Supporting Information

Intrinsic-to-Extrinsic Emission Tuning in Luminescent Cu Nanoclusters by *in-situ* Ligand Engineering†

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Section 1:

1.1. Synthesis of 1-OT capped CuNC, 3-MPA capped CuNC and AA capped CuNC

Synthesis of 1-OT capped CuNC

In a typical experiment, 4 ml of 10 mM $CuSO_4.5H_2O$ solution was prepared in methanol solvent and was taken in a 25 ml round bottom (RB) flask. 20.8 µl of 1-OT was dissolved in ~150 ul of 0.6 M methanolic NaOH and the resulting disperse was sonicated and added to the Cu^{2+} solution. It resulted into the formation of a white turbid solution (The conc. of OH^- ions and 1-OT in the final mixture becomes ~20 mM and ~30 mM respectively). The mixture was kept under inert condition and constant stirring at ~50-55°C temperature for 4-5 hrs. followed by centrifugation at 12000 rpm for 10 min. Resulting colourless supernatant appeared as blue emissive under UV light.

Synthesis of 3-MPA capped CuNC

In a typical experiment, 4 ml of 10 mM $CuSO_4.5H_2O$ solution was prepared in methanol solvent and was taken in a 25 ml round bottom (RB) flask. 10.4 µl of 3-MPA was dissolved in ~150 ul of 0.6 M methanolic NaOH and the resulting disperse was sonicated and added to the Cu^{2+} solution. It resulted into the formation of a white turbid solution (The conc. of OH^- ions and 3-MPA in the final mixture becomes ~20 mM and ~30 mM respectively). The mixture was kept under inert condition and constant stirring at ~50-55°C temperature for 4-5 hrs. followed by centrifugation at 12000 rpm for 10 min. Resulting colourless supernatant appeared as blue emissive under UV light.

Synthesis of AA capped CuNC

In a typical experiment, 4 ml of 10 mM $CuSO_4.5H_2O$ solution was prepared in methanol solvent and was taken in a 25 ml round bottom (RB) flask. 21.1 mg of AA was dissolved in ~150 ul of 0.6 M methanolic NaOH and the resulting disperse was sonicated and added to the Cu^{2+} solution. It resulted into the formation of a deep brown precipitate (The conc. of OH^- ions and AA in the final mixture becomes ~20 mM and ~30 mM respectively). The mixture was kept under inert condition and constant stirring at ~50-55°C temperature for 4-5 hrs. followed by centrifugation at 12000 rpm for 10 min. Resulting colourless supernatant appeared as blue emissive under UV light.

1.2. Synthesis of DHAA capped CuNCs

In a typical experiment, 4 ml of 10 mM $CuSO_4.5H_2O$ solution was prepared in methanol solvent and was taken in a 25 ml round bottom (RB) flask. 20.8 mg of DHAA was dissolved in ~250 ul of 0.6 M methanolic NaOH and the resulting disperse was sonicated and added to the Cu^{2+} solution resulting into instantaneous formation of a yellowish precipitate (The conc. of OH^- ions and DHAA in the final mixture becomes ~20 mM and ~30 mM respectively). 1 ml of hydrazine monohydrate was dropwise added to the mixture. The mixture was kept under inert condition and constant stirring at ~50-55˚C temperature for 24 hrs. Bigger particles and aggregates were removed by centrifugation at 8000 rpm for 10 min. Resulting yellowish green supernatant appeared as green emissive under UV light.

1.3. Synthesis of green-yellow emissive CuNC by following P2 and using 1-OT, 1,3-PDT and 1,6-NDT as capping ligands

Synthesis of green-yellow emissive CuNC from 1-OT capped CuNC.

4 ml of 10 mM $CuSO_4.5H_2O$ solution was prepared in methanol solvent and was taken in a 25 ml RB flask. 20.8 ul of 1-OT was dissolved in 250 ul of 0.6 M methanolic NaOH and added to the solution in RB flask so that conc. of OH^- ions and 1-OT in the resulting solution becomes ~40 mM and ~30 mM respectively. White precipitate was formed instantaneously, followed by an addition of 14 mg (20 mM) of solid L-ascorbic acid into the mixture. The mixture was kept under inert condition and constant stirring at 50-55˚C temperature for 24 hrs. After that, the mixture was centrifuged at 12000 rpm for 10 min. and resulting yellowish green supernatant appeared as bright green emissive under UV light.

Synthesis of green-yellow emissive CuNC from 1-PDT capped CuNC.

4 ml of 10 mM $CuSO_4.5H_2O$ solution was prepared in methanol solvent and was taken in a 25 ml RB flask. 12 ul of 1,3-PDT was dissolved in 250 ul of 0.6 M methanolic NaOH and added to the solution in RB flask so that conc. of OH^- ions and 1,3-PDT in the resulting solution becomes ~40 mM and ~30 mM respectively. White precipitate was formed instantaneously, followed by an addition of 14 mg (20 mM) of solid L-ascorbic acid into the mixture. The mixture was kept under inert condition and constant stirring at 50-55˚C temperature for 24 hrs. After that, the mixture was centrifuged at 12000 rpm for 10 min. and resulting yellowish green supernatant appeared as bright green emissive under UV light.

Synthesis of green-yellow emissive CuNC from 1,9-NDT capped CuNC.

4 ml of 10 mM $CuSO_4.5H_2O$ solution was prepared in methanol solvent and was taken in a 25 ml RB flask. 24.2 ul of 1,9-NDT was dissolved in 250 ul of 0.6 M methanolic NaOH and added to the solution in RB flask so that conc. of OH^- ions and 1,9-NDT in the resulting solution becomes ~40 mM and ~30 mM respectively. White precipitate was formed instantaneously, followed by an addition of 14 mg (20 mM) of solid L-ascorbic acid into the mixture. The mixture was kept under inert condition and constant stirring at 50-55°C temperature for 24 hrs. After that, the mixture was centrifuged at 12000 rpm for 10 min. and resulting yellowish green supernatant appeared as bright green emissive under UV light.

1.4. Quantum yield determination of BCuNC, GCuNC and RCuNC.

Relative quantum yield of BCuNC and GCuNC were calculated using the following equation[1],

$$\phi_s = \phi_r \frac{I_s}{I_r} \cdot \frac{A_r}{A_s} \cdot \frac{\eta_s^2}{\eta_r^2} \tag{1}$$

Where, ϕ_s = relative quantum yield of the sample, ϕ_r = relative quantum yield of the reference, I_s = Integrated PL intensity of the sample, I_r = Integrated PL intensity of the reference, A_r = absorbance value of the reference at excitation wavelength, A_s = absorbance value of the sample at excitation wavelength, η_s = refractive index of the solvent for the sample (in our case methanol), η_r = refractive index of the solvent for the reference (in our case ethanol).

The calculated relative quantum yield of BCuNC was found to be **0.10 (10%)**, and relative quantum yield of GCuNC was found to be **0.30 (30%)**.

Where quantum yield of references are as following,

POPOP (for BCuNC) = 0.97 (97%)[2]
Coumarin 30 (for GCuNC) = 0.67 (67%)[3].

Absolute quantum yield of RCuNC was measured by using integrating sphere method and found to be 3% (absolute error $\pm\ 0.047$, relative error $\pm\ 0.02625$).

1.5. Calculation of macroscopic rate constant for the formation of GCuNC

Figure 3d was plotted by collecting fluorescence intensities at corresponding time from **figure S17a**. where, F = fluorescence intensities at reaction time of 2, 6, 10, 14, 18, 22, 26 hrs respectively, collected at 520 nm and F_0 = fluorescence intensity at reaction time of 2 hrs. F/F_0 vs. reaction time (hrs) was plotted and fitted with a sigmoid function (eq. 2) by using Igor Pro 6.0 software.

$$y = b + \frac{y_{max}}{1 + e^{\frac{x_{half} - x}{k}}} \qquad (2)$$

Where, k is the macroscopic rate constant of the corresponding process, b is the base value of y, y_{max} is the maximum value of y and x_{half} is the value of x at $y = \frac{y_{max} - b}{2}$.

