

Supplementary Information

Self-Healing Heterometallic Supramolecular Polymers Constructed by Hierarchical Assembly of Triply Orthogonal Interactions with Tunable Photophysical Properties

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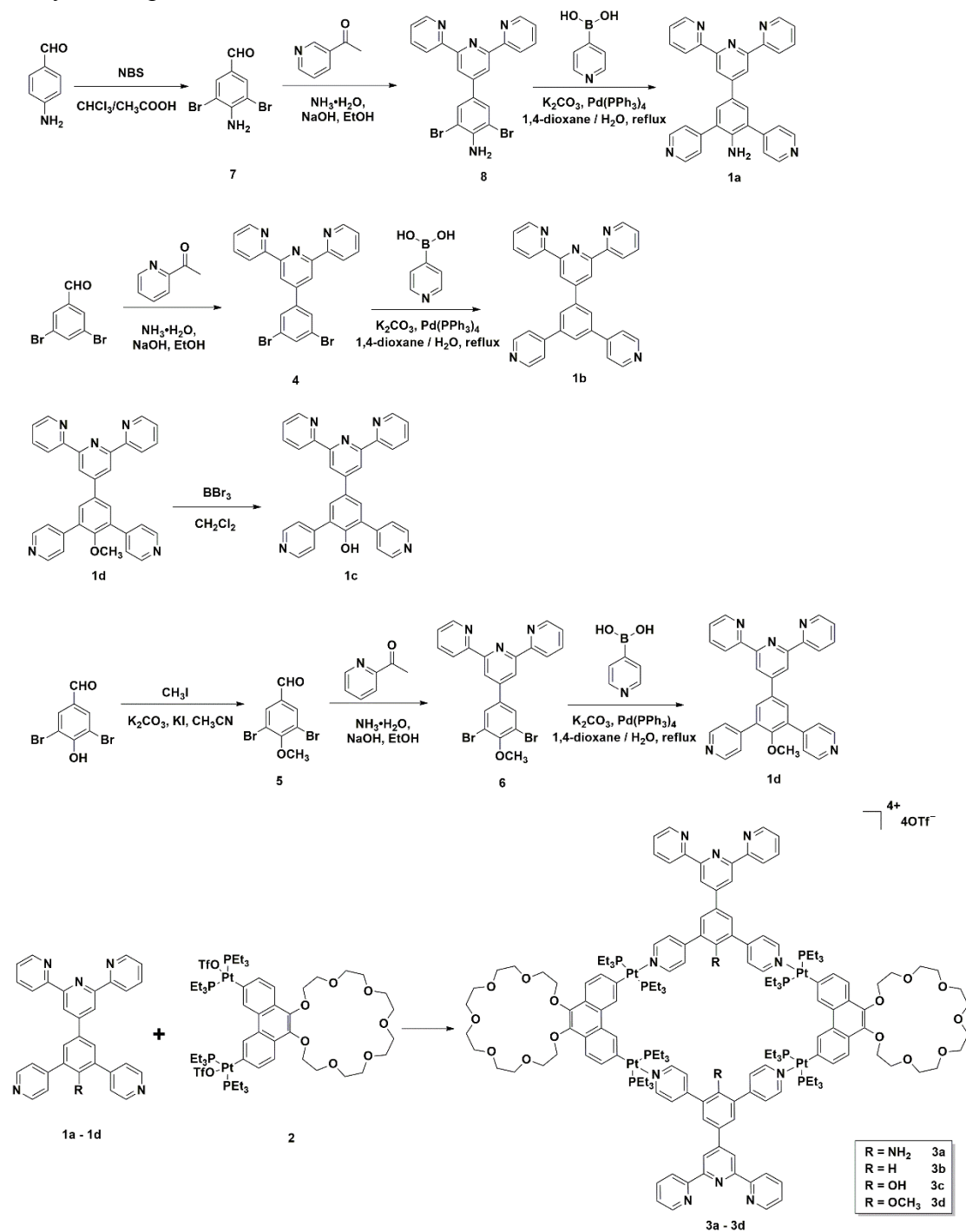
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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Energy Chemical. Compounds **2**^[S1] and **4**^[S2] were prepared according to the literature. NMR spectra were recorded on a Varian Unity 400 MHz or a Bruker Advance 500 MHz spectrometer. ¹H and ¹³C NMR chemical shifts are reported relative to residual solvent signals, and ³¹P{¹H} NMR chemical shifts are referenced to an external unlocked sample of 85% H₃PO₄ ($\delta = 0.0$ ppm). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer and 6530 Q-TOF LC/MS. The melting points were collected on a YRT-3 automatic melting point apparatus. The UV-Vis absorption spectra were measured by a Hitachi U-5300 absorption spectrophotometer. The fluorescent emission spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800. Dynamic light scattering experiments were performed using a Nano ZS90 instrument with a He-Ne laser (633 nm) and 90° collecting optics. The data were analyzed using the Malvern Dispersion Technology Software 5.10. Rheological data were obtained by using an ARES-G2 rheometer (Waters) with plate-plate geometry (diameter of 25 mm, gap is 300 μ m). Oscillatory frequency sweep experiments were performed from 0.1 rad s⁻¹ to 100 rad s⁻¹ with a strain in the linear region at 20 °C. The scanning frequency of self-healing experiments were performed with 10 rad s⁻¹ at 20 °C.

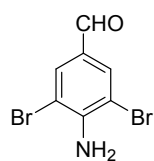
2. Synthetic procedures and characterization data.



Scheme S1 Synthetic routes to ligands **1a-1d** and metallacycles **3a-3d**.

2.1 Synthesis of compound **1a**

2.1.1 Synthesis of compound **7**



4-Aminobenzaldehyde (200.0 mg, 1.65 mmol) was dissolved in chloroform/glacial acetic acid (10 mL, 1/1, v/v) under ice bath. *N*-bromosuccinimide (NBS) was added in portions and the mixture was stirred at room temperature overnight. After

removing the solvent, water (100 mL) was added and the mixture was extracted with CH₂Cl₂ for

three times. The combined organic layer was dried over anhydrous MgSO_4 . After filtration, the solvent was removed by reduced pressure. The crude product was purified by flash column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as the eluent to afford compound **7** (70 mg, 65%) as a white solid. ^1H NMR (500 MHz, CDCl_3 , 298K): δ 9.61 (s, 1H), 7.84 (s, 2H), 5.11 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 298K): 187.0, 146.0, 132.7, 127.3, 107.0. ESI-HRMS $[\mathbf{7} + \text{H}]^+$: calcd. for $[\text{C}_7\text{H}_6\text{Br}_2\text{NO}]^+$ 277.8816, found 277.8810.

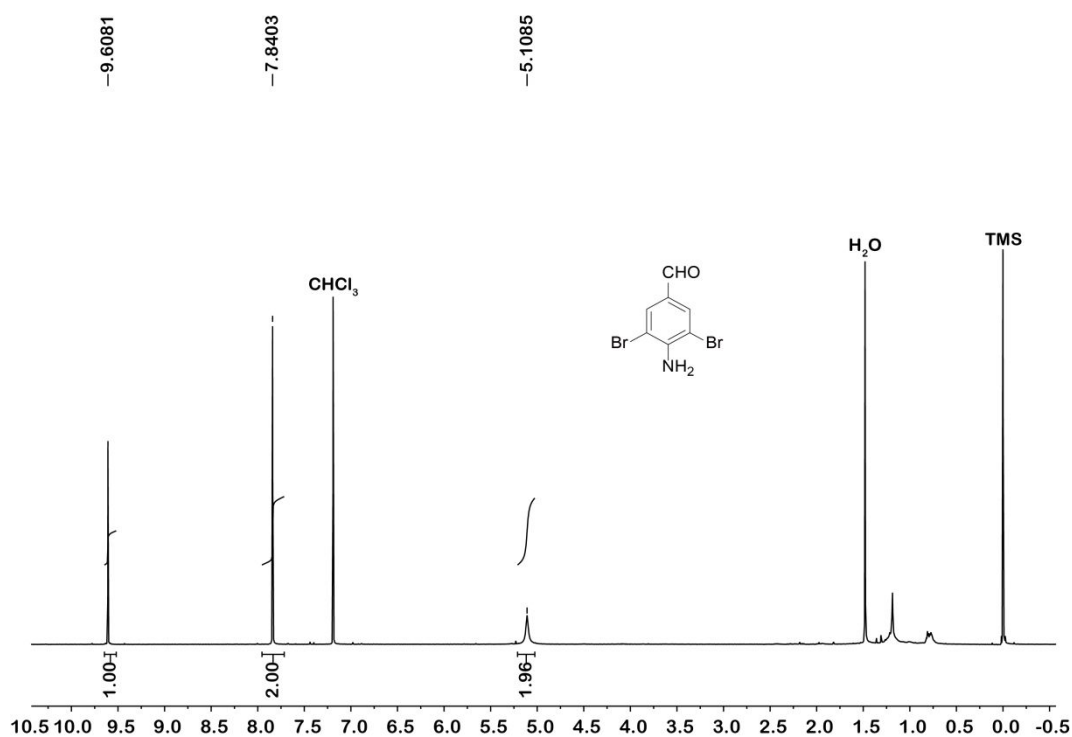


Fig. S1 ^1H NMR spectrum (500 MHz, CDCl_3 , 298K) of compound **7**.

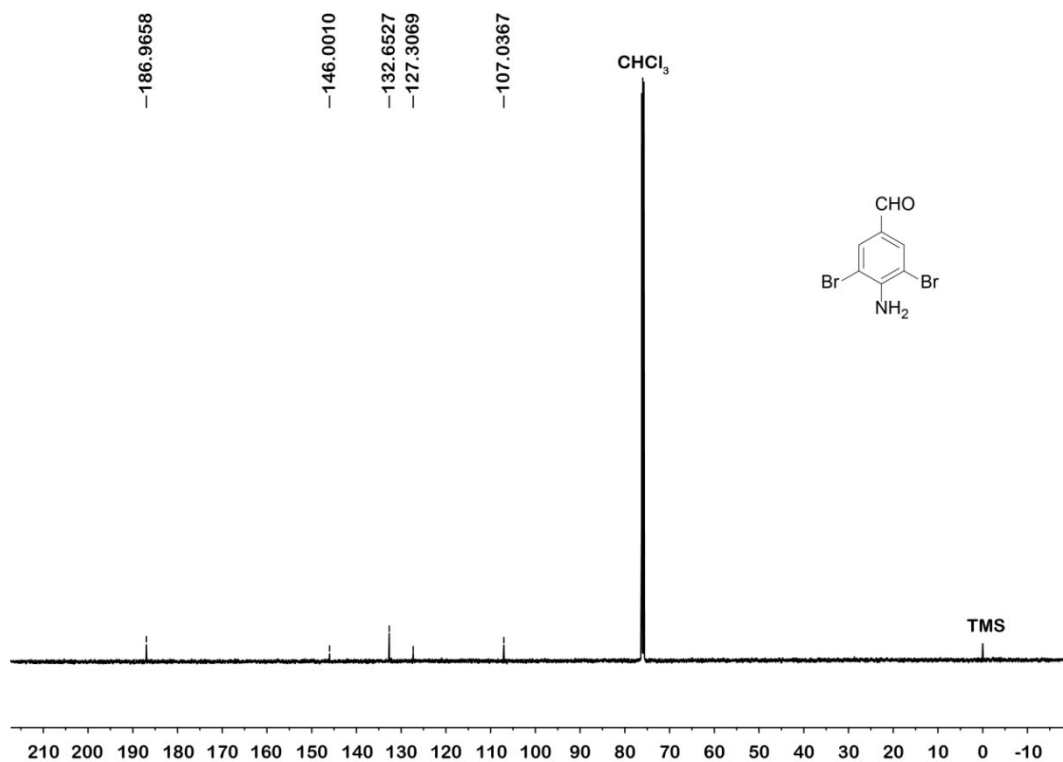


Fig. S2 ^{13}C NMR spectrum (125 MHz, CDCl_3 , 298K) of compound **7**.

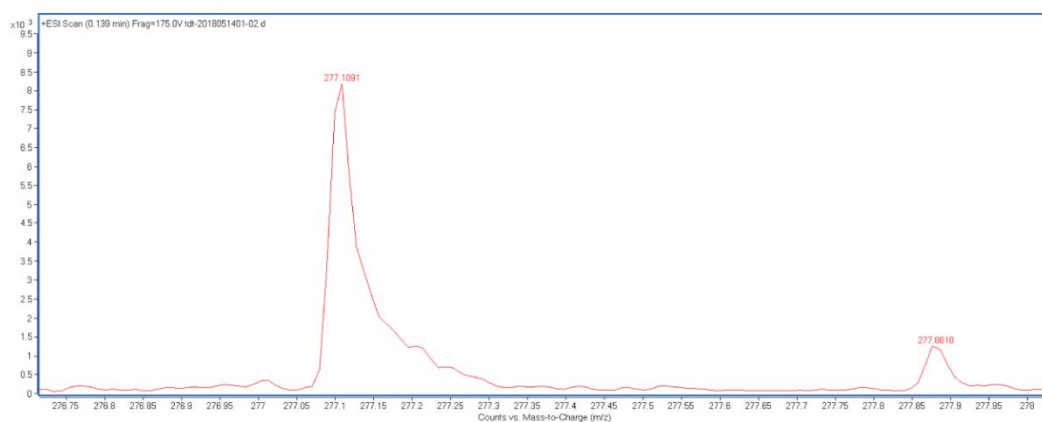
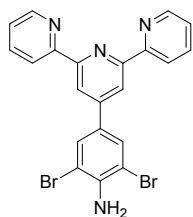


Fig. S3 ESI-HRMS spectrum of compound **7**.

2.1.2 Synthesis of compound **8**



2-Acetylpyridine (87.2 mg, 0.72 mmol) was added to a stirred solution of compound **7** (100.2 mg, 0.36 mmol) in ethanol (30 mL), and then NaOH (280.1 mg, 2.52 mmol) was added. After the mixture was stirred at room temperature overnight, $\text{NH}_3 \cdot \text{H}_2\text{O}$ (15.3 mg, 0.9 mmol) was added and the mixture was then

heated at 65 °C for 24 h. After the mixture was cooled down and filtered, the solid was collected

and washed with ethanol for three times to afford compound **8** (130 mg, 75%) as a white solid. ^1H NMR (500 MHz, CDCl_3 , 298K): δ 8.66 (d, $J = 5.7$ Hz, 2H), 8.57 (d, $J = 9.1$ Hz, 2H), 8.52 (s, 2H), 7.90 (s, 2H), 7.79 (td, $J = 7.7, 1.8$ Hz, 2H), 7.28 (ddd, $J = 7.5, 4.7, 1.2$ Hz, 2H), 4.68 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 298K): 156.1, 156.0, 149.1, 147.6, 142.7, 136.9, 130.4, 129.7, 123.9, 121.4, 117.6, 109.1. ESI-HRMS [**8** + H] $^+$: calcd. for $[\text{C}_{21}\text{H}_{15}\text{Br}_2\text{N}_4]^+$ 480.9663, found 480.9651.

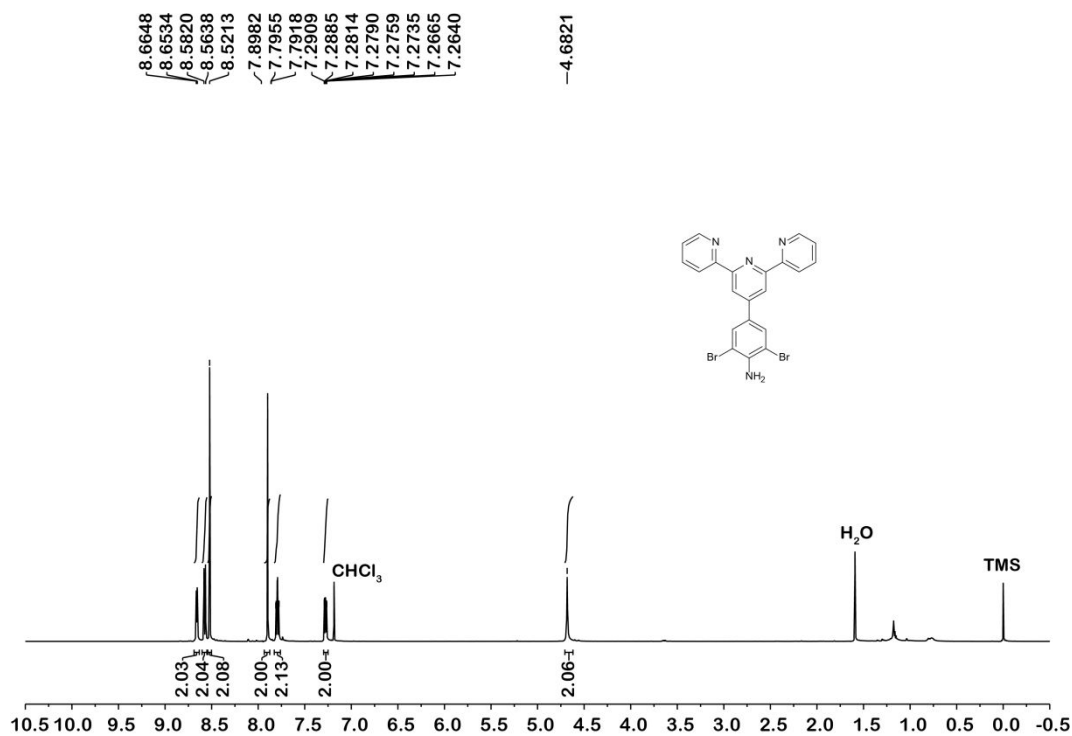


Fig. S4 ^1H NMR spectrum (500 MHz, CDCl_3 , 298K) of compound **8**.

