

## Electronic Supplementary Information

### **A 3D/3D hetero-interpenetrated MOF with a novel (3,9)-c net and 6-c lcy net for the fluorescence detection of carbaryl**

Rong Shi,<sup>a</sup> Ze-Ming Xu,<sup>a</sup> Chen Cao,<sup>a</sup> Zheng Niu<sup>\*a</sup> and Jian-Ping Lang<sup>\*a,b</sup>

<sup>a</sup> *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Jiangsu, Suzhou, 215123, China*

<sup>b</sup> *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

\*E-mail: [jplang@suda.edu.cn](mailto:jplang@suda.edu.cn); [nkniu Zheng@163.com](mailto:nkniu Zheng@163.com)

## Table of Contents

<b>Experimental</b> .....	S3
<b>Materials and instruments</b> .....	S3
<b>Synthesis of H<sub>2</sub>L</b> .....	S3
<b>Fig. S1</b> Synthesis process of ligand H <sub>2</sub> L.....	S4
<b>Fig. S2</b> The <sup>1</sup> H NMR of H <sub>2</sub> L (400 MHz, DMSO- <i>d</i> <sub>6</sub> ).....	S4
<b>Synthesis of 1</b> .....	S4
<b>Fig. S3</b> The IR spectrum of <b>1</b> .....	S5
<b>Single-crystal X-ray crystallography</b> .....	S5
<b>Table S1</b> Summary of crystal data and structural refinement parameters for <b>1</b> .....	S5
<b>Fig. S4</b> (a) The asymmetric unit of <b>lcy</b> net. (b) The asymmetric unit of (3,9)-c net. (c) The coordination mode of H <sub>2</sub> L ligand in <b>1</b> .....	S6
<b>Fig. S5</b> (a) The [Zn <sub>4</sub> (μ <sub>4</sub> -O)(CO <sub>2</sub> ) <sub>6</sub> ] cluster of <b>1</b> . (b) The 9-c [Zn <sub>6</sub> (μ <sub>3</sub> -OH) <sub>3</sub> (O <sub>2</sub> C-) <sub>9</sub> ] cluster of <b>1</b> . (c) The [Zn <sub>2</sub> (O <sub>2</sub> C-) <sub>3</sub> (DEF) <sub>3</sub> (H <sub>2</sub> O)] cluster of <b>1</b> .....	S7
<b>Fig. S6</b> The unit cell diagram of <b>1</b> view along the <i>a</i> -axis.....	S7
<b>N<sub>2</sub> sorption experiments of 1</b> .....	S8
<b>Fig. S7</b> The TGA curve of <b>1</b> .....	S8
<b>Fig. S8</b> Solid-state UV spectrum of <b>1</b> .....	S9
<b>Fig. S9</b> (a) The luminescence emission spectra of H <sub>2</sub> L. (b) The luminescence emission spectra of <b>1</b> .....	S9
<b>Fig. S10</b> The X-Ray powder diffraction patterns of <b>1</b> .....	S10
<b>Fig. S11</b> (a-c) High-resolution electron images of <b>1</b> . (d) The SAED pattern of <b>1</b> .....	S10
<b>Fig. S12</b> The luminescence excitation and emission spectra of carbaryl (λ <sub>ex</sub> = 334 nm, λ <sub>em</sub> = 400 nm).....	S11
<b>Fig. S13</b> The X-Ray powder diffraction patterns after the sensor performance test of <b>1</b> .....	S11
<b>Carbaryl titration experiments of 1</b> .....	S12
<b>References</b> .....	S12

