

Electronic Supplementary Information (ESI)

for

When Cu_4I_4 cubane meets $\text{Cu}_3(\text{pyrazolate})_3$ triangle: dynamic interplay between two classical luminophores functioning in a reversibly thermochromic coordination polymer

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Experimental 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 tetramethylsilane 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.

The diffuse reflectance solid-state UV-Vis spectrum was recorded on a Lambda950 UV/Vis/NIR spectrophotometer of Perkin Elmer using pure powder sample. 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, a red-sensitive Peltier-cooled Hamamatsu R928P photomultiplier tube (PMT), and a closed cycle cryostat (Advanced Research Systems). The corrections of excitation and emission for the detector response were performed ranging from 200-900 nm. 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. Lifetime data were fitted with triple exponential decay functions. The goodness of the nonlinear least-squares fit was judged by the reduced χ^2 value (<1.2 in most of the cases), the randomness of the residuals, and the autocorrelation function (Seeing Table S3 and Fig. S8). In all cases, 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. S4).

Synthesis:

3-(4-pyridyl)-5-*p*-tolyl-1-H-pyrazole (HL)

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

1-(4-pyridyl)-3-(*p*-tolyl)-1,3-propanedione

To a suspension of newly prepared C₂H₅ONa (3.4g, 0.05mol) in 100 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 3.5 mL (about 3.5g, 0.025mol) 4-acetyltoluene was slowly added to the mixture. After completing the addition, the mixture was kept with stirring for about 10 hours equipped with drying tube. Then the solvent was evaporated completely under reduced pressure. The residual was dissolved in 100 mL diluted acetic acid solution (3 mol·L⁻¹), and left it in refrigerator under 0-4 °C for about 5 hours and then filtered. Yellow solids were obtained and dried in vacuo to give 3.10 g primary product of 1-(4-pyridyl)-3-(*p*-tolyl)-1,3-propanedione. Yield: 52.0 %, mp: 118-120 °C. IR (ν/cm⁻¹): 3367 w, 3117 w, 3047 w, 3019 w, 2913 w, 2855 w, 1610 vs, 1479 vs, 1421 s, 1217 m, 1127 m, 1008 m, 821 m, 800 s, 710 m. ¹H NMR (400 MHz, CDCl₃, 298K): δ 8.79 (dd, *J* = 4.5, 1.6 Hz, 2H, CHpy), 7.91 (d, *J* = 8.3 Hz, 2H, CHpy), 7.78 (dd, *J* = 4.5, 1.7 Hz, 2H, CHph), 7.31 (d, *J* = 8.0 Hz, 2H, CHph), 6.86 (s, 1H, CH_{C=CH}), 2.45 (s, 3H, CH₃).

3-(4-pyridyl)-5-*p*-tolyl-1-H-pyrazole

2.39 g (0.01 mol) 1-(4-pyridyl)-3-(*p*-tolyl)-1,3-propanedione was added in ethanol (50 mL) and the mixture was treated with an excess of hydrazine (80 %, 3 mL), and then was refluxed for 10 hours. The solution was kept standing in air to evaporate the ethanol solvent. Several days later, nearly colorless microcrystalline solids were obtained and dried in vacuo to give 1.62 g product. Yield 68.9%, mp: 245-246°C. IR(ν/cm⁻¹): 3423 s, 3191 w, 3113 m, 3011 m, 2913 m, 2852 m, 1605 vs, 1507 s, 1467 m, 1180 m, 1000 m, 960 m, 830 m, 788 s, 694 s. ¹H NMR (400 MHz, MeOD, 298 K): δ 8.56 (d, *J* = 4.2 Hz, 2H, CHpy), 7.88 (d, *J* = 4.0 Hz, 2H, CHpy), 7.67 (d, *J* = 8.0 Hz, 2H, CHph), 7.29 (d, *J* = 7.5 Hz, 2H, CHph), 7.16 (s, 1H, CHpz), 2.39 (s, 3H, CH₃).

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.

Complex $[\text{Cu}_4\text{L}_4(\text{NH}_3)\text{Cu}_3\text{L}_3]_n$

A mixture of **HL** (47 mg, 0.2 mmol), CuI (76.2 mg, 0.4 mmol), C₂H₅OH (12 mL) and aqueous NH₃ (0.5 mL) was sealed in a 20-mL Teflon-lined reactor and heated in an oven at 180 °C for 72 hours and slowly cooled to room temperature at a rate of 5 °C·h⁻¹. Yellow block crystals were obtained. (yield: 51 % based on ligand). Anal. Calcd for C₄₅H₃₉Cu₇I₄N₁₀: C 32.32, H 2.35, N 8.38 %, Found: C 32.56, H 2.53, N 8.42 %. IR data (KBr, cm⁻¹): 3367 w, 3117 w, 3048 w, 3019 w, 2913 w, 2856 w, 1609 vs, 1479 vs, 1422 s, 1217 m, 1127 m, 1009 m, 821 m, 800 s, 710 m.

