

Electronic Supplementary Information (ESI) for *Chemical Communications*

Luminescence Thermochromism of Two Entangled Copper-Iodide Networks with Large Temperature-Respondent Emission Shift

Di Sun,^{*} Shuai Yuan, Hua Wang, Hai-Feng Lu, Sheng-Yu Feng, Dao-Feng Sun^{*}

Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, P. R. China

1. General Information.....	2
2. Synthesis of [Cu ₄ I ₄ (dmimpr) ₂] _n (1).....	3
3. Synthesis of [Cu ₆ I ₆ (dimb) ₃] _n (2).....	3
4. Crystal structure determination of 1 and 2.....	4
5. Table S1. Crystal Data Collection and Structure Refinement for 1 and 2.....	5
6. Table S2. Selected bond lengths (Å) in 1 and 2 at four different temperatures.....	7
7. Figure S1. The XRD patterns of 1 and 2.....	8
8. Figure S2. The TGA for 1 and 2.....	9
9. Figure S3. Excitation spectra for 1 and 2 at 298 K.....	10
10. Figure S4. The emission decay curve of 1 and 2 ($\lambda_{\text{ex}} = 365 \text{ nm}$) at 298 K. The green lines are the best fit to the data using a double-exponential function.....	11
11. Figure S5. The coordination environments of Cu(I) ions in 1.....	12
12. Figure S6. The coordination environments of Cu(I) ions in 2.....	13
13. Table S3: Cu···Cu distances [Å] and cell volumes [Å ³] in 1 and 2 at four different temperatures.....	14
14. Table S4 Comparison of luminescent shifts under 298 and 77K between the reported examples and 1 and 2 in this work.....	15
15. Figure S7. The plot of the overall variation tendency of emission maximum and Cu···Cu distance against the temperature.....	17
16. Figure S8. Temperature dependence of maximum emission wavelength of 1.....	18

1. General Information.

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were recorded on a Nicolet AVATAT FT-IR360 spectrometer as KBr pellets in the frequency range of 4000-400 cm^{-1} . The elemental analyses (C, H, N, S contents) were determined on a Vario EL III analyzer. Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with Cu K_{α} radiation equipped with an X'Celerator detector. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence Spectrophotometer equipped with dewar flask with a Suprasil quartz cold finger. Solid state quantum yields measurements were carried out using a Edinburgh FLS920 fluorescence spectrophotometer equipped with a xenon lamp, calibrated integrating sphere. Emission lifetimes were recorded with an Edinburgh FLS920 fluorescence spectrophotometer using the TCSPC (Time Correlated Single Photon Counting) method. Data were analyzed by exponential curve fitting. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 ° C under nitrogen atmosphere at a heating rate of 10° C/min.

2. Synthesis of $[\text{Cu}_4\text{I}_4(\text{dmimpr})_2]_n$ (**1**).

A mixture of CuI (19 mg, 0.10 mmol), dmimpr (4.4 mg, 0.02mmol), 1.5 mL DMF-CH₃CN (v:v = 1:1) were sealed in a glass tube, and heated to 120 °C in 10 hours, kept 120 °C for 50 hours then slowly cooled to 30 °C in 13 hours. The pale-yellow crystals were collected and washed with EtOH and dried in the air (yield: 80 %). Elemental analysis calcd (%) for **1** (C₁₁H₁₆Cu₂I₂N₄): C 22.58, H 2.76, N 9.57; found: C 22.18, H 2.36, N 9.66. Selected IR peaks (cm⁻¹): 3432 (s), 1616 (s), 1567 (s), 1494 (s), 1390 (m), 1347 (m), 756 (m) 649 (m).

3. Synthesis of $[\text{Cu}_6\text{I}_6(\text{dimb})_3]_n$ (**2**).

Synthesis of complex **2** was similar to that of **1** but using dimb (4.1 mg, 0.02 mmol) instead of dmimpr and heated to 130 °C rather than 120 °C. Pale-yellow crystals of **2** were collected and washed with EtOH and dried in the air (yield: 74 %). Elemental analysis calcd (%) for **2** (C₁₅H₂₁Cu₃I₃N₆): C 21.03, H 2.47, N 9.81; found: C 20.92, H 2.68, N 9.99. Selected IR peaks (cm⁻¹): 3432 (s), 1616 (s), 1567 (s), 1494 (s), 1390 (m), 1347 (m), 756 (m) 649 (m).

4. Crystal structure determination of **1** and **2**

Single crystals of the complexes **1** and **2** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for them were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo K α radiation source ($\lambda = 0.71073 \text{ \AA}$) at four different temperatures (100, 160, 220, 298K). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each, each frame corresponds to a 0.5° scan in 5 s, followed by spot integration and least-squares refinement. For **1** and **2**, data were measured using ω scans of 0.5° per frame for 10 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS. In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97 and refined on F^2 by full-matrix least-squares procedures with SHELXL-97. Atoms were located from iterative examination of difference F -maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. All structures were examined using the Addsym subroutine of PLATON to assure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table S1. Selected bond lengths and angles are collated in Table S2.

