Supporting Information

Light and Heat Dually Responded Luminescence in Organic Templated $CdSO_4$-type Halogeno(cyano)cuprates with Disorder of Halogenide/Cyanide

Shi-Li Li[†], Jie Wang[†], Fu-Qiang Zhang[†], Xian-Ming Zhang[†‡]*

Dr. S.-L. Li, J. Wang, Dr. Fu-Qiang Zhang, Prof. X.-M. Zhang

[†]School of Chemistry & Material Science, Shanxi Normal University, Linfen 041004, P. R. China

[‡]Institute of Crystalline Materials, Shanxi University, Taiyuan 030006 P. R. China

E-mail: zhangxm@dns.sxnu.edu.cn.

Contents

S1. The Tables in Supporting Information

Table S1. Bond Lengths (Å) and Angles (°) for **1**.

		1	
Cu(1)-N(1)	1.972(3)	Br(1)-Cu(1a)	2.6065(7)
Cu(1)-Br(1)	2.5341(6)	Br(2)-Cu(1b)	2.5518(6)
Cu(1)-Br(2)	2.5519(6)	Cu(1)-C(2)	1.969(7)
Cu(1)-Br(1a)	2.6066(7)	Cu(1)-N(1)	1.972(3)
N(1)-Cu(1)-Br(1)	115.86(9)	N(1)-Cu(1)-Br(1a)	111.50(10)
N(1)-Cu(1)-Br(2)	109.14(10)	Br(1)-Cu(1)-Br(1a)	99.72(2)
Br(1)-Cu(1)-Br(2)	115.73(4)	Br(2)-Cu(1)-Br(1a)	103.84(2)
N(2)-Cu(1)-Br(1)	110.0(2)	N(2)-Cu(1)-Br(1a)	105.6(4)

Symmetry codes: a) -x, -y+1, -z+1 b) -x, y, -z+1/2 c) -x+1/2, -y+1/2, -z+1 d) -x+1, y, -z+1/2

Table S2. Bond Lengths (Å) and Angles (°) for **2**.

		2	
Cu(1)-C(1)	1.940(4)	I(1)-Cu(1a)	2.7109(8)
Cu(1)-I(2)	2.5215(7)	I(2)-Cu(1b)	2.5215(7)
Cu(1)-I(1a)	2.7109(8)	Cu(1)-C(2)	1.873(8)
Cu(1)-I(1)	2.8065(9)	Cu(1)-C(1)	1.940(4)
C(1)-Cu(1)-I(2)	114.93(14)	C(1)-Cu(1)-I(1)	108.23(14)
C(1)-Cu(1)-I(1a)	114.53(13)	I(2)-Cu(1)-I(1)	103.51(3)
I(2)-Cu(1)-I(1a)	116.90(6)	I(1a)-Cu(1)-I(1)	95.70(2)
C(2)-Cu(1)-I(1)	106.9(4)	C(2)-Cu(1)-I(1a)	108.9(3)

Symmetry codes: a) -x+3/2, -y+1/2, -z+1 b) -x+1, -y, -z+1 c) -x+1, y, -z+1/2

Table S3. Emission lifetimes of compound **1** at 5 K.

Ex/nm	Em_1/nm	τ/μs	Em_2/nm	τ/μs
310	471	37.76	—	—
320	471	37.07	—	—
330	471	39.42	557	56.15
340	471	46.86	567	98.67
350	—	—	570	116.25
360	—	—	570	115.91
370	—	—	570	124.67
380	—	—	570	119.88
390	—	—	570	92.23

Table S4. Emission lifetimes of compound **1** at 50 K.

Ex/nm	Em_1/nm	τ/μs	Em_2/nm	τ/μs
310	473	37.22	—	—
320	473	36.17	—	—
330	473	36.70	552	57.88
340	473	38.87	557	95.81
350	—	—	567	113.34
360	—	—	567	112.70
370	—	—	567	115.49
380	—	—	567	112.28
390	—	—	567	101.29

Table S5. Emission lifetimes of compound **1** at 75 K.

