

*Electronic Supplementary Information for*

## **Fine-Tuning of the Optical Output in a Dual Responsive Catenane Switch**

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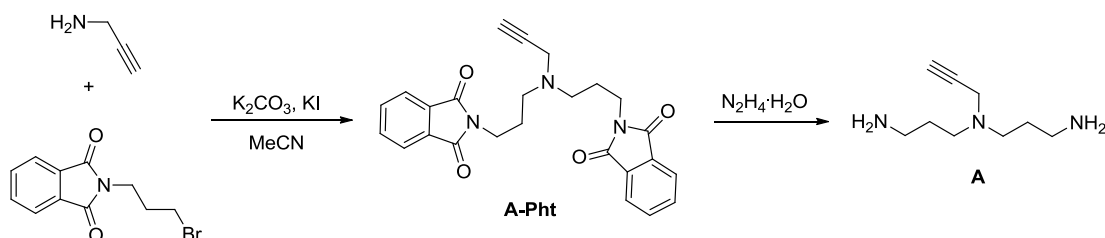
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## 1. Synthesis

*General.* All reagents were purchased from commercial suppliers (Dkmchem, J & K, Aldrich and Energy) and used without further purification unless otherwise noted. All the solvents were of analytical grade (ACI Labscan and DUKSAN Pure Chemicals). MeCN, CHCl<sub>3</sub> and MeOH were distilled over CaH<sub>2</sub> before use. **Phen-CHO** was synthesized according to literature procedures.<sup>1</sup> Thin layer chromatography (TLC) was performed on silica gel 60 F254 (Merck, Germany, Aluminium sheet) and column chromatography was carried out using silica gel 60F (Silicycle, Canada). ESI-MS were carried out using a Waters-Acquity UPLC H-Class system coupled with a QDa MS detector. HRMS spectra were obtained from a Waters Micromass Q-ToF Premier quadrupole time-of-flight tandem mass spectrometer. NMR spectra were recorded on Bruker DPX spectrometers with working frequencies of 400 MHz or 500 MHz for <sup>1</sup>H, and 100 MHz or 125 MHz for <sup>13</sup>C, respectively. Chemical shifts are reported in ppm and referenced to solvent residues (for <sup>1</sup>H: CDCl<sub>3</sub>: δ = 7.26 ppm, d<sub>6</sub>-DMSO: δ = 2.50 ppm, CD<sub>3</sub>OD: δ = 3.31 ppm; For <sup>13</sup>C: CDCl<sub>3</sub>: δ = 77.16 ppm, d<sub>6</sub>-DMSO: δ = 39.52 ppm, CD<sub>3</sub>OD: δ = 49.00 ppm).

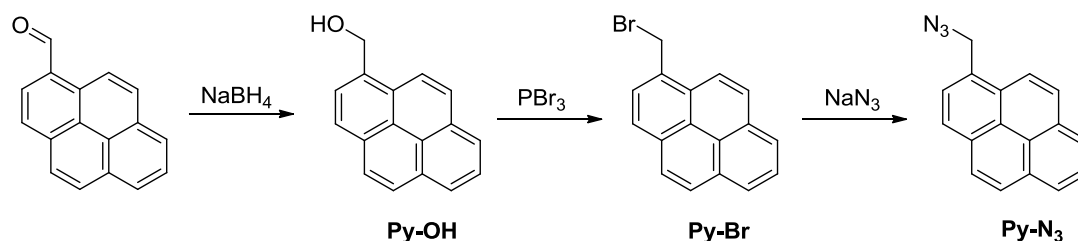


**Scheme S1.** Synthesis of **A-Pht** and **A**.

*Synthesis of A-Pht.* A mixture of propargylamine (0.55 g, 10 mmol), N-(3-bromopropyl)phthalimide (6.70 g, 25 mmol), K<sub>2</sub>CO<sub>3</sub> (4.14 g, 30 mmol) and KI (0.17 g, 1 mmol) in MeCN (100 mL) was heated at 80 °C for overnight. The reaction was cooled to room temperature and filtered, and the solvents were removed by a rotary evaporator. The residue was re-dissolved in 80 mL CH<sub>2</sub>Cl<sub>2</sub>, washed with water (2 x 100 mL) and brine (100 mL), dried over anhydrous MgSO<sub>4</sub> and filtered. Solvents were removed from the filtrate by a rotary evaporator and the residue was purified by a silica column using hexane/ethyl

acetate/CH<sub>2</sub>Cl<sub>2</sub> = 12:8:1 as the eluent. The product was obtained as a white solid. Yield: 3.56 g, 83%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ 7.86–7.79 (m, 8H), 3.58 (t, *J* = 7.1 Hz, 4H), 3.00 (t, *J* = 2.1 Hz, 1H), 2.42 (t, *J* = 6.8 Hz, 4H), 1.66 (quint, *J* = 6.9 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ 168.0, 134.3, 131.7, 123.0, 78.4, 75.7, 50.3, 35.7, 25.6. HRMS (ESI+): *m/z* calcd. for C<sub>25</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 430.1761, found: 430.1759.

**Synthesis of A.** Under an argon atmosphere, a mixture of **A-Pht** (1.0 g, 2.3 mmol) and hydrazine hydrate (0.7 mL, 14 mmol) in 50 mL MeOH was stirred for 24 hours at room temperature. The reaction mixture was filtered and solvents were removed from the filtrate using a rotary evaporator. The residue was re-dissolved in 30 mL CH<sub>2</sub>Cl<sub>2</sub> and filtered, and the solvent was removed from the filtrate. If white solid was observed, the residue was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered until a yellow oil was obtained upon solvent removal. Yield: 0.34 g, 88%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, 298 K) δ 3.39 (s, 1H), 3.28–3.26 (m, 2H), 2.63 (t, *J* = 7.1 Hz, 4H), 2.57–2.45 (m, 4H), 1.66–1.54 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ 52.5, 49.9, 42.2, 40.9, 31.1. HRMS (ESI+): *m/z* calcd. for C<sub>9</sub>H<sub>19</sub>N<sub>3</sub> [M+H]<sup>+</sup>: 170.1652, found: 170.1651.

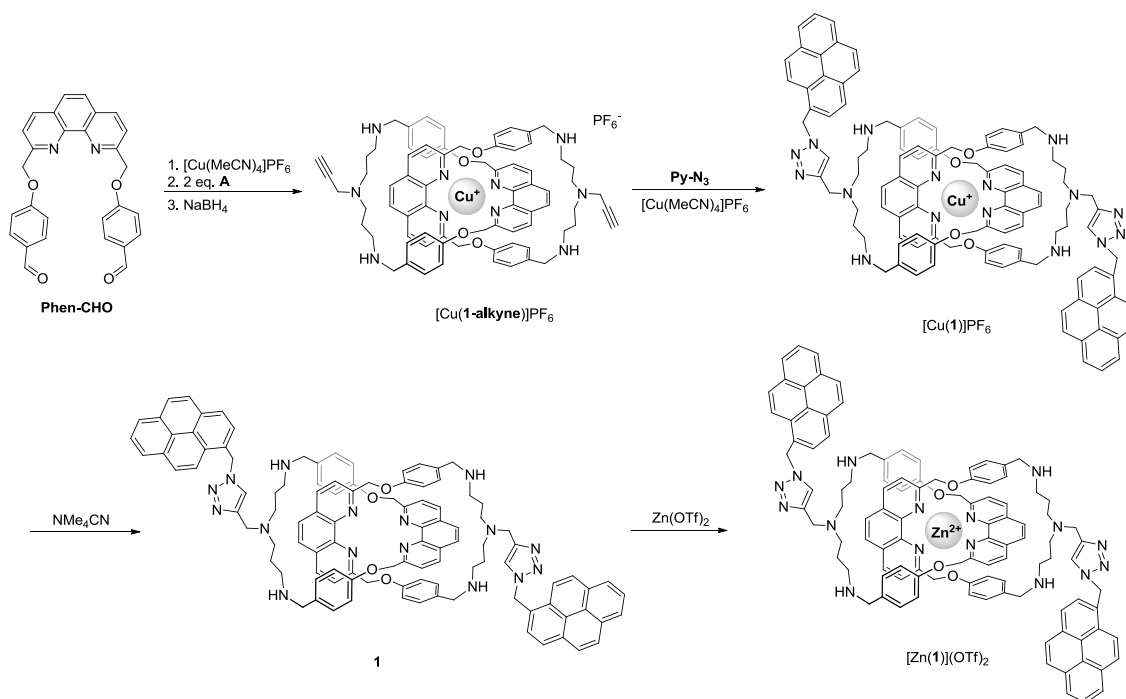


**Scheme S2.** Synthesis of **Py-OH** and **Py-N<sub>3</sub>**.

**Synthesis of Py-OH.** To a solution of 1-pyrenecarboxaldehyde (0.50 g, 2.2 mmol) in tetrahydrofuran (15 mL) cooled in an ice bath, NaBH<sub>4</sub> (0.2 mg, 4 mmol) was added. The reaction mixture was warmed to room temperature and stirred for overnight. Solvents were removed by a rotary evaporator and the residue was re-dissolved in 30 mL CH<sub>2</sub>Cl<sub>2</sub>, washed with water (2 x 50 mL) and brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. Solvents were removed from the filtrate to afford the product as a yellow powder.

Yield: 0.49 g, 95%.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ , 298 K)  $\delta$  8.39 (d,  $J = 9.2$  Hz, 1H), 8.32–8.26 (m, 3H), 8.23 (d,  $J = 9.3$  Hz, 1H), 8.14 (m,  $J = 8.0, 3.0$  Hz, 3H), 8.07 (t,  $J = 7.6$  Hz, 1H), 5.52 (t,  $J = 5.5$  Hz, 1H), 5.25 (d,  $J = 5.5$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ , 298 K)  $\delta$  136.0, 130.8, 130.4, 123.0, 127.7, 127.5, 127.2, 126.8, 126.2, 125.6, 125.1, 125.1, 124.7, 124.0, 123.9, 123.5, 61.3. HRMS (ESI+):  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{12}\text{O}$   $[\text{M}+\text{Na}]^+$ : 255.0780, found: 255.0780.

*Synthesis of Py-N<sub>3</sub>*. To a solution of **Py-OH** (0.49 g, 2.1 mmol) in toluene (40 mL) cooled in an ice bath, a solution of  $\text{PBr}_3$  (0.3 mL, 3.2 mmol) in toluene (10 mL) was added dropwisely. The mixture was warmed to room temperature and stirred for overnight. A saturated aq.  $\text{NaHCO}_3$  solution was added slowly until no gas evolution was observed. The organic phase was separated and the aqueous phase was extracted by  $\text{CH}_2\text{Cl}_2$  (30 mL) and combined with the toluene solution, washed with water (2 x 50 mL) and brine (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and filtered. Solvents were removed from the filtrate to afford the **Py-Br** as a yellow powder which was used in the next step without further purification. The obtained **Py-Br** was dissolved in *N,N*-dimethylformamide (20 mL) and  $\text{NaN}_3$  (0.28 g, 3.2 mmol) was added, the reaction mixture was stirred at room temperature for overnight. Water (100 mL) was added to the reaction mixture and the organic components were extracted by  $\text{CH}_2\text{Cl}_2$  (50 mL). The organic layer was washed with water (2 x 100 mL) and brine (100 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and filtered. Solvents were removed from the filtrate using a rotary evaporator to afford **Py-N<sub>3</sub>** as a yellow powder. Yield: 0.50 g, 92%.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ , 298 K)  $\delta$  8.42–8.31 (m, 5H), 8.25–8.18 (m, 2H), 8.18–8.10 (m, 2H), 5.23 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ , 298 K) 131.1, 130.7, 130.3, 129.0, 128.8, 128.1, 128.1, 127.8, 127.4, 126.5, 125.7, 125.6, 124.8, 124.1, 123.8, 123.2, 51.7. HRMS (EI+):  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{11}\text{N}_3$   $[\text{M}]^+$ : 257.0953, found: 257.0953.



**Scheme S3.** Synthesis of [Cu(1-alkyne)]PF<sub>6</sub>, [Cu(1)]PF<sub>6</sub>, **1** and [Zn(1)](OTf)<sub>2</sub>.

*Synthesis of [Cu(1-alkyne)]PF<sub>6</sub>.* Under an argon atmosphere, a mixture of **Phen-CHO** (0.54 g, 1.2 mmol) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (0.22 g, 0.6 mmol) in 300 mL of 5:3:2 CHCl<sub>3</sub>/CH<sub>3</sub>CN/CH<sub>3</sub>OH (150 mL/90 mL/60 mL) solvent mixture was stirred until a clear red solution was obtained, followed by addition of **A** (0.25 g, 1.5 mmol) and piperidine (0.5 mL). The reaction mixture was heated to 60 °C for 4 hours. An additional amount of **A** (0.05 g, 0.3 mmol) was added and the mixture was heating for another 4 hours. The reaction mixture was cooled in an ice bath and NaBH<sub>4</sub> (0.11 g, 3 mmol) was added. The mixture was stirred in the ice bath for 1 hour and warmed to room temperature. Solvents were removed by a rotary evaporator and the dark red residue was re-dissolved in 50 mL CH<sub>2</sub>Cl<sub>2</sub>, washed with water (2 x 100 mL) and brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed by a rotary evaporator to afford an orange solid, which was washed by ethyl acetate (3 x 20 mL) and re-dissolved in 30 mL CH<sub>3</sub>CN (30 mL). The solution was filtered, and the solvent was removed to afford [Cu(1-alkyne)]PF<sub>6</sub> as an orange powder which was further dried under vacuum. Yield: 0.43 g, 52%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ 8.55 (d, *J* = 8.1 Hz, 4H), 8.05 (d, *J* =

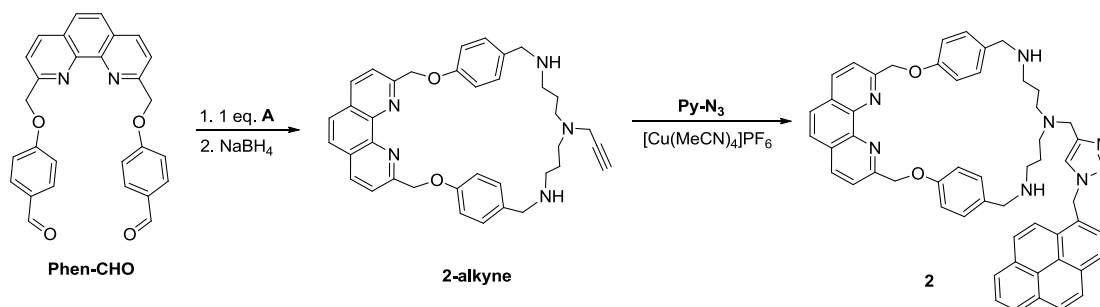
8.2 Hz, 4H), 7.91 (s, 4H), 6.40 (d,  $J = 8.3$  Hz, 8H), 5.79 (d,  $J = 8.3$  Hz, 8H), 4.84 (s, 8H), 3.53 (s, 4H), 3.15 (s, 2H), 2.67 (t,  $J = 6.5$  Hz, 8H), 1.73–1.66 (m, 8H)  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO- $d_6$ , 298 K)  $\delta$  155.7, 153.6, 142.5, 137.5, 132.4, 128.2, 127.5, 126.4, 125.6, 112.2, 78.1, 75.9, 70.6, 52.1, 52.0, 46.6, 27.8. HRMS (ESI+):  $m/z$  calcd. for  $\text{C}_{74}\text{H}_{78}\text{N}_{10}\text{O}_4\text{Cu}$   $[\text{M}]^+$ : 1233.5498, found: 1233.5500.

*Synthesis of [Cu(1)]PF<sub>6</sub>*. A mixture of [Cu(1-alkyne)]PF<sub>6</sub> (69 mg, 0.05 mmol), **Py-N<sub>3</sub>** (29 mg, 0.11 mmol) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (2 mg, 0.005 mmol) in 5 mL MeCN was stirred at room temperature for 24 hours under an argon atmosphere. The orange precipitate formed was collected by filtration and was washed by ethyl acetate (2 x 20 mL) and diethyl ether (10 mL). The orange solid was dried under vacuum. Yield: 49 mg, 52%.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , 298 K)  $\delta$  8.55 (d,  $J = 9.3$  Hz, 2H), 8.49 (d,  $J = 8.1$  Hz, 4H), 8.35–8.31 (m, 8H), 8.20 (q,  $J = 9.0$  Hz, 4H), 8.12–8.08 (m, 4H), 8.03 (d,  $J = 7.9$  Hz, 2H), 8.00 (d,  $J = 8.2$  Hz, 4H), 7.83 (s, 4H), 6.42 (s, 4H), 6.32 (d,  $J = 8.1$  Hz, 8H), 5.74 (d,  $J = 8.3$  Hz, 8H), 4.78 (s, 8H), 3.80 (s, 4H), 3.21 (s, 8H), 2.39 (br, 8H), 1.72 (br, 8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, DMSO- $d_6$ , 298 K)  $\delta$  155.7, 153.6, 142.4, 137.5, 132.4, 131.0, 130.8, 130.2, 129.4, 128.4, 128.2, 128.1, 127.8, 127.6, 127.5, 127.3, 126.5, 126.4, 125.8, 125.6, 125.5, 125.1, 124.1, 124.1, 123.8, 122.8, 121.7, 112.3, 70.6, 52.1, 50.9, 47.0, 45.1, 30.7, 27.7. HRMS (ESI+):  $m/z$  calcd. for  $\text{C}_{108}\text{H}_{101}\text{N}_{16}\text{O}_4\text{Cu}$   $[\text{M}+\text{H}]^{2+}$ : 874.8754, found: 874.8781.

*Synthesis of 1*. To a suspension of [Cu(1)]PF<sub>6</sub> (92 mg, 0.05 mmol) in 5 mL MeCN was added (NMe<sub>4</sub>)CN (100 mg, 1.0 mmol) and the mixture was stirred at room temperature for 12 hours. The white solid formed was collected by filtration and washed by deionized water (3 x 10 mL) and dried under vacuum to afford **1** as a white powder. Yield: 80 mg, 95%.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , 298 K)  $\delta$  8.39 (d,  $J = 8.2$  Hz, 4H), 8.26–8.23 (m, 4H), 8.12 (t,  $J = 9.0$  Hz, 8H), 8.05 (d,  $J = 6.3$  Hz, 4H), 8.01 (s, 2H), 7.85 (s, 4H), 7.71 (d,  $J = 8.2$  Hz, 6H), 6.67 (d,  $J = 8.3$  Hz, 8H), 6.55 (d,  $J = 8.2$  Hz, 8H), 6.20 (s, 4H), 5.12 (s, 8H), 3.14 (s, 8H), 1.95 (br, 8H), 1.88 (br, 8H), 1.19 (br, 8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, DMSO- $d_6$ , 298 K)  $\delta$  157.0, 156.6, 144.7, 143.8, 137.0, 133.1, 130.8, 130.7, 130.1, 129.2, 128.7, 128.1,

128.0, 127.9, 127.6, 127.2, 126.8, 126.4, 126.4, 125.6, 125.5, 124.8, 123.9, 123.9, 123.6, 122.4, 122.2, 114.7, 72.5, 52.2, 52.0, 50.7, 46.1, 45.8, 27.1. HRMS (ESI+):  $m/z$  calcd. for  $C_{108}H_{102}N_{16}O_4$   $[M+2H]^{2+}$ : 843.9145, found: 843.9163.