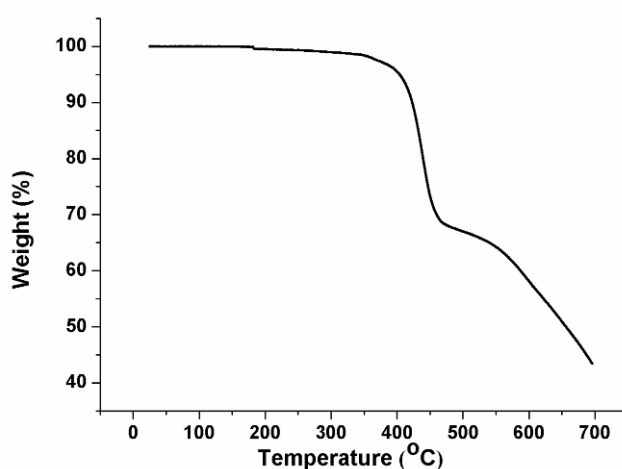


Fig. S1 Thermogravimetric plot of the complex.

Crystal Structure Determination

Single crystal data collection was performed on an Oxford Diffraction Gemini E (Enhance Mo X-Ray source, $K\alpha$, $\lambda = 0.71073 \text{ \AA}$) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature (293K) and under nitrogen stream (100 K) using the same crystal sample. The data was processed using CrysAlis RED, Oxford Diffraction Ltd (Version 1.171.34.44, release 25-10-2010 CrysAlis171 .NET). Structure were solved by direct methods (SHELXTL-97) and refined on F^2 using full-matrix least-squares (SHELXTL-97).⁴ 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. Crystal data and structure refinement for these complexes are summarized in Table S1. Selected bond lengths and angles are given in Table S2. CCDC 829986 (293 K) and 829987 (100 K) 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 complex in 293 K and 100K

Parameter	293 K	100 K
Chemical formula	C ₄₅ H ₃₉ N ₁₀ Cu ₇ I ₄	C ₄₅ H ₃₉ N ₁₀ Cu ₇ I ₄
Formula weight	1672.24	1672.24
Crystal system	Trigonal	Trigonal
Space group	<i>R</i> -3	<i>R</i> -3
<i>a</i> (Å)	18.4873(4)	18.4690(4)
<i>b</i> (Å)	18.4873(4)	18.4690(4)
<i>c</i> (Å)	25.7549(6)	25.3532(6)
α (deg)	90	90
β (deg)	120	120
γ (deg)	90	90
<i>V</i> (Å ³)	7623.2(3)	7489.5(3)
<i>Z</i>	6	6
<i>D</i> _{Calcd} (g·cm ⁻³)	2.186	2.225
μ (mm ⁻¹)	5.346	5.441
Reflections collected	6851	6667
Unique reflections	3741	3672
<i>R</i> _{int}	0.0230	0.0377
Goodness-of-fit on <i>F</i> ²	1.021	1.077
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0372	0.0402
w <i>R</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0705	0.0705
<i>R</i> ₁ ^a [all refl.]	0.0552	0.0588
w <i>R</i> ₂ ^b [all refl.]	0.0787	0.0811

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table S2. Selected bond lengths (Å), bond angles (°) for the complex in 293 K and 100 K

293K		100 K	
N1–Cu1	1.8656(4)	N1–Cu1	1.8692(3)
N2–Cu1B	1.8715(4)	N2–Cu1B	1.8708(3)
Cu1–Cu1A	3.2104(6)	Cu1–Cu1A	3.2240(6)
Cu1–Cu1E	3.6459(7)*	Cu1–Cu1E	3.5953(7)*
N1–Cu1–N2A	170.40(3)	N1–Cu1–N2A	170.34(3)
I1–Cu2	2.6490(5)	I1–Cu2	2.6441(3)
I2–Cu2	2.8043(6)	I2–Cu2	2.6726(7)
I2–Cu2D	2.6706(5)	I2–Cu2D	2.7835(1)
I2–Cu3	2.7023(5)	I2–Cu3	2.6877(1)
N3–Cu2	2.0233(4)	N3–Cu2	2.0298(8)
N4–Cu3	2.0409(4)	N4–Cu3	2.0518(3)
Cu2–Cu3	2.6477(5)	Cu2–Cu3	2.6171(3)
Cu2–Cu2C	2.6865(5)	Cu2–Cu2C	2.6542(6)
I2–Cu3–I2C	114.56(2)	I2–Cu3–I2C	114.85(2)
I2–Cu2–I2C	112.28(2)	I2–Cu2–I2C	112.28(2)
I2–Cu2–N3	101.34(2)	I2–Cu2–N3	106.15(2)
I2–Cu3–N4	103.70(2)	I2–Cu3–N4	103.32(2)