## Experimental

### Materials and instruments

All the reagents and solvents employed were used as obtained from Sigma-Aldrich and TCI fine chemicals. A slightly modified procedure was used for the synthesis of the H<sub>2</sub>L ligand. <sup>1</sup>H NMR spectra were recorded on a Jeol EX270 spectrometer operating at 270 MHz. Deuterated solvents were obtained from Cambridge Stable Isotopes and used without further purification. Elemental analyses (C, H and N) were carried out on a Carlo-Erba CHNO-S microanalyzer. Infrared (IR) spectra were recorded on a Varian 1000 spectrometer using KBr disks (4000-400 cm<sup>-1</sup>). Powder X-ray diffraction (PXRD) measurements were acquired on a PANalytical X'Pert PRO MPD system (PW3040/60) with Cu-K $\alpha$  radiation. UV-Visual absorption spectra were conducted on a JASCO model V-670 spectrometer. Luminescence spectra and quantum yields were obtained on a HORIBA PTI QuantaMaster40 Spectrofluorometer. Gas sorption isotherm measurements were carried out on the Micromeritics ASAP 2020. With the temperature was held persistently by liquid N<sub>2</sub> bath, N<sub>2</sub> isotherms were performed at 77 K. Thermogravimetric analyses (TGA) were conducted on a Q50 thermogravimetric analyzer under the N<sub>2</sub> atmosphere. TEM images were recorded on FEI talos F200x G2.

**Synthesis of H<sub>2</sub>L.** The ligand H<sub>2</sub>L was synthesized by a modified procedure.<sup>S1,S2</sup> A mixture of 33 mmol (4.5342 g) 4-aminobenzoic acid and 15 mmol (3.7446 g) bicyclo[2.2.2]oct-7-ene-2,3,5,6- tetracarboxylic acid dianhydride was added into a 500 mL round-bottom flask and then 300 mL of acetic acid was poured into the flask and refluxed at 140 °C for 12 h. After the mixture was cooled to room temperature, it was washed three times by distilled water and one time by ethanol. Finally, white powder product was obtained (Fig. S1). H<sub>2</sub>L was used for next procedures without further purification. The purity of the ligand was confirmed by <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm): 13.10 (s, 1 H), 8.02 (d, *J* = 12.00 Hz, 4 H), 7.32 (d, *J* = 8.00 Hz, 4 H), 6.33 (t, *J* = 4.00 Hz, 2 H), 3.54 (s, 2 H), 3.46 (s, 4 H) (Fig. S2).

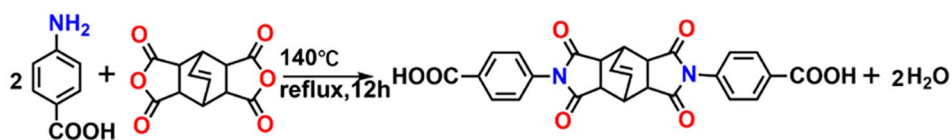


Fig. S1 Synthesis process of ligand H<sub>2</sub>L.

