Supporting Information

Unusual microporous polycatenane-like metal-organic frameworks for the luminescent sensing of Ln³⁺ cations and rapid adsorption of iodine

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S1. Materials and Instrumentation

Chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) was carried out with an X-ray diffractometer of Rigaku, Rint 2000. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000 °C at a ramp rate of 5 °C/min under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 spectrometer. ICP was measured by ICP-9000(N+M) (USA Thermo Jarrell-Ash Corp).

S2. Syntheses of Organic Ligands H₄Lⁿ



Scheme S1. Two-step synthesis routes of H_3L^1 .

Synthesis of H₃L¹.

The first step: A mixture of ethyl 4'-hydroxybiphenyl-4-carboxylate (3.96 g, 30.0 mmol), 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (7.26 g, 30.0 mmol), and K_2CO_3 (16.58 g, 120 mmol) in *N*,*N*-dimethylformamide (DMF) (50 mL) was heated under vigorous stirring at 120 °C for 72 h. The reaction mixture was cooled to room temperature and then poured into 200 mL of water. A white solid of triethyl 4',4",4"'-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tribiphenyl-4-carboxylate formed immediately, which was isolated by filtration in 92% yield after drying in vacuum.

The second step: In a round bottom flask, triethyl 4',4",4"'-(2,4,6-trimethylbenzene -1,3,5-triyl)tris(methylene)tribiphenyl-4-carboxylate (8.34 g, 10 mmol) was dissolved in tetrahydrofuran (THF) (150 mL) and a solution of KOH (11.22 g, 200 mmol) in H₂O (50 mL) was added. This mixture was refluxed for 12 h. After cooling down to room temperature, the THF was evaporated and the resulting water phase was acidified with conc. HCl until no further precipitate was detected. The slightly white solid4',4",4"'-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tribiphenyl-4-carboxy lic acid (H_3L^1) was collected by filtration, washed with water and dried in vacuum (91%). IR (cm⁻¹): 2982 (m), 1685 (s), 1602 (s), 1523 (m), 1492 (s), 1422 (m), 1236 (s), 1183 (s), 1114 (m), 1025 (w), 986 (m), 827 (m), 722 (w), 702 (w), 547 (w), 495 (w).



Scheme S2. Two-step synthesis routes of H_3L^2 .

Synthesis of H_3L^2 .

 H_3L^2 was prepared in the same way as H_3L^1 by using the corresponding ethyl 3-(4-hydroxyphenyl)acrylate instead of ethyl 4'-hydroxybiphenyl-4-carboxylate. IR (cm⁻¹): 2958 (m), 1679 (m), 1628 (s), 1598 (s), 1508 (s), 1423 (m), 1367 (m), 1305 (m), 1240 (s), 1167 (s), 1026 (w), 983 (m), 866 (w), 827 (m), 670 (w), 516 (w).

S3. Synthesis of Compounds.

Synthesis of IFMC-10.

A solid mixture of H_3L^1 (0.160 g, 0.2 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.119 g, 0.4 mmol) and HBF₄ (0.5 ml) was dissolved in DMF (10 mL) in a 15 mL Teflon-lined stainless steel container. The clear reaction solution was heated in an isotherm oven at 85 °C for 72 h resulting in yellow crystals, which were isolated by washing with DMF and were immersed in dichloromethane for 24 h. After the removal of dichloromethane by decanting, the sample was dried under a dynamic vacuum at room temperature overnight. Yield: 81% based on 1 mol of H_3L^1 . IR (cm⁻¹): 3028 (m), 2859 (m), 2797 (m), 2500 (w), 1591 (s), 1466 (m), 1362 (s), 1240 (m), 1187 (m), 1096 (w), 1025 (m), 986 (w), 898 (w), 800 (s).

Synthesis of IFMC-11.

Compound **IFMC-11** was prepared in the same way as compound **IFMC-10** by using the corresponding H_3L^2 instead of H_3L^1 . Yield: 75 % based on 1 mol of H_3L^2 . IR (cm⁻¹): 3438 (m), 2982 (m), 1658 (s), 1599 (s), 1508 (m), 1393 (s), 1299 (m), 1235 (s), 1170 (m), 1096 (w), 1025 (w), 984 (m), 869 (w), 830 (w), 803 (w), 4660 (w), 568 (w).

