Three novel Cu_6S_6 cluster-based coordination compounds: synthesis, framework modulation and the sensing for small molecules and Fe^{3+} ion

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Figure caption

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Table S1 Crystal and structure refinement data for compounds **1-3.**

Compound	**1**	**2**	**3**
Empirical formula	$C_{30}H_{30}Cu_6N_{12}S_6$	$C_{30}H_{30}Br_4Cu_{10}N_{12}S_6$	$C_{30}H_{30}Cu_{12}I_6N_{12}S_6$
Formula weight	1132.26	1706.06	2274.90
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$I2/m$	$P2_1/n$
a, Å	22.1787(8)	8.5779(3)	11.5116(4)
b, Å	11.5351(3)	17.6149(7)	11.0849(4)
c, Å	18.4943(6)	15.0573(6)	20.7805(7)
β, deg	114.620(2)	96.829	97.415(3)
Volume (Å^3)	4301.3(2)	2259.00(15)	2629.52(16)
Z	4	2	2
ρ_{calc}/gcm^{-3}	1.748	2.508	2.873
Absorption coeff.	3.243	8.463	8.544
θ range (°)	2.99 to 25.10	3.49 to 25.10	3.09 to 25.10
Reflections collected	16009	4405	9691
Unique	7571 [R(int) = 0.0273]	2082 (R(int) = 0.0335)	4680 (Rint = 0.0321)
Completeness	99.0 %	99.7 %	99.8%
Goodness-of-fit	1.103	1.018	0.905
R indexes [$I>2\sigma(I)$][a]	R1 = 0.0434 wR2 = 0.1057	R_1 = 0.0352 wR_2 = 0.0674	R_1 = 0.0302 wR_2 = 0.0478
R (all data)[a]	R1 = 0.0624 wR2 = 0.1182	R_1 = 0.0496 wR_2 =0.0739	R_1 = 0.0505 wR_2 = 0.0519

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)_2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 Bond lengths (Å) and Angles (deg) for compound **1-3**

Compound **1**			
Cu(1)-N(4)	2.023(7)	Cu(5)-S(5)	2.235(2)
Cu(1)-S(1)	2.229(2)	Cu(5)-S(6)	2.257(2)
Cu(1)-S(2)	2.249(2)	Cu(6)-N(9)	2.040(7)
Cu(2)-N(1)	2.013(7)	Cu(6)-S(4)	2.238(2)
Cu(2)-S(2)#1	2.243(2)	Cu(6)-S(6)#2	2.271(2)
