

Supporting Information

Instant room temperature synthesis of self-assembled emission-tunable gold nanoclusters: million-fold emission enhancement, and fluorimetric detection of Zn²⁺

Balamurugan, K.*†and Uday Maitra*

^aDepartment of Organic Chemistry, Indian Institute of Science, Bangalore,
560012, Karnataka, India,

Supporting Figures

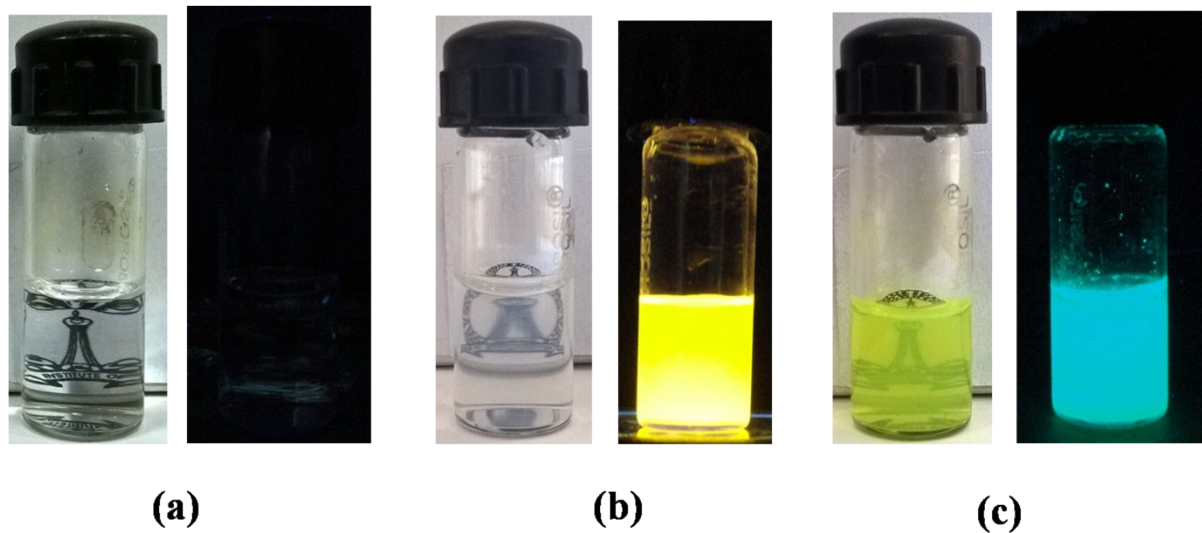


Figure S1. Photographs of (a) *nl*-NCs, (b) *Y*-NCs and (c) *G*-NCs under ambient light and under 365 nm hand held UV lamp.

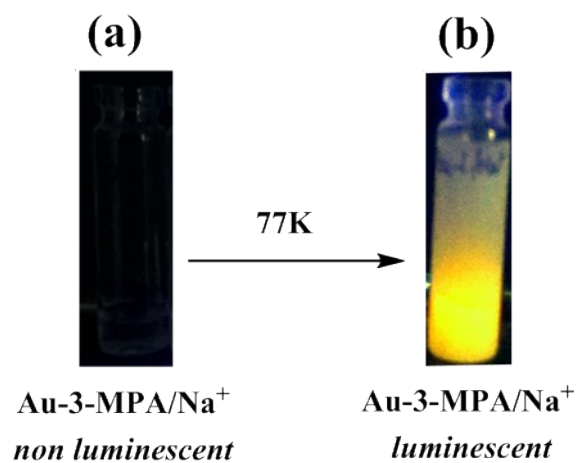


Figure S2. Photographs of Au NCs (a) at room temperature and (b) at 77 K (illuminated under 365 nm UV and photographed at room temperature).

