Supporting Information

Superstructures of Copper Nanoclusters as NIR TADF Emitters: Solvent-dependent Optical and Morphological Modulation

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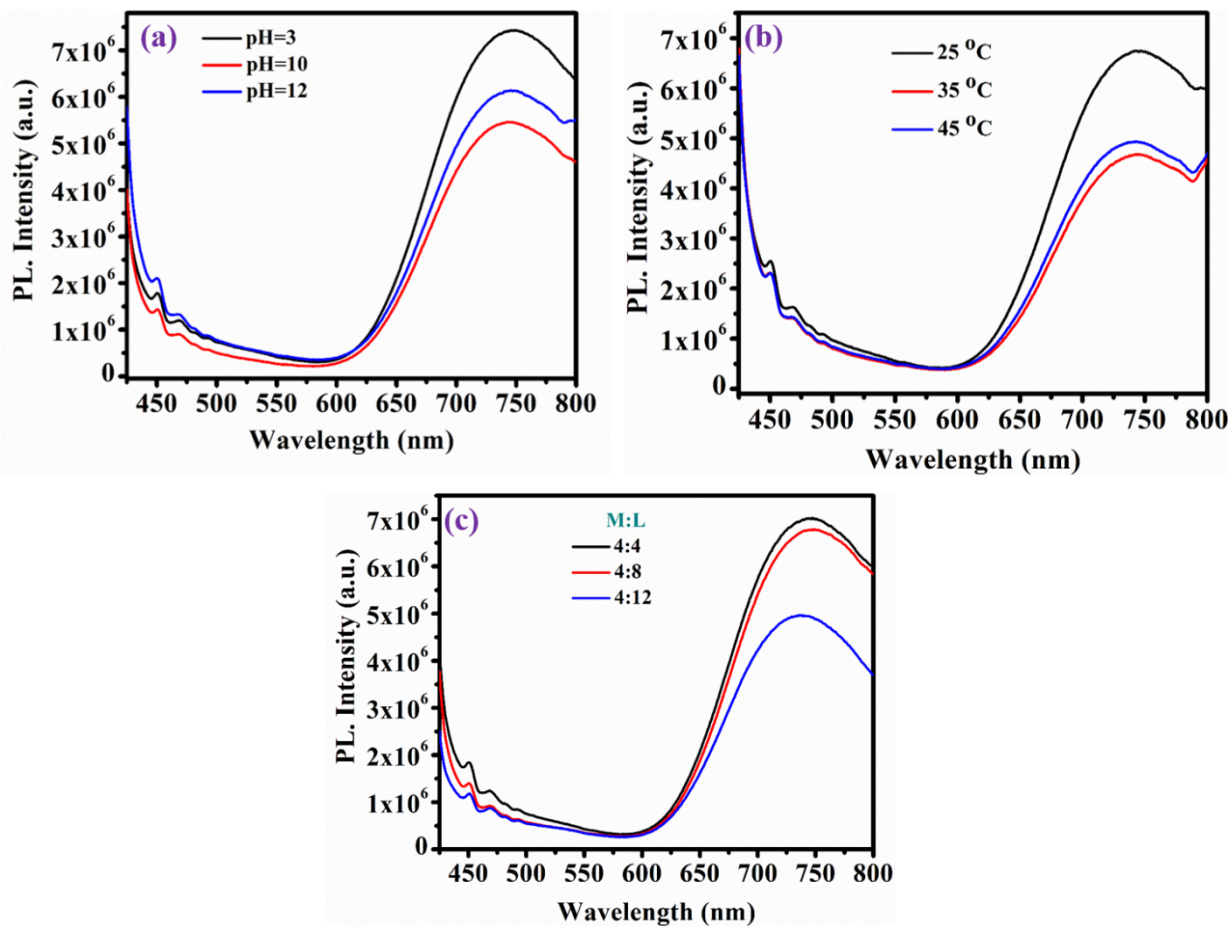*Indian Institute of Science Education and Research Bhopal*

