Supporting Information

Highly Sensitive and Selective Fluorescent Probe for Hg^{2+} in Ag(I)/Cu(II) 3D Supramolecular Architecture Based on Noncovalent Interactions

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Table S1 Crystal data and structure refinement parameters of compounds **1, 2** and **3**.

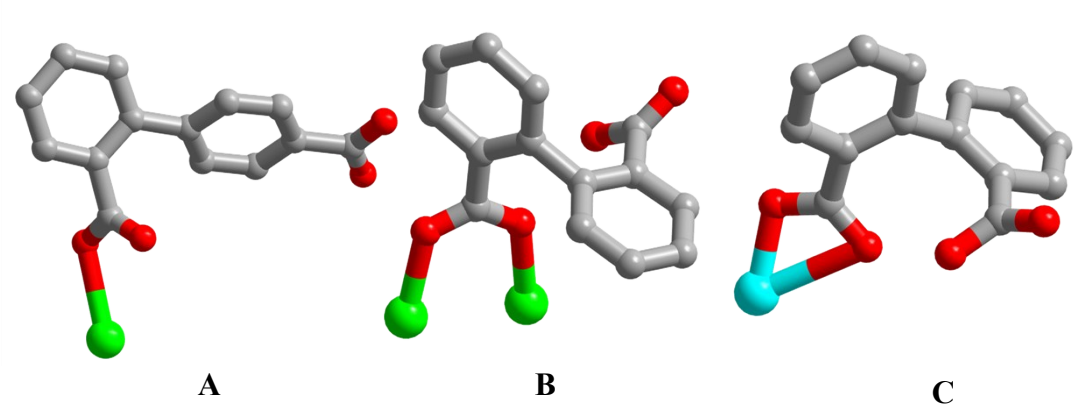
Identification code	**1**	**2**	**3**
Empirical formula	$C_{24}H_{17}AgN_2O_4$	$C_{19}H_{13}AgNO_4$	$C_{40}H_{28}CuN_4O_8$
Formula mass	505.27	427.17	756.21
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/c	*C*2/c	*P***Error!**
a (Å)	21.460(6)	29.457(9)	8.0398(16)
b (Å)	11.416(3)	14.831(5)	9.1650(18)
c (Å)	17.625(5)	7.499(2)	12.290(3)
α (˚)	90.00	90.00	111.73(3)
β (˚)	115.291(9)	99.616(5)	94.75(3)
γ (˚)	90.00	90.00	97.18(3)
V (Å^3)	3904.0(19)	3230.1(17)	826.4(3)
Z	8	8	1
D_c/(g cm^{-3})	1.719	1.703	1.519
μ (Mo Kα)/mm^{-1}	1.069	1.270	0.726
F(000)	2032	1600	389
Crystal size	0.16 x 0.14 x 0.12 mm	0.30 x 0.28 x 0.24 mm	0.32 x 0.15 x 0.12
θ range (°)	3.36 – 25.00	1.40 – 26.88	3.23 – 27.56
Limiting indices	$-25 \le h \le 25$	$-36 \le h \le 34$	$-10 \le h \le 10$
	$-11 \le k \le 13$	$-18 \le k \le 17$	$-11 \le k \le 11$
	$-20 \le l \le 20$	$-9 \le l \le 9$	$-15 \le l \le 15$
Data/Restraints/Parameters	3392 / 7 / 291	3188 / 0 / 229	3745 / 0 / 241
GOF on F^2	0.952	0.999	1.071
Final *R* indices [$I > 2\sigma(I)$]			
R_1[a]	0.0651	0.0566	0.0773
wR_2[b]	0.1526	0.1428	0.2085
R indices (all data)			
R_1	0.1079	0.0872	0.0885
wR_2	0.1265	0.1660	0.2142
CCDC	1477431	1477429	1477430

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$; [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

Table S2 Selected bond lengths [Å] and angles [°] for **1**, **2** and **3**.

