

Electronic Supplementary Information (ESI)

for

**Excimer and exciplex formation in a pair of bright
phosphorescent isomers constructed from $\text{Cu}_3(\text{Pyrazolate})_3$ and
 Cu_3I_3 coordination luminophores**

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General Experimental and Synthesis Section

Materials and physical measurements:

Commercially available chemicals were purchased and used without further purification. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000-400 cm^{-1} . $^1\text{H-NMR}$ spectroscopy was performed on a Bruker DPX 400 spectrometer using the TMS as internal standard. All δ values are given in ppm. Elemental analyses of C, H, and N were determined with the instrument Elementar Vario EL III CHNS analyzer. TG analysis were performed on a TA Instruments Q50 Thermogravimetric Analyzer under nitrogen flow of ($40 \text{ mL}\cdot\text{min}^{-1}$) at a typical heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. X-Ray power diffraction (XRPD) experiments were performed on a D8 Advance X-ray diffractometer.

Steady state photoluminescence spectra and lifetime measurements were measured by a single photon counting spectrometer on an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp, a μF900 microsecond flash lamp, and a closed cycle cryostat (Advanced Research Systems). The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments. In all cases, the crystalline samples were selected under microscope with 40 times amplification after washed by ethanol and acetonitrile and then dried. The purity of the samples is assured by elemental analysis and X-ray powder diffraction measurement (Fig. S13).

Synthetic Procedures

Ligands

The preparation of the ligand is similar to our previous works.^{1,2,3}

5-methyl-1-(4-pyridyl)-hexane-1,3-dione

To a suspension of NaH (1.5g, 80 % in oil, 0.05mol) in 50 mL anhydrous THF was added 3.5 mL (3.5g, 0.025mol) methyl isonicotinate. The mixture was stirred at room temperature for 10 min and then 3.1 mL (2.5g, 0.025mol) 4-methyl-2-pentanone was slowly added to the mixture. (Note: the reaction is exothermic and a great amount of

¹ S.-Z. Zhan, D. Li, X.-P. Zhou, X.-H. Zhou, *Inorg. Chem.* **2006**, *45*, 9163.

² S.-Z. Zhan, M. Li, J.-Z. Hou, J. Ni, D. Li, X.-C. Huang, *Chem. Eur. J.* **2008**, *14*, 8916.

³ S.-Z. Zhan, R. Peng, S.-H. Lin, S. W. Ng, D. Li, *CrystEngComm* **2010**, *12*, 1385.

hydrogen gas will release.) After completing the addition of 4-methyl-2-pentanone (about 30 min), the mixture was kept with stirring for about 10 hours, and then distilled the THF under reduced pressure. The residual was neutralized with 40mL diluted acetic acid ($2 \text{ mol}\cdot\text{L}^{-1}$). The mixture was extracted with ether ($20 \text{ mL}\times 3$), then combined the organic solution. The ether is allowed to evaporate overnight at room temperature in a hood. Brown oil intermediate products 5-methyl-1-(4-pyridyl)-hexane-1,3-dione was left.

3-(4-pyridyl)-5-isobutyl-1H-pyrazole

All the intermediate products was added in ethanol (50 mL) and the mixture was treated with an excess of hydrazine (80%, 5mL), then refluxed for 10 hours and the color of the solution became light yellow. After filtered, the solution was kept standing in air to evaporate the ethanol solvent. Several days later colorless block crystal was obtained. The block crystals were recrystallized in ethanol to give the ligands 1.82g HL; yielding 36%, mp: 164-166 °C. IR(v/cm^{-1}): 3100~3200 broad, 3060 m, 2770 ~ 2900 multi, 1605 vs, 1576 s, 1552 s, 1442 s, 1425 s, 1298 m, 1213 m, 1057 m, 1000 s, 937 s, 784 s, 681 s, 530 m. ^1H NMR (400 MHz, CD_3OD , 298K) δ 8.52 (d, $J = 5.1 \text{ Hz}$, 2H, CH_{py}), 7.80 (d, $J = 4.3 \text{ Hz}$, 2H, CH_{py}), 6.63 (s, 1H, CH_{pz}), 2.59 (d, $J = 7.0 \text{ Hz}$, 2H, CH_2), 1.98 (dp, $J = 13.6, 6.8 \text{ Hz}$, 1H, CH), 0.98 (d, $J = 6.6 \text{ Hz}$, 6H, CH_3).

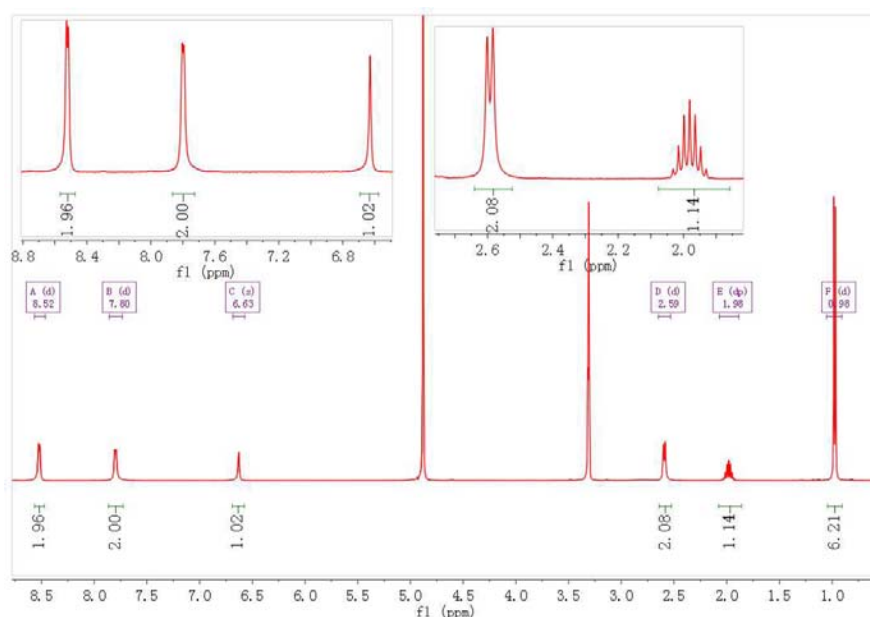


Fig. S1 ^1H NMR spectra of ligand

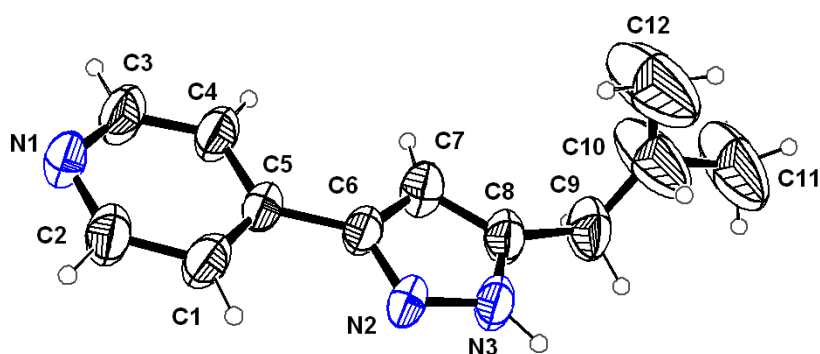


Fig. S2 ORTEP presentation of the molecular structure of ligand in the crystal. Thermal ellipsoids are drawn at 30% probability level.