Electronic Supplementary Information (ESI) for *Chemical Communications*

5. Table S1. Crystal Data Collection and Structure Refinement for 1 and 2.

1				
Temperature/K	100(2)	160(2)	220(2)	298(2)
Empirical formula	C ₁₁ H ₁₆ Cu ₂ I ₂ N ₄	C ₁₁ H ₁₆ Cu ₂ I ₂ N ₄	C ₁₁ H ₁₆ Cu ₂ I ₂ N ₄	C ₁₁ H ₁₆ Cu ₂ I ₂ N ₄
Formula weight	585.16	585.16	585.16	585.16
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	Pnn2	Pnn2	Pnn2	Pnn2
a/Å	17.6379(5)	17.6850(10)	17.7336(11)	17.9821(13)
b/Å	9.6123(5)	9.6255(5)	9.6470(6)	9.7493(7)
c/Å	9.8809(9)	9.8942(6)	9.9065(6)	10.0256(7)
α/°	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	90.00
γ/°	90.00	90.00	90.00	90.00
Volume/Å ³	1675.22(18)	1684.26(16)	1694.76(18)	1757.6(2)
Z	4	4	17	4
ρ _{calc} /mg/mm ³	2.320	2.308	2.293	2.211
μ/mm ⁻¹	6.216	6.183	6.145	5.925
F(000)	1096.0	1096.0	1096.0	1096.0
2θ range for data collection	4.62 to 50°	4.6 to 50°	4.6 to 49.98°	4.54 to 50°
Reflections collected	5340	5397	5437	5617
Independent reflections	1978[R(int) = 0.0165]	1989[R(int) = 0.0186]	1996[R(int) = 0.0188]	2094[R(int) = 0.0193]
Data/restraints/parameters	1978/1/174	1989/1/174	1996/1/174	2094/1/174
Goodness-of-fit on F ²	1.181	1.137	1.124	1.106
Final R indexes [I>=2σ (I)]	R ₁ = 0.0177, wR ₂ = 0.0441	R ₁ = 0.0186, wR ₂ = 0.0473	R ₁ = 0.0196, wR ₂ = 0.0513	R ₁ = 0.0215, wR ₂ = 0.0574
Final R indexes [all data]	R ₁ = 0.0177, wR ₂ = 0.0441	R ₁ = 0.0188, wR ₂ = 0.0473	R ₁ = 0.0199, wR ₂ = 0.0515	R ₁ = 0.0219, wR ₂ = 0.0577
Largest diff. peak/hole / e Å ⁻³	0.66/-0.84	0.55/-0.70	0.44/-0.65	0.55/-0.76
2				
Temperature/K	100(2)	160(2)	220(2)	298(2)
Empirical formula	C ₁₅ H ₂₁ Cu ₃ I ₃ N ₆	C ₁₅ H ₂₁ Cu ₃ I ₃ N ₆	C ₁₅ H ₂₁ Cu ₃ I ₃ N ₆	C ₁₅ H ₂₁ Cu ₃ I ₃ N ₆
Formula weight	856.70	856.70	856.70	856.70
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c
a/Å	25.146(3)	25.258(7)	25.367(11)	25.640(7)
b/Å	11.2465(14)	11.286(3)	11.290(5)	11.421(3)
c/Å	16.080(2)	16.119(4)	16.143(7)	16.219(5)