Bond length	(Å)	Bond angle	(°)
1			
Ag(1A)-N(1)	2.193(6)	N(1)-Ag(1A)-N(2)#1	159.7(3)
Ag(1A)-N(2)#1	2.214(6)	N(1)-Ag(1A)-O(2)	93.8(2)
Ag(1A)-O(2)	2.512(7)	N(2)#1-Ag(1A)-O(2)	105.9(2)
Ag(1B)-N(1)	2.201(6)	N(1)-Ag(1B)-N(2)#1	158.9(6)
Ag(1B)-N(2)#1	2.212(6)	N(1)-Ag(1B)-O(1)#2	106.6(4)
Ag(1B)-O(1)#2	2.572(11)	N(2)#1-Ag(1B)-O(1)#2	92.4(3)
Ag(1C)-N(1)	2.208(6)	N(1)-Ag(1B)-Ag(1B)#2	96.4(3)
Ag(1C)-N(2)#1	2.214(6)	N(2)#1-Ag(1B)-Ag(1B)#2	96.8(2)
Ag(1C)-O(2)	2.688(7)	O(1)#2-Ag(1B)-Ag(1B)#2	76.1(4)
Ag(1C)-Ag(1C)#2	2.807(9)	N(1)-Ag(1C)-N(2)#1	157.7(3)
Ag(1D)-N(1)	2.162(6)	N(1)-Ag(1C)-O(2)	88.8(2)
Ag(1D)-N(2)#1	2.187(6)	N(2)#1-Ag(1C)-O(2)	100.3(2)
N(2)-Ag(1B)#3	2.212(6)	N(1)-Ag(1C)-Ag(1C)#2	98.4(2)
N(2)-Ag(1A)#3	2.214(6)	N(2)#1-Ag(1C)-Ag(1C)#2	98.6(2)
O(1)-Ag(1B)#2	2.572(11)	O(2)-Ag(1C)-Ag(1C)#2	105.9(3)
		N(1)-Ag(1D)-N(2)#1	172.0(4)
2			
Ag(1)-O(1)	2.148(4)	O(1)-Ag(1)-O(1)#1	164.6(2)
Ag(1)-O(1)#1	2.149(4)	O(1)-Ag(1)-N(1)	97.71(10)
Ag(1)-N(1)	2.397(6)	O(1)-Ag(1)-Ag(2)	82.29(10)
Ag(1)-Ag(2)	2.9584(13)	N(1)-Ag(1)-Ag(2)	180.0
Ag(2)-O(2)	2.231(3)	O(2)-Ag(2)-O(2)#1	157.30(19)
Ag(2)-N(2)#2	2.392(6)	O(2)-Ag(2)-N(2)#2	101.35(9)
		O(2)-Ag(2)-Ag(1)	78.65(9)
3			
Cu(1)-N(2)	1.973(4)	N(2)-Cu(1)-N(2)#1	179.998(1)
Cu(1)-O(1)	1.978(4)	N(2)-Cu(1)-O(1)#1	88.07(17)
Cu(1)-O(2)	2.671(4)	N(2)-Cu(1)-O(1)	91.93(17)
		N(2)#1-Cu(1)-O(1)	88.07(17)
		O(1)#1-Cu(1)-O(1)	179.999(2)
		N(2)-Cu(1)-O(2)	96.09(16)
		N(2)#1-Cu(1)-O(2)	83.91(16)
		O(1)#1-Cu(1)-O(2)	125.72(14)
		O(1)-Cu(1)-O(2)	54.28(14)
		N(2)-Cu(1)-O(2)#1	83.91(16)
		N(2)#1-Cu(1)-O(2)#1	96.09(16)
		O(1)#1-Cu(1)-O(2)#1	54.28(14)
		O(1)-Cu(1)-O(2)#1	125.72(14)
		O(2)-Cu(1)-O(2)#1	180.00(18)

Symmetry transformations used to generate equivalent atoms: #1: –x, –y+2, –z; #2: –x, –y+1, –z+1.



