

# In situ generated dimethylamine constructs a robust hydrogen-bonded organic framework for selective fluorescence detection

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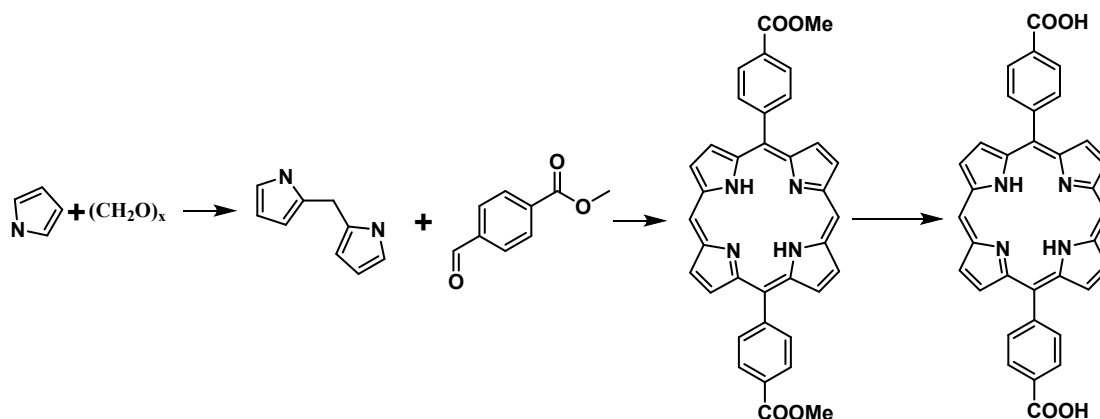
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## 1. Materials and Instruments:

All the chemicals were purchased from commercial sources and used without further purification unless otherwise stated. <sup>1</sup>H-NMR spectroscopy data were collected on a Bruker 600 spectrometer. The Single Crystal X-ray diffraction (SCXRD) data was collected on a Agilent Gemini E diffractometer (Mo, 50 kV 40 mA) and reduced by CrysAlisPro (Rigaku). The structures were solved by direct methods using SHELXS-97. Refinements were performed with SHELXL-2013 using fullmatrix least-squares calculations on F2, with anisotropic displacement parameters for all the nonhydrogen atoms. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/MAX powder X-ray diffractometer with a scan range of 2 theta from 3 to 25° using Cu Ka radiation (150 mA and 40 kV). Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209 F3 thermal analyzer under a N<sub>2</sub> atmosphere in the temperature range of 30-800 °C at a heating rate of 10 °C min<sup>-1</sup>. Transmission electron microscope (TEM) was recorded with a American Thermo Field (formerly FEI) Talos L120C at a voltage of 120 KV. UV-vis spectra were recorded with a Techcomp UV-2600 Spectrophotometer. Contact Angle (CA) data was recorded by BiolinFlex, Sweden, Theta; Luminescence spectra and lifetime measurements were measured by an Edinburgh FLS1000 spectrometer. The quantum yields were measured by use of an integrating sphere with an Edinburgh Instrument FLS1000 spectrometer.



**Fig. S1** The synthesis path of DBP.

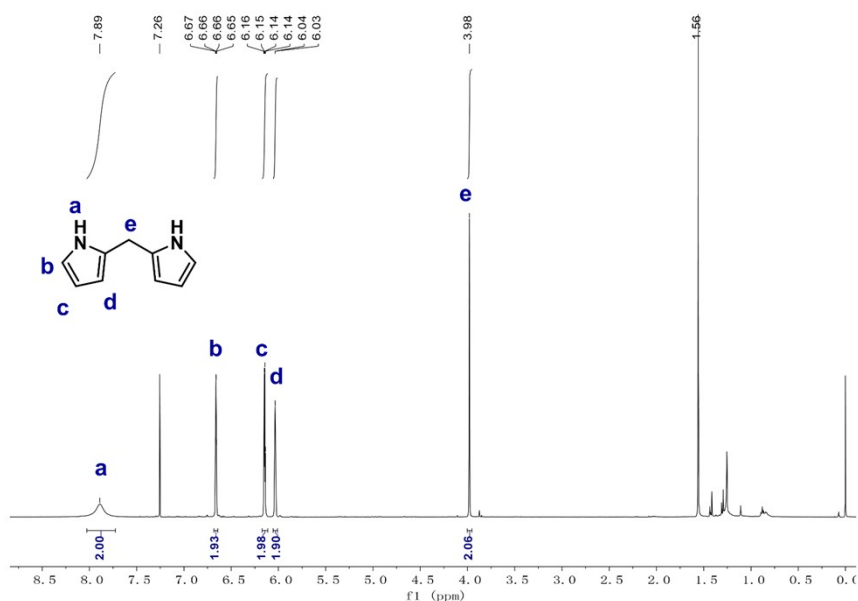
## 2. Synthesis

DBP was synthesized using a three-step method. Refer to the method reported by Lin et al for specific steps<sup>1</sup>. <sup>1</sup>H-NMR showed that DBP was synthesized successfully.

