

Supporting Information

**Isolation and Studies of Thioether-functionalized Pyrazole Derived
Cu(I)-based Cyclic Trinuclear Complex and Its Coordination
Polymers with [Cu₂I₂] and [BiBr₃] Nodes**

Zhi-Qing Lin,[‡] Sai-Li Zheng,[‡] Jieying Hu, Hua-Qun Zhou, Zihao Feng, Yonghe He,
Lai-Hon Chung*, Jun He*

*School of Chemical Engineering and Light Industry, Guangdong University of
Technology, Guangzhou 510006, Guangdong, China*

* Corresponding author.

[‡] These authors contributed equally to this work.

E-mail: laihonchung@gdut.edu.cn; junhe@gdut.edu.cn

Table of Contents

1. Experimental details	4
2. MOF syntheses	6
3. Crystallographic data	7
Table S1. Crystallographic data for the 1 , 2 and 3	7
Table S2. Selected bond lengths (Å) and bond angles (°) for 1	8
Table S3. Selected bond lengths (Å) and bond angles (°) for 2	8
Table S4. Selected bond lengths (Å) and bond angles (°) for 3	9
4. Additional Figures	9
Fig. S1 The synthetic route for 1	9
Fig. S2 The ¹ H NMR spectrum of compound HL in CDCl ₃	10
Fig. S3 The ¹³ C NMR spectrum of compound HL in CDCl ₃	10
Fig. S4 The ¹ H NMR spectrum of (a) 1 in CDCl ₃ and (b) the same sample standing for two days.	11
Fig. S5 The ¹³ C NMR spectrum of 1 in CDCl ₃	11
Fig. S6 Photographs of an as-made sample of 1 (a) under ambient light and (b) in dark upon 365-nm UV irradiation.	12
Fig. S7 PXRD patterns (Cu Kα, λ = 1.5418 Å) of (a) an as-made sample of 1 ; (b) a simulation from the single crystal structure of 1 .	12
Fig. S8 The FT-IR spectra of (a) the ligand HL, (b) an as-made sample of 1 , (c) an as-made sample of 2 .	13
Fig. S9 PXRD patterns (Cu Kα, λ = 1.5418 Å) of (a) an as-made sample of 2 ; (b) a simulation from the single crystal structure of 2 .	13
Fig. S10 Photographs of an as-made sample of 2 (a) under ambient light and (b) in dark upon 365-nm UV irradiation.	14
Fig. S11 Complex 1 shown by ORTEP diagram of 50% probability with H atoms omitted for clarity (Copper: orchid; Nitrogen: blue; Carbon: grey; Sulfur: orange).	14
Fig. S12 The asymmetric unit of 2 shown by ORTEP diagram of 50% probability with H atoms omitted for clarity (Copper: orchid; Nitrogen: blue; Carbon: grey; Sulfur: orange; Iodine: sea	

green).	15
Fig. S13 The asymmetric unit of 3 shown by ORTEP diagram of 50% probability with H atoms omitted for clarity (Copper: orchid; Nitrogen: blue; Carbon: grey; Sulfur: orange; Bismuth: dark purple; Bromine: brown).	15
Fig. S14 Room temperature emission spectra of 1 in the solid state ($\lambda_{\text{ex}} = 300\text{--}380$ nm).	16
Fig. S15 Room temperature excitation spectra of 1 in the solid state ($\lambda_{\text{em}} = 630$ and 660 nm for a and b).	16
Fig. S16 Room temperature emission spectra of (a) the ligand HL in the solid state ($\lambda_{\text{ex}} = 330$ nm) (b) HL in CHCl_3 , $[\text{HL}] = 2$ mg/mL ($\lambda_{\text{ex}} = 330$ nm).	17
Fig. S17 Room temperature emission spectra of 1 in CHCl_3 , ($\lambda_{\text{ex}} = 390$ nm for [1] of 10, 5, 2.5 mg/mL).	17
Fig. S18 Room temperature excitation spectra of 2 in the solid state ($\lambda_{\text{em}} = 620$ and 650 nm for a and b).	18
5. References	18

1. Experimental details

General procedure. Starting materials, reagents, and solvents were purchased from commercial sources (J&K, Aldrich and Acros) and used without further purification. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer, with working frequencies of 400 MHz for ^1H and 100 MHz for ^{13}C nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents, with tetramethylsilane (TMS) as the internal standard. Powder X-ray diffraction data were collected in reflection mode at room temperature on a Rigaku Smart Lab diffractometer with mixture of Cu-K α 1 ($\lambda = 1.54056\text{\AA}$) and Cu-K α 2 ($\lambda = 1.5418\text{\AA}$) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA. Fluorescence emission spectra were obtained with a FluoroMax-4 fluorescence photometer. Excited state lifetime of **1** and **2** were obtained with Edinburgh FLS980 photoluminescence spectrometer. Fluorescence images were acquired with a Zeiss Observer Z1 Research Microscope.

Single crystal X-ray crystallography.

For **1**, **2**, and **3**, data collections were conducted on a Bruker AXS SMART APEX CCD system using Mo K α ($\lambda = 0.71073\text{\AA}$) radiation at 100(2) K. All absorption corrections were performed using the SADABS program. The crystals of **1**, **2**, and **3** were immediately placed into grease after removal from the mother liquors. The structures of **1**, **2**, and **3** were solved by direct methods using SHELXTL 6.14.¹ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined in the riding model. All structures were refined by full-matrix least-squares on F_o^2 using SHELXTL 6.14. ORTEP representations were drawn using ORTEP version 2020.1.² For summaries of the X-ray crystallographic data, see Tables S1 below. CCDC 2088677–2088679 corresponding to **1–3** 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/datarequest/cif.

Synthesis of 3,5-dimethyl-4-(4-(methylthio)phenyl)-1H-pyrazole (HL).

