Photo induced chemical modification of surface ligands for aggregation and luminescence modulation of copper nanoclusters in presence of oxygen.

Srestha Basu,^{†a} Md. Wasim Nawaj^{†a}, Chirantan Gayen^a and Anumita Paul^{a*}

^aDepartment of Chemistry,

Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India.

Email: anumita@iitg.ac.in

Electronic Supplementary Information



Fig. S1 (A) Excitation spectrum of Cu NCs upon fixing emission at 610 nm. (B) Emission spectrum of Cu NCs upon fixing excitation at 365 nm.



Fig. S2 (A-B) Representative TEM images showing the presence of cysteine stabilized Cu NCs.



Fig. S3 UV-vis absorbance spectrum of as synthesized cysteine stabilized Cu NCs



Fig. S4 XPS core spectrum of (A) Cu 2p and (B) S 2p



Fig. S5: Luminescence spectra of Cu NCs (a) before and (b) after exposure to visible light for a day.



Fig. S6 (A) Decrease in photoluminescence intensity at 610 nm of Cu NCs as a function of excitation slit width (SW). The excitation wavelength was set at 365 nm. (B) Bar diagram showing that the percentage decrease in photoluminescence intensity of Cu NCs scales linearly with slit width after 1800 sec. The unit of slit width is arbitrary.

Slit width dependant quenching of luminescence of Cu NCs

In order to affirm the critical role of light in quenching of photoluminescence of Cu NCs under UV irradiation, slit width dependant photoluminescence change of Cu NCs was monitored. For example, keeping all experimental parameters same, the quenching of luminescence of Cu NCs for a time scale of 1800 sec, was monitored at slit widths of 5, 10 and 15. Interestingly, the decrease in photoluminescence intensity of Cu NCs was observed to have occurred to the maximum extent in case of slit width 15 followed by 10 and 5 (Fig. S6 A). Further, the percentage decrease in photoluminescence intensity of Cu NCs was calculated to be 81.5 % in case of slit width 15, 62.3 % in case of slit width 10 and 33.2 % in case of slit width 5 (Fig. S6 B). This clearly highlights that the quenching of luminescence of Cu NCs and the chemical process (aggregation of Cu NCs) responsible for the same has been triggered by light. Further, control experiments were performed, where the photoluminescence spectra of a dispersion of Cu NCs were captured at substantial intervals of time following incubation of the dispersion in dark (i.e. in absence of light) (Fig. S7). Interestingly upon being kept in dark, no significant change in luminescence of Cu NCs was observed for a period of 20 h. This further highlights the crucial role of 365 nm wavelength light in quenching of photoluminescence of Cu NCs.



Fig. S7 Emission spectra of Cu NCs (acquired at time intervals mentioned in figure legends) following incubation in dark.



Fig. S8 UV-vis absorption peak of the product obtained following exposure of Cu NCs to 365 nm UV irradiation for 2576 sec.



Fig. S9 Emission spectrum of Cu NCs acquired (a) initially and that following exposure of UV irradiation of duration (b) 230 sec, (c) 276 sec and (d) 322 sec at 365 nm in absence of air. Nitrogen gas was continuously bubbled through the sample to remove traces of dissolved aerial gases from the dispersion.



Fig. S10 FTIR spectra of (a) L cysteine and Cu NCs (b) before and (c) after UV irradiation.