**Synthesis of  $[Zn(1)](OTf)_2$ .** A mixture of **1** (26 mg, 0.014 mmol) and  $Zn(OTf)_2$  (7 mg, 0.02 mmol) were in 4 mL of 1:1  $CH_2Cl_2/CH_3CN$  (2 mL/2 mL) was stirred at room temperature for overnight. Diethyl ether (20 mL) was added and the white precipitate formed collected by filtration and washed by diethyl ether (2 x 20 mL). The white powder was dried under vacuum to afford  $[Zn(1)](OTf)_2$ . Yield: 24 mg, 92%.  $^1H$  NMR (500 MHz,  $DMSO-d_6$ , 298 K)  $\delta$  8.67 (d,  $J = 8.2$  Hz, 4H), 8.58 (d,  $J = 9.3$  Hz, 2H), 8.37–8.33 (m, 8H), 8.20 (m, 6H), 8.11 (m, 6H), 8.07 (d,  $J = 7.9$  Hz, 2H), 7.82 (s, 4H), 6.42 (d,  $J = 14.5$  Hz, 12H), 5.73 (d,  $J = 7.6$  Hz, 8H), 5.27 (s, 8H), 3.88 (s, 4H), 2.36 (br, 8H), 1.76 (br, 8H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $DMSO-d_6$ , 298 K)  $\delta$  156.1, 141.3, 138.5, 131.1, 130.8, 130.2, 129.3, 128.5, 128.3, 127.9, 127.6, 127.3, 126.9, 126.7, 125.9, 125.7, 125.5, 125.4, 125.4, 125.2, 125.1, 124.6, 124.1, 123.7, 122.8, 122.3, 119.1, 115.9, 115.8, 115.8, 70.7, 70.7, 70.6, 51.0, 30.0. HRMS (ESI+):  $m/z$  calcd. for  $C_{108}H_{100}N_{16}O_4Zn$   $[M]^{2+}$ : 875.3708, found: 875.3734.



#### Scheme S4. Synthesis of **2-alkyne** and **2**.

**Synthesis of 2-alkyne.** A mixture of **Phen-CHO** (180 mg, 0.4 mmol) and **A** (102 mg, 0.6 mmol) and piperidine (0.5 mL) in 250 mL of 5:3:2  $CHCl_3/CH_3CN/CH_3OH$  (125 mL/75 mL/50 mL) solvent mixture was heated at 60 °C for overnight. The reaction mixture was cooled in an ice bath and  $NaBH_4$  (46 mg, 1.2 mmol) was added and the mixture was stirred in the ice bath for 1 hour. The mixture was warmed to room temperature and

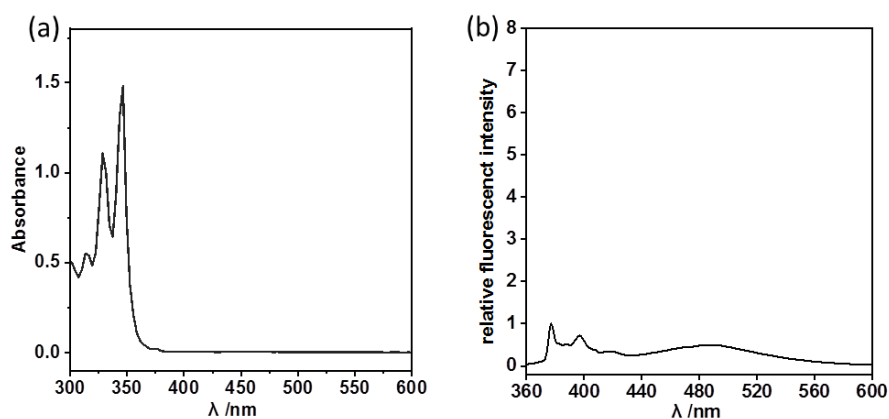
solvents were removed by a rotary evaporator. The yellow residue was purified by a silica column using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH/Et<sub>3</sub>N = 40:1:1 as the eluent to afford **2-alkyne** as a light yellow solid. Yield: 105 mg, 45%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 8.24 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.77 (s, 2H), 7.23–7.13 (m, 8H), 5.64 (s, 4H), 3.67 (s, 4H), 3.33 (d, *J* = 2.3 Hz, 1H), 2.64 (t, *J* = 6.5 Hz, 4H), 2.51 (t, *J* = 6.9 Hz, 4H), 1.66–1.58 (m, 4H), 1.25 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 158.1, 158.0, 145.4, 137.1, 129.5, 128.3, 126.5, 122.2, 115.9, 115.9, 73.1, 72.6, 53.2, 52.1, 47.6, 41.66, 27.4, 27.0. HRMS (ESI+): *m/z* calcd. for C<sub>37</sub>H<sub>39</sub>N<sub>5</sub>O<sub>2</sub> [M+Na]<sup>+</sup>: 608.2996, found: 608.2988.

*Synthesis of 2.* A mixture of **2-alkyne** (25 mg, 0.04 mmol), **Py-N<sub>3</sub>** (13 mg, 0.05 mmol) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (2 mg, 0.005 mmol) in 4 mL 3:1 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (3 mL/1 mL) solvent mixture was stirred at room temperature for overnight. A aqueous solution of ethylenediaminetetraacetic acid (EDTA) (29 mg, 0.1 mmol, 4 mL) was added and the reaction mixture was stirred for 1 hour. Solvents were removed by a rotary evaporator, and the yellow residue was re-dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>, washed with water (2 x 10 mL) and brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. Solvents were removed from the filtrate by a rotary evaporator and the yellow residue was purified by a silica column using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH/Et<sub>3</sub>N = 40:1:1 as the eluent to afford **2** as a white solid. Yield: 31 mg, 92%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ 8.47 (d, *J* = 8.2 Hz, 2H), 8.41 (d, *J* = 9.3 Hz, 1H), 8.28 (d, *J* = 7.7 Hz, 2H), 8.23 (dd, *J* = 8.6, 4.2 Hz, 2H), 8.14 (q, *J* = 9.0 Hz, 2H), 8.05 (t, *J* = 7.6 Hz, 1H), 7.93–7.88 (m, 5H), 7.84 (s, 1H), 7.11 (q, *J* = 8.8 Hz, 8H), 6.27 (s, 2H), 5.49 (s, 4H), 3.53 (s, 4H), 2.32 (t, *J* = 6.5 Hz, 4H), 2.26 (t, *J* = 6.5 Hz, 4H), 1.48–1.41 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>, 298 K) δ 157.2, 157.1, 144.6, 144.2, 137.2, 133.1, 131.0, 130.7, 130.2, 129.2, 129.0, 128.4, 128.2, 127.9, 127.8, 127.4, 127.3, 126.5, 125.7, 125.6, 125.0, 124.0, 123.7, 123.6, 122.7, 122.6, 115.2, 71.6, 52.3, 51.3, 50.8, 47.7, 46.8, 26.6. HRMS (ESI+): *m/z* calcd. for C<sub>54</sub>H<sub>51</sub>N<sub>8</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 843.4129, found: 843.4154.

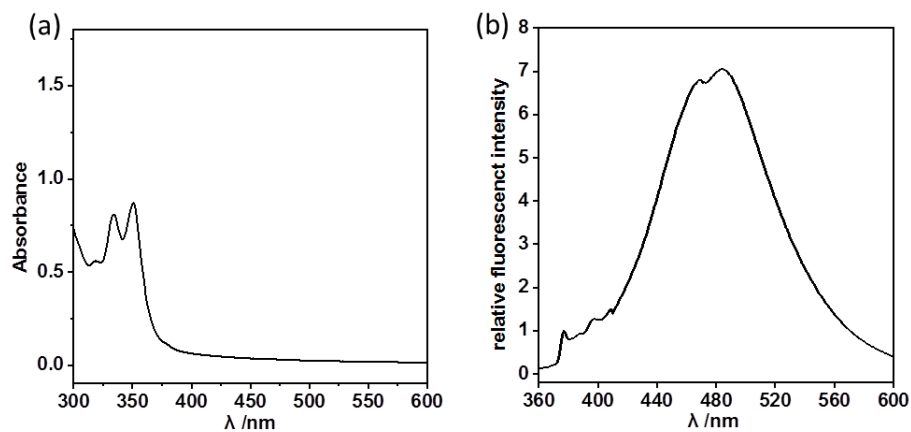


## 2. UV-Vis and Fluorescence Spectroscopy

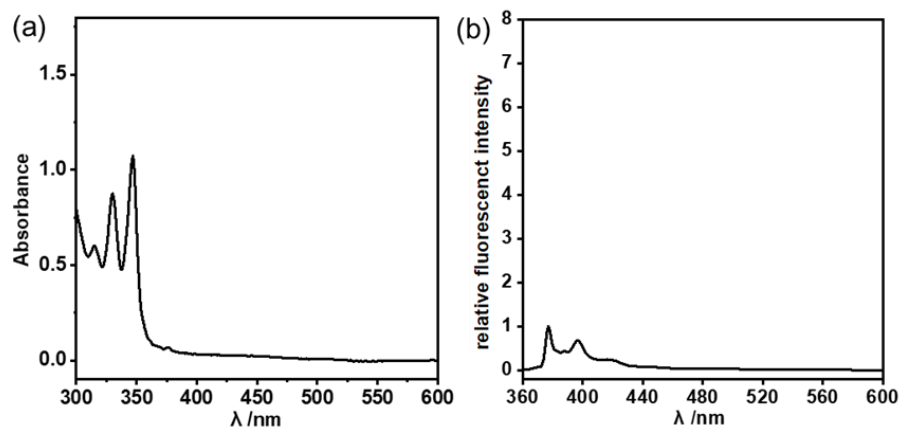
UV-Vis spectra were recorded by a Hitachi UH5300 UV-Vis spectrophotometer. Fluorescence spectra were recorded on an Edinburgh Instruments FS5 Spectrophotometer equipped with a 150 W CW Ozone-free xenon arc lamp and a Photomultiplier R928P detection unit with spectral coverage of 200–870 nm. Samples for emission measurement were contained in a quartz cuvette with a path length of 1 cm and 1.5 mL cell volume. The samples were excited at 340 nm and emission spectra were collected from 360 nm to 600 nm. Millipore water was used to prepare all aqueous solutions. Stock solutions of **1**, **2**, [Cu(**1**)]PF<sub>6</sub>, [Zn(**1**)](OTf)<sub>2</sub> at 1 mM were prepared in DMSO. Stock solutions of trifluoroacetic acid (1 mM), sodium chloride (100 mM), calcium chloride (1 mM) and lithium chloride (1 mM) were prepared in Millipore water. Samples for measurement were diluted by Millipore water and DMSO to the required concentrations and solvent composition. All the samples were mixed with a plastic disposable pipette prior to the collection of absorption and emission spectra.



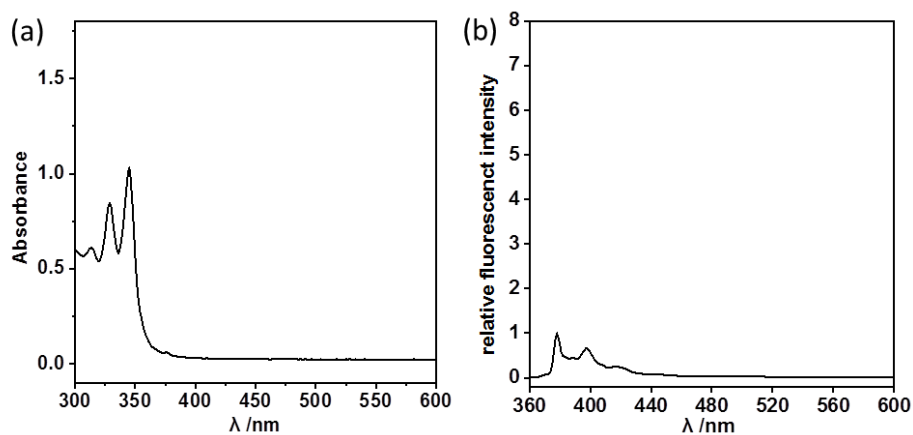
**Fig. S1.** (a) UV-Vis and (b) fluorescent spectra of a 25  $\mu$ M solution of **1** in DMSO at 298 K.



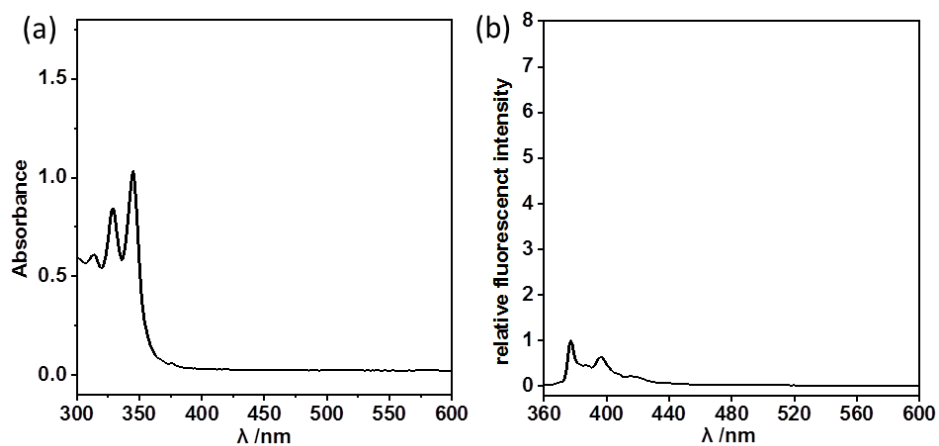
**Fig. S2.** (a) UV-Vis and (b) fluorescent spectra of a 25  $\mu\text{M}$  solution of **1** in 90% (v/v)  $\text{H}_2\text{O}/\text{DMSO}$  at 298 K.



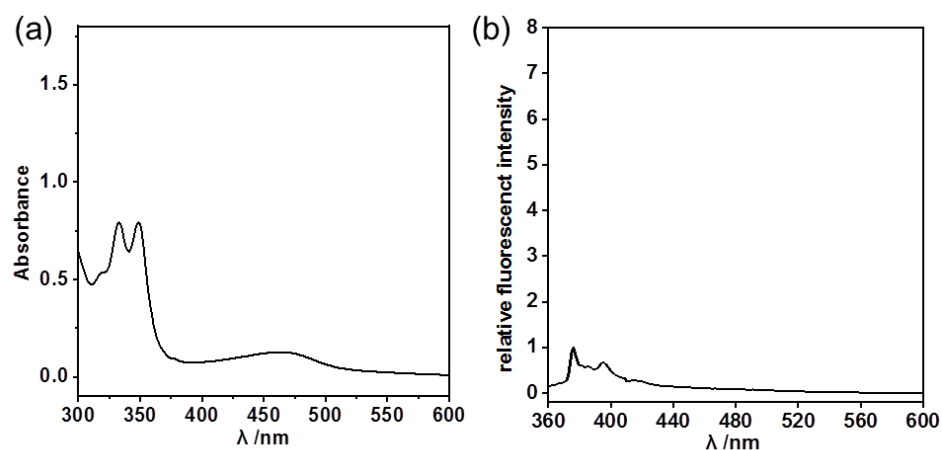
**Fig. S3.** (a) UV-Vis and (b) fluorescent spectra of a 50  $\mu\text{M}$  solution of **2** in DMSO at 298 K.



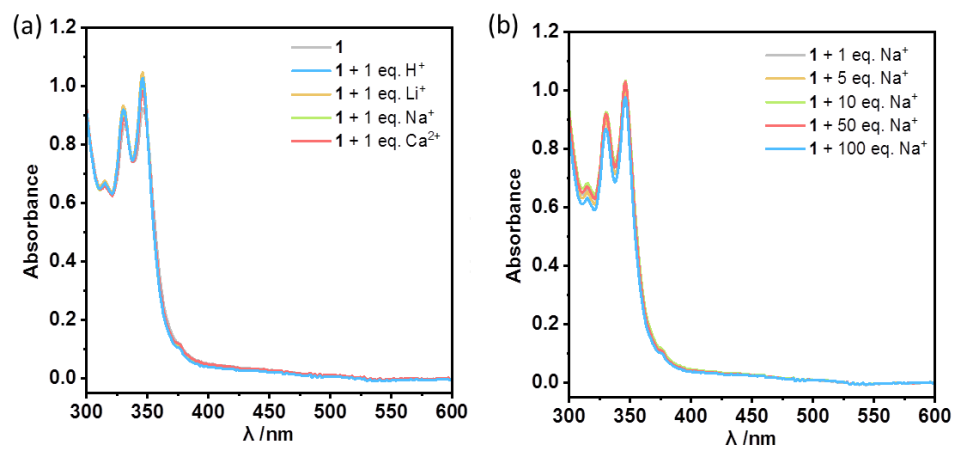
**Fig. S4.** (a) UV-Vis and (b) fluorescent spectra of a 25  $\mu\text{M}$  solution of  $[\text{Zn}(\mathbf{1})](\text{OTf})_2$  in DMSO at 298 K.



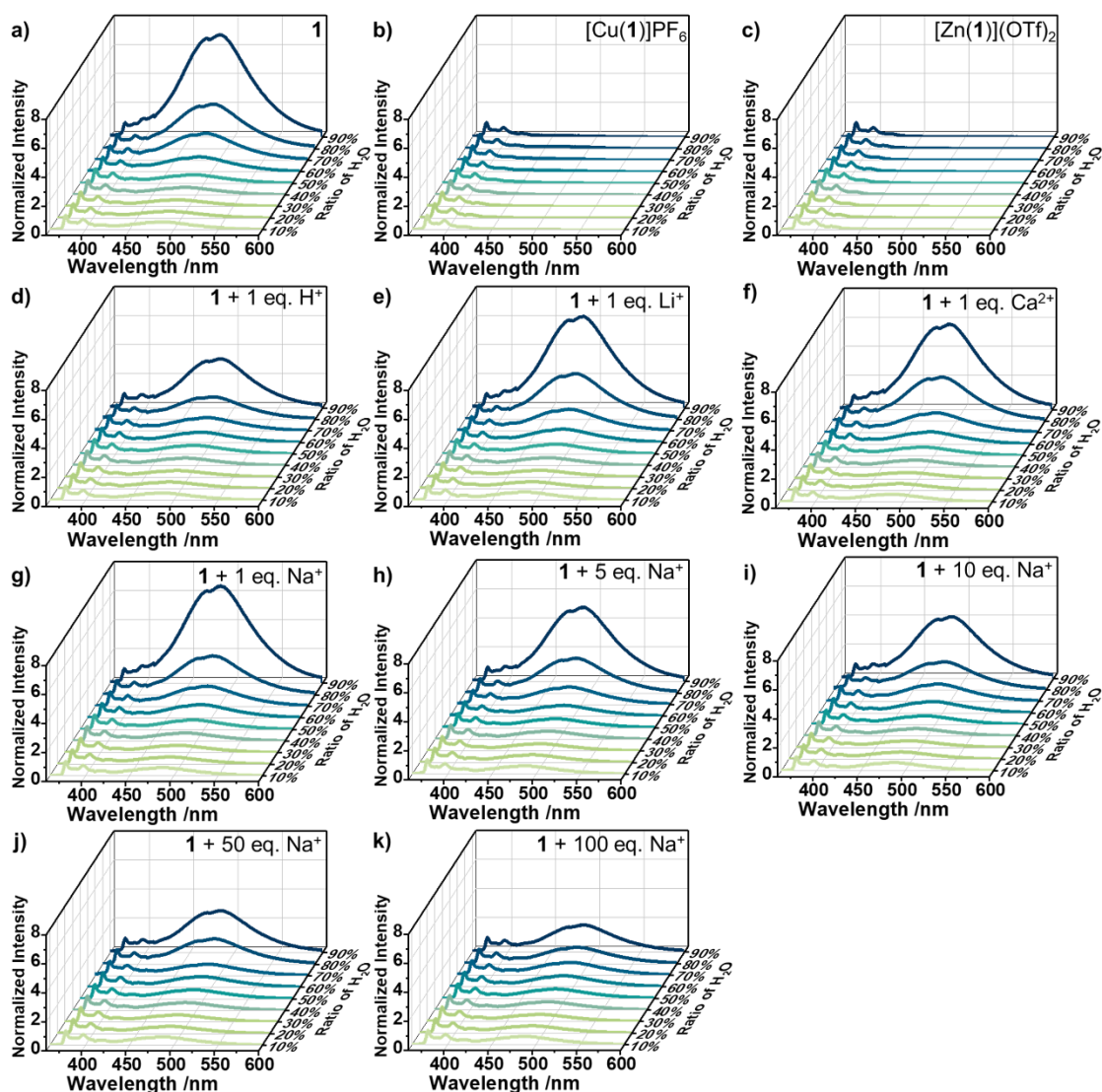
**Fig. S5.** (a) UV-Vis and (b) fluorescent spectra of a 25  $\mu\text{M}$  solution of  $[\text{Zn}(\mathbf{1})](\text{OTf})_2$  in 90% (v/v)  $\text{H}_2\text{O}/\text{DMSO}$  at 298 K.