3,5-dimethyl-4-iodopyrazole (222 mg, 1.0 mmol), 4-(methylthio)phenylboronic acid (336 mg, 2.0 mmol), tetrakis(triphenylphosphine)palladium (116 mg, 0.1 mmol) and K_2CO_3 (332 mg, 2.4 mmol) were loaded into a 50-mL two-neck round-bottom flask charged with a stirring bar. The flask was evacuated and re-filled by N_2 atmosphere for three cycles and degassed mixture of toluene (20 mL) and EtOH/ H_2O (4 mL, 1:1, v:v) was then transferred into the flask via a cannula. After being stirred at 110 °C for 24 h, the mixture was cooled to room temperature and poured into water (200 mL) and extracted by ethyl acetate (3 × 50 mL). The combined organic layer was then washed by water (3 × 150 mL), dried over anhydrous $MgSO_4$, and the organic solvent was removed via rotary evaporation. The residue was further purified by column chromatography (silica gel, eluent: dichloromethane/methanol, 80:1) to afford a white solid (HL, 159 mg, yield 73 % based on 3,5-dimethyl-4-iodopyrazole). 1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 6H), 2.52 (s, 3H), 7.20-7.23 (d, 2H), 7.31-7.33 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.59, 16.01, 117.76, 126.83, 128.67, 129.73, 130.80, 132.07, 136.06, 141.76. FT-IR (KBr pellet, v/cm^{-1}): 3170.17 (s), 3130.78 (m), 3071.68 (s), 3007.66 (m), 2968.26 (m), 2923.93 (s), 1913.93 (w), 1572.91 (s), 1525.48 (s), 1427.82 (s), 1308.07 (s), 1262.73 (s), 1097.63 (s), 1045.84 (s), 1000.52 (s), 831.65 (s), 753.96 (m), 692.45 (m), 540.31 (s), 494.99(s).

Synthesis of 1. To a glass tube, $Cu(NO_3)_2 \cdot 3H_2O$ (6 mg, 0.025 mmol), HL (5 mg, 0.023 mmol) and acetonitrile/ H_2O (1.25 mL, 1:4, v:v) were added. The mixture was sonicated for 5 min to form a well-dispersed solution. Then the tube was sealed by oxyhydrogen flame and heated at 140 °C in an oven for 24 h, followed by natural cooling to room temperature, during which bulk pale yellow single crystals suitable for single-crystal X ray diffraction were formed. The freshly prepared crystals were wash by acetonitrile (2 mL × 3) and then dried in air to afford the as-made product **2** as bulk pale-yellow block

(Yield: 47%). ^1H NMR (400 MHz, CDCl_3) δ 2.27 (s, 6H), 2.52 (s, 3H), 7.16-7.18 (d, 2H), 7.28-7.30 (d, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.38, 16.11, 116.95, 126.83, 129.52, 131.50, 135.42, 146.80. FT-IR (KBr pellet, v/cm^{-1}): 3445.57 (br), 2913.75 (s), 2164.70 (w), 1893.84 (w), 1597.64 (w), 1538.90 (s), 1487.55 (s), 1425.65 (s), 1342.89 (m), 1284.94 (w), 1094.51 (s), 1033.10 (s), 1011.04 (s), 967.31 (m), 830.64 (s), 566.15 (s), 516.94 (s).

2. MOF syntheses

Crystallization of 2. To a glass tube, **1** (3 mg), CuI (6 mg, 0.03 mmol) and acetonitrile (1 mL) were added. The mixture was sonicated for 5 min to form a well-dispersed suspension. Then the tube was sealed with a Teflon cap and heated at 120 °C in an oven for 48 h, followed by natural cooling to room temperature, during which bulk greyish yellow single crystals suitable for single-crystal X ray diffraction were formed. The freshly prepared crystals were wash by acetonitrile (2 mL \times 3) and then dried in air to afford the as-made product of **2** as bulk greyish yellow block (yield of 57 % based on **1**). FT-IR (KBr pellet, v/cm^{-1}): 3445.57 (br), 2913.75 (s), 1893.84 (w), 1597.64 (w), 1538.90 (s), 1487.55 (s), 1425.65 (s), 1342.89 (m), 1284.94 (w), 1094.51 (s), 1033.10 (s), 1011.04 (s), 967.31 (m), 830.64 (s), 566.15 (s), 516.94 (s).

Crystallization of 3. To a glass tube, **1** (3 mg), BiBr_3 (5 mg) and benzene (1 mL) were added. The mixture was sonicated for 5 min to form a well-dispersed suspension. Then the tube was sealed with a Teflon cap and heated at 85 °C in an oven for 48 h, followed by natural cooling to room temperature, during which bulk orange single crystals suitable for single-crystal X ray diffraction were formed. The freshly prepared crystals were wash by acetonitrile (2 mL \times 3) and then dried in air to afford the as-made product of **3** as bulk orange block (yield of 34 % based on **1**).

3. Crystallographic data

Table S1. Crystallographic data for the **1**, **2** and **3**.

Parameter	1	2	3
Empirical formula	C ₃₆ H ₃₉ Cu ₃ N ₆ S ₃	C ₃₆ H ₃₉ Cu ₄ IN ₆ S ₃	C ₃₆ H ₃₉ Cu ₃ N ₆ S ₃ BiBr ₃
Formula weight	842.53	1055.54	1330.30
Temperature/K	100(2)	100(2)	100(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	11.7791(14)	7.768(3)	7.5245(10)
<i>b</i> /Å	24.430(3)	16.625(6)	18.260(3)
<i>c</i> /Å	25.856(3)	17.603(7)	18.341(3)
<i>α</i> /°	83.560(2)	75.602(5)	118.114(2)
<i>β</i> /°	84.781(2)	89.685(6)	91.455(2)
<i>γ</i> /°	79.452(2)	86.205(6)	93.877(2)
V/Å³	7249.8(15)	2197.1(14)	2212.9(5)
Z	8	2	2
Dc/g·cm⁻³	1.544	1.596	1.997
μ/mm⁻¹	1.952	2.788	8.272
F(000)	3456	1052.1	1282
R₁^a(I>2σ(I))	0.0718	0.0921	0.0398
wR₂^b(all data)	0.1709	0.2120	0.0899
GOF	1.015	1.030	1.059

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

Table S2. Selected bond lengths (Å) and bond angles (°) for **1**.

