

Supporting Information

Thermally induced transformation of Cu₄I₄-based cluster to Cu₂I₂-based cluster under mild condition

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1. Experiment

1.1 Materials.

6,6'-dimethyl-2,2'-dipyridyl, N-bromosuccinimide(NBS), dibenzoyl peroxide(BPO), benzyl mercaptan, sodium hydroxide, CuI and $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ were purchased from commercial sources and used directly. Tetrachloromethane (CCl_4) was purified according to the standard procedures. Other solvents were commercially available and used without further purification. All reactions were performed under the atmosphere of argon using Schlenk techniques.

1.2 Synthesis

1.2.1 Synthesis of 6,6'-bis(bromomethyl)-2,2'-bipyridine

This compound was prepared according to a modified version of the procedure reported by Beves et al [1]. 6,6'-Dimethyl-2,2'-dipyridyl (2.00 g, 11.0 mmol), NBS (3.90 g, 22.0 mmol), and 150 mL of dry CCl_4 were mixed in a 250 mL flask and heated to 80 °C for 30 min under argon atmosphere. After BPO (44.0mg, 0.09 mmol) was added, the reaction mixture was further refluxed for 12 h. Subsequently, the reaction mixture was filtered, and the filtrate was dried in *vacuo*. The product was purified by recrystallization from CCl_4/MeOH . Yield: 1.60g (63%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.40 (d, 2H, J=8 Hz, Ar-H), 7.84 (d, 2H, J=8 Hz, Ar-H), 7.49 (t, 2H, J=8 Hz, Ar-H), 4.65 (s, 4H, CH_2). Elemental Analysis calcd (%) for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{Br}_2$: C 42.14, H 2.95, N 8.19; found: C 42.19, H 2.93, N 8.10.

1.2.2 Synthesis of 6,6'-bis((benzylthio)methyl)-2,2'-bipyridine (L)

This ligand **L** was prepared according to a modified literature procedure [2]. To a solution containing benzyl mercaptan (363.0 mg, 2.92 mmol) and sodium hydroxide (116.0mg, 2.92 mmol) in 20ml ethanol, 6,6'-bis(bromomethyl)-2,2'-bipyridine (0.5 g, 1.46 mmol) was added and the mixture was stirred for 30 min. Then the solution was allowed to stir at 85 °C for 12h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was extracted with dichloromethane and washed with water. After an evaporation of the solvent, crude product was collected as white solid. Yield: 0.37g (60.0%). ^1H NMR (CDCl_3 , 400 MHz): δ 8.37 (d, 2H, J = 4 Hz, Ar-H), 7.80 (t, 2H, J = 8 Hz, Ar-H), 7.39 (t, 6H, J = 4 Hz, Ar-H), 7.32 (t, 6H, J = 8 Hz, Ar-H), 3.84 (s, 4H, Bpy- CH_2), 3.77 (s, 4H, Ar- CH_2). Elemental Analysis calcd (%) for

C₂₆H₂₄N₂S₂: C 72.86, H 5.64, N 6.54; found: C 72.83, H 5.65, N 6.58.

1.2.3 Synthesis of compound 1

0.5 mL CH₂Cl₂ solution of **L** (20.0 mg, 0.047 mmol) was added to 3 mL CH₃CN solution of CuI (17.9 mg, 0.094 mmol). This solution was undisturbedly kept at room temperature, and the yellow-orange crystal appeared after 2 days. Yield: 22.7 mg (59.9%). Elemental Analysis calcd (%) for C₅₄H₅₂N₄S₄Cl₄Cu₄I₄: C 36.26, H 2.93, N 3.13; found: C 36.86, H 3.00, N 3.21.

1.2.4 Synthesis of compound 2

A mixture of CuI (17.9 mg, 0.094 mmol), **L** (20.0 mg, 0.047 mmol), and acetonitrile (5 mL) were stirred for 10 min. The suspension was then transferred into a glass flask and kept in 55 °C. The deep red crystals appeared after several days. The other solvents that we used such as methanol, ethanol, acetone, DMF, DMA, DMSO and benzonitrile could not trigger the transformation under the same reaction condition as acetonitrile. Yield: 21.8 mg (57.7%). Interestingly, compound **2** can also be obtained by keeping solid **1** in acetonitrile at 55°C for 1-2 weeks, during which the deep red crystals appeared. Elemental Analysis calcd (%) for C₅₂H₄₈N₄S₄Cu₄I₄: C 38.58, H 2.99, N 3.46; found: C 38.82, H 3.02, N 3.52.