**Fig. S6.** (a) UV-Vis and (b) fluorescent spectra of a 25  $\mu\text{M}$  solution of  $[\text{Cu}(\mathbf{1})]\text{PF}_6$  in 90% (v/v)  $\text{H}_2\text{O}/\text{DMSO}$  at 298 K.



**Fig. S7.** UV-Vis spectra of 25  $\mu\text{M}$  solutions of  $\mathbf{1}$  in the presence of (a) 1 eq. of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{CF}_3\text{COOH}$ ; and (b) 1 eq. 5 eq. 10 eq. 50 eq. and 100 eq. of  $\text{Na}^+$  in 90% (v/v)  $\text{H}_2\text{O}/\text{DMSO}$  at 298 K.



**Fig. S8.** Normalized fluorescent spectra of a) **1**; b)  $[\text{Cu}(\mathbf{1})]\text{PF}_6$ ; c)  $[\text{Zn}(\mathbf{1})](\text{OTf})_2$ ; d) **1** + 1 eq.  $\text{CF}_3\text{COOH}$ ; e) **1** + 1 eq. of  $\text{Li}^+$ ; f) **1** + 1 eq. of  $\text{Ca}^{2+}$ ; g) **1** + 1 eq. of  $\text{Na}^+$ ; h) **1** + 5 eq. of  $\text{Na}^+$ ; i) **1** + 10 eq. of  $\text{Na}^+$ ; j) **1** + 50 eq. of  $\text{Na}^+$ ; k) **1** + 100 eq. of  $\text{Na}^+$  in different percentages of  $\text{H}_2\text{O}$  in DMSO (v/v, 10% to 90%) at 298 K.

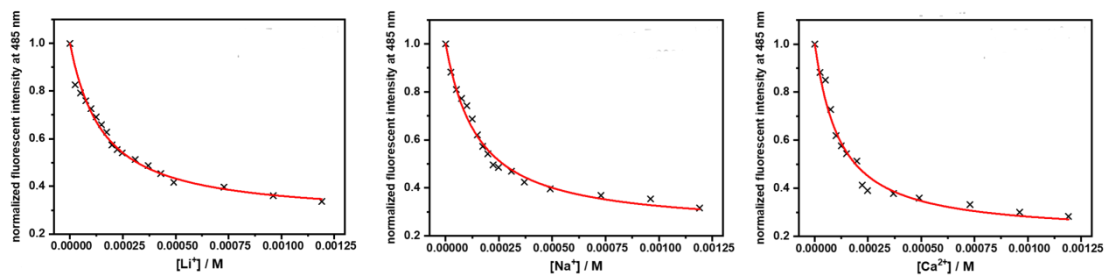
Association constants and stoichiometry of binding of **1** to H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup> were determined by fluorescent titration and Job's Plots respectively. All the measurements were conducted by using solutions of **1** in 97.5% (v/v) H<sub>2</sub>O/DMSO at 298 K at a final concentration of 25 μM. Stock solutions of 25 mM trifluoroacetic acid, LiCl, NaCl and CaCl<sub>2</sub> were prepared using a solution of 25 μM of **1** in 97.5% (v/v) H<sub>2</sub>O/DMSO.

The titration involved sequential additions of the guests using Eppendorf pipettes to a 1.000 mL aliquot of 25 μM of **1** in 97.5% (v/v) H<sub>2</sub>O/DMSO in a quartz cuvette. The solution were mixed well with a plastic disposable pipette prior to the collection of emission spectra. Emission spectra were collected from 360 nm to 600 nm.

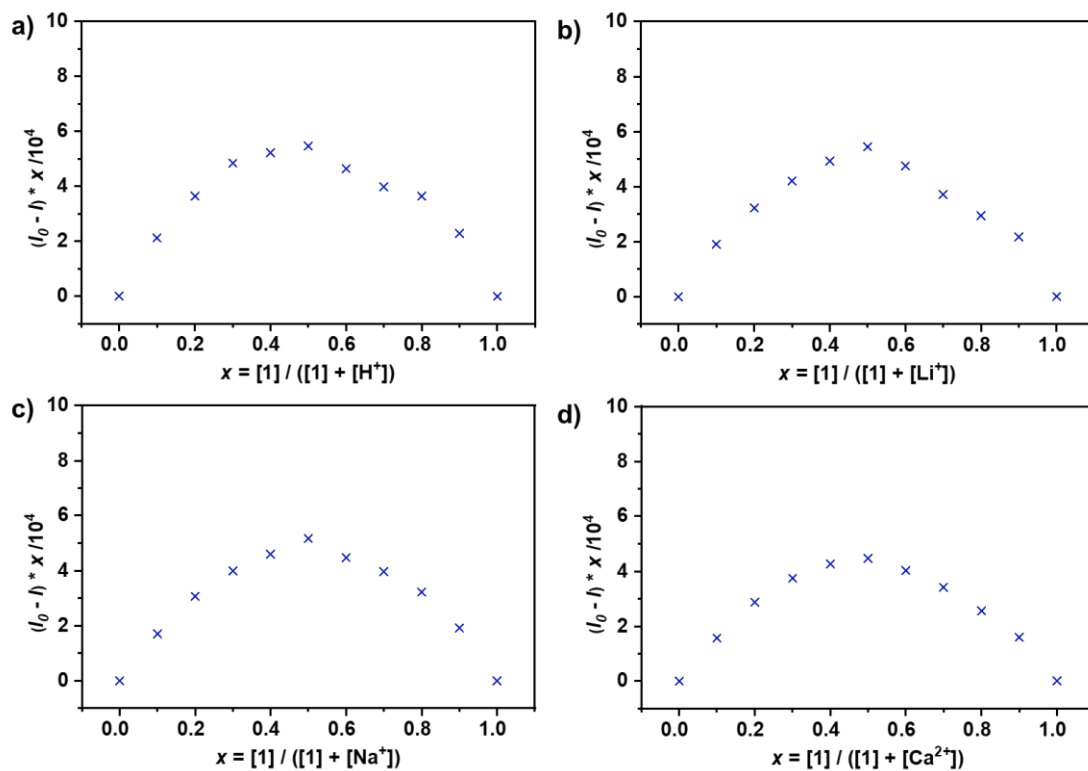
Association constant ( $K_a$ ) was obtained by nonlinear curve-fitting using the following equation in which  $I$  is the normalized emission intensity at 485 nm in each measurement;  $I_0$  is the normalized emission intensity of **1** in the absence of cation;  $[H]_0$  is the initial concentration of **1** (25 μM); and  $[G]$  is the equilibrium concentration of the cation guest. Fitting was performed using Origin 2018.

$$I = I_0 + \frac{I_c - I_0}{2 \times [H]_0} \times \left[ \left( [H]_0 + [G] + \frac{1}{K_a} \right) - \sqrt{\left( [H]_0 + [G] + \frac{1}{K_a} \right)^2 - 4 \times [H]_0 \times [G]} \right]$$

Due to the presence of multiple basic nitrogen sites in **1**, acid-base equilibrium involving **1** would be highly complex and association of **1** with H<sup>+</sup> may not be reliably obtained from fluorescence titration with acid. It has been reported that phenanthroline-based catenane has a pK<sub>a</sub> value of ~8.7,<sup>2</sup> which may be comparable to the secondary and tertiary aliphatic amines in **1**. Photophysical properties of the pyrene may also be sensitive to the protonation state of the nearby triazole.



**Fig. S9.** Non-linear curve-fitting for the titration of a)  $\text{Li}^+$ ; b)  $\text{Na}^+$ ; and c)  $\text{Ca}^{2+}$  to **1**.

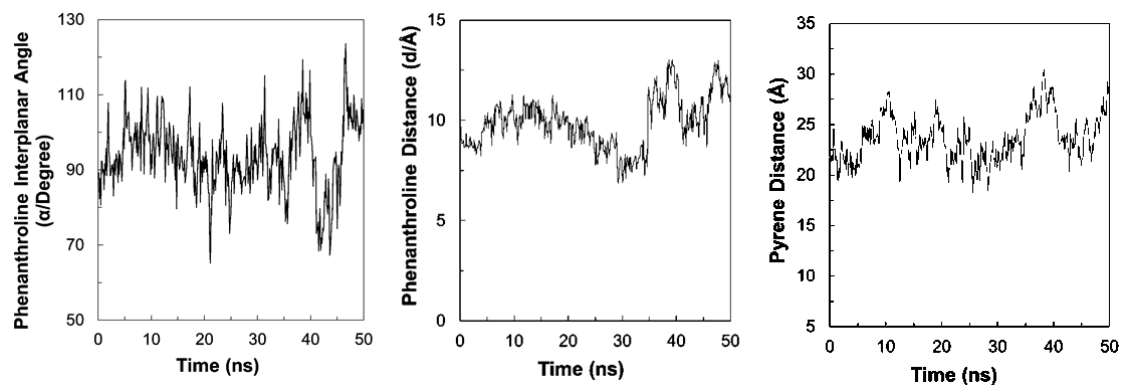


**Fig. S10.** Job's Plots for the binding of **1** with a)  $\text{H}^+$ ; b)  $\text{Li}^+$ ; c)  $\text{Na}^+$ ; d)  $\text{Ca}^{2+}$ .

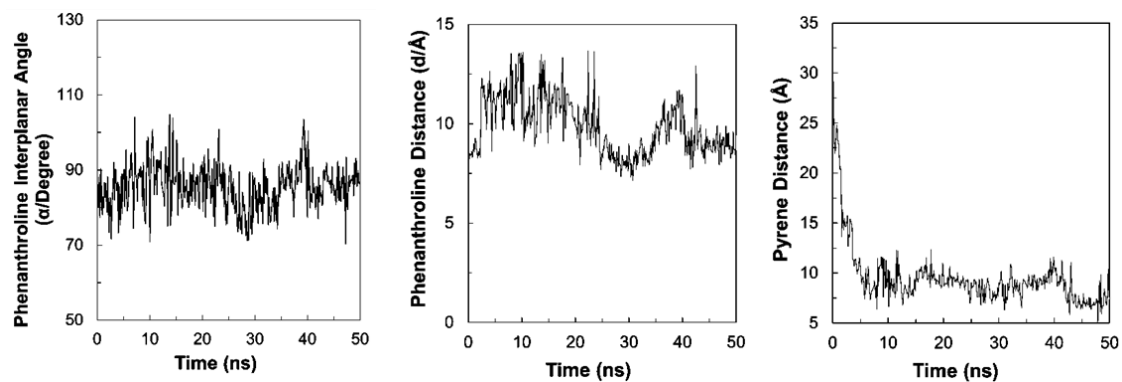
### 3. Molecular dynamics simulations

Structural dynamics of **1**, [Zn(**1**)]<sup>2+</sup> and [1·H]<sup>+</sup> were simulated using GROMACS (Version 2020.2) with a CHARMM27 force field.<sup>3,4</sup> Molecular structures were converted into Tripos molecule structure format (MOL2) using VEGA ZZ (Version 3.2.1.33).<sup>5</sup> In SwissParam module,<sup>6</sup> the Van der Waals parameters were extracted from the closest atom type in CHARMM22,<sup>7</sup> while the atomic charges were determined from Merck Molecular ForceField (MMFF).<sup>8-12</sup> Catenane **1** and its Zn<sup>2+</sup> complex were first placed in the centre of a 1 x 10<sup>6</sup> Å<sup>3</sup> box (100 Å x 100 Å x 100 Å) and solvated with approximately 32,000 TIP3P water molecules or 6,800 SwissParam parameterized DMSO molecules with a minimum solvent depth of 30 Å from the edge. To neutralize the net charge on [Zn(**1**)]<sup>2+</sup> and [1·H]<sup>+</sup>, two or one solvent molecules were replaced by the same number of Cl<sup>-</sup> counterions respectively with Van der Waals parameters taken from Ujaque's and Halgren's works.<sup>13,14</sup>

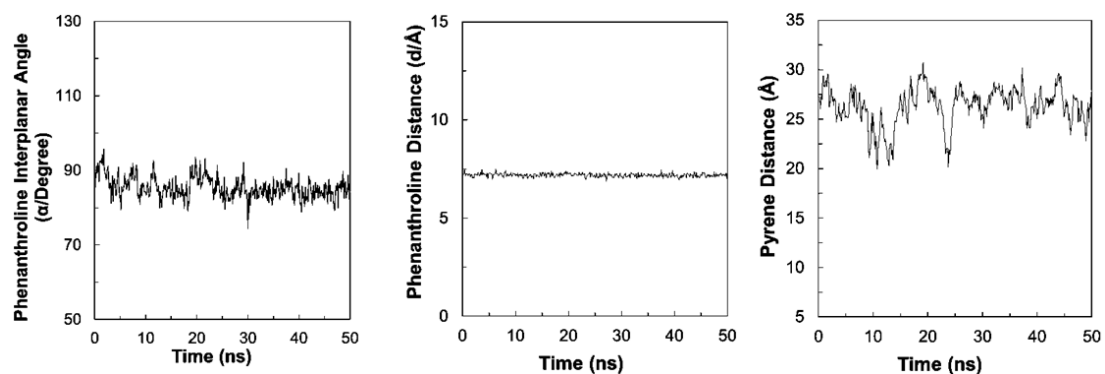
Simulations were carried out using the particle mesh Ewald technique (PME) with periodic boundary and a 12 Å nonbonded cutoff.<sup>15</sup> Bondings in the molecule were constrained with an LINCS algorithm with a time step of 2.5 fs.<sup>16</sup> The system was first pre-equilibrated with 50,000 steps until its maximum force was below 1000.0 kJ/mol/nm, and then equilibrated using NVT at 298 K by coupling all atoms to a Berendsen-thermostat with a time constant of 0.1 ps and a simulation trajectory of 2 ns. With NPT MD, temperature of the system was maintained at 298 K with Berendsen weak-coupling algorithm (time constant = 0.1 ps), while the pressure was kept at 1.0 bar under Parrinello–Rahman Lagrangian (time constant = 2.0 ps) for 2 ns. Isothermal compressibilities of water and DMSO were set at 4.50 x 10<sup>-5</sup> bar<sup>-1</sup> and 5.0 x 10<sup>-5</sup> bar<sup>-1</sup> respectively.<sup>17</sup> The pressure and temperature were kept the same under NPT ensemble and the simulation was allowed to run for a further 50 ns, while snapshots were saved every 5 ps to examine the reproducibility of key events and verify conformational changes. Dihedral angle between the two phenanthroline planes ( $\alpha$ ), and distances between the centroids of the two phenanthrolines ( $d$ ) and the pyrenes were measured.



**Fig. S11.** Evolution of  $\alpha$  (left),  $d$  (middle) and inter-pyrene distance (right) of **1** in DMSO.

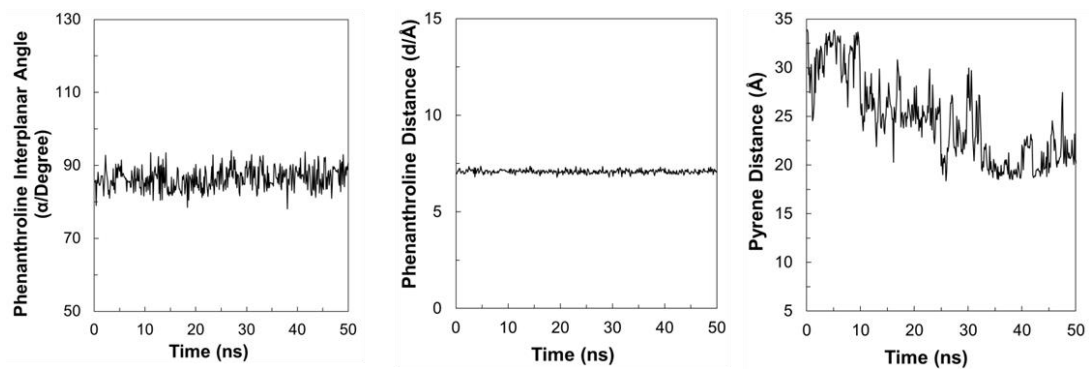


**Fig. S12.** Evolution of  $\alpha$  (left),  $d$  (middle) and inter-pyrene distance (right) of **1** in water.

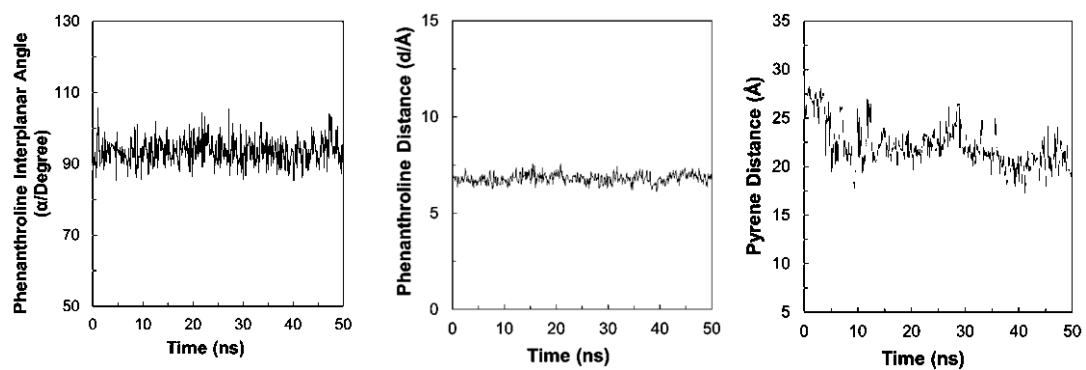


**Fig. S13.** Evolution of  $\alpha$  (left),  $d$  (middle) and inter-pyrene distance (right) of  $[\text{Zn}(\mathbf{1})]^{2+}$  in DMSO.

