

Supporting Information

A hydrostable Cu^{II} coordination network prepared hydrothermally as “turn-on” fluorescent sensor for S²⁻ and selective adsorbent for methylene blue

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Materials and Instruments

All reagents used were analytical reagents and commercially available. IR data were tested by using a Thermo Mattson FTIR spectrometer. Powder X-ray diffraction (PXRD) was obtained on a Rigaku D/Max 2200PC diffractometer with Cu K α radiation. Elemental analysis data of carbon, nitrogen, and hydrogen were tested using a Thermo Flash 2000 elemental analyzer. In a N₂ atmosphere, thermogravimetric analysis (TGA) was performed with a TGA/ NETZSCH STA449C instrument at a heating rate of 5 °C/min. Fluorescence data were collected by using F-7000 fluorescence spectrophotometer at F-7000 fluorescence spectrophotometer (Japan Hitachi company). The emission spectra of H₄L and **CuCP** in solid state at room were determined by putting the powdered solid samples between quartz plates under the exactly same experimental condition where the excitation and emission slits were 5 nm and 5 nm, voltage was 700 V and scan speeds were 1200 nm/min. Ultraviolet-visible (UV-vis) absorption spectral data were executed with a UV-1800 Shimadzu spectrophotometer.

The Synthesis Steps of CuCP

The synthesis of [Cu₂L(H₂O)₂]_n (**CuCP**). The mixture of H₄L (0.01 mmol, 4.1 mg), Cu(NO₃)₂·3H₂O (0.02 mmol) and 6 mL H₂O was sealed in a polytetrafluoroethylene liner high pressure reactor (25 mL) and heated at 140 °C for 3 days , and then cool to room temperature at a rate of 5 °C·h⁻¹. The green rod-shaped single crystal washed with water was collected by filtration and the test samples could be obtained by repeating the experiment.

Crystallographic Data Collection and Refinement

Single crystals of **CuCP** with approximate dimensions of $0.37 \times 0.15 \times 0.15 \text{ mm}^3$ suitable for X-ray diffraction were obtained in moderate yield by solvothermal method. Crystal data of **CuCP** was collected on a Bruker APEX-II CCD diffractometer (Cu K α radiation, $\lambda = 0.71073 \text{ \AA}$) at 100 K. Structures were solved by direct methods and refined by a full matrix least-squares technique based on F^2 using the SHELXL 2014 program.¹ All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. Disordered phenylic H and uncoordinated carboxyl H for **CuCP** was not located but are included in their formulas. Drawings of the molecules were performed with the program Diamond.³ Crystallographic data as well as details of data collection and refinement for these complexes are summarized in Table S1, important bond lengths are listed in Table S2.

Thermal Stability and Chemical Stability Experiments

The thermogravimetric analysis (TGA) experiment of **CuCP** at 25~800 °C was carried out under N₂ atmosphere to evaluate its thermal stability. The Powder X-ray diffraction (PXRD) experiments were performed to verify the chemical and water stability by soaking **CuCP** in deionized water for two weeks and aqueous solutions of different pH values (2 ~ 12) treated by HCl or NaOH for 48 hours.

Sorption Kinetics and isotherm

The linear forms of pseudo first and second order kinetic model are expressed as the following equations:

$\ln(Q_e - Q_t) = \ln Q_t - k_1 t$ Pseudo first order kinetic model

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 k_2} + \frac{t}{Q_e} \quad \text{Pseudo first order kinetic model}$$

where Q_e and Q_t are the amounts of MB (mg/g) adsorbed onto the adsorbent at equilibrium and at a given time t (min), respectively; k_1 and k_2 are the pseudo first and second order rate constants (g/mg/min), respectively.

The Langmuir isotherm is represented as following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m k_L} + \frac{C_e}{Q_m}$$

where C_e is the equilibrium iodine concentration (mg/L), Q_m is the maximum adsorption capacity (mg/g), k_L is the Langmuir adsorption isotherm constant (L/mg).