Cu(2)-S(3)	2.250(2)	Cu(1)-Cu(2)	2.7061(15)
Cu(3)-N(6)	2.049(7)	Cu(4)-Cu(5)	2.7358(15)
Cu(3)-S(1)#1	2.240(2)	Cu(5)-Cu(6)	2.7770(15)
Cu(3)-S(3)	2.269(2)	Cu(2)-Cu(3)#1	2.8079(15)
Cu(4)-N(11)	2.037(7)	Cu(4)-Cu(6)	2.9375(15)
Cu(4)-S(4)	2.241(2)	Cu(6)-Cu(4)#2	2.9566(15)
Cu(4)-S(5)#2	2.251(2)	Cu(3)-Cu(1)#1	2.9676(15)
Cu(5)-N(7)	2.013(7)	Cu(1)-Cu(3)	2.9875(15)
N(4)-Cu(1)-S(1)	124.7(2)	N(11)-Cu(4)-S(4)	121.0(2)
N(4)-Cu(1)-S(2)	109.9(2)	N(11)-Cu(4)-S(5)#2	109.8(2)
S(1)-Cu(1)-S(2)	118.14(9)	S(4)-Cu(4)-S(5)#2	120.27(9)
N(1)-Cu(2)-S(2)#1	121.4(2)	N(7)-Cu(5)-S(5)	124.1(2)
N(1)-Cu(2)-S(3)	120.6(2)	N(7)-Cu(5)-S(6)	119.3(2)
S(2)#1-Cu(2)-S(3)	111.38(9)	S(5)-Cu(5)-S(6)	110.49(9)
N(6)-Cu(3)-S(1)#1	119.7(2)	N(9)-Cu(6)-S(4)	121.5(2)
N(6)-Cu(3)-S(3)	108.8(2)	N(9)-Cu(6)-S(6)#2	110.0(2)
S(1)#1-Cu(3)-S(3)	121.51(9)	S(4)-Cu(6)-S(6)#2	118.92(9)
Compound **2**			
Cu(3)-N(4)	1.933(4)	Cu(2)-S(2)#2	2.2660(12)
Cu(4)-N(2)	2.031(5)	Br(1)-Cu(4)	2.3719(8)
Cu(1)-N(1)	2.037(5)	Cu(1)-Cu(2)	2.7988(9)
Cu(2)-N(3)	2.033(4)	Cu(2)-Cu(2)#4	2.7780(12)
Cu(1)-S(2)	2.2587(13)	Cu(2)-Cu(2)#3	3.0311(13)
Cu(2)-S(1)	2.2335(13)	S(1)-Cu(2)-S(2)#4	117.21(5)
N(3)-Cu(2)-S(2)#4	113.92(11)	N(4)-Cu(3)-N(4)#5	167.3(2)
N(1)-Cu(1)-S(2)	118.73(5)	N(2)-Cu(4)-Br(1)	119.87(3)
S(2)#1-Cu(1)-S(2)	114.38(7)	Br(1)#3-Cu(4)-Br(1)	118.62(5)
N(3)-Cu(2)-S(1)	118.93(11)	S(2)#3-Cu(1)-S(2)	114.38(7)
Compound **3**			
N(2)-Cu(6)#6	2.008(4)	Cu(5)-I(2)#7	2.7532(8)
N(3)-Cu(3)	1.995(4)	Cu(2)-S(1)	2.2485(14)
N(1)-Cu(1)	2.046(4)	Cu(2)-S(2)	2.2555(14)
N(6)-Cu(2)	2.037(4)	Cu(4)-S(3)	2.3563(14)
N(5)-Cu(5)	2.041(4)	Cu(1)-S(3)	2.2180(14)
I(1)-Cu(6)	2.5868(8)	Cu(1)-S(2)#8	2.2767(15)
I(1)-Cu(4)	2.6859(8)	Cu(3)-S(3)	2.2085(14)
I(1)-Cu(5)	2.7174(8)	Cu(3)-S(1)#8	2.2498(15)

