

Supporting Information

Self-assembly of zirconocene-based metal-organic capsules: structure, luminescence sensing of Fe³⁺ and iodine capture

Siyuan Chen, Shuangjing Cheng, Liang Zhao*, Chunyi Sun, Chao Qin* and Zhongmin Su*

Key Laboratory of Polyoxometalate Science, Institute of Functional Material Chemistry, National & Local United Engineering Laboratory for Power Battery, Northeast Normal University, Changchun, Jilin, 130024, P. R. China.

Materials and physical measurements

All the chemicals and solvents were purchased from chemical suppliers without further purification. The ligand H₂ADA was synthesized according to the literature.¹ Elemental analyses of (C, H, and N) were performed on a Per-Elmer 2400 CHN elemental analyzer. PXRD patterns were tested on a Siemens D5005 diffractometer with graphite monochromatized Cu K α ($\lambda=1.5418$ Å) radiation. The Fourier transform infrared (FT-IR) spectra were measured from 4000 to 400 cm⁻¹ using KBr pellets with an Alpha Centauri FT/IR spectrophotometer. Thermogravimetric analyses (TGA) of the samples were recorded on a Perkin-Elmer TG-7 analyzer and heated from 25 °C to 800 °C with a heating rate of 10 °C min⁻¹ under dry nitrogen flow. The UV-Vis absorption spectra were measured on a Shimadzu UV-2550 spectrophotometer in the wavelength range of 200-800 nm. Photoluminescence properties were measured on a fluorescence spectrophotometer (Cary Eclipse) at room temperature.

Synthesis and Method

Synthesis of Zr-MC-1 (1) 1, 4-benzenedicarboxylic acid (1, 4-H₂BDC) (20 mg, 0.12 mmol) and bis(cyclopentadienyl)zirconium dichloride (Cp₂ZrCl₂) (20 mg, 0.07 mmol) were dissolved in 1 mL N, N-diethylformamide (DMA) followed by the addition of 3 drops of H₂O. After sonication for 3 minutes, the clear solution of the mixture was heated at 65 °C for 10 h. After cooling to room temperature slowly, colorless cubic block crystals were obtained and washed with DMA three times. The yield is 75% based on 1, 4-H₂BDC. Elemental analysis (%) for C₅₈H₅₉Cl₂NO₂₂Zr₆, calcd: C 40.03, H 3.39, N 0.80; found: C 40.31, H 3.30, N 0.94. IR

(KBr, cm^{-1}): 3108 (m), 1624 (m), 1555 (s), 1504(m), 1406 (s), 1018(m), 813 (m), 749 (m), 696 (w), 607 (m), 547 (m), 507 (m), 471 (m), 411 (s).

Synthesis of Zr-MC-2 (2) 4, 4-stilbenedicarboxylic acid (4, 4-H₂SDC) (5 mg, 0.02 mmol) and bis(cyclopentadienyl)zirconium dichloride (Cp₂ZrCl₂) (17.5 mg, 0.06 mmol) were dissolved in 1 mL N, N-diethylformamide (DEF) and 6 drops of distilled water. After sonication for 3 minutes, the mixture was heated at 60 °C for 8 h. After cooling to room temperature slowly, colorless parallelogram crystals were obtained and washed with DEF three times. The yield is 80% based on 4, 4-H₂SDC. Elemental analysis (%) for C_{85.5}H_{83.5}Cl₂N_{2.5}O_{22.5}Zr₆, calcd: C 48.34, H 3.93, N 1.65; found: C 48.63, H 4.03, N 1.41. IR (KBr, cm^{-1}): 2975 (m), 1645 (m), 1604 (m), 1582(m), 1527 (s), 1420 (s), 1265 (m), 1182 (w), 1104 (w), 1017 (m), 815 (m), 786 (m), 711 (w), 614 (m), 475 (m), 437 (w).

Synthesis of Zr-MC-3 (3) Azobenzene-4, 4-dicarboxylic acid (4, 4-H₂ADA) (14 mg, 0.05 mmol) and bis(cyclopentadienyl)zirconium dichloride (Cp₂ZrCl₂) (20 mg, 0.07 mmol) were dissolved in 1.5 mL N, N-dimethylformamide (DMF) followed by the addition of 3 drops of H₂O. After sonication for 3 minutes, the clear solution of the mixture was heated at 60 °C for 10 h. After cooling to room temperature slowly, salmon fusiform crystals were obtained and washed with DMF three times. The yield is 83% based on 4, 4-H₂ADA. Elemental analysis (%) for C₇₈H₇₄Cl₂N₈O₂₂Zr₆, calcd: C 44.75, H 3.56, N 5.35; found: C 45.03, H 3.83, N 5.28. IR (KBr, cm^{-1}): 3430 (m), 1656 (m), 1592 (m), 1536(s), 1496 (w), 1421 (s), 1098 (w), 1015 (m), 872 (w), 814 (m), 791 (m), 711 (w), 611 (m), 475 (m).

