

Supporting information

A "off-on-off" fluorescence chemosensor for sensitive detection of Cu²⁺ in aqueous solution based on multiplet fluorescence emission mechanisms

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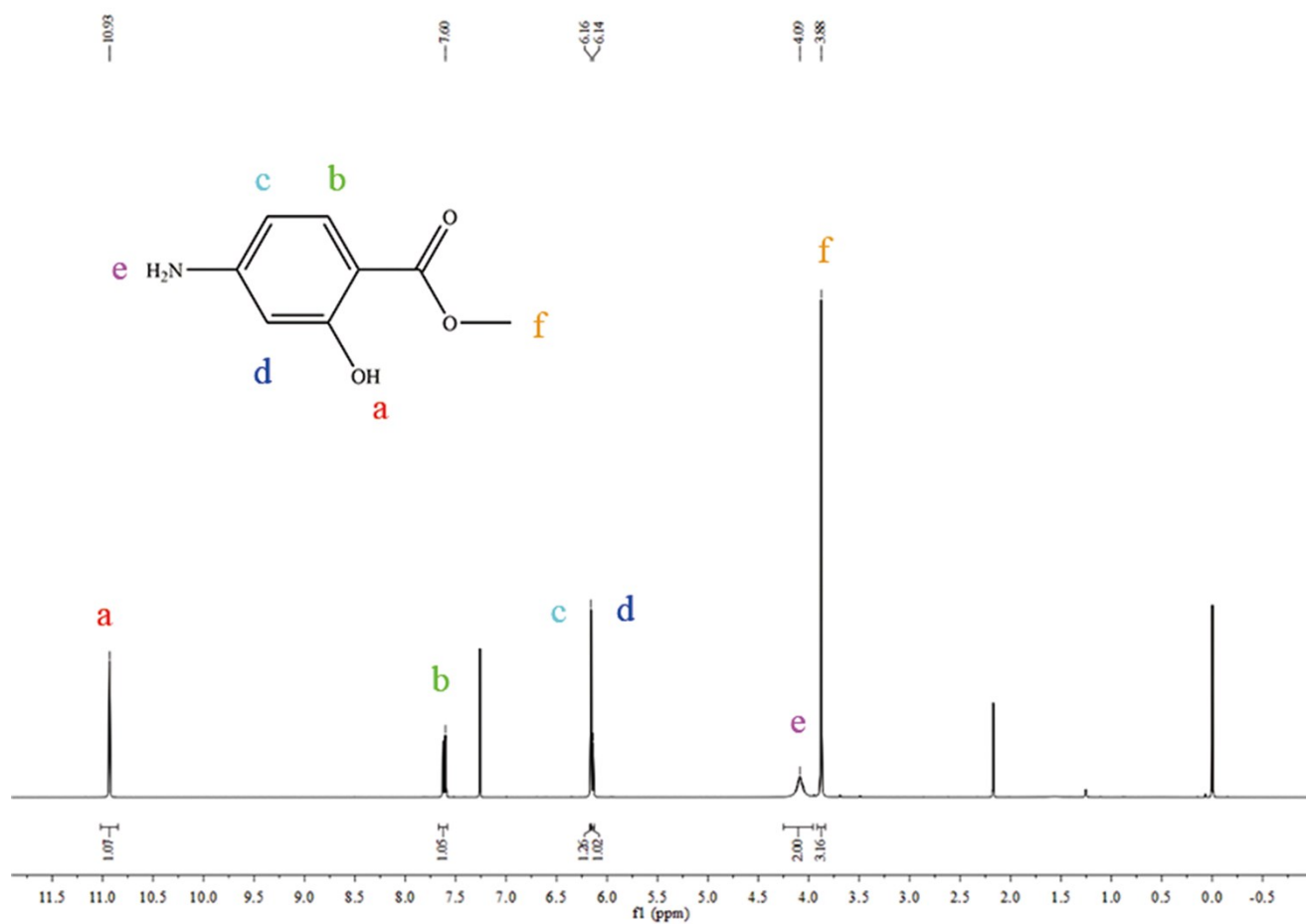


Figure S1. ^1H NMR spectrum of 4-amino-2-hydroxybenzoate.

