Room temperature phosphorescence and photochromism in a series of pyridine-based hybrid compounds

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Table S1. Selected bond lengths [Å] and angles [°] for compounds **1**-**4**.

Compound **1**			
Cd1–O1	2.348(7)	N3–Cd1–Cl2	84.6(2)
Cd1–N1	2.364(8)	O1–Cd1–Cl1	95.72(18)
Cd1–N3$^{\#1}$	2.411(7)	N1–Cd1–Cl1	91.2(2)
Cd1–Cl2	2.561(3)	N3–Cd1–Cl1	176.2(2)
Cd1–Cl1	2.578(3)	Cl2–Cd1–Cl1	99.11(9)
Cd1–Cl4$^{\#2}$	2.625(3)	O1–Cd1–Cl4	86.1(2)
Cd2–N2	2.322(9)	N1–Cd1–Cl4	170.0(2)
Cd2–Cl3	2.486(3)	N3–Cd1–Cl4	94.00(19)
Cd2–Cl4	2.568(3)	Cl2–Cd1–Cl4	90.37(9)
Cd2–Cl1$^{\#3}$	2.609(3)	Cl1–Cd1–Cl4	86.79(9)
Cd2–Cl2$^{\#4}$	2.748(3)	N2–Cd2–Cl3	97.2(2)
Cl1–Cd2$^{\#5}$	2.609(3)	N2–Cd2–Cl4	161.5(2)
Cl2–Cd2$^{\#2}$	2.748(3)	Cl3–Cd2–Cl4	97.78(11)
Cl4–Cd1$^{\#4}$	2.624(3)	N2–Cd2–Cl1	88.8(2)
N3–Cd1$^{\#1}$	2.411(7)	Cl3–Cd2–Cl1	102.03(10)
		Cl4–Cd2–Cl1	98.65(9)
O1–Cd1–N1	84.3(3)	N2–Cd2–Cl2	79.6(2)
O1–Cd1–N3	80.6(3)	Cl3–Cd2–Cl2	98.12(10)
N1–Cd1–N3	87.4(3)	Cl4–Cd2–Cl2	87.50(8)
O1–Cd1–Cl2	164.55(18)	Cl1–Cd2–Cl2	157.87(9)
N1–Cd1–Cl2	99.7(2)		
Cd1–O1	2.348(7)	N3–Cd1–Cl2	84.6(2)
Compound **2**			
Cd1–Cl1	2.5934(10)	N2–Cd1–Cl2	102.21(8)
Cd1–Cl2$^{\#1}$	2.6590(10)	N2–Cd1–Cl2	94.98(8)
Cd1–Cl2	2.6116(10)	N2–Cd1–Cl3	156.15(8)
Cd1–Cl3$^{\#2}$	2.6493(11)	N2–Cd1–N4	77.79(12)
Cd1–N2	2.365(3)	N4–Cd1–Cl1	97.97(9)
Cd1–N4$^{\#3}$	2.458(3)	N4–Cd1–Cl2	169.75(9)
Cd2–Cl1$^{\#4}$	2.6419(10)	N4–Cd1–Cl2	88.74(9)
Cd2–Cl1$^{\#1}$	2.6419(10)	N4–Cd1–Cl3	79.37(9)
Cd2–Cl3$^{\#5}$	2.6328(10)	Cl1–Cd2–Cl1	180.00(3)
Cd2–Cl3	2.6328(10)	Cl3–Cd2–Cl1	86.78(3)

