

Realizing Near White and Warm Light Emission of Cuprous Iodide Complexes by Alkyl-isomerization of Ligand

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Supporting Information

Experimental Section

Materials

CuI (98%, Aladdin), KI (99%, Aladdin), acetonitrile (99%, Aladdin), triethylene diamine (ted, 99%, Aladdin), 1-bromopropane (99%, Aladdin), 2-bromopropane (98%, Aladdin), 1-iodobutane (98%, Aladdin), 2-methyl-4-iodobutane (99%, Aladdin), ethyl acetate (99%, Aladdin). All reagents and solvents were used without further purification unless otherwise stated.

Synthesis of ligands.

Preparation of 1-propyl-1,4-diazabicyclo[2.2.2]octan-1-ium(L₁, *n*-pr-ted) :

Ted (5.6g, 50mmol) was first ultrasonically dissolved in 50 mL of acetonitrile, magnetically stirred at room temperature, and 1-bromopropane solution (6.15g, 50mmol) was added dropwise into it. The resulting solution was subjected to rotary evaporation to obtain a white solid. After 6 hours of reaction, the white solid was obtained by rotary evaporation, which was washed with ethyl acetate for several times and dried in vacuum. The yield was 92%.

Preparation of 1-isopropyl-1,4-diazabicyclo[2.2.2]octan-1-ium(L₂, *i*-pr-ted)

Ted (6.72g, 60mmol) was dissolved in 50 mL of acetonitrile ultrasonically, and the 2-bromopropane solution (7.38g, 60mmol) was weighed. After the two were mixed, they were magnetically stirred and refluxed at 65°C for 6 hours. After the reaction, the heating was stopped, and a white solid was obtained by rotary evaporation, which was washed with ethyl acetate for several times and dried in vacuum. The yield was 94%.

Preparation of 1-butyl-1,4-diazabicyclo[2.2.2]octan-1-ium(L₃, *n*-bu-ted)

Ted (6.72g, 60mmol) was dissolved in 50 mL acetonitrile ultrasonically in a 100 ml single-necked flask, and the 1-iodobutane solution (8.22g, 60mmol) was weighed. After the two were mixed, they were magnetically stirred and refluxed at 75°C for 6 hours. After the reaction, the heating was stopped, and a white solid was obtained by rotary evaporation, which was washed with ethyl acetate for several times and dried in vacuum. The yield was 98%.

Preparation of 1-isobutyl-1,4-diazabicyclo[2.2.2]octan-1-ium(L₄, *i*-bu-ted)

Ted (5.6g, 50mmol) was dissolved in 50 mL acetonitrile ultrasonically in a 100 ml single-necked flask, and the 2-methyl-4-iodobutane solution (9.2g, 60mmol) was weighed. After the two were mixed, they were magnetically stirred at room temperature. After the reaction, the white solid was obtained by rotary evaporation, which was washed with ethyl acetate for several times and dried in vacuum. The yield

was 96%.

Synthesis of Complexs 1-4

Synthesis of $\text{Cu}_4\text{I}_6(n\text{-pr-ted})_2(1)$. CuI (19mg) and the L_1 ligand (15.5mg) was dissolved in KI saturated solution (10mL) and a mixed solution of acetone(10mL)and acetonitrile (10mL), respectively. After ultrasound dissolved, the two solutions were mixed in the beaker, and the solvent was volatilized at room temperature. The block crystals were precipitated within two days and collected by filtration. **The yield was 61%. Anal. calcd. (%) for $\text{Cu}_4\text{I}_6(n\text{-pr-ted})_2$ (Mr: 1326.1): C, 16.30; H, 2.89; N, 4.22 Found: C,16.54; H, 2.53; N, 4.41.**

Synthesis of $\text{Cu}_5\text{I}_7(i\text{-pr-ted})_2(2)$. 19mg CuI was dissolved in 10mL KI saturated solution, then mix with 20mL mixed solvent (volume ratio of acetone: acetonitrile = 1: 1) containing 15.5 mg L_2 ligand in the beaker. A clear solution was obtained after ultrasound dissolved, which was slow volatilized at room temperature two days and then the needle- shaped crystal product was collected by filtration. **The yield was 54%. Anal. calcd. (%) for $\text{Cu}_5\text{I}_7(i\text{-pr-ted})_2$ (Mr: 1516.52): C, 14.26; H, 2.53; N,3.69 Found: C,14.03; H, 2.99; N, 3.77.**

Synthesis of $\text{Cu}_4\text{I}_6(n\text{-bu-ted})_2(3)$. 10mL KI saturated solution containing 19mg CuI was mixed with 20 mL mixed solvent (volume ratio of acetone: acetonitrile = 1: 1) containing 17.0 mg L_3 in the beaker. After the two solutions are thoroughly mixed, a clear solution was obtained, which was slow volatilized at room temperature overnight and then the block crystal product was collected by filtration. **The yield was 65%. Anal. calcd. (%) for $\text{Cu}_4\text{I}_6(n\text{-bu-ted})_2$ (Mr: 1354.13): C,17.74; H, 3.13; N, 4.14 Found: C,17.82; H, 2.98; N, 4.09.**

Synthesis of $\text{Cu}_6\text{I}_8(i\text{-bu-ted})_2(4)$. 17.0mg L_4 ligand was dissolved in 20 mL mixed solvent (volume ratio of acetone: acetonitrile = 1: 1), then the solution was mixed with 10 mL KI saturated solution containing 19mg CuI in the beaker. The mixture become a clear solution after ultrasound dissolved, and then it was slow volatilized at room temperature two day. The block crystal product was collected by filtration. **The yield was 55%. Anal. calcd. (%) for $\text{Cu}_6\text{I}_8(i\text{-bu-ted})_2$ (Mr: 677.07): C, 17.74; H, 3.13; N, 4.14 Found: C,17.62; H, 3.47; N, 4.25.**

Single crystal X-ray diffraction (SCXD).

Single crystal X-ray diffraction data of complexes 1-4 was collected by Bruker SMART APEX-II CCD diffractometer (Mo-K α , $\lambda = 0.71073 \text{ \AA}$) at room temperature. The structures were solved by direct methods using SIR-97 and refined by full-matrix least-

squares on F^2 using the SHELXL and Olex2 programs. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. These crystal data have been stored in the Cambridge Crystal Structure Database (CSD).

Powder X-ray diffraction (PXRD) analysis.

Powder X-ray diffraction (PXRD) patterns were measured on Ultima IV with $\text{CuK}\alpha$ radiation field emission ($\lambda=1.5406\text{\AA}$). Measurements were made in a 2θ range of $5-50^\circ$. The data were collected at room temperature with a scanning speed of $10^\circ/\text{min}$. The operating power was 40 kV/10 mA.

Photoluminescence spectra measurements and lifetime measurements.

Photoluminescence measurements of the complexes in the solid state were recorded using a FS5 fluorescence spectrophotometer at room temperature. The obtained sample powder was put into between two glass plates (which do not have emission in the visible range) for measurements. The lifetime decay data is also recorded a FS5 fluorescence spectrophotometer at room temperature. The lifetimes of the sample were extracted by fitting the decay curves in Origin with first, second or third order exponential decay functions with coefficient of determination (R^2) values larger than 0.99.

Thermogravimetric Analysis (TGA).

TG analyses were performed on powder samples by a Netzsch/TG209 F3 thermogravimeter. Pure powder samples were put into platinum pans and heated it from room temperature to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Optical Diffuse Reflectance Measurements.

Optical diffuse reflectance spectra were measured by a Shimadzu UV-3600 spectrophotometer with BaSO_4 powder as the standard (100% reflectance) at room temperature. The data were collected in the wavelength range of 300-800nm. In order to evaluate the band gap, the Kubelka-Munk function is used to collect and transform the data. The function conversion procedure is the same as reported in the past literature. The scattering coefficient (S) is considered to be a constant, because the average particle size of the measured sample is obviously greater than $5\ \mu\text{m}$.

Internal Quantum Yield Measurements

The room temperature internal quantum yields (IQYs) of samples in powder were measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics) with 150 W xenon monochromatic light source and 3.3 inch integrating

sphere. The sample to be measured is prepared by spreading the powder sample evenly on the bottom of the quartz sample holder.

DFT calculations.

Band structure (BS) and density of states (DOS) calculations were performed on sample employing density functional theory (DFT). The electronic properties of ligands were evaluated by density functional theory (DFT) computations using the Gaussian 09 suite of programs. A hybrid functional, B3LYP, was used for calculations. Ligands were optimized using 6-31+G* basis sets, respectively.

Table S1. Crystal data of complexes 1-4

Complex	1	2	3	4
Empirical Formula	C ₁₈ H ₃₈ Cu ₄ I ₆ N ₄	C ₁₈ H ₃₈ Cu ₅ I ₇ N ₄	C ₂₀ H ₄₂ Cu ₄ I ₆ N ₄	C ₁₀ H ₂₁ Cu ₂ I ₃ N ₂
FW	1326.10	1516.52	1354.13	677.07
Crystal system	cubic	monoclinic	orthorhombic	triclinic
Space Group	<i>Pa-3</i>	<i>Cm</i>	<i>Pbca</i>	<i>P-1</i>
a (Å)	14.7923(4)	14.1398(3)	13.8890(5)	7.9068(4)
b (Å)	14.7923(4)	16.8903(4)	14.9749(5)	8.6471(4)
c (Å)	14.7923(4)	8.6472(2)	16.1518(5)	13.3890(7)
α(°)	90	90	90	107.204
β(°)	90	109.129	90	102.168
γ(°)	90	90	90	99.198
V (Å³)	3236.7	1951.14	3359.35	830.26
Z	4	2	4	2
Dc (g/m⁻³)	2.721	2.581	2.677	2.708
μ (mm⁻¹)	8.331	8.233	8.029	8.122
F (000)	2432.0	1380.0	2496.0	624.0
θ range [°]	2.385 - 27.523	3.050 - 26.371	2.139 - 27.103	2.513-27.1
Collected reflections	24306	7866	25912	10088
Unique reflections	1248	3835	3700	3651
R1, wR2 [I > 2σ (I)]	0.0511, 0.1116	0.0027, 0.0529	0.0247, 0.0606	0.0301,0.0751
R1, wR2 [all data]	0.0776, 0.1267	0.0318, 0.0549	0.0296, 0.0632	0.0321,0.0763
GOF	1.034	1.000	1.043	1.174

