Electronic Supplementary Material (ESI) for RSC Advances.

Novel Zn(II)-thiazolone-based Solid Fluorescent Chemosensors: Naked-eye Detection for Acid/Base and Toluene

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Supporting Information

Preparation of Thiosemicarbazones (Precursors of Ligands)

Synthesis of Am4DH

2-Cyanopyridine (5.63 g, 0.054 mol) was dissolved in a solution of sodium (0.23 g, 0.01 mol) in MeOH (100 mL), which had been dried over $CaSO_4$, and the mixture stirred for 0.5 h. The thiosemicarbazide (5 g, 0.054 mol) was added in small portions to the resulting solution, then the mixture was refluxed for 4h and the resulting

yellowish solid was filtered off, washed and recrystallized from methanol. Yield: 6.38 g (ca. 60%). Selected IR data (KBr, cm^{-1}): 3420.6, 3360, 3233.9, 2988.7, 1661.6, 1610.1, 1588.7, 1542.2, 1480.5, 1464.4, 1435.7, 1381.1, 1298.3, 1251.6, 1151.6, 1130.2, 1049.1, 998.5, 852.8, 792.2, 744.1, 701.7, 619.1, 526.2, 460.5. ^{1}H NMR (d_6-DMSO, δ/ppm): 10.06 (s, 1H), 8.55 (d, 1H), 8.44 (d, 1H), 7.95 (s, 1H), 7.86−7.75 (m, 2H), 7.43 (dd, 1H), 6.92 (s, 2H). ^{13}C NMR (d_6-DMSO, δ/ppm): 176.64(s), 150.15 (s), 147.85 (s), 141.86−140.20 (m), 136.64 (s), 124.48 (s),121.10 (s).

Synthesis of Am4M

The same procedure as for Am4DH using 2-Cyanopyridine (4.90 g, 0.047 mol) dissolving in a solution of sodium (0.23 g, 0.01 mol) in MeOH (100 mL), and the mixture stirred for 0.5 h. The N(4)-methylthiosemicarbazide (5 g, 0.047 mol) was added in small portions to the resulting solution, then the mixture was refluxed for 4h and the resulting yellowish solid was filtered off, washed and recrystallized from methanol. Yield: 6.05 g (ca. 61.1%). Selected IR data (KBr, cm^{-1}): 3366, 3317, 3247, 3146, 3038, 1660, 1590, 1548, 1512, 1473, 1441, 1336, 1224, 1147, 1066, 1012, 996, 796, 565. ^{1}H NMR (d_6-DMSO, δ/ppm): 10.06 (s, 1H), 8.54 (t, 1H), 8.46 (d, 1H), 8.25 (t, 1H), 7.85 (t, 1H), 7.49−7.29 (m, 1H), 6.90 (s, 2H), 3.03 (d, 3H). ^{13}C NMR (d_6-DMSO, δ/ppm): 176.66 (d), 150.09 (d), 147.69 (d), 141.60 (d), 136.37 (d), 124.07 (d), 120.44 (d), 30.59−29.23 (m).

Synthesis of Am4E

The same procedure as for Am4DH using 2-Cyanopyridine (4.38 g, 0.042 mol) dissolving in a solution of sodium (0.23 g, 0.01 mol) in MeOH (100 mL), and the

mixture stirred for 0.5 h. The N(4)-ethylthiosemicarbazide (5 g, 0.042 mol) was added in small portions to the resulting solution, then the mixture was refluxed for 4h and the resulting yellowish solid was filtered off, washed and recrystallized from methanol. Yield: 6.66 g (ca. 71%). Selected IR data (KBr, cm^{-1}): 3343.3, 3280.1, 3231.4, 3183.9, 2974.1, 2932.8, 1661.6, 1609.4, 1589.9, 1542, 1506.8, 1471.1, 1441, 1483.7, 1371.8, 1315.2, 1270.5, 1237.5, 1150.7, 1092.4, 1049.4, 996.3, 967.2, 933.7, 796.6, 746.3, 710.5, 667.5, 620.6, 569.8, 496.8, 471.1. ^{1}H NMR (d_6-DMSO, δ/ppm): 10.00 (s, 1H), 8.61−8.49 (m, 1H), 8.45 (d, 1H), 8.33 (t, 1H), 7.85 (td, 1H), 7.44 (ddd, 1H), 6.92 (s, 2H), 3.61 (p, 2H), 1.15 (t, 3H). ^{13}C NMR (d_6-DMSO, δ/ppm): 175.61 (d), 149.81 (d), 147.23 (d), 141.67 (d), 136.59 (s), 123.98 (d), 120.59 (d), 38.07 (s), 14.86 (s).

Synthesis of 1, 3-thiazolidin-4-ones (ligands)

General Synthetic Route

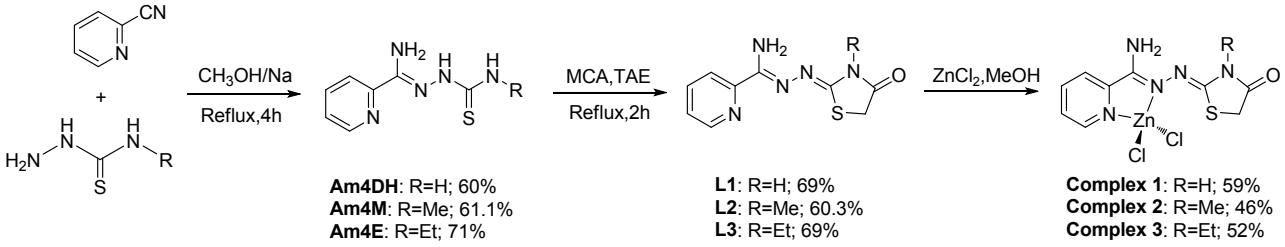
The Thiosemicarbazones were stirred with several drops of triethylamine in toluene solution, then a solution of chloroacetic acid in toluene was added. The mixture was refluxed for a minimum of 2 h to give the precipitate which was filtered off and washed with toluene for several times. The precipitate was recrystallized from ethanol to give pure products.