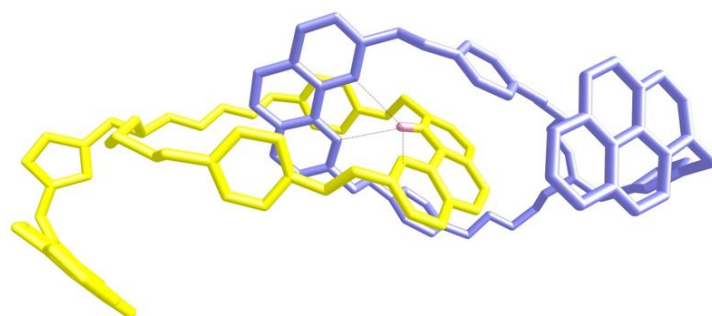




**Fig. S14.** Evolution of  $\alpha$  (left),  $d$  (middle) and inter-pyrene distance (right) of  $[\text{Zn}(\mathbf{1})]^{2+}$  in water.



**Fig. S15.** Evolution  $\alpha$  (left),  $d$  (middle) and inter-pyrene distance (right) of  $[\mathbf{1}\cdot\text{H}]^+$  in water.



**Fig. S16.** A representative structure of  $[\mathbf{1}\cdot\text{H}]^+$  obtained using MD simulations in water.

**Table S1.** Cartesian coordinates of **1** in DMSO obtained using MD simulations. Cartesian coordinates of solvent molecules and hydrogen atoms are excluded.

Atom Number	Atom Type	X Coordinate	Y Coordinate	Z Coordinate
1	C	30.07	23.23	36.88
2	C1	30.84	24.23	37.43
3	C2	30.43	25.59	37.33
4	C3	29.21	25.95	36.74
5	C4	28.39	24.93	36.16
6	C5	28.84	23.60	36.26
7	N	27.22	25.28	35.51
8	C6	26.49	24.23	35.02
9	C7	26.86	22.95	35.29
10	C8	28.03	22.55	35.86
11	C9	31.29	26.45	38.03
12	C10	30.86	27.76	38.11
13	C11	29.70	28.18	37.50
14	N1	28.94	27.32	36.79
15	C14	24.48	24.59	32.00
16	C15	24.84	24.26	30.69
17	C16	24.21	24.87	29.57
18	C17	23.28	25.88	29.80
19	C18	22.82	26.10	31.10
20	C19	23.40	25.54	32.24
21	C22	19.10	29.30	34.92
22	C23	20.13	30.20	34.49
23	C24	21.36	29.77	34.16
24	C25	21.84	28.46	34.52
25	C26	20.80	27.64	35.09
26	C27	19.42	28.04	35.29
27	N4	21.09	26.37	35.41
28	C28	20.21	25.48	35.97
29	C29	18.85	25.81	36.04
30	C30	18.47	27.12	35.73
31	C31	22.28	30.71	33.65
32	C32	23.62	30.31	33.32
33	C33	24.03	29.16	33.85
34	N5	23.20	28.17	34.33
35	C35	20.60	22.46	34.85
36	C36	26.96	27.93	31.98
37	C37	20.41	21.05	34.80
38	C38	21.04	20.28	33.79
39	C39	21.82	20.88	32.86
40	C40	22.10	22.26	32.96
41	C41	21.43	23.09	33.91
42	C42	28.08	27.63	32.74
43	C43	28.91	26.62	32.36
44	C44	28.81	26.11	31.02
45	C45	27.89	26.54	30.19
46	C46	26.89	27.37	30.70
47	C49	29.23	31.27	36.30
48	C50	28.68	30.61	35.20
49	C51	27.88	31.36	34.30
50	C52	27.75	32.76	34.48
51	C53	28.36	33.36	35.57

52	C54	29.04	32.64	36.53
53	C69	29.02	17.78	30.95
54	C70	29.90	17.12	31.70
55	N10	29.80	15.82	31.34
56	N11	28.82	15.61	30.53
57	N12	28.26	16.81	30.27
58	C72	30.07	13.63	32.51
59	C73	30.44	12.25	32.44
60	C74	29.83	11.35	33.40
61	C75	28.85	11.77	34.29
62	C76	28.51	13.11	34.28
63	C77	29.17	14.04	33.48
64	C78	31.33	11.68	31.55
65	C79	31.73	10.32	31.54
66	C80	31.06	9.43	32.34
67	C81	30.13	9.97	33.29
68	C82	29.41	9.07	34.09
69	C83	28.51	9.57	35.03
70	C84	28.11	10.87	35.06
71	C85	31.47	8.11	32.45
72	C86	30.88	7.24	33.38
73	C87	29.82	7.73	34.09
74	C89	26.11	33.09	26.77
75	C90	26.51	34.37	27.15
76	N13	27.69	34.59	26.52
77	N14	27.95	33.56	25.64
78	N15	26.93	32.70	25.73
79	C92	29.34	35.30	28.11
80	C93	30.46	34.47	28.23
81	C94	30.79	34.09	29.54
82	C95	30.12	34.63	30.66
83	C96	29.05	35.51	30.45
84	C97	28.67	35.88	29.15
85	C98	31.29	34.11	27.12
86	C99	32.46	33.34	27.39
87	C100	32.80	32.92	28.71
88	C101	31.95	33.32	29.75
89	C102	32.27	32.92	31.07
90	C103	31.44	33.29	32.10
91	C104	30.41	34.21	31.95
92	C105	33.93	32.13	28.97
93	C106	34.25	31.75	30.28
94	C107	33.36	32.04	31.33
95	C12	25.23	24.52	34.21
96	O	25.23	23.86	32.93
97	C13	29.20	29.54	37.89
98	O1	29.98	30.60	37.28
99	C20	22.74	26.50	28.54
100	C21	27.20	33.50	33.39
101	N2	23.33	27.84	28.37
102	N3	25.74	33.28	33.22
103	O2	19.88	23.06	35.94
104	C34	25.52	28.76	33.78
105	O3	26.00	28.78	32.42

106	C47	22.35	20.01	31.79
107	C48	29.77	25.00	30.58
108	N6	23.76	20.14	31.91
109	N7	29.26	23.67	30.78
110	C55	23.13	28.79	29.44
111	C56	25.23	33.74	31.93
112	C57	29.25	23.29	32.21
113	C58	24.24	19.15	32.84
114	C59	23.50	30.17	28.92
115	C60	24.99	30.43	28.99
116	N8	25.42	31.83	28.73
117	C61	24.98	32.84	29.74
118	C62	25.86	32.80	30.90
119	C63	25.71	19.42	33.09
120	C64	26.49	19.43	31.76
121	N9	27.85	19.87	31.90
122	C65	27.94	21.32	31.86
123	C66	29.24	21.84	32.48
124	C67	20.66	24.11	36.39
125	C68	25.08	32.24	27.30
126	C71	30.67	14.71	31.69
127	C88	28.81	19.23	30.89
128	C91	28.70	35.62	26.71

**Table S2.** Cartesian coordinates of **1** in water obtained using MD simulations. Cartesian coordinates of solvent molecules and hydrogen atoms are excluded.

Atom Number	Atom Type	X Coordinate	Y Coordinate	Z Coordinate
1	C	23.85	34.24	82.41
2	C1	25.15	34.08	82.02
3	C2	26.13	34.87	82.61
4	C3	25.88	35.83	83.62
5	C4	24.50	36.03	83.92
6	C5	23.44	35.18	83.34
7	N	24.12	37.05	84.79
8	C6	22.79	37.17	85.16
9	C7	21.73	36.36	84.67
10	C8	22.06	35.38	83.72
11	C9	27.45	34.62	82.20
12	C10	28.53	35.35	82.72
13	C11	28.21	36.22	83.74
14	N1	26.92	36.54	84.16
15	C14	21.45	40.25	86.67
16	C15	20.83	41.37	86.06
17	C16	20.75	42.58	86.74
18	C17	21.28	42.72	88.04
19	C18	21.99	41.60	88.59
20	C19	22.03	40.34	87.95
21	C22	24.17	33.89	91.72
22	C23	25.45	34.44	91.64
23	C24	25.66	35.30	90.58
24	C25	24.67	35.72	89.63
25	C26	23.39	35.07	89.73

26	C27	23.16	34.16	90.77
27	N4	22.36	35.40	88.84
28	C28	21.11	34.81	88.95
29	C29	20.87	33.93	90.03
30	C30	21.90	33.62	90.90
31	C31	27.02	35.81	90.38
32	C32	27.26	36.77	89.43
33	C33	26.20	37.19	88.68
34	N5	24.91	36.72	88.78
35	C35	18.71	36.89	87.16
36	C36	25.91	40.58	87.33
37	C37	18.05	36.09	86.25
38	C38	17.40	36.68	85.12
39	C39	17.39	38.06	84.97
40	C40	18.06	38.81	85.98
41	C41	18.71	38.26	87.04
42	C42	26.42	40.51	85.96
43	C43	26.16	41.53	84.99
44	C44	25.25	42.48	85.38
45	C45	24.67	42.48	86.68
46	C46	25.11	41.63	87.66
47	C49	29.75	39.13	84.84
48	C50	29.88	40.37	84.21
49	C51	29.91	41.60	84.97
50	C52	29.85	41.51	86.39
51	C53	29.78	40.27	86.91
52	C54	29.67	39.08	86.22
53	C69	23.97	38.66	80.89
54	C70	25.26	38.96	81.34
55	N10	26.06	38.83	80.26
56	N11	25.35	38.38	79.18
57	N12	24.04	38.38	79.53
58	C72	28.29	39.97	80.14
59	C73	29.67	39.96	79.98
60	C74	30.45	41.10	79.67
61	C75	29.79	42.37	79.60
62	C76	28.39	42.41	79.94
63	C77	27.66	41.23	80.27
64	C78	30.41	38.74	79.98
65	C79	31.80	38.63	79.89
66	C80	32.56	39.84	79.79
67	C81	31.86	41.04	79.54
68	C82	32.59	42.29	79.35
69	C83	31.92	43.49	79.28
70	C84	30.52	43.50	79.25
71	C85	33.96	39.76	79.75
72	C86	34.63	40.94	79.53
73	C87	33.99	42.21	79.38
74	C89	27.62	48.67	88.47
75	C90	28.97	48.63	88.71
76	N13	29.43	49.75	88.08
77	N14	28.41	50.46	87.52
78	N15	27.24	49.83	87.77
79	C92	31.67	49.01	87.46

80	C93	31.19	48.19	86.40
81	C94	31.78	46.91	86.22
82	C95	32.82	46.55	87.07
83	C96	33.27	47.35	88.19
84	C97	32.68	48.59	88.36
85	C98	30.19	48.59	85.43
86	C99	29.83	47.77	84.30
87	C100	30.49	46.54	84.18
88	C101	31.40	46.08	85.15
89	C102	32.09	44.85	84.98
90	C103	33.00	44.43	85.91
91	C104	33.35	45.30	86.99
92	C105	30.21	45.69	83.14
93	C106	30.87	44.49	82.91
94	C107	31.84	44.10	83.84
95	C12	22.62	38.23	86.18
96	O	21.64	39.23	85.72
97	C13	29.33	36.80	84.55
98	O1	29.78	38.05	84.01
99	C20	21.31	44.01	88.80
100	C21	30.11	42.75	87.22
101	N2	22.39	44.81	88.24
102	N3	28.88	43.41	87.50
103	O2	19.33	36.43	88.27
104	C34	26.44	38.29	87.69
105	O3	26.27	39.54	88.29
106	C47	16.72	38.75	83.82
107	C48	24.86	43.56	84.47
108	N6	17.69	39.47	82.99
109	N7	24.20	43.22	83.22
110	C55	22.59	46.04	89.08
111	C56	29.12	44.33	88.62
112	C57	22.86	42.95	83.54
113	C58	18.36	38.47	82.09
114	C59	23.75	46.87	88.61
115	C60	25.03	46.00	88.59
116	N8	26.20	46.70	88.11
117	C61	27.31	45.77	87.75
118	C62	27.86	45.00	88.94
119	C63	19.54	39.07	81.36
120	C64	20.68	39.40	82.41
121	N9	21.93	39.79	81.72
122	C65	22.62	40.67	82.67
123	C66	22.13	42.06	82.57
124	C67	20.02	35.17	87.95
125	C68	26.61	47.74	89.12
126	C71	27.52	38.67	80.36
127	C88	22.69	38.50	81.64
128	C91	30.78	50.18	87.88

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**Table S3.** Cartesian coordinates of  $[\text{Zn}(\mathbf{1})]^{2+}$  in DMSO obtained using MD simulations. Cartesian coordinates of solvent molecules and hydrogen atoms are excluded.

Atom Number	Atom Type	X Coordinate	Y Coordinate	Z Coordinate
1	C	31.98	24.73	34.28
2	C1	33.12	25.48	34.43
3	C2	33.26	26.65	33.64
4	C3	32.27	26.99	32.63
5	C4	31.19	26.10	32.49
6	C5	30.97	25.02	33.38
7	N	30.24	26.29	31.47
8	C6	29.08	25.54	31.48
9	C7	28.87	24.49	32.36
10	C8	29.85	24.17	33.35
11	C9	34.31	27.50	33.95
12	C10	34.32	28.75	33.24
13	C11	33.40	29.00	32.19
14	N1	32.40	28.13	31.87
15	C14	26.26	27.59	30.40
16	C15	25.96	27.36	29.02
17	C16	25.20	28.30	28.31
18	C17	24.77	29.46	29.05
19	C18	25.09	29.60	30.33
20	C19	25.78	28.66	31.04
21	C22	28.32	31.12	27.64
22	C23	28.47	30.27	26.58
23	C24	29.06	29.01	26.81
24	C25	29.36	28.58	28.17
25	C26	29.13	29.47	29.27
26	C27	28.58	30.75	28.94
27	N4	29.52	29.16	30.53
28	C28	29.12	30.00	31.55
29	C29	28.48	31.21	31.25
30	C30	28.30	31.62	29.99
31	C31	29.31	28.12	25.70
32	C32	29.80	26.87	25.98
33	C33	29.98	26.44	27.31
34	N5	29.86	27.27	28.35
35	C35	28.46	27.69	34.47
36	C36	30.41	23.12	28.84
37	C37	29.54	27.72	35.33
38	C38	29.69	26.74	36.31
39	C39	28.77	25.68	36.40
40	C40	27.69	25.71	35.55
41	C41	27.47	26.68	34.64
42	C42	30.94	22.62	30.03
43	C43	30.83	21.28	30.36
44	C44	29.94	20.49	29.55
45	C45	29.30	21.02	28.44
46	C46	29.54	22.39	28.01
47	C49	32.03	32.39	31.75
48	C50	31.06	33.04	32.55
49	C51	30.54	34.24	32.13
50	C52	31.02	34.82	30.94

51	C53	31.95	34.14	30.17
52	C54	32.51	32.92	30.58
53	C69	24.65	20.05	34.17
54	C70	24.46	18.88	34.85
55	N10	23.44	18.23	34.27
56	N11	22.97	18.99	33.22
57	N12	23.68	20.09	33.16
58	C72	22.47	15.93	34.14
59	C73	21.50	15.70	33.18
60	C74	21.54	14.57	32.36
61	C75	22.54	13.56	32.62
62	C76	23.57	13.81	33.55
63	C77	23.46	15.02	34.26
64	C78	20.45	16.62	32.93
65	C79	19.38	16.35	32.05
66	C80	19.40	15.17	31.38
67	C81	20.48	14.27	31.49
68	C82	20.40	13.05	30.78
69	C83	21.47	12.10	31.05
70	C84	22.47	12.36	31.93
71	C85	18.33	14.84	30.56
72	C86	18.38	13.72	29.80
73	C87	19.44	12.81	29.88
74	C89	23.94	38.13	29.23
75	C90	24.47	39.07	30.06
76	N13	24.60	40.17	29.26
77	N14	23.82	40.02	28.16
78	N15	23.49	38.80	28.08
79	C92	26.57	41.24	30.16
80	C93	27.57	40.71	29.33
81	C94	28.78	40.37	29.89
82	C95	29.02	40.52	31.27
83	C96	28.02	41.12	32.06
84	C97	26.78	41.43	31.48
85	C98	27.33	40.38	27.91
86	C99	28.35	40.01	27.12
87	C100	29.61	39.80	27.70
88	C101	29.80	39.90	29.06
89	C102	31.04	39.48	29.65
90	C103	31.21	39.50	31.06
91	C104	30.21	40.10	31.88
92	C105	30.56	39.21	26.88
93	C106	31.78	38.76	27.41
94	C107	32.02	38.87	28.79
95	C12	27.85	25.86	30.54
96	O	26.99	26.77	31.25
97	C13	33.31	30.37	31.63
98	O1	32.27	31.11	32.22
99	C20	23.75	30.42	28.51
100	C21	30.42	36.02	30.31
101	N2	24.12	31.86	28.79
102	N3	29.29	35.55	29.52
103	O2	28.15	28.65	33.40
104	C34	30.40	24.99	27.41



105	O3	30.36	24.50	28.79
106	C47	28.88	24.55	37.39
107	C48	29.59	19.09	29.94
108	N6	29.35	23.33	36.80
109	N7	28.64	19.11	31.02
110	C55	24.84	32.31	27.61
111	C56	28.61	36.73	28.92
112	C57	29.31	18.92	32.32
113	C58	28.84	22.13	37.49
114	C59	25.40	33.72	27.83
115	C60	24.47	34.52	28.68
116	N8	24.86	35.93	28.61
117	C61	26.15	36.19	29.29
118	C62	27.24	36.45	28.30
119	C63	27.71	21.33	36.85
120	C64	27.85	21.42	35.36
121	N9	26.92	20.50	34.68
122	C65	27.47	20.09	33.44
123	C66	28.40	18.84	33.50
124	C67	29.27	29.46	32.95
125	C68	23.78	36.65	29.37
126	C71	22.57	17.26	34.93
127	C88	25.63	21.13	34.54
128	C91	25.23	41.44	29.57
129	Zn	31.28	27.70	30.01

**Table S4.** Cartesian coordinates of  $[\text{Zn}(\mathbf{1})]^{2+}$  in water obtained using MD simulations. Cartesian coordinates of solvent molecules and hydrogen atoms are excluded.