Symmetry codes: A -y+1, +x-y+1, +z; B -x+y, -x+1, +z;
 C -y, +x-y, +z; D -x+y, -x, +z; E +y, -x+y+1, -z

* *intertrimer* Cu-Cu distances

Additional Figures and Structural Descriptions

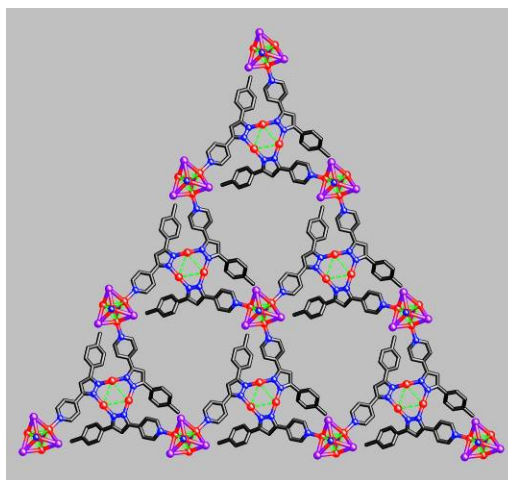
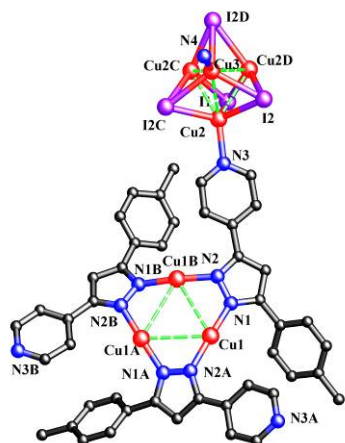


Fig. S2 (a) Coordination environment of the complex (symmetry codes: A $-y+1, +x-y+1, +z$; B $-x+y, -x+1, +z$; C $-y, +x-y, +z$; D $-x+y, -x, +z$). (b) The 2-D layer of the coordination polymers (color codes: Cu in red, N in blue, I in purple, C in black; H omitted).

