

# TetrazineBox: A Structurally Transformative ToolBox

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## Supporting Information

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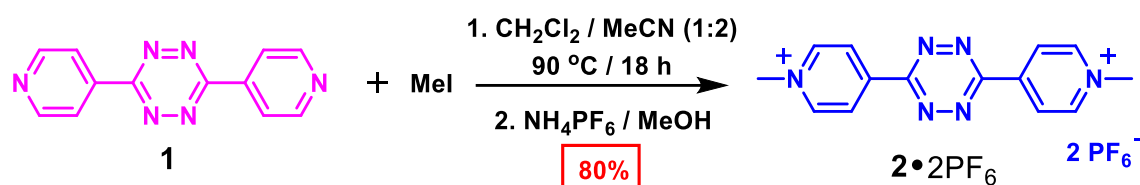
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## Section A. General Information

All commercially available reagents were used as received. Anhydrous MeCN and CH<sub>2</sub>Cl<sub>2</sub> were prepared by solvent drying system. 3,6-Di(4-pyridinyl)-1,2,4,5-tetrazine (**1**) was synthesized according to literature<sup>1</sup>. Bis(cyclopentadienyl)cobalt(II) was purchased from Sigma-Aldrich. UV–Vis–NIR absorption spectra were collected on a Shimadzu UV-3600 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 500 spectrometers, with working frequencies of 500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C nuclei, respectively. Chemical shifts were reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (DMSO-*d*<sub>6</sub>:  $\delta_{\text{H}} = 2.50$  and  $\delta_{\text{C}} = 39.5$  ppm; CD<sub>3</sub>CN:  $\delta_{\text{H}} = 1.94$  and  $\delta_{\text{C}} = 118.3$  ppm). Abbreviations are used in the description of NMR data as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet), coupling constant (*J*, Hz). EPR Spectra were recorded using a Bruker Elexsys E580 X-band EPR spectrometer. EPR Samples were prepared by titration with cobaltocene and the solution was transferred into 1.8 mm o.d. quartz tubes and sealed with a clear ridged UV doming epoxy in an Ar glovebox. High-resolution mass spectra (ESI-HRMS) were measured on a Finnigan LCQ iontrap mass spectrometer. Single-crystal X-ray diffraction (SCXRD) data were collected on a Bruker APEX-II CCD diffractometer.

## Section B. Synthetic Protocols

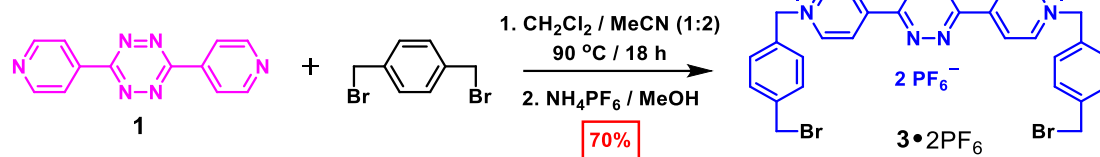
### 1. Synthesis of **2•2PF<sub>6</sub>**



**Scheme S1.** Synthesis of **2•2PF<sub>6</sub>**

**2•2PF<sub>6</sub>**: A solution of 3,6-di(4-pyridinyl)-1,2,4,5-tetrazine **1** (118 mg, 0.5 mmol) and methyl iodide (710 mg, 5 mmol) in the mixture of dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and anhydrous MeCN (40 mL) was heated to 90 °C for 18 h. The resulting red precipitate was collected by filtration, and washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The precipitate was then dissolved in anhydrous MeOH (200 mL) and the solution was filtered. A solution of NH<sub>4</sub>PF<sub>6</sub> (2 g) in anhydrous MeOH (20 mL) was added in the filtrate. The resulting red precipitate was collected by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and dried to give the product **2•2PF<sub>6</sub>** (222 mg, 0.4 mmol) in 80% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K)  $\delta_H$  = 9.16 (d,  $J$  = 6.17 Hz, 4H), 9.00 (d,  $J$  = 6.17 Hz, 4H), 4.49 (s, 4H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>SOCD<sub>3</sub>, 298 K)  $\delta_C$  = 161.8, 147.9, 145.9, 126.0, 125.6, 49.0; ESI-HRMS Calcd for C<sub>14</sub>H<sub>14</sub>F<sub>6</sub>N<sub>6</sub>P:  $m/z$  = 411.0916 [ $M + H$ ]<sup>+</sup>; found: 411.0917 [ $M + H$ ]<sup>+</sup>.

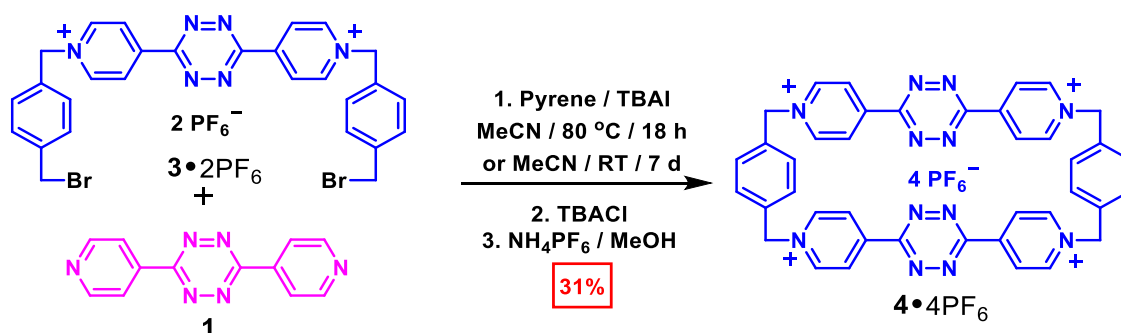
## 2. Synthesis of **3•2PF<sub>6</sub>**



**Scheme S2.** Synthesis of **3•2PF<sub>6</sub>**

**3•2PF<sub>6</sub>**: A solution of  $\alpha,\alpha'$ -dibromo-*p*-xylene (13.20 g, 50 mmol) and 3,6-di(4-pyridinyl)-1,2,4,5-tetrazine **1** (1.18 g, 5 mmol) in the mixture of dry  $\text{CH}_2\text{Cl}_2$  (80 mL) and anhydrous MeCN (160 mL) was heated to 90 °C for 18 h. The resulting red precipitate was collected by filtration, washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL). The precipitate was then dissolved in anhydrous MeOH (400 mL) and the solution was filtered. A solution of  $\text{NH}_4\text{PF}_6$  (8 g) in anhydrous MeOH (50 mL) was added in the filtrate. The resulting red precipitate was collected by filtration, washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL) and dried to give the product **3•2PF<sub>6</sub>** (3.13 g, 3.5 mmol) in 70% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K)  $\delta_{\text{H}} = 9.17$  (d,  $J = 6.46$  Hz, 4H), 9.10 (d,  $J = 6.46$  Hz, 4H), 7.60 (d,  $J = 8.02$  Hz, 4H), 7.55 (d,  $J = 8.02$  Hz, 4H), 5.91 (s, 4H), 4.65 (s, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , 298 K)  $\delta_{\text{C}} = 162.3, 147.6, 146.8, 141.1, 133.0, 130.8, 130.5, 127.5, 65.1, 33.1$ ; ESI-HRMS Calcd for  $\text{C}_{28}\text{H}_{24}\text{Br}_2\text{N}_6\text{F}_{12}\text{P}_2$ :  $m/z = 749.0045$  [ $M - \text{PF}_6$ ] $^+$ ; found: 749.0081 [ $M - \text{PF}_6$ ] $^+$ .

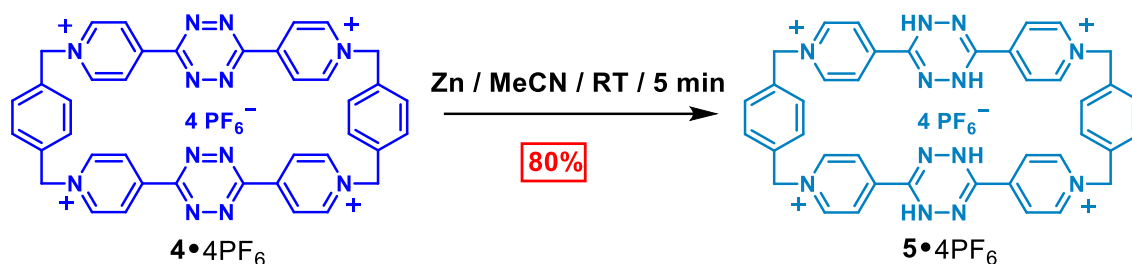
### 3. Synthesis of 4•4PF<sub>6</sub>



**Scheme S3.** Synthesis of 4•4PF<sub>6</sub>

**4•4PF<sub>6</sub>:** A template pyrene (1.51g, 6mmol) and a catalyst TBAI (111 mg, 0.3mmol) were added to a solution of **1** (894 g, 1 mmol) and **3•2PF<sub>6</sub>** in anhydrous MeCN (500 mL). The mixture was heated to 80 °C for 18 h or stirred at room temperature for 7 days. The resulting red precipitate was collected by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The precipitate was then dissolved in anhydrous MeOH (800 mL) and the solution was filtered. A solution of NH<sub>4</sub>PF<sub>6</sub> (2.5 g) in anhydrous MeOH (50 mL) was added to the filtrate. The resulting red precipitate was collected by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and dried. The analytically pure product **4•4PF<sub>6</sub>** (391 mg, 0.31 mmol), which was obtained in 31% yield, was isolated as a red powder by high-performance reverse-phase preparative C18 column chromatography (anhydrous MeCN and 5% CH<sub>2</sub>Cl<sub>2</sub> as eluent). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K) δ<sub>H</sub> = 8.93 (d, *J* = 7.00 Hz, 8H), 8.62 (d, *J* = 7.00 Hz, 8H), 7.67 (s, 8H), 7.67 (s, 8H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 298 K) δ<sub>C</sub> = 154.8, 151.5, 145.4, 136.5, 130.9, 127.8, 126.8, 64.9, 22.8; ESI-HRMS Calcd for C<sub>40</sub>H<sub>32</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>: *m/z* = 1115.1793 [*M* – PF<sub>6</sub>]<sup>+</sup>, 485.1073 [*M* – 2PF<sub>6</sub>]<sup>2+</sup>; found: 1115.1782 [*M* – PF<sub>6</sub>]<sup>+</sup>, 485.1077 [*M* – 2PF<sub>6</sub>]<sup>2+</sup>.

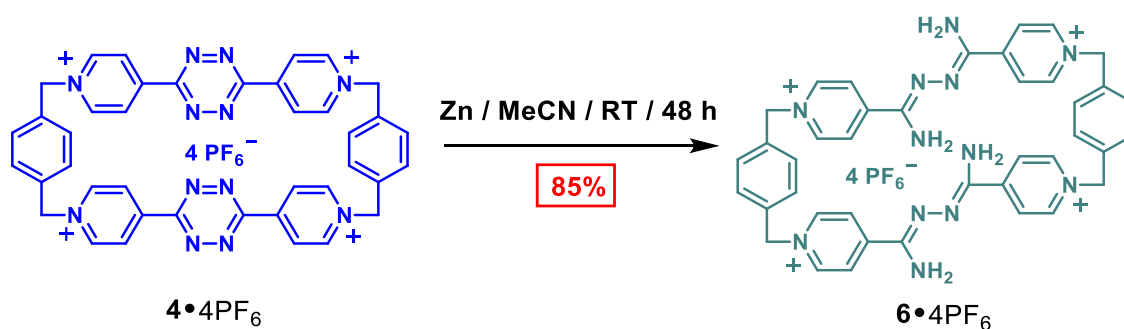
#### 4. Synthesis of 5•4PF<sub>6</sub>



**Scheme S4.** Synthesis of 5•4PF<sub>6</sub>

**5•4PF<sub>6</sub>:** Excess of activated Zn powder was added to a solution of 4•4PF<sub>6</sub> (10 mg, 0.008 mmol) in anhydrous MeCN (5 mL) in a N<sub>2</sub> glovebox. The mixture was stirred at room temperature for 5 min. The Zn powder was filtered off and the resulting clear filtrate was allowed to stand in a 1-ml vial in a N<sub>2</sub> glovebox. On slow vapor diffusion of *i*Pr<sub>2</sub>O into the MeCN solution during one day, the pure product 5•4PF<sub>6</sub> (8 mg, 0.0064 mmol) was afforded as red crystals in 80% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K)  $\delta_H$  = 8.79 (d, *J* = 7.02 Hz, 4H), 8.55 (s, 8H), 8.15 (d, *J* = 7.02 Hz, 8H), 7.56 (s, 8H), 5.73 (s, 8H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 298 K)  $\delta_C$  = 145.9, 145.4, 143.2, 135.7, 130.8, 125.5, 64.6.

#### 5. Synthesis of 6•4PF<sub>6</sub>

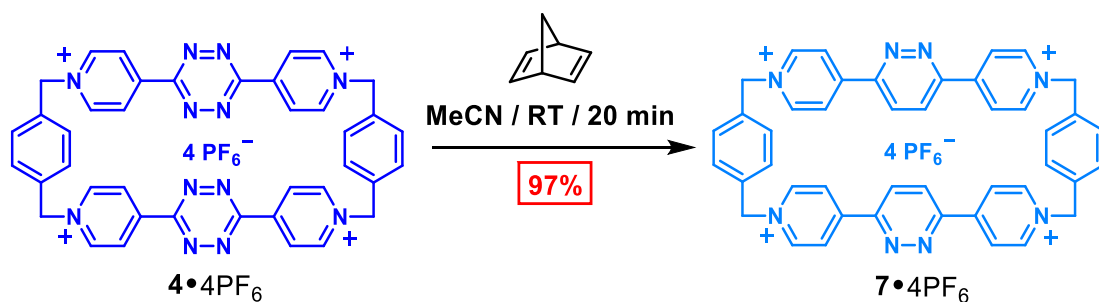


**Scheme S5.** Synthesis of 6•4PF<sub>6</sub>

**6•4PF<sub>6</sub>:** Excess of activated Zn powder was added to a solution of 4•4PF<sub>6</sub> (100 mg, 0.08 mmol) in anhydrous MeCN (25 mL) in a N<sub>2</sub> glovebox. The mixture was stirred at room temperature for 48 h. The Zn powder was filtered off, the resulting clear filtrate

was subjected to SiO<sub>2</sub> column chromatography (0.25% NH<sub>4</sub>PF<sub>6</sub> in MeCN as eluent). The pure product **6**•4PF<sub>6</sub> (86 mg, 0.068 mmol) was afforded as a red powder in 85% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K)  $\delta_H$  = 8.75 (d, *J* = 6.48 Hz, 8H), 8.33 (d, *J* = 6.48 Hz, 8H), 7.59 (s, 8H), 6.34 (s, 8H), 5.66 (s, 8H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 298 K)  $\delta_C$  = 152.0, 149.9, 144.3, 136.6, 130.7, 125.6, 64.7; ESI-HRMS Calcd for C<sub>40</sub>H<sub>32</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>: *m/z* = 1115.1793 [*M* – PF<sub>6</sub>]<sup>+</sup>, 485.1073 [*M* – 2PF<sub>6</sub>]<sup>2+</sup>; found: 1115.1782 [*M* – PF<sub>6</sub>]<sup>+</sup>, 485.1077 [*M* – 2PF<sub>6</sub>]<sup>2+</sup>.

## 6. Synthesis of **7**•4PF<sub>6</sub>



**Scheme S6.** Synthesis of **7**•4PF<sub>6</sub>

**7**•4PF<sub>6</sub>: Excess of norbornadiene (147 mg, 1.6 mmol) was added to a solution of **4**•4PF<sub>6</sub> (100 mg, 0.08 mmol) in anhydrous MeCN (25 mL). The mixture was stirred at room temperature for 20 min while N<sub>2</sub> was released. The mixture was subjected to SiO<sub>2</sub> column chromatography (0.25% NH<sub>4</sub>PF<sub>6</sub> in MeCN as eluent). The pure product **7**•4PF<sub>6</sub> (86 mg, 0.068 mmol) was afforded as a yellow powder in 97% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K)  $\delta_H$  = 8.90 (d, *J* = 6.92 Hz, 4H), 8.60 (d, *J* = 6.92 Hz, 8H), 8.44 (s, 4H), 7.63 (s, 8H), 5.77 (s, 8H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 298 K)  $\delta_C$  = 154.8, 151.5, 145.4, 136.5, 130.9, 127.8, 126.8, 64.9. ESI-HRMS Calcd for C<sub>44</sub>H<sub>36</sub>F<sub>24</sub>N<sub>8</sub>P<sub>4</sub>: *m/z* = 1111.1983 [*M* – PF<sub>6</sub>]<sup>+</sup>; found: 1111.1994 [*M* – PF<sub>6</sub>]<sup>+</sup>.

