Supporting Information

Metal ions determined geometrical configurations of metallocages with different emission properties

Zirui Zhai,^{‡a} Qixia Bai,^{‡a} Yu-Ming Guan,^a He Zhao,^b Tun Wu,^a Jingxian

Pang,^a Haoxuan Xu,^a Ting-Zheng Xie,^a Zhe Zhang,^{*a} Pingshan Wang^{*a}

^a Institute of Environmental Research at Greater Bay Area, Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, China

^b Hunan Key Laboratory of Micro & Nano Materials Interface Science; College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

*Corresponding authors: chemwps@csu.edu.cn, zhezhang2018@gzhu.edu.cn

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1. Schemes of preparation of ligand L and supramolecules



Scheme S1. Synthesis of ligand L.



Scheme S2. Self-assembly of Co₆L₄, Ni₆L₄, Zn₆L₄ and Cd₆L₄.



Scheme S3. Self-assembly of Fe_6L_4 .

2. Experimental section

General procedures. Chemicals were purchased from Bidepharm, Sigma/Aldrich, Energy Chemical, Alfa Aesar and used without further purification. Thin-layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al₂O₃ (IB-F) or SiO₂ (IB2-F) and visualized by UV light. Column chromatography was conducted using neutral Al₂O₃ (200-300 mesh) SiO₂ (200-300 mesh). ¹H, ¹³C, ¹H-¹H COSY and ¹H-¹H NOESY NMR spectra were recorded on a Bruker NMR. Different NMR solvents were purchased from Energy Chemical, J&K scientific and Sigma/Aldrich. ESI-MS and TWIM-MS were recorded with a Waters Synapt G2-Si tandem mass spectrometer, using solutions of 0.01 mg sample in 1 mL of CHCl₃/MeOH (1:3, v/v) for ligands or 0.5 mg sample in 1 mL of DMF/MeOH (3:1, v/v) for complexes.

TWIM-MS. The TWIM-MS experiments were performed under the following conditions: ESI capillary voltage, 2 kV; sample cone voltage, 35 V; source offset, 42 V; source temperature 150 °C; desolvation temperature, 250 °C; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N₂); source gas flow, 0 mL/min; trap gas flow, 3 mL/min; helium cell gas flow, 120 mL/min; ion mobility (IM) cell gas flow, 30 mL/min; sample flow rate, 8 μ L/min; IM traveling wave height, 25 V; and IM traveling wave velocity, 1200 m/s. Q was set in rf-only mode to transmit all ions produced by ESI into the triwave region for the acquisition of TWIM-MS data. Data were collected and analyzed by using MassLynx 4.2 and DriftScope 2.9.

TEM. Transmission electron microscopy tests were performed on the JEOL JEM-2100F equipment. The sample solutions were diluted to a concentration of 2×10^{-6} M using DMF, drop-casted onto a lacey carbon-covered Cu grid (300 mesh, purchased from Beijing Zhongjingkeyi Technology Co., Ltd.).

Molecular Modeling. Energy minimization of the macrocycles was conducted with the Materials Studio version 6.0 program, using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted.

UV-vis absorption, fluorescence properties and electroluminescence spectra. UV-vis absorption spectra were recorded on Thermo Fisher Scientific Evolution 201 spectrophotometer at room temperature (10^{-6} M in CHCl₃ or DMF) and were corrected with the background spectrum of the solvent. Fluorescence properties were performed on Edinburgh-FS5 Fluorescence spectrometer at 300 K (10^{-6} M or 10^{-5} M in DMF). The Commission International de I'Eclairage (CIE) coordinates of each sample were calculated on the basis of the international CIE standard.