Ligand 1 Yield: ca. 69%. Selected IR data (KBr, cm^{-1}): 3436.6, 3307.3, 3069, 2926.6, 2761.9, 1708.6, 1641.8, 1616, 1589.2, 1564, 1476.7, 1435.6, 1391.7 1333.8, 1241.3, 1201.5, 1134.5, 1047.8, 989.6, 884.4, 796.6, 742.4, 717.1, 621.2, 580.7, 508, 462.2. ^{1}H NMR (d_6-DMSO, δ/ppm): 11.65 (s, 1H), 8.73−8.47 (m, 1H), 8.10 (d, 2H), 7.89 (tt,

1H), 7.59−7.38 (m, 1H), 6.33 (d, 2H), 3.85 (s, 2H). ^{13}C NMR (d_6-DMSO, δ/ppm): 173.84 (s), 157.38 (s), 152.70 (s), 150.20 (s), 148.37 (s), 136.83 (s), 124.97 (s), 120.59 (s), 32.76 (s).

Ligand 2 Yield: ca. 60.3%. Selected IR data (KBr, cm^{-1}): 3466, 3345, 3052, 2998, 2939, 1705, 1610, 1562, 1529, 1469, 1423, 1372, 1318, 1251, 1225, 1122, 1038, 1014, 906, 808, 486. ^{1}H NMR (d_6-DMSO, δ/ppm): 8.63 (d, 1H), 8.13 (d, 1H), 7.91 (td, 1H), 7.53−7.45 (m, 1H), 6.69 (d, 2H), 3.96−3.84 (m, 2H), 3.36 (s, 3H). ^{13}C NMR (d_6-DMSO, δ/ppm): 171.95 (s), 156.52 (s), 153.58 (s), 150.30 (s), 148.36 (s), 136.85 (s), 125.01 (s), 120.70 (s), 31.96 (s), 29.25 (s).

Ligand 3 Yield: ca. 69%. Selected IR data (KBr, cm^{-1}): 3483, 3359.5, 3077.3, 2976, 2936.7, 1708.8, 1629, 1561.6, 1529.3, 1473.1, 1440.8, 1384.8, 1343.9, 1289.7, 1244.6, 1221.6, 1168.9, 1134.3, 1044.6, 1018.1, 995.5, 945.2, 900.4, 886, 807, 773.9, 754.4, 688.2, 634.3, 616, 599.8, 543.2, 500.8, 460.2. ^{1}H NMR (d_6-DMSO, δ/ppm): 8.63 (d, 1H), 8.13 (d, 1H), 7.91 (td, 1H), 7.50 (dd, 1H), 6.67 (d, 2H), 3.89 (d, 2H), 3.84 (q, 2H), 1.19 (t, 3H). ^{13}C NMR (d_6-DMSO, δ/ppm): 171.71 (s), 155.58 (d), 153.47 (s), 150.30 (s), 148.36 (s), 136.85 (s), 125.00 (s), 120.68 (s), 37.51 (s), 31.95 (s), 12.45 (s).



Am4DH: R=H; 60%
Am4M: R=Me; 61.1%
Am4E: R=Et; 71%

L1: R=H; 69%
L2: R=Me; 60.3%
L3: R=Et; 69%

Complex 1: R=H; 59%
Complex 2: R=Me; 46%
Complex 3: R=Et; 52%

Scheme S1. Synthetic route of **1-3**.

Table S1. Summary of Crystal Data for **1**−**3**.

Complex	$C_9H_9Cl_2ZnN_5OS$ (**1**)	$C_{10}H_{11}Cl_2ZnN_5OS$ (**2**)	$C_{11}H_{13}Cl_2ZnN_5OS$ (**3**)
Fw	389.59	385.57	399.59
crystal system	monoclinic	monoclinic	monoclinic
space group	*P2(1)/c*	*P2(1)/c*	*P2(1)/n*
a, Å	7.8176(16)	15.220(3)	11.624(2)
b, Å	10.961(2)	6.8071(14)	11.064(2)
c, Å	17.170(3)	15.097(3)	12.437(3)
α, º	90	90	90
β, º	92.17(3)	115.90(3)	100.48(3)
γ, º	90	90	90
V, Å^3	1470.2(5)	1407.1(5)	1572.8(5)
Z	4	4	4
ρ_{calcd}, g·cm^{-3}	1.760	1.820	1.688
T, K	113(2)	113(2)	113(2)
μ, mm^{-1}	2.182	2.274	2.038
F(000)	784	776	808
crystal size, mm	0.18 × 0.16 × 0.12	0.20 × 0.15 × 0.12	0.20 × 0.15 × 0.12
θ limits, º	2.20 to 27.94	2.70 to 28.05	2.48 to 27.94
reflections collected	14754	13199	15684
independent reflections	3520 [R(int) = 0.0485]	3285 [R(int) = 0.0593]	3741 [R(int) = 0.0400]
completeness to θ (%)	99.5%	96.9 %	99.1%
data/restraints/parameters	3520/3/189	3285/0/181	3741/0/191
Goodness on fit on F^2	0.938	0.990	1.002
R_1 ($I > 2\sigma(I)$)	0.0493	0.0454	0.0264
wR_2 (all data)	0.1043	0.1152	0.0641
largest diff. peak and hole, e Å^{-3}	0.453, -0.684	0.702, -1.026	0.609, -0.444

Table S2. Bond lengths [Å] and angles [˚] for **1**−**3**.

1					
Zn(1)-N(3)	2.065(2)	N(3)-Zn(1)-N(1)	79.96(10)	N(1)-Zn(1)-Cl(1)	112.76(8)
Zn(1)-N(1)	2.074(3)	N(3)-Zn(1)-Cl(2)	125.99(8)	Cl(2)-Zn(1)-Cl(1)	115.56(4)
Zn(1)-Cl(2)	2.2205(11)	N(1)-Zn(1)-Cl(2)	103.25(8)	C(6)-N(3)-Zn(1)	112.4(2)
Zn(1)-Cl(1)	2.2248(10)	N(3)-Zn(1)-Cl(1)	111.97(8)	N(4)-N(3)-Zn(1)	132.08(18)
2					
Zn(1)-N(3)	2.063(2)	N(3)-Zn(1)-N(1)	80.81(10)	N(1)-Zn(1)-Cl(2)	103.88(8)
Zn(1)-N(1)	2.064(3)	N(3)-Zn(1)-Cl(1)	110.40(7)	Cl(1)-Zn(1)-Cl(2)	115.67(4)
Zn(1)-Cl(1)	2.2267(8)	N(1)-Zn(1)-Cl(1)	114.01(8)	C(1)-N(1)-Zn(1)	127.3(2)
Zn(1)-Cl(2)	2.2323(10)	N(3)-Zn(1)-Cl(2)	125.93(7)	C(5)-N(1)-Zn(1)	112.87(19)
3					
Zn(1)-N(2)	2.0606(15)	N(2)-Zn(1)-N(1)	79.70(6)	N(1)-Zn(1)-Cl(1)	112.75(4)
Zn(1)-N(1)	2.0680(15)	N(2)-Zn(1)-Cl(2)	125.94(5)	Cl(2)-Zn(1)-Cl(1)	117.52(3)
Zn(1)-Cl(2)	2.2095(6)	N(1)-Zn(1)-Cl(2)	105.27(5)	C(1)-N(1)-Zn(1)	126.32(12)
Zn(1)-Cl(1)	2.2272(8)	N(2)-Zn(1)-Cl(1)	108.61(4)	C(5)-N(1)-Zn(1)	114.25(11)

