Supplementary Information

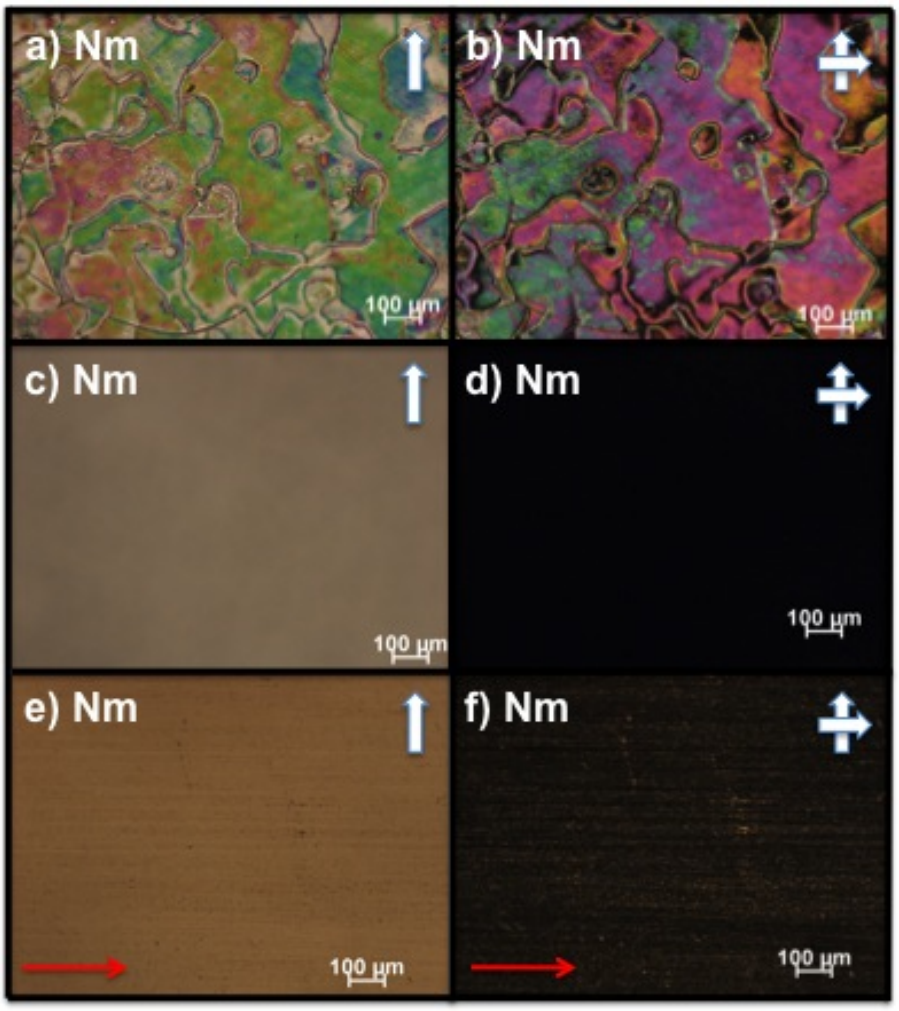

Figure S1: Polarized Optical Microscopy pictures of 5CB between untreated (a-b) and treated glass slides with an (c-d) homeotropic and (e-d) homogeneous parallel LC aligning organic layer. The 5CB are subject to the same treatment than the AuNP dispersions where the material is heated to the isotropic phase and mixed by moving and pressing the two slides together prior to be analyzed with the microscope. The single and crossed white arrows indicate the parallel and perpendicular orientations of the analyzer and the red arrow indicates the direction of the aligning layer at the surface of the glass slides.

