

Reversible Long-Range Assemblies in Gold Nanoparticles – Liquid Crystal Composites: Molecular Dynamics of the Gold Capping Layer

J. Milette, V. Toader, L.-P. Scheffer, R. B. Lennox and L. Reven

Centre for Self-assembled Chemical Structures, Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, QC, H4A 3B7, Canada, Jonathan.Milette@mail.McGill.ca.

ABSTRACT

Highly miscible mesogenic ligand capped gold nanoparticles (AuNPs) [1] that produce reversible long-range assemblies in nematic and smectic liquid crystal (LC) [2-3] were recently developed by our group. At the isotropic-to-nematic phase transition of cyanobiphenyl based liquid crystal, AuNP networks are formed with controllable dimension and topology. The molecular interactions driving the assembly and detected by nuclear magnetic resonance (NMR) spectroscopy are presented in this paper. The chain mobility of the ligand shell at gold surface was found to play a key role in the nanocrystal miscibility and assembly. The orientational orders of the selectively deuterated LC matrix and AuNP ligands, each separately followed by variable temperature deuterium NMR as a function of particle concentration, were also observed to be strongly correlated [4]. The mechanism of the nanoparticle structure formation is attributed to the coupling of the AuNP ligands to the LC matrix, inducing an isotropic-nematic biphasic state. Fine-tuning of these interactions through ligand and mesogen chemistry provides a route for major materials innovations by merging structured fluid physics and nanoscience.

Keywords: advanced materials, soft nanotechnology and colloids, applications of liquid crystalline materials

1 INTRODUCTION

Liquid crystalline nanocomposites can be used to spatially organize nanomaterials as well as to enhance the properties of both the nanomaterials and its liquid crystal (LC) host [5]. For colloidal particles dispersed in nematic LC, the long-range orientational distortion of the LC about the colloid governs the interparticle interactions [6]. These LC mediated particle interactions are predicted to diminish when the particle size is decreased to the nanometer scale, offering the possibility of forming well-defined structures through reversible association combined with tuning of the anchoring energies.

Studies of the LC mediated interactions between 100 nm NPs indicate that the nature of the surface anchoring strongly influences the short- and long- range interactions between the nanoparticles [7-8]. Thermally stable nanoparticle association can be achieved by using capping

ligands that provide very strong LC surface anchoring whereas weaker interparticle interactions offer the possibility of forming well defined structures through reversible association.

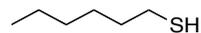
Table 1. (a) 4 to 5 nm Gold nanoparticles (AuNP) functionalized with a monolayer of (b) hexanethiol (HT), (c) dodecanethiol (DDT) or (d) CBO(CH₂)₁₂SH and a binary layer of HT and CBO(CH₂)₁₂SH are studied by ¹H and ¹³C NMR.

a) Gold nanoparticle samples

Samples	CBO(CH ₂) ₁₂ SH surface coverage/%
AuNP-0 ⁽¹⁾	0
AuNP-28	28
AuNP-49	49
AuNP-70	70
AuNP-100	100

(1) AuNP functionalized with hexanethiol (HT) or dodecanethiol (DDT)

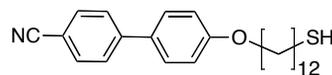
b) Hexanethiol (HT) ligand



c) Dodecanethiol (DDT) ligand



d) Liquid crystal (CBO(CH₂)₁₂SH) ligand



In this perspective, we developed a chemical method to tune the miscibility of gold nanoparticles in LC medium [1] in order to create long-range assemblies [2-3]. Compositionally tailored capping layers at the surface of 4-5 nm gold nanoparticles (AuNP) were produced to create a stable dispersion of individual particles in isotropic LC, such as 4'-pentyl-4-cyanobiphenyl (5CB) and 4'-octyl-4-cyanobiphenyl (8CB). Using ligand exchange reactions with 4-(N,N-dimethylamino)pyridine (DMAP) – capped AuNP precursors, NPs with ligand capping layers composed of

$\text{CH}_3(\text{CH}_2)_m\text{SH}$ ($m = 5, 11$) or 4'-(12-mercaptododecyloxy) biphenyl-4-carbonitrile ($\text{CBO}(\text{CH}_2)_{12}\text{SH}$) and their binary mixtures were prepared (Table 1). The NPs with a 1 : 1 $\text{CH}_3(\text{CH}_2)_5\text{SH}/\text{CBO}(\text{CH}_2)_{12}\text{SH}$ ratio were found to be completely miscible in isotropic 5CB up to at least 50 wt% Au (Figure 4 of reference [4]). When the composite is cooled to the nematic phase of 5CB or 8CB, AuNP networks made of branches and circular domains are formed by enrichment of the NPs at the nematic-isotropic liquid interfaces present at the clearing point. Controlled over the the dimensions, topology and LC defect structure of the networks were achieved by varying the particle concentration, cooling rate and film thickness (Figure 1). Different LC phase transitions produce different NP assemblies. Under conditions where the nematic network is suppressed, linear arrays of AuNPs with micron-scale periodicities appear at the nematic to smectic phase transition of 8CB over macroscopic areas.

