

## Supporting Information

### Hierarchical Self-Assembly of Discrete bis-[2]pseudorotaxanes Metallacycles with bis-pillar[5]arene via host-guest Interactions and Their Redox-Responsive Behavior

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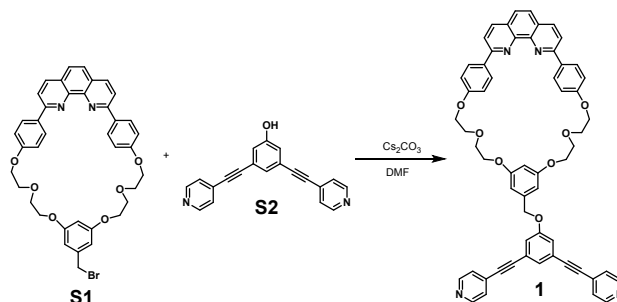
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## 1. Materials and methods

All solvents were dried according to standard procedures and all of them were degassed under N<sub>2</sub> for 30 minutes before use. All air-sensitive reactions were carried out under inert N<sub>2</sub> atmosphere. <sup>1</sup>H, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectra were recorded on Bruker 400MHz Spectrometer (<sup>1</sup>H: 400 MHz; <sup>31</sup>P: 161.9 MHz) and 500MHz Spectrometer (<sup>1</sup>H: 500MHz) at 298 K. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported relative to the residual solvent signals, and <sup>31</sup>P NMR resonances are referenced to an internal standard sample of 85% H<sub>3</sub>PO<sub>4</sub> (δ 0.0). 2D DOSY were recorded on Bruker 500 MHz Spectrometer (<sup>1</sup>H: 500MHz) at 298 K. UV-vis spectra were recorded in a quartz cell (light path 10 mm or 2 mm) on a Cary 50Bio UV-visible spectrophotometer. The SEM samples were prepared on clean Si substrates. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination. All the SEM images were obtained using a S-4800 (Hitachi Ltd.) with an accelerating voltage of 3.0-10.0 kV. The TEM samples were deposited on copper grids, followed by a slow evaporation in air at room temperature. All the TEM measurements were performed under a Tecnai G2 20 TWIN device.

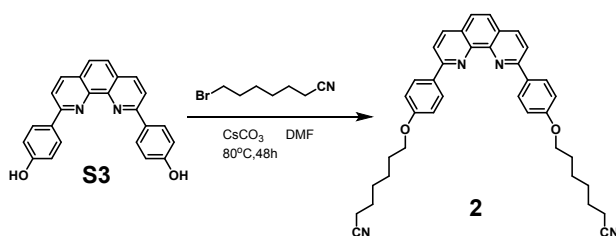
## 2. Synthetic experimental details and characterizations of new compounds

**Scheme S1.** The synthetic procedure for the macrocycle **1**.



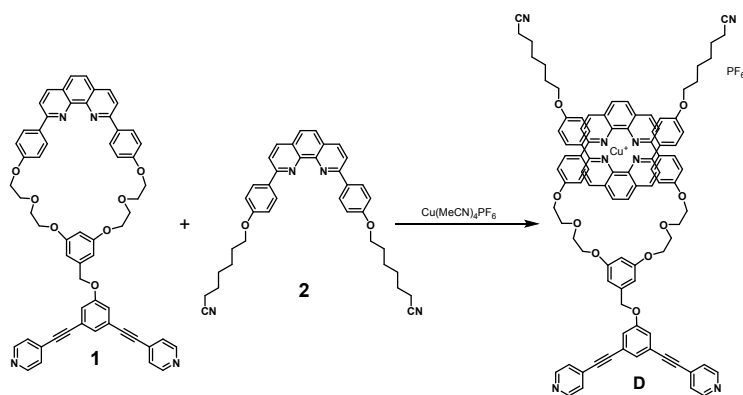
**Synthesis of macrocycle 1.** A 50 mL Schlenk flask was charged with macrocycle **S1** (300 mg, 0.423mmol),<sup>1</sup> Cs<sub>2</sub>CO<sub>3</sub>(163.6 mg, 0.846mmol), **S2** (150.7 mg, 0.508mmol), degassed, and back-filled three times with N<sub>2</sub>. Anhydrous DMF (20mL) were introduced into the reaction flask by syringe. The reaction was stirred under an inert atmosphere at 90°C for a night. The solvent was taken up in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O mixture (100/50 mL). The organic phase was washed with H<sub>2</sub>O (3×100 mL). The organic phases were collected and dried over MgSO<sub>4</sub>, and the solution was evaporated in vacuo. After column chromatography on SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH 0% to 2%), macrocycle **1** was obtained in 70% yield (273.8 mg). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-acetone) δ 8.66 (dd, 4H), 8.53 (d, 4H), 8.37 (d, 2H), 8.24 (d, 2H), 7.82 (s, 2H), 7.47 (dd, 4H), 7.20-7.08 (m, 5H), 6.91 (d, 2H), 6.63 (dd, 3H), 5.03 (s, 2H), 4.39-4.32 (m, 4H), 4.27-4.19 (m, 4H), 3.96 (dt, 8H). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-acetone) δ 161.28 (d), 159.30 (s), 156.29 (s), 150.91 (s), 146.87 (s), 140.09 (s), 137.54 (s), 133.28 (s), 131.28 (s), 129.62 (s), 128.40 (s), 128.02 (s), 126.50 (s), 126.19 (s), 124.02 (s), 119.59 (s), 116.38 (s), 106.60 (s), 101.44 (s), 92.87 (s), 87.73 (s), 70.66-70.17 (m), 68.92 (s), 68.57 (s).