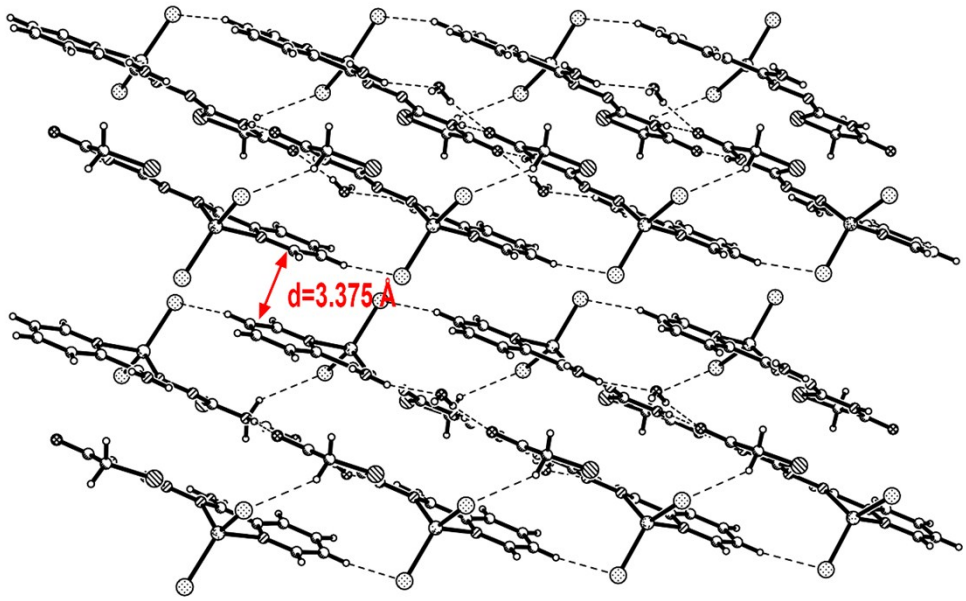


Fig. S1. A 3D supramolecular structure formed in **1**. Hydrogen atoms have been omitted for clarity. The dotted lines represent interplanar hydrogen bonds.

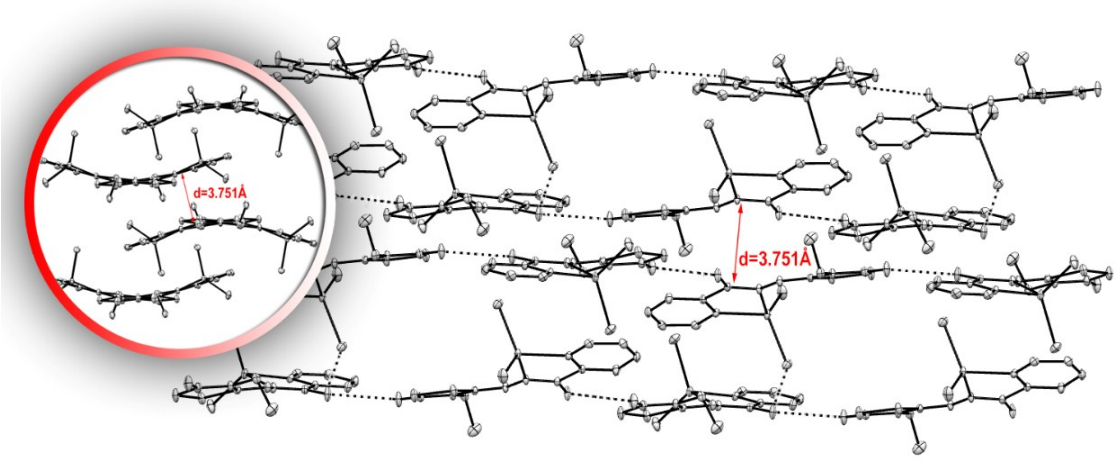


Fig. S2. Perspective views of molecular structures **1** through b (side view in inserted figure). Hydrogen atoms have been omitted for clarity. The dotted lines represent interplanar hydrogen bonds.

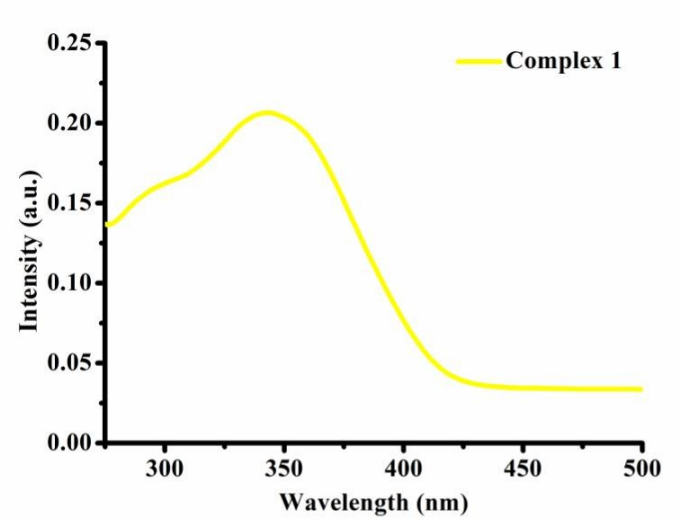


Fig. S3-1. Absorption spectra of **1** in solid state.

