

Formation of periodic stripe patterns in nematic liquid crystals doped with functionalized gold nanoparticles

Hao Qi and Torsten Hegmann*

Electronic Supplementary Information (ESI)

Synthesis of 12-sulfanyldodecyl (2*S*)-2-(6-methoxy-2-naphthyl) propanoate (**3b**)

12-bromododecyl (2*S*)-2-(6-methoxy-2-naphthyl) propanoate was synthesized according to a published procedure^{S1} using Naproxen (7.8 mmol, 1.8 g), 12-bromo-dodecan-1-ol (7.8 mmol, 2.0 g) and *p*-toluenesulfonic acid (9.8 mmol, 1.7 g) in toluene (50 ml). The mixture was refluxed for about 10 h under N₂ in a round bottom flask using a Dean-Stark trap. The reaction progress was monitored by TLC (hexane:ethyl acetate = 8:2). After the reaction was complete, the reaction mixture was cooled to room temperature, and then washed with water (3×). The organic layer was separated, dried (Na₂SO₄), and the solvent evaporated under reduced pressure. The crude residue was purified by column chromatography (hexane:ethyl acetate = 8:2) to afford 3.6 g (97%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.22 (m, br, 16H, CH₂), 1.44 (m, H, CH₂CH₂O), 1.62 (d, 3H, *J*=7.2Hz, CH₃CH), 1.88 (m, 2H, CH₂CH₂Br), 3.43 (t, 2H, *J*=6.8Hz, CH₂Br), 3.83 (m, 1H, CHCH₃), 3.93 (s, 3H, CH₃O), 4.10 (t, 2H, *J*=6.6Hz, OCH₂CH₂), 7.18 (m, 2H, Ar-*H*), 7.46 (d, 1H, *J*=8.5Hz, Ar-*H*), 7.70 (d, 2H, *J*=3.6Hz, Ar-*H*), 7.74 (s, 1H, Ar-*H*). ¹³C NMR (75 MHz, CDCl₃): δ 129.66, 128.63, 127.46, 126.31, 125.70, 119.32, 105.98, 65.28, 55.69, 45.95, 34.43, 33.25, 29.89, 29.17, 28.58, 26.19, 18.91. MS *m/z* (rel. int., %): 478 (7.1) [M]⁺, 396 (9.3), 185 (100), 170 (5.9), 141 (7.5).

3b was synthesized according to a procedure reported by Hu and co-workers.^{S2} Briefly, 12-bromododecyl (2*S*)-2-(6-methoxy-2-naphthyl) propanoate (2.5 mmol, 1.2g) was dissolved with freshly distilled dry THF (5 ml) and then cooled to -10 °C using an acetone/ice bath. To the resulting solution, hexamethyldisilathiane (3.0 mmol, 0.63ml) and TBAF (1M in THF, 2.76mmol, 2.76ml) were added under an inert-gas atmosphere. After the reaction was complete (TLC, hexane:ethyl acetate = 8:2), the mixture was allowed to warm to room temperature. Thereafter, the solution was partitioned between diethyl ether (100 ml) and saturated aqueous ammonium chloride (100 ml), the layers were separated, and the organic phase washed with water (50 ml). After evaporation of the solvent under reduced pressure, the crude residue was purified by column chromatography (hexane:ethyl acetate = 8:2) to yield 1.95 g of **3b** (60 %). *R_f* (hexane:ethylacetate = 9:1) 0.46 (disulfide **3a**: *R_f* (hexane:ethylacetate = 9:1) 0.2). [α]_D²⁰ +26.5°, (in comparison to (*S*)-Naproxen: [α]_D²⁰ +66 ± 2°, *c* 0.01 in chloroform source: Sigma-Aldrich). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.21-1.37 (m, br, 20H, CH₂, and overlapped 1H, SH), 1.58 (d, 3H, *J*=7.2Hz, CH₃CH), 2.53 (q, 2H, *J*=7.5Hz, CH₂SH), 3.88 (q, 1H, *J*=6.2Hz, CHCH₃), 3.93 (s, 3H, CH₃O), 4.08 (t, 2H, *J*=6.8Hz, CH₂O), 7.18 (m, 2H, Ar-*H*), 7.46 (d, 1H, *J*=1.8Hz, Ar-*H*), 7.70 (d, 2H, *J*=4.4Hz, Ar-*H*), 7.73 (s, 1H, Ar-*H*). ¹³C NMR (75 MHz, CDCl₃): δ 129.65, 127.45, 126.68, 126.30, 119.30, 105.97, 65.28, 55.68, 45.94, 34.45, 29.92, 29.47, 28.77, 26.31, 26.19, 25.05, 18.91. MS *m/z* (rel. int., %): 432 (3.4) [M]⁺, 230 (3.2), 212 (5.3), 185 (100), 171 (2.7), 155 (2.0), 141 (8.8).