Cd2–N3	2.298(3)	Cl3–Cd2–Cl1	86.78(3)
Cd2–N3$^{\#5}$	2.298(3)	Cl3–Cd2–Cl1	93.22(3)
Cl1–Cd2$^{\#2}$	2.6419(10)	Cl3–Cd2–Cl1	93.22(3)
Cl2–Cd1$^{\#1}$	2.6590(10)	Cl3–Cd2–Cl3	180.0
Cl3–Cd1$^{\#4}$	2.6493(11)	N3–Cd2–Cl1	91.43(9)
N4–Cd1$^{\#6}$	2.458(3)	N3–Cd2–Cl1	88.57(9)
		N3–Cd2–Cl1	91.43(9)
Cl1–Cd1–Cl2	92.27(3)	N3–Cd2–Cl1	88.57(9)
Cl1–Cd1–Cl2	172.82(3)	N3–Cd2–Cl3	92.81(9)
Cl1–Cd1–Cl3	87.44(3)	N3–Cd2–Cl3	87.19(9)
Cl2–Cd1–Cl2	81.04(3)	N3–Cd2–Cl3	92.81(9)
Cl2–Cd1–Cl3	101.49(4)	N3–Cd2–Cl3	87.19(9)
Cl3–Cd1–Cl2	91.31(3)	N3–Cd2–N3	180.0
Compound **3**			
Cd1–O1	2.294(3)	N2–Cd1–O3	87.85(11)
Cd1–O3	2.390(3)	N2–Cd1–O7	111.93(12)
Cd1–O7	2.499(4)	N3–Cd1–O1	91.34(10)
Cd1–N2	2.342(3)	N3–Cd1–O3	78.30(11)
Cd1–N3$^{\#1}$	2.331(3)	N3–Cd1–O7	74.26(12)
Cd1–N4$^{\#2}$	2.340(3)	N3–Cd1–N2	90.73(10)
		N4–Cd1–O1	89.61(11)
O3–Cd1–O1	82.10(13)	N4–Cd1–O3	122.77(11)
O7–Cd1–O1	78.91(13)	N4–Cd1–O7	85.16(12)
O7–Cd1–O3	146.01(12)	N4–Cd1–N2	92.31(10)
Compound **4**			
Cd1–O7Z	2.286(12)	N4–Cd1–O3W	85.8(5)
Cd1–N4	2.301(12)	N2–Cd1–O3W	76.3(5)
Cd1–N2$^{\#1}$	2.323(12)	O6T–Cd1–O3W	143.5(5)
Cd1–O6T	2.360(13)	N3–Cd1–O3W	113.3(6)
Cd1–N3$^{\#2}$	2.365(11)	O14E–Cd2–N9F	90.1(5)
Cd1–O3W	2.598(19)	O14E–Cd2–N11	95.2(5)
Cd2–O14E	2.269(11)	N9F–Cd2–N11	157.3(5)
Cd2–N9F$^{\#3}$	2.328(13)	O14E–Cd2–N10A	161.5(5)
Cd2–N11	2.368(13)	N9F–Cd2–N10A	88.0(5)
Cd2–N10A$^{\#4}$	2.370(12)	N11–Cd2–N10A	93.6(5)

Cd2–O8V	2.549(15)	O14E–Cd2–O8V	80.6(5)
Cd2–O12	2.59(2)	N9F–Cd2–O8V	75.0(5)
Cd2–O11S	2.635(17)	N11–Cd2–O8V	84.0(4)
		N10A–Cd2–O8V	116.6(5)
O7Z–Cd1–N4	86.9(5)	O14E–Cd2–O12	84.1(6)
O7Z–Cd1–N2	94.5(5)	N9F–Cd2–O12	121.7(5)
N4–Cd1–N2	160.8(4)	N11–Cd2–O12	80.8(5)
O7Z–Cd1–O6T	82.1(6)	N10A–Cd2–O12	81.3(5)
N4–Cd1–O6T	119.8(5)	O8V–Cd2–O12	157.4(6)
N2–Cd1–O6T	79.3(5)	O14E–Cd2–O11S	76.0(5)
O7Z–Cd1–N3	173.4(5)	N9F–Cd2–O11S	74.4(5)
N4–Cd1–N3	92.7(4)	N11–Cd2–O11S	128.3(5)
N2–Cd1–N3	88.0(4)	N10A–Cd2–O11S	85.7(5)
O6T–Cd1–N3	92.4(5)	O8V–Cd2–O11S	141.1(5)

Symmetry codes for **1**: #1: 1-X, 1-Y, 1-Z; #2: 1.5-X, 0.5+Y, 1.5-Z; #3: -0.5+X, 0.5-Y, 0.5+Z; #4: 1.5-X, -0.5+Y, 1.5-Z; #5: 0.5+X, 0.5-Y, -0.5+Z.