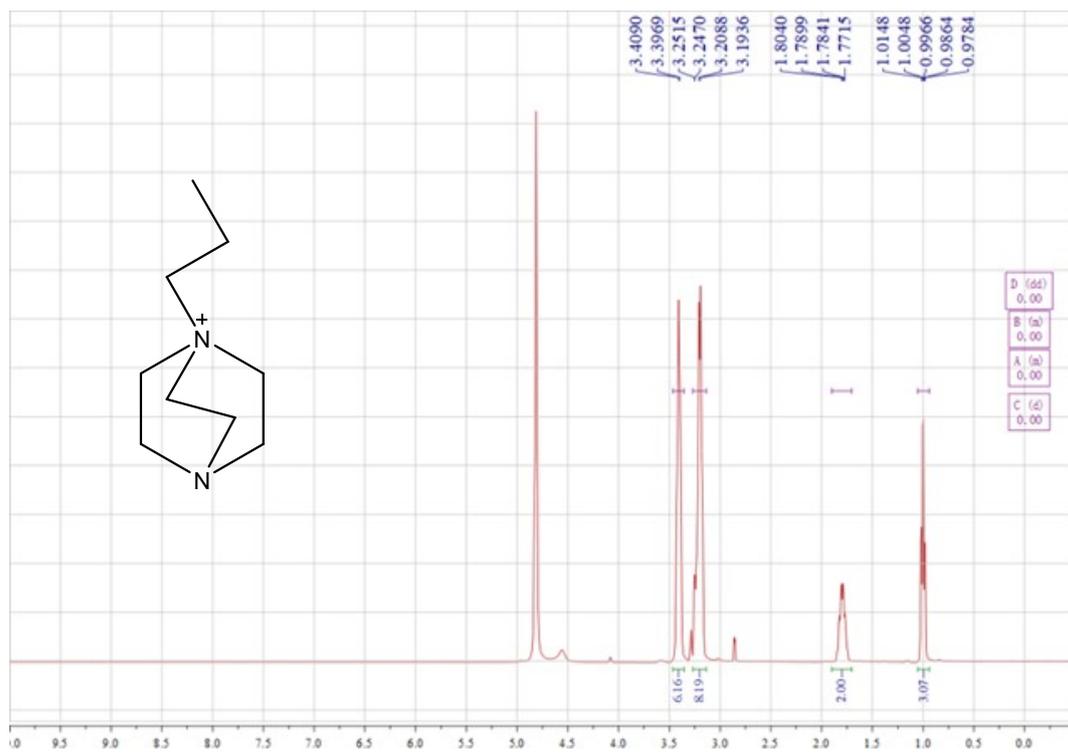


Fig.S1 1H NMR spectrum of organic ligand L_1

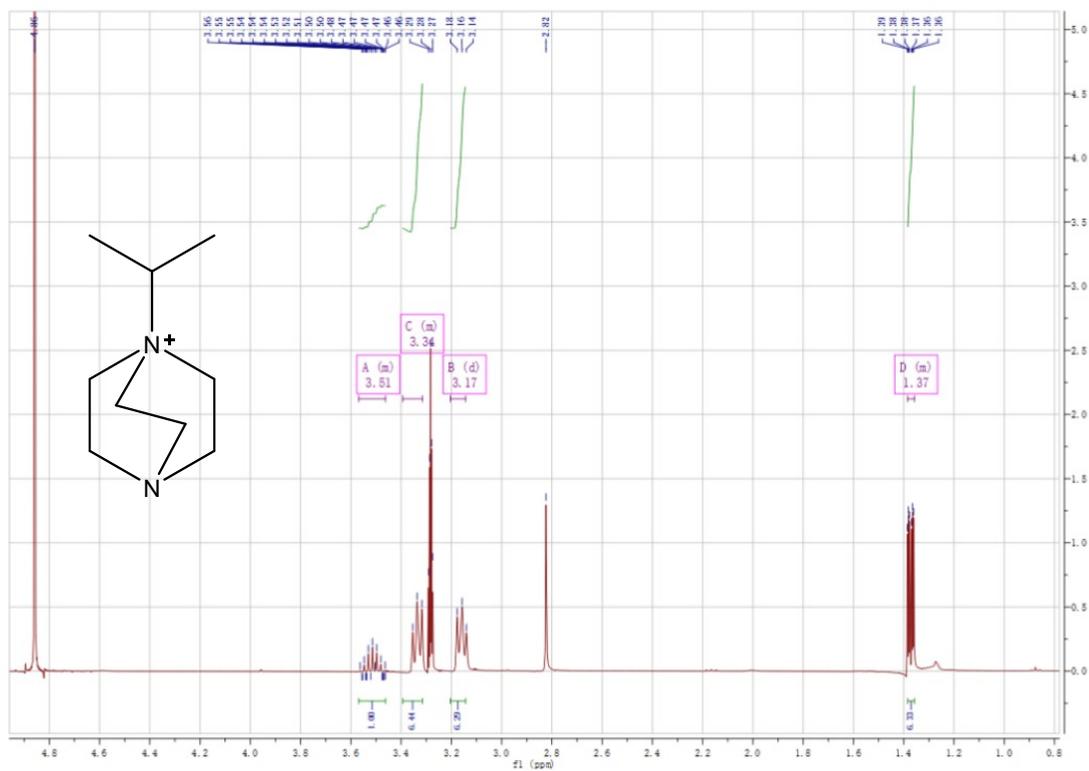


Fig.S2 1H NMR spectrum of organic ligand L_2

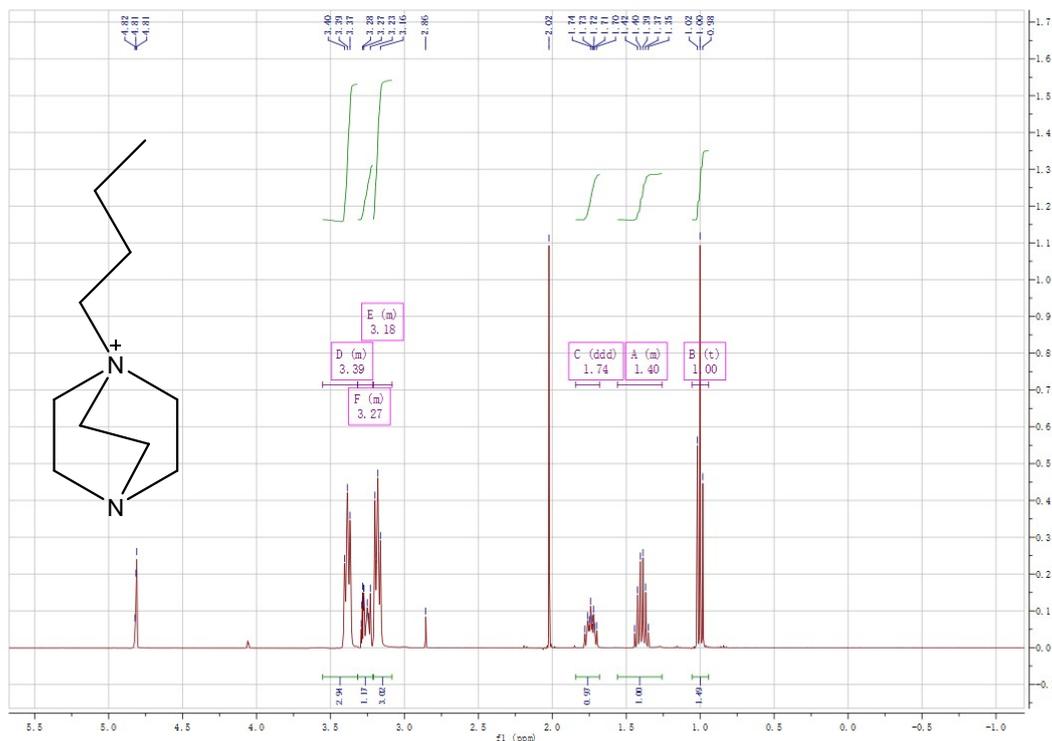


Fig.S3 1H NMR spectrum of organic ligand L_3

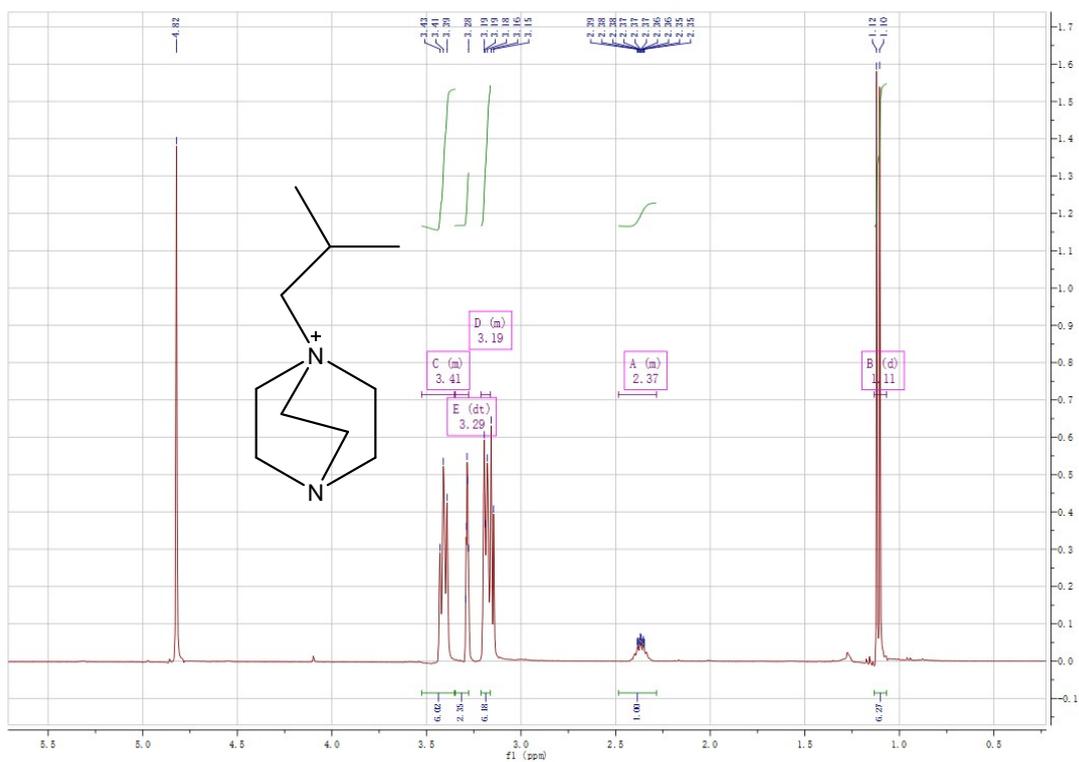


