

Effects of hydrophilic and hydrophobic gold nanoclusters on the stability and ordering of bolaamphiphilic liquid crystals

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Electronic Supplementary Information (ESI)

Synthesis of LCs

1 and **2** were synthesized based on a procedure reported by Tschierske and co-workers.^{S1}

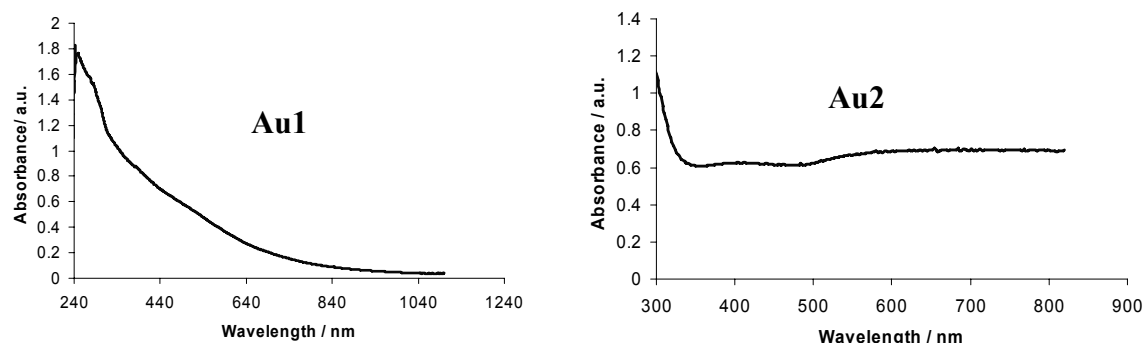
1: ¹H NMR (300 MHz, DMSO-D₆, δ, ppm): 7.53 (d, 2H, ³J=8.7Hz, Ar-H), 7.39 (m, 2H, Ar-H), 6.96 (m, 3H, Ar-H), 4.95 (d, 1H, ³J=5.1Hz, CHOH), 4.92 (d, 1H, ³J=5.1Hz, CHOH), 4.66 (m, CH₂OH), 4.05-3.78 (m, 6H, ArOCH₂, CHOH), 3.54-3.44 (m, 4H, CH₂OH), 2.22 (s, 3H, CH₃). ¹³C NMR (75MHz, DMSO-D₆, δ, ppm): 157.8, 156, 132.4, 131.8, 128.2, 127.1 (2C), 126.3, 124.4, 114.8 (2C), 111.7, 70.0 (2C), 69.9, 69.6, 62.8, 62.7, 16.1.

2: ¹H NMR (300 MHz, DMSO-D₆, δ, ppm): 7.52 (d, 2H, ³J=8.85Hz, Ar-H), 7.38-7.35 (m, 2H, Ar-H), 6.99-6.95 (2d, 3H, Ar-H), 4.91 (br, 1H, CHOH), 4.65 (br, 1H, CHOH), 4.05-3.85 (m, 6H, ArOCH₂, CHOH), 3.51-3.45 (m, 4H, CH₂OH), 2.61 (t, 2H, ³J=7.2Hz, Ar-CH₂), 1.57 (m, 2H, ArCH₂CH₂), 1.30-1.24 (m, 12H, CH₂), 0.85 (t, 3H, ³J=6.6Hz, CH₃). ¹³C NMR (75MHz, DMSO-D₆, δ, ppm): 158, 156, 132.4, 131.8, 130.9, 129, 127.2, 126.0, 114.8, 111.7, 70.0, 69.9, 69.6, 62.8, 62.7, 31.3, 29.0, 28.9, 28.7, 28.5, 28.1, 22.1, 14.0. MS m/z (rel. int., %): 460 (28) [M]⁺, 386 (20), 312 (45), 273 (6), 213 (7), 199 (50), 149 (26).

Thiol for Au2: 2-{2-[2-(5-Mercaptopentyloxy)ethoxy]ethoxy}ethanol was prepared according to a published procedure.^{S2} ¹H NMR (300 MHz, acetone-D₆, δ, ppm): 6.2 (br, 1H, CH₂OH), 3.61 (m, OCH₂CH₂O, 12H), 3.45 (t, 2H, ³J=6.2Hz, CH₂OCH₂CH₂), 2.53 (q, 2H, CH₂SH), 1.60 (m, 6H, CH₂). ¹³C NMR (75 MHz, acetone-D₆, δ, ppm): 72.8, 71.1, 70.73, 70.5, 70.3, 61.3, 34.2, 33.7, 29.6, 26.1. MS m/z (rel. int., %): 252 (0.1) [M]⁺, 133 (1.85), 119 (1.79), 103(1.76), 89 (22.73).