The parameters obtained from fitting are

$(F/F_0)_{base} = 0.68579 \pm 0.346$ $\qquad$ $k = 2.1421 \pm 0.241$ hrs^{-1}

$(F/F_0)_{max} = 12.055 \pm 0.443$

$(Reaction\ time)_{half} = 10.686 \pm 0.262$ hrs

Section 2: Figures and tables

(a)

(b)
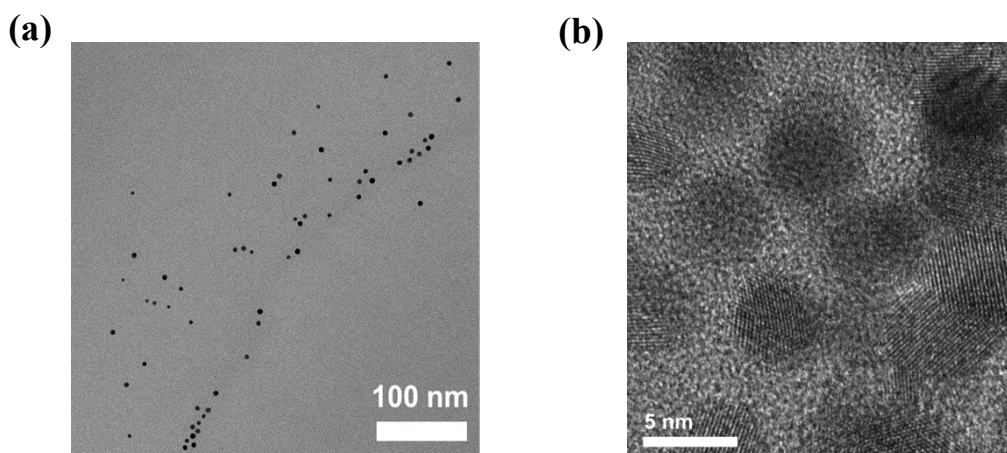
Fig. S1 HRTEM images of (a) BCuNC, (b) GCuNC.
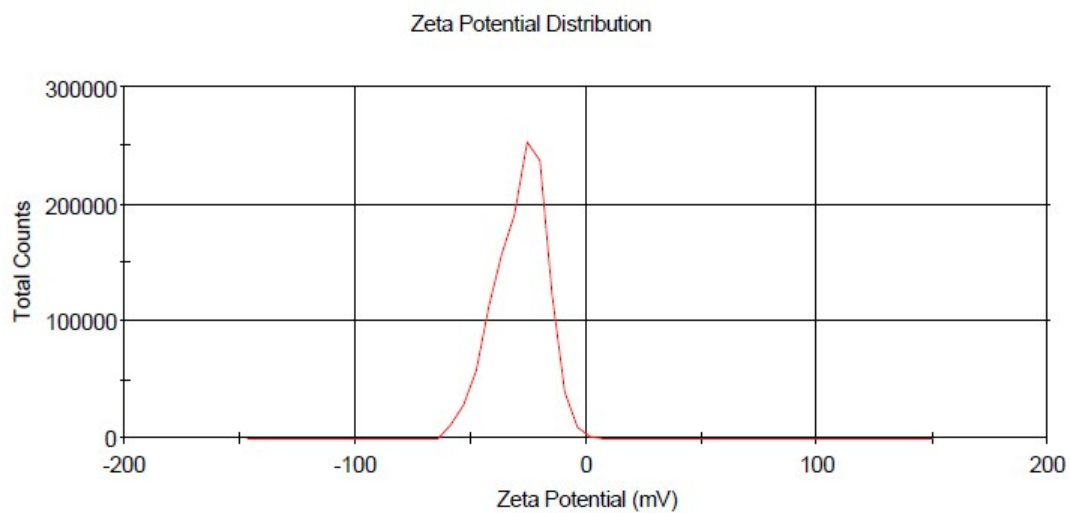
Fig. S2 Zeta potential distribution of BCuNC.
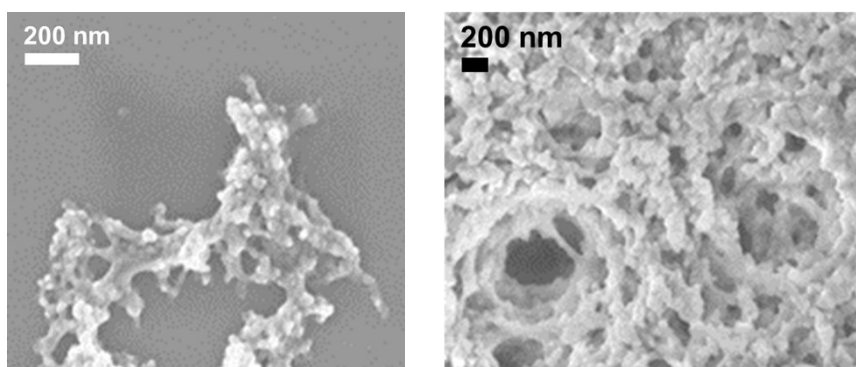
Fig. S3 FESEM images of RCuNC
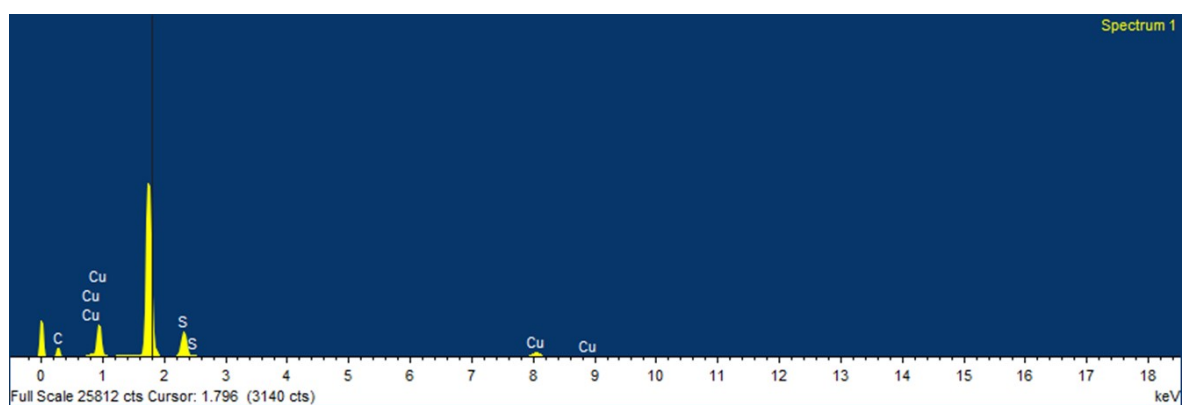
Fig. S4 EDX spectrum of RCuNC.

Table S1. Atomic and weight percentages of Cu, C and S in RCuNC, obtained from EDX analysis at the time of FESEM measurements.

Element	Weight%	Atomic%
C K	59.08	84.66
S K	16.02	8.60
Cu K	24.90	6.74
Totals	100.00	
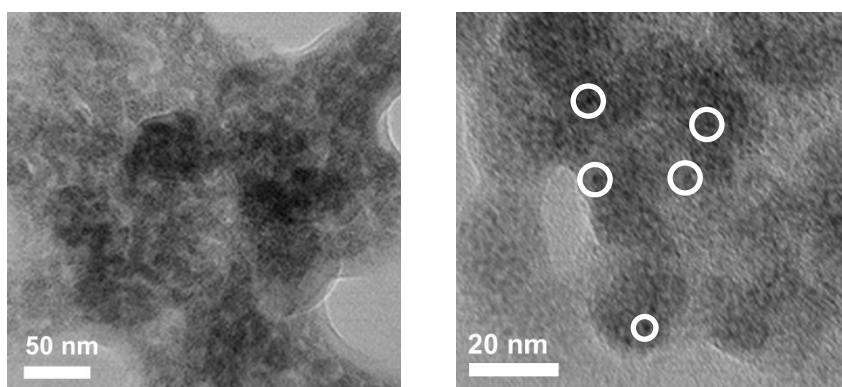
Fig. S5 HRTEM images of RCuNC. Small nanoclusters are marked under white circles.