Fig.S4 1H NMR spectrum of organic ligand L_4

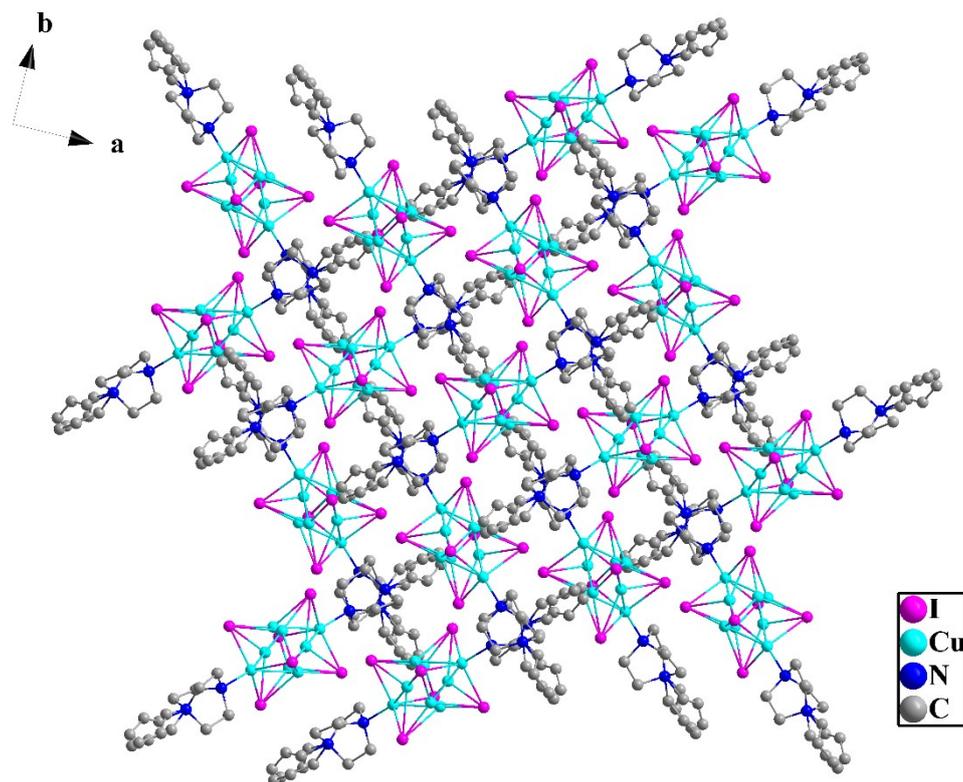


Fig.S5 Supramolecular network viewed along the c -axis of complex 1

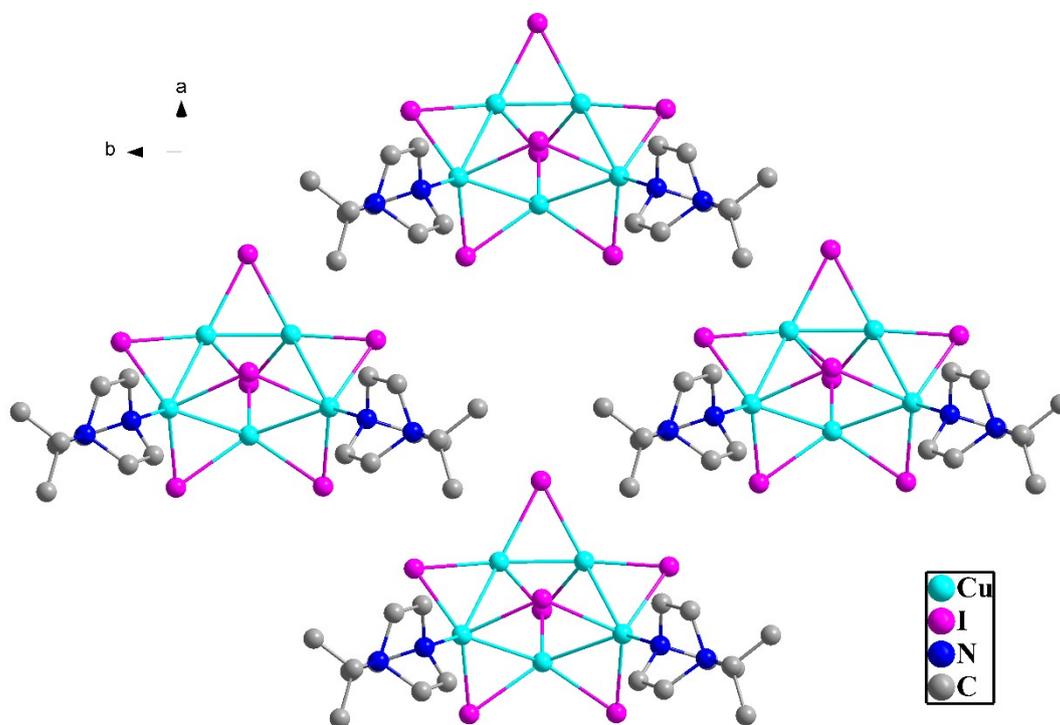


Fig.S6 Supramolecular network viewed along the c -axis of complex 2

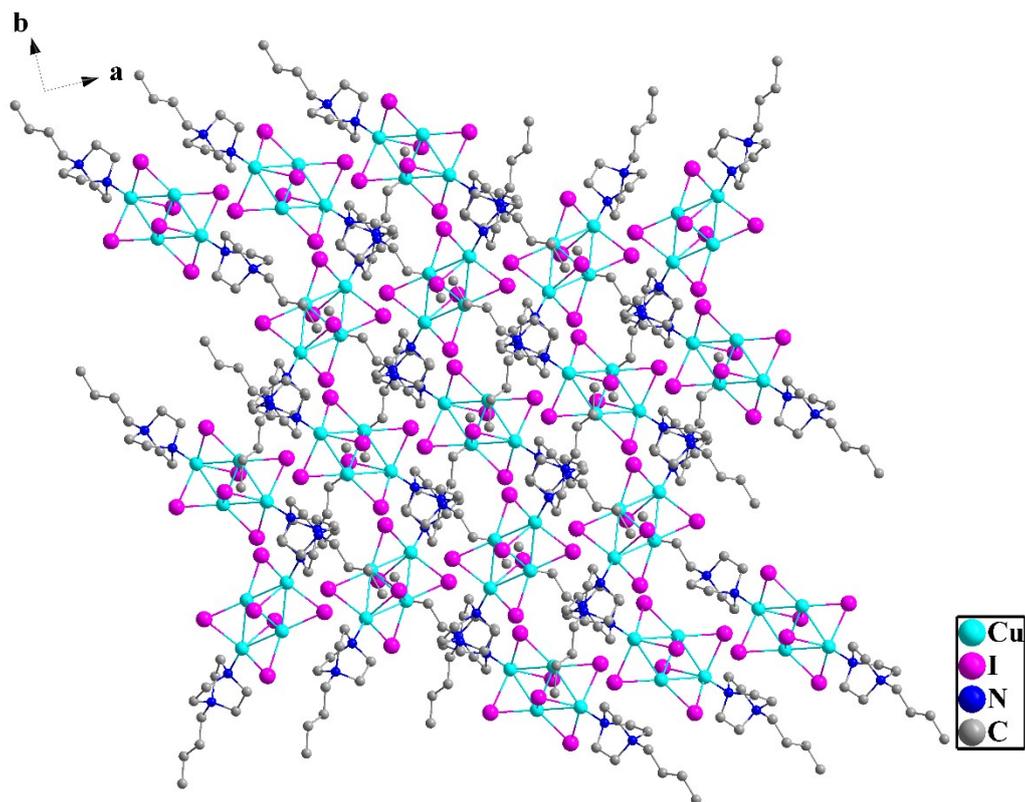


