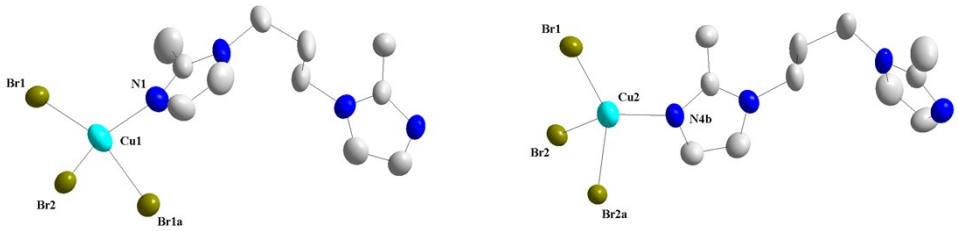
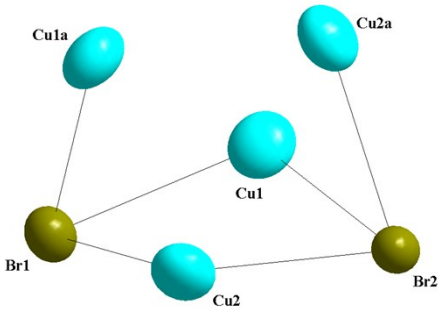
Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting information



(a)



(b)

Fig. S1 Coordination environments of Cu1, Cu2 (a) and bridging modes of Br1, Br2 (b) in **1**.

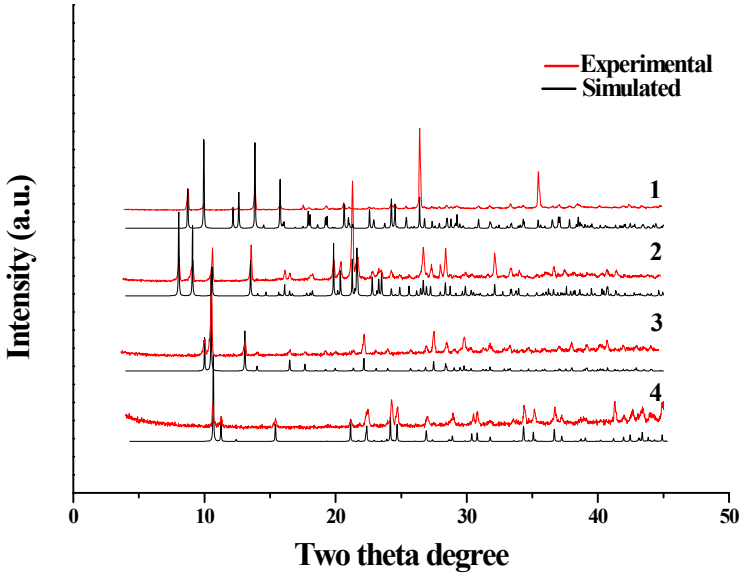


Fig. S2 Powder XRD patterns of **1**-**4**.