Ex/nm	Em_1/nm	τ/μs	Em_2/nm	τ/μs
310	473	37.27	—	—
320	473	37.98	—	—
330	473	34.85	545	51.62
340	473	34.87	555	96.88
350	—	—	558	100.18
360	—	—	563	105.93

370	—	—	563	115.44
380	—	—	563	112.62
390	—	—	563	107.67

Table S6. Emission lifetimes of compound **1** at 150 K.

Ex/nm	Em_1/nm	τ/μs	Em_2/nm	τ/μs
310	473	38.87	—	—
320	473	32.06	—	—
330	473	32.50	545	62.19
340	473	33.18	545	75.82
350	—	—	548	95.76
360	—	—	553	100.00
370	—	—	553	99.52
380	—	—	553	92.15
390	—	—	553	92.41

Table S7. Emission lifetimes of compound **1** at 200 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
310	488	46.17	360	544	86.92
320	488	33.81	370	544	98.96
330	488	37.22	380	544	100.13
340	535	67.68	390	544	84.54
350	544	82.71			

Table S8. Emission lifetimes of compound **1** at 250 K.

Ex/nm	Em/nm	τ /μs	Ex/nm	Em/nm	τ/μs
310	488	42.66	360	540	70.30
320	488	38.30	370	540	79.32
330	488	47.04	380	540	78.58
340	530	64.54	390	540	76.99
350	535	80.66			

Table S9. Emission lifetimes of compound **1** at 300 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs

295	495	72.45	350	535	70.76
310	495	65.54	360	535	69.83
320	497	57.42	370	535	70.12
330	514	63.62	380	535	69.16
340	531	69.56	390	535	69.29

Table S10. Emission lifetimes of compound **1** upon excitation at 365 nm from 300 K down to 5 K.

T/K	Em/nm	τ /μs	T/K	Em/nm	τ/μs
5	570	119.77	150	553	103.81
50	567	117.09	200	544	97.09
75	563	110.52	250	540	78.20
100	560	105.79	300	535	72.71

Table S11. Emission lifetimes of compound **2** at 5 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.63	360	505	5.52
330	478	4.26	370	505	5.54
340	494	5.26	380	505	5.84
350	498	5.84	390	505	5.67

Table S12. Emission lifetimes of compound **2** at 50 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.57	360	504	5.51
330	478	4.29	370	504	5.80
340	491	5.12	380	504	5.93
350	498	5.73	390	504	5.81

Table S13. Emission lifetimes of compound **2** at 75 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.70	360	504	5.44
330	478	4.54	370	504	5.83
340	488	4.96	380	504	5.70
350	498	5.70	390	504	5.64

Table S14. Emission lifetimes of compound **2** at 100 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.53	360	504	5.46
330	478	4.77	370	504	5.81
340	486	5.31	380	504	5.73
350	495	5.81	390	504	5.71

Table S15. Emission lifetimes of compound **2** at 150 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.71	360	504	5.45
330	478	4.96	370	504	5.84
340	485	5.27	380	504	5.77
350	495	5.71	390	504	5.72

Table S16. Emission lifetimes of compound **2** at 200 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.38	360	503	5.41
330	478	5.07	370	503	5.82
340	484	4.84	380	503	5.76
350	495	5.59	390	503	5.70

Table S17. Emission lifetimes of compound **2** at 250 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.47	360	502	5.27
330	478	4.52	370	502	5.75
340	484	4.75	380	502	5.74
350	495	5.05	390	502	5.72

Table S18. Emission lifetimes of compound **2** at 275 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	4.47	360	502	5.27
330	478	4.52	370	502	5.75
340	484	4.75	380	502	5.74
350	495	5.05	390	502	5.72

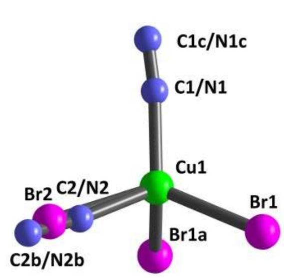
Table S19. Emission lifetimes of compound **2** at 300 K.