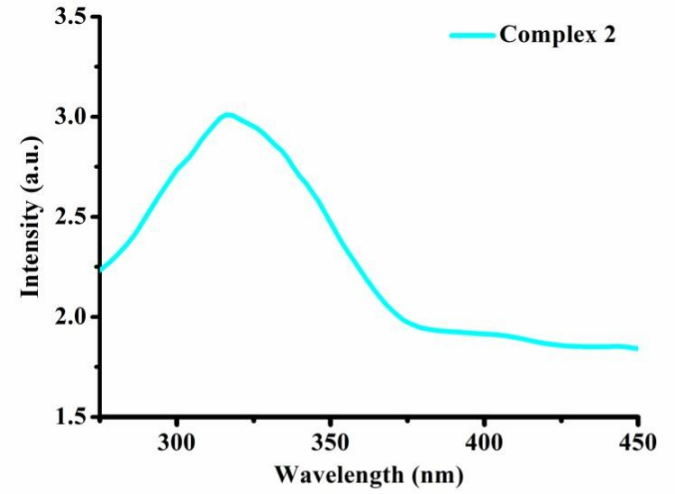


Fig. S3-2. Absorption spectra of **2** in solid state.

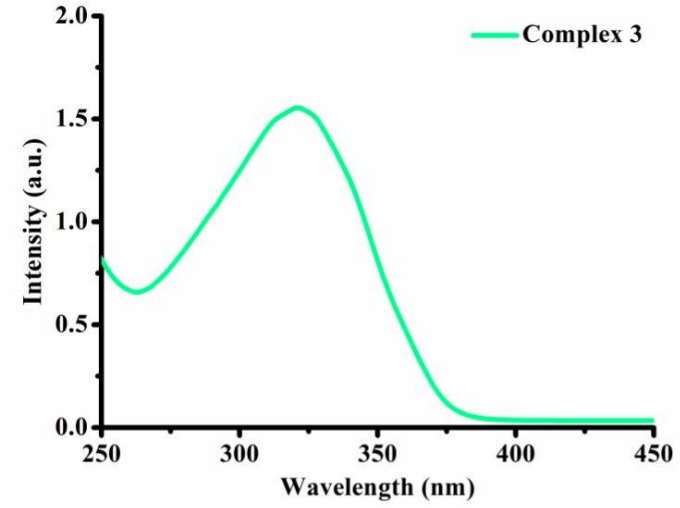


Fig. S3-3. Absorption spectra of **3** in solid state.

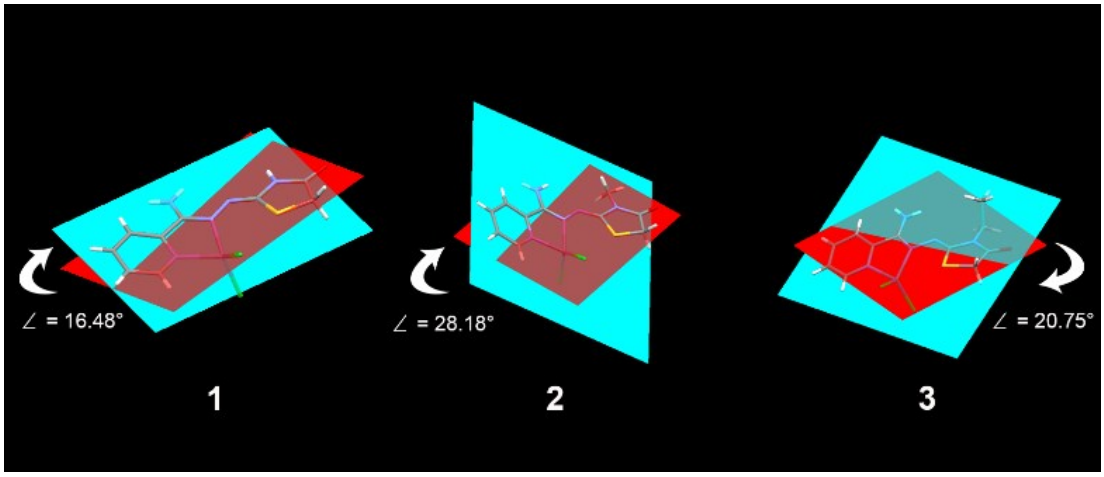


Fig. S4. Torsion angles [°] for **1**−**3**.

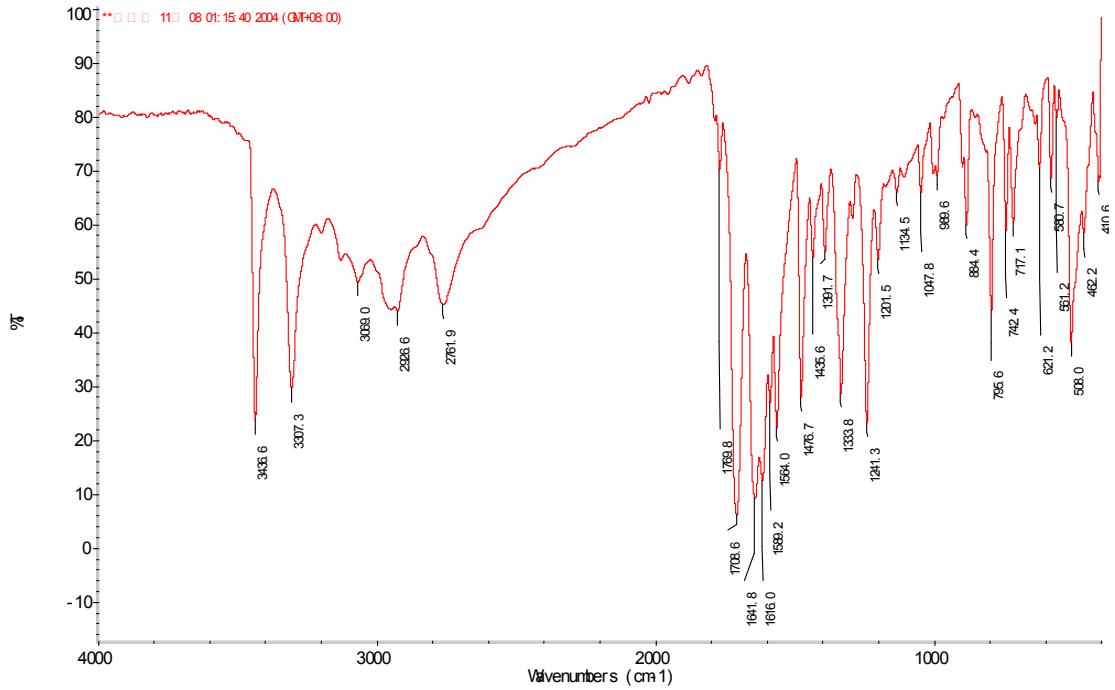


Fig. S5-1. IR spectrum of Ligand 1.

