Electronic Supplementary Material (ESI) for Dalton Transactions

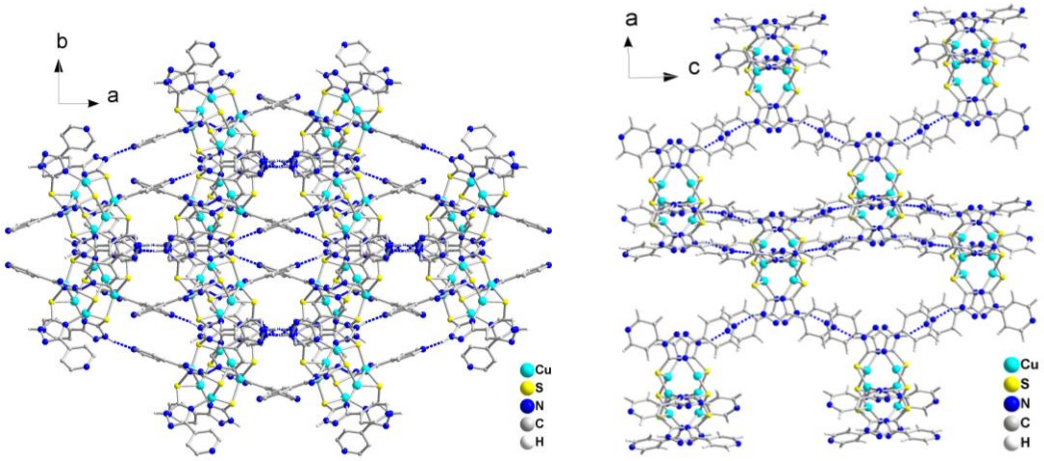
Supplementary Information

The Unusual Thermochromic NIR Luminescence of Cu(I) Clusters: Tuned by Cu-Cu Interactions and Packing Modes

Xiao-Chen Shan,[a b] Fei-Long Jiang,[a] Da-Qiang Yuan,[a] Ming-Yan Wu,[a] Shu-Quan Zhang[a b] and Mao-Chun Hong *[a]

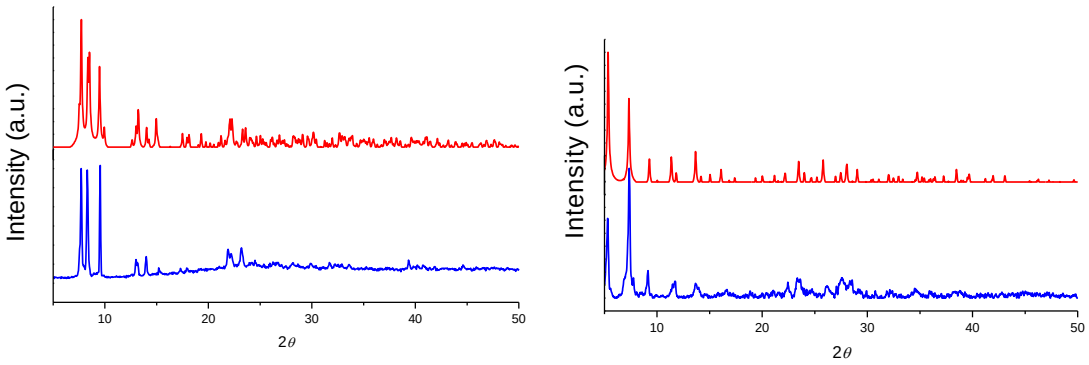
[a] State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China. E-mail: hmc@fjirsm.ac.cn; Fax: +86-591-83794946; Tel: +86-591-83792460

[b] Graduate School of the Chinese Academy of Sciences, Beijing, 100049, China



(a) (b)

Fig. S1 The 3D structure through hydrogen bonding (marked in blue dot lines) in compound **1** (a) along *c* axis and **2** (b) along *b* axis. Solvent molecules are omitted for clarity.