1.3 Physical measurements

¹H-NMR spectra was recorded on a Bruker AV 400 instrument. Chemical shifts were reported in parts per million (ppm) from TMS with the solvent resonance as internal standard. Excitation and emission spectra were recorded on a Jasco FP-6500 at room temperature. Elemental analysis (C, H, N) was measured on a Perkin-Elmer elemental analyser.

1.4 X-ray structure determinations

The crystal data for compounds **1** and **2** were collected on BL17B at the Shanghai Synchrotron Radiation Facility (SSRF) (Shanghai, China) and processed with HKL3000. The structures were solved by direct methods and refined by full-matrix least squares using the SHELXTL crystallographic software package [3]. Anisotropic displacement parameters were applied to all non-hydrogen atoms. In all the cases, hydrogen atoms were placed in calculated positions and

allowed to ride on their parent atoms. Crystal data for compounds **1** and **2** are listed in Table S1.

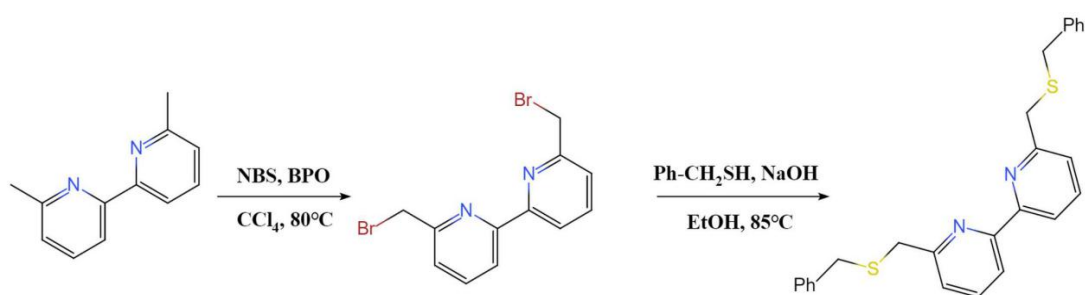
Table S1 Crystal data and collection parameters for compounds **1** and **2**.

	1	2
Empirical formula	C ₅₄ H ₅₂ Cl ₄ Cu ₄ I ₄ N ₄ S ₄	C ₅₂ H ₄₈ Cu ₄ I ₄ N ₄ S ₄
Formula weight	1788.84	1570.60
Temperature/K	100K	293K
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	10.284(2)	10.0310(9)
<i>b</i> /Å	11.994(2)	10.9399(10)
<i>c</i> /Å	13.416(3)	14.2340(12)
α /°	78.78(3)	85.488(2)
β /°	75.53(3)	70.252(2)
γ /°	65.58(3)	73.990(2)
Volume/Å ³	1451.2(6)	1412.9(2)
<i>Z</i>	1	1
<i>D</i> _x ,g/cm ³	2.047	1.846
μ /mm ⁻¹	3.943	3.855
<i>F</i> (000)	864.0	780.0
Crystal size/mm ³	0.22 × 0.2 × 0.15	0.15 × 0.1 × 0.08
Independent reflections	4993 [<i>R</i> _{int} = 0.058]	6472 [<i>R</i> _{int} = 0.0150]
GoF	1.001	1.028
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0525, <i>wR</i> ₂ = 0.1574	<i>R</i> ₁ = 0.0244, <i>wR</i> ₂ = 0.0532
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0525, <i>wR</i> ₂ = 0.1574	<i>R</i> ₁ = 0.0333, <i>wR</i> ₂ = 0.0567

1.5 Computational Detail:

All density functional theory calculations were performed in the Gaussian 16 software[1] with the theoretical level of B3LYP-D3BJ method, together with the effective core potential basic set of LANL2DZ (for Cu and I elements) and all-electron basic set of 6-31G(d) for other elements. Time-dependent DFT calculations were further conducted. The first excite state were also optimized and result in the emission energy by the formula: $\Delta E = E_E^{ES}(Q_0^{ES}) - E_{NE}^{GS}(Q_0^{ES})$. $E_E^{ES}(Q_0^{ES})$ is the energy of excite state with equilibrium status at the relaxed excite-state geometry, $E_{NE}^{GS}(Q_0^{ES})$ is the energy of the ground state with non-equilibrium status at the relaxed excite-state geometry.