Electronic Supplementary Information (ESI) for *Chemical Communications*

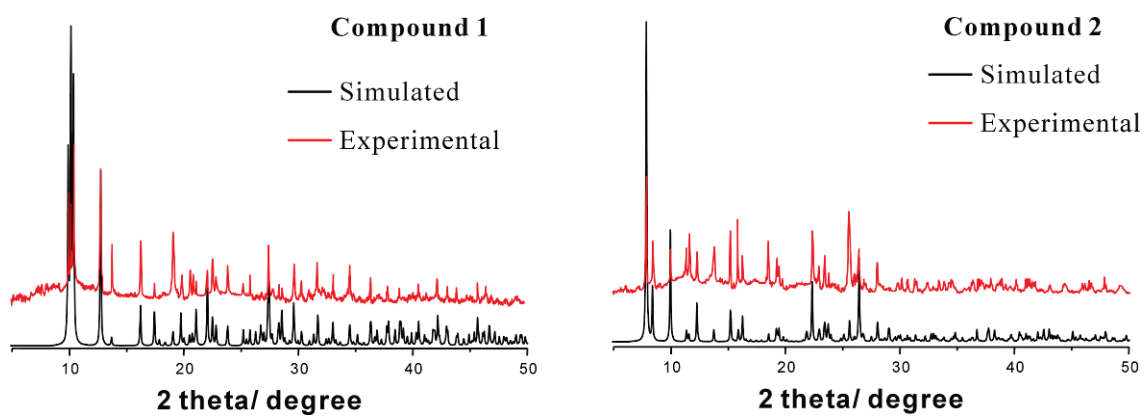
$\alpha/^\circ$	90.00	90.00	90.00	90.00
$\beta/^\circ$	101.206(2)	101.063(4)	100.920(7)	100.823(5)
$\gamma/^\circ$	90.00	90.00	90.00	90.00
Volume/ \AA^3	4460.9(10)	4510(2)	4539(3)	4665(2)
Z	8	8	8	8
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	2.551	2.524	2.507	2.440
μ/mm^{-1}	7.000	6.924	6.879	6.694
F(000)	3192.0	3192.0	3192.0	3192.0
2 θ range for data collection	3.98 to 50°	3.28 to 50°	3.28 to 50°	3.92 to 50°
Reflections collected	8628	8744	8835	10182
Independent reflections	3894[R(int) = 0.0429]	3932[R(int) = 0.0437]	3951[R(int) = 0.0516]	4117[R(int) = 0.0391]
Data/restraints/parameters	3894/90/280	3932/90/280	3951/90/280	4117/90/280
Goodness-of-fit on F2	1.009	1.015	1.067	1.019
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0414, wR2 = 0.0925	R1 = 0.0425, wR2 = 0.0983	R1 = 0.0504, wR2 = 0.1249	R1 = 0.0506, wR2 = 0.1424
Final R indexes [all data]	R1 = 0.0636, wR2 = 0.1017	R1 = 0.0709, wR2 = 0.1227	R1 = 0.0911, wR2 = 0.1681	R1 = 0.0841, wR2 = 0.1688
Largest diff. peak/hole / e \AA^{-3}	1.16/-0.94	1.02/-0.88	1.10/-1.22	1.87/-1.27

Electronic Supplementary Information (ESI) for *Chemical Communications*

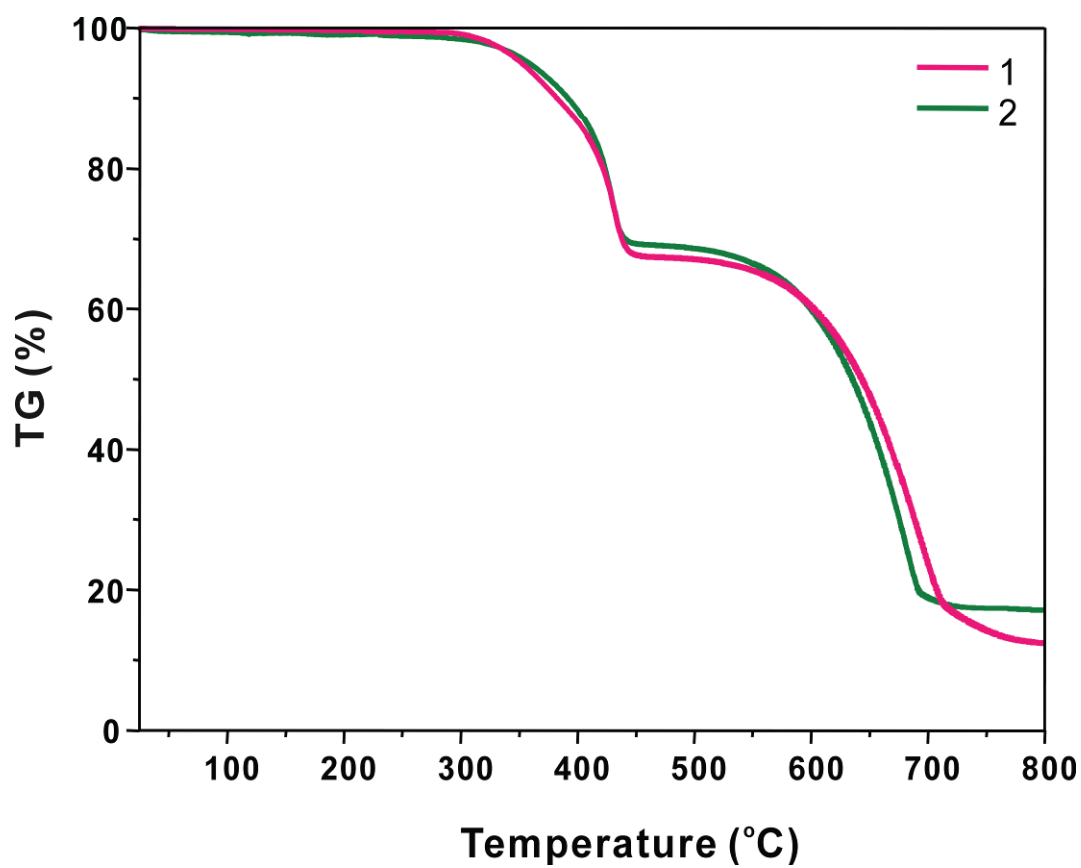
6. Table S2. Selected bond lengths (Å) in 1 and 2 at four different temperatures.

