Electronic Supplementary Material (ESI) for ChemComm.

ESI material for

Circularly polarized luminescence in chiral silver nanoclusters

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Experimental Section

General

All chemicals were commercially available and were used without purification. *R*, *S*- and racemic-α-lipoic acids, silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were purchased from TCI (*S*-lipoid acid is currently unavailable from TCI). Absorption and emission spectra were measured using a JASCO V-670 spectrophotometer and using a HITACHI F-7000 spectrofluorometer, respectively. Absolute fluorescence quantum yields of compounds were determined using a Hamamatsu C9920-02. CD and CPL spectra were measured using a JASCO J-725 spectropolarimeter and a homemade CPL spectroscopy system,[1] respectively.

Synthesis and purification of Ag NCs

Ag NCs were synthesized following previously reported procedure with modifications.[2] 100 mg of lipoic acid (5.0×10^{-4} mol, *R*- and *S*-forms in total) was mixed in 5 ml of deionized water in a vial and stirred. To the stirring solution 19 mg of $NaBH_4$ (5.0×10^{-4} mol) in 1 ml of deionized water was added in a dropwise manner. The solution was allowed to stir vigorously until a transparent solution with light-yellow color was formed. This indicates the formation of soluble DHLA in solution. To the stirring DHLA solution, 2 ml of 0.1 M aqueous $AgNO_3$ was added. The reduction of Ag^+ was carried out by adding 19 mg of $NaBH_4$ (5.0×10^{-4} mol) in 1 ml of deionized water dropwise under stirring. After the completion of reduction, the solution was kept stirring for 8 h. The color of solution changed from dark brown into bright orange indicating the formation of NCs. Addition of equiamount acetonitrile to this aqueous solution resulted in the precipitation of inorganic salts and ligand, which was removed by centrifugation at a speed of 3500 rpm for 4 min. The solvent was removed and the residue subjected to

freeze drying to obtain NCs as red solid powder. The powder could be dissolved in aqueous medium for further investigations. Bright-red emission observed when exposed to UV light confirms the formation of silver clusters.

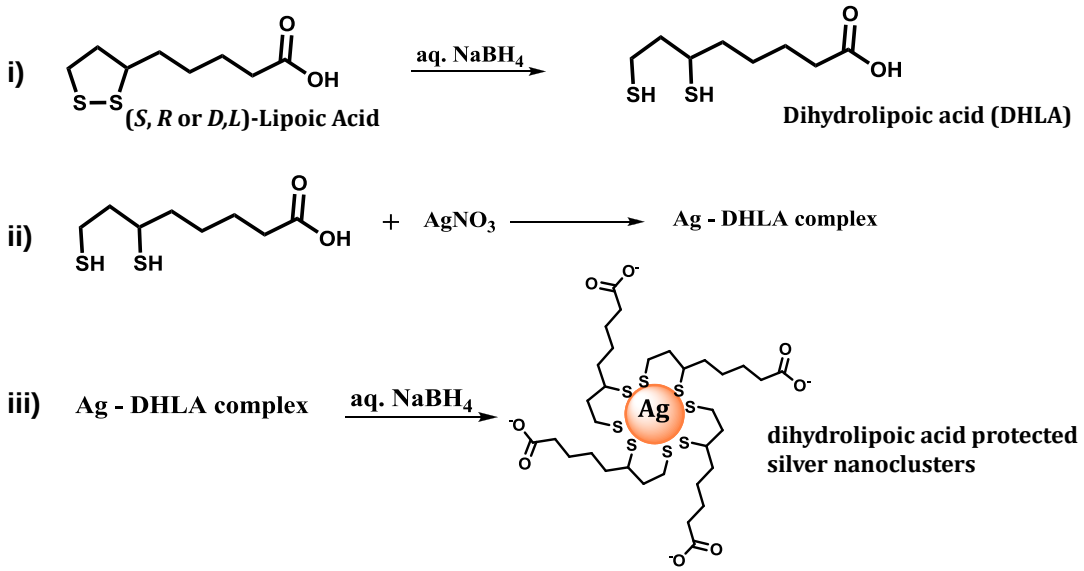

Fig. S1 Scheme illustrating the synthesis of *R*-, *S*- or *rac*-NCs.