2. Scheme S1. Synthetic route to L



Scheme S1. Synthetic route to L

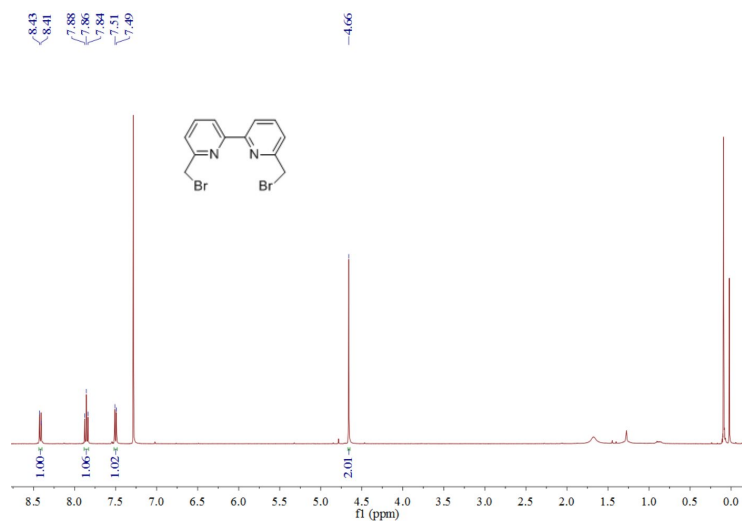


Fig. S1-1. $^1\text{H-NMR}$ spectrum for 6,6'-bis(bromomethyl)-2,2'-bipyridine

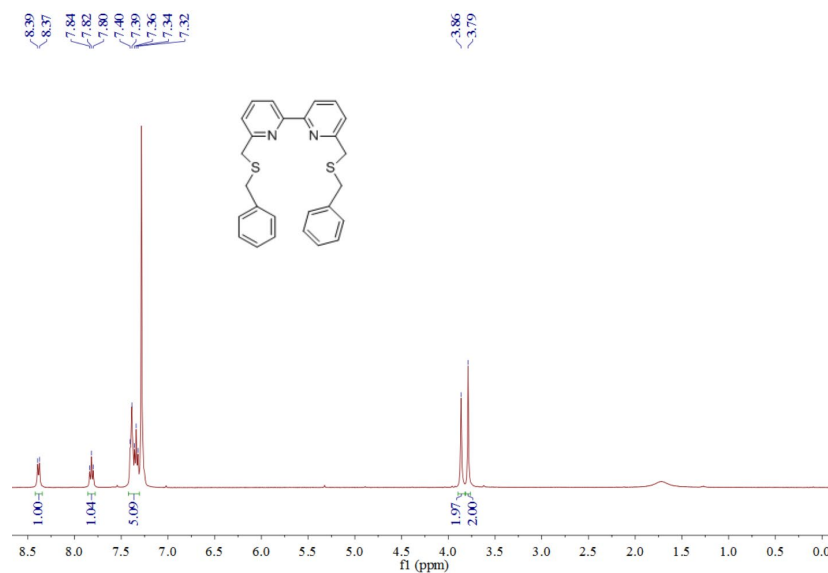
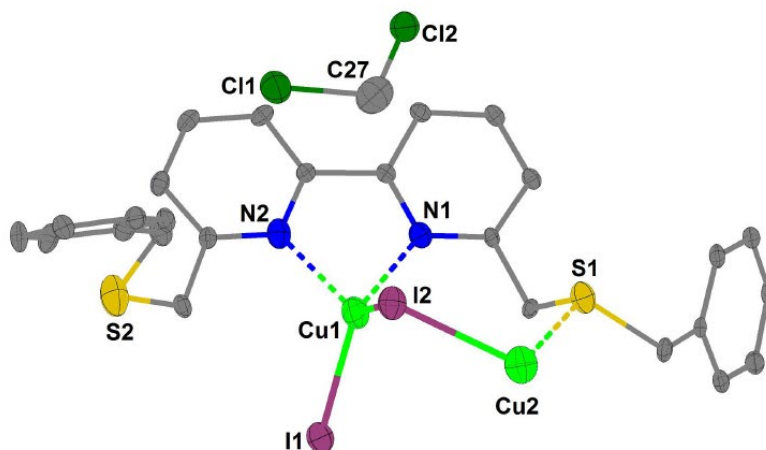