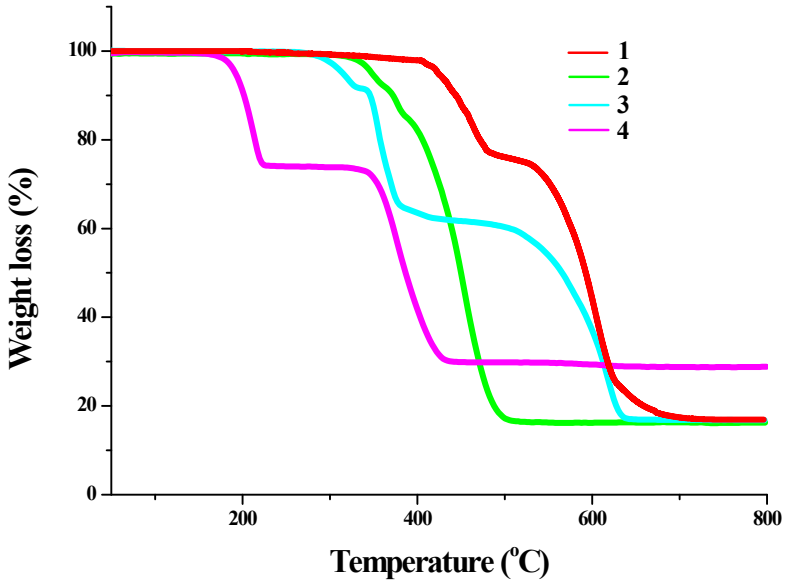
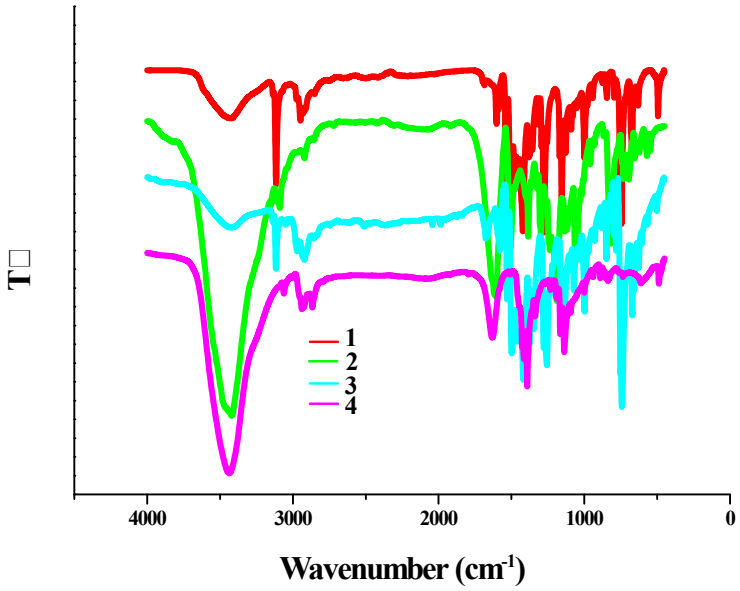


Fig. S3 TG curves of **1**-**4**.



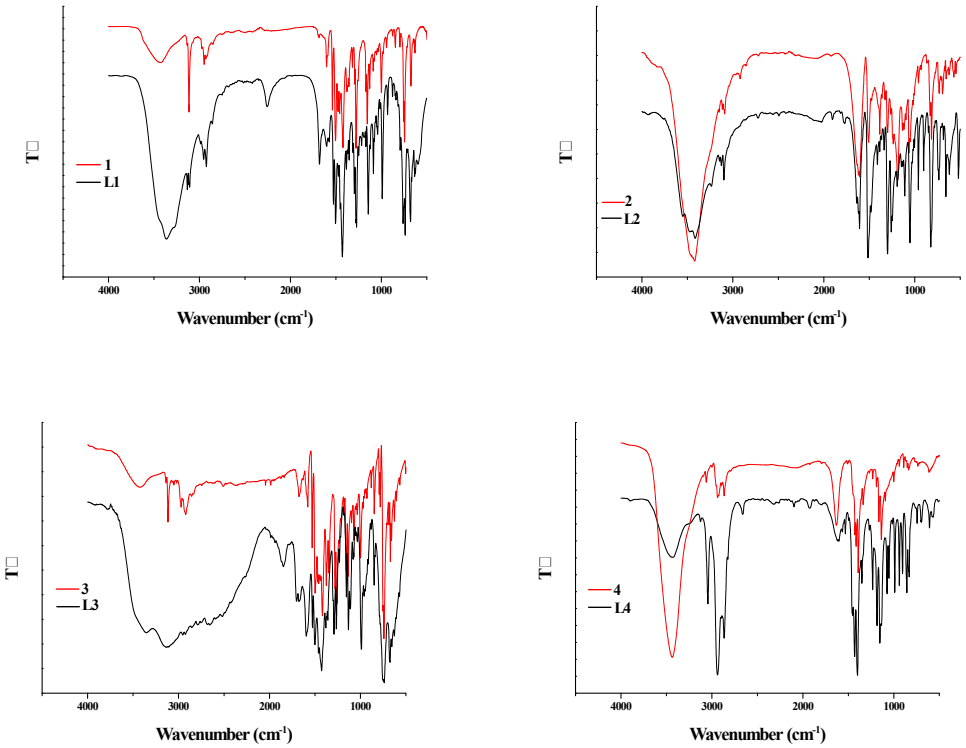
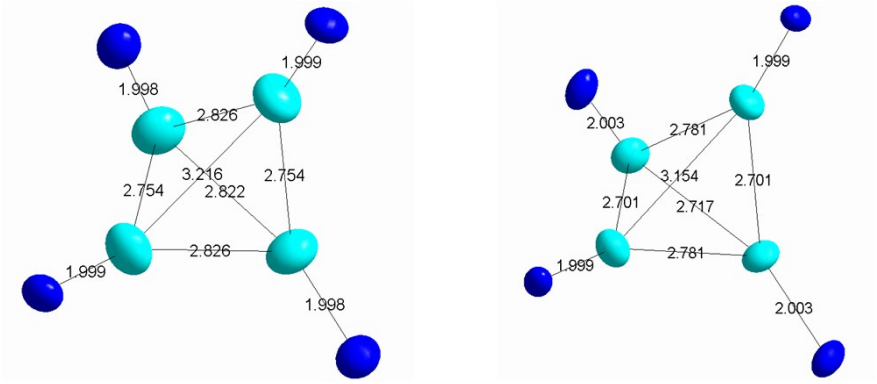
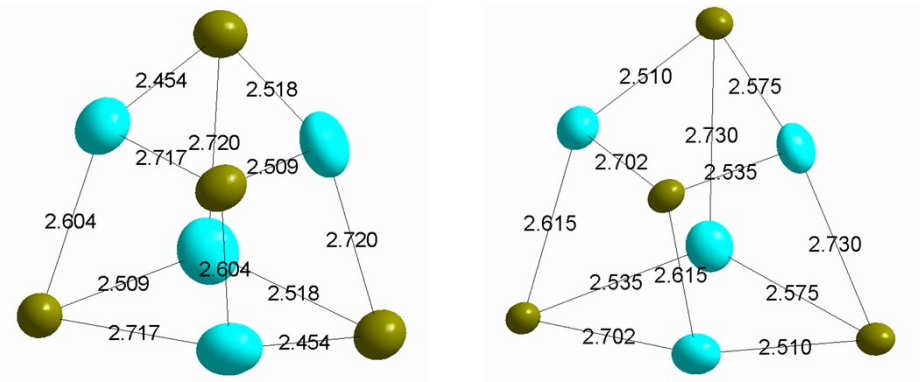