Note: The *R* and *S*-(α)-lipoic acids were used for the synthesis of different sets of NC solutions. The lipoic acid was reduced to dihydrolipoic acid (DHLA) using sodium borohydride and the DHLA was in turn used for the stabilization of the clusters. The carboxylate group of DHLA renders solubility for the clusters in polar solvents and the strong interaction of thiol with Ag provides good control over the cluster size.

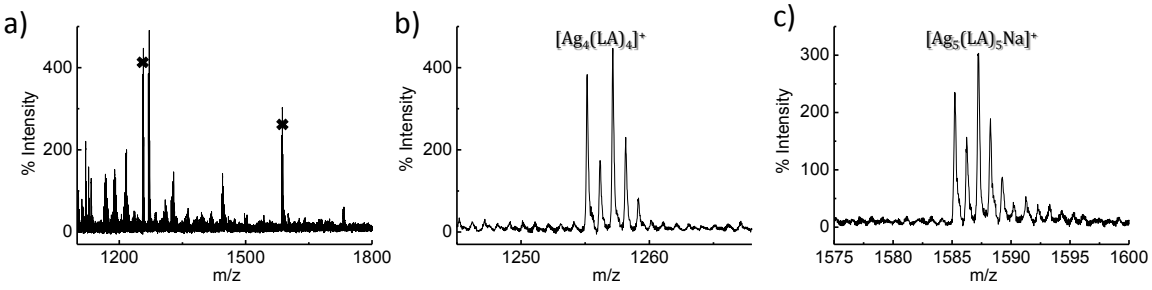

Fig. S2 High-resolution mass spectra (HR-MS) of fluorescent Ag NCs, showing the presence of Ag_4 and Ag_5 clusters. (LA corresponds to the ligand DHLA)

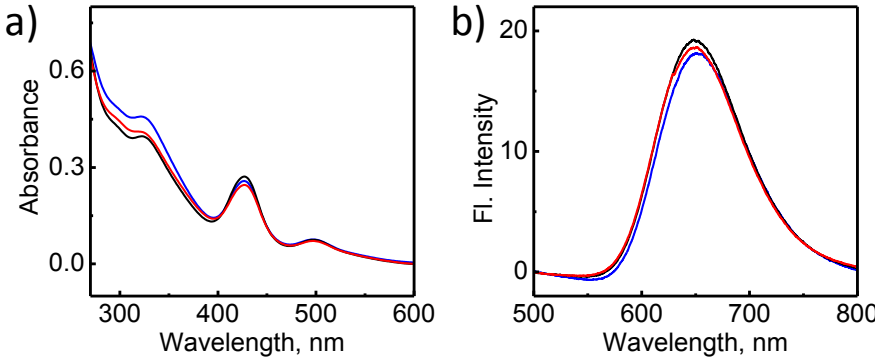

Fig. S3 (a) Absorption and (b) fluorescence spectra of silver NCs capped with *R*- (red traces), *S*- (blue traces) and *rac*- (black traces) dihydro-lipoic acid.