	100K	160K	220K	298K
1				
Cu1—N1	2.018 (5)	2.019 (5)	2.021 (5)	2.039 (5)
Cu1—I2	2.6037 (8)	2.6018 (8)	2.6000 (9)	2.6240 (10)
Cu1—I1 ⁱ	2.7346 (7)	2.7393 (7)	2.7455 (8)	2.7815 (9)
Cu1—I1	2.7584 (7)	2.7626 (7)	2.7678 (8)	2.7986 (9)
Cu2—N3 ⁱⁱ	2.009 (5)	2.006 (5)	2.006 (5)	2.029 (6)
Cu2—I1	2.6591 (9)	2.6658 (8)	2.6651 (10)	2.6931 (11)
Cu2—I2	2.6666 (7)	2.6709 (13)	2.6664 (8)	2.6877 (10)
Cu2—I2 ⁱ	2.7826 (7)	2.7902 (8)	2.7976 (8)	2.8361 (10)
Symmetry codes: (i) $-x+1, -y, z$; (ii) $x, y-1, z+1$.				
2				
Cu1—N5	2.013 (7)	2.017 (8)	2.000 (11)	2.021 (9)
Cu1—I1 ⁱ	2.6586 (12)	2.6596 (15)	2.651 (2)	2.6568 (18)
Cu1—I2	2.7137 (12)	2.7178 (15)	2.718 (2)	2.7374 (18)
Cu1—I1	2.7706 (13)	2.7816 (16)	2.791 (2)	2.8101 (19)
Cu2—N1	2.011 (7)	2.013 (8)	2.024 (10)	2.031 (8)
Cu2—I2 ⁱ	2.6071 (12)	2.6087 (15)	2.612 (2)	2.6214 (17)
Cu2—I1	2.6866 (12)	2.6990 (15)	2.705 (2)	2.7356 (17)
Cu2—I2	2.7639 (12)	2.7680 (14)	2.765 (2)	2.7707 (16)
Cu3—N4	1.938 (7)	1.937 (8)	1.945 (10)	1.945 (9)
Cu3—I3 ⁱⁱ	2.5677 (13)	2.455 (2)	2.566 (2)	2.5749 (19)
Cu3—I3	2.5753 (12)	2.5729 (15)	2.573 (2)	2.5816 (18)
Symmetry codes: (i) $-x, y, -z-1/2$; (ii) $-x-1/2, -y+1/2, -z+1$.				

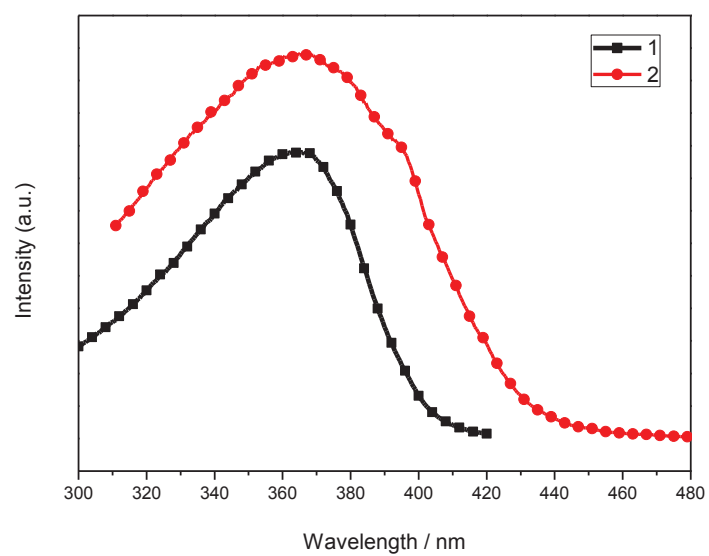
7. Figure S1. The XRD patterns of 1 and 2.