Fig.S7 Supramolecular network viewed along the *c*-axis of complex 3

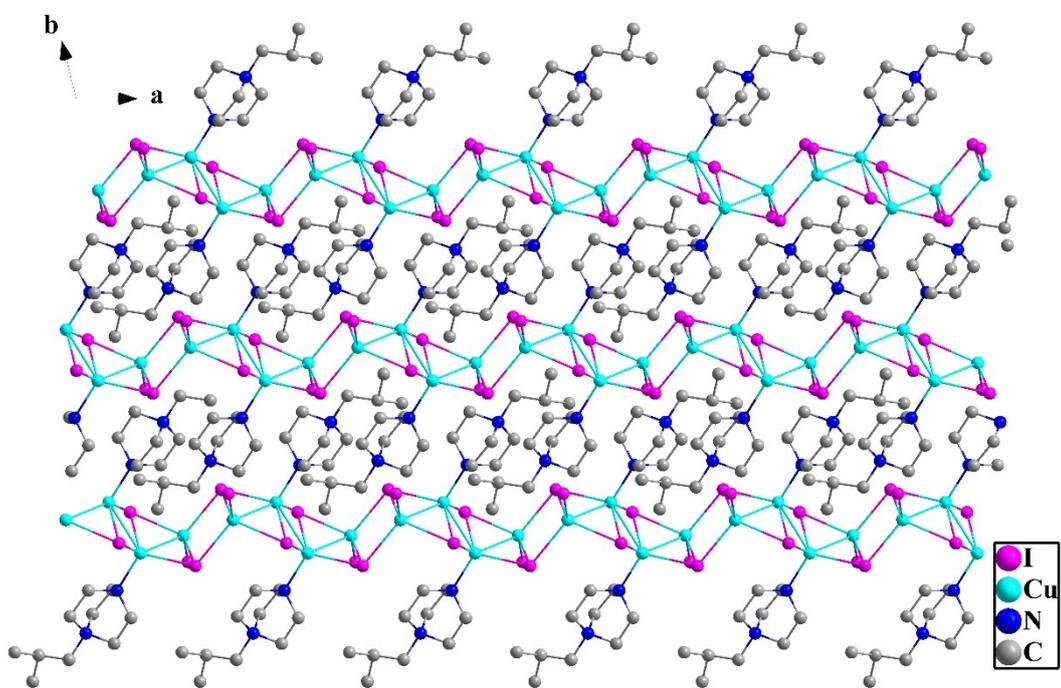


Fig.S8 Supramolecular network viewed along the *b*-axis of complex 4

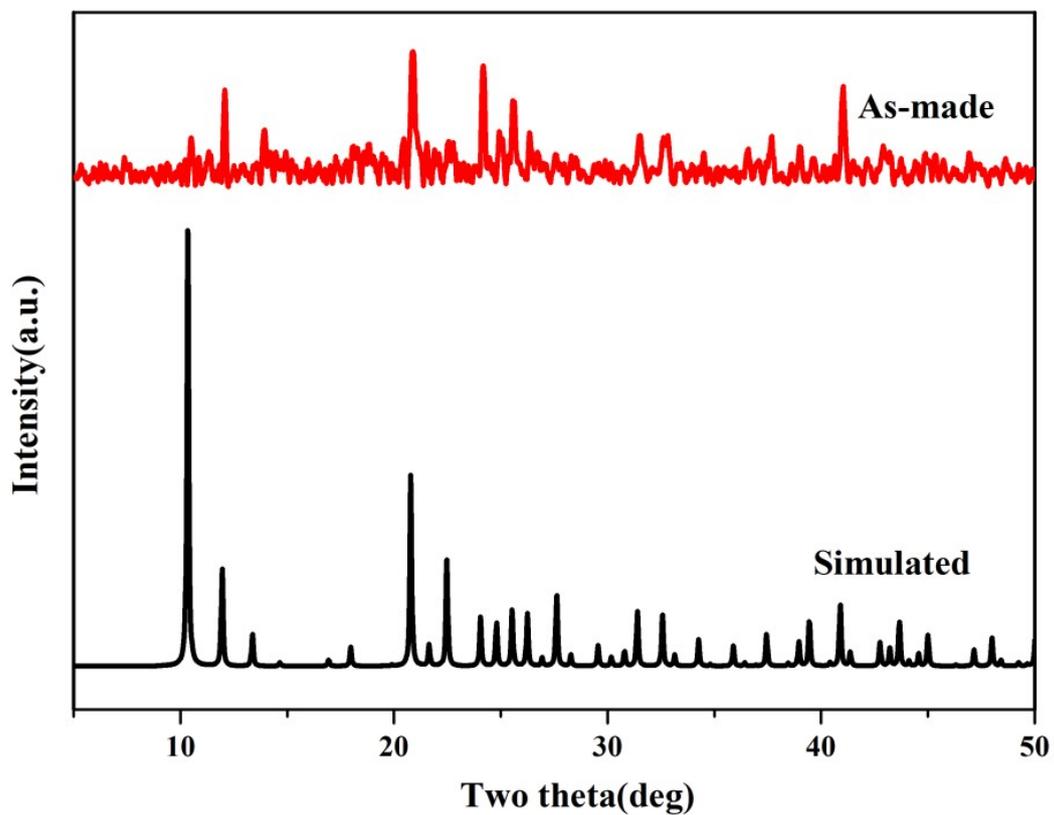


Fig.S9 PXR D patterns of complex 1

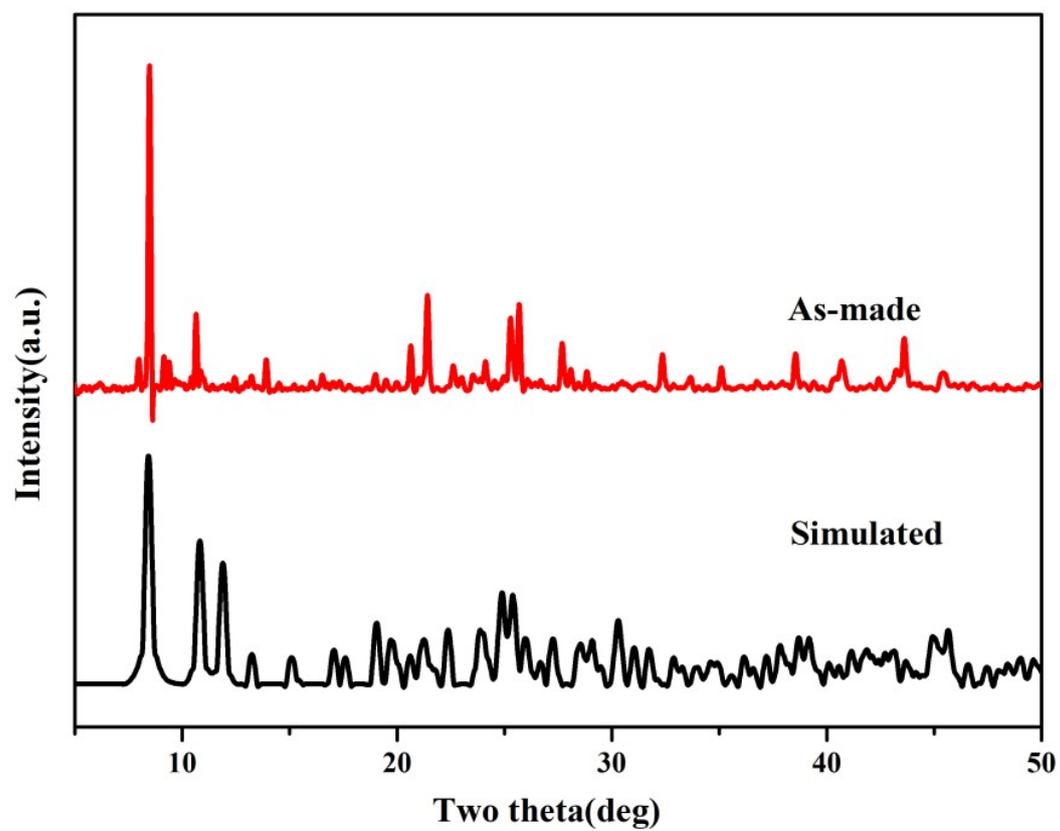


Fig.S10 PXR D patterns of complex 2