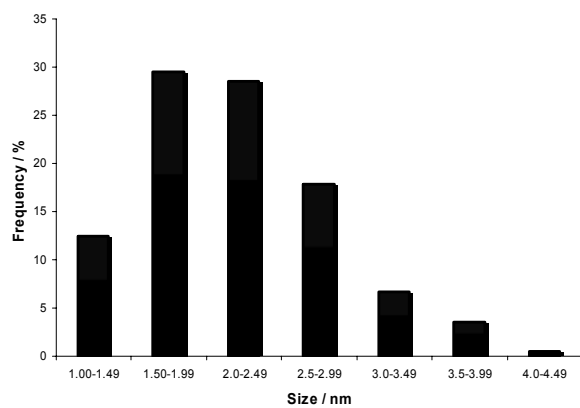
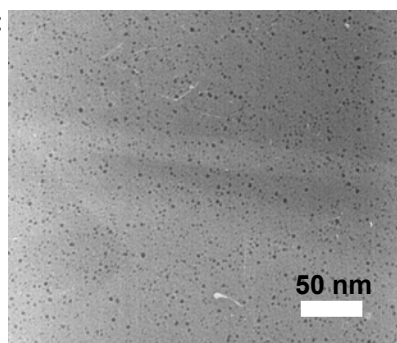
Gold nanoclusters characterization:

UV-vis (Fig. S1)

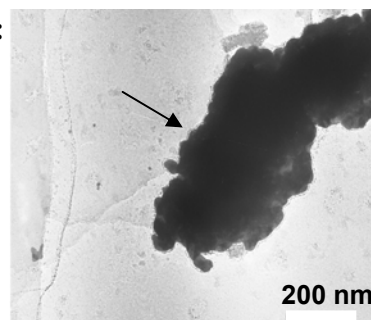


TEM (Fig. S2)

Au1:

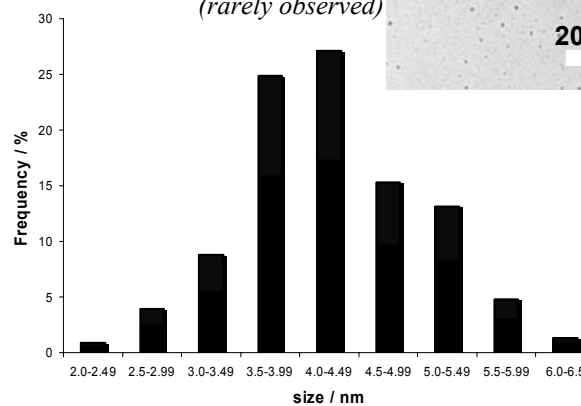
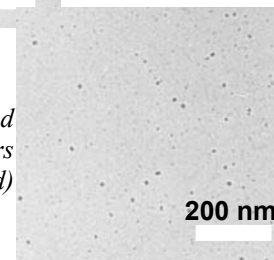


Au2:

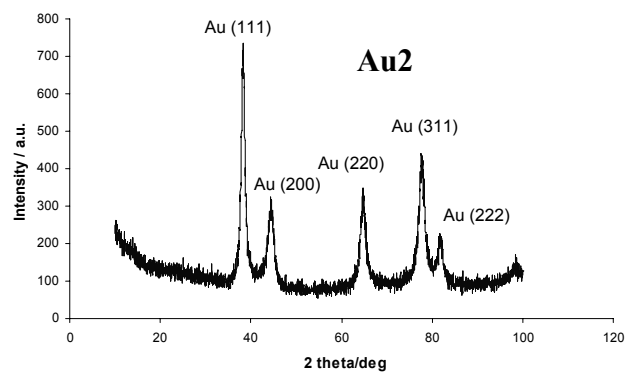
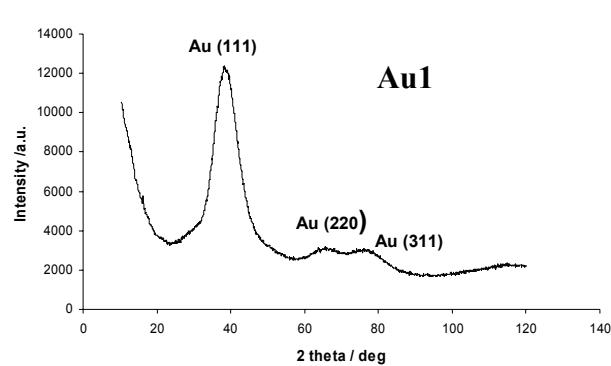


aggregates of Au2

some isolated Au2 clusters (rarely observed)