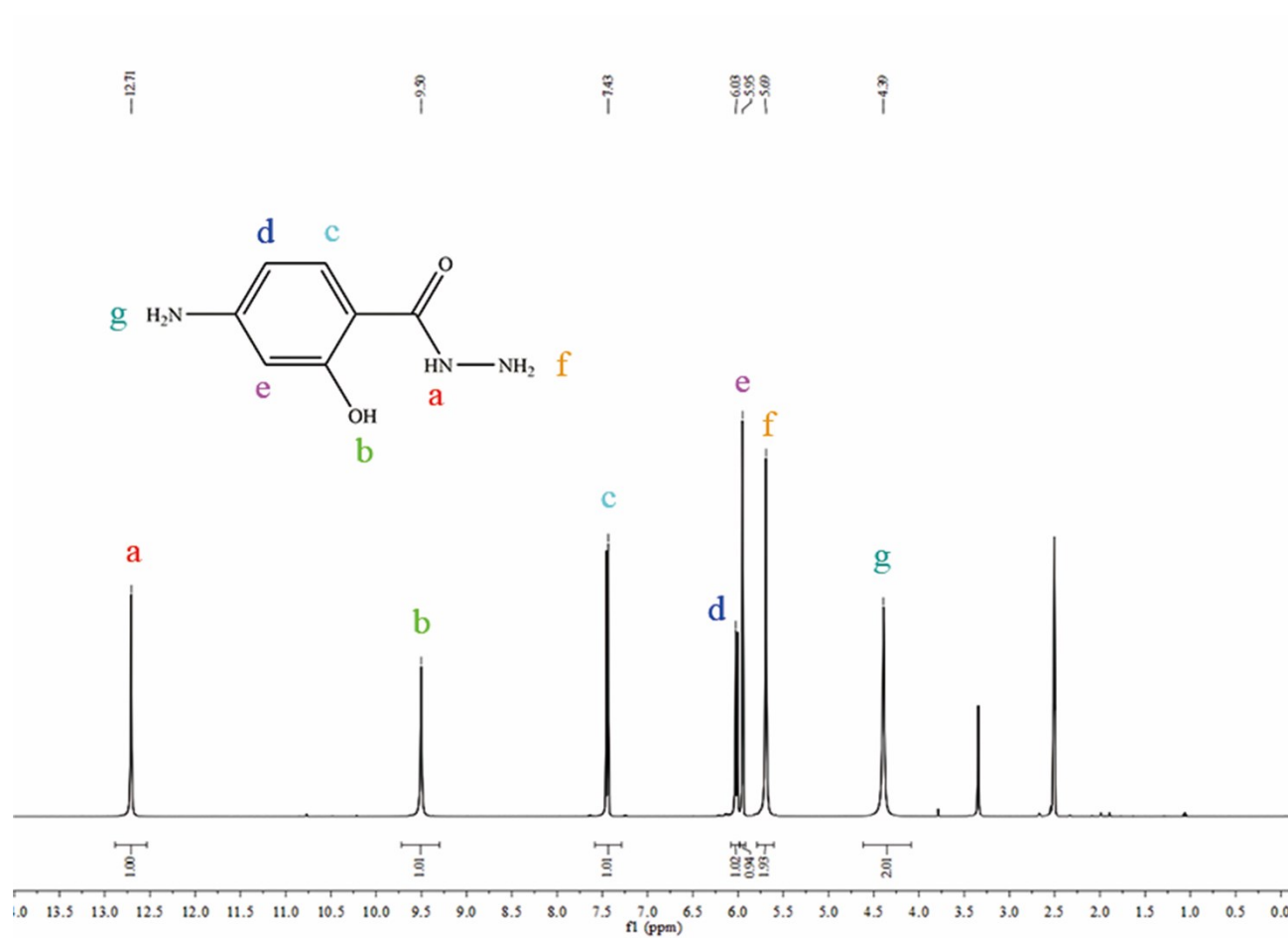


Figure S2. ^1H NMR spectrum of 4-Aminosalicylhydrazide.

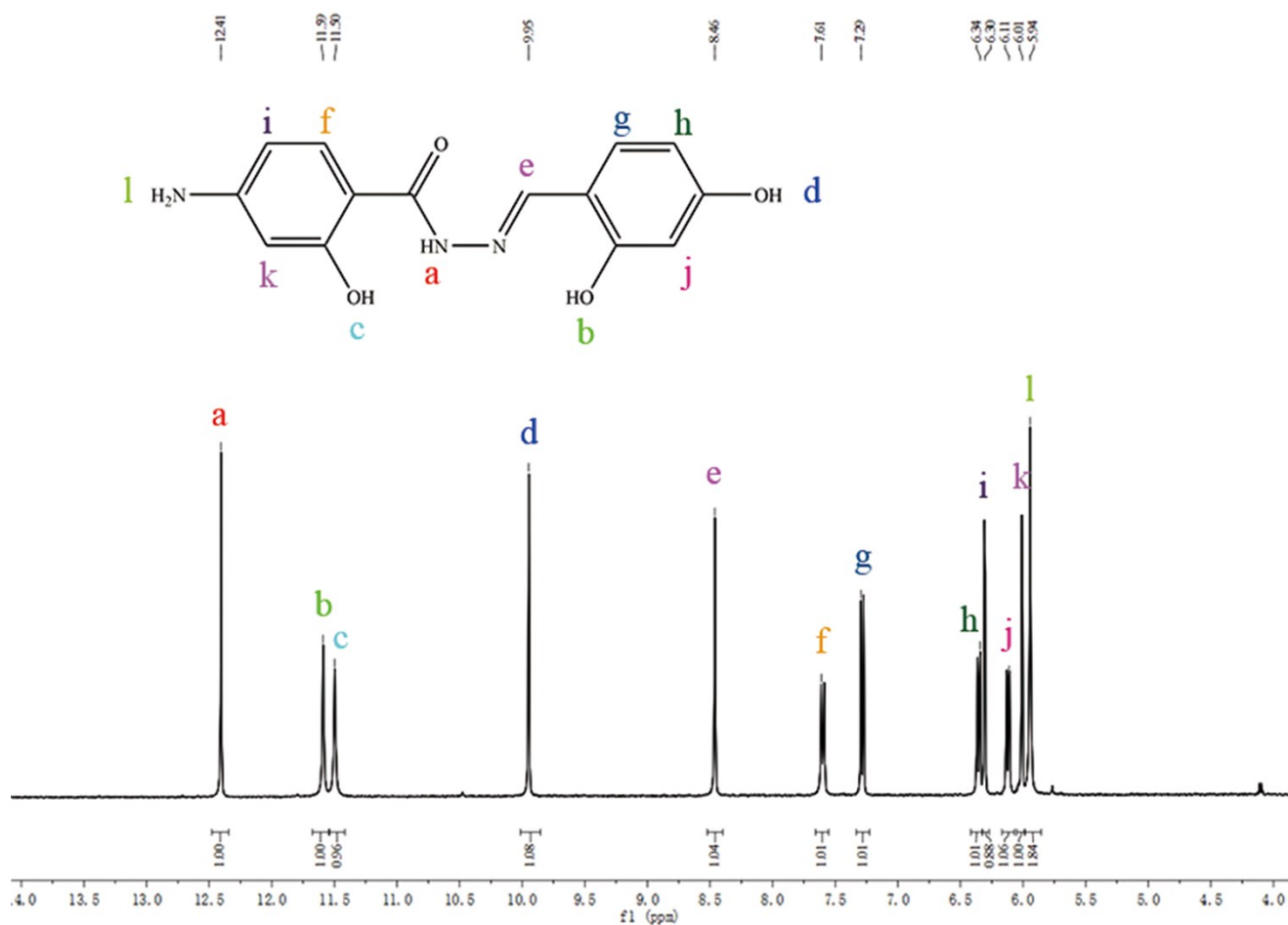


Figure S3. ^1H NMR spectrum of (E)-4-amino-N'-(2,4-dihydroxybenzylidene)-2-hydroxybenzohydrazide (AHBH).

