

Detecting, Visualizing, and Measuring Gold Nanoparticle Chirality Using Helical Pitch Measurements in Nematic Liquid Crystal Phases

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Supporting Information – SI

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Materials and Methods:

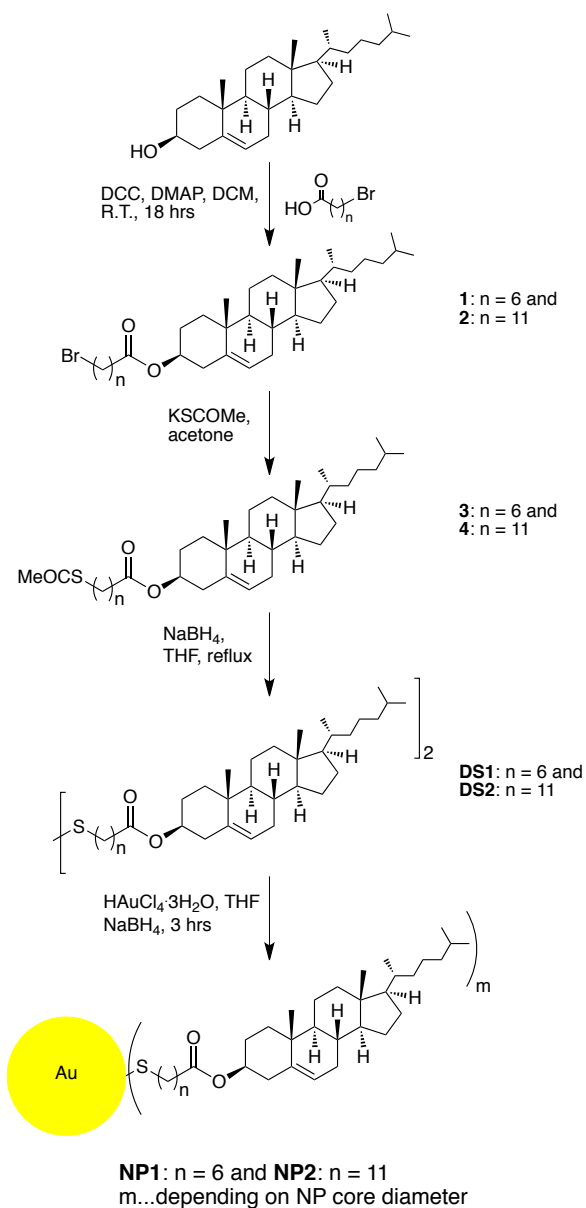
All reactions were carried out under nitrogen atmosphere unless stated otherwise. The organic compounds **1** to **5**, disulfide **1** (**DS1**) and disulfide **2** (**DS2**) were synthesized following procedures reported earlier¹⁻³ (see Schemes 1 and 2 for details). **Ligand 3** was synthesized according to a method reported in the literature⁴.

Materials:

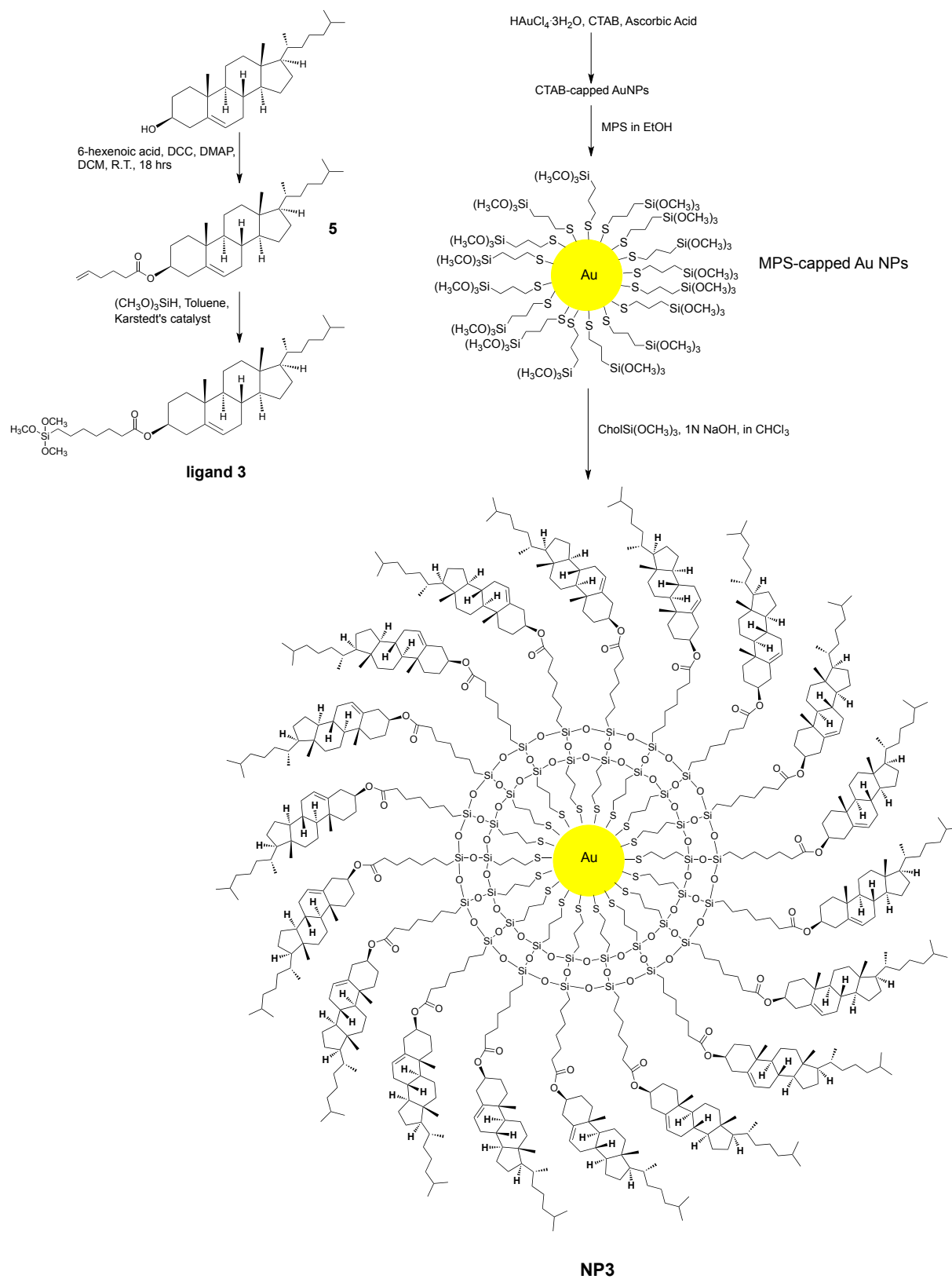
All solvents used for the synthesis and purification were EMD Millipore grade purified by a PureSolv solvent purification system (Innovative Technology Inc.). Tetrahydrofuran (THF) was dried over benzophenone-sodium and distilled under nitrogen. Acetone was dried overnight over activated molecular sieves (4 Å). For the NP synthesis, all reagents were purchased from Sigma Aldrich except for hydrogen tetrachloroaurate (HAuCl₄, Alfa-Aesar). Cholesterol, 4-dimethylamino pyridine (DMAP), dicyclohexylcarbodiimide (DCC), 6-bromohexanoic acid, 11-bromoundecanoic acid, potassium thioacetate, sodium sulphate, sodium, 3-(mercaptopropyl)trimethoxysilane, sodium hydroxide, hexadecyltrimethylammonium bromide (CTAB), and sodium borohydride were purchased from Sigma-Aldrich. Deionized water, DI (Millipore, resistivity 18.1 Ω) was used.

Methods:

Visible absorption spectra of the NPs in toluene were recorded using a dual cell OLIS14 Clarity spectrophotometer. Circular Dichroism (CD) measurements were performed using an OLIS spectrometer (1 cm path length quartz cuvette). Transmission electron microscopy (TEM) analysis was performed with a FEI Tecnai TF20 TEM instrument at an accelerating voltage of 200 kV. Samples were prepared by evaporating a drop of dilute toluene solution of particles onto a carbon-coated copper TEM grid (400 mesh) and dried overnight. The ¹H NMR spectra were recorded in CDCl₃ at ambient temperature on a Bruker DMX 400 MHz spectrometer and referenced internally to residual solvent peaks at 7.26 (¹H). Polarized optical microscopy (POM) images were taken on Olympus BX-53 equipped with a Linkam LTS420E heating/cooling stage.



Scheme S1: Synthesis of **disulfide 1 (DS1)**, **disulfide 2 (DS2)**, and the corresponding gold NPs, **NP1** and **NP2**.



Scheme S2: Synthesis of ligand 3 and NP3.

Detailed synthetic information

Cholesteryl 6-bromohexanoate, **1**:

Cholesterol (1.0 g, 2.6 mmol) was dissolved in dry dichloromethane (25 mL) followed by addition of 6-bromohexanoic acid (0.75 g, 3.85 mmol). Then, 4-dimethylaminopyridine (20 mg, 0.16 mmol) and dicyclohexylcarbodiimide, DCC (0.64 g, 3.1 mmol) were added and the mixture was stirred at room temperature for 18 hours. The dicyclohexylurea formed was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was dissolved in hexane and any undissolved solid was discarded. The formed precipitate was washed profusely with ethanol. Finally, the crude product was purified by recrystallization from ethanol to give off-white solid. ¹H NMR (300 MHz, CDCl₃, δ/ppm): 0.67 (s, 3H, CH₃), 0.8-2.05 (m, 44H, Br-CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH, CH₂), 2.26-2.38 (m, 4H, C=C-CH₂-CH-O, CO₂-CH₂), 3.41 (t, 2H, Br-CH₂-CH₂, J=6.7 Hz), 4.56- 4.71 (m, 1H, O-CH), 5.35- 5.41 (d, 1H, C=CH, J= 4.5 Hz).

2:

Synthesized as described above for compound **1**. Quantities: Cholesterol (1.0 g, 2.6mmol), 11-bromoundecanoic acid (1.02g, 3.87mmol) dimethylaminopyridine, DMAP (20mg, 0.16mmol) and dicyclohexylcarbodiimide (0.64g, 3.1mmol). ¹H NMR (300 MHz, CDCl₃, δ/ppm): 0.67 (s, 3H, CH₃), 0.81-2.05 (m, 54H, Br-CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH, CH₂), 2.26-2.37 (m, 4H, C=C-CH₂-CH-O, CO₂-CH₂), 3.41 (t, 2H, Br-CH₂-CH₂, J=6.8 Hz), 4.56- 4.71 (m, 1H, O-CH), 5.35- 5.41 (d, 1H, C=CH, J= 4.4 Hz).

6-(cholesterylloxycarbonyl)hexyl thioacetate, **3**:

Compound **1** (1.0 g, 1.77 mmol) and potassium thioacetate (0.24 g, 2.12 mmol) were dissolved in dry acetone (20 mL). The reaction was allowed to reflux for 18 hours. After the reaction had finished, the solvent was evaporated and the residue was dissolved in dichloromethane and washed with water to remove the excess potassium thioacetate. Then, the collected organic layer was dried using sodium sulfate and after evaporation of solvent **CHSC-6** was obtained as pale white powder. ¹H NMR (CDCl₃, 300 MHz, δ/ppm): 0.67 (s, 3H, CH₃), 0.8-2.08 (m, 44H, -S-CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH, CH₂), 2.24-2.39 (m, 7H, C=C-CH₂-CH-O, CO₂-CH₂ and -S-C=O-CH₃), 2.87 (t, 2H, -S-CH₂, J= 7.2 Hz), 4.54-4.68 (m, 1H, O-CH), 5.35-5.42 (d, 1H, C=CH, J= 5.2 Hz).