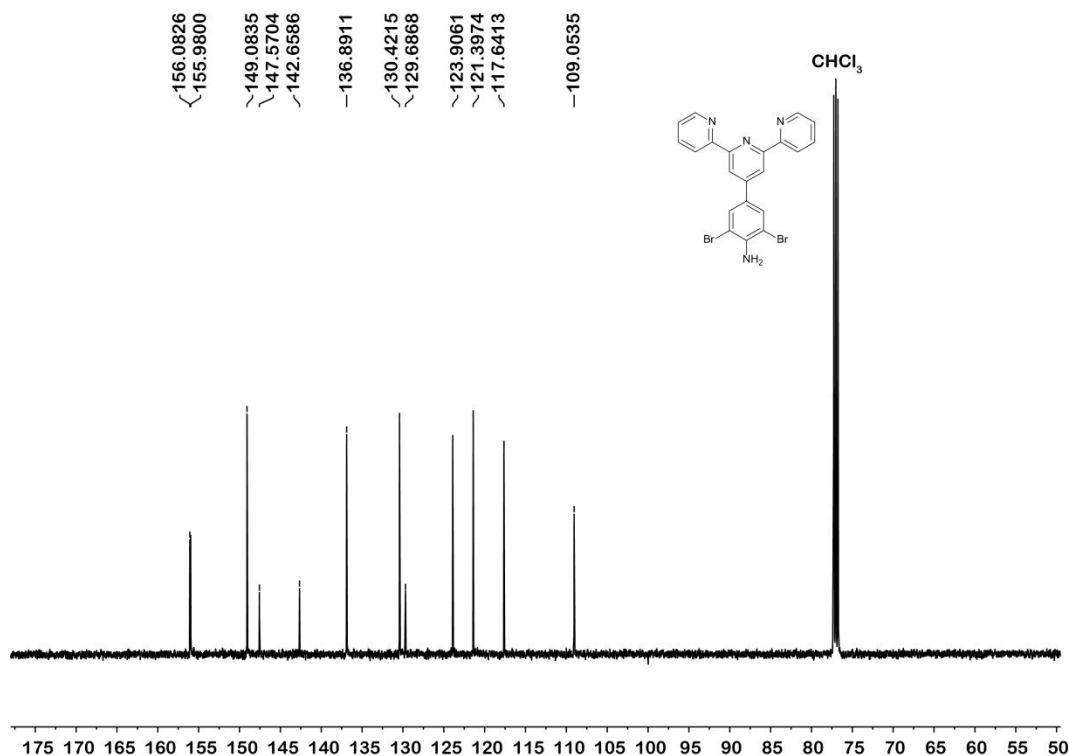


Fig. S5 ¹³C NMR spectrum (125 MHz, CDCl₃, 298K) of compound **8**.

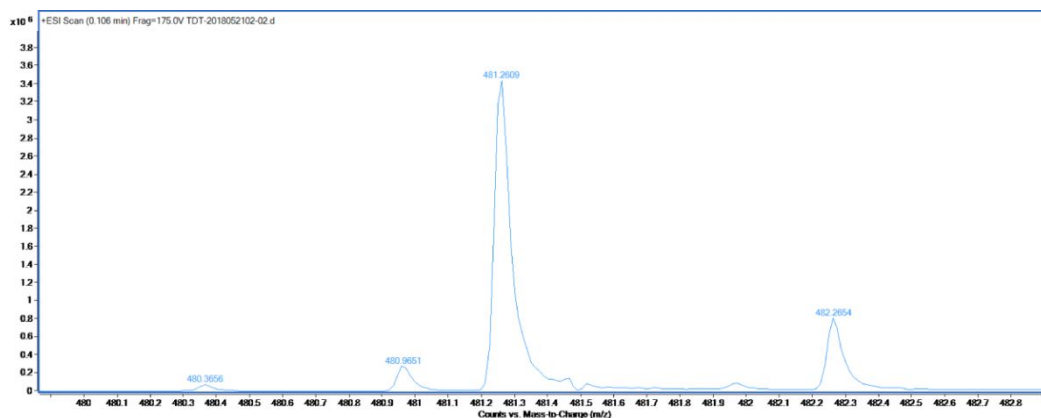
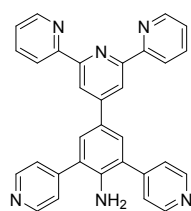


Fig. S6 ESI-HRMS spectrum of compound **8**.

2.1.3 Synthesis of compound **1a**



Compound **8** (100.0 mg, 0.21 mmol), 4-pyridineboronic acid (118.0 mg, 0.96 mmol), K₂CO₃ (265.7 mg, 1.93 mmol), Pd(PPh₃)₄ (19.6 mg, 0.02 mmol) were dissolved in 1,4-dioxane/H₂O (30 mL, 4/1, v/v) under nitrogen. The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the solvent was removed in vacuo. Then the mixture was extracted with CH₂Cl₂ for three times, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography with CH₂Cl₂/CH₃OH (5:1, v/v) as the eluent to afford

compound **9** (57 mg, 57%) as a white solid. ^1H NMR (500 MHz, CDCl_3 , 298K): δ 8.72 (d, $J = 5.0$ Hz, 4H), 8.70–8.57 (m, 6H), 7.85 (t, $J = 7.8$ Hz, 2H), 7.73 (s, 2H), 7.51 (d, $J = 5.0$ Hz, 4H), 7.32 (t, $J = 6.0$ Hz, 2H), 4.08 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 298K): δ 155.9, 155.6, 150.3, 148.7, 148.6, 146.6, 140.9, 136.6, 128.8, 128.3, 125.4, 123.9, 123.6, 121.1, 117.3. ESI-HRMS [**1a** + H] $^+$: calcd. for $[\text{C}_{31}\text{H}_{23}\text{N}_6]^+$ 479.1984, found 479.1986.

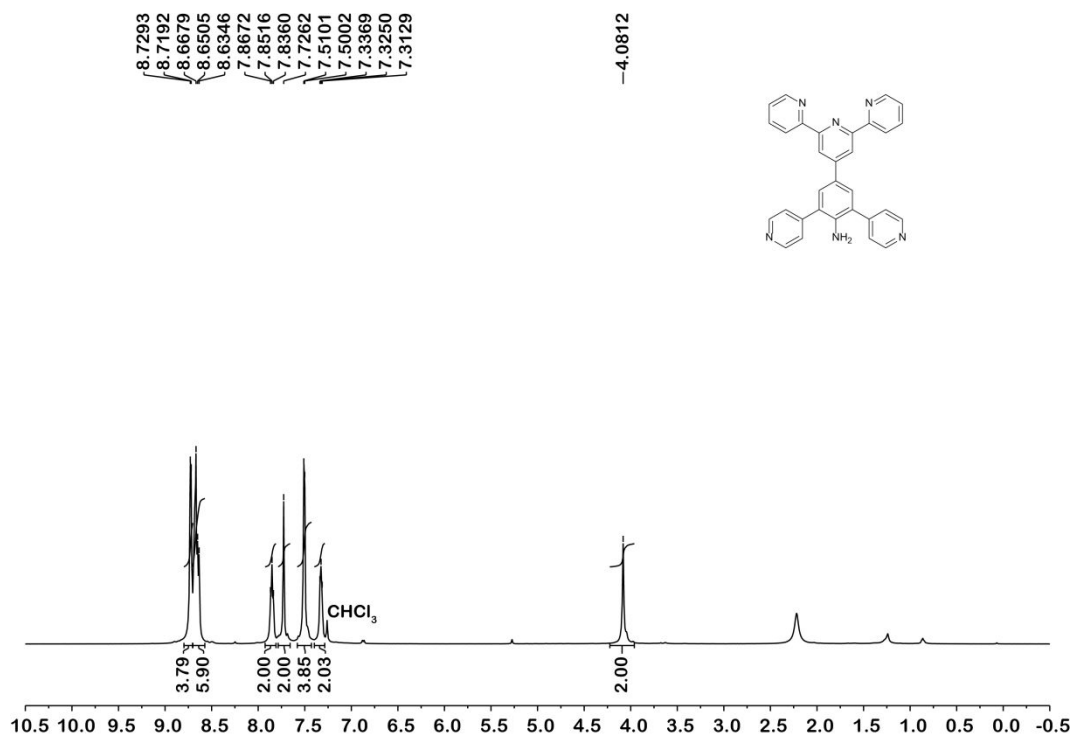


Fig. S7 ^1H NMR spectrum (500 MHz, CDCl_3 , 298K) of compound **1a**.

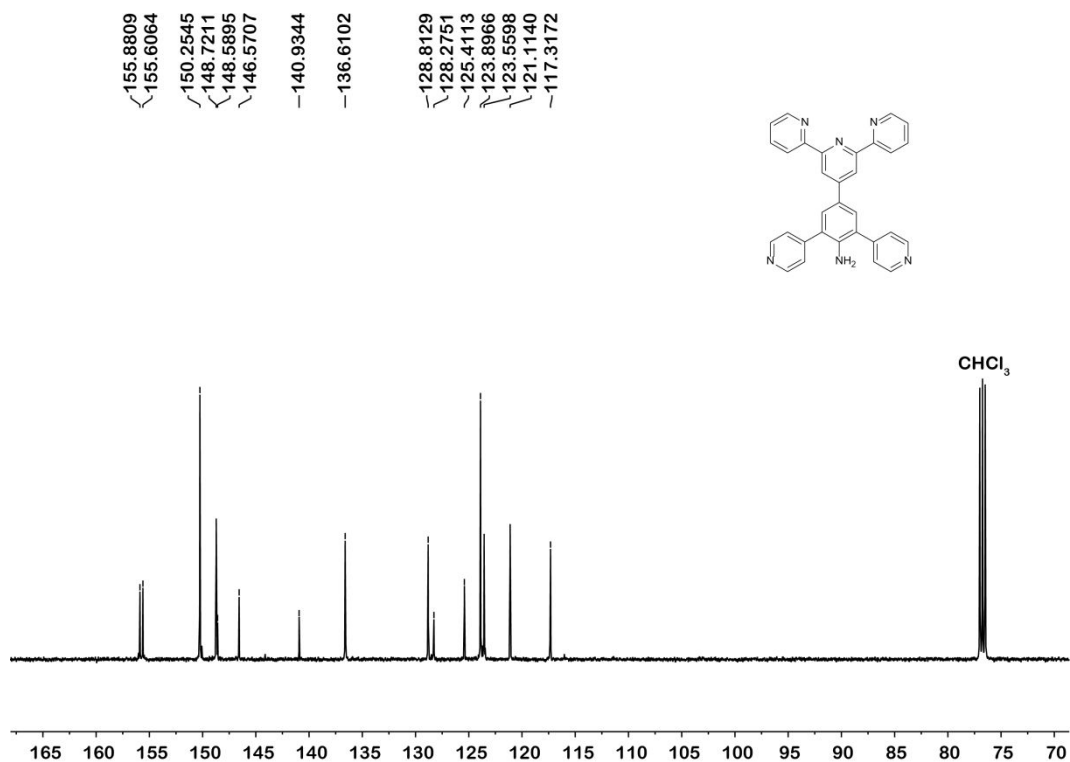


Fig. S8 ¹³C NMR spectrum (125 MHz, CDCl₃, 298K) of compound **1a**.

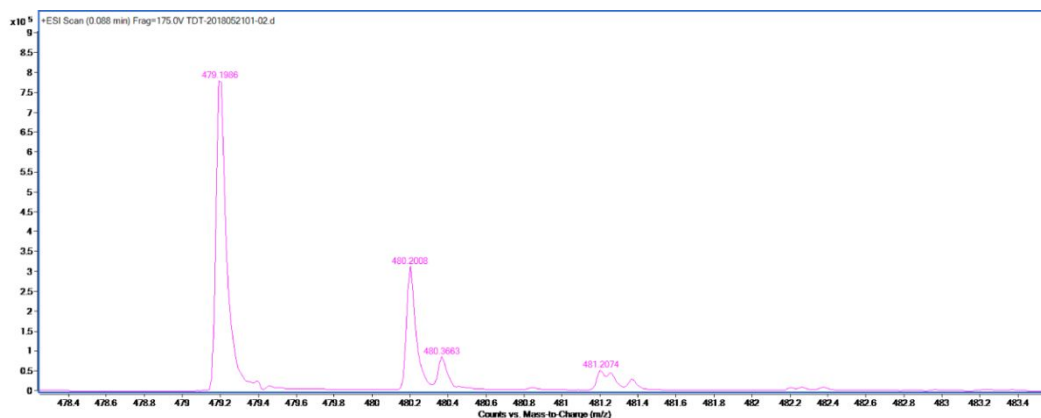
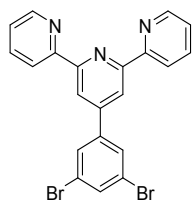


Fig. S9 ESI-HRMS spectrum of compound **1a**.

2.2 Synthesis of compound **1b**

2.2.1 Synthesis of compound **4**



2-Acetylpyridine (87.2 mg, 0.72 mmol) was added to a stirred solution of **3**, 5-dibromobenzaldehyde (90.0 mg, 0.34 mmol) (100.2 mg, 0.36 mmol) in ethanol (30 mL), and then NaOH (100.8 mg, 2.52 mmol) was added. After the mixture was stirred at room temperature overnight, NH₃·H₂O (15.3 mg, 0.9 mmol) were added and the mixture was heated at 65 °C for 24 h. Then the mixture was cooled

down and filtered. The solid was collected and washed with ethanol for three times to afford compound **4** (105 mg, 66%) as a white solid. ^1H NMR (500 MHz, CDCl_3 , 298K): δ 8.67 (dd, $J = 4.8, 0.9$ Hz, 2H), 8.60 (d, $J = 7.9$ Hz, 2H), 8.58 (s, 2H), 7.89 (d, $J = 1.7$ Hz, 2H), 7.82 (td, $J = 7.7, 1.8$ Hz, 2H), 7.68 (t, $J = 1.7$ Hz, 1H), 7.30 (ddd, $J = 7.5, 4.7, 1.2$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 298K): δ 156.2, 155.7, 149.2, 137.0, 134.4, 129.1, 124.1, 123.6, 121.4, 118.7. ESI-HRMS [**4** + H] $^+$: calcd. for $[\text{C}_{21}\text{H}_{14}\text{Br}_2\text{N}_3]^+$ 465.9549, found 465.9554.

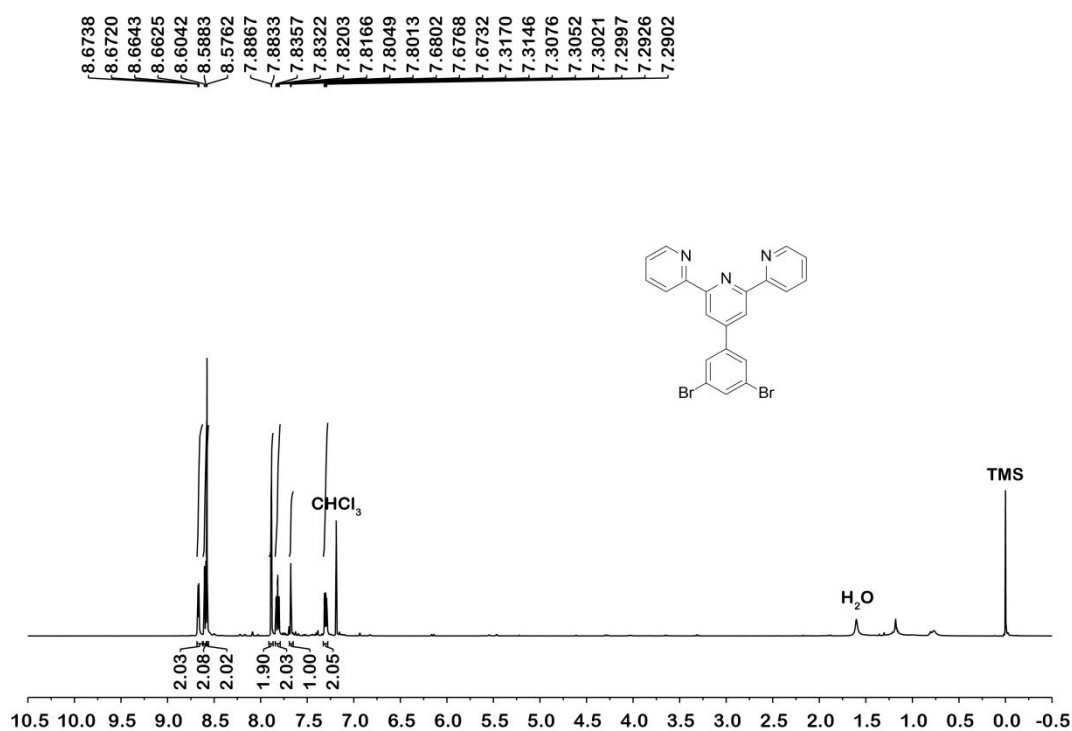


Fig. S10 ^1H NMR spectrum (500 MHz, CDCl_3 , 298K) of compound **4**.