(a) (b)

Fig. S2 Simulated (red) and measured (blue) PXRD patterns of **1** (a) and **2** (b)

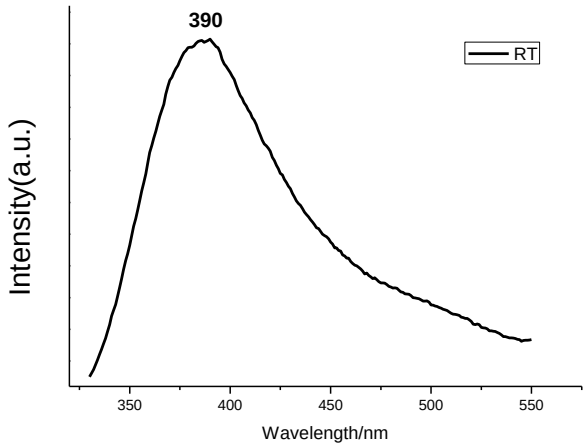


Fig. S3 Emission spectrum of 4-Hptt at room temperature under excitation of 290 nm.

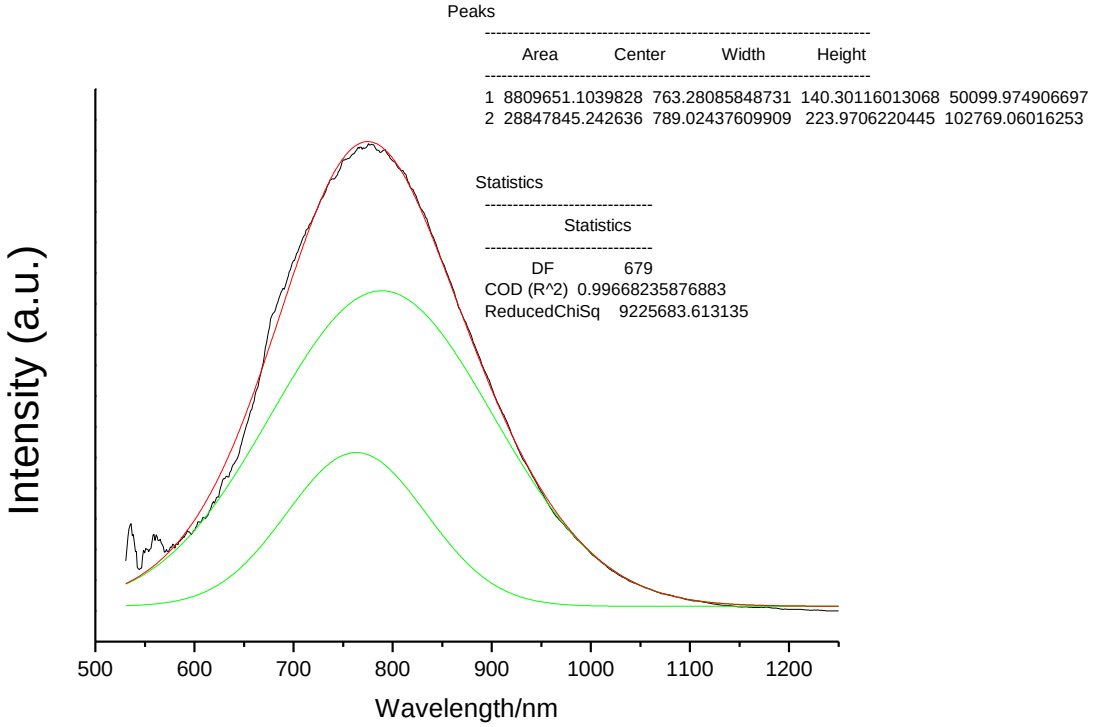


Fig. S4 Emission spectra of compound **2** and the fitted Gaussian profile excited by 360 nm at room temperature (Black: measured spectrum, Red: Gauss fitting result, Green: Gauss fitting peaks of 763 nm and 789 nm respectively.)