Cu(1)–N(1)	1.856(5)	Cu(1)–N(6)	1.855(6)
Cu(2)–N(2)	1.847(5)	Cu(2)–N(3)	1.859(5)
Cu(3)–N(4)	1.858(5)	Cu(3)–N(5)	1.854(5)
N(1)–Cu(1)–N(6)	177.4(2)	N(2)–Cu(2)–N(3)	174.7(2)
N(4)–Cu(3)–N(5)	176.2(2)		
Intramolecular Cu...Cu distance			
Cu(1)...Cu(2)	3.250	Cu(1)...Cu(3)	3.175
Cu(2)...Cu(3)	3.176	Cu(4)...Cu(5)	3.213
Cu(4)...Cu(6)	3.243	Cu(5)...Cu(6)	3.151
Intermolecular Cu...Cu distance			
Cu(1)...Cu(4)	3.212	Cu(3)...Cu(6)	3.065
Cu(2)...Cu(5)	3.170		

Table S3. Selected bond lengths (Å) and bond angles (°) for **2**.

Cu(1)–N(1)	1.888(9)	Cu(1)–N(6)	1.878(9)
Cu(2)–N(2)	1.886(10)	Cu(2)–N(3)	1.872(10)
Cu(3)–N(4)	1.879(10)	Cu(3)–N(5)	1.863(9)
Cu–S	2.328(4)–2.349(5)	Cu–I	2.606(19)–2.635(2)
N(1)–Cu(1)–N(6)	179.3(4)	N(4)–Cu(3)–N(5)	175.2(4)
N(2)–Cu(2)–N(3)	177.9(4)	S(2)–Cu(4)–S(3)	113.22(15)
I–Cu(4)–I	117.56(7)		
Intramolecular Cu...Cu distances			
Cu(1)...Cu(2)	3.256	Cu(1)...Cu(3)	3.185
Cu(2)...Cu(3)	3.232	Cu(1')...Cu(2')	3.218
Cu(1')...Cu(3')	3.226	Cu(2')...Cu(3')	3.152
Intermolecular Cu...Cu distances			
Cu(1)...Cu(2')	3.138	Cu(1')...Cu(2)	3.138

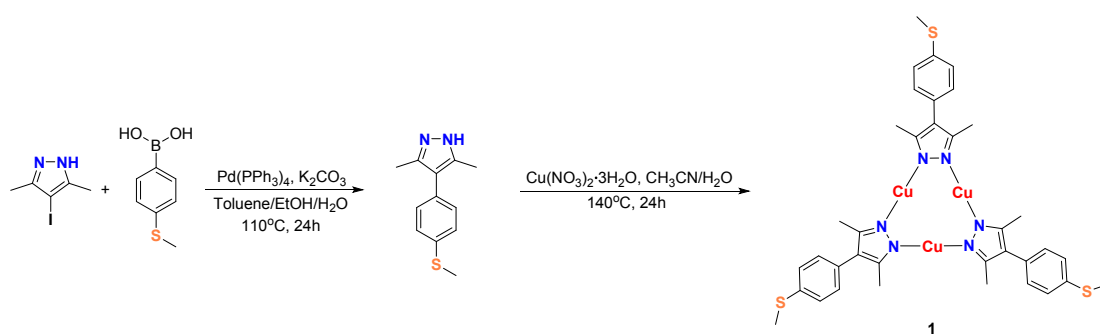
Symmetry Code: +1–x, +1–y, –z; +1+x, –y, –1+z; –1+x, +y, +1+z

Table S4. Selected bond lengths (Å) and bond angles (°) for **3**.

Cu(1)–N(1)	1.852(4)	Cu(1)–N(6)	1.861(4)
Cu(2)–N(2)	1.858(4)	Cu(2)–N(3)	1.858(4)
Cu(3)–N(4)	1.853(4)	Cu(3)–N(5)	1.851(4)
Bi–S	3.239–3.299	Bi–Br	2.6325(7)–2.6665(7)
N(1)–Cu(1)–N(6)	178.3(2)	N(2)–Cu(2)–N(3)	177.47(19)
N(4)–Cu(3)–N(5)	172.40(19)	Br–Bi–Br	92.67(2)–95.15(2)
S–Bi–S	89.58		
Intramolecular Cu...Cu distances			
Cu(1)...Cu(2)	3.286	Cu(1)...Cu(3)	3.176
Cu(2)...Cu(3)	3.170	Cu(1')...Cu(2')	3.218
Cu(1')...Cu(3')	3.226	Cu(2')...Cu(3')	3.152
Intermolecular Cu...Cu distances			
Cu(1)...Cu(2')	2.987	Cu(1')...Cu(2)	2.987

Symmetry Code: +1–x, +2–y, +1–z; –x, +2–y, +2–z

4. Additional Figures

**Fig. S1** The synthetic route for **1**.

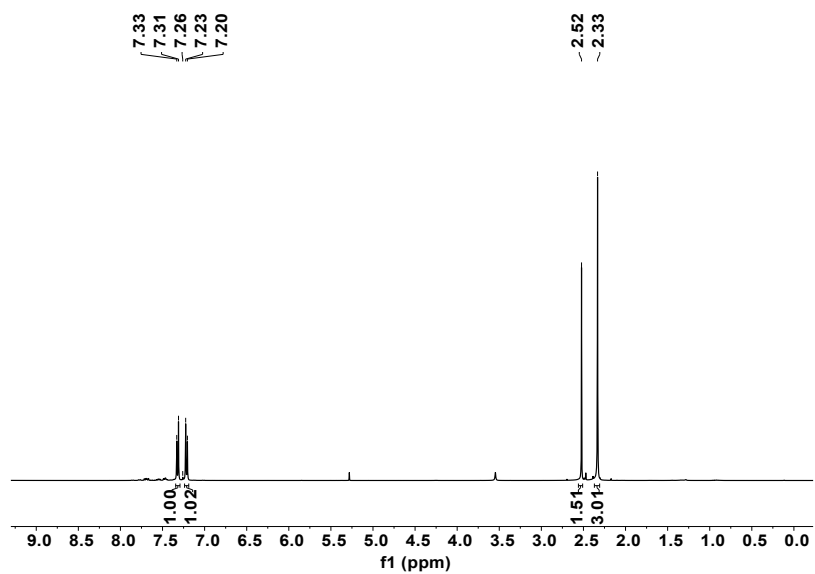


Fig. S2 The ^1H NMR spectrum of compound HL in CDCl_3 .