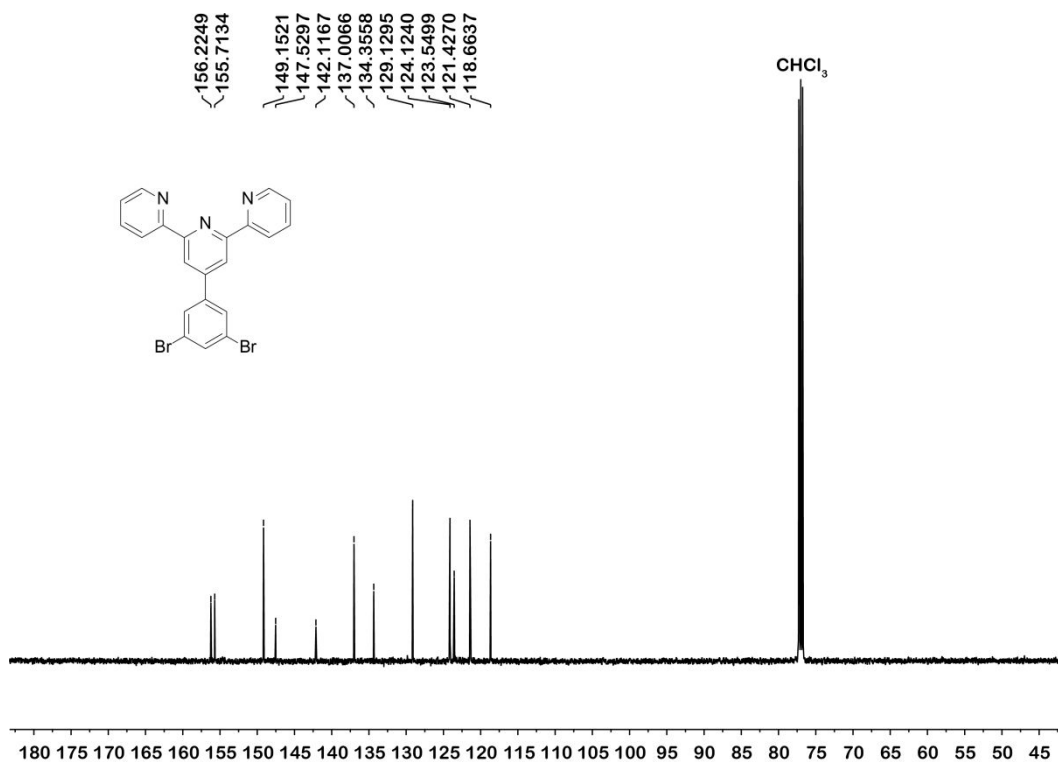


Fig. S11 ¹³C NMR spectrum (500 MHz, CDCl₃, 298K) of compound 4.

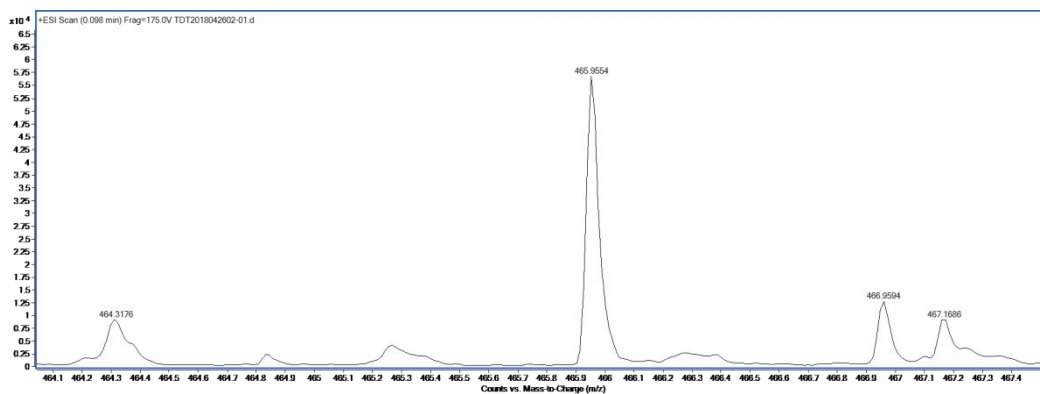
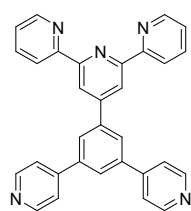


Fig. S12 ESI-HRMS spectrum of compound 4.

2.2.2 Synthesis of compound 1b



4 (98.0 mg, 0.21 mmol), 4-pyridineboronic acid (118.0 mg, 0.96 mmol), K₂CO₃ (265.7 mg, 1.93 mmol), Pd(PPh₃)₄ (19.6 mg, 0.02 mmol) were dissolved in 1,4-dioxane/H₂O (30 mL, 4/1, v/v) under nitrogen. The mixture was stirred at 80 °C for 24 h. After cooling, the solvent was removed in vacuo, and then the mixture was extracted with CH₂Cl₂ for three times. The combined organic layer was dried over anhydrous Na₂SO₄. After filtration, the solvent was removed by rotation. The crude

product was purified by flash column chromatography with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (10:1, v/v) as the eluent to afford compound **1b** (65 mg, 67%) as a white solid. m. p. 250.3–258.9 °C. ^1H NMR (500 MHz, CDCl_3 , 298K): δ 8.75 (s, 2H), 8.70 (dd, $J = 4.5, 1.8$ Hz, 6H), 8.65 (d, $J = 7.9$ Hz, 2H), 8.10 (s, 2H), 7.86 (dt, $J = 7.7, 1.8$ Hz, 3H), 7.60 (d, $J = 6.2$ Hz, 4H), 7.34 (dd, $J = 6.3, 4.7$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 298K): δ 156.2, 155.9, 150.4, 149.2, 147.5, 140.1, 137.0, 126.6, 126.3, 124.1, 121.9, 121.5, 119.0. ESI-HRMS [**1b** + H] $^+$: calcd. for $[\text{C}_{31}\text{H}_{22}\text{N}_5]^+$ 464.1870, found 464.1876.

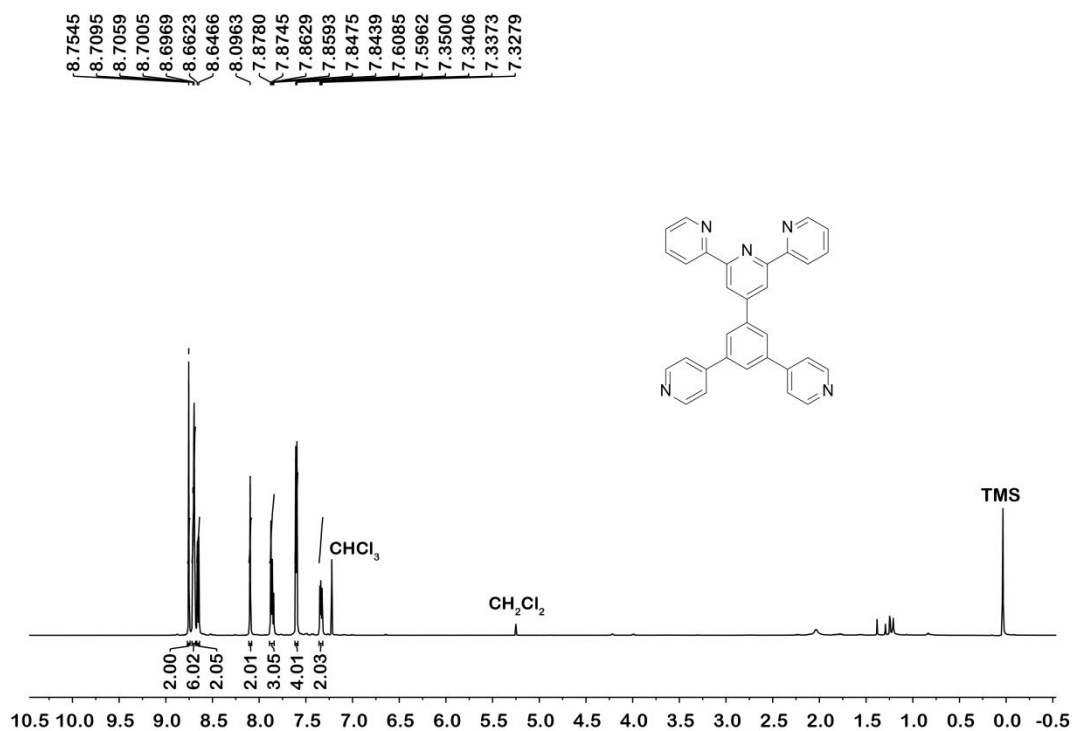


Fig. S13 ^1H NMR spectrum (500 MHz, CDCl_3 , 298K) of compound **1b**.

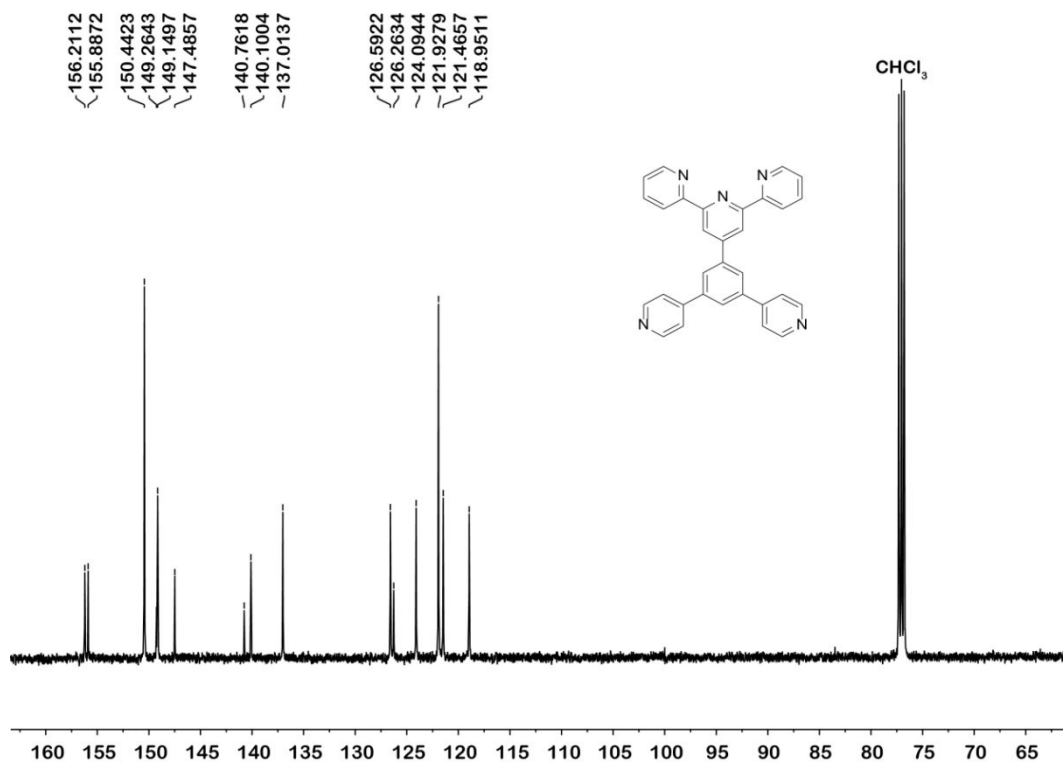


Fig. S14 ¹³C NMR spectrum (500 MHz, CDCl₃, 298K) of compound **1b**.

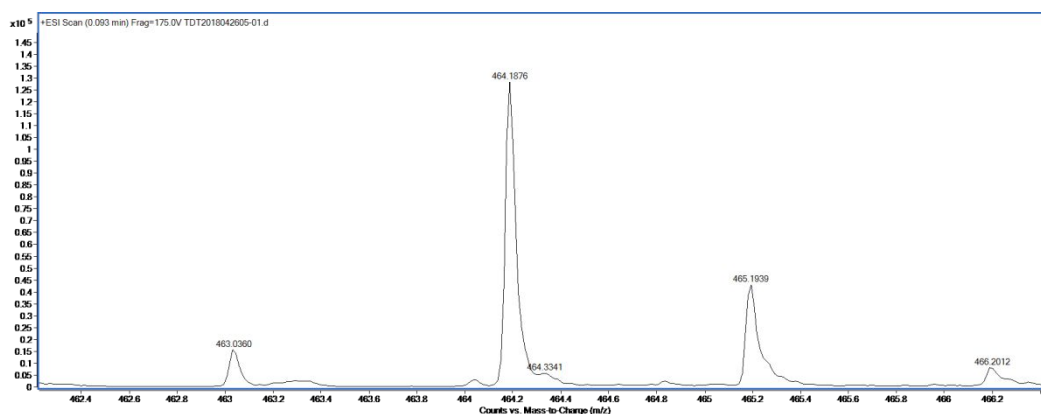
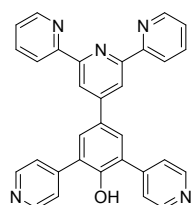


Fig. S15 ESI-HRMS spectrum of compound **1b**.

2.3 Synthesis of compound **1c**



Boron tribromide solution (500.0 mg, 2.00 mmol) was added dropwise to a stirred solution of compound **1d** (99.2 mg, 0.20 mmol) in dichloromethane (10 mL) at -78 °C for 30 minutes. After the mixture was stirred at room temperature overnight, the reaction mixture was quenched by the addition of saturated NaHCO₃ solution (100 mL). The mixture was filtered to afford compound **1c** (70 mg, 73%) as a magenta powder. m. p. 289.1–289.9 °C. ¹H NMR (500 MHz, DMSO-*d*₆, 298K): δ 9.02 (d, *J* = 6.6 Hz, 4H), 8.87 (s, 2H), 8.79 (d, *J* = 4.9 Hz, 4H), 8.39 (d, *J* = 6.7 Hz, 4H), 8.23 (s, 2H),

8.16 (d, $J = 7.5$ Hz, 2H), 7.63 (t, $J = 6.2$ Hz, 2H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, 298K): δ 155.106, 154.2, 153.7, 148.9, 143.1, 142.1, 139.5, 132.2, 130.8, 128.1, 127.7, 127.1, 125.6, 122.4, 119.1. ESI-HR-MS [$\mathbf{1c} + \text{H}$] $^+$: calcd. for $[\text{C}_{31}\text{H}_{22}\text{N}_5\text{O}]^+$ 479.1866, found 479.1875.

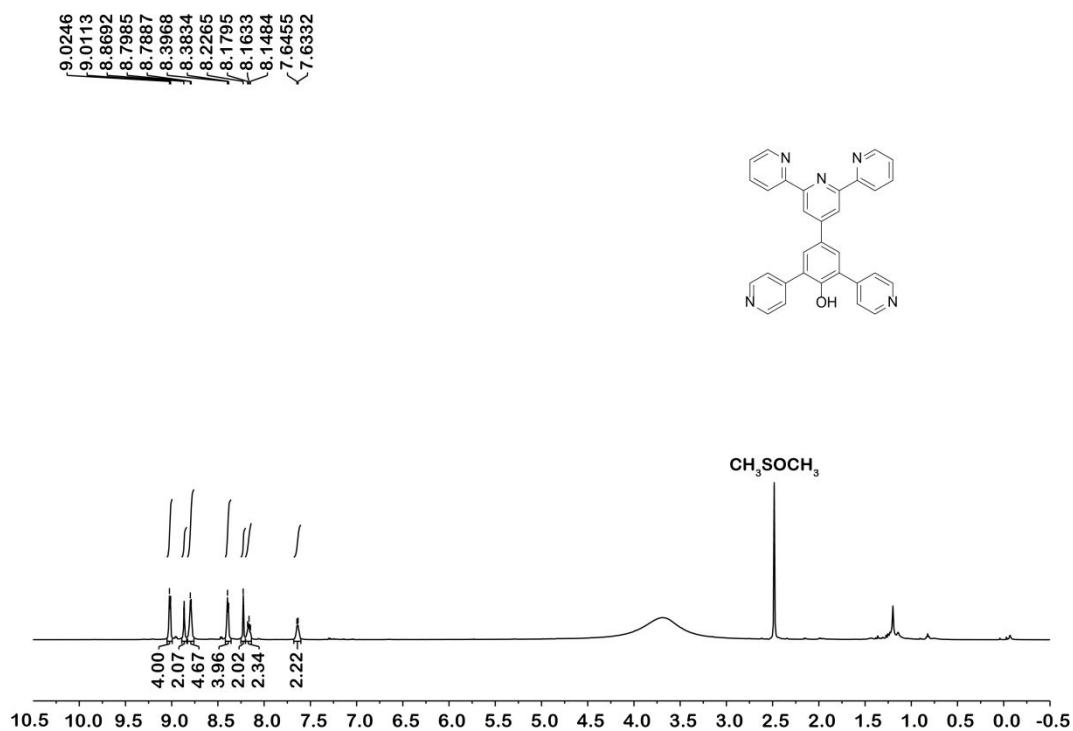


Fig. S16 ^1H NMR spectrum (500 MHz, $\text{DMSO-}d_6$, 293K) of compound **1c**.