Symmetry codes for **2**: #1: 1-X, -Y, 1-Z; #2: -1+X, +Y, +Z; #3: 1-X, -0.5+Y, 0.5-Z; #4: 1+X, +Y, +Z; #5: 2-X, -Y, 1-Z; #6: 1-X, 0.5+Y, 0.5-Z.

Symmetry codes for **3**: #1: 0.5+X, 1.5-Y, 1-Z; #2: 1-X, 1-Y, 1-Z; #3: -0.5+X, 1.5-Y, 1-Z.

Symmetry codes for **4**: #1: +X, 0.5-Y, -0.5+Z; #2: 1-X, 1-Y, 1-Z; #3: +X, 0.5-Y, 0.5+Z; #4: 2-X, 1-Y, 2-Z.

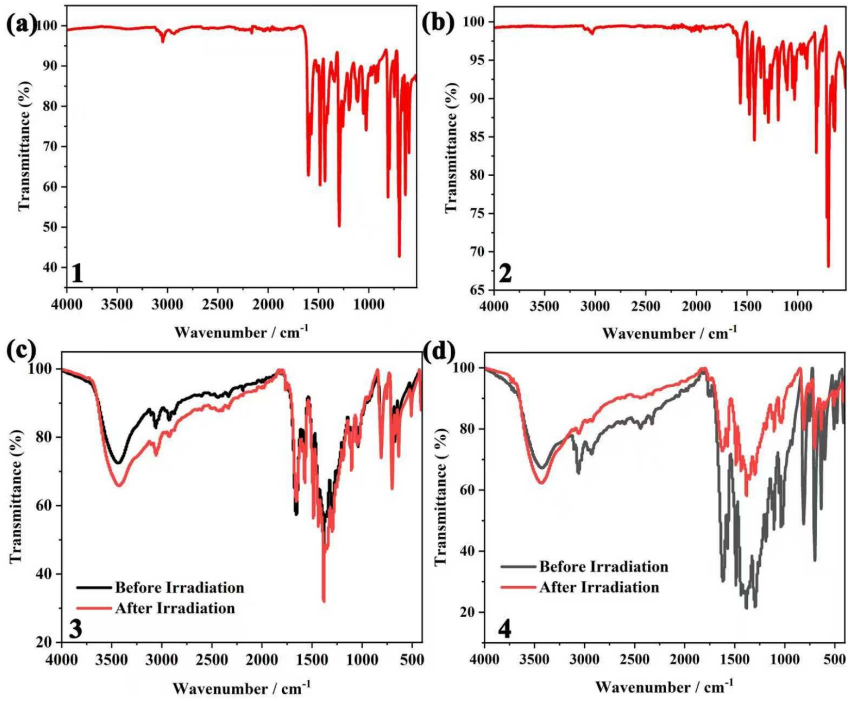

Fig. S1 (a-d) IR curves of compounds **1-4**.

Note: The peak around 3500 cm^{-1} corresponds to the stretching vibration of O-H bonds, which is likely attributed to the sample's absorption of trace moisture. The absorption near 3000 cm^{-1} arises from the stretching vibration of unsaturated C-H bonds on the pyridine rings. The peaks in the range of 1400–1700 cm^{-1} are assigned to the stretching vibrations of C=C and C=N bonds. The absorption near 1200 cm^{-1} is ascribed to the stretching vibration of C-N single bonds. The absorption peaks below 900 cm^{-1} are primarily associated with the out-of-plane bending vibrations of the aromatic ring.