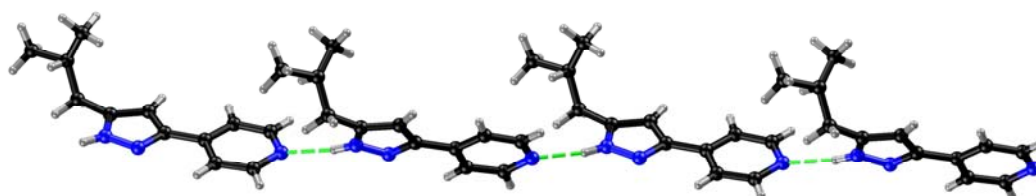


Fig. S3 1-D chain constructed by N...H Hydrogen bonds (dotted green stick) in ligand crystal.

Complexes

A mixture of HL (40.6 mg, 0.2 mmol), CuI (76.2 mg, 0.4 mmol) 8 mL water, 4 mL ethanol adding 5 drops of aqueous NH_3 was sealed in a 20-mL Teflon-lined reactor and heated in an oven at 140 °C for 72 hours and slowly cooled to room temperature at a rate of 5 °C·h⁻¹. Bright yellow block crystal and light yellow column crystal were obtained (total yield 31.2 mg, about 43.1 % based on HL). Anal. Calcd for complex **1** (bright yellow block) $\text{C}_{72}\text{H}_{86}\text{Cu}_9\text{I}_3\text{N}_{18}\text{O}$: C 39.81; H 3.99; N 11.61 %. Found: C 39.62; H 3.81; N 11.58 %. IR data (KBr, cm^{-1}) 3416 broad, 2954 vs, 2917 w, 2868 w, 1606 s, 1536 w, 1491 m, 1450 m, 1213 m, 1139 w, 829 m, 784 w, 547 m. Anal. Calcd for complex **2** (light yellow column) $\text{C}_{72}\text{H}_{84}\text{Cu}_9\text{I}_3\text{N}_{18}$: C 40.14; H 3.93; N 11.70 %, Found: C 40.01; H 3.81; N 11.75 %. IR data (KBr, cm^{-1}) 2954 vs, 2917 w, 2864 w, 1614 vs, 1536 w, 1491 m, 1450 m, 1213 m, 1143 w, 825 m, 768 w, 547 m.

Crystallographic Section

Crystal structure determination: Suitable crystals were mounted with glue at the end of a glass fiber. Diffraction data were collected at room temperature (293K) for ligand and under the cold nitrogen stream (100 K) for complexes with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3 and Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Multi-scan absorptions were applied. The structures were solved by the direct methods and refined by full-matrix least-square refinements based on F^2 . All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Structure solutions and refinements were performed with the SHELXL-97 package.⁴ Crystal data and structure refinement details for these complexes are summarized in Table S1. Selected bond lengths and angles are given in Table S2. CCDC 838375 (HL), 838376 (1) and 838377 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

⁴ G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

Table S1 Crystal data and structure refinement for the ligand and complexes

Parameter	HL	Complex 1	Complex 2
Chemical formula	C ₁₂ H ₁₅ N ₃	C ₇₂ H ₈₆ Cu ₉ I ₃ N ₁₈ O	C ₇₂ H ₈₆ Cu ₉ I ₃ N ₁₈
Formula weight	201.27	2172.15	2154.13
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Fdd2</i>	<i>P-1</i>	<i>P-1</i>
Temperature	293(2) K	100 K	100 K
<i>a</i> (Å)	17.241(3)	13.6702(2)	14.6484(3)
<i>b</i> (Å)	34.415(5)	17.3216(3)	14.7423(5)
<i>c</i> (Å)	8.1449(12)	17.4721(2)	21.7997(4)
α (deg)	90	84.6490(10)	90.488(2)
β (deg)	90	79.6620(10)	100.351(18)
γ (deg)	90	77.6360(10)	117.859(3)
<i>V</i> (Å ³)	4832.8(13)	3969.18(10)	4071.10(18)
<i>Z</i>	16	2	2
D _{Calcd} (g·cm ⁻³)	1.106	1.817	1.757
μ (mm ⁻¹)	0.068	3.581	3.490
Reflections collected	7325	51231	35810
Unique reflections	2203	18116	14325
R _{int}	0.0476	0.0498	0.0417
Goodness-of-fit on F ²	0.994	1.058	1.091
R1 ^a [I > 2 σ (I)]	0.0611	0.0453	0.0415
wR2 ^b [I > 2 σ (I)]	0.1631	0.1117	0.0823
R1 ^a [all refl.]	0.1248	0.0806	0.0629
wR2 ^b [all refl.]	0.2047	0.1380	0.0926

^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. Bond lengths and bond angles of the ligand crystal.

Bond lengths		Bond Angles	
N(1)-C(3)	1.311(6)	C(3)-N(1)-C(2)	114.3(3)
N(1)-C(2)	1.316(5)	C(6)-N(2)-N(3)	104.4(3)
N(2)-C(6)	1.317(5)	N(2)-N(3)-C(8)	113.9(3)
N(2)-N(3)	1.342(4)	C(2)-C(1)-C(5)	119.5(4)
N(3)-C(8)	1.344(5)	N(1)-C(2)-C(1)	125.1(4)
C(1)-C(2)	1.369(6)	N(1)-C(3)-C(4)	125.5(4)
C(1)-C(5)	1.384(6)	C(5)-C(4)-C(3)	119.7(4)
C(3)-C(4)	1.370(6)	C(4)-C(5)-C(1)	115.8(3)
C(4)-C(5)	1.365(6)	C(4)-C(5)-C(6)	122.8(4)
C(5)-C(6)	1.468(4)	C(1)-C(5)-C(6)	121.4(3)
C(6)-C(7)	1.401(6)	N(2)-C(6)-C(7)	110.8(3)
C(7)-C(8)	1.370(5)	N(2)-C(6)-C(5)	120.0(4)
C(8)-C(9)	1.495(6)	C(7)-C(6)-C(5)	129.2(4)
C(9)-C(10)	1.403(10)	C(8)-C(7)-C(6)	106.1(4)
C(10)-C(12)	1.298(13)	N(3)-C(8)-C(7)	104.8(3)
C(10)-C(11)	1.520(10)	N(3)-C(8)-C(9)	122.4(4)
		C(7)-C(8)-C(9)	132.8(5)
		C(10)-C(9)-C(8)	119.2(5)
		C(12)-C(10)-C(9)	133.0(7)
		C(12)-C(10)-C(11)	114.3(7)
		C(9)-C(10)-C(11)	112.6(7)

Table S3. Selected bond lengths and bond angles in Complex 1 and Complex 2.

