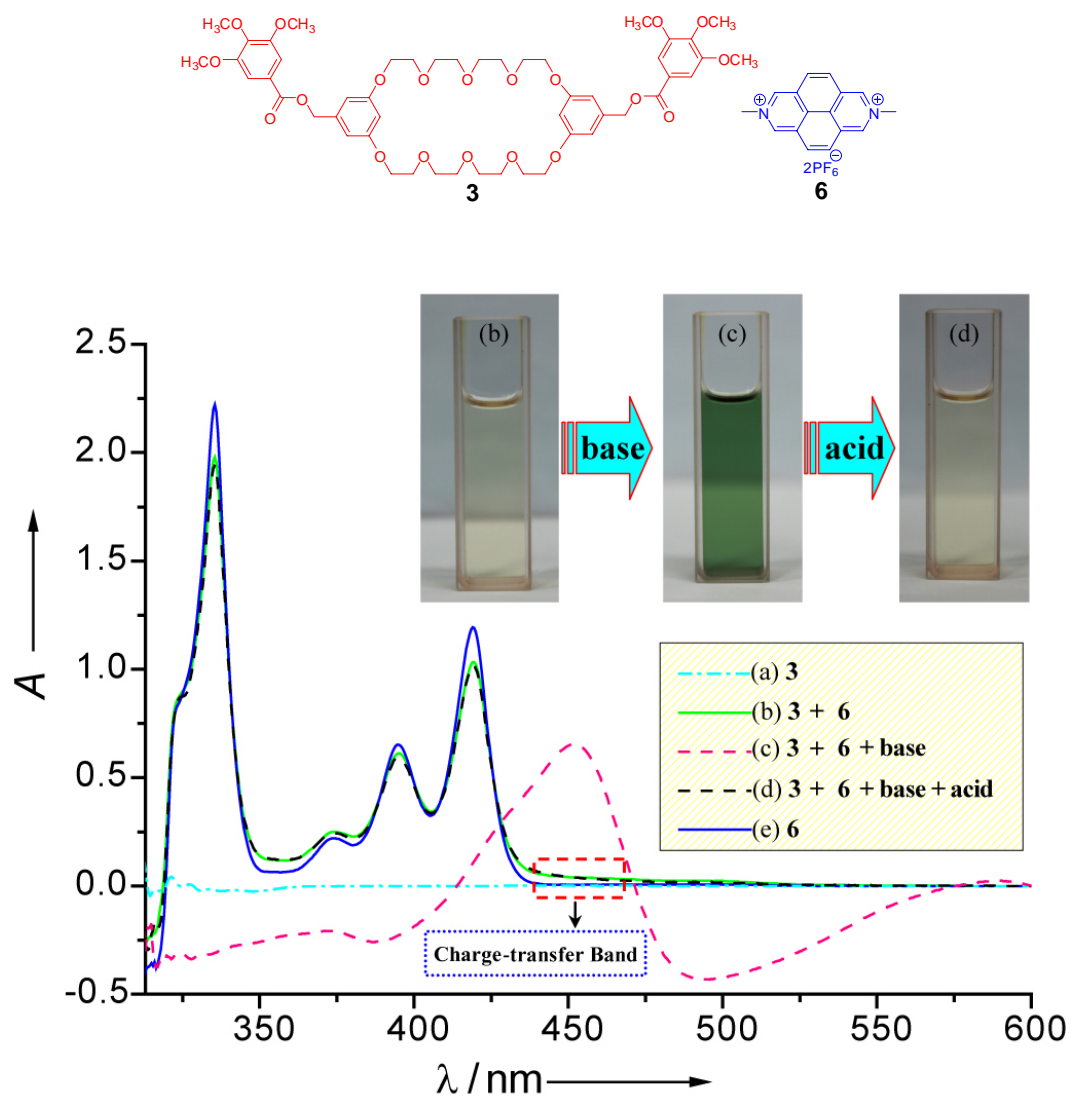


Fig. S14. UV-vis absorption spectra of (a) 5.00×10^{-5} M **3**; (b) 5.00×10^{-5} M **3** + 5.00×10^{-5} M **6**; (c) after addition of Et₂NH (10.0 equiv.) to b; (d) after addition of CF₃COOH (10.0 equiv.) to c; (e) 5.00×10^{-5} M **6**.

8. X-ray crystal data for 3⇨6

Crystallographic data: block, yellow, $0.28 \times 0.23 \times 0.16 \text{ mm}^3$, $\text{C}_{70}\text{H}_{84}\text{F}_{12}\text{N}_4\text{O}_{20}\text{P}_2$, FW 1591.35, triclinic, space group $P\bar{1}$, $a = 11.1390(9)$, $b = 11.9736(7)$, $c = 15.3398(10) \text{ \AA}$, $\alpha = 110.014(6)^\circ$, $\beta = 106.655(7)^\circ$, $\gamma = 94.675(6)^\circ$, $V = 1804.7(2) \text{ \AA}^3$, $Z = 1$, $D_c = 1.464 \text{ g cm}^{-3}$, $T = 120 (2) \text{ K}$, $\mu = 1.488 \text{ mm}^{-1}$, 11309 measured reflections, 6105 independent reflections, 492 parameters, 0 restraints, $F(000) = 830$, $R(\text{int}) = 0.0446$, $R_1 = 0.0730$, $wR_1 = 0.1443$ (all data), $R_2 = 0.0504$, $wR_2 = 0.1279 [I > 2\sigma(I)]$, max. residual density $0.905 \text{ e}\cdot\text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.023. CCDC 879994.

9. X-ray crystal data for 3⇨7

Crystallographic data: platelet, yellow, $0.45 \times 0.38 \times 0.22 \text{ mm}^3$, $\text{C}_{68}\text{H}_{82}\text{F}_{12}\text{N}_4\text{O}_{20}\text{P}_2$, FW 1565.32, monoclinic, space group Cc , $a = 17.9964(10)$, $b = 13.7356(6)$, $c = 32.6891(15) \text{ \AA}$, $\alpha = 90.00(17)^\circ$, $\beta = 102.548(5)^\circ$, $\gamma = 90.00^\circ$, $V = 7887.5 (7) \text{ \AA}^3$, $Z = 4$, $D_c = 1.318 \text{ g cm}^{-3}$, $T = 140 (2) \text{ K}$, $\mu = 0.152 \text{ mm}^{-1}$, 18075 measured reflections, 10629 independent reflections, 963 parameters, 68 restraints, $F(000) = 3264$, $R(\text{int}) = 0.0319$, $R_1 = 0.1110$, $wR_1 = 0.2672$ (all data), $R_2 = 0.0802$, $wR_2 = 0.2294 [I > 2\sigma(I)]$, max. residual density $1.384 \text{ e}\cdot\text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.038. CCDC 879994.

References:

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