I(2)-Cu(4)	2.5799(8)	Cu(5)-Cu(6)	2.5530(10)
I(2)-Cu(4)#7	2.6600(8)	Cu(4)-Cu(5)	2.6063(10)
I(2)-Cu(5)#7	2.7532(8)	Cu(2)-Cu(3)	2.7422(10)
I(3)-Cu(6)	2.5196(8)	Cu(2)-Cu(1)	2.8652(9)
I(3)-Cu(5)	2.6271(8)	Cu(4)-Cu(4)#7	2.8118(14)
Cu(4)-I(2)#7	2.6600(8)	Cu(1)-Cu(3)#8	2.9496(10)
N(6)-Cu(2)-S(1)	117.10(12)	N(5)-Cu(5)-I(2)#7	106.44(11)
N(6)-Cu(2)-S(2)	118.51(12)	I(3)-Cu(5)-I(2)#7	106.27(3)
S(1)-Cu(2)-S(2)	114.73(5)	I(1)-Cu(5)-I(2)#7	111.90(3)
S(3)-Cu(4)-I(2)	108.49(4)	N(1)-Cu(1)-S(3)	125.38(12)
S(3)-Cu(4)-I(2)#7	106.10(4)	N(1)-Cu(1)-S(2)#8	107.54(12)
I(2)-Cu(4)-I(2)#7	115.12(3)	S(3)-Cu(1)-S(2)#8	120.81(6)
S(3)-Cu(4)-I(1)	98.92(4)	N(3)-Cu(3)-S(3)	123.82(13)
I(2)-Cu(4)-I(1)	110.60(3)	N(3)-Cu(3)-S(1)#8	111.78(14)
I(2)#7-Cu(4)-I(1)	115.96(3)	S(3)-Cu(3)-S(1)#8	118.63(5)
N(5)-Cu(5)-I(3)	109.35(12)	N(2)#9-Cu(6)-I(3)	130.76(13)
N(5)-Cu(5)-I(1)	109.80(12)	N(2)#9-Cu(6)-I(1)	107.85(13)
I(3)-Cu(5)-I(1)	112.83(3)	I(3)-Cu(6)-I(1)	121.37(3)

Symmetry transformations: #1 -x+1, -y, -z+1; #2 -x, -y+1, -z+2; #3 x, 2-y, z; #4 2-x, y, 2-z; #5 1-x, y, 2-z; #6 x, y+1, z; #7 2-x, -y, 2-z; #8 2-x, 1-y, 2-z; #9 x, y-1, z.