Complex 1		Complex 2	
Bond lengths			
Cu1-N1	1.981(5)	Cu1-N1	1.996(5)
Cu1-I2	2.5127(8)	Cu1-I2	2.5350(9)
Cu1-I3	2.620(4)	Cu1-I3	2.5403(9)
Cu2-N10	1.996(5)	Cu2-N10	1.991(5)
Cu2-I1	2.5282(10)	Cu2-I1	2.5286(8)
Cu2-I3	2.590(4)	Cu2-I3	2.5643(9)
Cu3-N4	2.017(5)	Cu3-N4	2.054(4)
Cu3-N13	2.053(5)	Cu3-N13	2.065(5)
Cu3-I1	2.6409(8)	Cu3-I1	2.6294(9)
Cu3-I2	2.6645(9)	Cu3-I2	2.6745(8)
Cu1-Cu2	2.5619(11)	Cu1-Cu2	2.5885(11)
Cu1-Cu3	3.1311(7)	Cu1-Cu3	3.0500(11)
Cu2-Cu3	3.3164(3)	Cu2-Cu3	2.9433(11)
Cu4-N2	1.854(5)	Cu4-N2	1.858(5)
Cu4-N5	1.853(5)	Cu4-N5	1.859(5)
Cu5-N6	1.911(5)	Cu5-N6	1.867(5)
Cu5-N8	1.910(5)	Cu5-N9	1.874(5)
Cu6-N3	1.854(5)	Cu6-N3	1.865(4)
Cu6-N9	1.838(5)	Cu6-N8	1.862(5)
Cu5-N16#1	2.120(5)		
Cu7-N11	1.865(5)	Cu7-N11	1.857(4)
Cu7-N14	1.857(5)	Cu7-N14	1.861(4)
Cu8-N12	1.871(5)	Cu8-N12	1.868(5)
Cu8-N18	1.866(4)	Cu8-N17	1.868(5)
Cu9-N15	1.887(4)	Cu9-N15	1.873(5)
Cu9-N17	1.885(4)	Cu9-N18	1.874(5)
Cu4-Cu5	3.1000(8)	Cu4-Cu5	3.24407(7)
Cu4-Cu6	3.1384(9)	Cu4-Cu6	3.11998(7)
Cu5-Cu6	3.1631(3)	Cu5-Cu6	3.12062(7)
Cu7-Cu8	3.0910(10)	Cu7-Cu8	3.18648(7)
Cu8-Cu9	3.1958(5)	Cu8-Cu9	3.14412(7)
Cu7-Cu9	3.2783(1)	Cu7-Cu9	3.19342(7)
Cu8-Cu9#2	2.9867(10)		
Cu7-I1#3	3.8570(1)	Cu7-I1#2	3.90467(9)
Cu8-I1#3	3.3583(1)	Cu8-I1#2	3.25152(7)
Cu9-I1#3	3.3927(5)	Cu9-I1#2	3.31896(7)
Q1-I1#3	3.0273(2)	Q1-I1#2	2.9863(8)
		Cu4-I2#1	3.65040(8)
		Cu5-I2#1	3.16712(7)
		Cu6-I2#1	3.36649(7)

		Q1-I2#1	2.8688(3)
Bond angles			
N1-Cu1-I2	136.38(15)	N1-Cu1-I2	118.68(15)
N1-Cu1-I3	109.37(16)	N1-Cu1-I3	118.40(15)
I2-Cu1-I3	113.03(6)	I2-Cu1-I3	121.91(3)
N10-Cu2-I1	116.08(15)	N10-Cu2-I1	118.48(14)
N10-Cu2-I3	115.65(16)	N10-Cu2-I3	119.33(14)
I1-Cu2-I3	128.27(7)	I1-Cu2-I3	120.36(3)
N4-Cu3-N13	121.84(19)	N13-Cu3-N4	106.42(18)
N4-Cu3-I1	109.77(13)	N4-Cu3-I1	109.80(14)
N13-Cu3-I1	101.82(13)	N13-Cu3-I1	103.80(14)
N4-Cu3-I2	102.69(15)	N4-Cu3-I2	102.75(13)
N13-Cu3-I2	105.18(14)	N13-Cu3-I2	104.82(13)
I1-Cu3-I2	116.26(3)	I1-Cu3-I2	127.68(3)
N2-Cu4-N5	178.6(2)	N2-Cu4-N5	178.9(2)
N6-Cu5-N8	152.1(2)	N6-Cu5-N9	161.4(2)
N9-Cu6-N3	177.1(3)	N8-Cu6-N3	175.3(2)
N11-Cu7-N14	177.75(19)	N11-Cu7-N14	178.9(2)
N18-Cu8-N12	173.0(2)	N17-Cu8-N12	171.4(2)
N17-Cu9-N15	178.0(2)	N15-Cu9-N18	165.1(2)
N17-Cu9-Cu8#2	78.77(14)		
N15-Cu9-Cu8#2	102.66(13)		
N8-Cu5-N16#1	101.0(2)		
N6-Cu5-N16#1	106.3(2)		
N18-Cu8-Cu9#2	79.06(13)		
N12-Cu8-Cu9#2	105.68(14)		
Q1: the center of Cu7Cu8Cu9 Symmetry codes: #1 x+1, y, z+1 #2 -x, -y+1, -z #3: -x+1, -y+1,-z		Q1: the center of Cu7Cu8Cu9 Q2: the center of Cu4Cu5Cu6 Symmetry codes: #1: -x+1, -y+1, -z+1 #2 x+1, -y+1, -z+2	

Table S4. Hydrogen bonds lengths and angles in complex 1 and complex 2.

