Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A butterfly shaped $Eu_4(OH)_2$ cluster-based luminescent metal-organic framework with lewis basic triazole sites demonstrating turn off sensing to organic amines

Jie-Ru Wang, Jin Fu, Yu-Juan Zhang, Jia-Chen Liang, Rui-Sha Zhou,* Si-Min Gong, Jiang-Feng Song*

Department of Chemistry, North University of China, Taiyuan, Shanxi, 030051, P.R. China

* Corresponding author.

rszhou0713@nuc.edu.cn (R.S. Zhou), jfsong0129@nuc.edu.cn (J. F. Song)

Figure captions:

Fig. S1 The 3D filling diagram of compound **1** with isosceles triangular channels, and all uncoordinated triazole units are omitted for clarity.

Fig. S2 N_2 adsorption−desorption isotherms of compound **1**.

Fig. S3 Three sides of isosceles triangular channels, (a) and (b) both constructed by -($Eu_4(OH)_2$-ox)$_n$- chains and taip$_1^{2-}$ anions. (c) constructed by -($Eu_4(OH)_2$-ox)$_n$- chain and taip$_2^{2-}$ anions.

Fig. S4 Two kinds of parallelograms constructed by isosceles triangular channels in compound **1**.

Fig. S5 Experimental and simulated PXRD diagrams of compound **1**.

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Fig. S23 PXRD patterns of compound **1** after five cycles.

Fig. S24 PXRD patterns of **1** after soaking in organic amines with concentration of 0.1 M for 24 hours.

Fig. S25 UV absorption spectra of different organic amines and excited spectrum of compound **1**.

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Fig. S27 The fluorescence spectra of H_2taip in ethanol and organic amines.

Fig. S28 IR spectra of organic amines, compound **1** and compound **1** after sensing organic amines.

Fig. S29 Luminescence decay curves of compound **1** (a) in EtOH, (b) in EDA, (c) in DEA, (d) in TMA, (e) in TEA, and (f) in aniline.

Table S1 Selected bond lengths (Å) and angles (°) for **1**.

Table S2 The three-dimensional dimensions of TEA, aniline, TMA, DEA and EDA.

Table S3 HOMO and LUMO energy levels of H_2taip and organic amines.

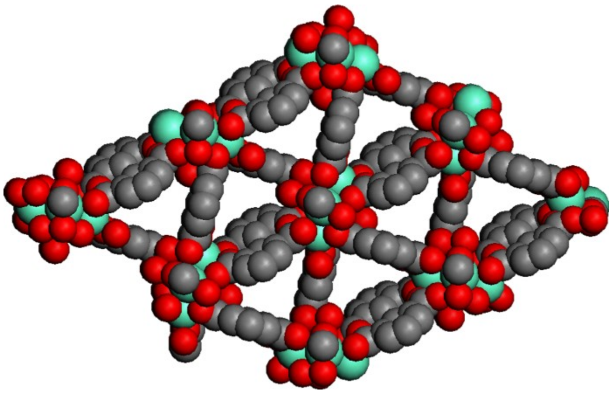


Fig. S1 The 3D filling diagram of compound **1** with isosceles triangular channels, and all uncoordinated triazole units are omitted for clarity.

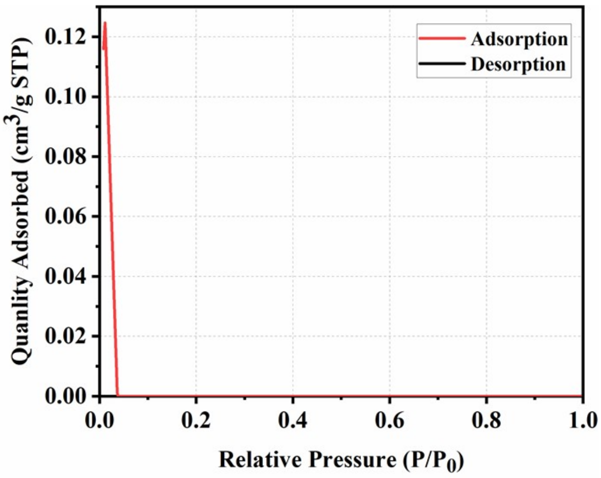


Fig. S2 N_2 adsorption−desorption isotherms of compound **1**.

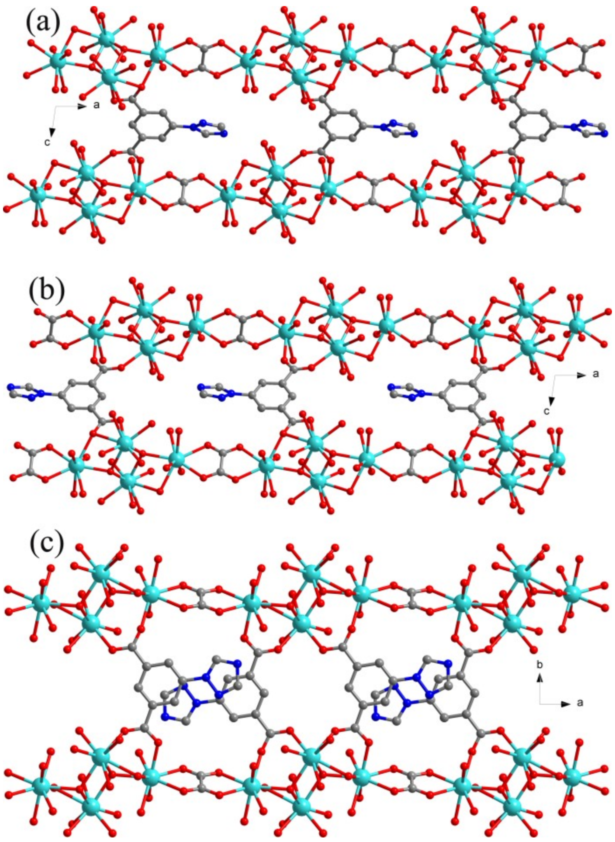


Fig. S3 Three sides of isosceles triangular channels, (a) and (b) both constructed by -$(Eu_4(OH)_2\text{-ox})_n$- chains and $taip_1^{2-}$ anions. (c) constructed by -$(Eu_4(OH)_2\text{-ox})_n$- chain and $taip_2^{2-}$ anions.