Wide-angle Powder XRD of Au1 and Au2 (Fig. S3)

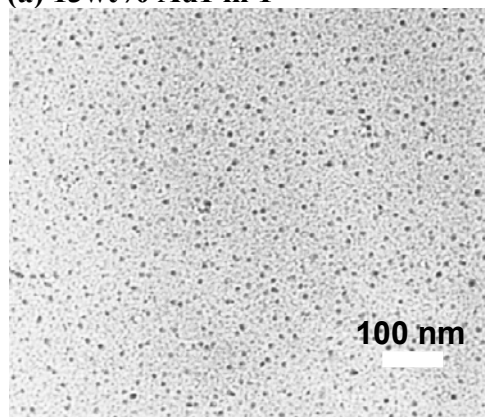


TEM of annealed mixtures (more detailed and larger images):

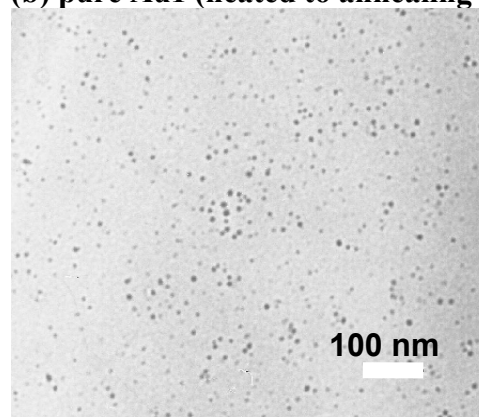
Although some areas in the TEM images appear to show organization of the nanoclusters over shorter length scales [two examples are shown in Figs. S4(b) and (d)], and one could argue about self-assembly on such shorter length scales, x-ray scattering at low and ultra-low angles did not reveal any bulk, long range periodic ordering of the gold nanoclusters. The original size of the **Au1** is about 2 nm, but increases upon heating to ca. 4 nm. For the **Au2** clusters, no change in size was observed. Hence, in the final mixtures with **2**, both nanoparticles are similar in size, and effects on the LC ordering are primarily a result of interactions with the hydrophilic or hydrophobic monolayers. The reason for the difference of this size-effect between the larger (**Au2**) and the smaller clusters (**Au1**) was explained by the fact that smaller nanoclusters have larger chemical potentials and, as a result thereof, have a greater tendency to sinter and change size.^{S3} A detailed discussion of size change of gold particles upon heating in LCs will be included in the following paper.

TEM image of mixture of gold nanoclusters in LCs (Fig. S4)

