Supporting Information

Dual Emissive Optically Active Gold Nanoclusters Endowed with Circularly Polarized Phosphorescence

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Experimental Section

Materials

Polyvinyl alcohol, and D/L-cysteine hydrochloride monohydrate were purchased from TCI chemicals. Tetrachloroauric acid ($HAuCl_4.3H_2O$) was purchased from Sigma-Aldrich. Solvents, including acetone and DMF, were purchased from Spectrochem Pvt. Ltd. Milli-Q water was used for all experiments. All the chemicals were used without further purification.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded on the Perkin Elmer FT-IR spectrometer. The solution state UV-visible spectra were measured on Cary UV-visible Multicell Peltier. The fluorescence measurements were performed on JASCO spectrofluorometer- FP-8500. CD spectra were recorded on JASCO J-1500 CD spectrometer. The CPL measurements were done using JASCO CPL-300 CPL spectrometer. The lifetime measurements were performed on the Edinburg FLS-1000 fluorescence spectrometer by exciting the sample at 375 nm. The absolute quantum yield measurements were obtained using the integrating sphere in an Edinburg FLS-1000 instrument. High Resolution Mass Spectrometry (HRMS) was analysed on Agilent LC/Q-TOF and TEM images were captured using FEI Tecnai G2 20 S-twin electron microscope with an acceleration voltage of 200 kV.

Synthesis of Chiral Gold Nanoclusters

D-cysteine and L-cysteine capped gold nanoclusters (D-AuNC and L-AuNC) were synthesized by a modified process through the addition of 0.1 M of $HAuCl_4$ into 79.7 mM and 85.4 mM aqueous solution of L-cysteine hydrochloride monohydrate and D-cysteine hydrochloride monohydrate, respectively, under vigorous stirring at 23°C in methanol bath. The system was kept under continuous stirring in the dark for 24 hours. The solution was then stored under cool conditions until further use.

Preparation of PVA Films

200 mg of PVA was added into 1.5 mL of water followed by stirring at 80 °C in a water bath for 1.5 h. Upon the solution reaching to room temperature, 2.5 mL of cluster solution was added into it followed by gentle stirring overnight. The solution was then drop casted on a petri dish and allowed to dry at room temperature under dark.

Assembly of Au nanoclusters: The assembly of chiral AuNCs was performed by dispersing 200 µL of NCs in water to the acetone solution. The assembly process was monitored using UV-visible and fluorescence measurements. Aggregate morphology was analysed using TEM.

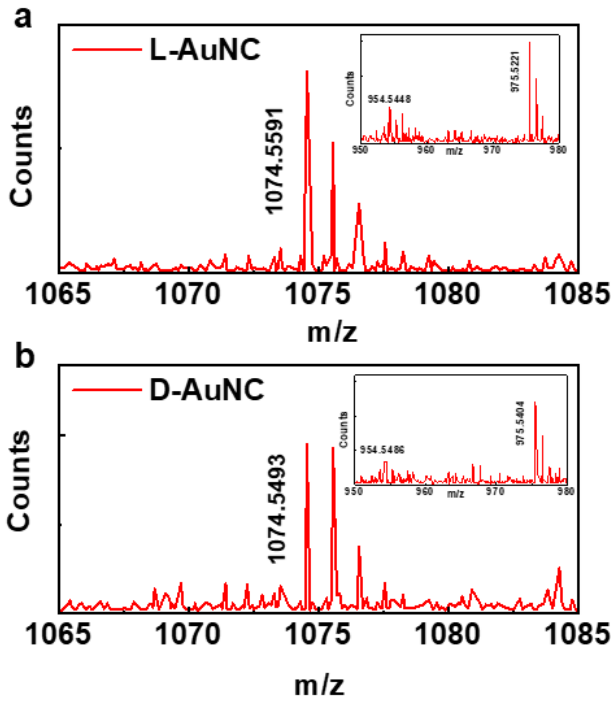

Fig. S1. HRMS plot of (a) L-AuNCs and (b) D-AuNCs.