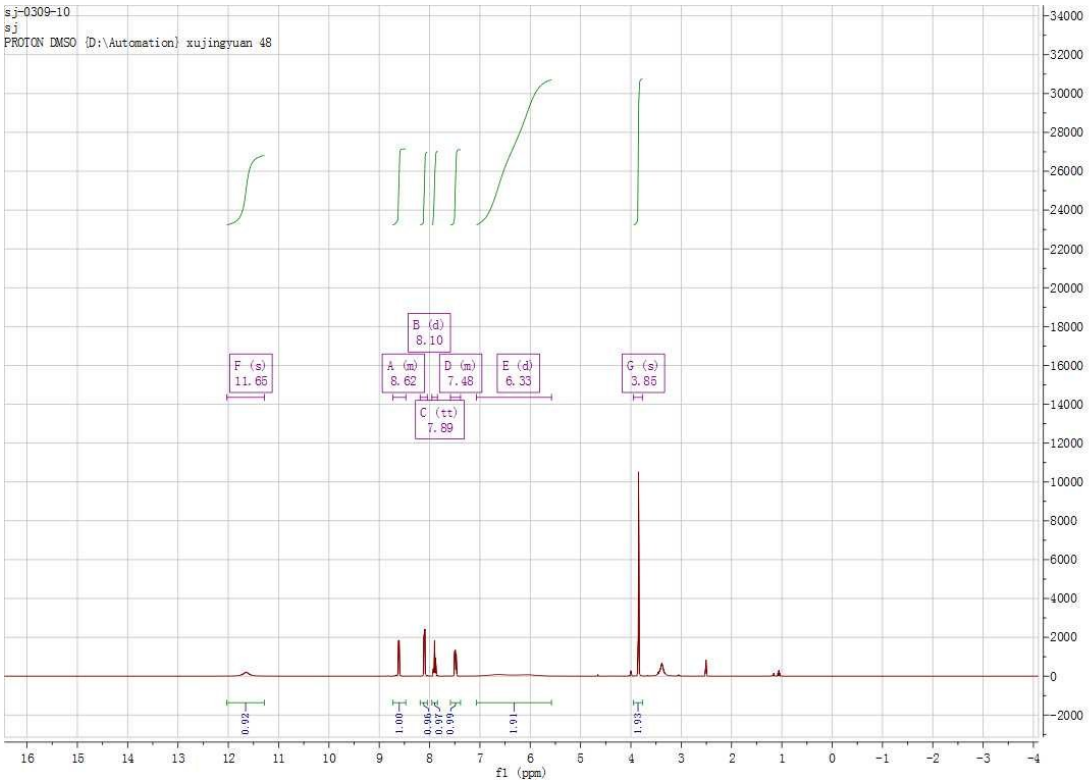


Fig. S5-2. ^{1}H NMR spectrum of Ligand 1.

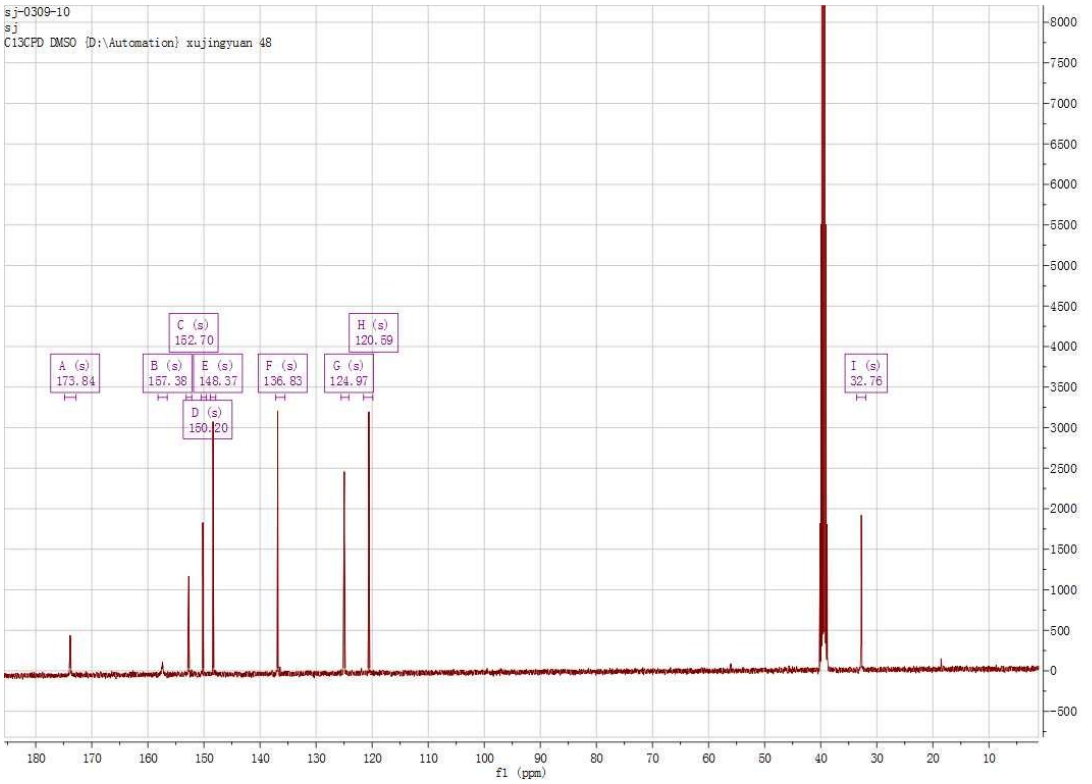


Fig. S5-3. ^{13}C NMR spectrum of Ligand 1.