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Figure S1. Optimization of the reaction conditions for the CuNCs preparation in water. (a) pH optimization; (b) temperature optimization; (c) metal-to-ligand concentration optimization. All the spectra were taken at the excitation wavelength of 410 nm.
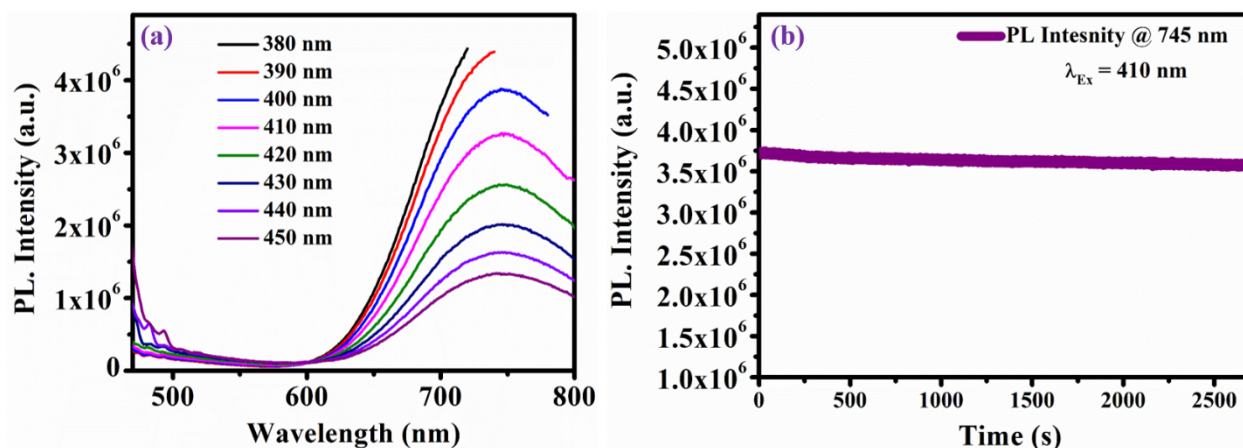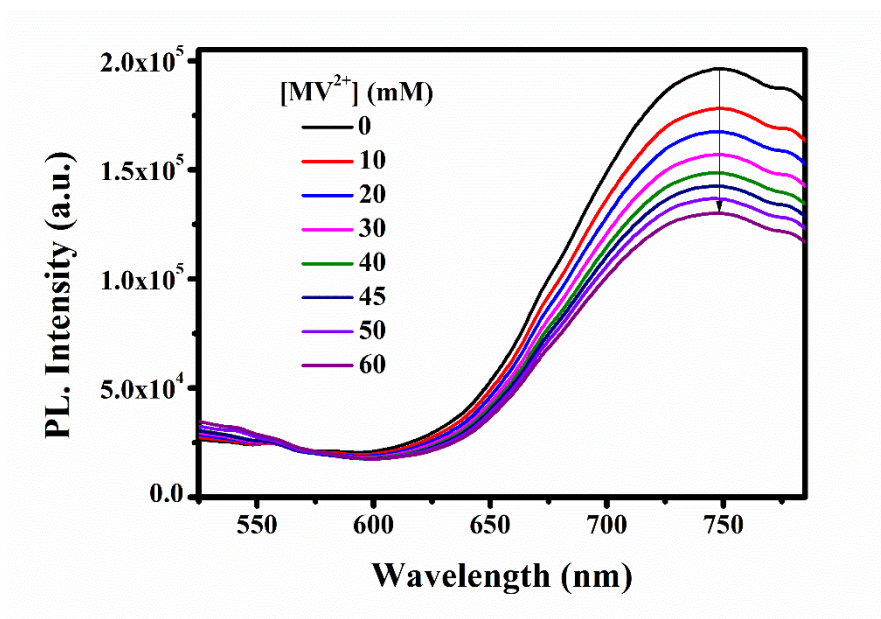
Figure S2. (a) Excitation-dependent emission spectra; (b) photostability (monitored for ~45 minutes; upon exciting the sample at 410 nm) of the as-prepared R-CuNCs after re-dissolving in DMSO.
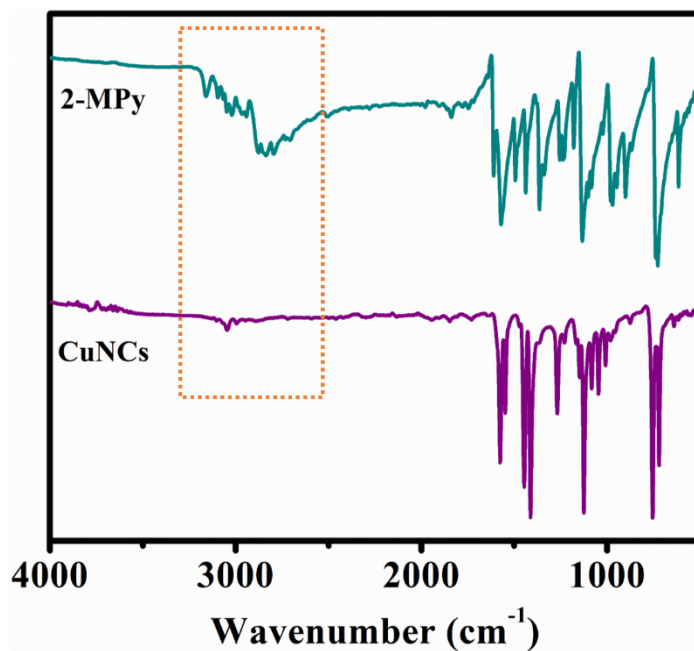
Table S1. Lifetime decay fitting parameters of R-CuNCs.

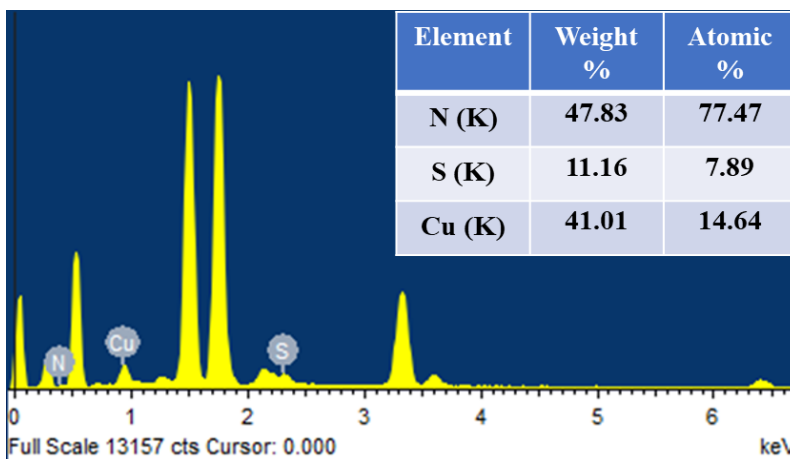| CuNCs	α (%)	τ (μs)	$<\tau>$[a] (μs)	χ^2
R-CuNCs	100	3.90	3.90	1.04

[a] ±5%

Figure S3. Photoluminescence profiles depicting the quenching of the PL intensity of the R-CuNCs upon the addition of MV^{2+}. The samples were excited at 410 nm.

Figure S4: FT-IR spectra of the as-prepared CuNCs (lower panel), and the ligand, 2-MPy only (upper panel).