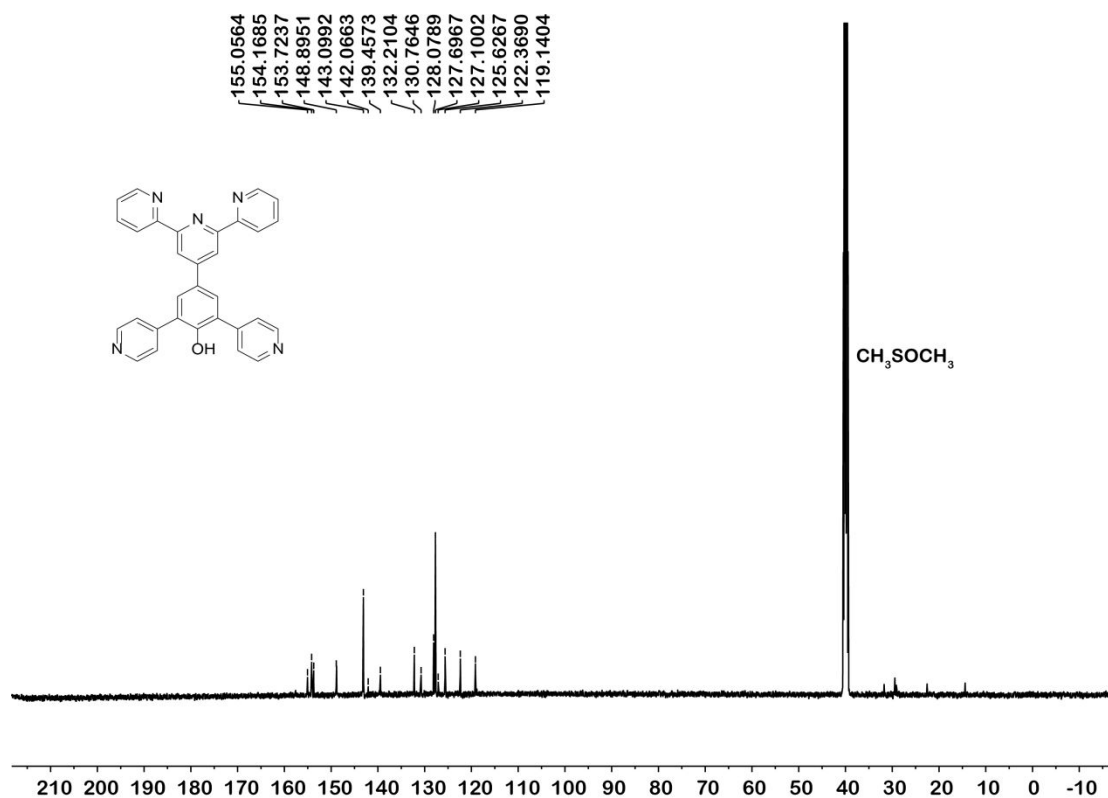


Fig. S17 ^{13}C NMR spectrum (125 MHz, $\text{DMSO-}d_6$, 298K) of compound **1c**.

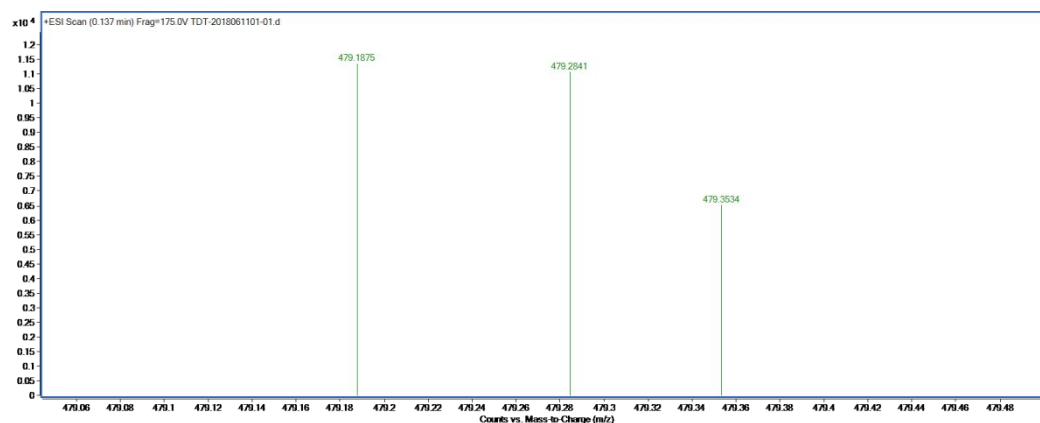
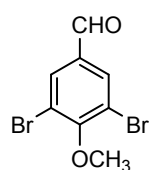


Fig. S18 ESI-HRMS spectrum of compound **1c**.

2.4 Synthesis of compound **1d**

2.4.1 Synthesis of compound **5**



3,5-Dibromo-4-hydroxybenzaldehyde (510.0 mg, 1.82 mmol), potassium carbonate (1254.9 mg, 9.10 mmol), potassium iodide (5.2 mg, 0.04 mmol) and methyl iodide (1133.0 mg, 7.28 mmol) were dissolved in acetonitrile (30 mL) and

the mixture was refluxed for 24 h. The solvent was removed by decompression, and the mixture was extracted with CH_2Cl_2 for three times. The combined organic layer was dried with anhydrous

Na₂SO₄. After filtration, the solvent was removed by rotation. The crude product was purified by flash column chromatography with petroleum ether/CH₂Cl₂ (5/1, v/v) as the eluent to afford compound **5** (480 mg, 90%) as yellow product. ¹H NMR (500 MHz, CDCl₃, 298K): δ 9.79 (s, 1H), 7.96 (s, 2H), 3.90 (s, 3H).

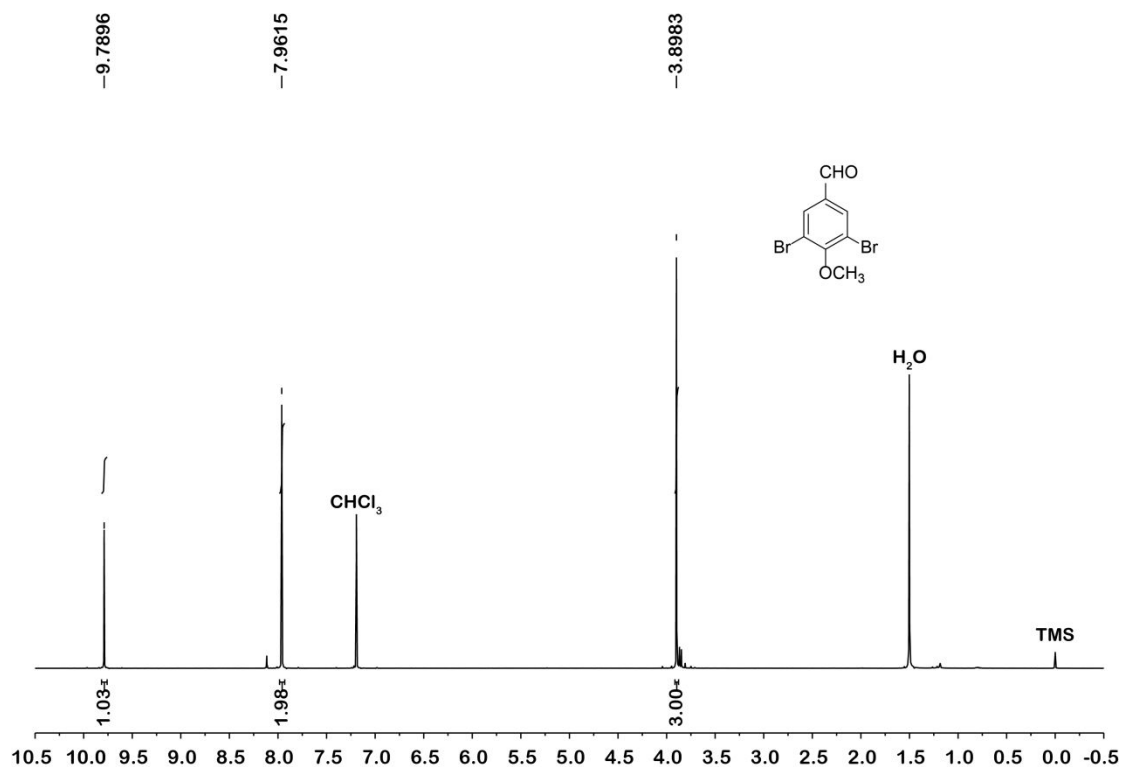
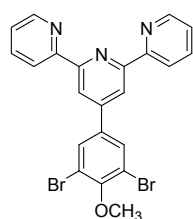


Fig. S19 ¹H NMR spectrum (500 MHz, CDCl₃, 298K) of compound **5**.

2.4.2 Synthesis of compound **6**



2-Acetylpyridine (87.2 mg, 0.72 mmol) and NaOH (100.8 mg, 2.52 mmol) were added into the ethanol solution of **5** (100.0 mg, 0.34 mmol, 30 mL). After the mixture was stirred at room temperature overnight, NH₃·H₂O (15.3 mg, 0.9 mmol) were added and the mixture was heated at 65 °C for another 24 h. After the mixture was cooled down and filtered, the crude product was collected, and washed with ethanol for three times to afford compound **6** (115 mg, 68%) as a white solid. ¹H NMR (500 MHz, CDCl₃, 298K): δ 8.74 (d, *J* = 4.1 Hz, 2H), 8.66 (d, *J* = 7.9 Hz, 2H), 8.63 (s, 2H), 8.04 (s, 2H), 7.89 (td, *J* = 7.7, 1.8 Hz, 2H), 7.37 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 2H), 3.96 (s, 3H). ¹³C NMR (125 MHz,

CDCl₃, 298K): δ 156.2, 155.8, 149.2, 137.1, 137.0, 131.4, 124.1, 121.4, 118.8, 118.5, 60.8.

ESI-HRMS [6 + H]⁺: calcd. for [C₂₂H₁₅Br₂N₃O]⁺ 497.9640, found 497.9598.

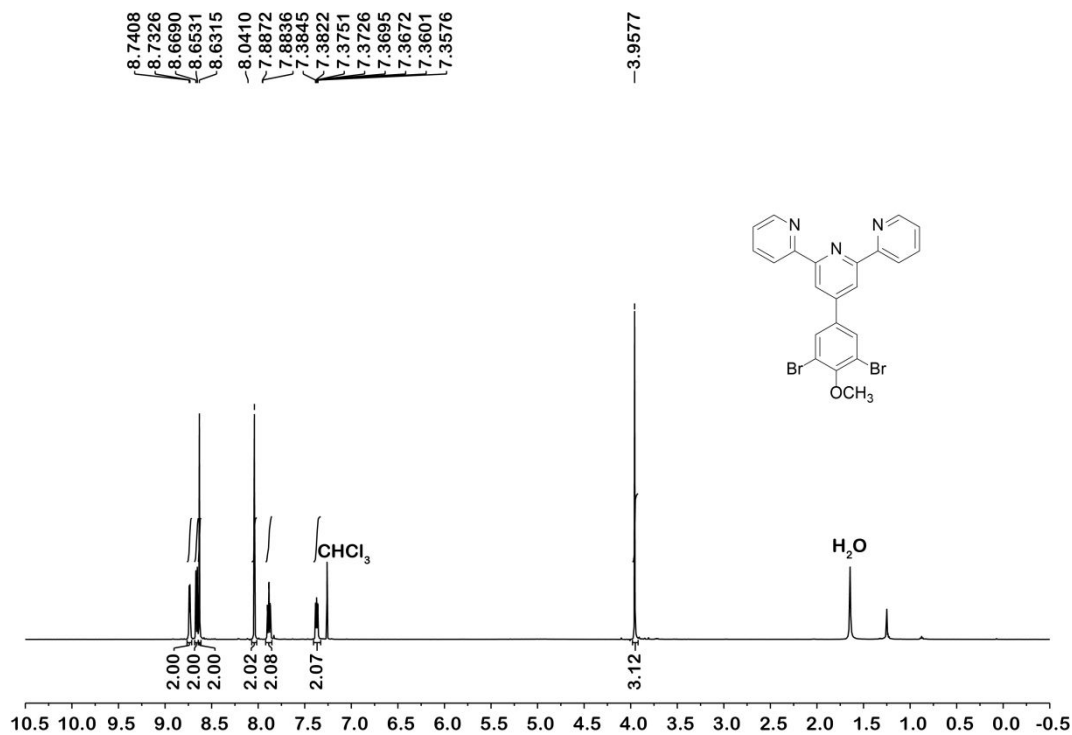


Fig. S20 ¹H NMR spectrum (500 MHz, CDCl₃, 298K) of compound 6.

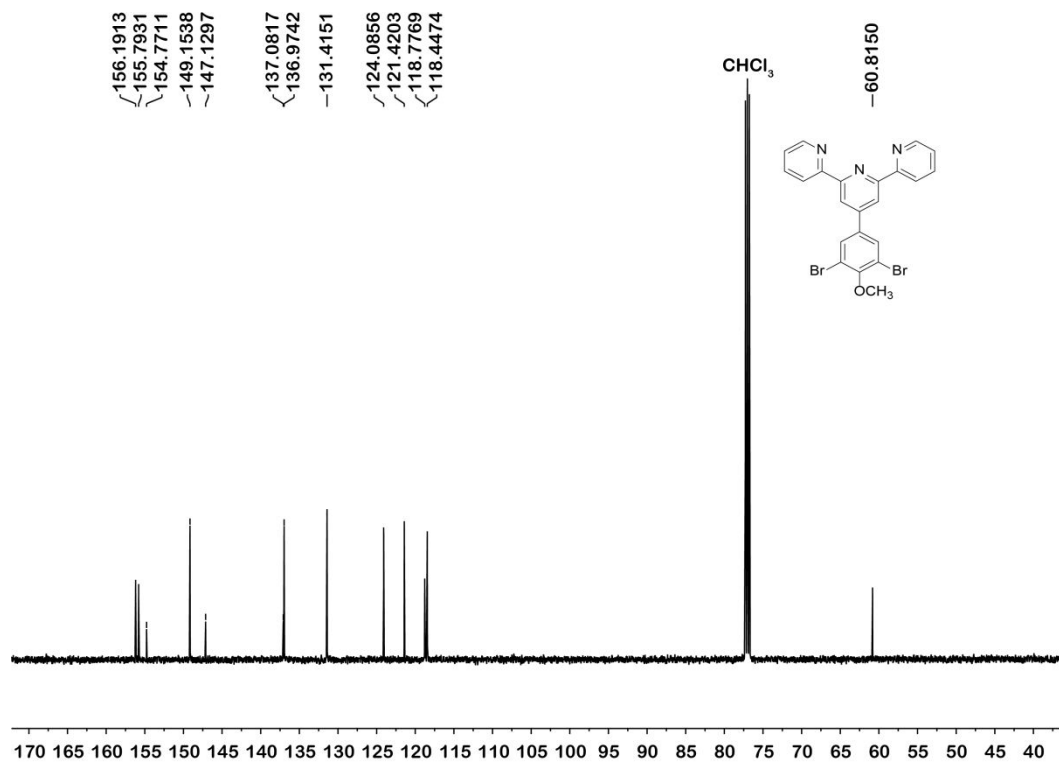


Fig. S21 ¹³C NMR spectrum (125 MHz, CDCl₃, 298K) of compound 6.

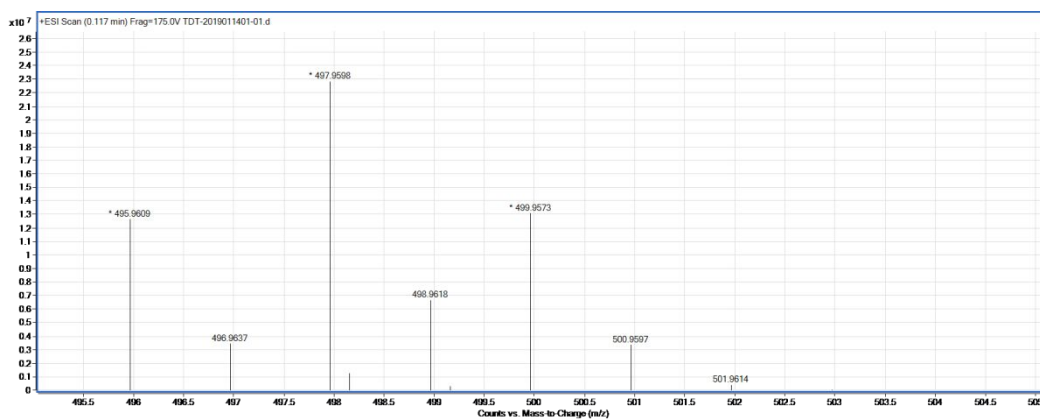
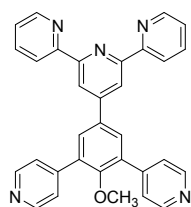


Fig. S22 ESI-HRMS spectrum of compound **6**.

2.4.3 Synthesis of compound **1d**



6 (104.4 mg, 0.21 mmol), 4-pyridineboronic acid (118.0 mg, 0.96 mmol), K_2CO_3 (265.7 mg, 1.93 mmol), $Pd(PPh_3)_4$ (19.6 mg, 0.02 mmol) were dissolved in the mixture of 1,4-dioxane/ H_2O (30 mL, 4/1, v/v) under nitrogen. The mixture was stirred at 80 °C for 24 h. After cooling, the solvent was

removed in vacuo, and the mixture was then extracted with CH_2Cl_2 for three times. The combined organic layer was dried with anhydrous Na_2SO_4 . After filtration, the solvent was removed by rotation. The crude product was purified by flash column chromatography with CH_2Cl_2/CH_3OH (10:1, v/v) as the eluent to afford compound **1d** (60 mg, 58%) as a white solid. m. p. 262.3–262.9 °C. 1H NMR (500 MHz, $CDCl_3$, 298K): δ 8.74 (d, $J = 2.0$ Hz, 4H), 8.73 (s, 3H), 8.72 (s, 2H), 8.69 (d, $J = 8.0$ Hz, 2H), 7.94–7.86 (m, 4H), 7.63 (d, $J = 4.6$ Hz, 4H), 7.39–7.34 (m, 2H), 3.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ 156.2, 155.9, 155.9, 149.9, 149.1, 148.7, 145.7, 137.0, 135.4, 133.9, 130.0, 124.1, 124.0, 121.5, 118.6, 61.3. ESI-HRMS [**1d** + H]⁺: calcd. for $[C_{32}H_{24}N_5O]^+$ 494.1975, found 494.1978.