S4. X-ray Crystallography

Single-crystal X-ray diffraction data for **IFMC-10** and **IFMC-11** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated MoK_{α} radiation ($\lambda = 0.71069$ Å) at 293K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97¹ and refined by full-matrix least-squares techniques using the SHELXL-97 program² within WINGX.³ Non-hydrogen atoms were refined with anisotropic temperature parameters. The SQUEEZE program implemented in PLATON was used to remove these electron densities for **IFMC-10**. Thus, all of electron densities from free solvent molecules have been "squeezed" out, while for the coordinated water molecules.⁴

The detailed crystallographic data and structure refinement parameters for **IFMC-10** (CCDC 855123) and **IFMC-11** (CCDC 855124) as following:

Table S1. Crystal data and structure refinements for compounds IFMC-10 and IFMC-11.

Compound	IFMC-10	IFMC-11
Formula	$C_{54}H_{48}N_2O_{14}Zn_2$	$C_{39.6}H_{36.4}N_{1.2}O_{13.2}Zn_2$
Formula weight	<mark>1079.68</mark>	<mark>870.94</mark>
Crystal system	Tetragonal	Tetragonal
Space group	<u>141/a</u>	<u>I41/a</u>
<mark>λ (Å)</mark>	<mark>0.71069</mark>	<mark>0.71069</mark>
a (Å)	25.502(4)	24.337(3)
<mark>b (Å)</mark>	25.502(4)	24.337(3)
<u>с (Å)</u>	49.611(7)	39.257(4)
<mark>α (°)</mark>	<mark>90</mark>	<mark>90</mark>
<mark>β (°)</mark>	<mark>90</mark>	<mark>90</mark>
<mark>γ (°)</mark>	<mark>90</mark>	<mark>90</mark>
V(Å ³)	32265(8)	23252(4)
z	<mark>16</mark>	<mark>16</mark>
d _{calc} (Mg cm ⁻³)	<mark>0.889</mark>	<mark>0.995</mark>
$\mu(\text{mm}^{-1})$	<mark>0.638</mark>	<mark>0.870</mark>
<u><i>T</i>(K)</u>	<mark>293(2)</mark>	<mark>293(2)</mark>
F(000)	<mark>8928</mark>	7167
Reflections	135406 / 18397	<mark>99484 / 13128</mark>
collected/unique	$[R_{int} = 0.0934]$	$[R_{int} = 0.0715]$
Data/restraints/parameters	<mark>18397 / 1 / 567</mark>	<mark>13128 / 19 / 459</mark>
$R_1, wR_2 [I > 2\sigma(I)]$	<mark>0.0906, 0.2611</mark>	<mark>0.1497, 0.3887</mark>
R_1 , wR_2 (all data)	<mark>0.2846, 0.3250</mark>	<mark>0.2642, 0.4431</mark>
Goodness-of-fit	<mark>0.894</mark>	1.227



Fig. S1 The coordination environment of Zn in IFMC-10 (a) and IFMC-11 (b), respectively.



Fig. S2 (a) and (b) View of the (6,3) layer showing hexagon window with the corresponding sizes in **IFMC-10** and **IFMC-11**, respectively.



Fig. S3 The sizes of porous in the 2D \rightarrow 2D nets in IFMC-10 (a) and IFMC-11 (b). The $(L^1)^{3-}$ or $(L^2)^{3-}$ ligands link three $[Zn_2(CO_2)_3]$ units to generate a 2D infinite wavelike (6,3) layer, with the dimensions of three sizes and the longest diagonal in the large 6-membered ring being 15.86Å, 15.86Å, 15.86Å and 34.25Å in IFMC-10 (a) and 13.75Å, 13.78Å, 13.87Å and 29.51Å in IFMC-11 (b), respectively.



Fig. S4 Space-filling views of IFMC-10 (a) and IFMC-11 (b).

Although **IFMC-10** and **IFMC-11** are isostructural, there are some structural differences. Comparing **IFMC-10** with **IFMC-11**, the different length of carboxylate ligands are may be due to the diversities of the sizes for the 6-membered rings, layer's thickness, the sizes for rhombic windows in the 2D interpenetrating layers and et. al. Because H_3L^1 is longer than H_3L^2 , the corresponding sizes in **IFMC-10** are longer than those in **IFMC-11**. **IFMC-10** possesses large elliptic pores of $13.28\text{Å} \times 6.91\text{\AA}$

(the longest and the shortest distances), which are larger than $9.06\text{\AA} \times 6.79\text{\AA}$ in IFMC-11.