Atom Number	Atom Type	X Coordinate	Y Coordinate	Z Coordinate
1	C	45.67	80.12	-62.70
2	C1	45.33	80.25	-61.41
3	C2	46.34	80.20	-60.40
4	C3	47.71	80.12	-60.70
5	C4	48.11	80.08	-62.16
6	C5	47.02	80.01	-63.08
7	N	49.37	80.08	-62.60
8	C6	49.58	79.90	-63.94
9	C7	48.58	79.80	-64.89
10	C8	47.25	79.84	-64.47
11	C9	45.91	80.20	-59.11
12	C10	46.88	80.11	-58.12
13	C11	48.25	79.98	-58.36
14	N1	48.70	80.11	-59.69
15	C14	53.00	78.75	-63.98
16	C15	53.80	79.91	-64.28
17	C16	55.23	79.96	-64.02
18	C17	55.74	78.88	-63.26
19	C18	54.88	77.74	-62.97
20	C19	53.55	77.68	-63.33
21	C22	54.65	79.21	-57.81
22	C23	54.57	80.55	-57.40
23	C24	53.50	81.36	-57.66
24	C25	52.45	80.92	-58.51

25	C26	52.53	79.55	-59.01
26	C27	53.62	78.68	-58.59
27	N4	51.46	79.01	-59.86
28	C28	51.55	77.64	-60.22
29	C29	52.57	76.82	-59.76
30	C30	53.61	77.35	-59.02
31	C31	53.39	82.64	-57.07
32	C32	52.18	83.31	-57.21
33	C33	51.20	82.83	-58.03
34	N5	51.31	81.64	-58.74
35	C35	48.02	76.77	-60.76
36	C36	47.86	83.54	-56.82
37	C37	46.98	76.92	-59.85
38	C38	45.64	76.93	-60.27
39	C39	45.41	76.71	-61.67
40	C40	46.48	76.68	-62.59
41	C41	47.79	76.59	-62.11
42	C42	47.13	83.27	-55.67
43	C43	45.75	83.22	-55.67
44	C44	45.06	83.49	-56.86
45	C45	45.76	84.00	-57.99
46	C46	47.14	84.03	-57.94
47	C49	50.32	77.59	-56.32
48	C50	50.57	76.22	-56.58
49	C51	51.65	75.54	-55.98
50	C52	52.57	76.28	-55.20
51	C53	52.33	77.65	-54.96
52	C54	51.25	78.27	-55.52
53	C69	39.15	77.72	-59.39
54	C70	39.84	76.94	-58.50
55	N10	39.19	75.73	-58.46
56	N11	38.05	75.84	-59.15
57	N12	37.93	77.05	-59.71
58	C72	40.99	74.07	-58.55
59	C73	41.20	73.73	-59.91
60	C74	42.51	73.38	-60.35
61	C75	43.55	73.30	-59.42
62	C76	43.30	73.64	-58.08
63	C77	42.05	74.05	-57.67
64	C78	40.16	73.92	-60.82
65	C79	40.35	73.58	-62.20
66	C80	41.59	73.17	-62.66
67	C81	42.62	73.03	-61.74
68	C82	43.85	72.57	-62.18
69	C83	44.96	72.59	-61.30
70	C84	44.83	73.06	-59.99
71	C85	41.72	72.79	-64.00
72	C86	42.94	72.16	-64.41
73	C87	44.03	72.16	-63.49
74	C89	58.58	79.26	-55.13
75	C90	57.43	79.67	-54.42
76	N13	57.84	79.64	-53.11
77	N14	59.09	79.24	-53.02
78	N15	59.57	79.03	-54.23

79	C92	55.71	79.99	-52.00
80	C93	54.96	81.08	-52.52
81	C94	53.52	81.03	-52.47
82	C95	52.84	79.86	-51.99
83	C96	53.64	78.73	-51.65
84	C97	55.03	78.83	-51.57
85	C98	55.58	82.18	-53.08
86	C99	54.73	83.26	-53.50
87	C100	53.38	83.20	-53.52
88	C101	52.72	82.04	-53.07
89	C102	51.32	81.92	-52.97
90	C103	50.71	80.82	-52.50
91	C104	51.47	79.79	-52.01
92	C105	52.55	84.24	-54.05
93	C106	51.17	84.11	-54.04
94	C107	50.57	82.96	-53.52
95	C12	51.01	79.94	-64.41
96	O	51.65	78.77	-63.89
97	C13	49.24	79.61	-57.26
98	O1	49.25	78.17	-57.05
99	C20	57.19	78.98	-62.87
100	C21	53.65	75.54	-54.50
101	N2	57.44	79.47	-61.56
102	N3	54.75	75.08	-55.39
103	O2	49.29	76.72	-60.11
104	C34	49.87	83.51	-58.08
105	O3	49.21	83.41	-56.80
106	C47	44.00	76.44	-62.02
107	C48	43.58	83.35	-56.91
108	N6	43.22	77.68	-62.26
109	N7	43.20	82.11	-57.58
110	C55	57.43	78.28	-60.68
111	C56	55.69	76.22	-55.55
112	C57	41.75	82.06	-57.44
113	C58	41.85	77.28	-61.91
114	C59	57.70	78.78	-59.27
115	C60	57.77	77.63	-58.36
116	N8	57.75	77.93	-56.95
117	C61	58.10	76.68	-56.24
118	C62	56.95	75.63	-56.23
119	C63	40.87	78.34	-62.24
120	C64	41.03	79.65	-61.51
121	N9	40.67	79.56	-60.05
122	C65	41.09	80.84	-59.40
123	C66	41.16	80.72	-57.88
124	C67	50.43	76.95	-60.95
125	C68	58.82	78.90	-56.56
126	C71	39.63	74.45	-57.98
127	C88	39.30	79.20	-59.80
128	C91	57.20	79.93	-51.91
129	Zn	50.53	80.77	-60.68

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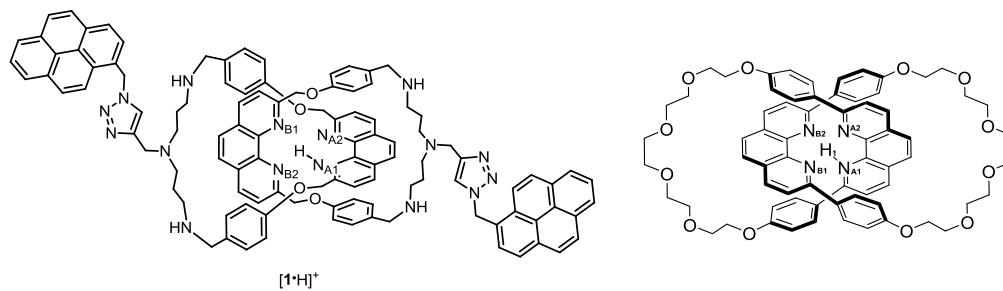
**Table S5.** Cartesian coordinates of [1-H]<sup>+</sup> in water obtained using MD simulations. Cartesian coordinates of solvent molecules and hydrogen atoms are excluded.

Atom Number	Atom Type	X Coordinate	Y Coordinate	Z Coordinate
1	C	29.99	25.42	24.36
2	C1	28.74	25.36	24.96
3	C2	27.79	26.30	24.69
4	C3	28.03	27.37	23.80
5	C4	29.37	27.55	23.30
6	C5	30.31	26.50	23.56
7	N	29.68	28.70	22.63
8	C6	30.92	28.80	22.22
9	C7	31.90	27.82	22.32
10	C8	31.63	26.66	23.01
11	C9	26.53	26.10	25.20
12	C10	25.50	26.94	24.76
13	C11	25.80	28.04	23.92
14	N1	27.04	28.29	23.43
15	C14	31.23	31.26	19.61
16	C15	31.89	32.40	20.19
17	C16	32.07	33.56	19.39
18	C17	31.74	33.54	18.08
19	C18	31.08	32.42	17.44
20	C19	30.89	31.30	18.23
21	C22	29.26	34.52	21.90
22	C23	29.69	34.53	23.18
23	C24	29.41	33.50	24.12
24	C25	28.78	32.33	23.63
25	C26	28.34	32.33	22.28
26	C27	28.50	33.42	21.41
27	N4	27.77	31.19	21.79
28	C28	27.27	31.09	20.49
29	C29	27.40	32.21	19.64
30	C30	28.05	33.41	20.12
31	C31	29.98	33.50	25.38
32	C32	29.78	32.46	26.24
33	C33	29.11	31.30	25.78
34	N5	28.62	31.21	24.52
35	C35	27.43	27.57	20.00
36	C36	29.96	28.19	27.53
37	C37	26.14	27.07	20.31
38	C38	26.10	25.71	20.73
39	C39	27.20	24.92	20.71
40	C40	28.44	25.41	20.31
41	C41	28.58	26.77	20.08
42	C42	28.71	27.64	27.93
43	C43	28.72	26.40	28.53
44	C44	29.91	25.74	28.71
45	C45	31.18	26.30	28.35
46	C46	31.20	27.49	27.69
47	C49	24.41	31.13	23.17
48	C50	23.84	31.09	21.86
49	C51	23.90	32.25	21.13
50	C52	24.35	33.43	21.77

51	C53	24.89	33.41	23.02
52	C54	24.89	32.27	23.69
53	C69	25.61	18.91	27.44
54	C70	25.28	19.21	28.76
55	N10	25.19	18.01	29.38
56	N11	25.42	17.01	28.50
57	N12	25.72	17.53	27.31
58	C72	23.69	16.79	31.08
59	C73	22.49	17.22	31.66
60	C74	21.43	16.24	31.89
61	C75	21.59	14.88	31.54
62	C76	22.78	14.56	30.83
63	C77	23.85	15.45	30.70
64	C78	22.22	18.59	31.99
65	C79	20.99	19.02	32.59
66	C80	20.06	18.04	32.98
67	C81	20.20	16.64	32.53
68	C82	19.23	15.73	32.91
69	C83	19.46	14.40	32.61
70	C84	20.55	14.00	31.90
71	C85	18.89	18.40	33.66
72	C86	18.04	17.40	34.04
73	C87	18.12	16.11	33.63
74	C89	27.26	41.30	19.32
75	C90	27.25	41.98	20.52
76	N13	25.92	42.32	20.65
77	N14	25.29	42.02	19.51
78	N15	26.12	41.55	18.64
79	C92	24.66	41.37	22.45
80	C93	25.48	40.53	23.28
81	C94	24.98	39.27	23.63
82	C95	23.69	38.88	23.19
83	C96	22.90	39.78	22.45
84	C97	23.43	40.96	22.05
85	C98	26.70	40.94	23.84
86	C99	27.52	40.16	24.61
87	C100	27.15	38.80	24.76
88	C101	25.86	38.41	24.29
89	C102	25.37	37.10	24.54
90	C103	24.11	36.68	24.15
91	C104	23.28	37.56	23.44
92	C105	27.99	37.84	25.28
93	C106	27.52	36.56	25.50
94	C107	26.22	36.19	25.22
95	C12	31.41	30.07	21.65
96	O	30.80	30.13	20.35
97	C13	24.69	28.83	23.33
98	O1	24.39	30.04	24.08
99	C20	31.72	34.84	17.33
100	C21	24.54	34.62	20.86
101	N2	30.65	35.64	17.85
102	N3	25.83	35.26	21.09
103	H	27.73	30.41	22.44
104	O2	27.65	28.87	19.52

105	C34	28.92	30.16	26.73
106	O3	30.11	29.36	26.75
107	C47	27.23	23.51	21.12
108	C48	29.91	24.31	29.10
109	N6	27.12	23.41	22.53
110	N7	29.62	23.45	27.92
111	C55	30.86	37.02	17.37
112	C56	25.91	36.48	20.28
113	C57	30.00	22.07	28.05
114	C58	27.45	22.07	22.87
115	C59	29.62	37.84	17.74
116	C60	29.61	38.35	19.15
117	N8	28.47	39.16	19.62
118	C61	27.24	38.35	19.55
119	C62	27.23	37.15	20.43
120	C63	27.24	21.82	24.34
121	C64	27.65	20.36	24.64
122	N9	27.40	20.02	26.11
123	C65	27.88	21.11	27.03
124	C66	29.43	21.19	26.99
125	C67	26.69	29.79	20.03
126	C68	28.26	40.33	18.74
127	C71	24.87	17.73	30.80
128	C88	25.91	19.77	26.25
129	C91	25.20	42.60	21.83

**Table S6.** Comparison of the H1–N(phenanthroline) distances in protonated [2]catenenes.



H <sub>1</sub> -N <sub>A1</sub>	0.77	0.78 <sup>2</sup>
H <sub>1</sub> -N <sub>A2</sub>	2.35	2.35 <sup>2</sup>
H <sub>1</sub> -N <sub>B1</sub>	2.53	2.49 <sup>2</sup>
H <sub>1</sub> -N <sub>B2</sub>	3.25	3.20 <sup>2</sup>

## 4. NMR Spectra

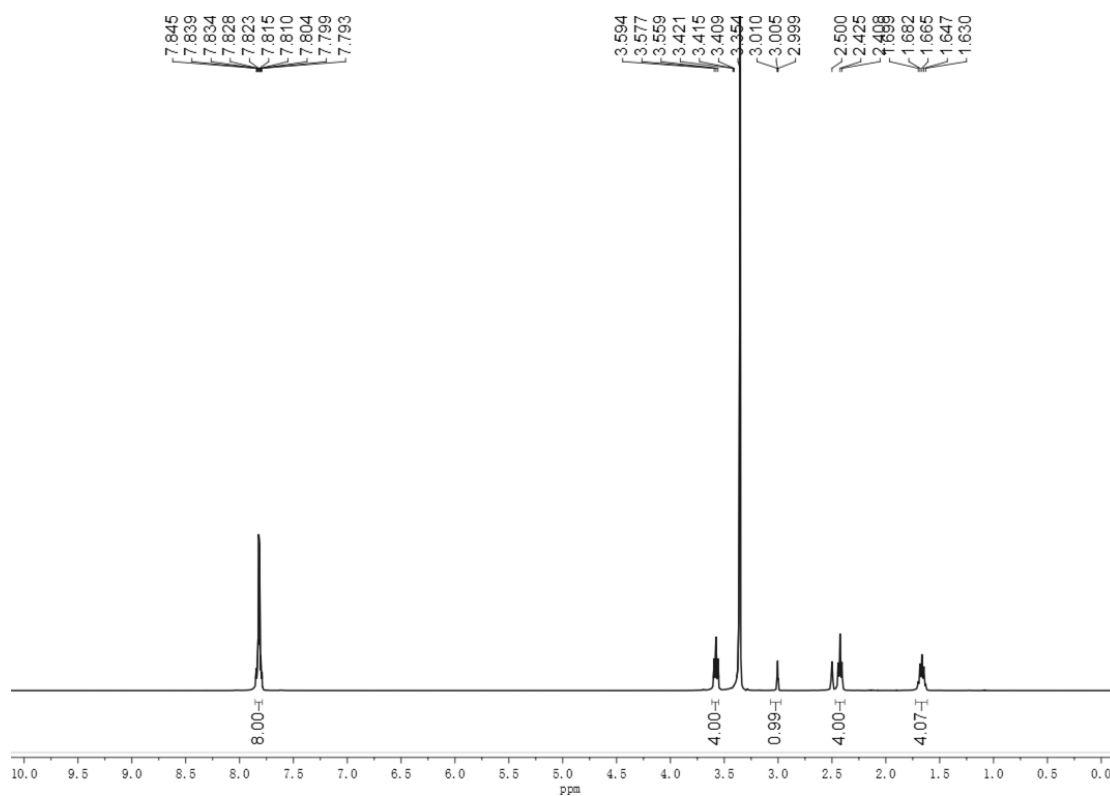


Fig. S17.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **A-Pht**.

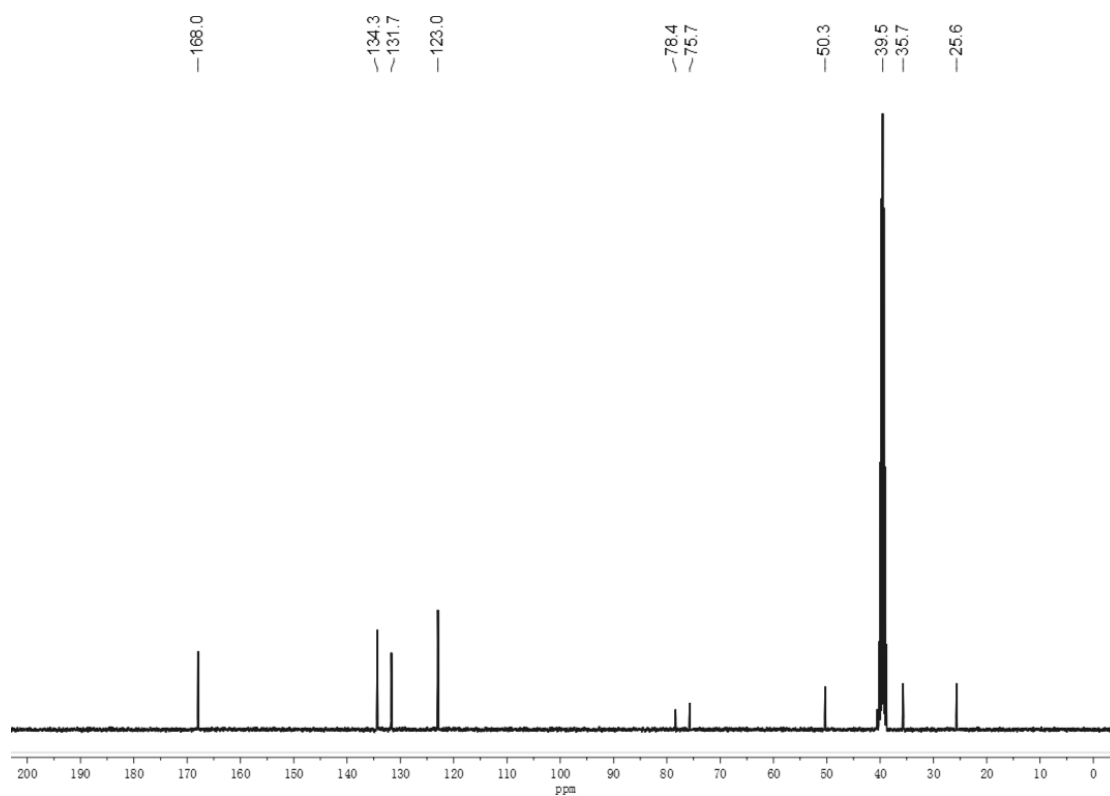
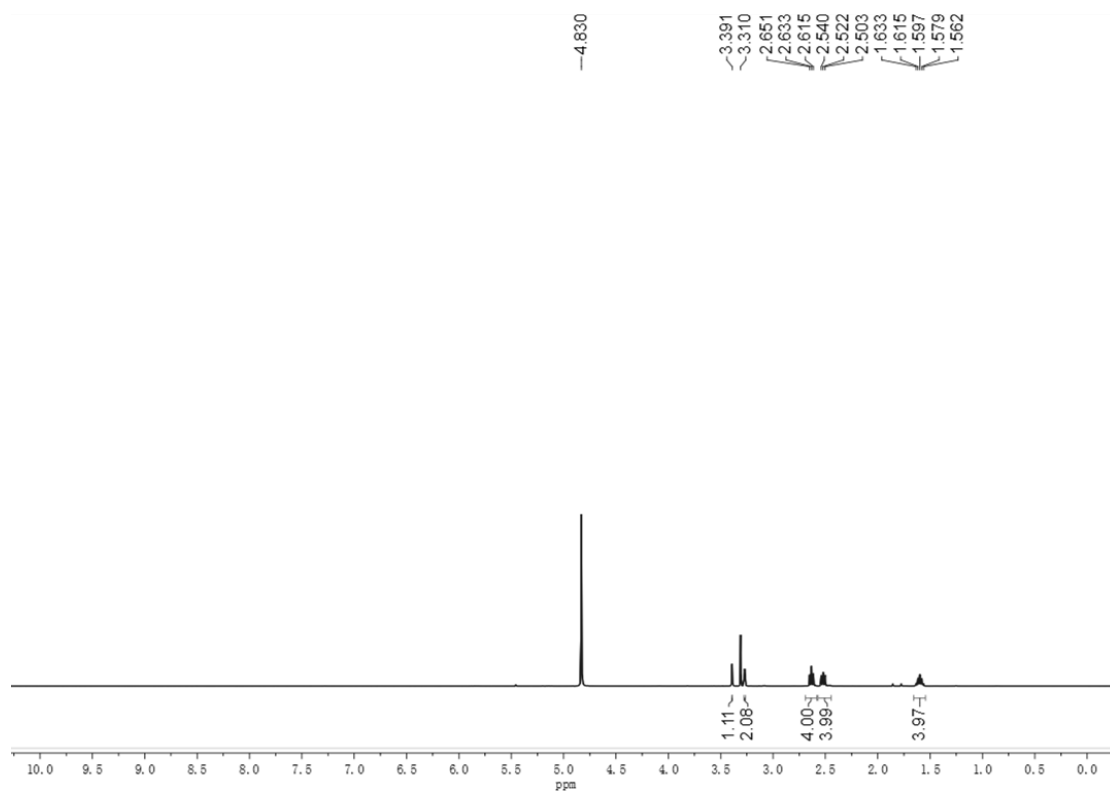
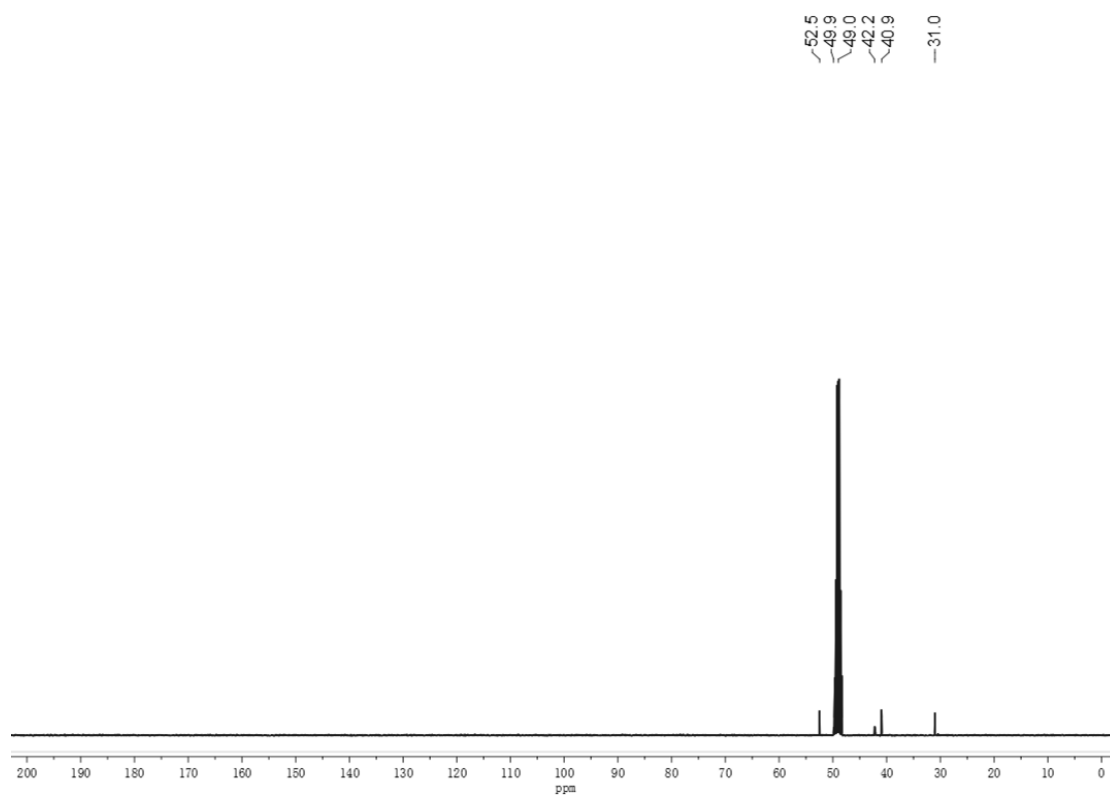