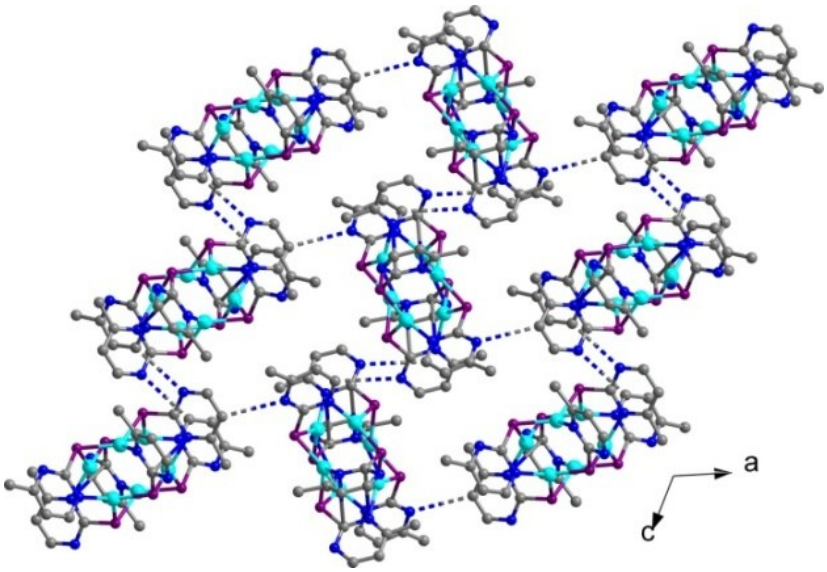

Fig. S1 The 3D supramolecular network in compound **1.**

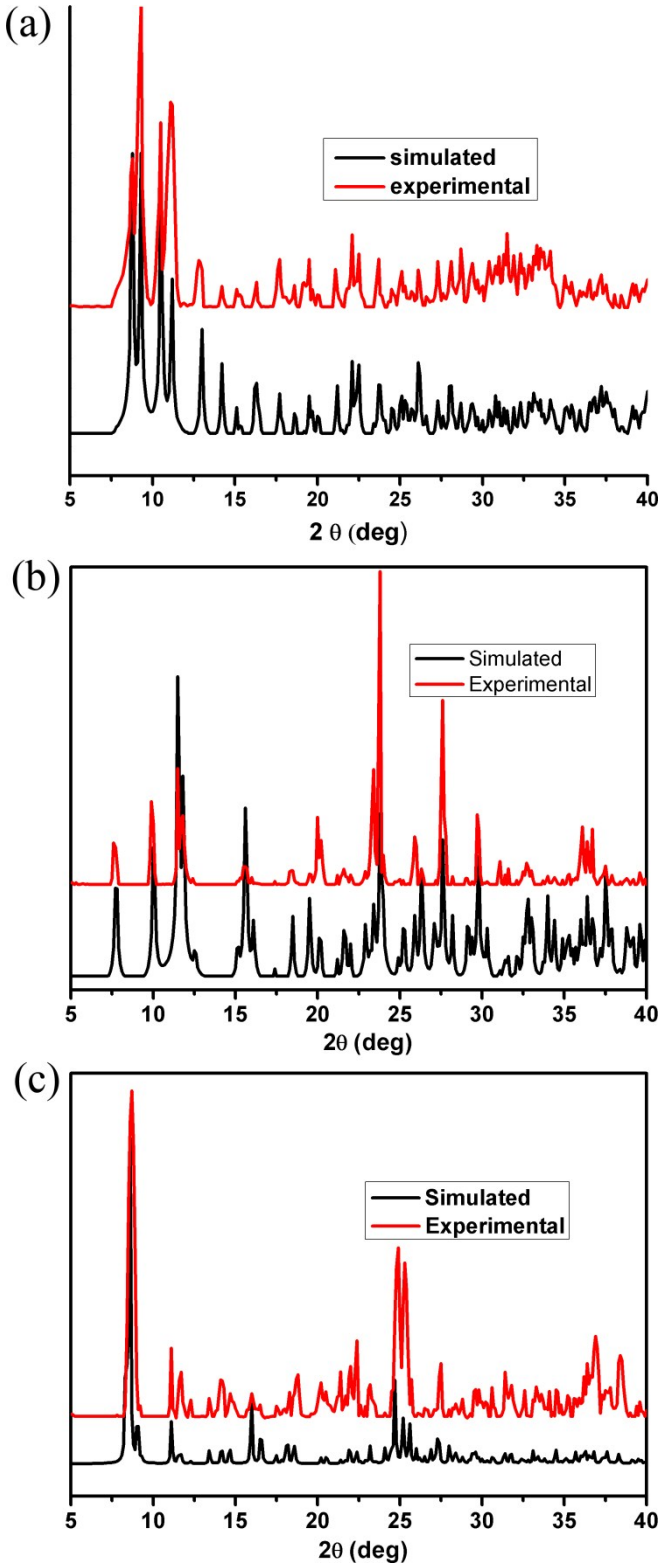

Fig. S2 Experimental and simulated X-ray diffraction patterns (a) for compound **1**, (b) for compound **2**, (c) for compound **3.**