### 2.1. Synthesis of DPM (Dipyrromethane)<sup>2</sup>:

Add 500 mL of freshly distilled pyrrole (7.2 mol) to a 1 L flask. Add paraformaldehyde (1.74 g, 58 mmol) to the flask and degas the mixture for 20 min. Heat the mixture at 60 °C to dissolve most of the solids. Cool to room temperature and slowly add 0.53 mL of trifluoroacetic acid (TFA) to the solution. After stirring the reaction mixture for 1 h, add 812 mg of sodium hydroxide and stir the reaction mixture for another 45 minutes. The pyrrole was steamed off by spinning at 80 °C, the remaining solids were dissolved with dichloromethane, transferred to a 250 mL separating funnel and extracted with water three times, and the crude product was

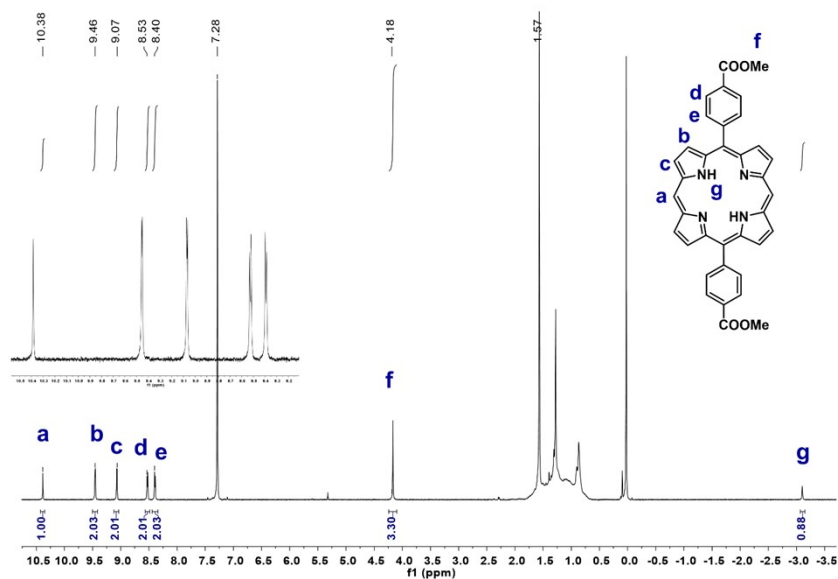
purified by silica gel column chromatography, and petroleum ether and dichloromethane were used as the eluate to obtain a gray-white product. (Fig. S2)



**Fig. S2** <sup>1</sup>H-NMR spectrum of the synthesized DPM in CDCl<sub>3</sub>.

## 2.2. Synthesis of Me<sub>2</sub>DBP:

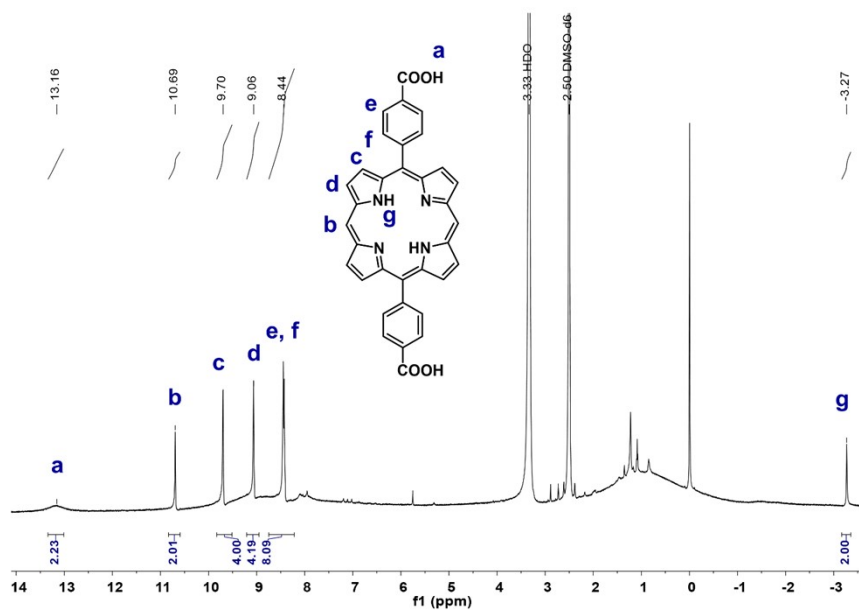
4-(methoxycarbonyl) benzaldehyde (1.20 g, 7.3 mmol) and dipyrrolemethane (1.07 g, 7.3 mmol) were added to a three-mouth flask. Add 1 L of anhydrous dichloromethane (DCM) to the flask. Trifluoroacetic acid was added dropwise (0.34 mL, 4.4 mmol). Stir the mixture at room temperature for 4 h. Add 2.49 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 11.0 mmol) to the reaction mixture and stir the mixture for another 1 hour. Triethylamine is added to neutralize the reaction mixture. Remove the solvent with a rotary evaporator. Dichloromethane was used as the eluate and purified by column chromatography to obtain purple crystals as the product 5,15-bis(p-methylbenzoate) porphyrin (Me<sub>2</sub>DBP) (Fig. S3).



**Fig. S3** <sup>1</sup>H-NMR spectrum of the synthesized Me<sub>2</sub>DBP in CDCl<sub>3</sub>.

### 2.3. Synthesis of DBP:

The above Me<sub>2</sub>DBP (399 mg, 0.69 mmol) was dissolved in a mixture of tetrahydrofuran (THF) and methanol (90 mL, 1:1 vol/vol). Add potassium hydroxide in water (14 mL, 2 M). Heat the solution to reflux overnight under nitrogen protection. The organic solvent was removed with a rotary evaporator, transferred to a separating funnel, extracted three times with methylene chloride, and then neutralized to pH = 3 with hydrochloric acid (3 M). The product was collected by centrifugation and washed with water and ether, and dried under vacuum to obtain a maroon solid of 5, 15-dicarboxyphenylporphyrin DBP (Fig. S4).