Fig. S4 IR spectra of **1**-**4**.



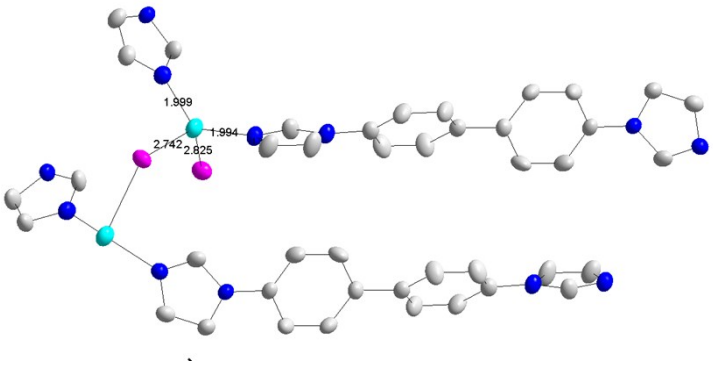
(a) **(b)**

Fig. S5 Plots showing Cu-N and Cu···Cu distances at 299 K (a) and 173 K (b) in **1**.

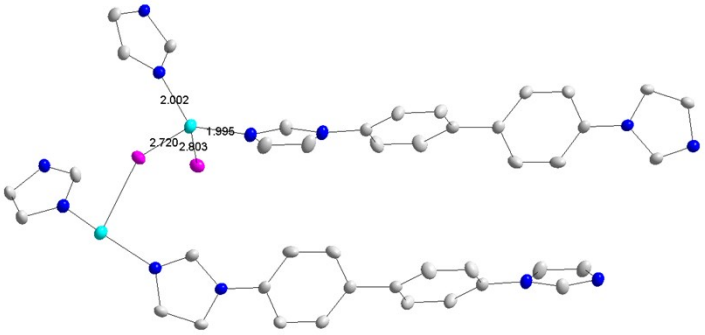


(a) **(b)**

Fig. S6 Plots showing Cu-Br distances at 299 K (a) and 173 K (b) in **1**.