Scheme S1 Coordination modes and configurations of H_2pdc ligands in compounds **1**, **2** and **3**.

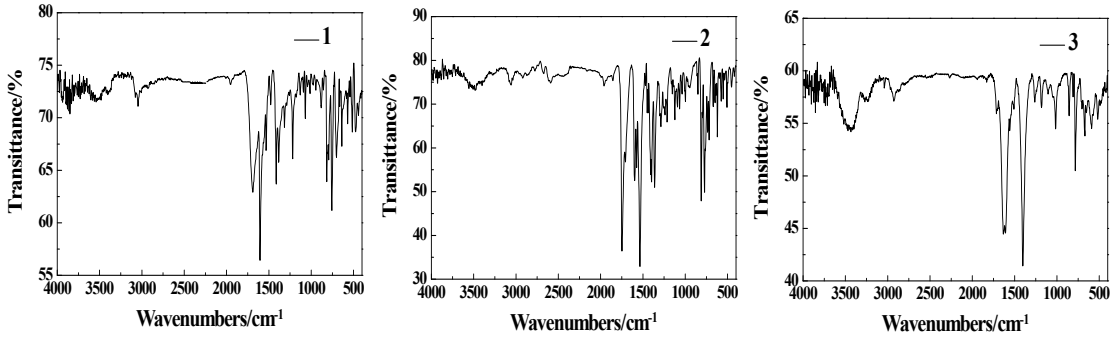


Fig. S1 The IR spectra of **1**, **2** and **3**.

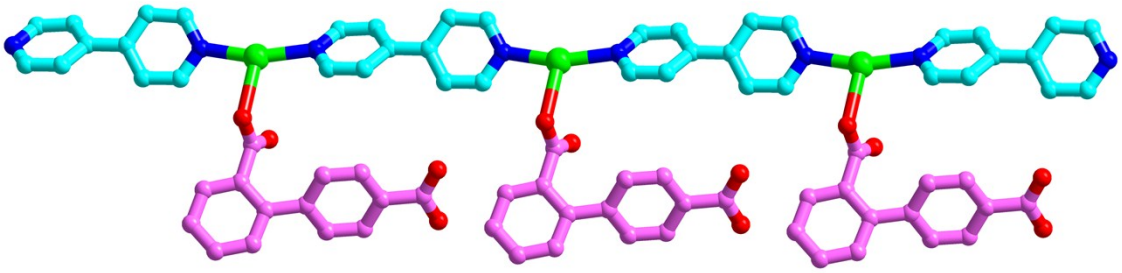


Fig. S2 The 1D chain of **1**.

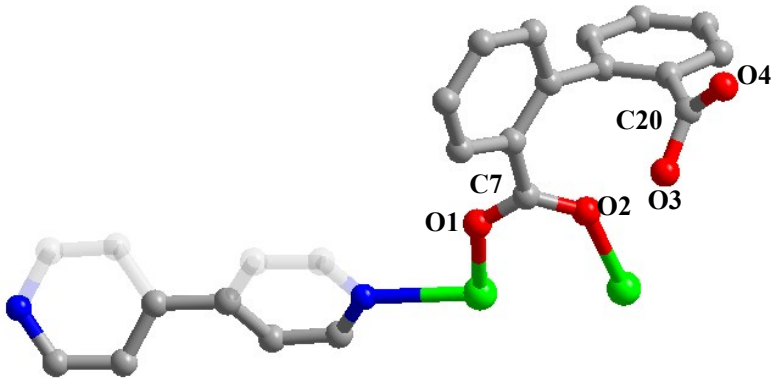


Fig.S3 The structural unit of **2** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity) symmetric components in 60% transparency.