Element	Weight %	Atomic %
N (K)	47.83	77.47
S (K)	11.16	7.89
Cu (K)	41.01	14.64

Full Scale 13157 cts Cursor: 0.000

Figure S5: SEM EDX analysis of as-prepared R-CuNCs. The inset represents the presence of Cu, N and S along with their weight % and atomic %.
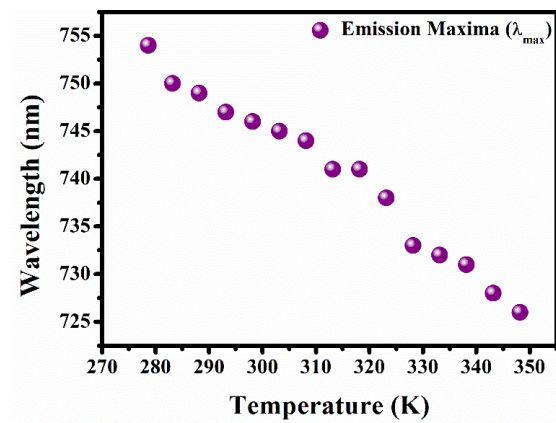
Figure S6. Blue shift in the emission maxima of R-CuNCs as a function of increasing temperature.
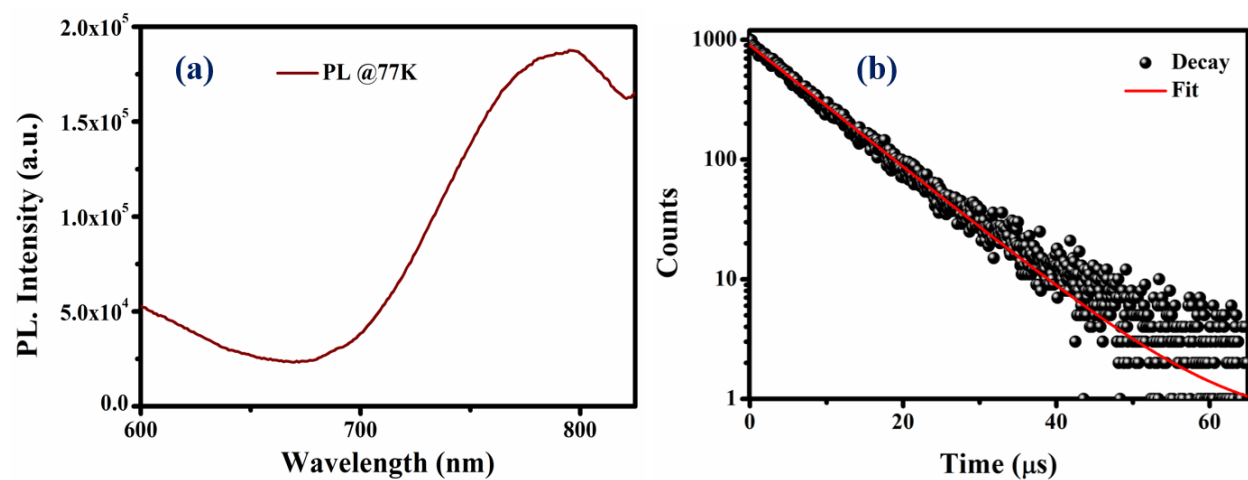
Table S2. Lifetime data fitting parameters of R-CuNCs upon increasing temperature from 278.15 K to 348.15 K.

Temperature (K)	α (%)	τ (μs)	$<\tau>^a$ (μs)	χ^2
278.15	100	4.118	4.118	1.01
283.15	100	4.004	4.004	1.00
288.15	100	3.873	3.873	1.00
293.15	100	3.766	3.766	1.00
298.15	100	3.667	3.667	1.00
303.15	100	3.599	3.599	1.01
308.15	100	3.514	3.514	1.02
313.15	100	3.427	3.427	1.01
318.15	100	3.349	3.349	1.00
323.15	100	3.275	3.275	1.01
328.15	100	3.213	3.213	1.01
333.15	100	3.138	3.138	1.00
338.15	100	3.085	3.085	1.01
343.15	100	3.008	3.008	1.01
348.15	100	2.957	2.957	1.02

[a] $\pm 5\%$

Table S3. TADF model fitting parameters for the average lifetime *vs* temperature plot for the R-CuNCs.