## Section C. X-Ray Crystallographic Characterization

All the single crystals were obtained by slow vapor diffusion of *i*Pr<sub>2</sub>O into solutions of **2**•2PF<sub>6</sub>, **4**•4PF<sub>6</sub>, **5**•4PF<sub>6</sub>, **6**•4PF<sub>6</sub>, and **7**•4PF<sub>6</sub> in MeCN after two days, respectively. Single crystals of host-guest complexes (**pyrene**⊂**TzBox**•4PF<sub>6</sub>, **perylene**⊂**TzBox**•4PF<sub>6</sub>, **pyrene**⊂**DzBox**•4PF<sub>6</sub>, and **perylene**⊂**DzBox**•4PF<sub>6</sub>) were obtained by slow vapor diffusion of *i*Pr<sub>2</sub>O into MeCN solutions containing 1:1 ratios of hosts to guests at room temperature. Single crystals suitable for X-ray crystallography were selected and mounted in an inert oil and transferred to the cold N<sub>2</sub> gas stream of a Bruker Kappa APEX CCD area detector diffractometer. The crystals were kept at 100 K during the data collection. Using Olex2<sup>2</sup>, structures were resolved with the XT<sup>3</sup> structure solution program employing Dual Space and refined with the XL<sup>4</sup> refinement package using least squares minimization. All crystallographic data for the structures reported here have been deposited on to the Cambridge Crystallographic Data Centre (CCDC) and can be downloaded free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). The crystallographic information, structural parameters for **2**•2PF<sub>6</sub>, **4**•4PF<sub>6</sub>, **5**•4PF<sub>6</sub>, **6**•4PF<sub>6</sub>, **7**•4PF<sub>6</sub>, **pyrene**⊂**TzBox**•4PF<sub>6</sub>, **perylene**⊂**TzBox**•4PF<sub>6</sub>, **pyrene**⊂**DzBox**•4PF<sub>6</sub>, and **perylene**⊂**DzBox**•4PF<sub>6</sub> are as follows.

**2**•2PF<sub>6</sub> Crystal Parameters. [C<sub>14</sub>H<sub>14</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>]. Triclinic, space group *P*-1, *a* = 7.8767(6), *b* = 9.0304(8), *c* = 14.5443(12) Å, *α* = 75.627(4), *β* = 82.233(4), *γ* = 82.011(4)°, *V* = 986.95(14) Å<sup>3</sup>, *Z* = 2, *T* = 100 (2) K, *ρ*<sub>calc</sub> = 1.872 g cm<sup>-3</sup>. The final *R*<sub>1</sub> was 0.0277 and *wR*<sub>2</sub> was 0.0714 (all data). CCDC number 1972857.

**4**•4PF<sub>6</sub> Crystal Parameters. [C<sub>54</sub>H<sub>53</sub>F<sub>24</sub>N<sub>19</sub>P<sub>4</sub>]. Monoclinic, space group *P*12<sub>1</sub>/*c*1, *a* = 17.4620(7), *b* = 20.4049(7), *c* = 19.1126(7) Å, *α* = 90, *β* = 90.954(2), *γ* = 90°, *V* = 6809.1(5) Å<sup>3</sup>, *Z* = 4, *T* = 100 (2) K, *ρ*<sub>calc</sub> = 1.510 g cm<sup>-3</sup>. The final *R*<sub>1</sub> was 0.0628 and *wR*<sub>2</sub> was 0.1770 (all data). CCDC number 1972858.

**5**•4PF<sub>6</sub> Crystal Parameters. [C<sub>26</sub>H<sub>27</sub>F<sub>12</sub>N<sub>9</sub>P<sub>2</sub>]. Triclinic, space group *P*-1, *a* = 10.3447(4),



$b = 11.4860(4)$ ,  $c = 17.3882(6)$  Å,  $\alpha = 104.290(2)$ ,  $\beta = 94.193(2)$ ,  $\gamma = 112.848(2)^\circ$ ,  $V = 1811.71(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 100$  (2) K,  $\rho_{\text{calc}} = 1.385$  g cm<sup>-3</sup>. The final  $R_1$  was 0.0516 and  $wR_2$  was 0.1422 (all data). CCDC number 1972862.

**6•4PF<sub>6</sub>** Crystal Parameters. [C<sub>40</sub>H<sub>40</sub>F<sub>18</sub>N<sub>12</sub>P<sub>3</sub>]. Monoclinic, space group  $C12/c1$ ,  $a = 16.1323(5)$ ,  $b = 11.4829(4)$ ,  $c = 30.2137(9)$  Å,  $\alpha = 90$ ,  $\beta = 101.490(2)$ ,  $\gamma = 90^\circ$ ,  $V = 5484.8(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 100$  (2) K,  $\rho_{\text{calc}} = 1.361$  cm<sup>-3</sup>. The final  $R_1$  was 0.0405 and  $wR_2$  was 0.1091 (all data). CCDC number 1972863.

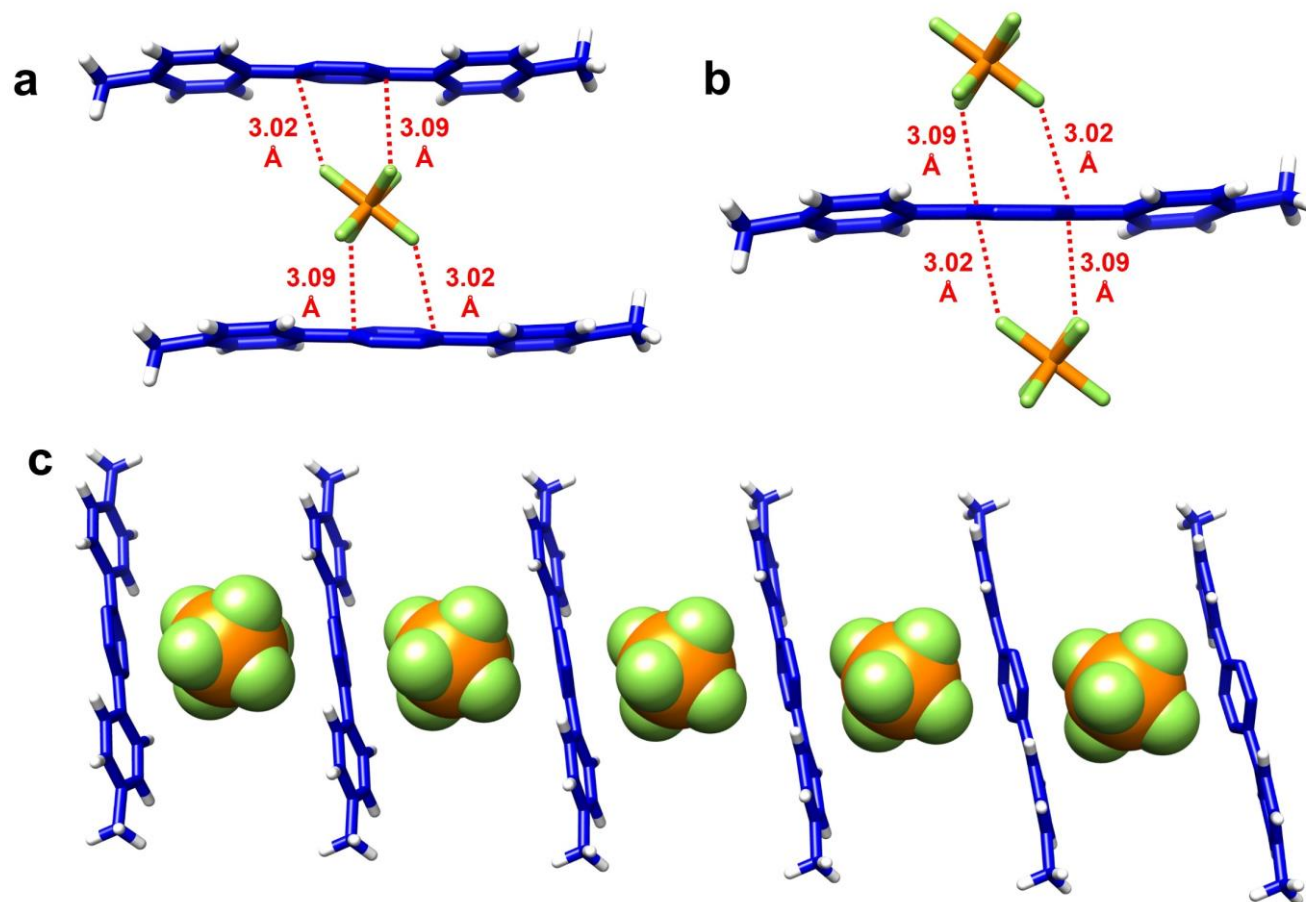
**7•4PF<sub>6</sub>** Crystal Parameters. [C<sub>46</sub>H<sub>39</sub>F<sub>24</sub>N<sub>9</sub>P<sub>4</sub>]. Triclinic, space group  $P-1$ ,  $a = 13.3898(4)$ ,  $b = 14.5809(4)$ ,  $c = 15.0625(4)$  Å,  $\alpha = 106.7410(10)$ ,  $\beta = 99.5330(10)$ ,  $\gamma = 110.0920(10)^\circ$ ,  $V = 2527.68(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 100$  (2) K,  $\rho_{\text{calc}} = 1.705$  g cm<sup>-3</sup>. The final  $R_1$  was 0.0607 and  $wR_2$  was 0.1704 (all data). CCDC number 1972859.

**Pyrene⊂TzBox•4PF<sub>6</sub>** Crystal Parameters. [C<sub>64</sub>H<sub>54</sub>F<sub>24</sub>N<sub>18</sub>P<sub>4</sub>]. Triclinic, space group  $P-1$ ,  $a = 10.8605(4)$ ,  $b = 13.1591(5)$ ,  $c = 13.4694(5)$  Å,  $\alpha = 81.307(2)$ ,  $\beta = 87.8564(18)$ ,  $\gamma = 67.7952(17)^\circ$ ,  $V = 1761.33(12)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 100(2)$  K,  $\rho_{\text{calc}} = 1.534$  g cm<sup>-3</sup>. The final  $R_1$  was 0.0644 and  $wR_2$  was 0.1839 (all data). CCDC number 1972860.

**Perylene⊂TzBox•4PF<sub>6</sub>** Crystal Parameters. [C<sub>68</sub>H<sub>56</sub>F<sub>24</sub>N<sub>16</sub>P<sub>4</sub>]. Triclinic, space group  $P-1$ ,  $a = 10.8276(8)$ ,  $b = 13.2652(9)$ ,  $c = 13.6121(10)$  Å,  $\alpha = 81.996(3)$ ,  $\beta = 89.523(3)$ ,  $\gamma = 67.586(3)^\circ$ ,  $V = 1787.7(2)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 100(2)$  K,  $\rho_{\text{calc}} = 1.558$  g cm<sup>-3</sup>. The final  $R_1$  was 0.0507 and  $wR_2$  was 0.1403 (all data). CCDC number 1972864.

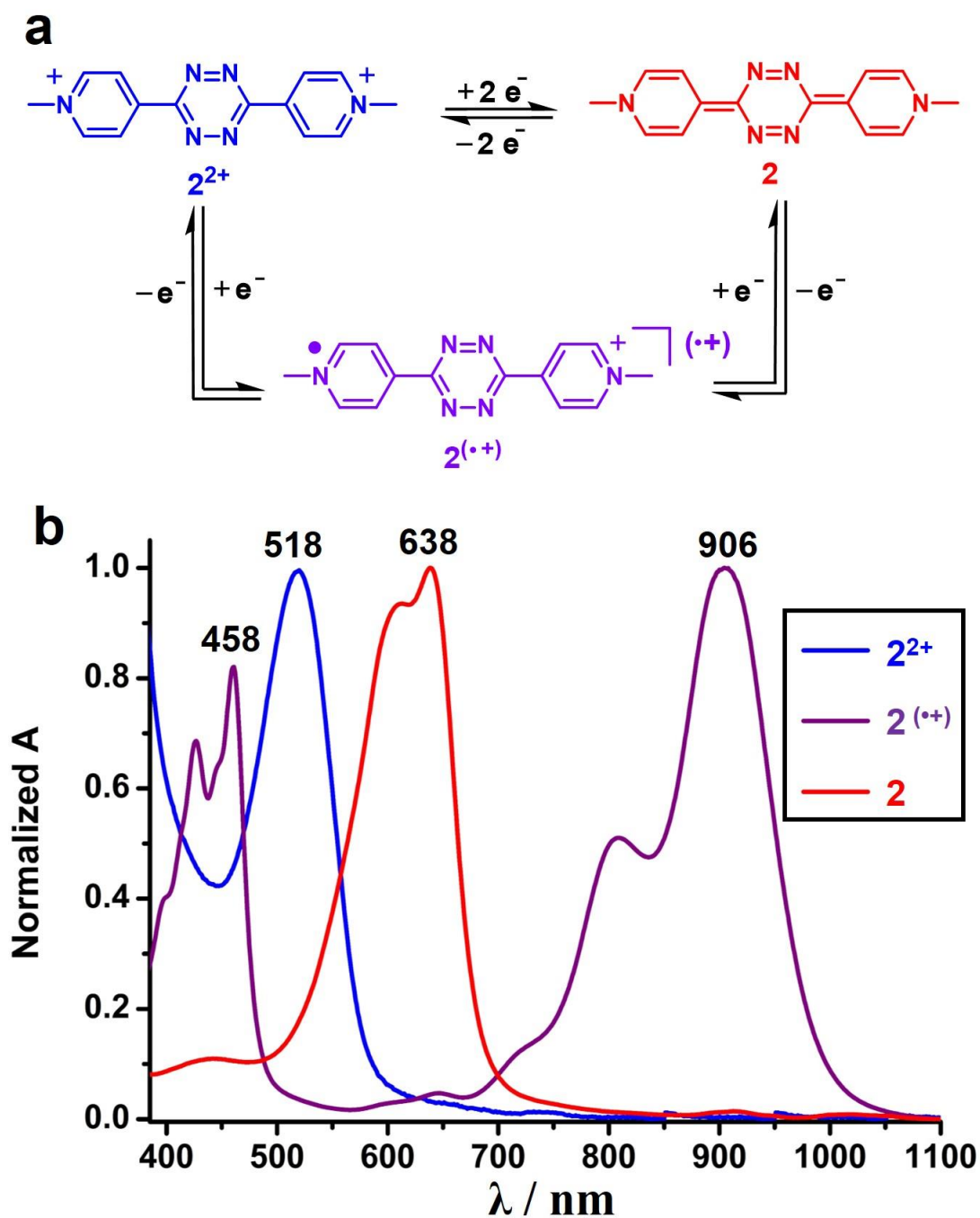
**Pyrene⊂DzBox•4PF<sub>6</sub>** Crystal Parameters. [C<sub>68</sub>H<sub>58</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>]. Triclinic, space group  $P-1$ ,  $a = 10.4268(5)$ ,  $b = 11.1641(5)$ ,  $c = 17.3653(8)$  Å,  $\alpha = 74.541(3)$ ,  $\beta = 80.014(3)$ ,  $\gamma = 63.639(2)^\circ$ ,  $V = 1742.15(15)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 100(2)$  K,  $\rho_{\text{calc}} = 1.547$  g cm<sup>-3</sup>. The final  $R_1$  was 0.0609 and  $wR_2$  was 0.1699 (all data). CCDC number 1972861.

**Perylene⊂DzBox•4PF<sub>6</sub>** Crystal Parameters. [C<sub>72</sub>H<sub>60</sub>F<sub>24</sub>N<sub>12</sub>P<sub>4</sub>]. Triclinic, space group  $P-1$ ,  $a = 10.4662(5)$ ,  $b = 11.0351(5)$ ,  $c = 17.4251(8)$  Å,  $\alpha = 74.1610(15)$ ,  $\beta = 78.6350(15)$ ,  $\gamma = 65.1600(10)^\circ$ ,  $V = 1749.15(14)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 100(2)$  K,  $\rho_{\text{calc}} = 1.5883$  g cm<sup>-3</sup>. The final  $R_1$  was 0.0454 and  $wR_2$  was 0.1191 (all data). CCDC number 1972865.