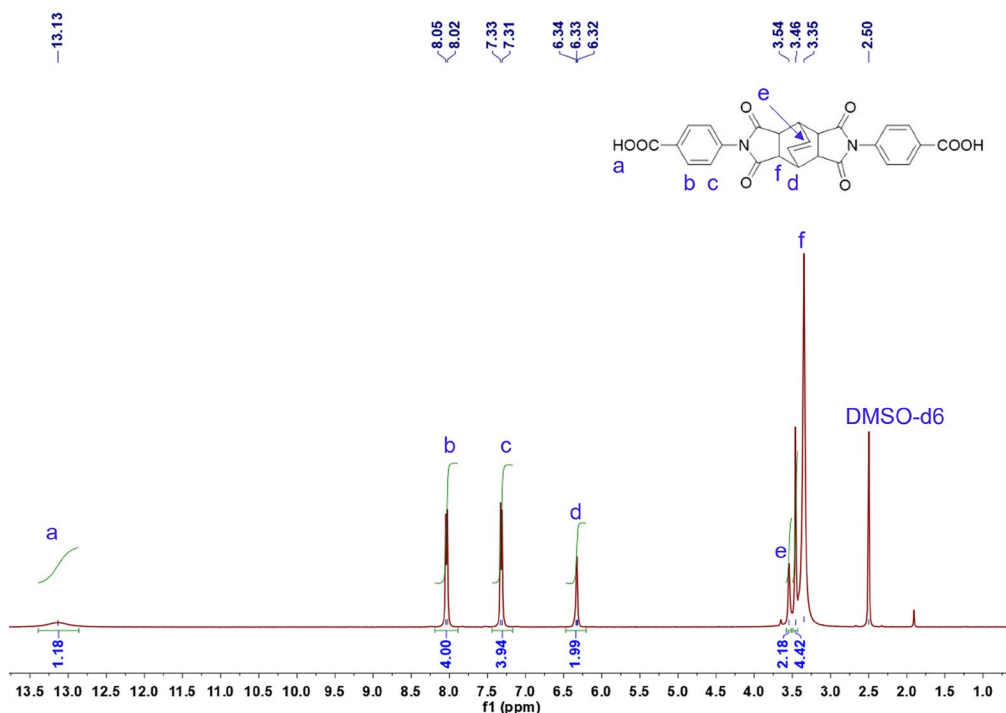
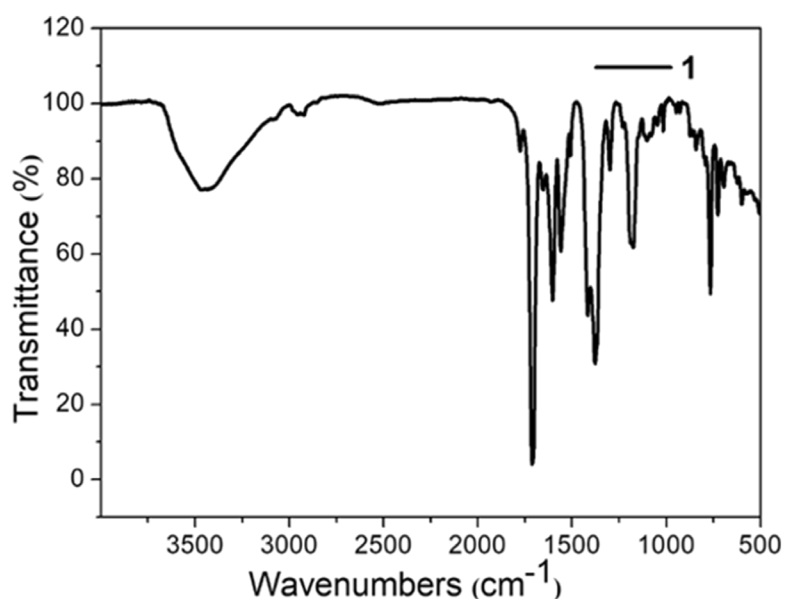


Fig. S2 The <sup>1</sup>H NMR of H<sub>2</sub>L (400 MHz, DMSO-*d*<sub>6</sub>).

**Synthesis of 1.** The mixture of H<sub>2</sub>L (0.05 mmol, 0.0243 g), Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol, 0.0372 g), 2 mL *N,N*-diethylformamide (DEF) and 1 mL ethanol were added into the glass beaker. The mixture was then sonicated for a half hour until all of the solid material got dissolved and stirred for one hour, resulting in a clear colorless solution. Finally, the mixture was sealed into a 25 mL Teflon-lined autoclave. After being heated at 100 °C for 24 hours, it was cooled to room temperature. Colorless block crystals were obtained. Yield: 70% based on Zn. Element analysis (%) found (calcd.) for **1**: C, 51.70 (51.79), H, 4.68 (4.61), N, 6.18 (6.23). IR (KBr, v/cm<sup>-1</sup>): 3473 (br), 2960 (w), 1776 (w), 1714 (vs), 1654 (d), 1604 (w), 1560 (m), 1510 (w), 1418 (m), 1379 (s), 1299 (w), 1191 (s), 1175 (s), 766 (s), 728 (m), 696 (w), 600 (w) (Fig. S3).