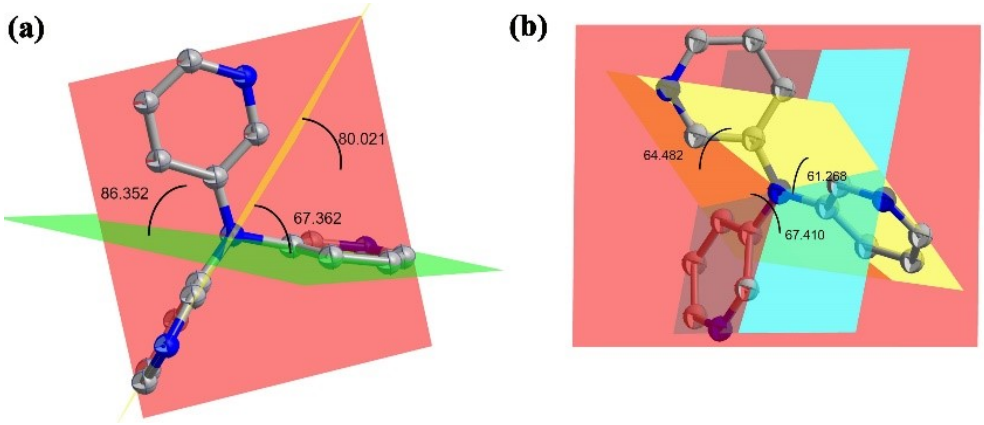

Fig. S2 Dihedral angles of TPA ligand in compounds **1** (a) and **2** (b).

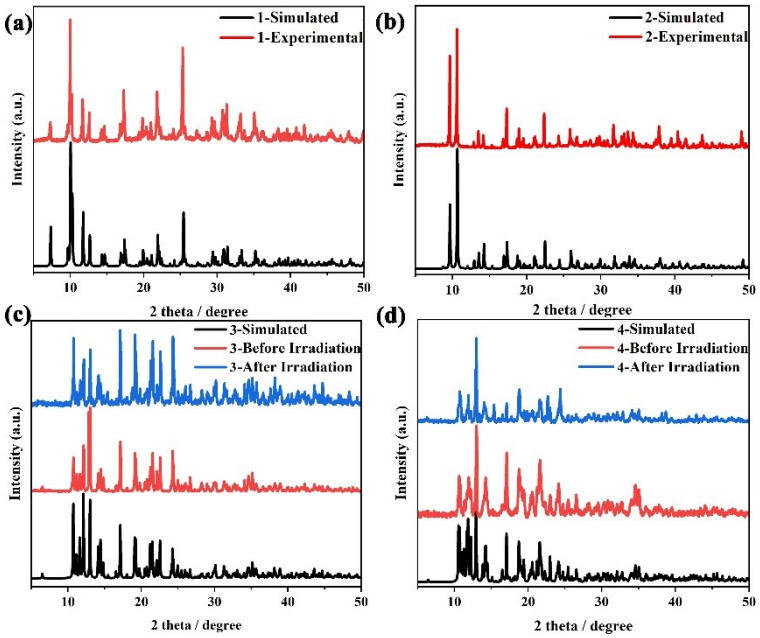

Fig. S3 PXRD patterns of the compounds **1**-**4**.