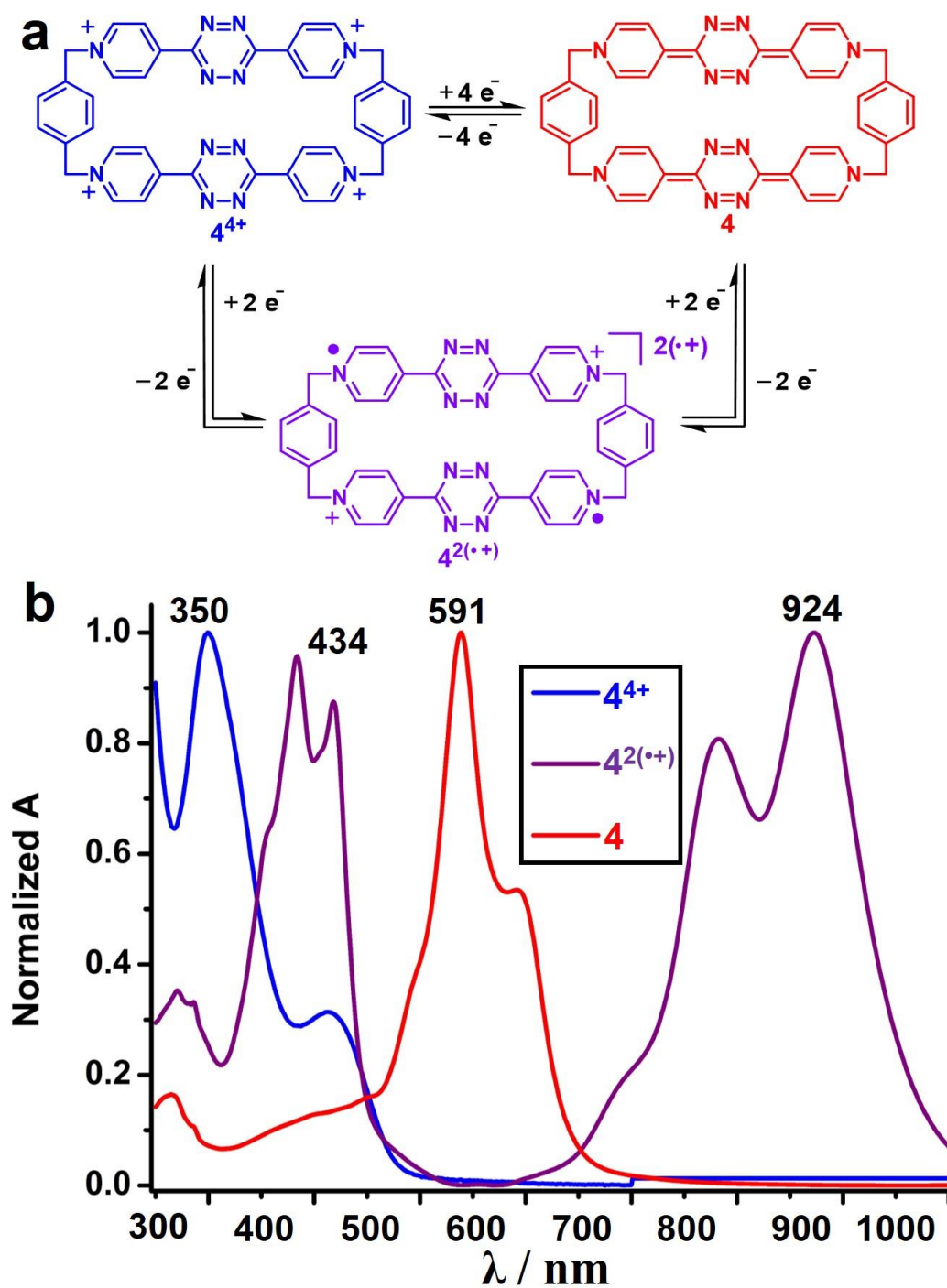


**Figure S1.** The multiple anion– $\pi$  interactions between  $\text{PF}_6^-$  counterions and  $\pi$  electron-deficient  $2^{2+}$  fragments in the superstructures of  $2 \cdot 2\text{PF}_6$ . **(a)** One  $\text{PF}_6^-$  counterion interacts with two  $2^{2+}$  fragments. **(b)** One  $2^{2+}$  fragment interacts with two  $\text{PF}_6^-$  counterions. **(c)**  $2^{2+}$  fragments and  $\text{PF}_6^-$  counterions assemble into a 1D superstructure.

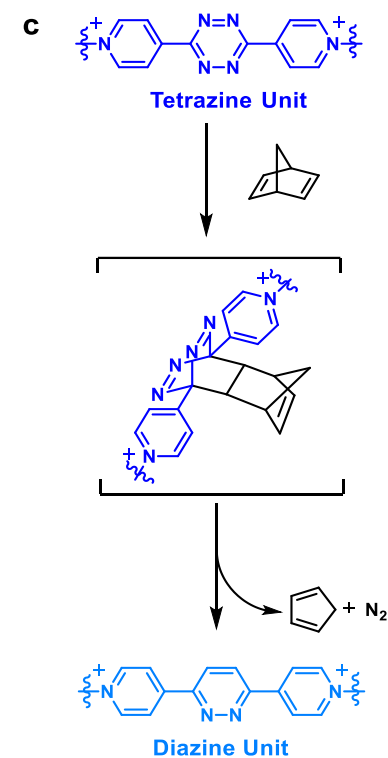
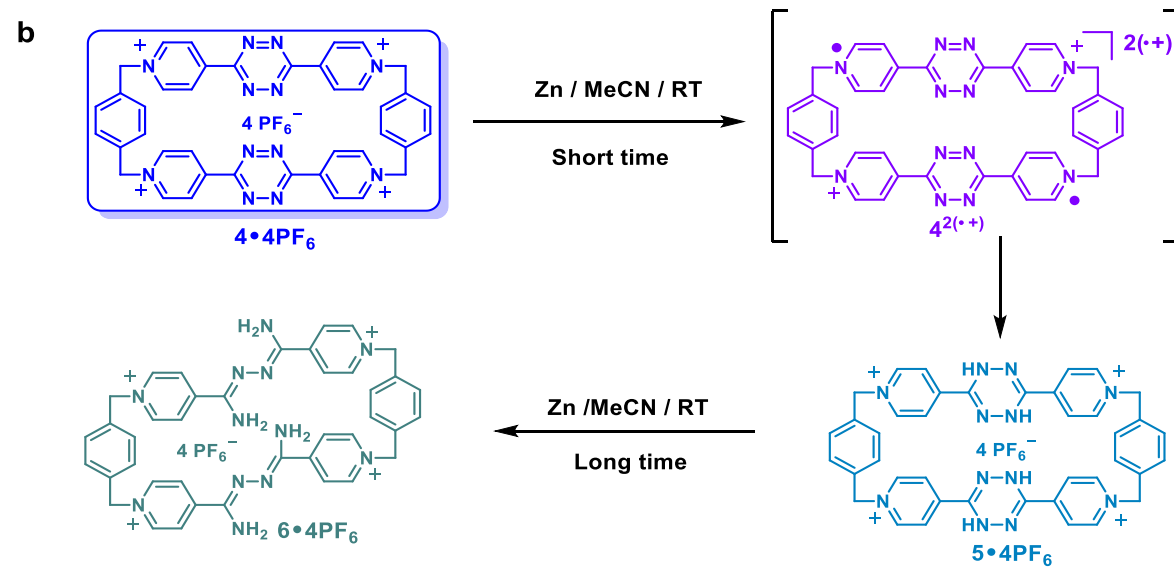
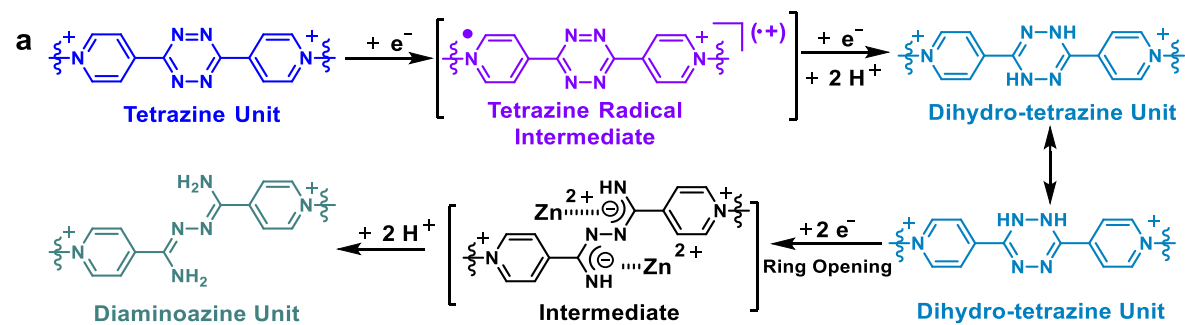
## Section D. Redox Chemistry and UV–Vis–NIR Spectra



**Figure S2.** (a) Structural formulas of the three redox states of  $2 \cdot 2\text{PF}_6$ . (b) Normalized UV–Vis–NIR absorption spectra of  $2^{2+/(•+)/0}$ , which were obtained by the stepwise addition of 0, 1.0, and 2.0 equiv of  $\text{CoCp}_2$ . All spectra were recorded in Ar-purged DMF solutions at 298 K.



**Figure S3.** (a) Structural formulas of the three redox states of  $4\bullet 4\text{PF}_6$ . (b) Normalized UV-Vis-NIR absorption spectra of  $4^{4+/2(•+)/0}$ , which were obtained by the stepwise addition of 0, 2.0, and 4.0 equiv of  $\text{CoCp}_2$ . All spectra were recorded in Ar-purged DMF solutions at 298 K.



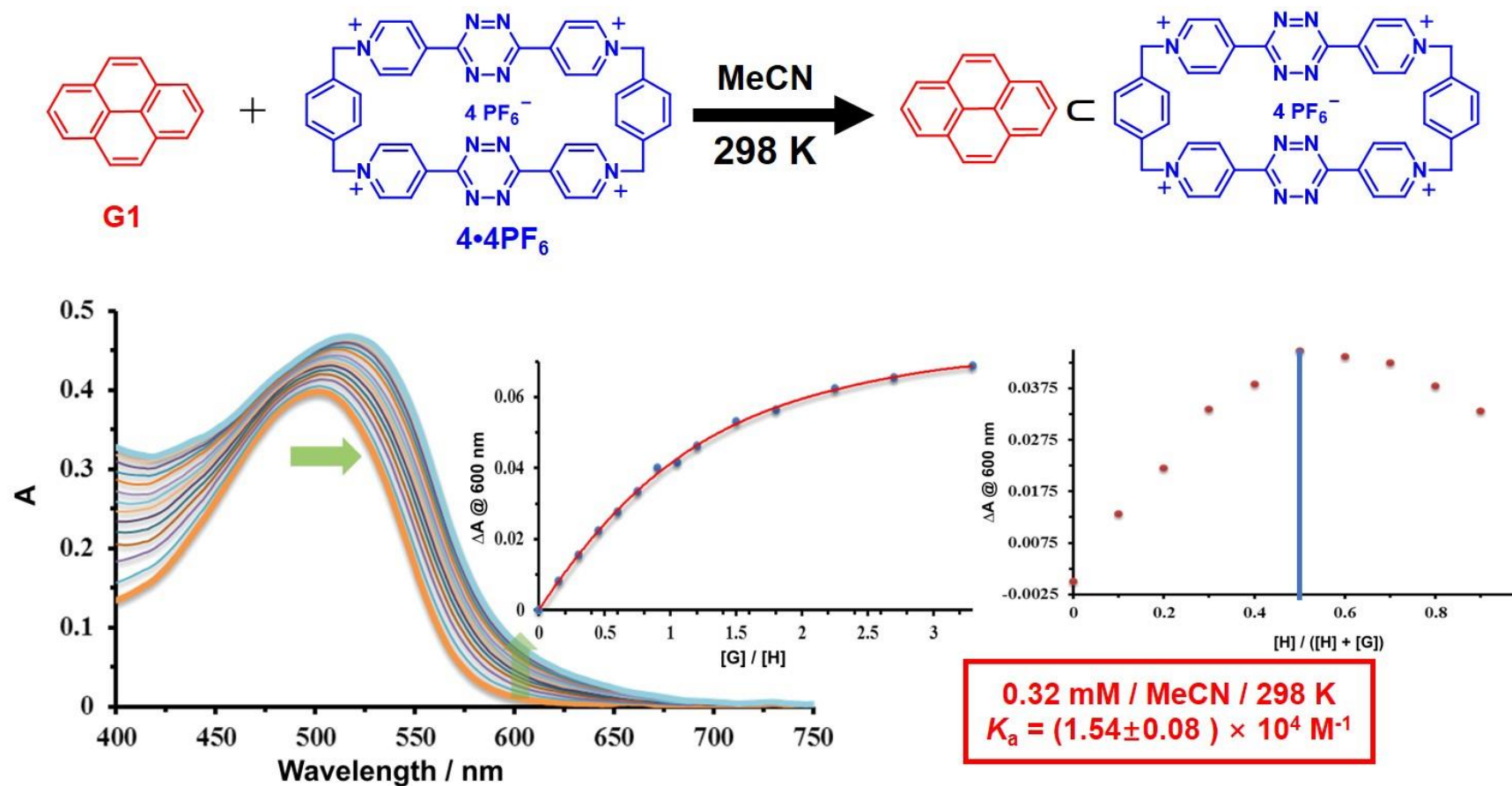
Inverse Electron-Demand Diels-Alder (IEDDA) Reaction

**Scheme S7.** (a) The mechanism for the metal-mediated reduction, in which radical intermediates are involved. (b) Box-to-box transformation. (c) inverse electron-demand Diels-Alder (IEDDA) reaction.

**Table S1.** The Heights, Widths and Lengths of **TzBox<sup>4+</sup>**, **DzBox<sup>4+</sup>**, **DHTzBox<sup>4+</sup>**, and **DAzBox<sup>4+</sup>**.

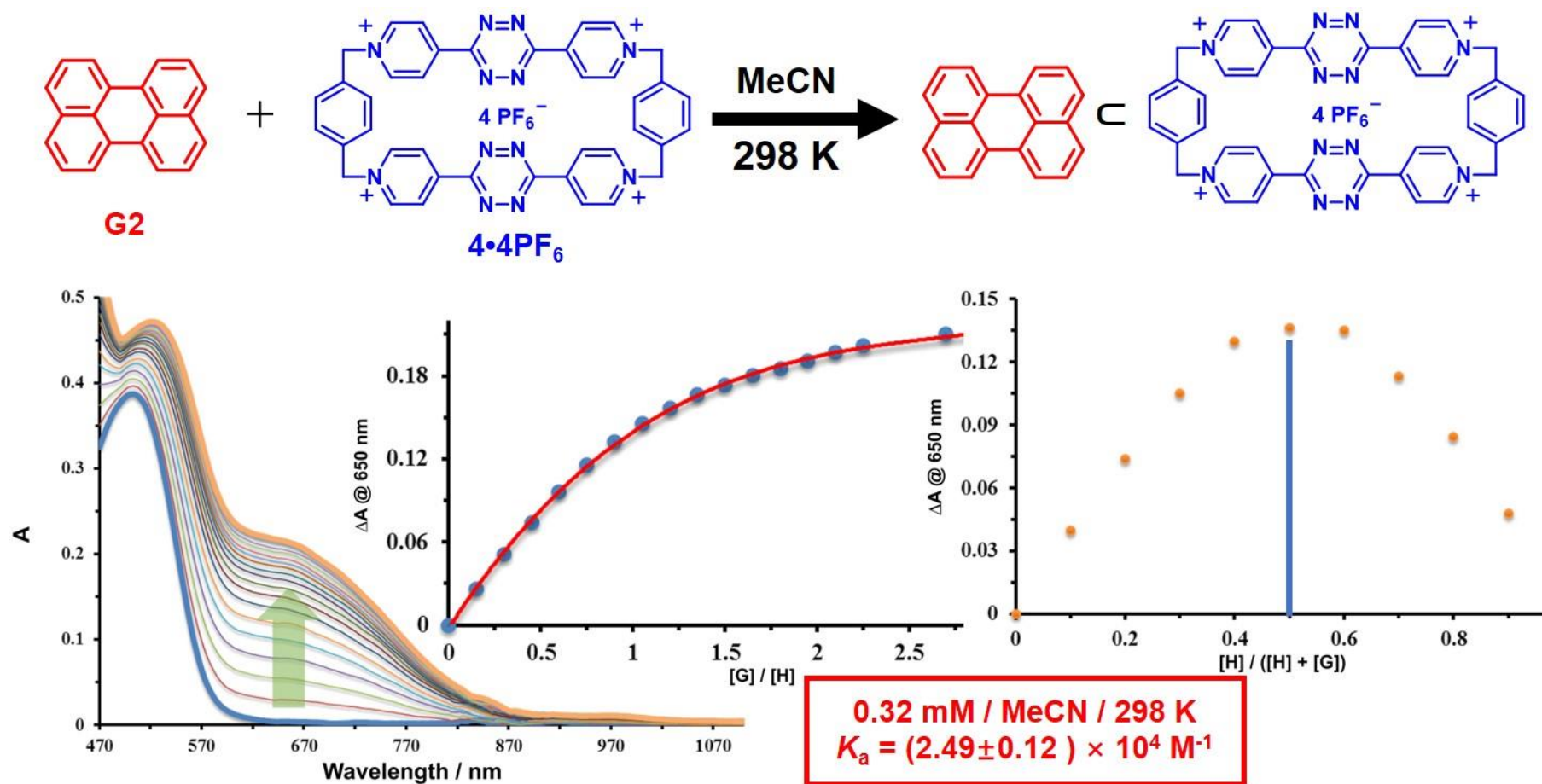
	Height (Å)	Width (Å)	Length (Å)
<b>TzBox<sup>4+</sup></b>	4.53	7.29	14.15
<b>DzBox<sup>4+</sup></b>	4.33	6.99	14.49
<b>DHTzBox<sup>4+</sup></b>	4.03	9.31	13.77
<b>DAzBox<sup>4+</sup></b>	5.69	7.12	14.38