**Fig. S3** The IR spectrum of **1**.

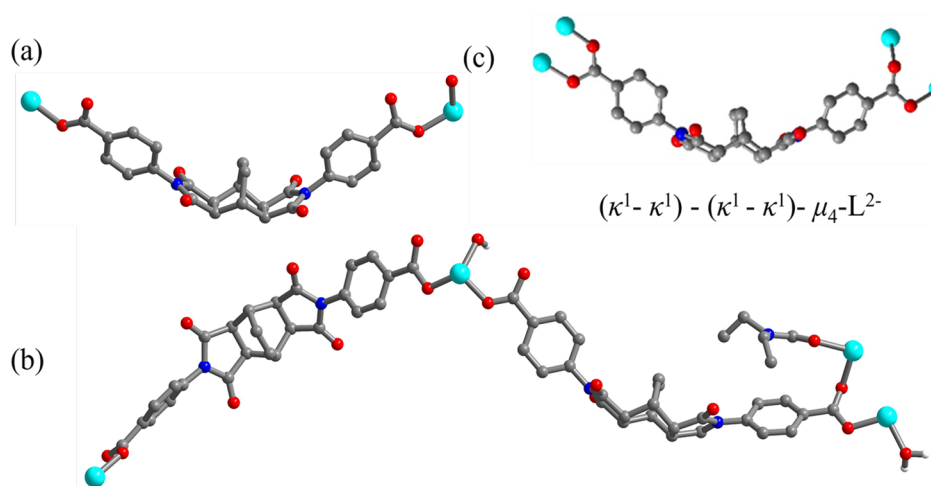
**Single-crystal X-ray crystallography.** One single crystal of **1** suitable for single-crystal X-ray diffraction was mounted on a Bruker Smart CCD diffractometer with a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by intrinsic phasing (SHELXT)<sup>S3,S4</sup> and refined by full-matrix least squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically. DFIX restraints were applied to keep the bond length (C89-C87, C86-C89, C86-C88, C87-N6, C86-N6, C54-C55, C56-C57 bonds 1.5  $\text{\AA}$ , O12-H11A bond 3.2  $\text{\AA}$ ) in reasonable ranges. There is an Alert level A “a solvent accessible void in the structure”, which is attributed to some solvent molecules that could not be located. The important crystallographic data and refinement details for **1** were summarized in Table S1.

**Table S1** Summary of crystal data and structural refinement parameters for **1**.

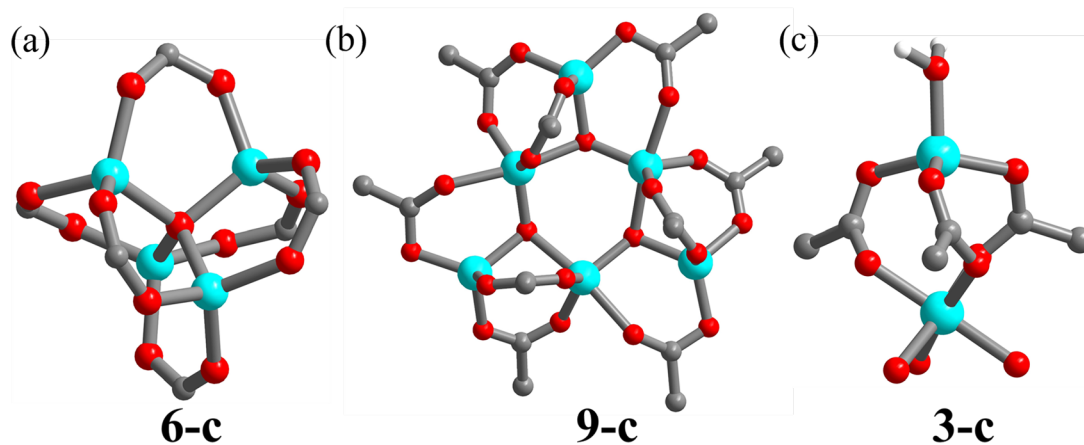
<b>1</b>	
Formula	C <sub>517</sub> H <sub>416</sub> Cl <sub>3</sub> N <sub>46</sub> O <sub>192</sub> Zn <sub>24</sub>
$F_w$	12021.11
Crystal system	Cubic
Space group	$P2_13$
$a$ ( $\text{\AA}$ )	32.520(5)
$b$ ( $\text{\AA}$ )	32.520(5)
$c$ ( $\text{\AA}$ )	32.520(5)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	90
$\gamma$ ( $^\circ$ )	90
$V$ ( $\text{\AA}^3$ )	34392(16)

$Z$	2
$D_c$ (g/cm <sup>3</sup> )	1.161
$\mu$ (mm <sup>-1</sup> )	0.908
$R_{int}$	0.0831
GOF <sup>c</sup> on $F^2$	0.9892
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0555, 0.1464
$R_1, wR_2$ (all data)	0.0625, 0.1514
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.549, -0.658