The Freundlich isotherm is represented as following equation:

$$\ln Q_e = \ln k_F + \frac{1}{n} \ln C_e$$

where the k_F and n are the Freundlich adsorption isotherm constants.

Table S1. Crystal data and structure refinement parameters for **CuCP**.

Compound	CuCP
CCDC number	20114829
Empirical formula	C ₁₀ H ₁₀ NO ₇ Cu
Temperature (K)	173.20(10)
Formula weight	318.98
Diffraction	CuK α (1.54184 Å)
Crystal system, Space group	Monoclinic, C2/c
Unit cell dimensions	$a = 14.0500(9)$ Å $b = 5.0906(3)$ Å; $\beta = 104.268(6)^\circ$ $c = 26.2723(16)$ Å
$V/\text{Å}^3, Z$	1821.1(2), 8
$D_{\text{calcd}}/\text{Mg m}^{-3}$	2.070
μ/mm^{-1}	3.543
$F(000)$	1136
θ range for data collection	$3.472^\circ \sim 66.548^\circ$
index ranges, hkl	$-16 \leq h \leq 15; -6 \leq k \leq 6; -30 \leq l \leq 31$
Independent reflections (R_{int})	0.0586
Completeness	97.7%
Reflections unique / collected	1773 / 1773
Data / restraints / params	1773 / 0 / 156
Goodness-of-fit on F^2	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0447, wR_2 = 0.1248$
R indicCs (all data)	$R_1 = 0.0456, wR_2 = 0.1257$

Table S2. Selected bond lengths (Å) and angles ($^\circ$) for **CuCP**.

Cu1–O1 1.985(3)	Cu1–O3 2.161(3)	Cu1–O3 1.939(3)	Cu1–O5 2.218(3)	Cu1–N1 1.893(4)
O1–Cu1–O5 98.35(13)	O1–Cu1–O3 159.50(12)	O3–Cu1–O 1 97.45(13)	O3–Cu1–N3 99.29(8)	
O3–Cu1–O5 89.37(12)	O3–Cu1–O5 102.89(13)	N1–Cu1–O5 97.75(13)	N1–Cu1–O3 78.59(13)	
N1–Cu1–O3 159.25(15)	N1–Cu1–O1 81.5(19)			

Table S3. Cartesian coordinates of H₄L optimized structures by DFT.

B3LYP/6–31G in gas phase, Charge = 0 Multiplicity = 3

C	1.38592	-0.0008	0.00032	C	3.63679	1.20042	-0.00677
C	0.67534	-1.20984	0.00779	C	3.63675	-1.20253	0.00694
C	-0.71794	-1.20706	0.00627	C	5.04274	1.14923	-0.00737
C	-1.41721	-0.00032	0.00004	H	3.11688	2.16686	-0.01178
C	-0.71755	1.20615	-0.00609	C	5.04276	-1.15085	0.0056
C	0.67578	1.20845	-0.0074	H	3.1172	-2.16917	0.01278
H	1.22328	-2.1641	0.00721	N	5.7446	-0.00069	-0.00134
H	-1.26652	-2.16039	0.0089	C	5.87883	2.44248	-0.01524
H	-1.26578	2.15968	-0.00879	C	5.87922	-2.44387	0.01246
H	1.224	2.16254	-0.00667	O	5.22448	3.71397	-0.02205
C	-2.95721	-0.00008	-0.00009	H	4.59219	3.75283	0.69927
C	-3.65454	1.20829	-0.00633	O	7.13588	2.38418	-0.01571
C	-3.6549	-1.20786	0.00591	O	5.22524	-3.71554	0.0203
C	-5.04925	1.20879	-0.00587	H	4.50362	-3.70869	-0.6128
H	-3.10419	2.16032	-0.01028	O	7.13625	-2.38521	0.01119
C	-5.05004	-1.20754	0.00537	O	-5.10246	-3.77819	0.01758
H	-3.10545	-2.16034	0.01065	H	-5.72444	-4.50945	0.01522
N	-5.74727	0.00051	-0.00039	O	-7.07746	2.54772	-0.01148
C	-5.81998	-2.54124	0.01142	O	-5.10145	3.77945	-0.01789
C	-5.81907	2.54256	-0.01187	H	-5.72331	4.51076	-0.00915
O	-7.07836	-2.54629	0.01095	C	2.92592	-0.0011	0.00066

Table S4. Selected bond lengths (Å) and angles (°) of Na₄L optimized structure by DFT.