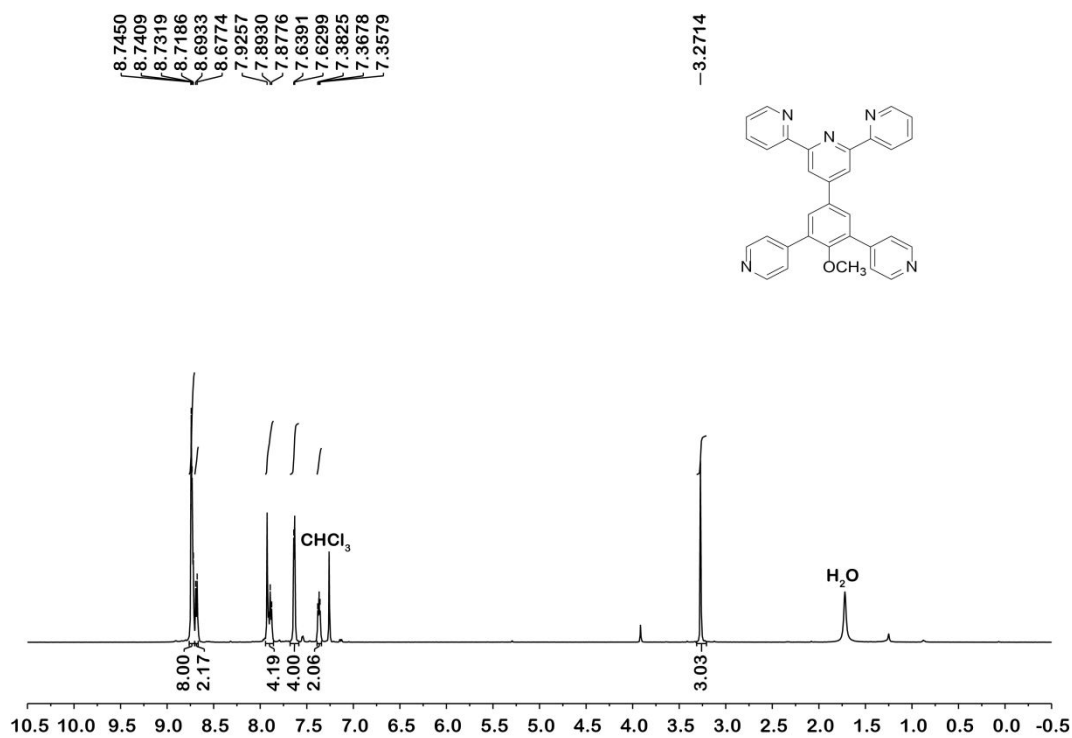


Fig. S23 ¹H NMR spectrum (500 MHz, CDCl₃, 298K) of compound **1d**.

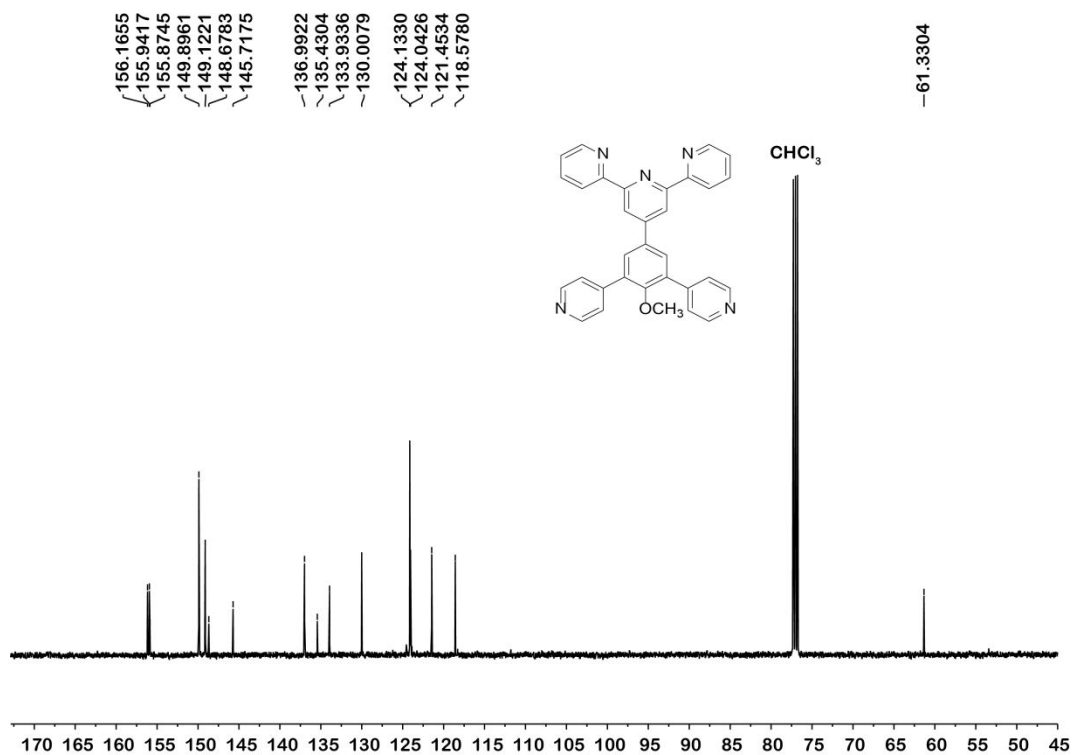


Fig. S24 ¹³C NMR spectrum (125 MHz, CDCl₃, 298K) of compound **1d**.

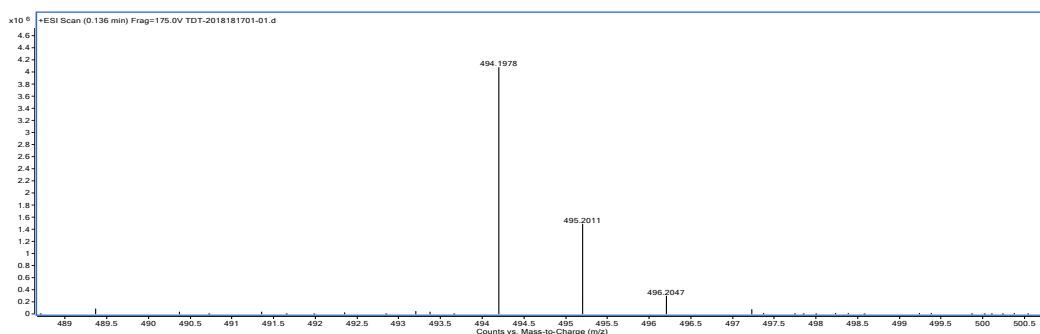
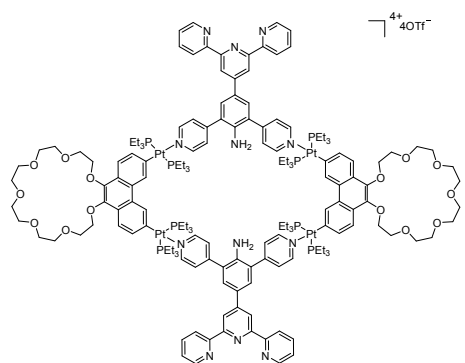


Fig. S25 ESI-HRMS spectrum of compound **1d**.

2.5 Synthesis of metallacycle **3a**



1a (4.78 mg, 10.0 μmol) and **2** (16.14 mg, 10.0 μmol) were dissolved in DMSO (0.5 mL) and heated at 65 $^{\circ}\text{C}$ for 12 h and then cooled to room temperature. To the resulting homogeneous solution, toluene (0.5 mL) and diethyl ether (ca. 7 mL) were added to obtain the desired product **3a** (15.30 mg, 83%) as a yellow solid precipitate.

^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 9.00 (s, 2H), 8.90 (s, 2H), 8.75 (s, 4H), 8.64 (s, 6H), 8.45 (s, 4H), 8.34 (d, $J = 11.2$ Hz, 12H), 8.10 (s, 4H), 8.00 (s, 10H), 7.65 (s, 6H), 7.35 (s, 2H), 4.41 (s, 6H), 4.03 (s, 8H), 3.82 (s, 8H), 3.73 (s, 8H), 3.67 (s, 18H), 1.44 (s, 48H), 1.21 (s, 72H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ 14.10 ppm (s, $^1J_{\text{Pt-P}} = 2678.1$ Hz). ESI-TOF-MS [**3a** – 3OTf] $^{3+}$: calcd. for $[\text{C}_{163}\text{H}_{221}\text{N}_{12}\text{O}_{17}\text{P}_8\text{Pt}_4\text{F}_3\text{S}]^{3+}$ 1247.11, found 1247.20.

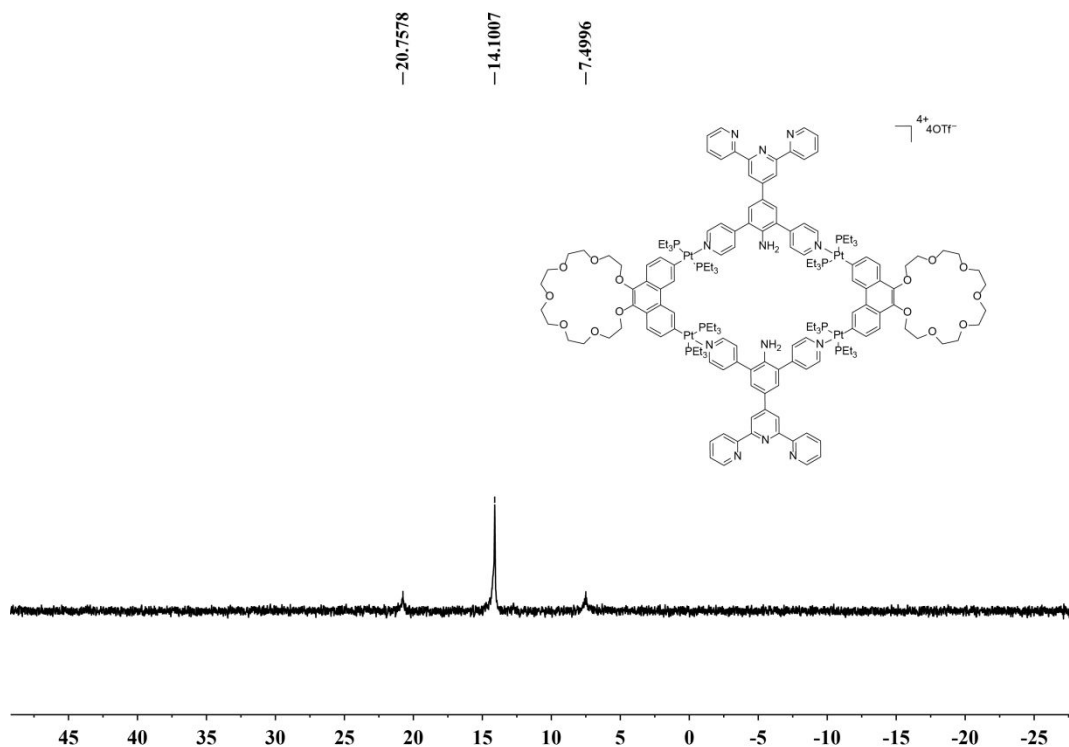


Fig. S26 $^{31}P\{^1H\}$ NMR spectrum (202 MHz, CD_2Cl_2 , 298K) of **3a**.

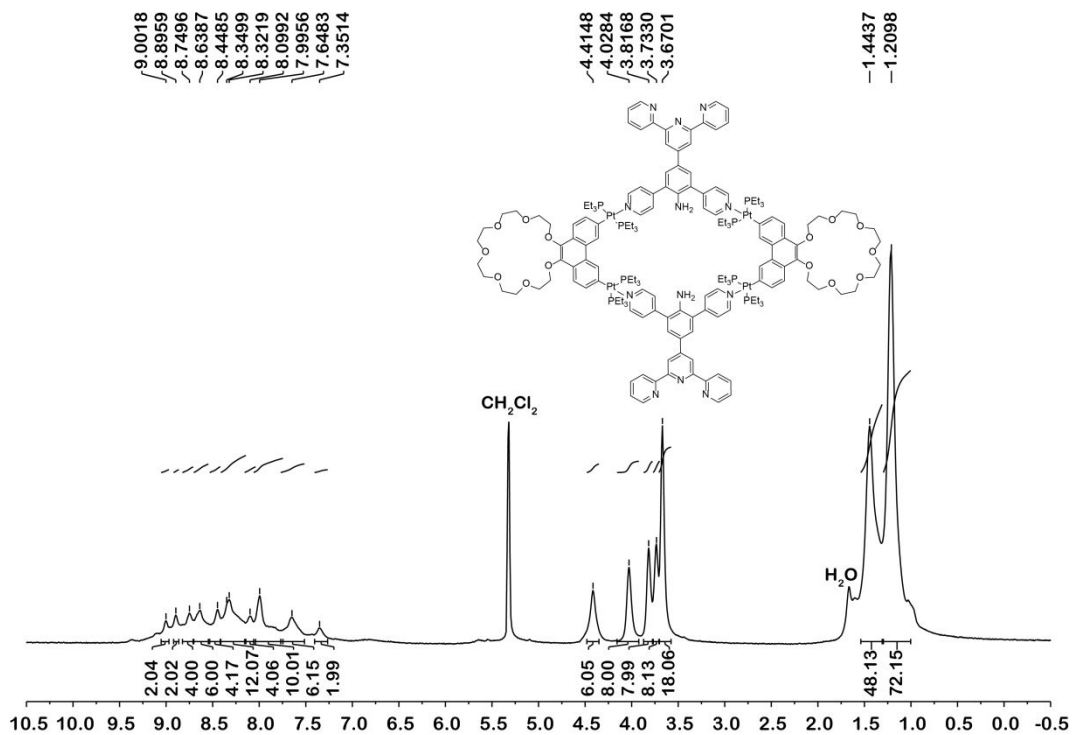


Fig. S27 1H NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of **3a**.

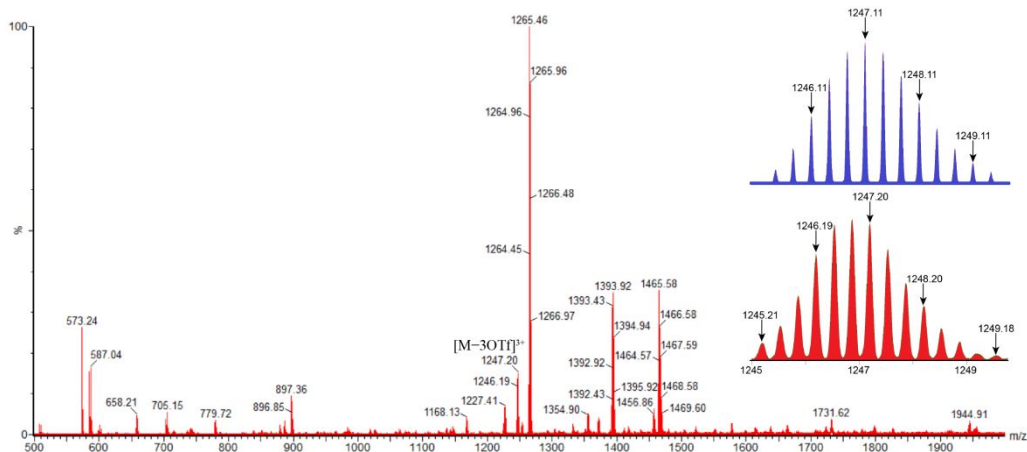


Fig. S28 ESI-TOF-MS of **3a**. Inset: calculated (blue) and experimental (red) ESI-TOF-MS spectra of metallacycle **3a** $[M-3OTf]^{3+}$.

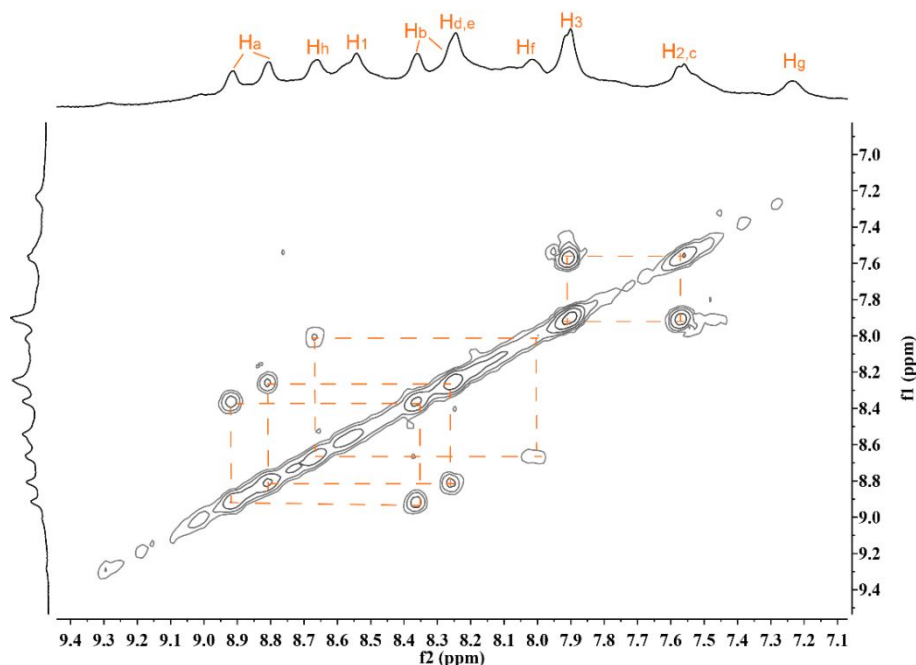
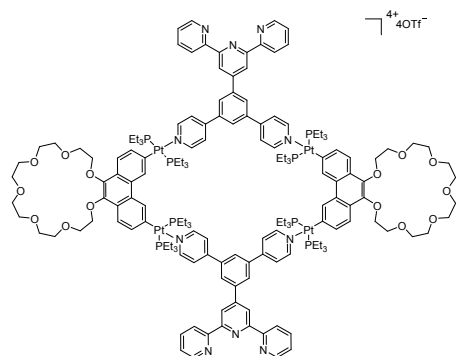


Fig. S29 Partial COSY spectra (CD_3CN/CD_2Cl_2 , 1/1 v/v, 298 K, 400 MHz) of **3a**.