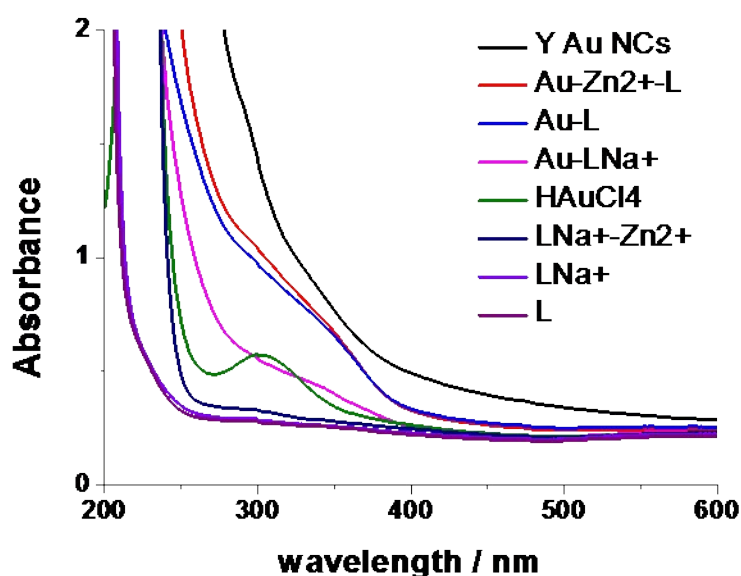


Figure S3. Absorption spectra of Au NCs and control samples. $\text{LNa}^+ = 3\text{-MPA}/\text{Na}^+$. Concentrations: Au(0.5mM), Zn^{2+} (3mM), and LNa^+ (3.5mM).

Photophysical characterization of Y-NCs along with control samples

The nature of the carboxylic group on NCs surface plays a crucial role in deciding the luminescence property of the material. Throughout the study ligand was used in its deprotonated form (LNa^+), which upon coordination to Zn^{2+} contributes to the luminescence immensely. For comparison and justification for choosing LNa^+ , we have carried out photophysical characterization of the control samples (Au-LNa^+ , Au-L , Au-L-Zn^{2+}) along with Y-NCs ($\text{Au-LNa}^+\text{-Zn}^{2+}$). Experimentally the samples (Au-L , Au-L-Zn^{2+}) having ligand in its non-ionized form were found to be colloidal solution indicating aggregation of NCs, as is the case for $\text{Au-LNa}^+\text{-Zn}^{2+}$. This observation is supported from the absorbance data (Figure S4a), where baseline and absorbance (LMCT) intensity bands in the range 300-380 nm increases. The order of increased baseline scattering extracted from absorbance data was noticed to be $\text{Au-L}/\text{Na}^+\text{-Zn}^{2+} > \text{Au-L-Zn}^{2+} > \text{Au-L} > \text{Au-L}/\text{Na}^+$. The observed trend is directly related to the extent of shielding of the carboxylate ($-\text{COO}^-$) group by either H^+ or Zn^{2+} . The -

COO⁻ bound by H⁺ or Zn²⁺ prevents the non-radiative relaxation and in turn activating the T₁ radiative relaxation by aggregation. The extent to which H⁺ and Zn²⁺ enhance the emission is summarized in photoemission spectra (Figure S4b and c). Sample having free (Au-L/Na⁺) -COO⁻ shows negligible emission as expected. Au-L and Au-L-Zn²⁺ having ligand in COOH form shows ~fold increase in intensity when compared to Au-L/Na⁺ resulting from protonation of the free COO⁻ of the ligand. In case of Au-L/Na⁺-Zn²⁺ (Y-NCs) the emission enhancement was found to be million fold (Figure S4c). The strong binding ability of Zn²⁺ to -COO⁻ and its coordination to neighbouring ligands on the same NCs results in such major difference in intensity between -COOH and -COOZn type surface ligands. Figure S4b and c shows negligible difference in intensity between Au-L, Au-L-Zn²⁺, as the addition of Zn²⁺ to protonated ligand (-COOH) doesn't give any room for coordination. For same reasons the absorbance feature of these NCs samples showed no change. The noisy emission profile of the control samples (Figure S4b) is due to extremely poor luminescence. Emission intensity is directly related to the degree of aggregation, which is in turn related to the electrostatic interaction between the ligand and Zn²⁺.