O31–Na39	2.321	O38–Na41	2.247	C28–O37–Na41	88.74
O32–Na39	2.248	O35–Na42	2.351	C29–O31–Na39	87.07
O33–Na40	2.28	O36–Na42	2.247	C29–O32–Na39	89.64
O34–Na40	2.247	O37–Na41	2.250	C30–O33–Na40	87.94
C30–O34–Na40	88.98	C27–O36–Na42	90.19	C27–O35–Na42	86.31
C28–O38–Na41	88.38	O31–C39–O39	60.54		

Table S5. Kinetic model and adsorption isotherm parameters for the adsorption.

Model	Parameters	k	Q_{cal}	R^2
Pseudo first order model		0.015 min ⁻¹	376.57 mg/g	0.82
Pseudo second order model		0.006 g/mg/min	380.32 mg/g	0.99
Langmuir isotherm		0.036 L/mg	375.97 mg/g	0.99
Freundlich isotherm		0.19 mg/g	395.67 mg/g	0.90

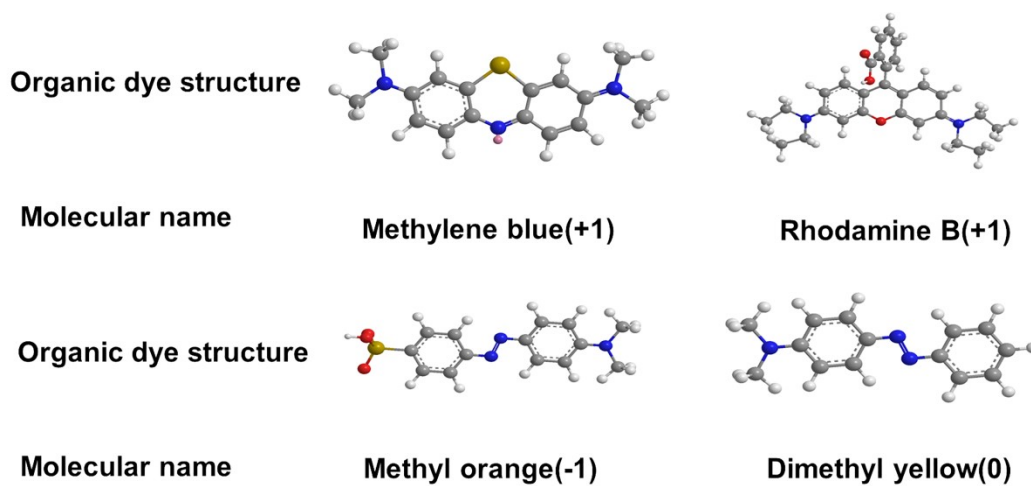


Fig. S1. The molecular structures of four dyes used.

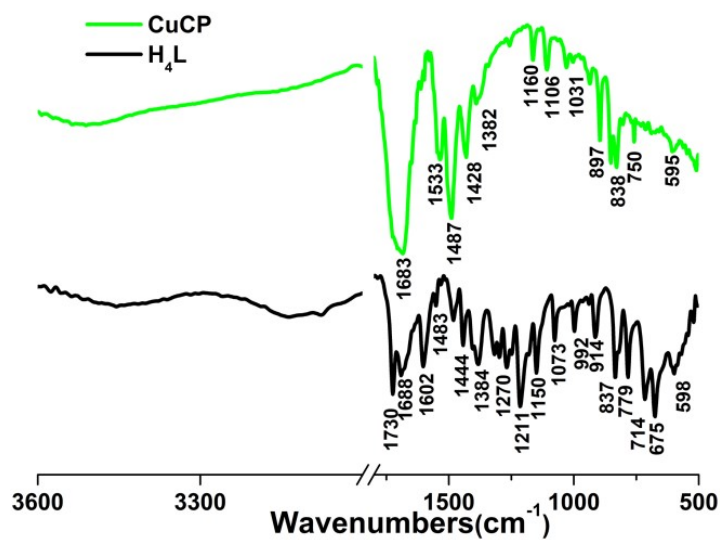


Fig. S2. IR spectra of H₄L and CuCP in solid state.