Fig. S18.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **A-Pht**.



**Fig. S19.**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ , 298 K) spectrum of **A**.



**Fig. S20.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ , 298 K) spectrum of **A**.



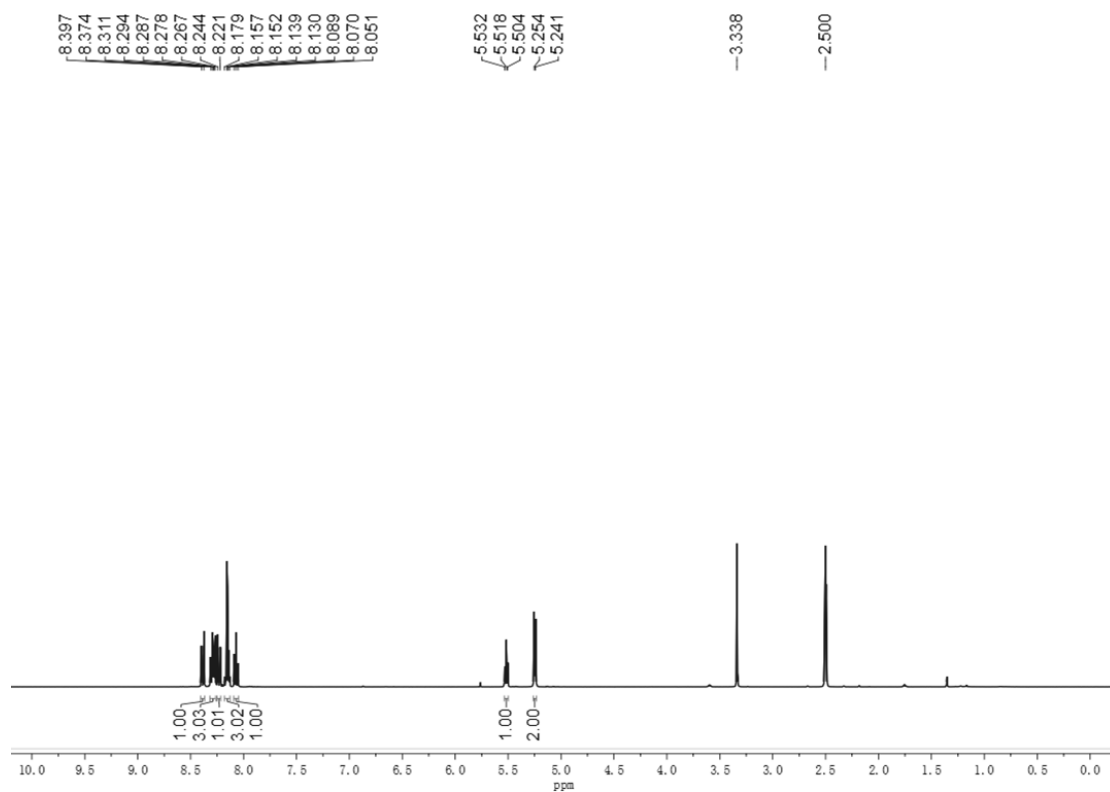


Fig. S21.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **Py-OH**.

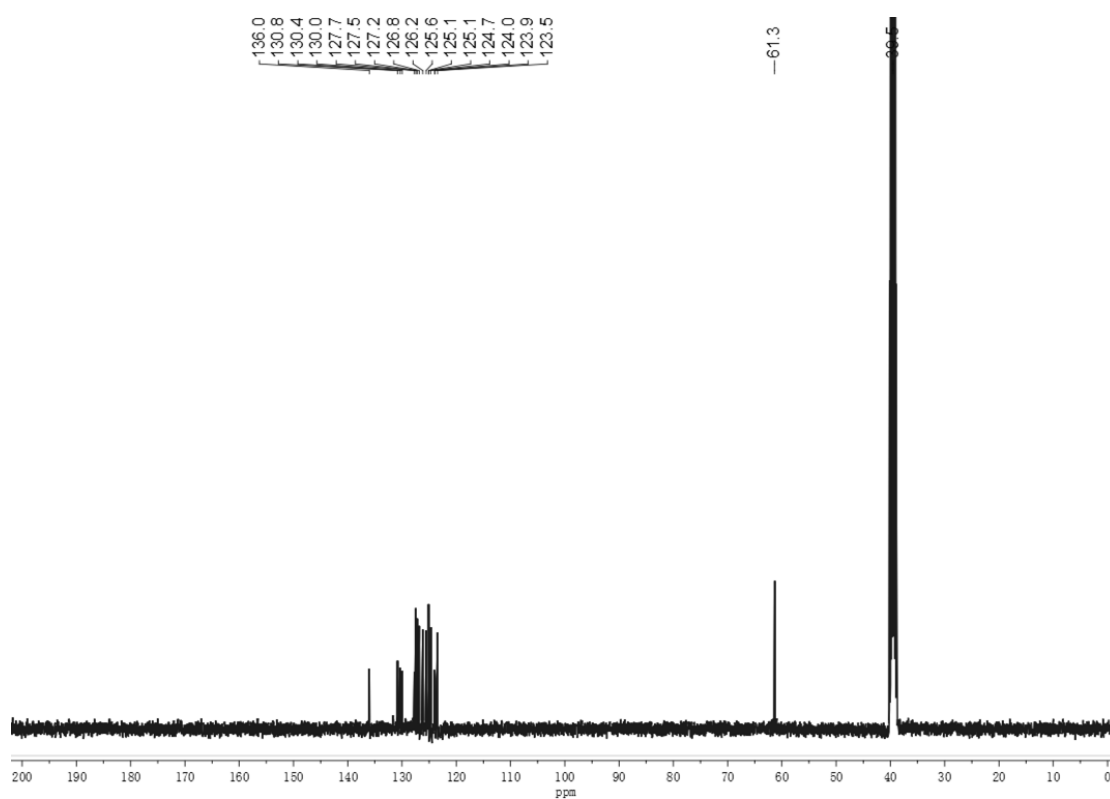
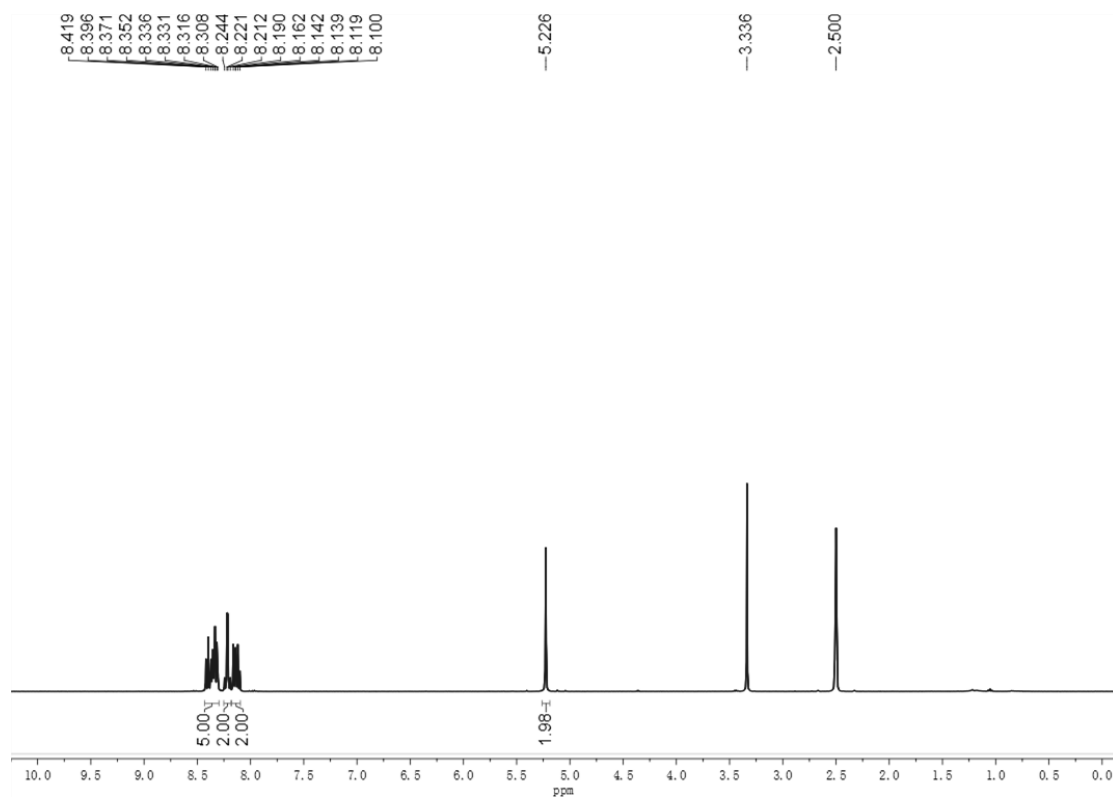
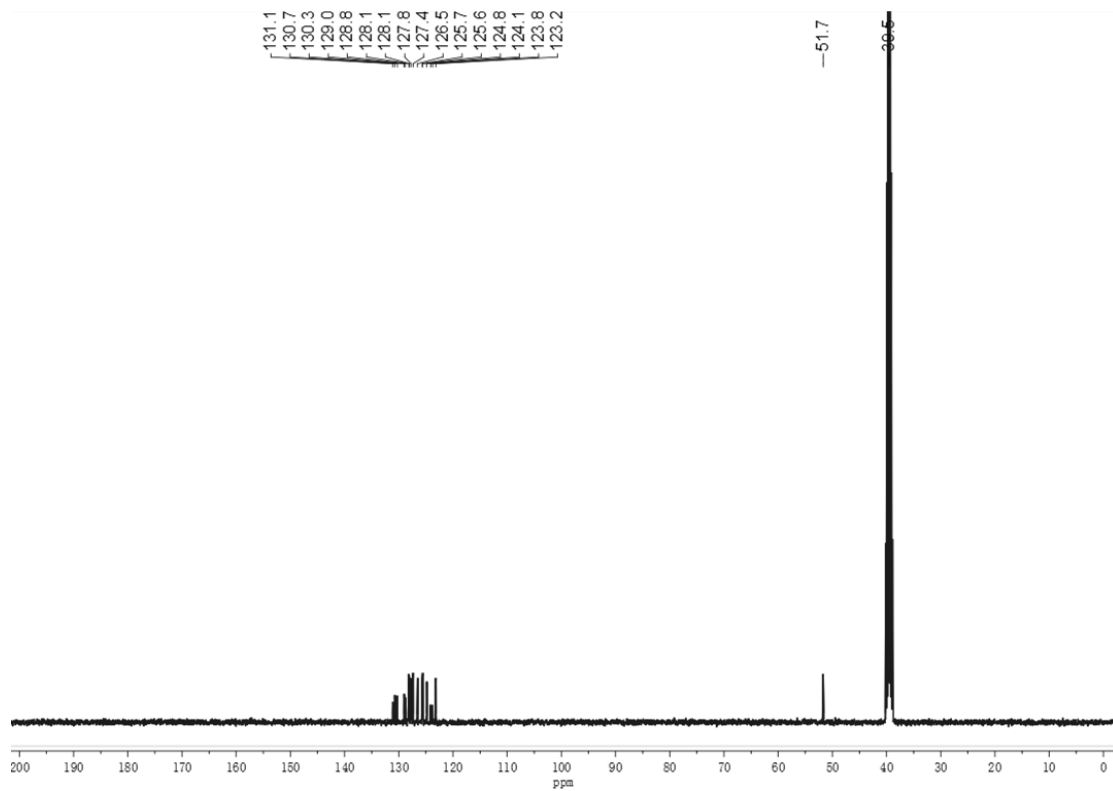


Fig. S22.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **Py-OH**.



**Fig S23.**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **Py-N<sub>3</sub>**.



**Fig. S24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **Py-N<sub>3</sub>**.

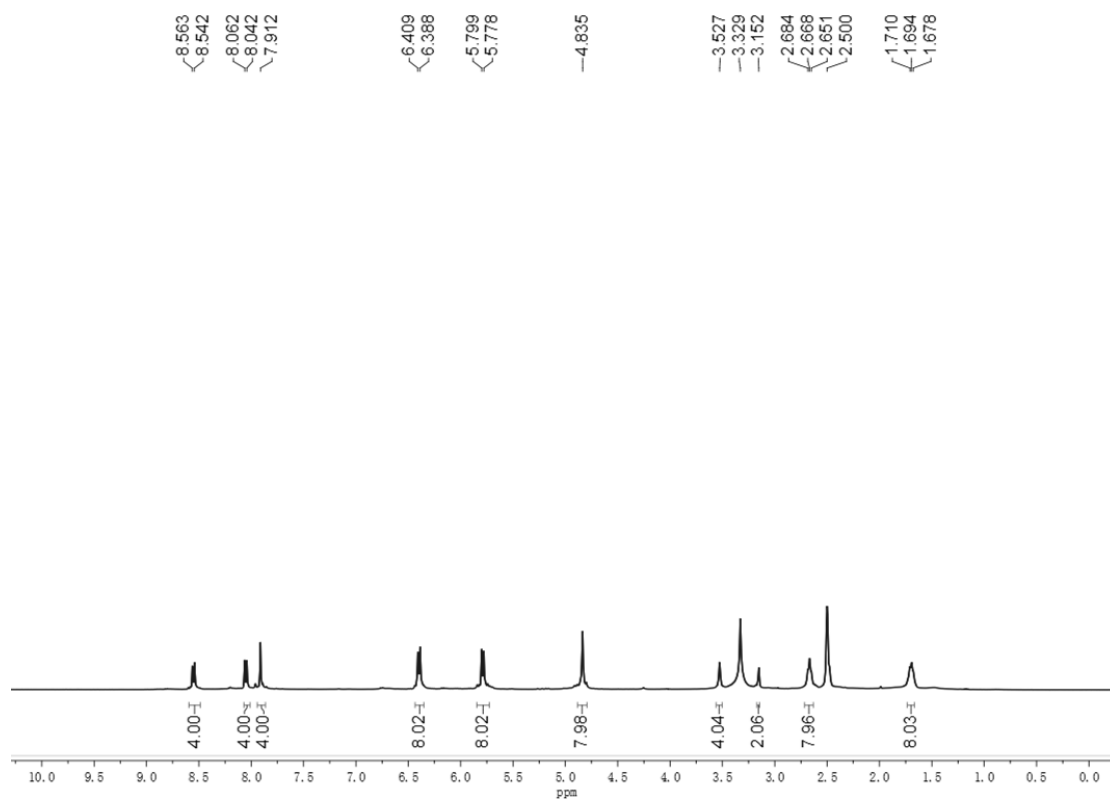


Fig. S25.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of  $[\text{Cu}(\text{1-alkyne})]\text{PF}_6$ .

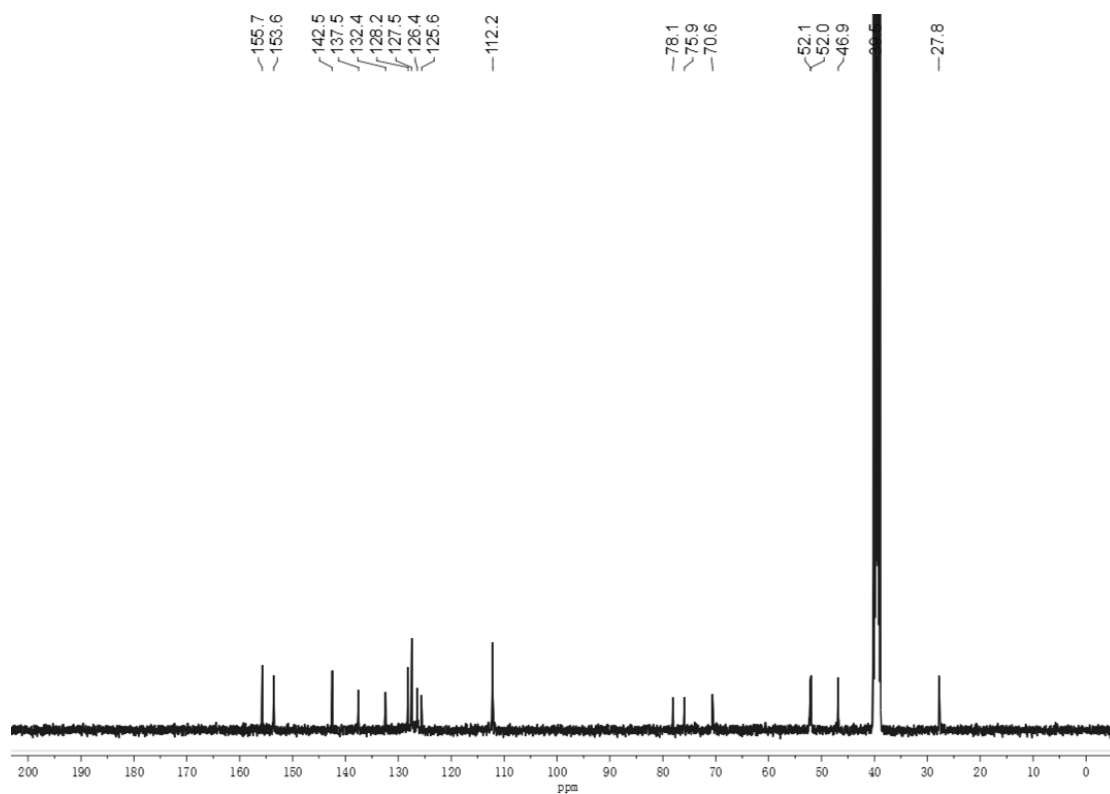


Fig. S26.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of  $[\text{Cu}(\text{1-alkyne})]\text{PF}_6$ .