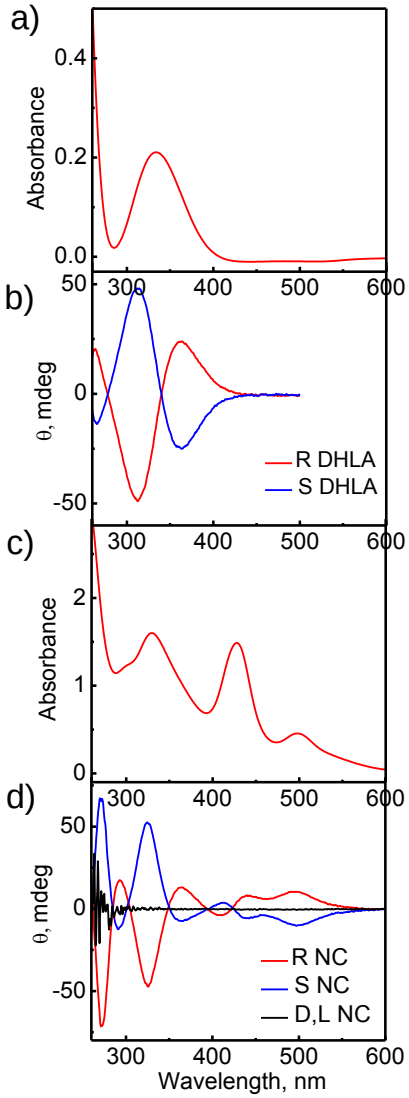

Fig. S4 (a) Absorption and (b) CD spectra of *R* (red traces) and *S* (blue traces) DHLA in water and (c,d) the respective spectra of silver NCs capped with the corresponding ligands (shown for comparison).

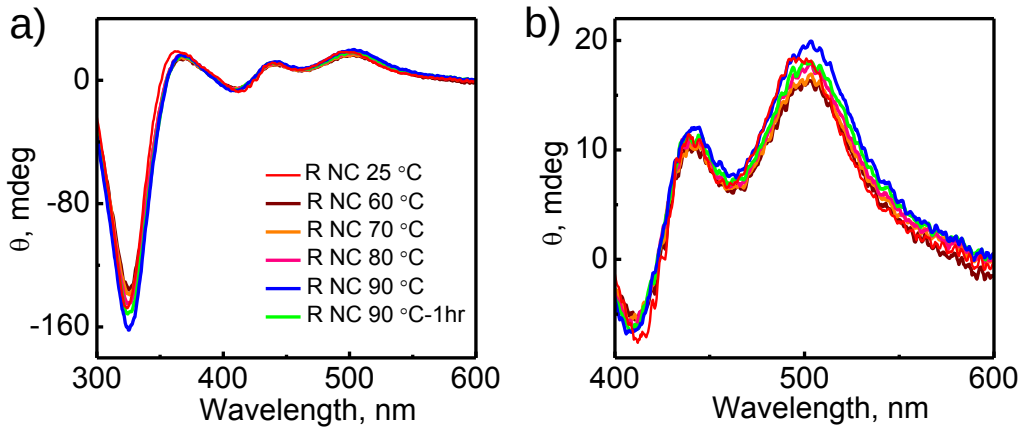

Fig. S5 CD spectral changes of *R* NC at varying temperature depicting the stability of NCs to elevated temperatures. (b) The spectral changes at the corresponding NC region. Note: No noticeable changes observed on heating confirm (i) the stability of NCs at elevated temperature.

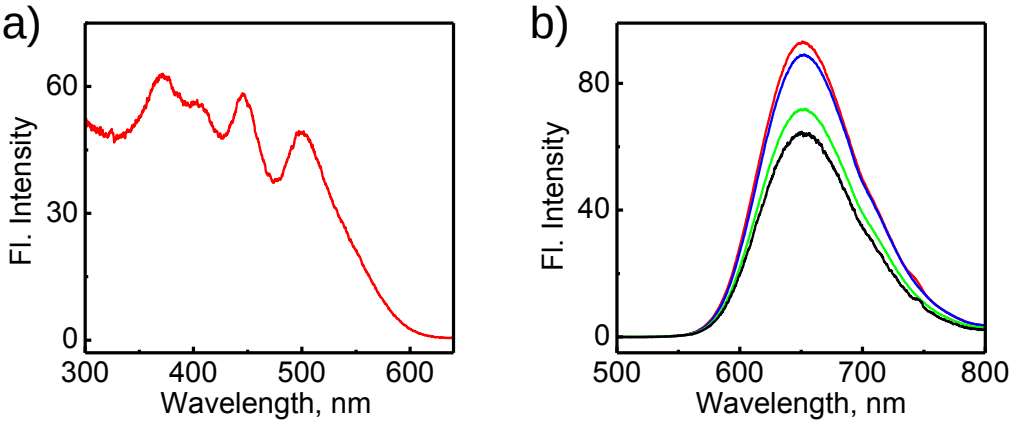

Fig. S6 (a) Excitation spectrum of silver NCs capped with *R* lipoic acid collected (emission monitored at 650 nm) and (b) fluorescence spectra of corresponding NCs collected after exciting at 330 (red), 370 (blue), 430 (green) and 490 nm black).