**Fig. S4**  $^1\text{H-NMR}$  spectrum of the synthesized DBP in  $\text{DMSO-}d_6$ .

### 3. Crystal data.

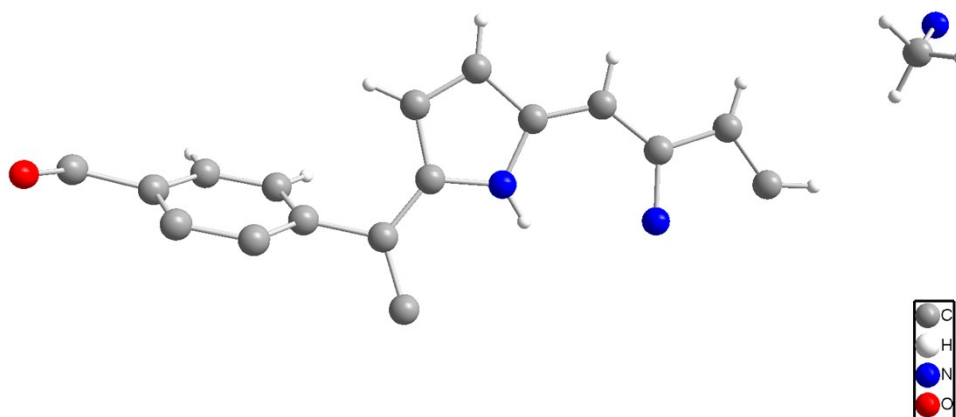
Crystal data and structure refinement for DBP-HOF and DBP-HOF-acid (DBP-HOF after soaking in 3 M HCl) are summarized in Table S1.

**Table S1** Crystal data

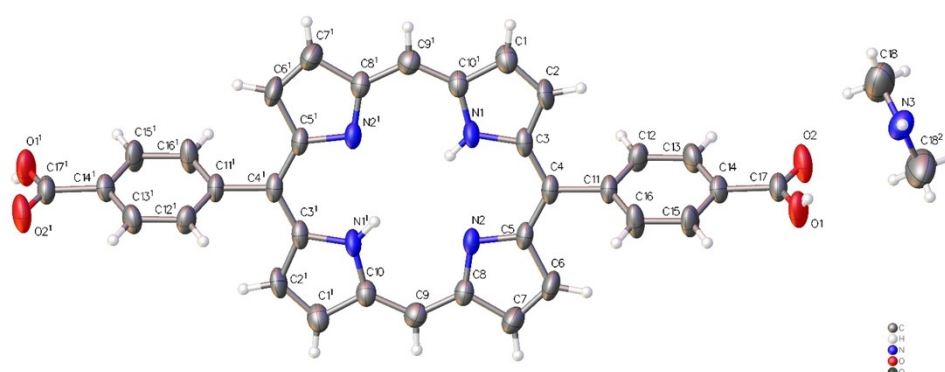
Identification code	DBP-HOF	DBP-HOF-acid
Empirical formula	C <sub>36</sub> H <sub>29</sub> N <sub>5</sub> O <sub>4</sub>	C <sub>36</sub> H <sub>29</sub> N <sub>5</sub> O <sub>4</sub>
CCDC number	2307357	2308077
Formula weight	595.64	595.64
Temperature/K	293(2)	296.15
Crystal system	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
a/Å	36.623(6)	36.466(7)
b/Å	8.325(2)	8.2745(15)
c/Å	10.0606(14)	10.0269(18)
α/°	90	90
β/°	97.746(13)	97.792(3)
γ/°	90	90
Volume/Å <sup>3</sup>	3039.3(10)	2997.5(9)
Z	4	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.302	1.320
μ/mm <sup>-1</sup>	0.087	0.088
F(000)	1248.0	1248.0
Crystal size/mm <sup>3</sup>	0.21 × 0.15 × 0.09	0.1 × 0.1 × 0.1
Radiation	synchrotron (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.95 to 48.994	4.51 to 55.284
Index ranges	-39 ≤ h ≤ 42, -9 ≤ k ≤ 6, -11 ≤ l ≤ 11	-42 ≤ h ≤ 45, -7 ≤ k ≤ 10, -12 ≤ l ≤ 13
Reflections collected	5257	8783
Independent reflections	2473 [R <sub>int</sub> = 0.0569, R <sub>sigma</sub> = 0.1060]	3403 [R <sub>int</sub> = 0.0275, R <sub>sigma</sub> = 0.0352]
Data/restraints/parameters	2473/4/213	3403/0/206
Goodness-of-fit on F <sup>2</sup>	0.981	1.030
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0626, wR <sub>2</sub> = 0.0969	R <sub>1</sub> = 0.0469, wR <sub>2</sub> = 0.1139
Final R indexes [all data]	R <sub>1</sub> = 0.1314, wR <sub>2</sub> = 0.1206	R <sub>1</sub> = 0.0799, wR <sub>2</sub> = 0.1312
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.16	0.13/-0.24

#### 4. Structure of DBP-HOF

Hydrogen bond information of DBP-HOF (Where D represents the hydrogen bond donor and A represents the hydrogen bond acceptor) are showed in Table S2.