**Scheme S2.** Synthesis route of the phen derivative **2**.



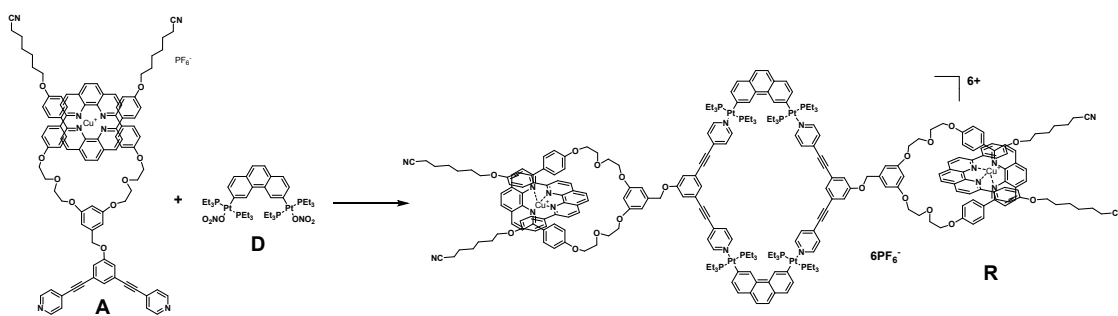
**Synthesis of phen derivative 2.** A 50 mL Schlenk flask was charged with **S3** (300 mg, 0.824mmol),<sup>2</sup>  $\text{Cs}_2\text{CO}_3$  (636.26mg, 3.3mmol), degassed, and back-filled three times with  $\text{N}_2$ . Anhydrous DMF (20mL) and 7-Bromoheptanenitrile (0.3 mL, 1.98mmol) were introduced into the reaction flask by syringe. The reaction was stirred under an inert atmosphere at  $80^\circ\text{C}$  for 48h. The solvent was taken up in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  mixture (100/50 mL). The organic phase was washed with  $\text{H}_2\text{O}$  ( $3 \times 100$  mL). The organic phases were collected and dried over  $\text{MgSO}_4$ , and the solution was evaporated in vacuo. After column chromatography on  $\text{SiO}_2$  ( $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$  0% to 1%), phen derivative **2** was obtained in 90% yield (432.2 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (d, 4H), 8.29 (d, 2H), 8.10 (d, 2H), 7.76 (s, 2H), 7.10 (d, 4H), 4.09 (t, 4H), 2.39 (t, 4H), 1.85 (s, 6H), 1.73 (s, 4H), 1.58 (d, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.48 (s), 156.28 (s), 145.45 (s), 137.12 (s), 131.72 (s), 129.08 (s), 127.57 (s), 125.68 (s), 119.79 (s), 119.57 (s), 114.78 (s), 67.72(s), 29.01 (s), 28.48 (s), 25.39 (d), 17.15 (s). HRMS (ESI): Exact mass calcd. For  $\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_2$ : 582.75, Found: 583.3.

**Scheme S3.** The synthetic procedure for the pseudorotaxane-containing donor building blocks **4**.



**Synthesis of phen derivative D.**<sup>2</sup> In a Schlenk flask, 1 equiv of macrocycle **1** (100mg, 0.108mmol) was dissolved under argon in a 1:1 mixture of dichloromethane and acetonitrile. After addition of 1 equiv of  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (40.4mg, 0.108mmol), the reaction was stirred at room temperature under argon for 15 min. In a second Schlenk flask, 1 equiv of **2** (63.1mg, 0.108mmol) was dissolved in dichloromethane and cannula filtered into the first solution. The solution was stirred under argon at room temperature for an additional 30 min, followed by removal of the solvent in vacuo. Final purification was achieved by precipitation with dichloromethane/pentane and silica gel column chromatography using dichloromethane/methanol (96:4) to yield a dark red, crystalline solid **D** in quantitative yield.  $^1\text{H}$  NMR (400 MHz,  $d_6$ -acetone)  $\delta$  8.74-8.51 (m, 7H), 8.19 (d, 4H), 8.00 (d, 2H), 7.91 (d, 2H), 7.57 (d, 4H), 7.52-7.38 (m, 8H), 7.37-7.31 (m, 3H), 6.92 (s, 3H), 6.11 (dd, 8H), 5.27 (s, 2H), 4.45-4.36 (m, 4H), 3.99-3.93 (m, 4H), 3.66 (dd, 12H), 2.53 (t, 4H), 1.78-1.62 (m, 8H), 1.53 (ddd, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -acetone)  $\delta$  161.23 (s), 160.45 (s), 160.07 (s), 159.62 (s), 157.35 (s), 156.77 (s), 150.85 (s), 144.23 (d), 140.43 (s), 138.18 (s), 137.97 (s), 132.86 (s), 131.89 (s), 131.05 (s), 130.19 (d), 128.87 (s), 128.43 (s), 127.39 (s), 126.94 (s), 124.92 (d), 124.56 (s), 120.80 (s), 119.94 (s), 113.70 (s), 106.41 (s), 103.16 (s), 92.75 (s), 88.10 (s), 70.78 (s), 70.40 (s), 69.81 (s), 68.49 (s), 68.21 (s), 68.11 (d), 26.04 (d), 17.13 (s). MALDI-TOF-MS of **D**:  $m/z$  calcd for  $[\text{C}_{97}\text{H}_{84}\text{N}_8\text{O}_9\text{Cu}]^+$  ( $[\text{M}-\text{PF}_6^-]$ ): 1569.33, Found: 1568.5.