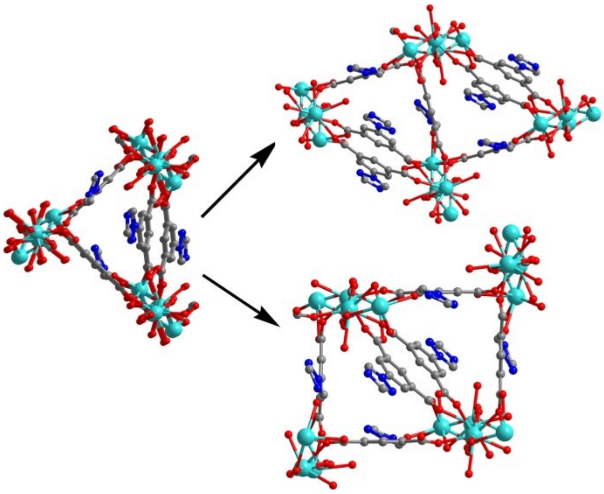


Fig. S4 Two kinds of parallelograms constructed by isosceles triangular channels in compound **1**.

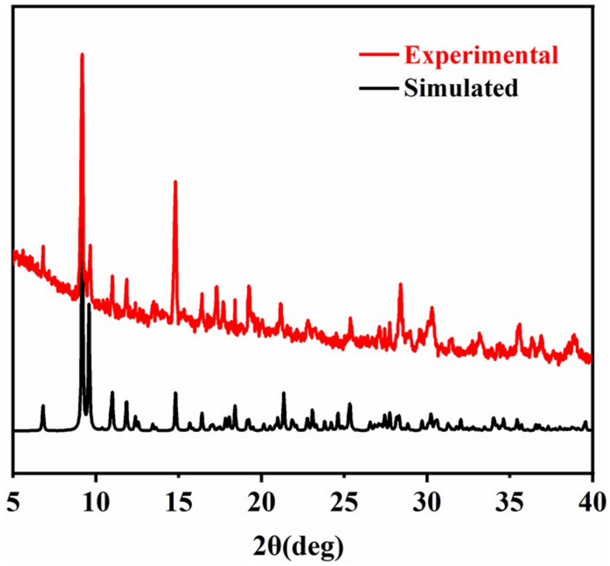


Fig. S5 Experimental and simulated PXRD diagrams of compound **1**.

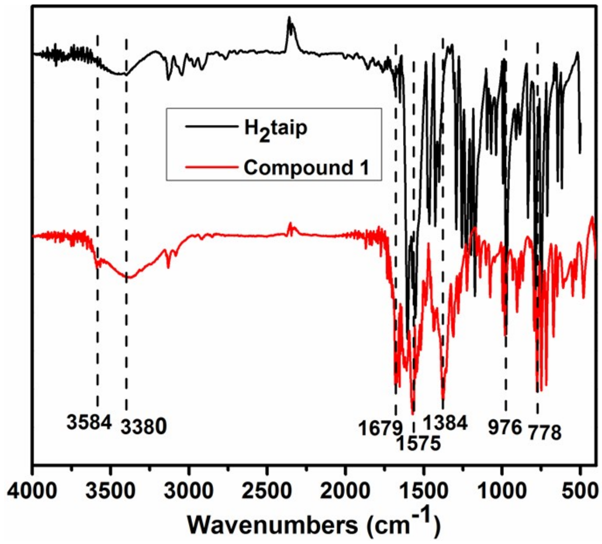


Fig. S6 Infrared spectra of compound **1** and H_2taip.

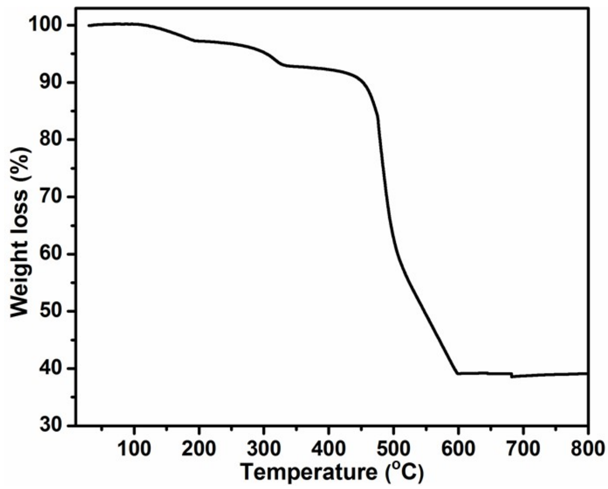


Fig. S7 Thermogravimetric curve of compound **1**.

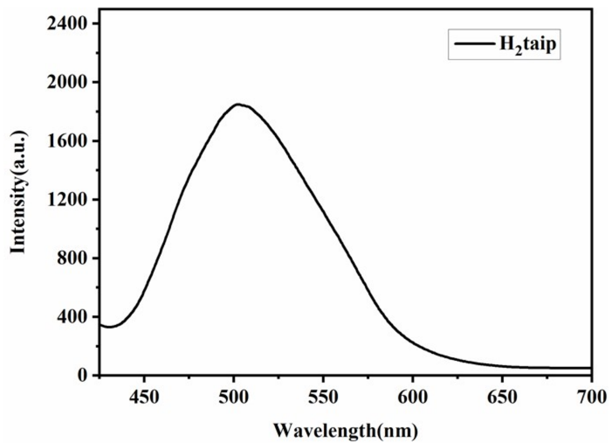


Fig. S8 The emission spectra of H_2taip in the solid state.