4:

Synthesized as described above for compound **3**. Quantities: Compound **2** (1.0 g, 1.56 mmol) and potassium thioacetate (0.26 g, 2.27 mmol). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 0.68 (s, 3H, CH₃), 0.83-2.07 (m, 54H, -S-CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH, CH₂), 2.21-2.35 (m, 7H, C=C-CH₂-CH-O, CO₂-CH₂ and -S-C=O-CH₃), 2.86 (t, 2H, -S-CH₂, J= 7.3 Hz), 4.53- 4.70 (m, 1H, O-CH), 5.33- 5.42 (d, 1H, C=CH, J=4.9 Hz).

6-(cholesterylloxycarbonyl)hexyl disulfide, **Disulfide 1 (DS1)**:

Compound **3** (1.0 g, 1.8 mmol) and sodium borohydride (0.67 g, 17.71 mmol) were dissolved in THF (15 mL) and reaction was refluxed for 24 hours. The solvent was evaporated and precipitate formed was washed once with water and hot ethanol for several times. ¹H NMR (400 MHz, CDCl₃, δ/ppm): 0.68 (s, 3H, CH₃), 0.83-2.07 (m, 88H, -S-CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH, CH₂), 2.25-2.38 (m, 8H, C=C-CH₂-CH-O, CO₂-CH₂), 2.69 (t, 4H, -S-CH₂, J=7.2 Hz), 4.53- 4.69 (m, 2H, O-CH), 5.34- 5.41 (d, 1H, C=CH, J= 4.8 Hz). Phase transition temperatures: Cr 116 N* 133 Iso [S1].

Disulfide 2 (DS₂):

Synthesized as described above for **DS₁**. Quantities: Compound **4** (1.0 g, 1.6 mmol) and sodium borohydride (1.20 g, 31 mmol). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 0.69 (s, 3H, CH₃), 0.83-2.07 (m, 108H, -S-CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH₂, CH₂), 2.22-2.36 (m, 8H, C=C-CH₂-CH-O, CO₂-CH₂), 2.63 (t, 4H, -S-CH₂, J= 7.3 Hz), 4.54- 4.69 (m, 2H, O-CH), 5.33- 5.40 (d, 1H, C=CH, J=4.7 Hz). Phase transition temperatures: Cr 99 (97 SmA*) N* 110 Iso [S₁].

5:

Synthesized as described above for compound **1**. Quantities: Cholesterol (10.0 g, 25.9 mmol), 5-hexenoic acid (3.54 g, 31.1 mol), 4-dimethylaminopyridine (0.05 g, 0.40 mmol) and dicyclohexylcarbodiimide (6.30 g, 30.5 mmol). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 0.69 (s, 3H, CH₃), 0.85-2.17 (m, 43H, -CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH₂, CH₂), 2.20-2.40 (m, 4H, C=C-CH₂-CH-O, CO₂-CH₂), 4.57- 4.66 (m, 1H, cholesteryl-O-CH), 4.96- 5.08 (m, 2H, -CH₂-CH=CH₂), 5.35- 5.41 (d, 1H, cholesteryl-C=CH, J=4.8 Hz), 5.73- 5.85 (m, 1H, -CH₂-CH=CH₂).

Ligand 3:

Compound **5** (1 g, 2.07 mmol) was dissolved in dry toluene (25 ml). Trimethoxysilane (0.13 g, 1.04 mmol) was added and solution was allowed to stir for 30 minutes at room temperature. Then, 1,1,3,3-tetramethyldisiloxane Pt-complex (Karstedt's catalyst) in xylene (7.89 mg, 0.021 mmol) was added and reaction was allowed to stir for 24 hours at room temperature. The excess of trimethoxysilane and solvent were removed under reduced pressure. The residue was dissolved in dichloromethane/ethyl acetate (1:1) and any undissolved part was discarded. The filtrate was collected and solvent is removed under reduced pressure to obtain sticky off-white solid. ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 0.69 (s, 3H, CH₃), 0.68- 0.65 (m, 1.57H -CH₂-Si-(OCH₃)₃), 0.85-2.17 (m, xH, -CH₂-CH₂, CO₂-CH₂-CH₂, cholesteryl-CH₂, CH₂), 2.25-2.36 (m, 4H, C=C-CH₂-CH-O, CO₂-CH₂), 3.58 (s, 9H, -Si-(OCH₃)₃), 4.57- 4.68 (m, 1H, O-CH), 5.37- 5.41 (d, 1H, cholesteryl-C=CH, J=4.6 Hz).

Synthesis of Au nanoparticles (NP1 and NP2): All glasswares used for synthesis and storage of nanoparticles were cleaned with *aqua regia*, rinsed with deionized water (Millipore, resistivity 18.1 Ω), acetone, *iso*-propanol and dried at 120 °C overnight. The Au nanoparticles **NP1** and **NP2** were synthesized following a modified one-phase Brust-Schiffrin approach⁶. **DS1** (0.131 g, 0.127 mmol) was added to $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (50 mg, 0.126 mmol) dissolved in freshly distilled THF (5 mL). The mixture was allowed to stir vigorously for fifteen minutes. Then, sodium borohydride (0.03 g, 0.872 mmol), dissolved in DI water (1 mL) was added and the color immediately changed to reddish-brown. The reaction mixture was allowed to stir for three hours. Thereafter, solvent was removed under reduced pressure. Thus obtained nanoparticles were profusely washed with hexane, ethyl acetate, acetone and DI water. The centrifugation and decantation was done thrice. The purified NPs were dissolved in hexane (5 mL) and dialyzed (Spectra/Por Dialysis membrane MWCO: 6-8,000) against hexane to remove unreacted materials. Then, the solvent was removed under reduced pressure and the particles were dried under nitrogen.

NP2 were synthesized under similar conditions using **DS2** as ligand. Briefly, **DS2** (0.15 mg, 0.127 mmol) was added to $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (50 mg, 0.126 mmol) dissolved in freshly distilled THF (5 mL). The mixture was allowed to stir vigorously for fifteen minutes. Then, sodium borohydride (0.024 g, 0.634 mmol), dissolved in DI water (1 mL) was added and the color immediately changed to reddish-brown. The purification steps were same as for **NP1**.

CTAB capped NP synthesis: These gold nanoparticles were synthesized according to modified non-seeding method^{4,5}. Hydrogen tetrachloroaurate (110 mg, 0.28 mmol) was dissolved in 250 mL DI water, to which CTAB (18.22 g, 50 mmol) was added and mixed with strong stirring at 30 °C. Then, silver nitrate (0.01M, 25 mL) and ascorbic acid (0.1M, 25 mL) were subsequently added followed by gentle stirring to obtain a colorless solution. Finally, an ice-cold aqueous solution of sodium borohydride (0.1mM, 2 mL) was added and solution was stirred gently for 12 hours at 30 °C. The solution turned wine red after 3-4 minutes. The resulting suspension was centrifuged (11,000 rpm, 20 minutes) at 35 °C to remove excess of CTAB and thus obtained precipitate was re-dispersed in 100 mL DI water.

Synthesis of Au nanoparticles (NP3): The synthesis of these NPs was done utilizing a modified silane conjugation method⁷. A 3 mL aqueous solution of as prepared CTAB capped gold nanoparticles was washed with chloroform. Then, 120 μL 3-(mercaptopropyl)trimethoxysilane (10 mmol solution in ethanol) was added and stirred for thirty minutes. Then, **ligand 3** (0.05 g, 0.081 mmol) dissolved in 3 mL chloroform was added, which was followed by subsequent addition of 1N sodium hydroxide (30 μL in water). The reaction mixture was allowed to stir vigorously. After stirring for 2 hours the gold nanoparticles were phase transferred. The solution was allowed to stir for 12 hours to ensure complete transfer. Then, the organic layer was separated and centrifuged (11,000 rpm, 15 min) to remove the excess ligand. The nanoparticle precipitate was dissolved in chloroform and centrifuged twice.

Calculations

Calculations for nanoparticle molecular weight and number of ligands: The average molecular weight was calculated following the method of Gelbart *et al.*⁸:

Volume of gold atom $V_g = 17 \text{ \AA}^3$

Surface Area assumed: 21.4 \AA^2

Mol. Wt. Au: 196.96 g/mol

Mol. Wt. of Cholesterol thiol1: 516.87 g/mol

Mol. Wt. of Cholesterol thiol2: 587 g/mol

Mol. Wt. of cholesterolthiol3: 755.26 g/mol

1. NP1

Average size from TEM: 1.77 nm

Radius of Au core from TEM: 8.85 Å

No. of gold atom at interface: $4 \times 3.14 \times (8.85)^3 / 3 \times V_g = 170.70$

Number of cholesterolthiol1 on surface, $n_{\text{thiol}} = 4 \times \pi \times (8.85)^2 / 21.4 = 45.96$

M. Wt. of total no. of gold atoms: $196.96 \times 170 = 33622.29165$

M. Wt. of total no. cholesterolthiol 1 on surface : $516.87 \times 45.96 = 23759.85211$

Molecular weight of particles, NP1: 57382.14 g/mol.

Total moles of cholesterolthiol 1: 0.414063514

Mol% of cholesterolthiol 1: 41.40 %

2. NP2

Average size from TEM: 5.54 nm

Radius of Au core from TEM: 27.7 Å

No. of gold atom at interface: $4 \times 3.14 \times (27.7)^3 / 3 \times V_g = 5234.30$

Number of cholesterolthiol2 on surface, $n_{\text{thiol}} = 4 \times \pi \times (27.7)^2 / 21.4 = 450.33$

M. Wt. of total no. of gold atoms: $196.96 \times 5234.30 = 1030948.108$

M. Wt. of total no. cholesterolthiol 1 on surface : $587 \times 450.33 = 264346.464$

Molecular weight of particles, NP2: 1295294.57 g/mol.

Total moles of cholesterolthiol1: 0.204082121

Mol% of cholesterolthiol2: 20.40 %

3. NP3

Average size from TEM: 10.09 nm

Radius of Au core from TEM: 50.45 Å

No. of gold atom at interface: $4 \times 3.14 \times (50.45)^3 / 3 \times V_g = 31622.99$

Number of cholesterolthiol3 on surface, $n_{\text{thiol}} = 4 \times \pi \times (50.45)^2 / 21.4 = 1493.81$

M. Wt. of total no. of gold atoms: $196.96 \times 31622.99 = 6228464.746$

M. Wt. of total no. ligand 3 on surface : $755.26 \times 1493.81 = 1128222.331$

Molecular weight of particles, NP3: 7356687.07 g/mol.

Total moles of **cholesterolthiolsilane 3**: 0.153360109

Mol% of cholesterolthiolsilane 3: 15.33 %

Above data were used to calculate and estimate (due to the size distribution) the molar concentration of chiral ligand in a particular LC-NP mixture.

Table S1. Mol% of Chiral Ligand present in NP-LC composites.