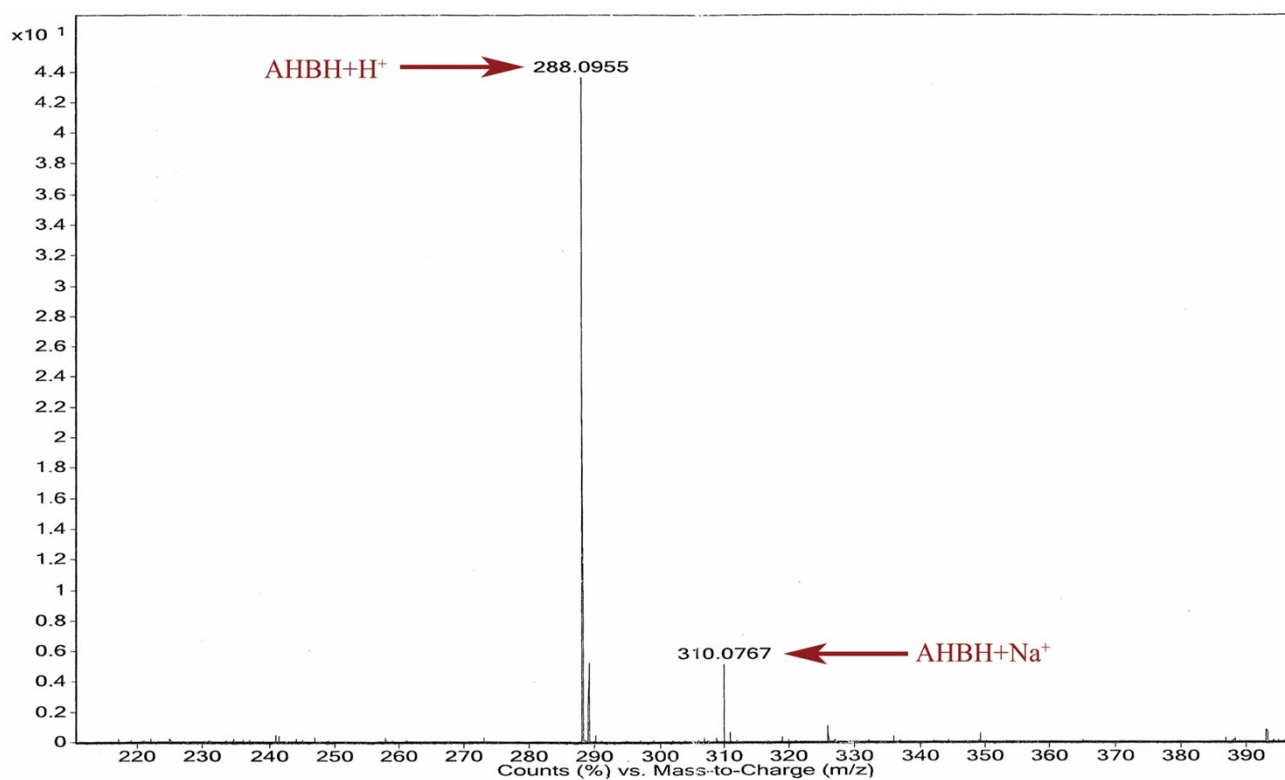


Figure S4. HRMS spectrum of (E)-4-amino-N'-(2,4-dihydroxybenzylidene)-2-hydroxybenzohydrazide (AHBH).

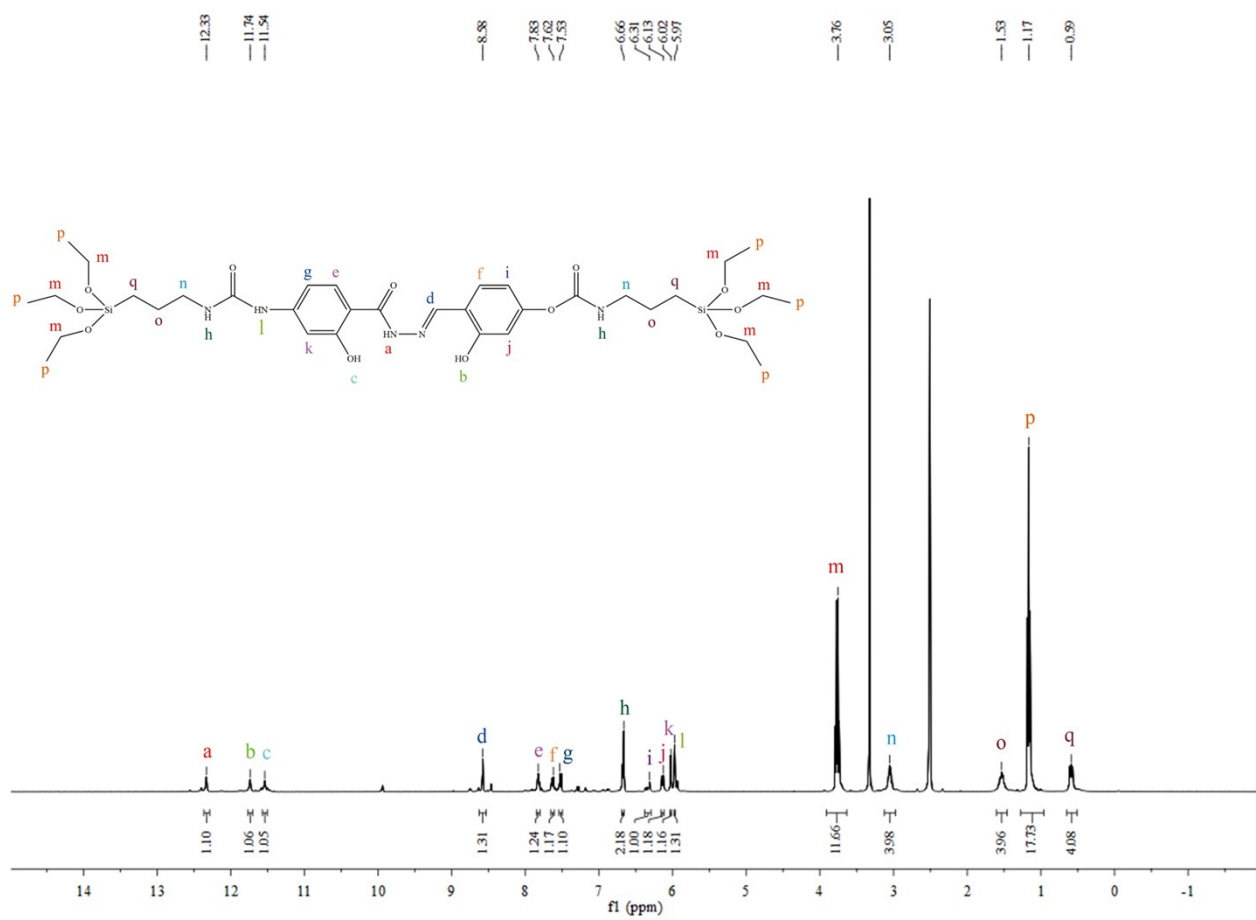


Figure S5. ^1H NMR spectrum of AHBH-Si.