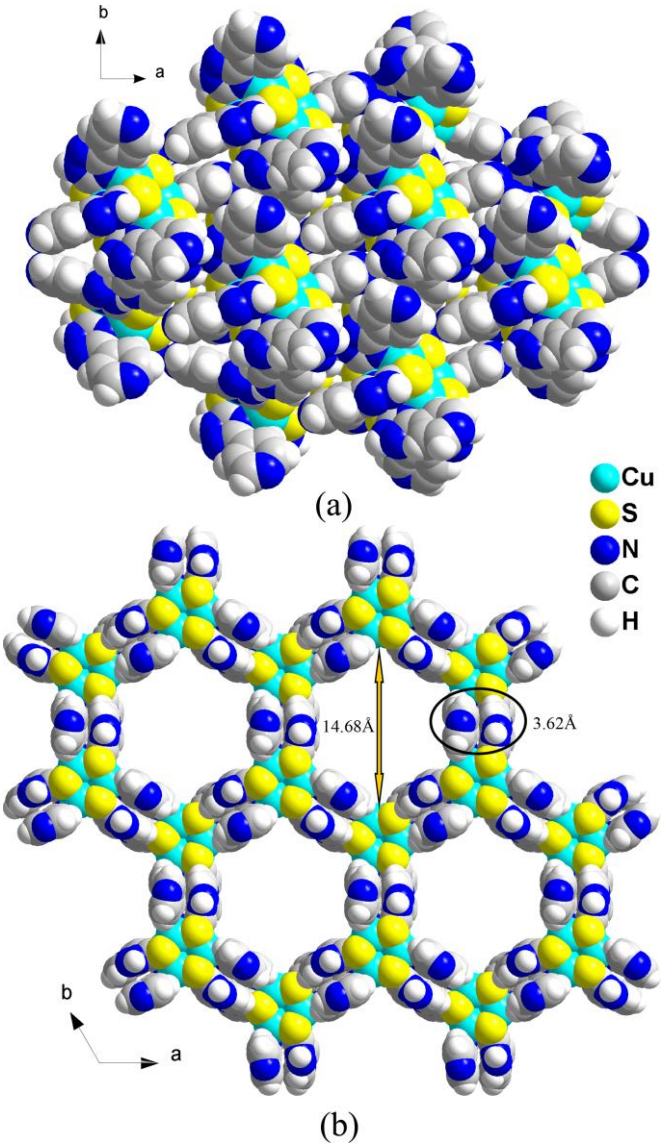


Fig. S5 Space-filling representations of supramolecule **1** (a) along *c* axis and **2** (b) with large hexagonal pores along *c* axis. Solvent molecules are omitted for clarity.

Table S1. Selected bond lengths (Å) and angles (°) for **1**[a]

Bond lengths (Å)			
Cu1—N1	2.012 (3)	S3—C15	1.745 (4)
Cu1—S3	2.2281 (11)	S2—C8	1.739 (4)
Cu1—S2^{i}	2.2644 (11)	S2—Cu1^{i}	2.2644 (11)
Cu1—Cu2	2.8495 (7)	S1—C1	1.742 (4)
Cu2—N5	2.010 (3)	S1—Cu2^{i}	2.2487 (12)
Cu2—S3	2.2368 (10)	N9—C15	1.345 (4)
Cu2—S1^{i}	2.2487 (12)	N9—C16	1.378 (5)
Cu2—Cu3	2.9500 (7)	N11—C16	1.312 (5)
Cu3—N9	1.981 (3)	C2—N3	1.322 (5)
Cu3—S1	2.2465 (11)	C2—N1	1.368 (5)
Cu3—S2	2.2705 (10)	N1—C1	1.341 (4)
N10—C15	1.335 (5)	N3—N2	1.362 (4)
N10—N11	1.369 (5)	N2—C1	1.338 (5)
N6—C8	1.343 (5)	N5—C9	1.370 (5)
N6—N7	1.365 (4)	C9—N7	1.319 (5)
N5—C8	1.348 (4)		
Angles (^{o})			
N1—Cu1—S3	120.58 (10)	S3—Cu2—Cu3	82.70 (3)
N1—Cu1—S2^{i}	107.43 (10)	S1i—Cu2—Cu3	126.32 (3)
S3—Cu1—S2^{i}	128.57 (4)	Cu1—Cu2—Cu3	64.177 (18)
N1—Cu1—Cu2	141.27 (10)	N9—Cu3—S1	124.82 (11)
S3—Cu1—Cu2	50.48 (3)	N9—Cu3—S2	122.97 (11)
S2i—Cu1—Cu2	101.10 (3)	S1—Cu3—S2	108.96 (4)
N5—Cu2—S3	120.64 (10)	N9—Cu3—Cu2	82.15 (10)
N5—Cu2—S1^{i}	107.24 (10)	S1—Cu3—Cu2	124.82 (3)
S3—Cu2—S1^{i}	127.91 (4)	S2—Cu3—Cu2	82.20 (3)
N5—Cu2—Cu1	144.31 (10)	C15—S3—Cu1	104.25 (13)
S3—Cu2—Cu1	50.21 (3)	C15—S3—Cu2	100.62 (13)
S1^{i}—Cu2—Cu1	100.01 (3)	Cu1—S3—Cu2	79.32 (3)