LC-NP Mixture		0.5 Weight% of NPs	5.0 Weight% of NPs
		Mol% of Chiral Ligand present in NP-LC composite	Mol% of Chiral Ligand present in NP-LC composite
1	NP₁ + LC₁	9.108E-04	9.455E-03
2	DS₁ + LC₁	0.121	1.25
3	NP₂ + LC₁	1.976E-05	2.068E-04
4	DS₂ + LC₁	0.107	1.10
5	NP₃ + LC₁	2.614E-06	3.003E-02
6	ligand 3 + LC₁	0.198	2.08
7	NP₁ + LC₂	1.441E-03	1.496E-02
8	DS₁ + LC₂	0.194	2.04
9	NP₂ + LC₂	3.140E-05	3.289E-04
10	DS₂ + LC₂	0.170	1.75
11	NP₃ + LC₂	4.172E-06	3.004E-02
12	ligand 3 + LC₂	0.321	3.24

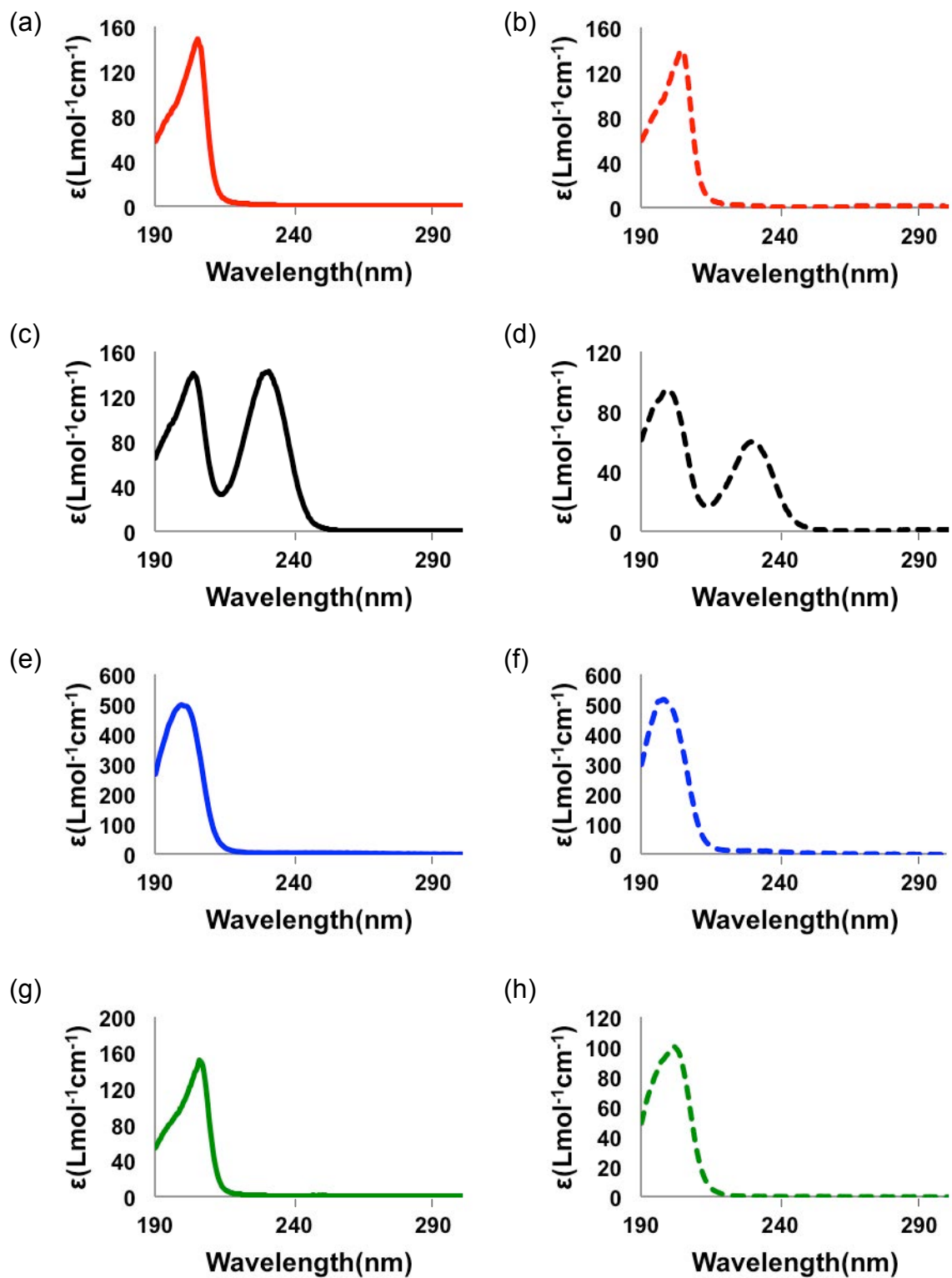


Figure S1. UV-absorbance spectra of: (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **DS1**, (f) **DS2**, (g) **5**, and (h) **ligand 3** in cyclohexane.

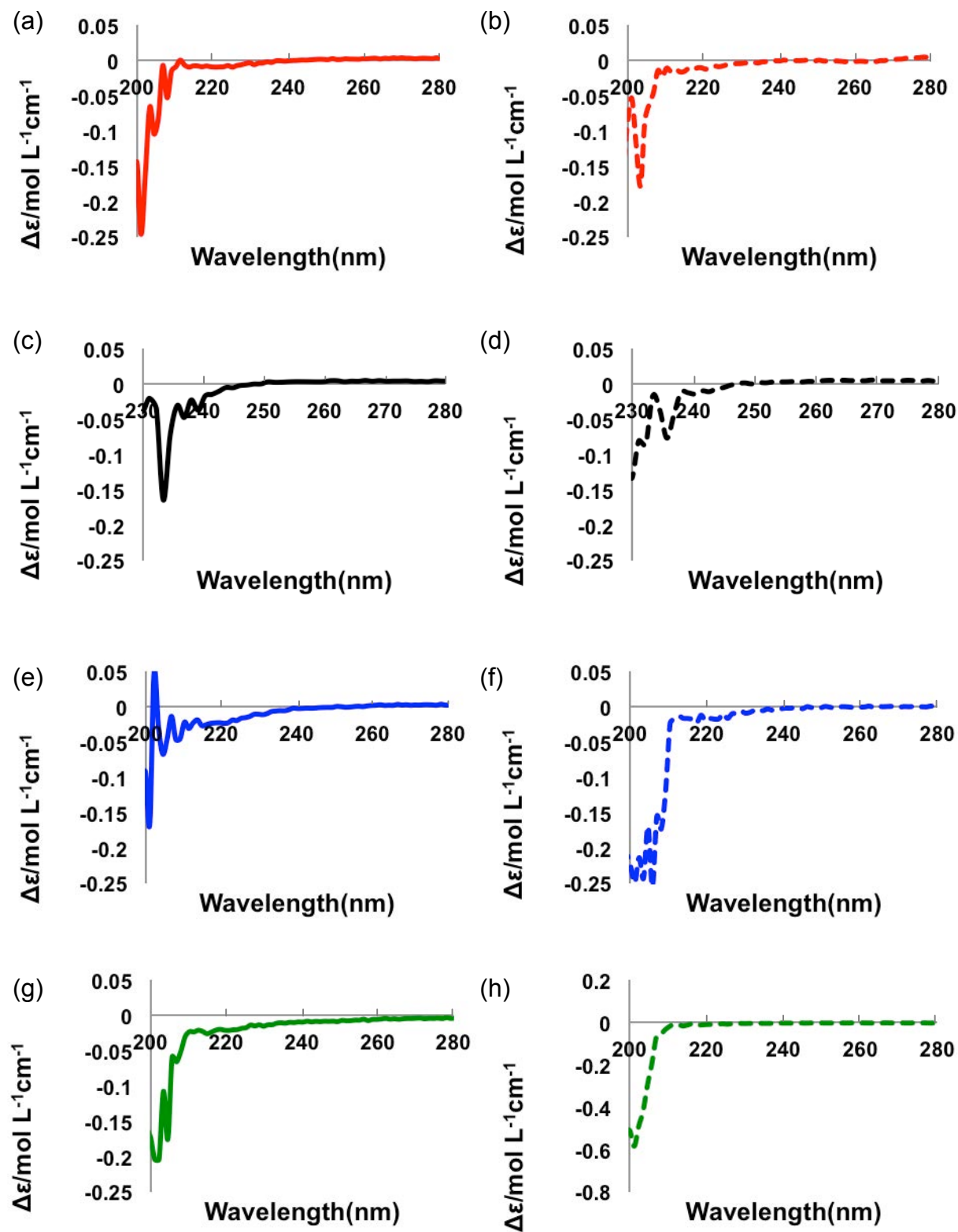


Figure S2. CD of: (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **DS1**, (f) **DS2**, (g) **5**, and (h) **ligand 3** in cyclohexane.

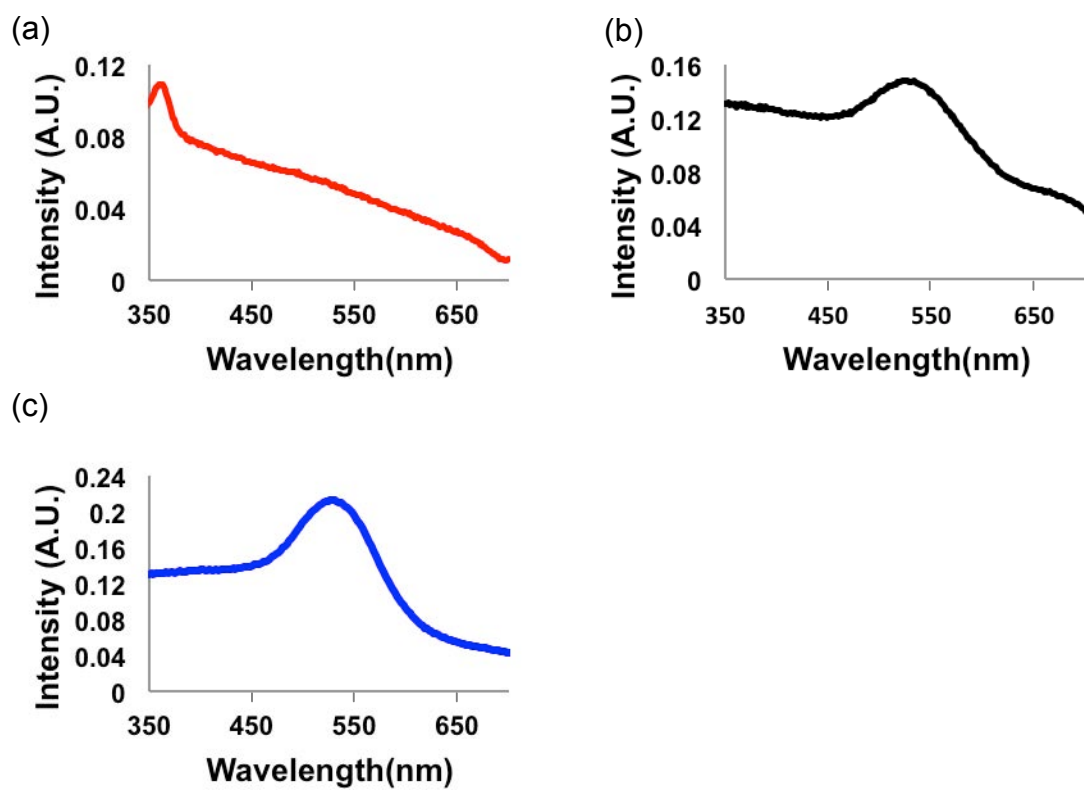


Figure S3. Vis-absorbance spectra of: (a) NP1, (b) NP2, and (c) NP3 in toluene.