**Fig. S5** Asymmetric structure of DBP-HOF.

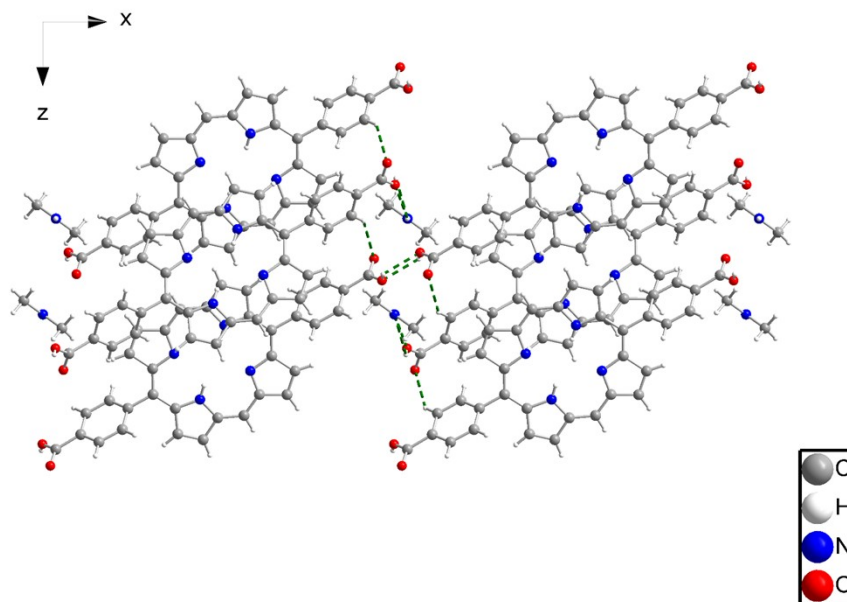


**Fig. S6** The numbering of the C, N, O atoms.

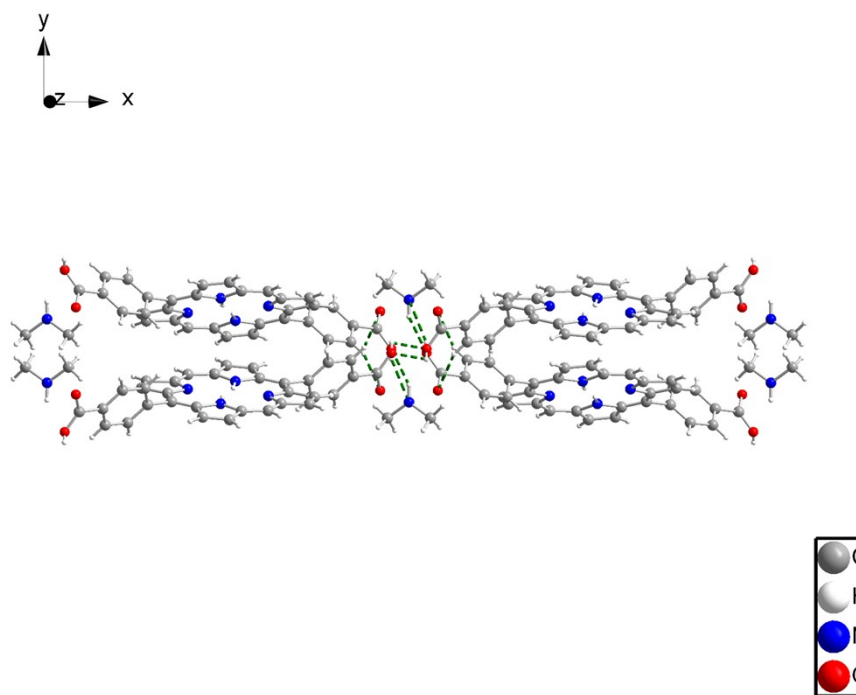
**Table S2** Hydrogen bond information

Hydrogen bond types	Distance between D and A	Distance between H and A	Angle
O-H $\cdots$ N	3.26 Å	3.06 Å	133.94°
N-H $\cdots$ O	3.26 Å	2.61 Å	104.22°
O-H $\cdots$ O	2.47 Å	2.25 Å	103.19°
C-H $\cdots$ O	3.53 Å	2.74 Å	104.10°





**Fig. S7** Crystal structure and hydrogen bond connection in direction b.



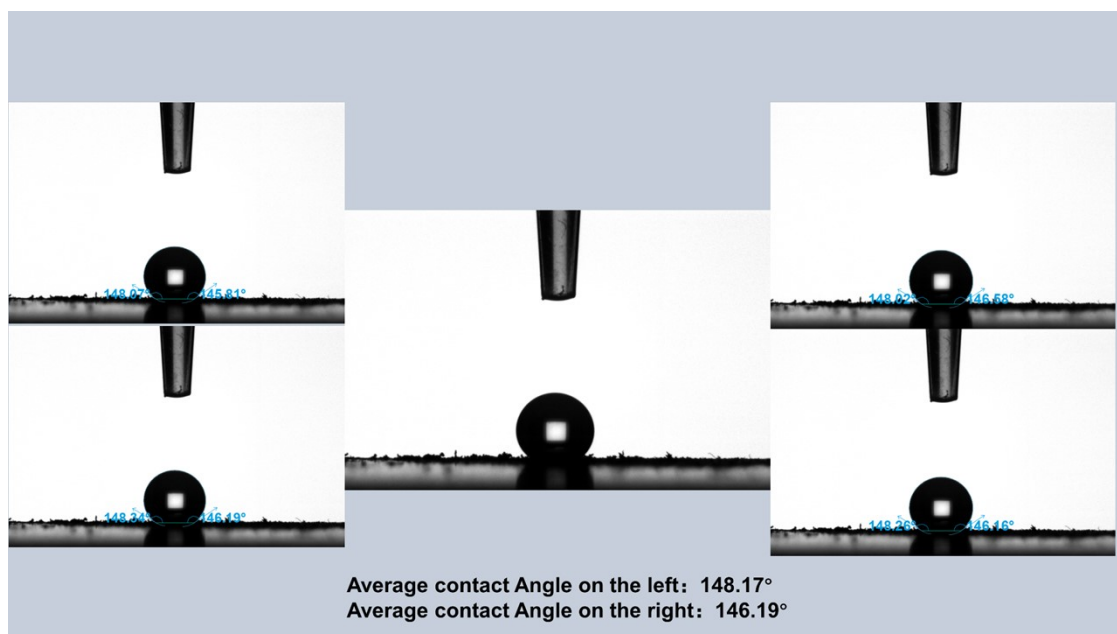
**Fig. S8** Crystal structure and hydrogen bond connection in direction c.