**Scheme S4.** The synthetic procedure for the supramolecular [2+2] rhomboidal metallacycle **R**.



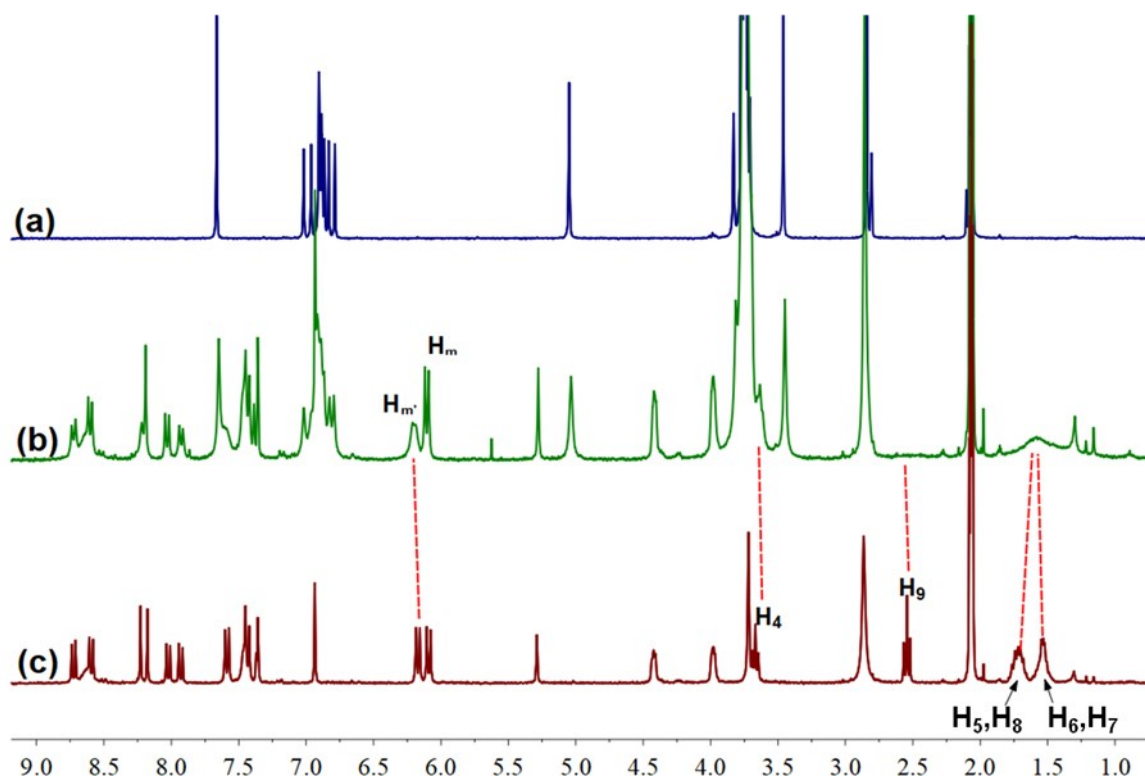
**Synthesis of metallacycle R.** Self-assembly of supramolecular [2+2] rhomboidal metallacycle **R** from ligand **D** and diplatinum acceptor **A**. The dipyrindyl donor ligand **D** (15 mg, 8.75  $\mu\text{mol}$ ) and 60° organoplatinum acceptor **A** (10.18 mg, 8.75  $\mu\text{mol}$ ) were weighed accurately into a glass vial. To the vial was added 2.5 mL acetone and 0.4 mL H<sub>2</sub>O, and the reaction solution was stirred at room temperature for 8 hours. The PF<sub>6</sub><sup>-</sup> salt of **R** was synthesized by dissolving the NO<sub>3</sub><sup>-</sup> salt of **R** in acetone/H<sub>2</sub>O and adding a saturated aqueous solution of KPF<sub>6</sub> to precipitate the product, which was collected by vacuum filtration. <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-acetone)  $\delta$  8.99 (dd,  $J = 24.0, 5.7$  Hz, 4H), 8.64 (s, 2H), 8.56 (dd,  $J = 23.2, 8.4$  Hz, 4H), 8.08 (d,  $J = 6.8$  Hz, 4H), 7.90-7.82 (m, 6H), 7.79 (dd,  $J = 5.6, 1.5$  Hz, 2H), 7.62 (dd,  $J = 7.2, 4.7$  Hz, 3H), 7.58-7.50 (m, 4H), 7.47 (d,  $J = 8.6$  Hz, 4H), 7.41 (d,  $J = 1.2$  Hz, 2H), 7.31 (d,  $J = 8.6$  Hz, 4H), 6.81 (dd,  $J = 12.2, 2.0$  Hz, 3H), 6.01 (dd,  $J = 28.4, 8.7$  Hz, 8H), 5.18 (s, 2H), 4.32-4.25 (m, 4H), 3.89-3.83 (m, 4H), 3.66-3.47 (m, 13H), 2.39 (t,  $J = 7.0$  Hz, 4H), 1.57 (tt,  $J = 13.5, 6.6$  Hz, 9H), 1.45-1.27 (m, 24H), 1.16-1.02 (m, 36H). <sup>13</sup>C NMR (101 MHz, *d*<sub>6</sub>-acetone)  $\delta$  161.16, 160.41, 160.05, 159.85, 157.37, 156.80, 153.41, 144.27, 144.20, 140.22, 138.21, 137.93, 134.52, 132.87, 131.92, 130.57, 130.20, 130.08, 129.80, 129.34, 128.89, 128.85, 128.40, 127.39, 126.88, 126.07, 124.99, 124.85, 123.98, 120.91, 120.68, 113.71, 113.68, 106.25, 103.08, 96.97, 87.12, 70.90, 70.32, 69.78, 68.45, 68.15, 67.99, 26.01, 25.90, 17.04, 13.27, 13.13, 13.00, 7.91. <sup>31</sup>P NMR (acetone-*d*<sub>6</sub>, 161.9 MHz):  $\delta$  14.48 ppm. ESI-MS:  $m/z$ : 1882.27 [M-3PF<sub>6</sub>]<sup>3+</sup>, 1376.56 [M-4PF<sub>6</sub>]<sup>4+</sup>, 1072.33 [M-5PF<sub>6</sub>]<sup>5+</sup>.

## Reference:

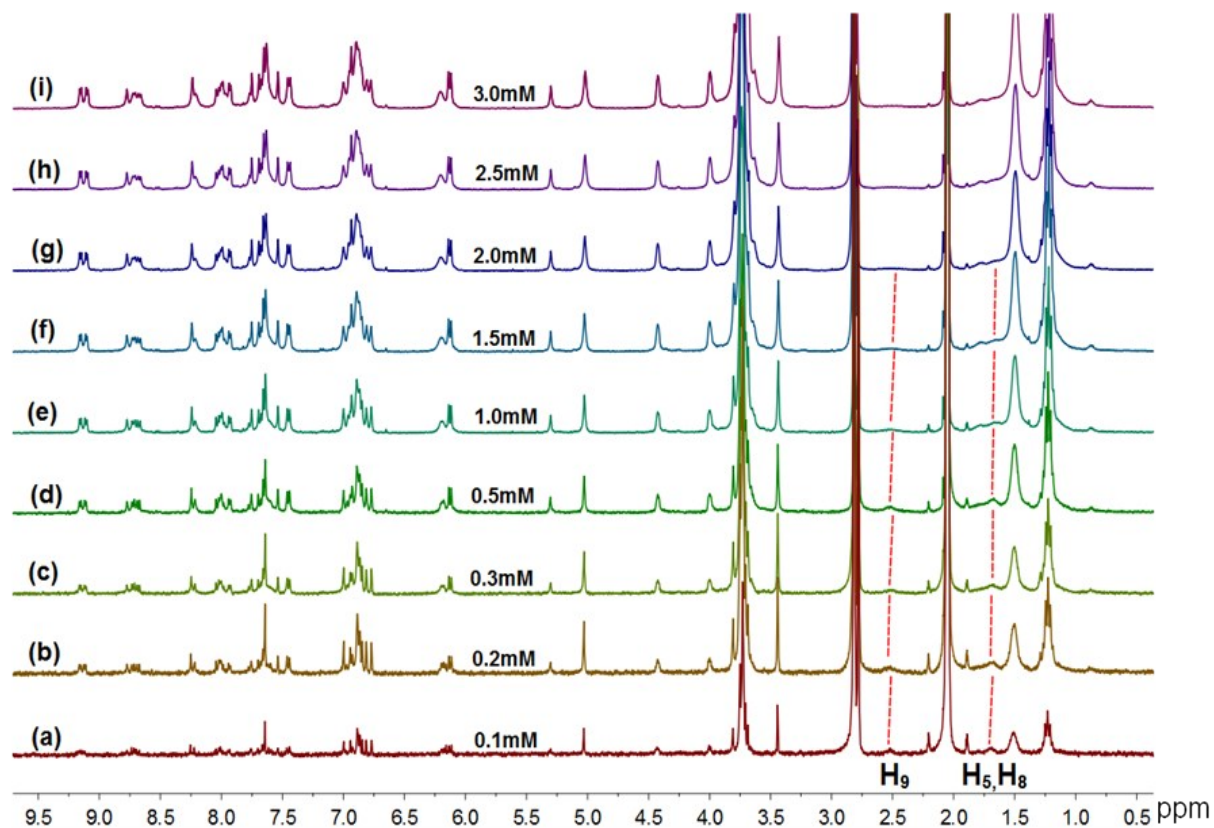
- [1] M. C. Jimenez-Molero, C. Dietrich-Buchecker, J.-P. Sauvage. *Chem. Eur. J.* 2002, **8**, 1456-1466.
- [2] C. O. Dietrich-Buchecker, J.-P. Sauvage. *Tetrahedron Letters*, 1983, **24**, 5095-5098.