N5—Cu2—Cu3	81.04 (9)	C8—S2—Cu1^{i}	102.31 (14)
C15—N10—N11	110.9 (3)	C8—S2—Cu3	101.85 (12)
C16—N11—N10	102.9 (3)	Cu1^{i}—S2—Cu3	96.91 (4)
N10—C15—N9	108.8 (3)	C1—S1—Cu3	106.56 (13)
N10—C15—S3	124.7 (3)	C1—S1—Cu2^{i}	102.45 (15)
N9—C15—S3	126.5 (3)	Cu3—S1—Cu2^{i}	98.35 (4)
N3—C2—N1	113.9 (3)	C15—N9—C16	103.5 (3)
N3—C2—C3	122.2 (3)	C15—N9—Cu3	122.9 (3)
N1—C2—C3	123.8 (3)	C16—N9—Cu3	133.6 (3)
N11—C16—N9	114.0 (4)	N2—C1—N1	108.8 (3)
C1—N1—C2	103.7 (3)	N2—C1—S1	124.5 (3)
C1—N1—Cu1	119.2 (2)	N1—C1—S1	126.8 (3)
C2—N1—Cu1	133.9 (2)	C8—N6—N7	110.4 (3)
C2—N3—N2	102.8 (3)	C8—N5—C9	103.8 (3)
C1—N2—N3	110.9 (3)	C8—N5—Cu2	121.6 (3)
N6—C8—N5	108.7 (3)	C9—N5—Cu2	132.1 (2)
N6—C8—S2	125.1 (3)	C9—N7—N6	103.3 (3)
N5—C8—S2	126.1 (3)	N7—C9—N5	113.7 (3)

[a]Symmetry codes: (i) 1/2-x, 3/2-y, 1-z; (ii) 1/2-x, 1/2-y, 1-z; (iii) -x, y, 3/2-z.

Table S2. Selected bond lengths (Å) and angles (°) for **2** [a]

Bond lengths (Å)			
Cu1—N1^{i}	2.004 (3)	N2—C1	1.320 (5)
Cu1—S1	2.2140 (11)	N2—N3	1.359 (5)
Cu1—S1^{ii}	2.3121 (12)	N3—C2	1.336 (5)
N1—Cu1^{i}	2.004 (3)	N1—C1	1.349 (4)
S1—Cu1^{iii}	2.3121 (12)	N1—C2	1.361 (5)
S1—C1	1.749 (4)	C3—C2	1.478 (5)
Angles (^{o})			
N1^{i}—Cu1—S1	130.63 (11)	C1—N1—C2	103.7 (3)
N1^{i}—Cu1—S1^{ii}	107.87 (11)	C1—N2—N3	111.8 (3)
S1—Cu1—S1^{ii}	118.68 (6)	C2—N3—N2	102.1 (4)
C1—S1—Cu1	107.47 (14)	N2—C1—N1	108.7 (3)
C1—S1—Cu1^{iii}	96.80 (14)	N2—C1—S1	124.1 (3)
Cu1—S1—Cu1^{iii}	92.85 (5)	N1—C1—S1	126.8 (3)
C1—N1—Cu1^{i}	122.5 (3)	N3—C2—N1	113.7 (3)
C2—N1—Cu1^{i}	132.6 (2)	N3—C2—C3	121.7 (4)

[a]Symmetry codes: (i) -x+y, y, 1/2-z; (ii) -x+y, 1-x, z; (iii) 1-y, 1+x-y, z.

Table S3. Hydrogen bonding distances (Å) and angle (°) data for **1**[a]-**2**[b]

Compound **1**[a]	D—H	H...A	D...A	D—H...A
N6—H6'...N12[i]	0.86	1.94	2.730 (4)	153.3
N10—H10'...N4[ii]	1.00	1.82	2.802 (4)	169.8
N2—H2'...N8[iii]	0.88	2.04	2.740 (5)	136.1
Compund **2**[b]	D—H	H...A	D...A	D—H...A
N2—H2...N4[i]	0.82	1.98	2.797 (5)	174.1

[a]Symmetry codes: (i) 1/2-x, 1/2+y, 3/2-z; (ii) -x, y, 1/2-z; (iii) 1/2+x, -1/2+y, z.

[b]Symmetry codes: (i) x, y, z.