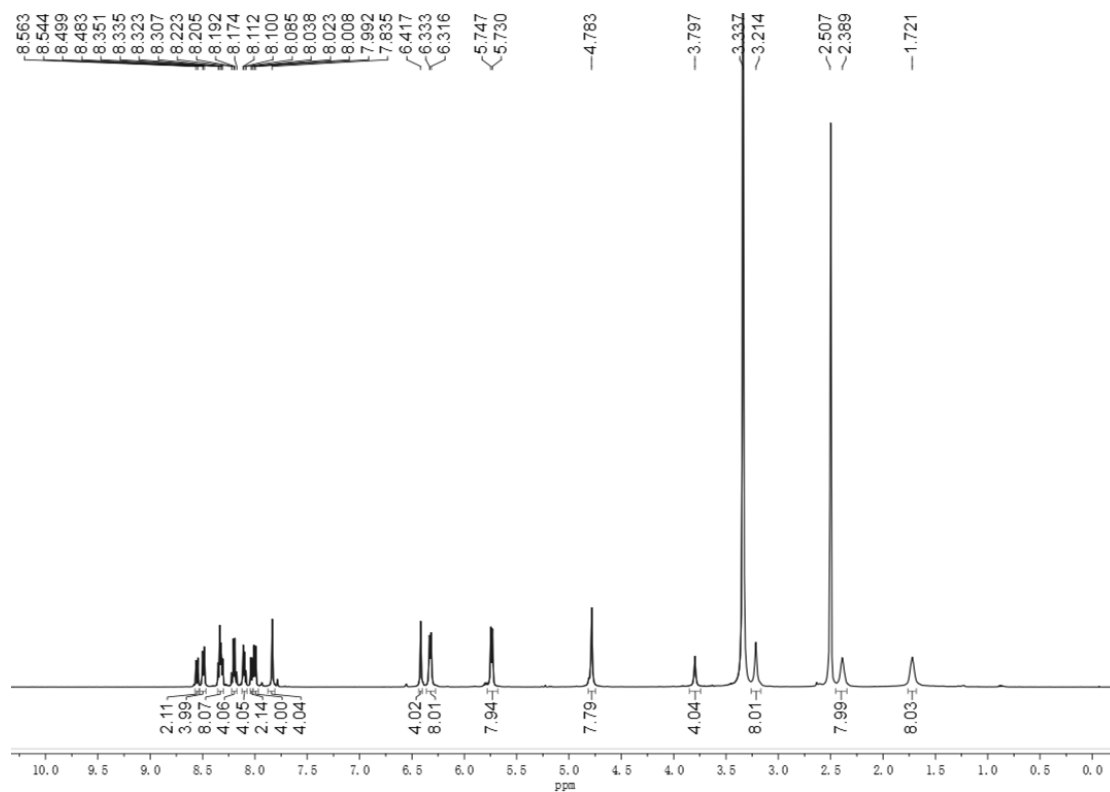


Fig. S27.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of  $[\text{Cu}(1)]\text{PF}_6$ .

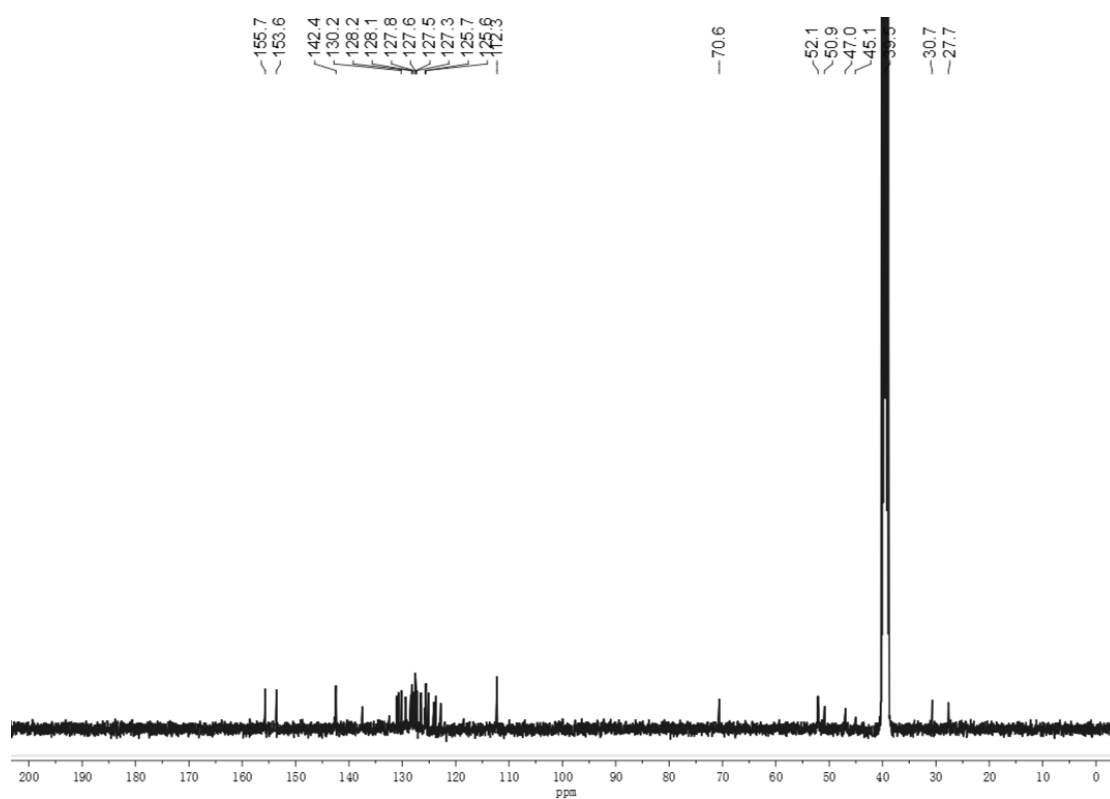


Fig. S28.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of  $[\text{Cu}(1)]\text{PF}_6$ .

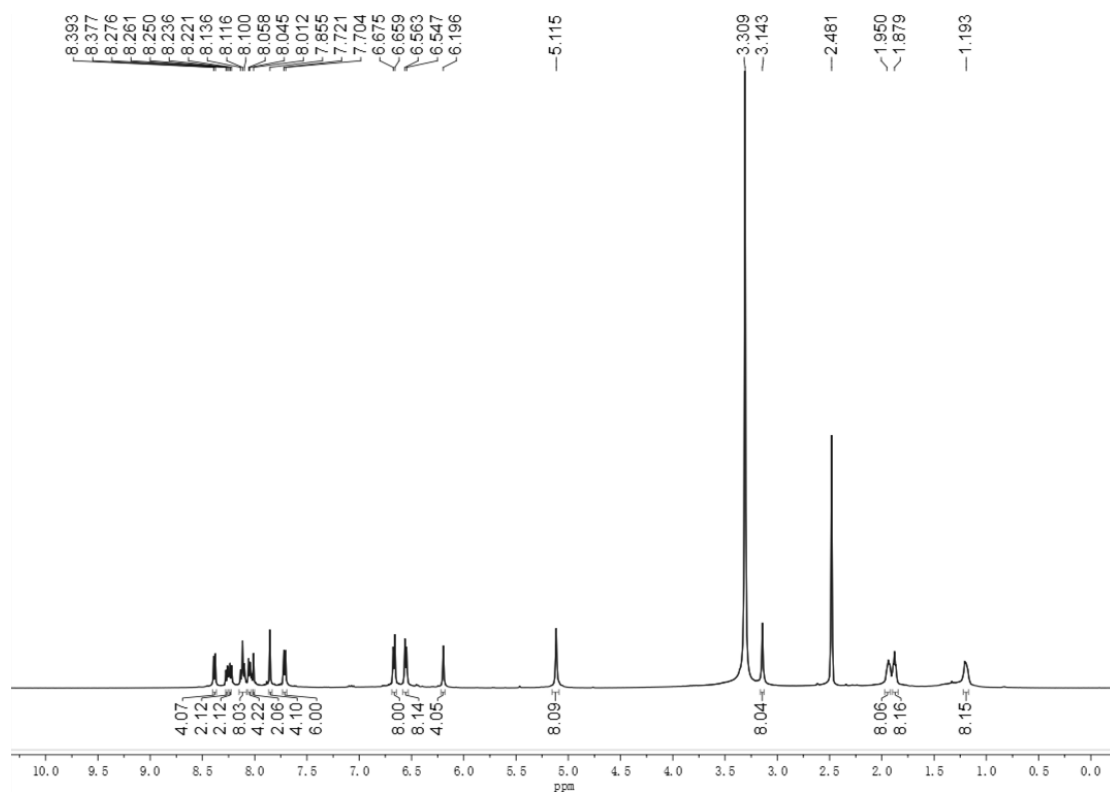


Fig. S29.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **1**.

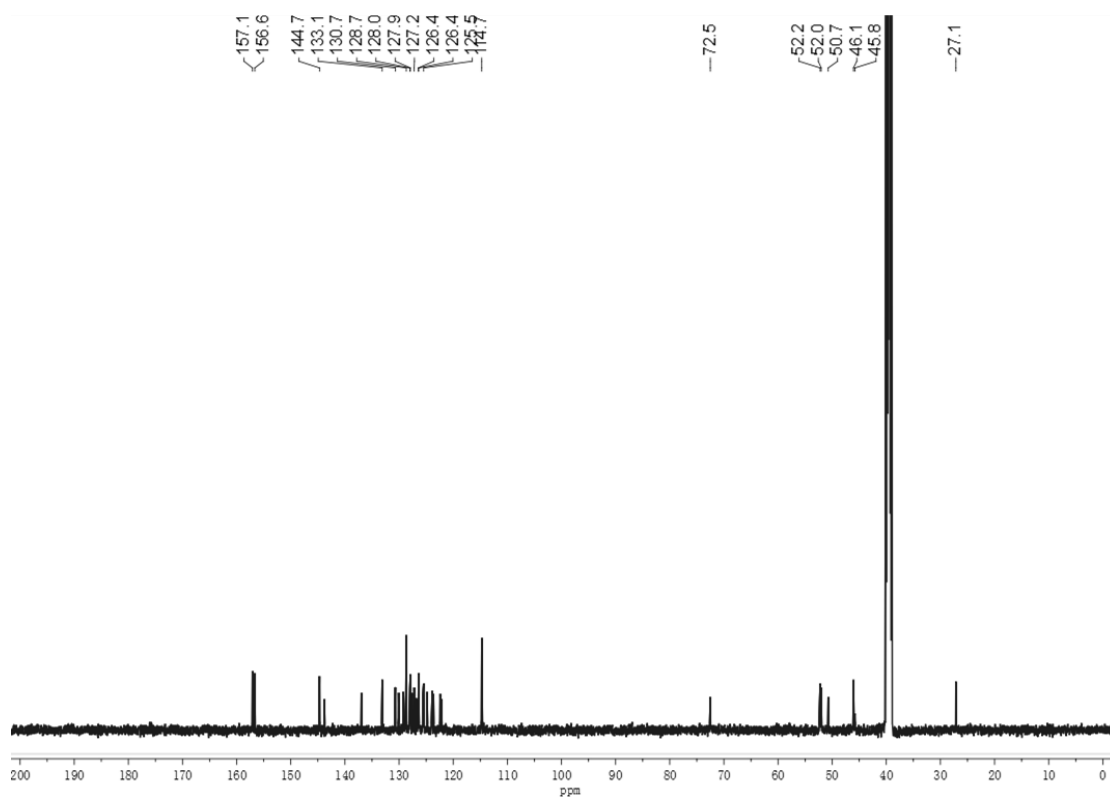


Fig. S30.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **1**.

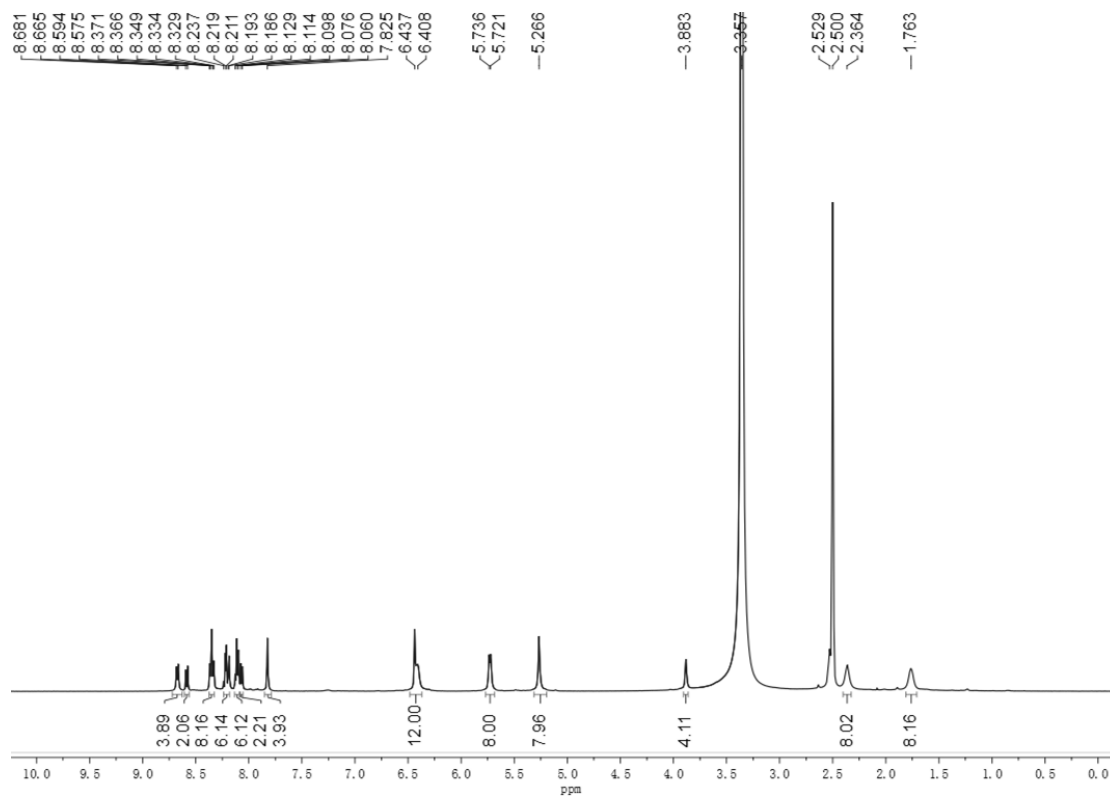


Fig. S31.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of  $[\text{Zn}(\mathbf{1})](\text{OTf})_2$ .