Ex/nm	Em/nm	τ/μs	Ex/nm	Em/nm	τ/μs
320	478	3.58	360	495	4.84
330	478	2.92	370	502	5.78
340	482	3.41	380	502	6.11
350	493	3.85	390	502	6.22

Table S20. The engergy gap of the exctation from the singlet ground state to the triplet ecited state ($S_0 \rightarrow T_1$) for sixteen different geometries caused by disorder bromide and cyanide.

Label of the geomtry	Orbitals related to exctation (>90%)	Engery gap (eV)
C2Br2	110→115	3.42
C2N2-a	90→93	3.64
C2N2-b	90→93	3.71
C2N2-c	91→94	3.64
C2NBr-a	100→104	3.36
C2NBr-b	102→105	3.51
C2NBr-c	100→104	3.51
C3N	91→94	3.58
C4	91→94	3.53
CN2Br-a	103→105	3.38
CN2Br-b	100→104	3.38
CN2Br-c	103→105	3.49
CN3	90→93	3.71
CNBr2	110→115	3.28
N2Br2	114→115	3.20
N4	89→93	3.71

S2. The Figures in Supporting Information



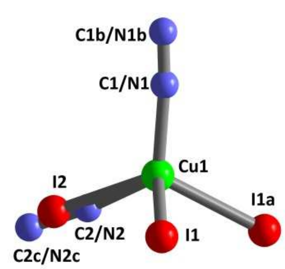


Figure S1. View of the coordination environments of Cu(I) atoms in **1** (left) and **2** (right).

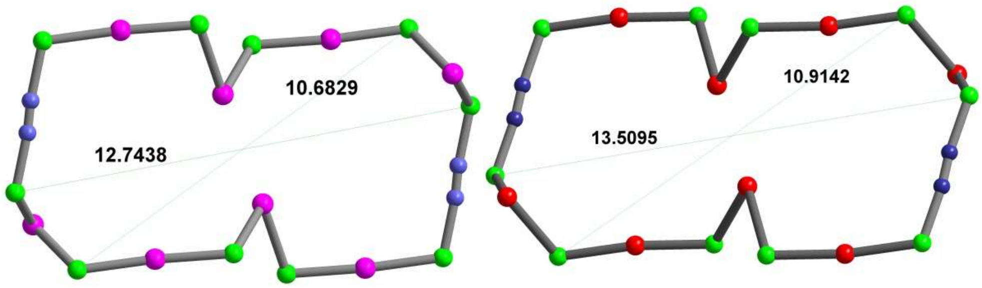


Figure S2. View of 10-membered dumbbell-shaped ring in **1** (left) and **2** (right).

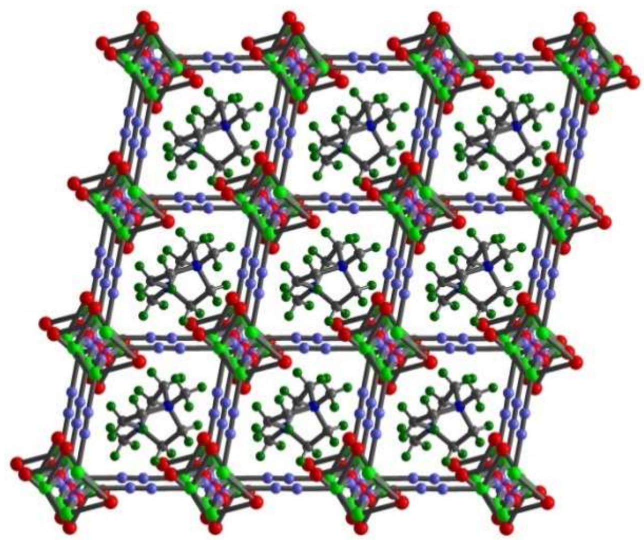


Figure S3. 3D open anionic framework showing the channels filled by organic templates in **2**.