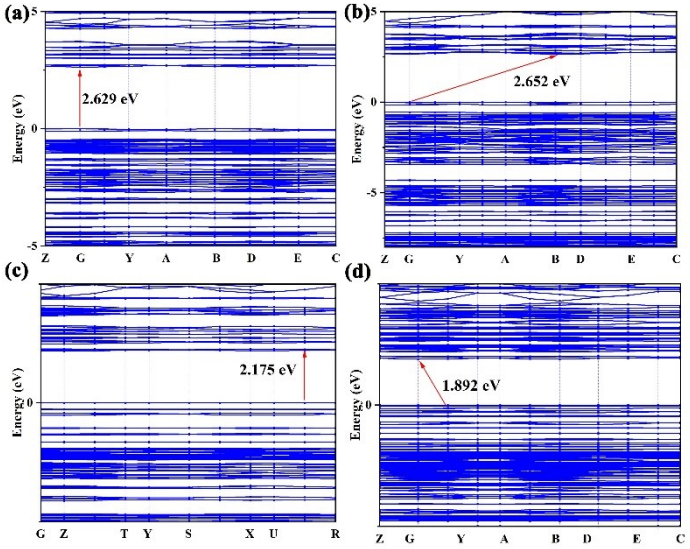

Fig. S4 Energy band calculations for compounds **1** (a), **2** (b), **3** (c) and **4** (d).

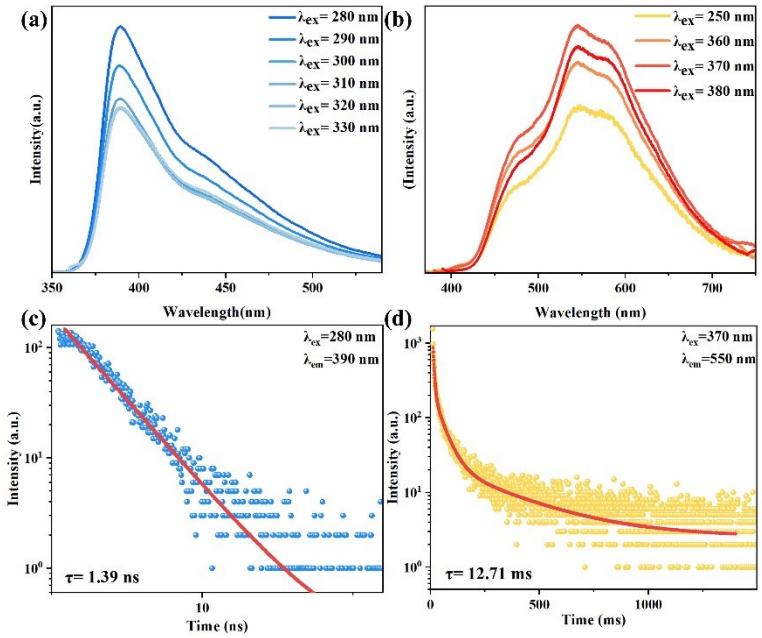

Fig. S5 (a, b) Prompt and delayed spectra of solid TPA; (c, d) fluorescence and phosphorescence decay curve for TPA.

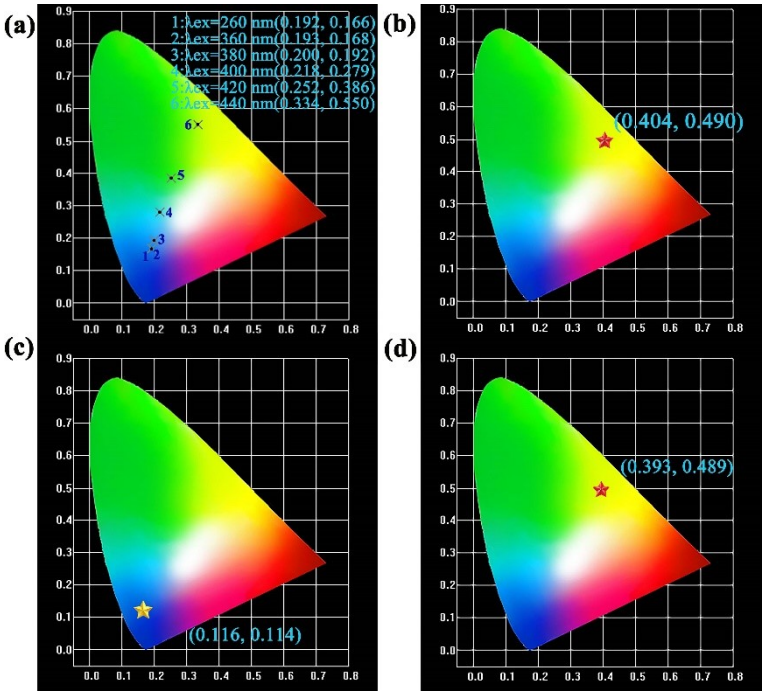

Fig. S6 (a, c) Fluorescence CIE chromaticity of **1** and **2**; (b, d) Phosphorescence CIE chromaticity of **1** and **2**.