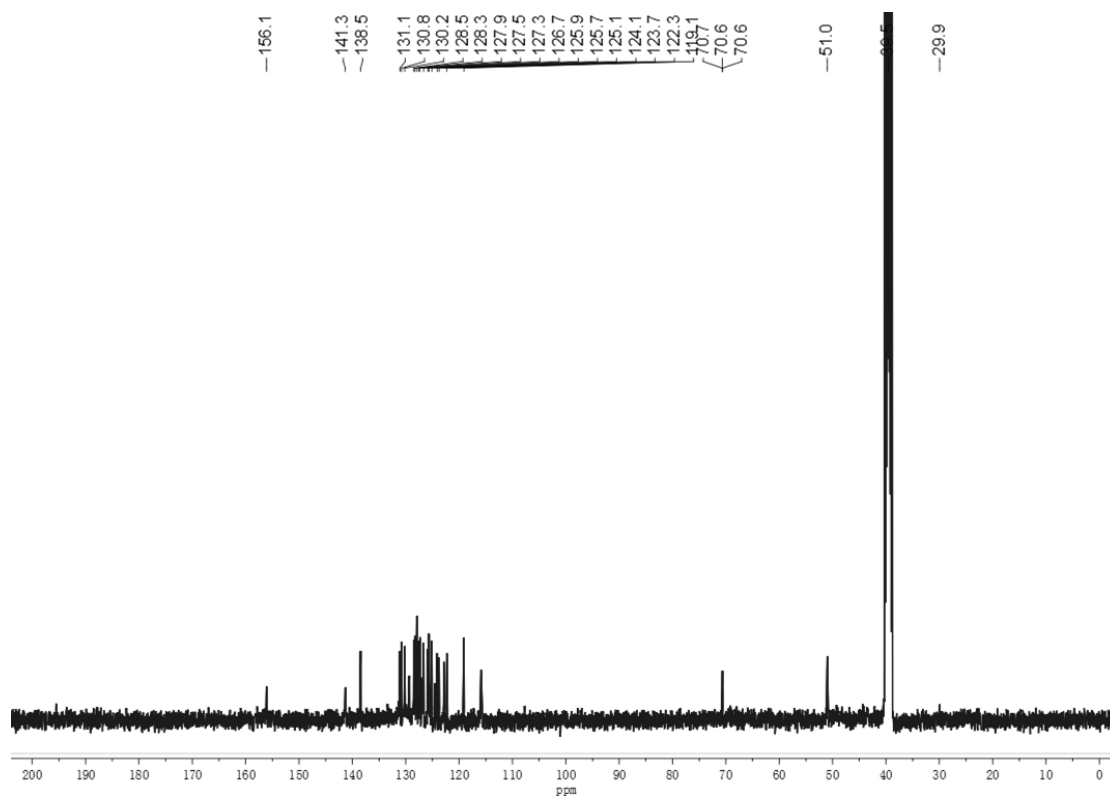
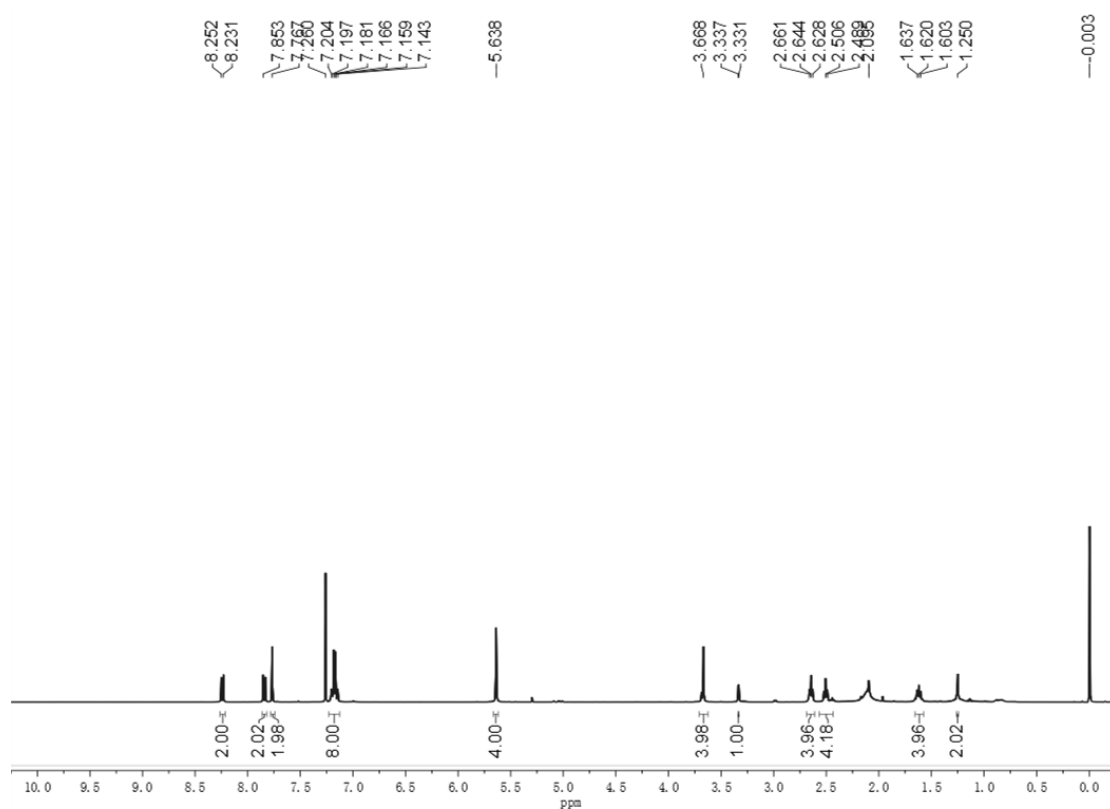
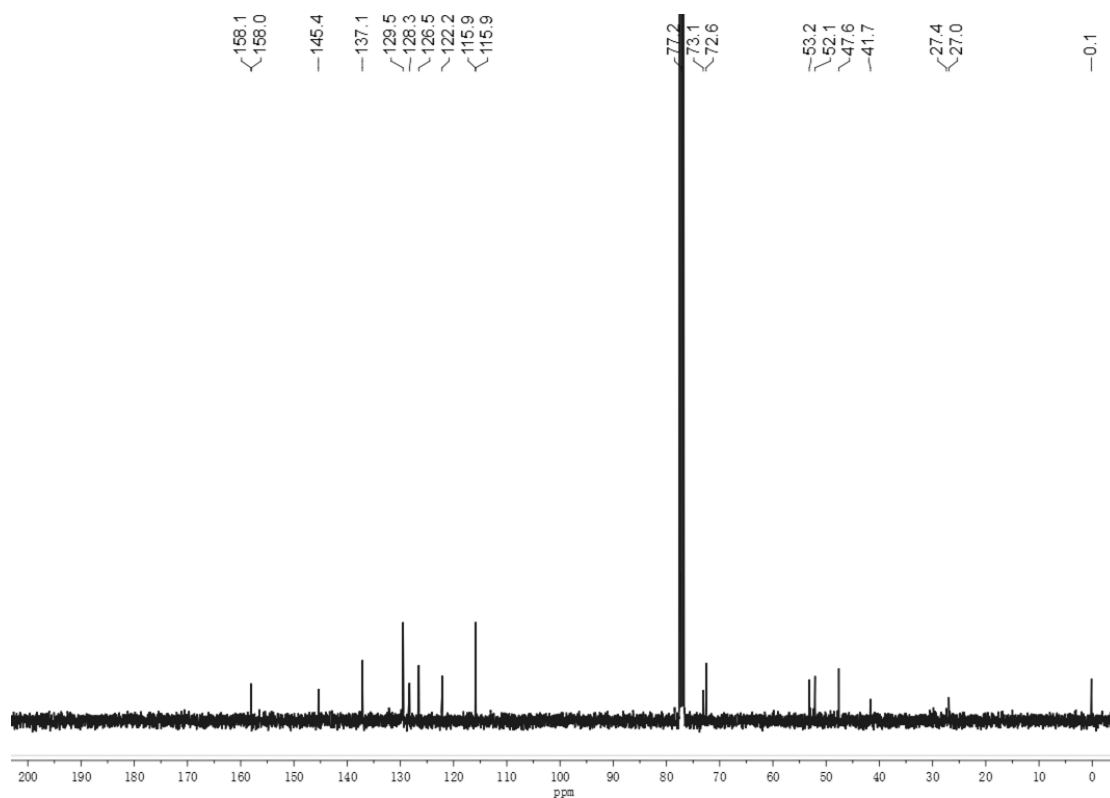


Fig. S32.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of  $[\text{Zn}(\mathbf{1})](\text{OTf})_2$ .



**Fig. S33.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K) spectrum of **2-Alkyne**.



**Fig. S34.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K) spectrum of **2-Alkyne**.

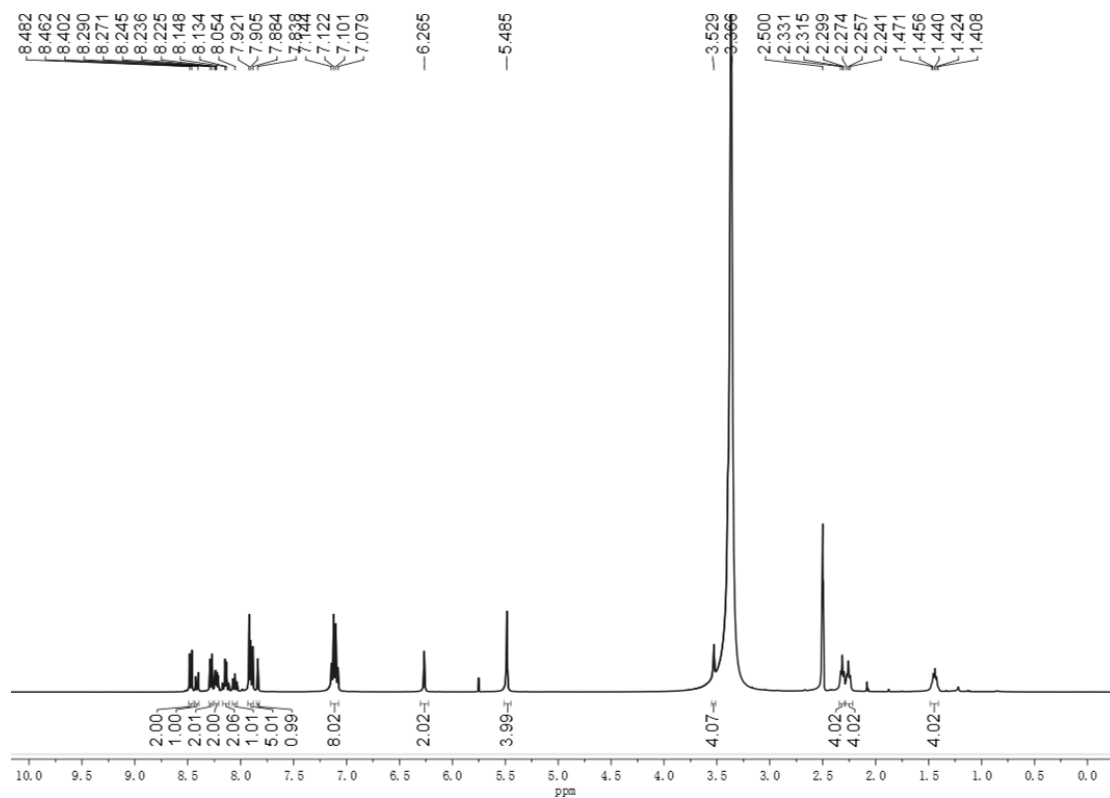


Fig. S35.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ , 298 K) spectrum of **2**.

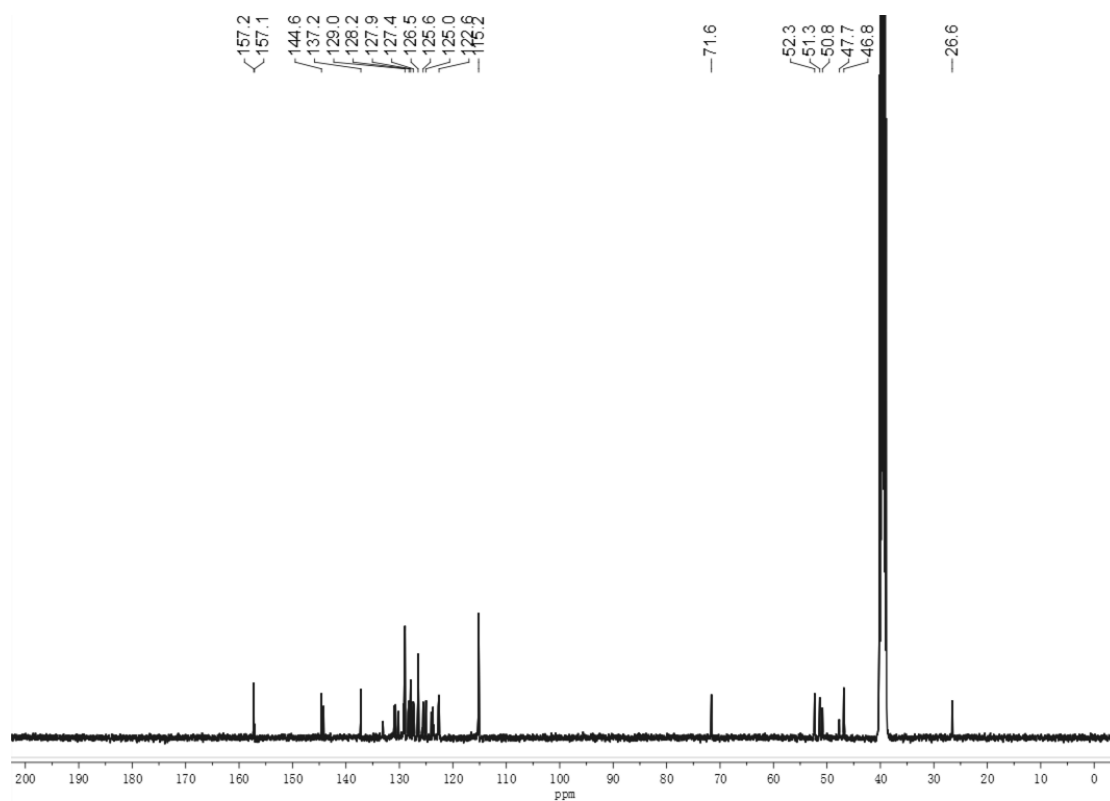
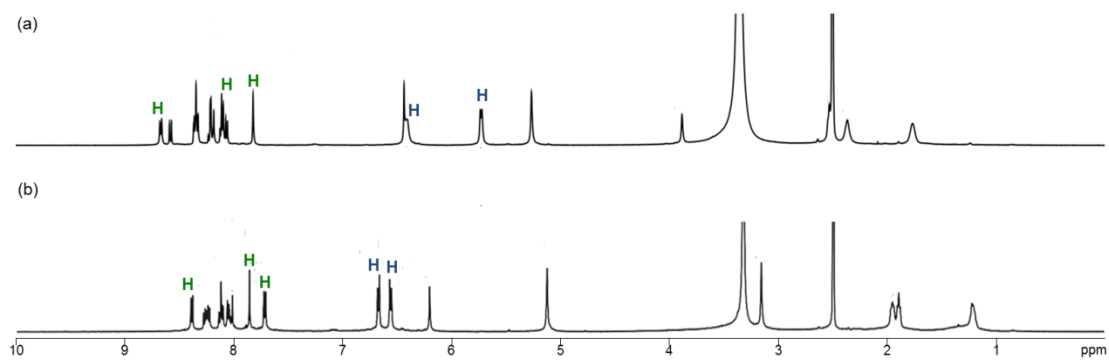
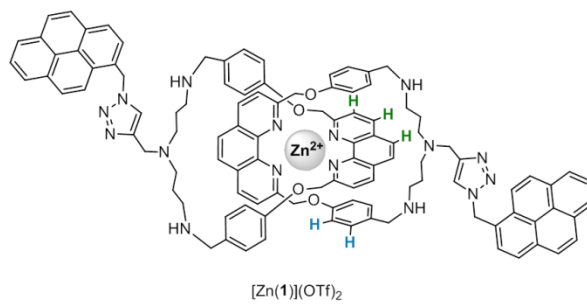


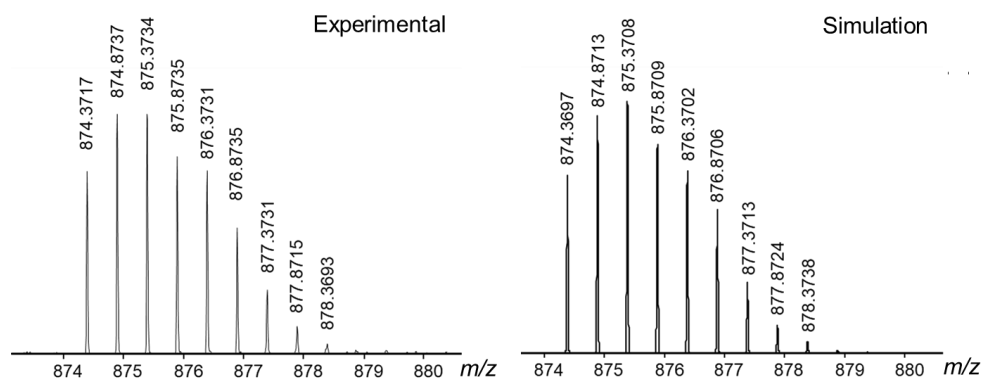
Fig. S36.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K) spectrum of **2**.



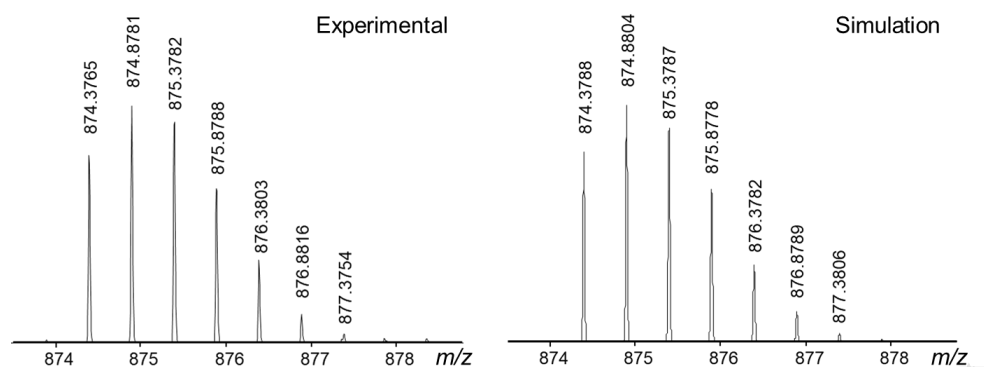


**Fig. S37.** Comparison of the <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K) of (a) [Zn(1)](OTf)<sub>2</sub> and (b) **1**. The upfield shifted aryl proton signals upon Zn<sup>2+</sup> coordination is consistent with the parallel stacking arrangement with the phenanthroline.

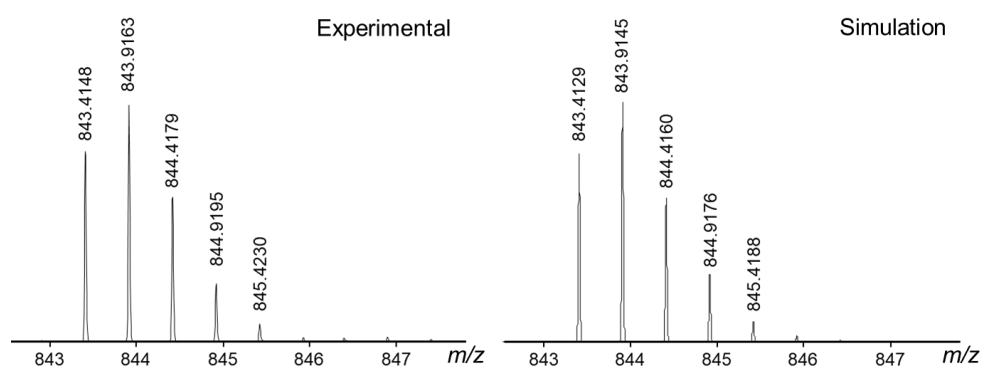
## 5. High Resolution Mass Spectra



**Fig. S38.** HRMS of  $[\text{Zn}(\mathbf{1})]^{2+}$  at  $m/z = 875.3734$  (left: experimental; right: simulation).



**Fig. S39.** HRMS of  $[\text{Cu}(\mathbf{1})+\text{H}]^{2+}$  at  $m/z = 874.8781$  (left: experimental; right: simulation).



**Fig. S40.** HRMS of  $[\mathbf{1}+2\text{H}]^{2+}$  at  $m/z = 843.9163$  (left: experimental; right: simulation).

## 6. References

1. C.-C. Yee, A. W. H. Ng, H. Y. Au-Yeung, *Chem. Commun.* 2019, **55**, 6169
2. M. Cesario, C. O. Dietrich, A. Edel, J. Guilhem, J. P. Kintzinger, C. Pascard and J. P. Sauvage, *J. Am. Chem. Soc.*, 1986, **108**, 6250
3. H. J. Berendsen, D. van der Spoel, R. van Drunen, *Comput. Phys. Commun.* 1995, **91**, 43
4. A. D. MacKerell Jr, N. Banavali, N. Foloppe, *Biopolymers* 2000, **56**, 257
5. A. Pedretti, L. Villa, G. Vistoli, *J. Mol. Graphics Modell.* 2002, **21**, 47
6. V. Zoete, M. A. Cuendet, A. Grosdidier, O. Michielin, *J. Comput. Chem.* 2011, **32**, 2359
7. A. D. MacKerell Jr, D. Bashford, M. Bellott, R. L. Dunbrack Jr, J. D. Evanseck, M. J. Field, S. Fischer, J. Gao, H. Guo, S. Ha, *J. Phys. Chem. B* 1998, **102**, 3586
8. T. A. Halgren, *J. Comput. Chem.* 1996, **17**, 490
9. T. A. Halgren, *J. Comput. Chem.* 1996, **17**, 520
10. T. A. Halgren, *J. Comput. Chem.* 1996, **17**, 553
11. T. A. Halgren, *J. Comput. Chem.* 1996, **17**, 616
12. T. A. Halgren, R. B. Nachbar, *J. Comput. Chem.* 1996, **17**, 587
13. G. Ujaque, F. Maseras, O. Eisenstein, *Theor. Chem. Acc.* 1997, **96**, 146
14. T. A. Halgren, *J. Am. Chem. Soc.* 1992, **114**, 7827
15. P. P. Ewald, *Ann. Phys.* 1921, **369**, 253
16. B. Hess, H. Bekker, H. J. Berendsen, J. G. Fraaije, *J. Comput. Chem.* 1997, **18**, 1463
17. S. Kumar, S. Sarkar, B. Bagchi, *J. Chem. Phys.* 2020, **152**, 164507