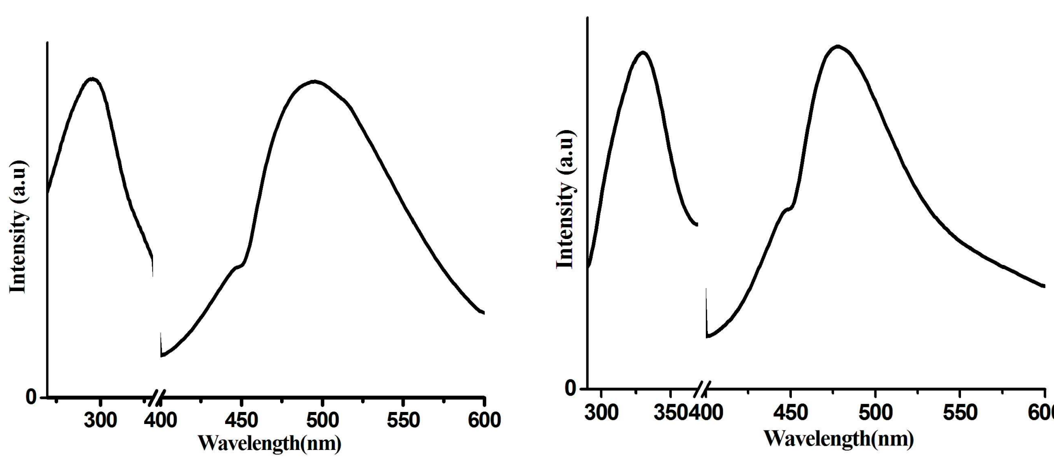


Figure S4.The solid-state luminescence spectra of **1** (λ_{ex} = 295 nm, left) and **2** (λ_{ex} = 330 nm, right).

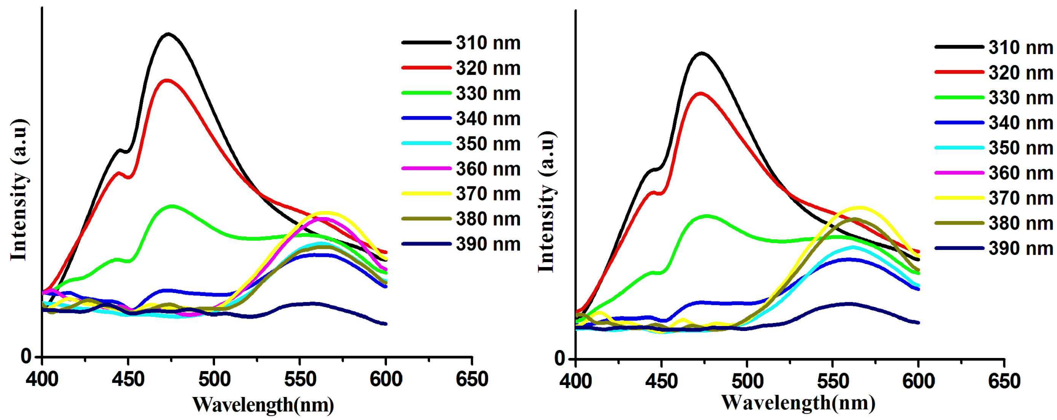


Figure S5.The solid-state luminescence spectra of compound **1** by varying excitation lights at 5 K (left) and 50 K (right).

