Metallacycle-cored supramolecular assemblies with tunable fluorescence including white-light emission

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PHYSICAL SCIENCES: Chemistry

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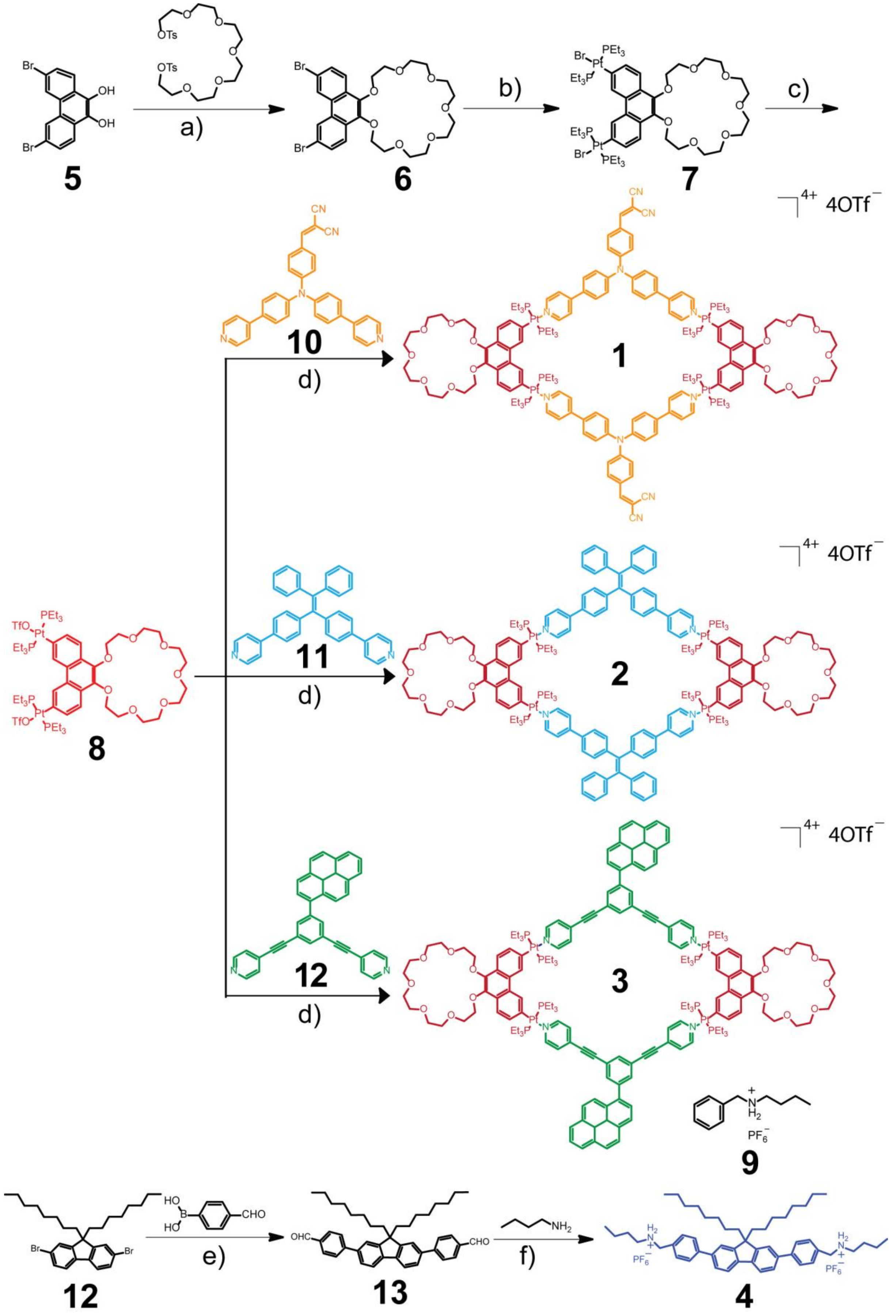
Section A. Materials/General Methods/Instrumentation

1. Gerneral materials and instrumentation

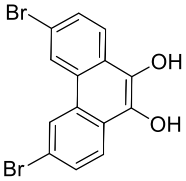
All reagents and deuterated solvents were commercially available and used without further purification. Compounds **5**,[S1] hexa(ethylene glycol) ditosylate,[S2] Pt(PEt_3)$_4$,[S3] **9**,[S4] **10**,[S5] **11**[S6] and 4,4'-((5-bromo-1,3-phenylene)bis(ethyne-2,1-diyl))dipyridine[S7] were prepared according to the literature procedures. NMR spectra were recorded on a Varian Unity 300 MHz or 400 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P{^{1}H} NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. The UV-Vis experiments were conducted on a Hitachi U-4100 absorption spectrophotometer. The fluorescent experiments were conducted on a Hitachi F-7000 fluorescence spectrophotometer. Quantum yields were determined using quinine sulfate at 365 nm (Φ_F = 56%).

Section B. Synthetic Procedures and Characterization Data



Scheme S1. Synthetic routes of rhomboidal metallacycles **1**, **2**, **3** and bis-ammonium salt **4** and chemical structures of compounds used in this study. Conditions: a) K_2CO_3, CH_3CN, reflux, 72 h; 64%; b) $Pt(PEt_3)_4$, toluene, 95 °C, 72 h; 68%; c) AgOTf, CH_2Cl_2, room temperature, 12 h; 95%; d) CH_2Cl_2, room temperature, 12 h; 90-96%; e) K_2CO_3, $Pd(PPh_3)_4$, dioxane/water (2:1), 90 °C, 48 h; 63%; f) (i) *n*-butylamine, CH_3OH, reflux, 12h; (ii) $NaBH_4$, room temperature, 24 h; (iii) HCl (aq) and (iv) NH_4PF_6 (aq); 27% in four steps.

*1. Synthesis of compound **5***



Compound **5** was synthesized according to literature procedure.[S1] The ^1H NMR of **5** matches well with the reported data. ^1H NMR (400 MHz, DMSO, 295K): 9.26 (br, 2H, ArO*H*), 9.00 (s, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H).

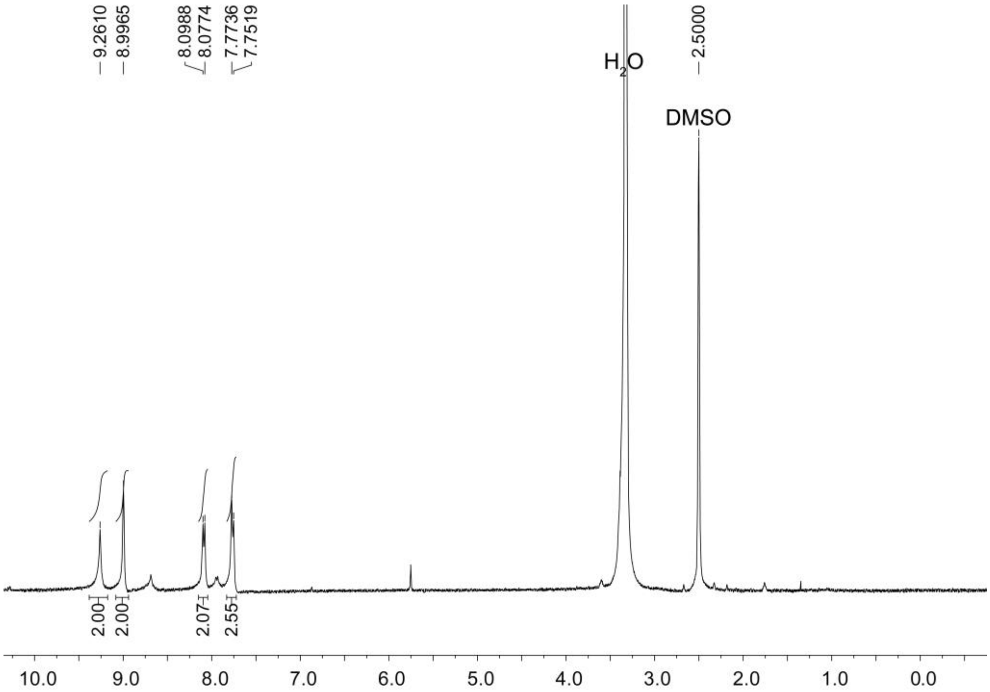
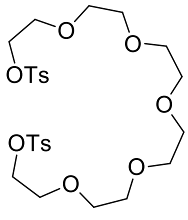


Figure S1. ^1H NMR spectrum (400 MHz, DMSO, 295 K) recorded for **5**.

2. Synthesis of hexa(ethylene glycol) ditosylate



Hexa(ethylene glycol) ditosylate was synthesized according to literature procedure.[S2] The ^1H NMR of hexa(ethylene glycol) ditosylate matches well with the reported data. ^1H NMR (400 MHz, $CDCl_3$, 295K): 7.79 (d, *J* = 8.2 Hz, 4H), 7.34 (d, *J* = 8.2 Hz, 4H), 4.15 (t, *J* = 4.8 Hz, 4H), 3.68 (t, *J* = 4.8 Hz, 4H), 3.60–3.63 (m, 8H), 3.57–3.59 (m, 8H), 2.44 (s, 6H).

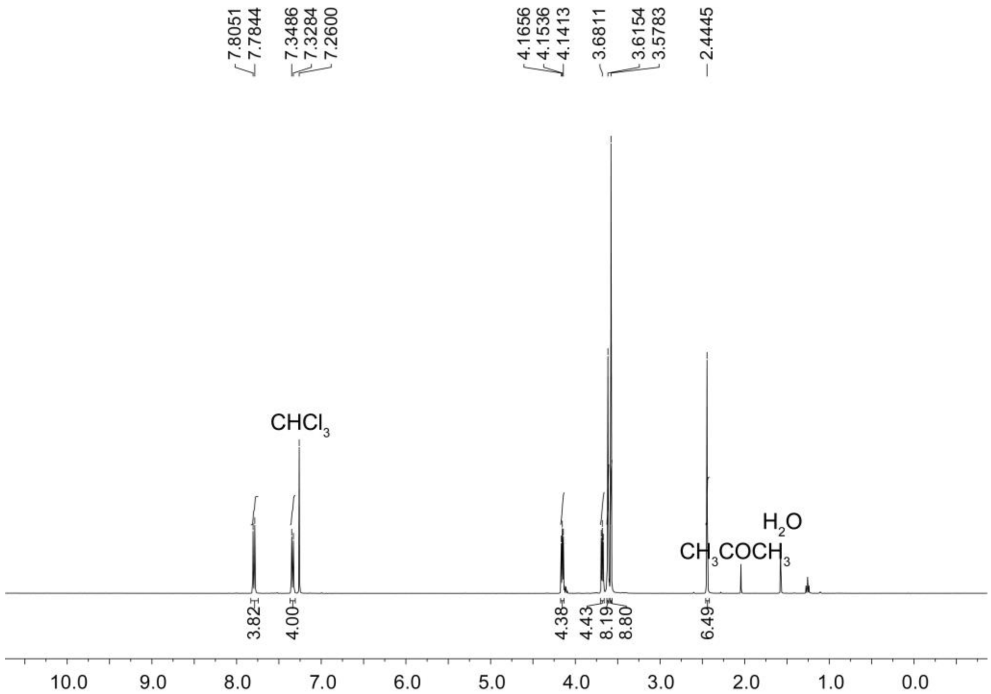
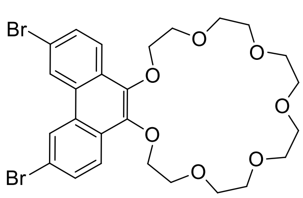


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 295 K) recorded for hexa(ethylene glycol) ditosylate.

*3. Synthesis of compound **6***



Compound **5** (500 mg, 1.36 mmol), hexa(ethylene glycol) ditosylate (802 mg, 1.36 mmol), K_2CO_3 (563 mg, 4.08 mmol) and KPF_6 (375 mg, 2.04 mmol) were added into CH_3CN (30 mL) and the whole reaction mixture was heated at reflux for 72 h under nitrogen. Then the system was cooled down and filtered. The filtrate was collected and the solvent was removed with a rotaevaporator. H_2O (100 mL) was added and the mixture was extracted by ethyl acetate (50 mL × 3), dried over anhydrous Na_2SO_4 and then concentrated. The residue was purified by silica gel flash column chromatography (CH_2Cl_2/ethyl acetate, *v*/*v* 1:4) to provide compound **6** (534 mg, 64%) as a white solid. M. P. 160.5–162.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 295K): 8.64 (d, J = 1.7 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 7.70 (dd, J_1 = 8.8 Hz, J_2 = 1.7 Hz, 2H), 4.42 (t, J = 4.3 Hz, 4H), 4.00 (t, J = 4.3 Hz, 4H), 3.77–3.85 (m, 4H), 3.71–3.77 (m, 4H), 3.66–3.71 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, 295K): 142.6, 130.2, 128.5, 128.1, 125.0, 124.1, 120.2, 72.4, 71.1, 70.5, 70.4, 70.2. ESI-HR-MS: *m*/*z* 637.0221 [**6** + Na]$^+$, calcd. for $[C_{26}H_{30}Br_2O_7Na]^+$, 637.0236.

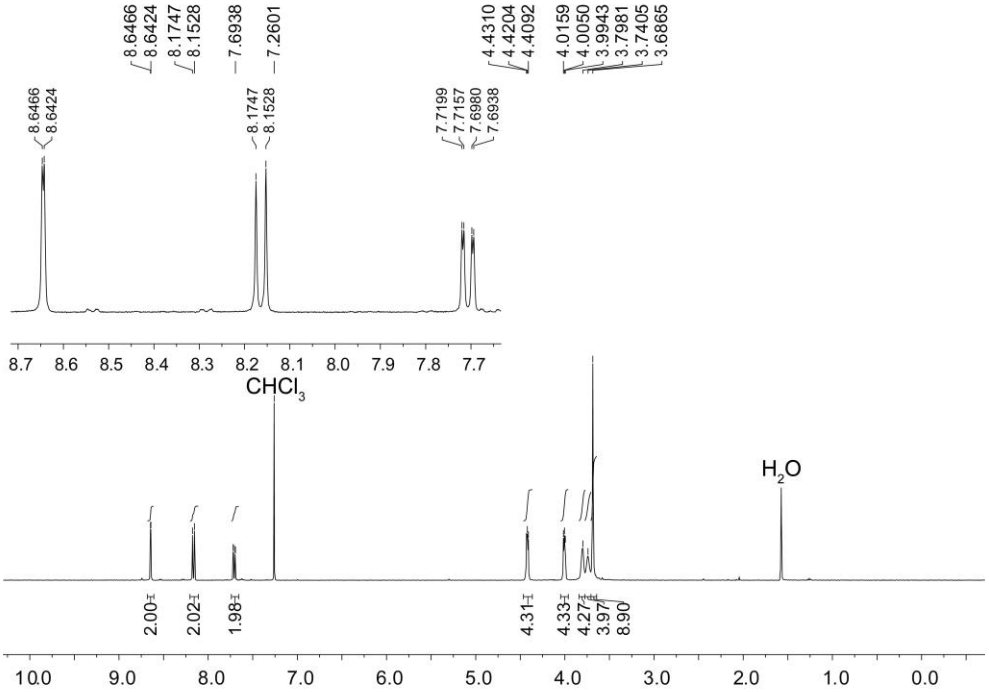


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 295 K) recorded for **6**.