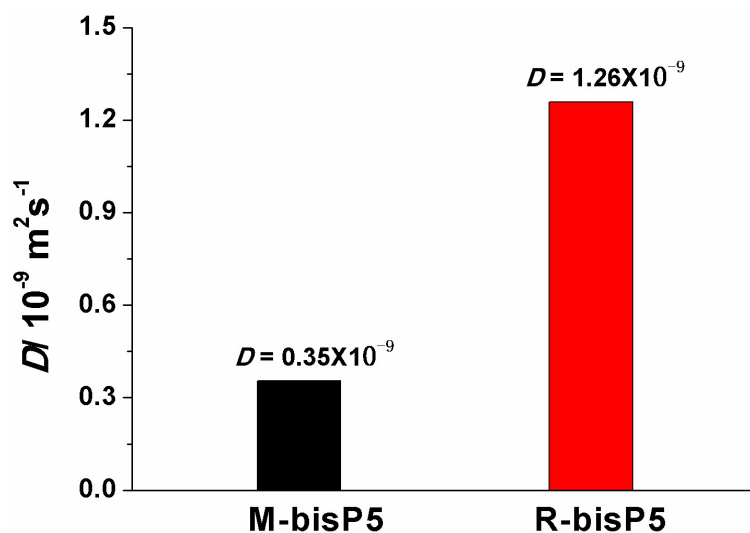




**Figure S3.** <sup>1</sup>H NMR spectra (500 MHz, acetone-d<sub>6</sub>, 296 K) of (a) 6.25 mM **bisP5**, (b) 6.25 mM **D** + 6.25 mM **bisP5**, and (c) 6.25 mM **D**.

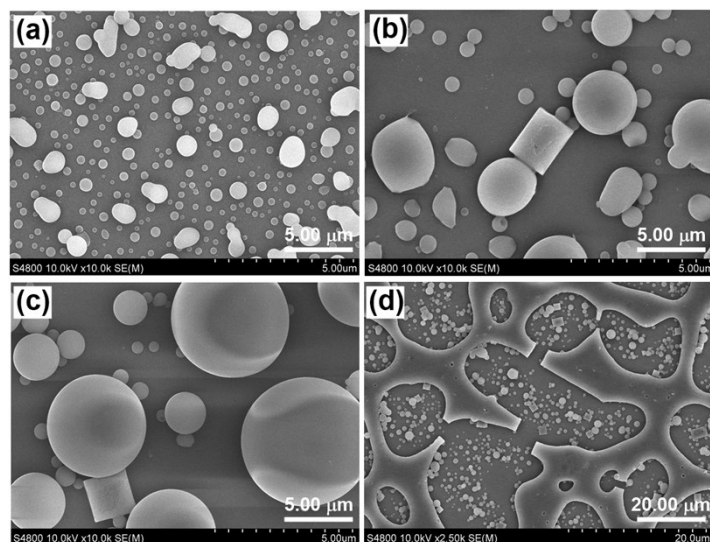


**Figure S4.**  $^1\text{H}$  NMR spectra (400 MHz, acetone- $d_6$ , 296 K) of  $\text{R}\rhd(\text{bisP5})_2$  at different concentrations: (a) 0.1 mM, (b) 0.2 mM, (c) 0.3 mM, (d) 0.5 mM, (e) 1.0 mM, (f) 1.5 mM, (g) 2.0 mM, (h) 2.5 mM, (i) 3.0 mM.

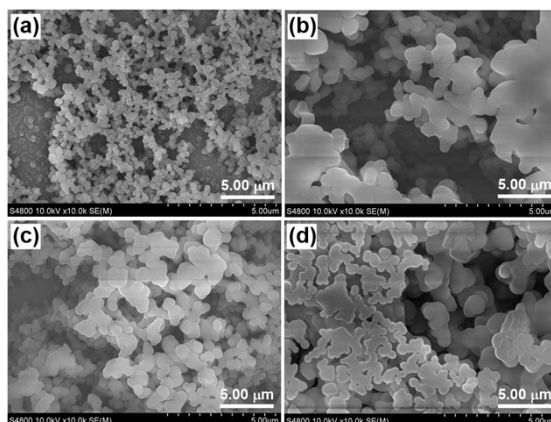


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**Figure S5.** 2-D DOSY (500 MHz, 296 K) plot of solutions in acetone- $d_6$  of the  $\text{R}\rhd(\text{bisP5})_2$  and  $\text{M}\rhd(\text{bisP5})_2$  ( $[\text{Cu}(\text{phenanthroline})_2]^+$  unit = 6 mM).