(a)　　　**(b)**
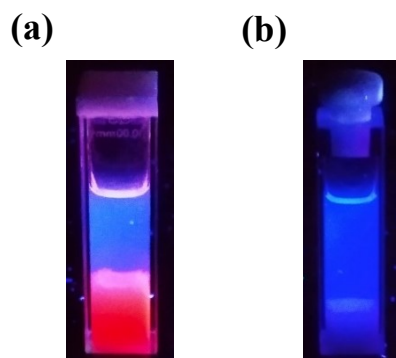
Fig. S6 (a) Blue emissive supernatant and red emissive precipitate when synthesized by using 1,6-HDT. (b) Only blue emissive supernatant when synthesized by using 1-octanethiol.
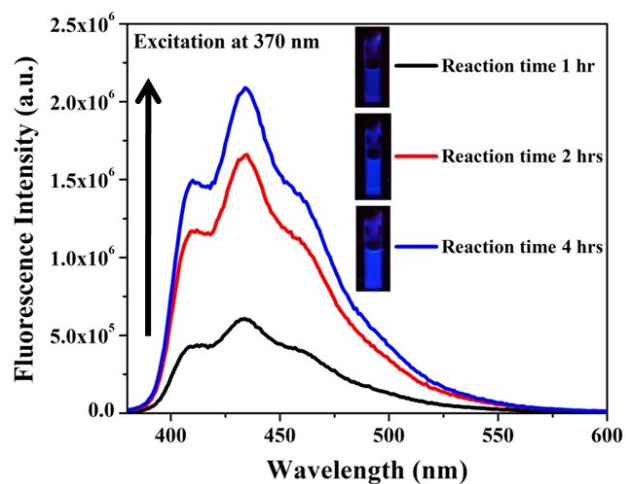
Fig. S7 Time dependent evolution of BCuNC in **P1.**
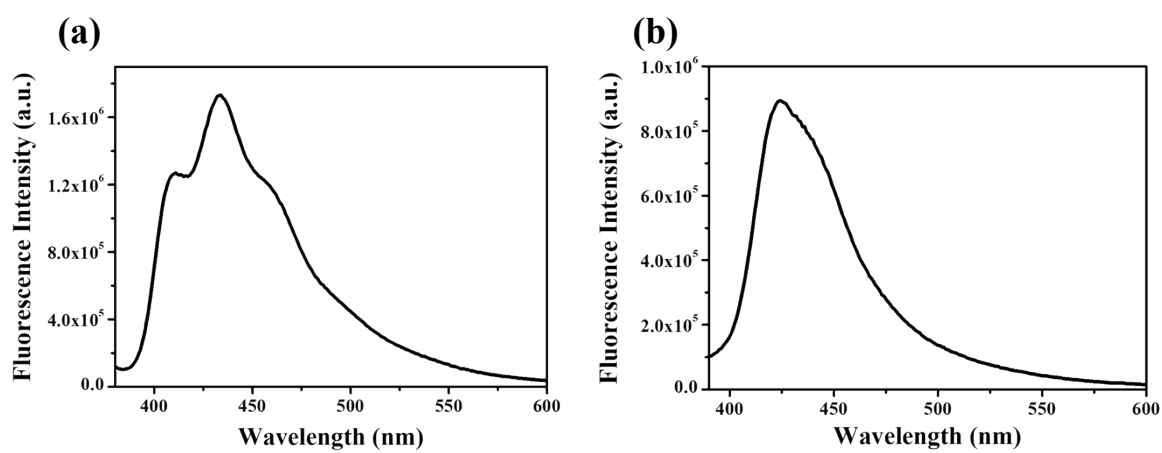
Fig. S8 Emission spectra of BCuNC in (a) *n*-hexane, (b) water.
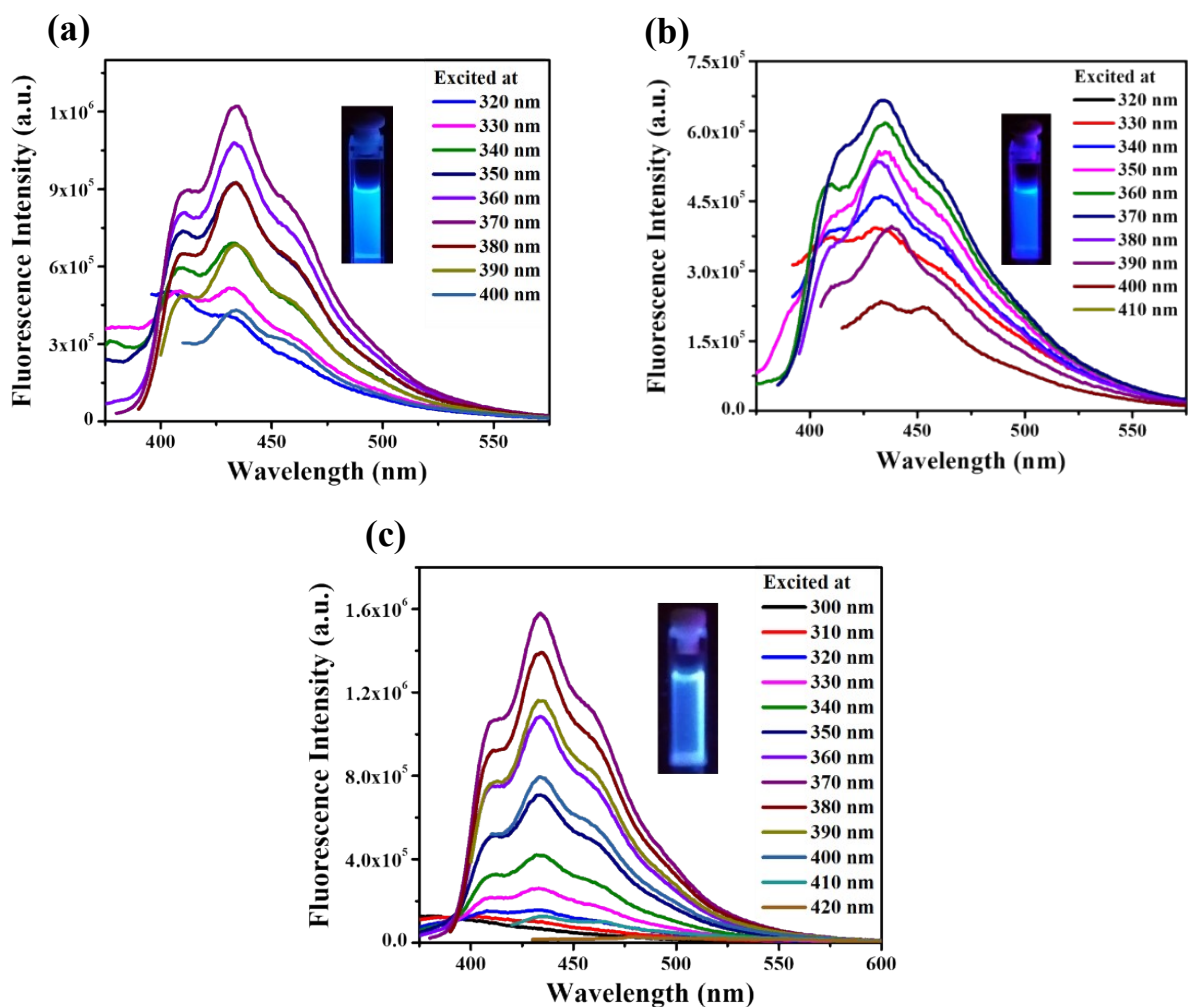
Fig. S9 Excitation independent emission from several ligand capped blue emissive CuNC. Emission spectra of (a) 1-OT capped CuNC, (b) 3-MPA capped CuNC, (c) AA capped CuNC.
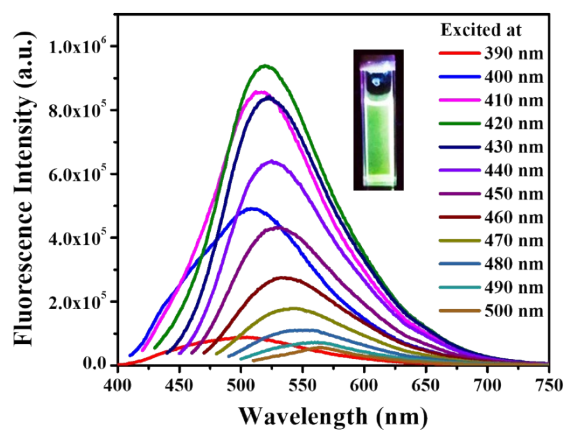