	Bond angles		Bond lengths	
Complex 1	C26-H26...O1w	162.06(8)	H26...O1w	2.5577(7)
	C43-H43...O1w	137.04(6)	H43...O1w	2.5873(4)
	O1w-H1w1...N7A	147.25(1)	H1w1...N7A	2.0788(6)
Complex 2	C49-H49...N16A	135.91(5)	H49...N16A	2.5913(3)

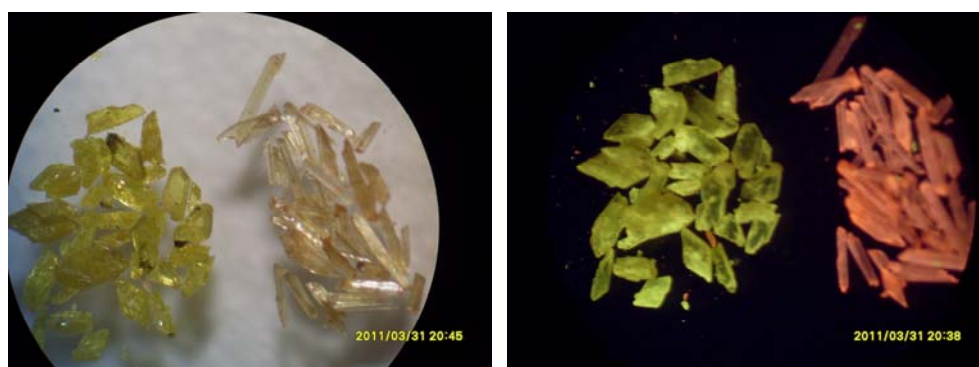
Discussion for synthesis of the complexes

In the reaction mixture, we increased the amount of water from 0:1 to 1:0 (volume ration of water and ethanol with total volume of 12 mL), with attempts to afford the two complexes separately. But the two complexes were always concomitantly obtained. Without ethanol, sometimes only complex **1** was obtained with very low yield, sometimes neither complex **1** nor complex **2** was obtained. The adding of ethanol could increase the total yield. From this point of view, it seems that water acts a key role in the formation of complex **1**. Further investigation of influence of water on the formation of the two complexes is still in progress.

Discussion for hydrogen bonds of the complexes

In complex **1**, two neighbouring crystallized water molecules act as not only hydrogen acceptors but also hydrogen donors, to form six hydrogen bonds with four $[\text{Cu}_3\text{L}_3]$ units around them (**Fig. S7a**). As a whole, the crystallized water molecules act as connector linking these 1-D double chains (**Fig. S5b**) to form 2-D layer structures (**Fig. S7b**). Compared with complex **1**, hydrogen bonds in complex **2** is much weaker, and only one type of weak hydrogen bonds, C49-H49...N16A, exist between two coordination molecules in complex **1** (**Fig. S7c**). So the hydrogen bonds play a key role probably in the formation of complex **1**.

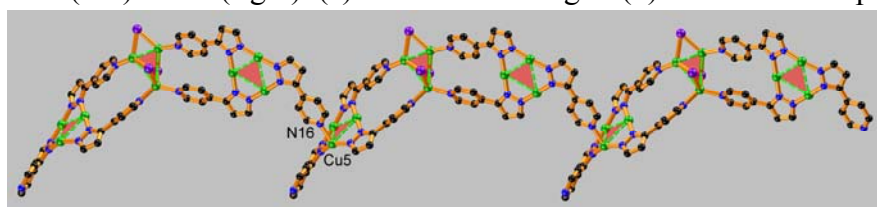
Additional Figures



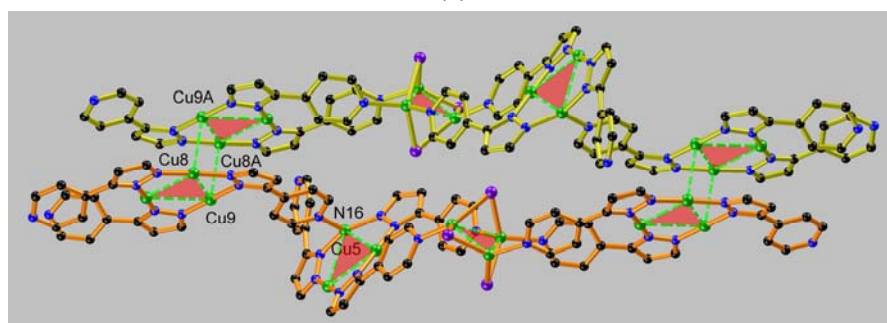
(a)

(b)

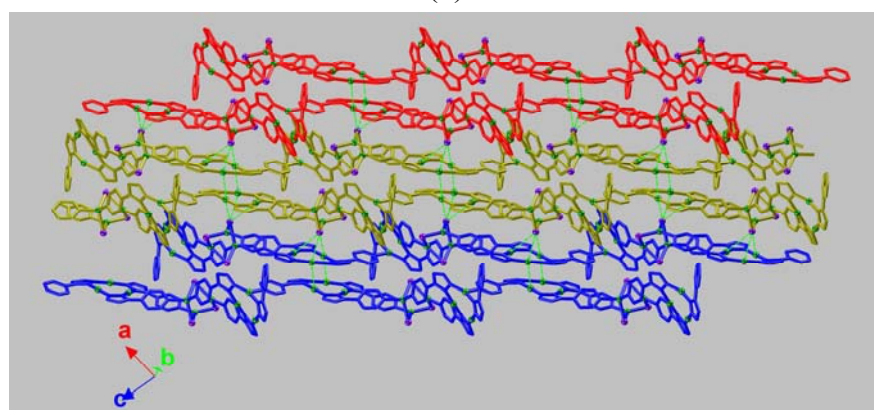
Fig. S4 Photograph of the crystal samples under microscope (amplified 40 times) for complex **1** (left) and **2** (right). (a) Under natural light. (b) Under UV lamp (365 nm).