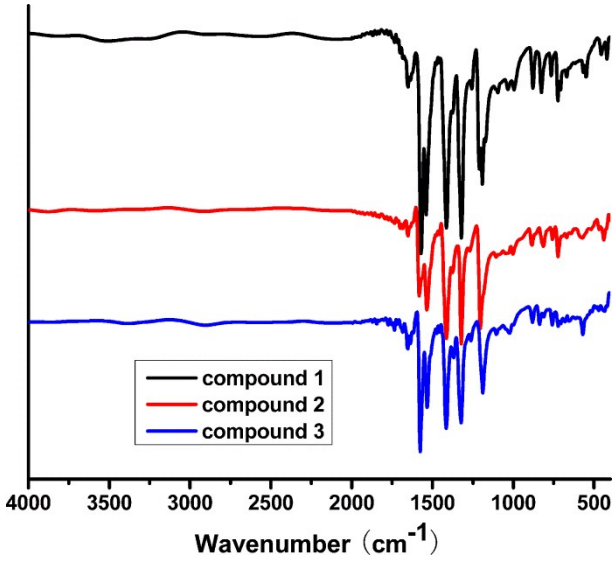

Fig. S3 The IR spectra of compounds **1-3.**

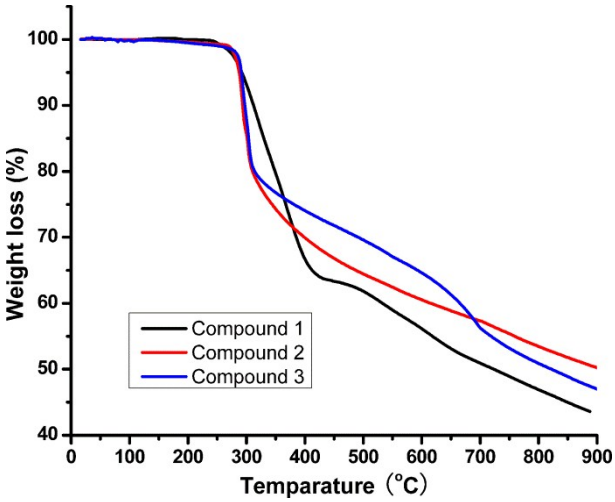

Fig. S4 The TGA polts of compounds **1-3.**

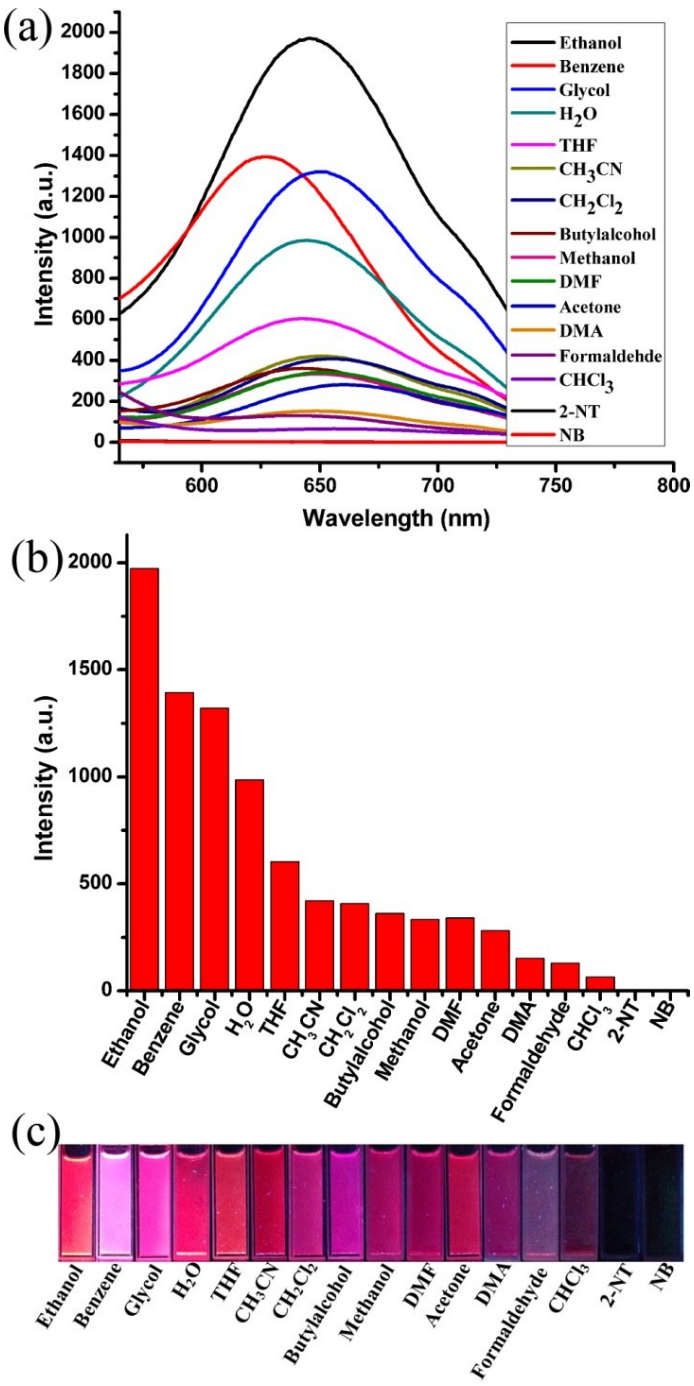

Fig. S5 (a) Emission spectra, (b) Emission intensities, (c) the luminescence photographs of compound **2** in different solvent emulsions under UV light.