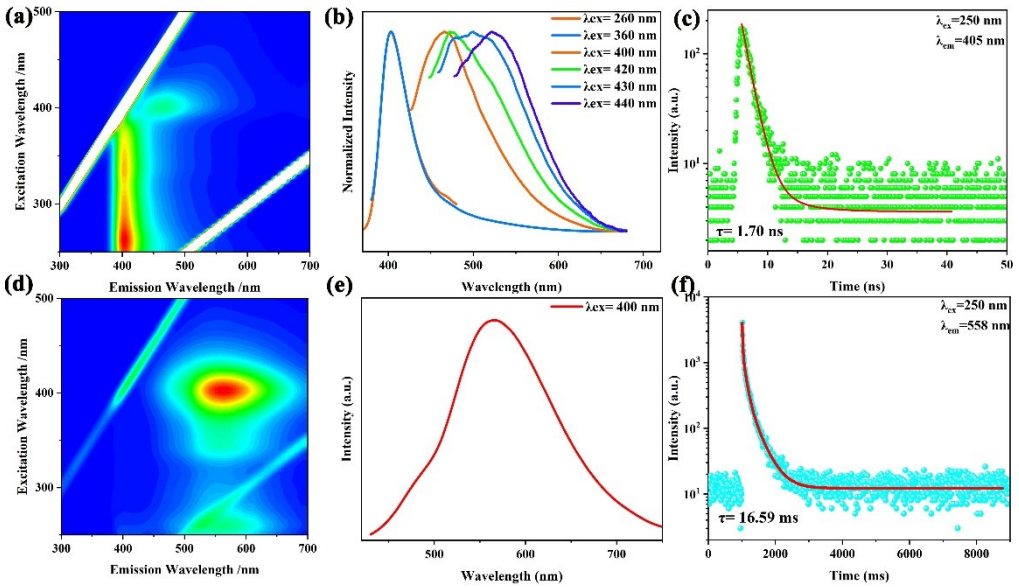

Fig. S7 (a, d) Prompt and delayed excitation-emission mapping of **3**; (b, e) normalized fluorescence and phosphorescence spectra of **3**; (c) immediate time-resolved decay curve for **3**; (f) phosphorescence decay curve for **3**.

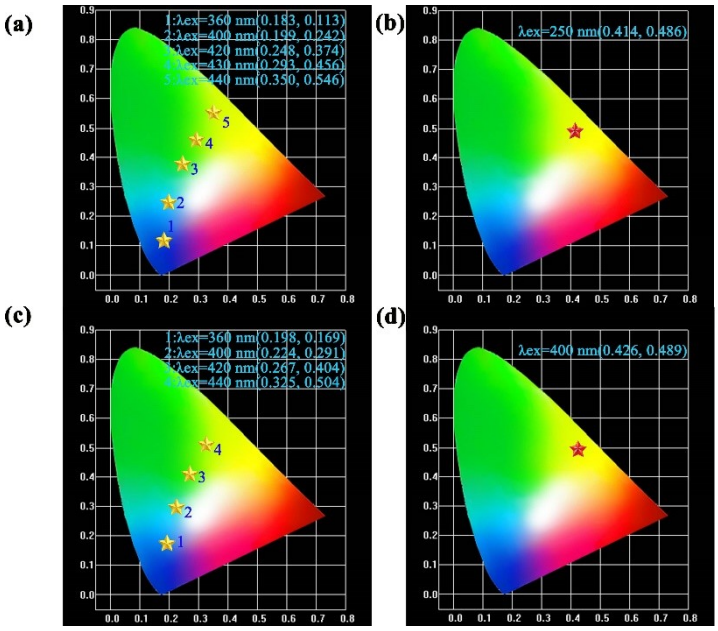

Fig. S8 (a, c) Fluorescence CIE chromaticity of **3** and **4**; (b, e) Phosphorescence CIE chromaticity of **3** and **4**.