Fig. S1-2. $^1\text{H-NMR}$ spectrum for 6,6'-bis(bromomethyl)-2,2'-bipyridine

3. Figure S2. Asymmetric unit of **1**



4. Transformation of 1 to 2.

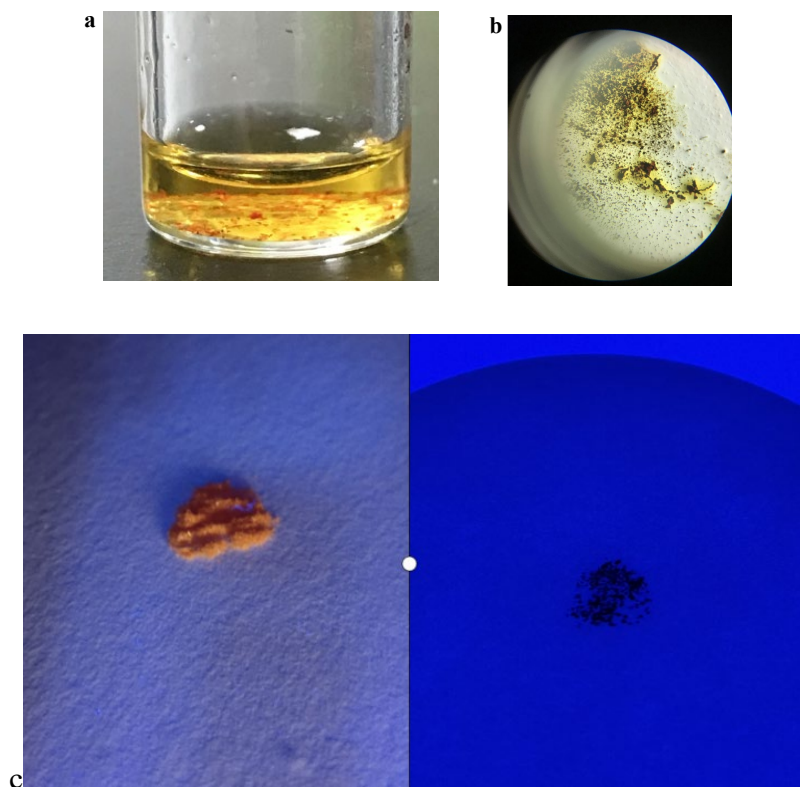


Figure S3. (a) Crystals of **1** before heating at 328K; (b) Crystals viewed from the bottom of the vial after heating for two weeks; (c) photo of two samples under UV light.

5.