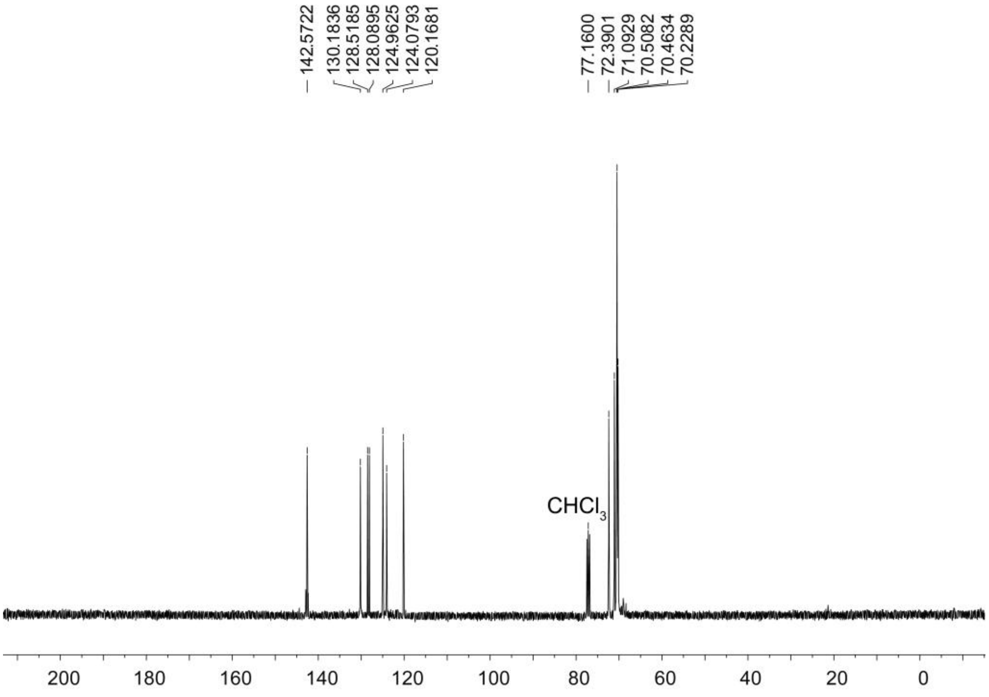


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 295 K) recorded for **6**.

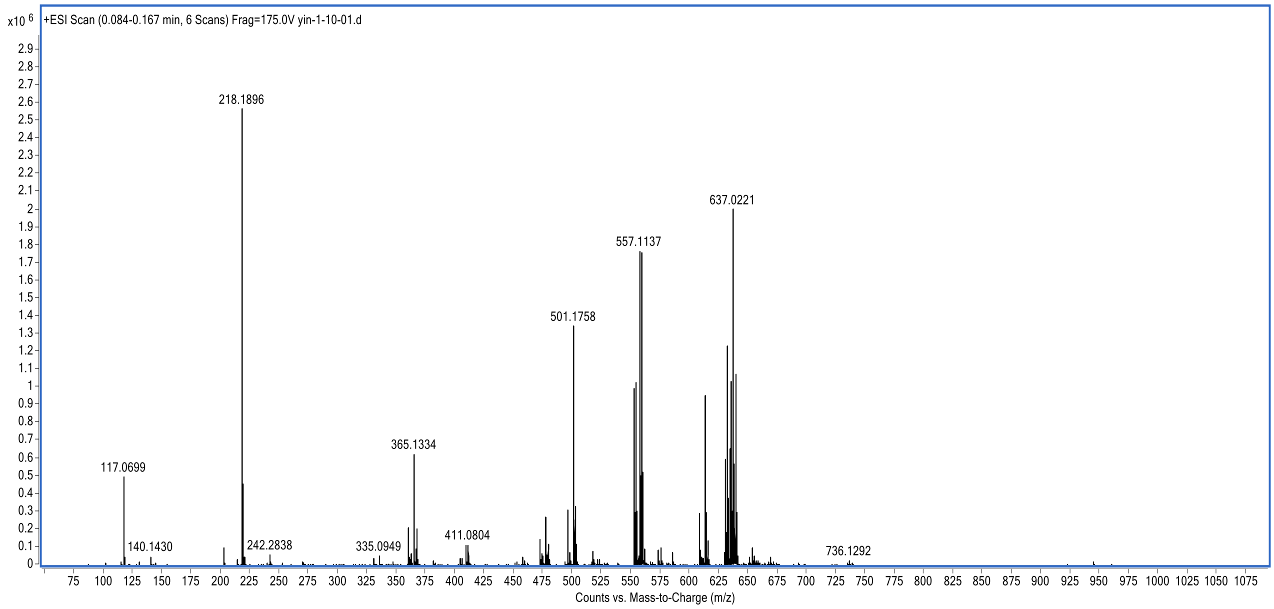
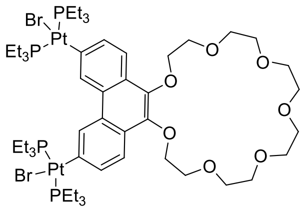


Figure S5. ESI-HR-MS spectrum of **6**.

*4. Synthesis of compound **7***



Compound **6** (0.44 g, 0.72 mmol) and Pt(PEt$_3$)$_4$ (1.30 g, 1.95 mmol) were added into a 100 mL Schlenk flask and charged with nitrogen. Freshly distilled toluene (40 mL) was added to the flask under nitrogen by syringe, and the resulting mixture was heated at 95 °C for 72 h. After cooling, the solvent was removed in vacuo to give a crude product, which was purified by flash column chromatography (CH$_2$Cl$_2$/ethyl acetate, *v*/*v* 1:3) to afford **7** as a white solid (0.72 g, 68%). M. P. 248.6–250.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 295K): 8.46 (s, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.41 (t, *J* = 4.3 Hz, 4H), 4.03 (t, *J* = 4.3 Hz, 4H), 3.83–3.88 (m, 4H), 3.77–3.82 (m, 4H), 3.68–3.74 (m, 8H), 1.59–1.73 (m, 24H), 1.01–1.13 (m, 36H). ^{13}C NMR (100 MHz, CDCl$_3$, 295K): 141.3, 137.4, 136.3, 129.2, 128.4, 124.8, 120.7, 72.3, 71.4, 71.3, 71.0, 70.8, 70.8, 14.2, 7.9. ESI-HR-MS: *m*/*z* 1465.4180 [**7** + H]$^+$, calcd. for [C$_{50}$H$_{91}$Br$_2$O$_7$P$_4$Pt$_2$]$^+$, 1465.3275.

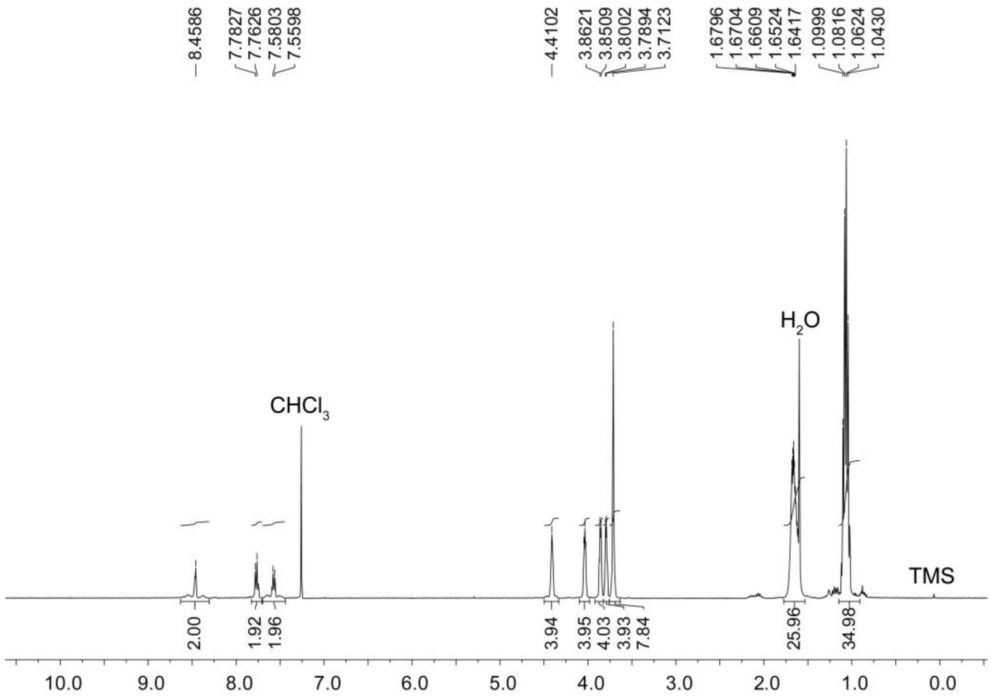


Figure S6. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 295 K) recorded for **7**.

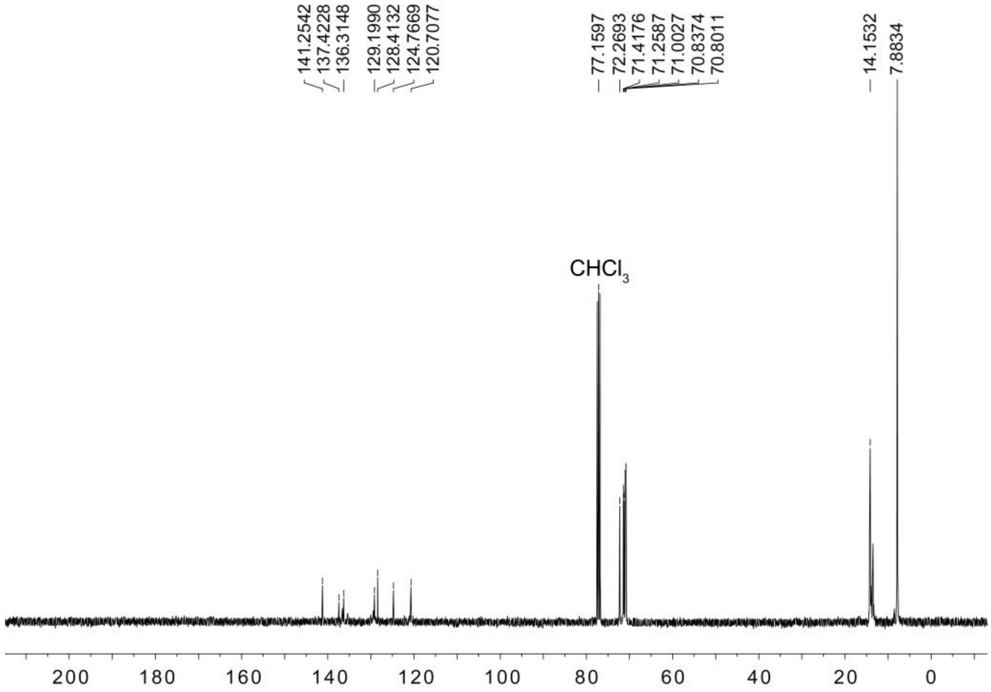


Figure S7. ^{13}C NMR spectrum (100 MHz, CDCl$_3$, 295 K) recorded for **7**.

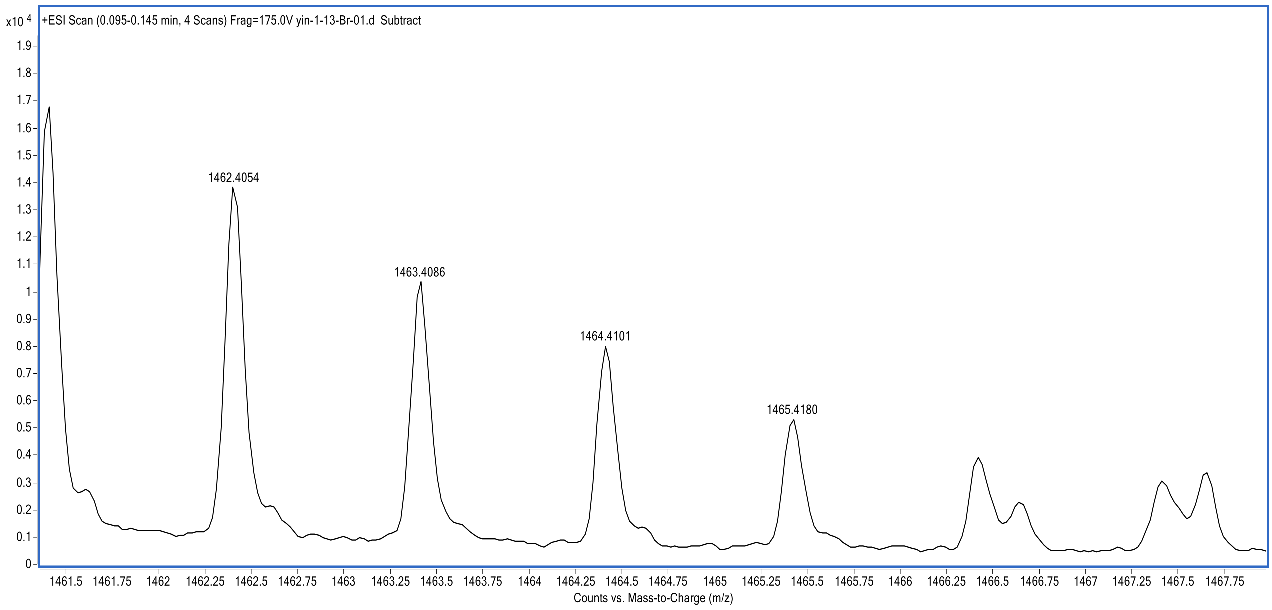
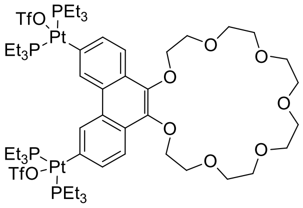


Figure S8. Electrospray ionization mass spectrum of **7**.

*5. Synthesis of compound **8***



Compound **7** (60 mg, 0.04 mmol) and AgOTf (18 mg, 0.12 mmol) were placed in a 5 mL vial, and then freshly distilled CH_2Cl_2 (4 mL) was added. The resulting mixture was stirred in the dark at room temperature for 12 h. After filtering off the heavy creasy precipitate, a clear solution was obtianed. Then the solvent was removed under a flow of nitrogen to afford **8** as a brown solid (62 mg, 95%). M. P. 216.7–219.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 295K): 8.33 (s, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 4.40–4.46 (m, 4H), 4.07–4.16 (m, 4H), 3.90–3.98 (m, 4H), 3.72–3.85 (m, 12H), 1.50–1.73 (m, 24H), 1.06–1.20 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 295K): 141.3, 135.0, 127.9, 125.3, 121.1, 72.1, 71.2, 71.0, 70.8, 70.6, 70.5, 13.6, 7.6. ^{31}P{^{1}H} NMR (121.4 MHz, CD_3COCD_3, 295 K) δ (ppm): 17.97 ppm (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2830.5 Hz). ESI-HR-MS: *m*/*z* 1638.4294 [**8** + Na]$^+$, calcd. for $[C_{52}H_{90}F_6O_{13}P_4Pt_2Na]^+$, 1638.3872.

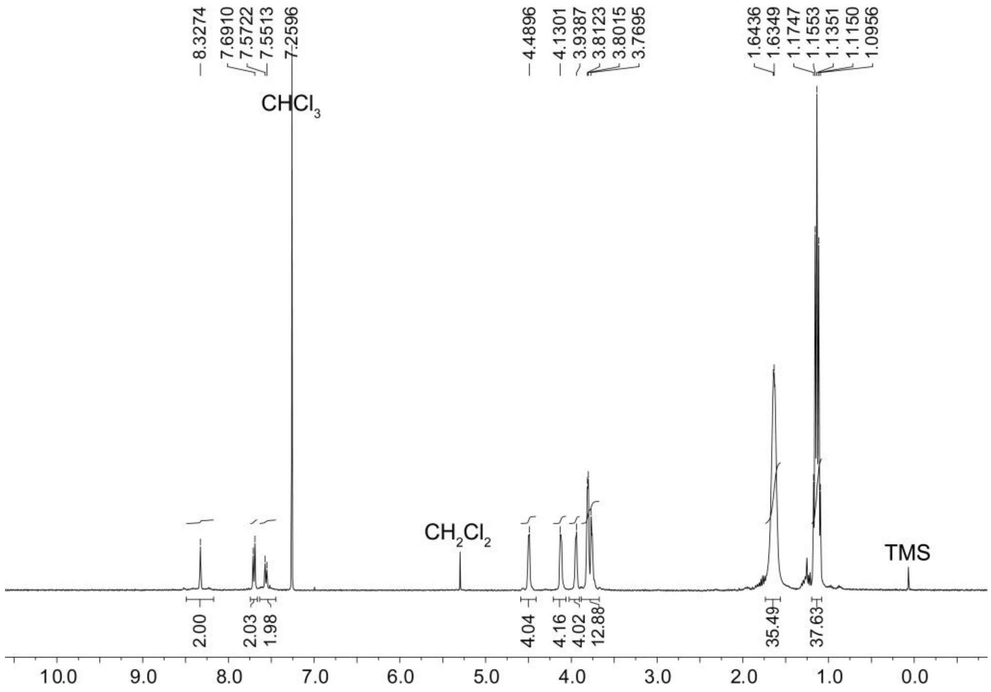


Figure S9. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 295 K) recorded for **8**.