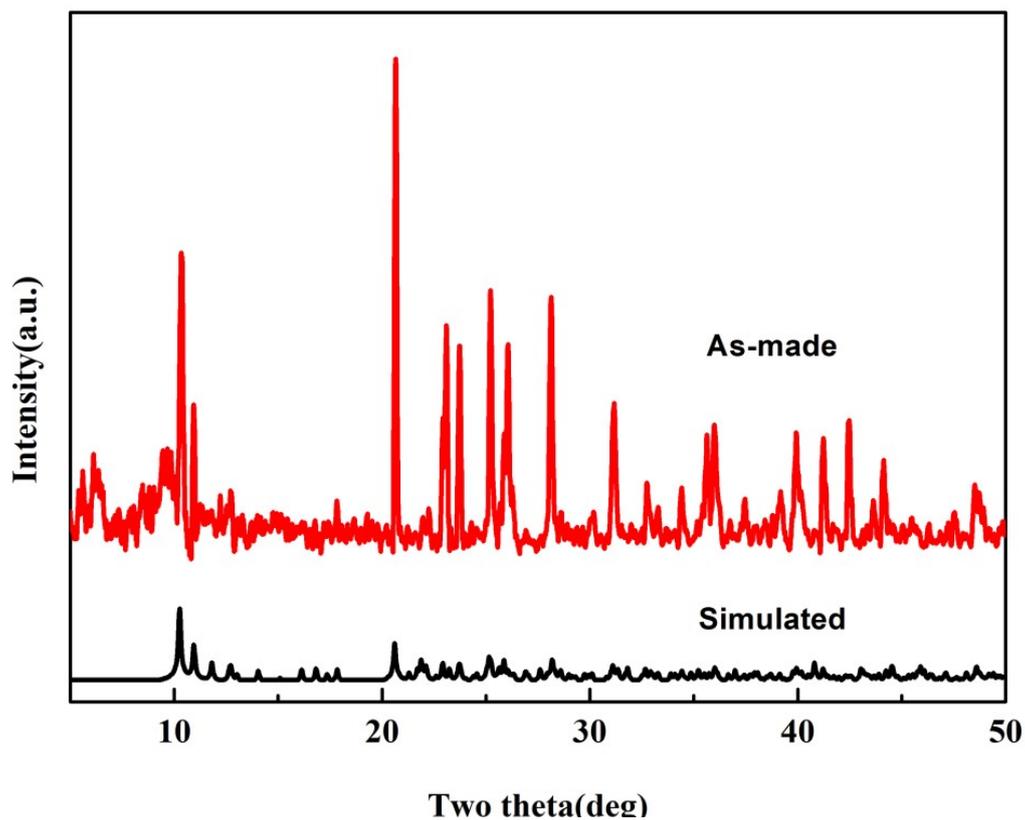


Fig.S11 PXRD patterns of complex 3

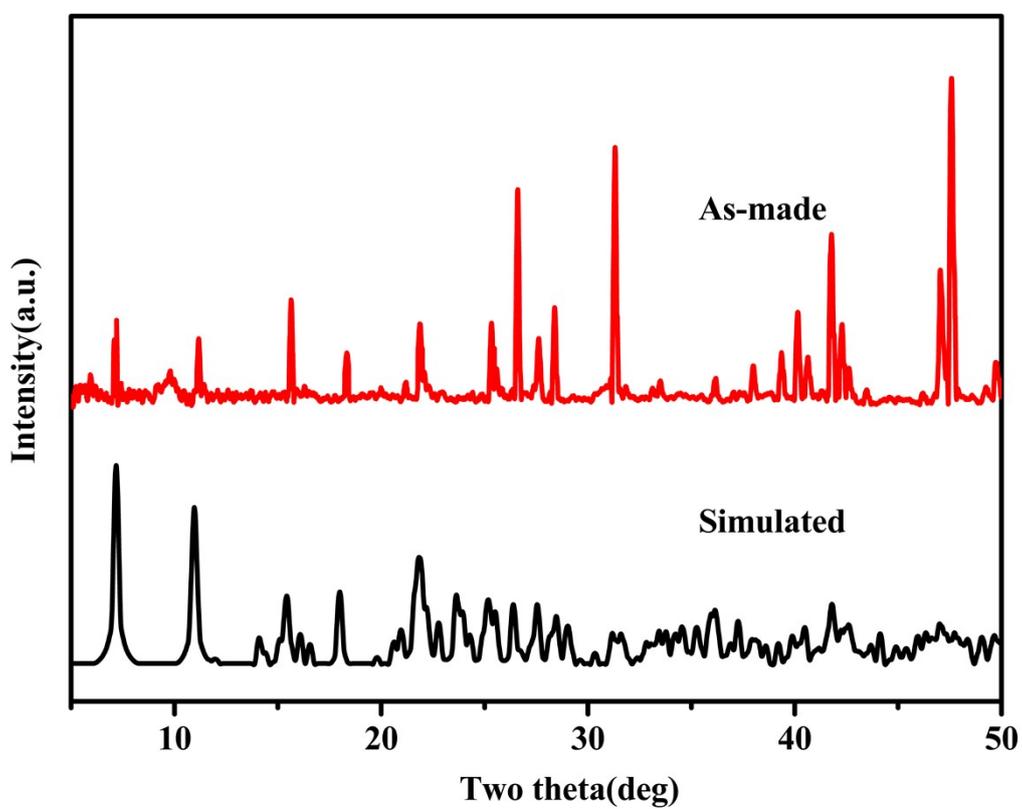


Fig.S12 PXRD patterns of complex 4

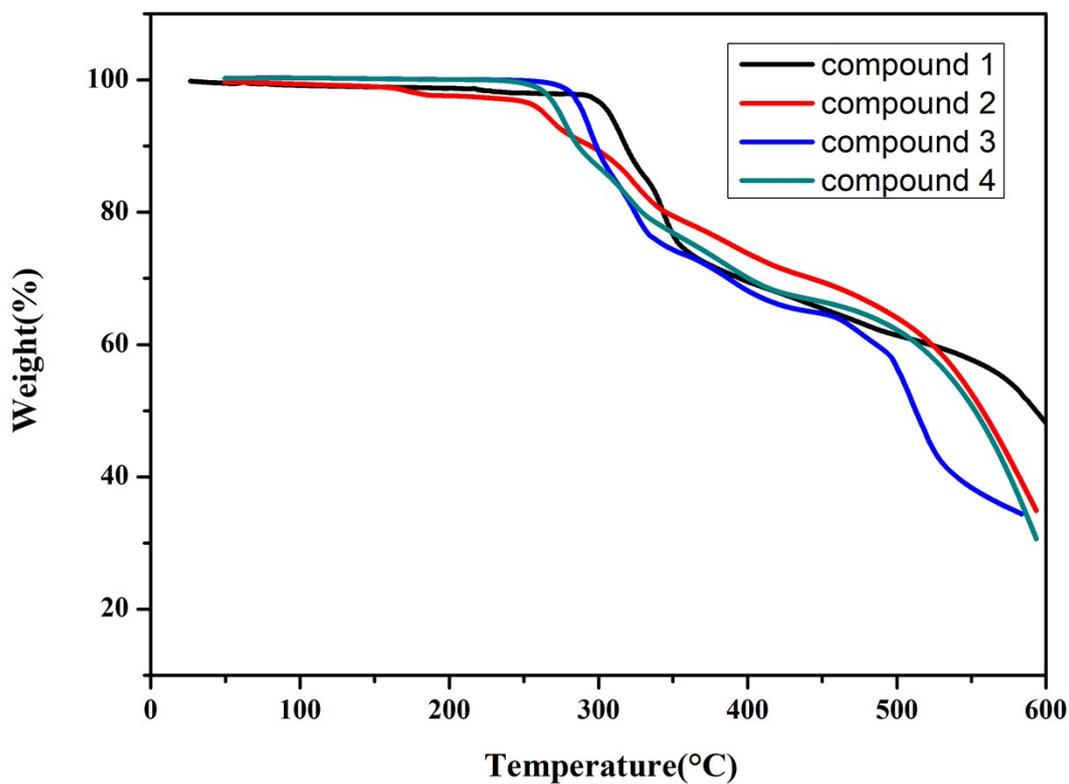


Fig.S13 TGA curves of complexes 1-4

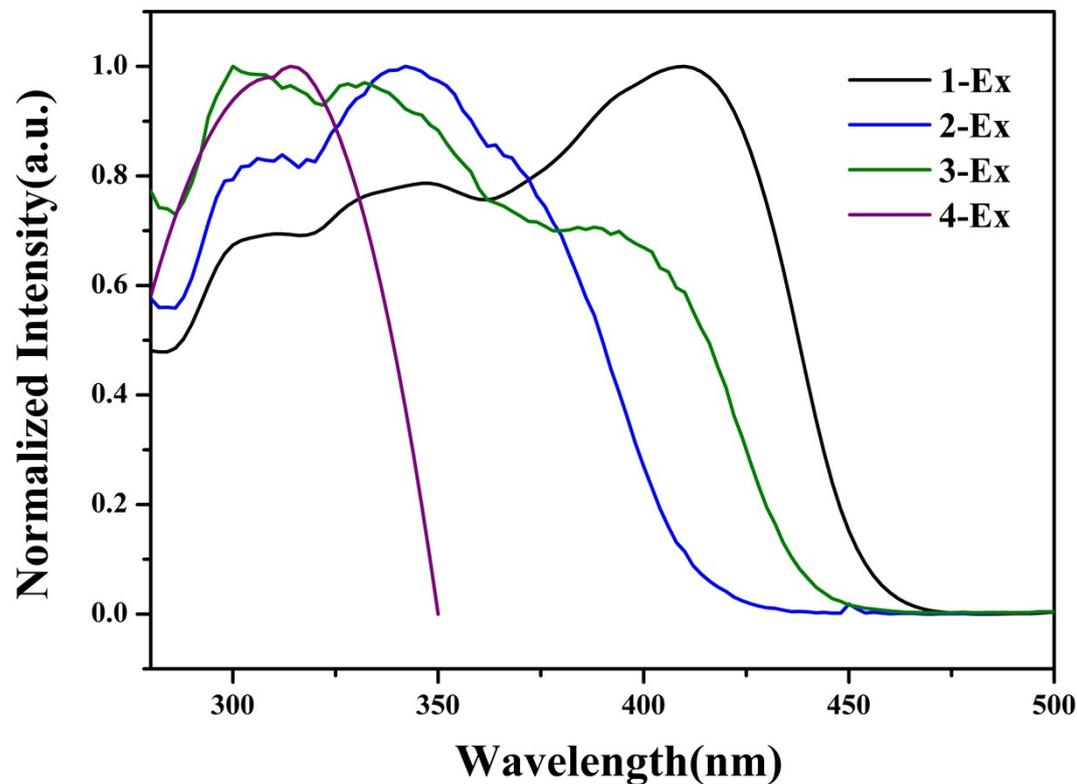


Fig.S14 Excitation spectra of complexes 1-4