Single-crystal X-ray Crystallography

Single-crystal X-ray diffraction data for **1-3** were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program.² The structures of **1-3** were solved by direct methods and refined on F^2 by full-matrix least-squares methods by using the SHELXL-2014 program.³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. The SQUEEZE routine of the PLATON software suite was used to remove the disordered solvent molecules of **1-3**. We calculated the final chemical formula using the elemental analysis and TGA data.

Chemical sensing of metal ions

Titration experiments of metal ions were carried out by adding different concentration of metal salt solutions (10 μL) into the methyl alcohol solution (1 mL) containing **Zr-MC-2** (1 mg/mL) at intervals of 5 minutes.

Fluorescence spectra were recorded after the addition of metal salt solutions. The excitation wavelength is 330 nm.

The fluorescence quenching was analyzed using the Stern-Volmer equations:

$$I_0/I = 1 + K_{sv} [Q]$$

where I_0 and I are the fluorescence intensity, in the absence and presence of analyte, respectively,

K_{sv} is the Stern-Volmer quenching constant and $[Q]$ is the concentration of analyte. The quenching percentage was calculated using the equation as follows:

$$\text{Fluorescence quenching \%} = (1 - I/I_0) \times 100 \%$$

where I_0 is the initial fluorescence intensity in the absence of metal ions, I is the fluorescence intensity in the presence of corresponding analyte.

Notes and references

- 1 Y. Hong, Z. Gao, M. Chen, J. Hao and S. Dong, *Langmuir*, 2018, **34**, 9435-9441.
- 2 R. H. Blessing, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, **51**, 33-38.
- 3 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3-8.

Figures

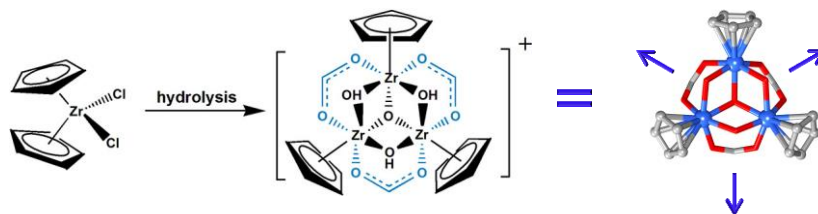


Fig. S1 Diagrammatic sketch of the formation of trinuclear $\text{Cp}_3\text{Zr}_3(\mu_3\text{-O})(\mu_2\text{-OH})_3$ SBU.

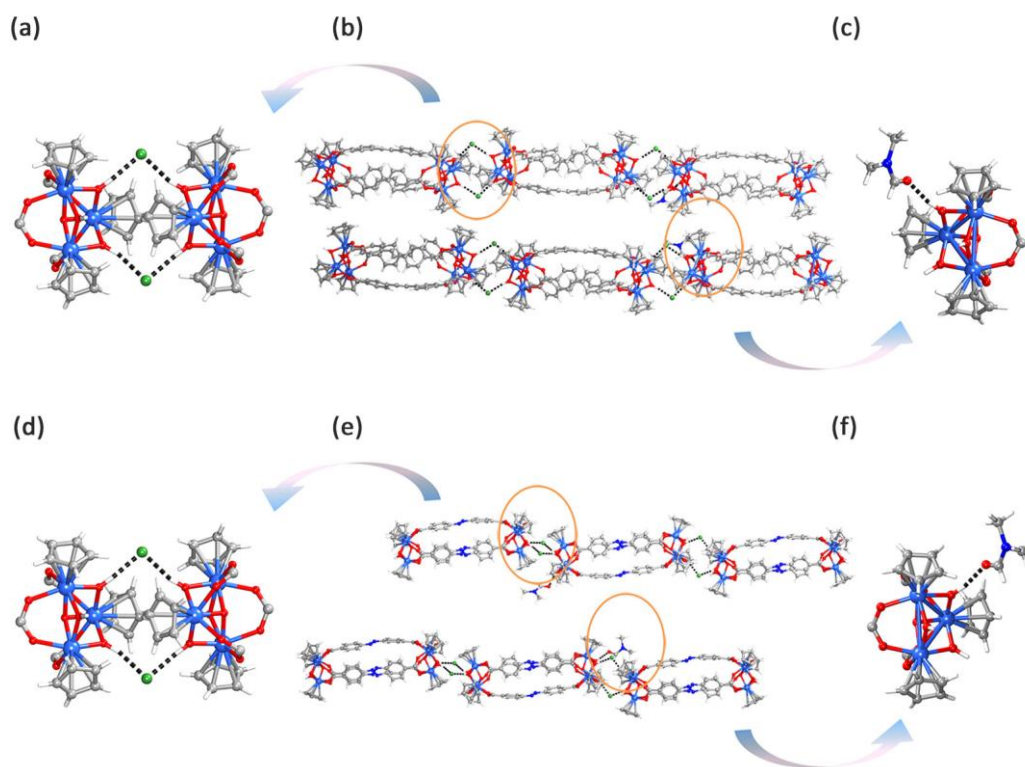


Fig. S2 Hydrogen bonds in **Zr-MC-2** (a) (c) and 3D stacking of **Zr-MC-2** (b); Hydrogen bonds in **Zr-MC-3** (d) (f) and 3D stacking of **Zr-MC-3** (e).