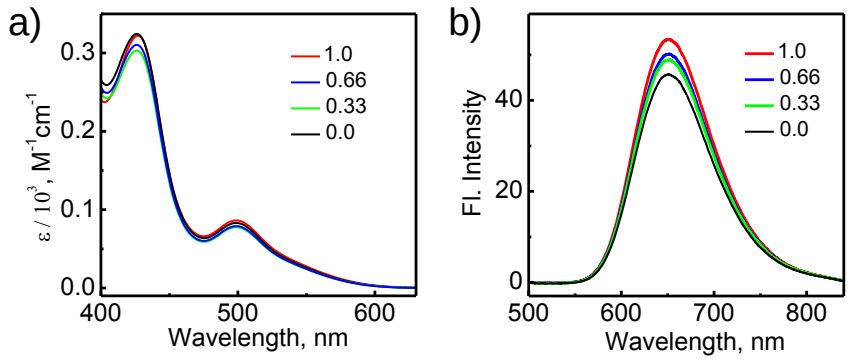

Fig. S7 (a) Absorption and (b) fluorescence spectra of the NCs synthesized using DHLA solution at different *ee*.

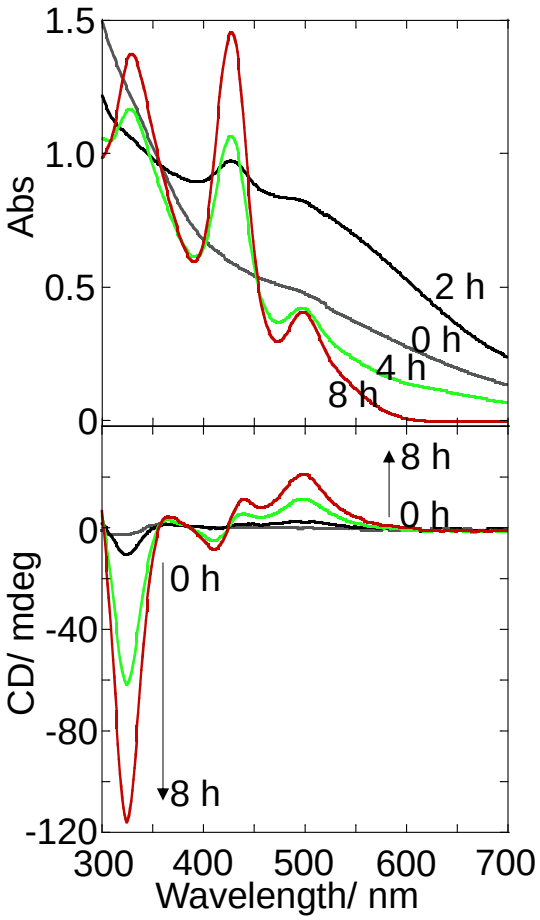

Fig. S8 Time dependent (a) absorption and (b) CD spectra of the *R*-NCs during the synthesis.

Note: A broad absorption band was observed at ~430 nm after addition of $NaBH_4$ to an aqueous mixture of $AgNO_3$ and DHLA. The absorption gradually becomes sharper with the progress of the reaction.

References

1. H. Tsumatori, T. Nakashima and T. Kawai, *Org. Lett.*, 2010, **12**, 2362 –2365.

2. B. Adhikari and A. Banerjee, *Chem. Mater.*, 2010, **22**, 4364–4371.