2.5 Synthesis of metallacycle **3b**



1b (4.43 mg, 10.0 μ mol) and **2** (16.14 mg, 10.0 μ mol) were dissolved in 0.5 mL of DMSO and heated at 65 $^{\circ}C$ for 12 h and then cooled to room temperature. To the resulting homogeneous solution, toluene (0.5 mL) and diethyl ether (ca. 7 mL) were added to obtain the

desired product **3b** (14.62 mg, 81%) as a yellow solid precipitate. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ 8.99 (s, 4H), 8.95 (s, 4H), 8.93–8.91 (m, 2H), 8.88 (s, 4H), 8.81 (s, 12H), 8.53 (s, 8H), 8.07 (d, $J = 18.1$ Hz, 8H), 7.94 (d, $J = 8.0$ Hz, 4H), 7.63 (d, $J = 8.3$ Hz, 4H), 7.27 (s, 4H), 4.35 (s, 8H), 3.96 (s, 8H), 3.75 (s, 8H), 3.67 (s, 8H), 3.60 (s, 16H), 1.37 (s, 48H), 1.15 (t, $J = 8.5$ Hz, 72H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 298 K): δ 13.98 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2681.7$ Hz). ESI-TOF-MS [**3b** – 3OTf] $^{3+}$: calcd. for $[\text{C}_{163}\text{H}_{219}\text{N}_{10}\text{O}_{17}\text{P}_8\text{Pt}_4\text{F}_3\text{S}]^{3+}$ 1236.76, found 1236.86.

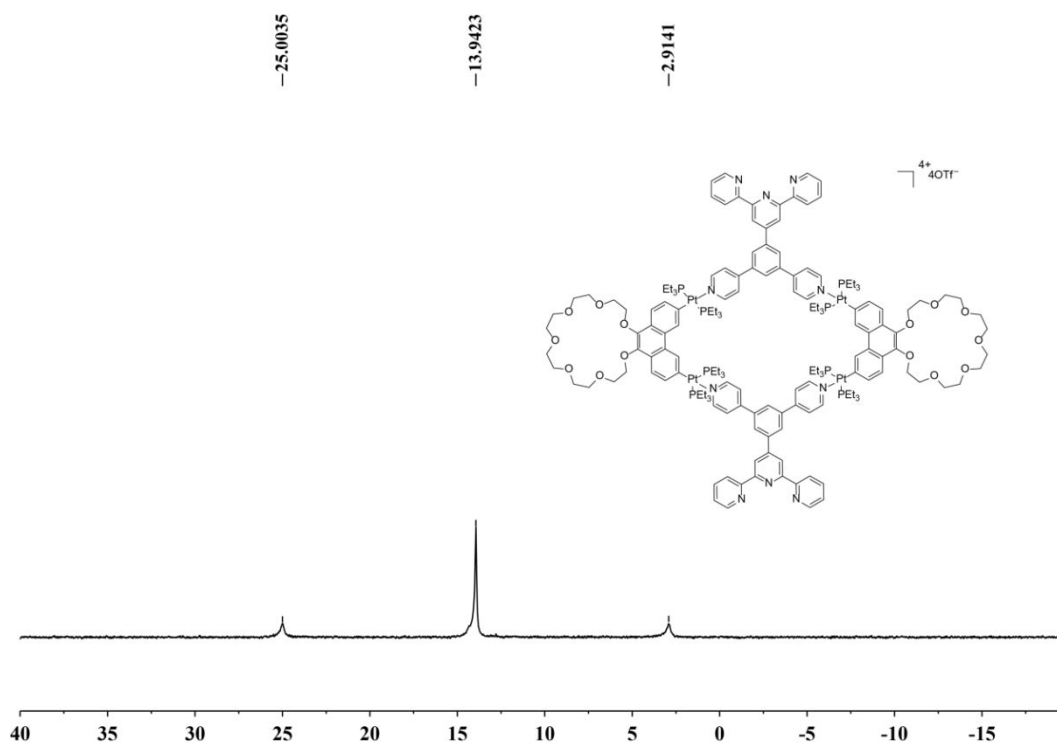


Fig. S30 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.4 MHz, CD_2Cl_2 , 298K) of **3b**.

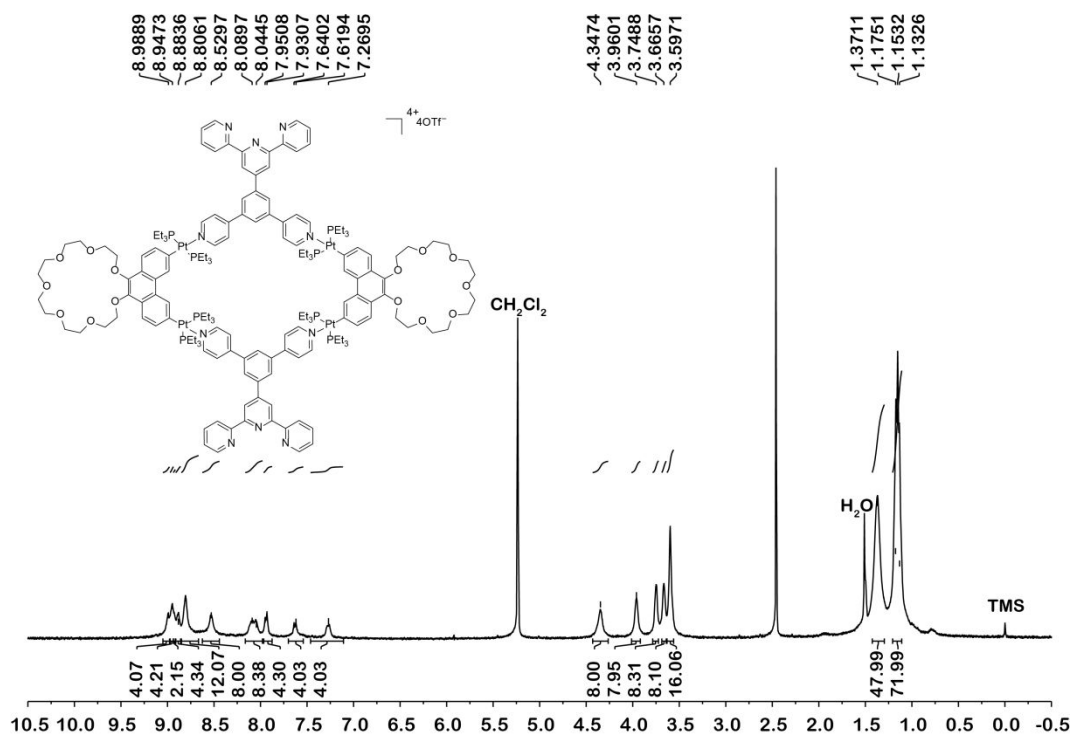


Fig. S31 ¹H NMR spectrum (400 MHz, CD₂Cl₂, 298K) of **3b**.

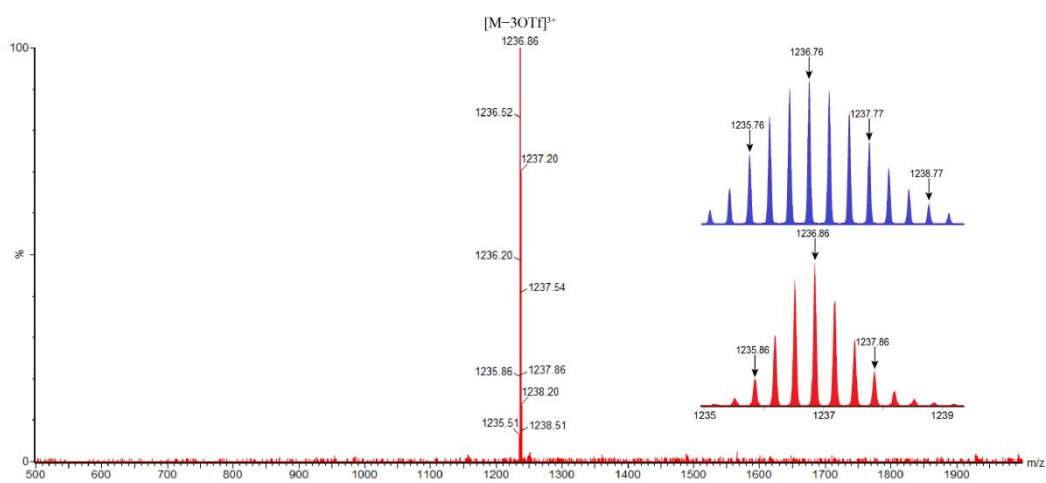
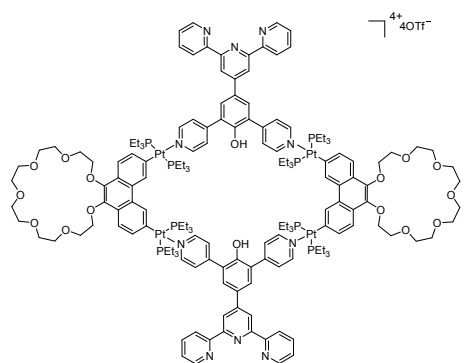


Fig. S32 ESI-TOF-MS of **3b**. Inset: calculated (blue) and experimental (red) ESI-TOF-MS spectra of metallacycle **3b** [M-3OTf]³⁺.

2.7 Synthesis of metallacycle **3c**



1c (4.43 mg, 10.0 μmol) and **2** (16.14 mg, 10.0 μmol) were dissolved in 0.5 mL of DMSO and heated at 50 $^{\circ}\text{C}$ for 12 h and then cooled to room temperature. To the resulting homogeneous solution, toluene (0.5 mL) and diethyl ether (ca. 7 mL) were added to obtain the desired product **3c** (16.15 mg, 88%) as a yellow solid precipitate.

^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ 9.69 (s, 2H), 9.25 (d, $J = 4.0$ Hz, 4H), 9.12 (s, 6H), 8.80 (dd, $J = 17.2, 6.0$ Hz, 10H), 8.71 (s, 4H), 8.57 (s, 2H), 8.45 (d, $J = 6.4$ Hz, 4H), 8.40 (d, $J = 5.9$ Hz, 3H), 8.30 (s, 6H), 8.01 (d, $J = 6.6$ Hz, 4H), 7.87 (d, $J = 8.2$ Hz, 4H), 7.69–7.50 (m, 6H), 4.35 (s, 8H), 3.97 (s, 8H), 3.72 (s, 8H), 3.65–3.52 (m, 24H), 1.43–1.26 (m, 48H), 1.18–1.05 (m, 72H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ 13.52 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2655.8$ Hz). ESI-TOF-MS [**3c** – 3OTf + 2Na – 2H] $^{3+}$: calcd. for $[\text{C}_{163}\text{H}_{216}\text{N}_{10}\text{O}_{19}\text{P}_8\text{Pt}_4\text{F}_3\text{SNa}_2]^{3+}$ 1262.08, found 1262.18.

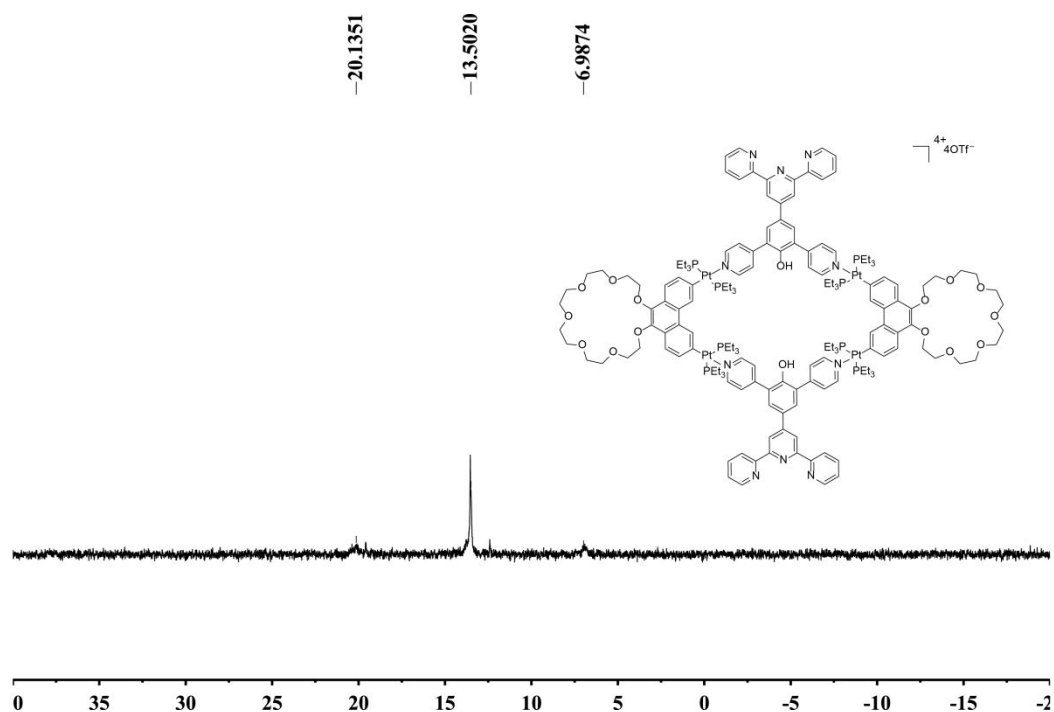


Fig. S33 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, CD_2Cl_2 , 298K) of **3c**.

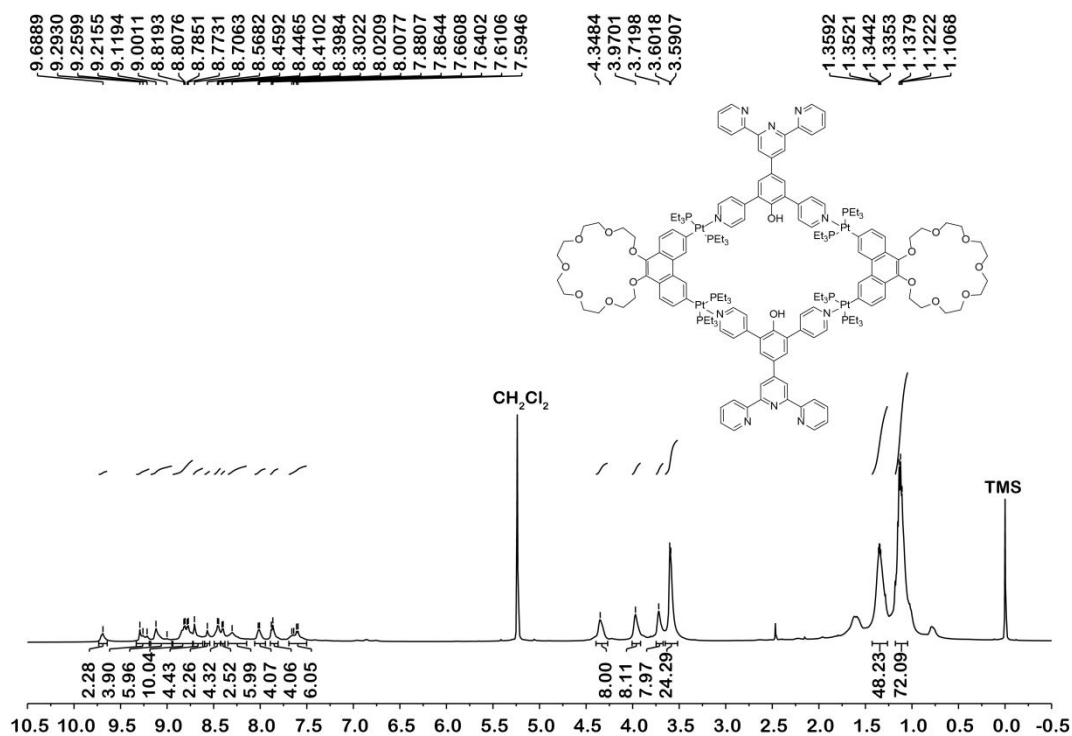


Fig. S34 $^1\text{H NMR}$ spectrum (500 MHz, CD_2Cl_2 , 293K) of **3c**.