## 5. Synthetic conditions of DBP-HOF

Entry	CH <sub>3</sub> COOAg (mg)	H <sub>2</sub> DBP (mg)	DMF (mL)	HCl(3M) ( $\mu$ L)	Reaction Time(h)	Temperature ( $^{\circ}$ C)	Phases	Date
1	0	5	1	0	24	80	×	3.18
2	0	5	1	0	24	100	×	3.18
3	0	5	1	0	24	120	×	3.18
4	2	5	1	0	24	80	×	3.18
5	6	5	1	0	24	80	×	3.18
6	2	5	1	50	24	80	×	3.18
7	6	5	1	50	24	80	×	3.18
8	2	5	1	100	24	80	×	3.18
9	6	5	1	100	24	80	×	3.18
10	2	5	1	0	24	100	×	3.18
11	6	5	1	0	24	100	×	3.18
12	2	5	1	50	24	100	×	3.18
13	6	5	1	50	24	100	×	3.18
14	2	5	1	100	24	100	×	3.18
15	6	5	1	100	24	100	×	3.18
16	2	5	1	0	24	120	×	3.18
17	6	5	1	0	24	120	×	3.18
18	2	5	1	50	24	120	√	3.18
19	6	5	1	50	24	120	√	3.18
20	2	5	1	100	24	120	√	3.18
21	0	5	1	50	24	100	×	3.22
22	0	5	1	100	24	100	×	3.22
23	0	5	1	150	24	100	×	3.22
24	2	5	1	50	24	100	×	3.22
25	2	5	1	100	24	100	×	3.22
26	2	5	1	150	24	100	×	3.22
27	0	5	1	50	24	120	×	3.22
28	0	5	1	100	24	120	×	3.22
29	0	5	1	150	24	120	×	3.22
30	2	5	1	50	24	120	√	3.22
31	2	5	1	100	24	120	√	3.22
32	2	5	1	150	24	120	√	3.22
33	0	5	1	50	24	140	×	3.22
34	0	5	1	100	24	140	×	3.22
35	0	5	1	150	24	140	×	3.22
36	2	5	1	50	24	140	√	3.22
37	2	5	1	100	24	140	√	3.22
38	2	5	1	150	24	140	√	3.22
39	6	5	1	100	24	120	√	3.18
40	0	5	1	100	24	100	×	3.24
41	0	5	1	200	24	100	×	3.24