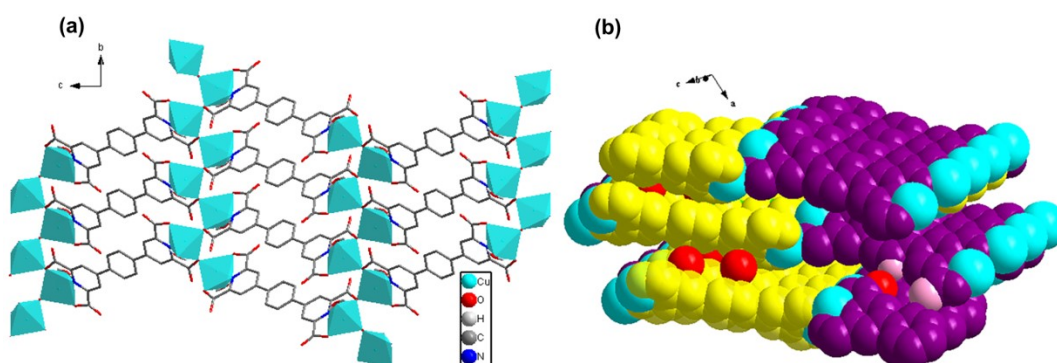


Fig. S3. (a) The 2D network of CuCP viewed along a-axis. (b) The 3D supramolecular architecture of CuCP constructed by multiple C-H...O hydrogen bonds.

Sample: L-Cu-----BET
 Operator:
 Submitter:
 File: D:\005-477.SMP

Started: 7/22/2021 10:47:34PM
 Completed: 7/22/2021 11:57:26PM
 Report Time: 9/22/2021 15:09:11PM
 Warm Free Space: 20.1496 cm³?Measured
 Equilibration Interval: 10 s
 Sample Density: 1.900 g/cm³

Analysis Adsorptive: N₂
 Analysis Bath Temp.: -195.800
 Sample Mass: 0.0901 g
 Cold Free Space: 59.9514 cm³?Measured
 Low Pressure Dose: None
 Automatic Degas: No

Summary Report

Surface Area

Single point surface area at P/P₀ = 0.046838711: 1.4468 m²/g

BET Surface Area: 1.4593 m²/g

Fig. S4. The summary report of N₂ adsorption determination for CuCP.