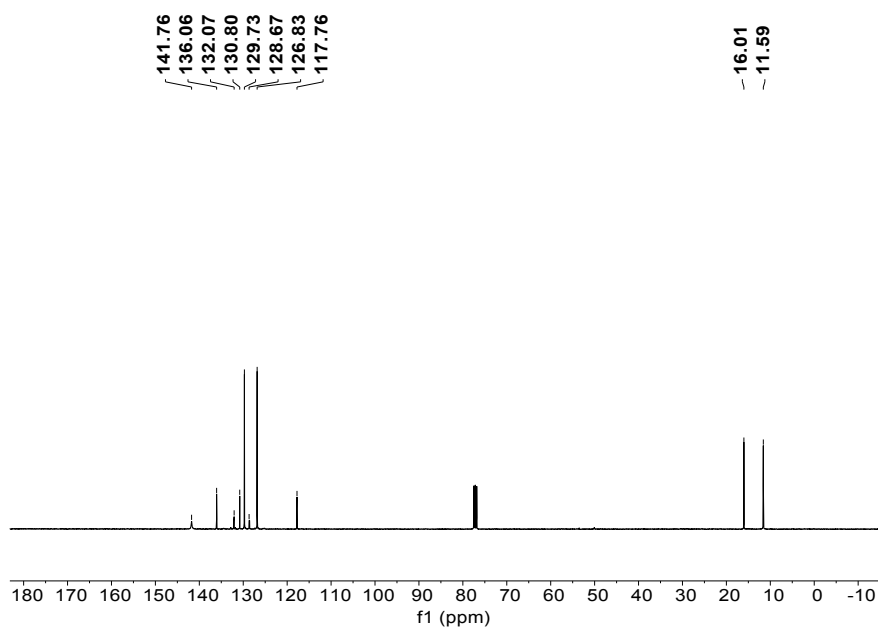


Fig. S3 The ^{13}C NMR spectrum of compound HL in CDCl_3 .

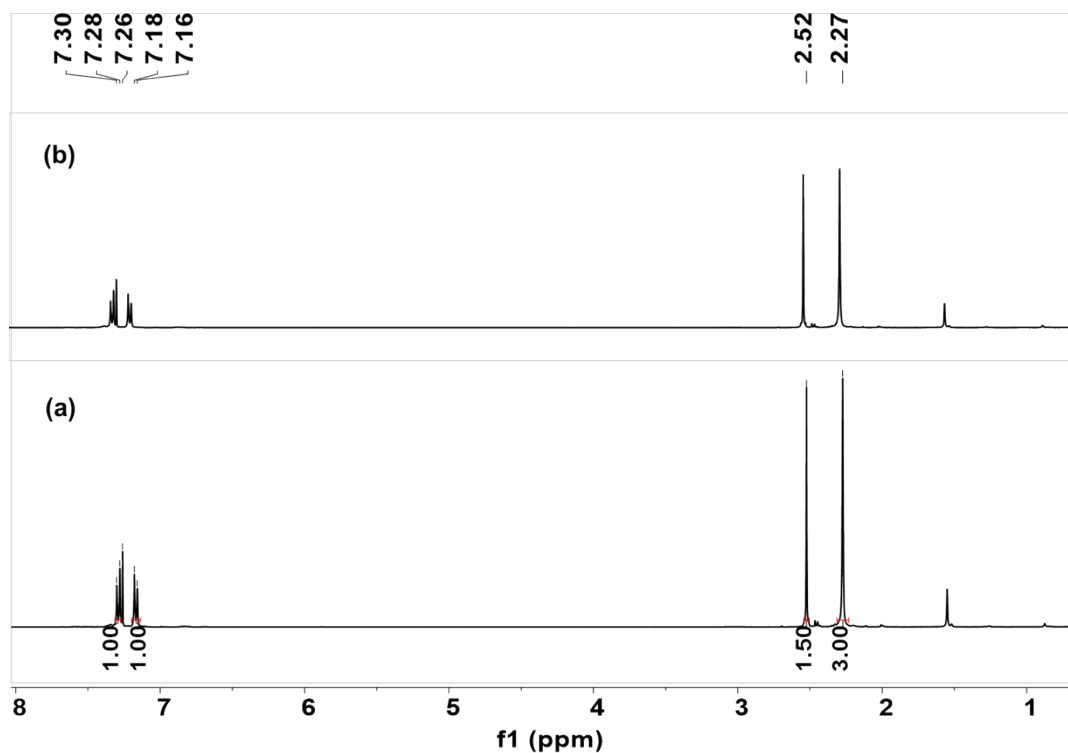


Fig. S4 The ^1H NMR spectrum of (a) **1** in CDCl_3 and (b) the same sample standing for two days.