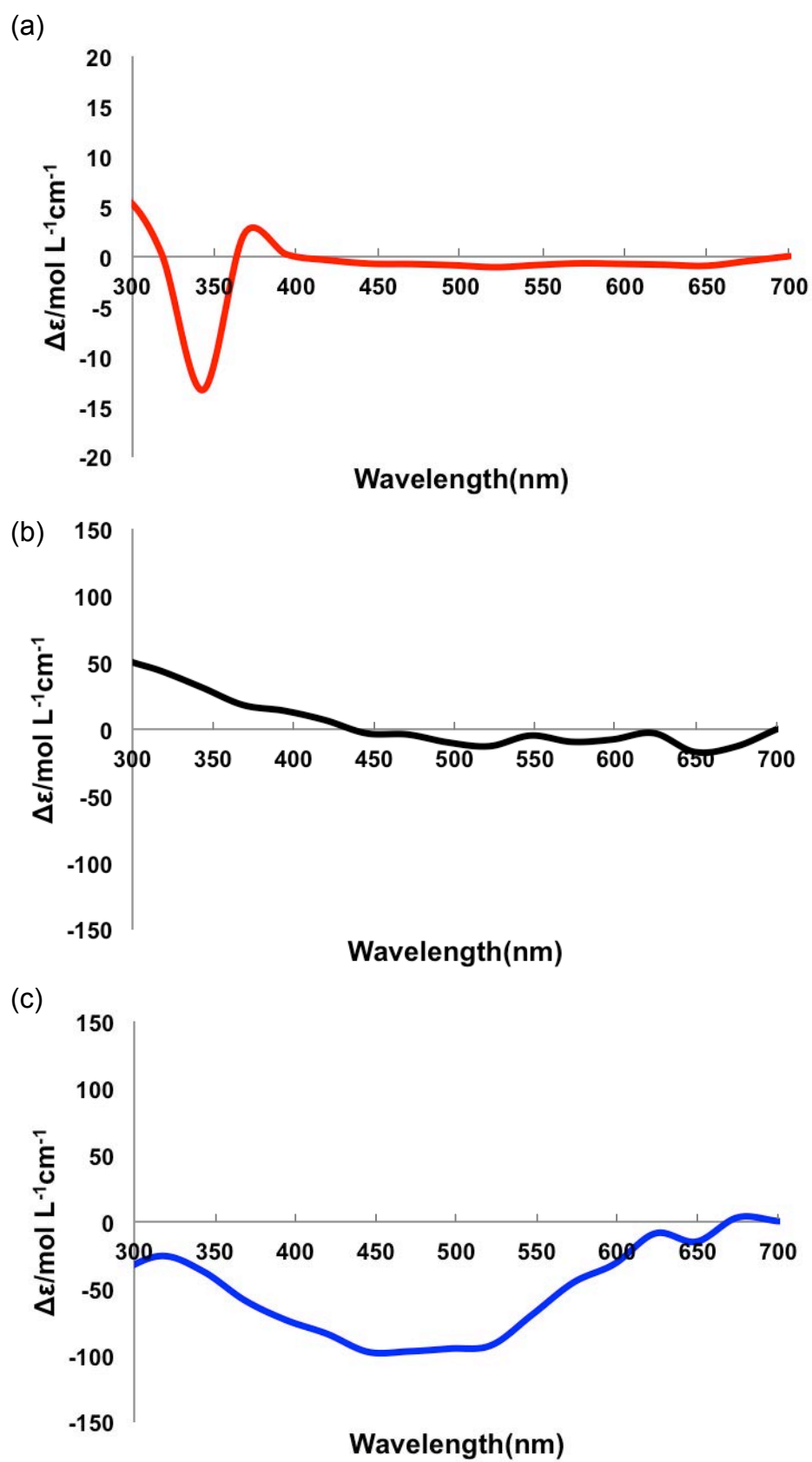


Figure S4. CD spectra of: (a) NP1, (b) NP2, and (c) NP3 in chloroform.

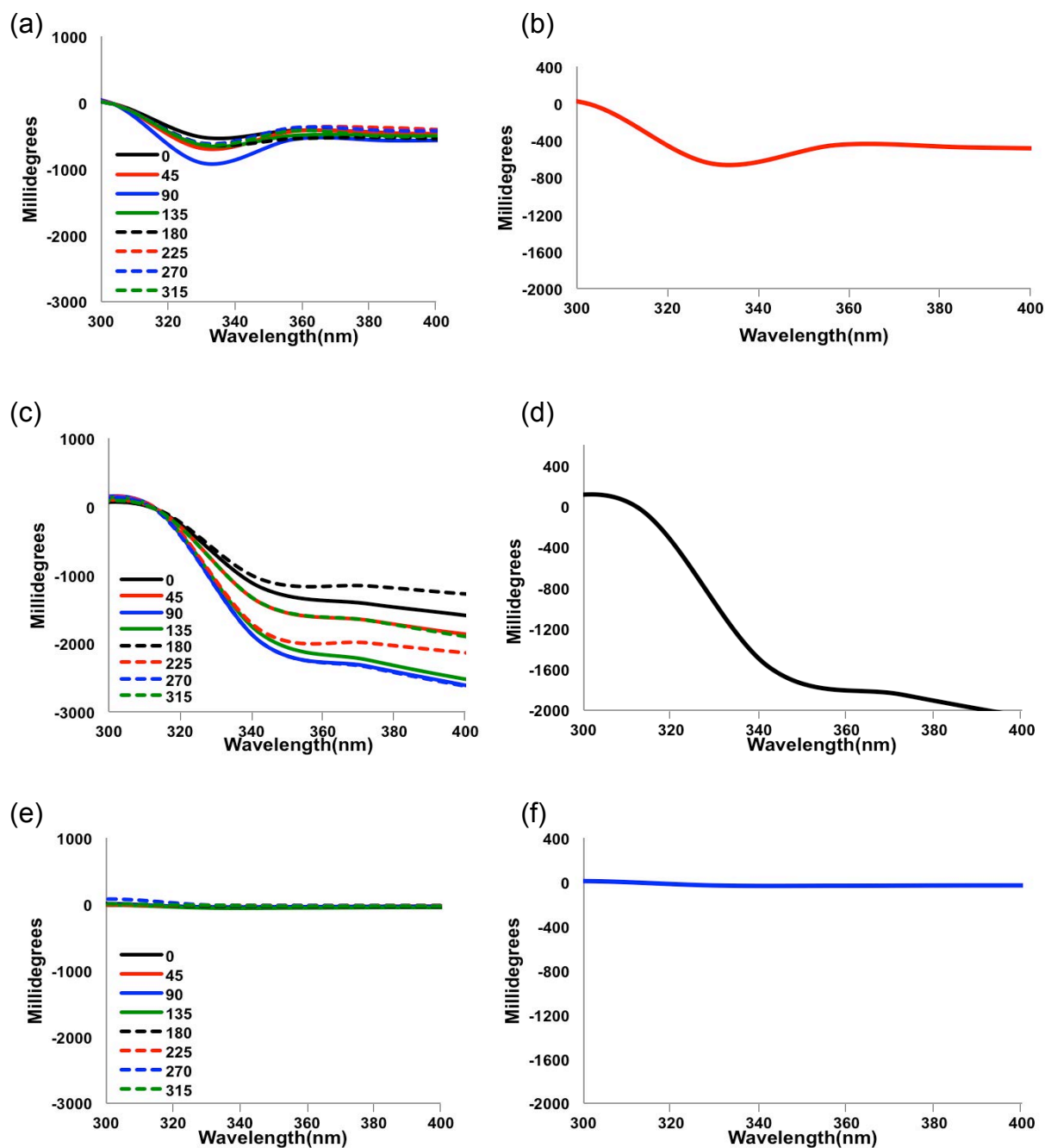


Figure S5. Thin film (10 micron) CD spectra (at 30 °C) of LC1 doped with 0.5wt% of: (a) NP₁ (at different rotation angles), (b) NP₁ (sum negative), (c) NP₂ (at different rotation angles), (d) NP₂ (sum negative), (e) NP₃ (at different rotation angles), and (f) NP₃ (sum zero).

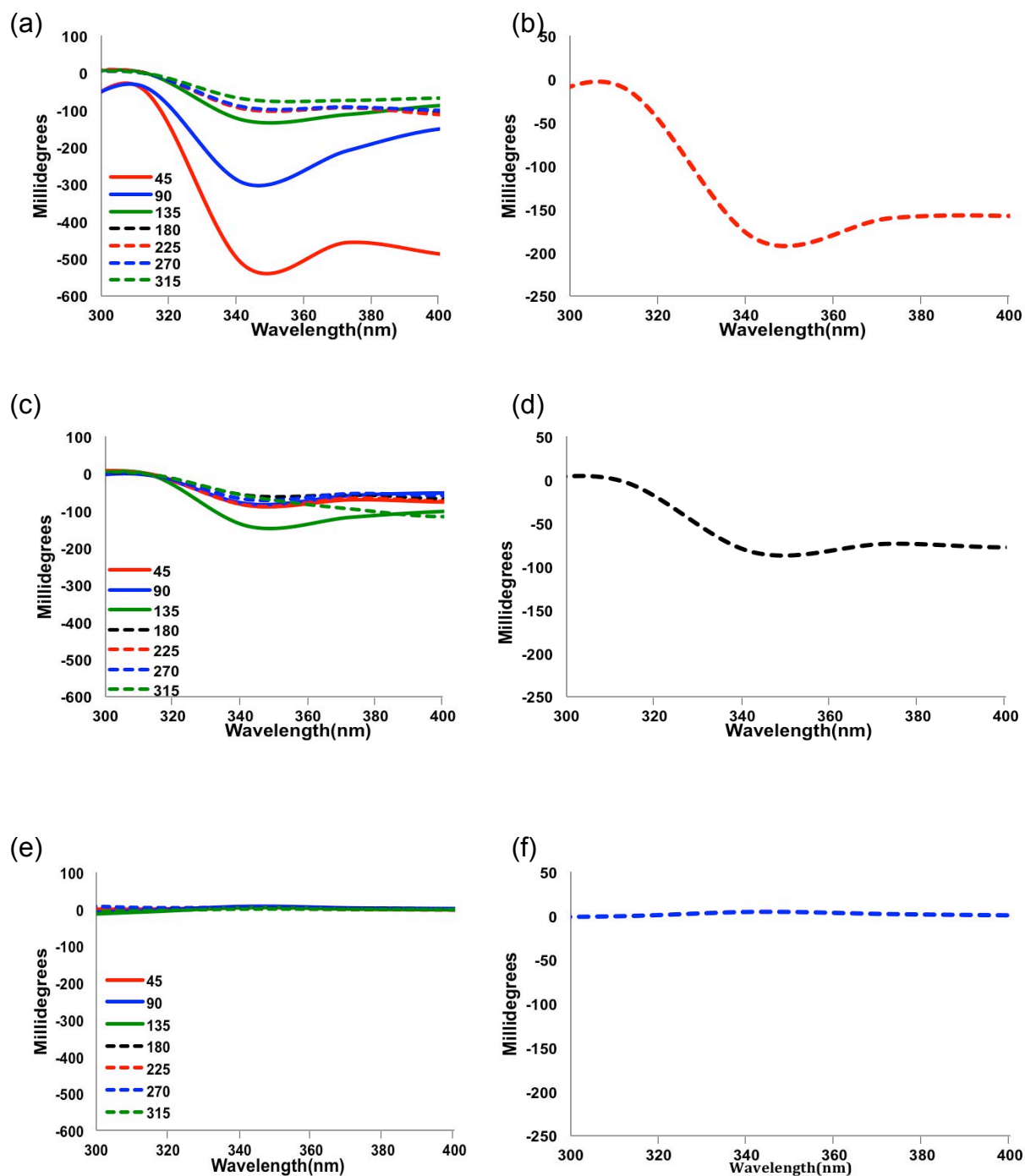


Figure S6. Thin film (10 micron) CD spectra of LC₂ (at 66 °C) doped with 0.5 wt% of: (a) NP₁ (at different rotation angles), (b) NP₁ (sum negative), (c) NP₂ (at different rotation angles), (d) NP₂ (sum negative), (e) NP₃ (at different rotation angles), and (f) NP₃ (sum zero).