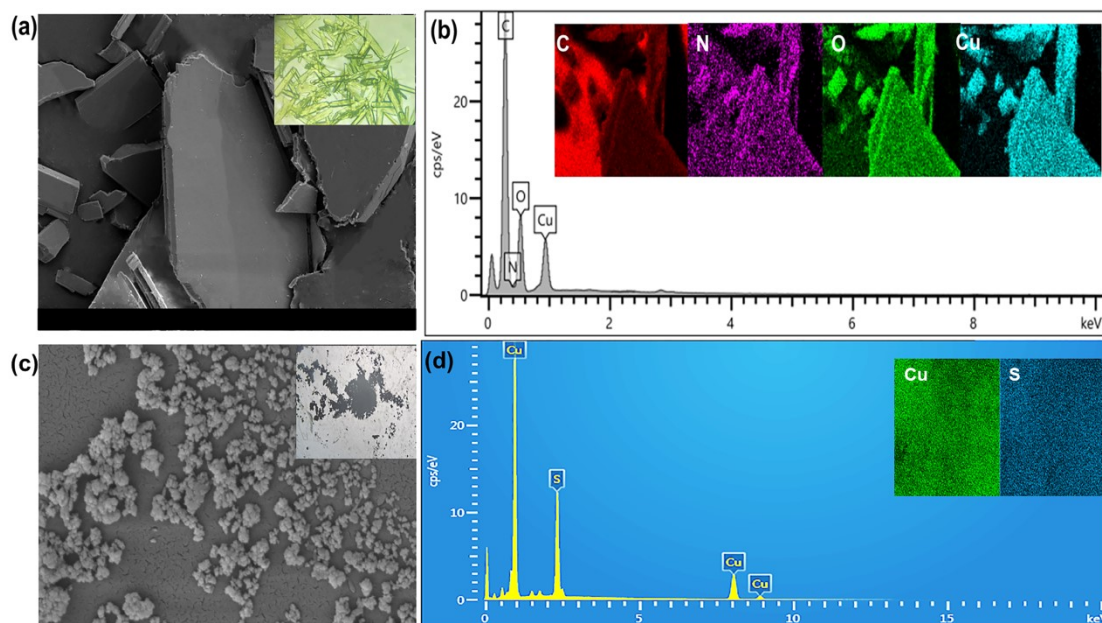


Fig. S5. The SEM image (a) (Inset: crystal image of CuCP) and elemental analysis of CuCP (b) (Inset: crystal image of Na₂S treated CuCP); The SEM (c) and elemental analysis of the black sediments obtained upon CuCP treated with Na₂S (d).

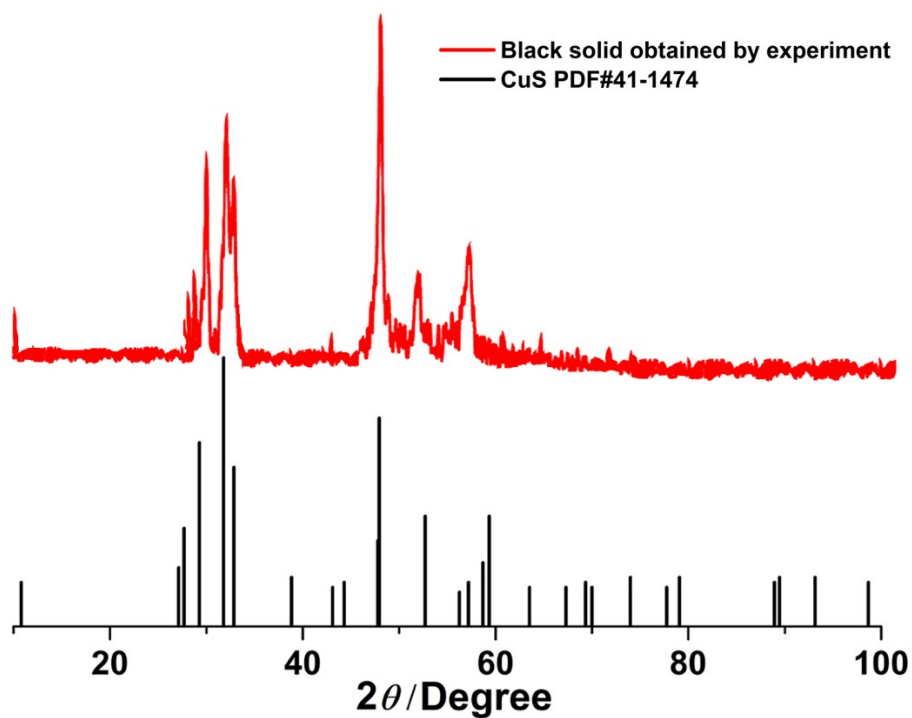


Fig. S6. The PXRD patterns of black solid obtained upon **CuCP** treated with Na_2S and the standard pattern of **CuS** (PDF41-1474).