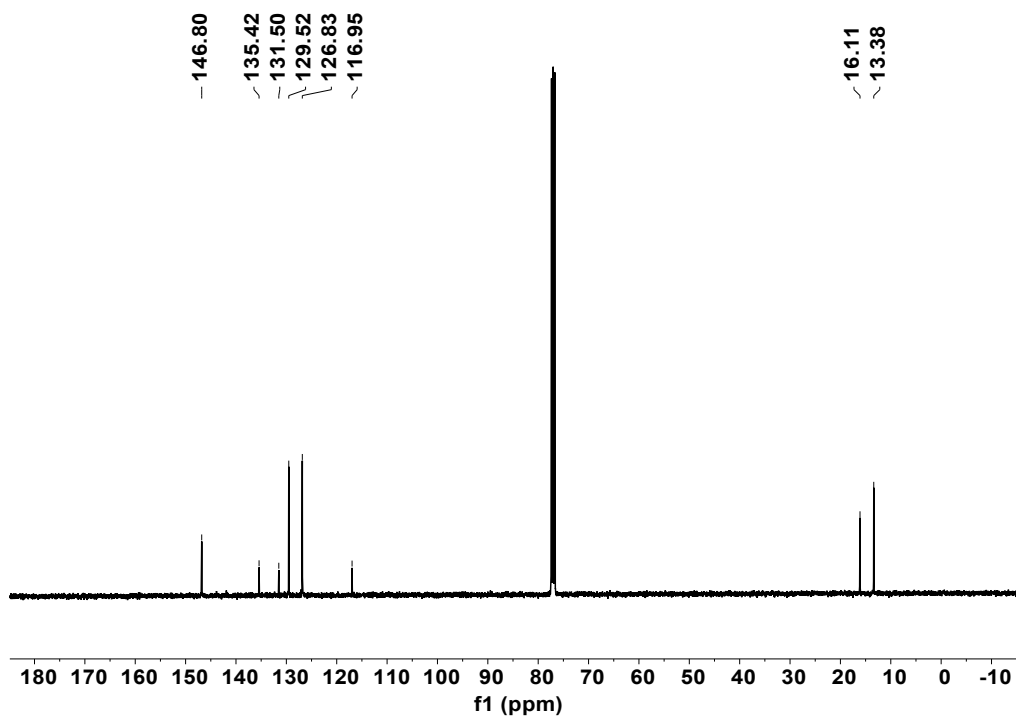


Fig. S5 The ^{13}C NMR spectrum of **1** in CDCl_3 .

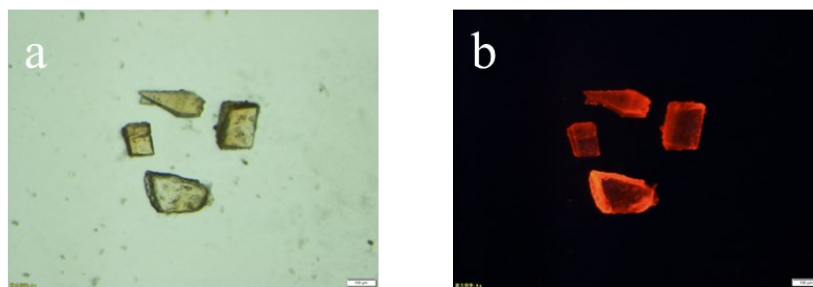


Fig. S6 Photographs of an as-made sample of **1** (a) under ambient light and (b) in dark upon 365-nm UV irradiation.

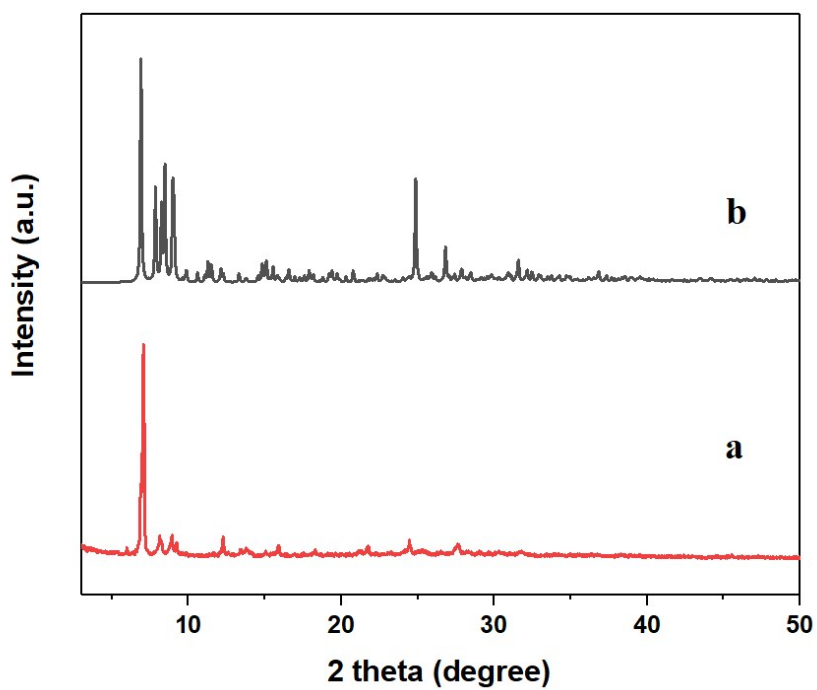


Fig. S7 PXRD patterns (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) of (a) an as-made sample of **1**; (b) a simulation from the single crystal structure of **1**.