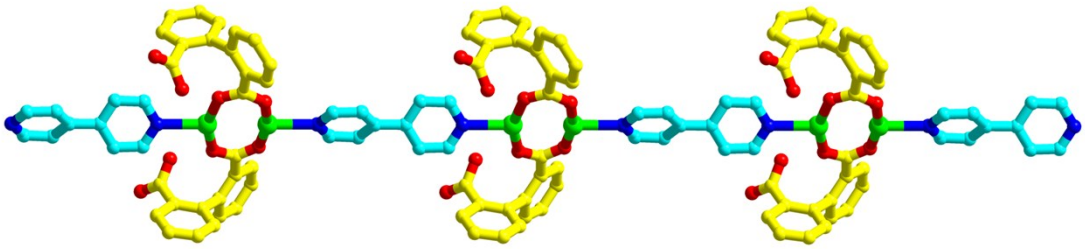


Fig. S4 The 1D chain of **2**.

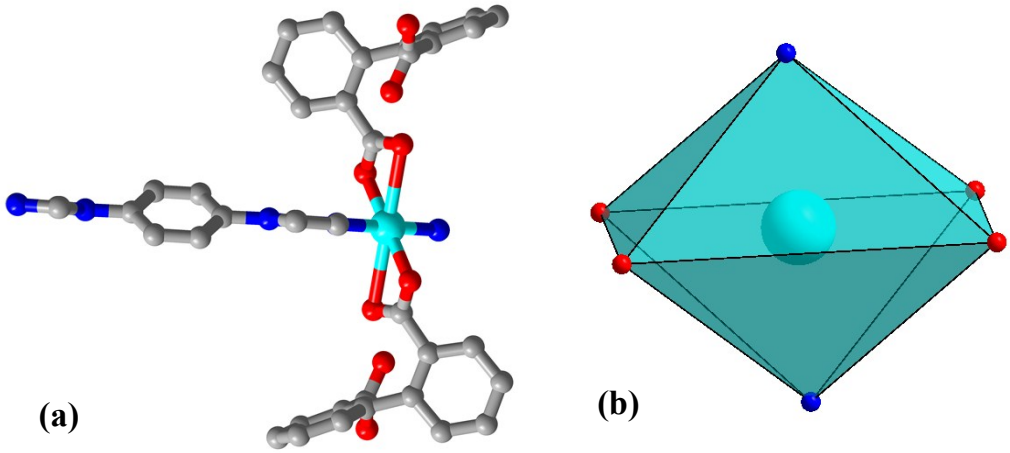


Fig. S5 (a) The structural unit of **3** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity). (b) Polyhedral representation of the coordination sphere of the Cu^{2+} centre.

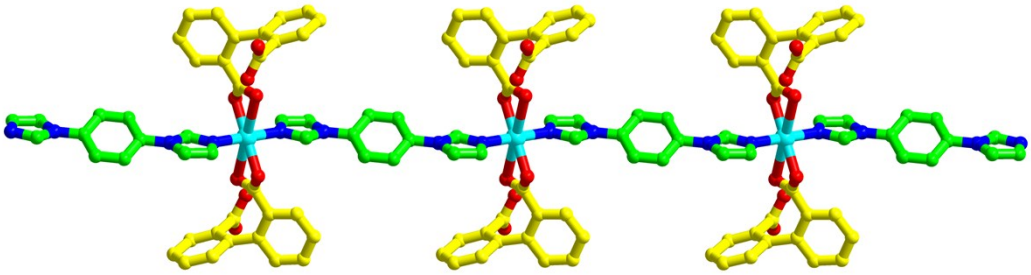


Fig. S6 The 1D chain of **3**.