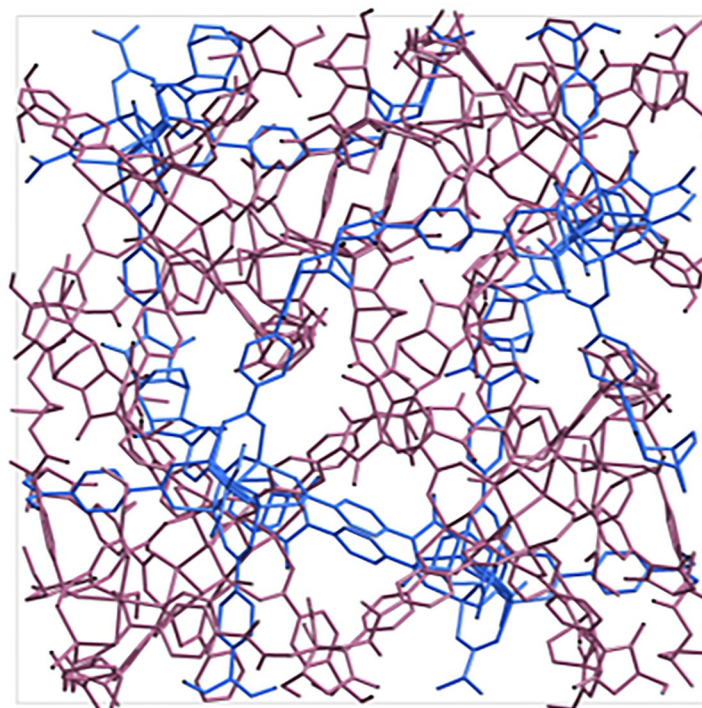
<sup>a</sup> $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ . <sup>b</sup> $wR = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$ . <sup>c</sup>GOF =  $\{\Sigma w((F_o^2 - F_c^2)^2) / (n-p)\}^{1/2}$ , where  $n$  = number of reflections and  $p$  = total number of parameters refined.



**Fig. S4** (a) The asymmetric unit of **Icy** net. (b) The asymmetric unit of (3,9)-**c** net. (c) The coordination mode of **H<sub>2</sub>L** ligand in **1**. The hydrogen atoms have been omitted for clarify.

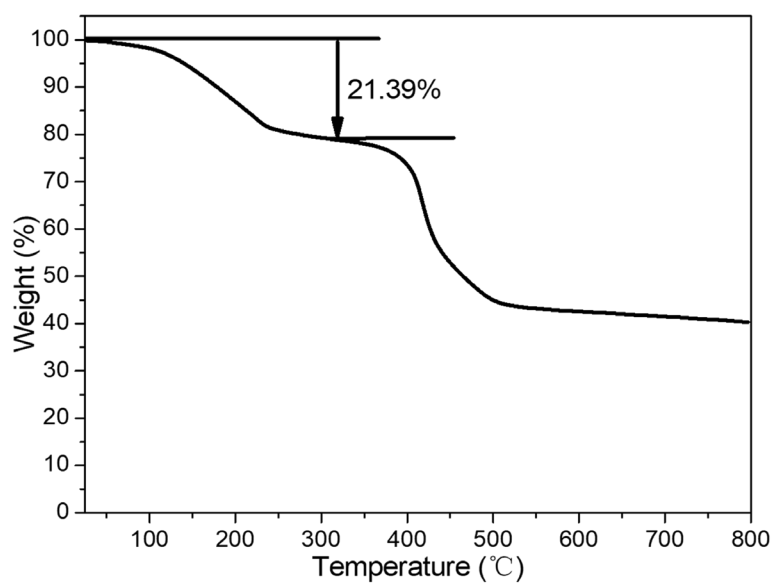


**Fig. S5** (a) The  $[Zn_4(\mu_4-O)(CO_2)_6]$  cluster of **1**. (b) The 9-c  $[Zn_6(\mu_3-OH)_3(O_2C-)_9]$  cluster of **1**. (c) The  $[Zn_2(O_2C-)_3(DEF)_3(H_2O)]$  cluster of **1**. The hydrogen atoms have been omitted for clarify.