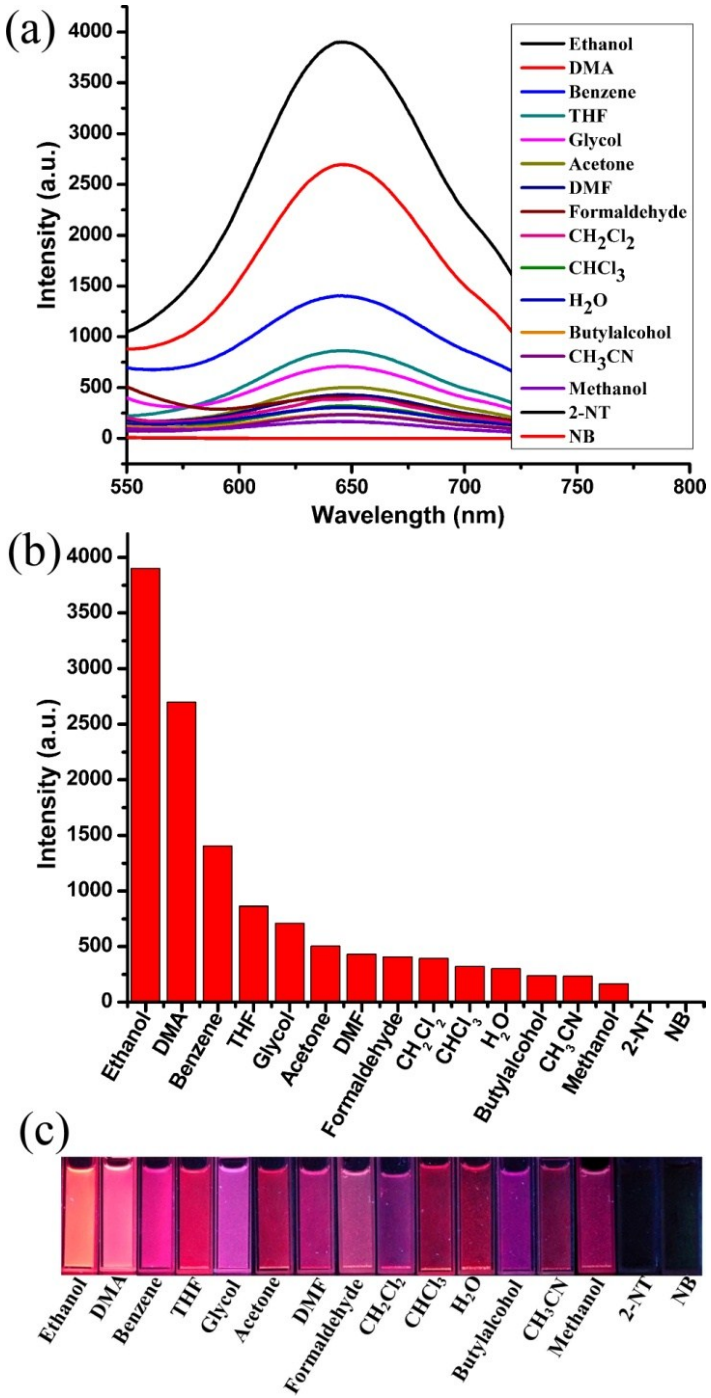

Fig. S6 (a) Emission spectra, (b) Emission intensities, (c) the luminescence photographs of compound **3** in different solvent emulsions under UV light.

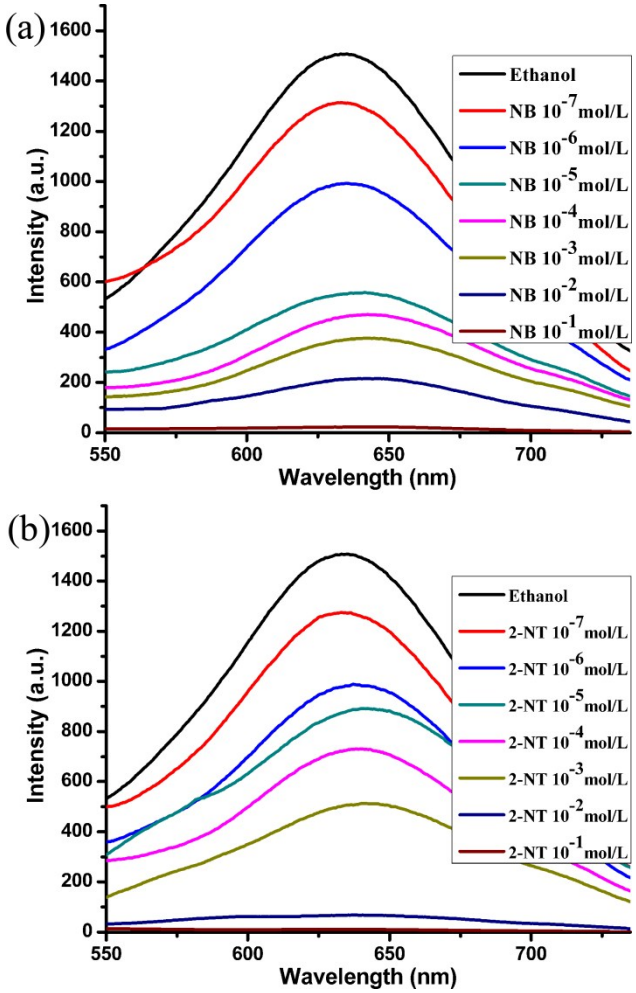

Fig. S7 Fluorescence titration of compound **2** dispersed in ethanol by gradual addition of analytes in ethanol, (a) NB, (b) 2-NT.