3. Synthesis of the compounds and supramolecules



Compound 1 was synthesized by dissolving 1-indanone (1.36 g, 10.3 mmol) in the mixture of HCl (3.16 mL, 0.1 mmol) and CH₃COOH (5.89 mL, 0.10 mmol), under an argon atmosphere. After stirring at 100 °C for 16 h, the mixture was poured into ice water and filtered. The solid was washed with water, acetone and CH₂Cl₂ to get compound 1 as a white solid (0.98 g, 72%). ¹H NMR (CDCl₃, 500 MHz): δ (ppm): 7.98 - 7.96 (d, *J* = 8Hz, 3H, Ph-*H*^{*a*}), 7.71 - 7.00 (d, *J* = 4Hz, 3H, Ph-*H*^{*b*}), 7.53 - 7.49 (t, *J* = 16Hz, 3H, Ph-*H*^{*c*}), 7.42 - 7.38 (t, *J* = 16Hz, 3H, Ph-*H*^{*d*}), 4.29 (s, 6H, Ph-*H*^{*e*}). ¹³C NMR (125 MHz, CDCl₃, 300 K, ppm) δ 81.51 (s), 81.19 (s), 80.87 (s), 52.62 (m).



Compound 2 was synthesized as follow. Firstly, 18-crown-6 (45 mg, 0.17 mmol) was added in the ice-cold suspension of Compound 1 (0.20 g, 0.57 mmol) and tBuOK (0.82 g, 7.31 mmol) in dry THF (15 mL) under an argon atmosphere. Then, iodoethane (0.75 mL, 9.36 mmol) was added dropwise, and the mixture was heated at 40 °C for another 2 h. Finally, the solution was cooled to 0 °C followed by adding iodoethane (0.75 mL, 9.36 mmol) again and heated at 40 °C for 20 h. After cooling to room temperature, the solution was poured into water and extracted with ethyl acetate. The organic phase was washed with saturated salt water and dried with anhydrous sodium sulfate. The solvent

was evaporated, and the residue was purified by silica gel column chromatography using petroleum ether as the eluent. Compound **2** is yellow solid (0.25 g, 85%). ¹H NMR (CDCl₃, 500 MHz): δ (ppm): 8.36 - 8.35 (d, J = 4Hz, 3H, Ph- H^a), 7.47 - 7.45 (d, J = 8Hz, 3H, Ph- H^b), 7.40 - 7.37 (m, J = 12Hz, 6H, Ph- H^c , Ph- H^d), 3.04 - 3.00 (d, J = 8Hz, 6H, Ph- H^e), 2.17 - 2.13 (d, 6H, Ph- H^f), 0.22 - 0.19(t, 18H, Ph- H^g). ¹³C NMR (125 MHz, CDCl₃, 300 K, ppm) δ 152.88 (s), 143.92 (s), 140.69 (s), 126.67 (s), 126.63, (s) 126.50 (s), 56.76 (s), 30.06 (s), 8.71 (s).



Compound 3 was synthesized under an air atmosphere. Typically, bromine (0.31 mL, 6 mmol) was added dropwise to a solution of compound **2** (0.51 g, 1 mmol) in CHCl₃ (10 mL) at 0 °C and stirred at room temperature for 16 h in the dark. Then the excess of bromine was removed by bubbling argon through the solution. The solution was poured into water and extracted with CH₂Cl₂. The combined organic phase was washed with saturated salt water and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residue was purified by silica gel column chromatography using petroleum ether as the eluent. The further purification of the product was carried out by recrystallization from ethanol to get Compound **3** as a white solid (0.70 g, 94%). ¹H NMR (CDCl₃, 500 MHz): δ (ppm): 8.17 - 8.15 (d, *J* = 8Hz, 3H, Ph-*H*^{*a*}), 7.57 (s, 3H, Ph-*H*^{*b*}), 7.53 - 7.51 (d, *J* = 8Hz, 3H, Ph-*H*^{*e*}), 2.93 - 2.89 (d, *J* = 12Hz, 6H, Ph-*H*^{*d*}), 2.12 - 2.08 (d, *J* = 12Hz, 6H, Ph-*H*^{*e*}), 0.22 - 0.19 (t, *J* = 12Hz, 18H, Ph-*H*^{*f*}). ¹³C NMR (125 MHz, CDCl₃, 300 K, ppm) δ 155.10 (s), 143.99 (s), 139.17 (s), 138.18 (s), 129.53 (s), 125.66 (s), 121.20 (s), 57.04 (s), 29.37 (s), 8.49 (s).