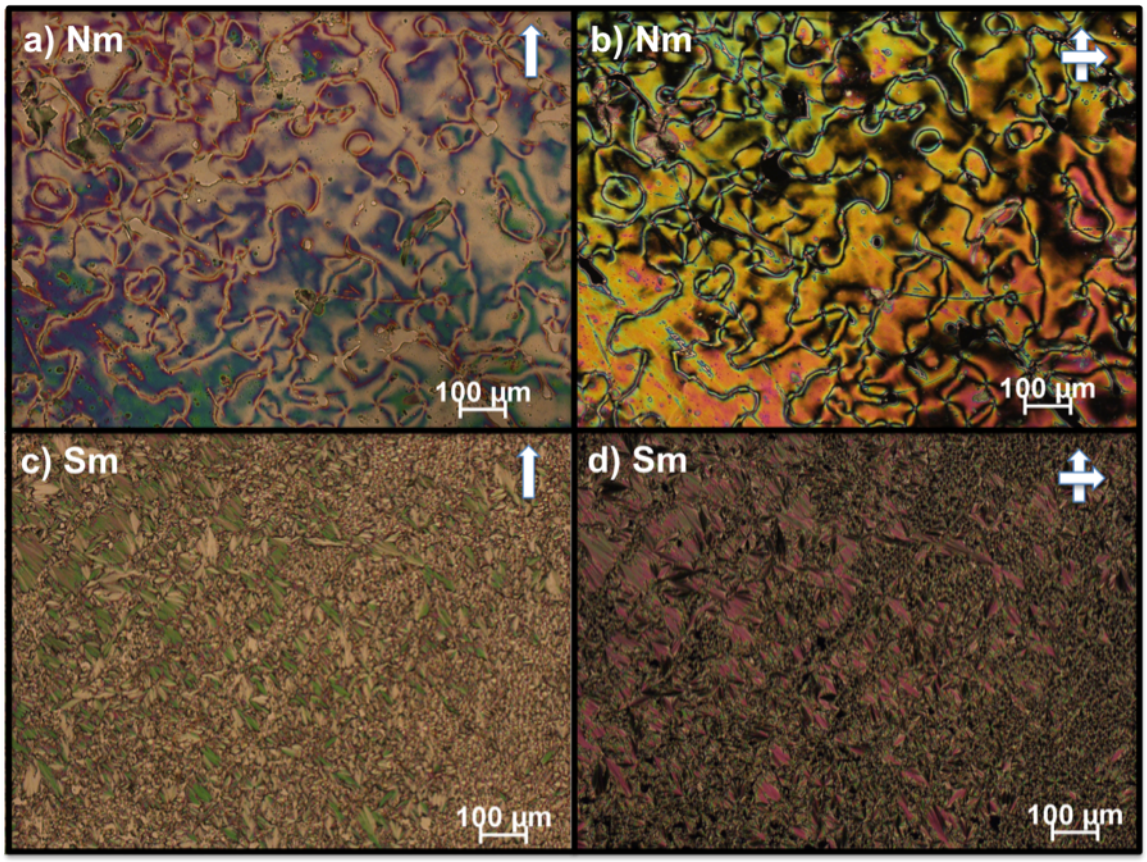

Figure S2: Polarized Optical Microscopy pictures of 8CB between untreated in the nematic (a, b) and smectic (c, d) phases.