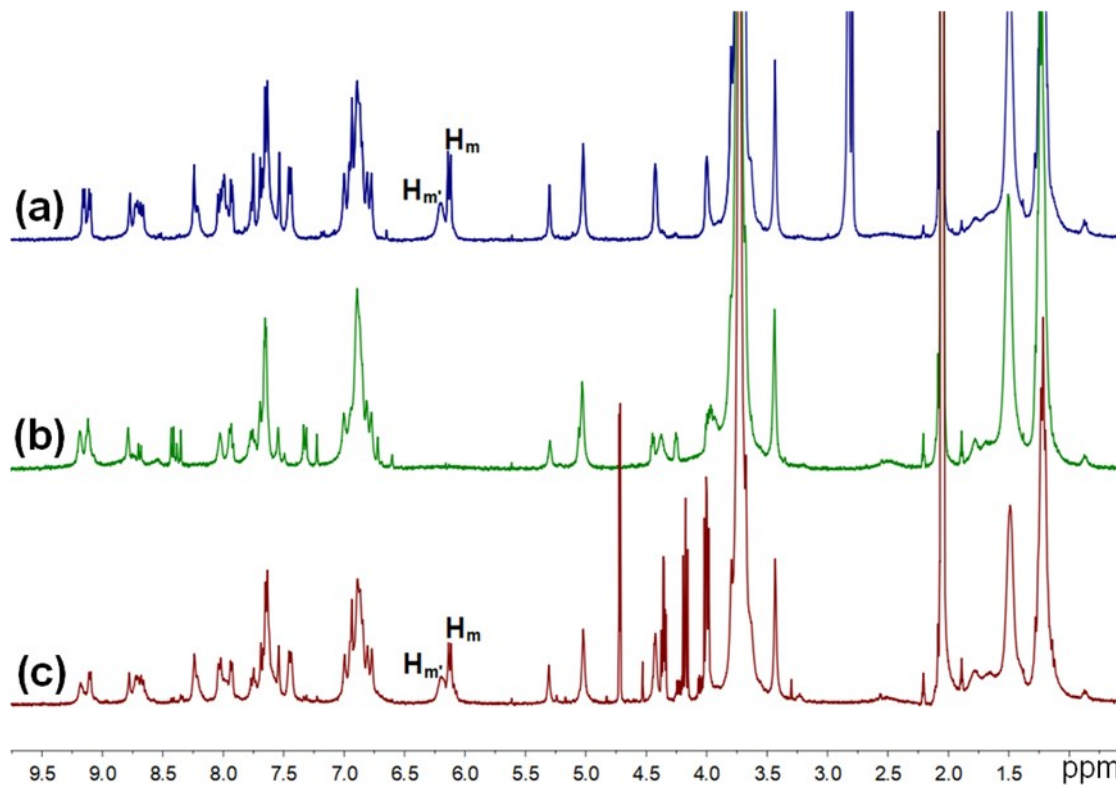


**Figure S6.** Concentration-dependent SEM images of rhomboidal metallacycles **R**: (a) ca. 1.0 mM; (b) 2.0 mM; (c) ca. 3.0 mM; (d) ca. 4.0 mM.

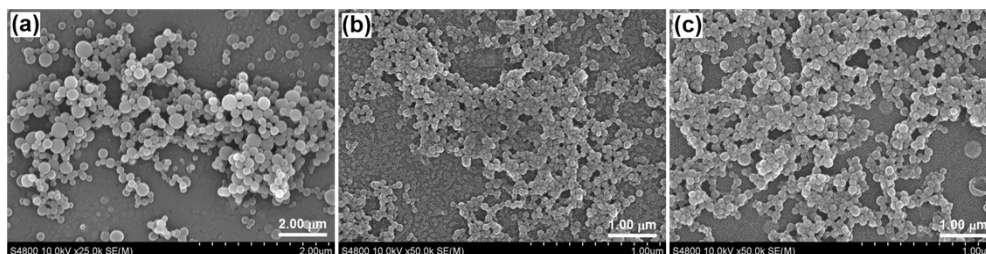


**5 Figure S7.** Concentration-dependent SEM images of supramolecular polymers **R⇌(bisPD)<sub>2</sub>**: (a) ca. 1.0 mM; (b) 2.0 mM; (c) ca. 3.0 mM; (d) ca. 4.0 mM.

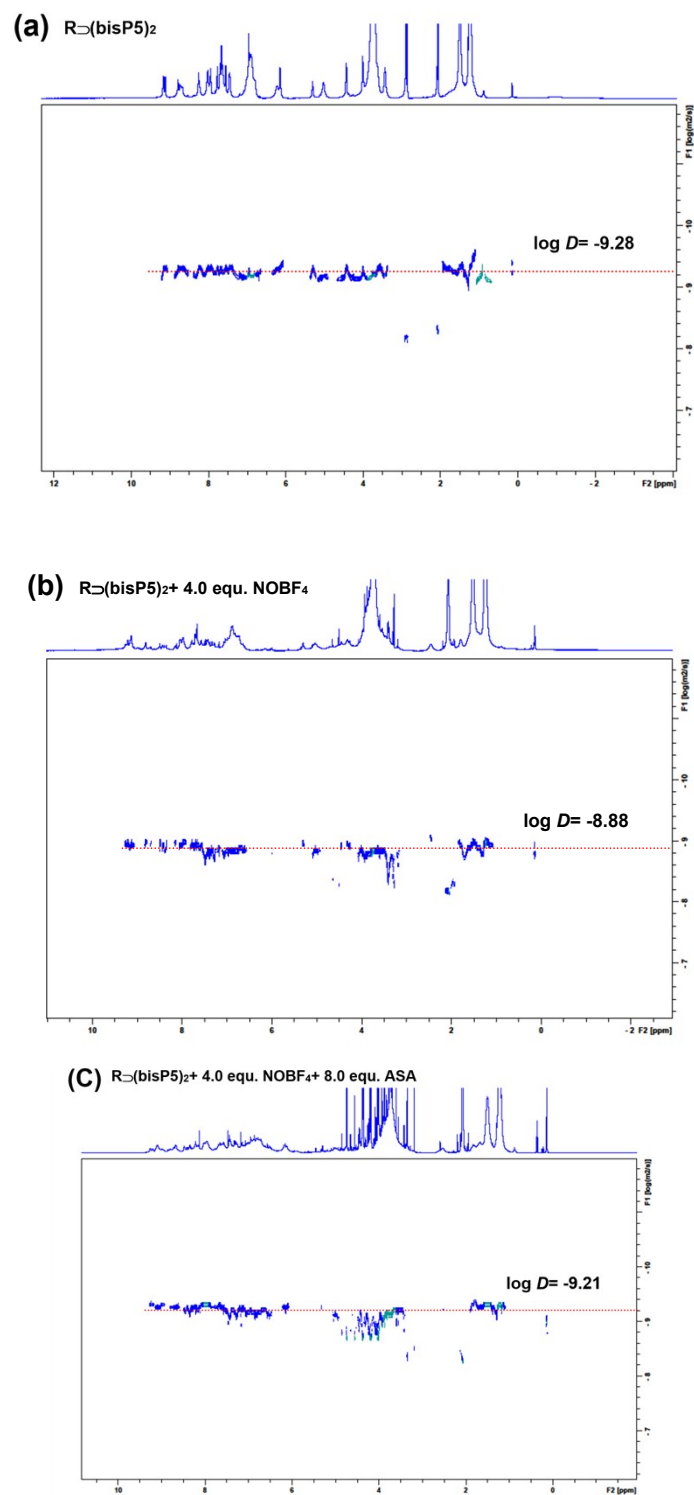
#### 4. Stimuli-responsive supramolecular polymers



**Figure S8.**  $^1\text{H}$  NMR spectra (500 MHz, acetone- $d_6$ , 296 K) of (a)  $\text{R}\supset(\text{bisP5})_2$  (3 mM), (b)  $\text{R}\supset(\text{bisP5})_2$  + 4.0 equiv  $\text{NOBF}_4$ , (c)  $\text{R}\supset(\text{bisP5})_2$  + 4.0 equiv  $\text{NOBF}_4$  + 8.0 equiv ASA.



**Figure S9.** SEM images of supramolecular polymers in acetone (a) 0.1 mM  $\text{R}\supset(\text{bisP5})_2$ , (b) 0.1 mM  $\text{R}\supset(\text{bisP5})_2$  + 4.0 equiv  $\text{NOBF}_4$ , (c) 0.1 mM  $\text{R}\supset(\text{bisP5})_2$  + 4.0 equiv  $\text{NOBF}_4$  + 8.0 equiv ASA.