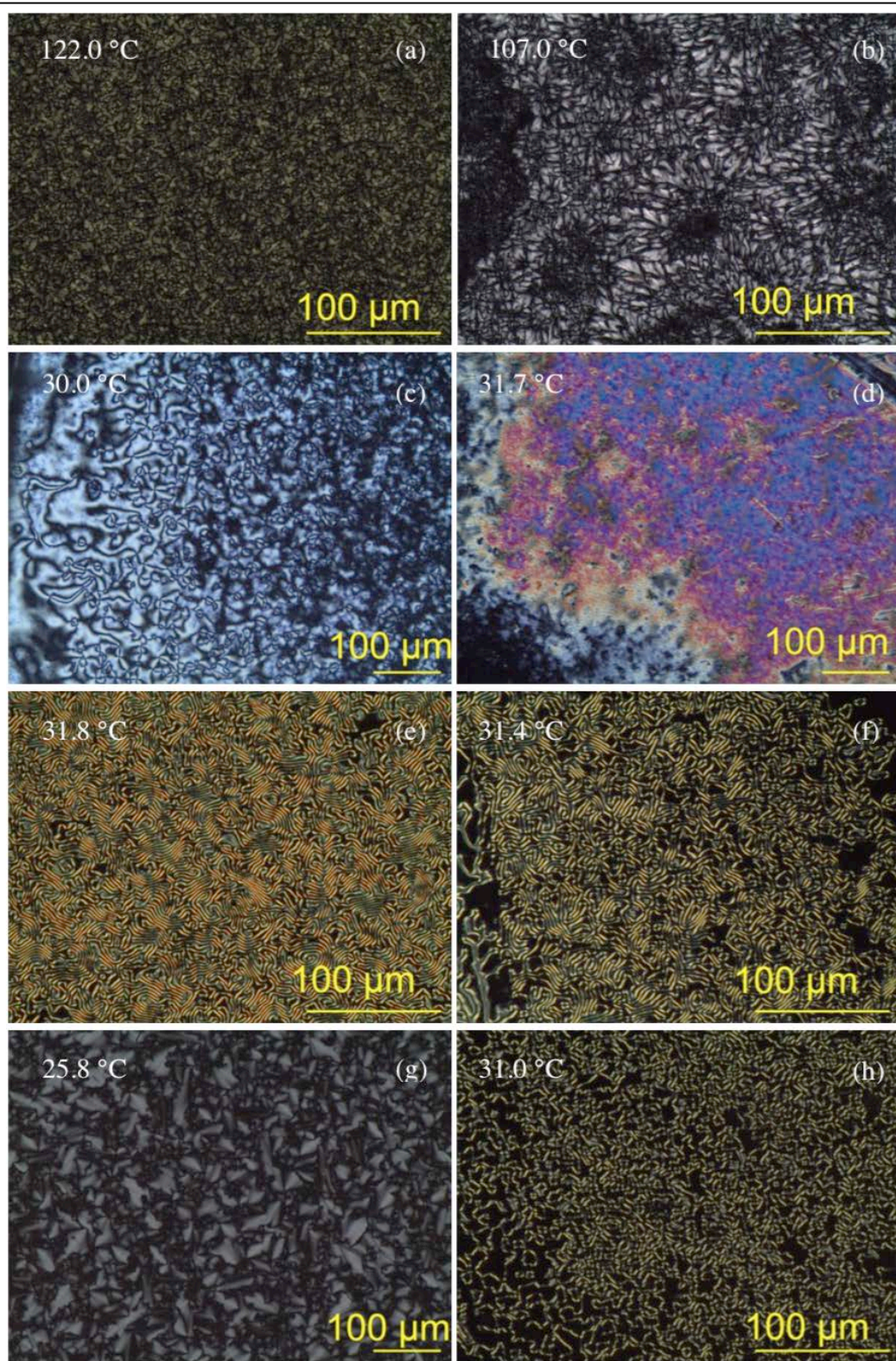


Figure S7. POM micrographs (crossed polarizers) between untreated glass slides of: (a) **DS1**, (b) **DS2**, (c) **LC1** doped with 0.5wt% **DS1**, (d) **LC1** doped with 0.5wt% **DS2**, (e) **LC1** doped with 5wt% **DS1**, (f) **LC1** doped with 5wt% **DS2**, (g) **Ligand 3**, and (h) **LC1** doped with 5wt% **ligand 3**.

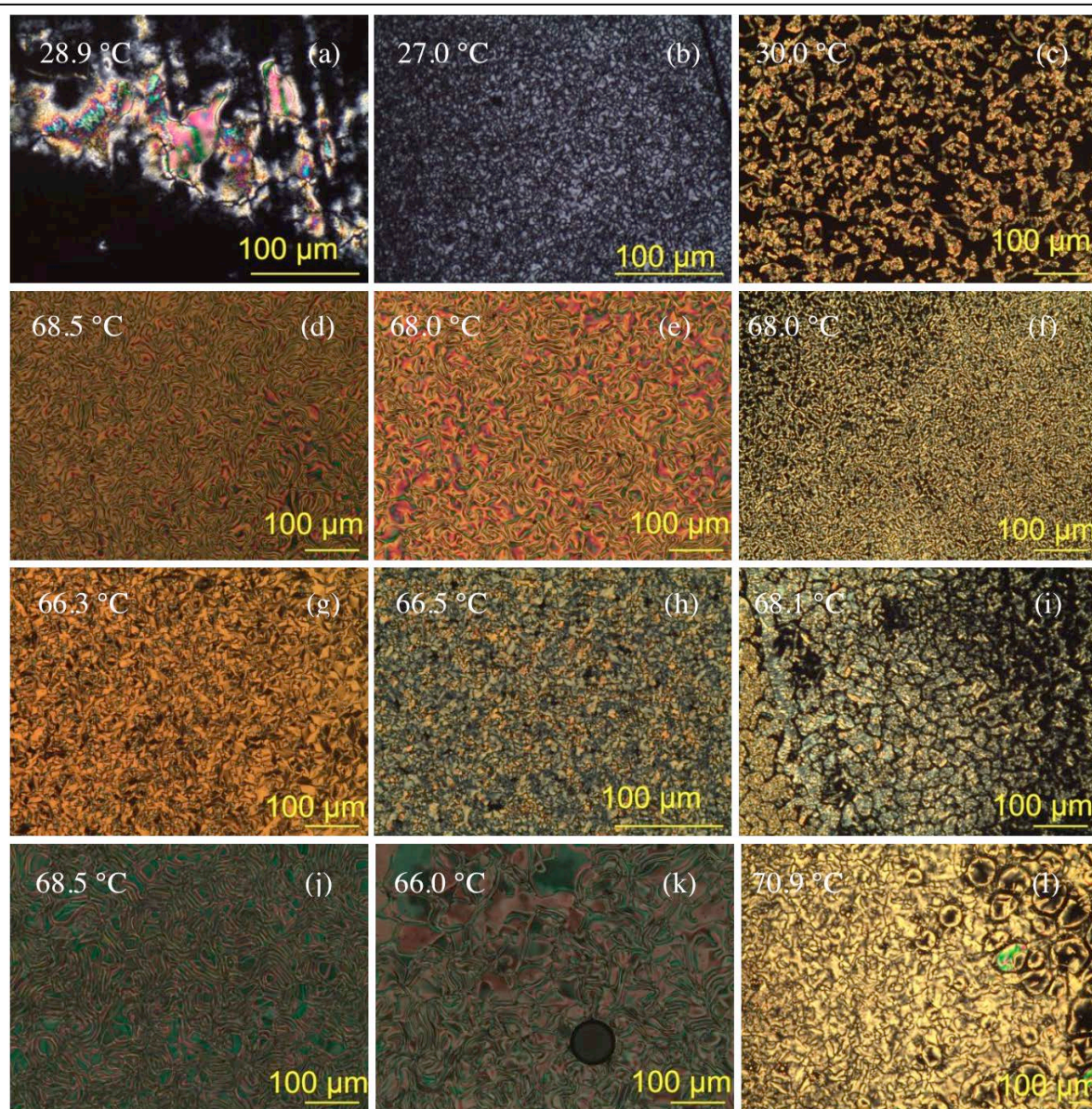


Figure S8. POM micrographs (crossed polarizers) between untreated glass slides of: (a) LC1 doped with 0.5wt% NP1, (b) LC1 doped with 0.5wt% NP2, (c) LC1 doped with 0.5wt% NP3, (d) LC2 doped with 0.5wt% NP1, (e) LC2 doped with 0.5wt% NP2, (f) LC2 doped with 0.5wt% NP3, (g) LC2 doped with 5wt% NP1, (h) LC2 doped with 5wt% NP2, (i) LC2 doped with 5wt% NP3, (j) LC2 doped with 0.5wt% NP1 (quartz cell), (k) LC2 doped with 0.5wt% NP2 (quartz cell), and (l) LC2 doped with 0.5wt% NP3 (quartz cell).

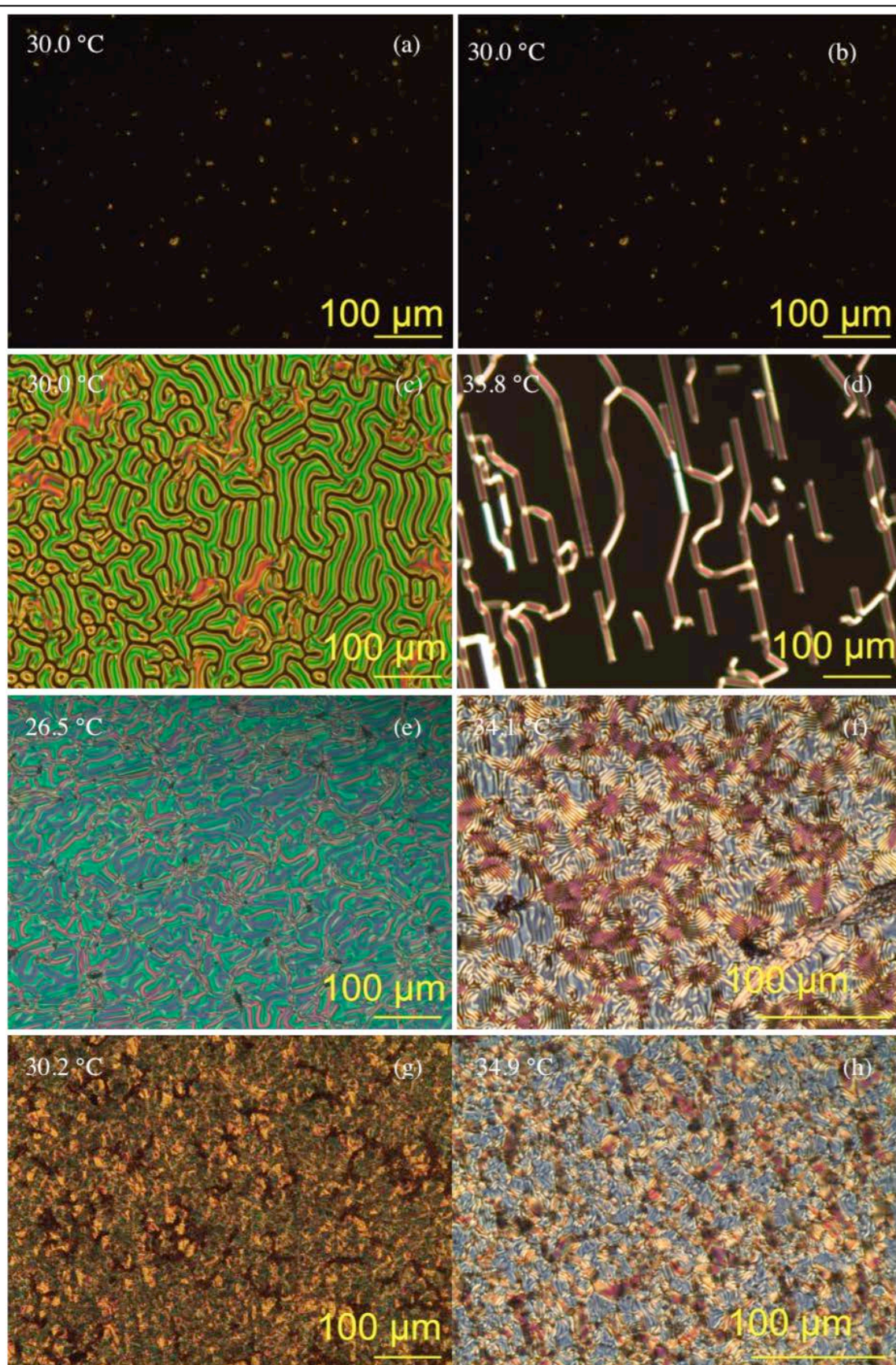


Figure S9. POM micrographs (crossed polarizers) of LC1 doped with: (a) **NP1** (0.5wt%), (b) **NP2** (0.5wt%), (c) **NP1** (2.5wt%), (d) **NP2** (2.5wt%), (e) **NP1** (5wt%), (f) **NP2** (5wt%), (g) **NP1** (10wt%), and (h) **NP2** (10wt%) in homeotropic cells.