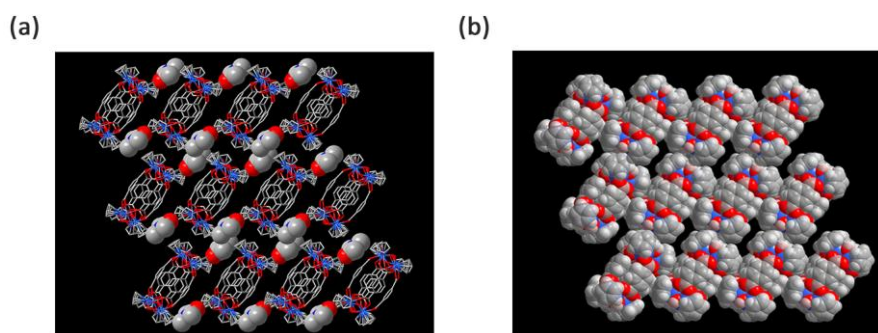


Fig. S3 (a) (b) 3D Packing patterns of **Zr-MC-1**. The potential solvent accessible area of the coordination framework, calculated by the PLATON program, is 24.8% for **Zr-MC-1**. (Probe radius = 1.2 Å)

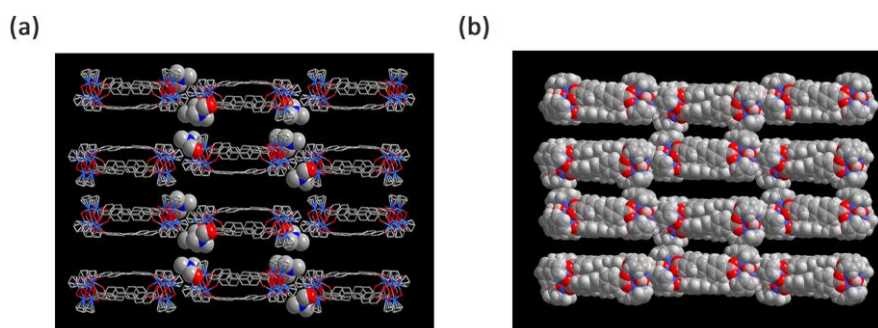


Fig. S4 (a) (b) 3D Packing patterns of **Zr-MC-2**. The potential solvent accessible area of the coordination framework, calculated by the PLATON program, is 28.0% for **Zr-MC-2**. (Probe radius = 1.2 Å)

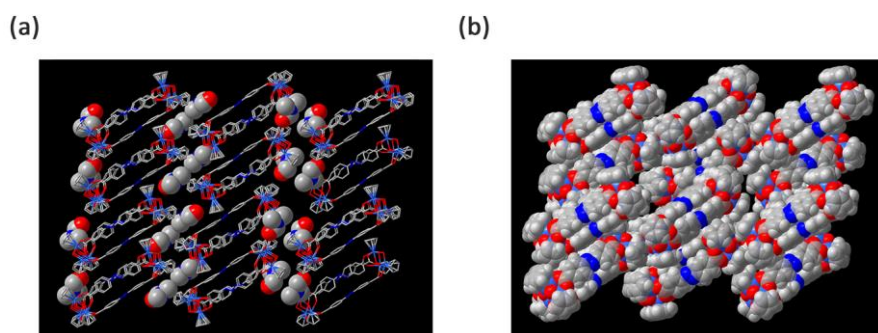


Fig. S5 (a) (b) 3D Packing patterns of **Zr-MC-3**. The potential solvent accessible area of the coordination framework, calculated by the PLATON program, is 8.7% for **Zr-MC-3**. (Probe radius = 1.2 Å)