Gold nanoparticle characterization (Au1-Au4)

UV-vis

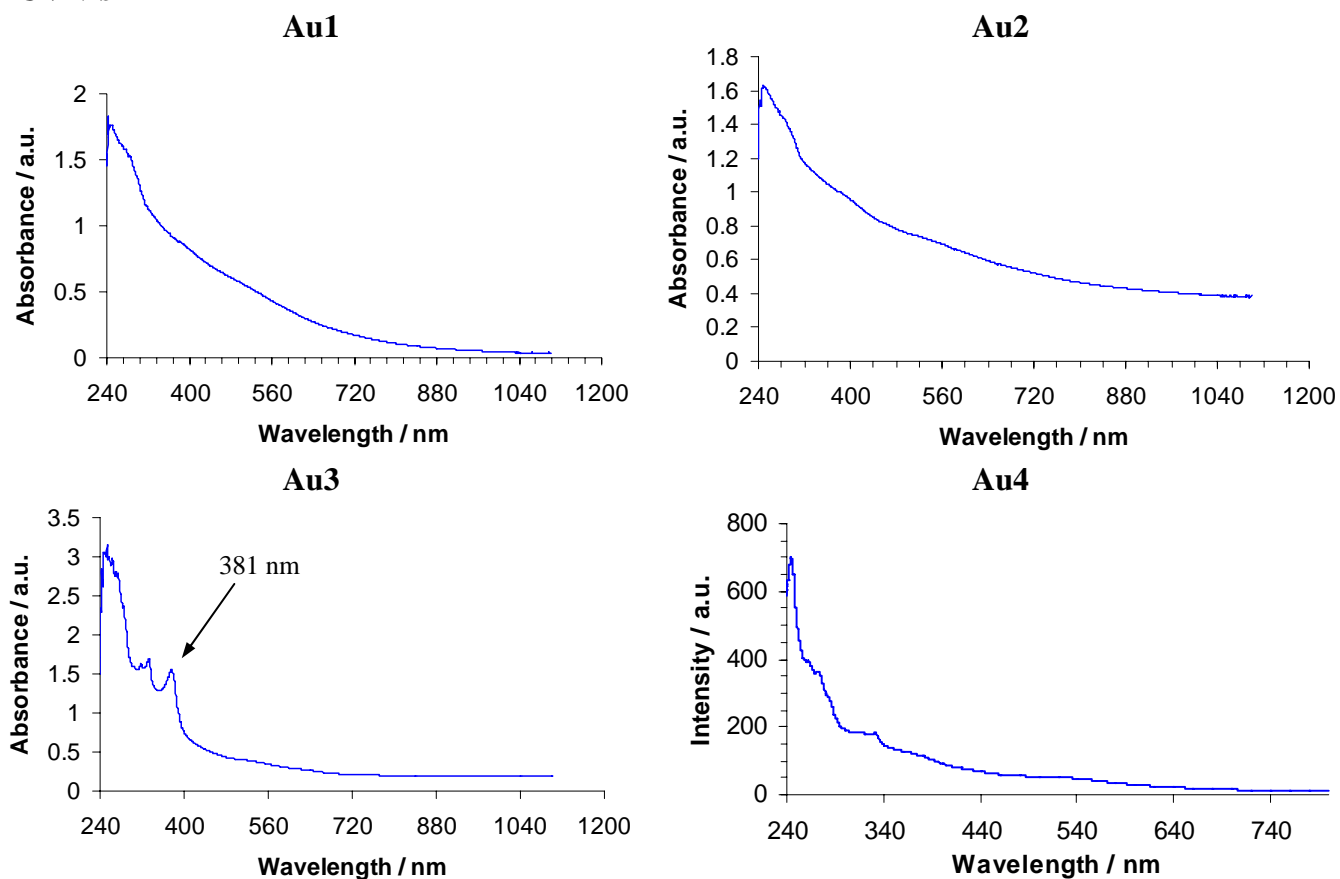
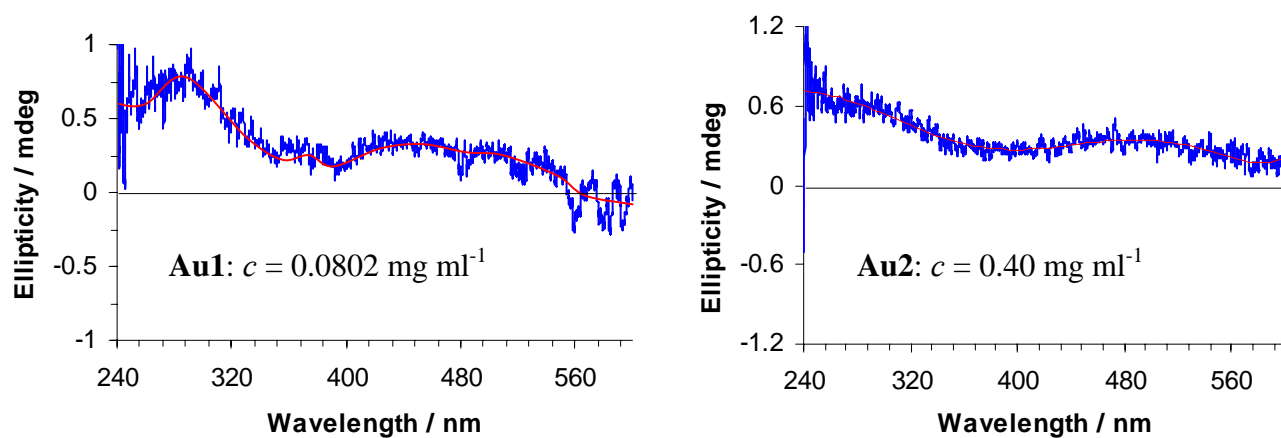