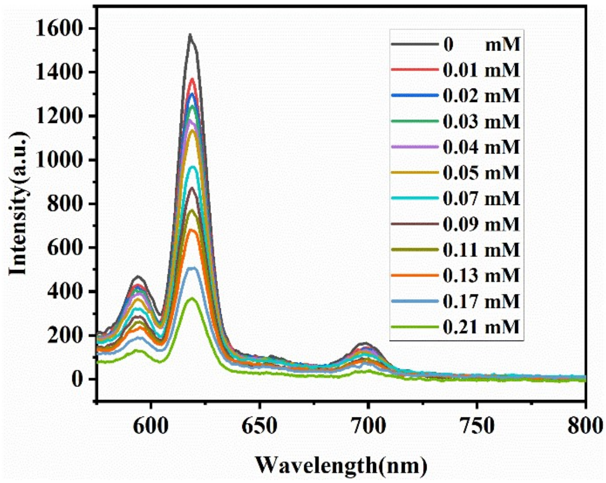


Fig. S9 The photoluminescence spectra of **1**-ethanol emulsion with incremental addition of EDA (0.01 M).

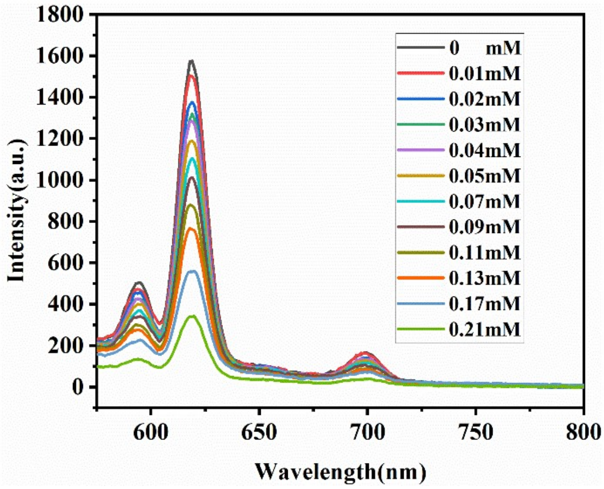


Fig. S10 The photoluminescence spectra of **1**-ethanol emulsion with incremental addition of DEA (0.01 M).

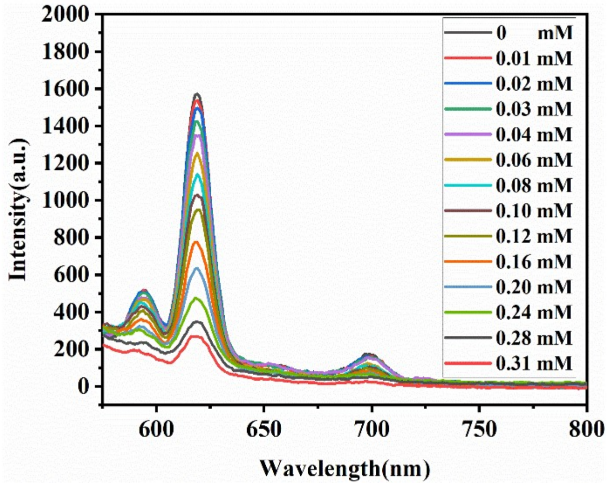


Fig. S11 The photoluminescence spectra of **1**-ethanol emulsion with incremental addition of TMA (0.01 M).

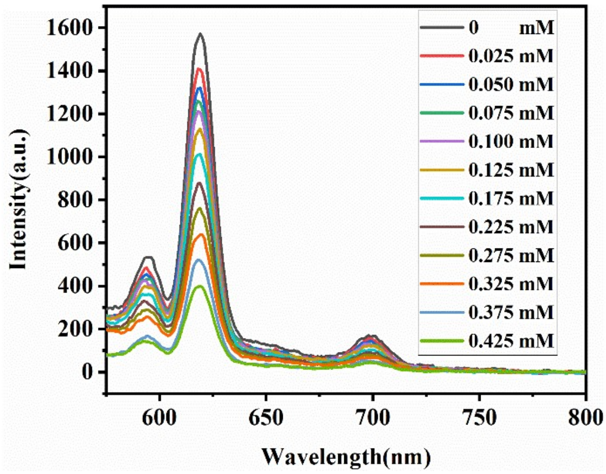


Fig. S12 The photoluminescence spectra of **1**-ethanol emulsion with incremental addition of TEA (0.01 M).

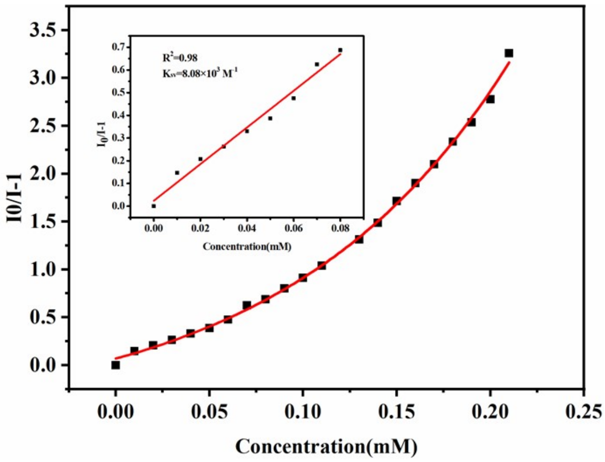


Fig. S13 Stern-Volmer plot for the luminescence intensity of **1**-ethanol emulsion upon the addition of EDA solution.

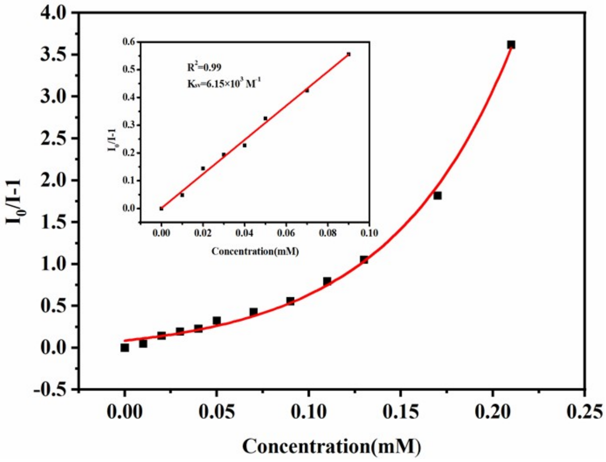


Fig. S14 Stern-Volmer plot for the luminescence intensity of **1**-ethanol emulsion upon the addition of DEA solution.