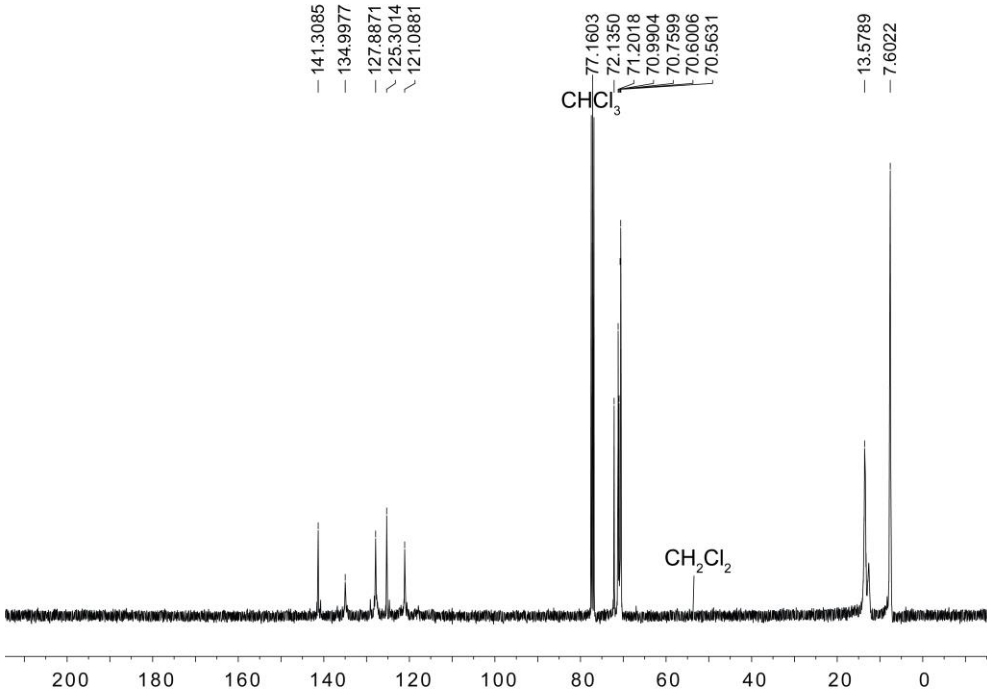


Figure S10. ^{13}C NMR spectrum (100 MHz, CDCl$_3$, 295 K) recorded for **8**.

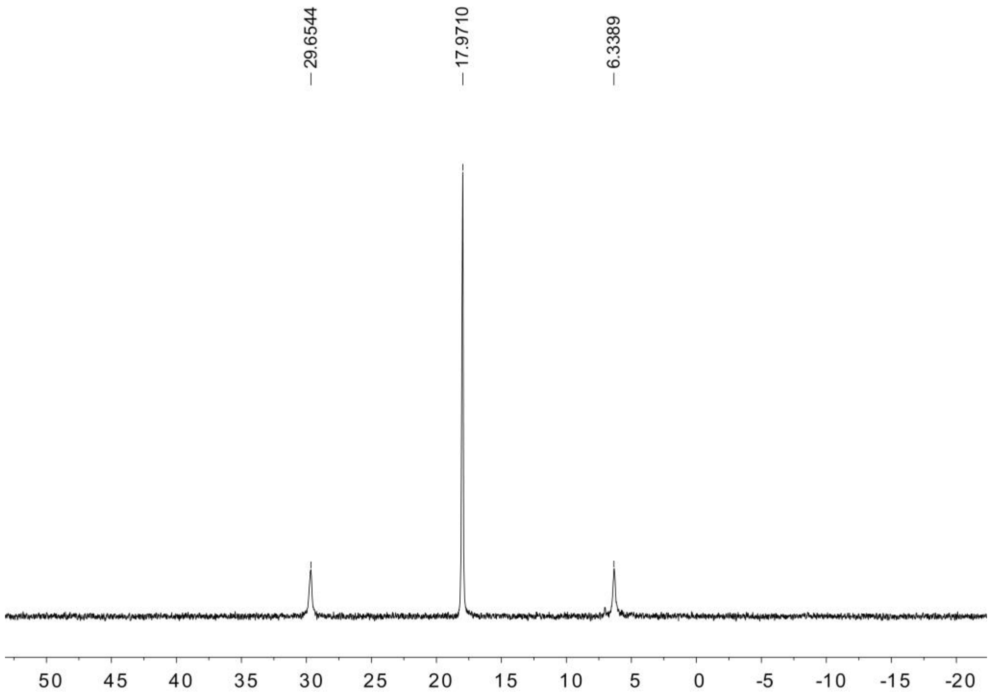


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum (121.4 MHz, CD_3COCD_3, 295 K) recorded for **8**.

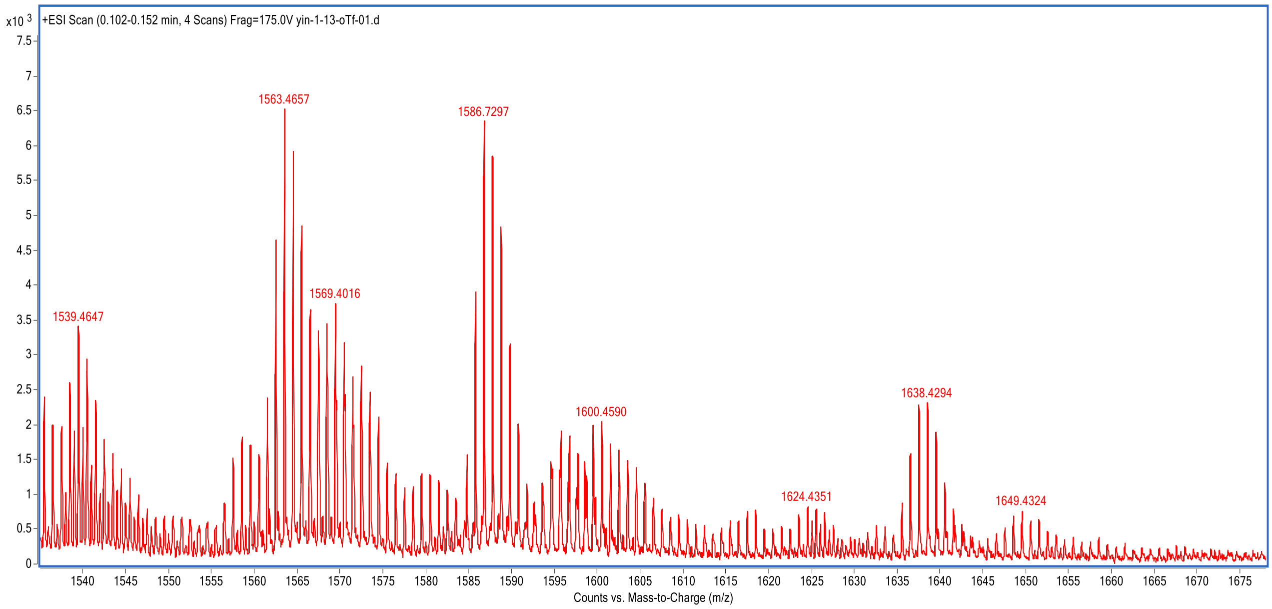
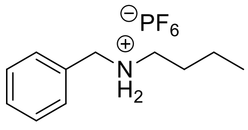


Figure S12. Electrospray ionization mass spectrum of **8**.

6. Synthesis of Compound 9



Compound **9** was synthesized according to literature procedure.[S4] The ^{1}H NMR of **9** matches well with the reported data. ^{1}H NMR (400 MHz, CD_3COCD_3, 295K): 7.55–7.63 (m, 2H), 7.45–7.51 (m, 3H), 4.58 (s, 2H), 3.43 (t, *J* = 7.9 Hz, 2H), 2.51 (br, 2H, NH_2), 1.82–1.92 (m, 2H), 1.42–1.53 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H).

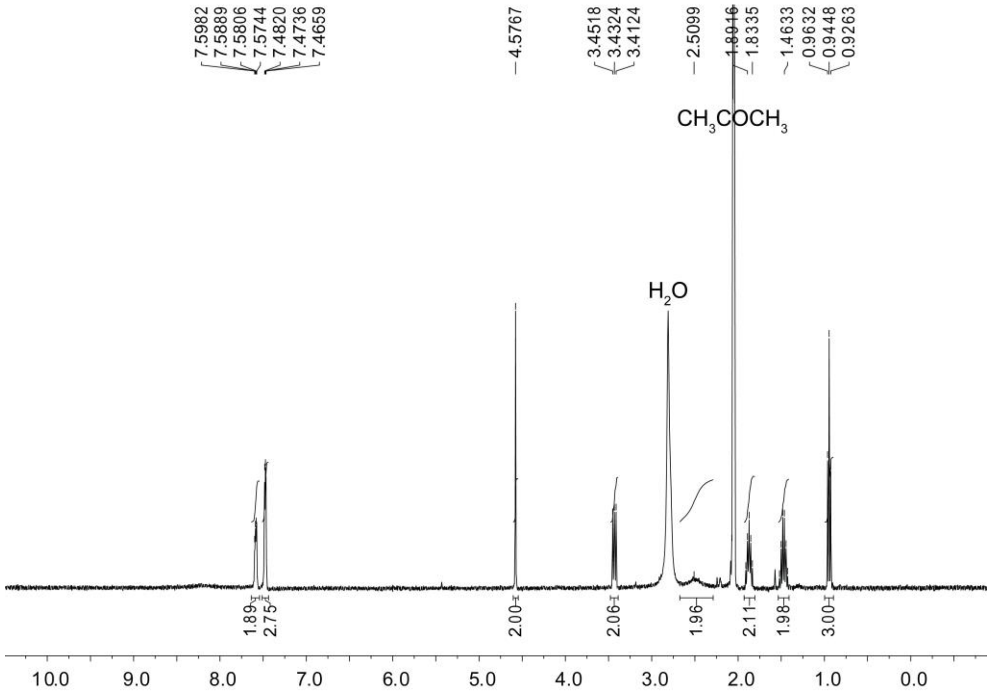
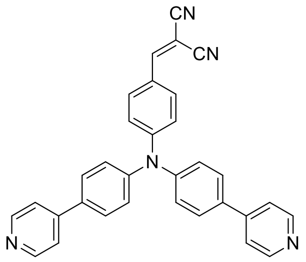


Figure S13. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, 295 K) recorded for **9**.

7. Synthesis of compound **10**



Compound **10** was synthesized according to literature procedure.[S5] The ^{1}H NMR of **10** matches well with the reported data. ^{1}H NMR (400 MHz, CH_2Cl_2, 295K): 8.63 (dd, J_1 = 6.1 Hz, J_2 = 1.6 Hz, 4H), 7.80 (d, J = 8.9 Hz, 2H), 7.68 (d, J = 8.6 Hz, 4H), 7.61 (s, 1H), 7.51 (dd, J_1 = 6.1 Hz, J_2 = 1.6 Hz, 4H), 7.31 (d, J = 8.6 Hz, 4H), 7.11 (d, J = 8.9 Hz, 2H).

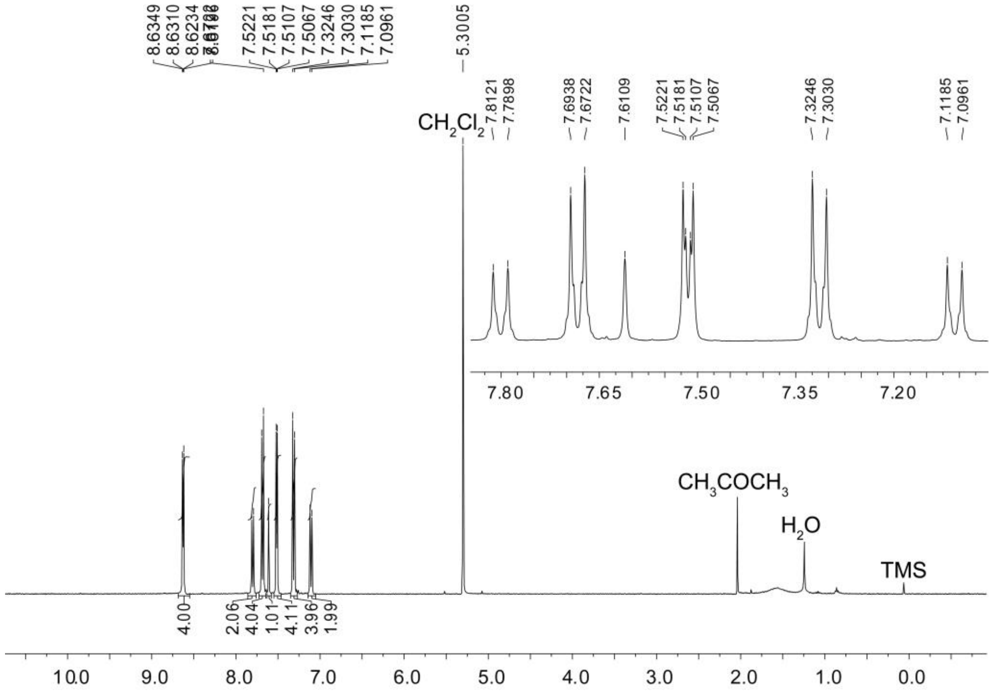
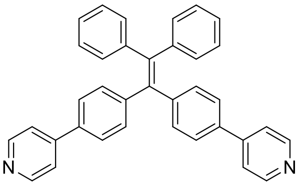


Figure S14. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 295 K) recorded for **10**.

8. Synthesis of compound ***11***



Compound **11** was synthesized according to literature procedure.[S6] The ^{1}H NMR of **11** matches well with the reported data. ^{1}H NMR (400 MHz, CD_3COCD_3, 295K): 8.60 (d, *J* = 6.0 Hz, 4H), 7.61–7.64 (m, 4H), 7.59–7.61 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 4H), 7.13–7.19 (m, 6H), 7.09–7.13 (m, 4H).

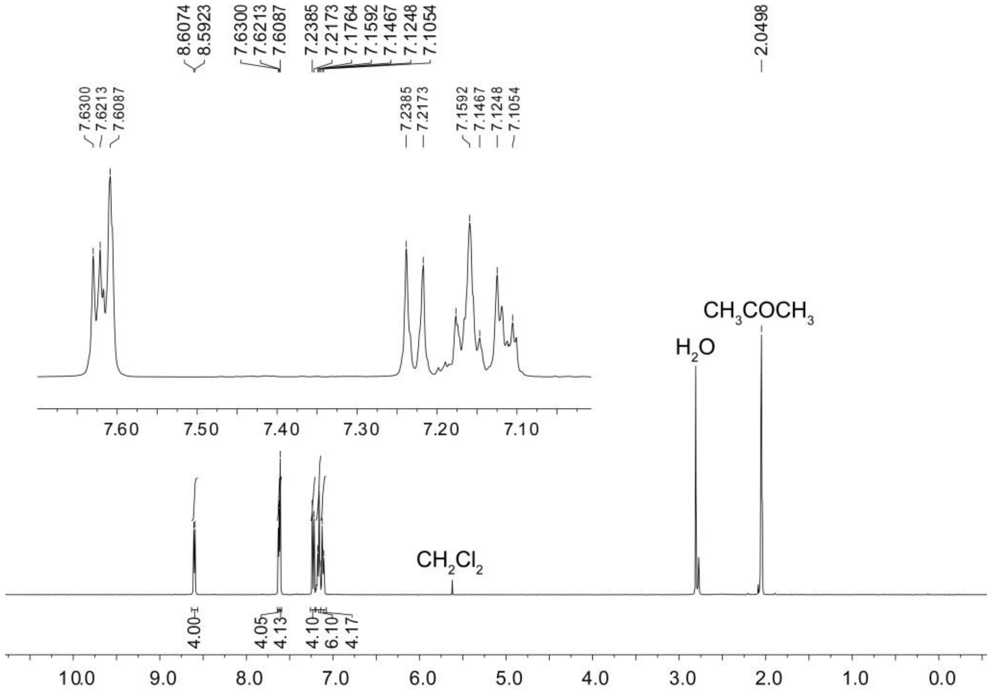
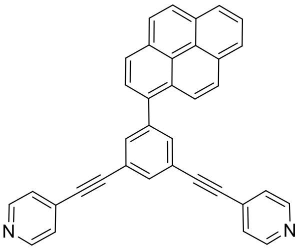


Figure S15. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, 295 K) recorded for **11**.