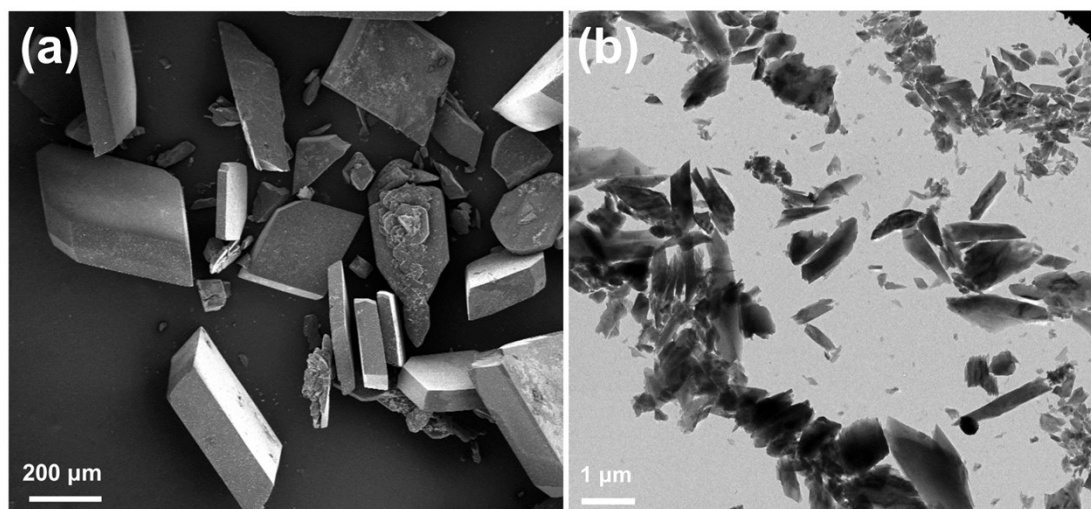
**Fig. S9** Synthesis of DBP-HOF

## 6. Hydrophobicity of DBP-HOF

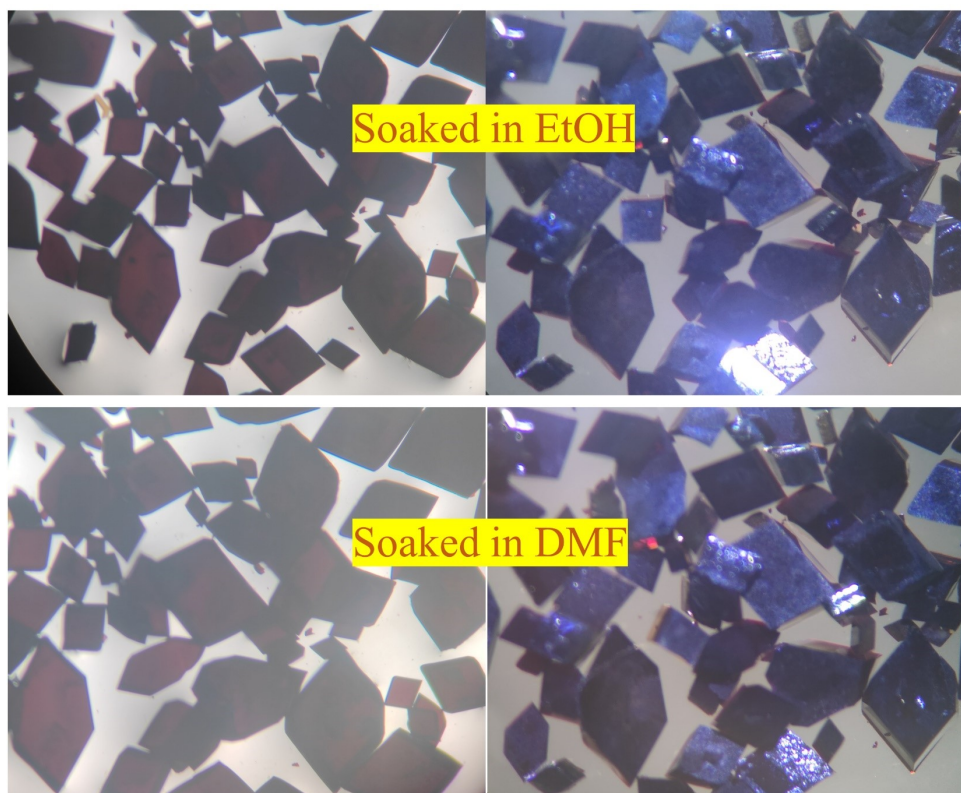


**Fig. S10** Contact Angle test of DBP-HOF

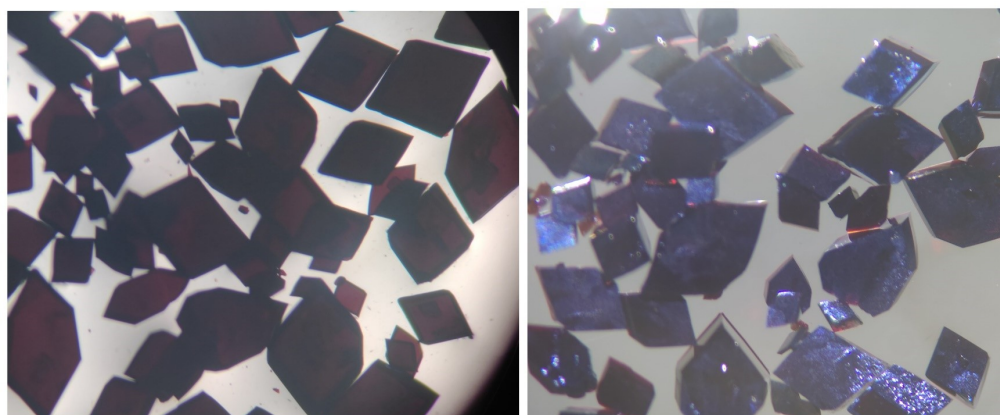
## 7. Morphology and chemical stability of DBP-HOF



**Fig. S11** (a) SEM image and (b) TEM image of DBP-HOF after two weeks immersion in EtOH.



**Fig. S12** DBP-HOF under optical microscope during organic solvent immersion.



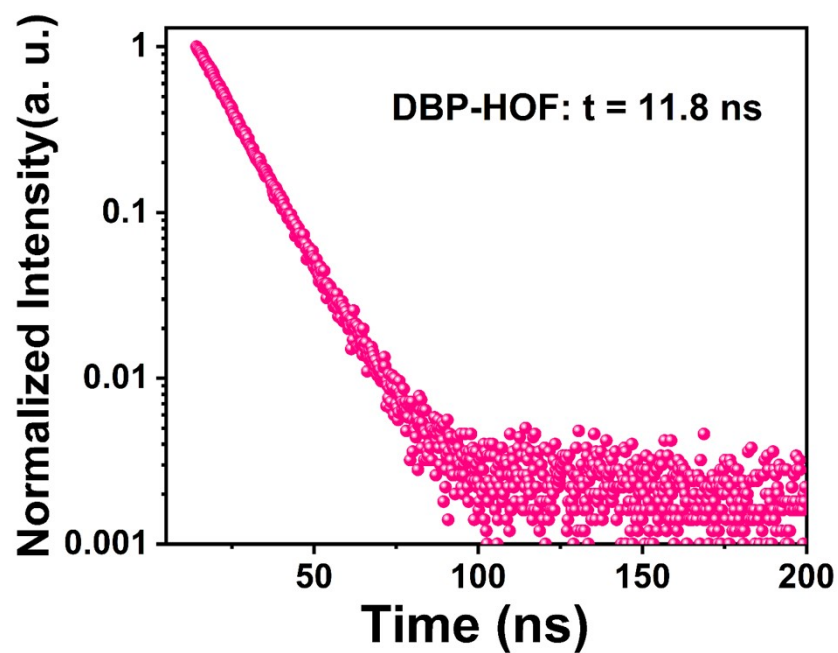
**Fig. S13** DBP-HOF under optical microscope during water immersion.

## 8. Optical properties of DBP-HOF

**Eq. S1.** Decay curves of DBP-HOF-2 ( $\lambda_{em} = 698$  nm,  $\lambda_{ex} = 365$  nm) and the lifetime values can be expressed by the formula:

$$I_t = I_0 \exp\left(-\frac{t}{\tau}\right) + C \quad (1)$$

In this formula,  $I_t$  is the luminescence intensity at time  $t$ ,  $I_0$  is the initial luminescence intensity,  $t$  is the time,  $C$  is constant, and  $\tau$  is the decay time for the exponential components.