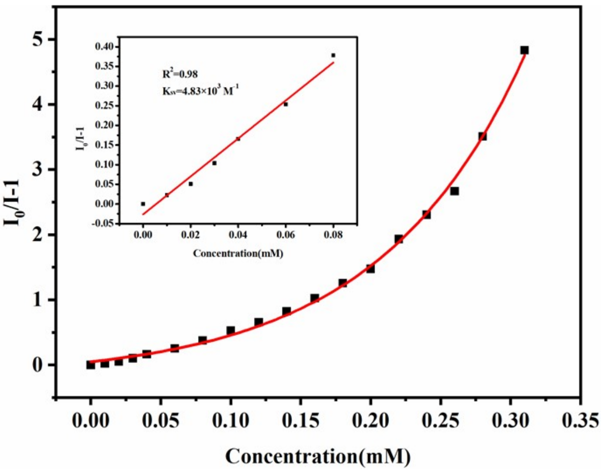


Fig. S15 Stern-Volmer plot for the luminescence intensity of **1**-ethanol emulsion upon the addition of TMA solution.

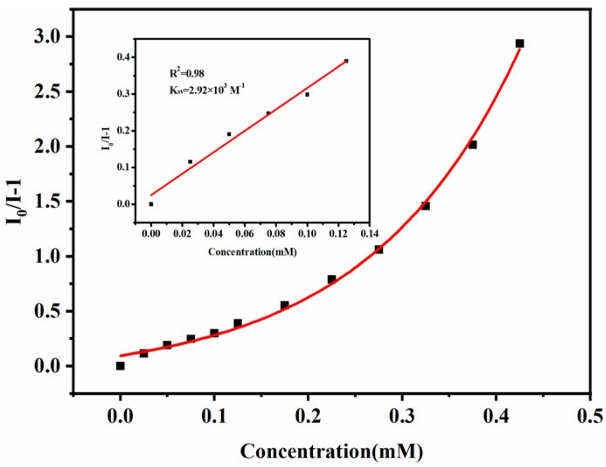
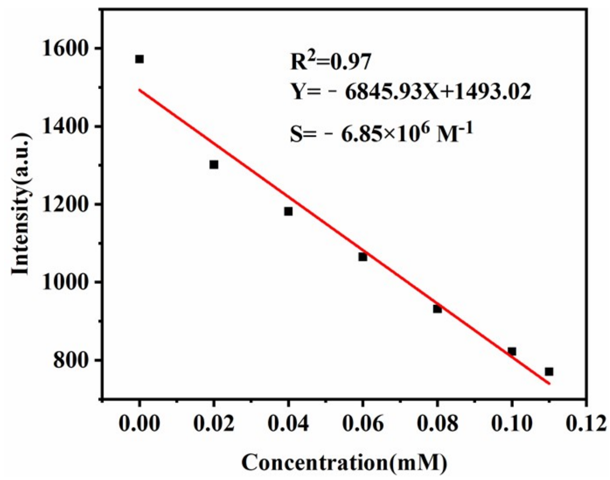


Fig. S16 Stern-Volmer plot for the luminescence intensity of **1**-ethanol emulsion upon the addition of TEA solution.

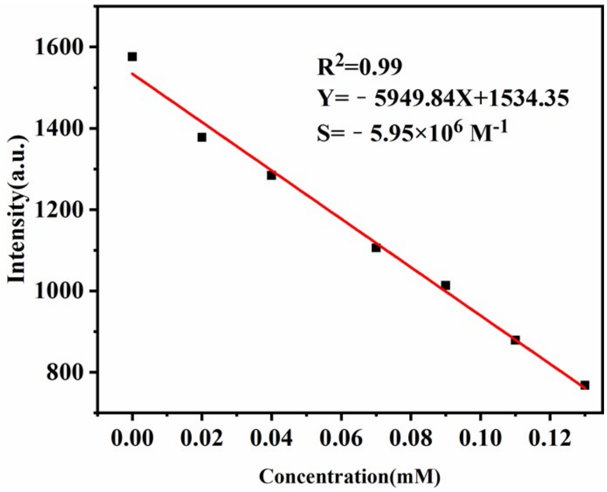


Linear Equation: Y=-6845.93X+1493.02 R^2=0.97

Slope=-6.85×10^6 M^{-1}

Limit detection: 3δ/Slope=4.29×10^{-7} M; δ=0.98(N=10)

Fig. S17 The fitting curve of the luminescence intensity of **1** at different EDA concentration.

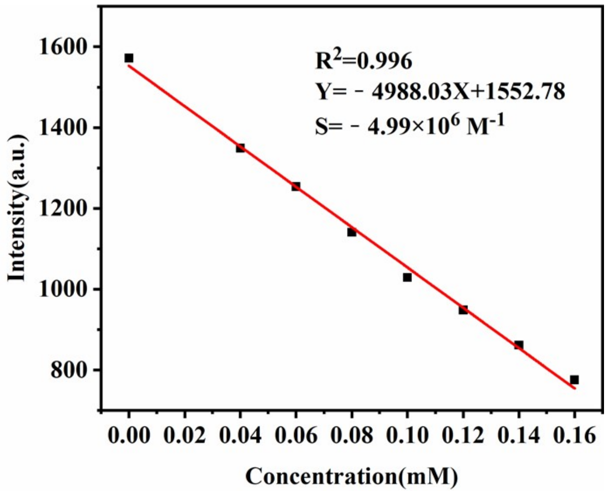


Linear Equation: Y=-5949.84X+1534.35 R^2=0.99

Slope=-5.95×10^6 M^{-1}

Limit detection: 3δ/Slope=4.94×10^{-7} M; δ=0.98(N=10)

Fig. S18 The fitting curve of the luminescence intensity of **1** at different DEA concentration.