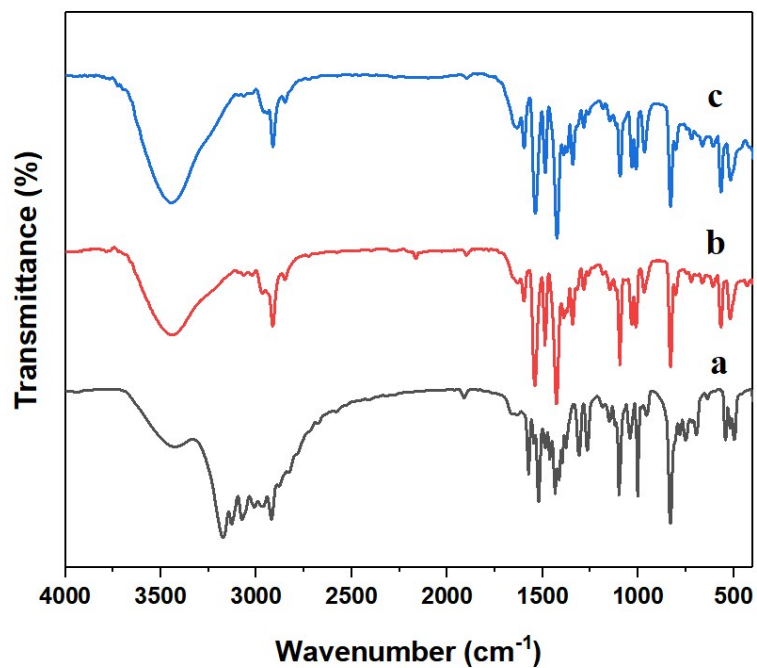


Fig. S8 The FT-IR spectra of (a) the ligand HL, (b) an as-made sample of **1**, (c) an as-made sample of **2**.

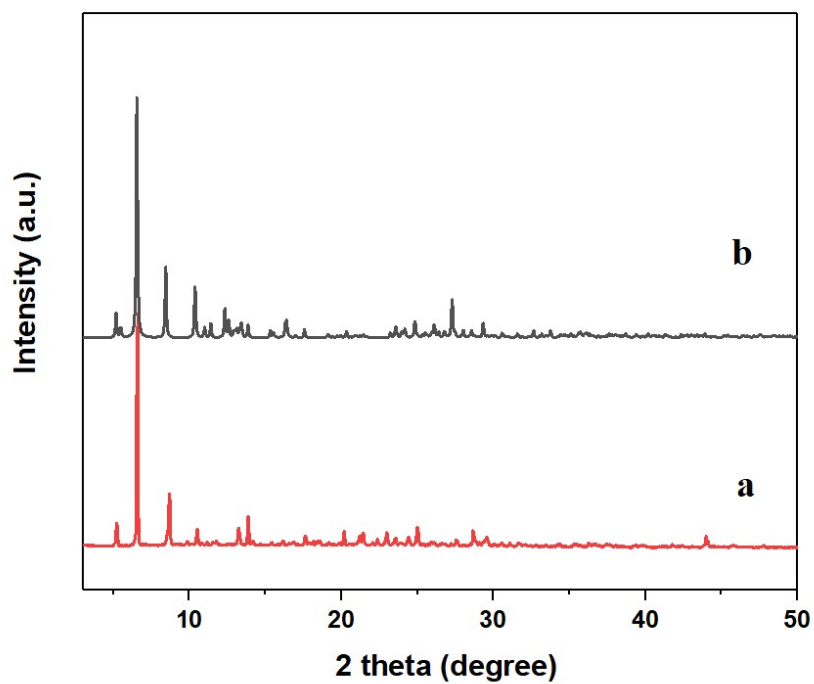


Fig. S9 PXRD patterns (Cu K α , $\lambda = 1.5418 \text{ \AA}$) of (a) an as-made sample of **2**; (b) a simulation from the single crystal structure of **2**.



Fig. S10 Photographs of an as-made sample of **2** (a) under ambient light and (b) in dark upon 365-nm UV irradiation.

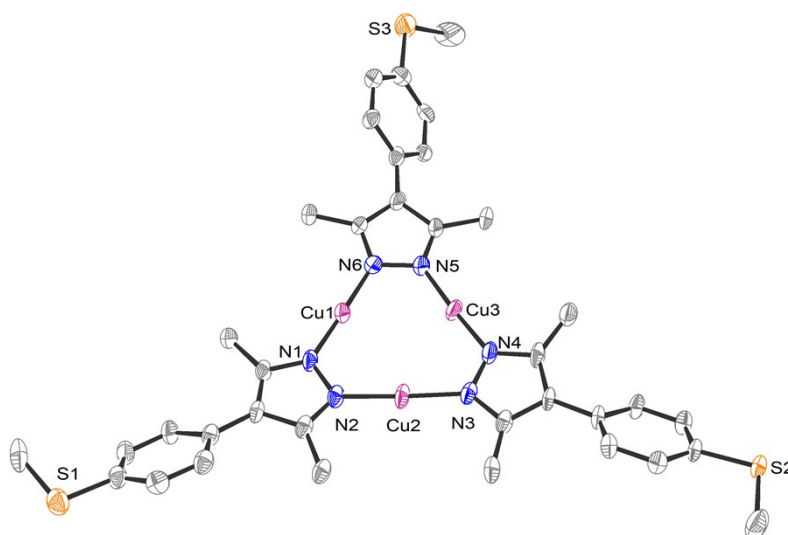


Fig. S11 Complex **1** shown by ORTEP diagram of 50% probability with H atoms omitted for clarity (Copper: orchid; Nitrogen: blue; Carbon: grey; Sulfur: orange).

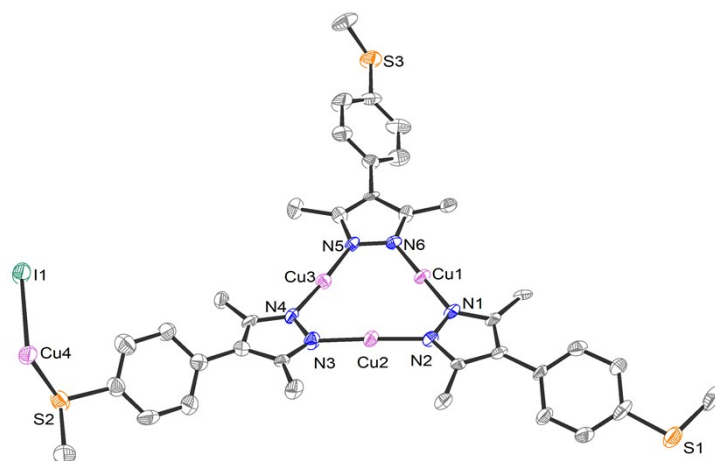


Fig. S12 The asymmetric unit of **2** shown by ORTEP diagram of 50% probability with H atoms omitted for clarity (Copper: orchid; Nitrogen: blue; Carbon: grey; Sulfur: orange; Iodine: sea green).