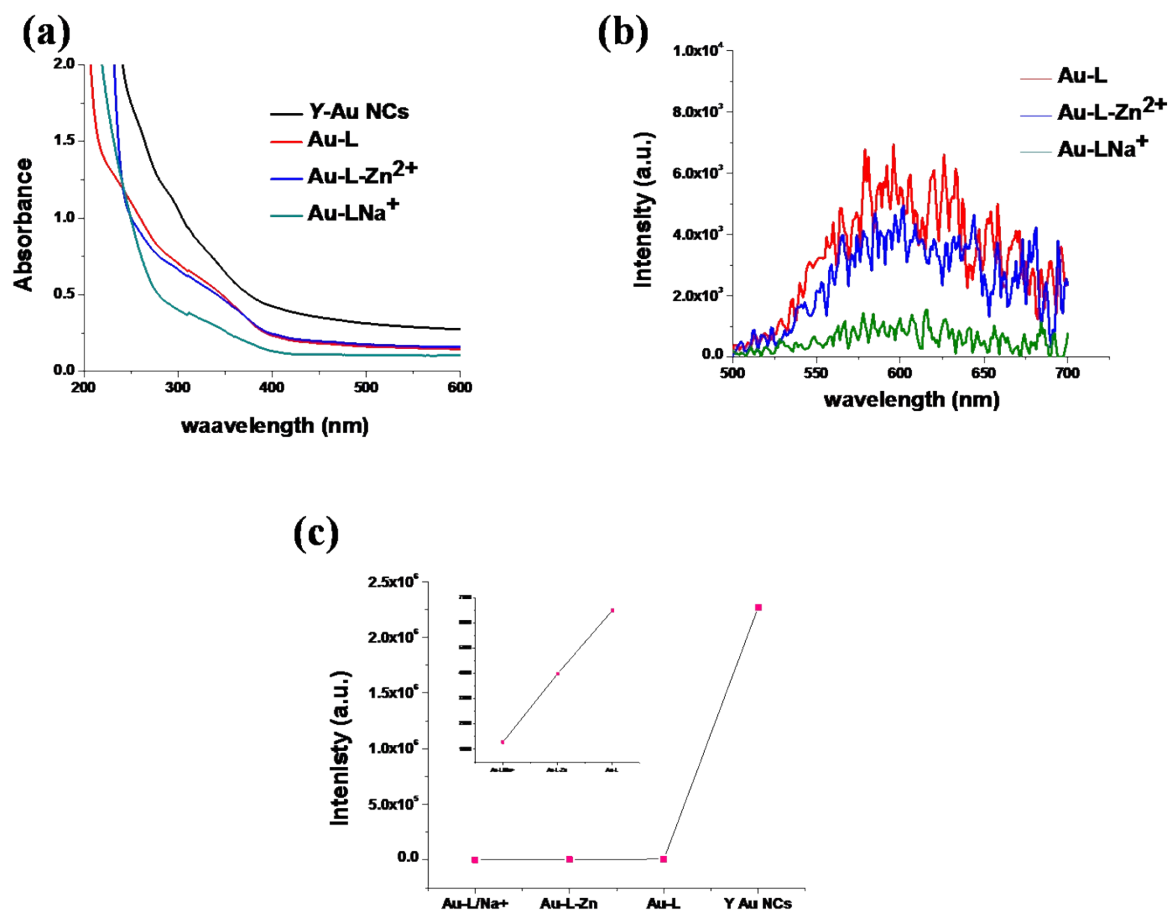


Figure S4. (a) Absorption spectra of Y-NCs and control samples, (b) emission spectra (except Au-L/Na⁺-Zn²⁺) and (c) intensity vs. NCs plot of Au-L/Na⁺, Au-L/Na⁺-Zn²⁺, Au-L & Au-L+-Zn²⁺, inset Au-L/Na⁺, Au-L & Au-L+-Zn²⁺