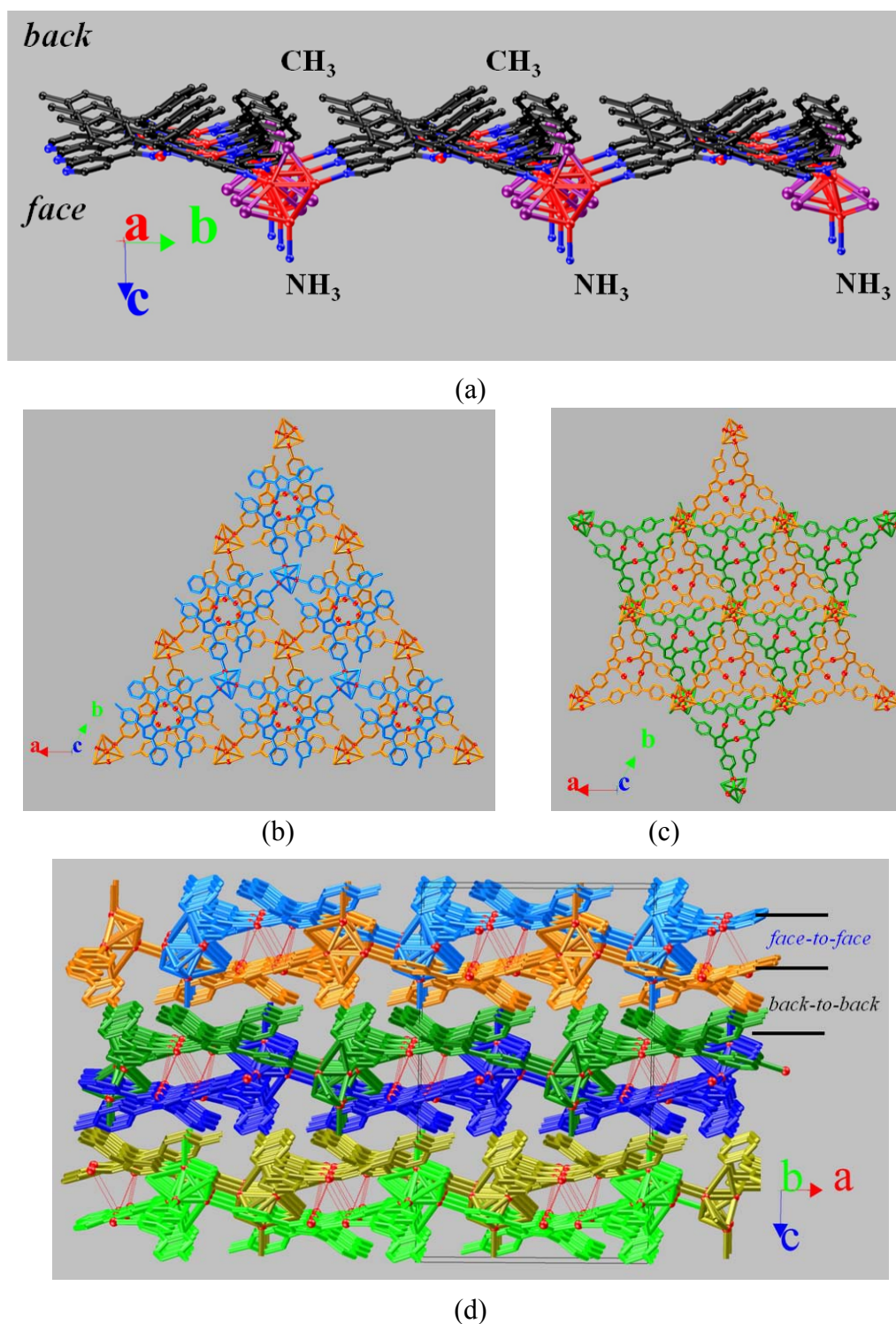


Fig. S3 Packing diagrams of the complex. (a) Single layer of the complex showing all NH₃ on the face side and CH₃ on the back side. (b) The face-to-face double layers showing Cu₃ – Cu₃, Cu₄ – V, and V – Cu₄ packing patterns along c axis. (c) The back-to-back double layers showing Cu₄ – Cu₄, Cu₃ – V, and V – Cu₃ packing patterns along c axis. (d) The packing diagram of layer-by-layer showing the face-to-face and back-to-back packing patterns alternately.

Description of Fig. S3:

These layers consist of three parts: $\text{Cu}_3(\text{Pz})_3$ units (Cu_3), Cu_4I_4 units (Cu_4), and the vacant areas (V) surrounded by three Cu_4I_4 units and three $\text{Cu}_3(\text{Pz})_3$ units. Here we labeled the side of methyl groups stretching as back and the side of NH_3 molecules as face (Fig. S2a). The 2-D layers are packed along c axis with face-to-face and back-to-back packing modes alternately (Fig. S2b and S2c) between the adjacent two layers through centrosymmetry and translation operation with translation vector $[1, -1, -1]$. Between the two face-to-face packing double-layers, the three parts show $\text{Cu}_3 - \text{Cu}_3$, $\text{Cu}_4 - \text{V}$ and $\text{V} - \text{Cu}_4$ packing patterns along c axis (Fig. S2b), and $\text{Cu}_3 - \text{Cu}_3$ units exhibit centrosymmetric staggered conformation, leading to an anti-triangular-prism geometry. The *intertrimer* Cu-Cu distance between the two adjacent face-to-face packing layers is 3.646 Å, the centroid distance is 3.140 Å (Fig. S2d), and the angle of N-Cu-N is 170.4°. These parameters are even slightly smaller than those of optimized geometry of ground states in the staggered conformation, indicating the possible strong *intertrimer* cuprophilic interactions. Of the back-to-back packing modes, the complex shows another packing pattern along c axis: $\text{Cu}_4 - \text{Cu}_4$, $\text{Cu}_3 - \text{V}$, $\text{V} - \text{Cu}_3$ (Fig. S2c). The distance between the two neighboring Cu_3 planes centers is 4.94 Å (Fig. S2d).

Physical measurements

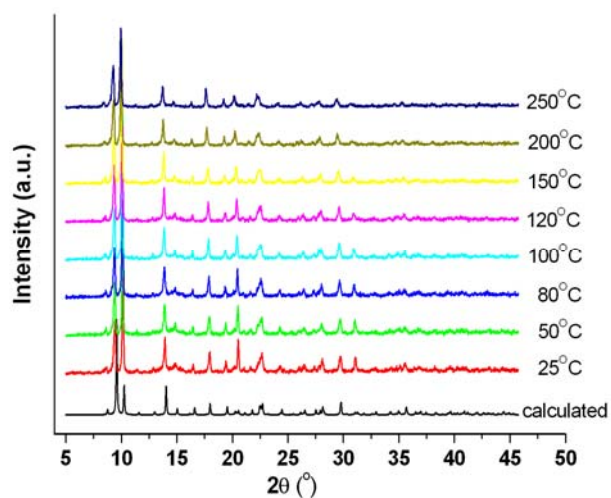


Fig. S4 Comparison of experimental PXD for bulk sample at different temperatures to calculated pattern from single-crystal X-ray data of the complex.