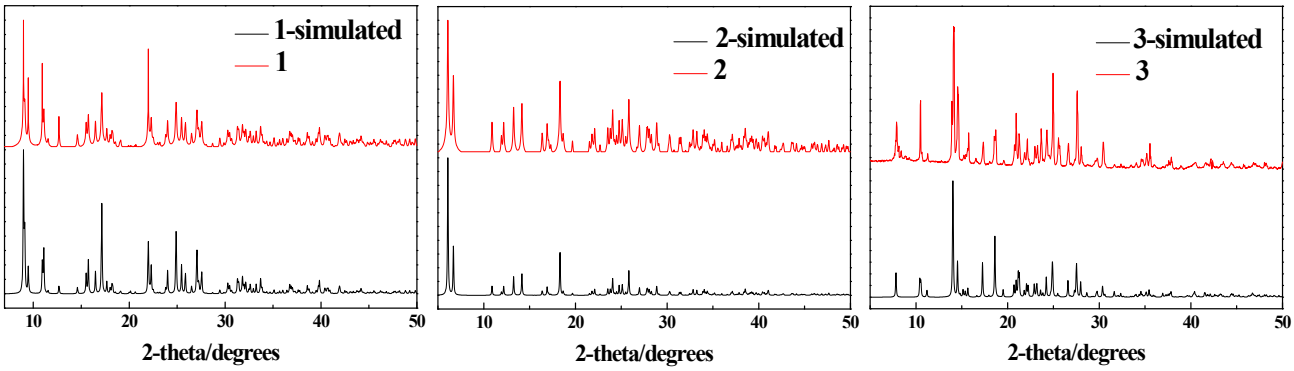


Fig. S7 The PXRD patterns of **1**, **2** and **3** with the relevant simulated patterns.

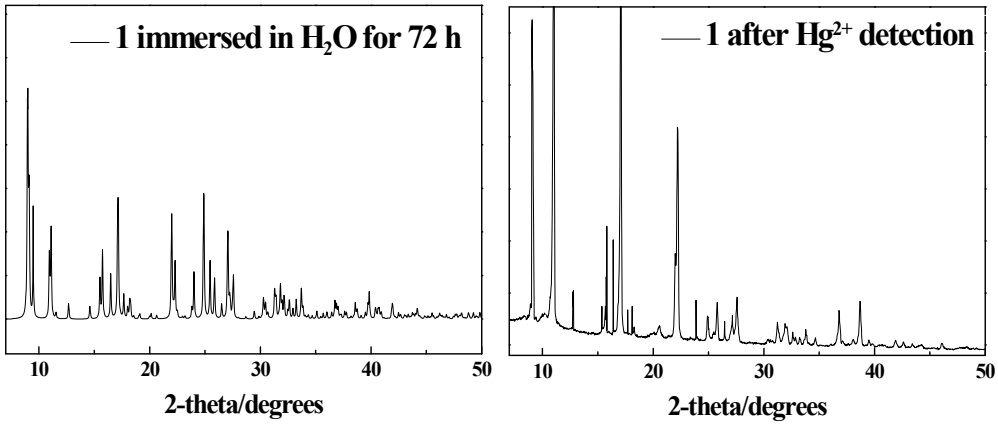


Fig. S8 The PXRD patterns of **1** immersed in H_2O for 72 h and the sample **1** detected Hg^{2+} ion.