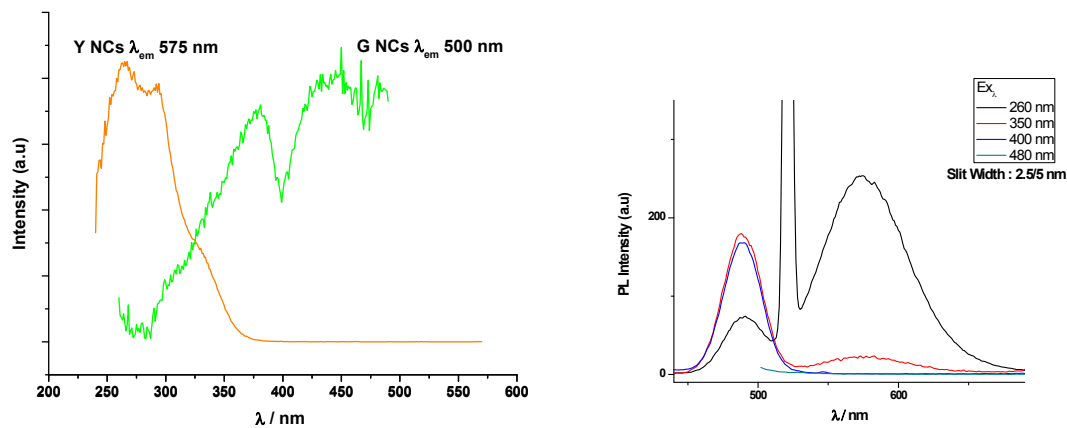


Figure S5.(a) Excitation spectra of yellow and green emitting Au NCs, (b) emission spectra of yellow and green emitting Au NCs as a function of excitation wavelength. The peak at 520 nm in the emission spectra is a the overtone band from the instrument upon excitation at 260 nm.

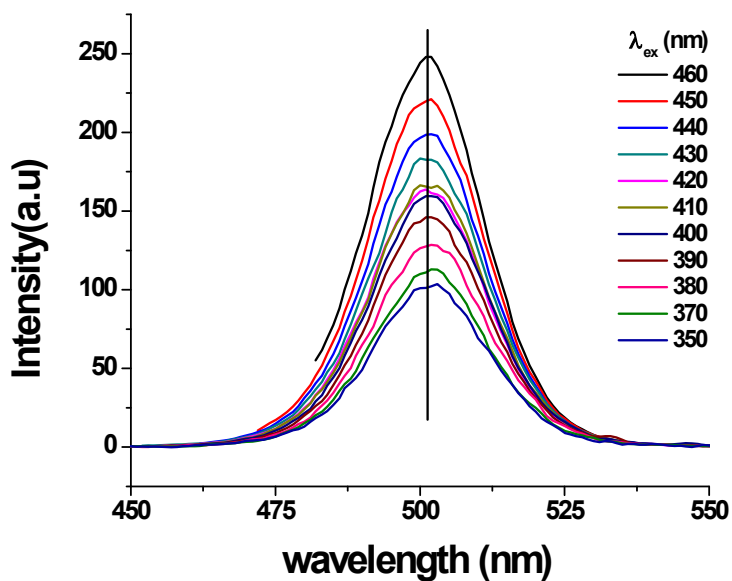


Figure S6.Excitation wavelength dependent emission spectra of G-NCs.