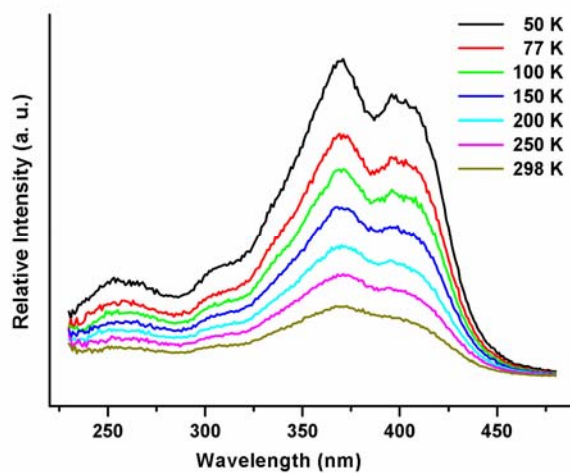


Fig. S5 Solid state excitation spectra monitored by 530 nm under various temperatures.

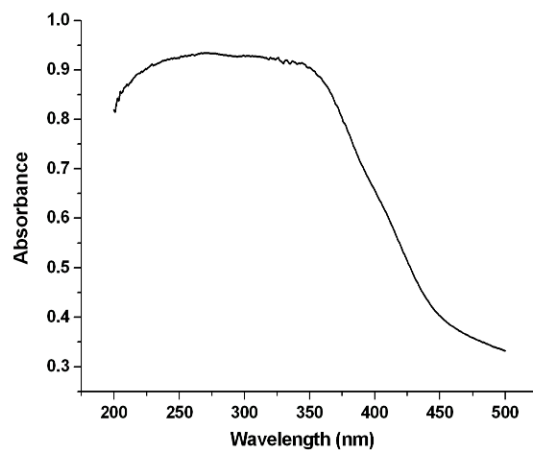


Fig. S6 Solid-state diffuse reflectance UV-Vis spectrum of the complex at room temperature.

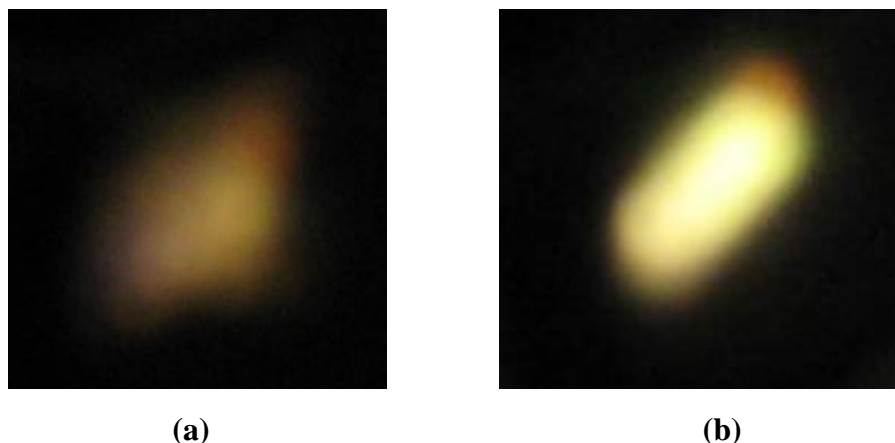
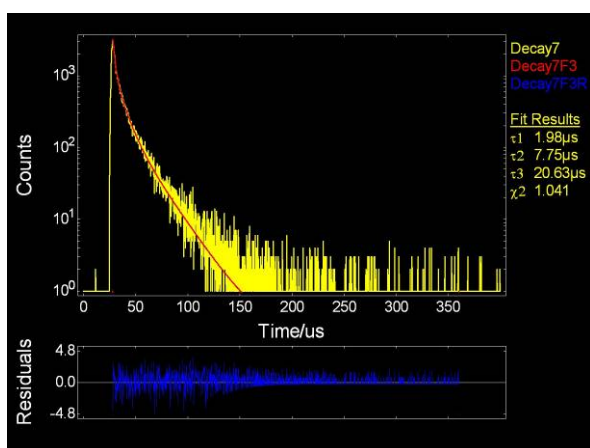
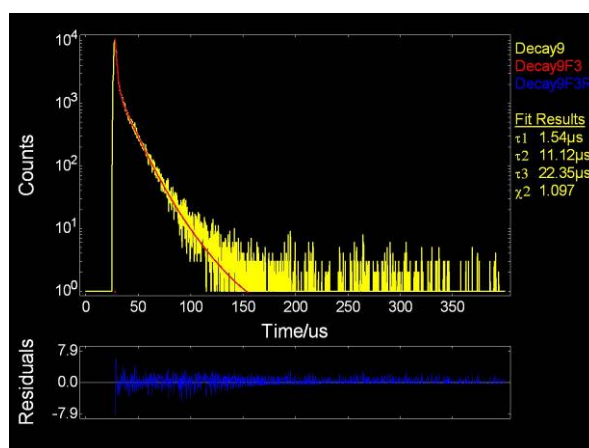


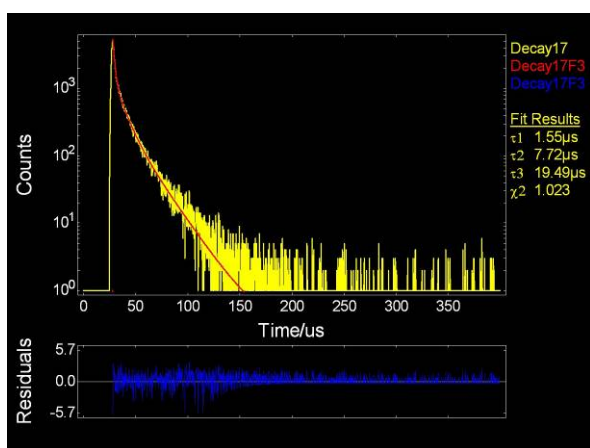
Fig. S7 Photoluminescence images of the complex under the irradiation of 270 nm (a) and 370 nm (b) in the spectrometer.