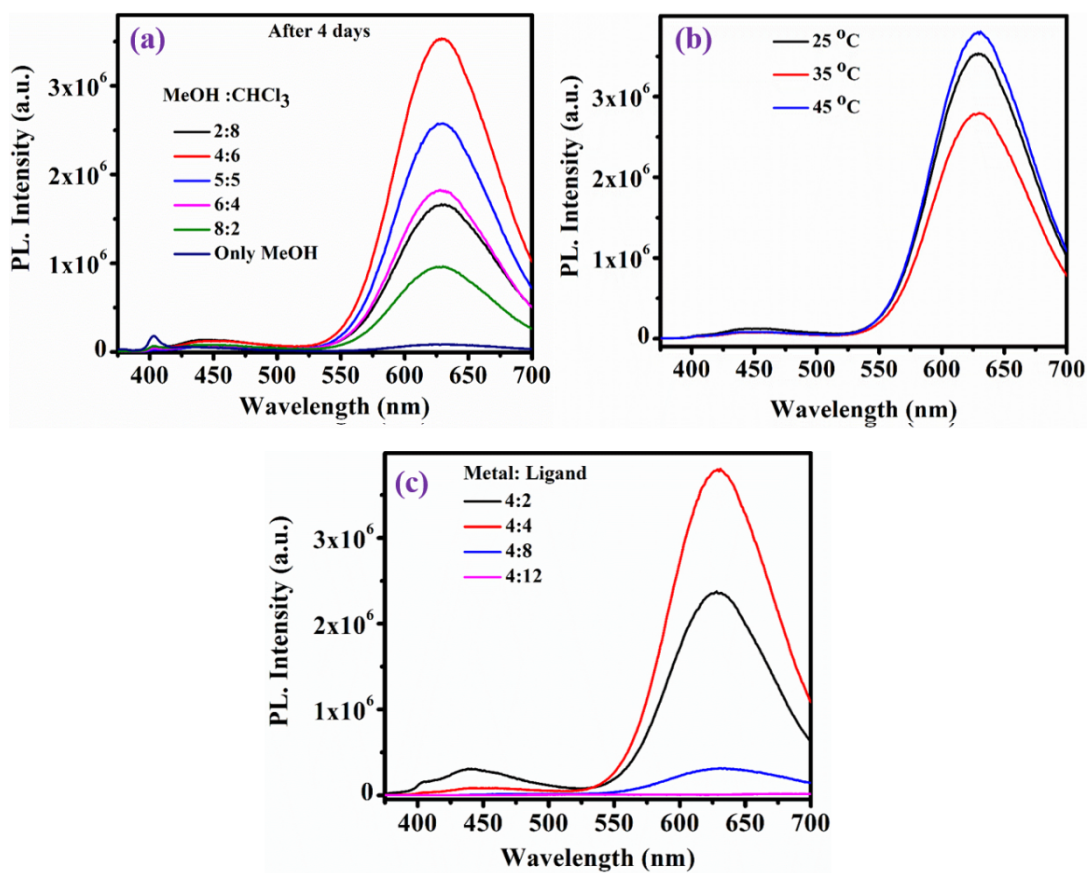| $\Delta E\ (S_1-T_1)$ (meV)	$\tau(T_1)$ (μs)	$\tau(S_1)$ (ns)	R^2
58.2	11.60	177.85	0.9989

Figure S7. (a) Photoluminescence profile and, (b) lifetime decay profile of R-CuNCs, at 77 K temperature.

Table S4. Lifetime decay fitting parameters for R-CuNCs at 77 K temperature.

| Temperature (K)	α (%)	τ (μs)	$<\tau>^a$ (μs)	χ^2
77	100	8.53	8.53	1.01

[a] ±5%

Figure S8. Optimization of reaction conditions for the preparation of CuNCs in MeOH-CHCl$_3$ solvent mixture resulting in the formation of the O-CuNCs. (a) MeOH to CHCl$_3$ solvent ratio optimization, spectra were taken after 4 days of the preparation of the CuNCs to check the stability; (b) reaction temperature optimization; and (c) metal-to-ligand concentration optimization. All the spectra were taken at λ_{ex} = 360 nm.
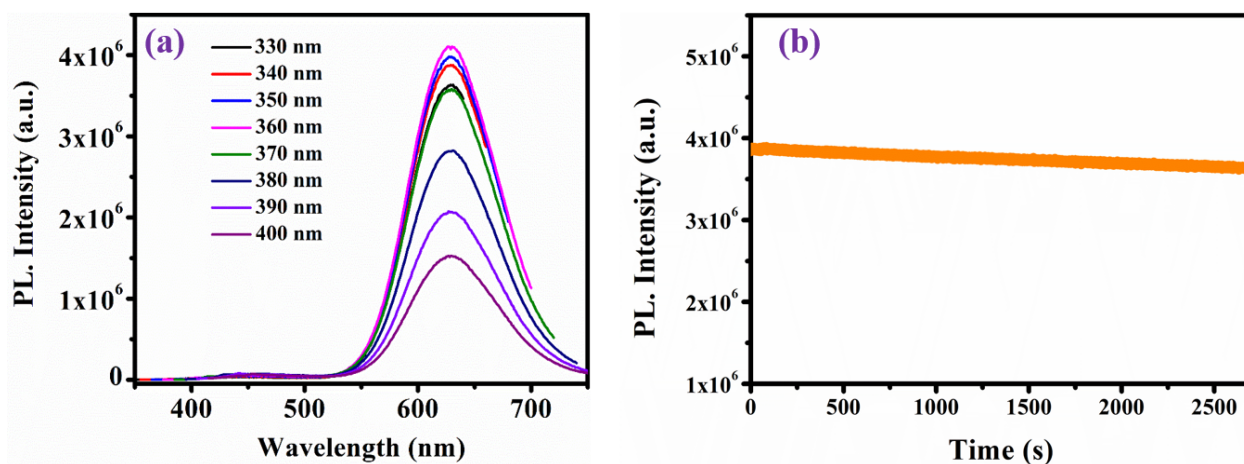
Figure S9. (a) Excitation-dependent emission spectra; (b) photostability study upon excitation at 360 nm for ~30 minutes of as-prepared CuNCs in MeOH-CHCl$_3$ solvent mixture.
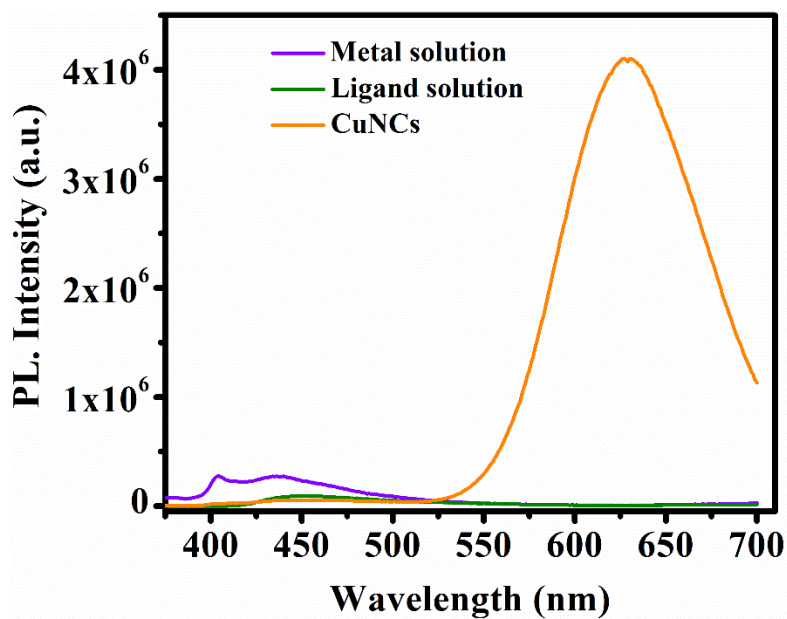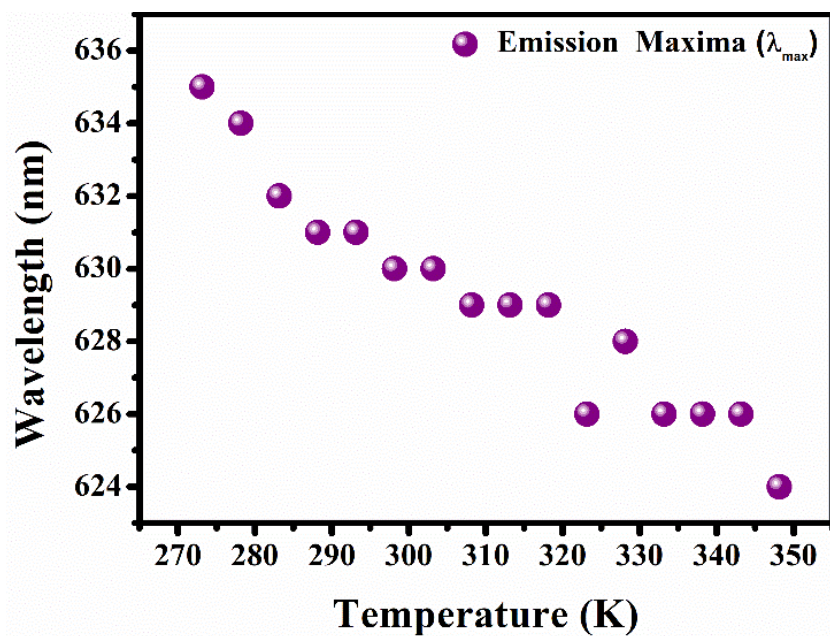