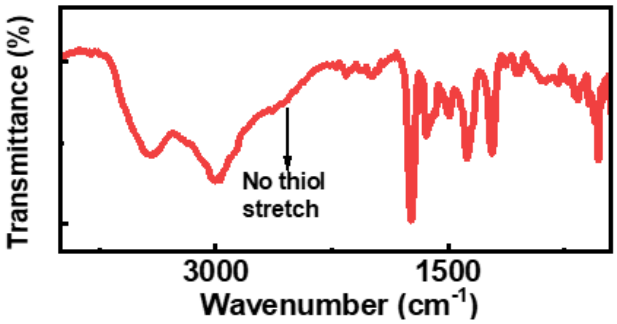

Fig. S2. FT-IR plot of L-AuNCs dispersed in water.

FTIR measurements showed strong and broad band from 2800 to 3500 cm^{-1} that could be assigned to the carboxylic O-H and C-H stretch. The stretching band around 3000 cm^{-1} corresponds to NH_2 group whereas the C=O stretching, N-H stretching, and N-H bending were observed around 1736 cm^{-1}, 3270-3530 cm^{-1}, 1580-1650 cm^{-1}, respectively. The absence of thiol stretching (-SH) around 2584-2598 cm^{-1} suggested a strong Au-thiol interaction in the clusters.

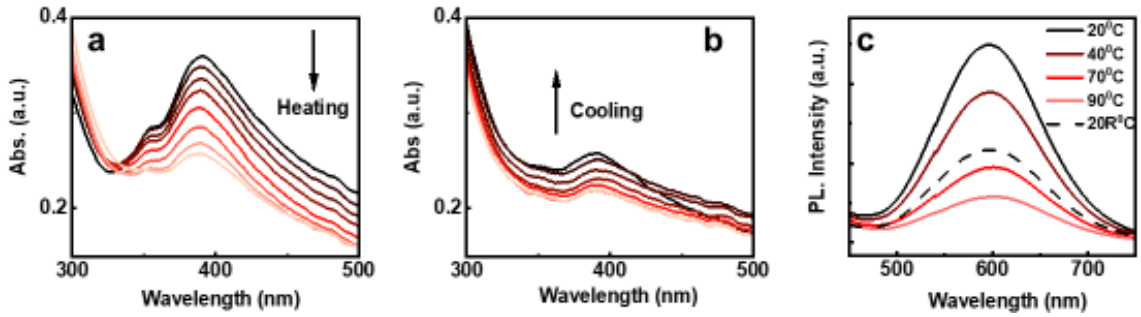

Fig. S3. Temperature dependent absorption plot by (a) increasing the temperature from 20°C to 90°C and (b) for the cooling cycle. (c) Temperature dependent emission spectra.

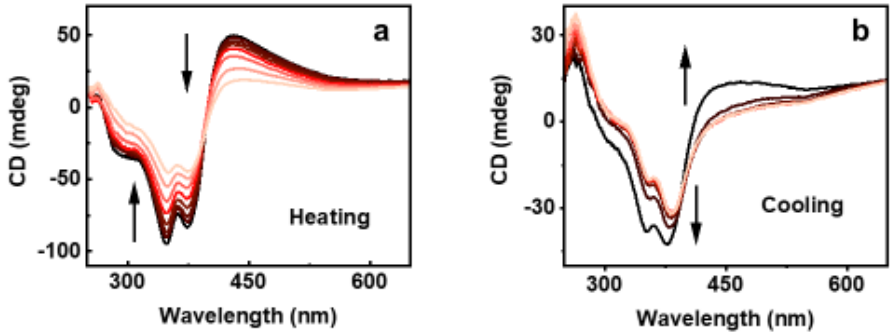

Fig. S4. CD spectral changes of AuNC for (a) heating cycle from 20°C to 90°C and the (b) for cooling from 90°C to 20°C.