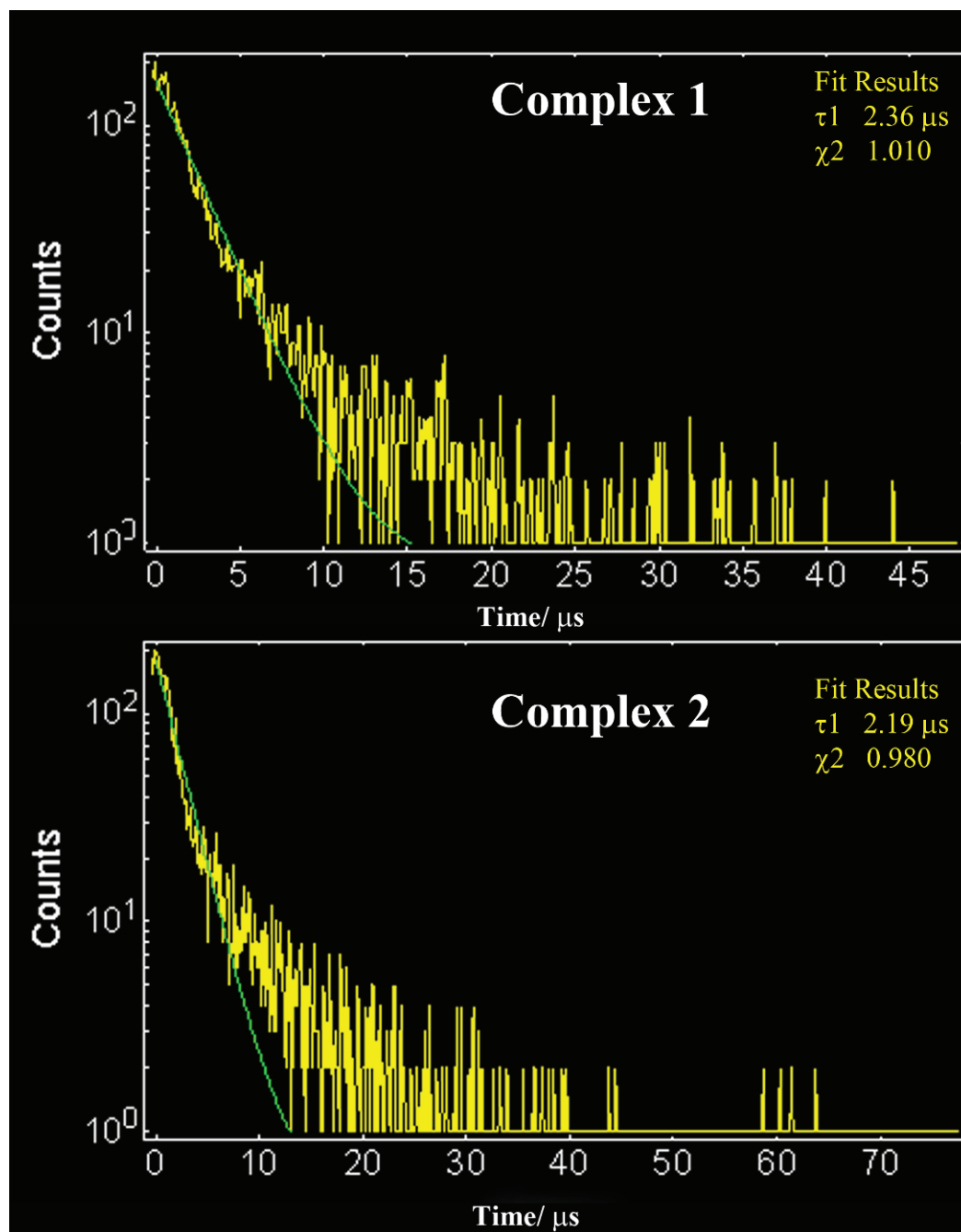
8. Figure S2. The TGA for 1 and 2.



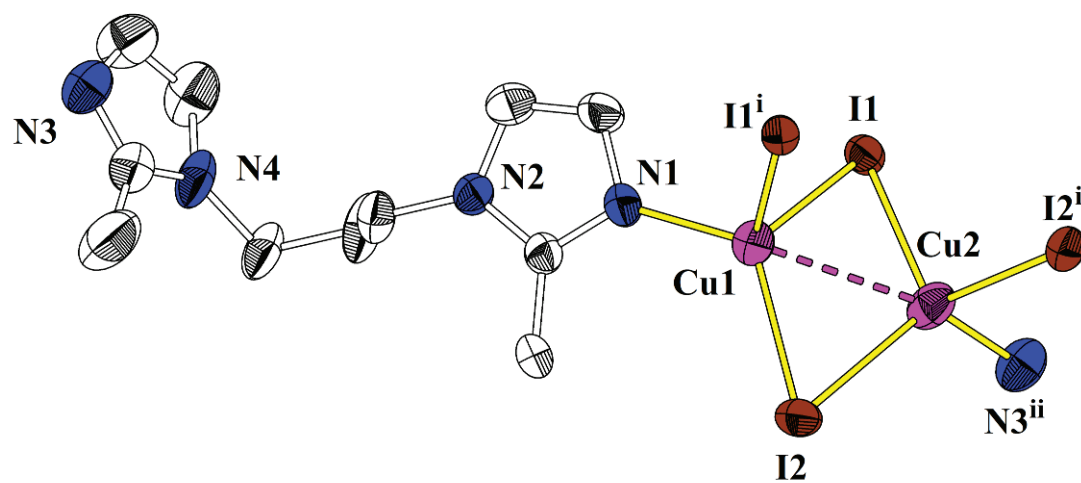
9. Figure S3. Excitation spectra for 1 and 2 at 298 K.