Figure S10. Control experiments to establish that the PL property of the CuNCs is an exclusive property of the system and not due to the ligand and metal solution as they do not exhibit any PL intensities.

Table S5. Lifetime decay fitting parameters of O-CuNCs.

CuNCs	α (%)	τ (ns)	$<\tau>^a$ (ns)	χ^2
O-CuNCs	100	491	491	1.01

[a] $\pm 5\%$

**Figure S11:** Blue shift in the emission maxima of O-CuNCs upon increasing temperature from 273.15 K to 348.15 K.

Table S6. Lifetime data fitting parameters for O-CuNCs upon increasing temperature from 278.15 K to 348.15 K.

| Temperature (K)	α (%)	τ (µs)	$<\tau>$a (µs)	χ^2
278.15	100	0.605	0.605	1.01
283.15	100	0.570	0.570	1
288.15	100	0.539	0.539	1
293.15	100	0.508	0.508	1.01
298.15	100	0.476	0.476	1.01
303.15	100	0.436	0.436	1
308.15	100	0.407	0.407	1
313.15	100	0.374	0.374	1.01
318.15	100	0.342	0.342	1.02
323.15	100	0.319	0.319	1.01
328.15	100	0.287	0.287	1.03
333.15	100	0.240	0.240	1.01
338.15	100	0.214	0.214	1.02
343.15	100	0.185	0.185	1.02
348.15	100	0.145	0.145	1

a ±5%

Table S7. TADF model fitting parameters for the average lifetime *vs* temperature plot for O-CuNCs.