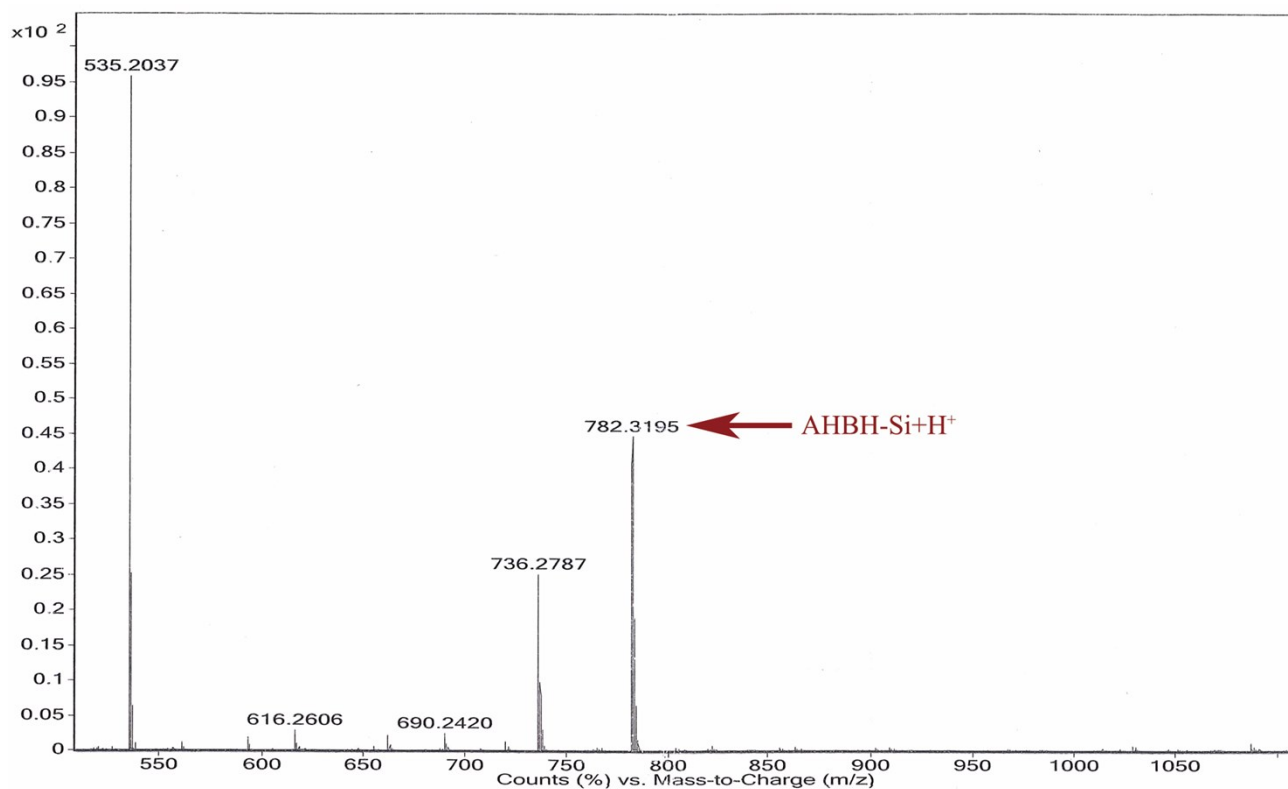


Figure S6. HRMS spectrum of AHBH-Si.

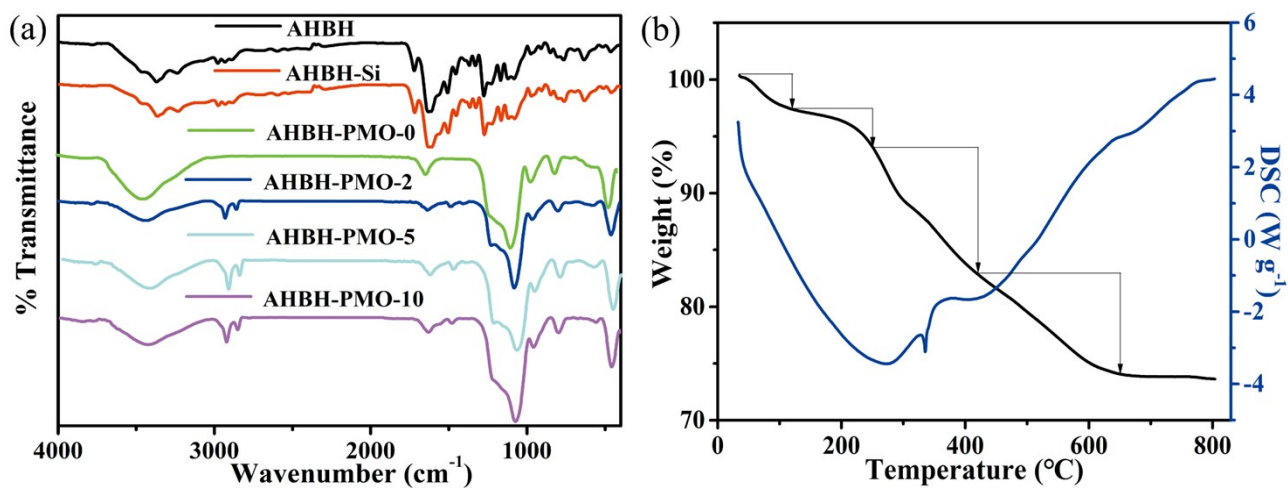


Figure S7. (a) FT-IR spectra of AHBH, AHBH-Si and AHBH-PMO-X after extraction, X=0, 2, 5, 10, respectively. (X is the quality fraction of AHBH-Si). (b) TGA/DSC of AHBH-PMO-10.