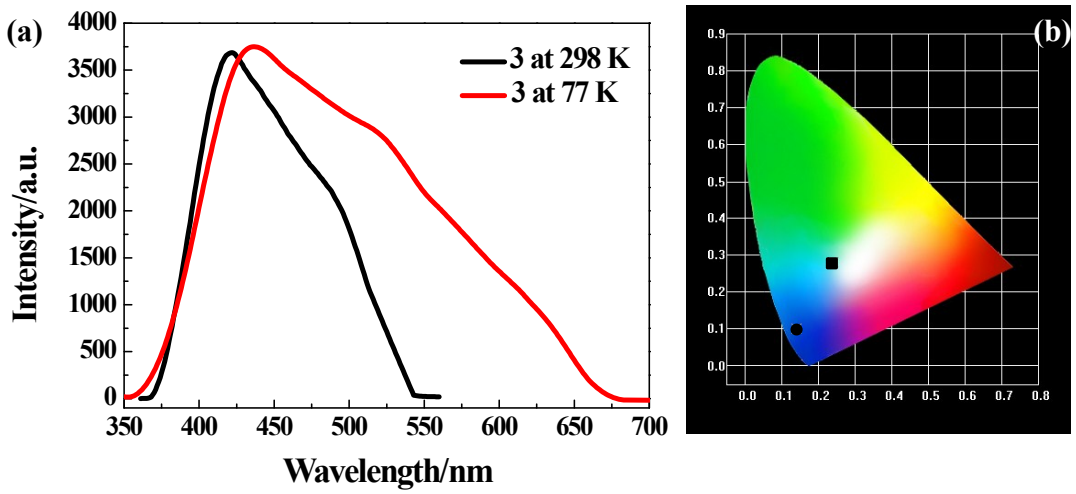


Fig. S9 (a) Emission spectra of compound **3** in the solid state at 298 K and 77 K; (b) The corresponding color coordinate diagram of emission for **3** (circle symbol for 298 K and square symbol for 77 K).

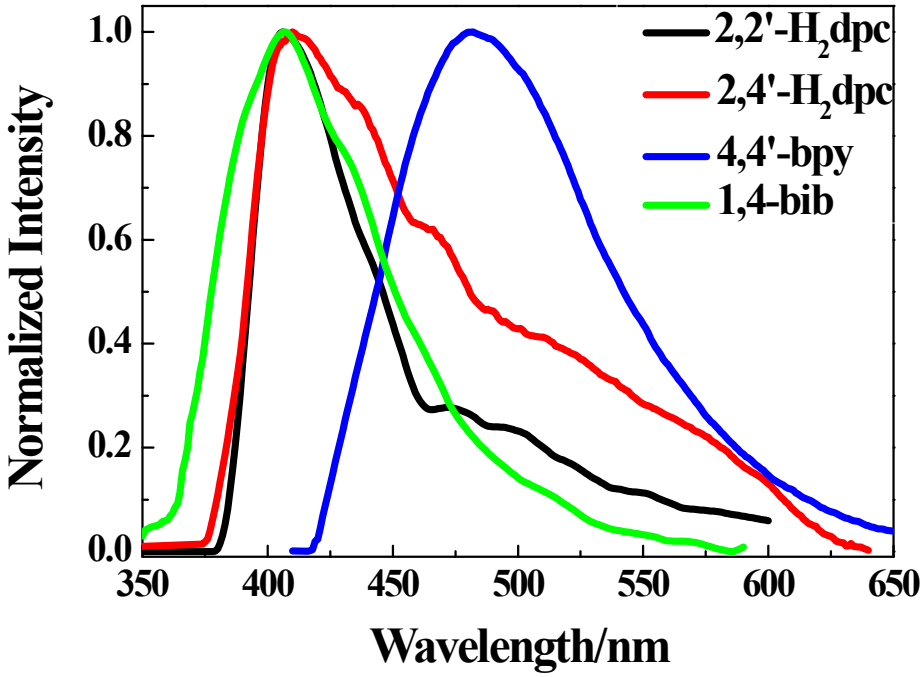


Fig. S10 Emission spectra of ligands in the solid state at 298 K.

Table S3 Luminescent data for **1**, **2, 3** in the solid state at 298 K and 77K, and corresponding ligands at 298 K.