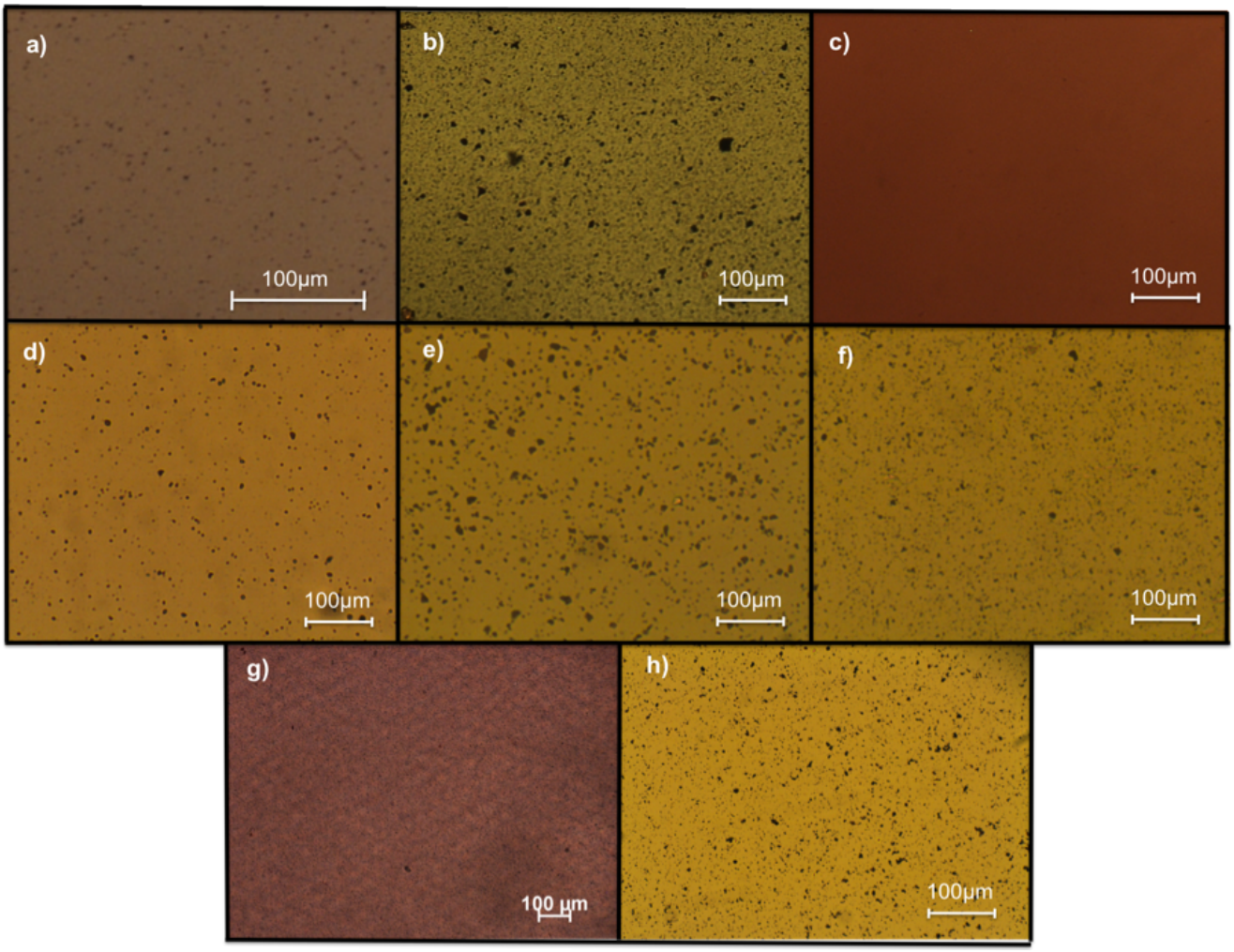

Figure S3: POM images of 1.0 wt% Au dispersions of AuNPs with (a) $CBO(CH_2)_{12}SH$ (100%) (b) $CBO(CH_2)_{12}SH$ (70%)/ $CH_3(CH_2)_5SH$(30%) (c) $CBO(CH_2)_{12}SH$ (49%)/ $CH_3(CH_2)_5SH$ (51%) (d) $CBO(CH_2)_{12}SH$(28%)/ $CH_3(CH_2)_5SH$ (72%) (e) $CH_3(CH_2)_5SH$ (100%), (f) $CH_3(CH_2)_{11}SH$ (100%), (g) $CBO(CH_2)_8SH$ (100%) and (h) $CBO(CH_2)_{16}SH$ (100%) in 5CB in the isotropic phase and between untreated glass slides.

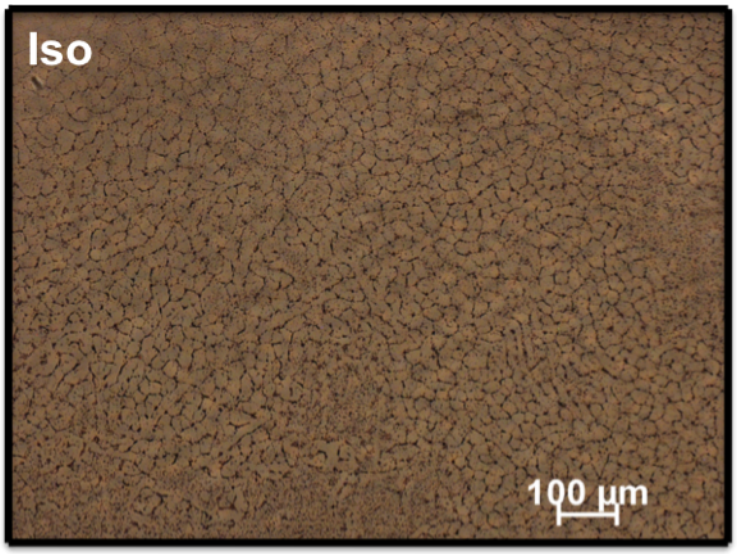

Figure S4: Polarized Optical Microscopy pictures of 5 wt% dispersions of $CBO(CH_2)_{16}SH$-AuNPs in isotropic 5CB between untreated glass slides. The network formed at T_{N-I} when cooling at 1.0 °/min becomes visible when the sample is heated back to the isotropic phase.