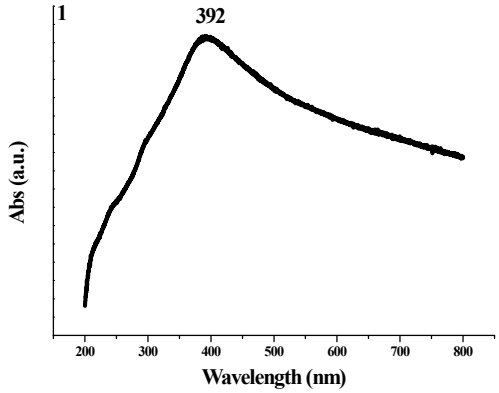


(a)



(b)

Fig. S7 Plots showing Cu-I and Cu-N distances at 297 K (a) and 173 K (b) in **2**.



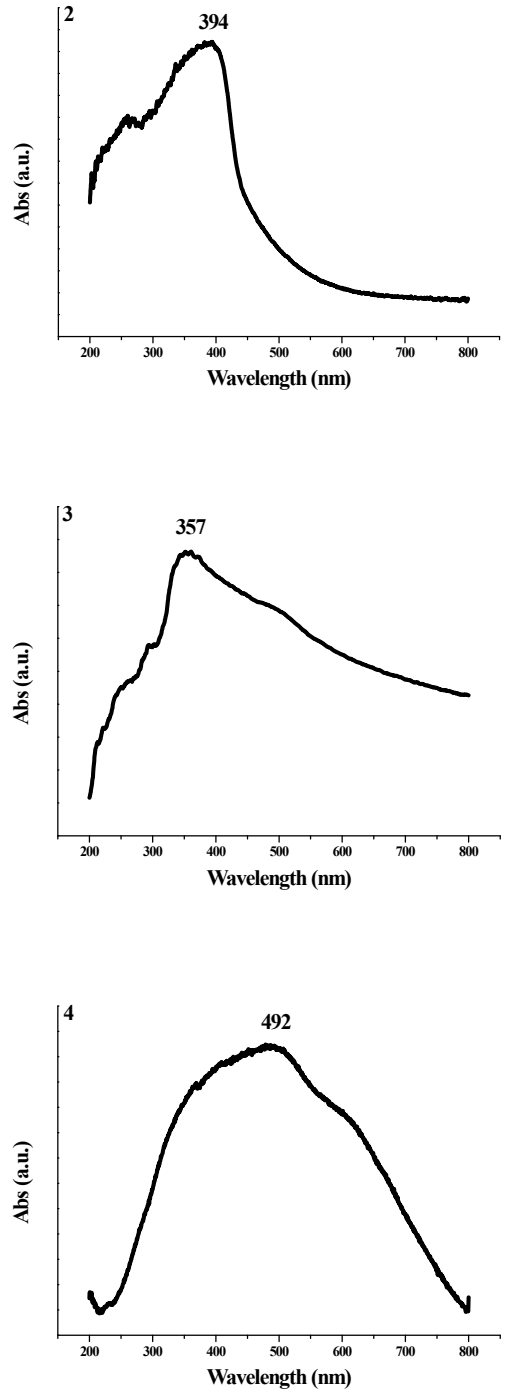


Fig. S8 Solid-state UV-vis spectra of **1**-**4** at room temperature.

