Supplementary information

Rapid and Specific Luminescent Sensing of Cu(I) Ion with Porphyrinic Metal-Organic Framework

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Experimental section

Chemicals and materials

All the chemicals were commercially available reagents of analytical grade unless otherwise specified, and were used without further purification. Metal ions were used as nitrate salts. All solutions were prepared using purified water purchased from Hangzhou Wahaha Group (Hangzhou, China).

Synthesis of *meso*-tetra (4-carboxyphenyl) porphyrin (TCPP)

The preparation of TCPP was carried out following the previously described procedure with slightly modifications^{1, 2}. Briefly, in a 250 mL round-bottom flask equipped with magnetic stirrer, 1.5 g of 4-formylbenzoic acid (10 mmol) was added to 50 mL of propionic acid. The mixture was stirred and heated to 80 °C at which temperature the aldehyde fully dissolved. Then a propionic acid solution (10 mL) of freshly distilled pyrrole (0.7 mL, 10 mmol) was added dropwise to the reaction mixture. The resultant dark mixture was refluxed with continued stirring for 2 h. After cooling to room temperature, the reaction flask was placed in the freezer overnight to aid precipitation of the porphyrin. The solid product was then separated by filtration and was washed several times with dichloromethane (DCM) followed by a small amount of distilled water in order to remove unreacted propionic acid and impurities. After that, the resulting purple solid was collected and dried overnight (about 50% yield).

¹H-NMR (400 MHz, DMSO-d₆): δ 8.86 (8H, s, β-H), 8.36 (16H, dd, o+m ArH), 2.93 (2H, s, NH). ¹³C-NMR (101 MHz, DMSO-d₆): δ 167.5, 145.3, 134.4, 130.5, 127.8, 119.2. Mass

Spectrum (MALDI-MS): Calculated (M) 790.206, Observed (M+1) 791.116. UV-Vis (DMF): 415, 517, 554, 586 and 647 nm.

Synthesis of MOF-525

The MOF-525 nanocrystals were synthesized by a facile solvothermal process following the procedure³. Briefly, in a 20 mL scintillation vial, 1.35 g of benzoic acid and 105 mg of zirconyl chloride octahydrate were dissolved in 8 mL of N, N-dimethylformamide (DMF) by sonication. The clear solution was heated at 80 °C for 2 h. After cooling down to room temperature, 47 mg of TCPP was added into the solution, and the mixture was sonicated for 20 min. Thereafter, the vial was closed with a urea cap and heated at 80 °C for 24 h. After cooling down, the microcrystalline powder was filtered and washed with DMF for three times by centrifugation. After the last wash, 10 mL of DMF was added into the centrifuge tube, and a concentrated suspension could be obtained by sonication. Then a small amount of concentrated suspension was diluted with 1.0 M NaOH aqueous solution to digest the MOF-525. And the concentration of TCPP in the obtained solution was estimated by UV-Vis spectroscopy with Beer-Lambert law based on the extinction coefficient of H₄TCPP (Fig. S4). The original concentration of MOF-525 could be calculated as about 6000 mg·L⁻¹ according to the molecular formula of MOF material. Considering the product loss during the washing process, the concentration of obtained MOF slightly varies in parallel vials. Then, a certain amount of DMF was added into appropriate volume of the concentrated suspension to obtain the stock solution of 600 $mg \cdot L^{-1}$. It was preserved under dark condition for further use.

For material characterizations purpose, the activation process of the MOF-525 nanocrystals is required. After last wash of DMF, the sample was then washed with acetone twice and socked in acetone for 24 h. Finally, the dark red powder was obtained after dried overnight.

Material characterization and instruments

Nuclear magnetic resonance (¹H-NMR and ¹³C-NMR) spectra were recorded on a Bruker 400 MHz apparatus at 298 K. Mass spectrum was performed on a Bruker Ultraflex MALDI-TOF mass spectrometer by using 2,5-dihydroxybenzoic acid as a matrix. The crystalline phases of the products were determined by powder X-ray diffraction (PXRD) measurement using a Rigaku D/Max 2000 diffractometer equipped with monochromatic Cu K α radiation ($\lambda = 1.5406$ Å). All patterns were obtained at an accelerating potential of 40 kV and a tube current of 100 mA with a scanning rate of 2°/min. Thermogravimetric analysis (TGA) was carried out using a simultaneous thermal analysis instrument SDT Q600 at a heat rate of 10 °C/min up to 600 °C under air atmosphere. The N₂ adsorptiondesorption isotherms were collected on a Micromeritics ASAP 2020M apparatus with prior degassing under vacuum at 120 °C. Scan electron microscopy (SEM) images were obtained by ZEISS Merlin Compact field-emission scanning electron microscope. UV-Vis absorption spectra were recorded with a PE Lambda 35 spectrophotometer in the wavelength range of 350-700 nm.