9. Synthesis of compound ***12***



4,4'-((5-bromo-1,3-phenylene)-bis(ethyne-2,1-diyl))dipyridine (430 mg, 1.20 mmol),[S7] 1-pyrenylboronic acid (595 mg, 2.40 mmol), $Pd(PPh_3)_4$ (139 mg, 0.12 mmol), and K_2CO_3 (828 mg, 6.00 mmol) were added into a 100 mL Schlenk flask and then charged with nitrogen. Degassed dioxane (30 mL) and degassed H_2O (15 mL) were added to the flask under nitrogen by syringe. The reaction mixture was stirred at 90 °C for 48 h under nitrogen atmosphere. After cooling, the product was concentrated and purified by flash column chromatography with CH_2Cl_2:CH_3OH (40:1, *v*/*v*) as the eluent to afford compound **12** (513 mg, 89%) as white powder. M. P. 218.7–221.1 ºC. ^{1}H NMR (400 MHz, CD_3COCD_3, 295K): 8.65 (dd, J_1 = 6.0 Hz, J_2 = 1.4 Hz, 4H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 7.6 Hz, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.26 (s, 2H), 8.24 (d, *J* = 9.4 Hz, 1H), 8.09–8.18 (m, 3H), 7.98 (t, *J* = 1.4 Hz, 1H), 7.94 (d, *J* = 1.4 Hz, 2H), 7.54 (dd, J_1 = 6.0 Hz, J_2 = 1.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 295K): 149.9, 142.2, 135.0, 134.4, 133.8, 131.4, 131.1, 130.9, 130.8, 128.4, 128.2, 127.9, 127.3, 126.3, 125.5, 124.9, 124.8, 124.4, 123.0, 92.7, 87.8. HR-MS: *m*/*z* 481.1705 ([**12** + H]$^+$, calcd. for $[C_{36}H_{21}N_2]^+$, 481.2626.

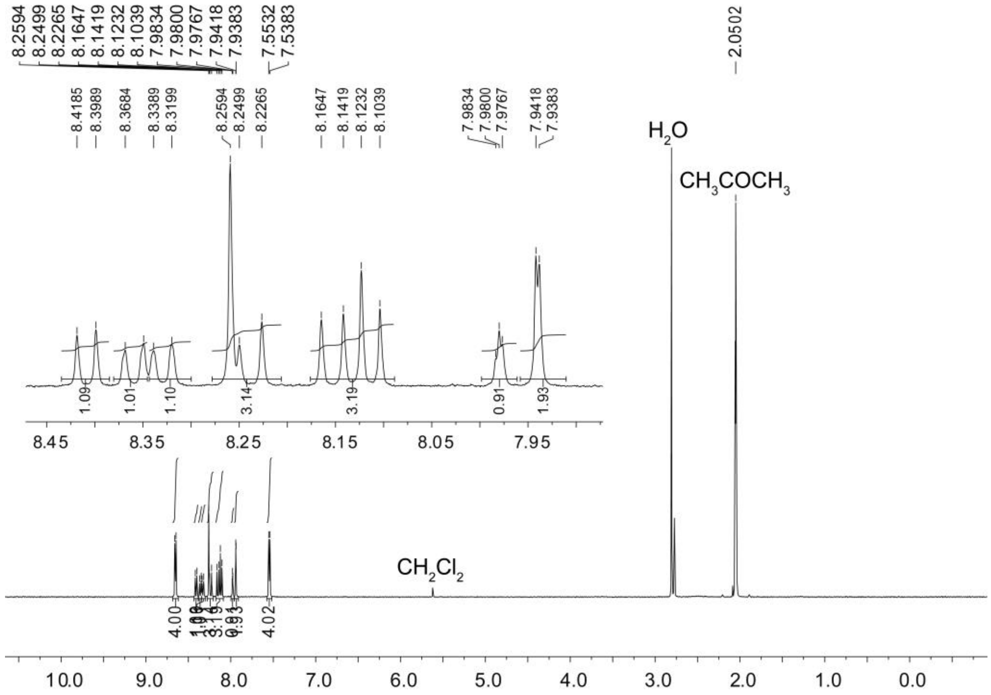


Figure S16. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, 295 K) recorded for **12**.

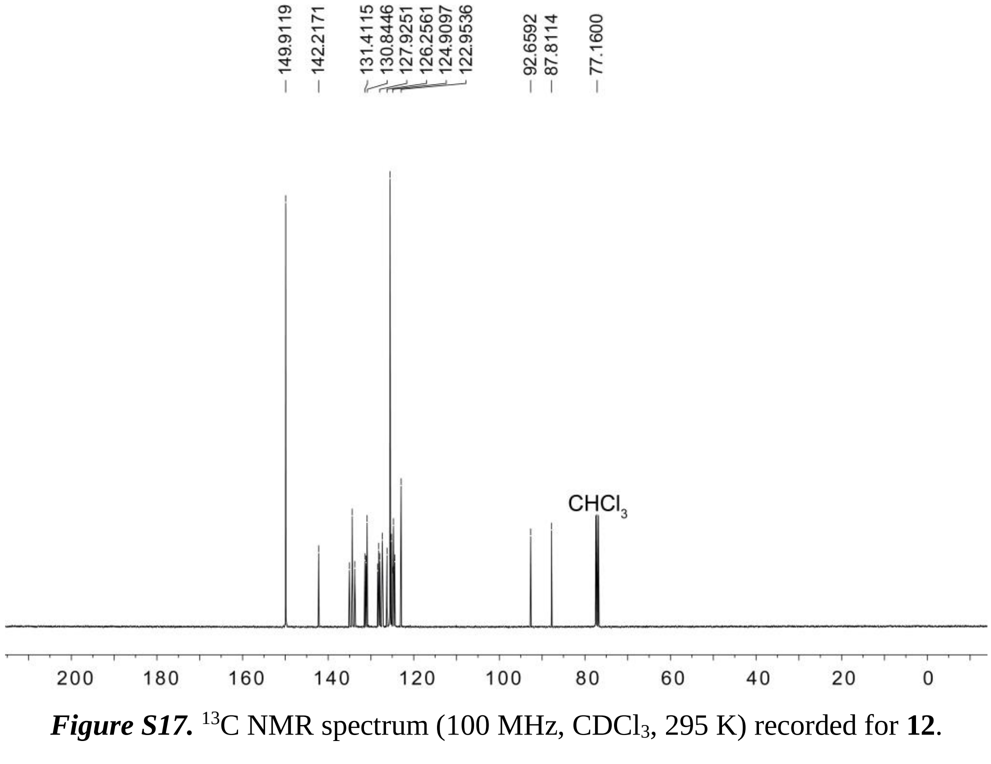


Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 295 K) recorded for **12**.

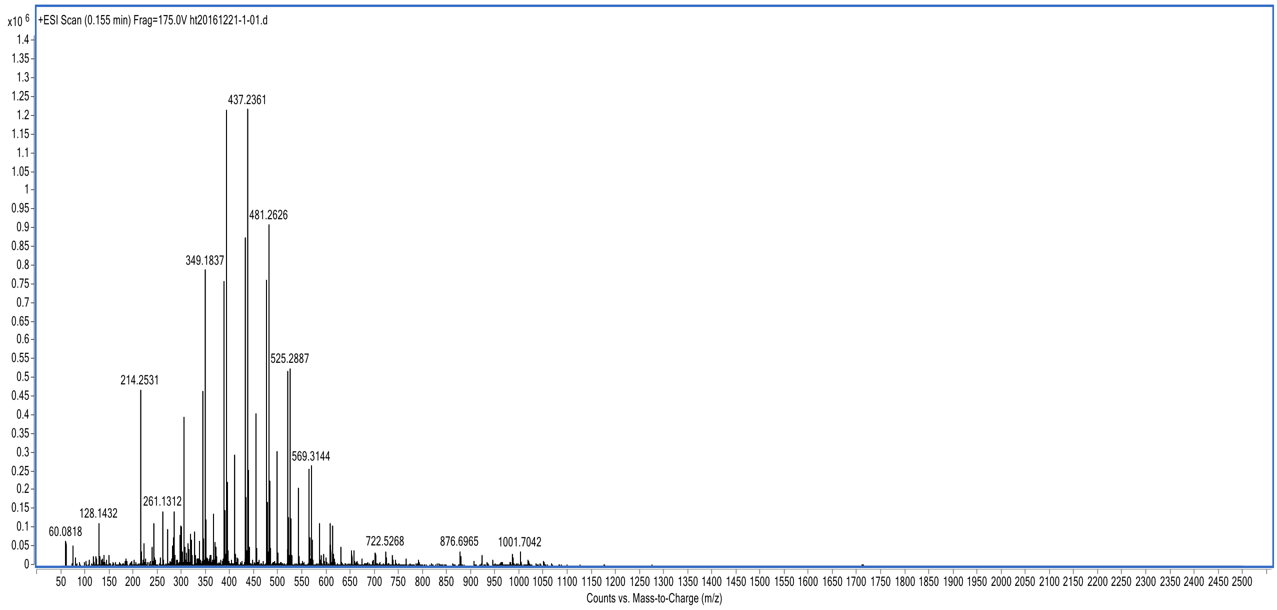
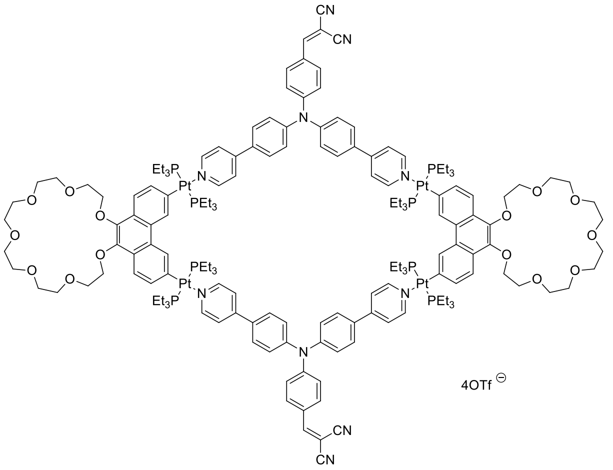


Figure S18. Electrospray ionization mass spectrum of **12**.

*10. Synthesis of rhomboidal metallacycle **1***



Compound **8** (30.39 mg, 18.81 μmol) and **10** (8.95 mg, 18.81 μmol) were dissolved in dry CH_2Cl_2 (2.0 mL) in a 5 mL vial. The reaction mixture was stirred for 12 h at room temperature. Diethyl ether (10 mL) was added to the resulting homogeneous solution to precipitate the product. The obtained product was dried under reduced pressure as a red solid (36.58 mg, 93%). ^{1}H NMR (400 MHz, CD_3COCD_3, 295K): 9.11 (dd, J_1 = 12.1 Hz, J_2 = 5.4 Hz, 8H), 8.70 (s, 4H), 8.18 (d, J = 5.6 Hz, 8H), 8.01–8.23 (m, 18H), 7.82 (d, J = 8.5 Hz, 4H), 7.49 (d, J = 7.8 Hz, 8H), 7.29 (d, J = 7.8 Hz, 4H), 4.37–4.48 (m, 8H), 3.97–4.07 (m, 8H), 3.74–3.83 (m, 8H), 3.69–3.74 (m, 8H), 3.56–3.68 (m, 16H), 1.41–1.66 (m, 48H), 1.15–1.34 (m, 72H). ^{31}P{^{1}H} NMR (121.4 MHz, CD_3COCD_3, 295 K) δ (ppm): 14.17 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt–P}}$ = 2674.2 Hz). ESI-TOF-MS: *m/z* 896.3092 [**1** – 4OTf]$^{4+}$, 1244.7423 [**1** – 3OTf]$^{3+}$, 1941.5898 [**1** – 2OTf]$^{2+}$.

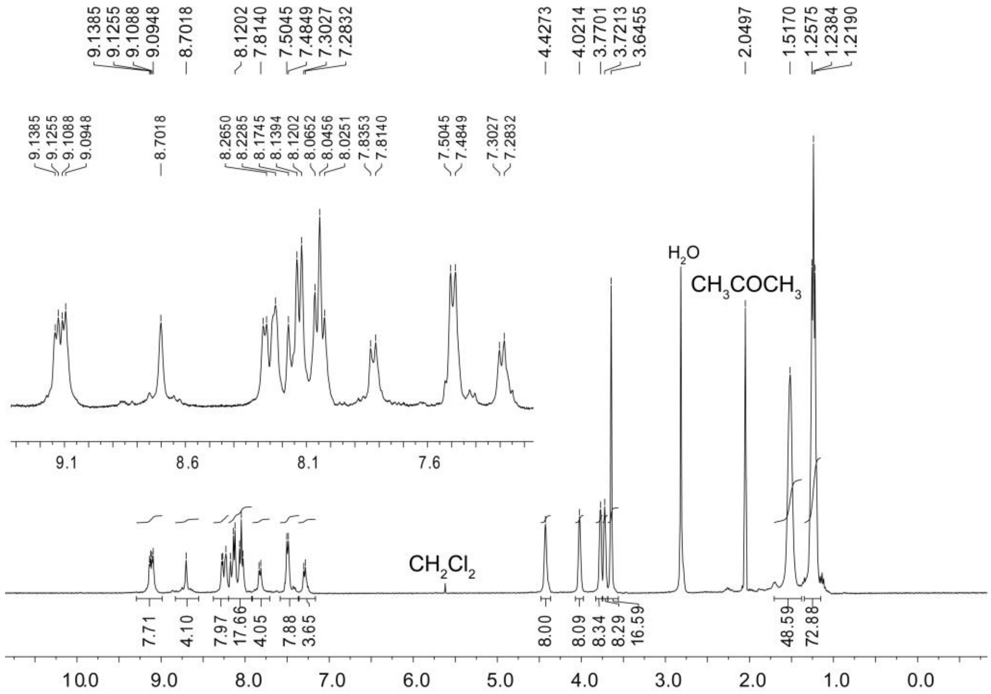


Figure S19. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, 295 K) recorded for **1**.