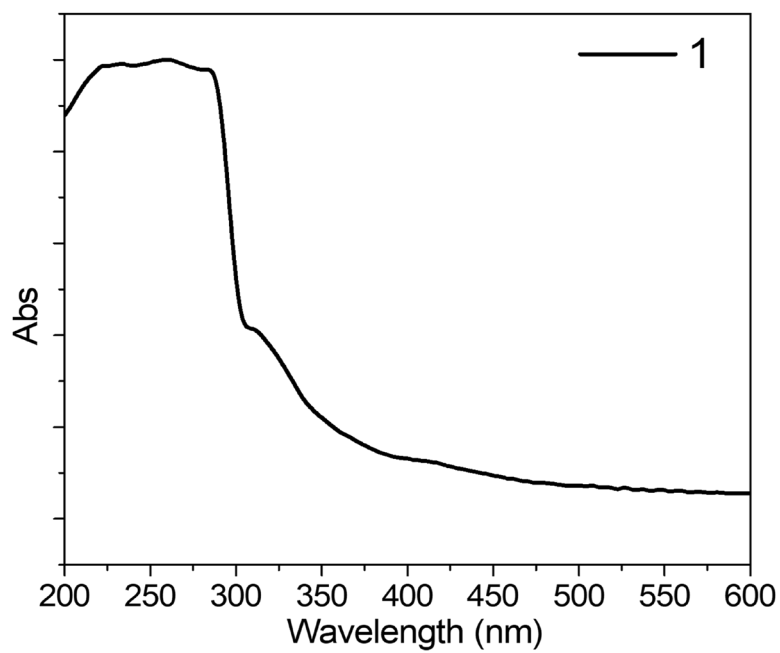
**Fig. S6** The unit cell diagram of **1** view along the  $a$ -axis. The hydrogen atoms have been omitted for clarify.

**N<sub>2</sub> sorption experiments of 1.** Before sorption experiment, the as-prepared sample of 1 was soaked in DMF, heated at 80 °C for 24 hours, and refreshed by using the solvent DMF every eight hours. After that, DMF was replaced by methanol under the same heating conditions to get rid of DMF. Then each sample was immersed into DCM, and refreshed by using the solvent every two hours. For the activation with supercritical N<sub>2</sub>, the DCM-containing samples were activated at room temperature under reduced pressure (10 μmHg) overnight before carrying out the sorption measurements.

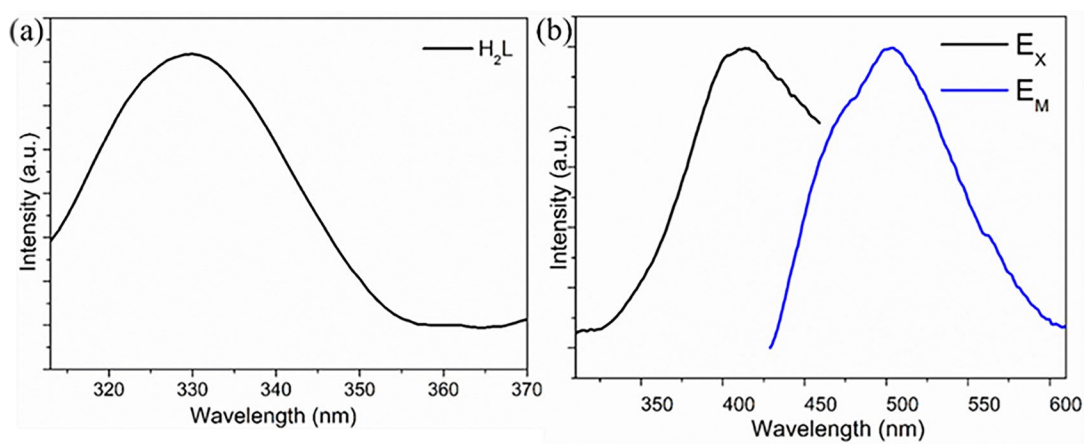


**Fig. S7** The TGA curve of **1**. The weight loss is 21.39%, which can correspond to the guest and coordinated DEF and water molecules.