Ligand L, Compound 3 (410 mg, 0.6 mmol), and 3-tripyridine-phenylboric acid (968.7 mg, 2.7 mmol), sodium carbonate (523.8 mg, 4.9 mmol) and Pd(PPh₃)₂Cl₂ (95 mg, 0.09 mmol) were added to a 500 mL three-neck flask, and the entire reaction system was vacuumized and replaced with nitrogen three times to ensure that the entire reaction system was in a nitrogen atmosphere. Under these conditions, 120 mL toluene, 24 mL tert-butanol and 48 mL water were injected into the flask with a needle, followed by ultrasound to ensure that the reactants were evenly dispersed, and the reaction was stirred at 80 °C for 3 days. At the end of the reaction, it was cooled to room temperature and extracted with dichloromethane and saturated salt water to collect the organic phase. The organic phase was dried with anhydrous Na₂SO₄ and the solvent was removed by vacuum distillation. The crude product had poor solubility, so it was purified by dry column chromatography (SiO₂), and DCM/MeOH (100:0.5, v/v) was used as the eluent to obtain 687.3 mg white solid (70% yield). ¹H NMR (500 MHz, CDCl₃, 300 K, ppm) δ 8.83 (s, 6H, tpy- $H^{3',5'}$), 8.77 - 8.76 (d, J = 4Hz, 6H, tpy- $H^{6.6''}$), 8.72 - 8.70 (d, J = 8 Hz, 6H, tpy- $H^{3,3''}$), 8.51 - 8.49 (d, J = 8 Hz, 3H, Ph- H^{i}), 8.23 (s, 3H, Ph-Hg) 7.92 - 7.78 (m, 18H, tpy-H^{4,4}", Ph-H^d, Ph-H^h, Ph-H^b, Ph-H^e), 7.67 - 7.64 $(t, J = 12 \text{ Hz}, 3\text{H}, \text{Ph-H}^{f}), 7.39 - 7.36 (t, J = 12 \text{ Hz}, 6\text{H}, tpy-H^{5,5''}), 3.17 - 3.12 (d, J = 12 \text{ Hz}, 6\text{H}, tpy-H^{5,5''})$ 20 Hz, 6H, Ph- H^k), 2.35 - 2.30 (d, J = 20 Hz, 6H, Ph- H^j), 0.38 - 0.34 (t, J = 16Hz, 18H, Ph-H¹). 13C NMR (101 MHz, CDCl₃, 300 K) δ 156.34 (s), 156.03 (s), 153.72 (s), 150.64 (s), 149.17 (s), 144.53 (s), 129.43 (s), 127.93 (s), 126.38 (s), 125.68 (s), 123.86

(s), 121.46 (s), 119.26 (s), 57.11 (s), 29.70 (s), 8.78 (s). ESI-TOF (m/z): Calcd. for [C₁₀₂H₈₁N₉+H] ⁺: 1432.16. Found: 1432.16.