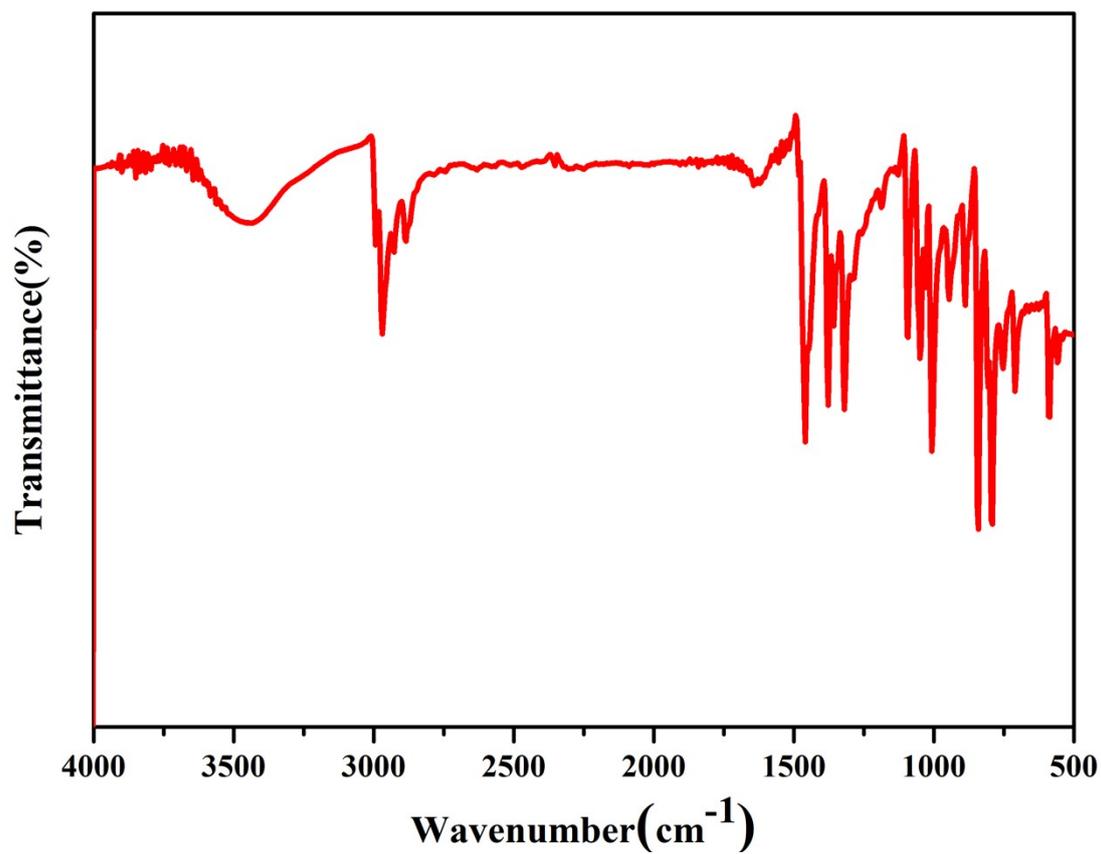


Fig.S15 IR spectrum of Complex 1

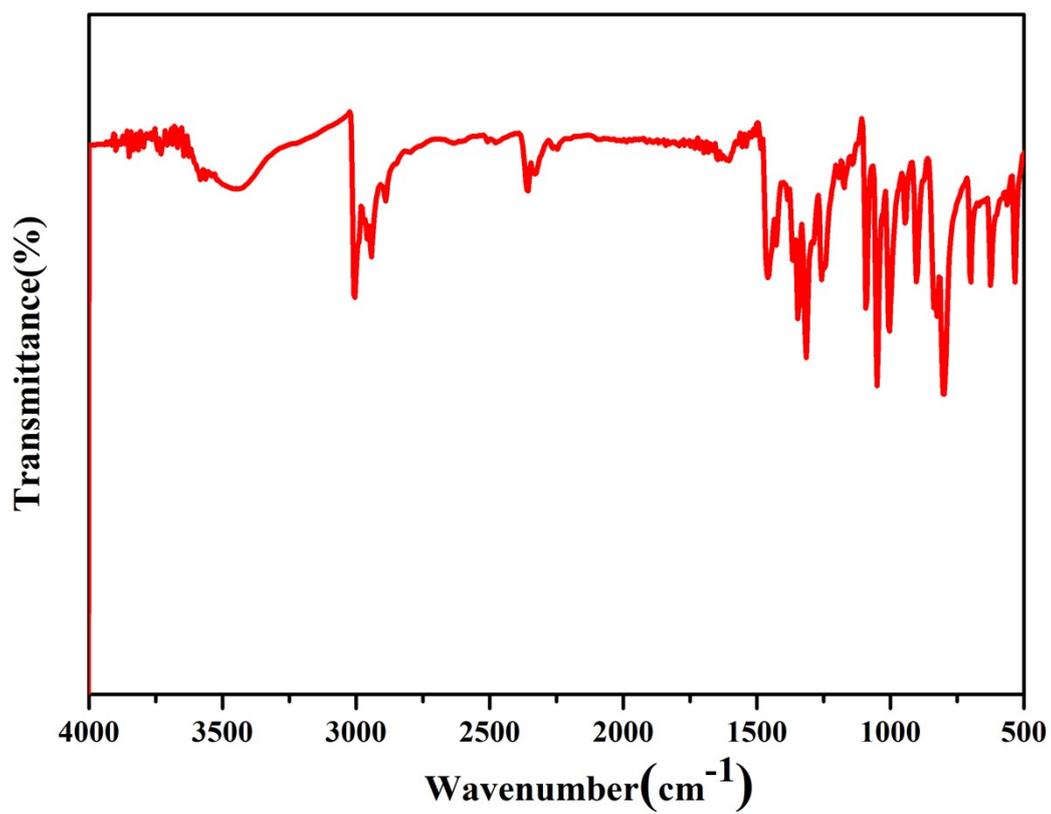


Fig.S16 IR spectrum of Complex 2

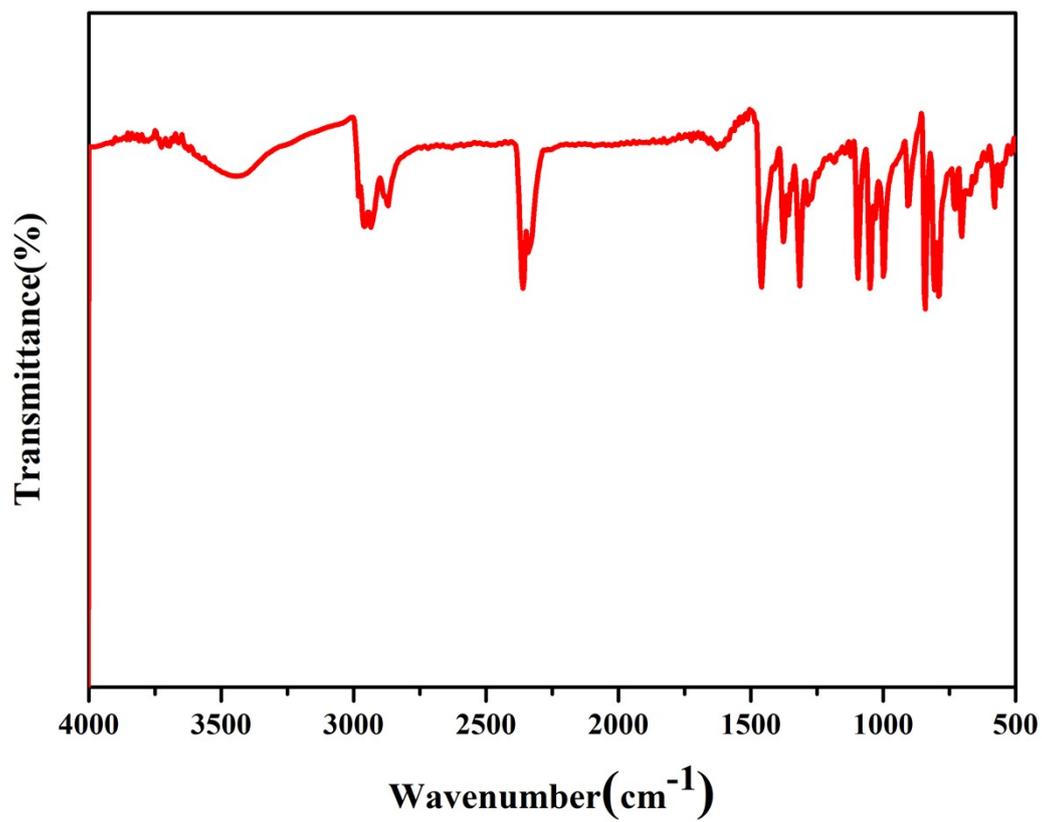


Fig.S17 IR spectrum of Complex 3

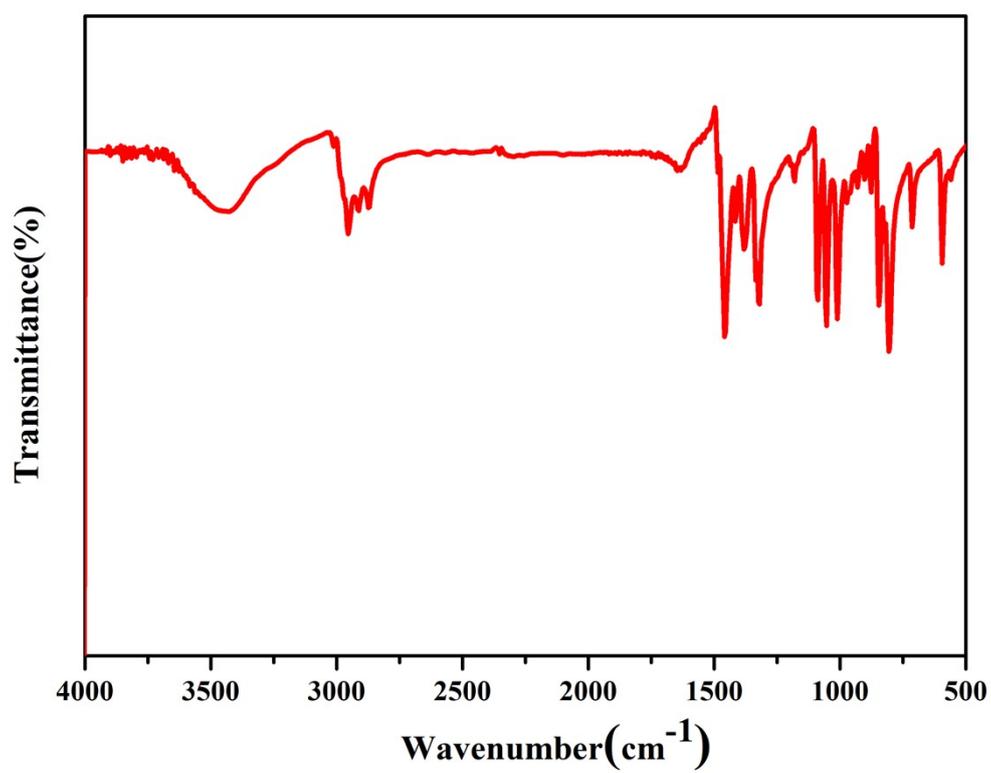


Fig.S18 IR spectrum of Complex 4