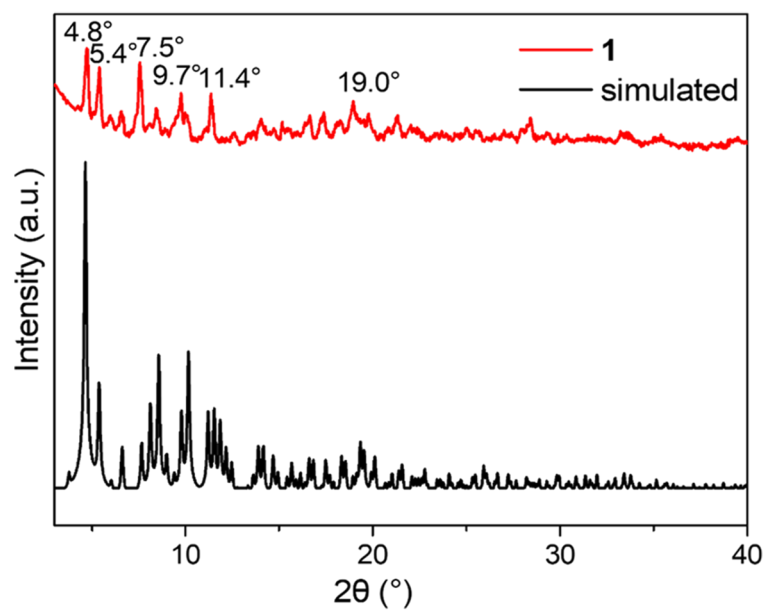




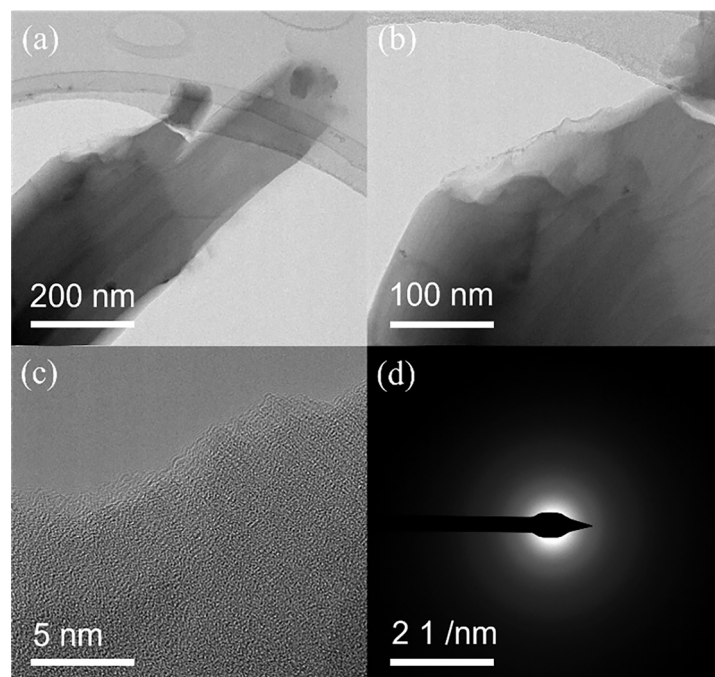
**Fig. S8** Solid-state UV spectrum of **1**.