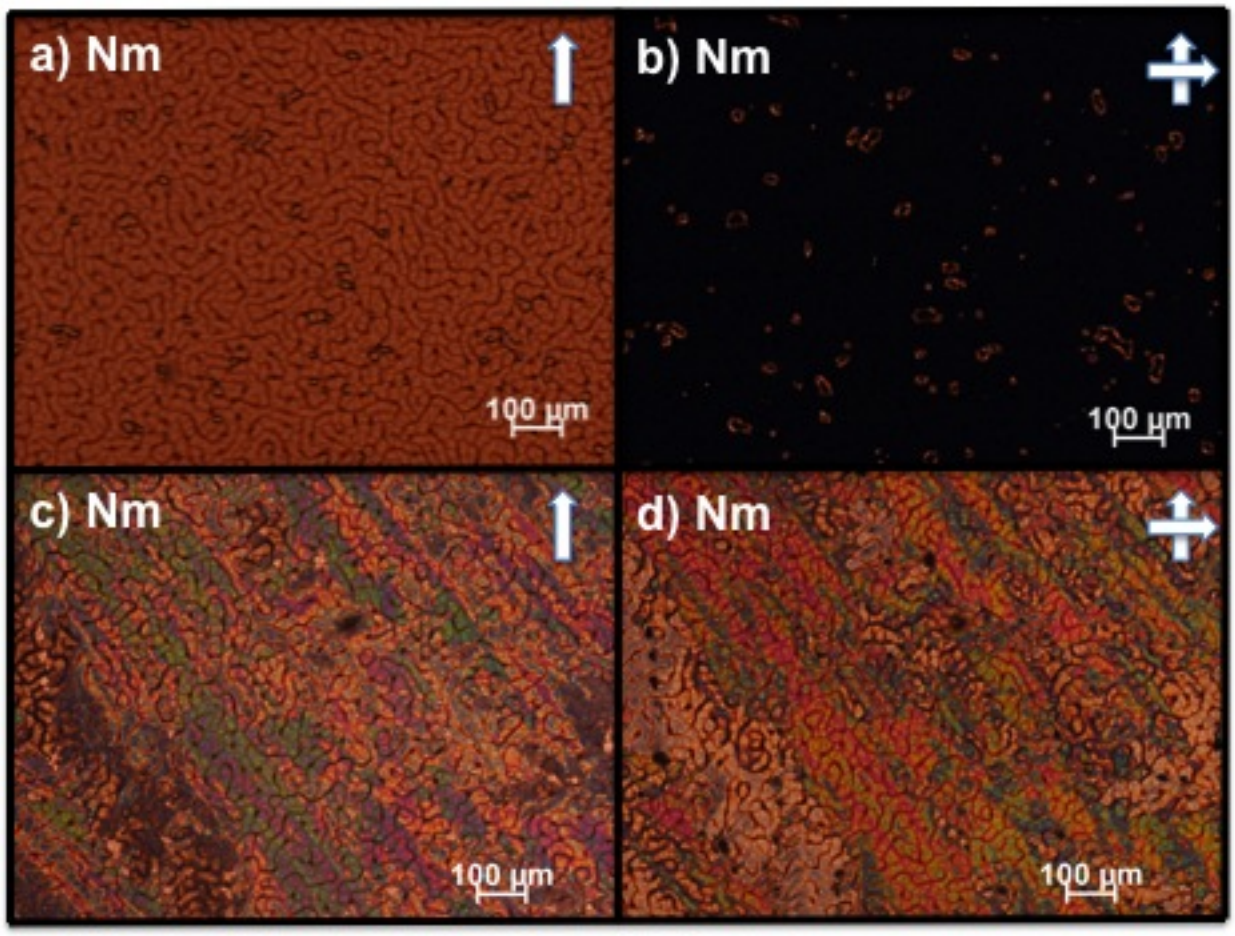

Figure S5: Polarized Optical Microscopy pictures of 5 wt%. dispersion of AuNPs with 1:1 $CBO(CH_2)_{12}SH$:$CH_3(CH_2)_5SH$ surface ligands in nematic 5CB using untreated slides after (a-b) cooling at 1.0°/min from the isotropic phase and (c-d) heating from the crystalline phase (single arrow = parallel analyzer; crossed arrows = perpendicular analyzer; scale bars = 100µm).