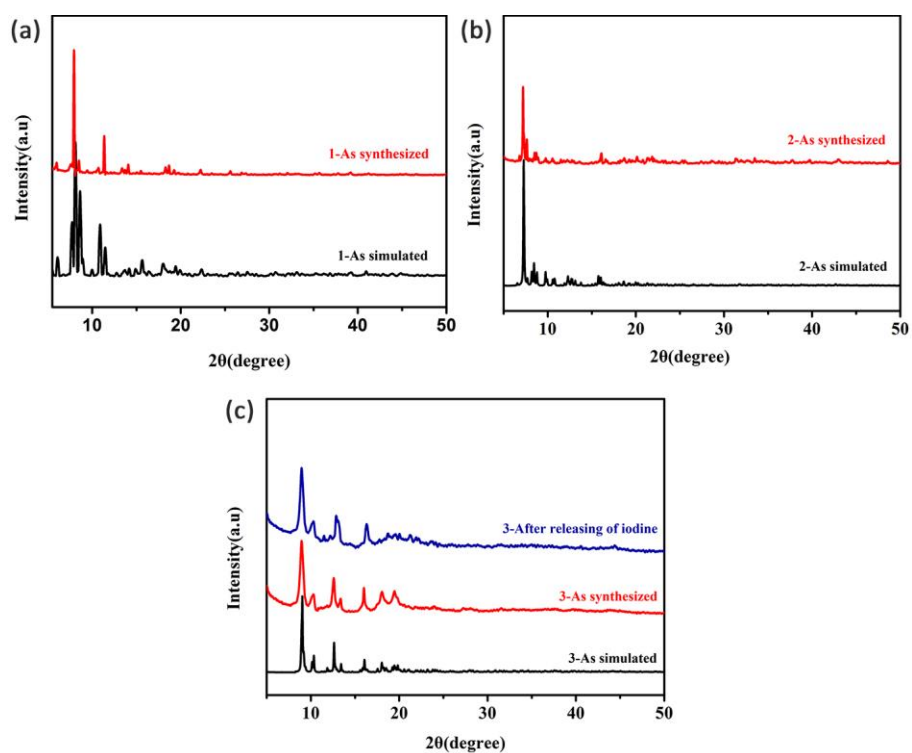


Fig. S6 PXR D patterns of **Zr-MC-1** (a), **Zr-MC-2** (b), and **Zr-MC-3** (c) with simulated (black), the synthesized (red) and recovered sample (blue).

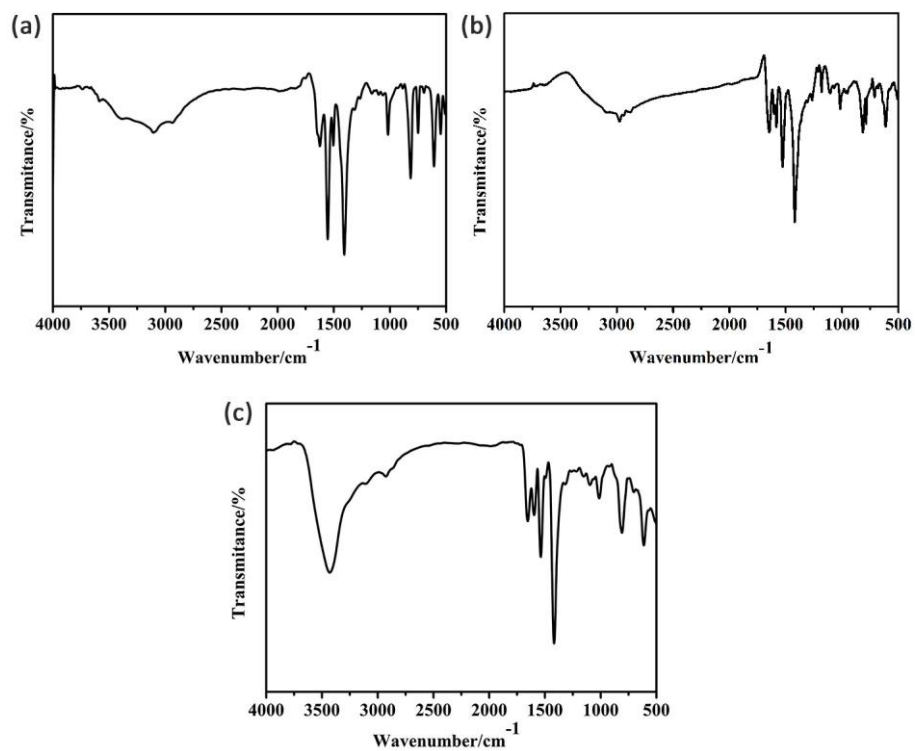


Fig. S7 IR spectra of **Zr-MC-1** (a), **Zr-MC-2** (b), and **Zr-MC-3** (c).