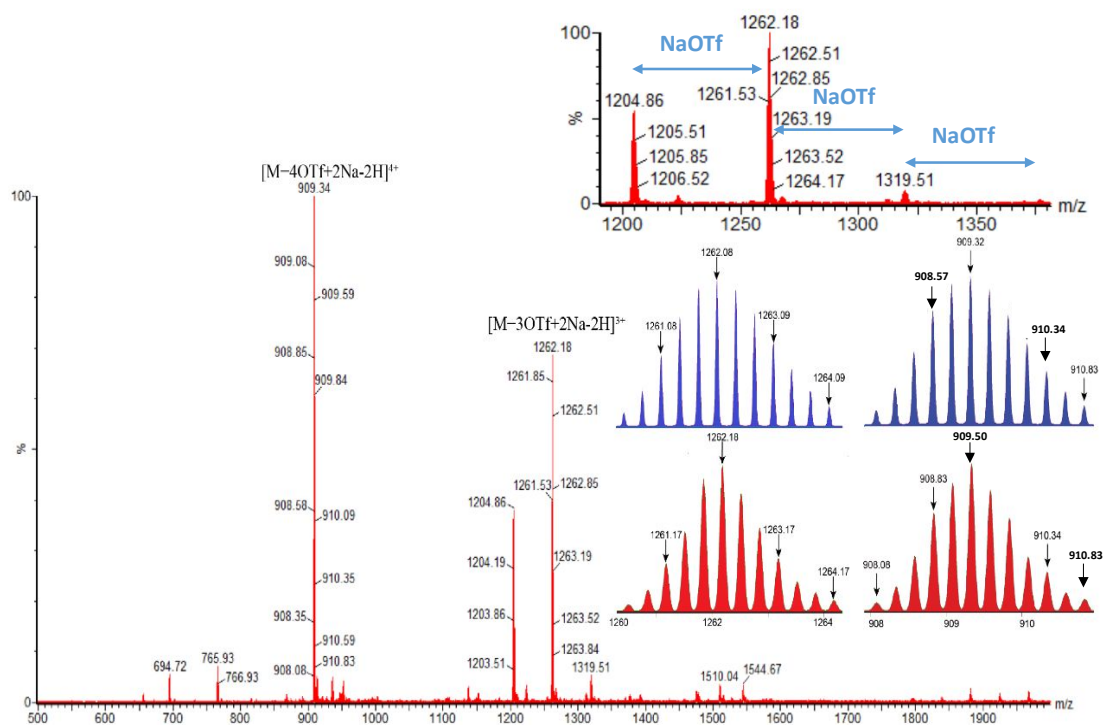
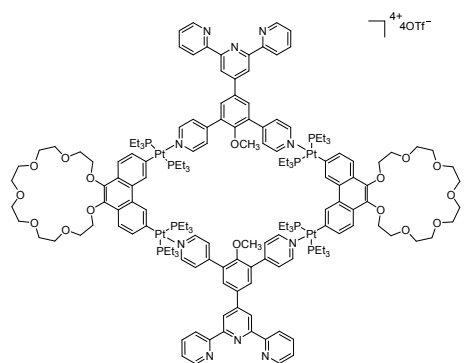


Fig. S35 ESI-TOF-MS of **3c**. Inset: calculated (blue) and experimental (red) ESI-TOF-MS spectra of metallacycle **3c** $[\text{M}-3\text{OTf}+2\text{Na}-2\text{H}]^{3+}$ and $[\text{M}-4\text{OTf}+2\text{Na}-2\text{H}]^{4+}$.

2.8 Synthesis of metallacycle **3d**



1d (4.93 mg, 10.0 μmol) and **2** (16.14 mg, 10.0 μmol) were dissolved in 0.5 mL of DMSO and heated at 65 $^{\circ}\text{C}$ for 12 h and then cooled to room temperature. To the resulting homogeneous solution, toluene (0.5 mL) and diethyl ether (ca. 7 mL) were added to obtain the desired product **3d** (12.4 mg, 67%) as a yellow solid precipitate.

^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ 9.17 (s, 4H), 9.00 (s, 4H), 8.90 (s, 4H), 8.80 (s, 5H), 8.75 (s, 6H), 8.59 (s, 8H), 8.15 (s, 8H), 8.05 (d, $J = 8.3$ Hz, 4H), 7.67 (d, $J = 8.3$ Hz, 6H), 7.34 (s, 4H), 4.46 (s, 8H), 4.07 (s, 9H), 3.87 (s, 9H), 3.79 (s, 8H), 3.71 (s, 16H), 3.45 (s, 6H), 1.57–1.40 (m, 48H), 1.33–1.19 (m, 72H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): δ 12.94 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2689.9$ Hz). ESI-TOF-MS [**3d** - 3OTf] $^{3+}$: calcd. for $[\text{C}_{165}\text{H}_{223}\text{N}_{10}\text{O}_{19}\text{P}_8\text{Pt}_4\text{F}_3\text{S}]^{3+}$ 1256.77, found 1256.87.

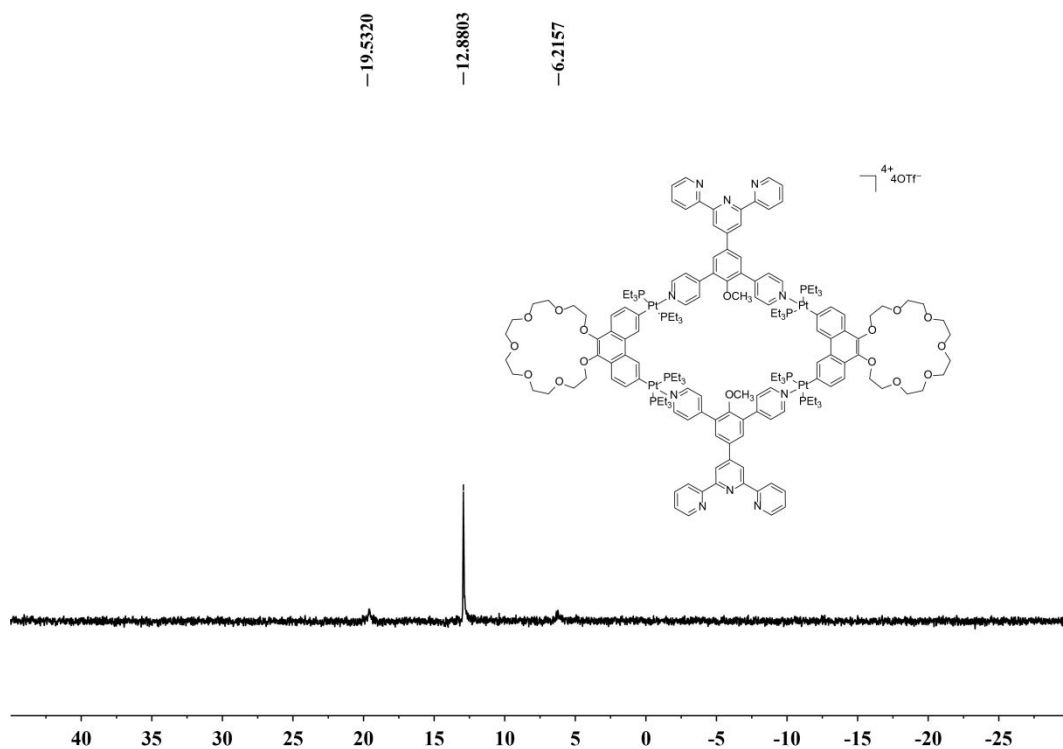


Fig. S36 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, CD_2Cl_2 , 298K) of **3d**.

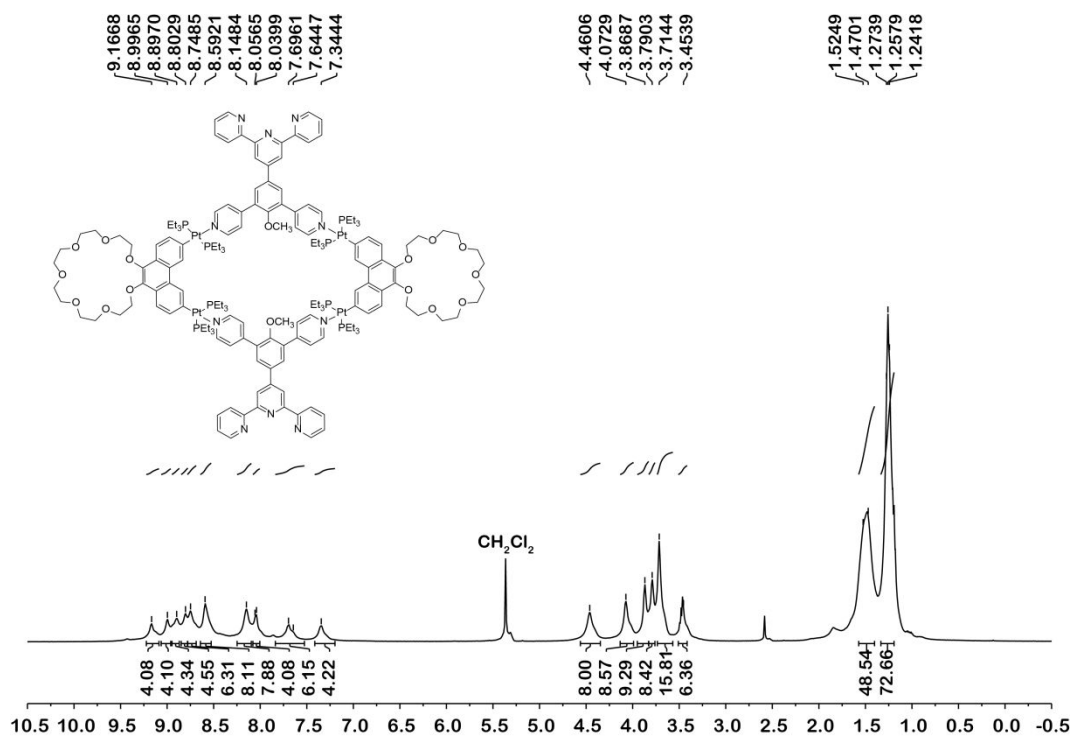


Fig. S37 $^1\text{H NMR}$ spectrum (500 MHz, CD_2Cl_2 , 293K) of **3d**.

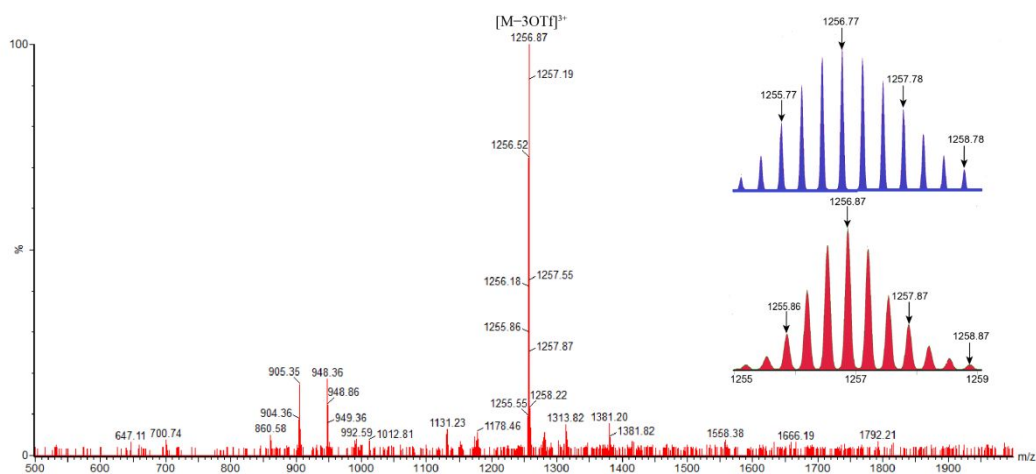
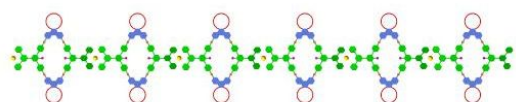


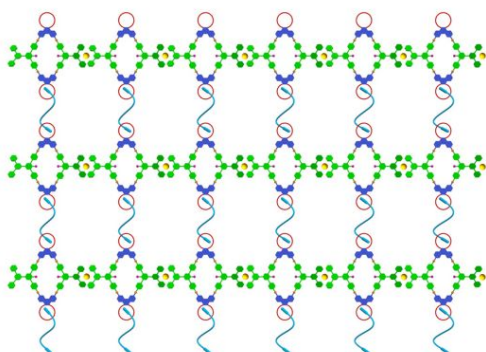
Fig. S38 ESI-TOF-MS of **3d**. Inset: calculated (blue) and experimental (red) ESI-TOF-MS spectra of metallacycle **3d** $[\text{M}-3\text{OTf}]^{3+}$.

2.9 Synthesis of the linear supramolecular polymer **4a**



3a (21.16 mg, 5.0 μmol) and $\text{Zn}(\text{OTf})_2$ (1.8 mg, 5.0 μmol) were dissolved in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1/1, v/v, 0.5 mL).

2.10 Synthesis of the cross-linked supramolecular polymer **6a**



3a (21.16 mg, 5.0 μmol), $\text{Zn}(\text{OTf})_2$ (1.8 mg, 5.0 μmol) and bis-ammonium salt **5** (3.7 mg, 5.0 μmol) were dissolved in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1/1, v/v, 0.5 mL) to form the cross-linked supramolecular polymer immediately. By increasing the concentration, the gel was formed at the concentration of B21C7 unit of 240 mM in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1/1, v/v).

3. Complexation study between **1a** and $\text{Zn}(\text{OTf})_2$

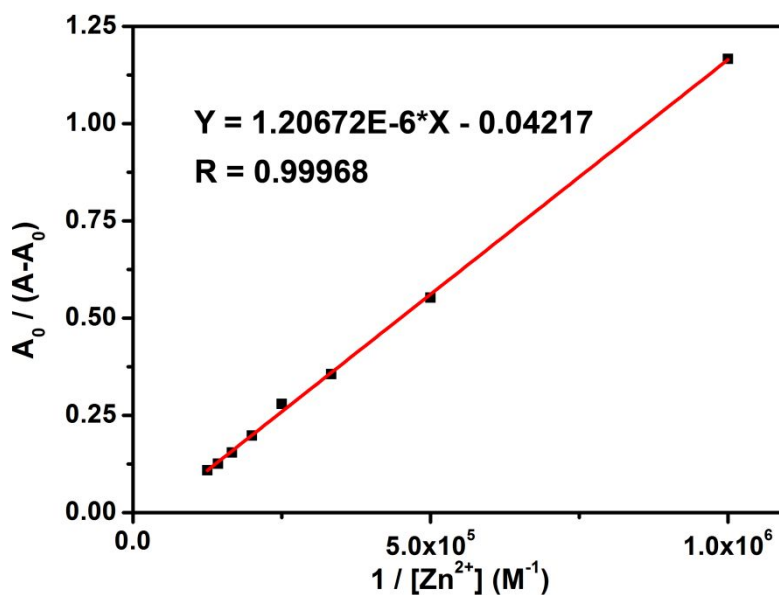


Fig. S39 The plot of the modified Benesi-Hildebrand equation $A_0/(A-A_0) = (a/(b-a)) ((1/K_s) [\text{Zn}^{2+}]^{-1} + 1)$ for the complexation between **1a** and $\text{Zn}(\text{OTf})_2$ using UV-Vis titration data in the high initial concentration of **1a**. Here a and b are constants while A and A_0 refer to the absorbance at $\lambda = 326$ nm with concentration of $[\text{Zn}^{2+}]$ and 0, respectively.^{S3}

4. Concentration-dependent ¹H NMR of **3a** and $\text{Zn}(\text{OTf})_2$

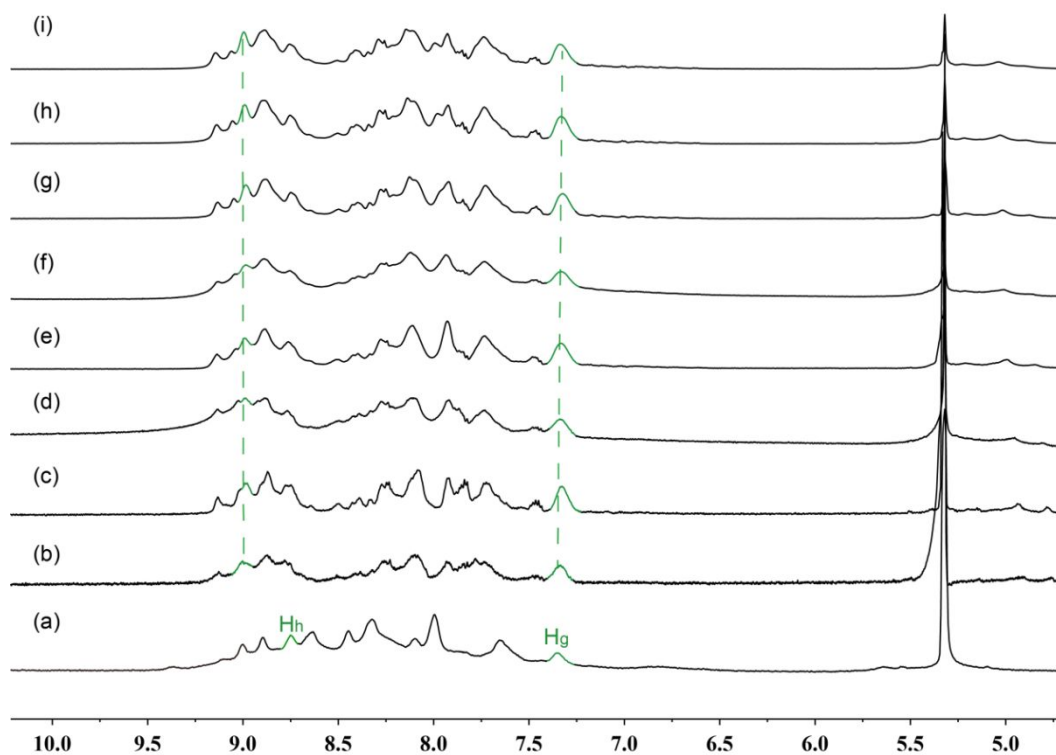


Fig. S40 Partial ^1H NMR spectra ($\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2 = 1/1$, v/v , 298 K, 500 MHz) of (a) **3a** and equal molar $\text{Zn}(\text{OTf})_2$ and **3a** at the concentration of (b) 1 mM (c) 5 mM (d) 10 mM (e) 20 mM (f) 30 mM (g) 40 mM (h) 50 mM (i) 60 mM.