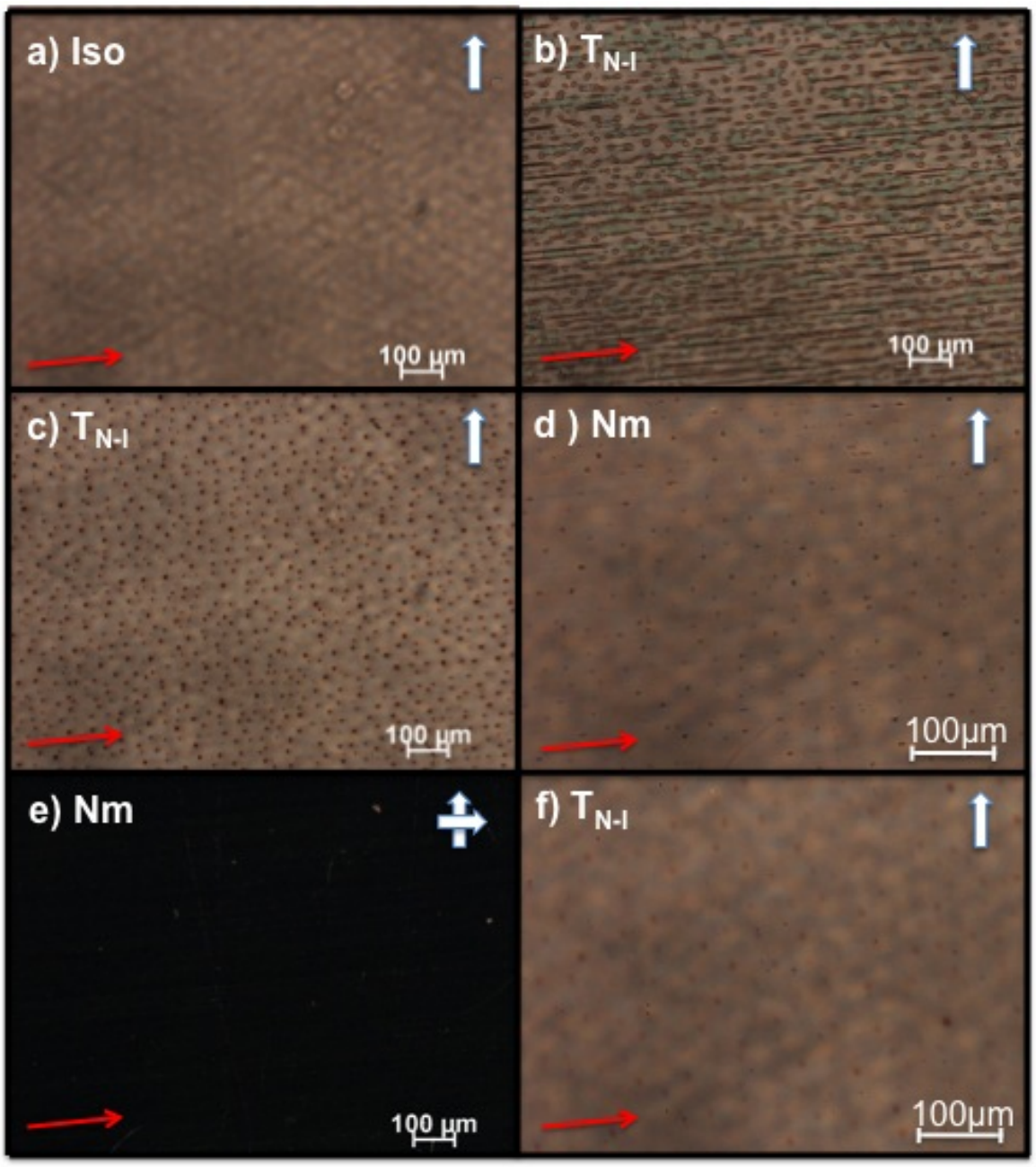

Figure S6: POM pictures of 1 wt%. dispersion of AuNPs with 1:1 CBO(CH2)12SH:CH3(CH2)5SH surface ligands in nematic 5CB between homogeneous glass plates (single arrow = parallel analyzer; crossed arrows = perpendicular analyzer; red arrows = direction of the aligning layer). The AuNPs dissolved in the isotropic phase (a) and phase separate at T_{N-I} (b-c) to form evenly dispersed aggregates in the nematic (d) and trigger the homeotropic alignment of the bulk LC (e). When heated back to the isotropic phase, the aggregates dissolve in the LC at T_{N-I} (f) making the aggregates formation reversible. The cooling rate between the isotropic and nematic phases is 1.0 °/min.