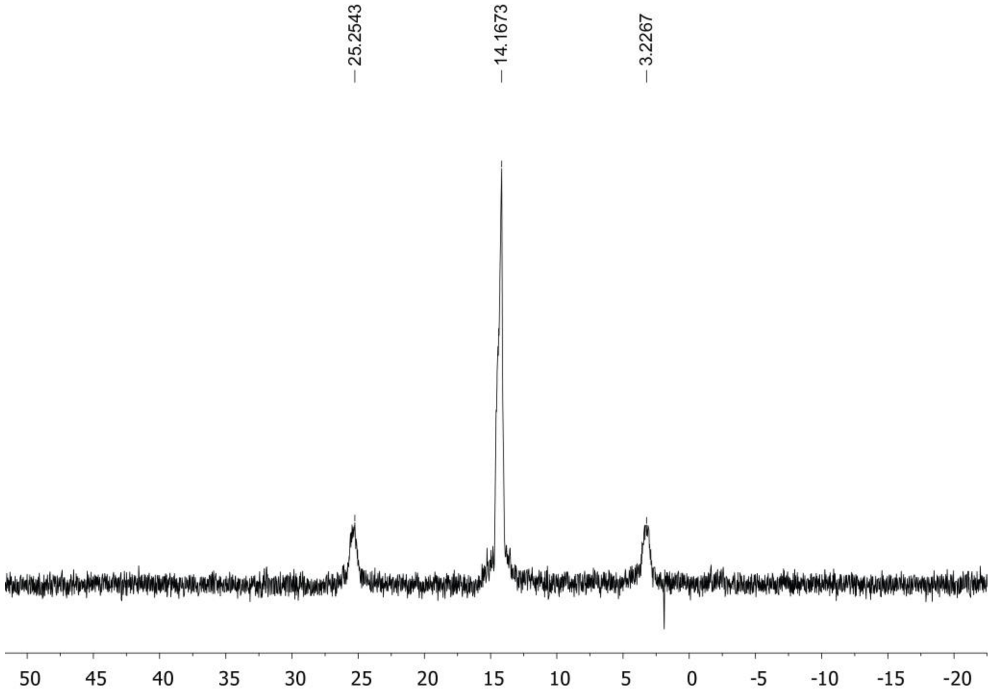


Figure S20. ^{31}P{^{1}H} NMR spectrum (121.4 MHz, CD_3COCD_3, 295 K) recorded for **1**.

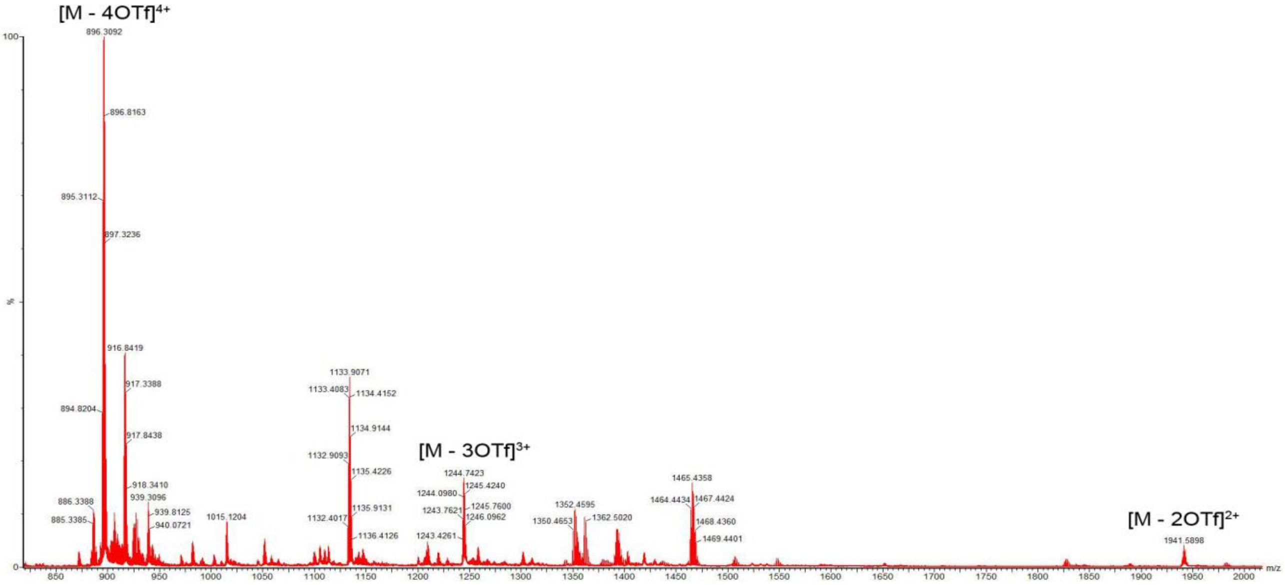
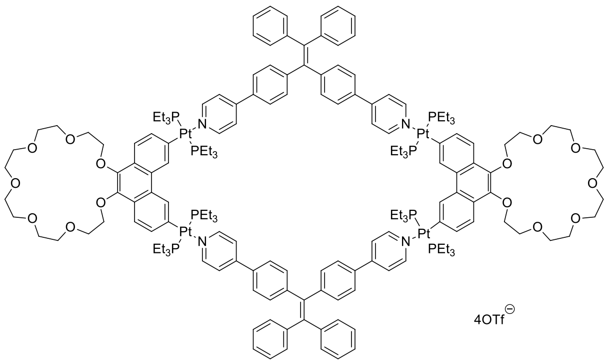


Figure S21. ESI-TOF-MS of **1**.

*11. Synthesis of rhomboidal metallacycle **2***



Compound **8** (30.39 mg, 18.81 μmol) and **11** (9.15 mg, 18.81 μmol) were dissolved in dry CH_2Cl_2 (2.0 mL) in a 5 mL vial. The reaction mixture was stirred for 12 h at room temperature. Diethyl ether (10 mL) was added to the resulting homogeneous solution to precipitate the product. The obtained product was dried under reduced pressure as a yellow solid (37.96 mg, 96%). ^{1}H NMR (400 MHz, CD_3COCD_3, 295K): 9.06 (t, J = 6.2 Hz, 8H), 8.68 (s, 4H), 8.15 (dd, J_1 = 16.7 Hz, J_2 = 5.3 Hz, 8H), 8.04 (d, J = 8.4 Hz, 4H), 7.86 (d, J = 8.2 Hz, 8H), 7.82 (d, J = 8.6 Hz, 4H), 7.33 (d, J = 8.2 Hz, 8H), 7.10–7.29 (m, 20H), 4.37–4.52 (m, 8H), 3.98–4.08 (m, 8H), 3.75–3.82 (m, 8H), 3.68–3.75 (m, 8H), 3.61–3.68 (m, 16H), 1.41–1.62 (m, 48H), 1.14–1.30 (m, 72H). ^{31}P{^{1}H} NMR (121.4 MHz, CD_3COCD_3, 295 K) δ (ppm): 14.69 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt–P}}$ = 2784.6 Hz). ESI-TOF-MS: *m*/*z* 901.3514 [**2** – 4OTf]$^{4+}$, 1252.1193 [**2** – 3OTf]$^{3+}$, 1952.6388 [**2** – 2OTf]$^{2+}$.

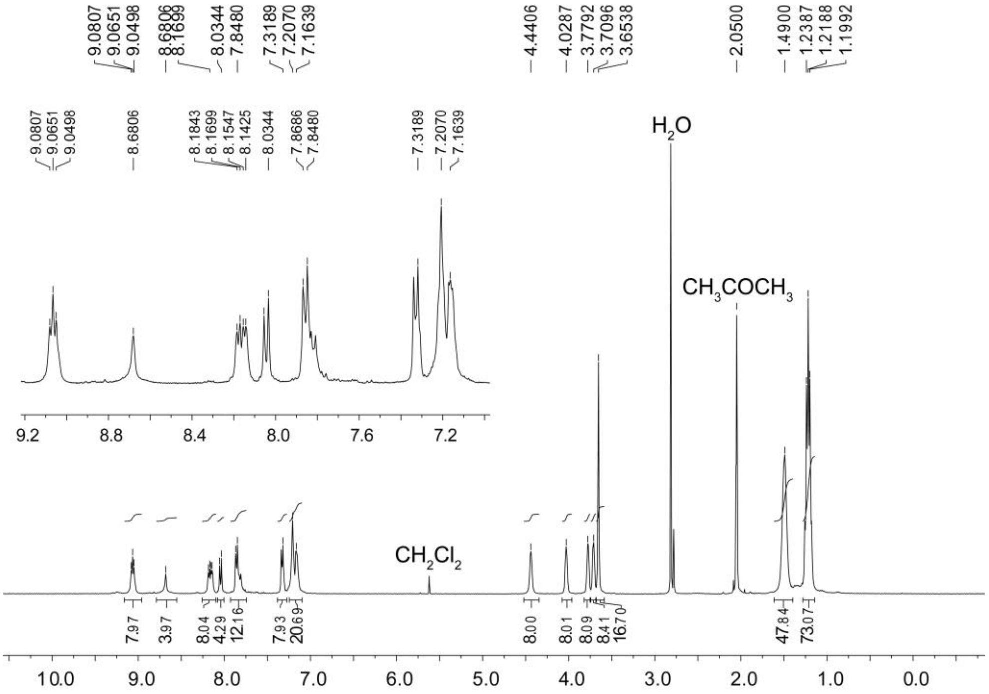


Figure S22. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, 295 K) recorded for **2**.

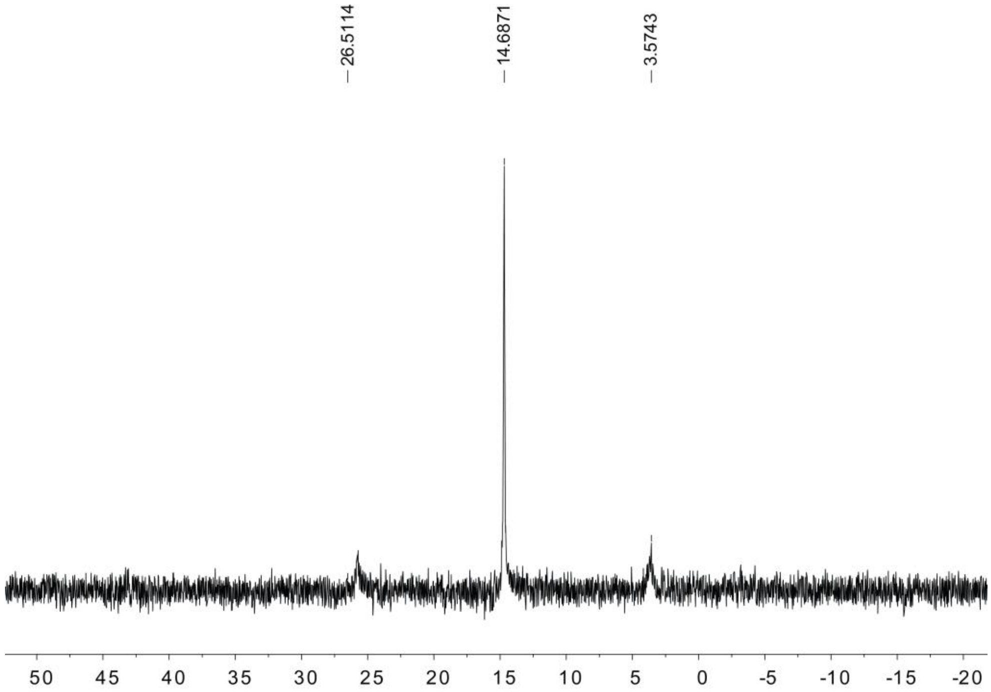


Figure S23. ^{31}P{^{1}H} NMR spectrum (121.4 MHz, CD_3COCD_3, 295 K) recorded for **2**.

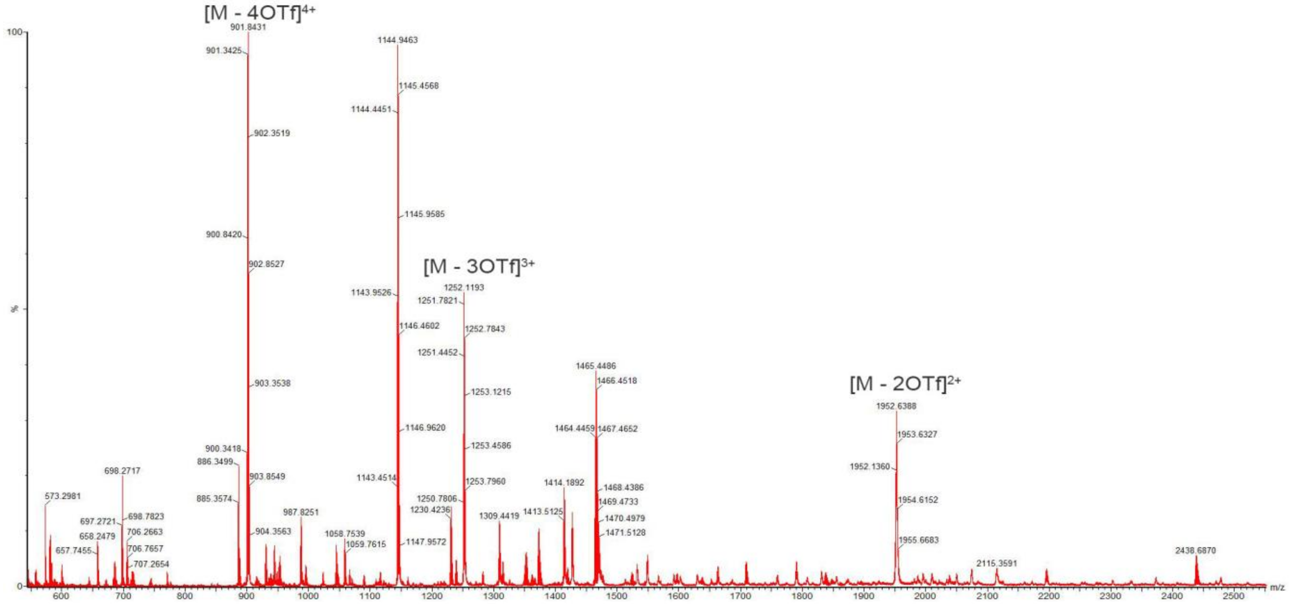
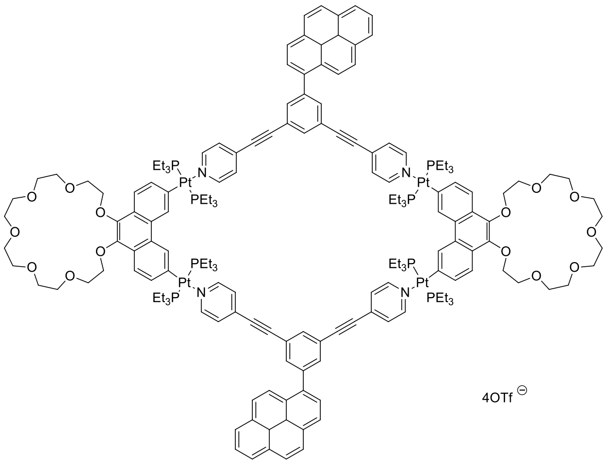


Figure S24. ESI-TOF-MS of **2**.

12. Synthesis of rhomboidal metallacycle ***3***



Compound **8** (30.39 mg, 18.81 μmol) and **12** (9.08 mg, 18.81 μmol) were dissolved in dry CH_2Cl_2 (2.0 mL) in a 5 mL vial. The reaction mixture was stirred for 12 h at room temperature. Diethyl ether (10 mL) was added to the resulting homogeneous solution to precipitate the product. The obtained product was dried under reduced pressure as a yellow solid (35.48 mg, 90%). ^{1}H NMR (400 MHz, CD_3COCD_3, 295K): 9.09–9.30 (m, 8H), 8.69 (s, 4H), 8.21–8.47 (m, 12H), 7.94–8.18 (m, 24H), 7.79 (d, J = 7.0 Hz, 4H), 4.35–4.50 (m, 8H), 3.97–4.07 (m, 8H), 3.74–3.82 (m, 8H), 3.67–3.74 (m, 8H), 3.57–3.67 (m, 16H), 1.36–1.61 (m, 48H), 1.07–1.31 (m, 72H). ^{31}P{^{1}H} NMR (121.4 MHz, CD_3COCD_3, 295 K) δ (ppm): 13.89 ppm (s, ^{195}Pt satellites, $^1J_{Pt–P}$ = 2655.5 Hz). ESI-TOF-MS: m/z 898.3780 [**3** – 4OTf]$^{4+}$, 1247.4213 [**3** – 3OTf]$^{3+}$, 1945.6079 [**3** – 2OTf]$^{2+}$.