**Fig. S14** Attenuation curves of DBP-HOF.

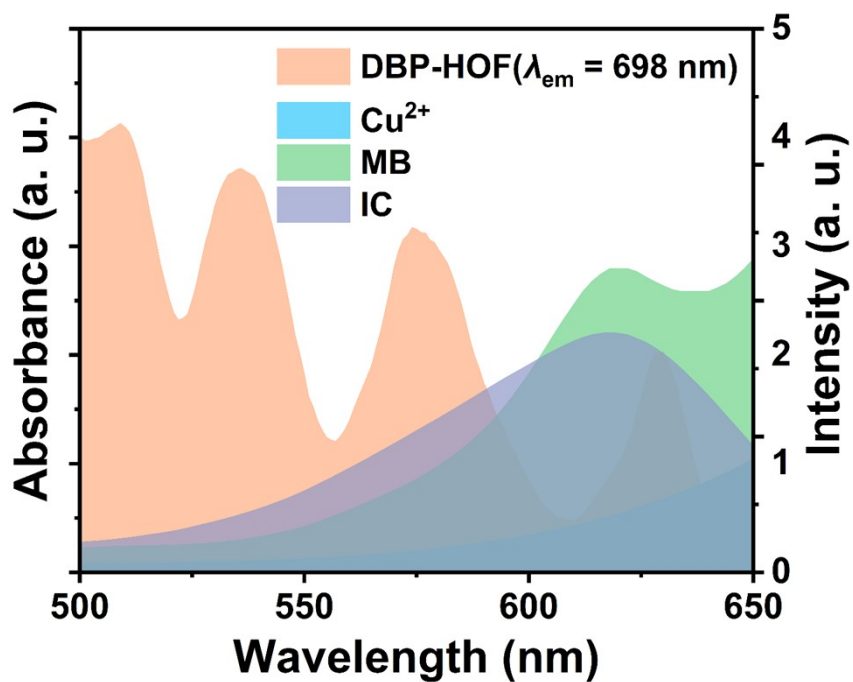


Fig. S15 Excitation spectrum of DBP-HOF and UV-vis spectra of  $\text{Cu}^{2+}$ , MB, and IC.

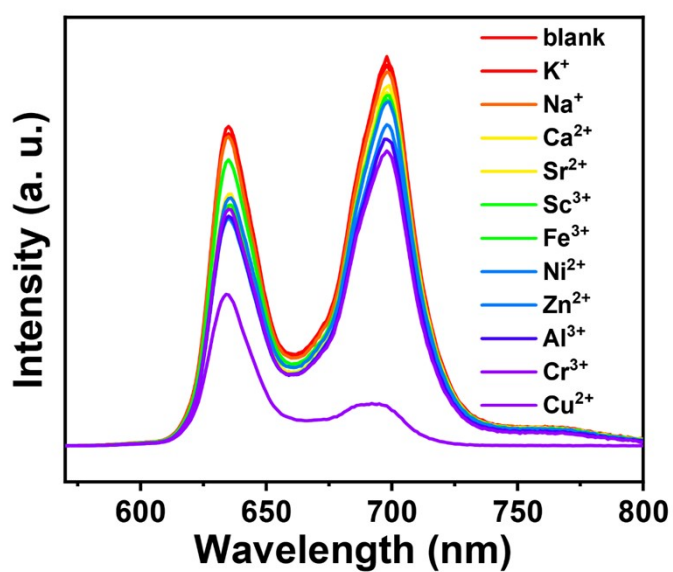


Fig. S16 DBP-HOF was used as a fluorescent probe to study the transmission spectra of aqueous solutions containing different metal ions ( $\lambda_{\text{ex}}=365$  nm, The concentration of all metal ions is 100 nM).

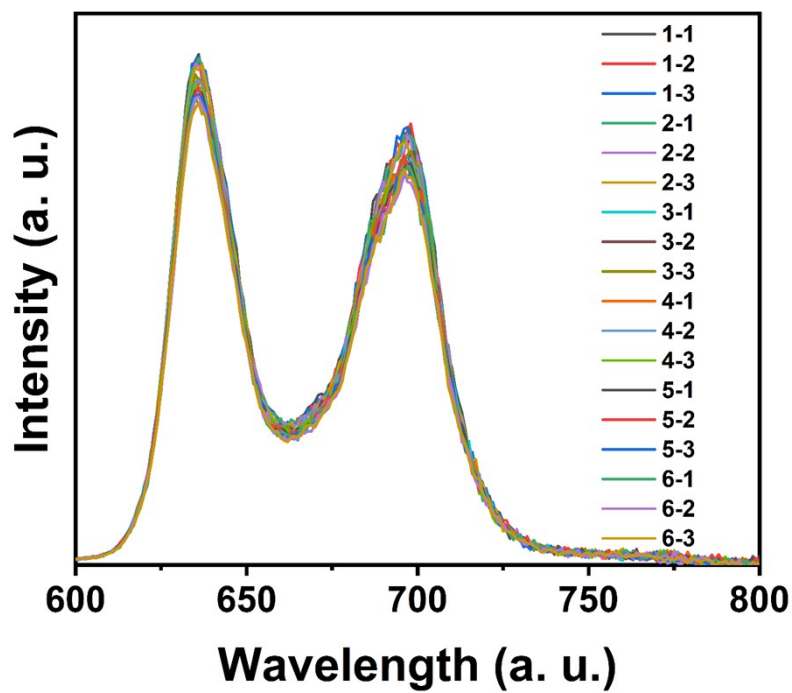


Fig. S17 Recyclability test of DBP-HOF towards the sensing of  $\text{Cu}^{2+}$  at 698 nm.