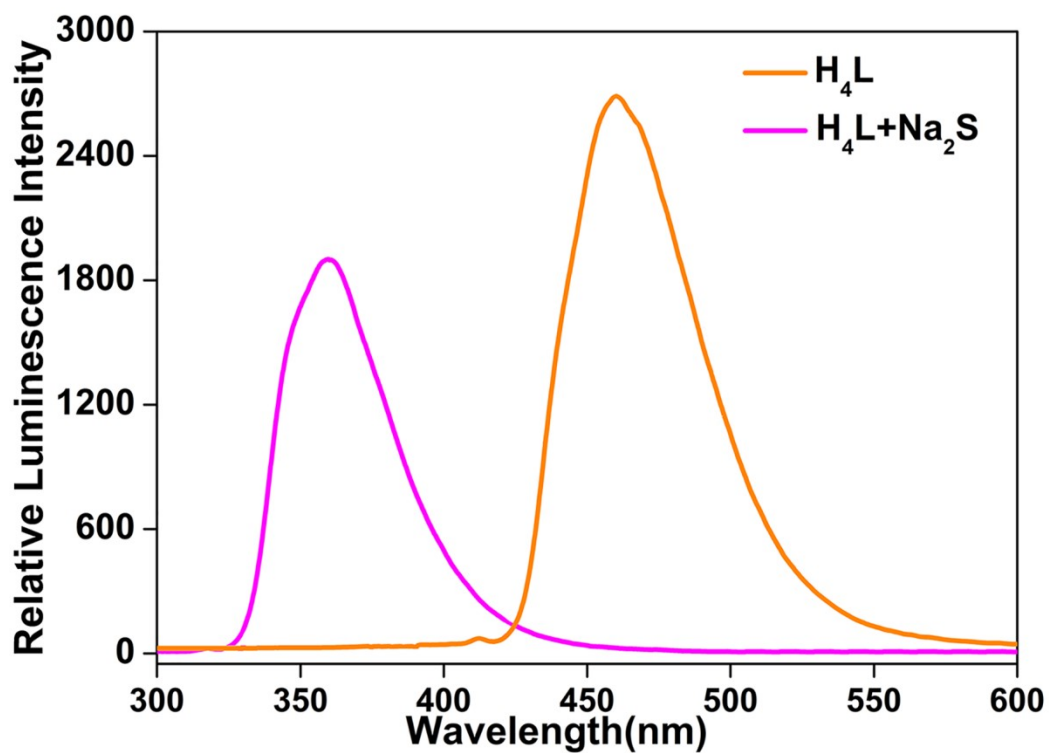


Fig. S7. The emission spectra of H_4L in water and that upon addition of Na_2S when excited at 320nm.

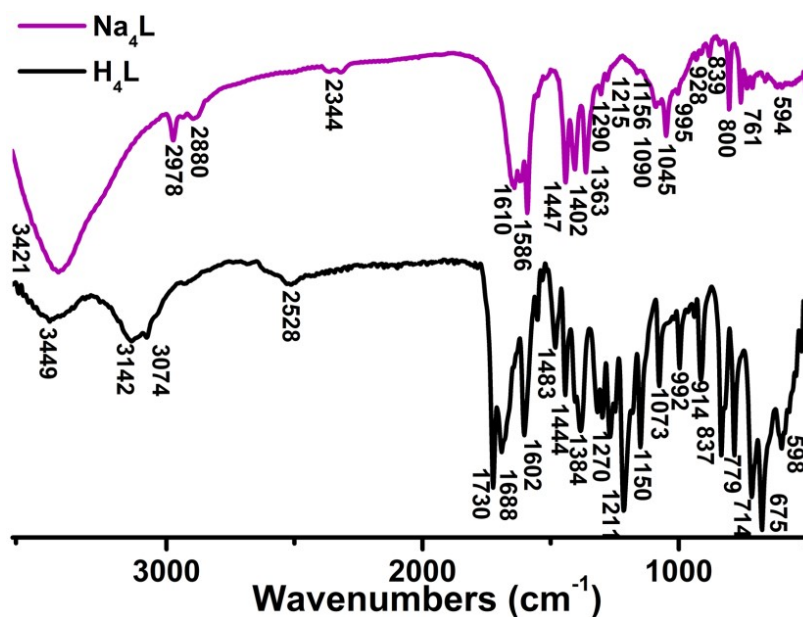


Fig. S8. The IR spectrum of H_4L and Na_4L obtained from Na_2S recognized by **CuCP**.