### Section E. Regulatable Binding Affinities



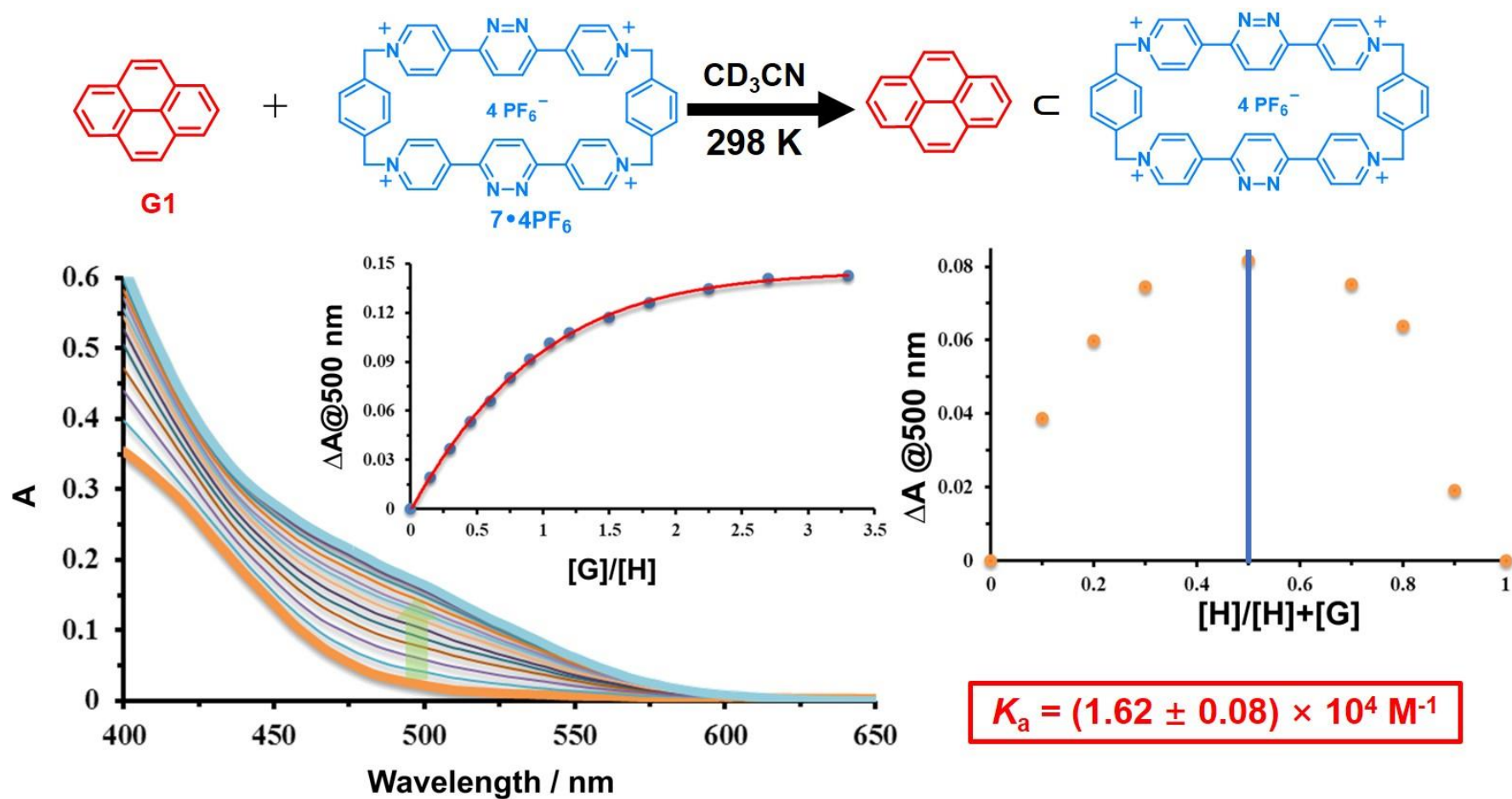
**Figure S4.** UV–Vis absorption spectrum of **4•4PF<sub>6</sub>** titrated by **pyrene** in MeCN solution at room temperature. A charge-transfer (CT) band appears. Job plot experiments 1:1 stoichiometry. The binding constant  $K_a$  was calculated to be  $(1.54 \pm 0.08) \times 10^4 \text{ M}^{-1}$ .



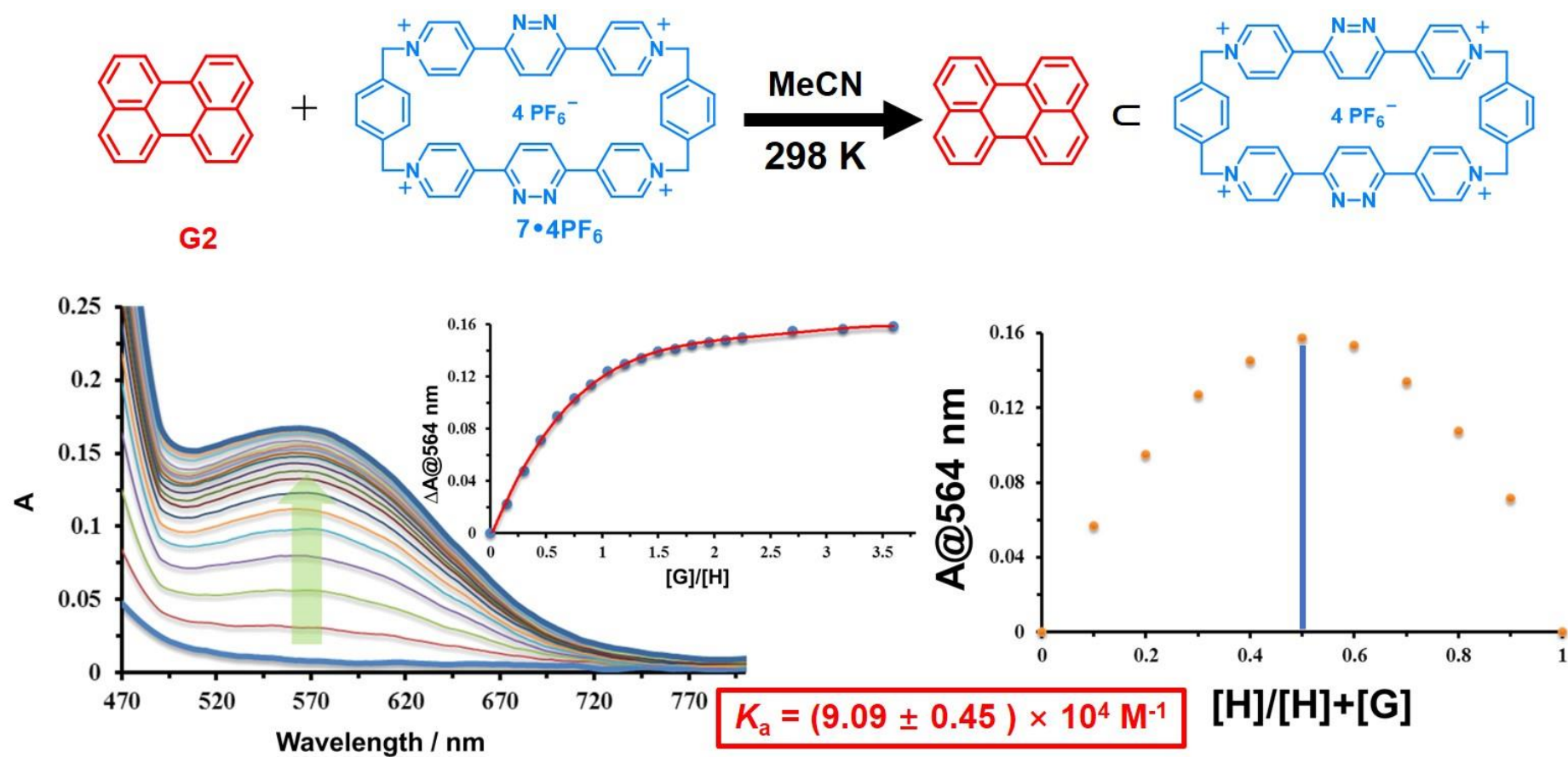


**Figure S5.** UV–Vis absorption spectrum of 4•4PF<sub>6</sub> titrated by **perylene** in MeCN solution at room temperature. A charge-transfer (CT) band at around 650 nm appears. Job plot experiments 1:1 stoichiometry. The binding constant  $K_a$  was calculated to be  $(2.49 \pm 0.12) \times 10^4 \text{ M}^{-1}$ .

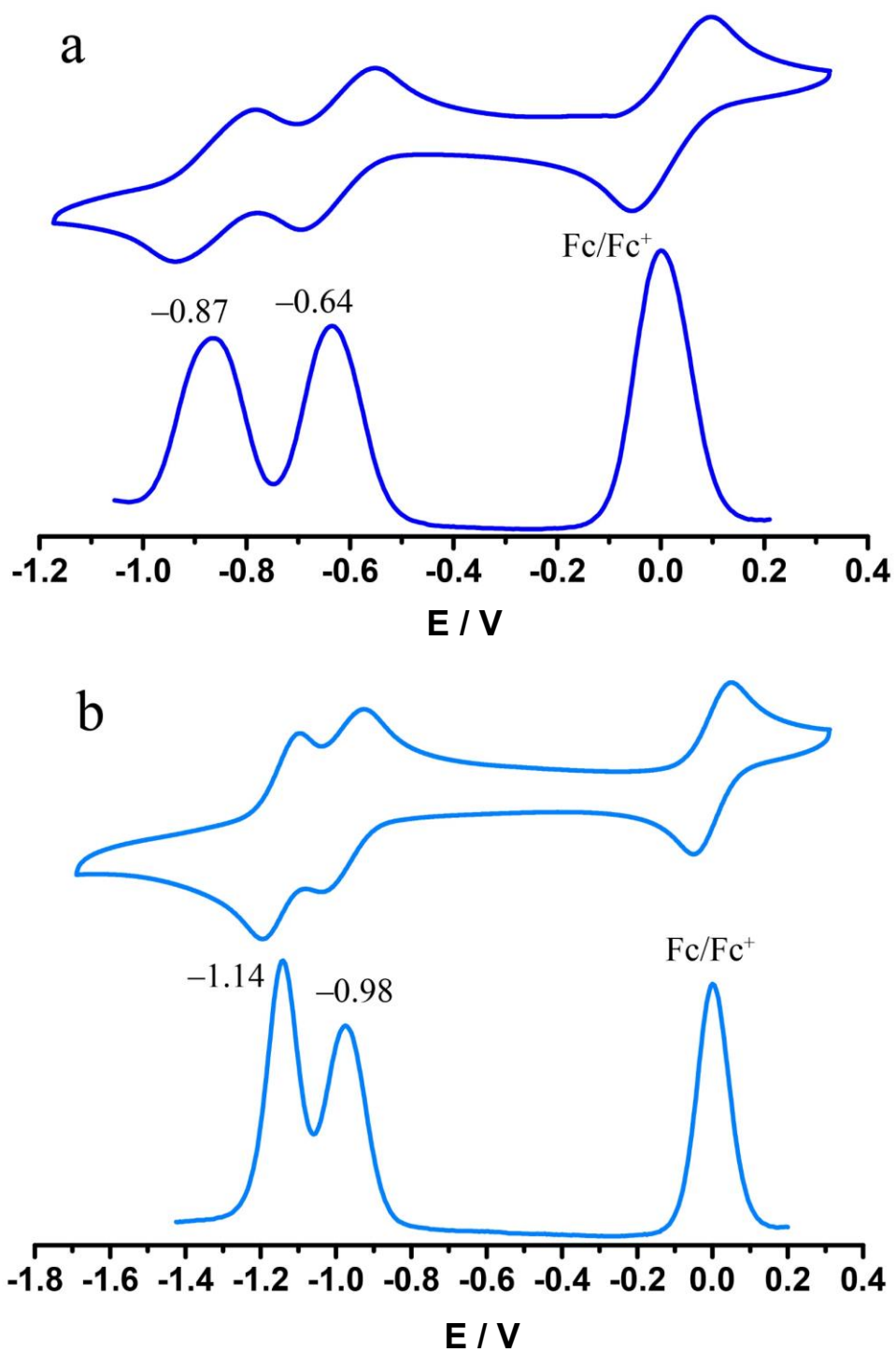




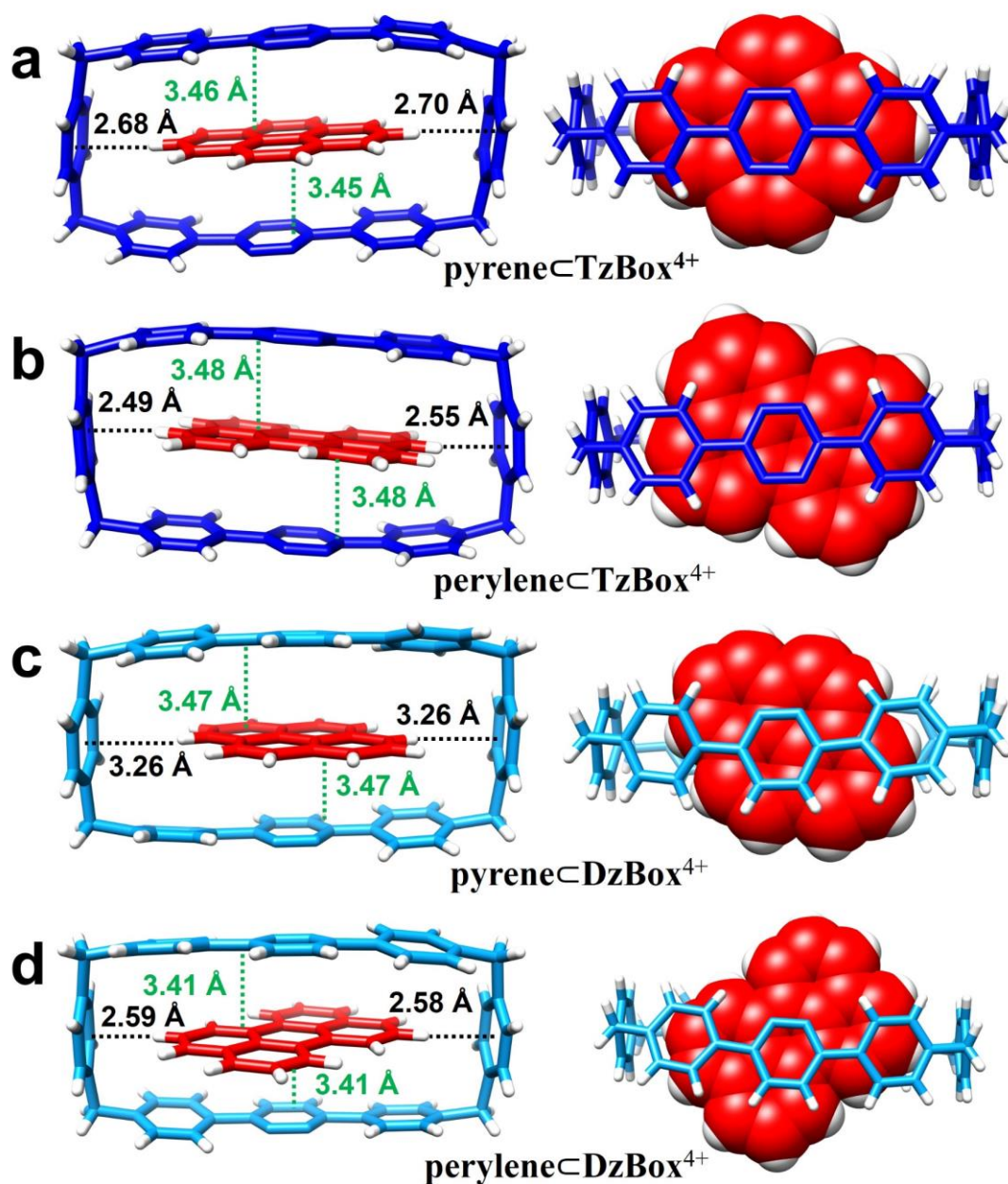
**Figure S6.** UV–Vis absorption spectrum of 4•4PF<sub>6</sub> titrated by **pyrene** in MeCN solution at room temperature. A charge-transfer (CT) band at around 500 nm appears. Job plot experiments 1:1 stoichiometry. The binding constant  $K_a$  was calculated to be  $(1.62 \pm 0.08) \times 10^4 \text{ M}^{-1}$ .



**Figure S7.** UV–Vis absorption spectrum of **7•4PF<sub>6</sub>** titrated by **perylene** in MeCN solution at room temperature. A charge-transfer (CT) band at around 564 nm appears. Job plot experiments 1:1 stoichiometry. The binding constant  $K_a$  was calculated to be  $(9.09 \pm 0.45) \times 10^4 \text{ M}^{-1}$ .