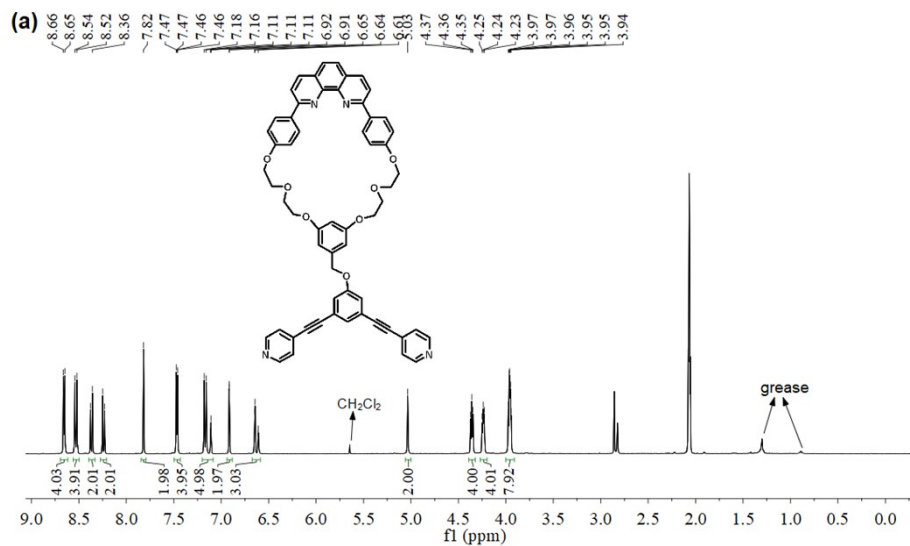


**Figure S10.** 2-D DOSY (500 MHz, 296 K) plot of solutions in acetone- $d_6$  of a 4.5mM solution of the 5  $R\text{-(bisP5)}_2$  (a) and of its oxidized form Cu(II)N4 (b), and  $R\text{-(bisP5)}_2 + 4.0$  equiv  $\text{NOBF}_4 + 8.0$  equiv ASA (c).

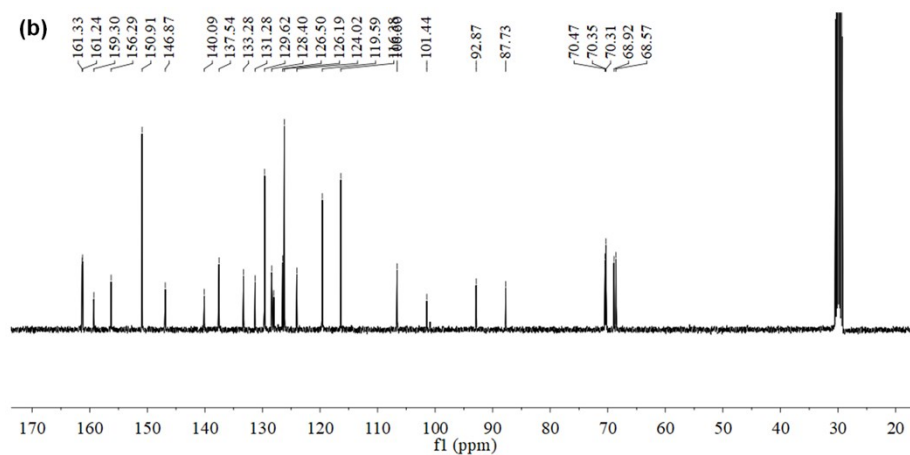
**Table S1** Diffusion coefficient ( $D$ ) values of the redox-responsive supramolecular polymers  $M\supset(\text{bisP5})_3$  and  $R\supset(\text{bisP5})_2$ .

	Original state Cu(I)N4	Oxidation state Cu(II)N4	Reduction state Cu(I)N4
$M\supset(\text{bisP5})_3$	$0.3 \times 10^{-9} \text{ m}^2\text{s}^{-1}$	$1.55 \times 10^{-9} \text{ m}^2\text{s}^{-1}$	$0.28 \times 10^{-9} \text{ m}^2\text{s}^{-1}$
$R\supset(\text{bisP5})_2$	$0.52 \times 10^{-9} \text{ m}^2\text{s}^{-1}$	$1.32 \times 10^{-9} \text{ m}^2\text{s}^{-1}$	$0.62 \times 10^{-9} \text{ m}^2\text{s}^{-1}$

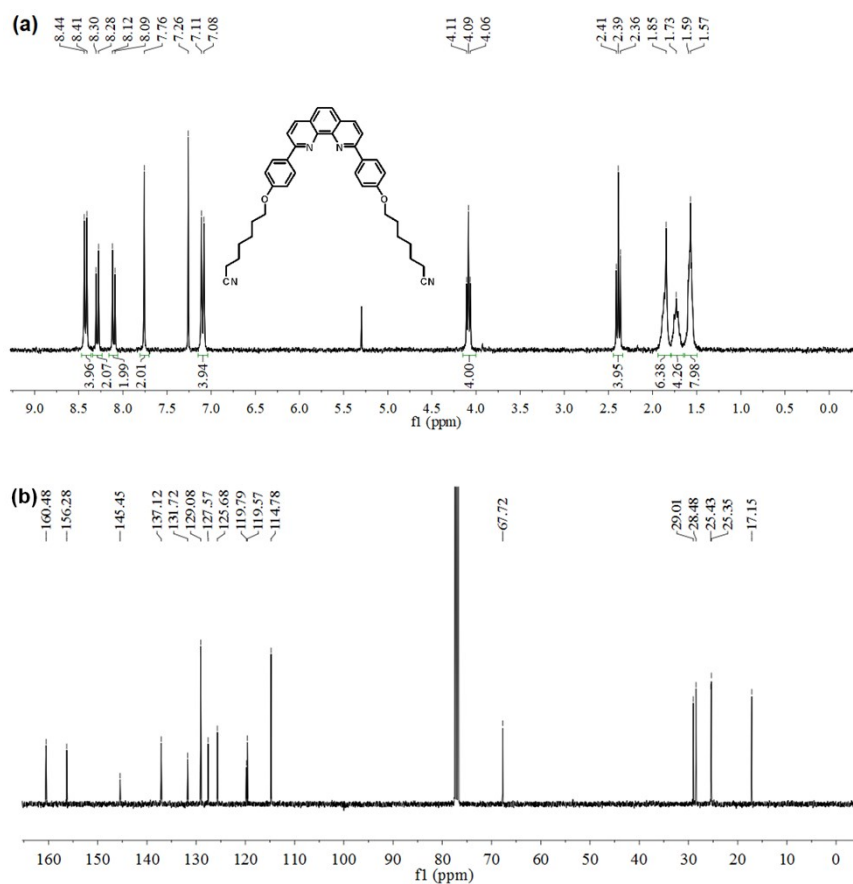
## 5. Multiple nuclear NMR ( $^1\text{H}$ and $^{13}\text{C}$ NMR) spectra and MS of new compounds.