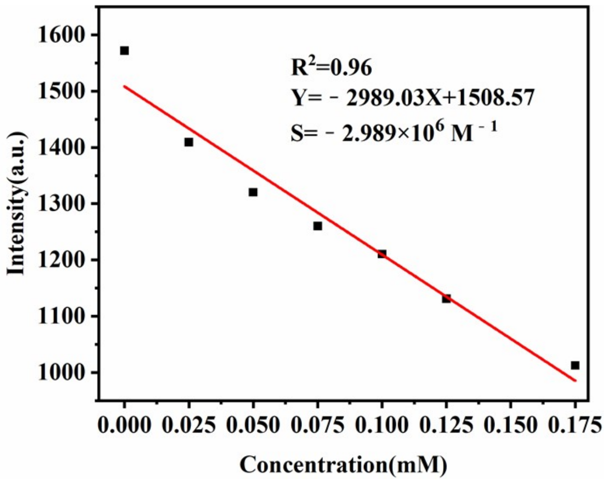


Linear Equation: Y=-4988.03X+1552.78 R^2=0.996

Slope=-4.99×10^6 M^{-1}

Limit detection: 3δ/Slope=5.89×10^{-7} M; δ=0.98(N=10)

Fig. S19 The fitting curve of the luminescence intensity of **1** at different TMA concentration.

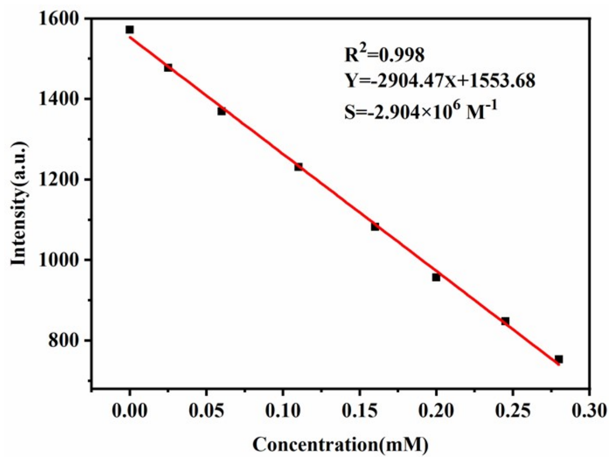


Linear Equation: Y=-2989.03X+1508.57 R^2=0.96

Slope=-2.989×10^6 M^{-1}

Limit detection: 3δ/Slope=9.84×10^{-7} M; δ=0.98(N=10)

Fig. S20 The fitting curve of the luminescence intensity of **1** at different TEA concentration.



Linear Equation: Y=-2904.47X+1553.68 R^2=0.998

Slope=-2.904×10^{6} M^{-1}

Limit detection: 3δ/Slope=1.012×10^{-6} M; δ=0.98(N=10)

Fig. S21 The fitting curve of the luminescence intensity of **1** at different aniline concentration.

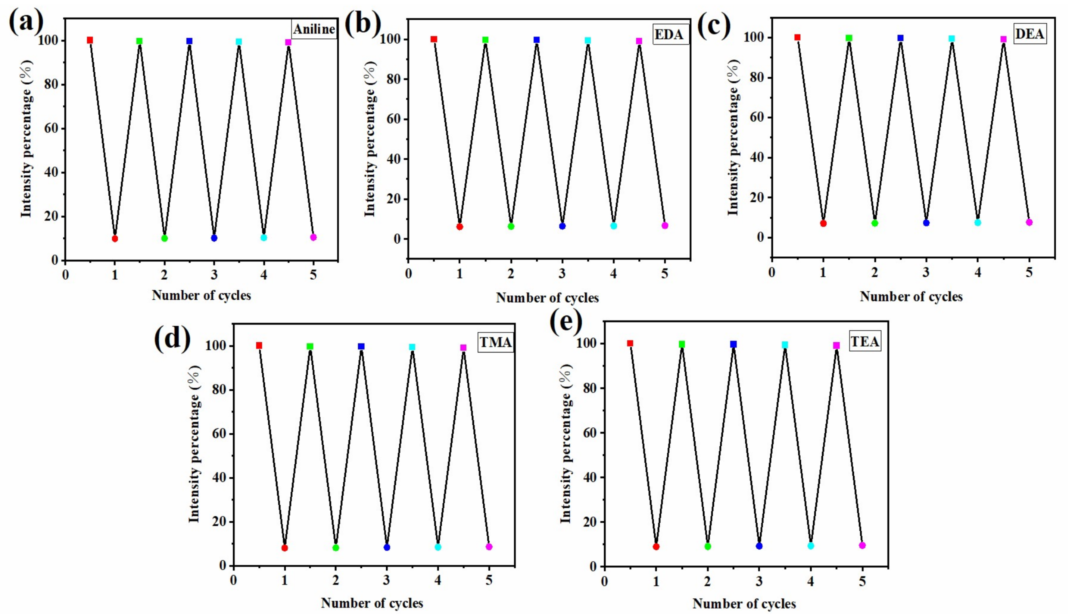


Fig. S22 The luminescence intensity of compound **1** after five cycles (a) for aniline, (b) for EDA, (c) for DEA, (d) for TMA, and (e) for TEA.

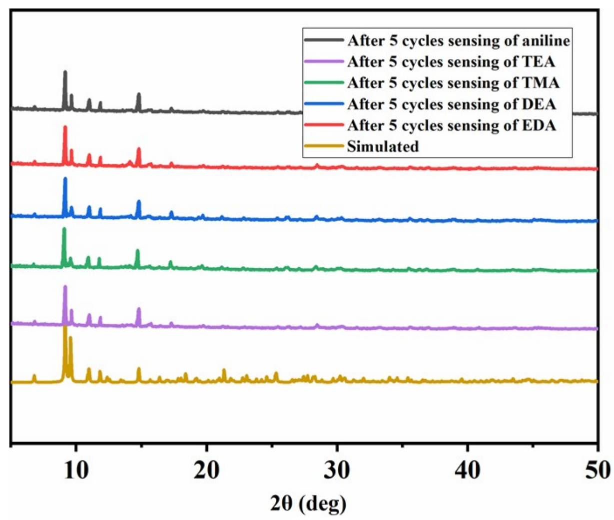


Fig. S23 PXRD patterns of compound **1** after five cycles.