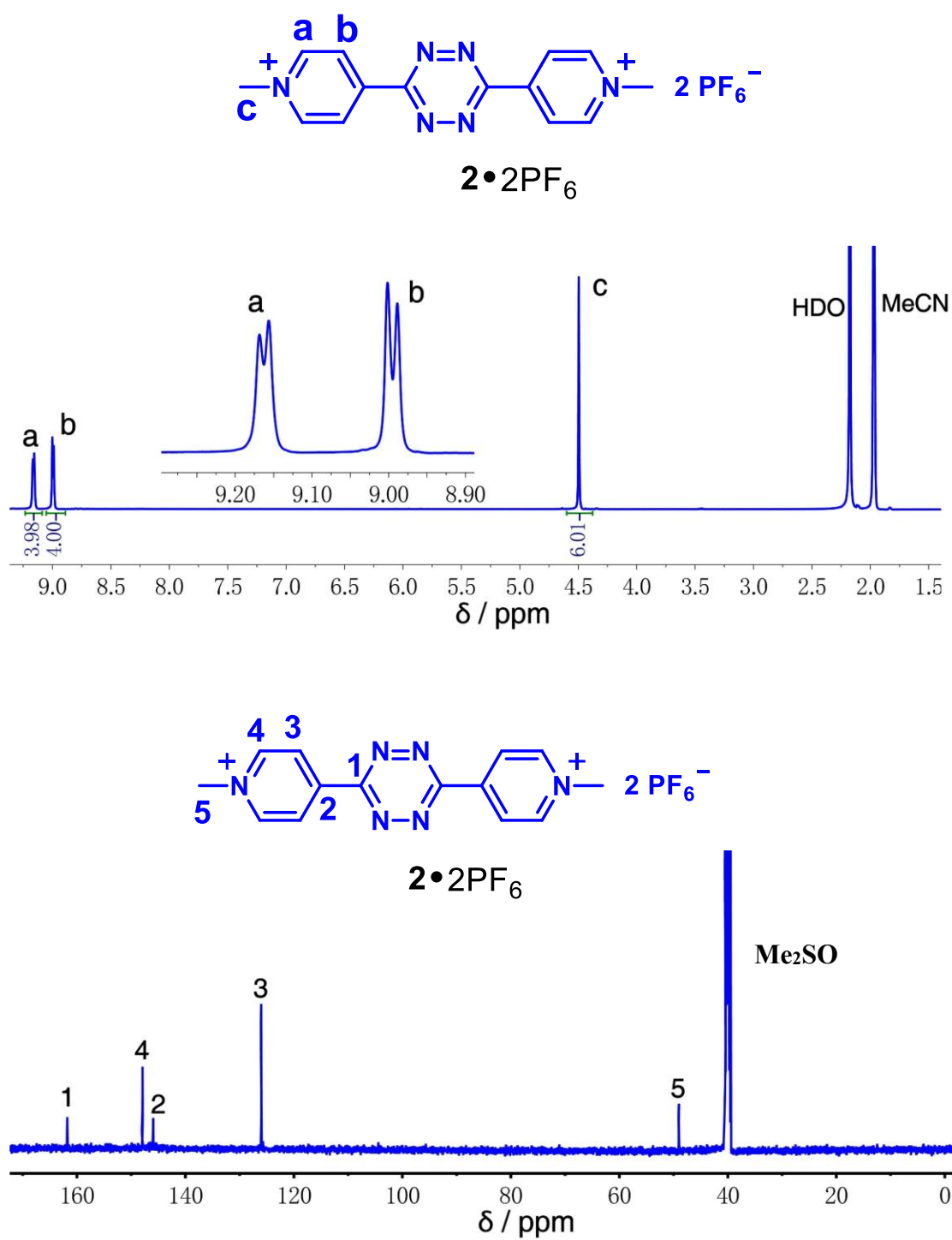


**Figure S8.** Cyclic voltammogram (CV) and differential pulse voltammetry (DPV) of (a) **TzBox**•4PF<sub>6</sub> and (b) **DzBox**•4PF<sub>6</sub> with their reduction potentials highlighted.

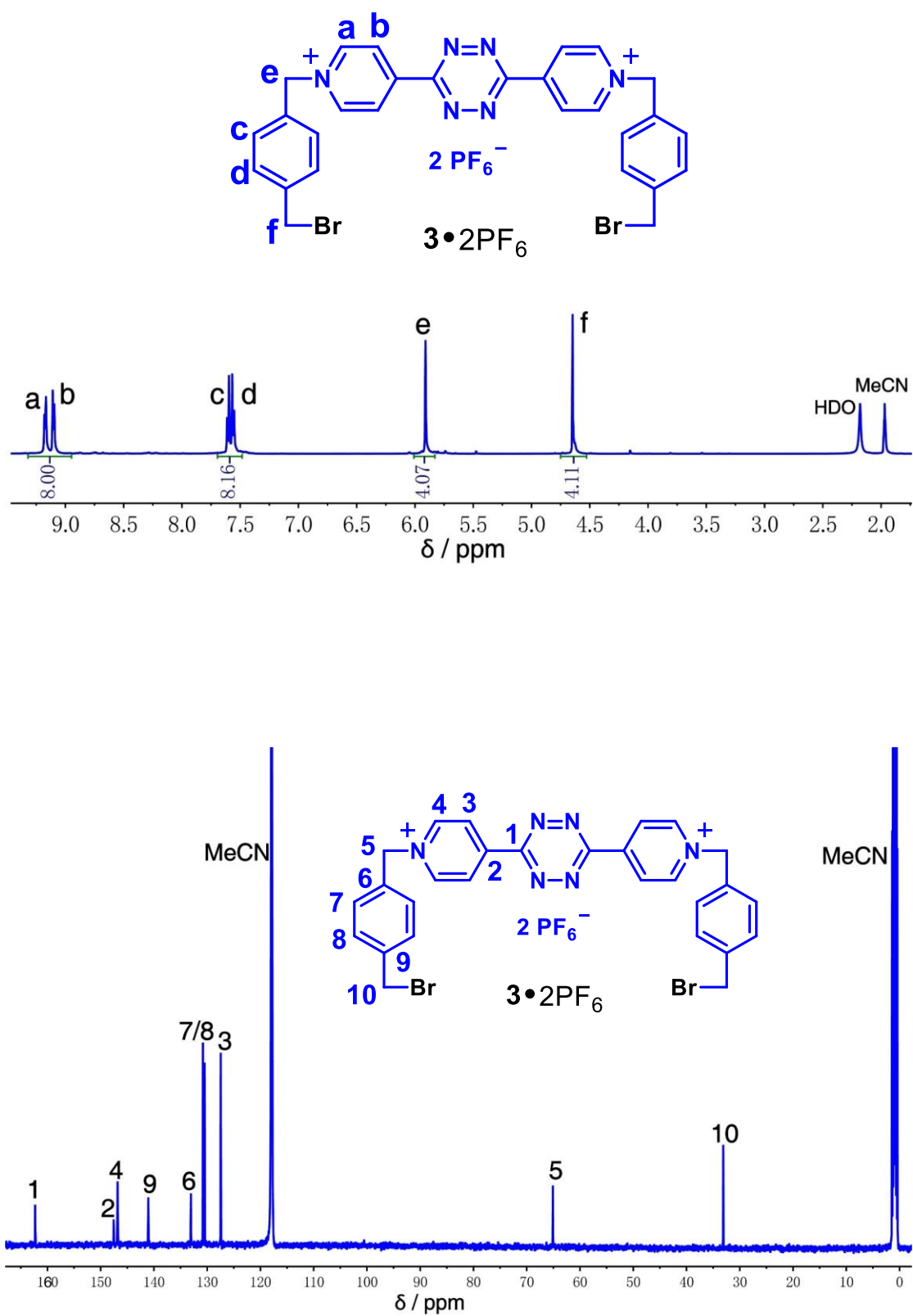


**Figure S9.** Tubular and mixed tubular/space-filling representations single crystal superstructures of the 1:1 inclusion complexes formed by  $[\pi \cdots \pi]$  interactions and  $[\text{C}-\text{H} \cdots \pi]$  interactions. (a) The  $\text{pyrene} \subset \text{TzBox}^{4+}$  1:1 inclusion complex. (b) The  $\text{peryene} \subset \text{TzBox}^{4+}$  1:1 inclusion complex. (c) The  $\text{pyrene} \subset \text{DzBox}^{4+}$  1:1 inclusion complex. (d) The  $\text{peryene} \subset \text{DzBox}^{4+}$  1:1 inclusion complex.

## Section F. NMR Spectroscopy

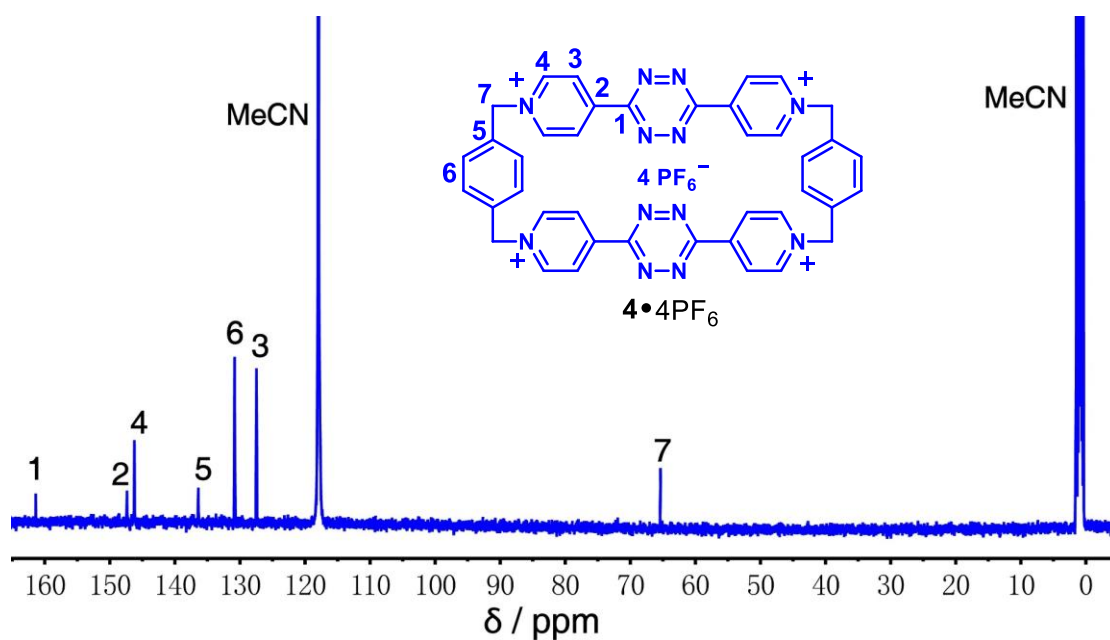
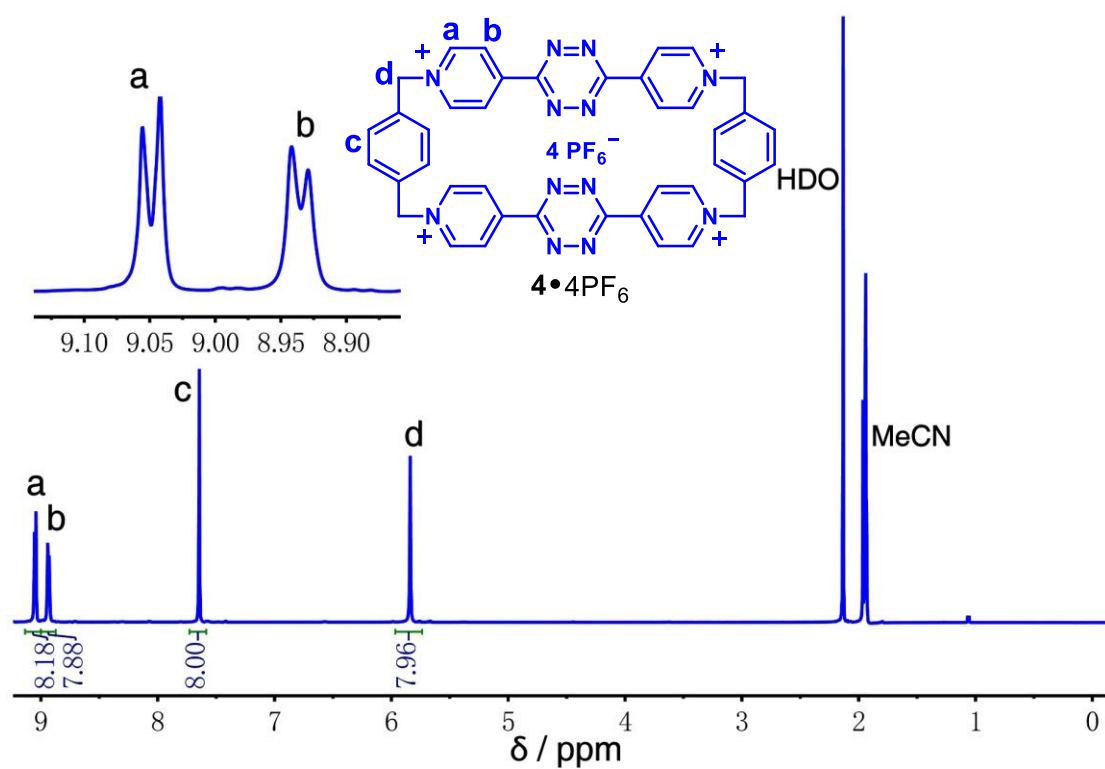