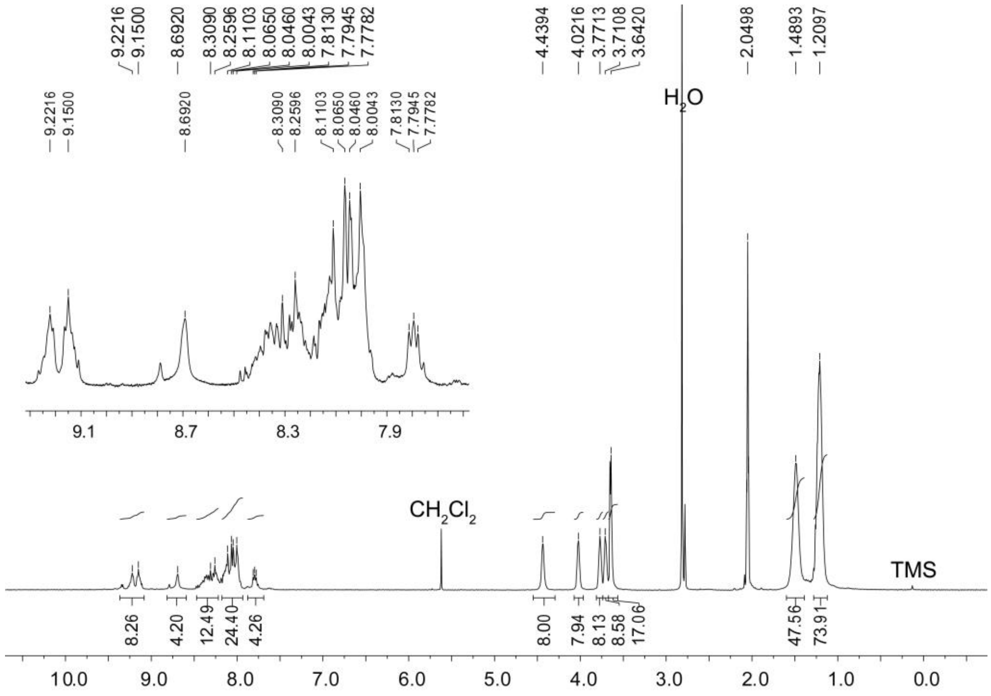


Figure S25. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, 295 K) recorded for **3**.

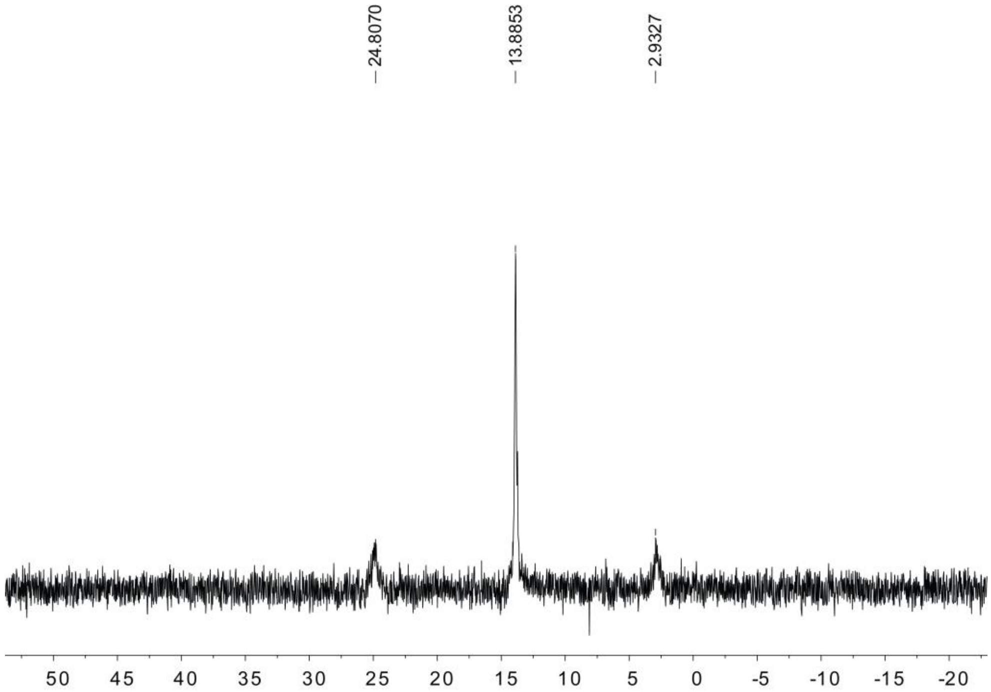


Figure S26. ^{31}P{^{1}H} NMR spectrum (121.4 MHz, CD_3COCD_3, 295 K) recorded for **3**.

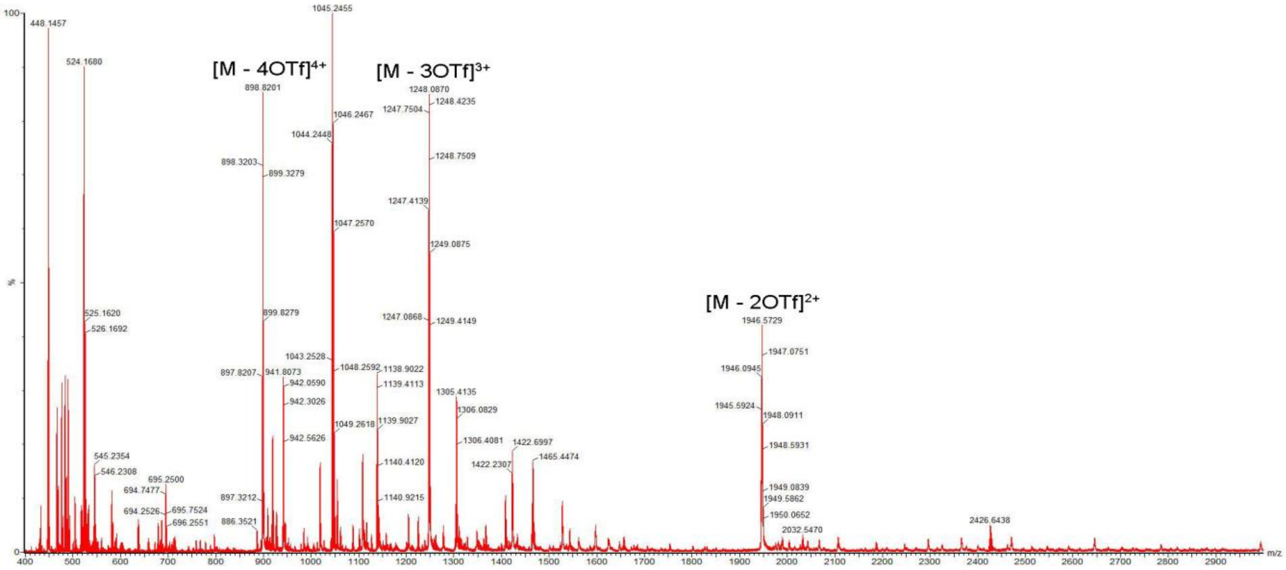
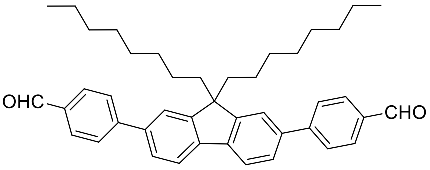


Figure S26. ESI-TOF-MS of **3**.

13. Synthesis of compound ***14***



Compound **13** (1.09 g, 2.0 mmol), (4-formylphenyl)boronic acid (0.90 g, 6.0 mmol), $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol), and K_2CO_3 (2.76 g, 20.0 mmol) were added into a 100 mL Schlenk flask and then charged with nitrogen. Degassed dioxane (60 mL) and H_2O (30 mL) were added to the flask under nitrogen by syringe. The reaction mixture was stirred at 90 °C for 48 h under nitrogen atmosphere. After cooling, the product was concentrated and purified by flash column chromatography with CH_2Cl_2:hexane (1:2, v/v) as the eluent to afford compound **13** (0.75 g, 63%) as white powder. M. P. 76.3–78.6 ^{o}C. ^{1}H NMR (400 MHz, CD_2Cl_2, 295K): 10.19 (s, 4H), 7.99 (d, J = 8.3 Hz, 4H), 7.81–7.89 (m, 6H), 7.62–7.70 (m, 4H), 2.03–2.18 (m, 4H), 1.00–1.34 (m, 24H), 0.79 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 295K): 191.1, 151.3, 146.3, 140.0, 138.0, 134.2, 129.4, 126.8, 125.7, 120.8, 119.6, 54.6, 39.4, 30.8, 29.0, 28.2, 22.9, 21.7, 13.1. ESI-HR-MS: m/z 599.3895 [**14** + H]$^{+}$, calcd. for $[C_{43}H_{51}O_2]^{+}$, 599.3889.

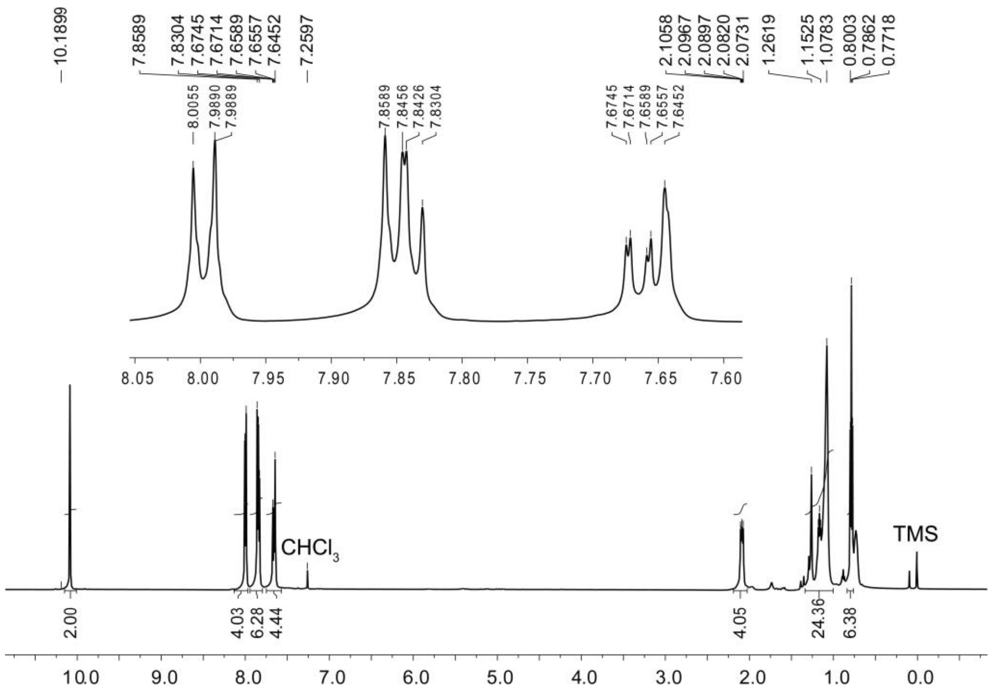


Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 295 K) recorded for **14**.

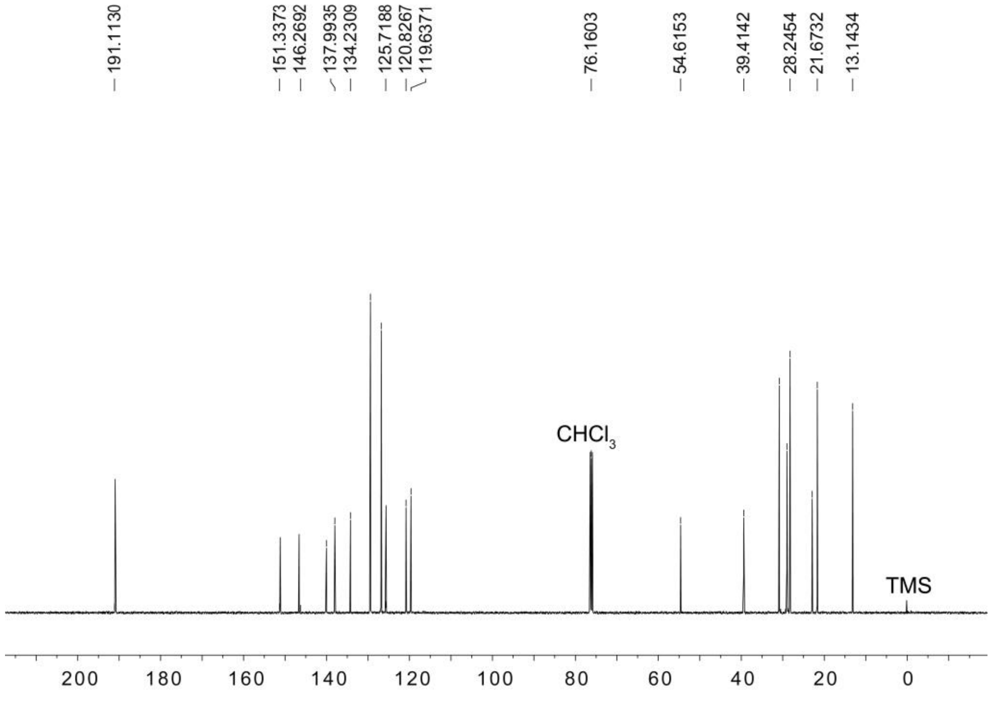


Figure S29. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 295 K) recorded for **14**.

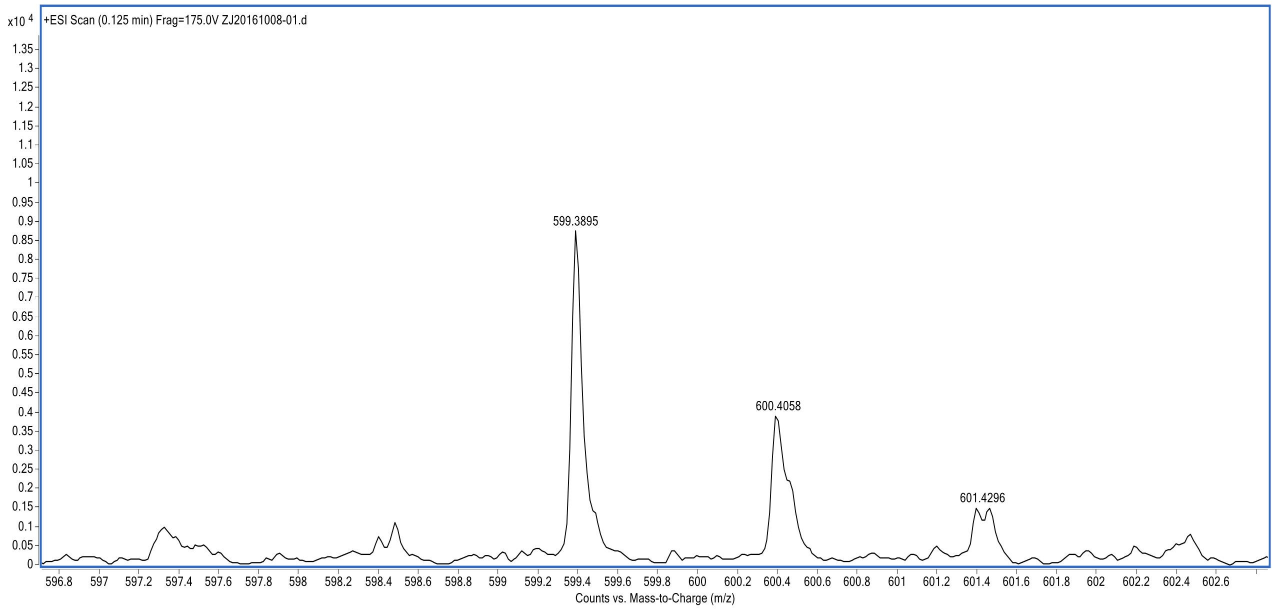
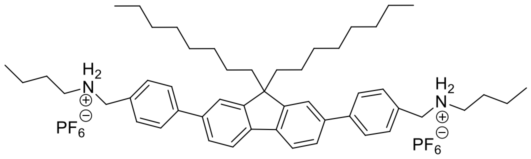


Figure S30. Electrospray ionization mass spectrum of **14**.