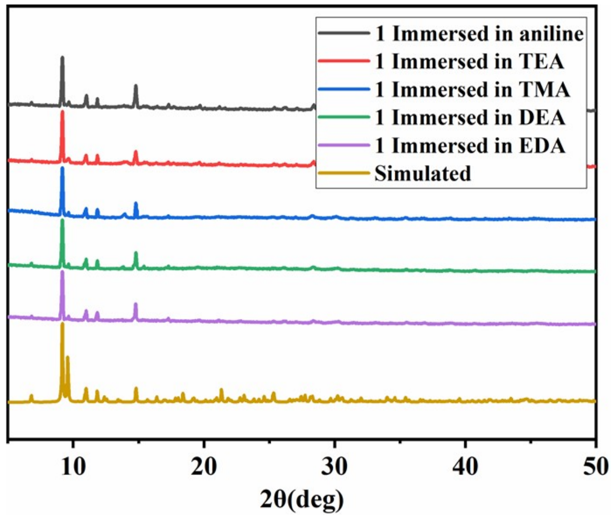


Fig. S24 PXRD patterns of **1** after soaking in organic amines with concentration of 0.1 M for 24 hours.

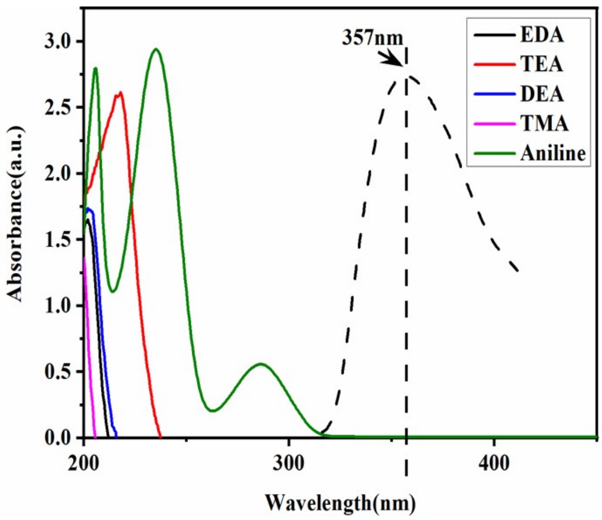


Fig. S25 UV absorption spectra of different organic amines and excited spectrum of compound **1**.

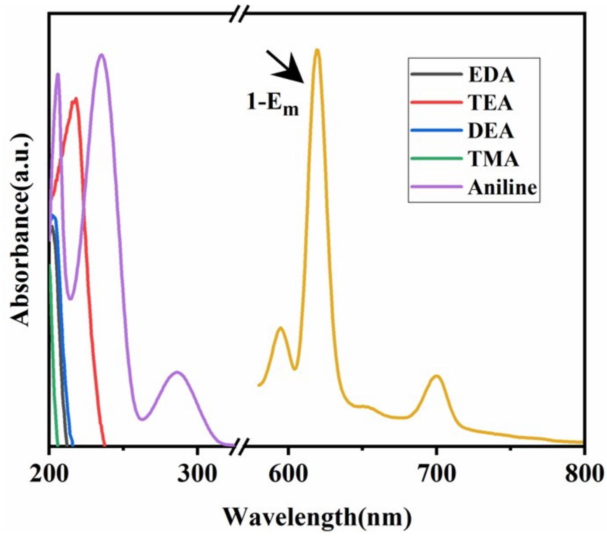


Fig. S26 The absorption spectra of organic amine ethanol solution and emission spectrum of compound **1**.

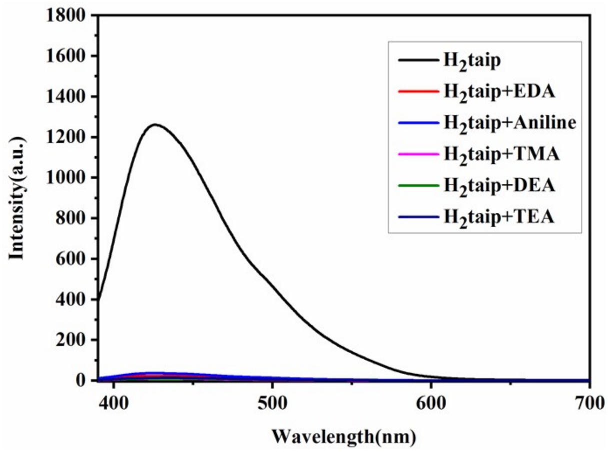


Fig. S27 The fluorescence spectra of H_2taip in ethanol and organic amines.