ΔE (S_1-T_1) (meV)	$\tau(T_1)$ (µs)	$\tau(S_1)$ (ns)	R^2
199.03	1.34	0.10	0.97323
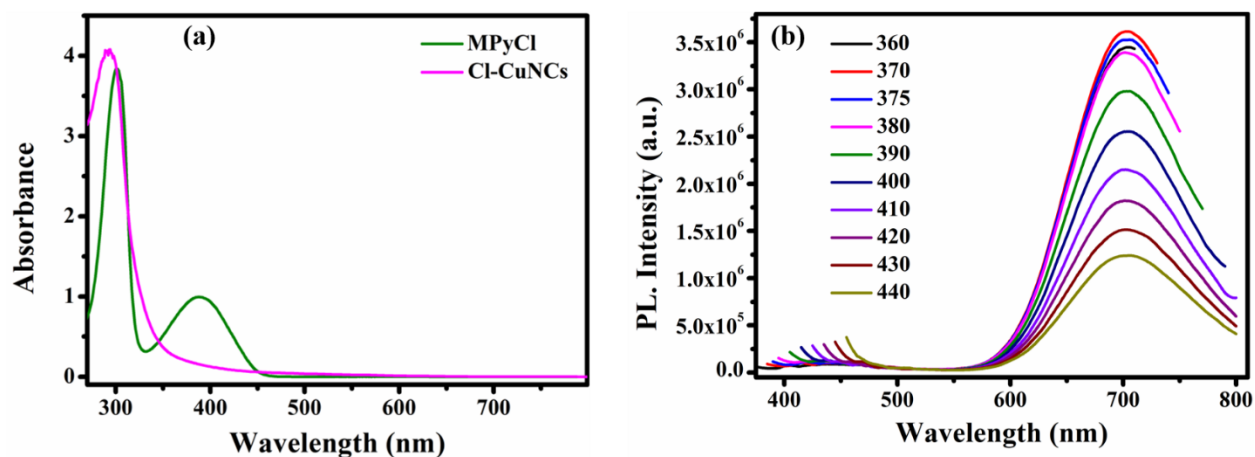
Figure S12. Photophysical studies of 5-Cl-2-MPy templated CuNCs (Cl-CuNCs). (a) Absorption spectra of Cl-CuNCs, and MPyCl (ligand); (b) excitation-dependent emission spectra representing maximum PL intensity upon 370 nm excitation.
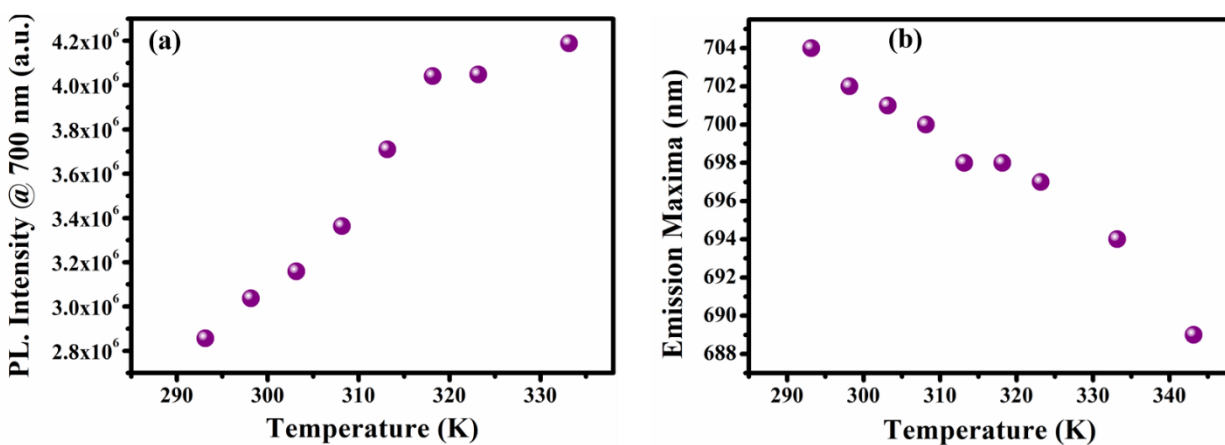
Figure S13. Temperature-dependent studies of 5-Cl-2-MPy templated CuNCs (Cl-CuNCs). (a) PL intensity at 700 nm as a function of increasing temperature; (b) the variation in the emission maxima as a function of temperature representing the blue shift in emission maxima upon increasing temperature.

Table S8. Lifetime decay fitting parameters for the temperature dependent lifetime studies on Cl-CuNCs.

Temperature	α	τ	$<\tau>^a$	χ^2

| (K)	(%)	(µs)	(µs)	
293.15	100	6.385	6.385	1.02
295.15	100	6.341	6.341	1.04
298.15	100	6.230	6.230	1.04
303.15	100	6.050	6.050	1.04
308.15	100	5.888	5.888	1.02
313.15	100	5.773	5.773	1.01
318.15	100	5.629	5.629	1.00
323.15	100	5.469	5.469	1.00
328.15	100	5.354	5.354	1.00
333.15	100	5.203	5.203	1.00
338.15	100	5.079	5.079	1.04