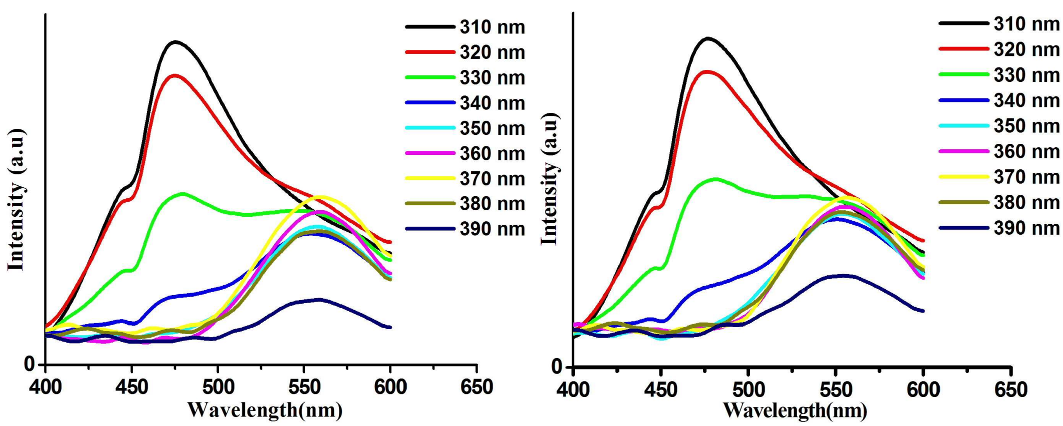


Figure S6. The solid-state luminescence spectra of compound **1** by varying excitation lights at 75 K (left) and 100 K (right).

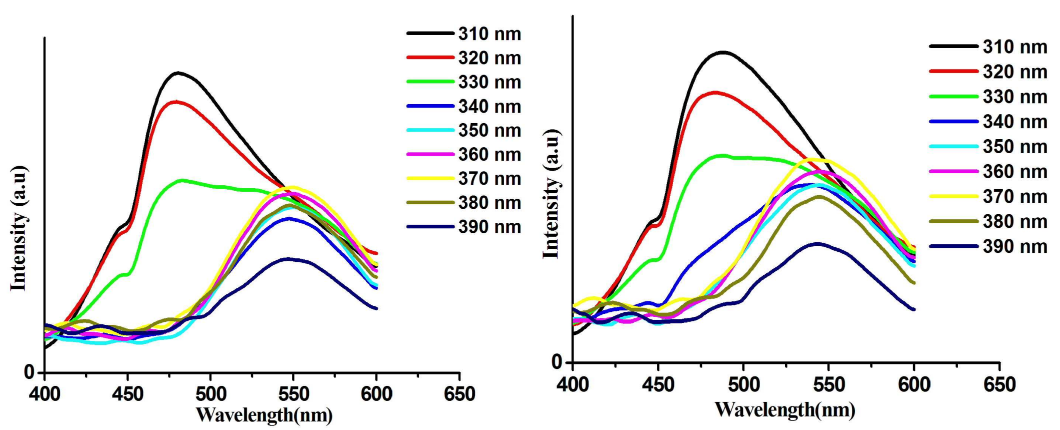


Figure S7. The solid-state luminescence spectra of compound **1** by varying excitation lights at 150 K (left) and 200 K (right).

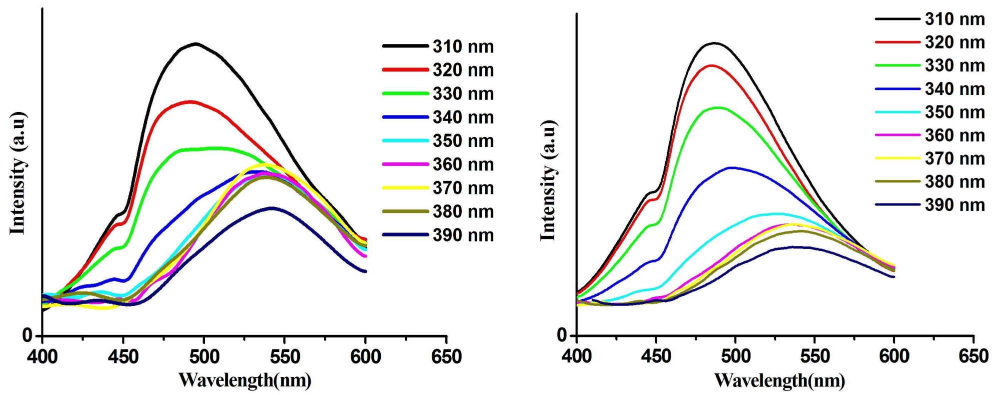


Figure S8. The solid-state luminescence spectra of compound **1** by varying excitation lights at 250 K (left) and 300 K (right).