**Figure S10.** <sup>1</sup>H (top) and <sup>13</sup>C(bottom) NMR spectra of **2•2PF<sub>6</sub>**.



**Figure S11.** <sup>1</sup>H (top) and <sup>13</sup>C(bottom) NMR spectra of **3**•2PF<sub>6</sub>.





**Figure S12.** <sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of 4•4PF<sub>6</sub>.

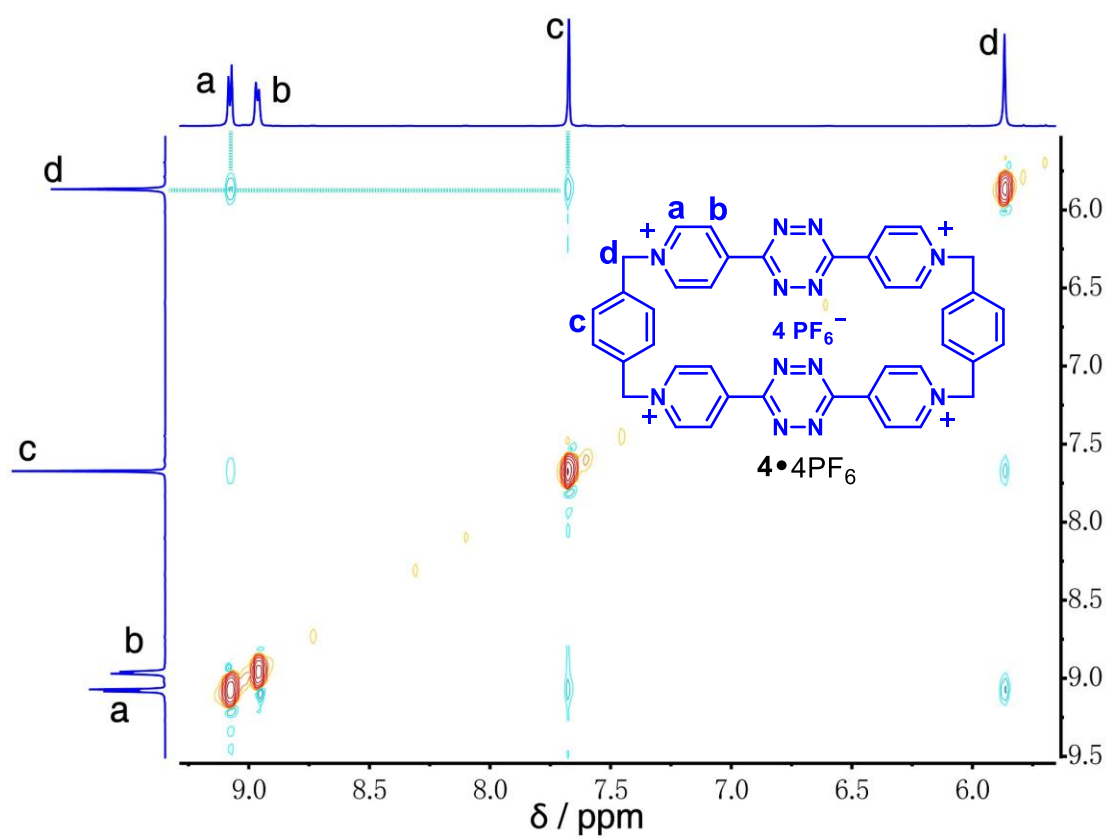
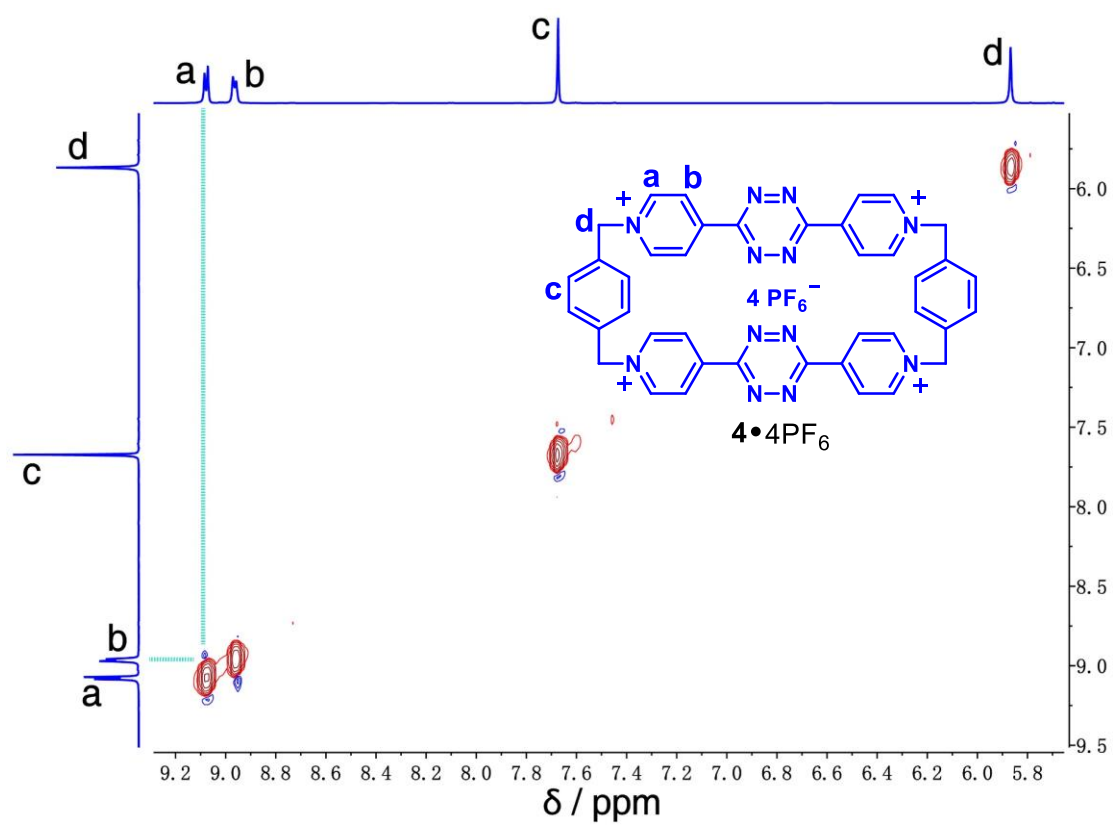
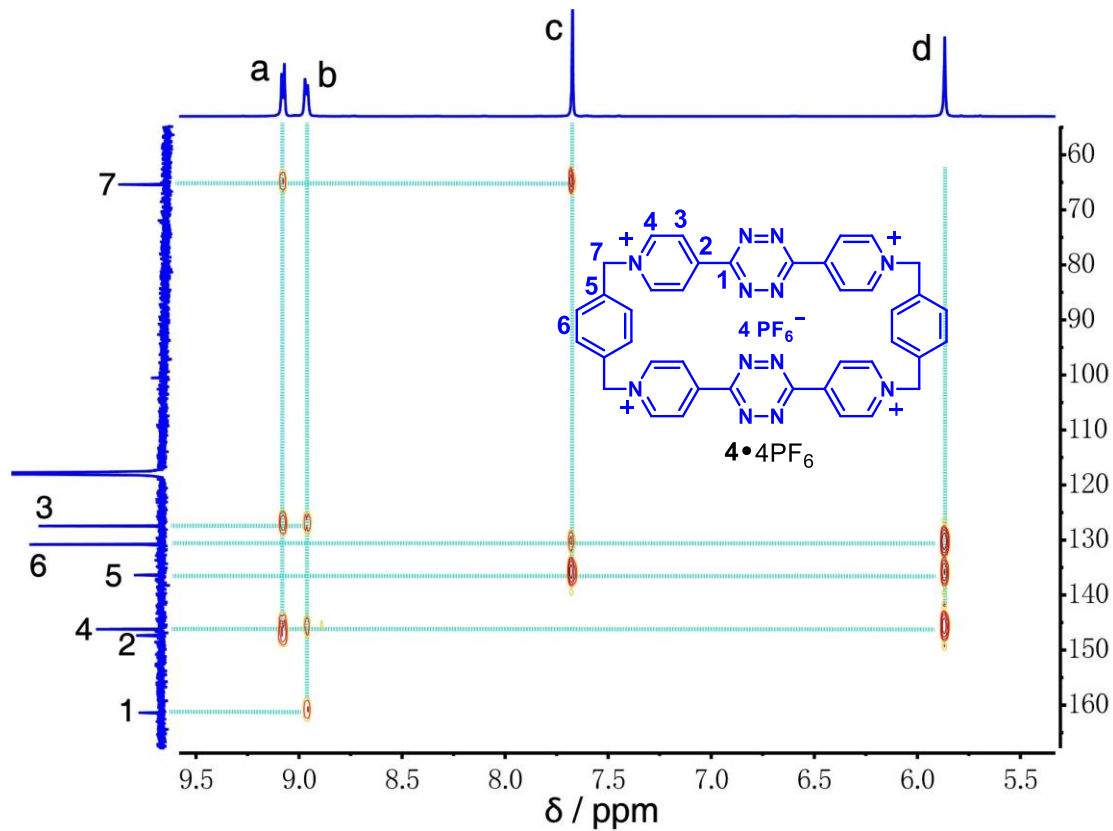
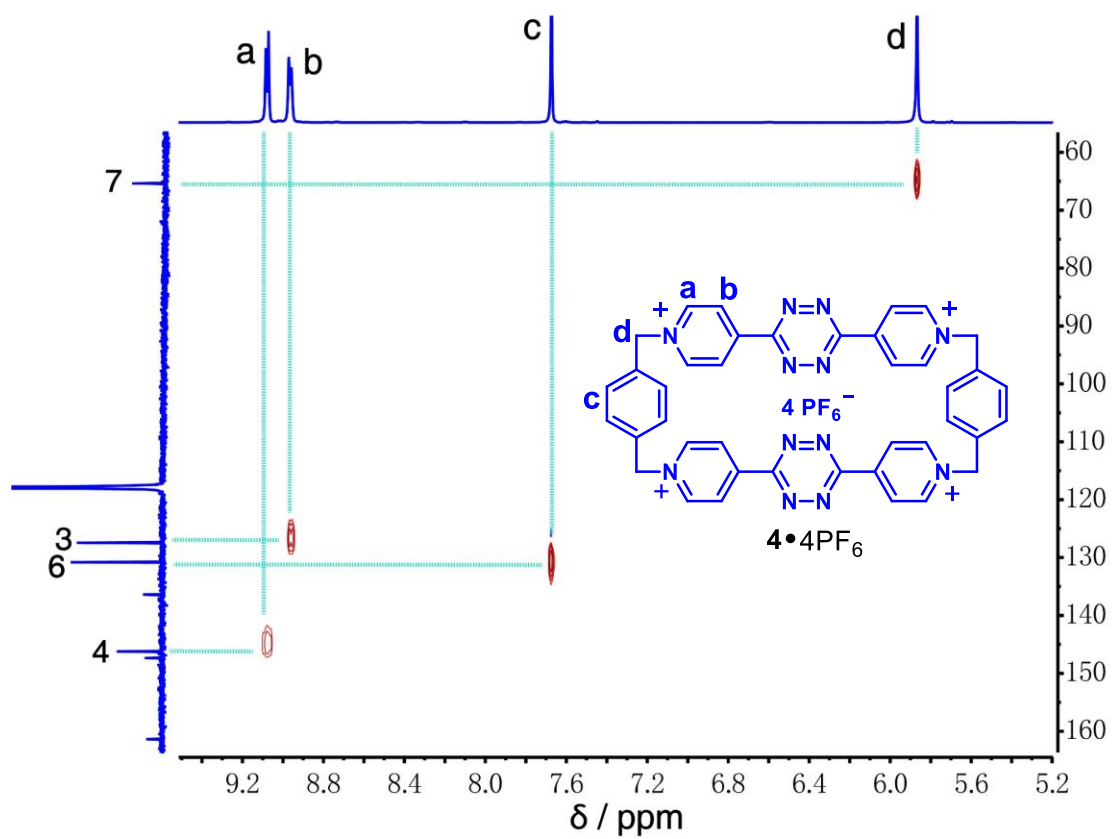
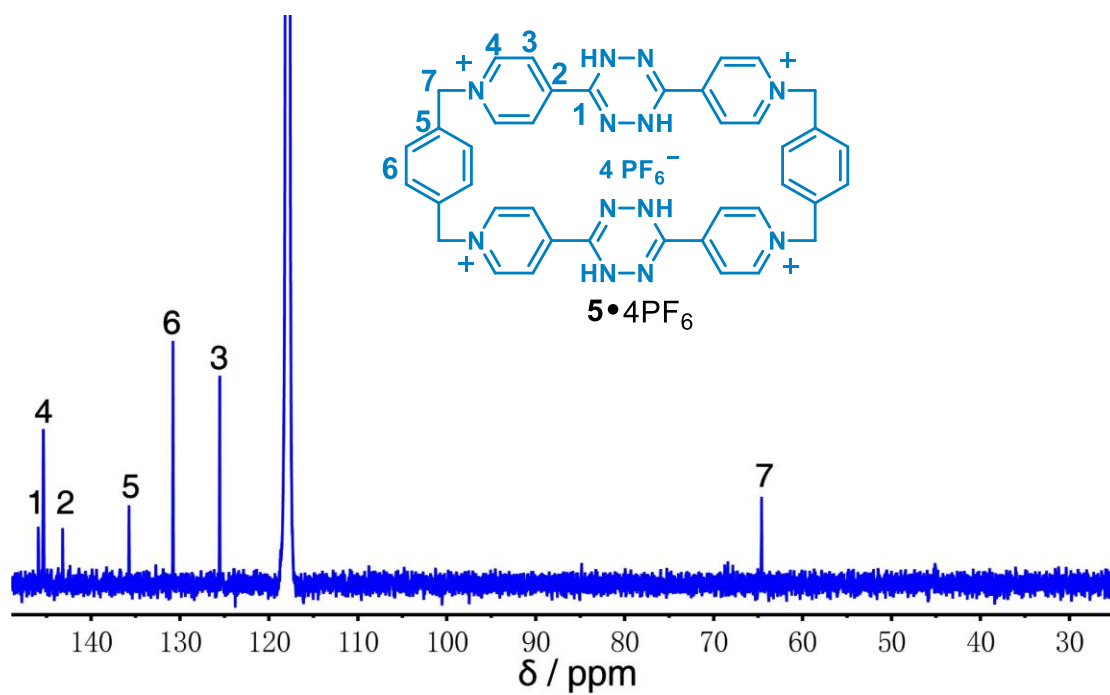
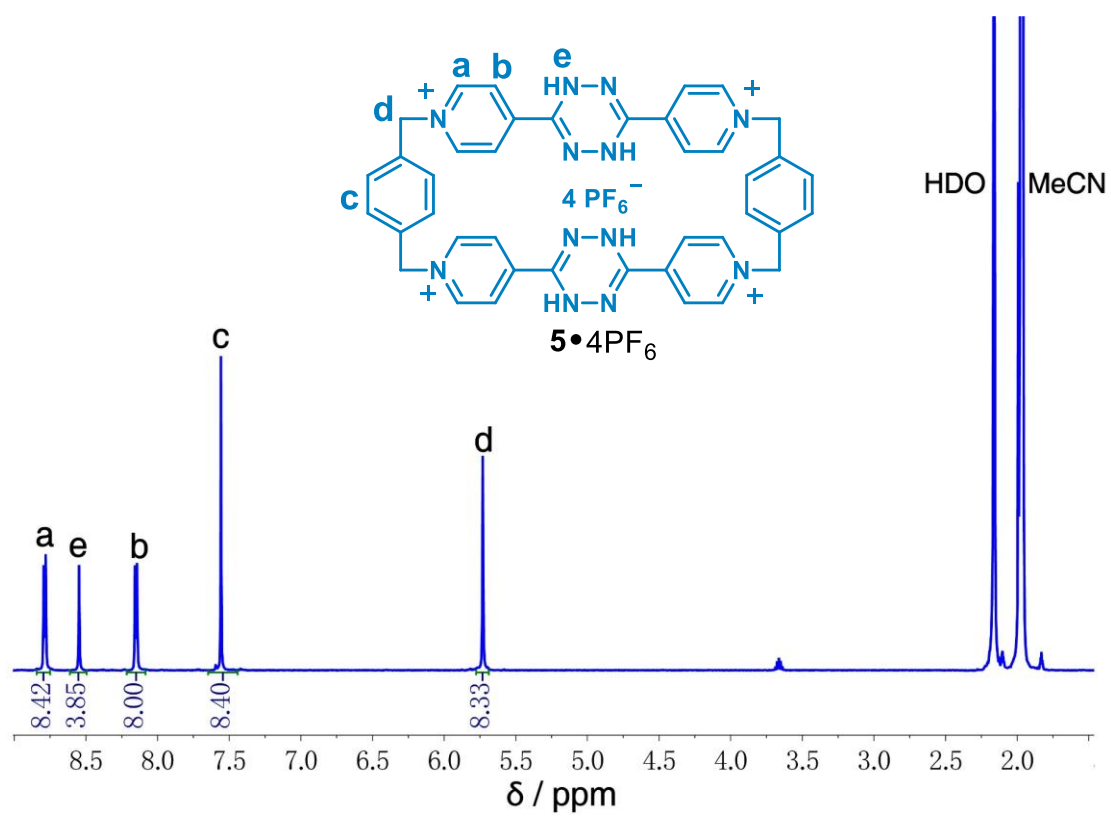


Figure S13. H-H COSY (top) and NOSY (bottom) NMR spectra of  $4\bullet 4PF_6$ .

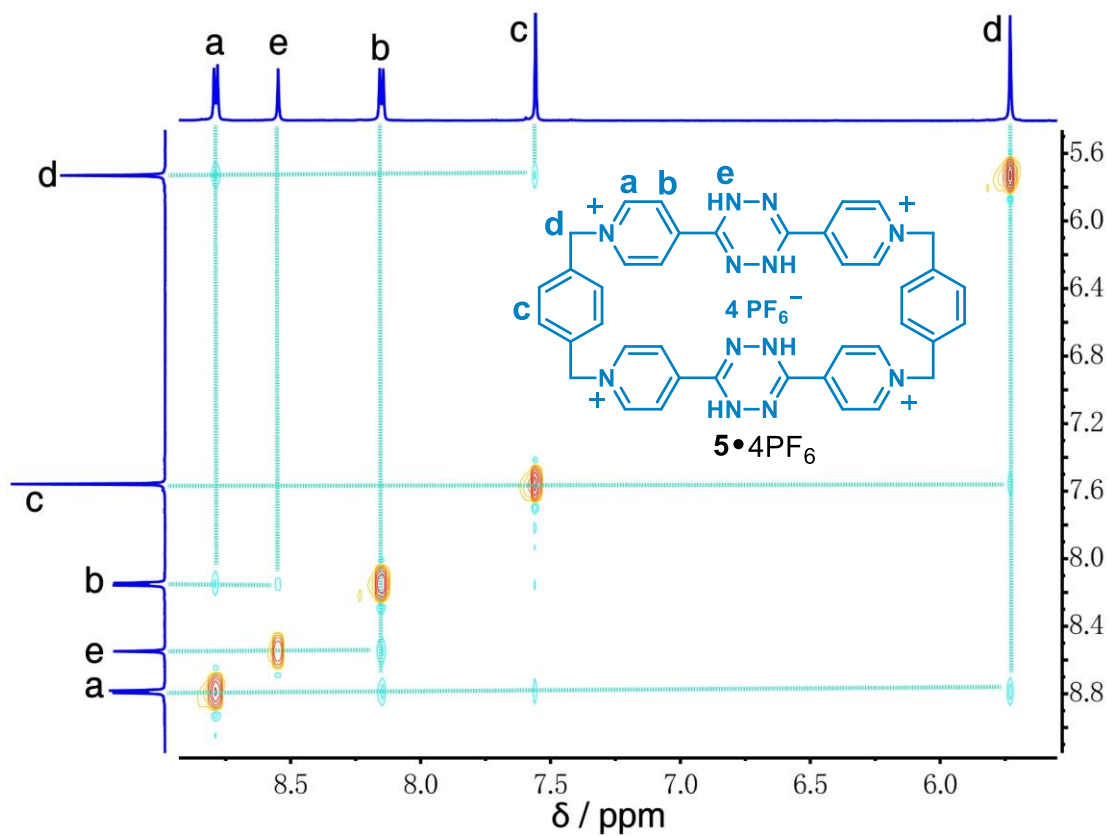
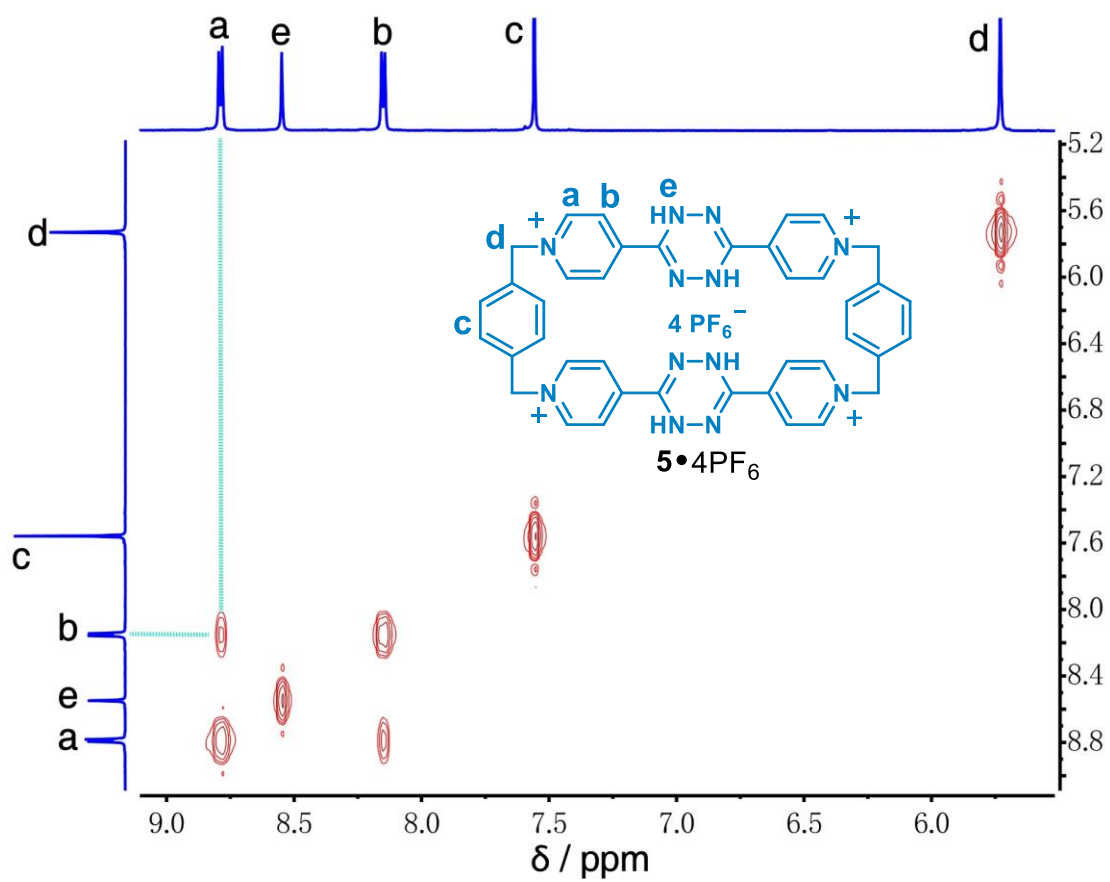