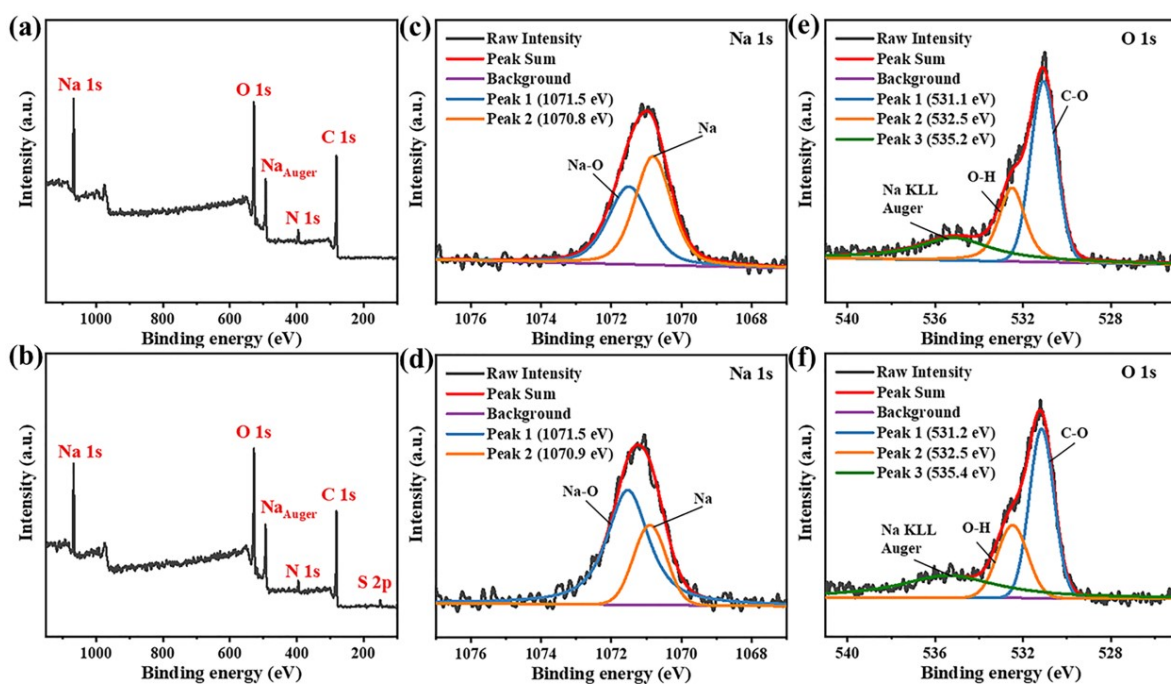


Fig. S9. The XPS spectrum of the white solid obtained from the Na_2S treated **CuCP** suspension (a) as well as that obtained from the reaction of H_4L and NaOH(b); Na 1s XPS for the white solid obtained from the Na_2S treated **CuCP** suspension (c) as well as that obtained from the reaction of H_4L and NaOH(d); O 1s XPS for the white solid obtained from the Na_2S treated **CuCP** suspension (e) as well as that obtained from the reaction of H_4L and NaOH(f).