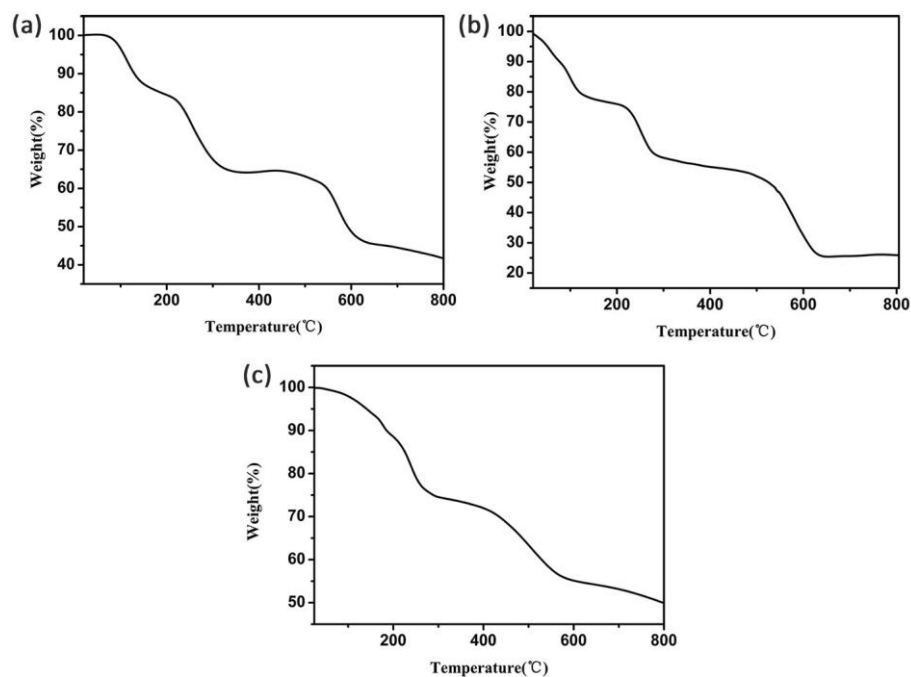


Fig. S8 TGA of Zr-MC-1 (a), Zr-MC-2 (b), and Zr-MC-3 (c).

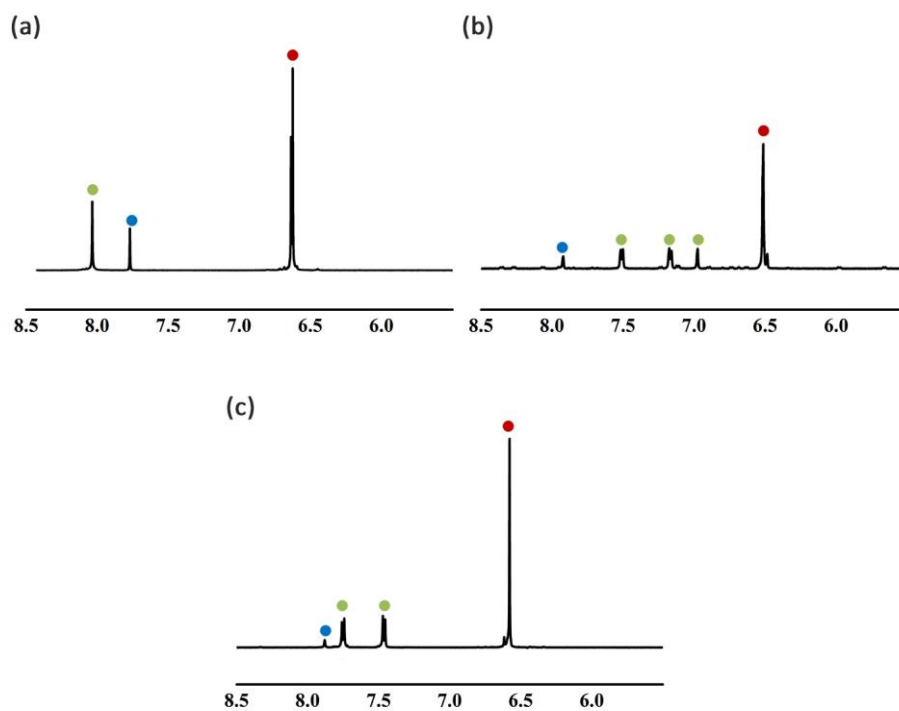


Fig. S9 ^1H NMR analysis of Zr-MC-1 (a), Zr-MC-2 (b), and Zr-MC-3 (c) in Methanol- d_4 . Blue, green, and red dots indicate residual DMF, ligand, and cyclopentadienyl resonances, respectively.