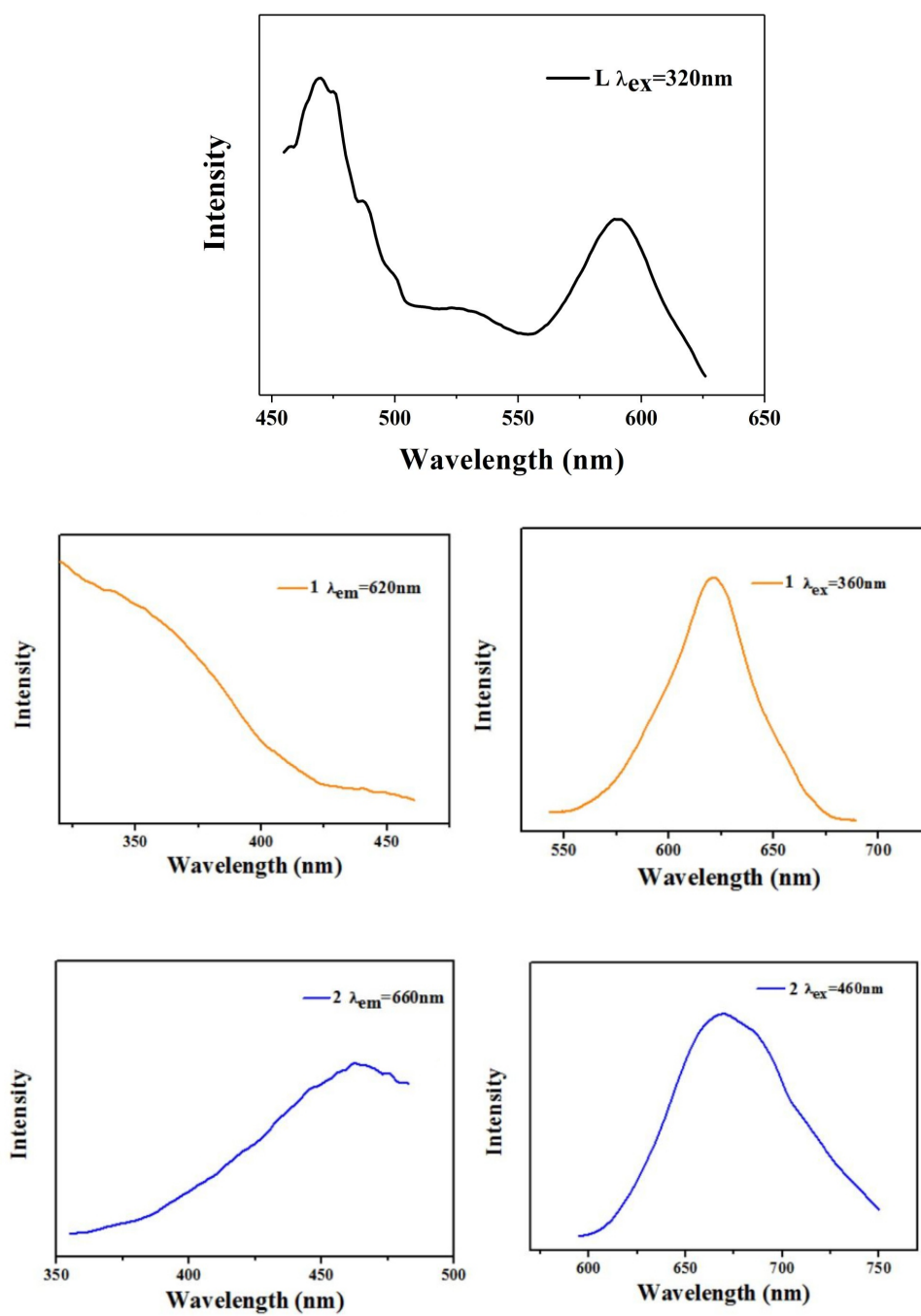


Fig. S4. Solid-state emission spectrum for L, 1 and 2 at room temperature.