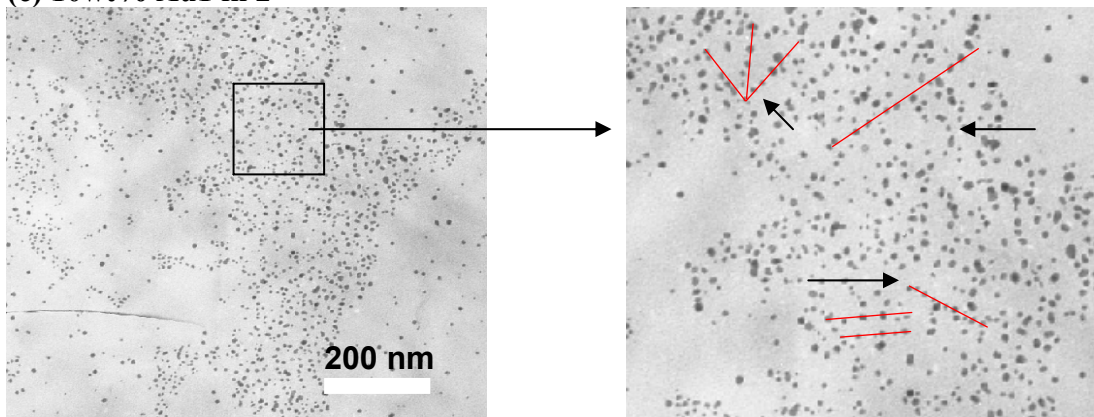
(a) 13wt% Au1 in 1



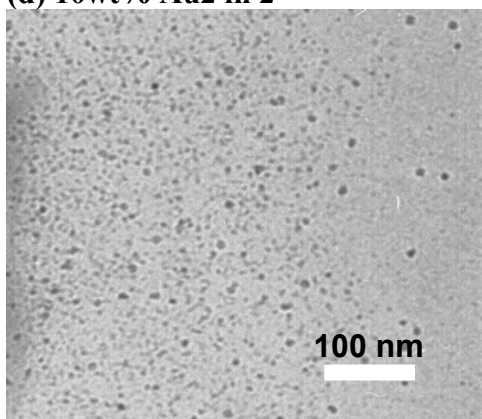
(b) pure Au1 (heated to annealing *T*)



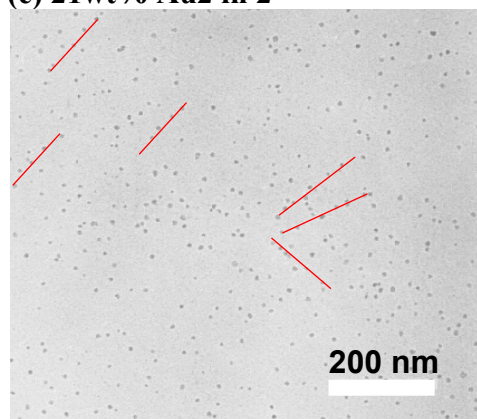
(c) 10wt% Au1 in 2



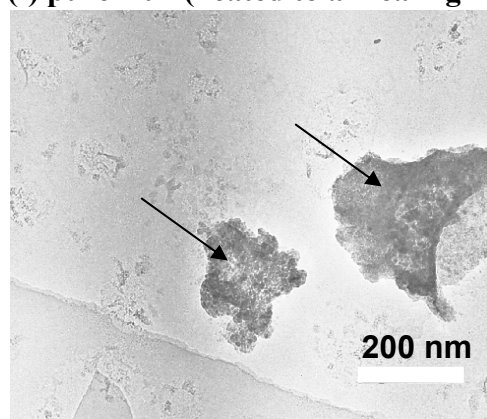
(d) 10wt% Au₂ in 2



(e) 21wt% Au₂ in 2

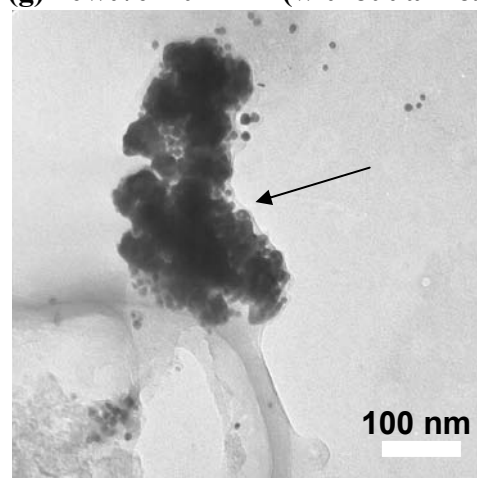


(f) pure Au₂ (heated to annealing *T*)



(Notice particle aggregates)