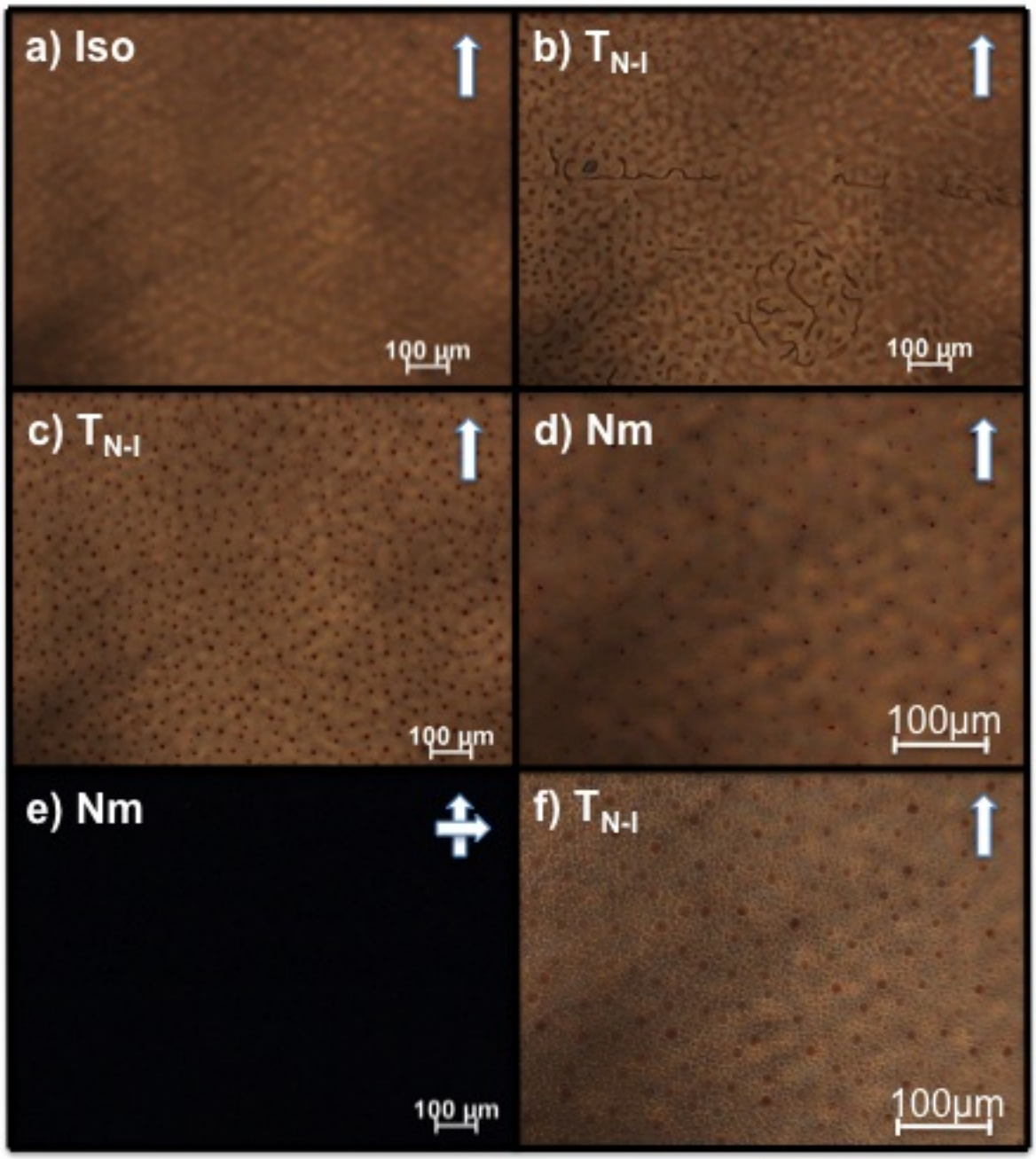

Figure S7: POM pictures of 1 wt%. dispersion of AuNPs with 1:1 CBO(CH2)12SH:CH3(CH2)5SH surface ligands in nematic 5CB between homeotropic glass plates (single arrow = parallel analyzer; crossed arrows = perpendicular analyzer). The AuNPs dissolved in the isotropic phase (a) and phase separate at T_{N-I} (b-c) to form evenly dispersed aggregates in the nematic (d) and trigger the homeotropic alignment of the bulk LC (e). When heated back to the isotropic phase, the aggregates dissolve in the LC at T_{N-I} (f) making the aggregates formation reversible. The cooling rate between the isotropic and nematic phases is 1.0 °/min.