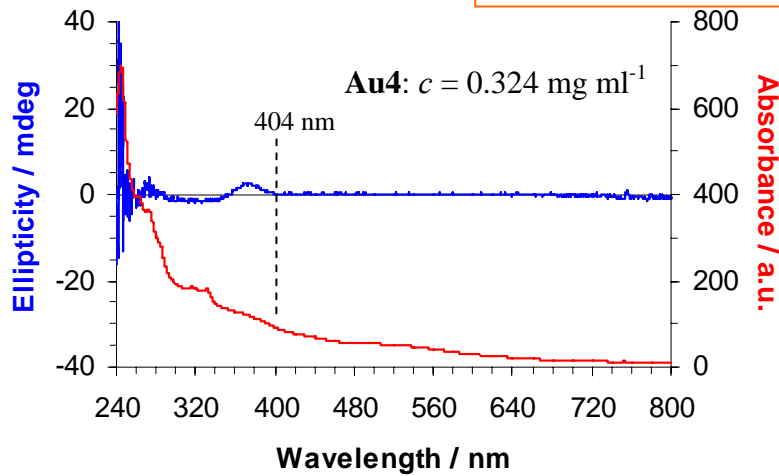
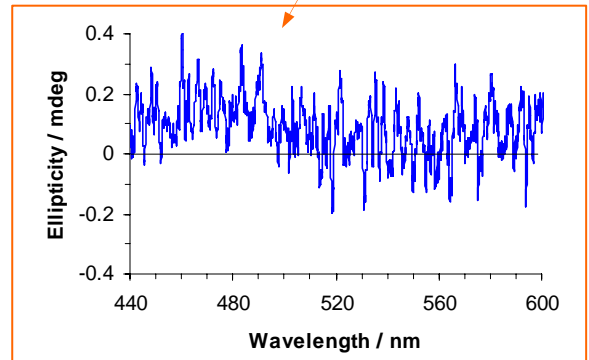
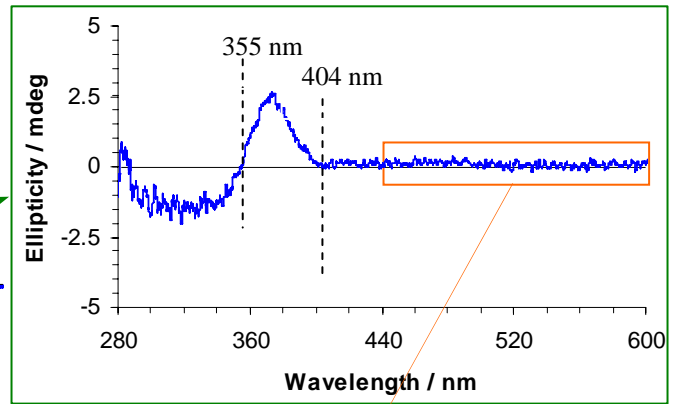