10. Figure S4. The emission decay curve of 1 and 2 ($\lambda_{\text{ex}} = 365 \text{ nm}$) at 298 K. The green lines are the best fit to the data using a double-exponential function

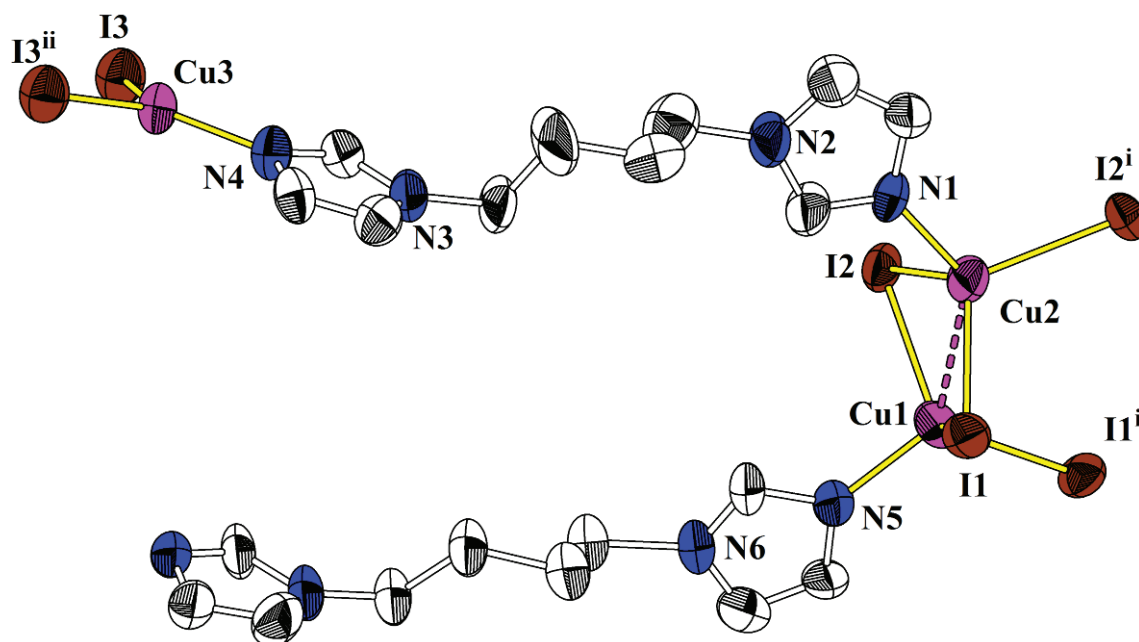


11. Figure S5. The coordination environments of Cu(I) ions in 1.



Symmetry codes: (i) $-x+1, -y, z$; (ii) $x, y-1, z+1$.

12. Figure S6. The coordination environments of Cu(I) ions in **2**.



Symmetry codes: (i) $-x, y, -z-1/2$; (ii) $-x-1/2, -y+1/2, -z+1$.

Electronic Supplementary Information (ESI) for ChemComm

13. Table S3: Cu...Cu distances [\AA] and cell volumes [\AA^3] in **1 and **2** at four different temperatures.**

	100K	160K	220K	298K
1				
Cu1...Cu2	2.6965(10)	2.7142(10)	2.7336(11)	2.7817(12)
Cu1...Cu2 ⁱ	2.7911(10)	2.8103(10)	2.8307(11)	2.8840(12)
Cu2...Cu2 ⁱ	2.6545(13)	2.6709(13)	2.6902(14)	2.7486(16)
Mean	2.7140	2.7318	2.7515	2.8048
Unit Cell	1675.22(18)	1684.26(16)	1694.76(18)	1757.6(2)
2				
Cu1...Cu2	2.6623(15)	2.6763(17)	2.688(2)	2.723(2)
Cu1...Cu2 ⁱ	2.6531(15)	2.6733(18)	2.686(2)	2.715(2)
Cu1...Cu1 ⁱ	2.862(2)	2.876(3)	2.875(4)	2.882(3)
Cu2...Cu2 ⁱ	2.717(2)	2.721(2)	2.721(3)	2.721(3)
Cu3...Cu3 ⁱⁱ	2.450(2)	2.455(2)	2.460(3)	2.480(3)
Mean	2.669	2.680	2.686	2.704
Unit Cell	4460.9(10)	4510(2)	4539(3)	4665(2)

Symmetry codes: (i) $-x+1, -y, z$ for **1**; (i) $-x, y, -z-1/2$; (ii) $-x-1/2, -y+1/2, -z+1$ for **2**.