*14. Synthesis of bis-ammonium salt **4***



Compound **14** (1.20 g, 2.00 mmol) and *n*-butylamine (0.29 g, 4.00 mmol) were dissolved into CH_3OH (100 mL) and then the reaction mixture was heated at reflux for 12 h. After cooling to room temperature, $NaBH_4$ (0.23 g, 6.00 mol) was slowly added to the above solution. The mixture was stirred at room temperature for another 24 h. HCl (1 mol/L, 20 mL) was added to the reaction mixture until there is no more precipitate comes out. The precipitate was filtered and dissolved in water. Then saturated aqueous NH_4PF_6 solution was added to give a precipitate which was collected and washed with large excess of water to afford **4** (0.54 g, 27% in four steps) as a white solid. M. P.: 237.5–239.3 ^{o}C. ^{1}H NMR (400 MHz, DMSO, 295K): 9.02 (br, 4H, N*H*$_2$), 7.92 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 4H), 7.79 (s, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 4H), 4.20 (s, 4H), 2.81–3.04 (m, 4H), 1.98–2.21 (m, 4H), 1.55–1.71 (m, 4H), 1.27–1.42 (m, 4H), 0.92–1.25 (m, 20H), 0.90 (t, *J* = 7.3 Hz, 6H), 0.72 (t, *J* = 6.9 Hz, 6H), 0.48–0.65 (m, 4H). ^{13}C NMR (100 MHz, DMSO, 295K): 151.4, 140.9, 139.9, 138.4, 130.9, 130.6, 126.9, 125.8, 121.1, 120.5, 55.1, 49.6, 46.1, 31.1, 29.1, 28.4, 27.4, 23.3, 22.0, 19.3, 13.9, 13.5. ESI-HR-MS: *m*/*z* 1003.5049 [**4** - H]$^-$, calcd. for $[C_{51}H_{73}F_{12}N_2P_2]^-$, 1003.5057.

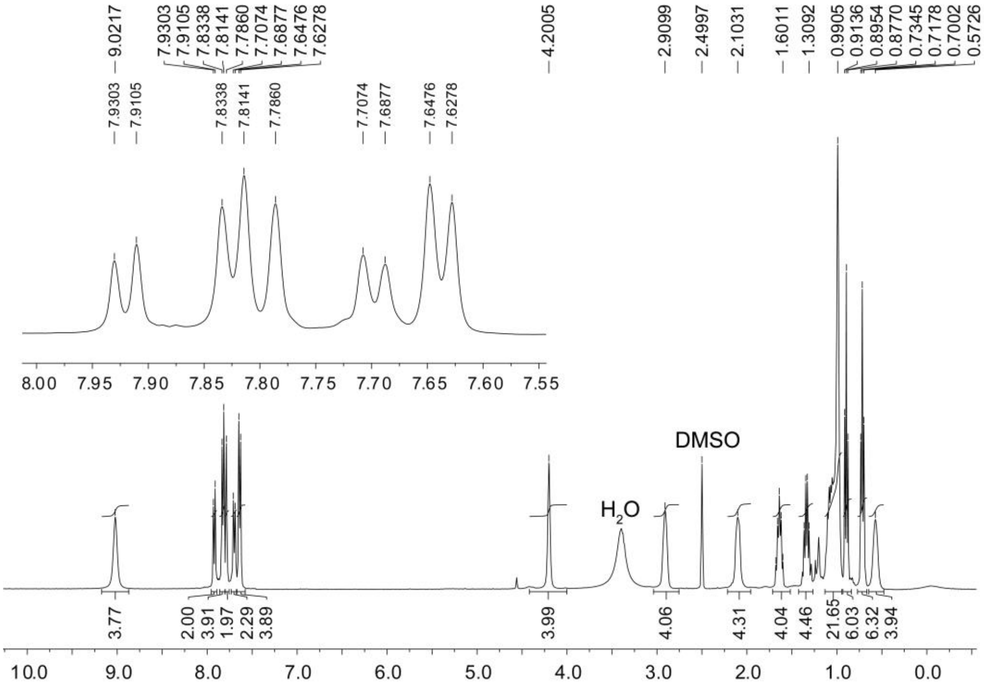


Figure S31. ^{1}H NMR spectrum (400 MHz, DMSO, 295 K) recorded for **4**.

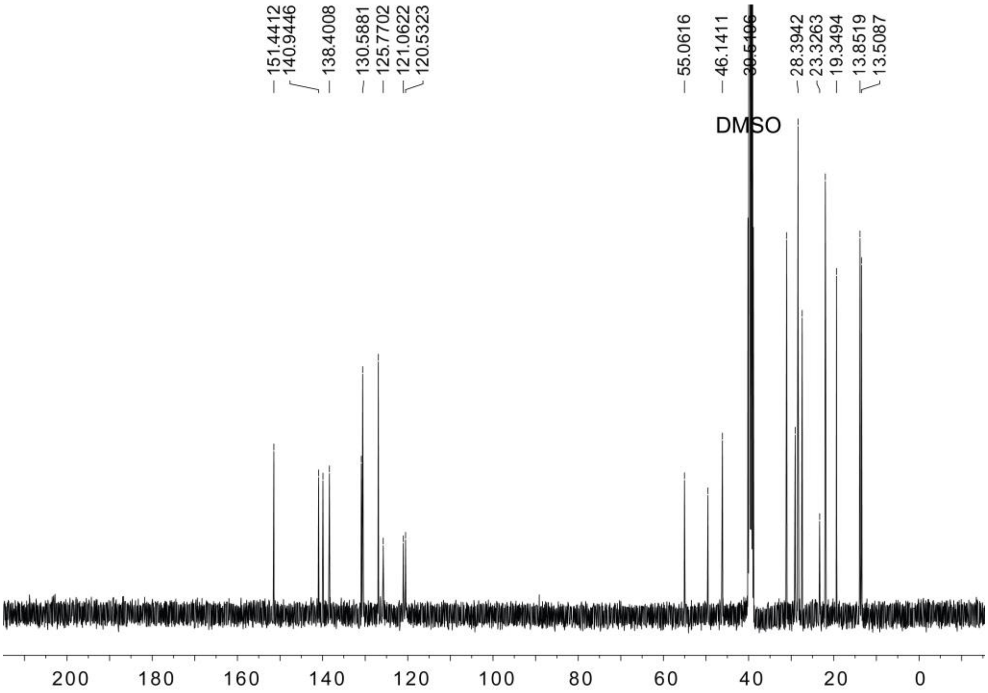


Figure S32. ^{13}C NMR spectrum (100 MHz, DMSO, 295 K) recorded for **4**.

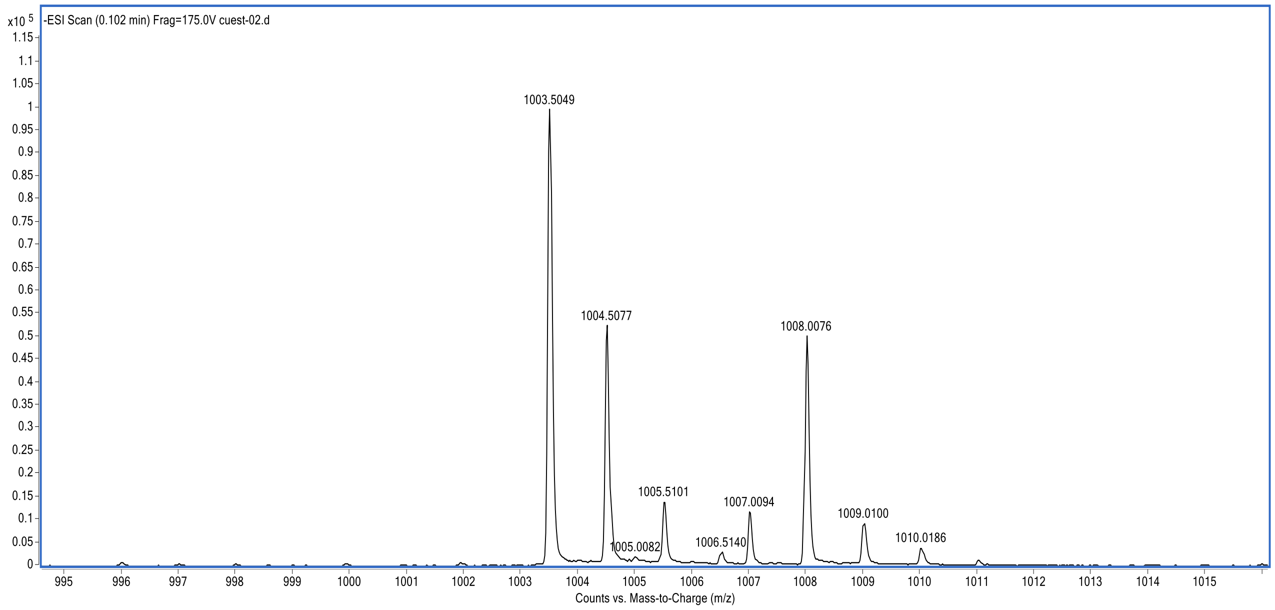


Figure S33. Electrospray ionization mass spectrum of **4**.

Section C. Host-guest complexation study between crown ether 8 and ammonium salt 9

*1. ^{1}H NMR spectra of an equimolar acetone solution of **8** and **9***

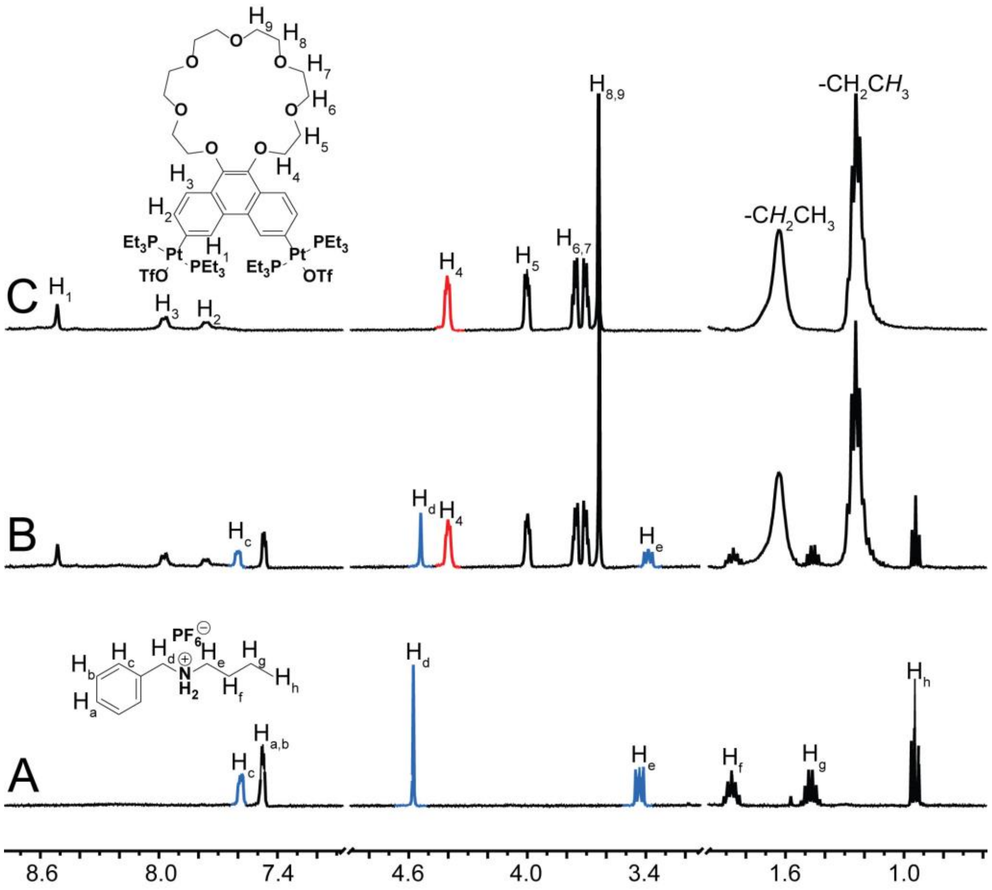


Figure S34. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 295 K) of (A) 2.00 mM **9**, (B) 2.00 mM **8** and **9**, (C) 2.00 mM **8**. Upfield shifts were observed for protons H_d, H_e of **9**, similar with benzo-21-crwon-7 (B21C7)-based system, indicating the formation of inclusion complex **8·9**.

2. *Determination of association constant (K_a) by ^{1}H NMR titration methods*

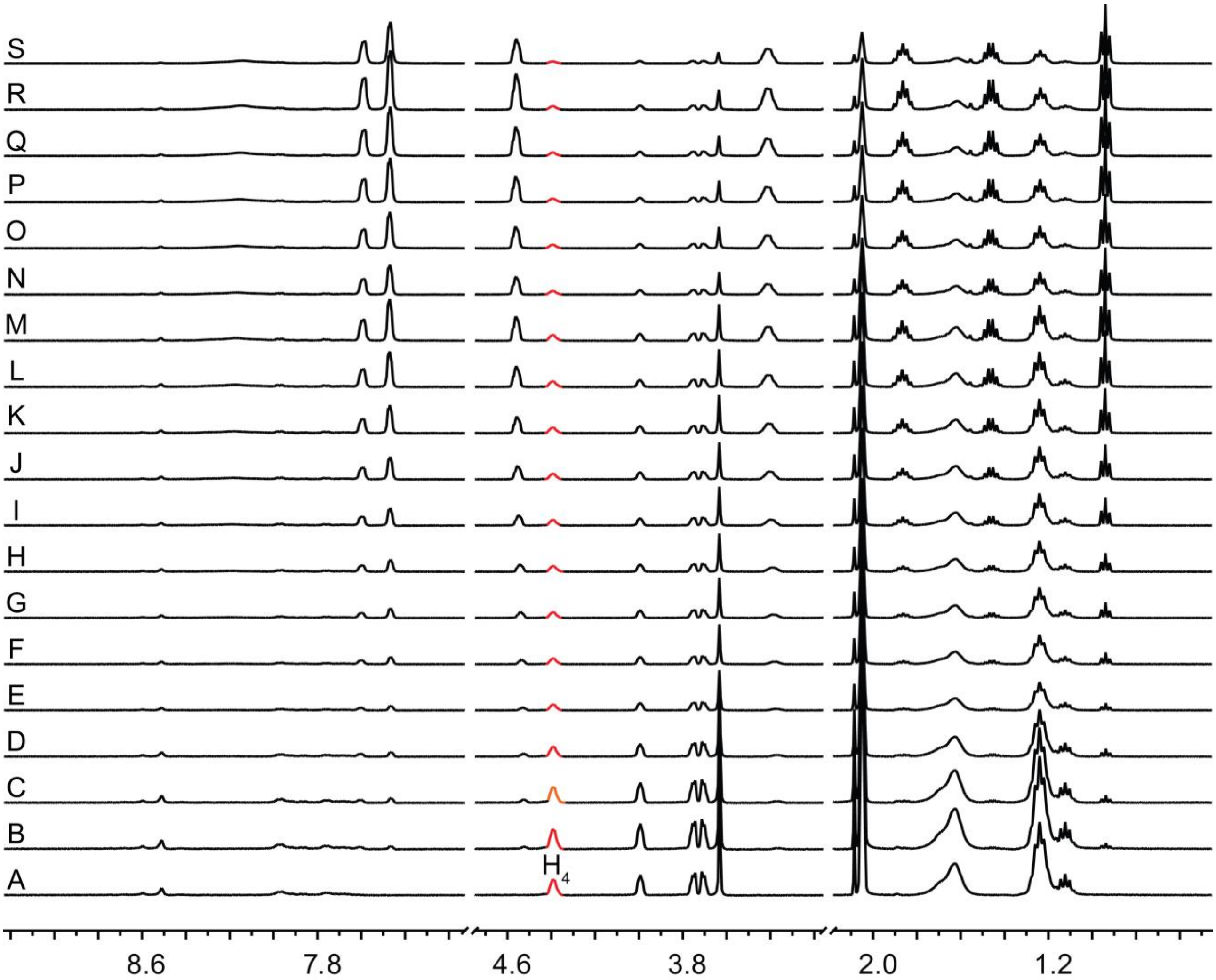


Figure S35. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 295 K) of **8** at a concentration of 2.00 mM upon the addition of **9**: (A) 0.00 mM, (B) 0.19 mM, (C) 0.32 mM, (D) 0.47 mM, (E) 0.76 mM, (F) 1.23 mM, (G) 1.65 mM, (H) 2.06 mM, (I) 2.95 mM, (J) 3.92 mM, (K) 4.85 mM, (L) 6.06 mM, (M) 7.07 mM, (N) 8.43 mM, (O) 10.08 mM, (P) 12.35 mM, (Q) 14.07 mM, (R) 16.67 mM, (S) 19.48 mM.