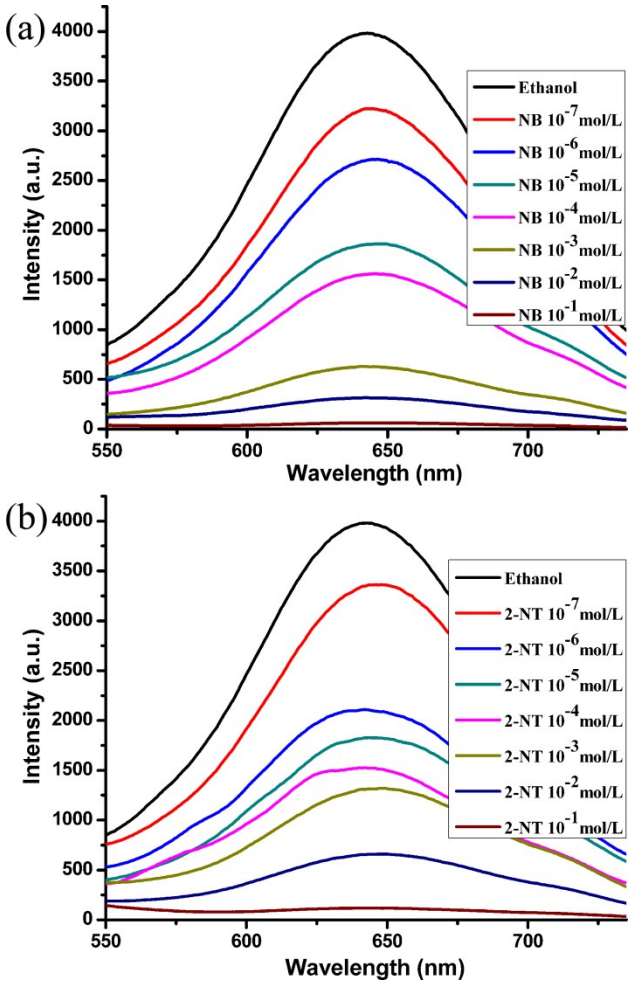

Fig. S8 Fluorescence titration of compound **3** dispersed in ethanol by gradual addition of analytes in ethanol, (a) NB, (b) 2-NT.

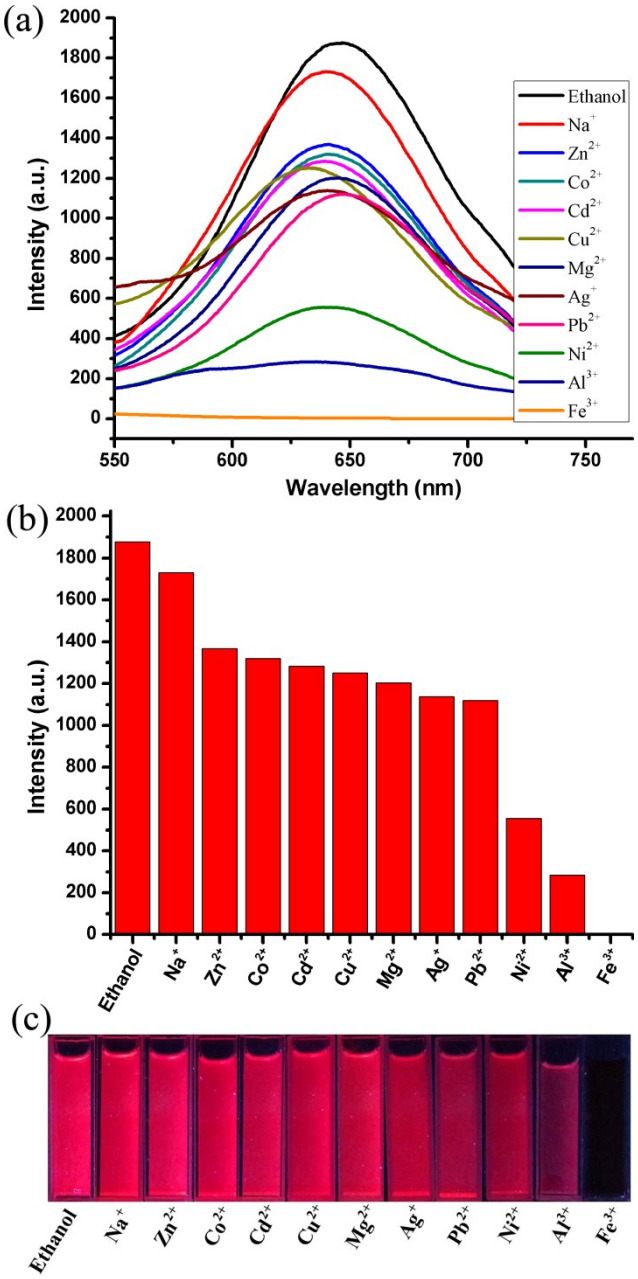

Fig. S9 (a) Emission spectra, (b) Emission intensities, (c) the luminescence photographs of compound **2** in ethanol emulsion containing different metal ions under UV light.