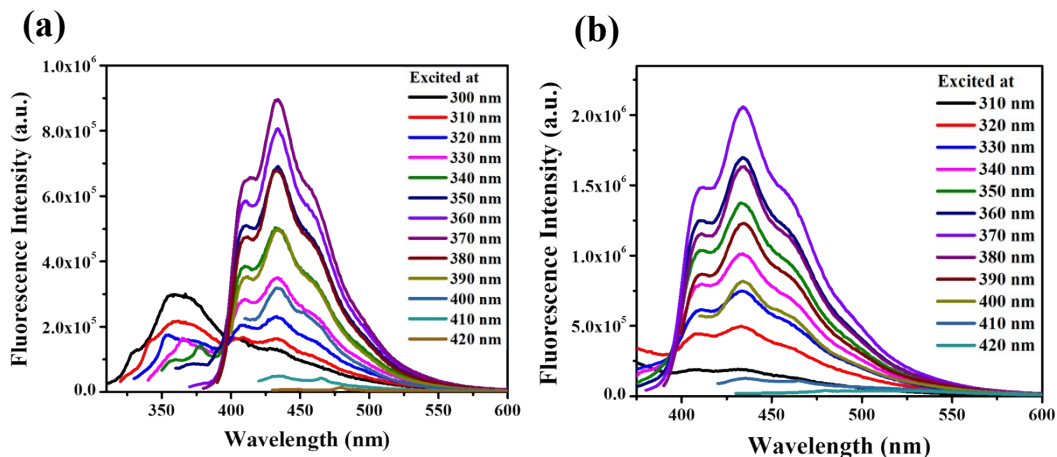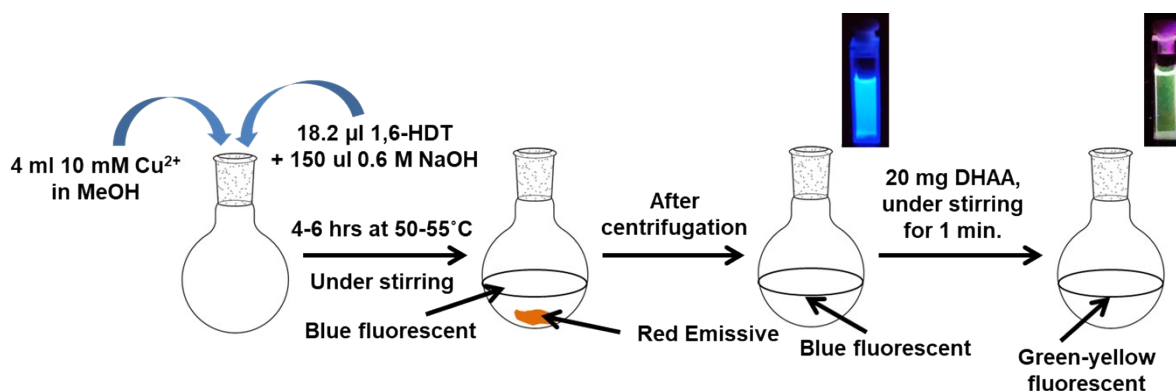**Fig. S10** Emission spectra of GCuNC (without normalization).

Fig. S11 Emission spectra of (a) 1,6-HDT capped CuNCs, (b) AA capped CuNC (Reaction time ~24 hrs). This indicates that either of 1,6-HDT or AA is not responsible for GCuNC formation. When both are present then only GCuNC is generated in longer reaction time.

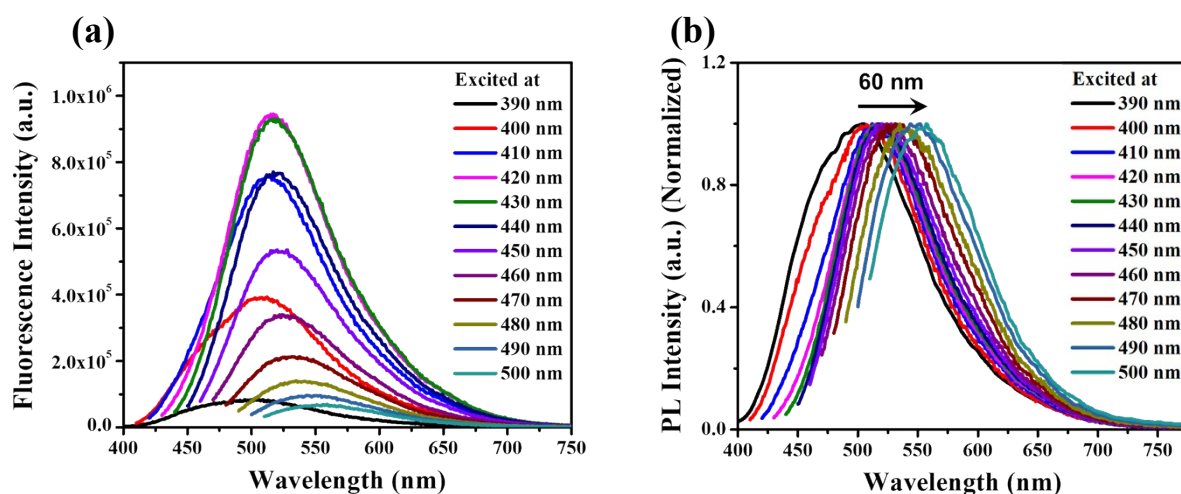**Scheme S1** Schematic representation of the cross-check experiment.

Fig. S12 (a) Emission spectra of green-yellow emissive CuNC from cross-check experiment. (b) Emission spectra of green-yellow emissive CuNC from cross-check experiment (normalized).
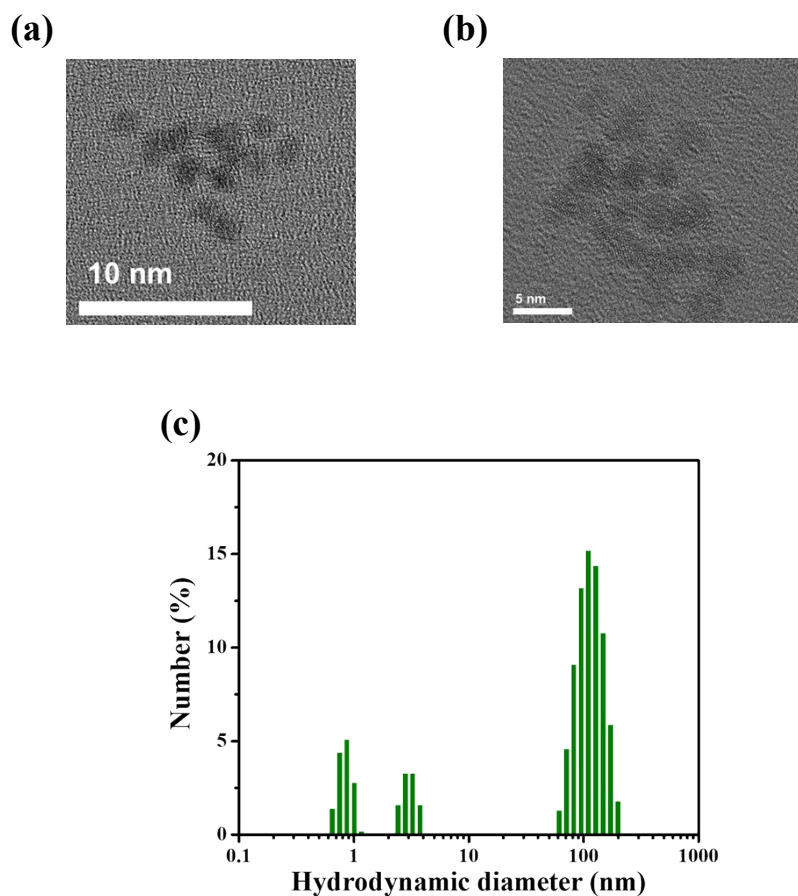
Fig. S13 (a), (b) HRTEM images of green-yellow emissive CuNC from cross-check experiment. (c) DLS size distribution of green-yellow emissive CuNC from cross-check experiment.
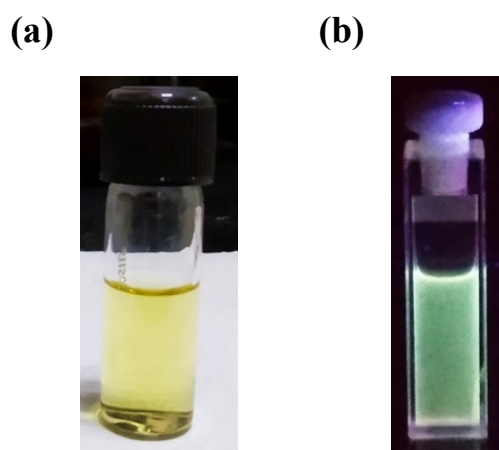