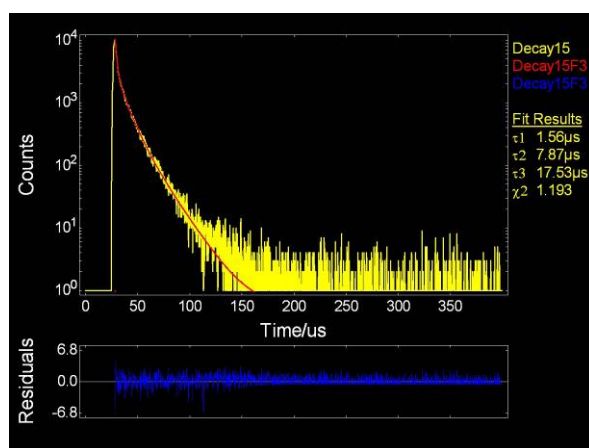
(a) 50 K Ex = 270 nm Em = 700 nm



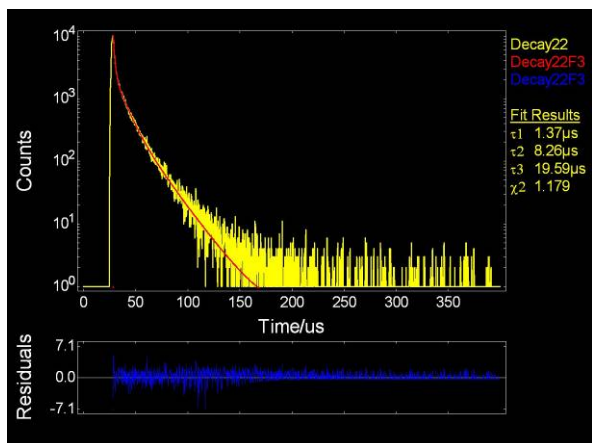
(b) 50 K Ex = 370 nm Em = 530 nm



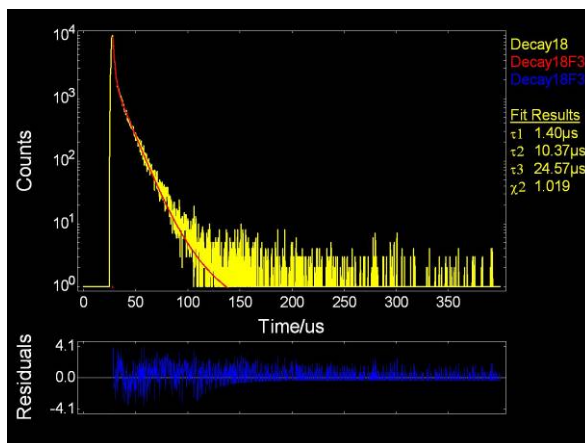
(c) 77 K Ex = 270 nm Em = 700 nm



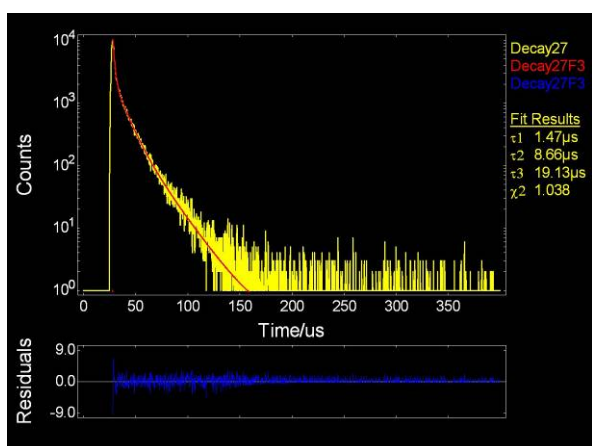
(d) 77 K Ex = 370 nm Em = 530 nm



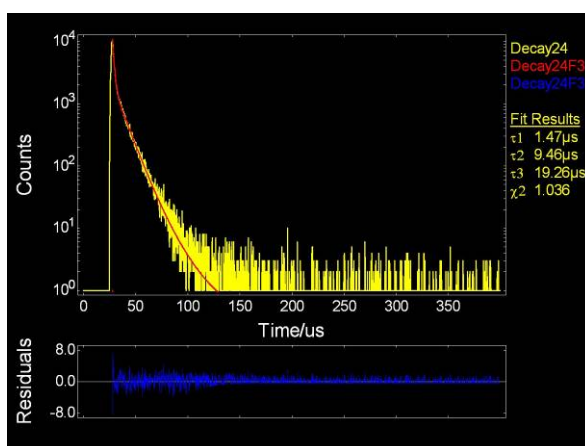
(e) 100 K Ex = 270 nm Em = 700 nm



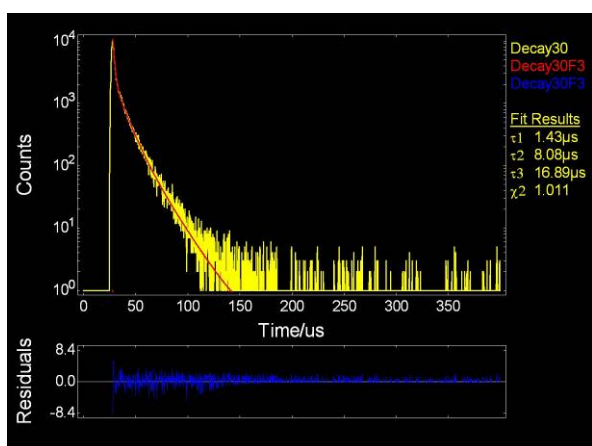
(f) 100 K Ex = 370 nm Em = 530 nm



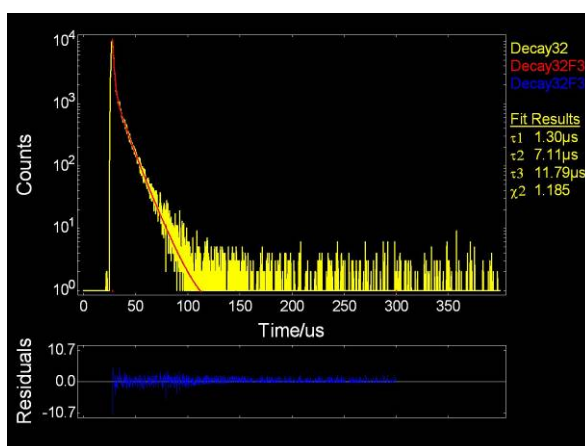
(g) 150 K Ex = 270 nm Em = 700 nm



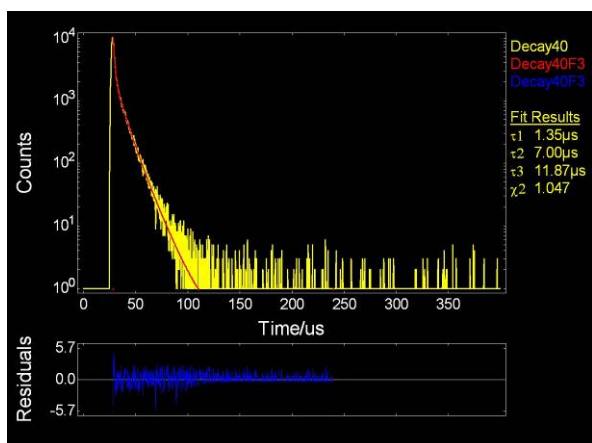
(h) 150 K Ex = 370 nm Em = 530 nm



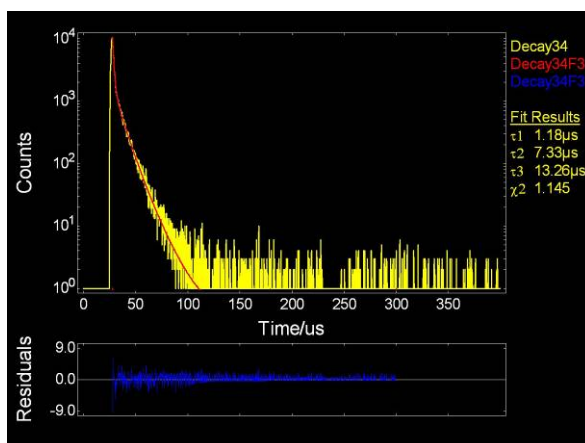
(i) 200 K Ex = 270 nm Em = 700 nm



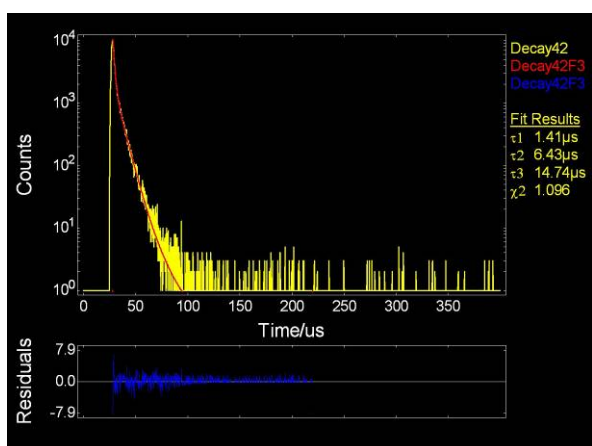
(j) 200 K Ex = 370 nm Em = 530 nm



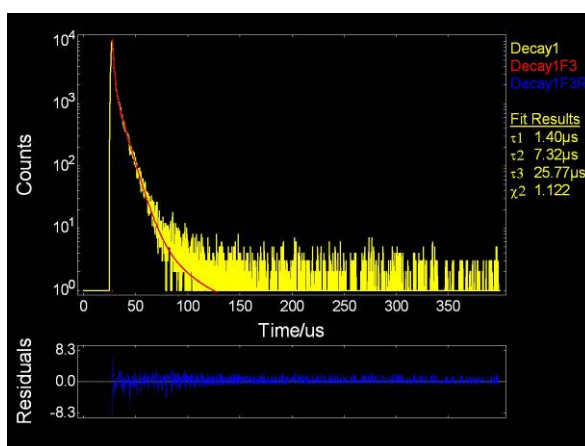
(k) 250 K Ex = 270 nm Em = 700 nm



(l) 250 K Ex = 370 nm Em = 530 nm



(m) 293 K Ex = 270 nm Em = 700 nm



(n) 293 K Ex = 370 nm Em = 530 nm