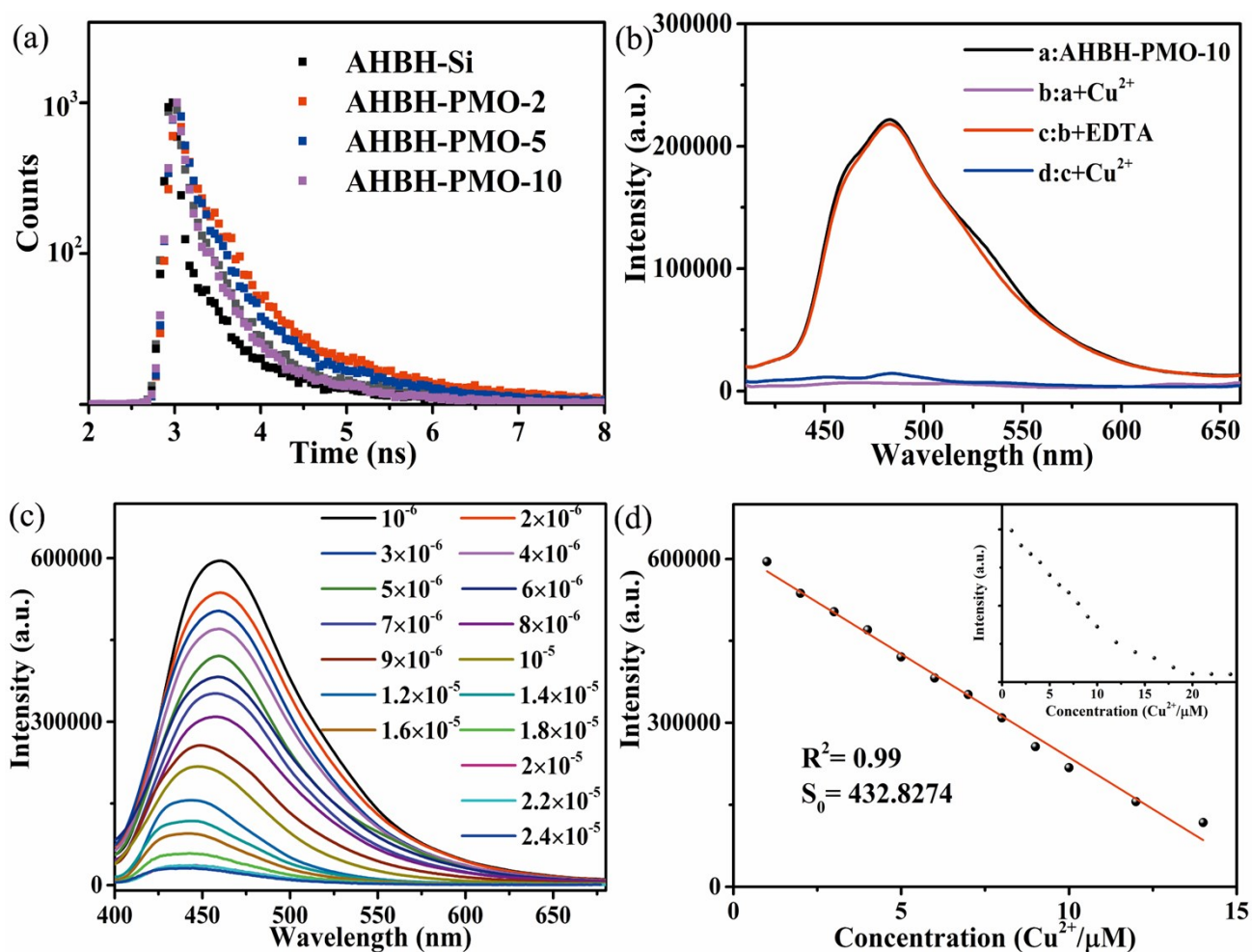
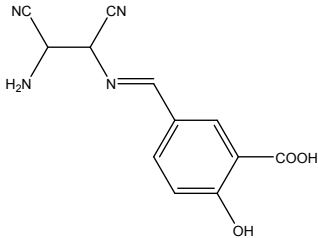
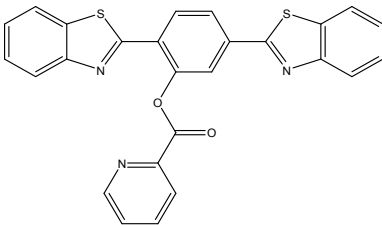
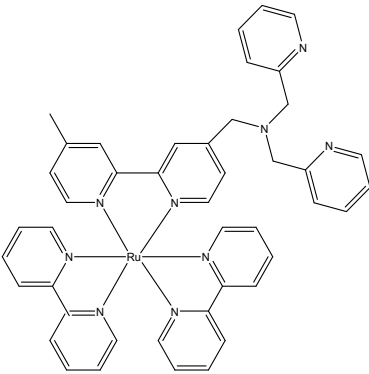
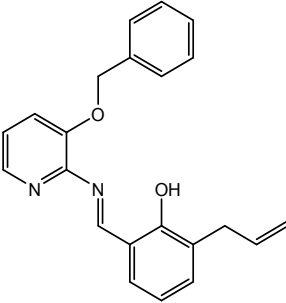


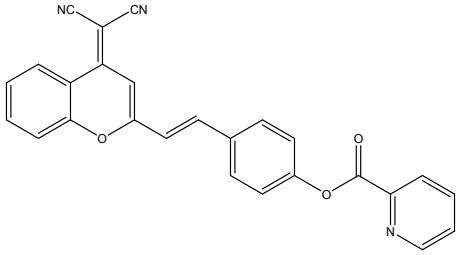
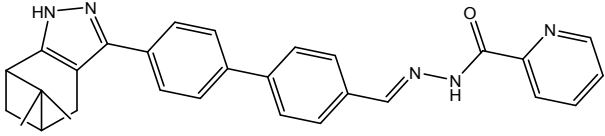
Figure S8. (a) Time-resolved fluorescence for the AHBH-Si and AHBH-PMOs. The fluorescence signal is collected at 482 nm, the excitation wavelength at 350 nm. (b) The reproductive test of AHBH-PMO-10 (2.25×10^{-4} M) in HEPES at pH=6.8. (c) Fluorescence spectra of AHBH (10^{-5} M) in THF: H_2O = 4:6 (v/v) with different concentrations of Cu^{2+} (10^{-6} - 2.4×10^{-5} M). (d) Linear relationship between AHBH (10^{-5} M) and the concentration of Cu^{2+} (10^{-6} - 2.4×10^{-5} M) in the solvent. Inset: The relationship between the concentration of AHBH (10^{-5} M) and Cu^{2+} (10^{-6} - 2.4×10^{-5} M) in the solvent.