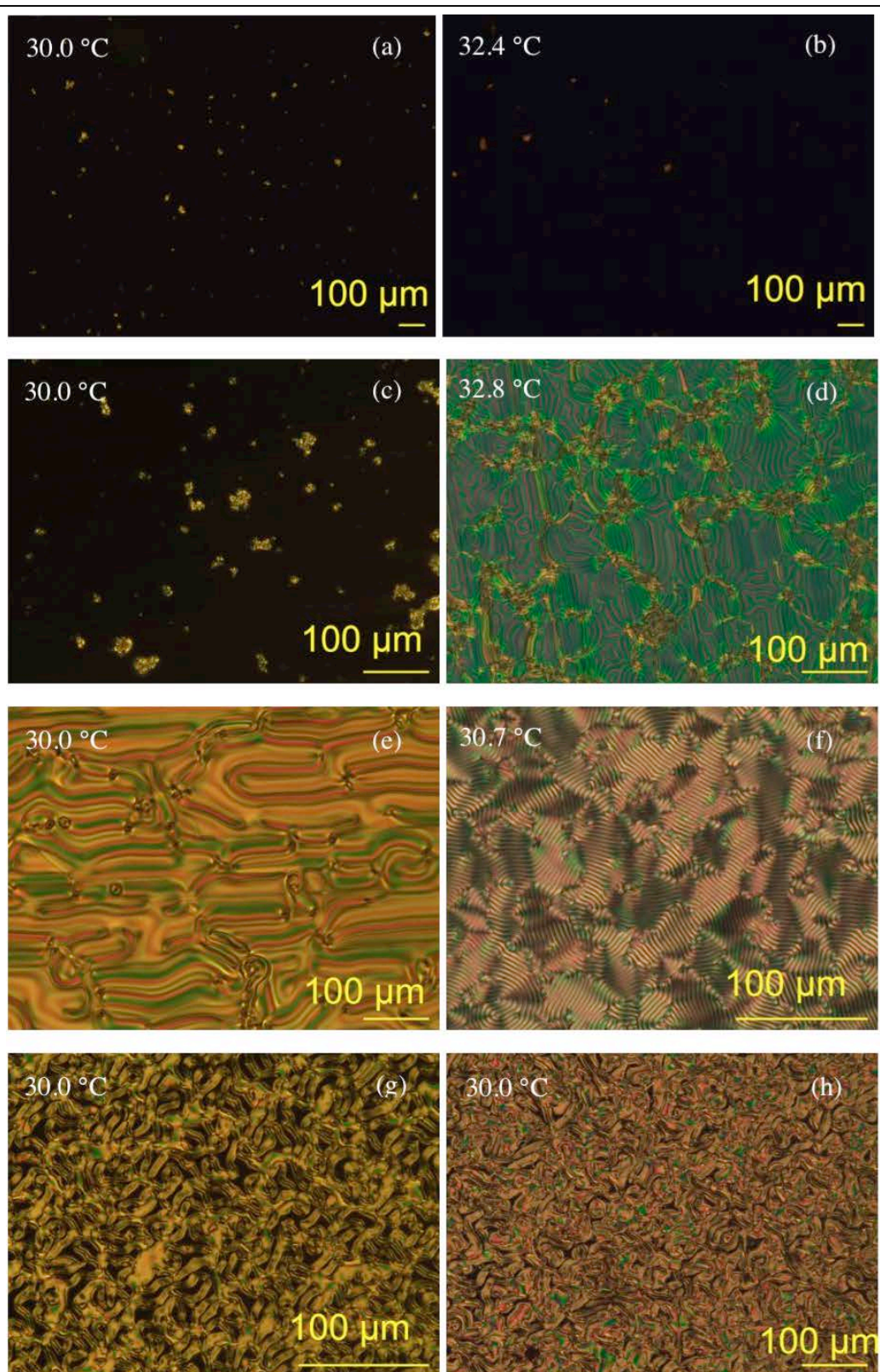


Figure S10. POM micrographs (crossed polarizers) of LC1 doped with: (a) **DS1** (0.5wt%), (b) **DS1** (5wt%), (c) **DS2** (0.5wt%), (d) **DS2** (5wt%), (e) **ligand 3** (0.5wt%), (f) **ligand 3** (5wt%), (g) **NP3** (0.5wt%), and (h) **NP3** (5wt%) in homeotropic cells.

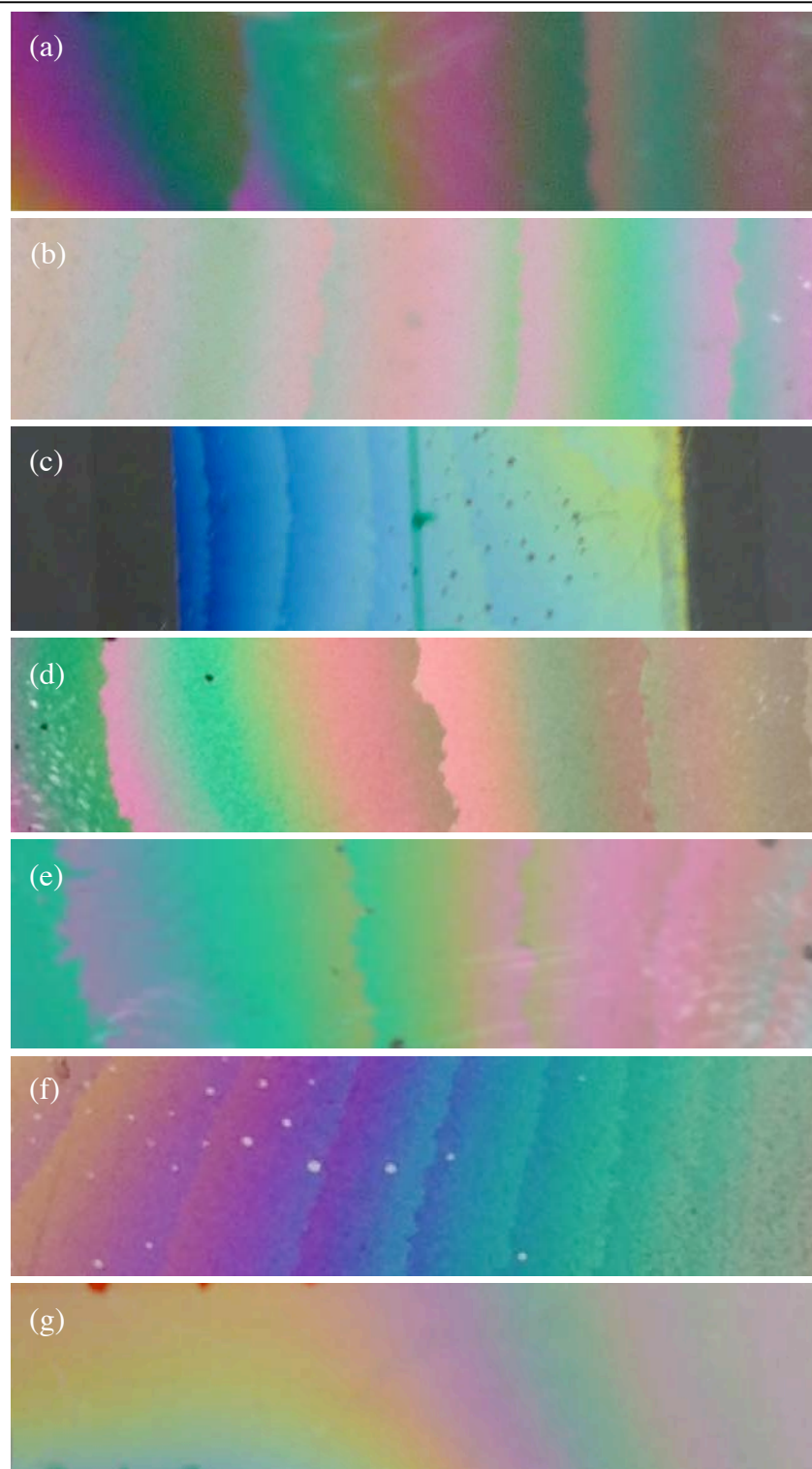


Figure S11. Images of Grandjean-Cano wedge cells (crossed polarizers) showing Grandjean steps (lines) of the induced N^* phase of LC1 doped with: (a) **NP1** (2.5wt%), (b) **NP1** (5wt%), (c) **NP1** (10wt%), (d) **NP2** (2.5wt%), (e) **NP2** (5wt%), (f) **NP2** (10wt%), and (g) **NP3** (5wt%).

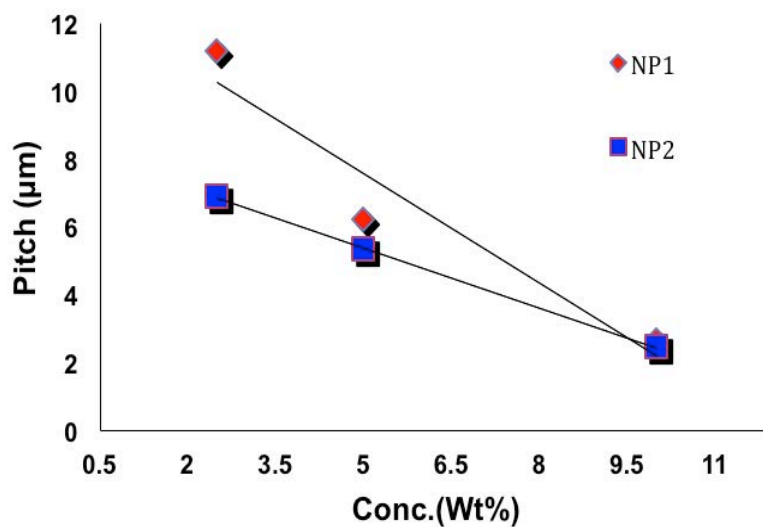


Figure S12. Pitch values for NP1 and NP2 at 2.5, 5 and 10wt% in LC1. Assuming a linear relationship, we can extrapolate when these p vs. conc. functions intersect and compare the effectiveness at the same number of chiral ligands in various LC-NP mixtures, see Table S2 below.

Table S2. Comparison of same chiral ligand mol% in the LC-NP mixtures.