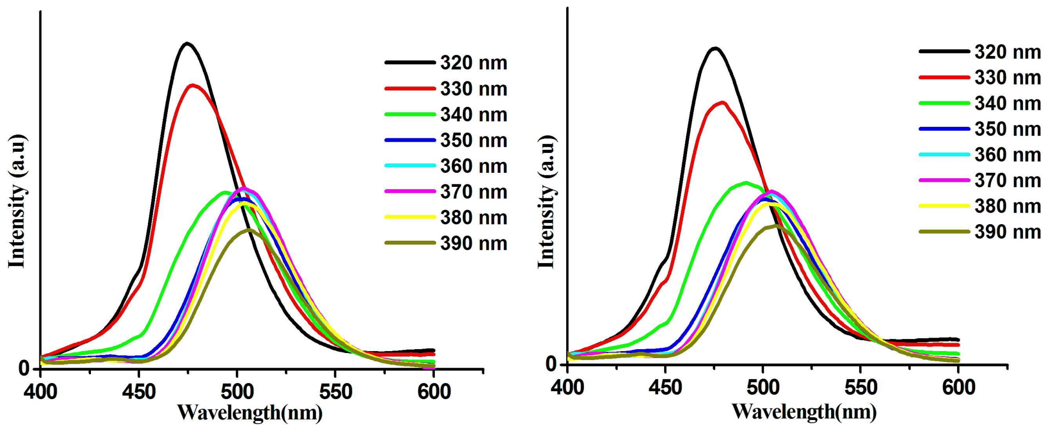


Figure S9. The solid-state luminescence spectra of compound **2** by varying excitation lights at 5 K (left) and 50 K (right).

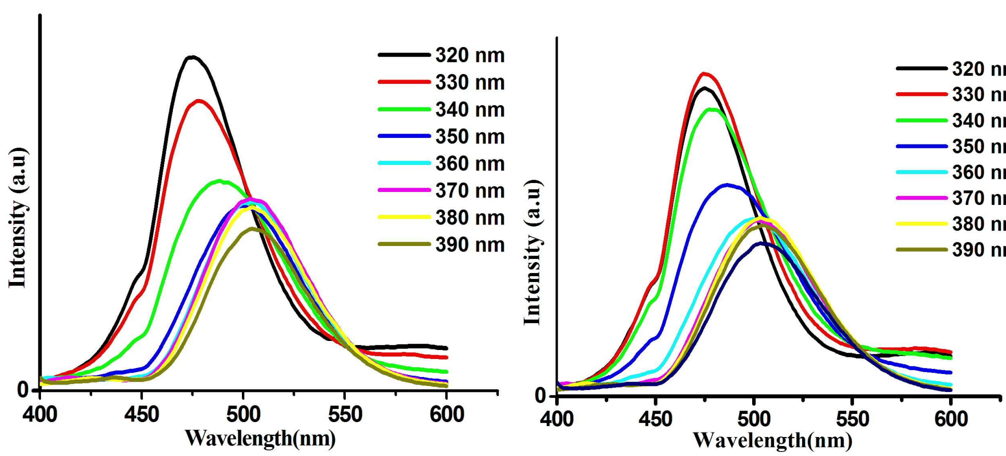


Figure S10. The solid-state luminescence spectra of compound **2** by varying excitation lights at 75 K (left) and 100 K (right).