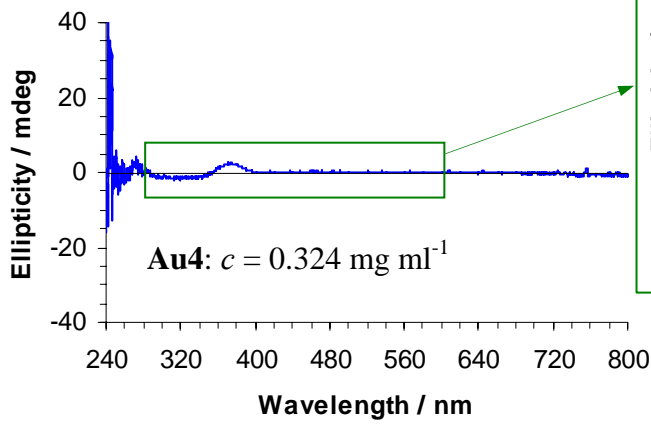
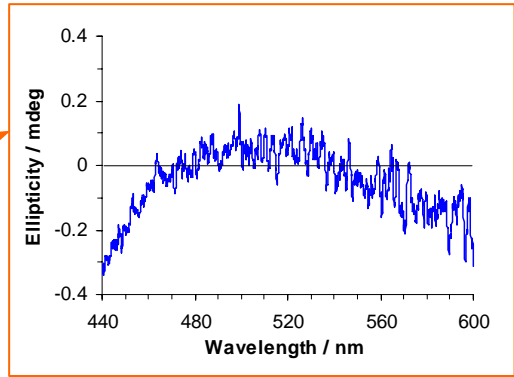
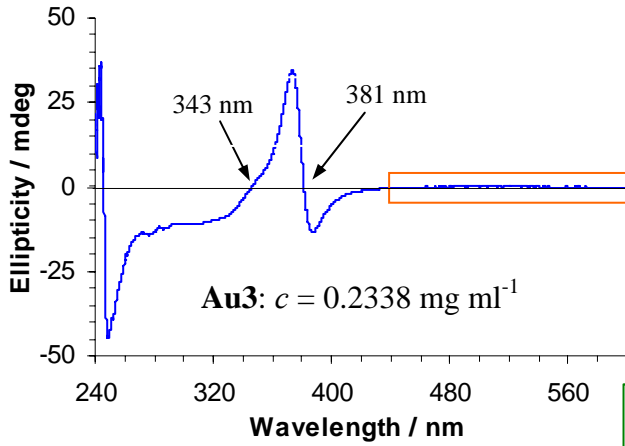