 ${}_{6}$ L₄: To a solution of ligand L (14 mg, 9.8 μmol) in CHCl₃ (6 mL), a solution of Fe(SO)₄·7H₂O (4.1 mg, 14.7 μmol) in MeOH (12 mL) was added, heat open for 20 minutes after adding ethylene glycol (15 mL). The mixture was stirred at 160 °C in thick-walled pressure resistant bottle for 8 h and then cooled to room temperature. then 10-fold excess NaSbF₆ was added for the anion exchange, a precipitate was formed and washed with water, dried in vacuum to give the product as a solid (18.6 mg, 94.3%). ESI-TOF (m/z): 1156.05 [M–6SbF₆-]⁶⁺ (calcd m/z: 1156.05), 970.19 [M–7SbF₆-]⁷⁺ (calcd m/z: 970.19), 830.79 [M–8SbF₆-]⁸⁺ (calcd m/z: 830.79), 722.37[M–9SbF₆-]⁹⁺ (calcd m/z: 722.37), 635.63 [M–10SbF₆-]¹⁰⁺ (calcd m/z: 635.63), 564.66 [M–11SbF₆-]¹¹⁺ (calcd m/z: 564.66), 505.53 [M–12SbF₆-]¹²⁺ (calcd m/z: 505.53).¹H NMR (500 MHz, CD₃CN, 300 K, ppm) δ 9.40 - 9.34 (br, 24H, tpy-*H*^{4,B3,5}), 8.79 - 8.69 (br, *J* = 40 Hz, 48H, tpy-*H*^{4,B3,3"}, Ph-*H*[§], 8.32 - 8.22 (br, *J* = 40 Hz, 48H, Ph-*H*^d, Ph-*H*^h, Ph-*H*[§], 8.00 - 7.93(br, *J* = 28 Hz, 36H, tpy-*H*^{4,B4,4"}, Ph-*H*^f), 7.32 - 7.12(br, *J* = 80Hz, 48H, tpy-*H*^{4,B6,6"}, tpy-*H*^{4,B5,5"}), 3.26(s, 24H, Ph-*H*^k), 2.55 (s, 24H, Ph-*H*^f), 0.40-0.37 (t, 72H, Ph-*H*^f).



Zn₆L₄: To a solution of ligand L (26 mg, 18.2 μmol) in CHCl₃ (6 mL), a solution of Zn(NO₃)₂·6H₂O (7.9 mg, 27.3 μmol) in MeOH (12 mL) was added. The mixture was stirred at 60 °C for 8 h and then cooled to room temperature. Then 10-fold excess NaSbF₆ was added for the anion exchange, a precipitate was formed and washed with water, dried in vacuum to give the product as a solid (30.0 mg, 96.0%). ESI-TOF (m/z): 1165.37 [M–6SbF₆-]⁶⁺ (calcd m/z: 1165.37), 978.31 [M–7SbF₆-]⁷⁺ (calcd m/z: 978.31), 837.76 [M–8SbF₆-]⁸⁺ (calcd m/z: 837.76), 728.67 [M–9SbF₆-]⁹⁺ (calcd m/z: 728.67), 641.20 [M–10SbF₆-]¹⁰⁺ (calcd m/z: 641.20), 569.82 [M–11SbF₆-]¹¹⁺ (calcd m/z: 569.82), 510.32 [M–12SbF₆-]¹²⁺ (calcd m/z: 510.32). ¹H NMR (500 MHz, CD₃CN, 300 K, ppm) δ 9.17 - 9.14 (br, 24H, tpy- $H^{4,B3',5'}$), 8.85 - 8.79 (br, 24H, tpy- $H^{4,B3,3'}$), 8.66 - 8.64 (br, 24H, Ph- H^i , Ph- H^s), 8.25 - 8.15 (br, 72H, tpy- $H^{4,B4,4''}$, Ph- H^i , Ph- H^h , Ph- H^b , Ph- H^e), 7.93 - 7.88 (br, J = 20Hz, 36H, tpy- $H^{4,B6,6''}$, Ph- H^i), 0.38 - 0.35 (t, 72H, Ph- H^i).