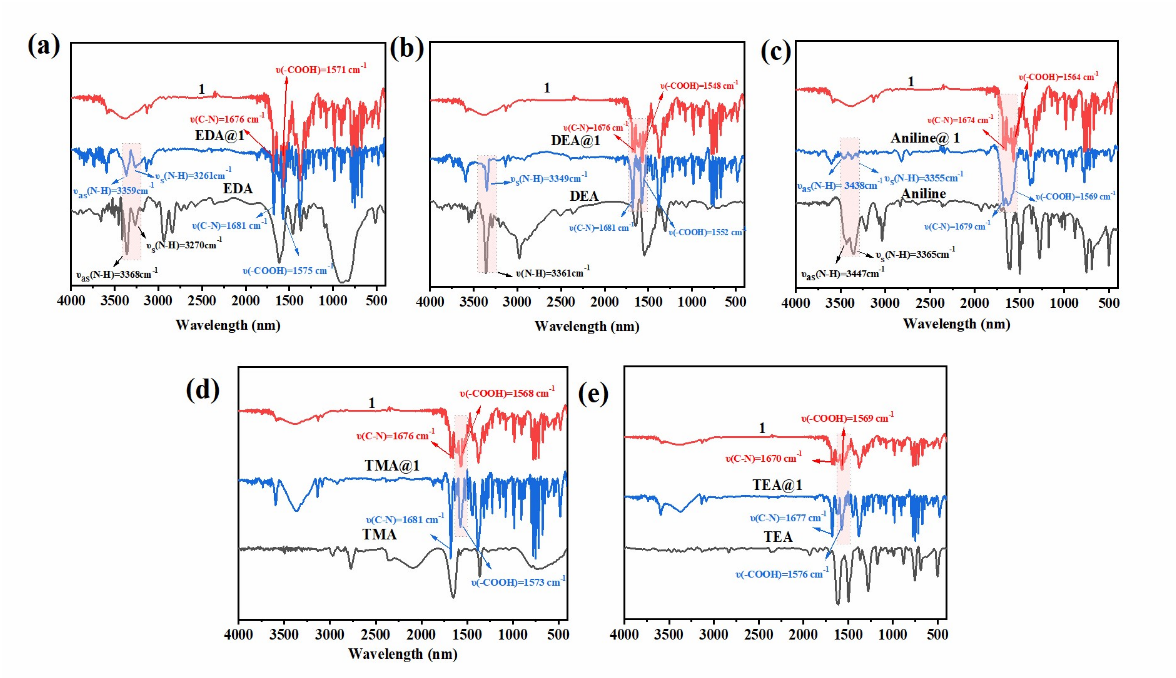


Fig. S28 IR spectra of organic amines, compound **1** and compound **1** after sensing organic amines.

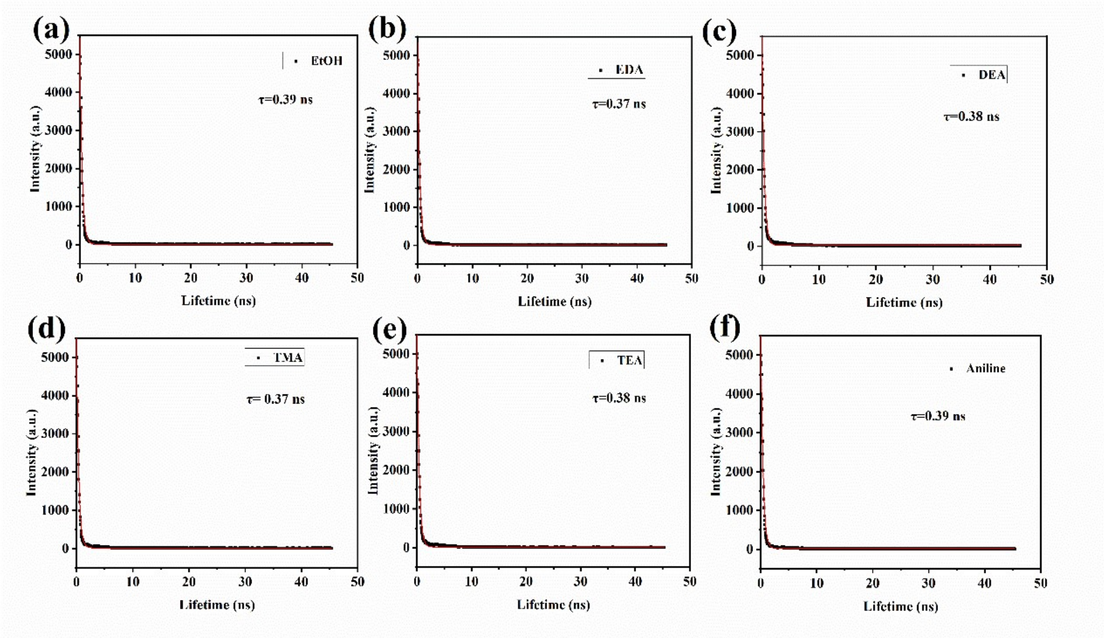


Fig. S29 Luminescence decay curves of compound **1** (a) in EtOH, (b) in EDA, (c) in DEA, (d) in TMA, (e) in TEA, and (f) in aniline.

Table S1 Selected bond lengths (Å) and angles (°) for **1**.