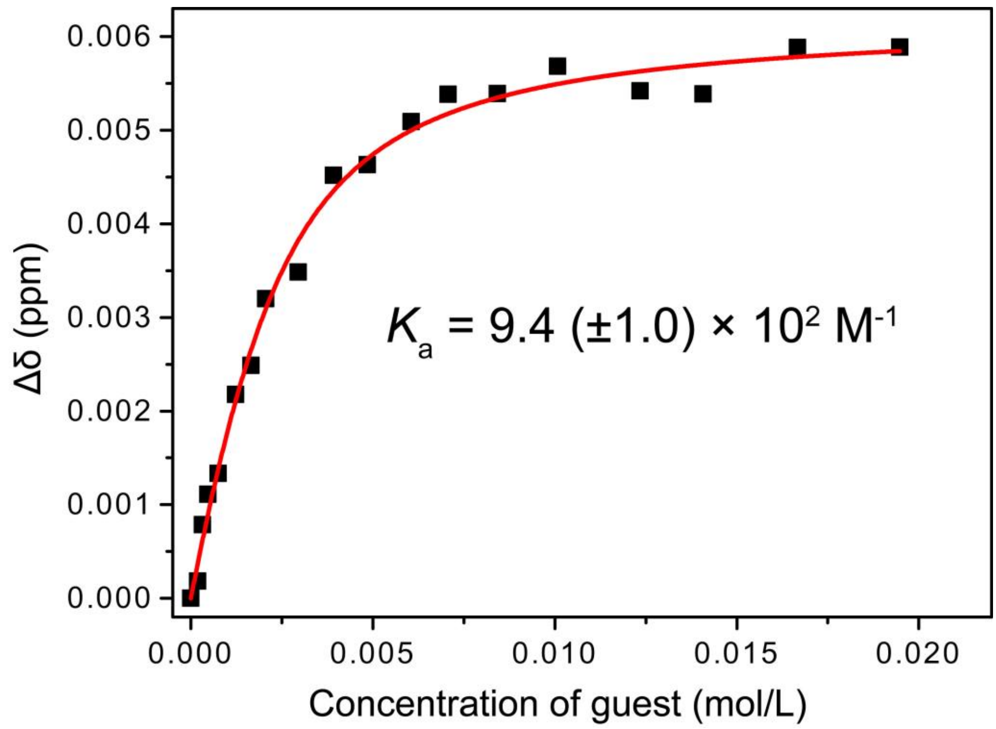


Figure S36. Non-linear fitting curve of the chemical shift changes of H_4 versus the concentration of **9**. The association constant K_a was calculated according to the following equation:

$$\Delta\delta = (\Delta\delta_{max}/[H]_0)\ (0.5[G] + 0.5\ ([H]_0+1/K_a) - (0.5([G]^2+(2[G](1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5}))$$

Where $\Delta\delta$ is the chemical shift change of H_4 on **8** upon titration, $\Delta\delta_{max}$ is the chemical shift change of H_4 when **8** is completely complexed, $[H]_0$ is the fixed concentration of **8** (0.002 mol/L), [G] is the concentration of added **9**. Based on the above equation, the association constant (K_a) of **8·9** was calculated to be 9.4 (± 1.0) × 10^2 M^{-1}.

Section D. The characterization of the supramolecular oligomers

1. *The size of the supramolecular oligomers by two-dimensional diffusion-ordered NMR (DOSY) method*

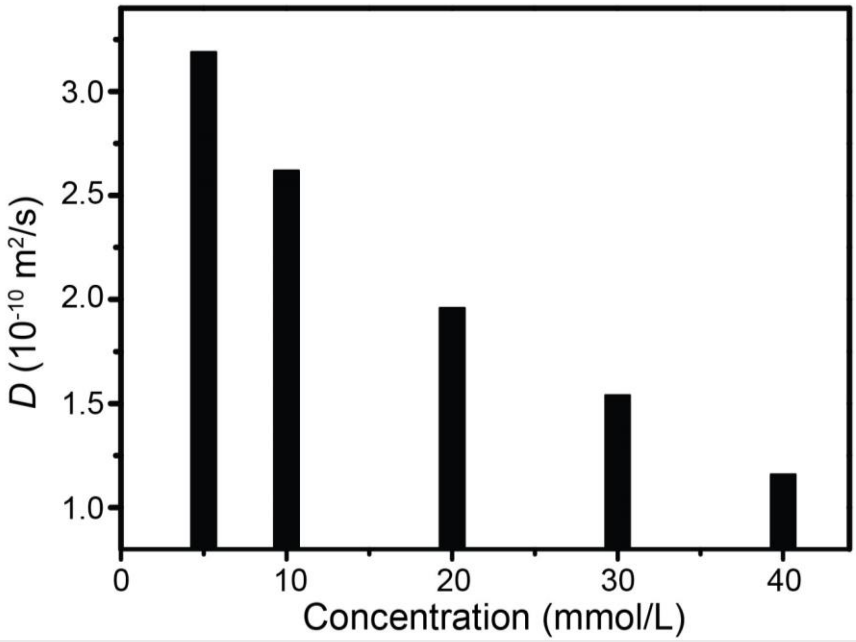


Figure S37. The measured weight average diffusion coefficient *D* of equal molar **4** and **1** at different concentrations.

Section E. The effect of counter-ions towards the assembly process

*1. Synthesis of bis-ammonium salt **4** with OTf$^-$ as counter ions*

Compound **4** (50 mg, 0.05 mmol) and AgOTf (200 mg, 1.31 mmol) were dissolved into the mixted solution of CH_3COCH_3 (4 mL) and H_2O (1 mL). The mixture was stirred at room temperature for 12 h. The filtrate was collected and the solvent was removed by N_2. The obtained solid was washed five times with water.

*2. The ^{1}H NMR spectra of the mixture of **1** and **4***

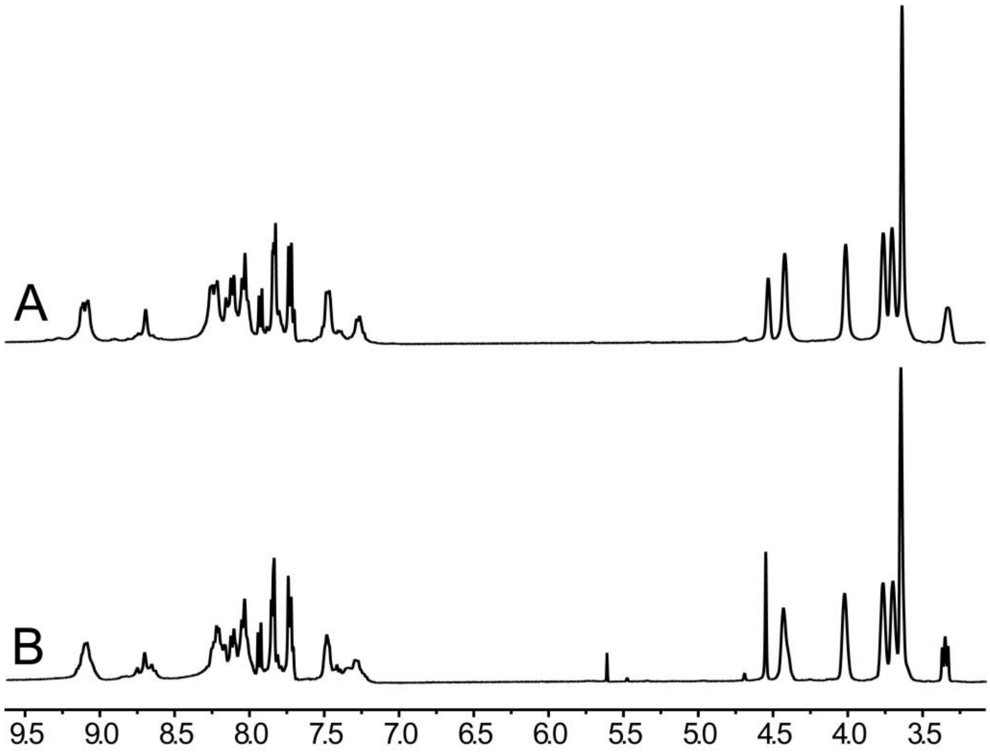


Figure S38. Partial ^{1}H NMR spectra (CD_3COCD_3, 295 K, 400 MHz) of equal molar **4** and **1** at the concentration of 5 mM. (*A*) both **1** and **4** with OTf^- as counter ions; (*B*) **1** with OTf^- and **4** with $PF6^-$ as the counter ions

Section F. The fluorescence properties of 1 and 4

*1. The aggregation-induced emission (AIE) property of **1***

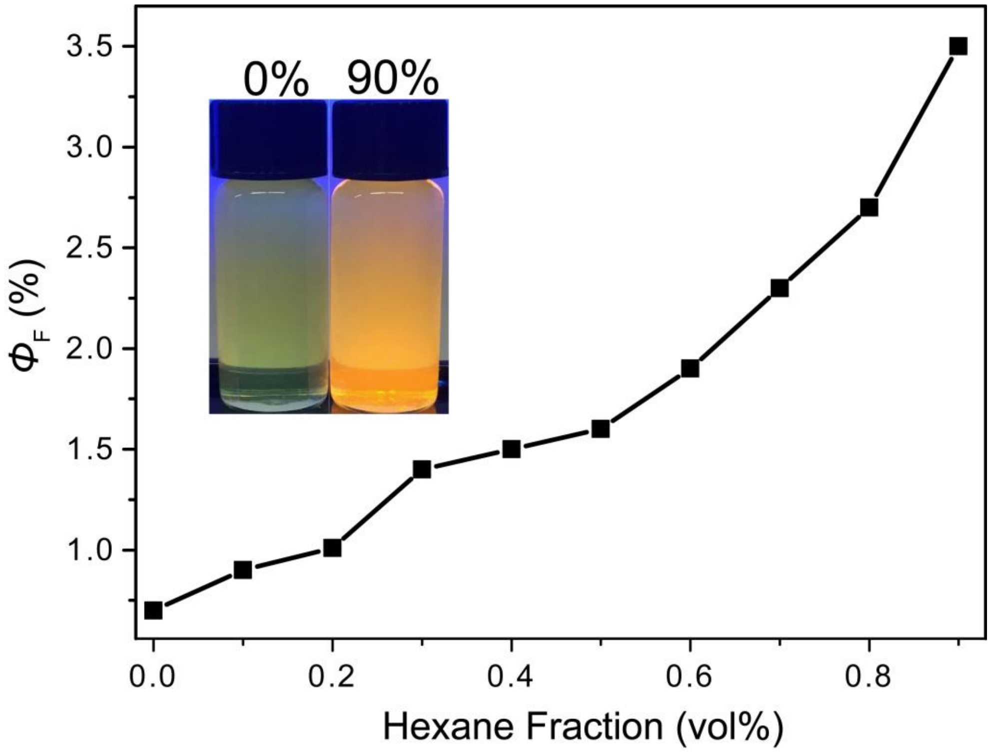


Figure S39. Fluorescence quantum yields of **1** versus hexane fraction in acetone/hexane mixtures (λ_{ex} = 365 nm, c = 10.0 μM) which were determined using quinine sulfate at 365 nm (Φ_F = 56%). Insets: photographs of **1** in acetone and 10%/90% acetone/hexane mixture upon excitation at 365 nm using an UV lamp at 298 K (c = 10.0 μM).

*2. The aggregation-caused quenching (ACQ) property of **4***

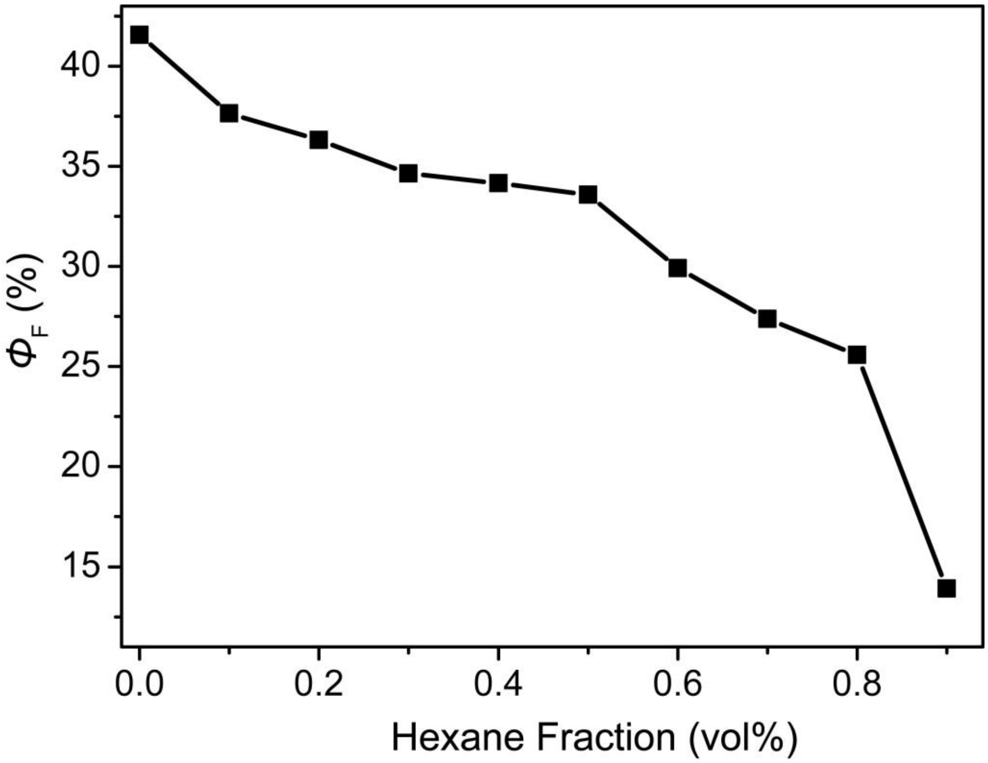


Figure S40. Fluorescence quantum yields of **4** versus hexane fraction in acetone/hexane mixtures (λ_{ex} = 365 nm, c = 10.0 μM) which were determined using quinine sulfate at 365 nm (Φ_F = 56%).

Section G. References

S1. Kim HJ, Lee E, Park HS, Lee M (2007) Dynamic Extension-Contraction Motion in Supramolecular Springs. *J Am Chem Soc* 129(36):10994–10995.

S2. Zhang CJ, et. al. (2007) Benzo-21-Crown-7/SecondaryDialkylammonium Salt [2]Pseudorotaxane- and [2]Rotaxane-Type Threaded Structures. *Org Lett* 9(26):5553–5556.

S3. Yoshida T, Matsuda T, Otsuka S, Parshall GW, Peet WG (1990) Tetrakis(Triethylphosphine)Platinum(0). *Inorg Synth* 28:122–123.

S4. Ashton PR, et. al. (1996) Pseudorotaxanes Formed between Secondary Dialkylammonium Salts and Crown Ethers. *Chem Eur J* 2(6):709–728.

S5. Qu Y, et. al. (2013) A New Triphenylamine Fluorescent Dye for Sensing of Cyanide Anion in Living Cell. *Tetrahedron Lett* 54(36):4942–4944.

S6. Yan XZ, et. al. (2015) A Suite of Tetraphenylethylene-Based Discrete Organoplatinum(II) Metallacycles: Controllable Structure and Stoichiometry, Aggregation-Induced Emission, and Nitroaromatics Sensing. *J Am Chem Soc* 137(48):15276–15286.

S7. Wei Wang, et. al. (2015) Discrete Stimuli-Responsive Multirotaxanes with Supramolecular Cores Constructed through a Modular Approach. *Chem Eur J* 21(16):6286–6294.