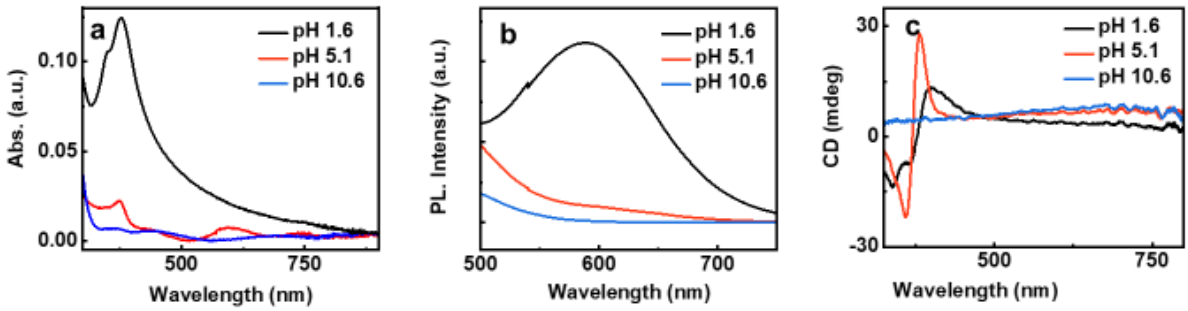

Fig. S5. (a) UV-visible, (b) luminescence, and (c) circular dichroism spectra of the clusters at varying pH.

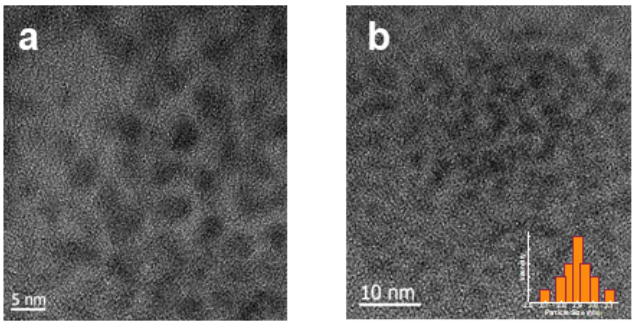

Fig. S6. TEM images of the nanoclusters at different magnifications. Inset in 'b' shows the particle size distribution.

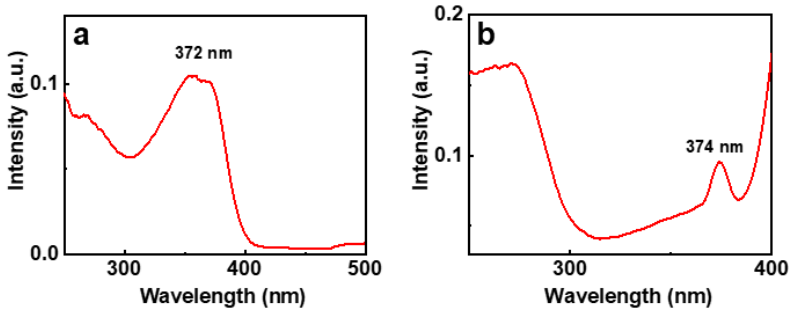

Fig. S7. Excitation spectra of the cluster solution corresponding to the (a) red and (b) blue emission peaks.

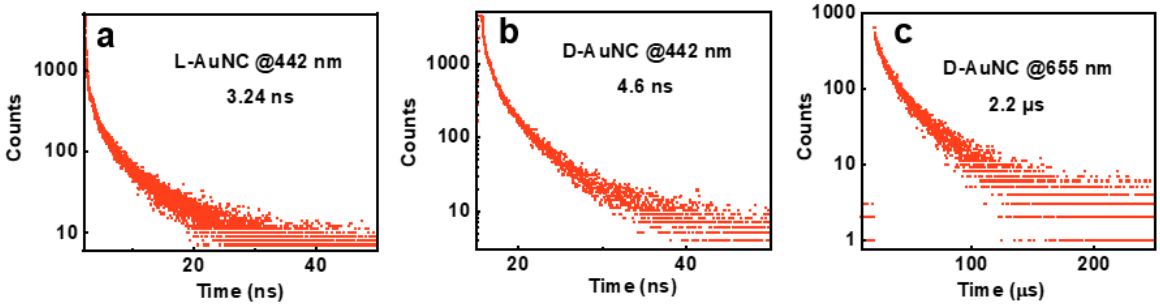

Fig. S8. (a) PL decay plot of L-AuNC corresponding to 442 nm emission. (b) PL lifetime decay plot of D-AuNC corresponding to (b) 442 nm and (c) 655 nm emission.