	1		
O(9)-Eu(1)#1	2.428(3)	O(4)-Eu(1)#8	2.485(3)
O(7)-Eu(1)#2	2.339(3)	O(4)-Eu(2)#9	2.590(3)
O(8)-Eu(2)#3	2.350(3)	O(3)-Eu(2)#9	2.461(3)
Eu(1)-O(5)	2.331(3)	Eu(2)-O(11)	2.435(2)
Eu(1)-O(1)	2.332(3)	Eu(2)-O(1W)	2.456(3)
Eu(1)-O(7)#4	2.339(3)	Eu(2)-O(3)#7	2.461(3)
Eu(1)-O(11)	2.392(2)	Eu(2)-O(4)#7	2.590(3)
Eu(1)-O(10)	2.400(3)	Eu(2)-O(8)#3	2.350(3)
Eu(1)-O(9)#1	2.428(3)	Eu(2)-O(11)#6	2.415(2)
Eu(1)-O(4)#5	2.485(3)	O(11)-Eu(2)#6	2.415(2)
Eu(1)-O(2W)	2.525(3)	Eu(2)-O(2)	2.362(3)
Eu(2)-O(6)	2.395(3)	O(2)-Eu(2)-O(4)#7	127.11(10)
O(5)-Eu(1)-O(1)	74.99(13)	O(6)-Eu(2)-O(4)#7	149.63(10)
O(5)-Eu(1)-O(7)#4	143.46(12)	O(11)#6-Eu(2)-O(4)#7	70.17(8)
O(1)-Eu(1)-O(7)#4	141.54(12)	O(11)-Eu(2)-O(4)#7	97.22(8)
O(5)-Eu(1)-O(11)	79.57(11)	O(1W)-Eu(2)-O(4)#7	71.28(11)
O(1)-Eu(1)-O(11)	88.04(11)	O(3)#7-Eu(2)-O(4)#7	51.24(8)
O(7)#4-Eu(1)-O(11)	97.36(10)	O(9)#1-Eu(1)-O(4)#5	139.49(10)
O(5)-Eu(1)-O(10)	77.09(12)	O(5)-Eu(1)-O(2W)	134.24(12)
O(1)-Eu(1)-O(10)	101.70(13)	O(1)-Eu(1)-O(2W)	71.26(13)
O(7)#4-Eu(1)-O(10)	91.59(12)	O(7)#4-Eu(1)-O(2W)	75.17(11)
O(11)-Eu(1)-O(10)	151.29(9)	O(11)-Eu(1)-O(4)#5	72.40(9)
O(5)-Eu(1)-O(9)#1	124.76(12)	O(10)-Eu(1)-O(4)#5	84.21(9)
O(1)-Eu(1)-O(9)#1	73.35(11)	O(11)-Eu(1)-O(2W)	69.41(9)
O(7)#4-Eu(1)-O(9)#1	79.41(11)	O(10)-Eu(1)-O(2W)	139.28(10)
O(11)-Eu(1)-O(9)#1	141.77(9)	O(9)#1-Eu(1)-O(2W)	73.02(10)
O(10)-Eu(1)-O(9)#1	66.69(9)	O(4)#5-Eu(1)-O(2W)	126.15(10)
O(5)-Eu(1)-O(4)#5	70.73(11)	O(7)#4-Eu(1)-O(4)#5	73.65(10)
O(1)-Eu(1)-O(4)#5	142.92(11)	O(8)#3-Eu(2)-O(1W)	73.62(14)
O(11)#6-Eu(2)-O(1W)	135.29(11)	O(2)-Eu(2)-O(1W)	72.59(12)
O(2)-Eu(2)-O(6)	79.41(13)	O(6)-Eu(2)-O(1W)	109.80(15)
O(8)#3-Eu(2)-O(11)#6	77.98(11)	O(11)-Eu(2)-O(1W)	139.69(13)
O(8)#3-Eu(2)-O(2)	124.18(12)	O(8)#3-Eu(2)-O(3)#7	127.58(10)
O(8)#3-Eu(2)-O(6)	72.04(12)	O(2)-Eu(2)-O(3)#7	82.42(11)
O(6)-Eu(2)-O(11)#6	92.93(12)	O(6)-Eu(2)-O(3)#7	159.10(11)
O(8)#3-Eu(2)-O(11)	144.02(11)	O(11)#6-Eu(2)-O(3)#7	98.18(9)
O(2)-Eu(2)-O(11)	86.42(10)	O(11)-Eu(2)-O(3)#7	69.29(9)

O(6)-Eu(2)-O(11)	99.20(11)	O(1W)-Eu(2)-O(3)#7	74.01(13)
O(11)#6-Eu(2)-O(11)	67.49(9)	O(8)#3-Eu(2)-O(4)#7	79.67(10)
O(2)-Eu(2)-O(11)#6	151.40(10)		

For compound **1**, #1 -x+2, -y+2, -z+2; #2 x, y-1, z; #3 -x+1, -y+1, -z+2; #4 x, 1+y, z; #5 x, -y+3/2, z+1/2; #6 -x+1, -y+2, -z+2; #7 -x+1, y+1/2, -z+3/2; #8 x, -y+3/2, z-1/2; #9 -x+1, y-1/2, -z+3/2.

Table S2 The three-dimensional dimensions of TEA, aniline, TMA, DEA and EDA.

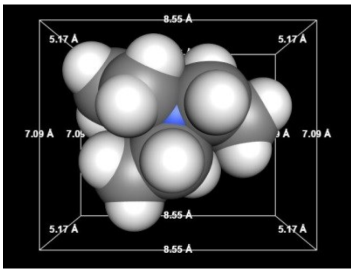
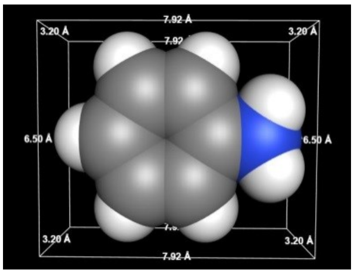
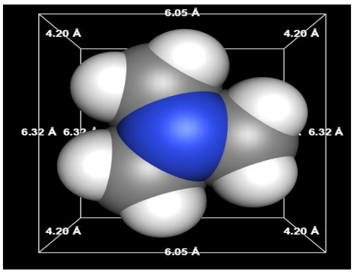
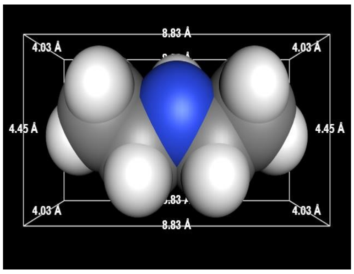
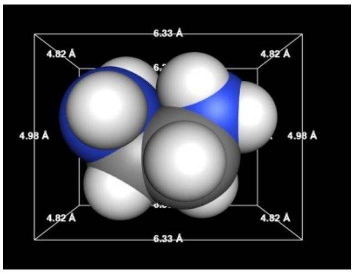
Organic amines	Three-Dimensional Size (Å^3)
	**8.551×7.087×5.167**
	**7.923×6.497×3.203**
	**6.046×6.324×4.197**
	**8.826×4.448×4.030**
	**6.331×4.982×4.820**

Table S3 HOMO and LUMO energy levels of H_2taip and organic amines.

	HOMO(H)	LUMO(H)	HOMO(eV)	LUMO(eV)	ΔE(eV)
H_2taip	-0.26631	-0.08411	-7.25	-2.29	4.96
aniline	-0.19871	0.00825	-5.41	0.22	5.63
EDA	-0.22661	0.08110	-6.17	2.21	8.38
TEA	-0.19880	0.07708	-5.41	2.10	7.51
TMA	-0.20715	0.08368	-5.64	2.28	7.92
DEA	-0.21517	0.08856	-5.86	2.41	8.28