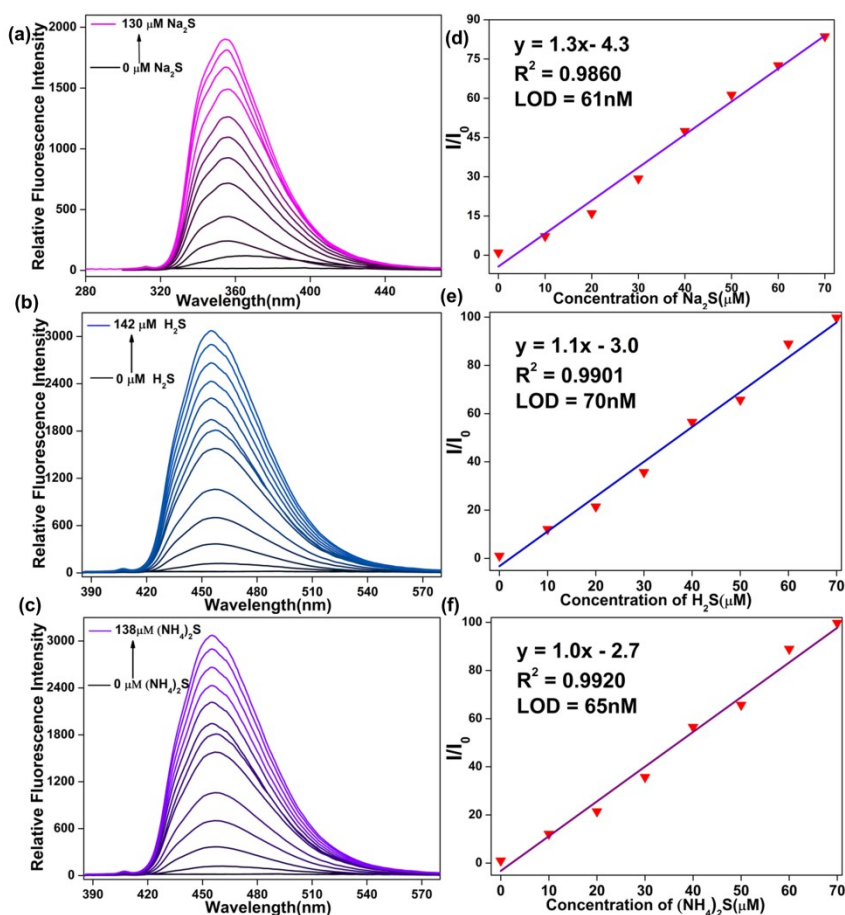


Fig. S10. The fluorescence response of CuCP to Na₂S(a), H₂S (b) and (NH₄)₂S (c) with concentrations ranging from 0~140 μM in tap water upon excited at 320 nm; The linear fitting observed at 0~70 μM for Na₂S(d), H₂S (e) and (NH₄)₂S (f) in tap water upon excited at 320 nm.

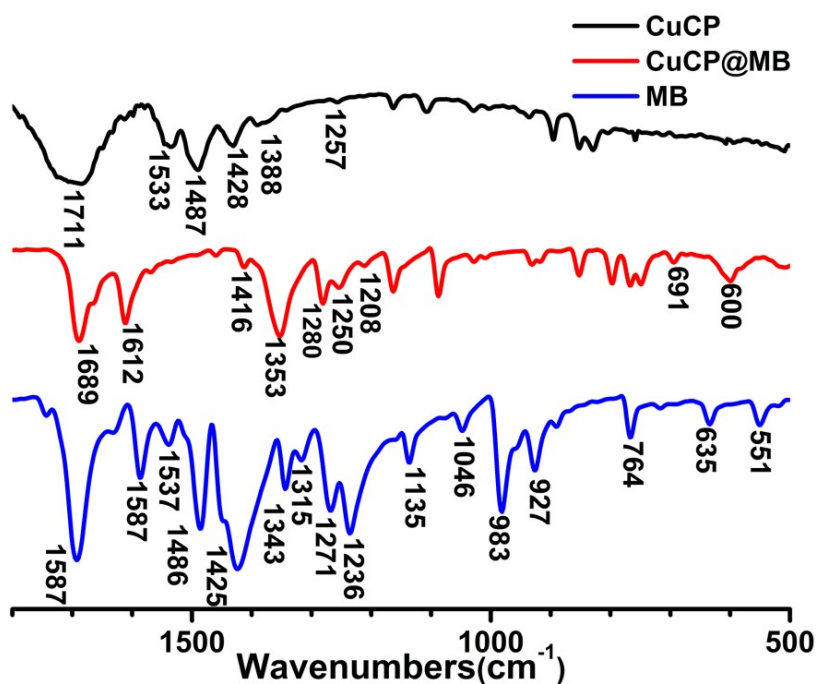


Fig. S11. The FT-IR spectra of MB, CuCP and CuCP@MB .

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3. DIAMOND. version 3.1; Crystal Impact: Bonn, Germany, 2004.