LC-NP mixture		Weight % of NPs in LC-NP mixture	Mol% of Chiral Ligand present in NP-LC composites
1	NP1 + LC1	9.53	0.019
2	NP2 + LC1	9.53	0.206
3	NP1 + LC1	5.00	0.0096
4	DS1 + LC1	0.03	0.0096
5	NP2 + LC1	69.89	0.0096
6	NP3 + LC1	5.00	0.030
7	NP1 + LC1	14.54	0.030
8	NP2 + LC1	88.55	0.030

Table S3. Average number of NPs per unit volume in LC1 for the 0.5wt% and 5wt% NP1-LC1 and NP2-LC1 mixtures.

wt% of NPs in LC1	0.5	5
	Number of NPs per unit volume LC1 (1/cm ³)	
NP1	5.31 E+16	5.51 E+17
NP2	2.33 E+15	2.45 E+16
NP3	4.12 E+14	5.34 E+15

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Appendix 1: ^1H NMR

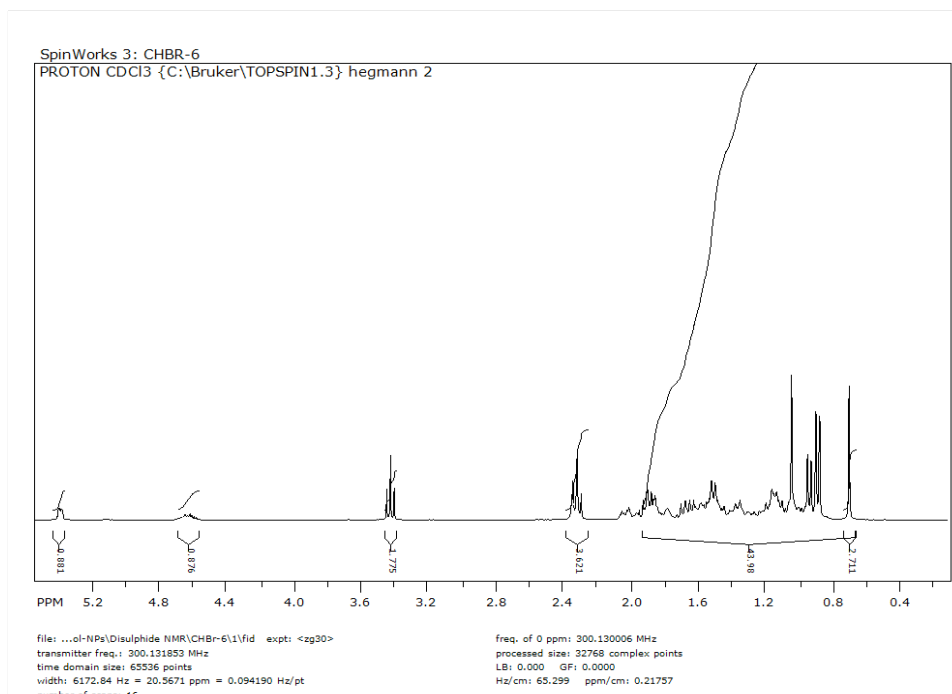


Figure A1. ^1H NMR spectrum of **1**.

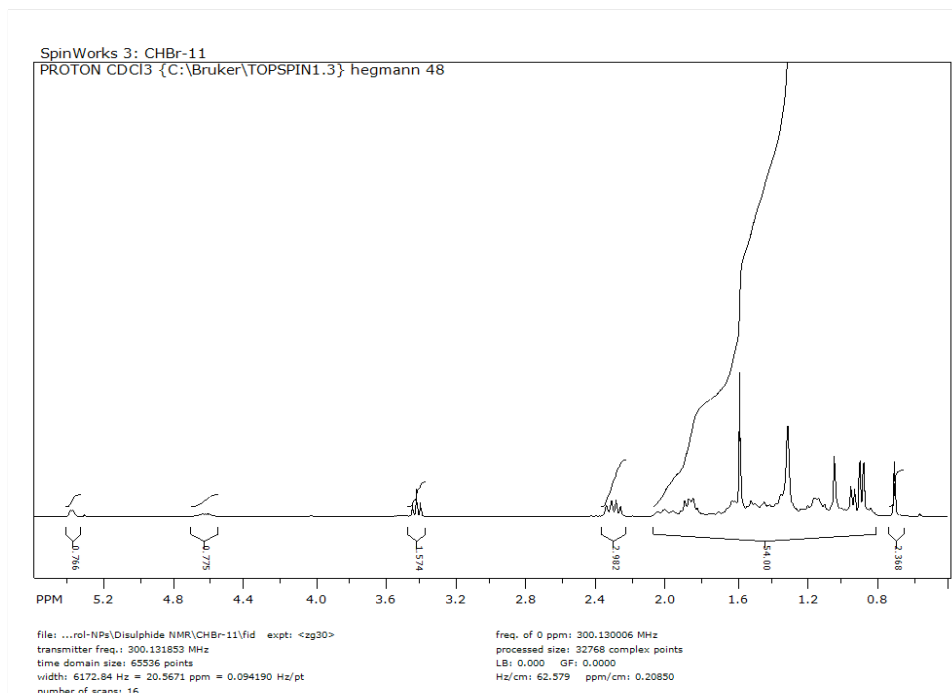


Figure A2. ^1H NMR spectrum of **2**.

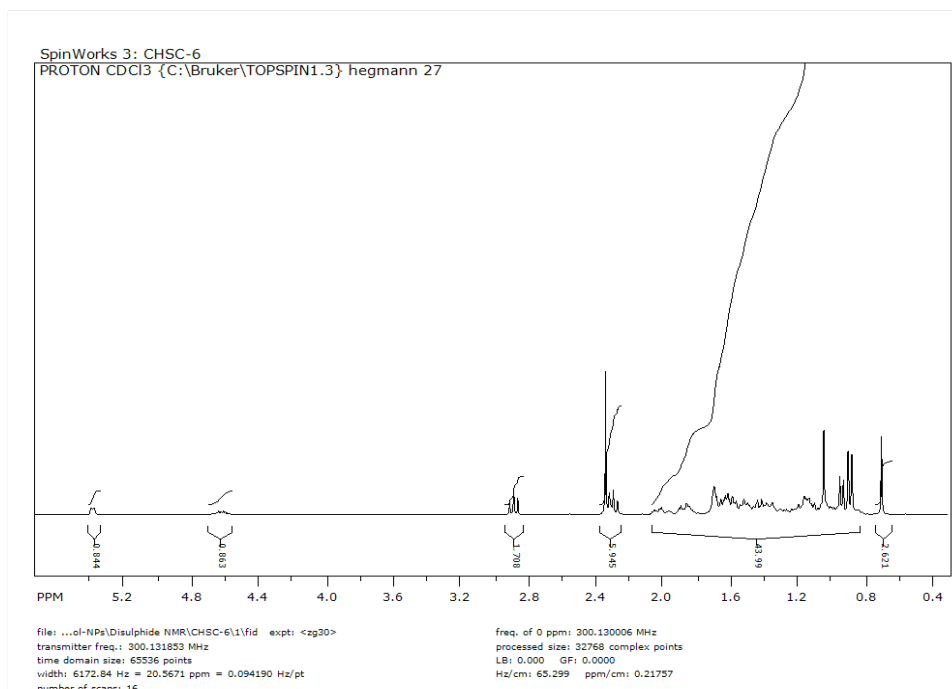


Figure A3. ¹H NMR spectrum of **3**.

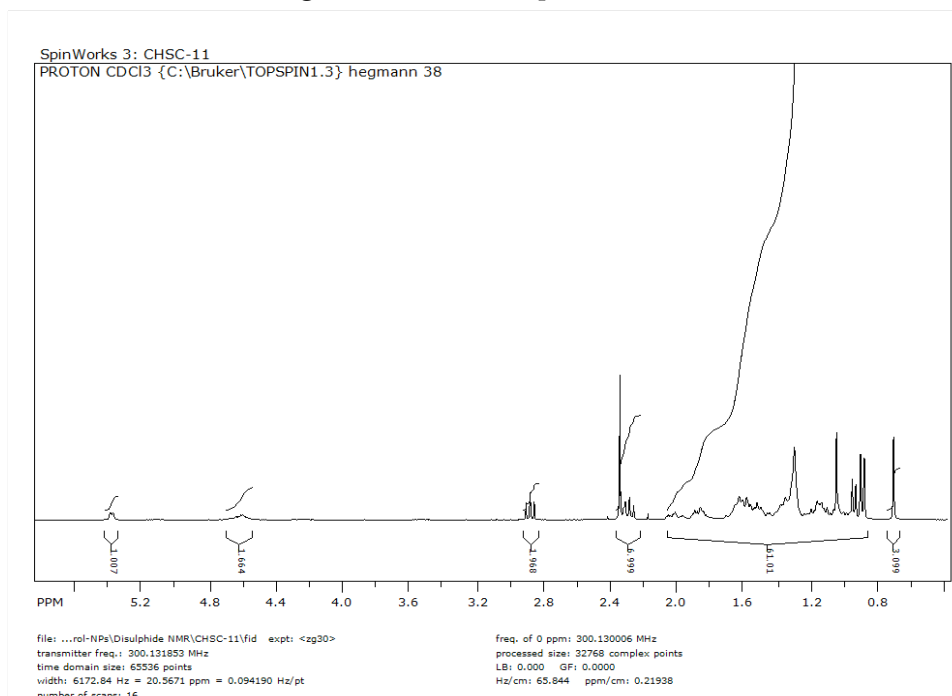


Figure A4. ¹H NMR spectrum of **4**.

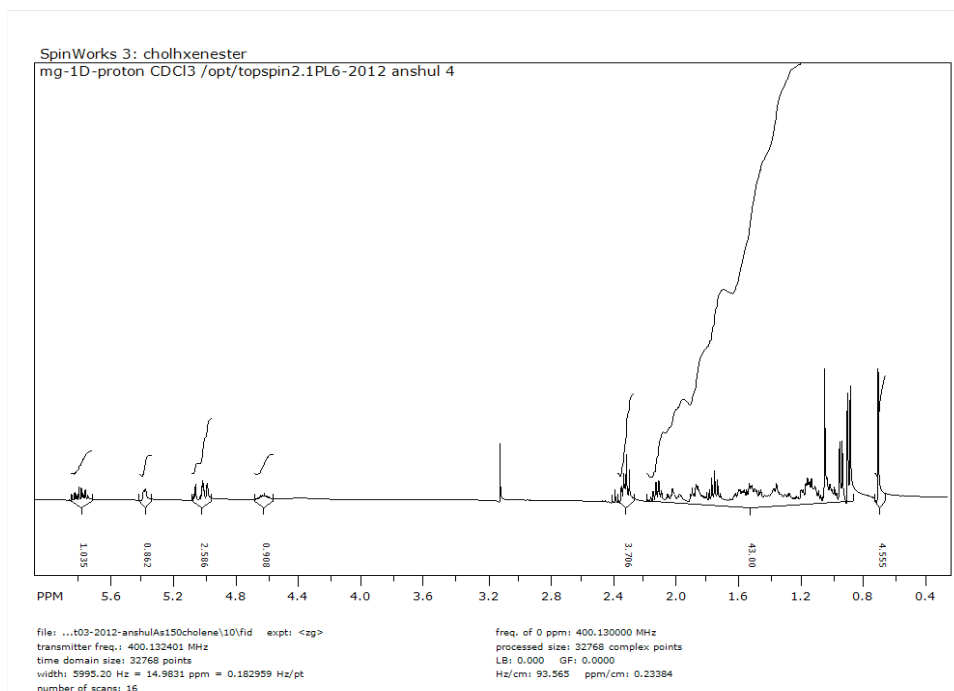


Figure A5. ¹H NMR spectrum of **5**.