(a)



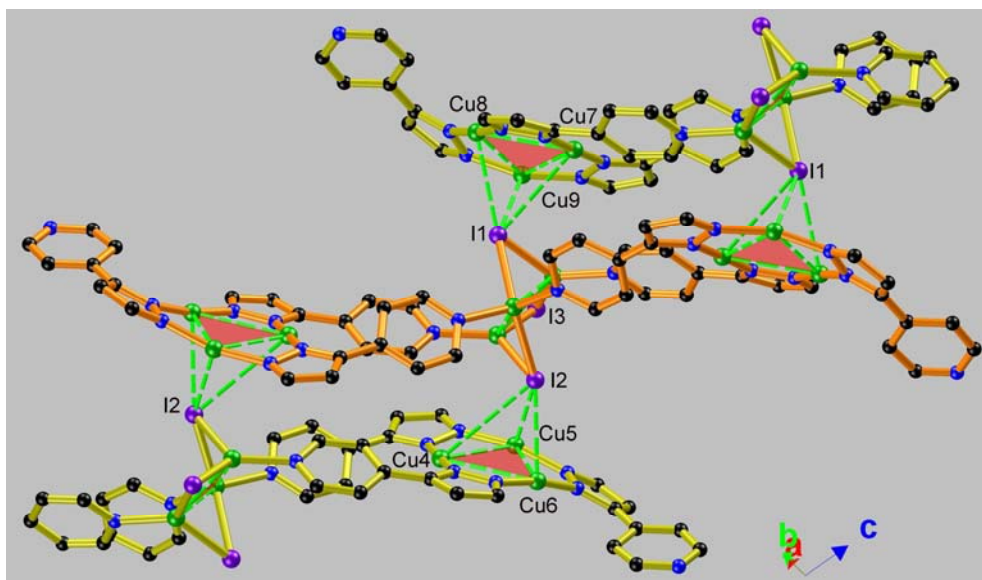
(b)



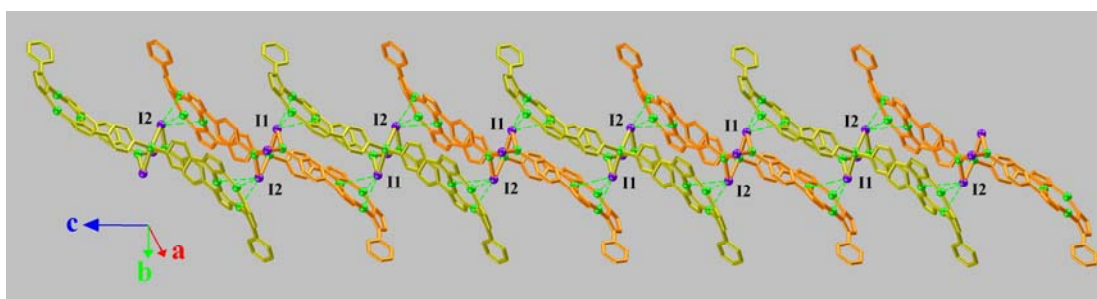
(c)

Fig. S5 Crystal structural diagram of complex **1**.

- 1-D chain constructed by Cu₃I₃(Cu₃Pz₃)₂ units through N16-Cu5 weak coordination bonds.
- 1-D double chains constructed by intertrimer Cu-Cu cuprophilic interactions.
- 2-D packing diagram through inter-double-chains I---Cu₃Pz₃ interactions.



(a)

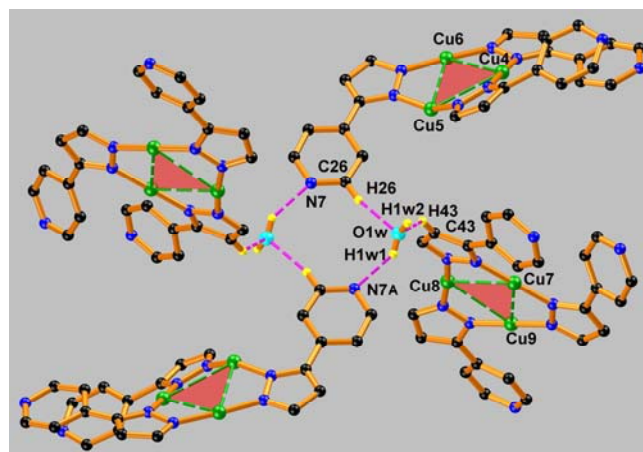


(b)

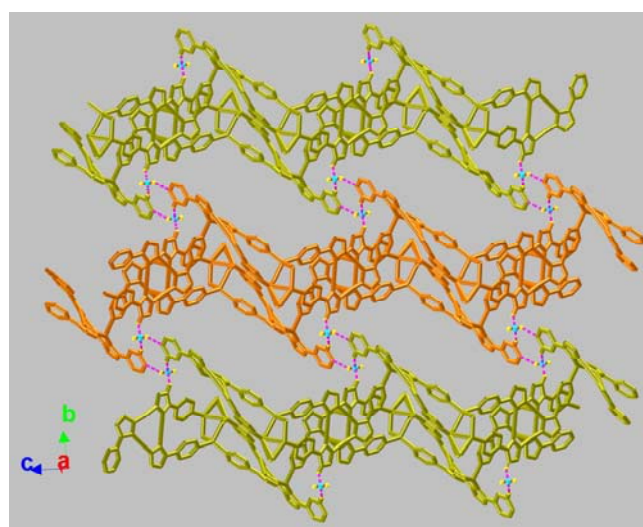
Fig. S6 Crystal structural diagram of complex 2.

(a) I---Cu₃Pz₃ interactions among these Cu₃Pz₃ units and Cu₃I₃ units.

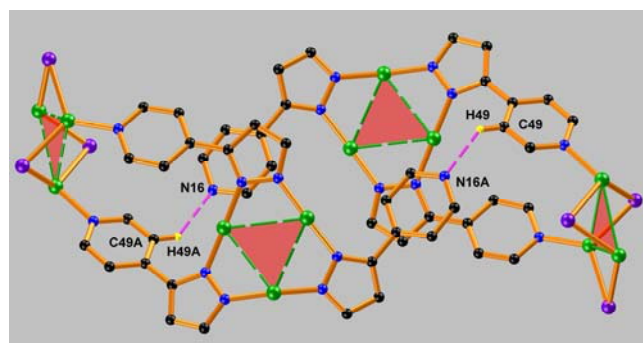
(b) 1-D chains constructed by I---Cu₃Pz₃ interactions.



(a)



(b)



(c)

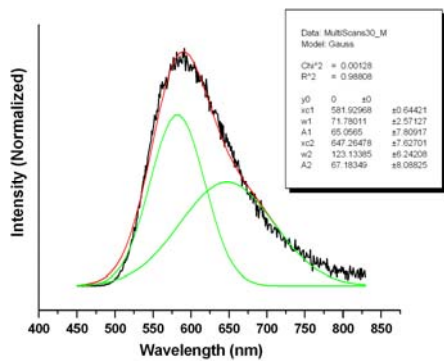
Fig. S7 Hydrogen bonds diagrams in the crystal structures of complex **1** (a and b) and complex **2** (c).