Cd₆L₄: To a solution of ligand L (2.9 mg, 2.03 µmol) in CHCl₃ (5 mL), a solution of Cd(NO₃)₂·4H₂O (0.937 mg, 3.05 µmol) in MeOH (10 mL) was added. The mixture was stirred at 60 °C for 8 h and then cooled to room temperature. Then 10fold excess NaSbF₆ was added for the anion exchange, a precipitate was formed and washed with water, dried in vacuum to give the product as a solid (3.61 mg, 96.5%). ESI-TOF (m/z): 1212.56 [M-6SbF₆-]⁶⁺ (calcd m/z: 1212.56), 1018.61 [M-7SbF₆-]⁷⁺ (calcd m/z: 1018.61), 873.16 [M-8SbF₆-]⁸⁺ (calcd m/z: 873.16), 760.02 [M-9SbF₆-]⁹⁺ (calcd m/z: 760.02), 669.51 [M–10SbF₆-]¹⁰⁺ (calcd m/z: 669.51), 595.46 $[M-11SbF_{6}-]^{11+}$ (calcd m/z: 595.46), 533.76 $[M-12SbF_{6}-]^{12+}$ (calcd m/z: 533.76). ¹H NMR (500 MHz, CD₃CN, 300 K, ppm), CD₃CN, 300 K, ppm) δ 9.09 (s, 24H, tpy- $H^{3',5'}$), 8.85-8.84 (d, 24H, tpy- $H^{3,3''}$), 8.64-8.58 (br, J = 24Hz, 24H, Ph- H^i , Ph- H^g), 8.24-8.16 (br, 96H, tpy-H^{4,4}", Ph-H^d, Ph-H^h, Ph-H^b, Ph-H^e, tpy-H^{6,6}"), 7.91-7.90 (br, 12H, Ph- H^{0}), 7.58-7.53 (br, 24H, tpy- $H^{5,5''}$), 3.20 (s, J = 12Hz, 24H, Ph- H^{k}), 2.49 (s, J12Hz, 24H, Ph-*H*^ℓ), 0.36-0.33 72H, Ph- H^l). (t,



4. ESI-MS spectra data of supramolecules (SbF₆⁻ as counterion)

Figure S1. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from $[Fe_6L_4]$ (SbF₆⁻ as counterion).



Figure S2. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from $[Zn_6L_4]$ (SbF₆-as counterion).



Figure S3. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from $[Cd_6L_4]$ (SbF₆-as counterion).

5. ¹H NMR, ¹³C NMR, ¹H-¹H COSY NMR, ¹H-¹H NOESY NMR, ¹H-¹H

DOSY NMR, Variable temperature NMR



ure **S5.** ¹³C NMR (101 MHz, CDCl₃, 300 K) spectrum of compound **1.**



Figure S7. ¹³C NMR (101 MHz, CDCl₃, 300 K) spectrum of compound 2.



Figure **S9.** ¹³C NMR (101 MHz, CDCl₃, 300 K) spectrum of compound **3.**



Figure S11. ¹³C NMR (101 MHz, CDCl₃, 300 K) spectrum of L.



Figure S12. ¹H NMR (500 MHz, CDCl₃, 300 K) spectrum of Fe₆L₄.



Figure S13. ¹H NMR (101 MHz, CDCl₃, 300 K) spectrum of Fe₆L₄ (aromatic region).



Figure S15. ¹H NMR (500 MHz, CDCl₃, 300 K) spectrum of Zn₆L₄ (aromatic region).



Figure S16. ¹H NMR (500 MHz, CDCl₃, 300 K) spectrum of Cd₆L₄.



gure S17. ¹H NMR (500 MHz, CDCl₃, 300 K) spectrum of Cd₆L₄(aromatic region).



Figure S18. ¹H NMR (500 MHz, DMSO-d₆, 300 K) spectrum of L.





Figure S19. ¹H NMR (500 MHz, DMSO-d₆, 300 K) spectrum of Fe₆L₄.

Figure S20. ¹H NMR (500 MHz, DMSO-d₆, 300 K) spectrum of Zn₆L₄.





Figure S21. ¹H NMR (500 MHz, DMSO-d₆, 300 K) spectrum of Cd₆L₄.

Figure **S22.** 2D COSY NMR (500 MHz, CDCN₃, 300 K) spectrum of Fe_6L_4 (aromatic region).



Figure **S23.** 2D NOESY NMR (500 MHz, CDCN₃, 300 K) spectrum of Fe_6L_4 (aromatic region).



Figure S24. 2D COSY NMR (500 MHz, CDCN₃, 300 K) spectrum of Cd_6L_4 (aromatic region).