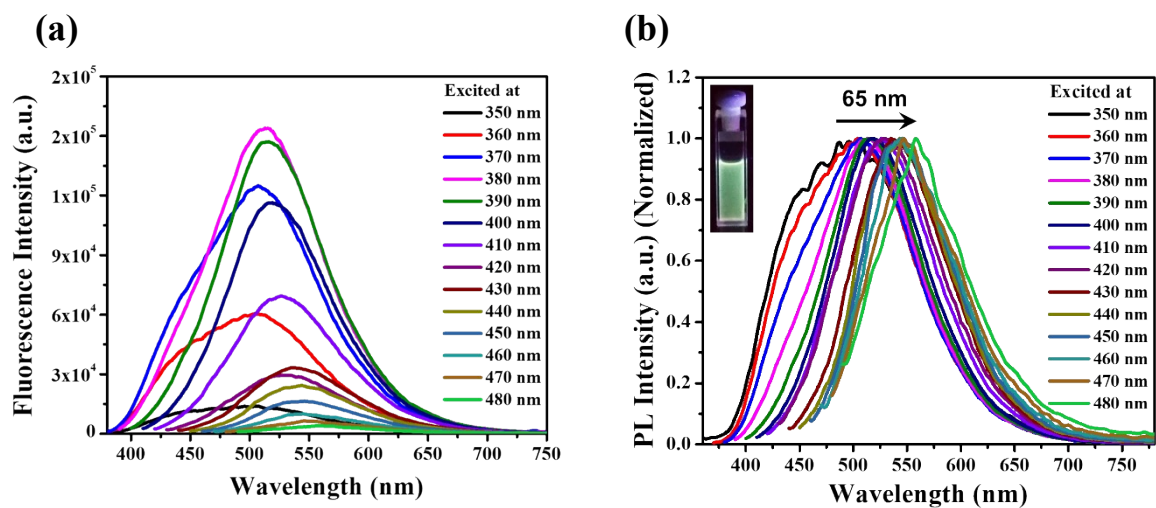**Fig. S14** DHAA capped CuNC (a) under day light, (b) under UV light.

Fig. S15 Emission spectra of DHAA capped CuNC (a) unnormalized, (b) normalized.
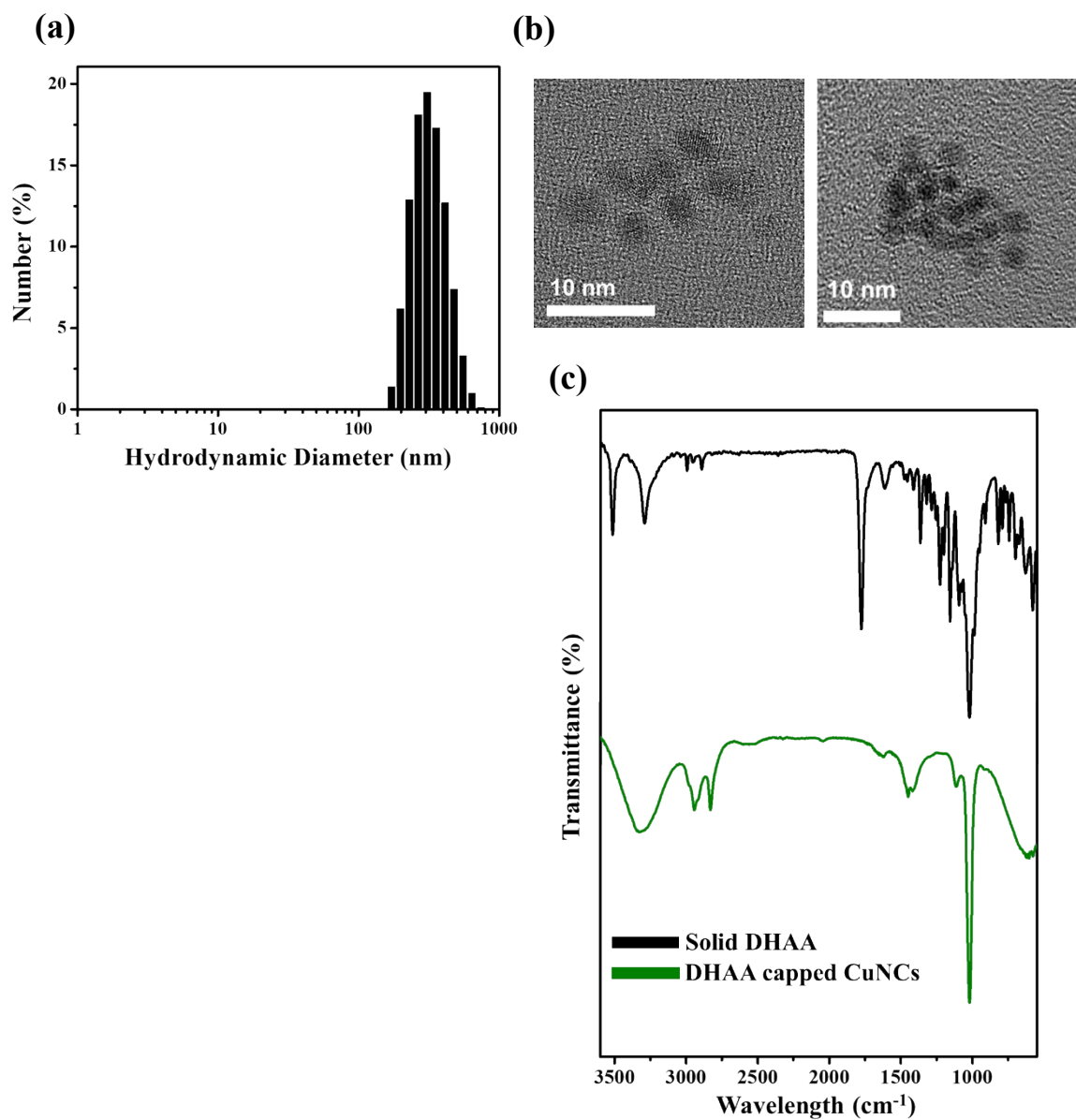
Fig. S16 (a) DLS size distribution and (b) HRTEM images and (c) FT-IR spectra of DHAA capped CuNC. The successful formation of DHAA capped CuNCs was further confirmed by FT-IR spectroscopy where the peak at 1320 cm^{-1} corresponds to O-H bending of primary and secondary alcohol group of DHAA powder, diminished upon the formation of Cu-O bond in DHAA capped CuNCs.
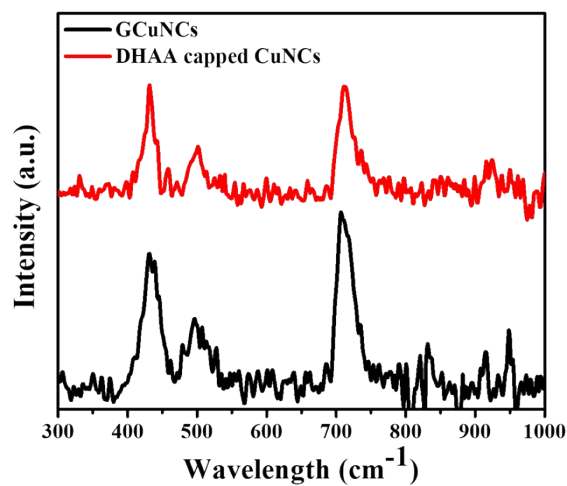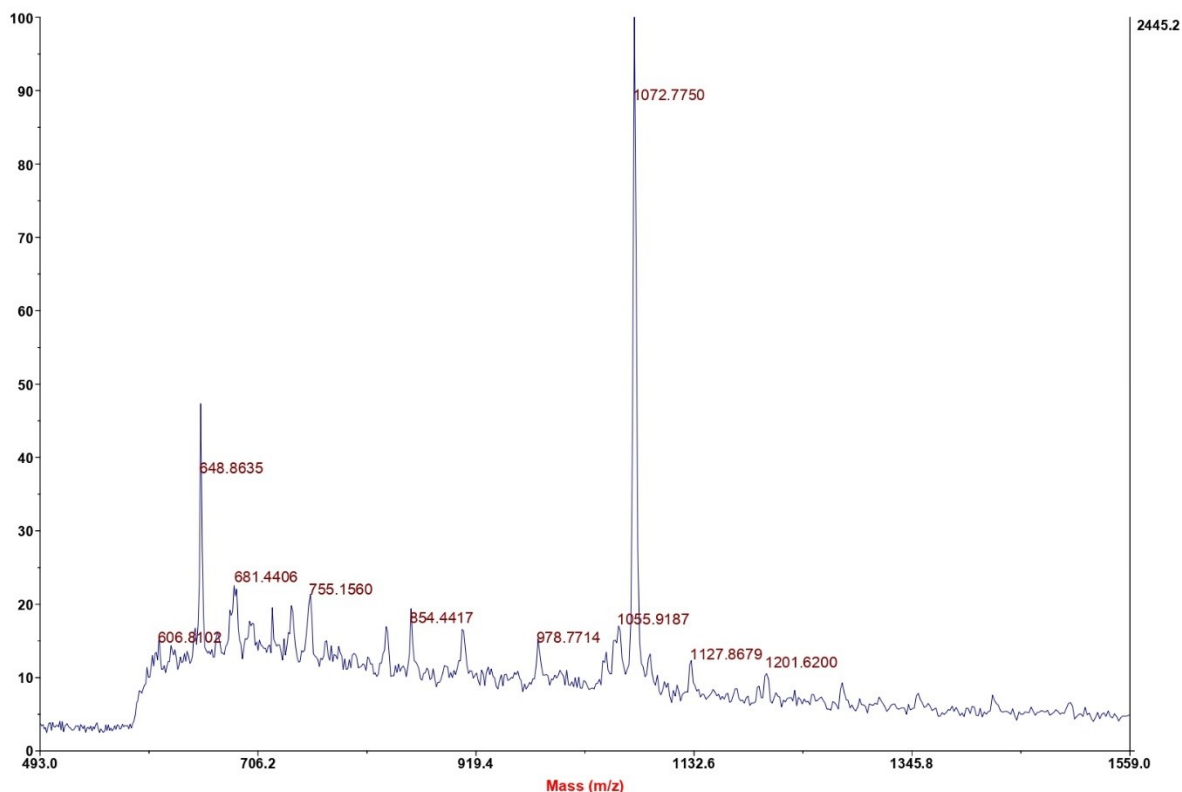