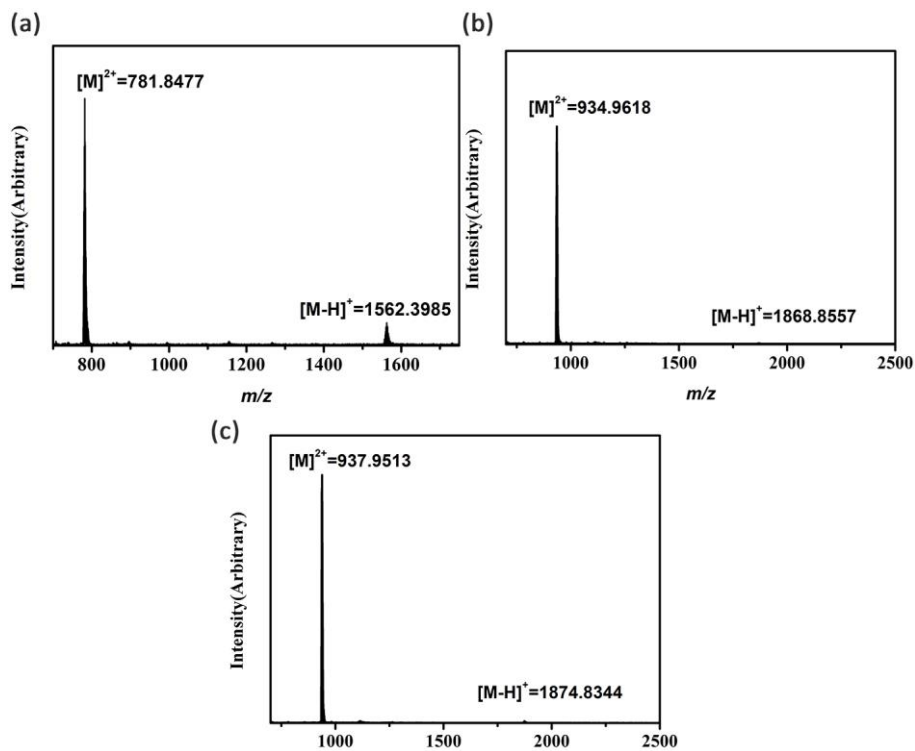


Fig. S10 Mass spectrometry image of Zr-MC-1 (a), Zr-MC-2 (b), and Zr-MC-3 (c) in methanol.

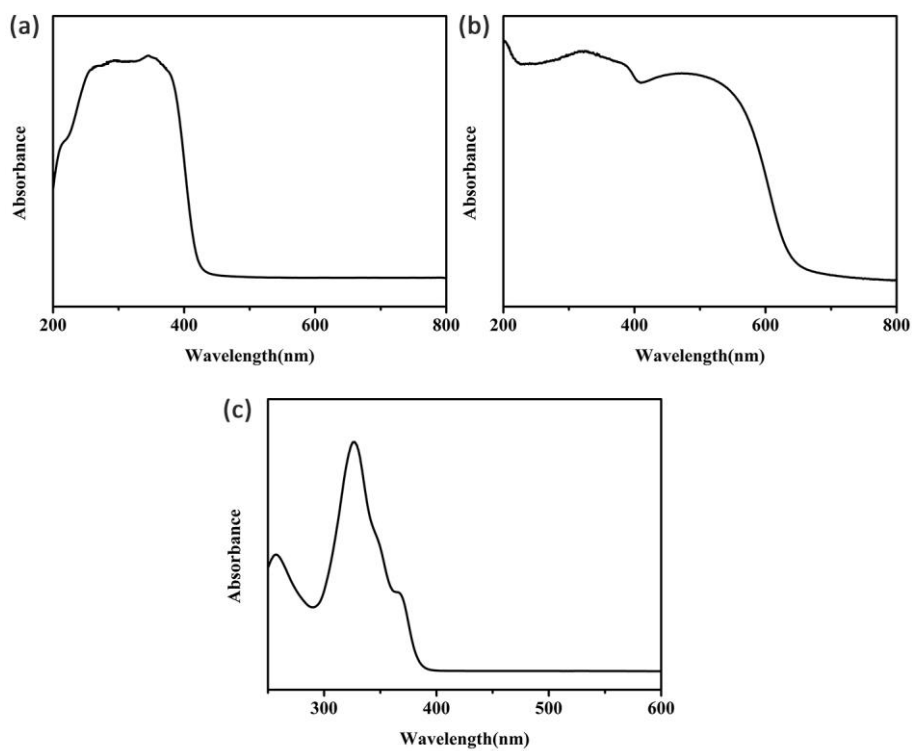


Fig. S11 Solid-state UV-Vis absorption spectra of Zr-MC-2 (a) and Zr-MC-3 (b). Liquid-state UV-Vis absorption spectra of Zr-MC-2 (c).



Fig. S12 Fluorescence photograph of Zr-MC-2 in the presence of the different metal ions under 365 nm UV-lamp.

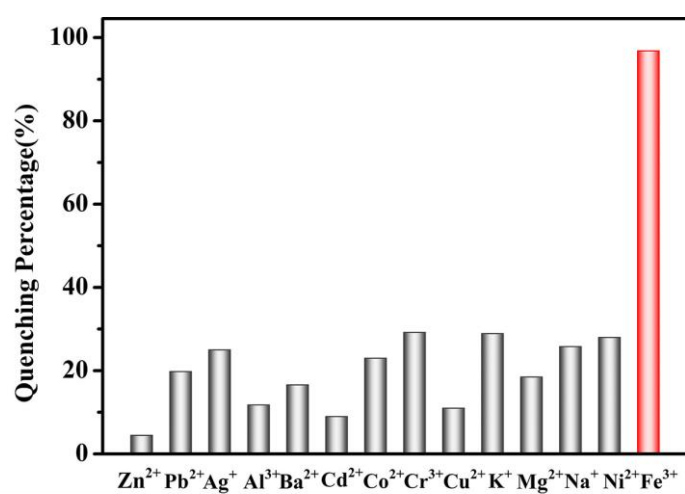


Fig. S13 Quenching efficiency of Zr-MC-2 after the addition different metal cations (300 μ M).