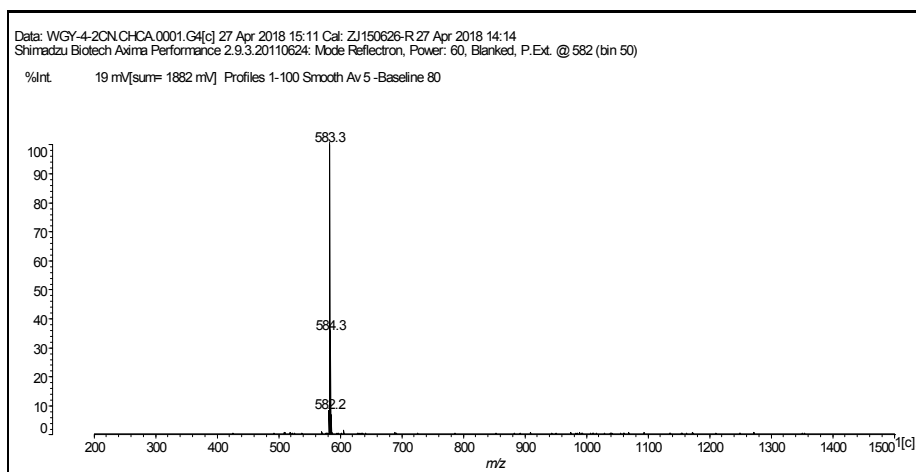
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**Figure S11.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of macrocycle **1** in  $\text{CD}_3\text{COCD}_3$ .

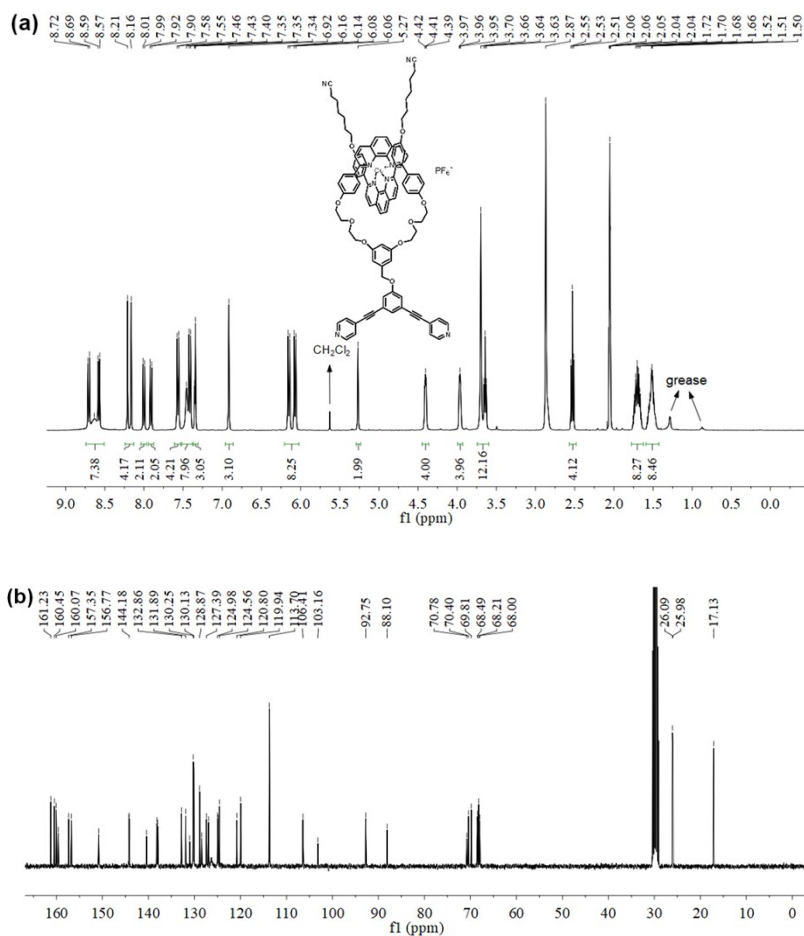


**Figure S12.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of the phenanthroline derivative **2** in  $\text{CD}_3\text{COCD}_3$ .

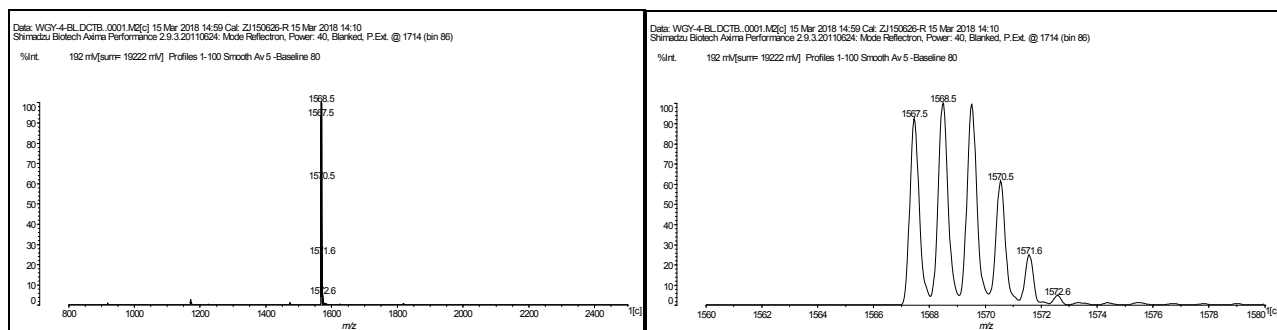


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**Figure S13.** ESI-TOF-MS of **2**: Exact mass calcd. For  $\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_2$ : 582.30, Found: 583.3.