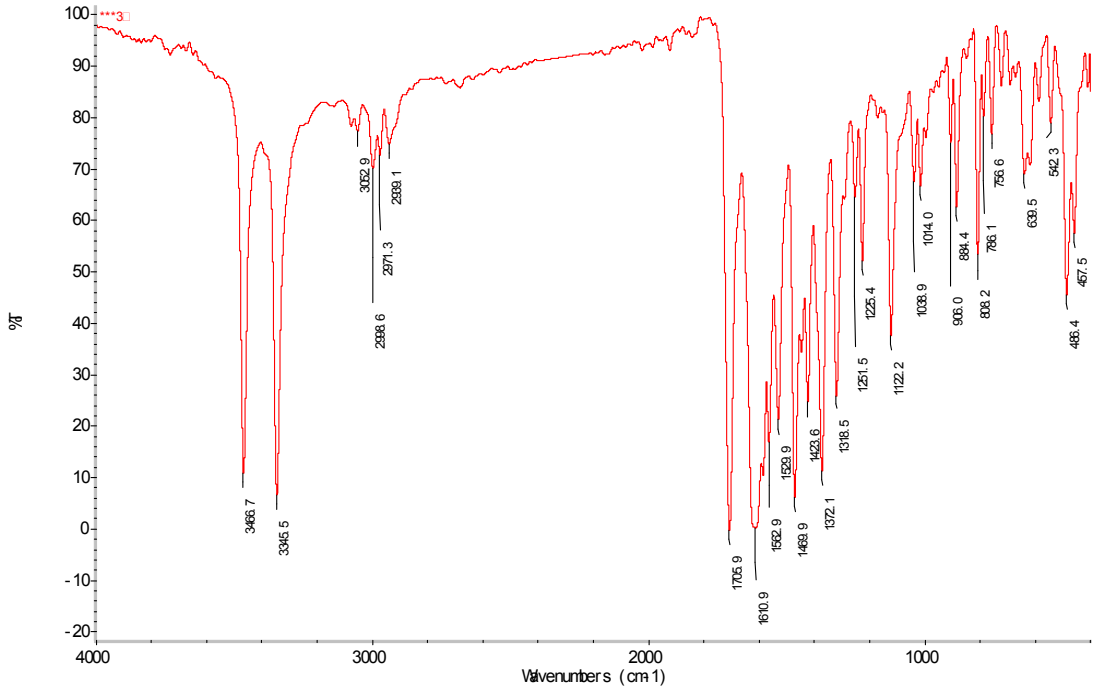


Fig. S6-1. IR spectrum of Ligand 2.

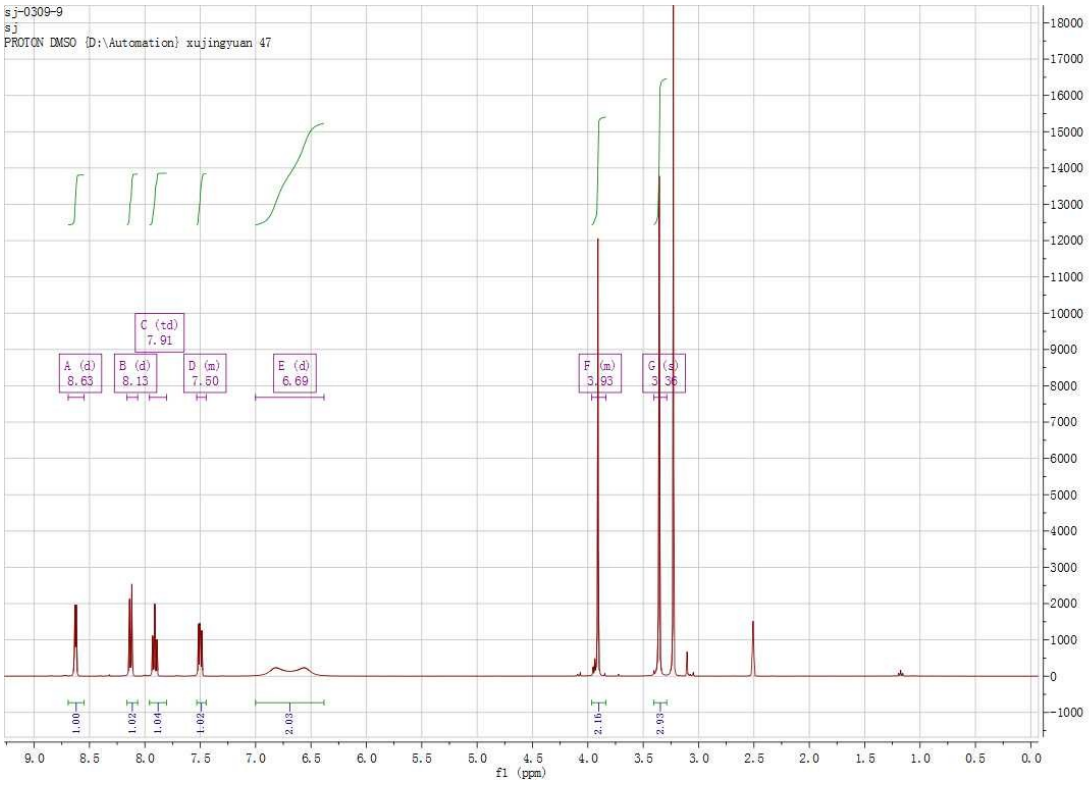


Fig. S6-2. ^{1}H NMR spectrum of Ligand 2.