[a] ±5%

**Table S9.** TADF model fitting parameters for the average lifetime *vs* temperature plot for Cl-CuNCs.

ΔE (S$_1$-T$_1$) (meV)	τ(T$_1$) (µs)	τ(S$_1$) (ns)	R^2
111.5	9.5	77.9	0.9986
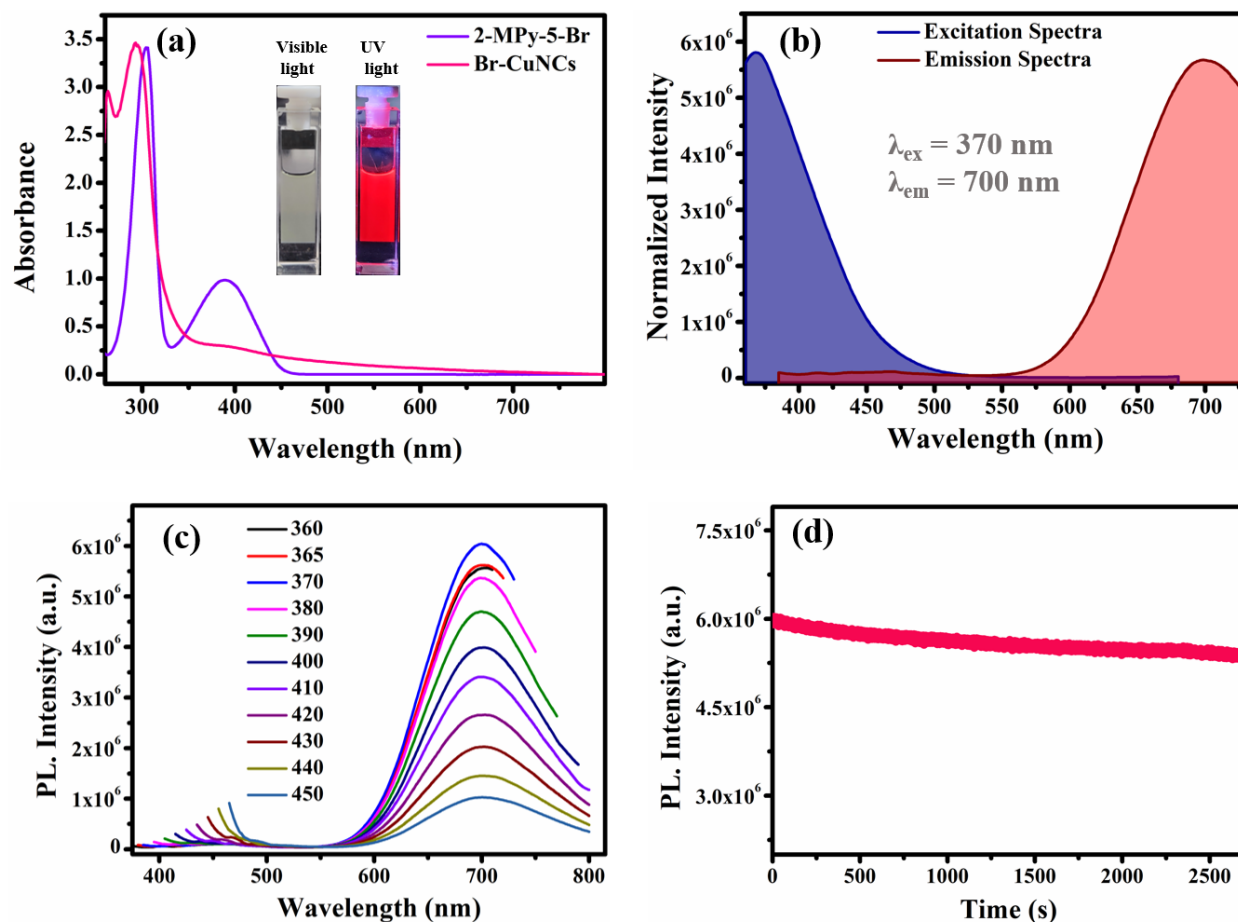
Figure S14. Photophysical studies of 5-Br-2-MPy templated CuNCs i.e., Br-CuNCs. (a) Absorption spectra of Br-CuNCs, and 5-Br-2-MPy (ligand); (b) excitation and emission spectra of Br-CuNCs, representing a large Stokes shift of 330 nm; (c) excitation-dependent emission spectra, representing maximum PL intensity upon 370 nm excitation; (d) photostability plot for the as-prepared CuNCs, monitored at 370 nm excitation wavelength at the emission maxima (700 nm) for ~45 mins.
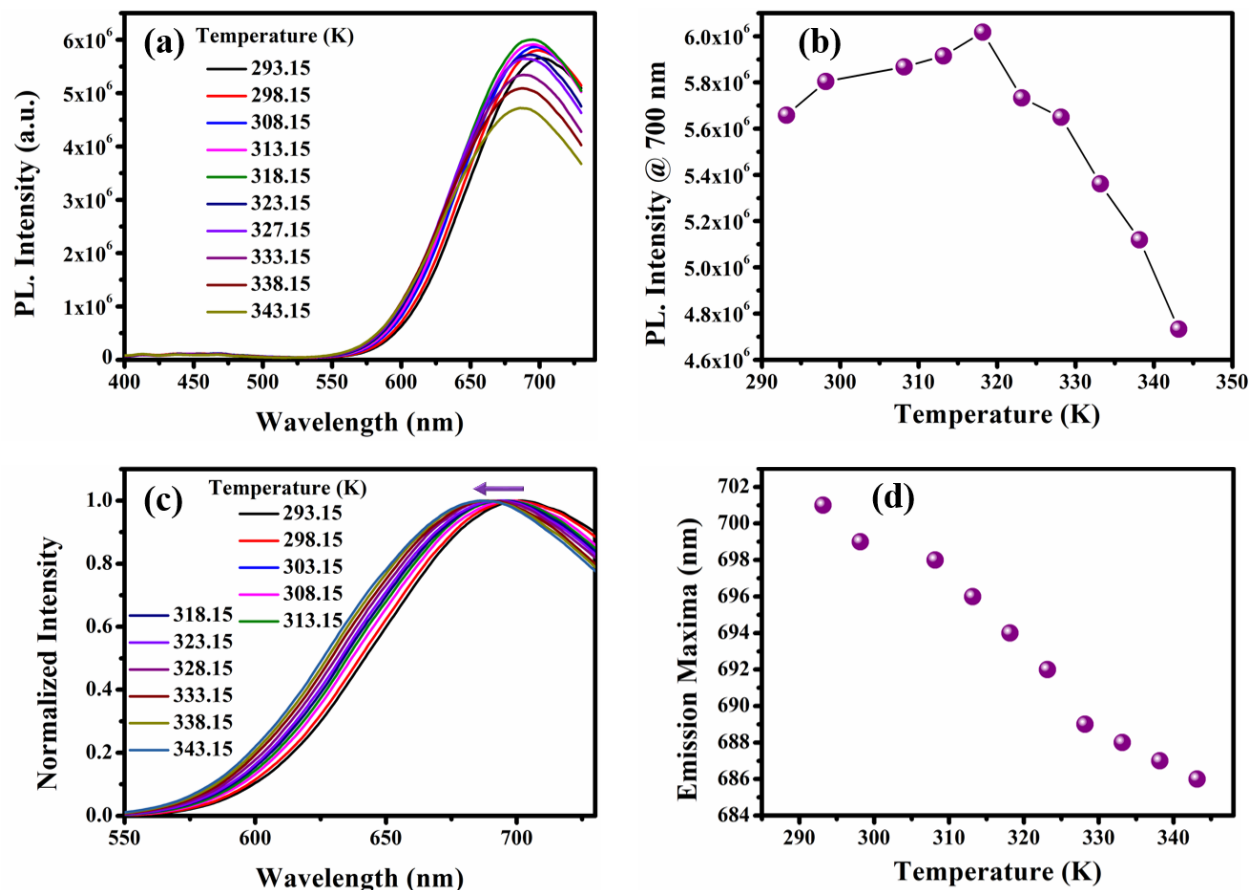
Figure S15. Temperature-dependent PL studies of 5-Br-2-MPy templated CuNCs. (a) PL intensity of Br-CuNCs as a function of temperature; (b) PL intensity at 700 nm as a function of temperature; (c) normalized plot of PL intensity *vs* wavelength, representing the blue shift upon increasing temperature; (d) the variation in the emission maxima as a function of temperature representing the blue shift in emission maxima upon increasing temperature.