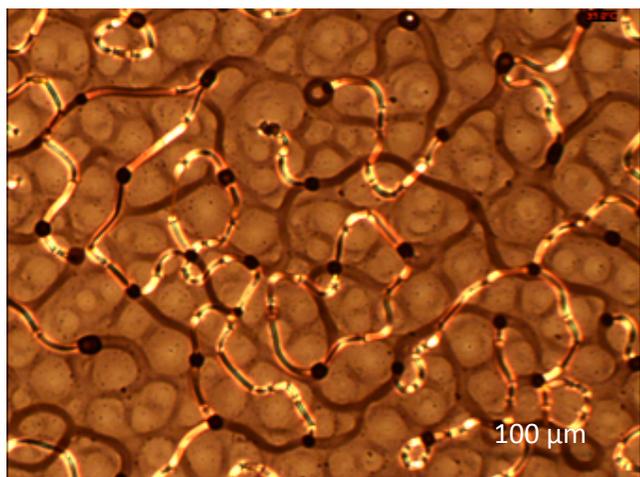


Figure 1. Polarized optical microscopy image of 1 wt% Au of AuNPs capped with a mix monolayer of $\text{CBOC}_{12}\text{SH}$ and hexanethiol (in a 1:1 ratio) and dispersed in the nematic phase of 5CB liquid crystal (parallel polarizers; scale bar = 100 μm).

The AuNPs capped with a monolayer and mix monolayer made of mesogenic ligands present an ideal model system to study the particles – liquid crystal interactions at the molecular level through multinuclear NMR spectroscopy. The ligand conformation and mobilities give insight as to why NPs with certain ligand compositions are miscible in LCs. ^{13}C chemical shifts provide information on chain conformation while the solid-state ^{13}C and ^1H NMR relaxation parameters probe the ligand dynamics.

2 EXPERIMENTAL

Sample preparation. The preparation of the gold nanoparticles [1] as well as their dispersion in liquid crystals [4] are reported in earlier publications.

NMR spectroscopy. The solid-state 100.5 MHz ^{13}C CP MAS spectra were run on a Varian 400 NMR spectrometer with a 7.5 mm T3 HX probe. A $5.0 \mu\text{s}$ ^1H 90° pulse width, a spinning frequency of 5 kHz and a pulse delay set to $\sim 5T_{1\text{H}}$ were used to acquire each spectrum with the number of scans varying between 2500 and 5000. An inversion-recovery pulse sequence with ^{13}C CP MAS detection was used to measure the proton $T_{1\text{H}}$ values. The variable contact time data were fitted to the equation of the decay of the ^1H spin-locked magnetization to determined T_{CH} and the proton $T_{1\rho}$ values.

3 RESULTS

As described previously, ligand exchange reactions formed the basis for synthesizing a family of LC-capped NPs for a rationalized miscibility in LC matrices [1]. The ratio of the two ligands, hexanethiol and $\text{CBO}(\text{CH}_2)_{12}\text{SH}$, plays a very strong role in determining miscibility of the AuNPs in cyanobiphenyl based liquid crystals. The hexanethiol acts as a spacer between the alkyl chains of $\text{CBO}(\text{CH}_2)_{12}\text{SH}$, serving to increase the free volume within the ligand shell. However there needs to be a sufficient number of cyanobiphenyl groups on the AuNPs to interact with the LC host molecules. Therefore we found that NPs with ligand shells composed of a 1:1 ratio of hexanethiol to $\text{CBO}(\text{CH}_2)_{12}\text{SH}$ showed the optimal miscibility. We would expect the NMR relaxation parameters to reflect an increase in chain mobility in the ligand shell provided by the hexanethiol spacer groups. The trend in the relative intensities of the aliphatic and aromatic signals in the solid-state ^1H and ^{13}C MAS NMR spectra of the AuNPs as a function of ligand composition mirrors the variation of the LC ligand content as measured by the iodine reaction analysis [1]. Selected ^1H and ^{13}C NMR relaxation parameters are presented in Table 2 for AuNPs capped with monolayers of dodecanethiol (DDT) or $\text{CBO}(\text{CH}_2)_{12}\text{SH}$ and the mixed monolayer AuNPs.