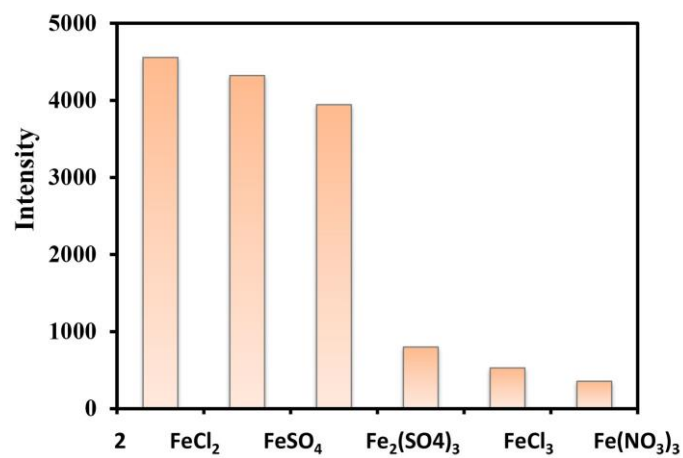


Fig. S14 Luminescence intensity of Zr-MC-2 (5 mg) immersed in the different metal salt solutions (5 mL).

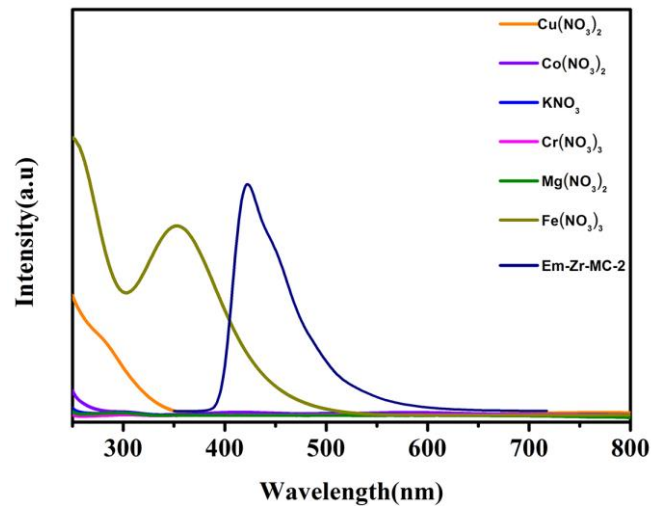


Fig. S15 Spectral overlap between the emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) or excitation ($\lambda_{\text{em}} = 435 \text{ nm}$) spectrum of **Zr-MC-2** and the absorption spectra of metal ions.

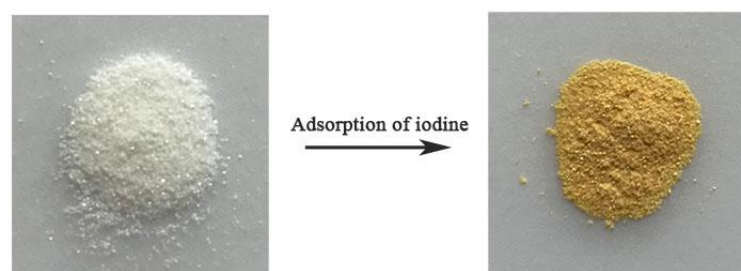


Fig. S16 Photographs of **Zr-MC-1** (left) and I_2 @**Zr-MC-1** (right).

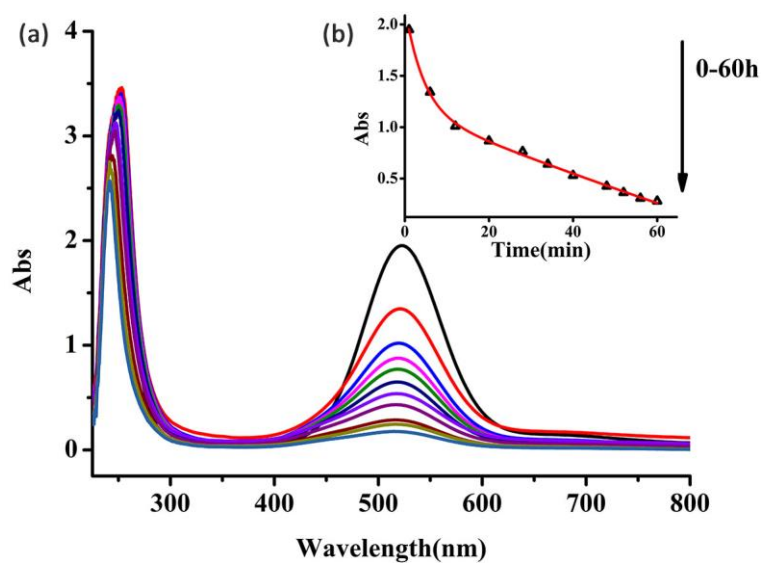


Fig. S17 (a) The UV-Vis spectra of **Zr-MC-1** for the adsorption process of iodine. (b) Absorption curves vs. time.