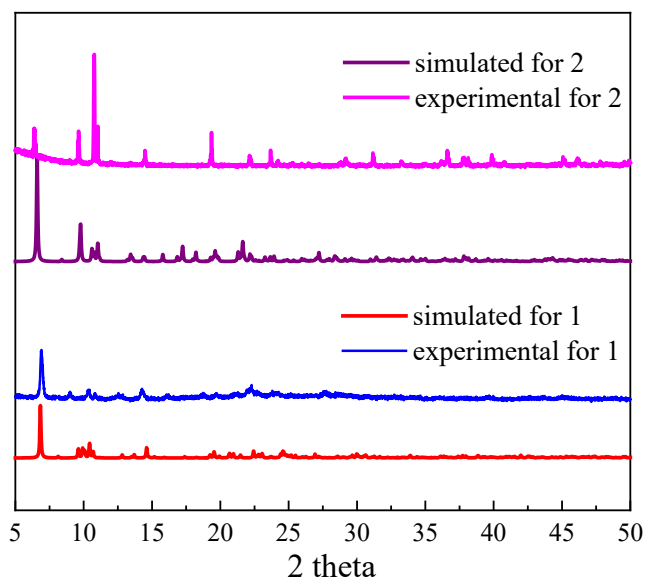


Fig. S5 XRD pattern of two solid sample of **1** and **2**

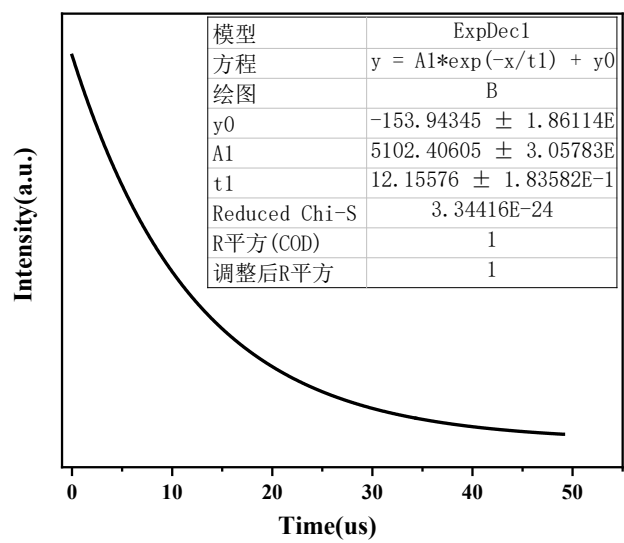


Fig.S6 Emission decay of **1**

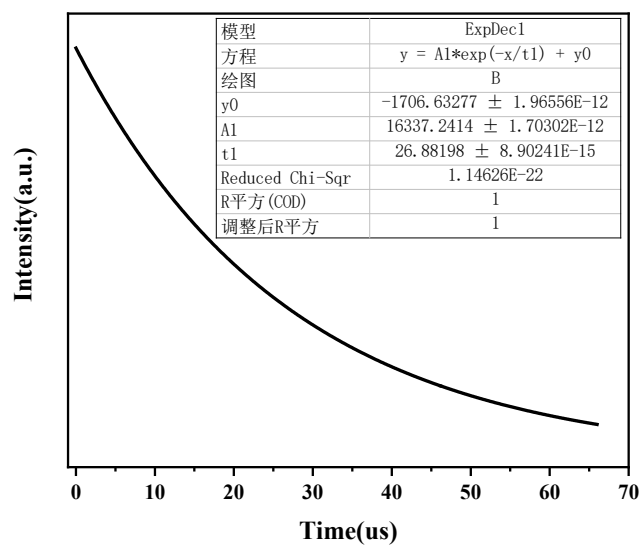
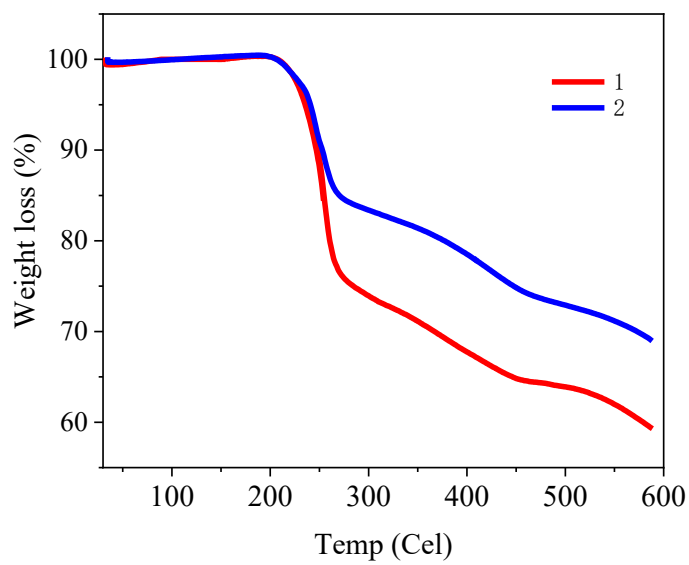


Fig.S7 Emission decay of 2



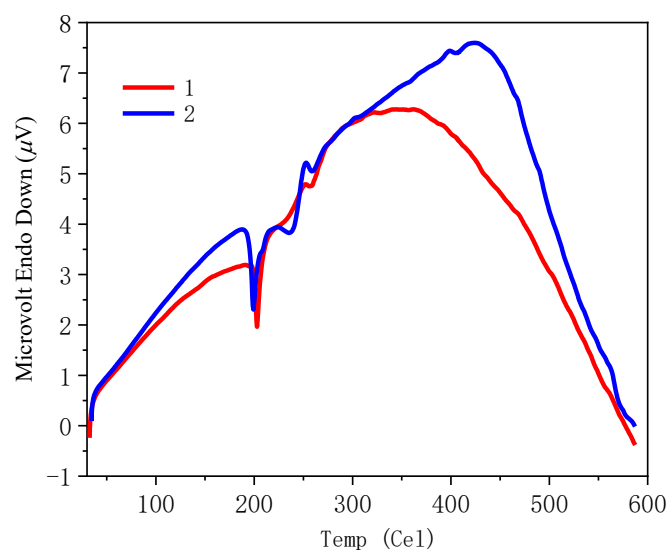


Fig.S8 TGA curves and DTA curves of 1 and 2

6.

Table S2. Energy level of frontier molecular orbital in the ground state.