Figure S1. UV-vis spectra of Au1-Au4.

CD





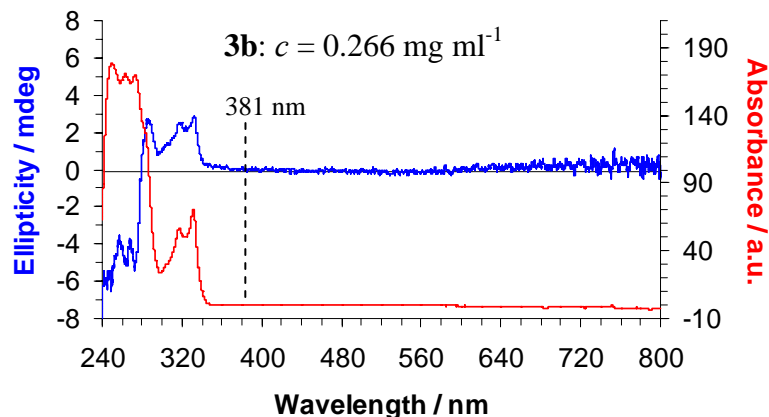


Fig. S2 CD spectra of Au1-Au4 and thiol **3b** in chloroform.

CD - Concentration Dependence for Au1 in CHCl₃

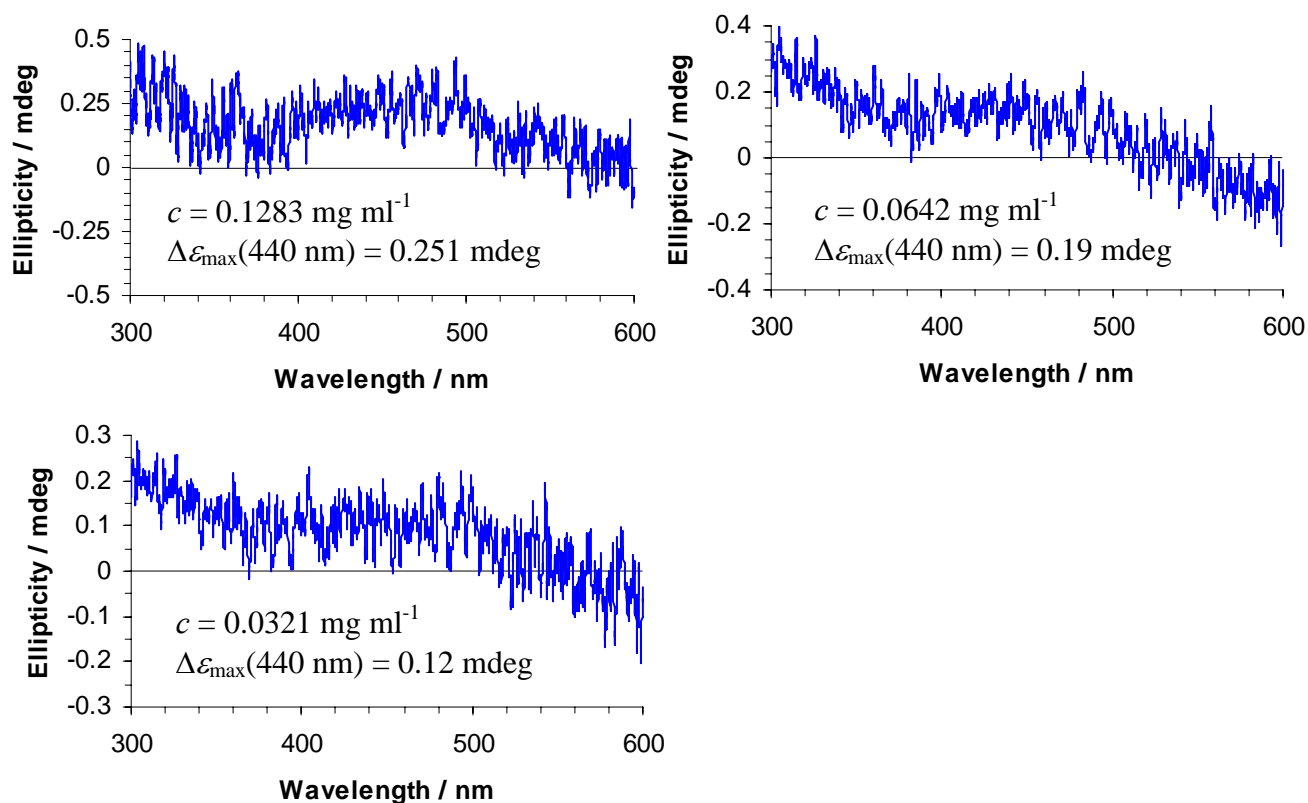


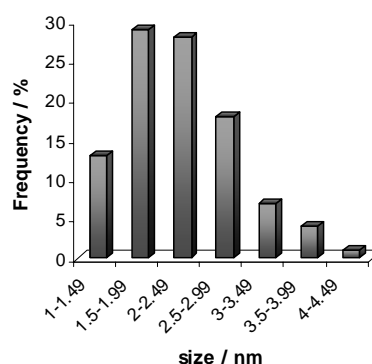
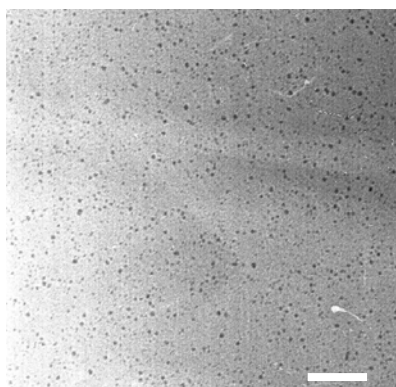
Fig. S3 CD spectra of Au1 in chloroform at three different concentrations.

Comment regarding CD

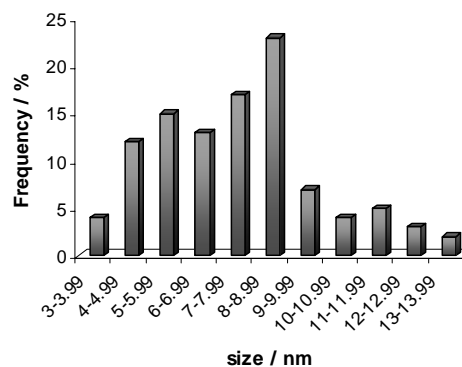
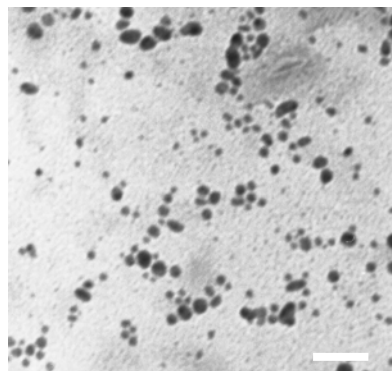
Since no chiral bias is present during the synthesis, both **Au1** and **Au2** should be obtained as a racemate, if the gold nanocluster core was chiral. The two different scenarios: (i) a chiral core due to thiolate induced lattice distortions, and (ii) a chiral adsorption pattern would average to zero in an ensemble of cluster adsorbates (parity conservation).^{S3} The most reasonable explanation for the

observed concentration-dependent CD at longer wavelength (where the thiol does not absorb) as well as for the higher $\Delta\epsilon_{\max}$ values for **Au3** in comparison to **Au4** draws from results of CD experiments on bio-macromolecules such as DNA aggregates, chloroplast, proteins, or viruses for which similar ‘anomalies’ were reported in the past.^{S4} This is that scattering (circular differential) and differential absorption both contribute to circular dichroism. However, scattering becomes increasingly important for particles/entities whose dimensions are greater than $1/20^{\text{th}}$ the wavelength of light.^{S5} Dynamic light scattering experiments at different time intervals after the preparation of the particle solutions indicate that all gold clusters discussed in this study do aggregate in solution (in the solvent used for CD). In this way, a higher concentration of particles in solution will naturally produce a higher number of particle aggregates or larger aggregates contributing to CD. In this way, the anomalous CD signals (so-called CD ‘artifacts’) are likely due to multiple scattering and dipole-dipole interactions of the dense particles,^{S6} which, in addition, continuously assemble into randomly shaped (anisometric) cluster aggregates. Yet again, this effect should average to zero, and one has to take into account that the measured CD is very weak. There are two more, but rather unlikely explanations for the observed CD. One would represent a parity violation (amplification of electro-weak forces due to the unique properties of gold nanostructures), and another one the presence of trace amounts of a chiral impurity during the cluster synthesis.^{S7}