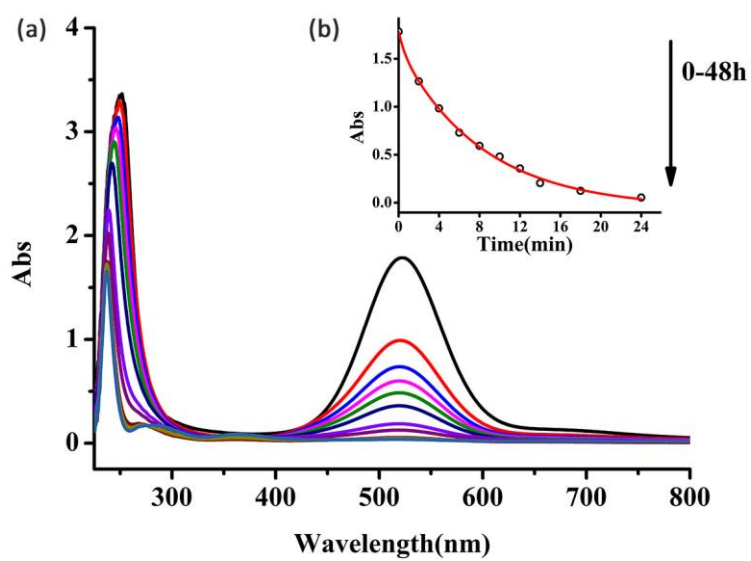


Fig. S18 (a) The UV-Vis spectra of **Zr-MC-3** for the adsorption process of iodine. (b) Absorption curves vs. time.

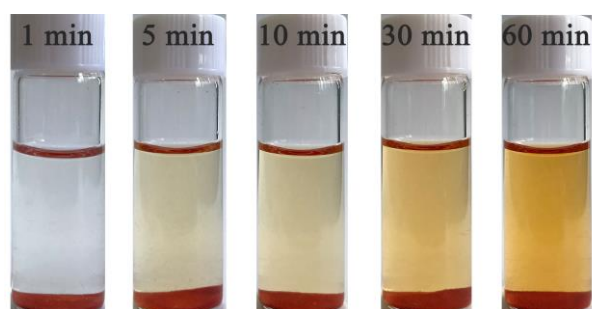


Fig. S19 Photographs of the I_2 release process over time of **Zr-MC-3** in 3 mL acetonitrile solution.

Table S1. Crystal data and structure refinement for **Zr-MC-1**, **Zr-MC-2**, and **Zr-MC-3**.

Complex	Zr-MC-1	Zr-MC-2	Zr-MC-3
Formula	C ₅₈ H ₅₉ Cl ₂ NO ₂₂ Zr ₆	C _{85.5} H _{83.5} Cl ₂ N _{2.5} O _{22.5} Zr ₆	C ₇₈ H ₇₄ Cl ₂ N ₈ O ₂₂ Zr ₆
Formula weight	1740.28	2124.26	2093.67
Temperature (K)	173.02	173.02	173.02
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P2 ₁ /c
<i>a</i> (Å)	14.7990(8)	10.7932(8)	39.583(5)
<i>b</i> (Å)	16.2691(10)	23.6272(15)	11.3619(16)
<i>c</i> (Å)	17.0541(9)	25.0116(18)	19.236(3)
α (°)	72.965(2)	67.089(3)	90
β (°)	80.879(3)	78.072(3)	91.681(8)
γ (°)	80.069(3)	77.205(3)	90
Volume (Å ³)	3841.6(4)	5677.5(7)	8648(2)
<i>Z</i>	2	2	4
ρ_{calc} (g/cm ³)	1.504	1.243	1.608
μ (mm ⁻¹)	0.917	0.634	6.911
<i>F</i> (000)	1728.0	2136.0	4192.0
Radiation	Mo K α (λ = 0.71073 Å)	Mo K α (λ = 0.71073 Å)	Cu K α (λ = 1.54178 Å)
2 θ range for data collection (°)	5.264 to 50.226	4.544 to 50.192	6.702 to 134.318
Reflections collected	66772	84261	60829
Independent reflections	13621	20012	14959
Goodness-of-fit on <i>F</i> ²	1.035	1.026	1.072
Final R indexes [<i>I</i> >= 2 σ (<i>I</i>)]	R ₁ = 0.0630 wR ₂ = 0.1449	R ₁ = 0.0693 wR ₂ = 0.1836	R ₁ = 0.0879 wR ₂ = 0.1809
Final R indexes (all data)	R ₁ = 0.1459 wR ₂ = 0.1963	R ₁ = 0.1111 wR ₂ = 0.2087	R ₁ = 0.1624 wR ₂ = 0.2102
R _{int}	0.1279	0.0937	0.1202

$${}^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^b wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}.$$