Orbital	1	2
LUMO+3	-1.333	-1.258
LUMO+2	-1.336	-1.259
LUMO+1	-1.997	-1.917
LUMO	-1.998	-1.918
HOMO	-4.968	-4.732
HOMO-1	-5.075	-4.776
HOMO-2	-5.076	-4.977
HOMO-3	-5.186	-4.993
gap	2.970	2.814

Table S3. Oscillator strengths and transitions of the peaks from experiment and TD-DFT calculations

$\lambda_{\text{Exp}}/\text{nm}$	$\lambda_{\text{DFT}}/\text{nm}$	f_{osc}	Transitions
1			
360	526.28	0.0036	HOMO-6→LUMO (15%) HOMO →LUMO+1 (52%)
	500.53	0.0052	HOMO-4→LUMO (40%) HOMO-4→LUMO (35%) HOMO→LUMO+1(20)
	489.94	0.0394	HOMO→LUMO+1 (33%) HOMO-1→LUMO (45%) HOMO-2→LUMO (35%)
	463.51	0.0080	HOMO-2→LUMO(46%) HOMO→LUMO+1(19%)
2			
460	590.43	0.0015	HOMO→LUMO(49%) HOMO-6→LUMO(16%)
	495.57	0.0387	HOMO-3→LUMO(51%) HOMO-4→LUMO+1(41%)
	482.57	0.0025	HOMO-5→LUMO(54%) HOMO-7→LUMO+1(30%)

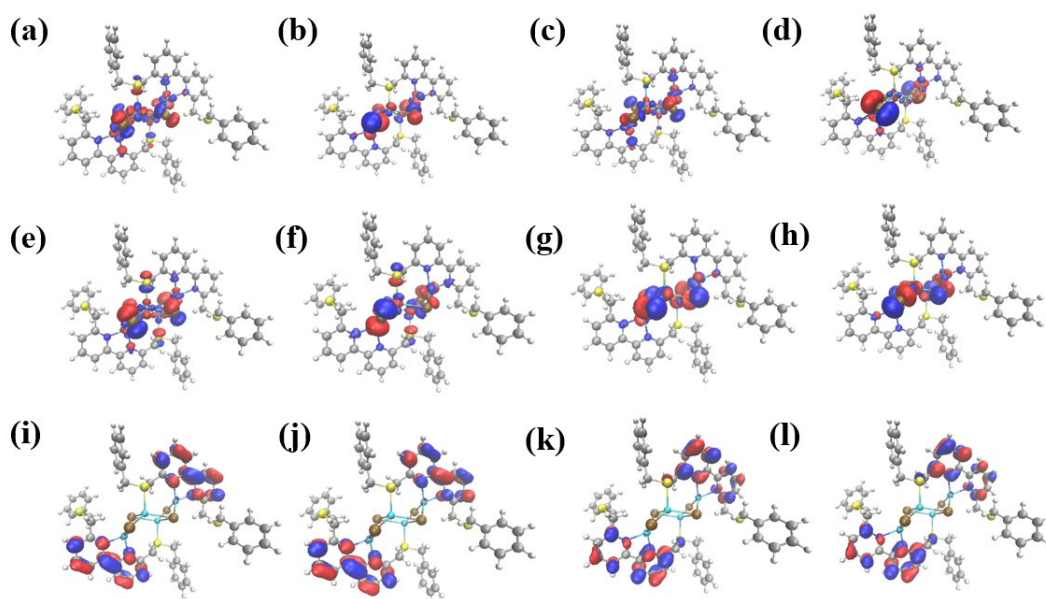


Figure S9. frontier molecular orbitals of **1**: HOMO-7(a), HOMO-6(b), HOMO-5(c), HOMO-4(d), HOMO-3I, HOMO-2(f), HOMO-1(g), HOMO(h), LUMO(i), LUMO+1(j), LUMO+2(k) and LUMO+3(l)