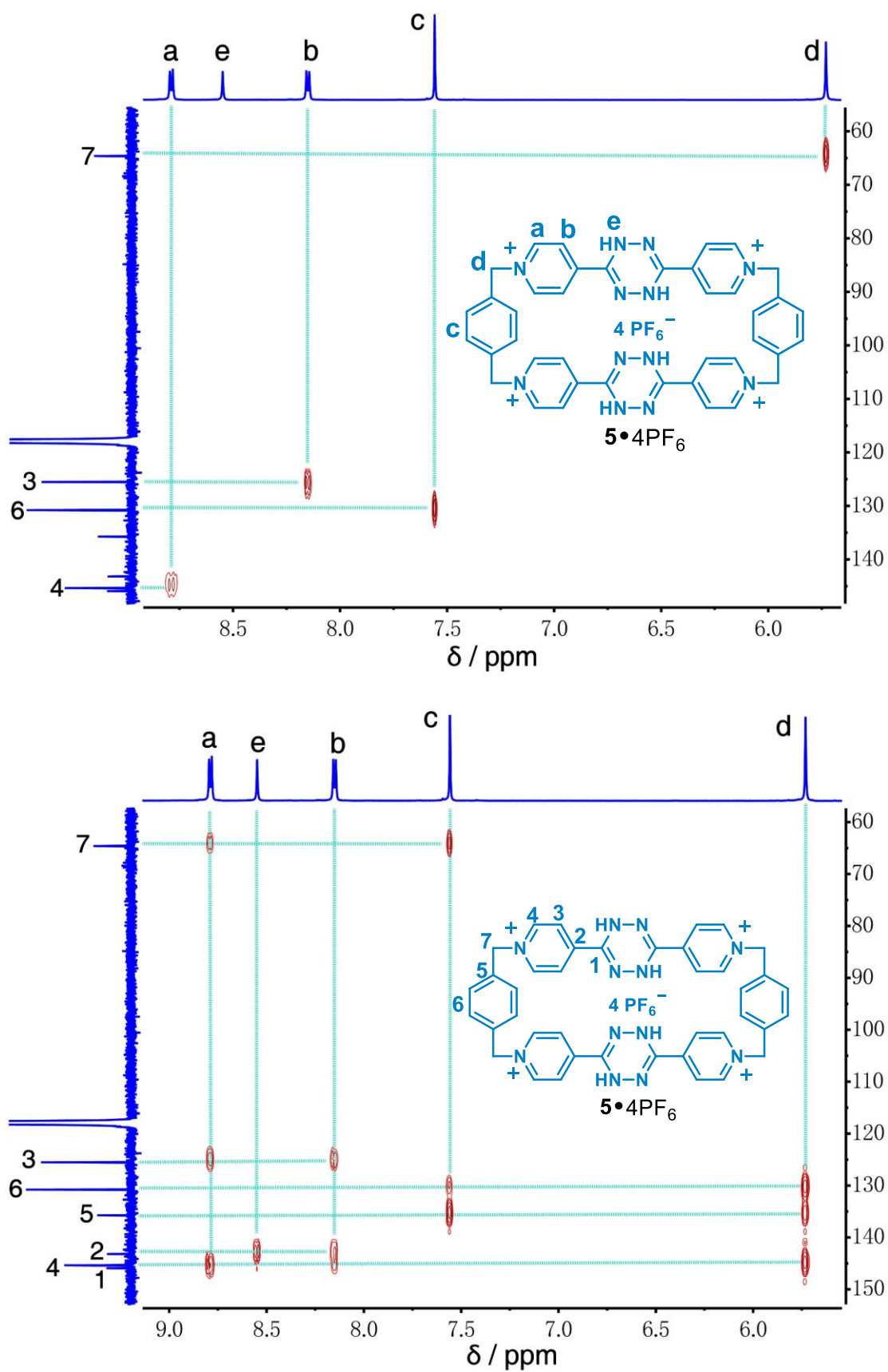
**Figure S14.** HSQC (top) and HMBC (bottom) NMR spectra of **4•4PF<sub>6</sub>**.



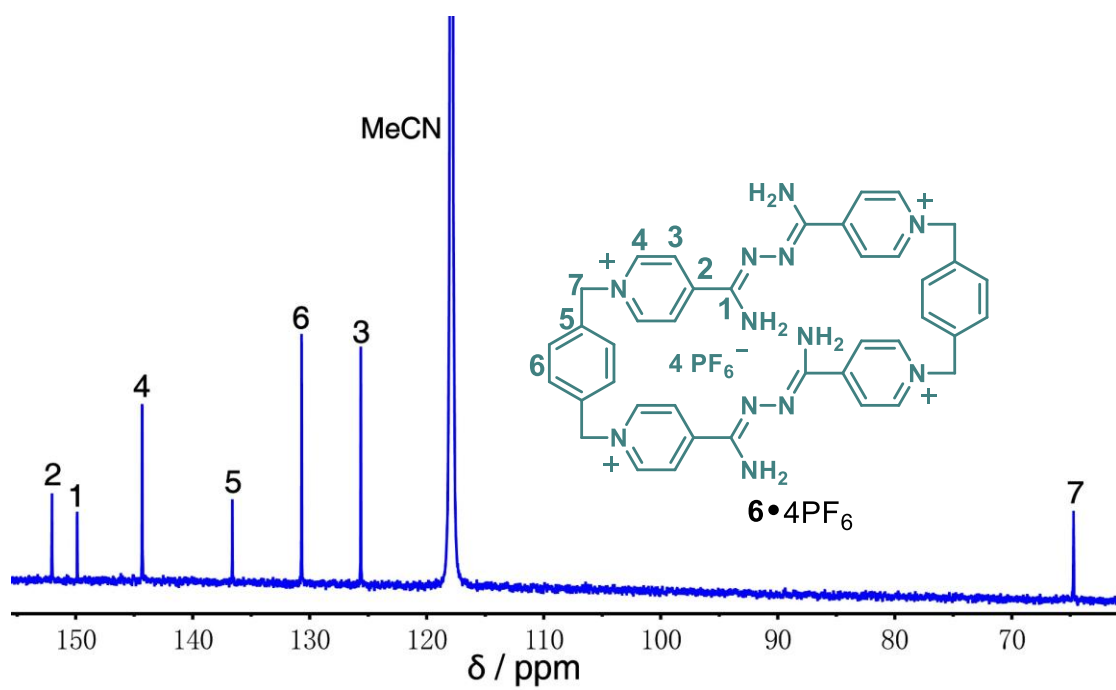
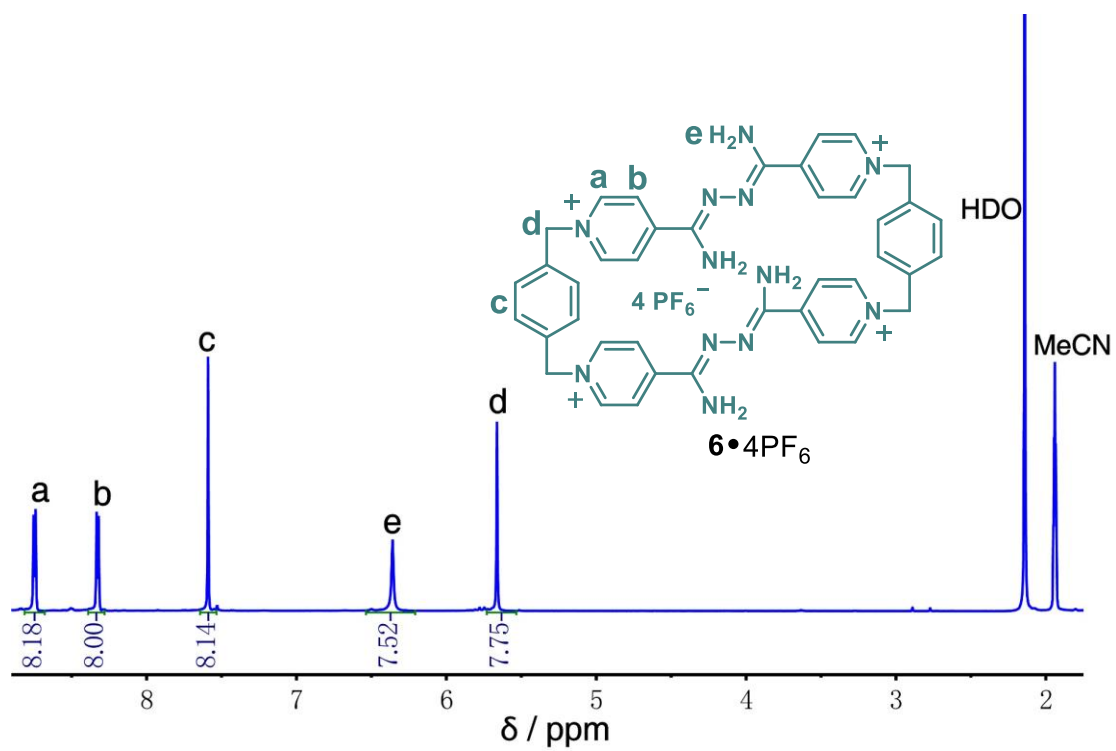
**Figure S15.** <sup>1</sup>H (top) and <sup>13</sup>C(bottom) NMR spectra of **5•4PF<sub>6</sub>**.



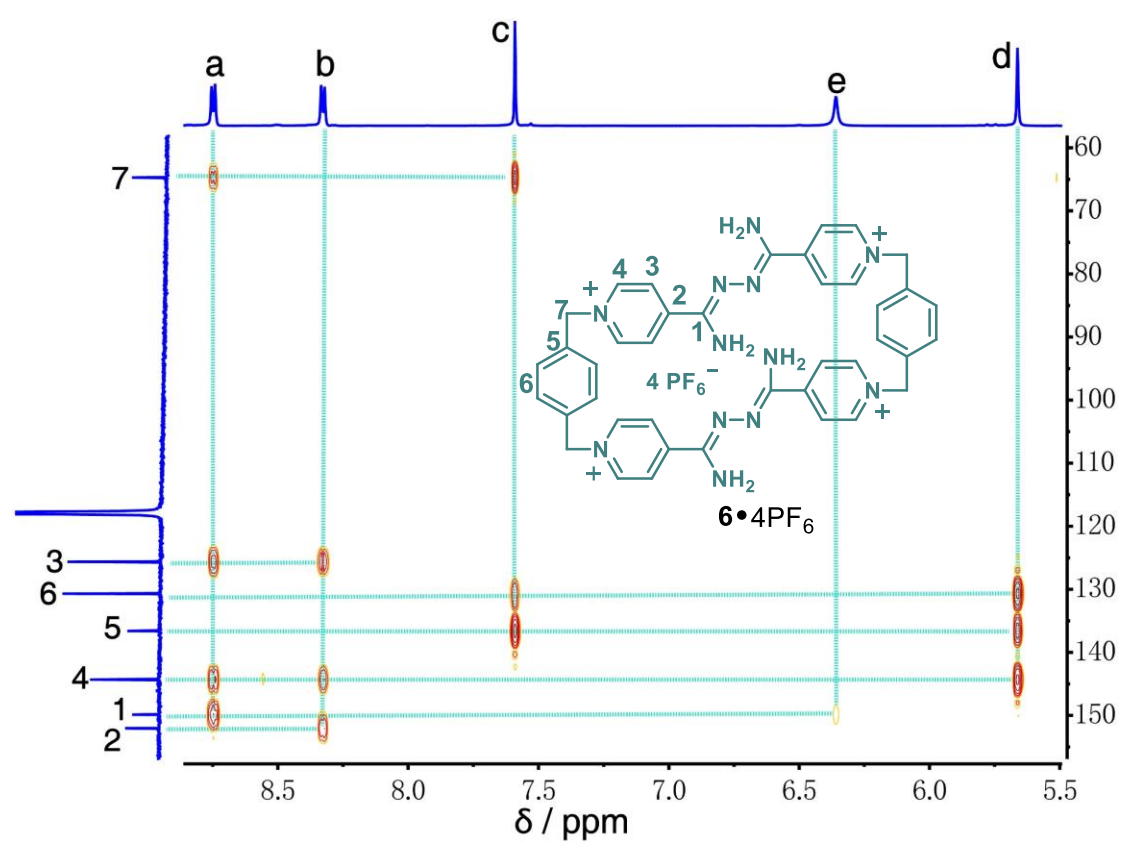
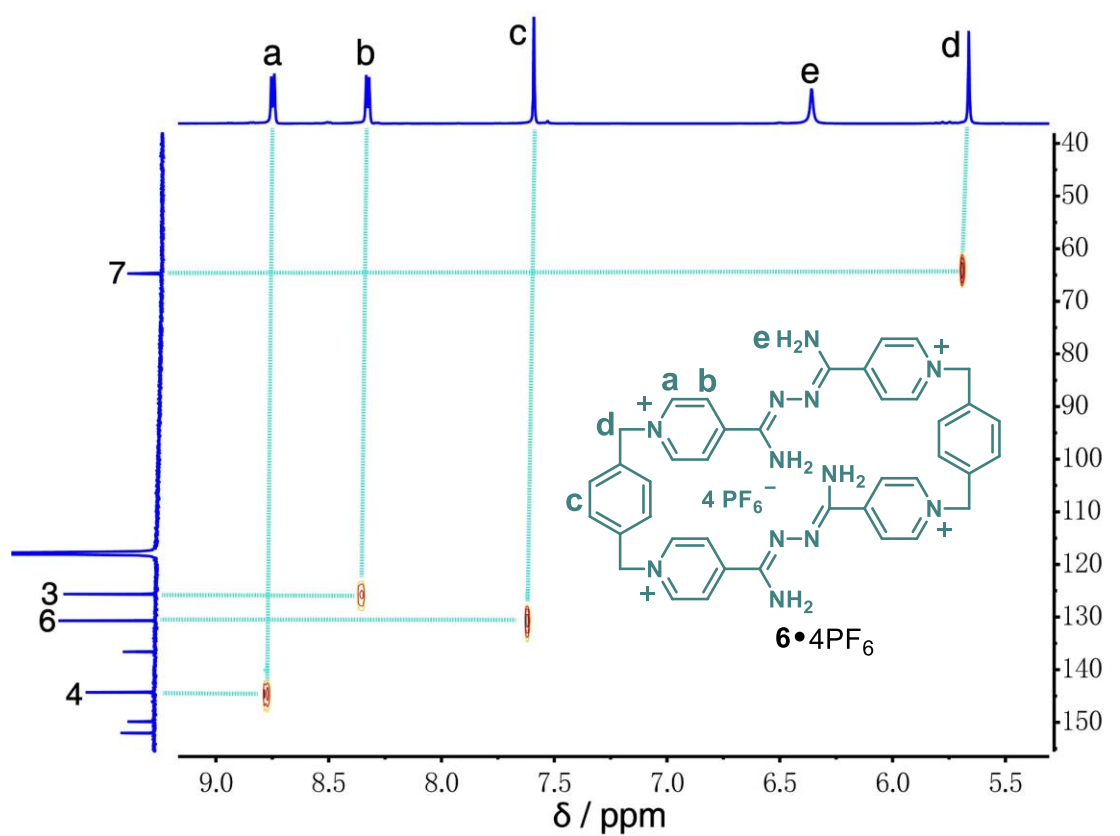
**Figure S16.** H-H COSY (top) and NOSY (bottom) NMR spectra of **5•4PF<sub>6</sub>**.