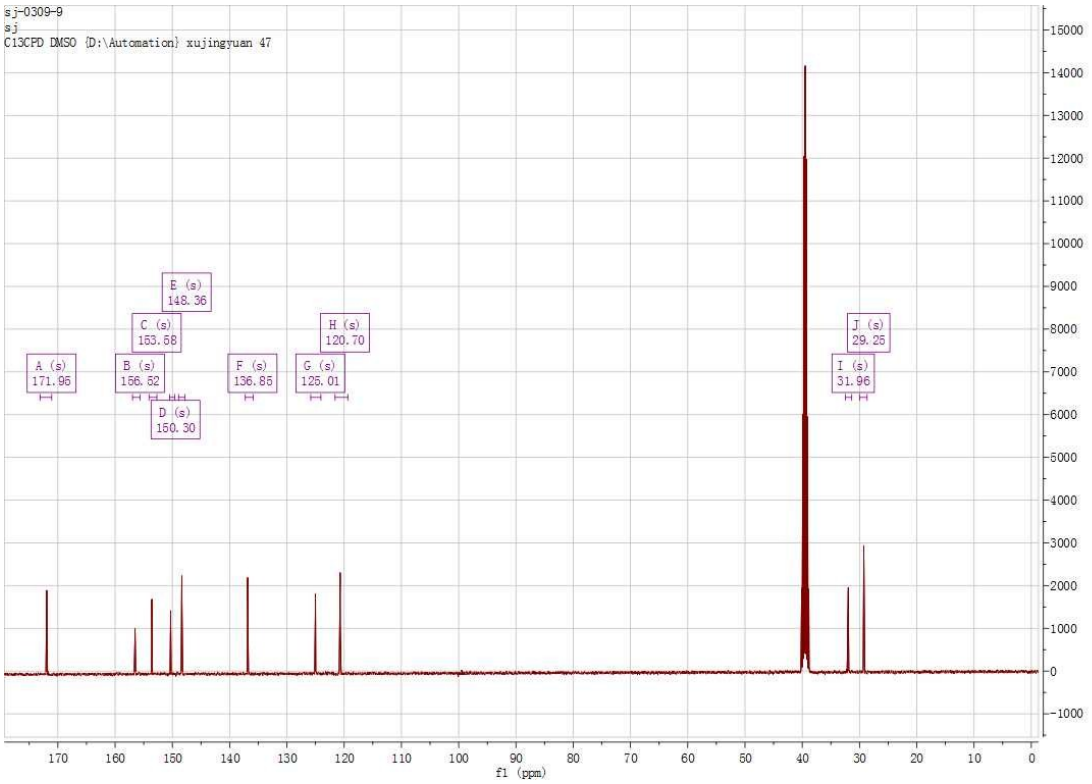


Fig. S6-3. ^{13}C NMR spectrum of Ligand 2.

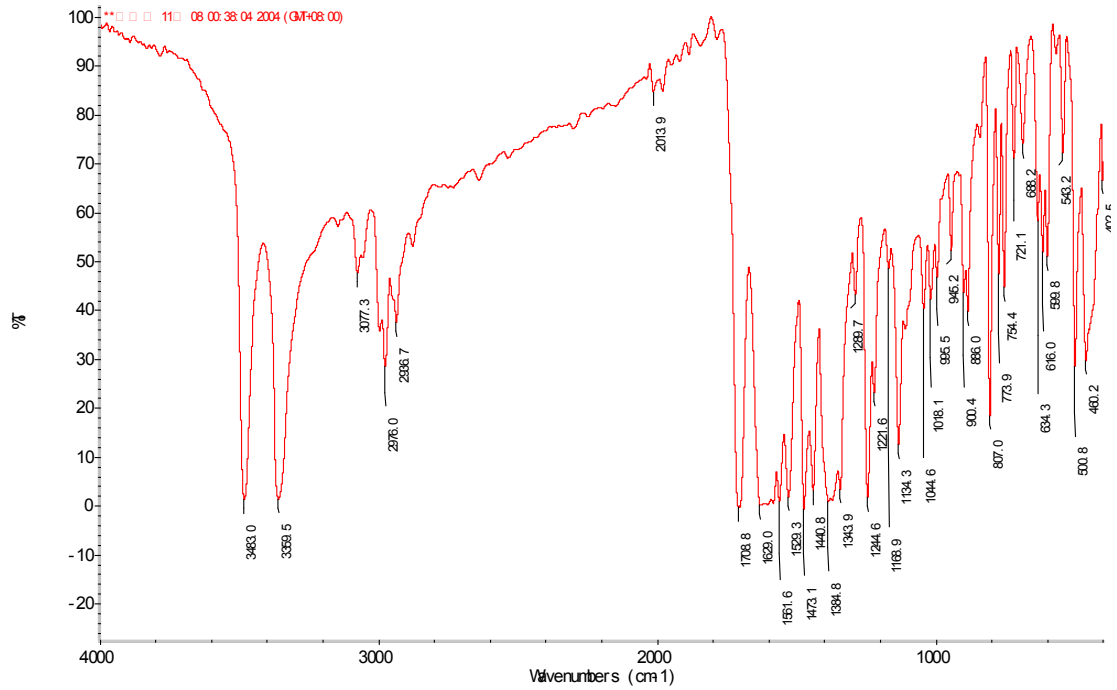


Fig. S7-1. IR spectrum of Ligand 3.

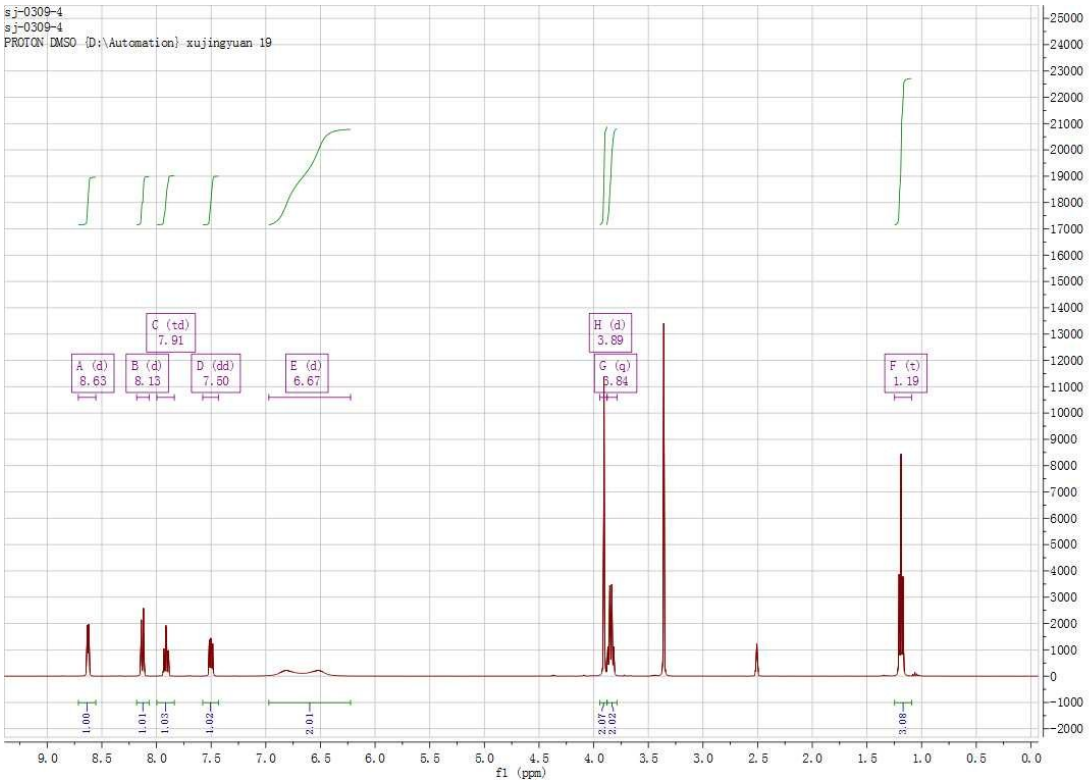


Fig. S7-2. ^{1}H NMR spectrum of Ligand 3.