Fig. S17 Raman spectra of GCuNC and DHAA capped CuNC.

Fig. S18 MALDI-TOF mass spectrum of GCuNC. Estimated compositions of GCuNC, $1072.77 = [Cu_7(DHAA)_3 - 3H^+]^+$, $1201.62 = [Cu_9(DHAA)_3 - H^+]^+$, $904.46 = [Cu_7(DHAA)_2 + K^+]^+$, $1127.86 = [Cu_8(DHAA)_3 - 10H^+]^+$.
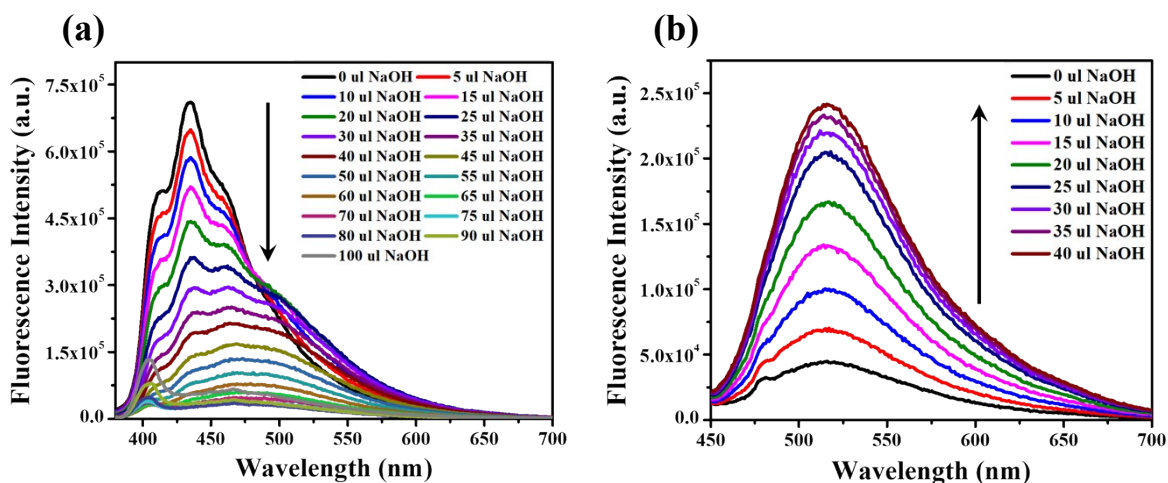

Fig. S19 Change in emission spectra during NaOH titration of BCuNC (synthesized by following P2 with reaction time of 2 hrs) (a) Emission spectra by exciting at 370 nm. (b) Emission spectra by exciting at 420 nm. Figure 3b was plotted by collecting PL intensity at every NaOH concentration from figure S17b.

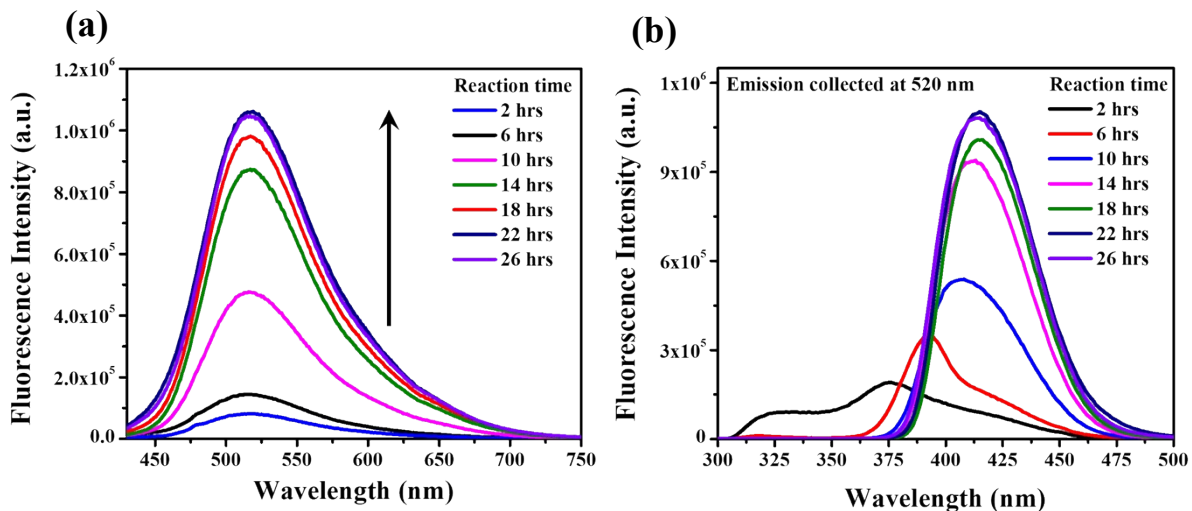**Fig. S20** (a) Emission spectra collected in different reaction time of P2 by exciting at 420 nm (excitation wavelength for GCuNC). (b) Excitation spectra collected at 520 nm (emission maxima of GCuNC) in different reaction time of P2.
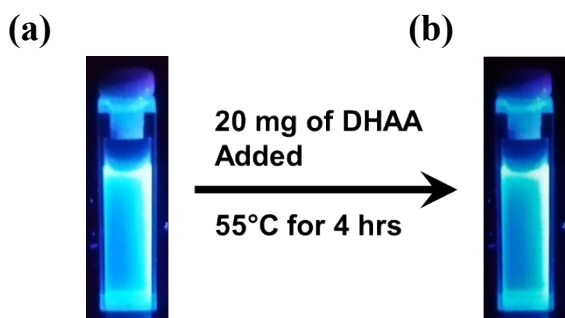

Fig. S21 (a) AA capped CuNC under UV light, (b) after addition of DHAA.
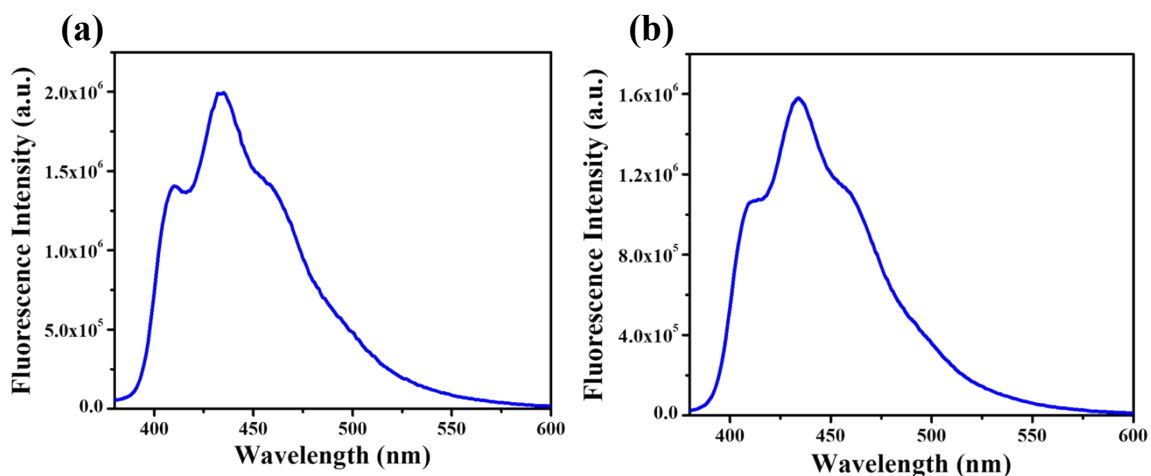