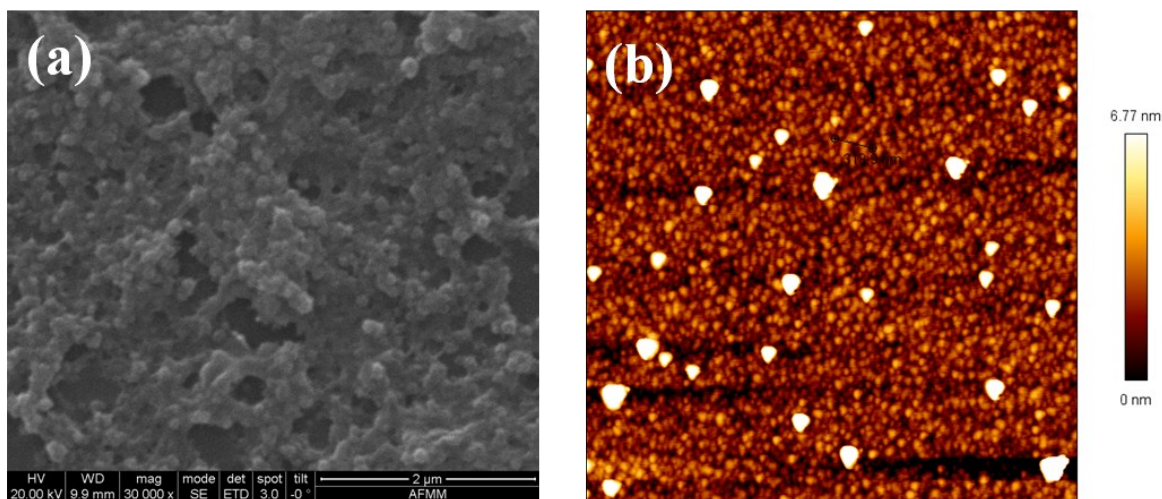


Figure S7.(a) SEM and (b) AFM images of G-NCs

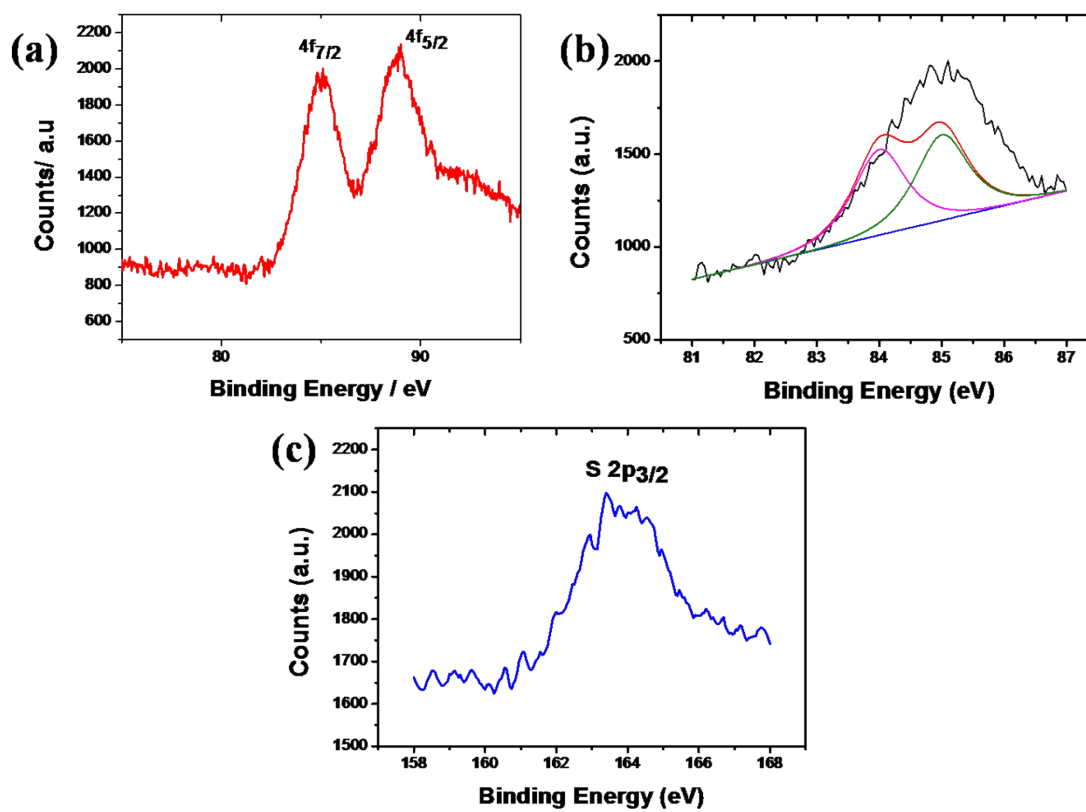


Figure S8. (a) Au 4f XPS spectra of