(a) C-H \cdots O (C26-H26 \cdots O1w and C43-H43 \cdots O1w) and N7 \cdots H1w1-O1w hydrogen bonds (purple dashed stick) in complex **1**. (Symmetry code: A -1-x, -y, -z)

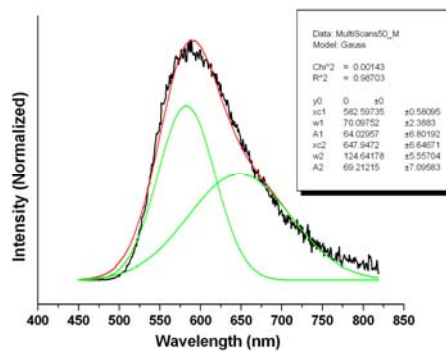
(b) 2-D layer structure constructed by hydrogen bonds (purple dashed stick) between these double-chains in complex **1**.

(c) C49-H49 \cdots N16A hydrogen bonds (purple dashed stick) between two coordination molecules in complex **2**. (Symmetry codes: A -x, -y, -2-z)

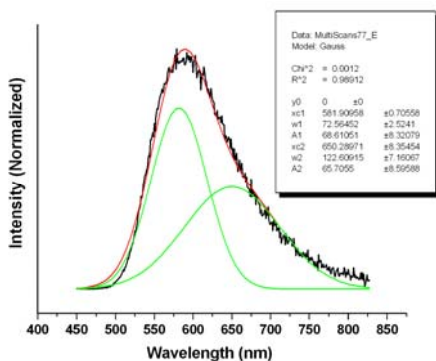
Physical Measurements



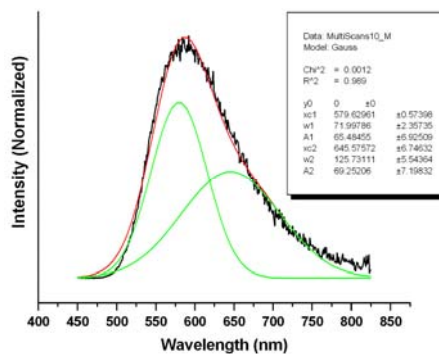
(a) 30 K



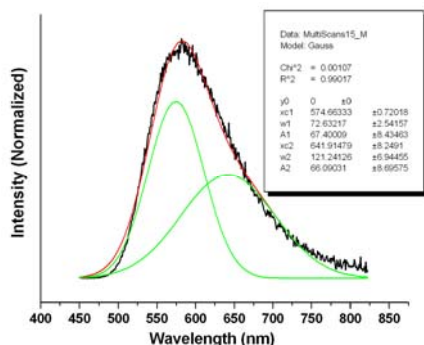
(b) 50K



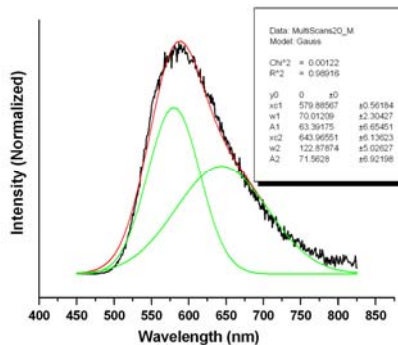
(c) 77K



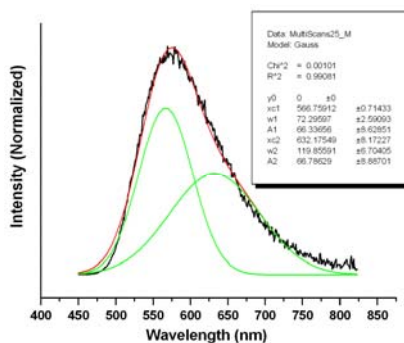
(d) 100K



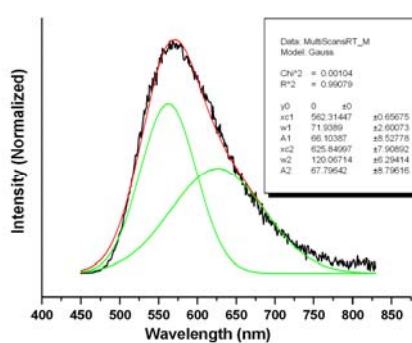
(e) 150K



(f) 200K



(g) 250K



(h) 298K

Fig. S8 Emission spectra of complex **1** and the fitted Gaussian profile at various temperatures excited by 380 nm. (Black: measured spectra, Red: Gauss fitting result, Green: Gauss fitting peak 1 and peak 2)

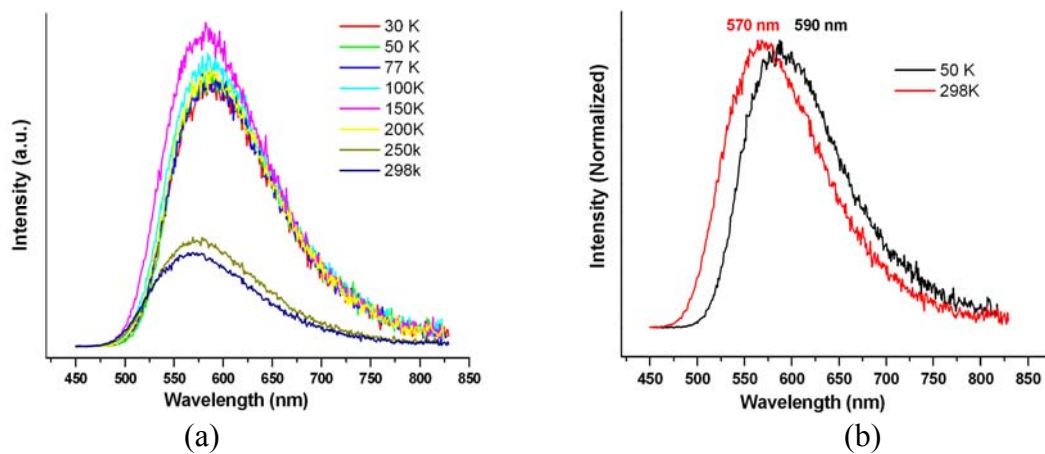
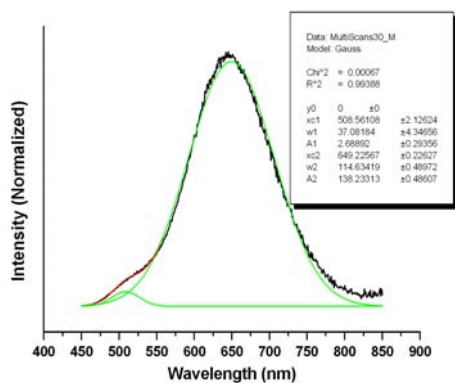
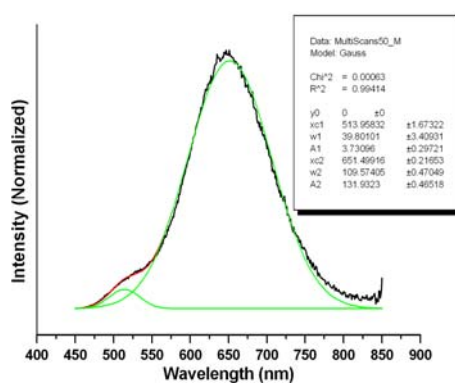