Table S1. Fluorescence lifetimes and quantum yields of AHBH-Si and AHBH-PMOs

	AHBH-Si	AHBH-PMO-2	AHBH-PMO-5	AHBH-PMO-10
τ_1/ns	0.13 (63.41%)	0.63 (44.48%)	0.44 (37.41%)	0.35 (47.44%)
τ_2/ns	0.50 (36.59%)	1.66 (55.52%)	1.34 (62.59%)	1.04 (52.56%)
τ/ns	0.26	1.20	1.00	0.71
$\Phi/\%$	2.23	6.23	12.21	17.05

Table S2. Comparative study of some recently reported copper sensors with present study.

S. No.	Structure	LOD	Reference
1		$2.19 \times 10^{-7} \text{ M}$	1
2		$1.97 \times 10^{-8} \text{ M}$	2
3		$4.00 \times 10^{-8} \text{ M}$	3
4		$8.81 \times 10^{-8} \text{ M}$	4
5	Tb ³⁺ @UiO-66-(COOH) ₂	$2.30 \times 10^{-7} \text{ M}$	5

6		$2.54 \times 10^{-8} \text{ M}$	6
7	N,S-CDs	$3.8 \times 10^{-8} \text{ M}$	7
8		$1.70 \times 10^{-8} \text{ M}$	8

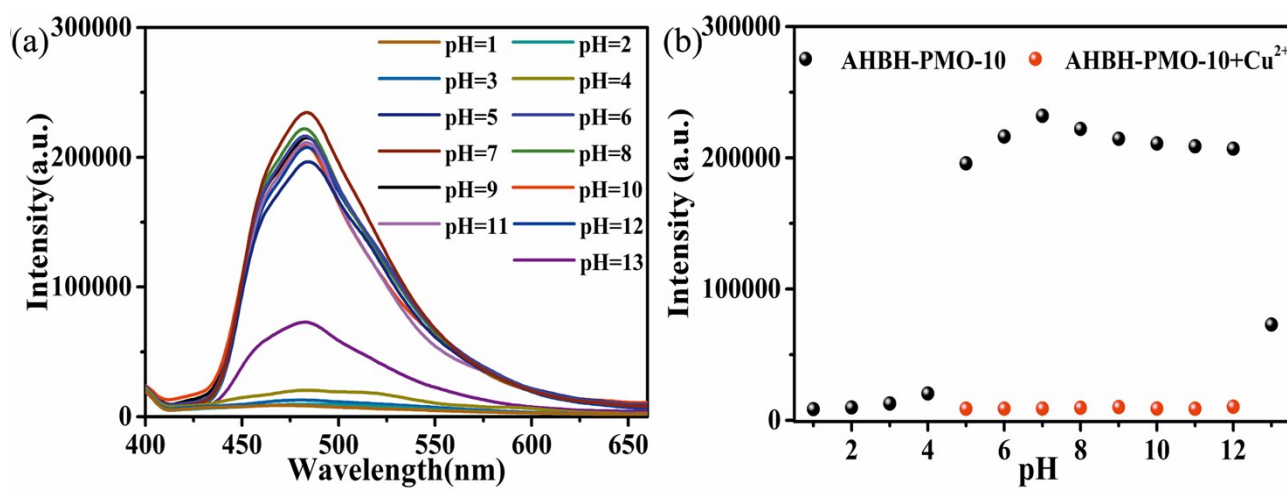


Figure S9. (a) Fluorescence emission spectra of AHBH-PMO-10 ($2.25 \times 10^{-4} \text{ M}$) in aqueous solution with different pH value. (b) Fluorescence intensity at 482 nm of AHBH-PMO-10 ($2.25 \times 10^{-4} \text{ M}$) in aqueous solution in the absence and presence of Cu^{2+} (10^{-6} M).

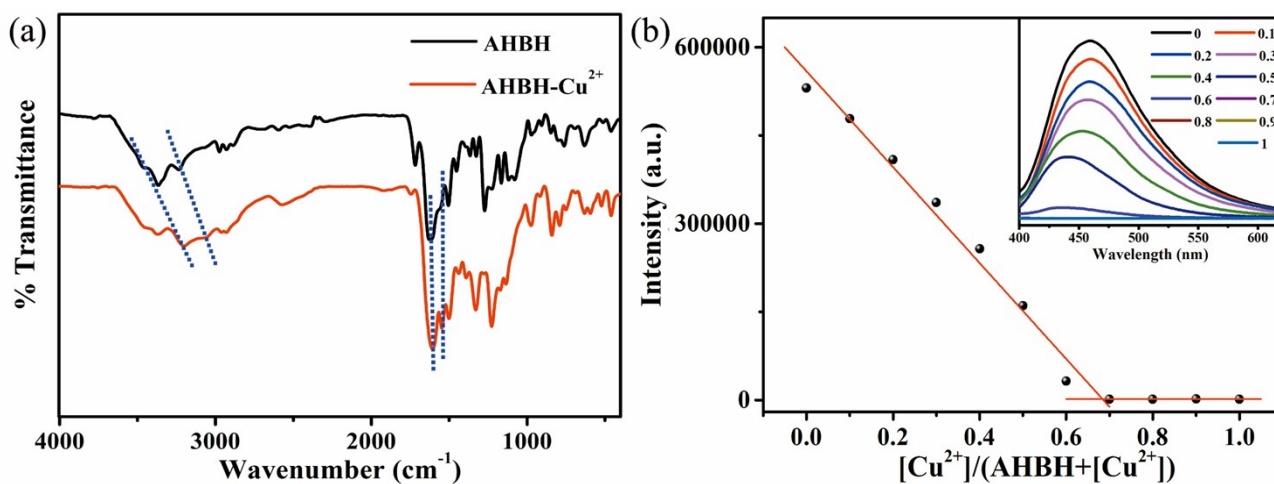


Figure S10. (a) FT-IR spectra of AHBH before (black) and after (red) adding Cu²⁺. (b) The job's plot of AHBH with molar fraction of Cu²⁺. Inset: Fluorescence spectra of solutions containing different molar fraction of Cu²⁺.