Fig. S22 Emission spectra of AA capped CuNC. (a) Before addition of DHAA, (b) after addition of DHAA.
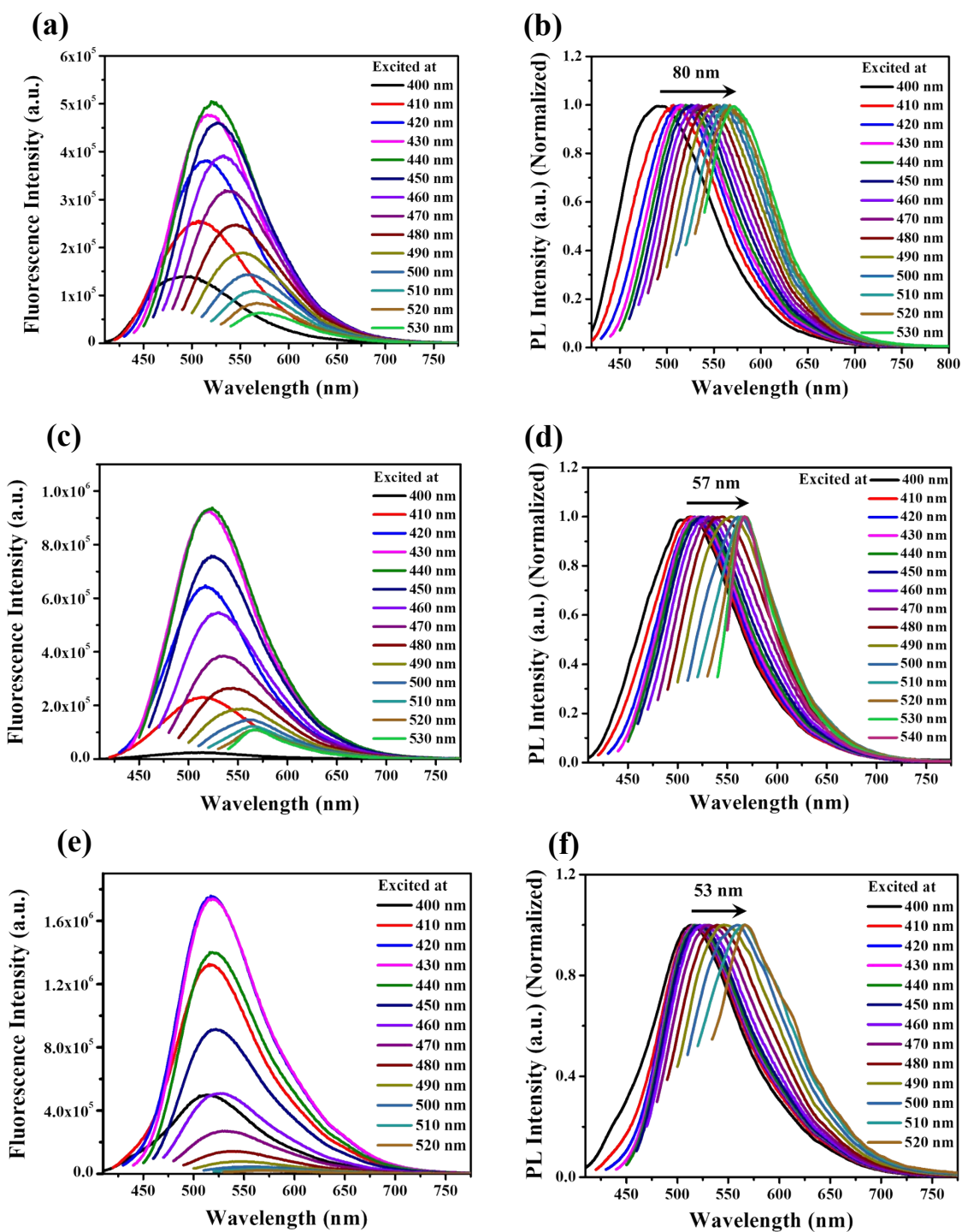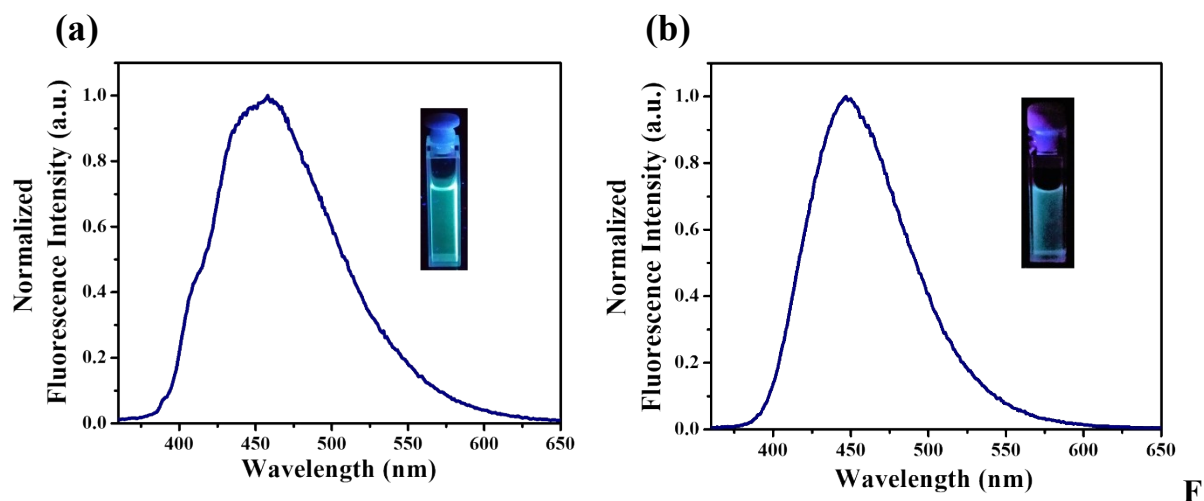
Fig. S23 Emission spectra of green yellow emissive CuNC by following P2 and using (a), (b) 1-OT as capping ligand; (c), (d) 1,3-PDT as capping ligand and (e), (f) 1,9-NDT as capping ligand.

(a)

(b)

F

ig. S24 Emission spectra of (a) cyan emissive CuNC by following P2 at 10 hrs of reaction time, (b) cyan emissive CuNC by capping with DHAA with a reaction time of 10-12 hrs by using the same protocol as 2C (section A).

Table S2. Lifetime fitting parameters of BCuNC and GCuNC obtained from TCSPC.

Sample	λ_{Em}	τ_1	α_1	τ_2	α_2	τ_3	α_3	$<\tau>$
BCuNC	410 nm	70.2 ps	0.62	1.39 ns	0.38	-	-	1.28 ns
BCuNC	435 nm	68.2 ps	0.54	1.39 ns	0.46	-	-	1.31 ns
BCuNC	460 nm	82.3 ps	0.51	1.4 ns	0.49	-	-	1.32 ns
GCuNC	520 nm	82.0 ps	0.76	0.875 ns	0.20	3.0 ns	0.04	1.45 ns

λ_{Em}	τ_1	α_1	τ_2	α_2	τ_3	α_3	$<\tau>$
450 nm	87.0 ps	0.53	997 ps	0.36	1.8 ns	0.11	1.19 ns
470 nm	84.5 ps	0.60	962 ps	0.32	2.1 ns	0.08	1.24 ns
490 nm	77.5 ps	0.71	952 ps	0.25	2.6 ns	0.05	1.34 ns
510 nm	85.9 ps	0.74	908 ps	0.22	2.8 ns	0.04	1.33 ns
530 nm	78.6 ps	0.78	852 ps	0.18	3.1 ns	0.04	1.53 ns
550 nm	81.9 ps	0.78	815 ps	0.17	3.0 ns	0.04	1.48 ns
570 nm	78.1 ps	0.79	798 ps	0.16	3.0 ns	0.04	1.50 ns
590 nm	80.3 ps	0.80	800 ps	0.16	3.0 ns	0.04	1.49 ns

Table S3. Wavelength dependent lifetime fitting parameters of GCuNC obtained from TCSPC.