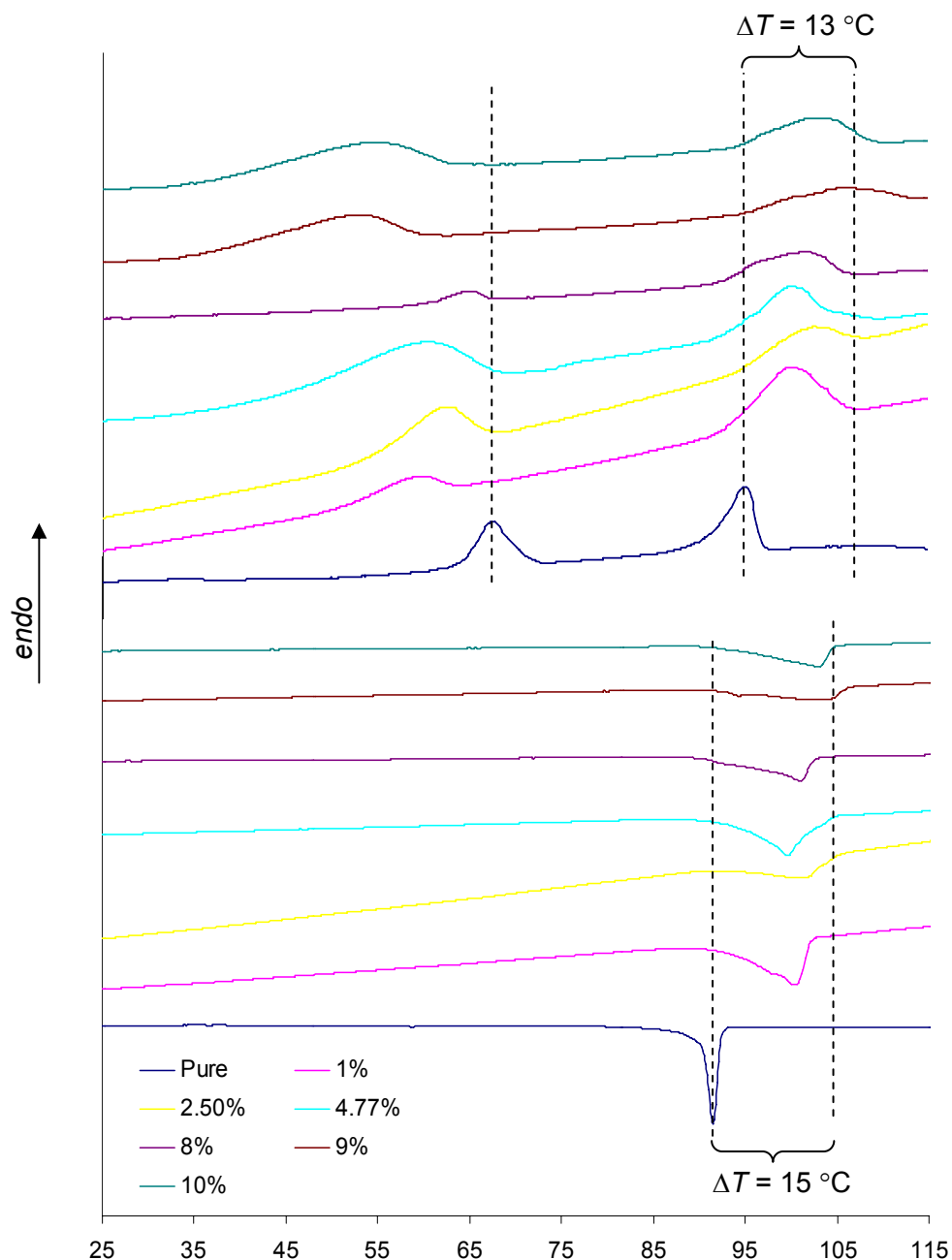
(g) 10wt% Au₂ in 2 (without annealing)



(Notice particle aggregates)

DSC for Au2 in 2 (Fig. S5)

Preparation of the samples requires annealing of the mixtures under a steady stream of dry N₂. Therefore, the DSC traces shown represent the second heating and second cooling run. As can be seen in the cooling runs by DSC, the samples do not crystallize over shorter periods of time, in some cases not for days. To ensure a measurable melting point in the second heating scan (first in the DSC instrument), ready, filled and closed sample pans were left in a desiccator to crystallize prior to DSC measurements.



NP Stability

Recent studies on the stability of thiolate-protected gold nanoparticles showed that thiols with a carbon chain longer than C6 begin to desorb from the gold nanoparticle surface above a threshold of 160 °C.^{S4} Therefore, we assume that during all mixing experiments with **2** no changes in the nanoparticle composition (surface) *via* desorption of thiolate takes place.

References

- (S1) M. Kölbl, T. Beyersdorff, X. Cheng, C. Tschierske, J. Kain and S. Diele, *J. Am. Chem. Soc.*, 2001, **123**, 6809.
- (S2) P. Chirakul, V. H. Perez-Luna, H. Owen and G. P. Lopez, *Langmuir*, 2002, **18**, 4324.
- (S3) M. M. Maye, W. Zheng, F. L. Leibowitz, N. K. Ly and C. Zhong, *Langmuir*, 2000, **16**, 490.
- (S4) M. Büttner, T. Belser and P. Oelhafen, *J. Phys. Chem. B*, 2005, **109**, 5464.

Figure 6 (main text) with enlarged segments