Electronic Supplementary Information (ESI) for ChemComm

14. Table S4 Comparison of luminescent shifts under 298 and 77K between the reported examples and 1 and 2 in this work.

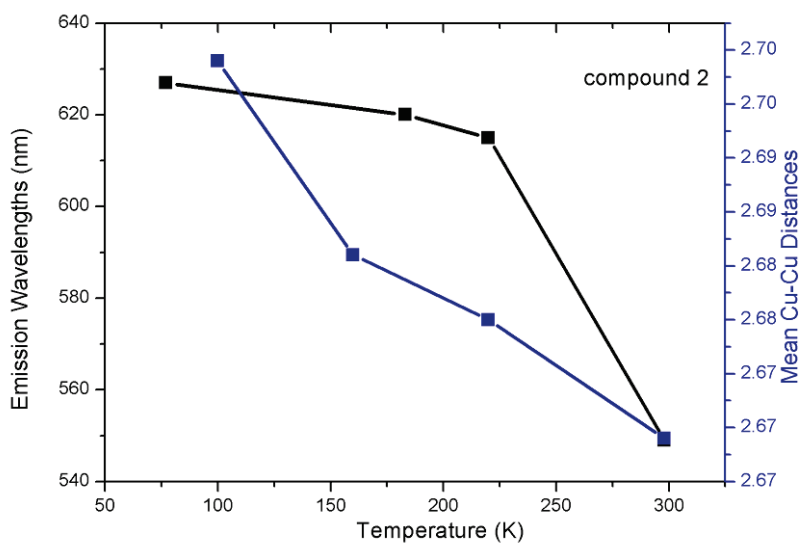
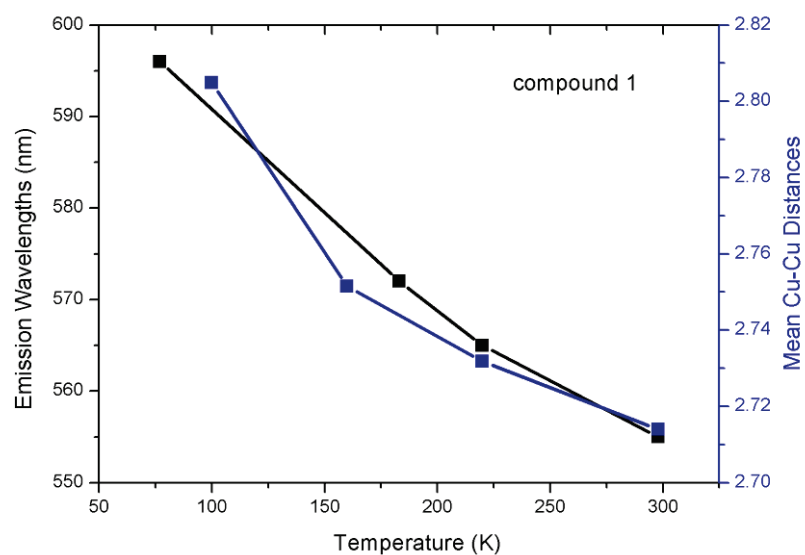
Compound	298K (nm)	77K (nm)	Δ Shift (nm)	Reference
[Cu ₄ I ₄ -(DABCO) ₂] (DABCO=1,4-diazabicyclo [2.2.2]octane)	580	590	10	Chem Eur. J. 2010, 16, 1553-1559
[Cu ₄ I ₄ -(DABCO) ₂] (DABCO=1,4-diazabicyclo [2.2.2]octane)	556	578	22	Chem Eur. J. 2010,16, 1553-1559
[(Cu ₆ I ₆)(μ-PhSCH ₂ C≡CCH ₂ SPh) ₃] _n	555	565	10	Dalton Trans. 2009, 948-955.
[Cu ₄ I ₄ (μ-PhS(CH ₂) ₄ SPh) ₂] _n	575	600	25	Dalton Trans. 2009, 948-955.
[Cu ₄ I ₄ (PPh ₃) ₄]	550	610	60	Chem. Commun., 2010, 46, 6302-6304
[Cu ₄ I ₄ (PPh ₃) ₄]	520	540	20	Chem. Commun., 2010, 46, 6302-6304
[(CuI) ₄ (N-Methylpiperazine) ₃] _n	593	580	13	Dalton Trans., 2012, 41, 11663-11674
[(CuBr) ₄ (N-Methylpiperazine) ₂] _n	589	619	30	Dalton Trans., 2012, 41, 11663-11674
[(CuI) ₄ (N-Methylpiperazine) ₂] _n	525	558	33	Dalton Trans., 2012, 41, 11663-11674
[(CuI) ₂ (N,N'-Diethylpiperazine)] _n	444	438	6	Dalton Trans., 2012, 41, 11663-11674
[(CuI) ₂ (N,N'-Dibenzylpiperazine)] _n	Non emissive	448		Dalton Trans., 2012, 41, 11663-11674
[(CuI) ₂ (N,N'-bis-Phenethylpiperazine)] _n	449	447	2	Dalton Trans., 2012, 41, 11663-11674
[(CuI) ₄ (N-Diphenylmethylpiperazine)] _n	573	605	32	Dalton Trans., 2012, 41,