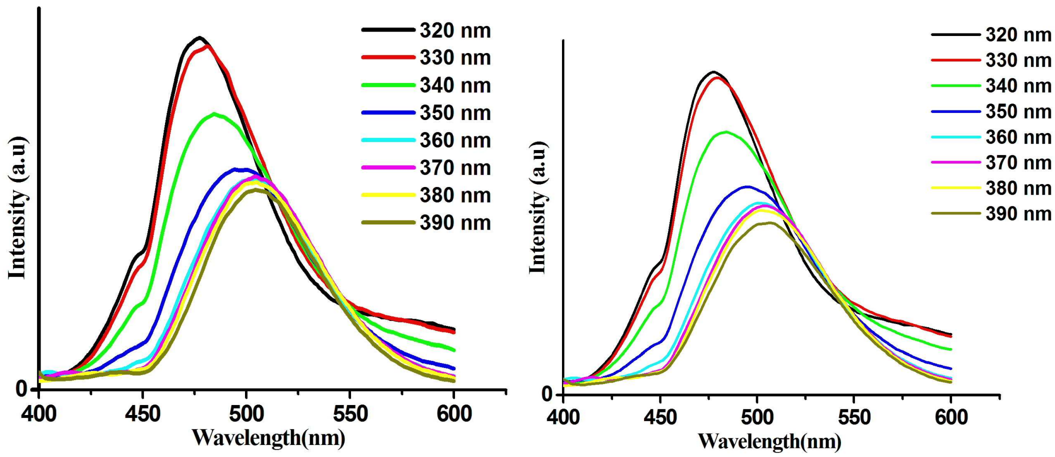


Figure S11. The solid-state luminescence spectra of compound **2** by varying excitation lights at 150 K (left) and 200 K (right).

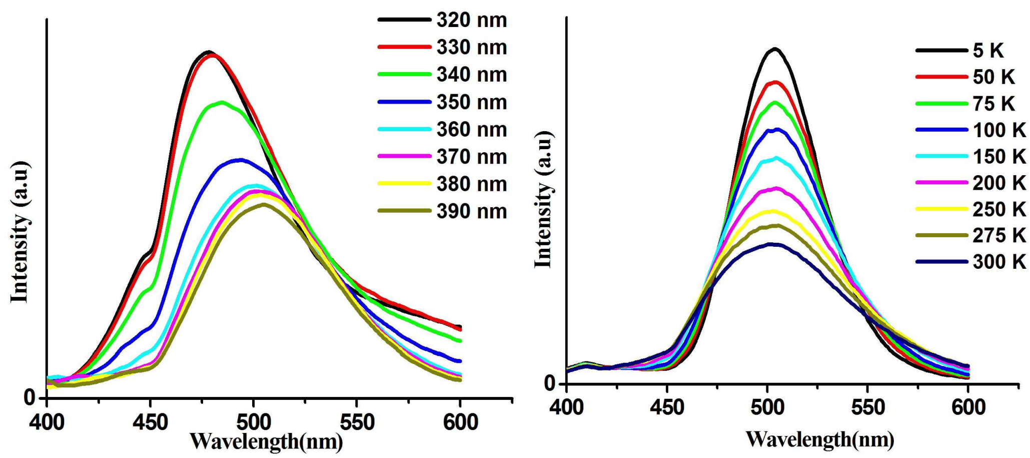


Figure S12. The solid-state luminescence spectra of compound **2** by varying excitation lights at 250 K (left) and upon 365 nm excitation from 300 K to 5 K (right).

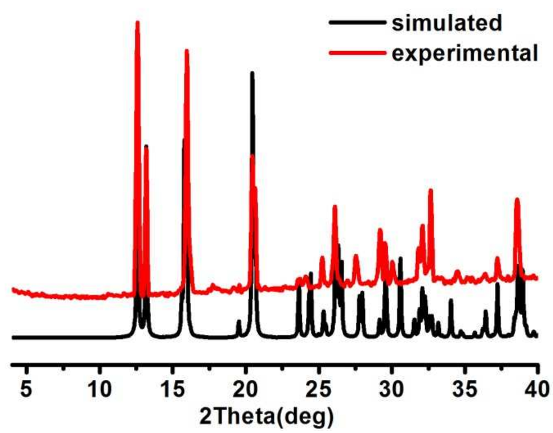


Figure S13. The PXRD patterns of simulated and experimental for **1**.