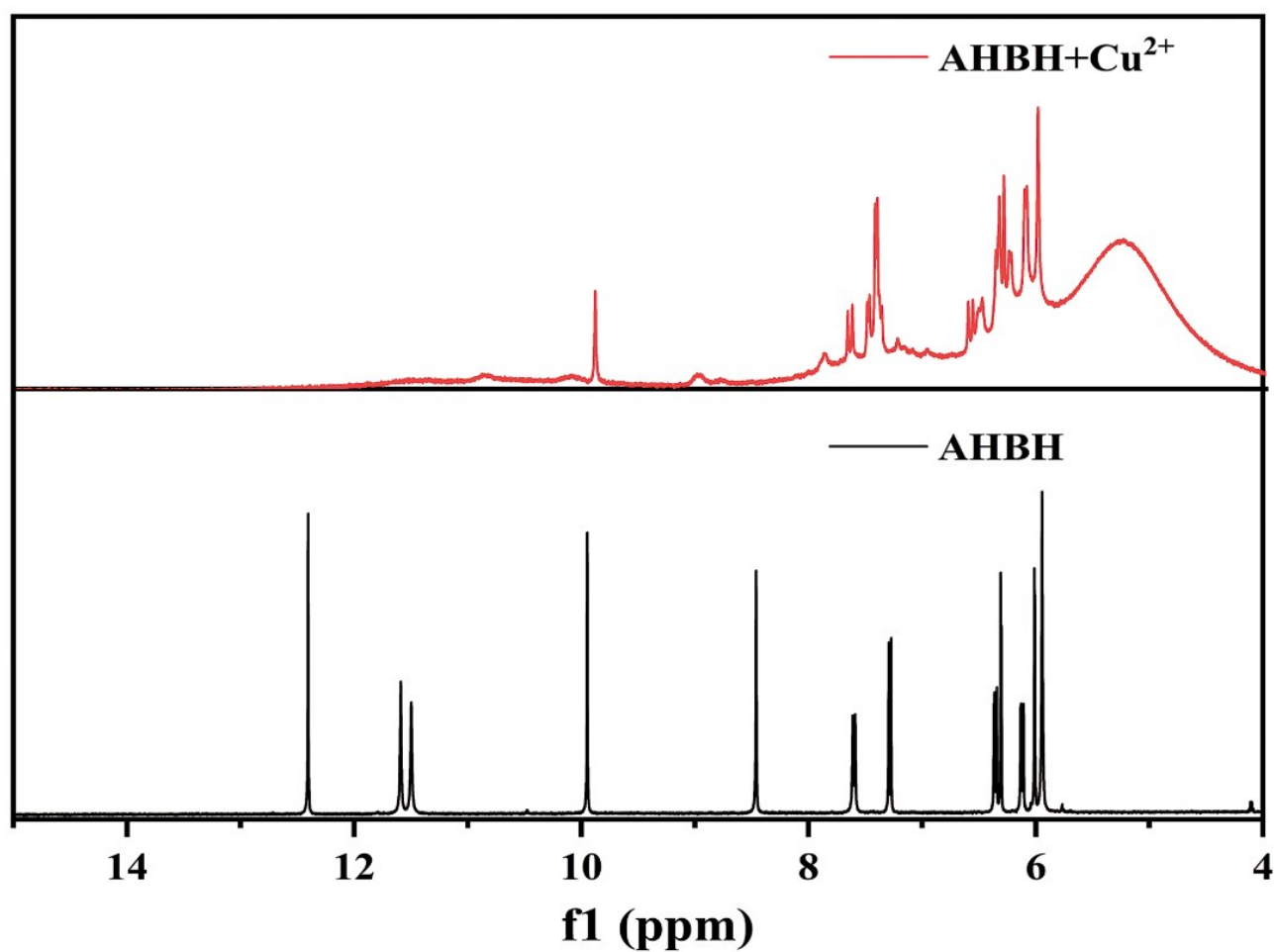


Figure S11. ¹H NMR spectra of AHBH before (black) and after (red) adding Cu²⁺ in DMSO-d₆.