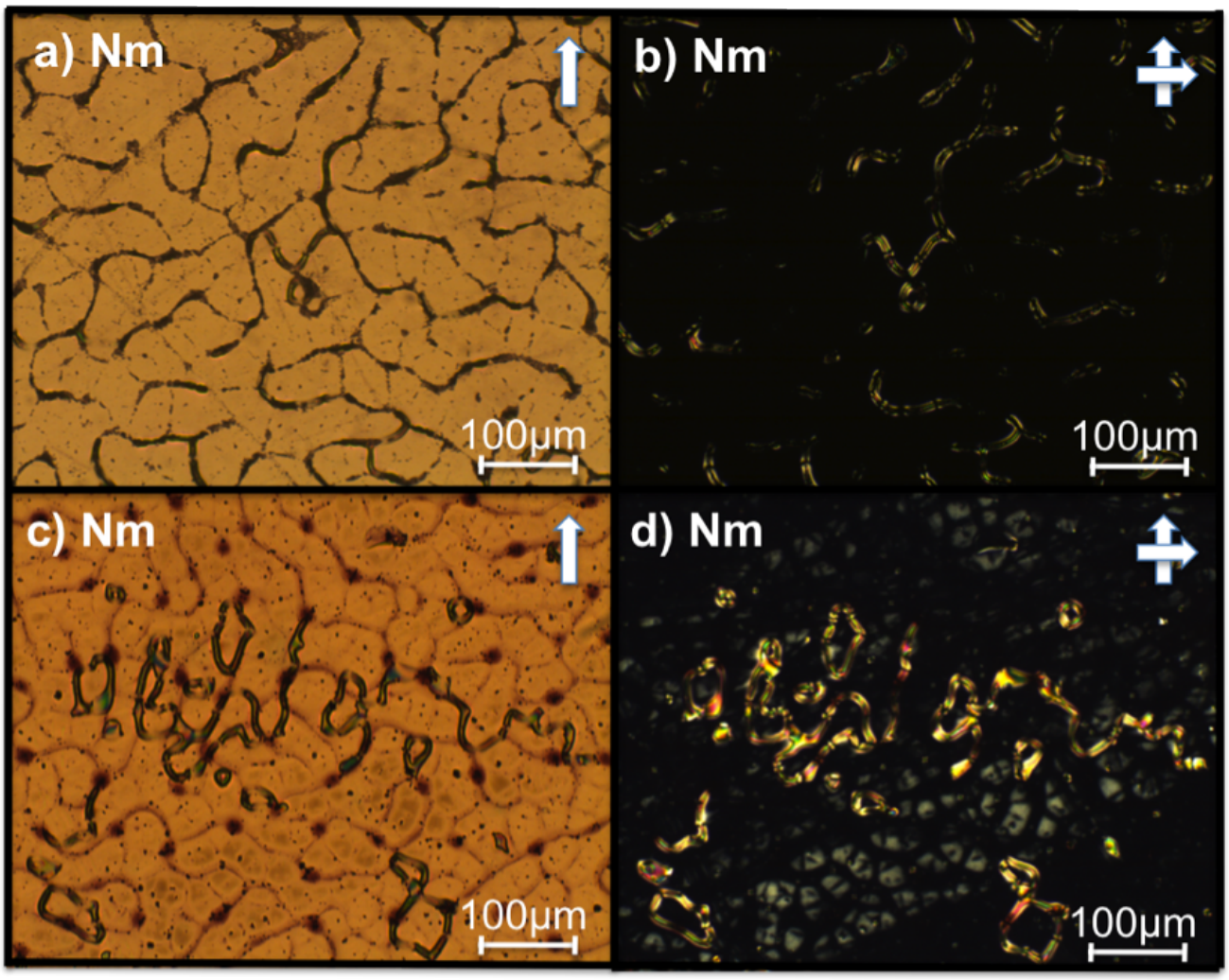

Figure S8: Polarized Optical Microscopy pictures of 1 wt%. dispersion of AuNPs with (a, b) 28:72 and (c, d) 70:30 $CBO(CH_2)_{12}SH$:$CH_3(CH_2)_5SH$ surface ligands in nematic 5CB using untreated slides (single arrow = parallel analyzer; crossed arrows = perpendicular analyzer; scale bars = 100µm). The cooling rate between the isotropic and nematic phases is 1.0°/min.