Figure S25. 2D NOESY NMR (500 MHz, CDCN₃, 300 K) spectrum of Cd_6L_4 (aromatic region).



Figure S27. DOSY NMR (500 MHz, CD₃CN 300 K) spectrum of Zn₆L₄.

 $R = \frac{kT}{6\pi\mu D}$



Figure **S28**. DOSY NMR (500 MHz, CD₃CN 300 K) spectrum of Cd_6L_4 .

$$\mathbf{R} = \frac{kT}{6\pi\mu D}$$

 $D = 10^{-9.5}$

- $k = 1.38 \times 10^{-23} \text{ N m K}^{-1}$
- T = 300 K
- $\mu = 3.43 \times 10^{-4} \text{ N m}^{-2} \text{ s (CD}_3 \text{CN)}$
- $R\approx 2.02\times 10^{-9}\,m$ =2.02 nm

The sphere's hydrodynamic radius was estimated according to the Stokes-Einstein Equation, where D is the diffusion constant, k is the Boltzmann's constant, T is the temperature, μ is the viscosity of solvents, and R is the radius.



Figure S30. ¹H NMR (500 MHz, CD₃CN) spectra of Zn₆L₄.



Figure S31. ¹H NMR (500 MHz, CD₃CN) spectra of Cd₆L₄.



Figure **S32**. (a), (b), (c) and (d) Four isomers of $\mathbb{Z}n_6L_4$. (e) Clockwise and anticlockwise rotation planes.

6. TEM images of supramolecular (SbF₆⁻ as counterion)



ure S33. TEM images of Fe_6L_4 on the lacey carbon coated Cu grid.



ure S34. TEM images of Zn_6L_4 on the lacey carbon coated Cu grid.



ure S35. TEM images of Cd_6L_4 on the lacey carbon coated Cu grid.



7. UV Vis and fluorescence emission spectra of L and supramolecules

Figure S36. (a) Fluorescence spectrum of Cd_6L_4 (($\lambda_{ex} = 325 \text{ nm}, c = 1.0 \times 10^{-6} \text{ M}$), (b) quantum yields of Cd_6L_4 , (c) photographs of Cd_6L_4 in DMF/CHCl₃ with various fractions.



Figure S37. (a) Fluorescence spectrum of $\mathbf{Zn}_6\mathbf{L}_4$ (($\lambda_{ex} = 325 \text{ nm}, c = 1.0 \times 10^{-5} \text{ M}$), (b) quantum yields of $\mathbf{Zn}_6\mathbf{L}_4$, (c) photographs of $\mathbf{Zn}_6\mathbf{L}_4$ in DMSO/CHCl₃ with various fractions.



Figure S38. (a) Fluorescence spectrum of Cd_6L_4 ($\lambda_{ex} = 325$ nm, c = 1.0×10^{-5} M), (b) quantum yields of Cd_6L_4 , (c) photographs of Cd_6L_4 in DMSO/CHCl₃ with various fractions.

Reference

 M.-Y. Wang, Q.-J. Zhang, Q.-Q. Shen, Q.-Y. Li and S.-J. Ren, *Chin. J. Polym. Sci.*, 2020, **38**, 151-157.

2. Y. Zeng, J. Shi, Z. Wang, X. Zhang, J. Li, H. Su, F. Fang, H. Zhang and M. Wang, *Inorg. Chem.*, 2023, **62**, 17150-17156.

3. Y.-T. Chan, X. Li, J. Yu, G. A. Carri, C. N. Moorefield, G. R. Newkome and C. Wesdemiotis, *J. Am. Chem. Soc.*, 2011, **133**, 11967-11976.

 C. Wang, X.-Q. Hao, M. Wang, C. Guo, B. Xu, E. N. Tan, Y.-Y. Zhang, Y. Yu, Z.-Y. Li, H.-B. Yang, M.-P. Song and X. Li, *Chem. Sci.*, 2014, 5, 1221-1226.