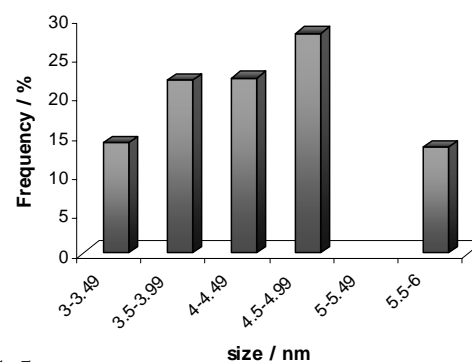
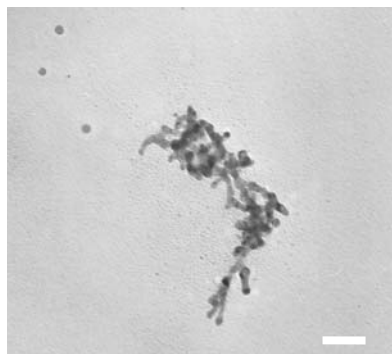
TEM Au1



Au2



Au3



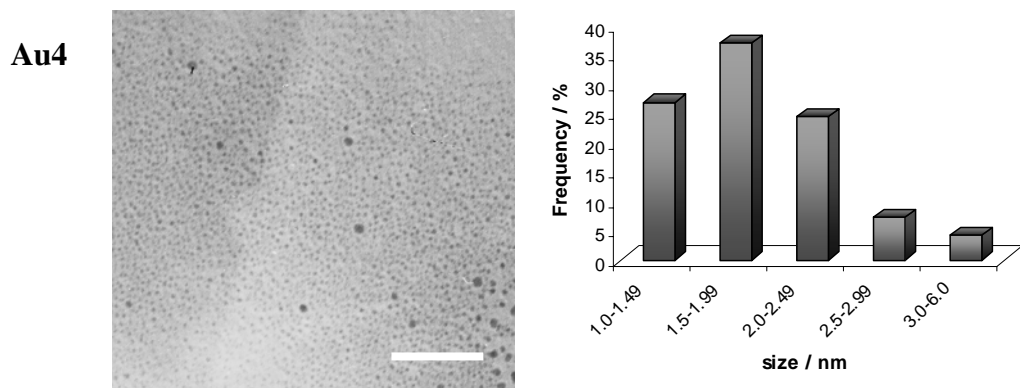


Fig. S4 TEM micrographs and size distribution of **Au1-Au4** (micrograph scale bars = 50 nm)