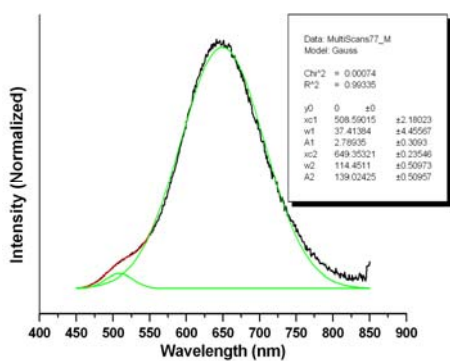
Fig. S9 (a) Temperature-dependent emission spectra of complex **1** from 298K to 30 K excited by 380 nm. (b) Normalized emission spectra at 298 K and 50 K showing the red shift upon decreasing temperature.



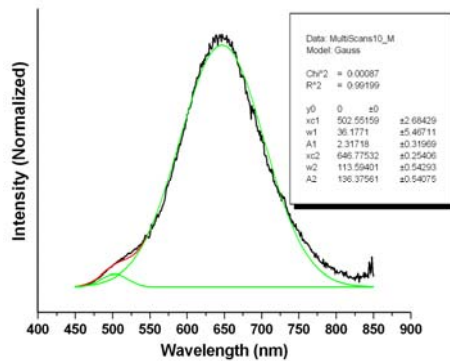
(a) 30 K



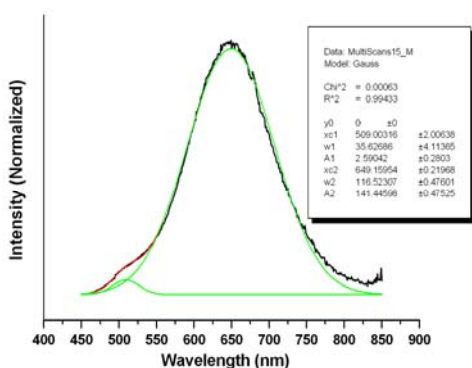
(b) 50 K



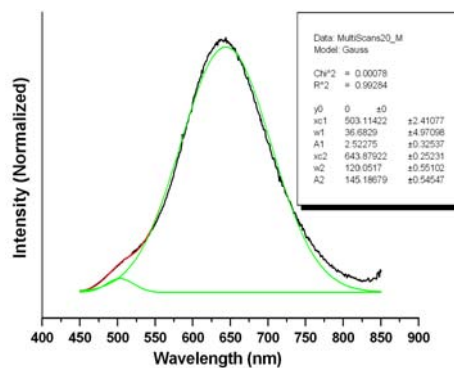
(c) 77 K



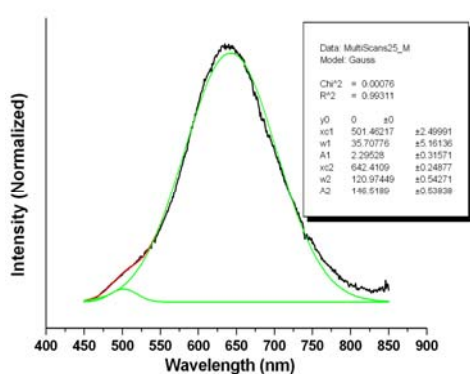
(d) 100 K



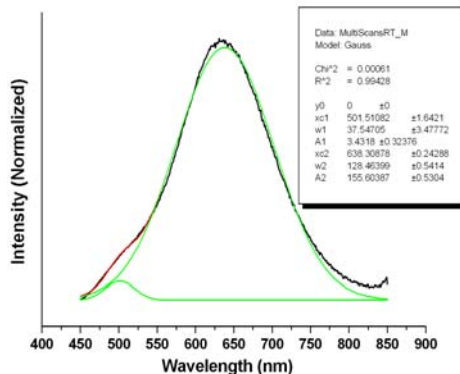
(e) 150 K



(f) 200 K



(g) 250 K



(h) 298 K

Fig. S10 Emission spectra of complex **2** and the fitted Gaussian profile at various temperatures excited by 380 nm. (Black: measured spectra, Red: Gauss fitting result, Green: Gauss fitting peak 1 and peak 2)

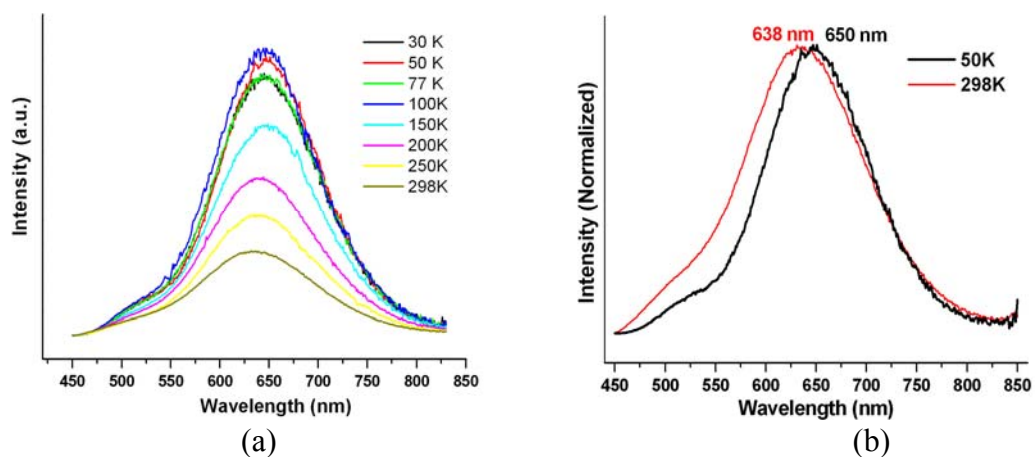


Fig. S11 (a) Temperature-dependent emission spectra of complex **2** from 298K to 30 K excited by 380 nm. (b) Normalized emission spectra at 298 K and 50 K showing red shift upon decreasing temperature.