5. Two-dimensional diffusion-ordered NMR spectroscopy (DOSY) and dynamic light scattering (DLS) results

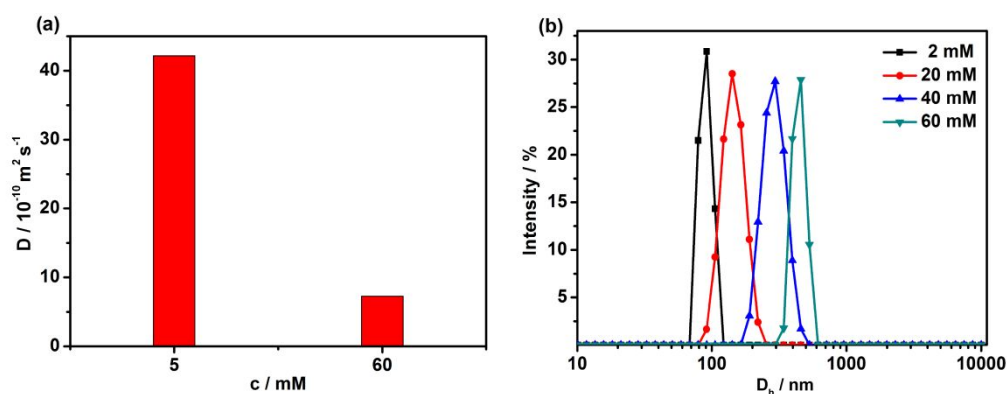


Fig. S41 (a) Concentration dependence of diffusion coefficient D ($\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2 = 1/1$, v/v , 298 K, 400 MHz) of **4a**; (b) Size distributions of **4a** at different B21C7 concentrations.

6. SEM images of **4**

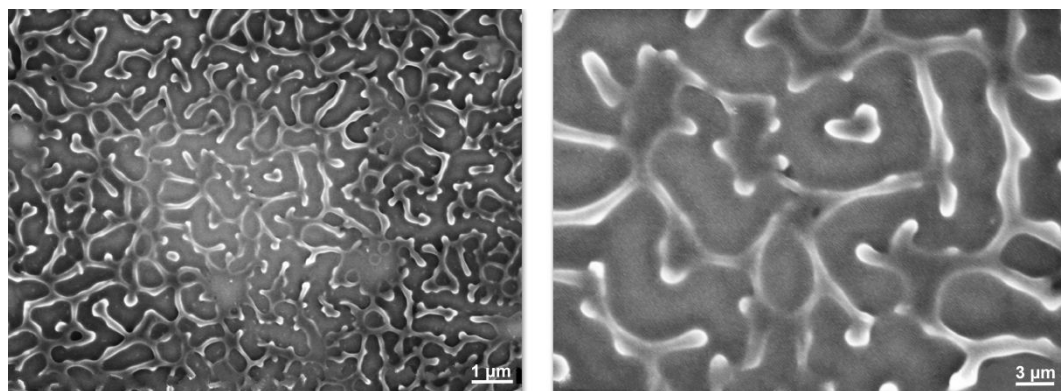


Fig. S42 SEM images of **4a**.

7. ^1H NMR spectra of **2** and **5**

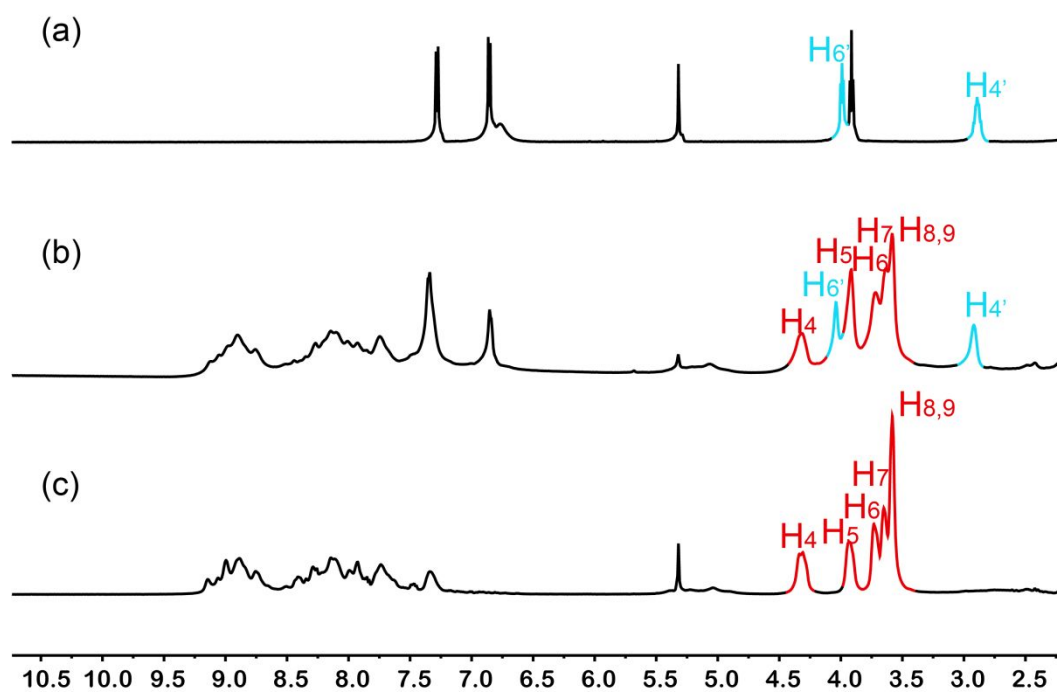


Fig. S43 Partial ^1H NMR spectra ($\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2 = 1/1$, v/v , 298 K, 500 MHz) of (a) 10.00 mM **5**, (b) 10.00 mM **5** and **2**, (c) 10.00 mM **2**.

8. Determination of the association constant between **2** and monofunction model compound **7** by ^1H NMR titration methods.

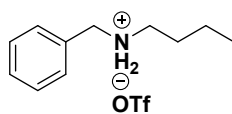


Fig. S44 Chemical structure of the monofunction model compound **7**

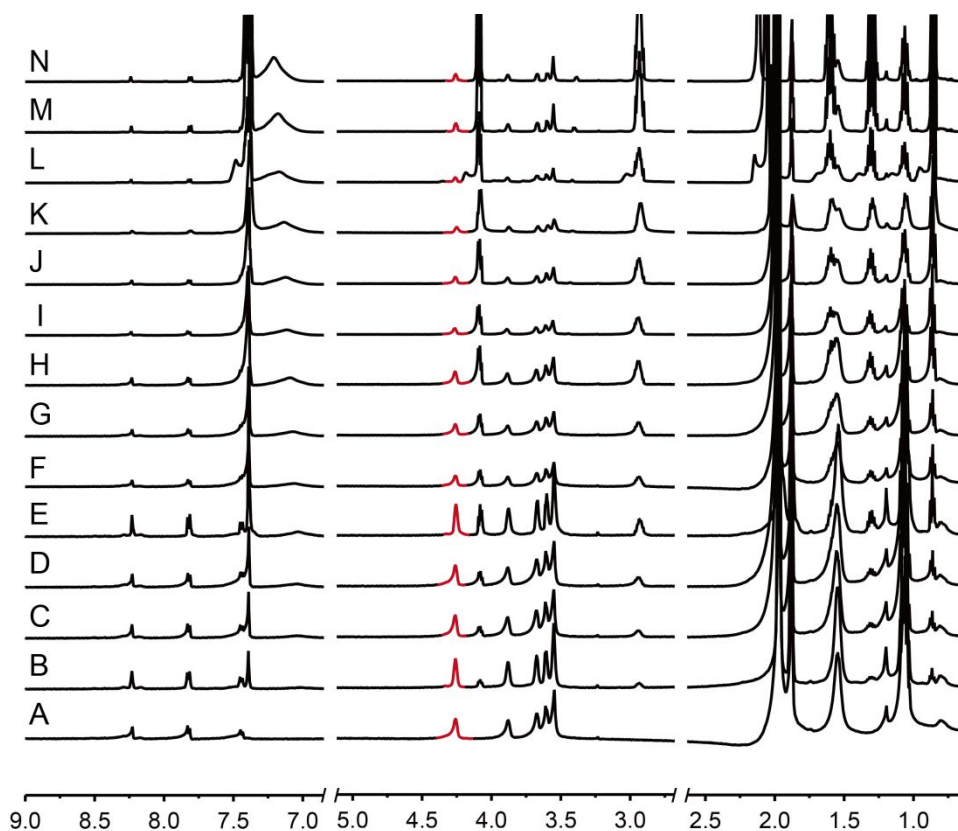


Fig. S45 ^1H NMR spectra (400 MHz, $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2 = 1/1$, v/v , 295 K) of **2** at a concentration of 2.00 mM upon the addition of **7**: (A) 0.00 mM, (B) 0.498 mM, (C) 0.990 mM, (D) 1.478 mM, (E) 1.961 mM, (F) 2.913 mM, (G) 3.846 mM, (H) 6.542 mM, (I) 9.910 mM, (J) 14.530 mM, (K) 20.635 mM, (L) 26.471 mM, (M) 35.897 mM, (N) 48.980 mM.

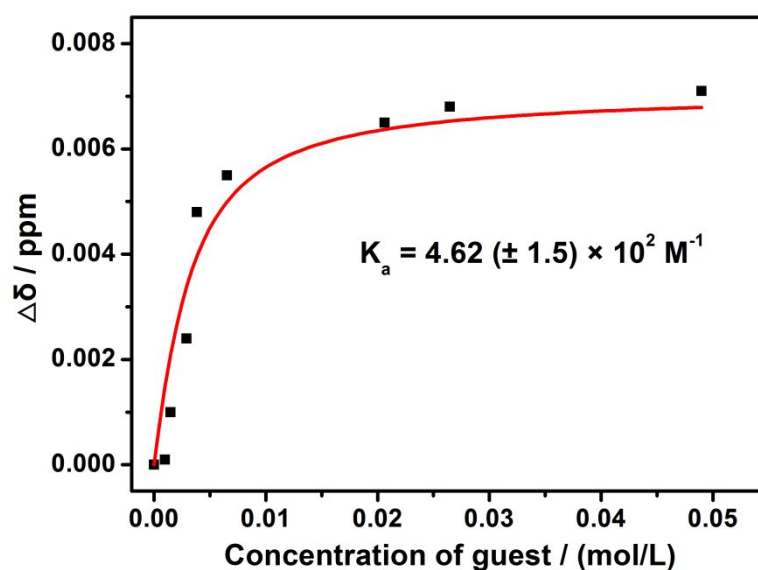


Fig. S46 Non-linear fitting curve of the chemical shift changes of H₄ versus the concentration of **2**.

The association constant K_a was calculated according to the following equation:

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

Where $\Delta\delta$ is the chemical shift change of H₄ on **2** upon titration, $\Delta\delta_{\text{max}}$ is the chemical shift change of H₄ when **2** is completely complexed, $[H]_0$ is the fixed concentration of **2** (0.002 mol/L), $[G]$ is the concentration of added **7**. Based on the above equation, the K_a of **2**·**7** was calculated to be 4.6 (± 1.5) $\times 10^2 \text{ M}^{-1}$.

9. The average diameters of **4a** and **6a**

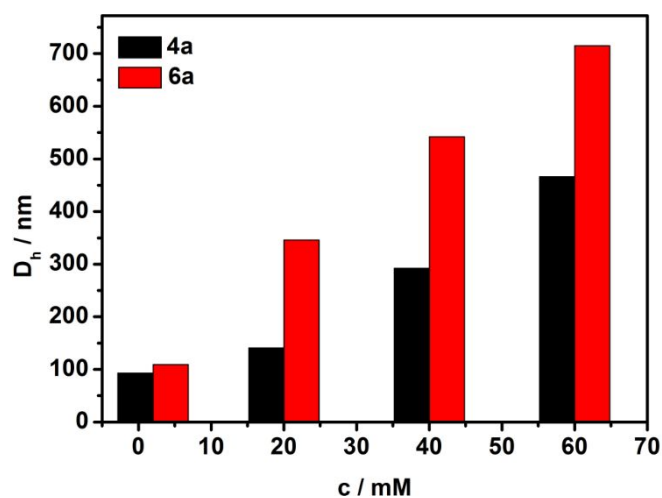


Fig. S47 Comparison of the average diameters of **4a** and **6a** under the same B21C7 concentrations.

10. Stimuli-responsiveness of the supramolecular gel

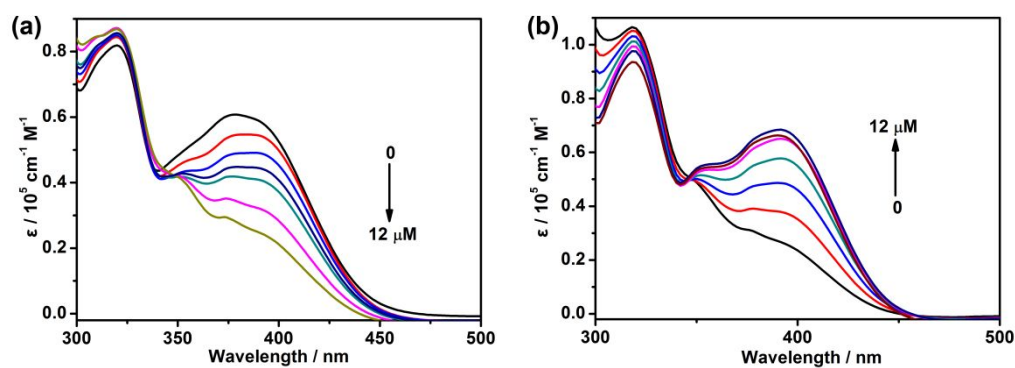


Fig. S48 Change in the UV/Vis absorption spectra of the cross-linked supramolecular polymer (10 μM) upon stepwise addition of 12 μM cyclen (a) and further stepwise addition of 12 μM of $\text{Zn}(\text{OTf})_2$ (b).

11. Optical characterization of ligands **1a-1d** and metallacycles **3a-3d**

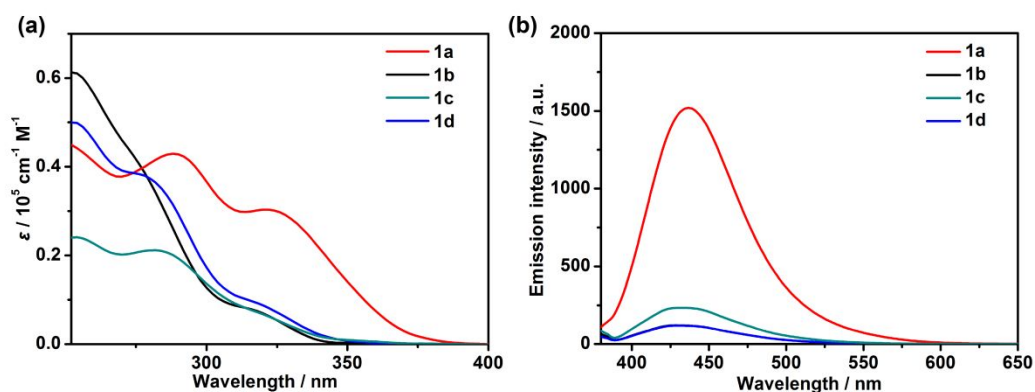


Fig. S49 (a) Absorption and (b) emission spectra of the precursor ligands.

Table S1 Main optical data of ligands **1a-1d** and metallacycles **3a-3d**.

Compound	$\lambda_{\text{ab, max}} / \text{nm} [\epsilon \times 10^3, \text{cm}^{-1} \text{M}^{-1}]$	$\lambda_{\text{em, max}} / \text{nm}$
1a	289 [43.1], 323 [30.3]	437
1b	318 [7.6]	428
1c	284 [21.1]	432
1d	281 [37.4], 318 [8.9]	428
3a	376 [26.1]	448
3b	354 [11.3], 372 [8.4]	430
3c	356 [23.4], 374 [14.5]	472
3d	354 [11.5], 372 [8.9]	436

12. References

- S1. Zhang, M.; Yin, S.; Zhang, J.; Zhou, Z.; Saha, M. L.; Lu, C.; Stang, P. J. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 3044.
- S2. Lu, C.; Zhang, M.; Tang, D.; Yan, X.; Zhang, Z.; Zhou, Z.; Song, B.; Wang, H.; Li, X.; Yin, S.; Sepehrpour, H.; Stang, P. J. *Am. Chem. Soc.* **2018**, *140*, 7674.
- S3. Benesi, H.A.; Hildebrand, J.H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.