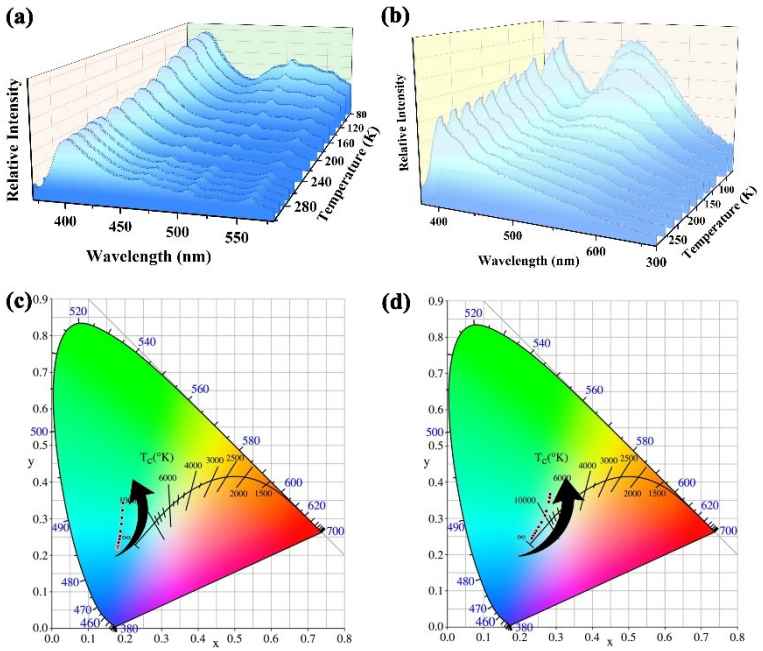

Fig. S9 (a, b) Prompt spectroscopy for compounds **3** and **4** with variable temperature; (c, d) the CIE coordinate graphs of **3** and **4** as the temperature decreased from 300 K to 77 K.

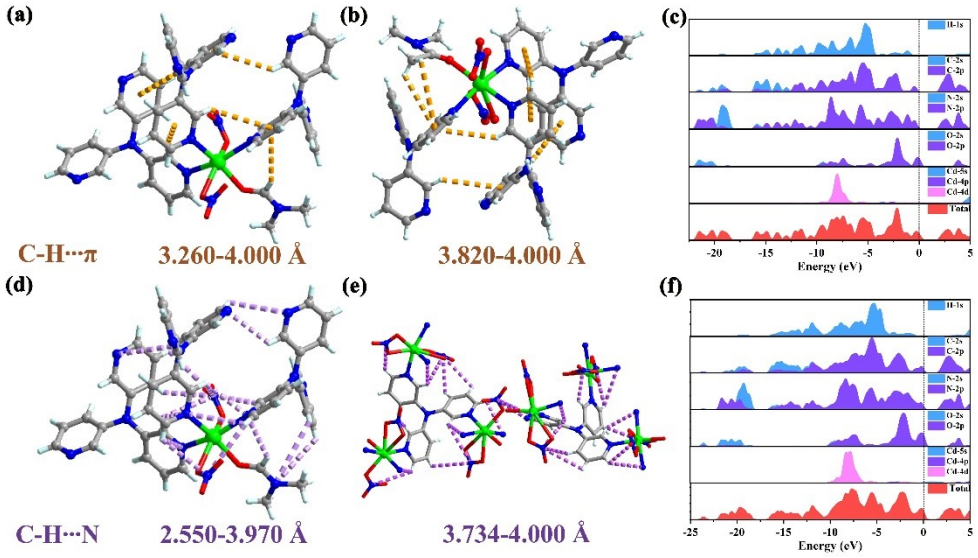

Fig. S10 (a, b, d, e) Intra-/intermolecular interactions in **3** and **4** derived from single-crystal X-ray diffraction data; (c, f) total and partial state densities for **3** and **4**.