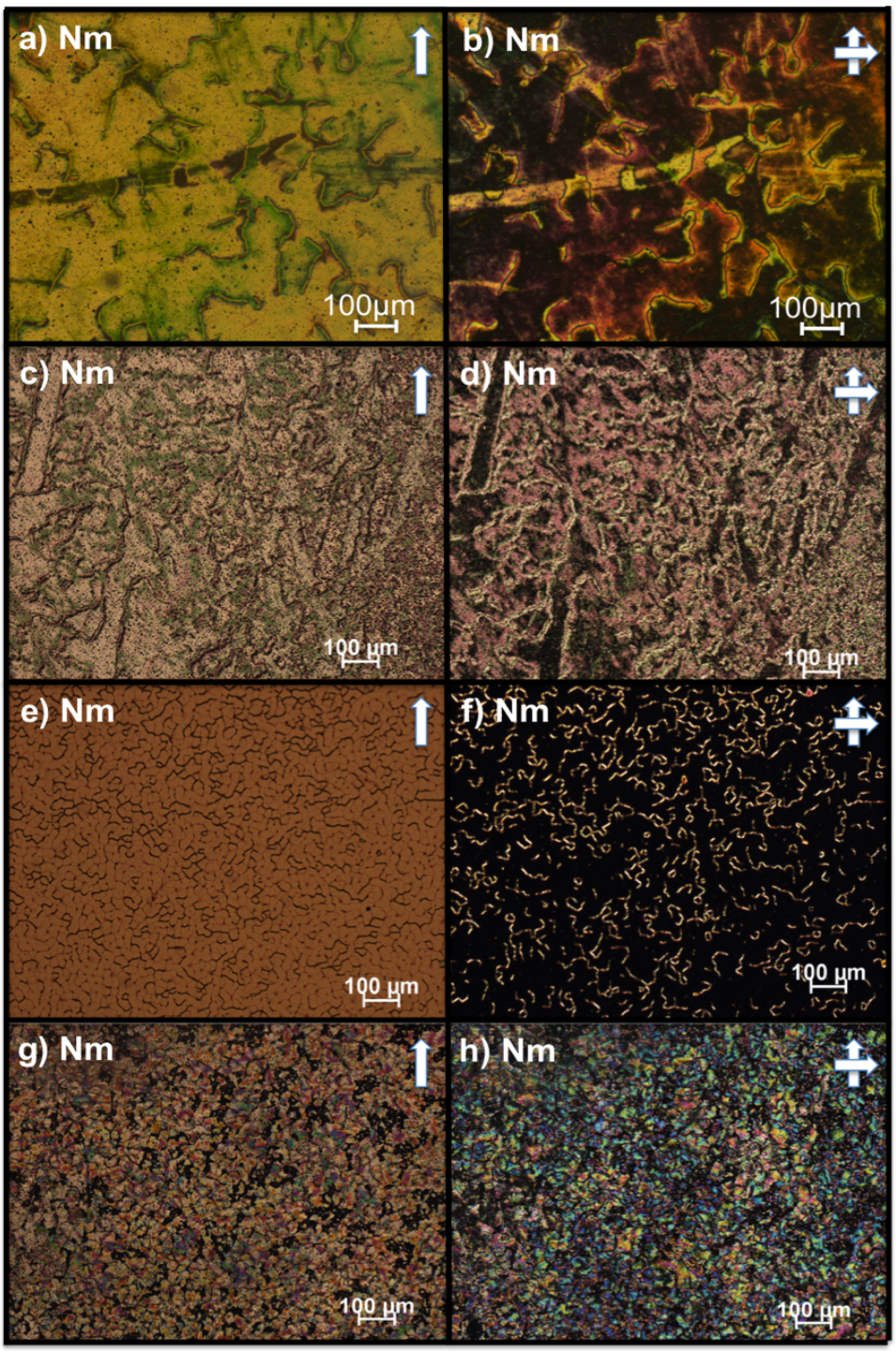

Figure S9: Polarized Optical Microscopy pictures of 1 wt%. dispersions of AuNPs with monolayer made of (a-b) $CH_3(CH_2)_5SH$, (c-d) $CBO(CH_2)_8SH$, (e-f) $CBO(CH_2)_{12}SH$ and (g-h) $CBO(CH_2)_{16}SH$ surface ligands in nematic 5CB using untreated slides (single arrow = parallel analyzer; crossed arrows = perpendicular analyzer; scale bars = 100µm). The cooling rate between the isotropic and nematic phases is 1.0 °/min.

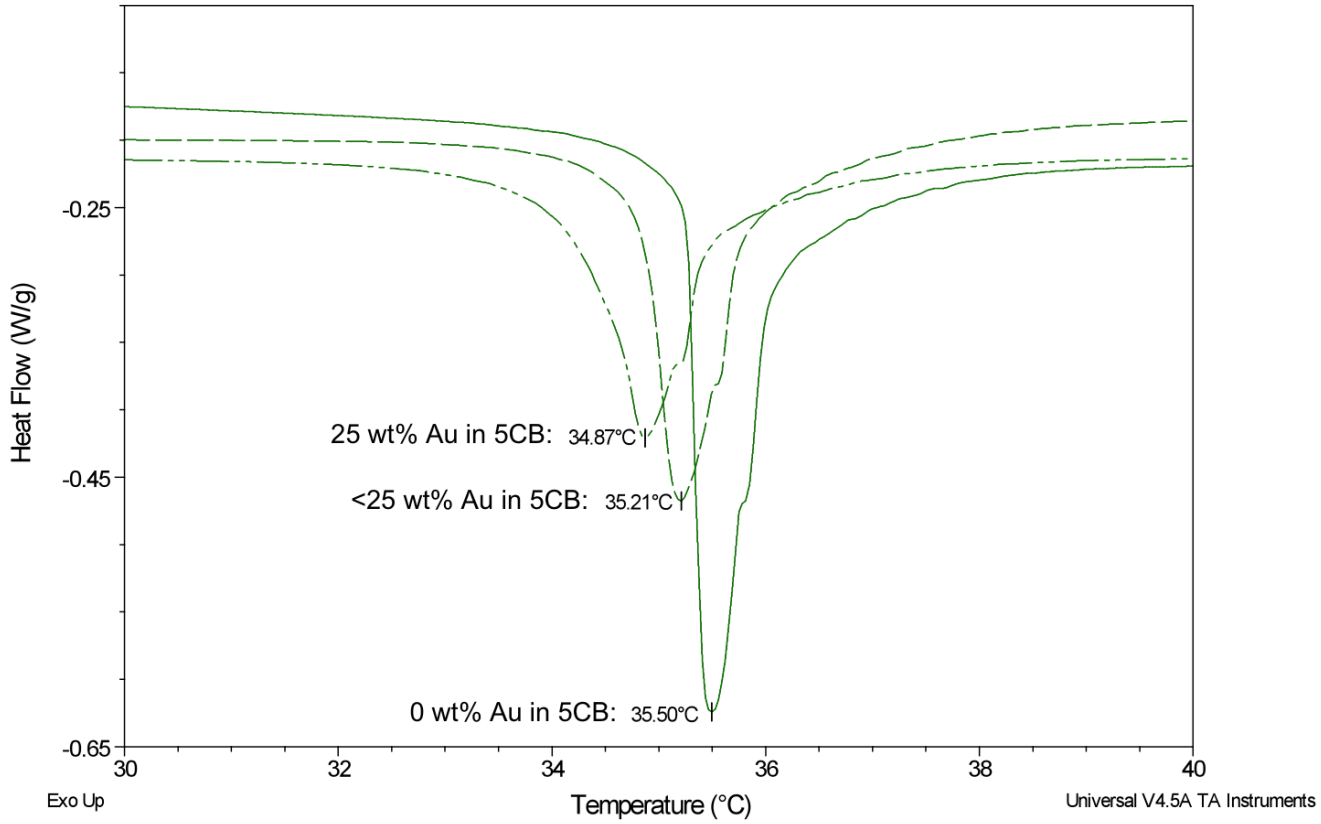

Figure S10. DSC thermogram of pure 5CB and two high concentration dispersions of the mixed monolayer 1:1 $CBO(CH_2)_{12}SH$:$CH_3(CH_2)_5SH$ AuNPs in 5CB.