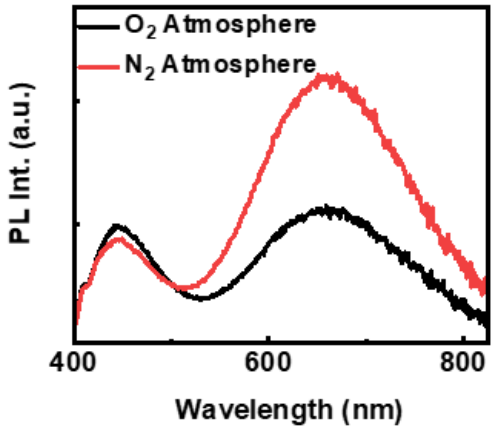

Fig. S9. PL spectra of the Au nanocluster solution collected under nitrogen (red trace) and oxygen (black trace) atmosphere.

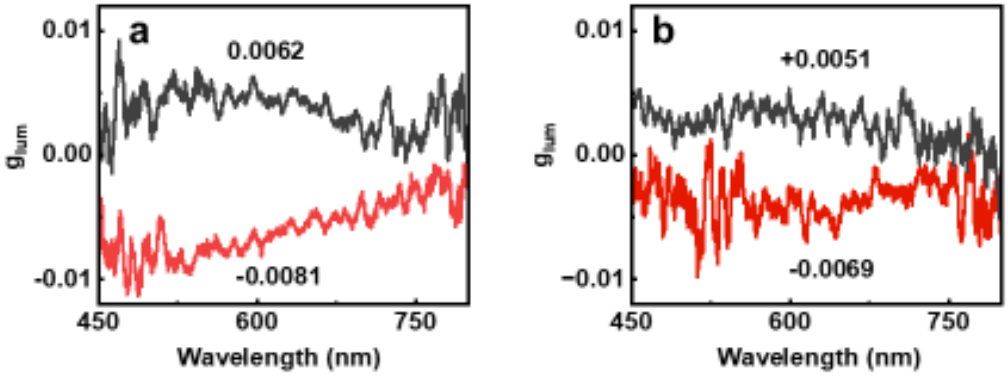

Fig. S10. (a) g_{lum} plot of the clusters dispersed in water. (b) g_{lum} plot of the clusters incorporated in PVA films. Black and red spectra correspond to AuNCs synthesized using D- and L-cysteine respectively.