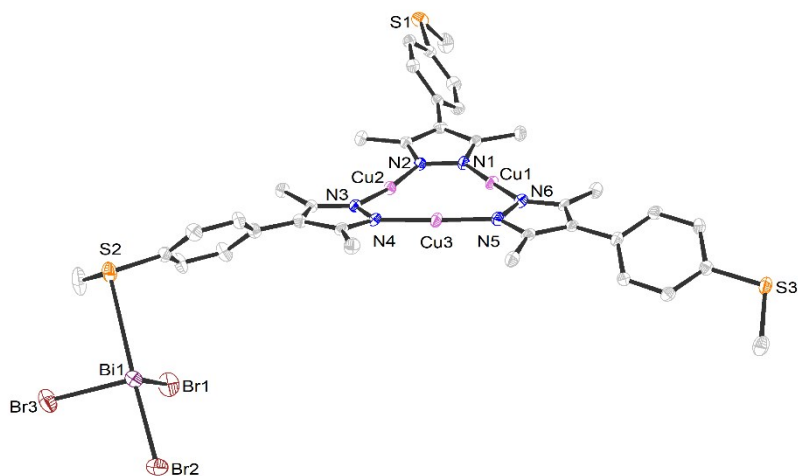


Fig. S13 The asymmetric unit of **3** shown by ORTEP diagram of 50% probability with H atoms omitted for clarity (Copper: orchid; Nitrogen: blue; Carbon: grey; Sulfur: orange; Bismuth: dark purple; Bromine: brown).

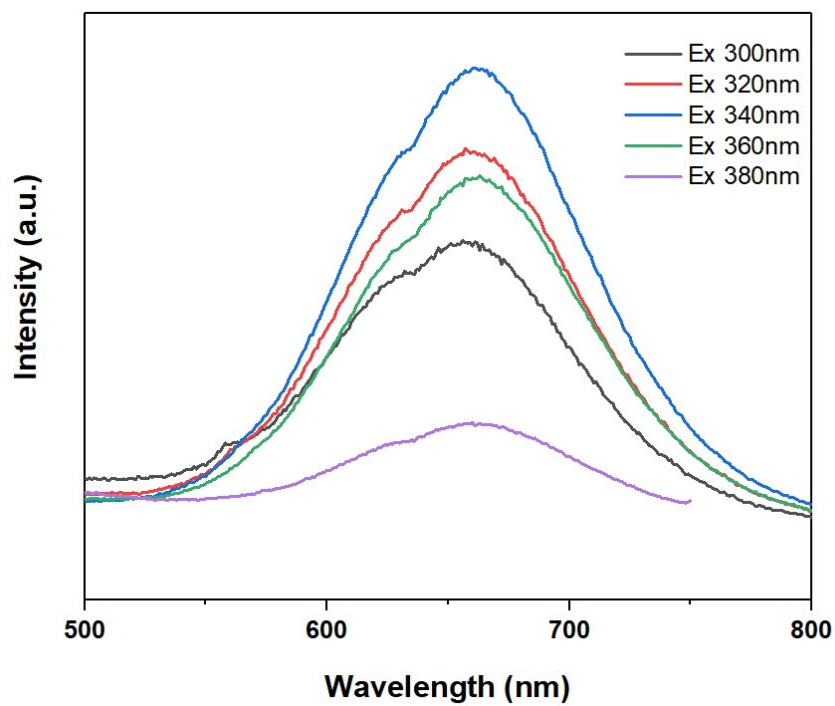


Fig. S14 Room temperature emission spectra of **1** in the solid state ($\lambda_{\text{ex}} = 300\text{--}380$ nm).

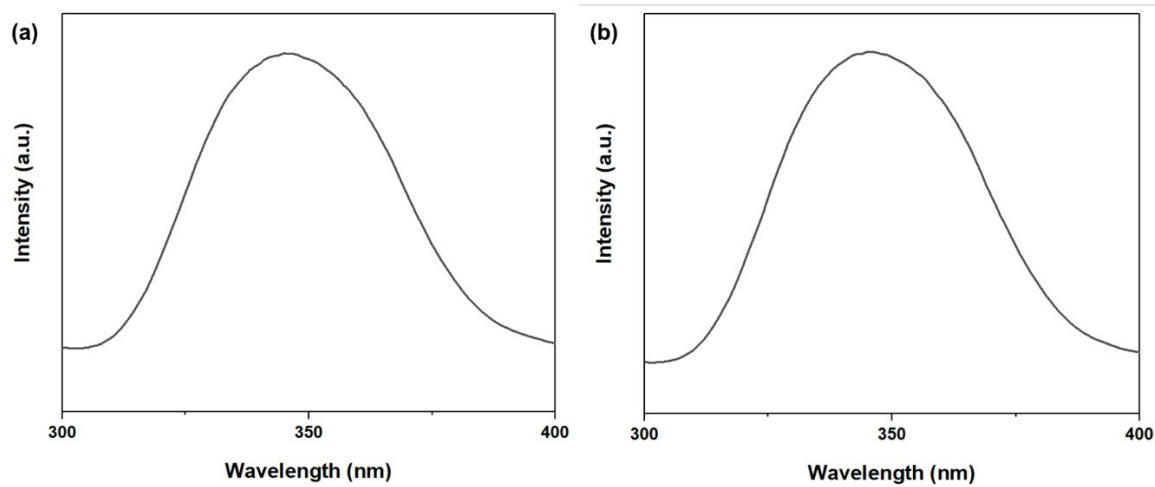


Fig. S15 Room temperature excitation spectra of **1** in the solid state ($\lambda_{\text{em}} = 630$ and 660 nm for a and b).