2.2.1 Hopf 6.3.2 Borromean 6.3.3 Torus This work

Fig. S5 Schematic representation of different links.



Fig. S6 The N₂ gas-sorption isotherms for IFMC-10 measured at 77 K, 1 atm (BET surface area: 185 m²/g; Langmuir surface area: 226 m²/g). The filled and open circles represent adsorption and desorption branches, respectively.



(b)

Fig. S7 X-Ray powder diffraction patterns of **Eu@IFMC-10**, **Sm@IFMC-10**, **Tb@IFMC-10** and simulated **IFMC-10** in the range of 5-50° and 5-20° for the simulated **IFMC-10** and as-synthesized **IFMC-10** (a), **IFMC-10** with I₂, as-synthesized and simulated **IFMC-10** (b), and as-synthesized and simulated **IFMC-11** (c) (5-50° and 5-20°), and X-ray thermodiffractogram of sample **IFMC-10** (d) and **IFMC-11** (e) (25-150 °C), X-Ray powder diffraction patterns for **IFMC-10** of adsorption and releasing Eu³⁺ (f), respectively. An X-ray thermodiffractometry experiment performed under air atmosphere between room temperature and 150 °C

for **IFMC-10** and **IFMC-11**. As shown in Fig. S7d and S7e, **IFMC-10** and **IFMC-11** are stable up to 100 °C and 80 °C, and the structural changes for **IFMC-10** and **IFMC-11** occur when the temperature rises, respectively.

(a)

(b)

(d)

(e)

Fig. S8 Solid-state photoluminescent spectra of **Eu@IFMC-10** (λ ex = 365 nm and λ em = 614) (a), **Sm@IFMC-10** (λ ex = 349 nm and λ em = 640) (b), **Tb@IFMC-10** (λ ex = 340 nm and λ em = 545) (c), H₃L¹ (λ ex = 364 and λ em = 420) (d), **IFMC-10** (λ ex = 350 nm and λ em = 402 and 550 nm) and the samples of Eu³⁺ adorption and release at room temperature (e), and I₂ adorption and release (f), respectively.

Fig. S9 Infrared spectra of fresh IFMC-10 and the samples of Eu^{3+} adsorption and release at room temperature.

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Fig. S10 The photographs for IFMC-10 of adsorption and releasing I_2 . The sample of $I_2@IFMC-10$ (0.1 g) was soaked in 20mL hexane, and replaced hexane (20 mL) per 20 min for 8 h. The PXRD and luminescent spectrum for the sample IFMC-10 releasing I_2 are similar to the fresh IFMC-10, which indicates that the mechanism for I_2 'insertion" is reversible. The photographs for IFMC-10 of adsorption I_2 and releasing I_2 are shown as Figure S10.

(a)

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(c)

Fig. S11 TGA curves of compound **IFMC-11** (a), **IFMC-10** (black) and Eu^{3+} -doped samples (red) (b), and **IFMC-10** (black) and I₂-doped samples (green) (c), respectively.

ICP	Eu@IFMC-10	Sm@IFMC-10	Tb@IFMC-10
Zn	10.5%	10.5%	10.4%
Ln	2.0%	2.1%	2.0%
Ln : Zn	1:5.25	1:5	1:5.2

ICP	I ₂ @IFMC-10
Zn	7.6%
Ι	3.8%
$I_2:Zn$	1:4

Table S3. ICP analysis for the IFMC-10 absorbing I₂.

ICP analysis shows that each unit cell in **IFMC-10** can accommodate about four I_2 molecules or 2.6 Ln^{3+} ions according to the Mol ratios of Ln/Zn and I_2/Zn .

References

- 1. G. M. Sheldrick, *SHELXS-97: Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.
- 2. G. M. Sheldrick, *SHELXL-97: Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
- 3. L. J. Farrugia, WINGX: A Windows Program for Crystal Structure Analysis; University of Glasgow: Glasgow, UK, 1988.
- 4. Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.*, 2003, **36**, 7.