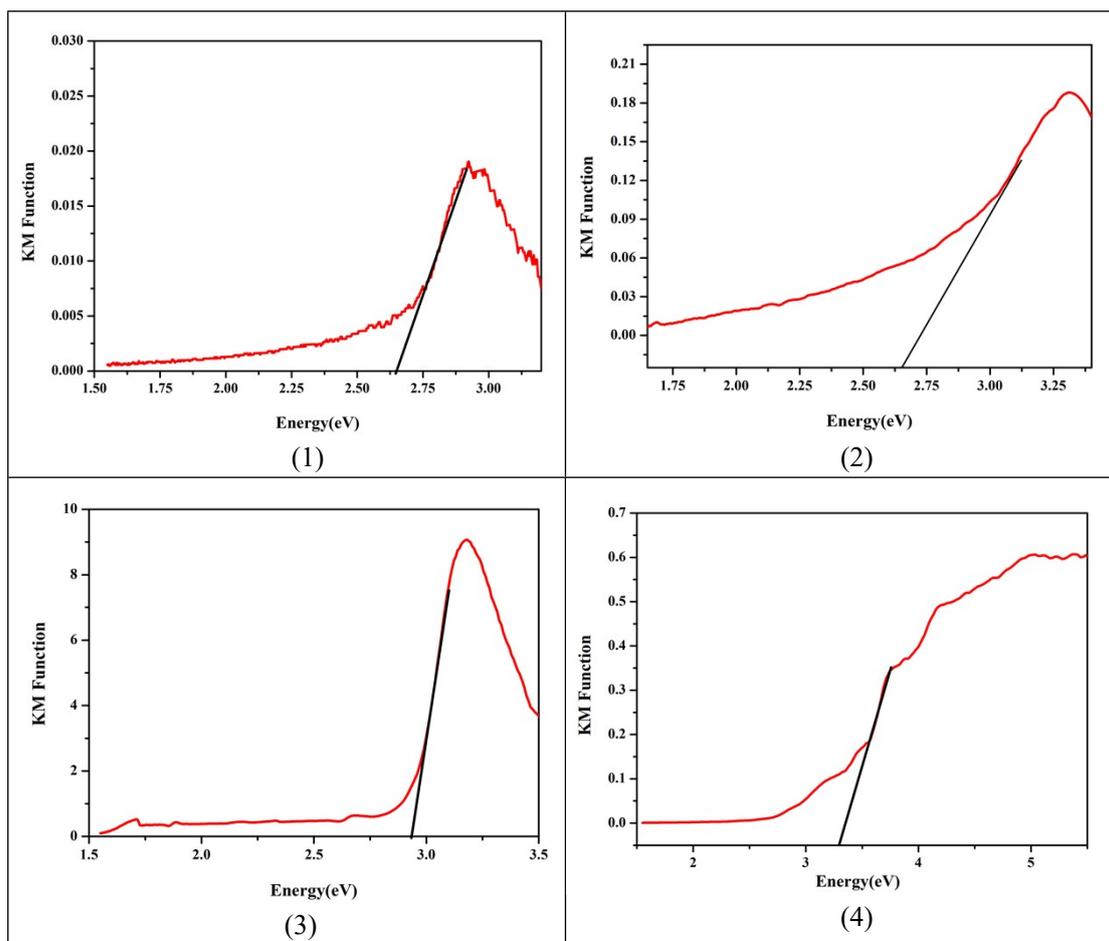


Fig.19 UV-vis absorption plots of Complexes 1- 4

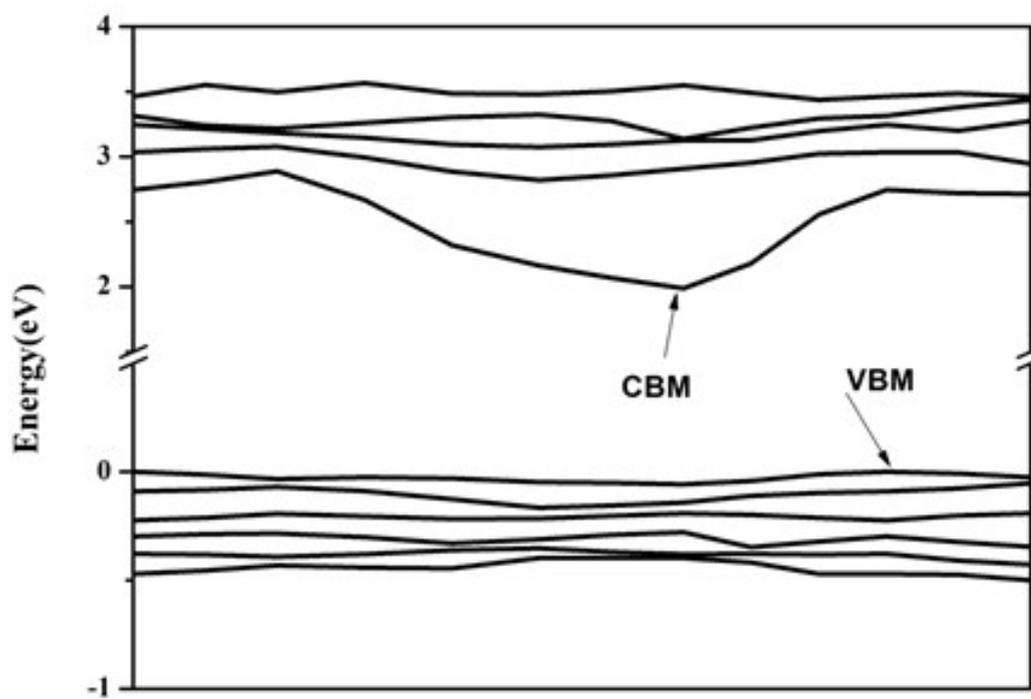


Fig.S20 Band structure of Complex 2

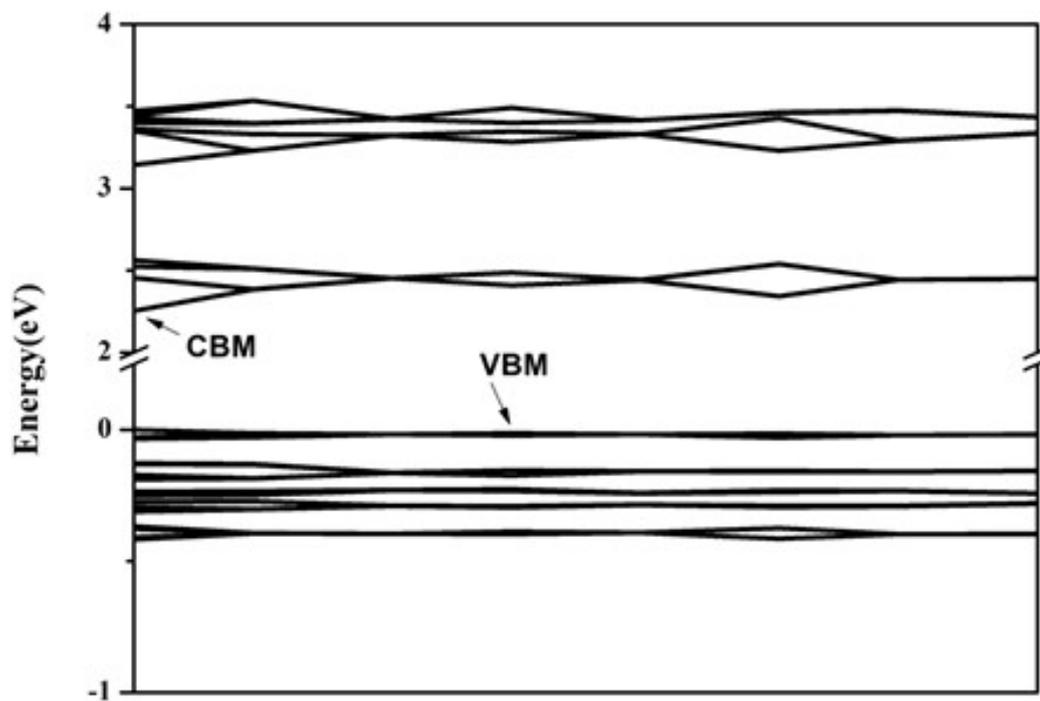


Fig.S21 Band structure of Complex 3

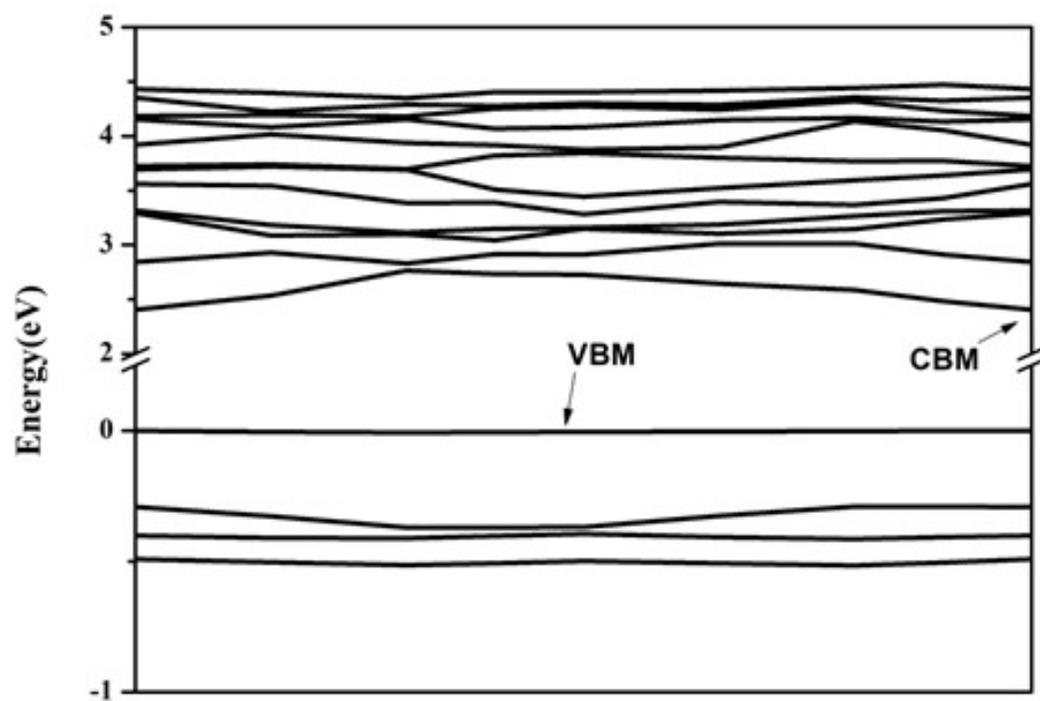


Fig.S22 Band structure of Complex 4