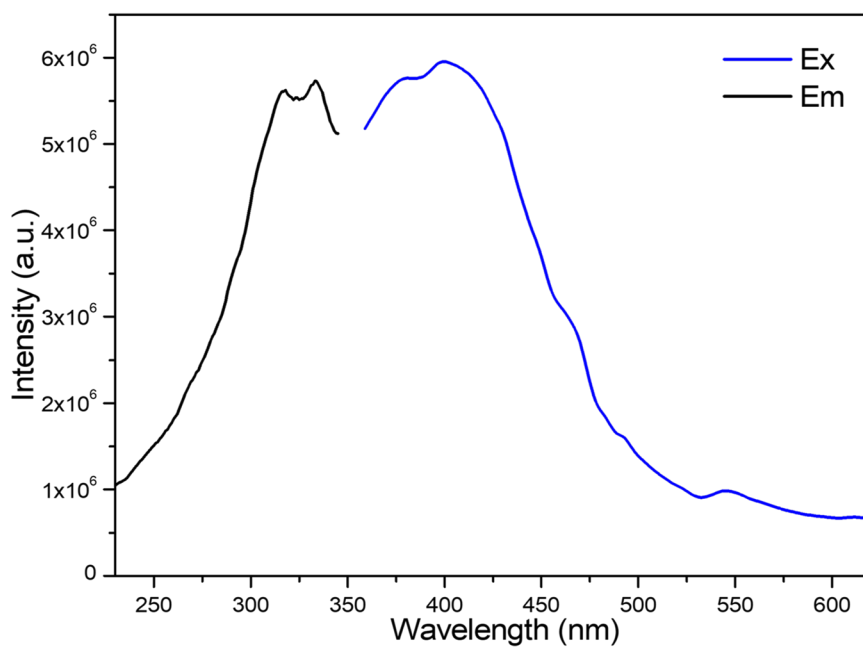
**Fig. S9** (a) The luminescence emission spectra of  $H_2L$ . (b) The luminescence emission spectra of **1**.



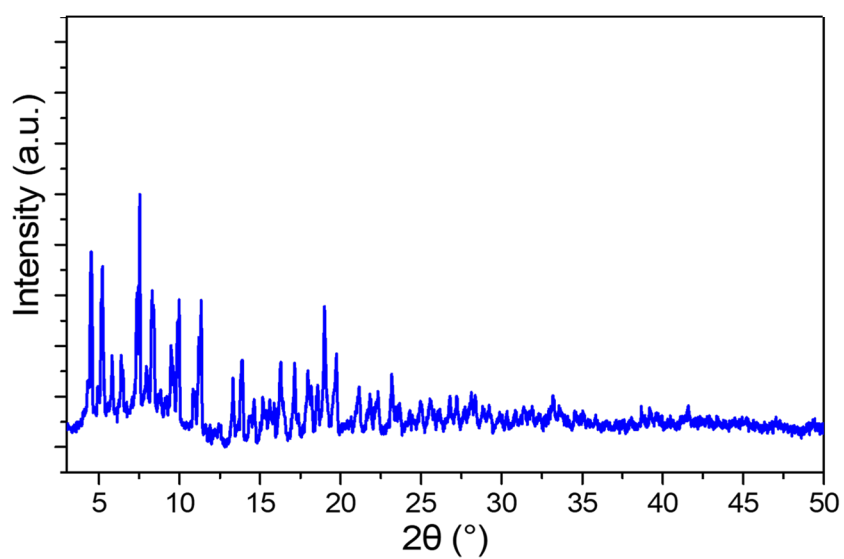
**Fig. S10** The X-Ray powder diffraction patterns of **1**.



**Fig. S11** (a-c) High-resolution electron images of **1**. (d) The SAED pattern of **1**.



**Fig. S12** The luminescence excitation and emission spectra of carbaryl ( $\lambda_{\text{ex}} = 334 \text{ nm}$ ,  $\lambda_{\text{em}} = 400 \text{ nm}$ ).



**Fig. S13** The X-Ray powder diffraction patterns after the sensor performance test of **1**.

**Carbaryl titration experiments of 1.** The as-prepared **1** was solvent-exchanged with DMF and dichloromethane (DCM). Then the crystals were obtained by vacuum filtration. The sample of **1** was well grinded into powder. The standard solution was prepared by addition of 0.4 mg finely grinded powder sample of **1** into 3 mL deionized DMF as the control group. The grinded powder of **1** was immersed in different concentrations of carbaryl DMF anhydrous solution with vigorously agitation using ultrasound overnight. Finally, the fluorescence spectrophotometer was used to collect the fluorescence data of the solution until the consistent results are observed.

## References

- S1 H. Lin, C. H. Deng, X. Qiu, X. Liu, J. G. Ma and P. Cheng, *Cryst. Growth Des.*, 2021, **21**(7), 3728-3735.
- S2 H. Li, J. Zhou, W. Shi, X. Zhang, Z. Zhang, M. Zhang and P. Cheng, *CrystEngComm*, 2014, **16**(5), 834-841.
- S3 G. M. Sheldrick, *Acta Cryst.*, 2008, **64**, 112-122.
- S4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.