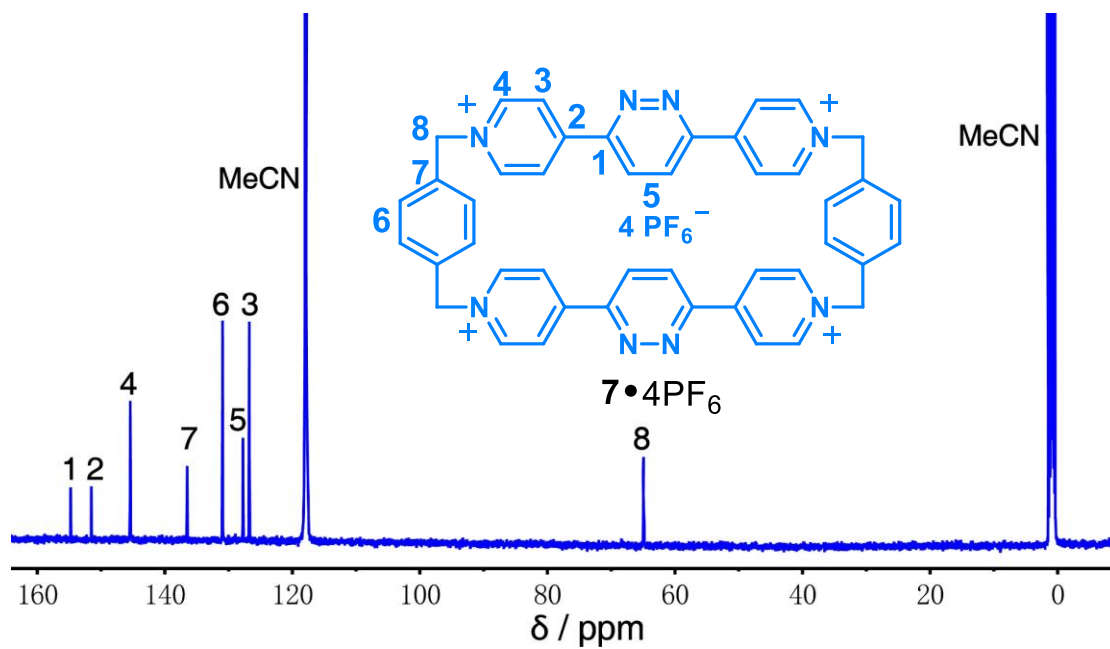
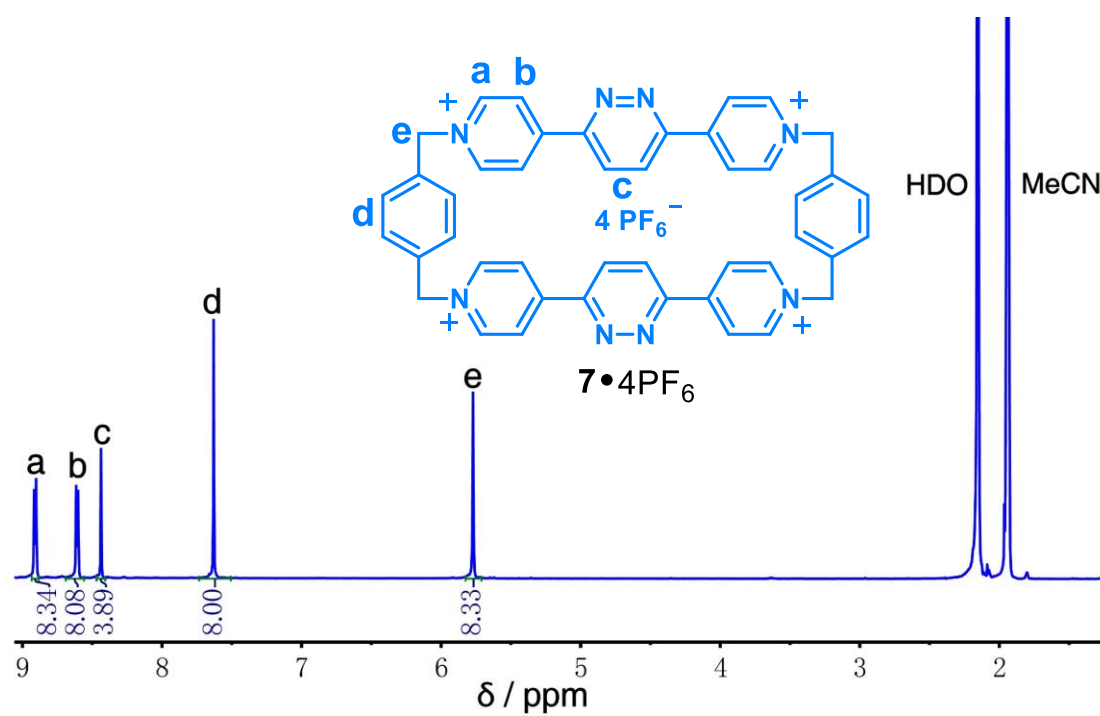
**Figure S17.** HSQC (top) and HMBC (bottom) NMR spectra of **5•4PF<sub>6</sub>**.



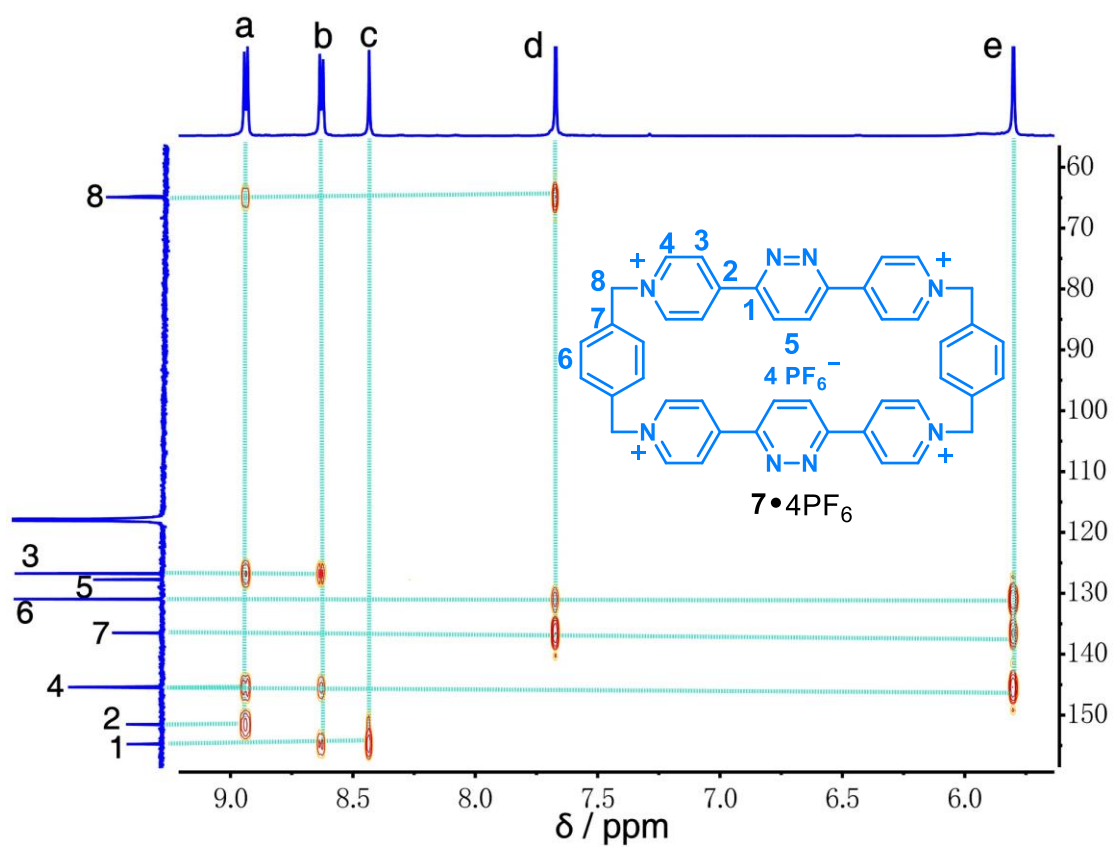
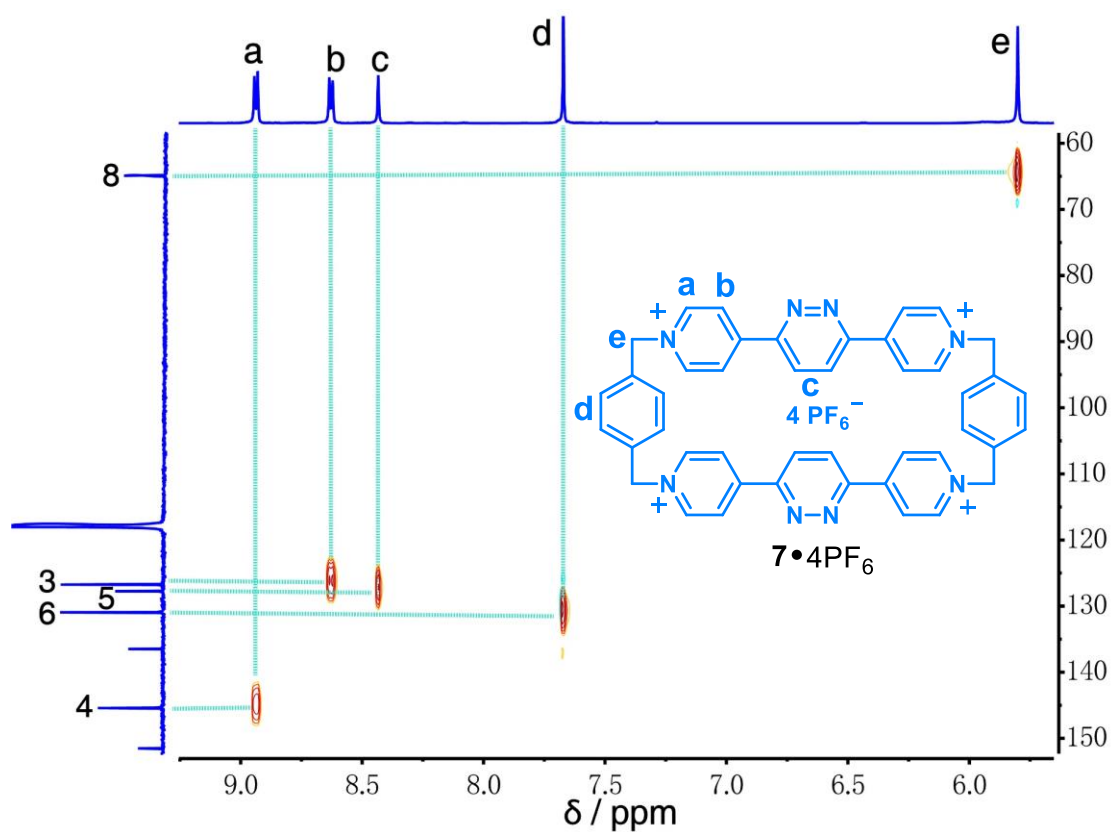
**Figure S18.** <sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of **6•4PF<sub>6</sub>**.



**Figure S19.** HSQC (top) and HMBC (bottom) NMR spectra of **6•4PF<sub>6</sub>**.

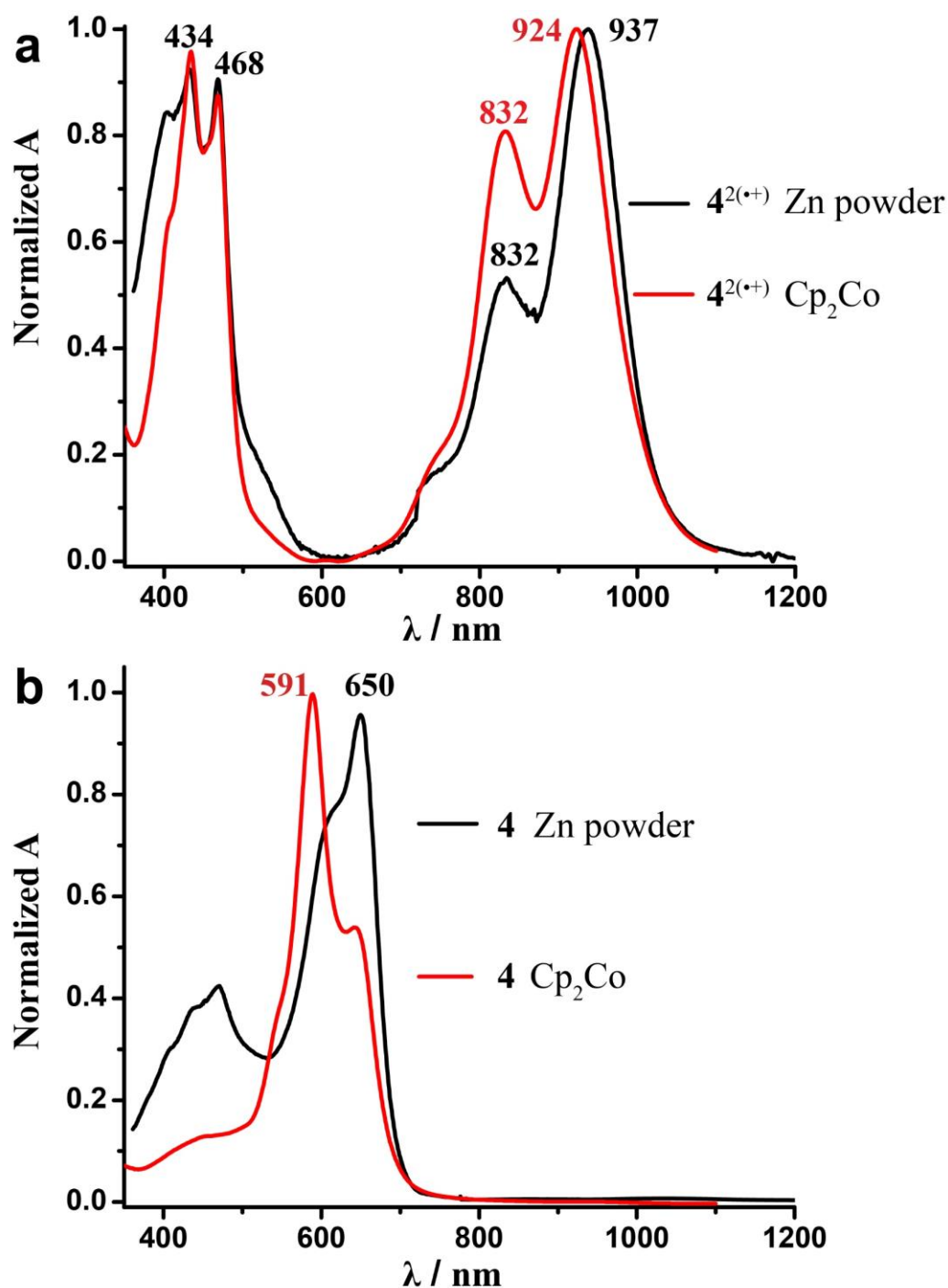


**Figure S20.** <sup>1</sup>H (top) and <sup>13</sup>C(bottom) NMR spectra of 7•4PF<sub>6</sub>.



**Figure S21.** HSQC (top) and HMBC (bottom) NMR spectra of **7•4PF<sub>6</sub>**.





**Figure S22.** (a) Normalized UV–Vis–NIR absorption spectra of  $4^{2(•+)}$ , which were obtained by addition of excess amounts ( $> 20$  equiv) of Zn powder in an Ar-purged dry MeCN solution (black line) and 2.0 equiv of  $\text{CoCp}_2$  in an Ar-purged dry DMF solution (red line). (b) Normalized UV–Vis–NIR absorption spectra of **4**, which were obtained by addition of excess amounts ( $> 20$  equiv) of Zn powder (black line) and 4.0 equiv of  $\text{CoCp}_2$  in Ar-purged DMF solutions (red line).

## Section G. References

- S1. Y.-C. He *et al.*, Luminescent Anionic Metal–Organic Framework with Potential Nitrobenzene Sensing. *Cryst. Growth Des.* **2014**, *14*, 3174–3178.
- S2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard, H. Puschmann, OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339–341.
- S3. G. Sheldrick, SHELXT–Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *71*, 3–8.
- S4. G. Sheldrick, A Short History of SHELX. *Acta Cryst.* **2008**, *64*, 112–122.