Electronic Supplementary Information (ESI) for ChemComm

				11663–11674
$[\text{Cu}_4\text{I}_4(\text{PPh}_3)_4] (\text{PPh}_3 = \text{triphenylphosphine})]_n$	545	587	42	Inorg. Chem. 2011, 50, 10682–10692
$[\text{Cu}_4\text{I}_4(\text{Pcpent}_3)_4] (\text{Pcpent}_3 = \text{tricyclopentylphosphine})$	523	515	8	Inorg. Chem. 2011, 50, 10682–10692
$[\text{Cu}_4\text{I}_4(\text{PPh}_2\text{Pr})_4] (\text{PPh}_2\text{Pr} = \text{diphenylpropylphosphine})$	560	566	6	Inorg. Chem. 2011, 50, 10682–10692
$[\{\text{Cu}(\mu_2\text{-I})_2\text{Cu}\}\{\mu\text{-PhS}(\text{CH}_2)_3\text{SPh}\}_2]_n$	440	440	0	Inorg. Chem. 2012, 51, 9917–9934
$[\text{Cu}_4\text{I}_4\{\mu\text{-PhS}(\text{CH}_2)_3\text{Ph}\}_2]_n$	520	525	5	Inorg. Chem. 2012, 51, 9917–9934
$[\text{Cu}_4\text{I}_4\{\mu\text{-PhS}(\text{CH}_2)_5\text{Ph}\}_2]_n$	560	555	5	Inorg. Chem. 2012, 51, 9917–9934
$[\{\text{Cu}(\mu_2\text{-I})_2\text{Cu}\}\{\mu\text{-PhS}(\text{CH}_2)_5\text{SPh}\}_2]_n$	440	440	0	Inorg. Chem. 2012, 51, 9917–9934
$[\{\text{Cu}(\mu_2\text{-I})_2\text{Cu}\}_2\{\mu\text{-p-TolS}(\text{CH}_2)_5\text{STol-p}\}_2]_n$	545	535	10	Inorg. Chem. 2012, 51, 9917–9934
$[\{\text{Cu}(\mu_2\text{-Br})_2\text{Cu}\}\{\mu\text{-PhS}(\text{CH}_2)_3\text{SPh}\}_2]_n$	480	490	10	Inorg. Chem. 2012, 51, 9917–9934
$[\text{Cu}_4\text{I}_4(\text{dmimpr})_2]_n$ (1) (dmimpr = 1,3-di(2-methyl-imidazol-1-yl)propane,)	555	596	41	This work
$[\text{Cu}_6\text{I}_6(\text{dimb})_3]_n$ (2) (dimb = 1,4-di(imidazol-1-yl)butane)	549	627	78	This work

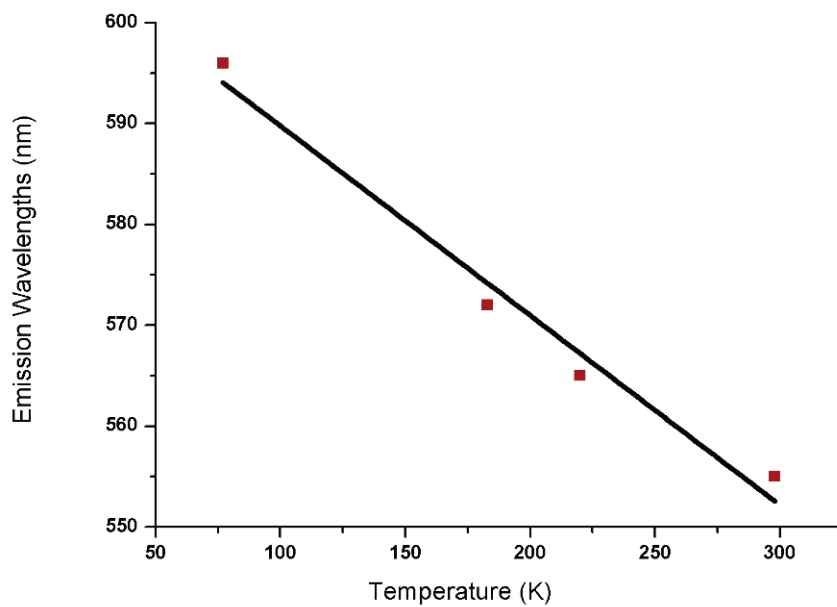
Electronic Supplementary Information (ESI) for ChemComm

15. Figure S7. The plot of the overall variation tendency of emission maximum and Cu···Cu distance against the temperature



Electronic Supplementary Information (ESI) for ChemComm

16. Figure S8. Temperature dependence of maximum emission wavelength of 1



Intercept		Slope		Statistics
Value	Standard Error	Value	Standard Error	Adj. R-Square
608.57685	4.09641	-0.18806	0.01949	0.96844