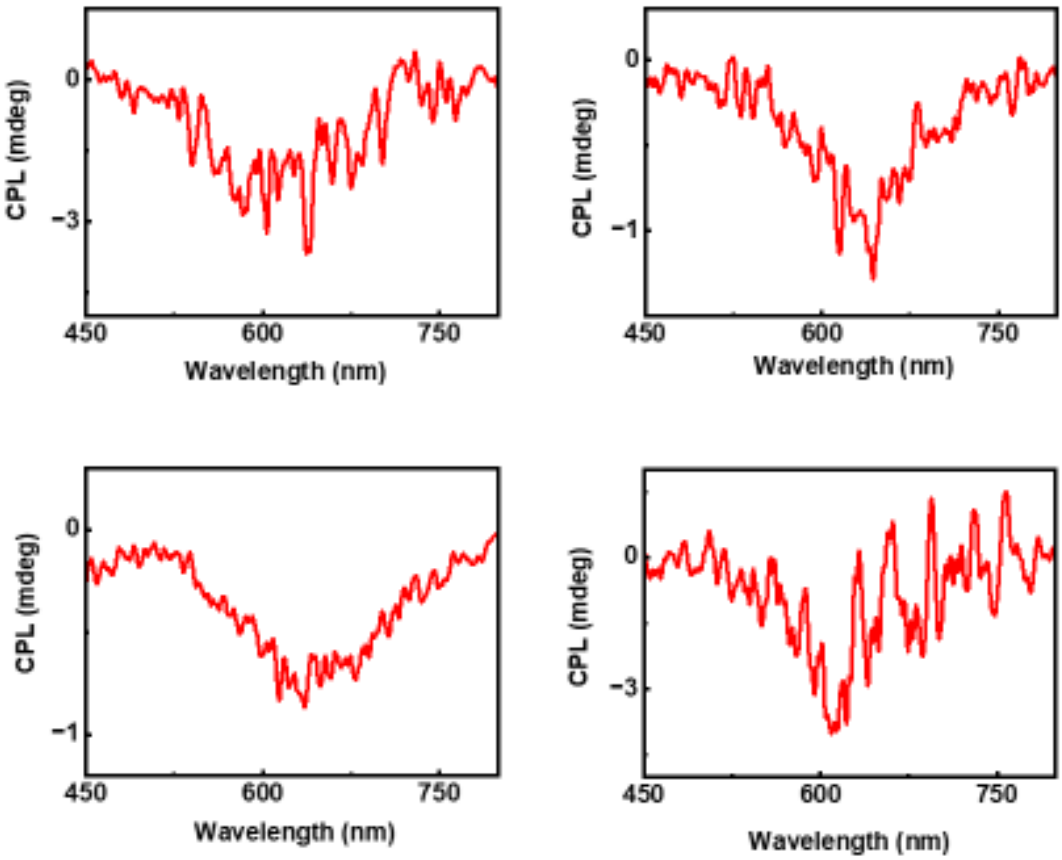

Fig. S11. CPL spectra collected from different positions on the PVA film incorporated with AuNCs synthesized using L-cysteine.

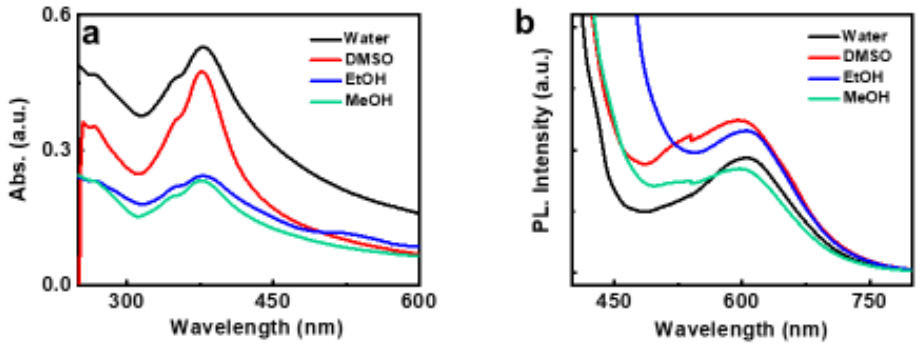

Fig. S12. (a) UV-visible and (b) luminescence spectra of L-AuNCs in solvents of varying polarity.

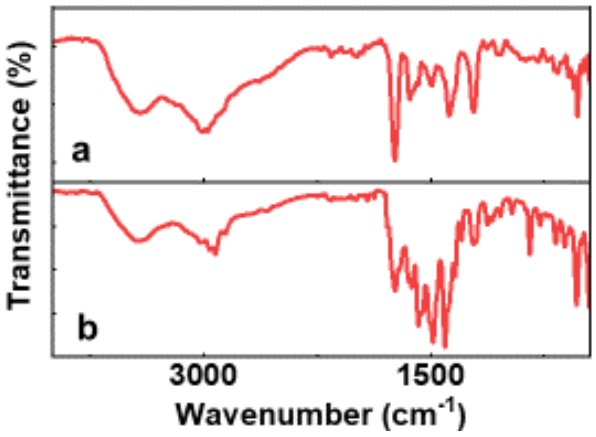

Fig. S13. FT-IR spectra of (a) monomeric AuNCs dispersed in water and (b) the aggregated clusters in acetone.