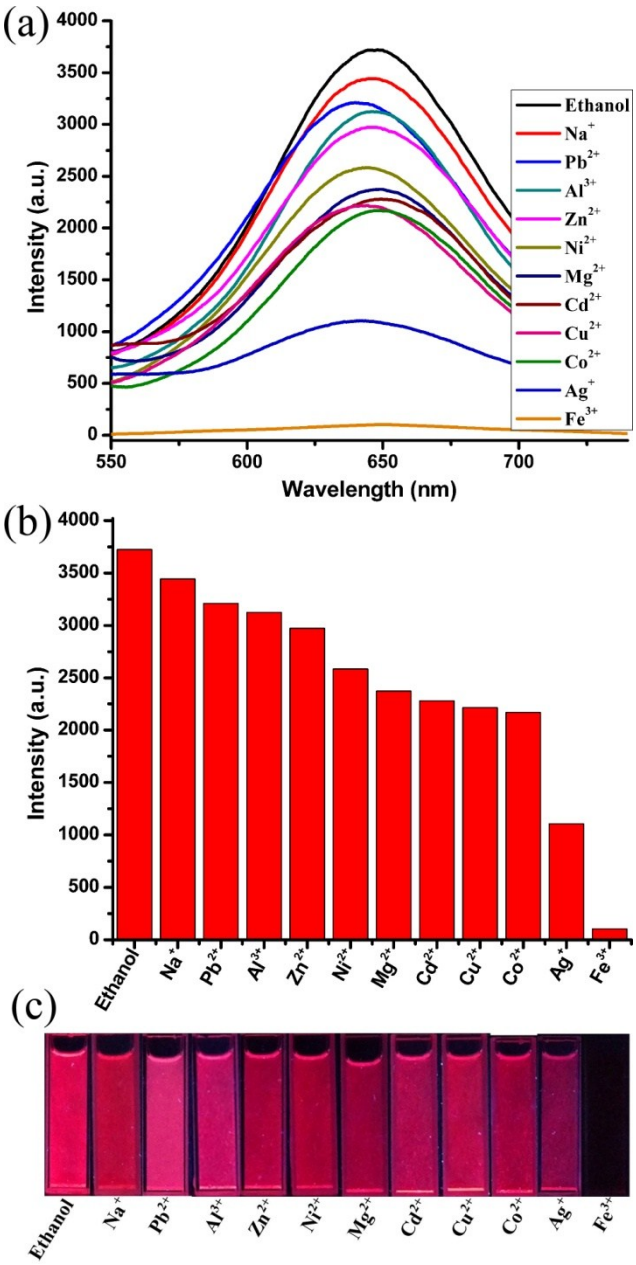

Fig. S10 (a) Emission spectra, (b) Emission intensities, (c) the luminescence photographs of compound **3** in ethanol emulsion containing different metal ions under UV light.

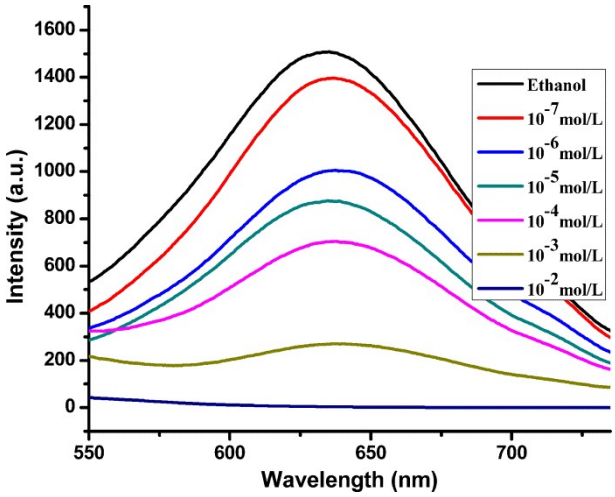

Fig. S11 Fluorescence titration of **2** dispersed in ethanol with the addition of different concentrations of Fe^{3+} (excited at 390 nm).

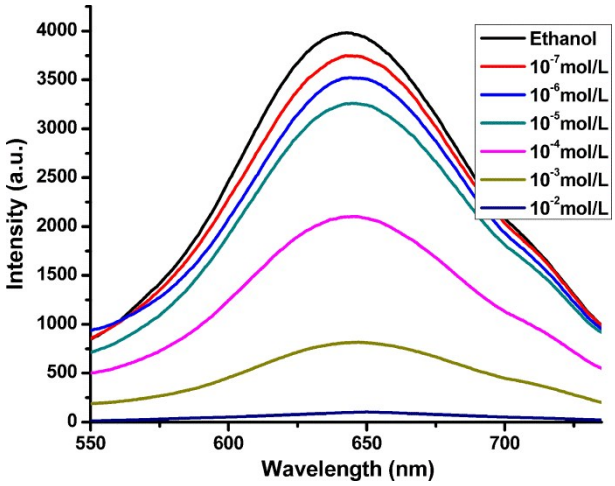

Fig. S12 Fluorescence titration of **3** dispersed in ethanol with the addition of different concentrations of Fe^{3+} (excited at 390 nm).