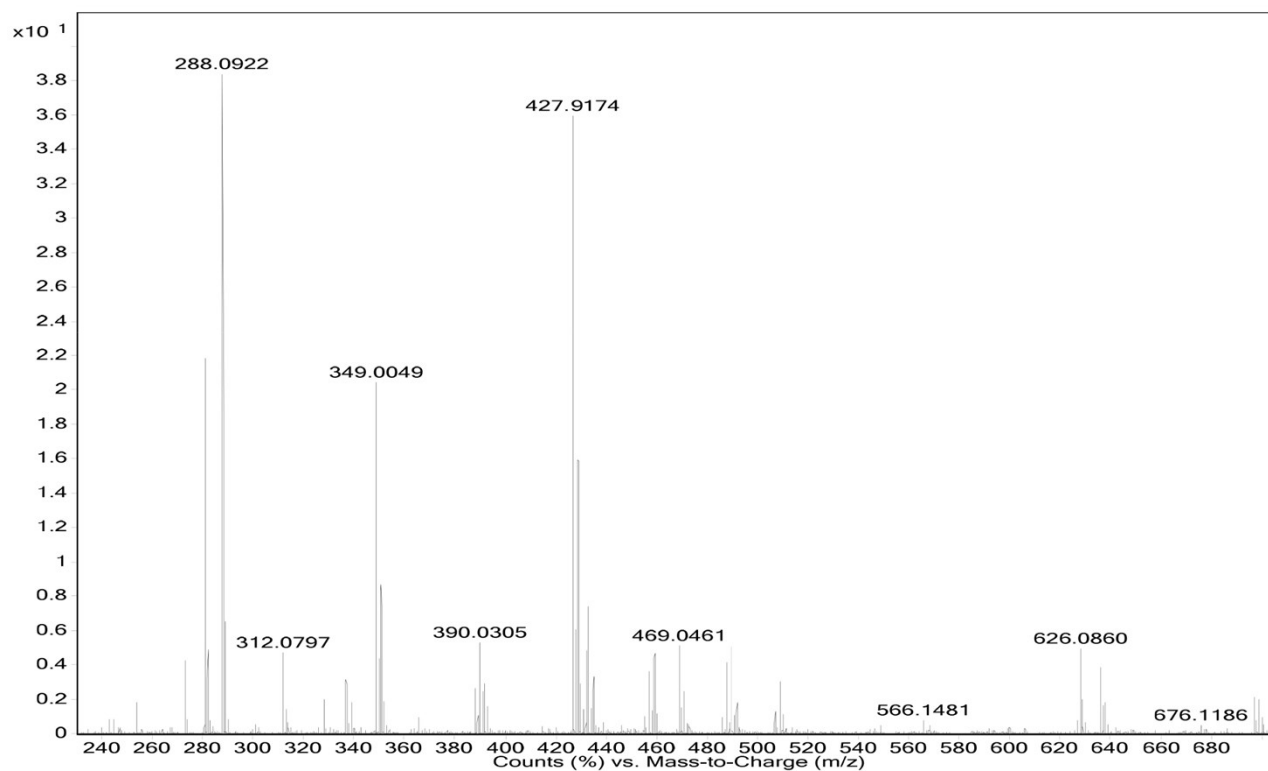
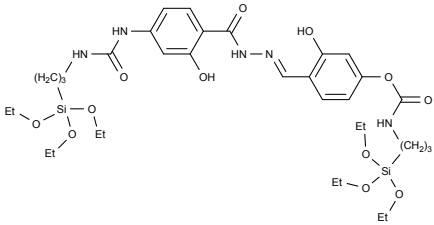
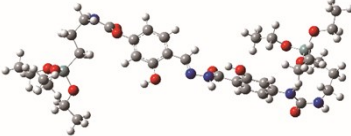
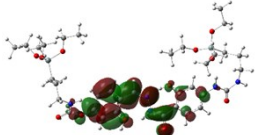
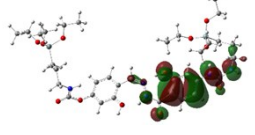
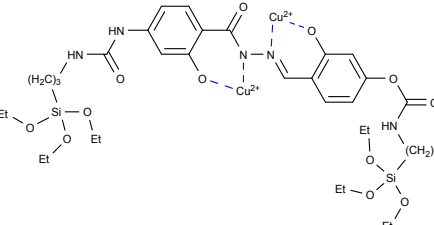
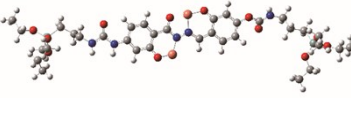
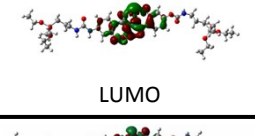
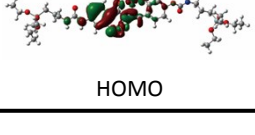
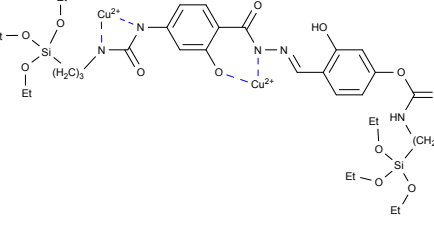
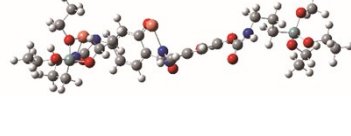
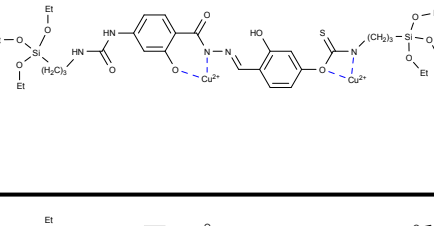
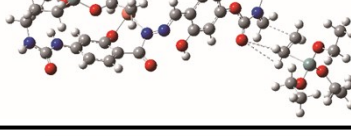
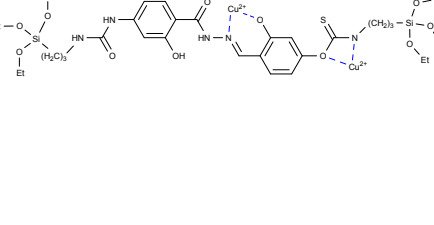
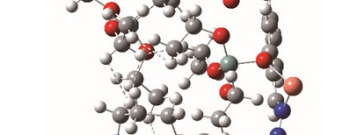


Figure S12. HRMS spectrum of AHBH with two equivalents of Cu^{2+} .

Table S3. The optimized structures and Frontier molecular orbitals of AHBH-Si and AHBH-Si-Cu²⁺ by density functional theory calculations under PEB0/6–31 G(d) level of theory.

Chemical Structure	Optimized Configuration	Frontier Orbital	$\Delta E/\text{eV}$
		 LUMO  HOMO	4.52
		 LUMO  HOMO	1.53
			
			
			

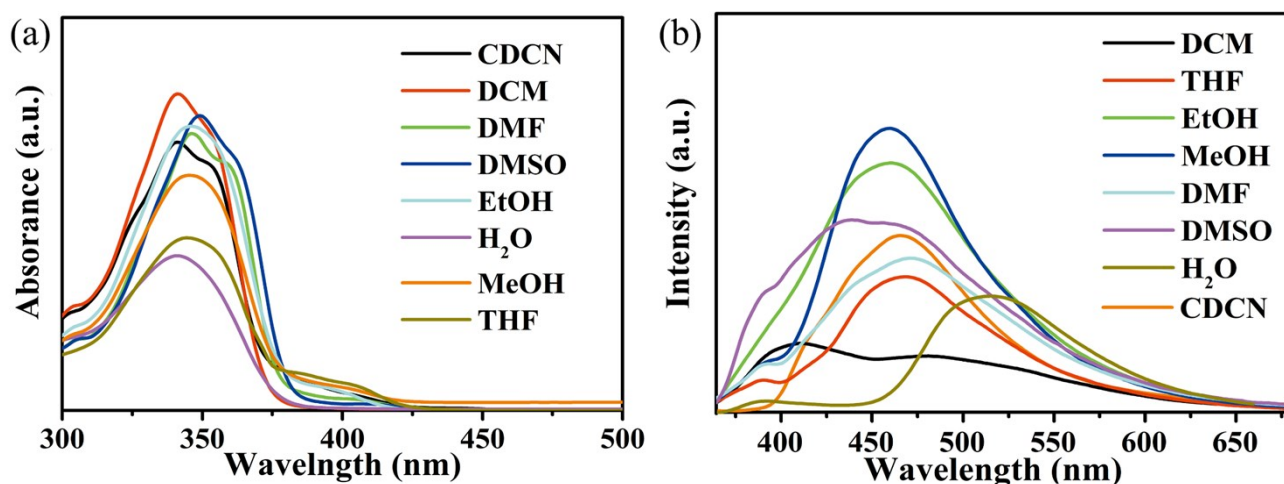


Figure S13. (a) UV-Vis absorption spectra of AHBH-Si in different solvents. (b) Fluorescence emission spectra of AHBH-Si in different solvents.

Table S4. UV-Vis and fluorescence emission characteristic peaks of AHBH-Si in different solvents

Solvent	DCM	THF	EtOH	MeOH	CDCN	DMF	DMSO	H ₂ O
UV-Vis/nm	341	345	346	346	341	347	349	341
						359	361	346
FL/nm	412	468	462	460	466	472	464	516
	487							

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