G-NCs, (b) deconvoluted Au 4f_{7/2} XPS spectra of G-NCs and (c) S p_{3/2} XPS spectra

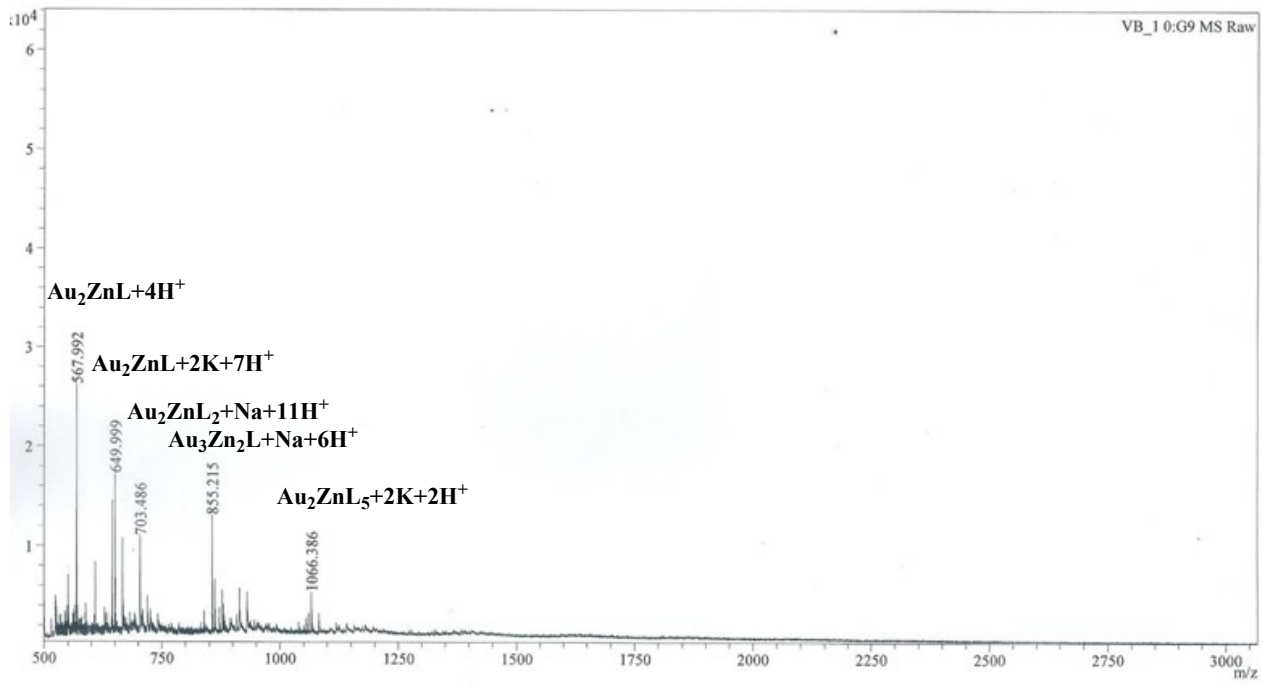
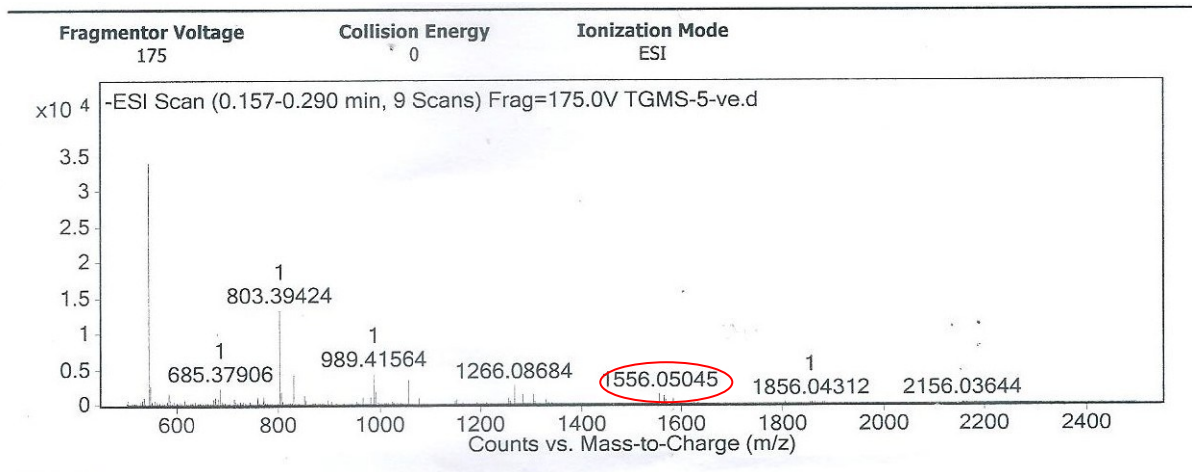