Compoud	Temperature (K)	Excitation (λ_{ex}, nm)	Emission (λ_{em}, nm)	CIE (x, y)
1	298	350	414	(0.14, 0.03)
	77	350	516	(0.29,0.34)
2	298	350	519	(0.29, 0.38)
	77	350	537	(0.30,0.43)
3	298	350	420	(0.14, 0.10)
	77	350	436	(0.24, 0.28)
2,2'-H_2dpc	298	300	410	(0.18,0.15)
2,4'-H_2dpc	298	300	412	(0.20,0.21)
4,4'-bpy	298	300	481	(0.21,0.32)
1,4-bib	298	300	403	(0.16, 0.08)

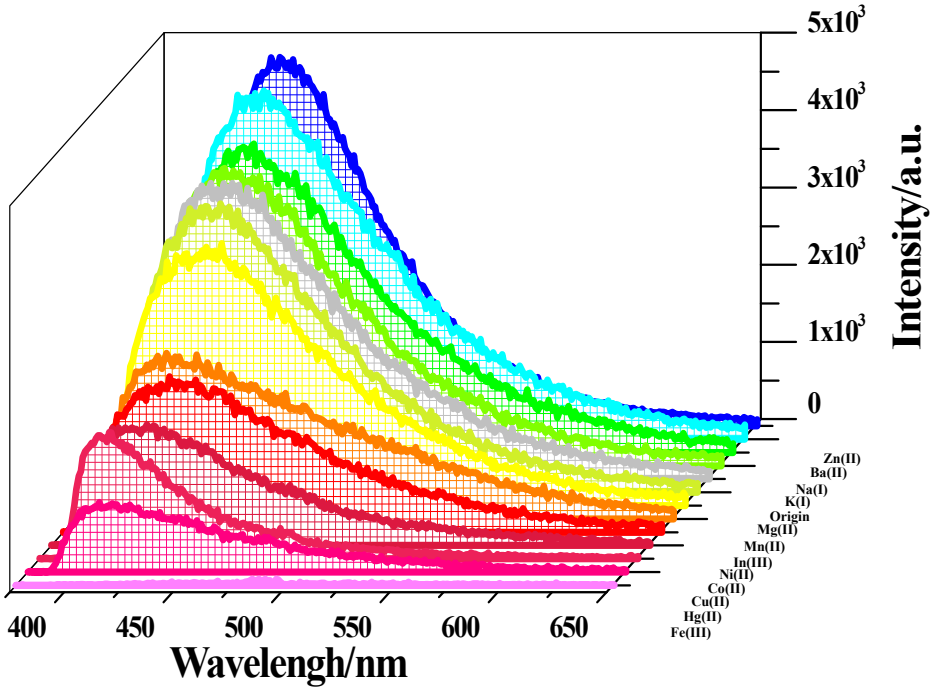


Fig. S11 Suspension-state PL spectra of **2** at 426 nm dispersed in aqueous solutions containing different metal ions (50μM) when excited at 320 nm.

Standard deviation and detection limit calculation

To calculate the standard deviation and detection limit of this detection method, compound **1** with fine particles was made into a suspension. Then, Hg^{2+} solution (5-100 μL, 100 μM) was added into the suspension and the fluorescent intensities were recorded. Standard deviation (σ) was calculated from five blank tests of **1** suspension and the detection limit was calculated via the formula: 3σ/m (m: the slope of the linear region).

Table S4 Standard deviation calculation and detection limit calculation.

Text 1 Fluorescence intensity	22206.56 a.u.
Text 2 Fluorescence intensity	22214.65 a.u.
Text 3 Fluorescence intensity	22208.56 a.u.
Text 4 Fluorescence intensity	22216.65 a.u.
Text 5 Fluorescence intensity	22212.35 a.u.
Standard Deviation (σ)	4.18
Slope (m)	1302.7022 μM^{-1}
Detection limit (3σ/m)	0.00963 μM