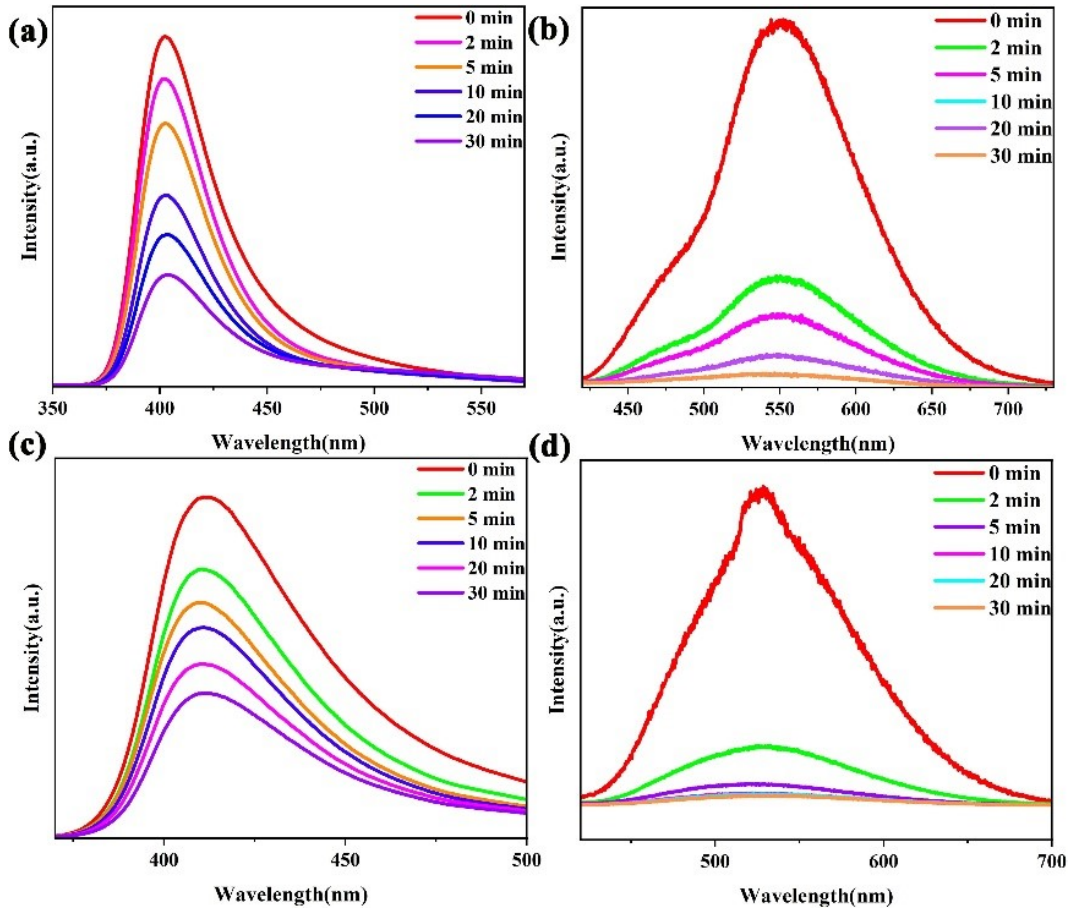

Fig. S11 (a, c) Fluorescence and phosphorescence spectra of compound **3** with the increase of irradiation time; (b, d) fluorescence and phosphorescence spectra of compound **4** with the increase of irradiation time.