Figure S9.(a)Negative mode ESI and(b) MALDI spectra of *G*-NCs.

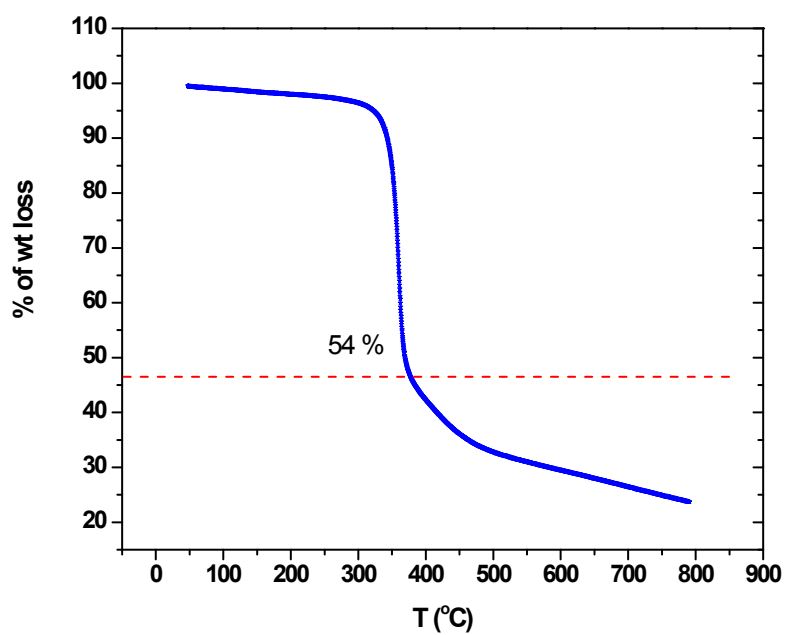


Figure S10. TGA plot of *G*-NCs.

