Supplementary Material (ESI) for CrystEngComm

Organic–Inorganic Hybrid Heterobridging Luminescent Copper(I) Polymer Exhibiting Thermochromic Behavior

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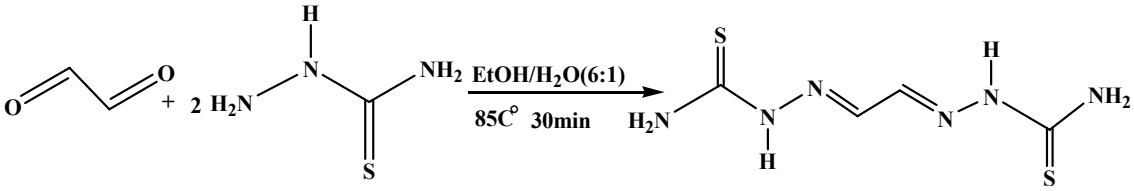
1. Experimental

1.1 Synthesis of Hgtsc

H*gtsc*(glyoxal-dithiosemicarbazone) was synthesized as reported in literature:[1]



1.2 Synthesis of $[Cu_2I_2(Hgtsc)]_n$· 2DMF (1A)

1A was synthesized by self-assembling reaction of CuI, NaI·$2H_2O$ and H*gtsc* in DMF solvent. Hgtsc (0.210g, 1.0 mmol), CuI (0.395g, 2mmol) and NaI•$2H_2O$(0.330g, 2mmol) were dissolved in 15mL DMF and stirred 20 min, and then the pH being adjusted to 4.0 by the addition of 10% HNO_3/DMF solution and continued stirring for another 1 h. The red clear solution formed was filtered and allowed to evaporate at room temperature, one week later, a kind of red crystalline product was formed yield 42% (0.31g, base on Cu). Calcd. for $C_{10}H_{24}N_8O_2S_2Cu_2I_2$ (733.41): C, 16.35; H, 3.27; N, 15.28%; found: C, 16.36; H, 3.27; N, 15.27%. IR (cm^{-1}): 3337 (m), 3005 (w), 2974(w),1634(w), 1592(s), 1515(s), 1305(m), 1083(m), 596(m).

1.3. Characterization

All the chemicals except Hgtsc were of reagent grade quality obtained from commercial sources and used without further purification. C, H, N analyses were carried out with a Vario EL III element analyzer. IR spectra were recorded on a Nicolet Co. Magna-IR 750 spectrometer with KBr pellets in the 4000–400 cm^{-1} regions. Optical diffuse reflectance spectra were measured on a

PE Lambda 35 UV-Vis spectrophotometer equipped with an integrating sphere at 293 K, and the $BaSO_4$ plate was used as the reference. The values of E_g were obtained with the use of a straightforward extrapolation method. Fluorescence spectra were carried out on a PW2424 spectrometer.

1.3 X-ray structure determination

A suitable red block crystal of as-synthesized compounds with the dimension of 0.20× 0.16 × 0.14 mm^3 was carefully selected and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was carried out on a Rigaku Weissenberg IP diffractometer with graphite-monochromated Mo-Ka (λ=0.71073Å) radiation at room temperature. An empirical absorption correction was applied using the SDAABS program. The structure was dissolved by the direct method and refined on F^2 by full-matrix least squares using SHELXTL97.[2] The hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Experimental details for the structure determination are presented in Table S1. Selected bond lengths and bond angles are listed in Table S2. Hydrogen details are given in Table S3.

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-634298. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; email:deposit@ccdc.cam.ac.uk).

Table S1 Crystal date and structure refinement summary for 1A

Formula	$C_{10}H_{24}N_8O_2S_2Cu_2I_2$
Formula weight	733.41
T (K)	293(2)
Crystal system	Monoclinic
Space group	C2/c
Z	8
a(Å)	23.125(3)
b(Å)	10.7039(7))
c(Å)	21.391(5)
β(°)	118.741(5)
Cell volume	4642.6(13)
Limiting indices	-30≤h≤30, -13≤k≤13, -27≤l≤27

μ(mm^{-1})	4.693
D_{calc} (Mg/m^3)	2.099
Reflections collected	17421
Independent reflections/Rint	5303/ 0.0242
Reflections observed	4415
F(000)	2800
Final R indices (I>2σ(I))[a]	R_1=0.0424, wR_2=0.1176
R indices(all data)	R_1=0.0526, wR_2=0.1261
S	1.117
(Δρ)max(e/Å^3)	1.450
(Δρ)min(e/Å^3)	-1.601

$$R_1 = \| F_0 | - | F_C \| / | F_0 |, wR_2 = [w(F^2_0 F^2_C)^2 / [w(F_0^2)^2]]^{1/2}$$