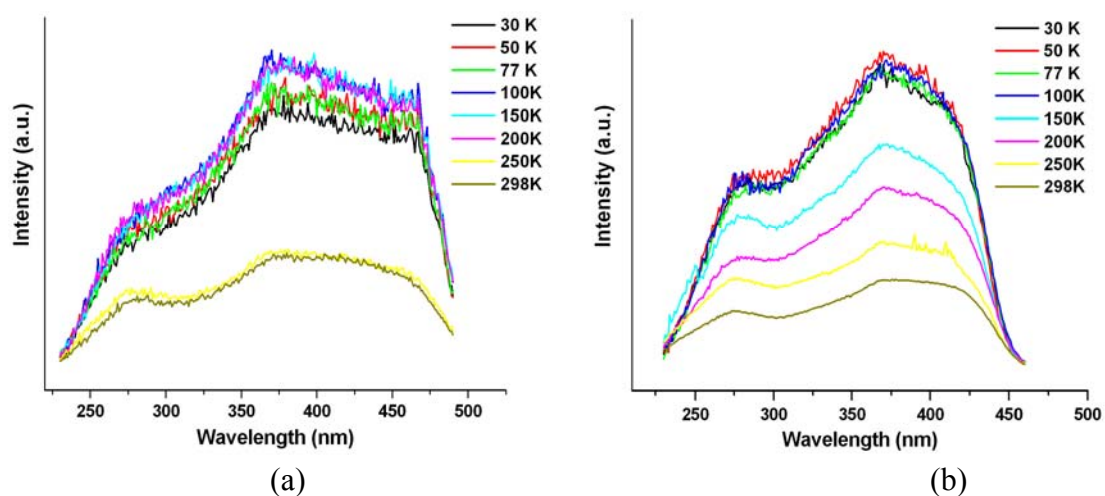


Fig. S12 Excitation spectra of complex **1** (a) monitored by 570 nm and complex **2** (b) monitored by 638 nm at various temperature.

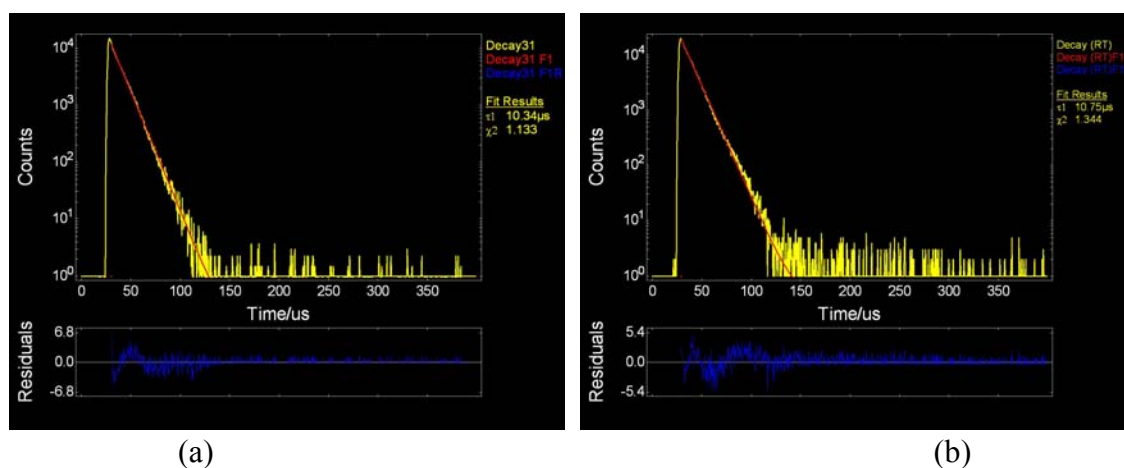


Fig. S13 Luminescence decay of the two complexes excited by 380 nm at 298 K. (a) Complex **1**, monitored by 570 nm. (b) Complex **2**, monitored by 638 nm.

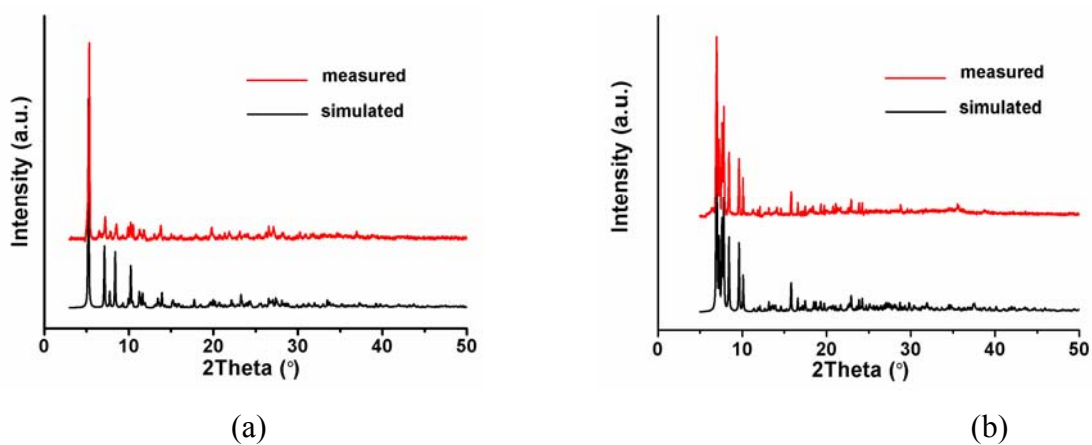


Fig. S14 Comparison of experimental PXD for bulk sample of complex **1** (a) and complex **2** (b) to their simulated pattern from single-crystal X-ray data.

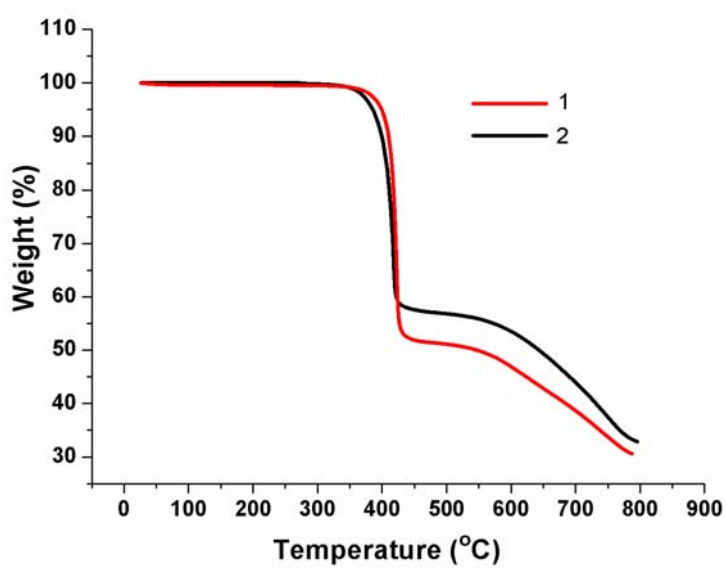


Fig. S15 TGA plot of isomer **1** (red) and isomer **2** (black).