Table S4. Lifetime fitting parameters of BCuNC and GCuNC obtained from femtosecond fluorescence up-conversion.

Sample	λ_{Em}	τ_1	α_1	τ_2	α_2	τ_3	α_3
BCuNC	410 nm	99 fs	97.40%	2.24 ps	2.51%	-	-
BCuNC	435 nm	297.4 fs	79.80%	2.98 ps	8.05%	67.4 ps	12.08%
BCuNC	460 nm	220 fs	56.96%	2.89 ps	25.94%	57.4 ps	17.08%
GCuNC	520 nm	7.0 ps	38.29%	82 ps	42.22%	875 ps	24.10%

Table S5. Lifetime fitting parameters of RCuNC obtained from TCSPC.

Sample	λ_{Em}	τ_1	α_1	τ_2	α_2	$<\tau>$
RCuNC	730 nm	0.51 μs	0.7	3.0 μs	0.3	2.29 μs

Table S6. Quantitative estimation data table derived from XPS data.

Element name	Peak BE eV	Area (P) CPS. eV	Atomic %
C1s	287.07	1188894.79	66.78
O1s	534.48	1058956.45	28.94
Na1s	1073.04	83570.29	0.97
Cu2p$_{1/2}$	952.78	12298.55	0.66
Cu2p$_{3/2}$	934.78	24195.45	2.64
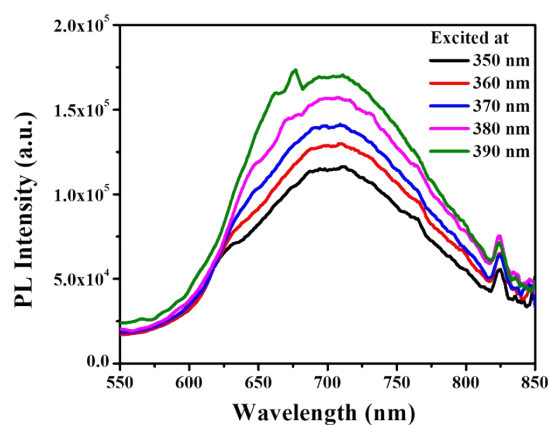
Fig. S25 Emission spectra of RCuNC at different excitation wavelengths.

(a)
4-5 hrs   14-16 hrs   22-24 hrs
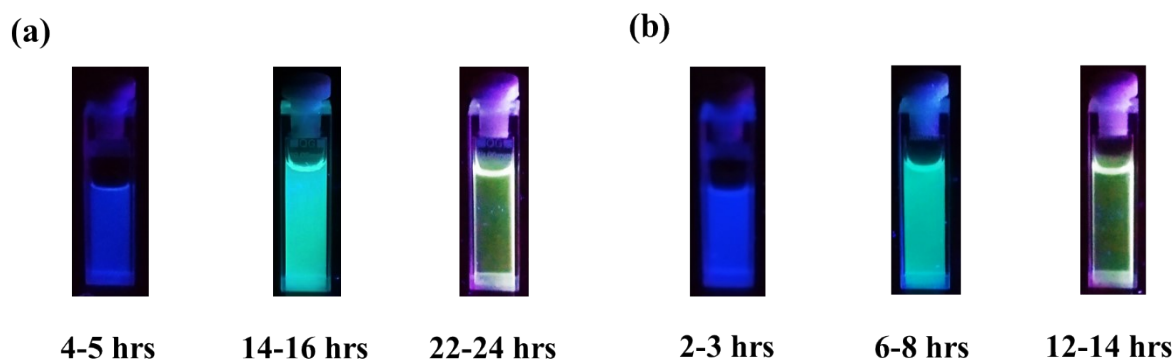
(b)
2-3 hrs   6-8 hrs   12-14 hrs

Fig. S26 (a) Sample images under UV light at different reaction times when concentration of AA was 20 mM. (b) Sample images under UV light at different reaction times when concentration of AA was 50 mM.
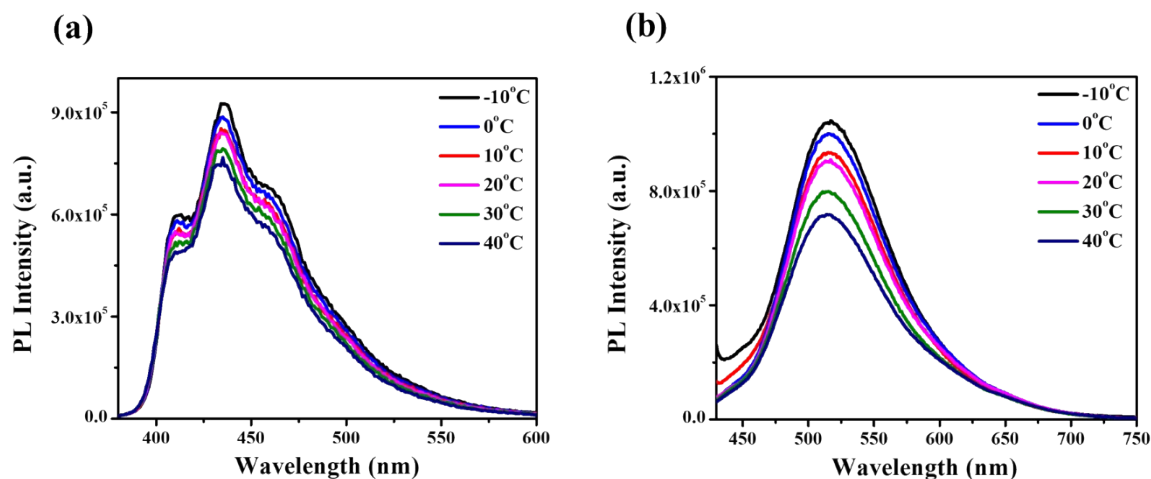
(a)

(b)

Fig. S27 Temperature dependent emission spectra of (a) BCuNC and (b) GCuNC.
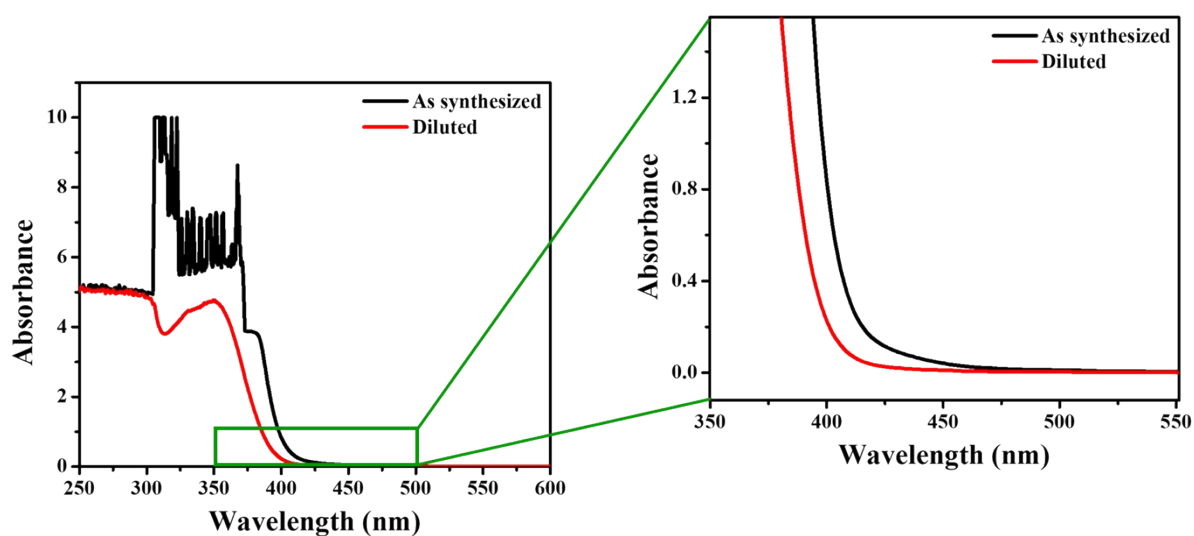

Fig S28. The absorption spectra of as synthesized and diluted GCuNC. Particularly for GCuNC, the ϵ (extinction coefficient) is reasonably high in lower wavelengths, as a result to get proper absorption spectra we had to dilute it to a great extent (~10-15 times). However, the dilution did not affect the features of the emission spectra except the intensity.

References

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3. G. Jones, W. R. Jackson, C. Y. Choi, W. R. Bergmark, *J. Phys. Chem.*, 1985, **89**, 294–300.