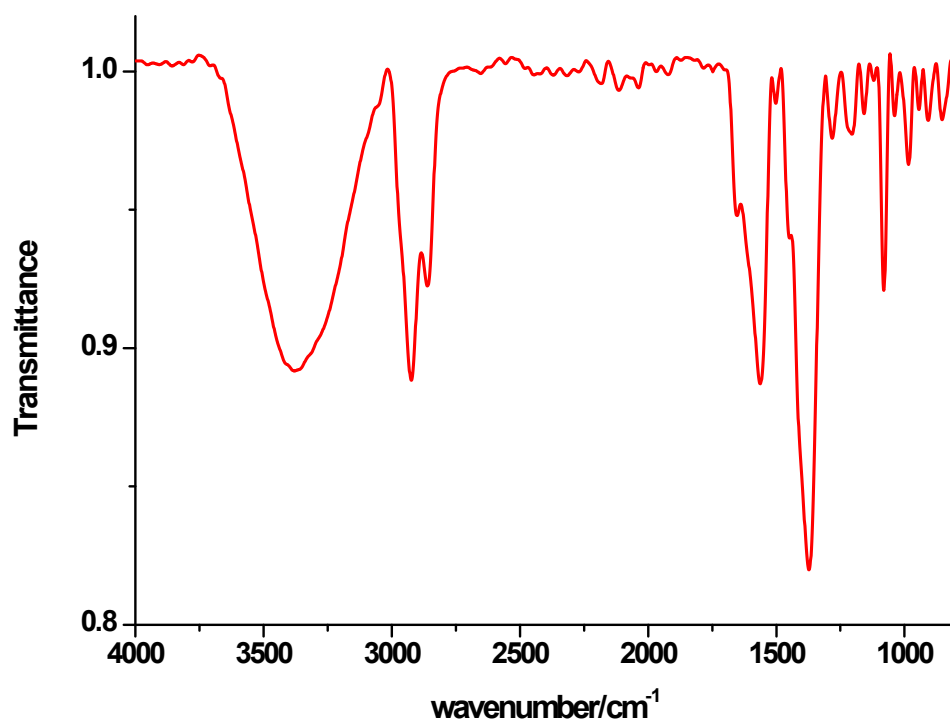


Figure S11. Infrared spectrum of *G*-NCs.

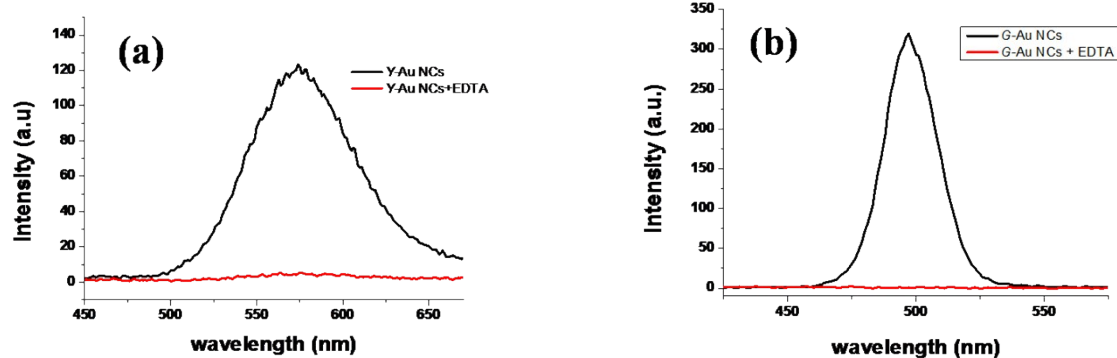


Figure S12. Emission spectra of (a) *Y*-NCs and (b) *G*-NCs in presence and absence of EDTA. EDTA: Zn^{2+} (1:1).

Table. 1 Elemental analysis data for *G*-NCs.

Sample	C (%)	H (%)	N (%)	S (%)
<i>G</i> -NCs	16.11	1.80	0.00	14.47

The percentage of ligand calculated from CNHS data was found to be 47%.