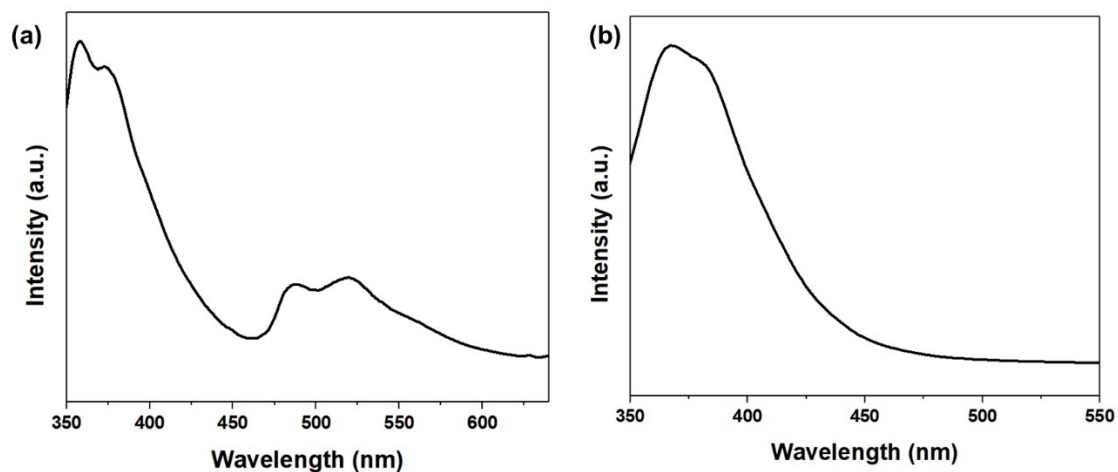


Fig. S16 Room temperature emission spectra of (a) the ligand HL in the solid state ($\lambda_{\text{ex}} = 330$ nm) (b) HL in CHCl₃, [HL] = 2 mg/mL ($\lambda_{\text{ex}} = 330$ nm).

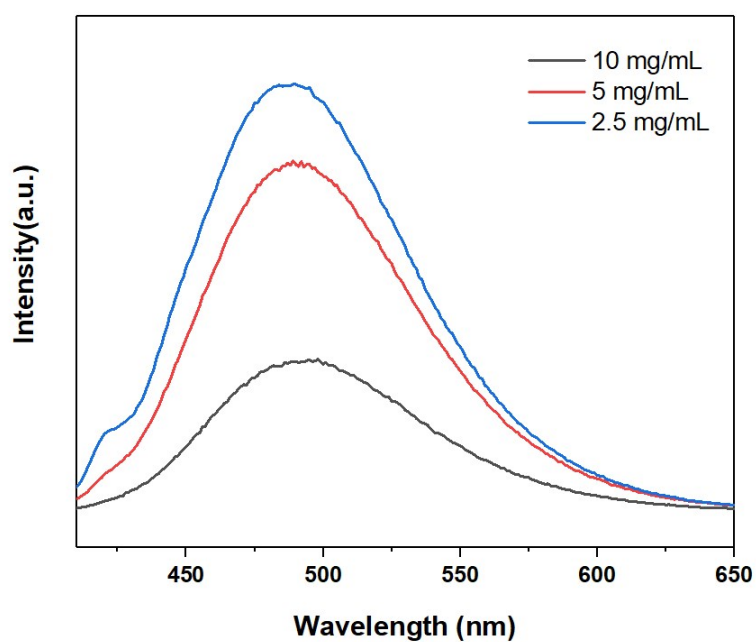


Fig. S17 Room temperature emission spectra of **1** in CHCl₃, ($\lambda_{\text{ex}} = 390$ nm for [**1**] of 10, 5, 2.5 mg/mL)

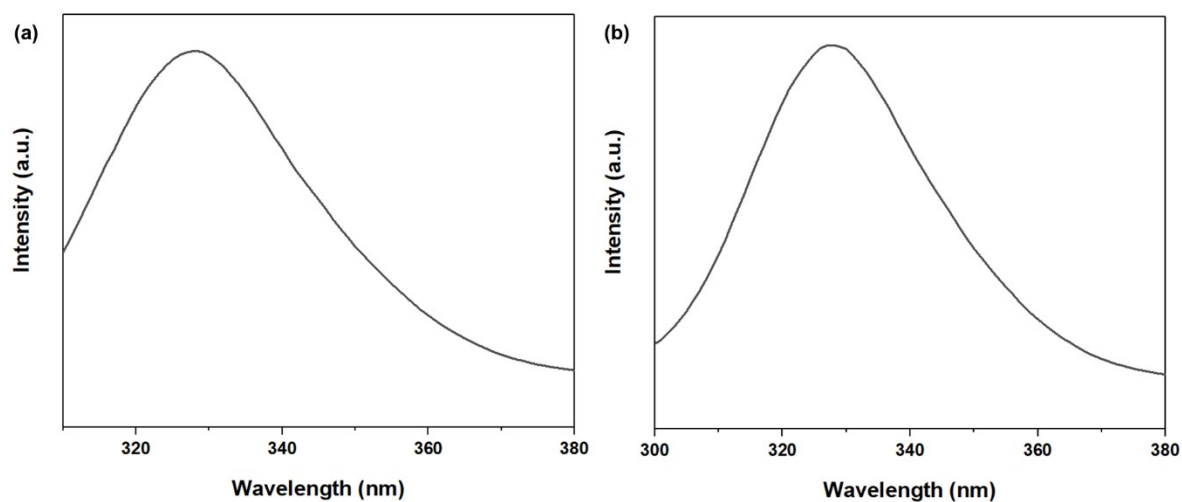


Fig. S18 Room temperature excitation spectra of **2** in the solid state ($\lambda_{\text{em}} = 620$ and 650 nm for a and b).

5. References

1. G. M. Sheldrick, SHELXTL, v. 6.14 Structure Determination Software Suite; Bruker AXS: Madison, WI, 2003.
2. L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849–854.