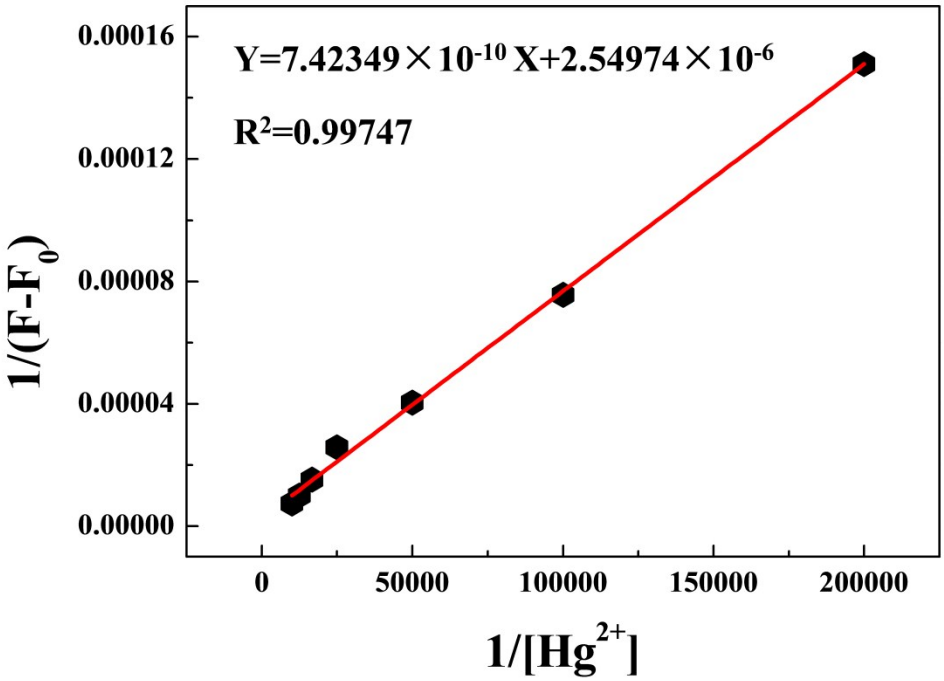


Fig. S12 Benesi–Hildebrand plot of **1** assuming 1:1 stoichiometry between **1** and Hg^{2+} in water. The association constant of **1**-Hg^{2+} is 3.44 × 10^3 M^{-1}.

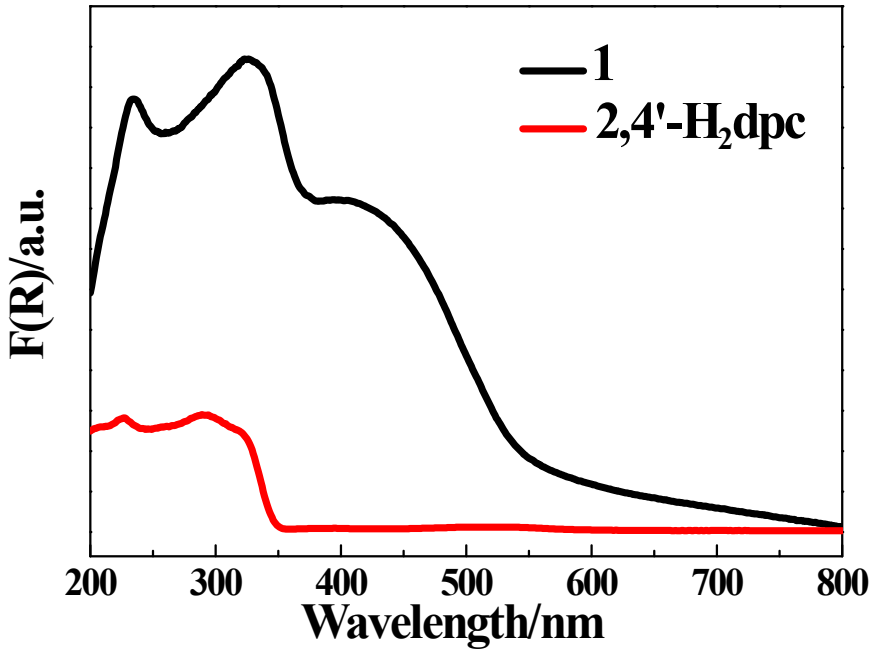


Fig. S13 Plots of UV-vis absorption spectra of **1** and 2,4'-H_2pdc ligand.