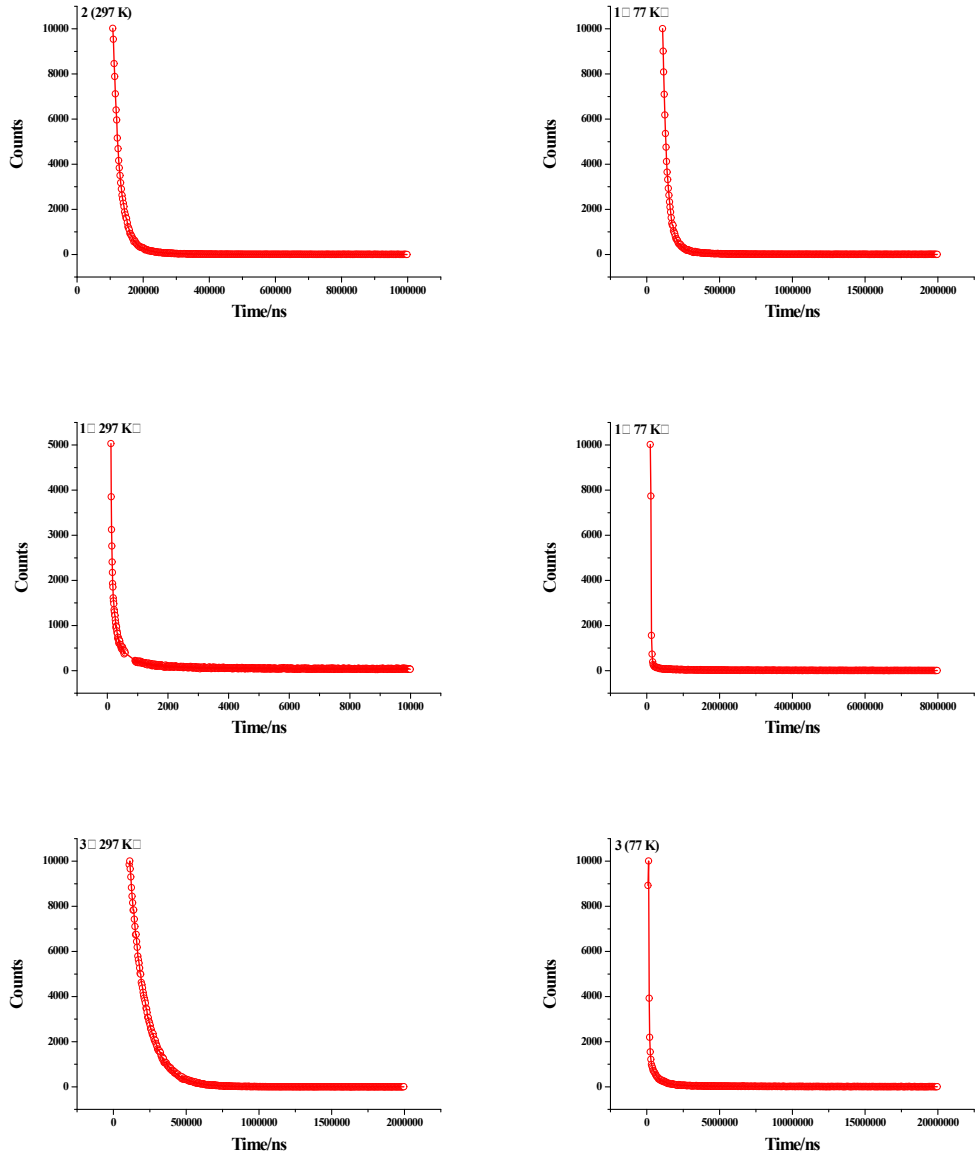


Fig. S9 Decay curves of **1**, **2** and **3** at 297 K and 77 K.

Table S1 Crystal data of **3** at 295 K

	3′
Formula	$C_{16}H_{18}N_4CuI$
M	456.79
T (K)	295(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.2408(4)
b (Å)	11.2282(4)
c (Å)	14.6987(5)
α (°)	90
β (°)	98.7760(10)

γ (°)	90
V (Å^3)	1670.35(11)
Z	4
D_c (g cm^{-3})	1.816
μ (mm^{-1})	3.157
Reflections collected	30816
Unique reflections	4140
R_{int}	0.1297
Gof	1.157
R_1, $I>2\sigma(I)$	0.0339
wR_2, all data	0.1105

Table S2 Photoluminescence lifetimes of **1**, **2** and **3** at 297 K and 77 K

	297 K	77 K
1	τ_1 = 19.38 μs, B1 = 9690.382	τ_1= 30.53 μs, B1 = 9613.146
	τ_2 = 68.35 μs, B2 = 664.031	τ_2 = 139.9 μs, B2 = 503.661
2	τ_1 = 46.05 ns, B1 = 2652.986	τ_1 = 9.211 μs, B1 = 40899.504
	τ_2 = 254 ns, B2 = 1295.133	τ_2 = 89.8 μs, B2 = 481.609
	τ_3 = 1.441 μs, B3 = 211.228	τ_3 = 1.240 ms, B3 = 77.596
3	τ_1 = 112.9 μs, B1 = 9650.912	τ_1= 49.03 μs, B1 = 6150.210
		τ_2 = 540.6 μs, B2 = 1156.404
		τ_3 = 3.848 ms, B3 = 77.005

The decay curves for **1** at 297 and 77K are fitted into a double exponential function. The decay curves for **2** at 297 K and 77 K are fitted into a triple exponential function. The decay curves for 3 at 297 K is fitted into a single exponential function, whereas the decay curve for **3** at 77 K is fitted into a triple exponential function. Bi is the pre-exponential function for the lifetime τ_i.