Fig. S8 Selected luminescence decay of the complex monitored at corresponding excitation/emission maxima under various temperatures.

Table S3. Lifetimes (τ) and corresponding fractional contributions (%) of the solid-state sample at various detection wavelengths and temperatures (χ^2 : fitting parameter).

	50K	77K	100K	150K	200K	250K	293K	T
Ex = 270 nm Em = 700 nm	1.041	1.023	1.179	1.038	1.011	1.047	1.096	χ^2
	1.98 (25.00)	1.55 (27.95)	1.37 (27.64)	1.47 (31.50)	1.43 (32.33)	1.35 (36.51)	1.41 (47.86)	τ_1 (μ s) (%)
	7.75 (41.00)	7.72 (36.79)	8.26 (39.59)	8.66 (41.73)	8.08 (42.00)	7.00 (39.61)	6.43 (48.89)	τ_2 (μ s) (%)
	20.63 (34.00)	19.49 (35.26)	19.59 (32.77)	19.13 (26.78)	16.89 (25.59)	11.87 (23.87)	14.74 (3.25)	τ_3 (μ s) (%)
Ex = 370 nm Em = 530 nm	1.097	1.193	1.019	1.036	1.185	1.145	1.122	χ^2
	1.54 (39.81)	1.56 (26.52)	1.40 (35.53)	1.47 (41.29)	1.30 (44.40)	1.18 (44.61)	1.40 (44.89)	τ_1 (μ s) (%)