Whereas the spin-lattice relaxation times, T_1 , are sensitive to molecular motional frequencies in the MHz range, the spin-lattice relaxation times in the rotating frame, $T_{1\rho}$, probe slower kHz motions. In the solid-state, the proton spin-lattice relaxation times reflect a common value due to spin diffusion. Since the rapidly rotating methyl group acts as a relaxation source, the proton T_1 values for all the AuNPs are similar except when capped with only LC ligands. ^{13}C relaxation parameters, due to chemical shift resolution and no spin diffusion, should in principle permit

Table 2. NMR Relaxation parameters of AuNPs and un-bound LC ligand.

Sample	AuNP DDT	AuNP 28	AuNP 49	AuNP 70	AuNP 100	CBO(CH ₂) ₁₂ SH
T _{1H} (s)	0.9	0.7	0.8	0.9	1.2	63
T _{1C} (s)	0.6	0.5	0.4	0.5	0.5	700
¹ H T _{1r} (ms)	8.2	2.1	1.9	2.3	4.7	-

selective measurement of the mobility of aromatic moieties of the LC ligands. Unfortunately the low sensitivity of ¹³C combined with a large chemical shift anisotropy (CSA) precluded accurate T1 measurements of the ring carbons, even with long acquisition times (Figure 2 of ref. [4]). The similar ¹³C T₁ values for the alkyl chains are not surprising given that C12 chains are too short to order into extended all trans conformations at room temperature according to previous studies of chain order/disorder transitions of alkanethiol capped AuNPs [9]. The proton spin-lattice relaxation times in the rotating frame, ¹H T_{1ρ}, were measured via the ¹³C signals for selectivity. The dependence of these values on the r.f. field strength indicates that the chain motion is on the slow side of the T_{1ρ} versus 1/T curve where smaller values indicate more mobility. These values do indicate increased chain mobility for the mixed monolayer AuNPs. However selective probing of the mobility of the LC ligands as well as NMR studies of the dispersions of these AuNPs in 5CB require isotopic labeling as described in reference [4].

4 CONCLUSIONS

High resolution ¹H and ¹³C solid-state NMR spectroscopy provides valuable insight into the molecular level interactions that are responsible for the assembly of nanoparticles into an ordered structure via the isotropic-nematic phase transition. The very high miscibility of the mixed monolayer AuNPs in isotropic 5CB was correlated with the enhanced mobility of the mesogenic ligands due to the presence of spacer ligands. The AuNP capping layer provides the strong LC surface anchoring and the weak interparticle interactions that are necessary to form long-range reversible assemblies in cyanobiphenyl liquid crystal.

5 ACKNOWLEDGEMENT

Funding for this research was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Fonds quebecois de la recherche sur la nature et les technologies (FQRNT). The authors thank Dr.

Frederick Morin (McGill University) for his help with the solid-state NMR.

6 REFERENCES

- [1] Millette, J.; Toader, V.; Lennox, R.B. and Reven, L. "Tuning the Miscibility of Gold Nanoparticles Dispersed in Liquid Crystals via the Thiol-for-DMAP Reaction" (2011) *J. Mater. Chem.*, 21, 9043-9050.
- [2] Millette, J.; Cowling, S.; Toader, V.; Lavigne, C.; Saez, I.M.; Lennox, R.B.; Goodby, J.W. and Reven, L. "Reversible Long Range Network Formation in Gold Nanoparticles – Nematic Liquid Crystal Composites" (2011) *Soft Matter*, 8, 173-179.
- [3] Millette, J.; Relaix, S.; Lavigne, C.; Toader, V.; Cowling, S.; Saez, I.M. ; Lennox, R.B.; Goodby, J.W. and Reven, L. "Reversible Long-Range Patterning of Gold Nanoparticles by Smectic Liquid Crystals" (2012) *Soft Matter*, 8, 2593-2598.
- [4] Millette, J.; Toader, V.; Soulé, E.; Lennox, R. B.; Rey, A.; Reven, L. "A Molecular and Thermodynamic View of the Assembly of Gold Nanoparticles in Nematic Liquid Crystals" (2013) *Langmuir*, 29 (4), 1258-1263.
- [5] O. Stamatoiu; J. Mirzaei; X. Feng and T. Hegmann "Nanoparticles in liquid crystals and liquid crystalline nanoparticles" (2012) *Top. Curr. Chem.*, 318, 331-393.
- [6] M. Ravnic "Colloidal structures in confined nematic liquid crystals" (2011) *Liquid Crystals Today*, 20, 77-84.
- [7] Y. Bai and N. L. Abbott "Recent Advances in Colloidal and Interfacial Phenomena Involving Liquid Crystals" (2010) *Langmuir*, 27, 5719-5738.
- [8] M. Skarabot and I. Musevic "Direct observation of interaction of nanoparticles in a nematic liquid crystal" (2010) *Soft Matter*, 6, 5476-5481.
- [9] A. Badia; R. B. Lennox and L. Reven "Dynamic View of Self-Assembled Monolayers" (2000) *Acc. Chem. Res.*, 33, 475-481.