XRD

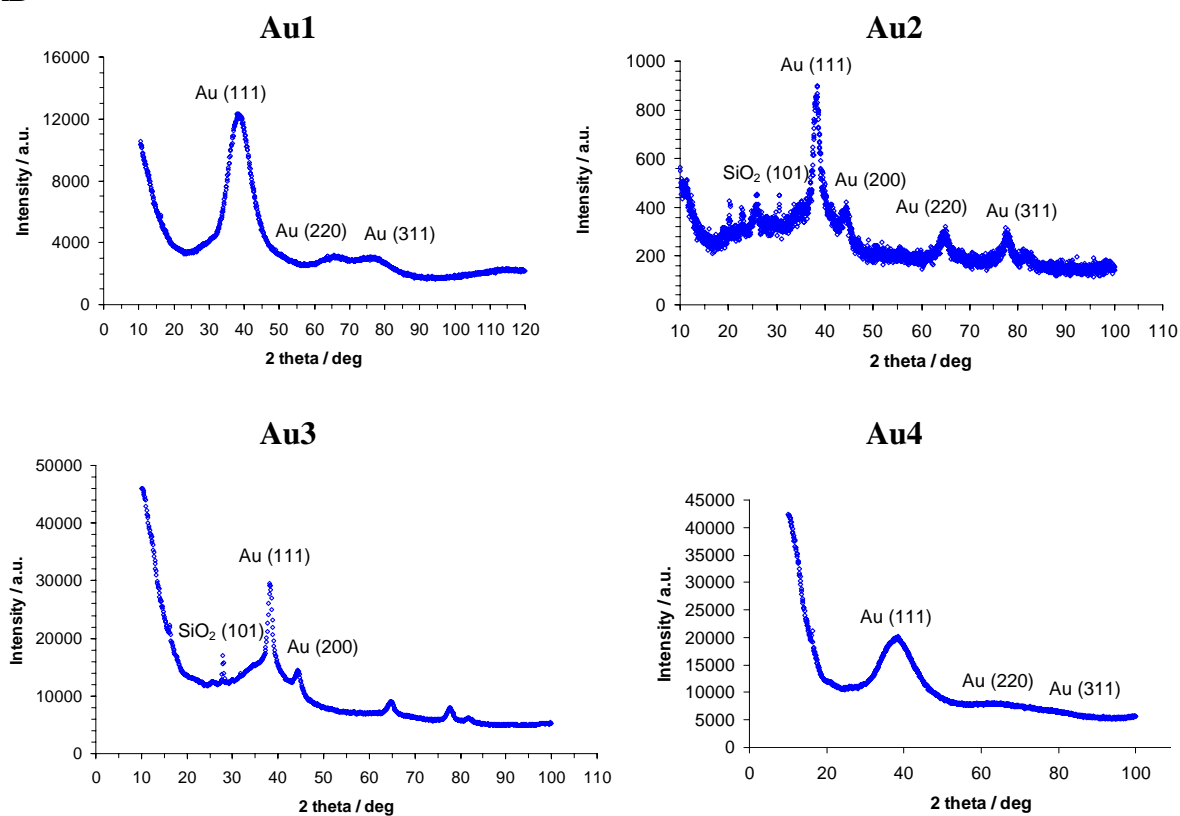


Fig. S5 Powder XRD pattern of **Au1-Au4**.

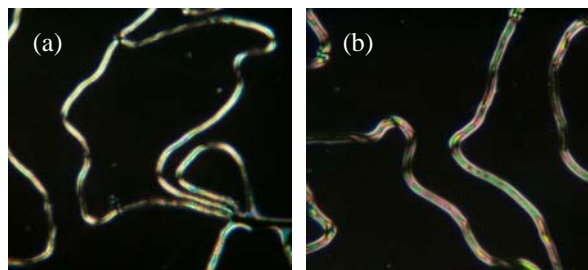


Fig. S6 POM micrographs of stripe pattern texture of the N phase of: (a) 5wt% **Au1** in **LC1** (64 °C), and (b) 5wt% **Au4** in **LC1** (56 °C) taken on cooling from the isotropic liquid phase.

References

- (S1) M. Kazemekaite, A. Bulovas, Z. Talaikyte, E. Butkus, V. Railaite, G. Niaura, A. Palaima and V. Razumas, *Tetrahedron Lett.*, 2004, **45**, 3551.
- (S2) J. Hu and M. A. Fox, *J. Org. Chem.*, 1999, **64**, 4959.
- (S3) M.-R. Goldsmith, C. B. George, G. Zuber, R. Naaman, D. H. Waldeck, P. Wipf and D. N. Beratan, *Phys. Chem. Chem. Phys.*, 2006, **8**, 63.
- (S4) O'Neil, J., personal communication.
- (S5) C. Bustamante, I. Tinoco Jr. and M. F. Maestre, *Proc. Natl. Acad. Sci. USA*, 1983, **80**, 3568, and additional references [33a,b] in main text.
- (S6) C. Bustamante, M. F. Maestre, D. Keller and I. Tinoco Jr., *J. Chem. Phys.*, 1984, **80**, 4817.
- (S7) In a test experiment, alkane thiolate capped nanoparticles synthesized in the presence of a chiral 'impurity' (we added one equivalent of **2**) gave the same CD and texture in **LC1** as alkane thiolate gold particles synthesized without the additional chiral component.