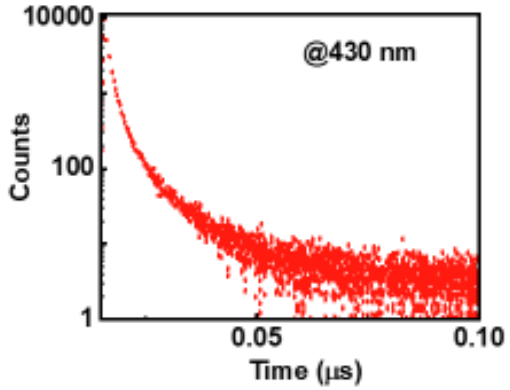

Fig. S14. Lifetime decay plot of the aggregated clusters at the emission maxima around 430 nm.

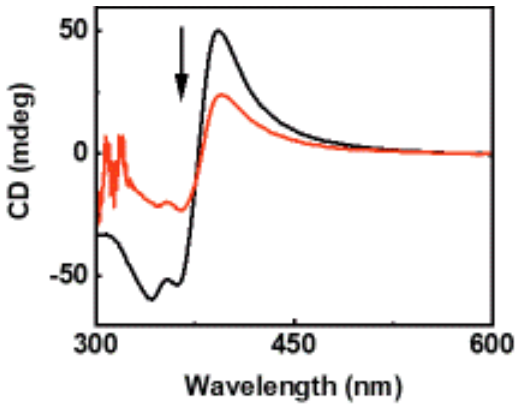

Fig. S15. CD spectra of the monomeric AuNCs dispersed in water (black trace) and the aggregated clusters in acetone (red trace).

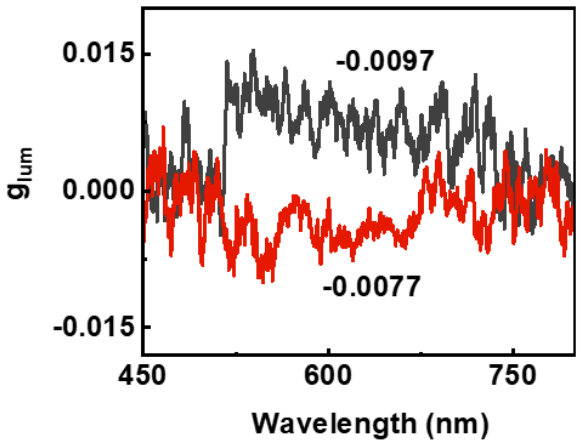

Fig. S16. g_{lum} plot of the AuNC aggregates incorporated PVA films. Black and red spectra correspond to AuNCs synthesized using D- and L-cysteine respectively.

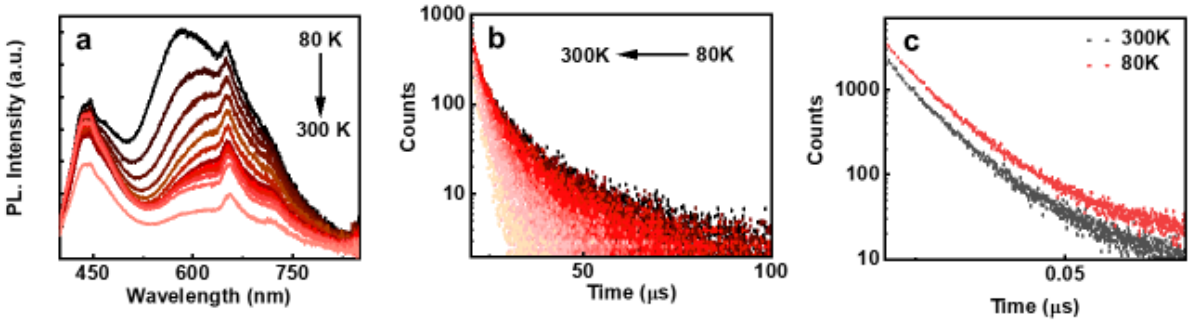

Fig. S17. Temperature dependent (a) PL and (b) lifetime plots (@650 nm) of the PVA film prepared by incorporating the assemblies of L-AuNCs. (c) Temperature dependent lifetime decay plot of the aggregated clusters incorporated PVA film at the emission maxima around 430 nm.