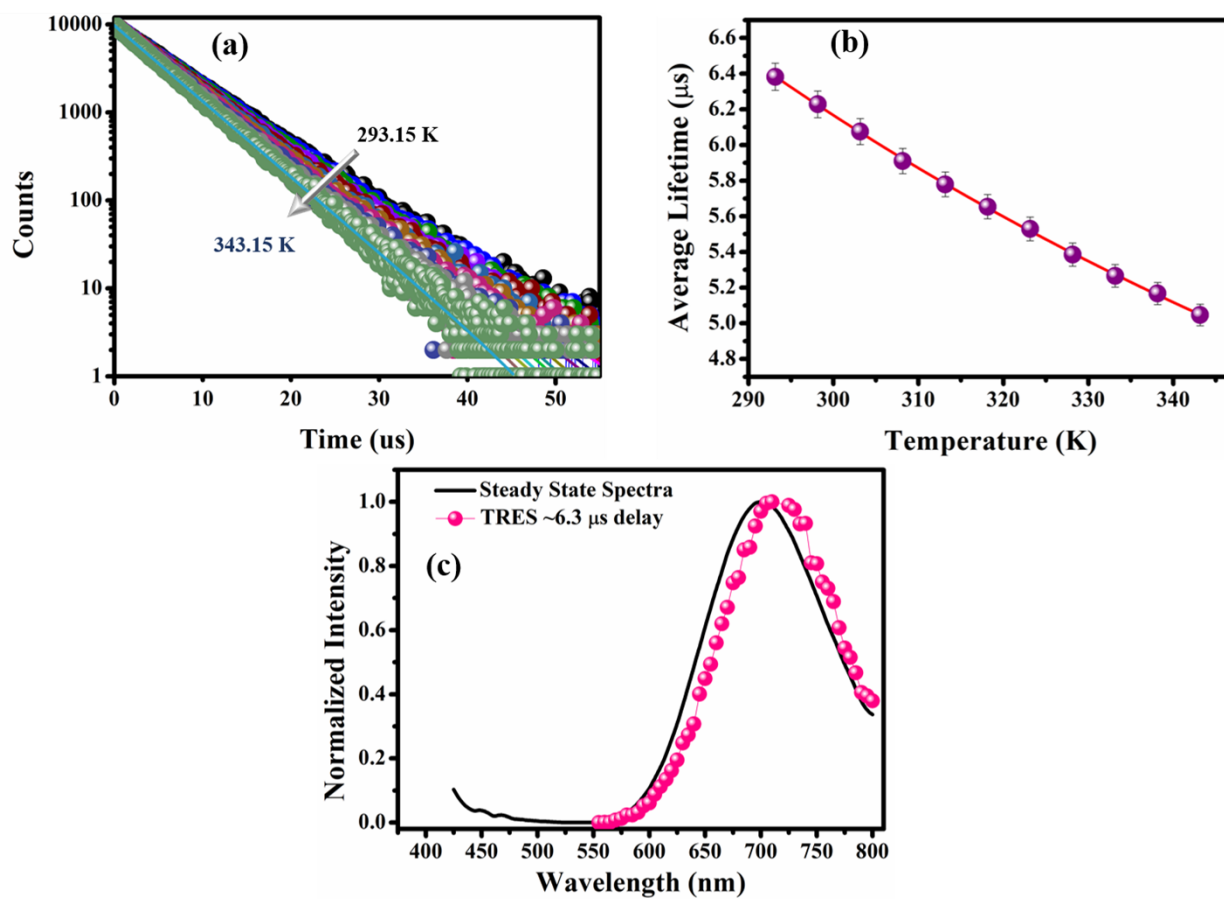
Figure S16. Temperature-dependent studies of 5-Br-2-MPy templated CuNCs. (a) Lifetime decay profile of Br-CuNCs as a function of temperature; (b) average lifetime *vs* temperature plot for the as-prepared CuNCs fitted using TADF model (error bars were determined based on three independent experiments); (c) TRES at a time delay of ~6.3 µs overlapping well with the steady state emission spectra.

Table S10. Lifetime decay fitting parameters for the temperature-dependent lifetime studies on Br-CuNCs.

Temperature (K)	α (%)	τ (µs)	$<τ>^a$ (µs)	$χ^2$
293.15	100	6.385	6.385	1.02
298.15	100	6.341	6.341	1.04
303.15	100	6.075	6.075	1.04
308.15	100	5.910	5.910	1.04
313.15	100	5.779	5.779	1.02
318.15	100	5.654	5.654	1.01
323.15	100	5.529	5.529	1.00
328.15	100	5.385	5.385	1.00
333.15	100	5.266	5.266	1.00
338.15	100	5.167	5.167	1.00
343.15	100	5.046	5.046	1.04

[a] ±5%

Table S11. TADF model fitting parameters for the average lifetime *vs* temperature plot for Br-CuNCs.

$ΔE (S_1-T_1)$ (meV)	$τ(T_1)$ (µs)	$τ(S_1)$ (ns)	R^2
67.4	15.03	246.5	0.9996