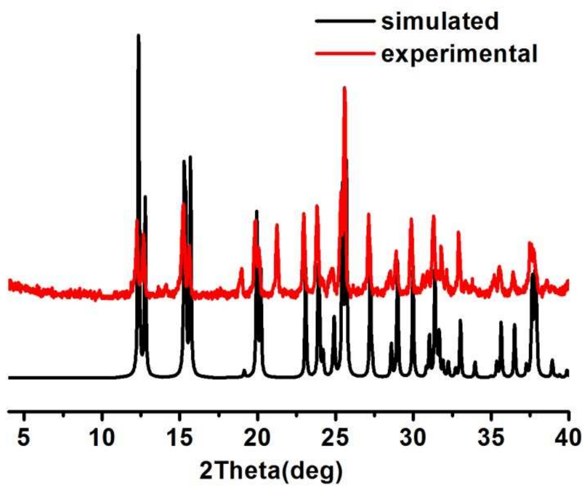


Figure S14. The PXRD patterns of simulated and experimental for **2**.

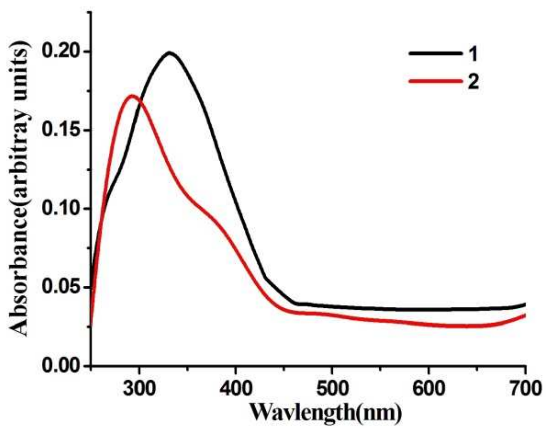


Figure S15. UV-vis diffuse reflectance spectra of **1** and **2**.

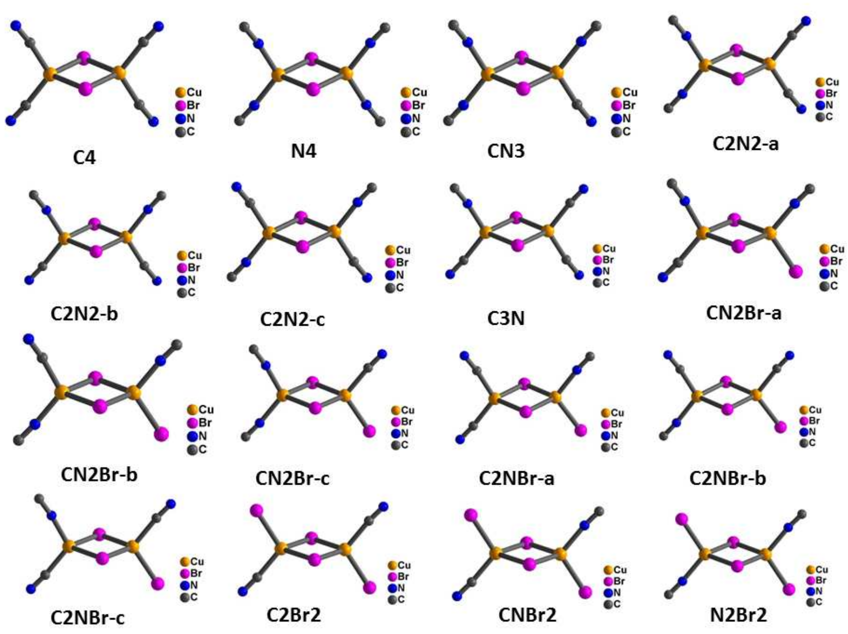


Figure S16. Sixteen different geometries Of Cu_2 cluster arising from disordered occupancy of the X^{-}/CN^{-} sites