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

Bonds	Dist. (Å)	Bonds	Dist. (Å)
Cu(1)−I(1)	2.643(3)	Cu(1)−I(2)	2.672(2)
Cu(1)−S(1)	2.468(4)	Cu(1)−S(1)^{i}	2.316(8)
Cu(2)−I(1)	2.683(3)	Cu(2)−I(2)	2.618(2)
Cu(2)−S(2)	2.348(4)	S(2)−Cu(2)^{ii}	2.456(9)
Cu(2)−S(2)^{ii}	2.456(9)	Cu(1)−Cu(1)^{i}	2.852(1)
Cu(1)−Cu(2)	2.728(1)	Cu(2)−Cu(2)^{ii}	2.655(2)
S(1)−C(1)	1.708(6)	S(2)−C(3)	1.722(5)
Angles	(º)	Angles	(º)
I(1)−Cu(1)−I(2)	113.82(3)	S(2)^{ii}−Cu(2)−I(2)	101.45(4)
S(1)−Cu(1)−I(1)	102.91(4)	S(2)−Cu(2)−S(2)^{ii}	112.95(5)
S(1)−Cu(1)−I(2)	108.34(4)	Cu(1)^{i}−S(1)−Cu(1)	73.12(4)
S(1)^{i}−Cu(1)−S(1)	92.49(3)	Cu(2)−S(2)−Cu(2)^{ii}	67.05(4)
S(1)^{i}−Cu(1)−I(1)	120.13(5)	Cu(1)−I(1)−Cu(2)	61.60(2)
S(1)^{i}−Cu(1)−I(2)	104.19(5)	Cu(2)−I(2)−Cu(1)	62.06(3)
I(2)−Cu(2)−I(1)	114.28(3)	S(2)−Cu(2)−I(1)	100.55(4)
S(2)−Cu(2)−I(2)	116.77(4)	S(2)^{ii}−Cu(2)−I(1)	111.32(4)

1A44((i) 0.5-x, -0.5-y, -z; (ii) 0.5-x, 0.5-y, -z; (iii) 1-x, -y, -z.

Symmetry codes:(i) 0.5-x, -0.5-y, -z; (ii) 0.5-x, 0.5-y, -z; (iii) 1-x, -y, -z

Table S3 Hydrogen bridging details of 1

D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/º	Symmetry transformations
N(2)–H(2)···I(1)	0.860	2.772	3.631	178.72	0.5-x, -0.5-x, -z
N(5)–H(5A)···I(2)	0.860	2.974	3.624	134.00	x, y, z
C(6)–H(6B)···I(2)	0.962	3.223	4.081	149.51	1-x, y, 0.5-z
N(1)–H(1B)···O(1)	0.916	1.903	2.813	168.90	x, y, z
N(4)–H(4A)···O(2)	0.942	2.093	2.959	152.21	1-x, y, 0.5-z

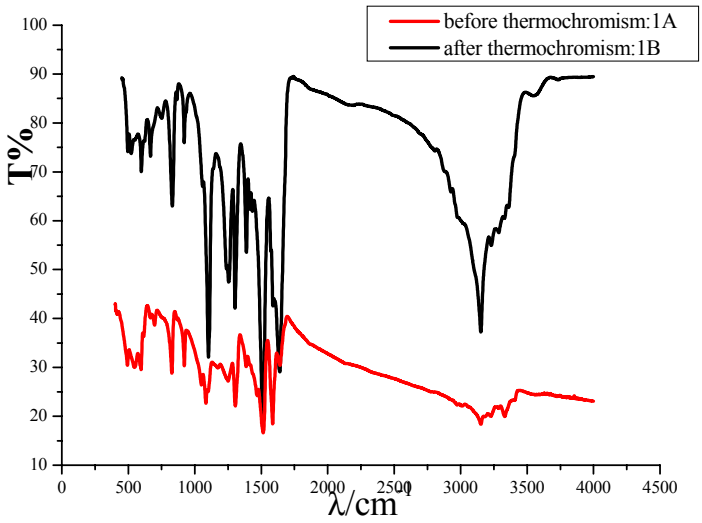


Fig. S1. IR spectra of 1Aand 1B

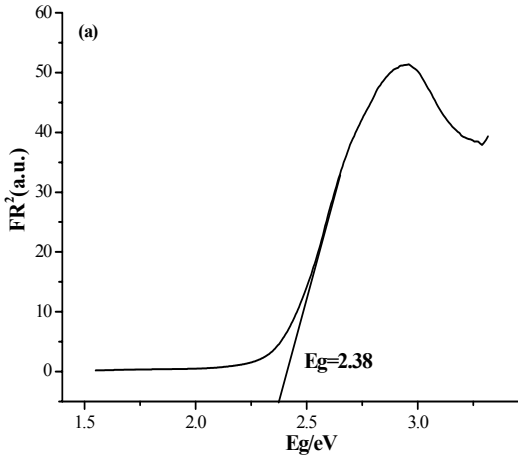


Fig.S2 Optical absorption spectra for 1

1 N. T. Akinchan, R. Akinchan, P. M. Drozdewski, Y. H. Yang, T. L. Klein, D. X. West, *Synth. React. Inorg. Met.-Org. Chem.* 1996, **26**, 1735.

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