	11.12 (49.82)	7.87 (43.21)	10.37 (60.80)	9.46 (53.14)	7.11 (27.43)	7.33 (40.73)	7.32 (53.26)	τ_2 (μ s) (%)
	22.35 (10.36)	17.53 (30.27)	24.57 (3.68)	19.26 (5.57)	11.79 (28.17)	13.26 (14.66)	25.77 (1.85)	τ_3 (μ s) (%)
Ex = 370 nm Em = 700 nm	1.227	1.376	1.505	1.220	1.164	1.384	1.054	χ^2
	1.85 (24.11)	2.07 (17.50)	1.66 (18.08)	1.54 (23.35)	1.58 (23.64)	1.89 (22.40)	2.43 (34.69)	τ_1 (μ s) (%)
	11.65 (67.29)	10.89 (67.52)	10.55 (32.66)	9.60 (50.76)	9.19 (39.30)	8.14 (37.20)	7.55 (63.92)	τ_2 (μ s) (%)
	29.78 (8.60)	28.02 (14.98)	24.61 (19.26)	20.26 (25.89)	16.62 (37.06)	12.54 (40.40)	21.37 (1.38)	τ_3 (μ s) (%)
Ex = 270 nm Em = 530 nm	1.058	1.012	1.015	1.046	1.027	1.189	1.035	χ^2
	1.08 (48.00)	0.99 (41.87)	1.06 (48.35)	1.09 (54.48)	1.04 (56.61)	0.99 (58.66)	0.93 (54.03)	τ_1 (μ s) (%)
	6.57 (33.12)	5.38 (38.29)	5.82 (35.34)	6.08 (35.61)	5.56 (32.03)	5.74 (33.56)	5.82 (44.39)	τ_2 (μ s) (%)
	17.06 (18.87)	15.69 (19.83)	14.84 (16.32)	15.45 (9.91)	13.24 (11.36)	13.90 (7.78)	27.66 (1.58)	τ_3 (μ s) (%)