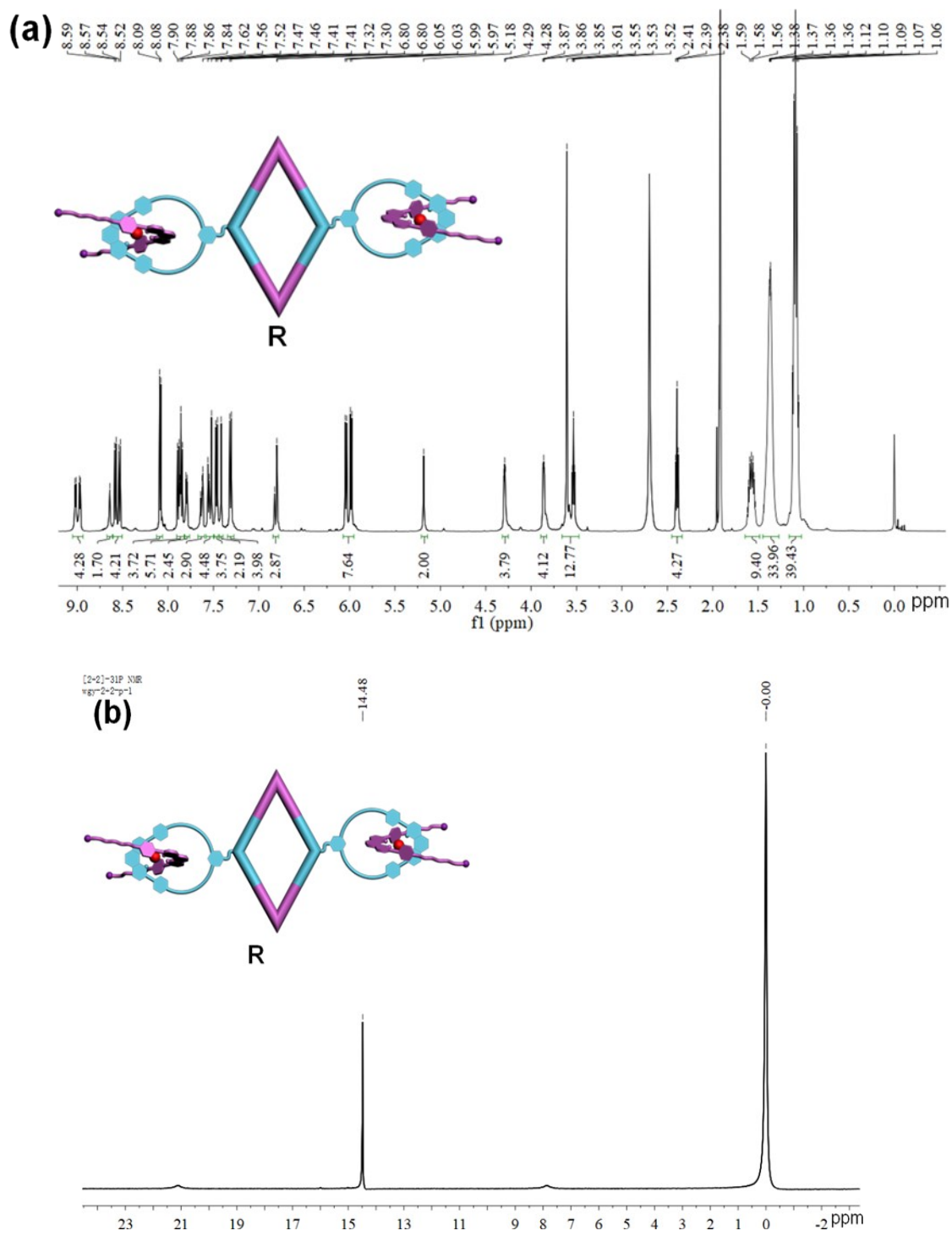


**Figure S14.** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of **D** in  $\text{CD}_3\text{COCD}_3$ .

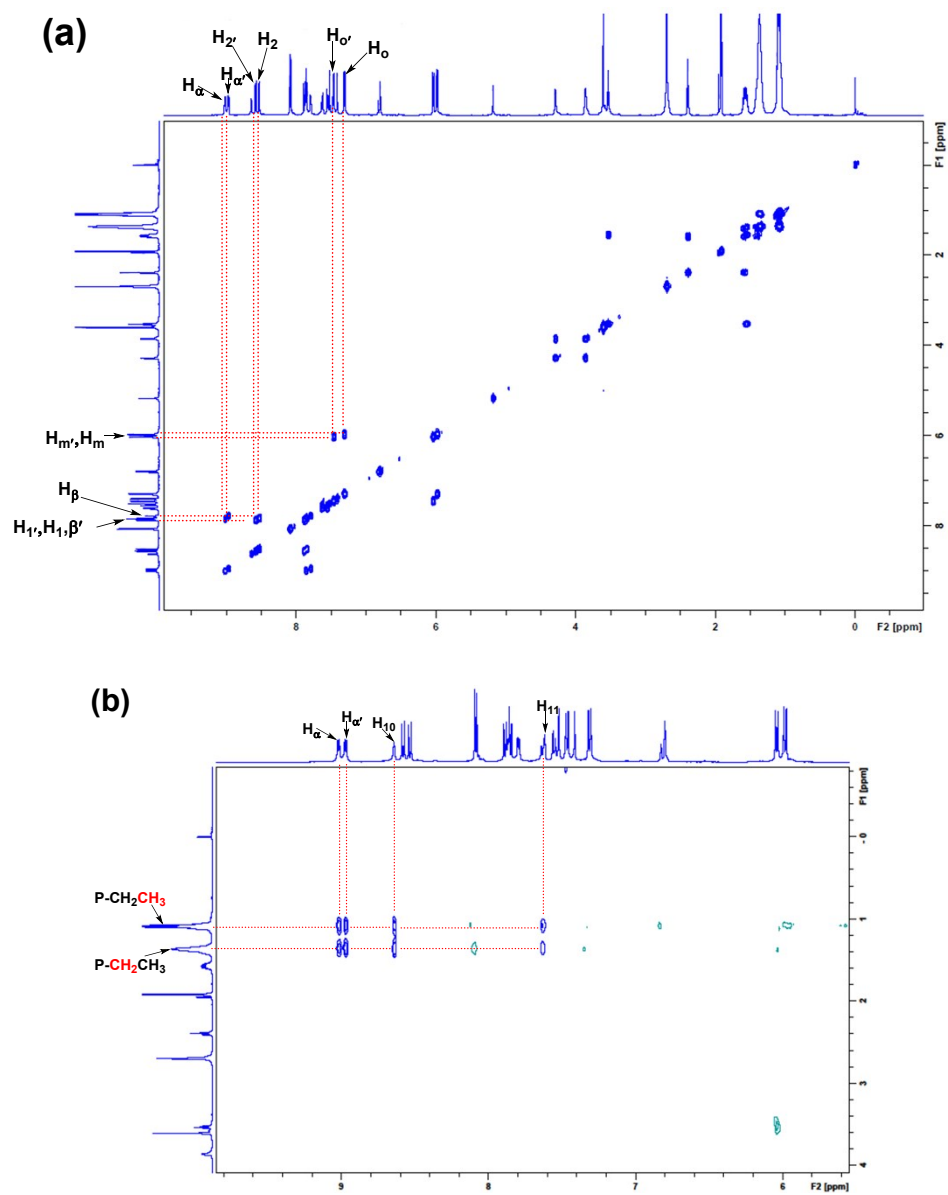


**5 Figure S15.** ESI-TOF-MS of **D**:  $m/z$  calcd for  $[\text{C}_{97}\text{H}_{84}\text{N}_8\text{O}_9\text{Cu}]^+$  ( $[\text{M}-\text{PF}_6]^+$ ): 1569.33, Found: 1568.5.





**Figure S16.** (a)  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the rhomboidal metallacycle **R** in  $\text{CD}_3\text{COCD}_3$ .



**Figure S17.** (a)  $^1\text{H}$ - $^1\text{H}$  COSY and (b) 2D NOESY NMR spectra of 3.0 mM rhomboidal metallacycle **R** in acetone- $d_6$  (500 MHz, 296 K).