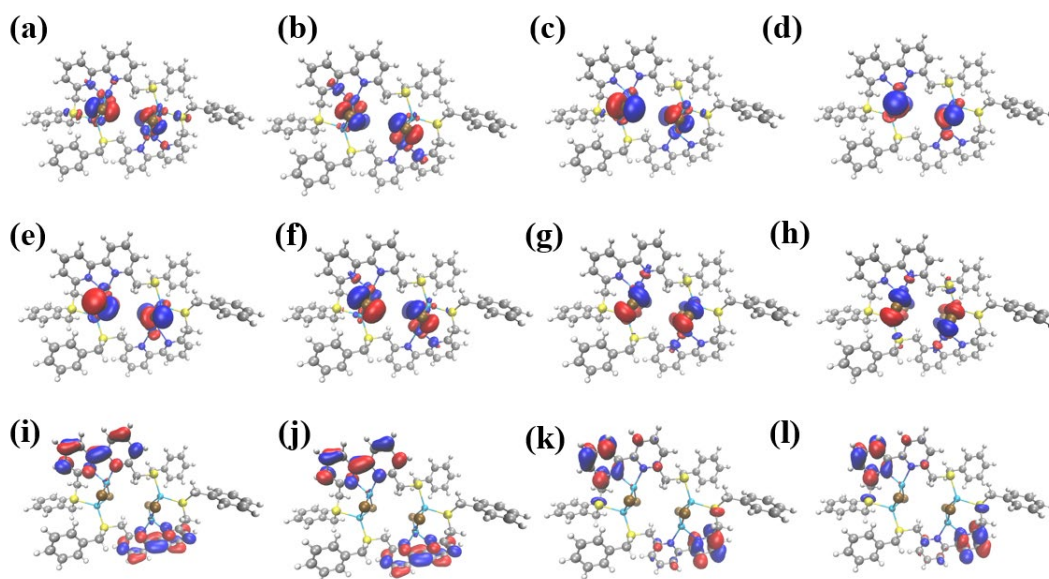


Figure S10. frontier molecular orbitals of **2**: HOMO-7(a), HOMO-6(b), HOMO-5(c), HOMO-4(d), HOMO-3I, HOMO-2(f), HOMO-1(g), HOMO(h), LUMO(i), LUMO+1(j), LUMO+2(k) and LUMO+3(l)

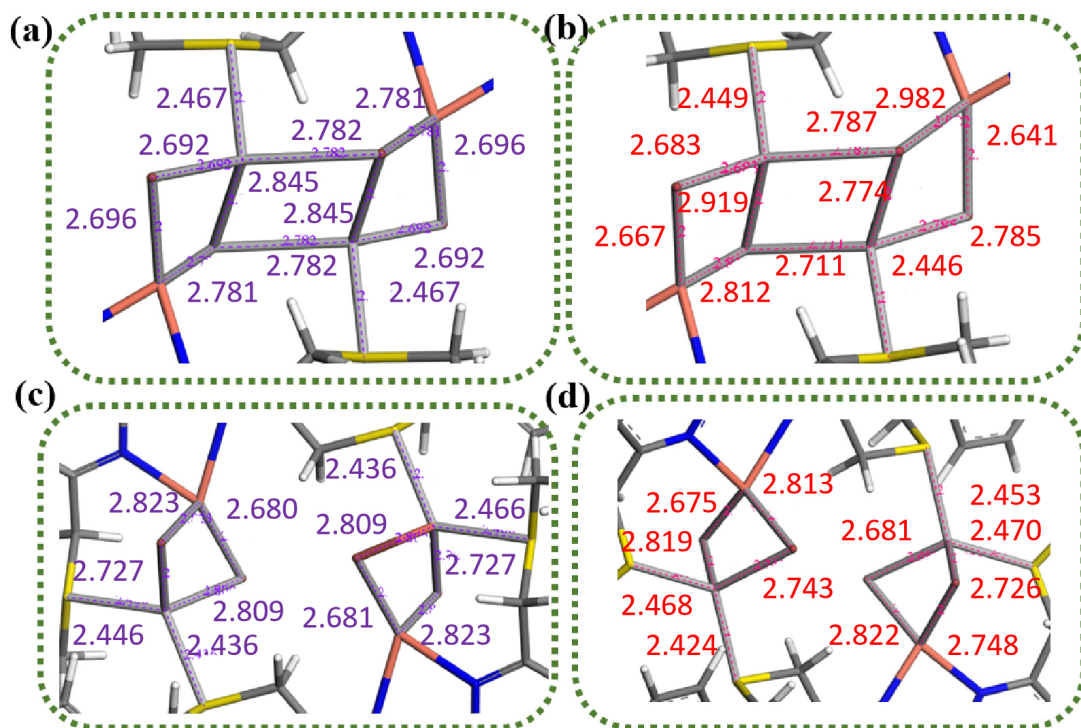


Figure S11. the selective bond of ground state (a for 1 and c for 2) and 1st excite state (b for 1 and d for 2)

References:

1. J. E. Beves, C. J. Campbell, D. A. Leigh, R. G. Pritchard, *Angew. Chem. Int. Ed.*, 2013, **52**, 6464.
2. A. Bonnot, F. Juvenal, A. Lapprand, D. Fortin, M. Knorr, P. D. Harvey, *Dalton. Trans.*, 2016, **45**, 11413.
3. G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Germany, 1997.