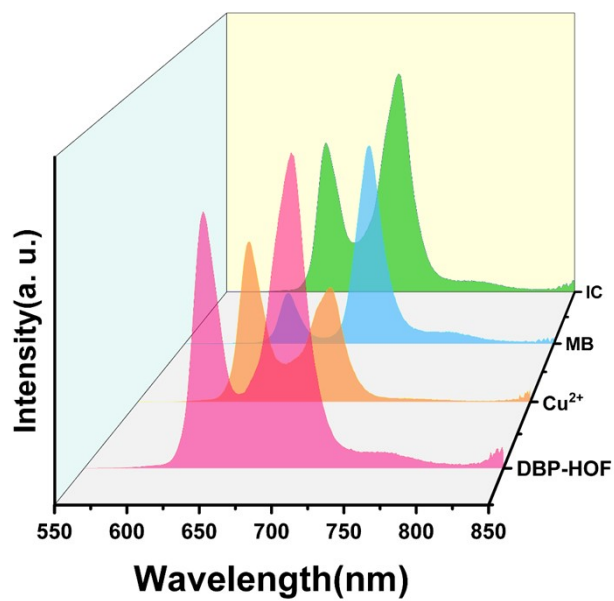
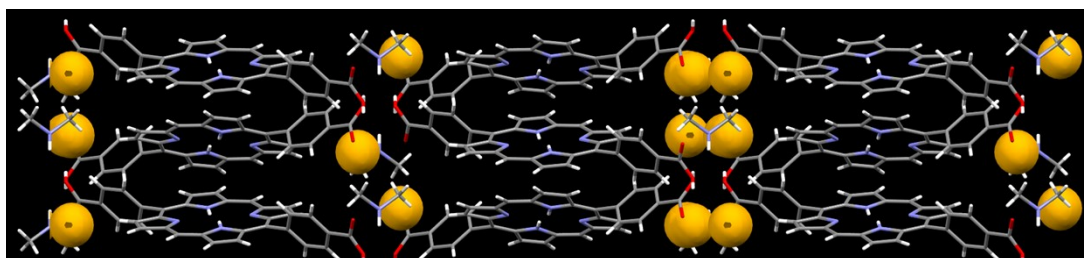
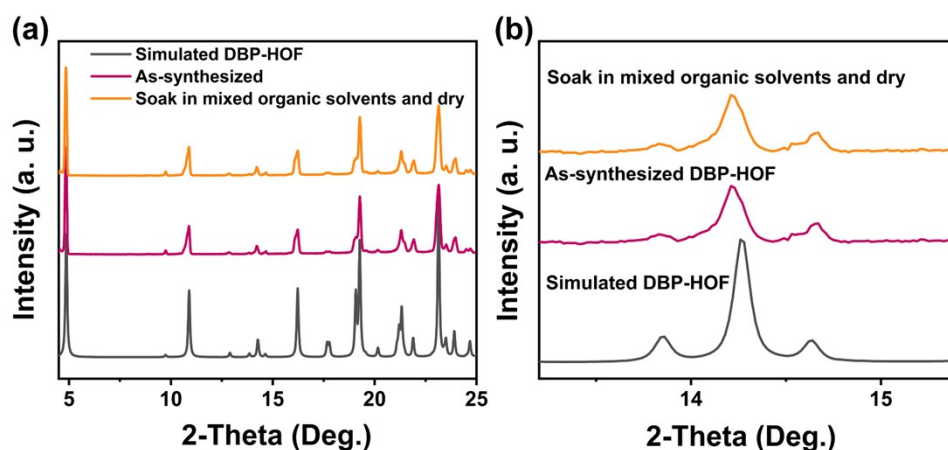


Fig. S18 Transmission spectra of aqueous  $\text{Cu}^{2+}$ , MB, and IC at certain concentrations.



**Fig. S19** Mercury shows the porosity (yellow ball) in the DBP-HOF structure.



**Fig. S20** (a) PXRD of DBP-HOF dried after immersion in a variety of organic solvents; PXRD of DBP-HOF around  $14^\circ 2\theta$  ( $^\circ$ ).

## 9. Detection

Detection of  $\text{Cu}^{2+}$ : 400 mg of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was weighed, and 10 mL of deionized water was added to prepare an aqueous solution of copper chloride of  $40 \text{ g L}^{-1}$ , after which aqueous solutions of copper chloride of different concentrations were prepared.

Detection of other metal ions: Aqueous solutions were prepared by replacing  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{SrCl}_2$ ,  $\text{ScCl}_3$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , respectively.

Detection of MB: 10 mg of MB was weighed, and 10 mL of deionized water was added to prepare an aqueous solution of MB of  $1 \text{ g L}^{-1}$ , after which aqueous solutions of MB of different concentrations were prepared.



Detection of IC: 10 mg of IC was weighed, and 10 mL of deionized water was added to prepare an aqueous solution of IC of  $1 \text{ g L}^{-1}$ , after which aqueous solutions of IC of different concentrations were prepared.

## References

1. Lu, K.; He, C.; Lin, W. *J Am Chem Soc* 2014, **136**, 16712–16715
2. Ren, Y.; Wang, M.; Yang, X.-Y.; Xu, W.-J.; Lei, Q.-J.; Zhang, J.; Wen, J.-X.; Gu, J.-X.; Chao, Z.-S.; Jin, H.-G. *Chemical Engineering Journal* 2022, **437**, 135150