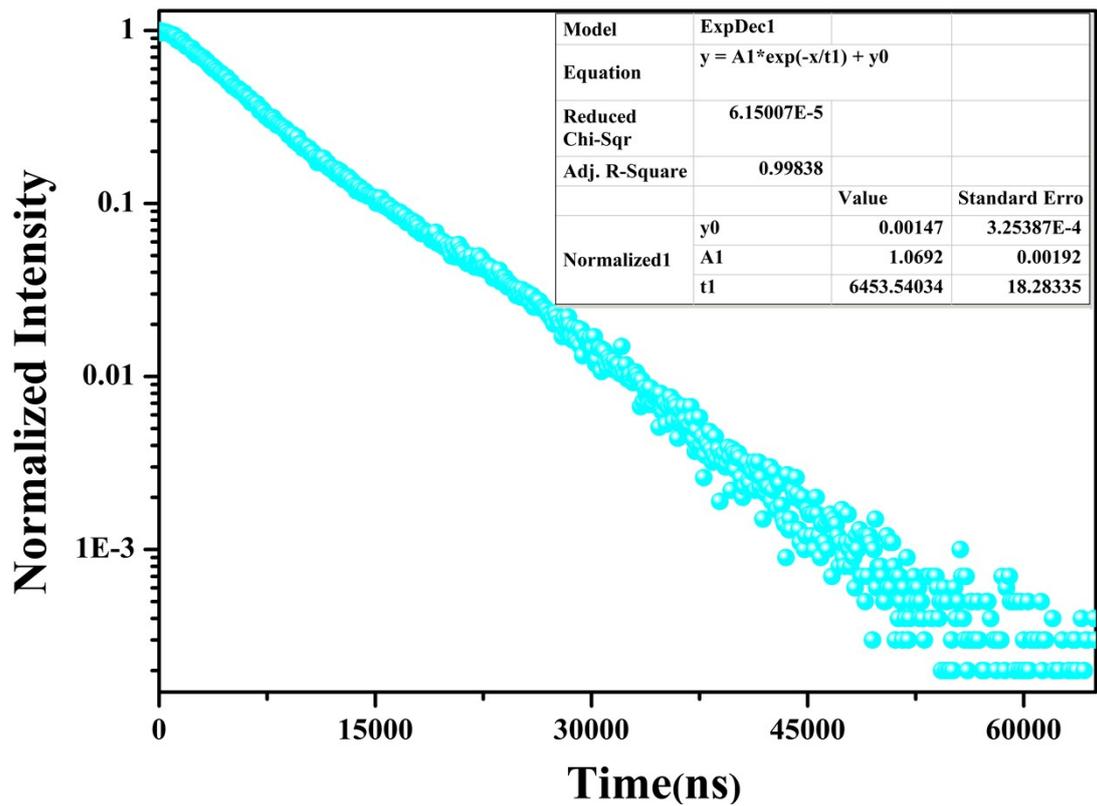


Fig.S23 Luminescence decay curve of 1

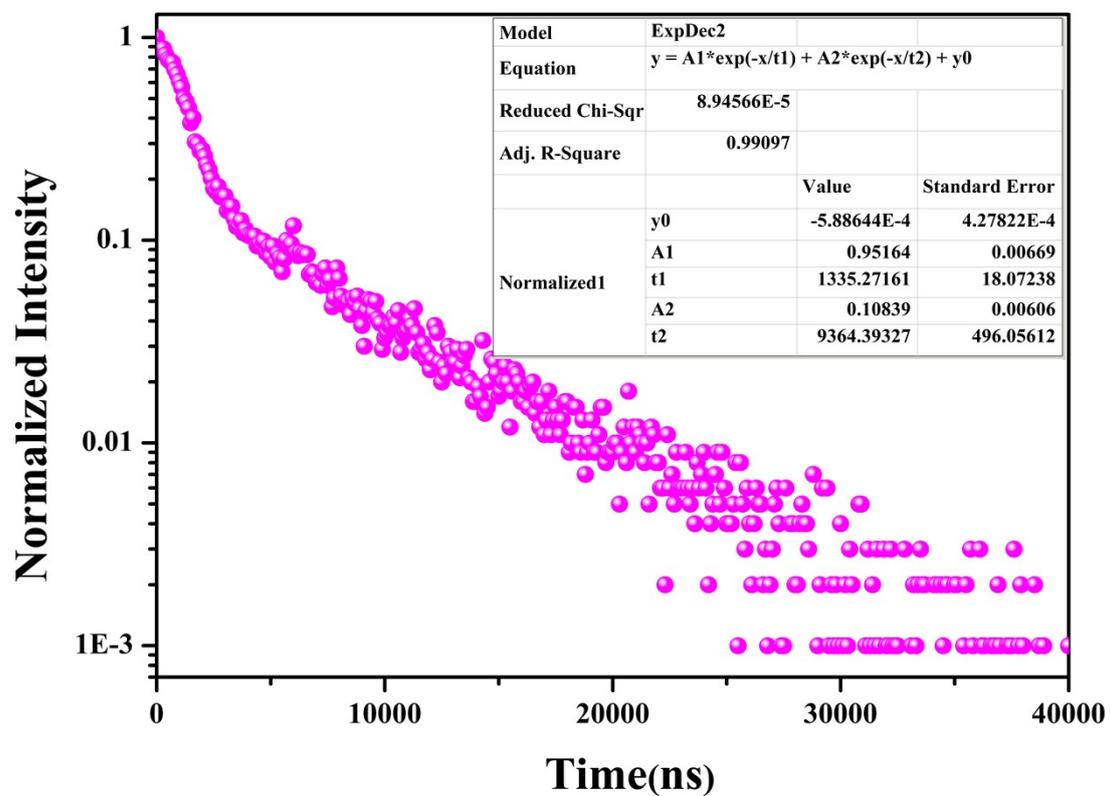


Fig.S24 Luminescent decay curve of 2

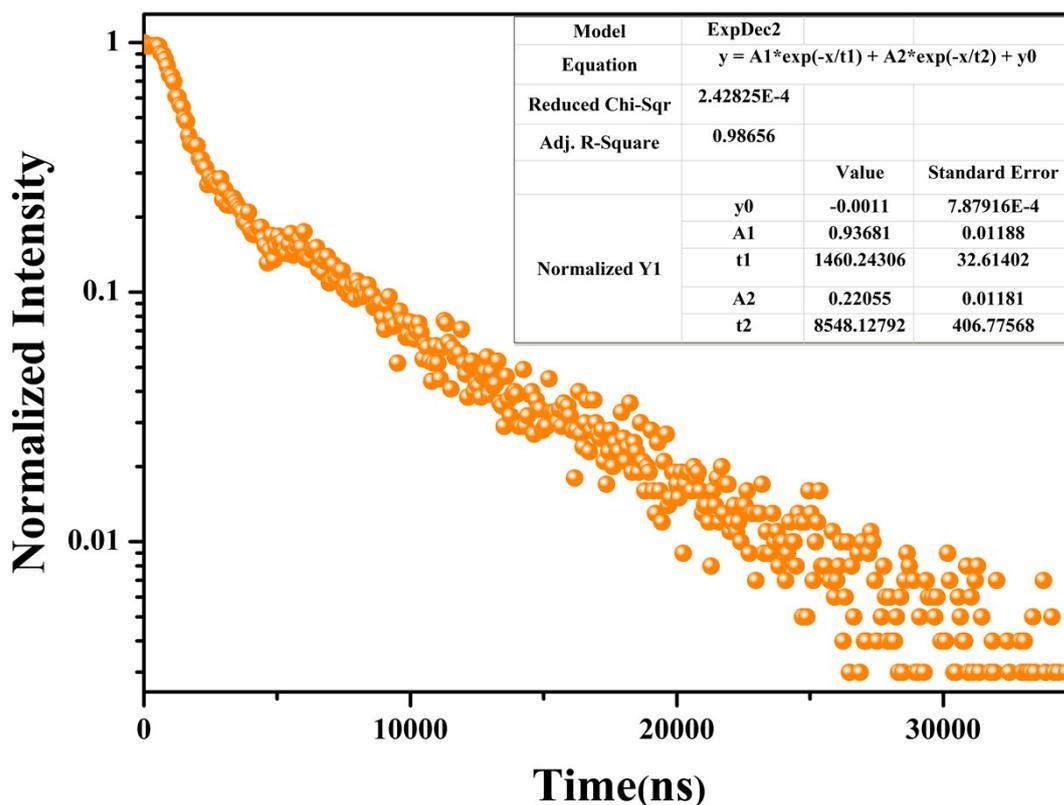


Fig.S25 Luminescent decay curve of 3

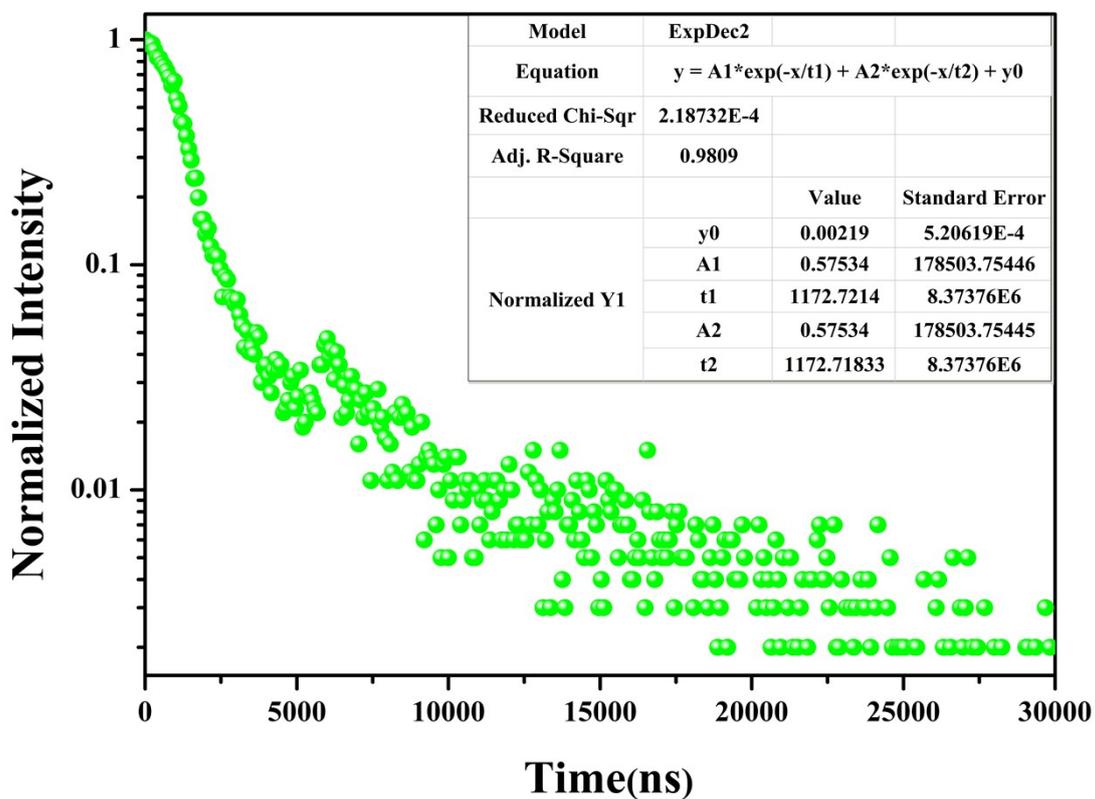


Fig.S26 Luminescent decay curve of 4