Luminescent sensing experiments

For the typical Cu(II) ion or other metal ions detection, 20 µL of MOF-525 stock solution

(600 mg·L⁻¹) was added into DMF and was mixed thoroughly. Then, the Cu(II) ion or other metal ions stock solutions were added to give a series of mixture solutions with different concentrations of analytes. The final Cu(II) ion concentrations were in the range from 0.1 to 1.2 mg·L⁻¹ (about 1.57 μ M to 18.88 μ M), and the final volumes of the prepared batches of solutions were kept at 2 mL. After mixing thoroughly at room temperature for 40 s, the fluorescence spectra were recorded with an emission wavelength in the range from 600 to 720 nm (excitation at $\lambda = 512$ nm). All of the fluorescent emission spectra were conducted on a Hitachi F-7000 spectrophotometer. In addition, the luminescence lifetimes (τ) were examined by a Edinburgh FLS980 spectrophotometer.

The recovery experiments were employed to evaluate the Cu(\mathbb{I}) ion concentration in real mineral and tap water samples. Typically, different concentrations of Cu(\mathbb{I}) ion (0, 0.4, 0.7 and 1.2 mg·L⁻¹) were added into real water samples and mixed with MOF suspension thoroughly then determined with a fluorescence measurement. The concentrations were calculated by the fluorescent response ($\lambda = 651$ nm) of spiked water samples and linear regression equation. All the experiments were repeated three times to get an average value.



Fig. S1 The ¹H-NMR spectrum of TCPP ligand.



Fig. S2 The ¹³C-NMR spectrum of TCPP ligand.



Fig. S3 The MALDI-MS spectrum of TCPP ligand.



Fig. S4 (a) UV-Vis spectra of different concentrations of TCPP in 1.0 M NaOH. (b) The calibration curve of the absorbance at 415 nm versus TCPP.



Fig. S5 The SEM image of MOF-525.



Fig. S6 The TGA plot of MOF-525.



Fig. S7 The UV-Vis spectrum of MOF-525 in DMF.



Fig. S8 The fluorescence spectra of blank MOF-525 (6 mg·L⁻¹) at different measurements.



Fig. S9 The calibration curve for fluorescence intensity against Cu(II) ion concentration.

MOF	LOD	Reference
MOF-525	67 nM	This work
Cd-MOF-74	78.7 μM	20174
$\{[Nd_2(NH_2-BDC)_3(DMF)_4]\}_n$	24.95 μM	2017 ⁵
MIL-53-L	10 µM	20166
UiO-66-NH ₂	2.5 μM	20167
PCN-222-Pd(II)	50 nM	20168
Eu ³⁺ @UiO-66-2COOH	1 nM	20169
${NH_2(CH_3)_2 \cdot Cd_{2.5}(L)_2(H_2O) \cdot (H_2O)}_n$	0.1 mM	2016 ¹⁰
$[Cd_2(PAM)_2(dpe)_2(H_2O)_2] \cdot 0.5(dpe)$	1 mM	201511
$[Eu(pdc)_{1.5}(DMF)] \cdot (DMF) \cdot 0.5(H_2O)_{0.5}$	10 µM	2015 ¹²
[Eu(HL)(L)(H ₂ O) ₂]·2H ₂ O	10 µM	2015 ¹³
[ZnL ₂]n	1 µM	2015 ¹⁴
[Cd(2-aip)(bpy)]·2DMF	10 mM	2015 ¹⁵
$\{[Mg_3(ndc)_{2.5}(HCO_2)_2(H_2O)][NH_2Me_2] \cdot 2H_2O \cdot DMF\}$	10 µM	2014 ¹⁶
[Eu ₃ (HCOO) ₂ (R-COO) ₈]	10 µM	201417
[Cd(H ₂ ttac)bpp] _n	0.63 mM	2014 ¹⁸
Eu(FBPT)(H ₂ O)(DMF)	10 µM	2013 ¹⁹
${Mg(DHT)(DMF)_2}_n$	10 µM	2012 ²⁰
$Zn(MeIM)_2 \cdot (DMF) \cdot (H_2O)_3$	1 mM	2011 ²¹
[NH ₄] ₂ [ZnL]·6H ₂ O	1 µM	2010 ²²
$[Eu(pdc)_{1.5}(dmf)] \cdot (DMF)_{0.5}(H_2O)_{0.5}$	0.1 µM	2009 ²³

Table S1 Previously reported various MOF-based sensors for Cu(${\rm I\!I}$) ion.

Samples	Spiked values (mg·L ⁻¹)	Detected values (mg·L ⁻¹)	Recovery (%) ^b	RSD (%) ^c
	0	ND ^d	-	-
Mineral water	0.40	0.37	92.0	5.8
	0.70	0.76	108.2	5.1
	1.0	1.1	105.5	7.4
Tap water	0	ND	-	-
	0.40	0.35	87.7	0.8
	0.70	0.67	96.2	0.5
	1.0	1.0	100.1	4.6

Table S2 The Cu(${\rm I\!I}$) ion determination in practical water samples (N^a=3).

a N is the repetitive measurement number. b Recovery (%) = $(C_{detected}/C_{spiked}) \times 100$. c RSD (%) are calculated based on measurements repeated N times. d ND is not detected.

Notes and references

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