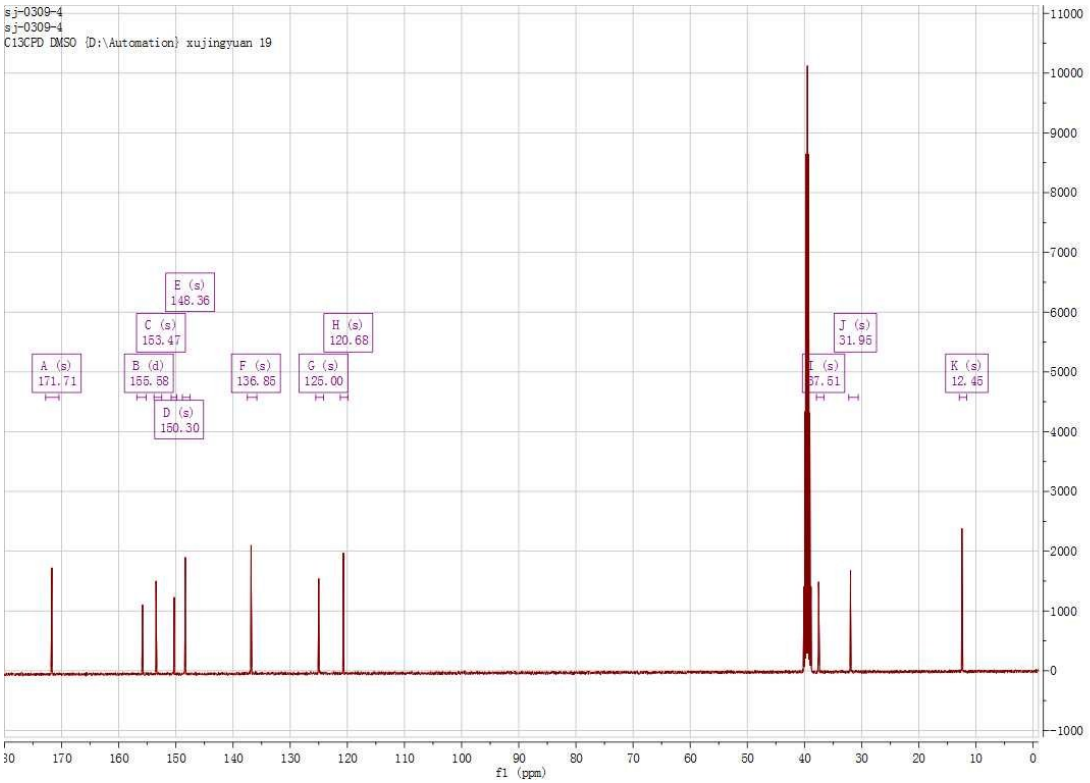


Fig. S7-3. ^{13}C NMR spectrum of Ligand 3.

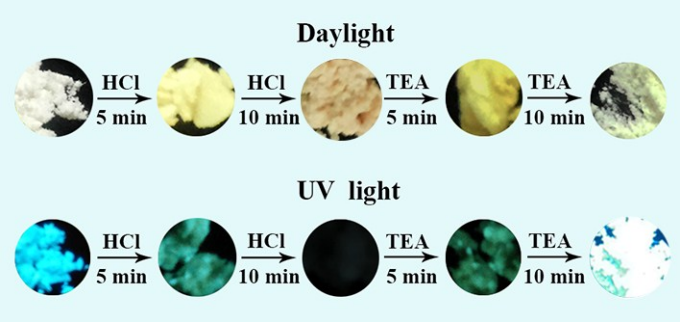


Fig. S8. Fluorescent dark and bright state of **2** switched by protonation/deprotonation process.

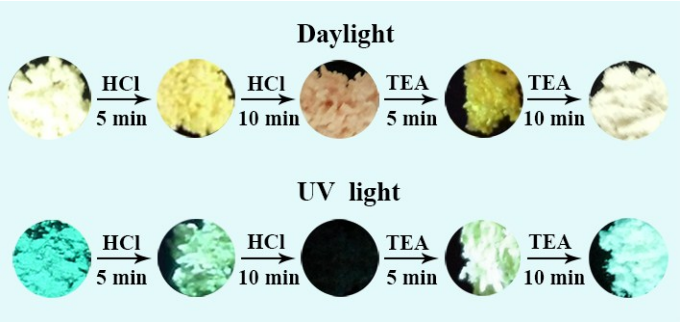


Fig. S9. Fluorescent dark and bright state of **3** switched by protonation/deprotonation process.

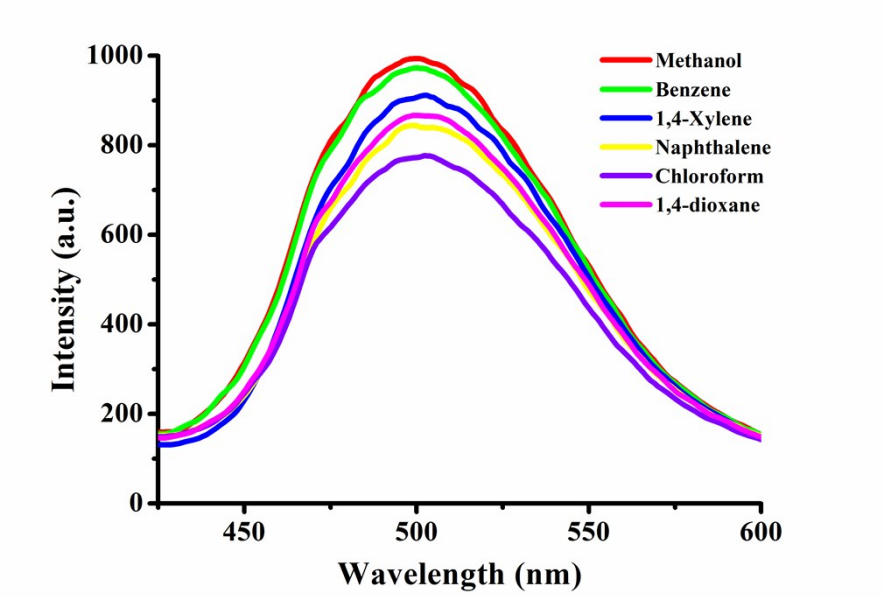


Fig. S10 Fluorescence intensity of powder **1** after different organic solution was added (organic solution:methanol = 1:9).