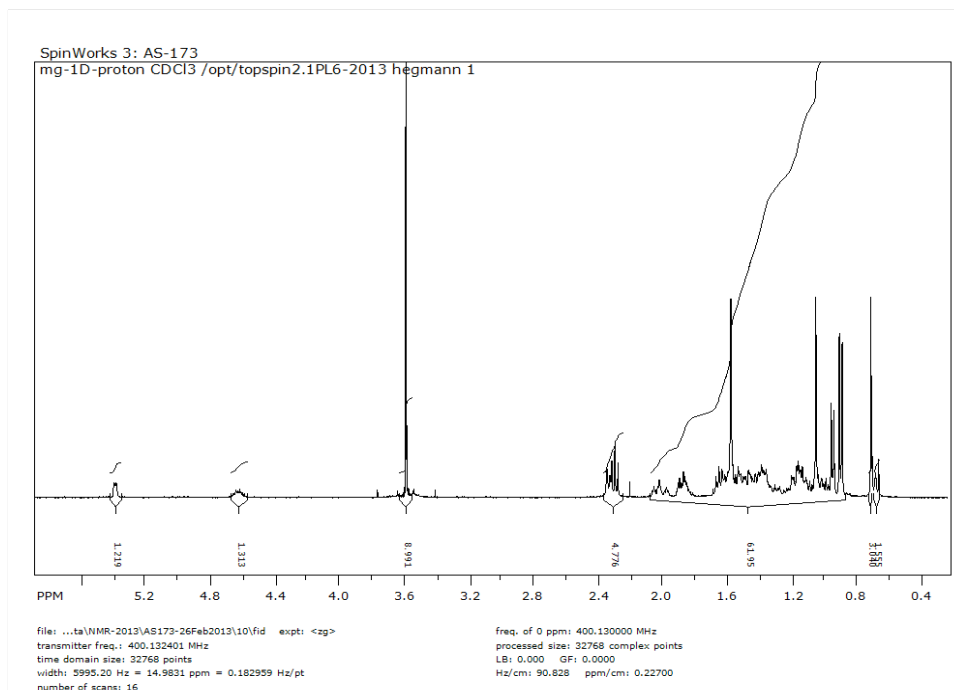


Figure A6. ¹H NMR spectrum of **ligand 3**.

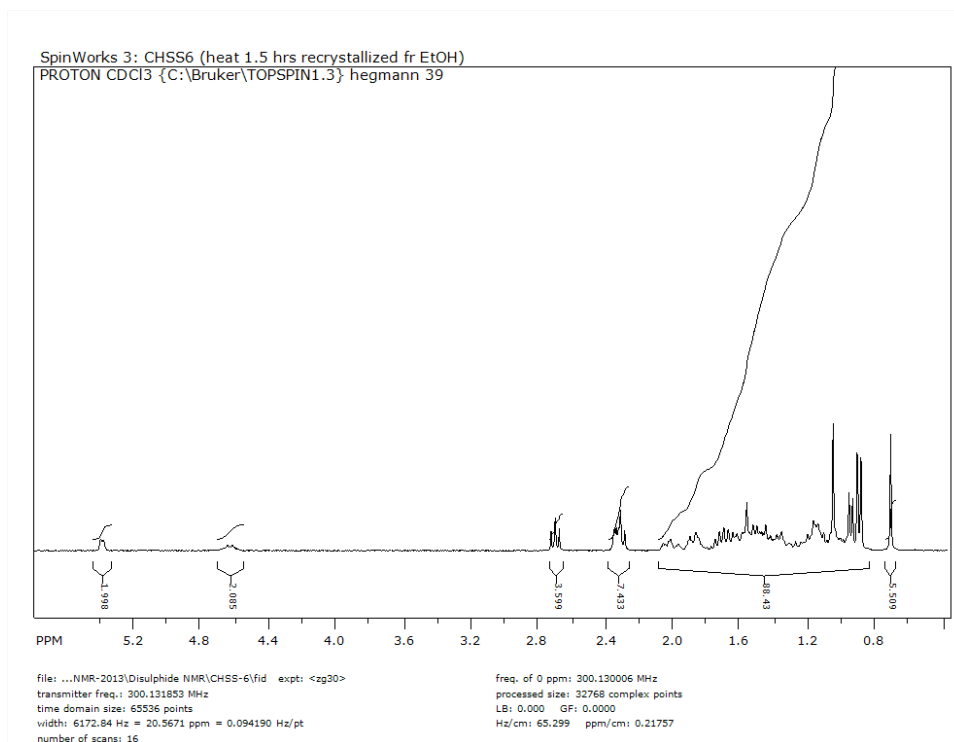


Figure A7. ¹H NMR spectrum of DS₁.

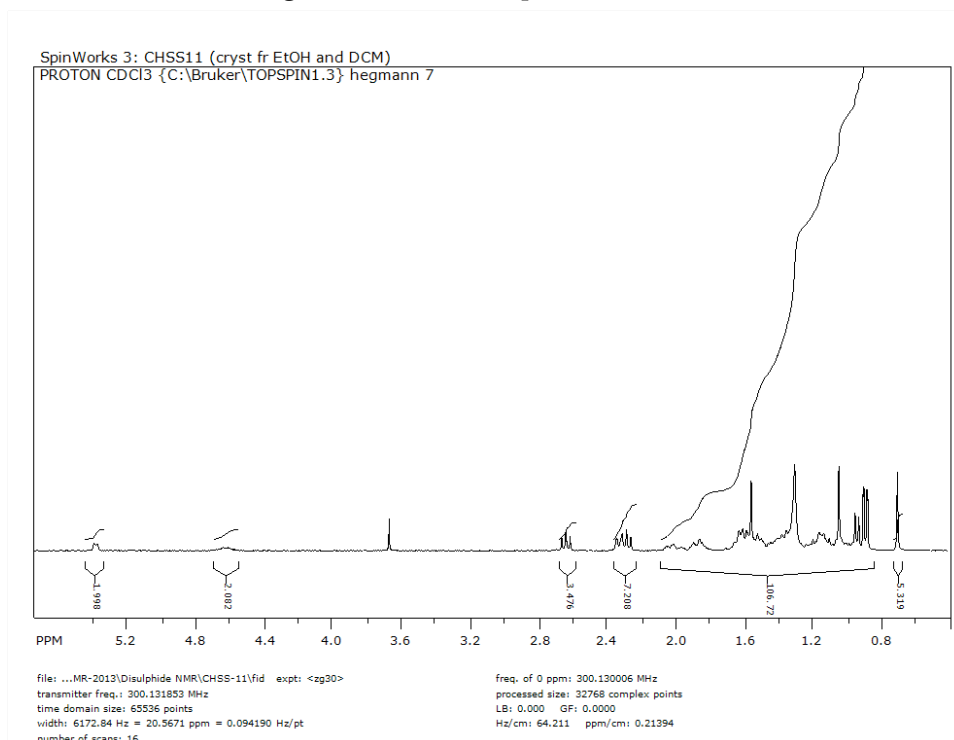


Figure A8. ¹H NMR spectrum of DS₂.

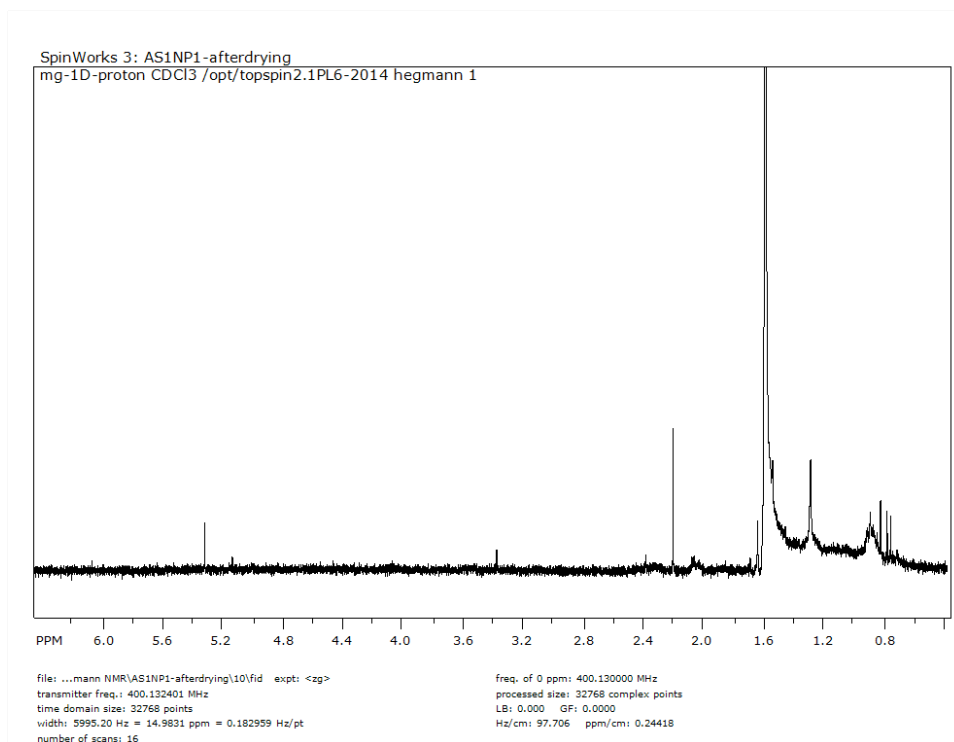


Figure A9. ¹H NMR spectrum of NP₁.

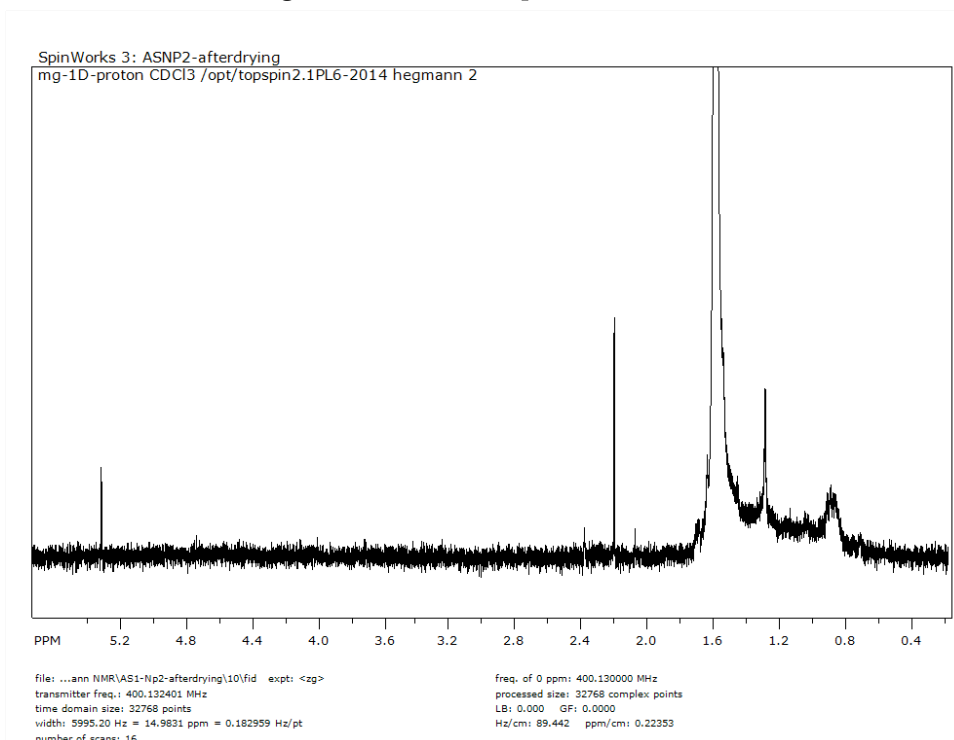


Figure A10. ¹H NMR spectrum NP₂.

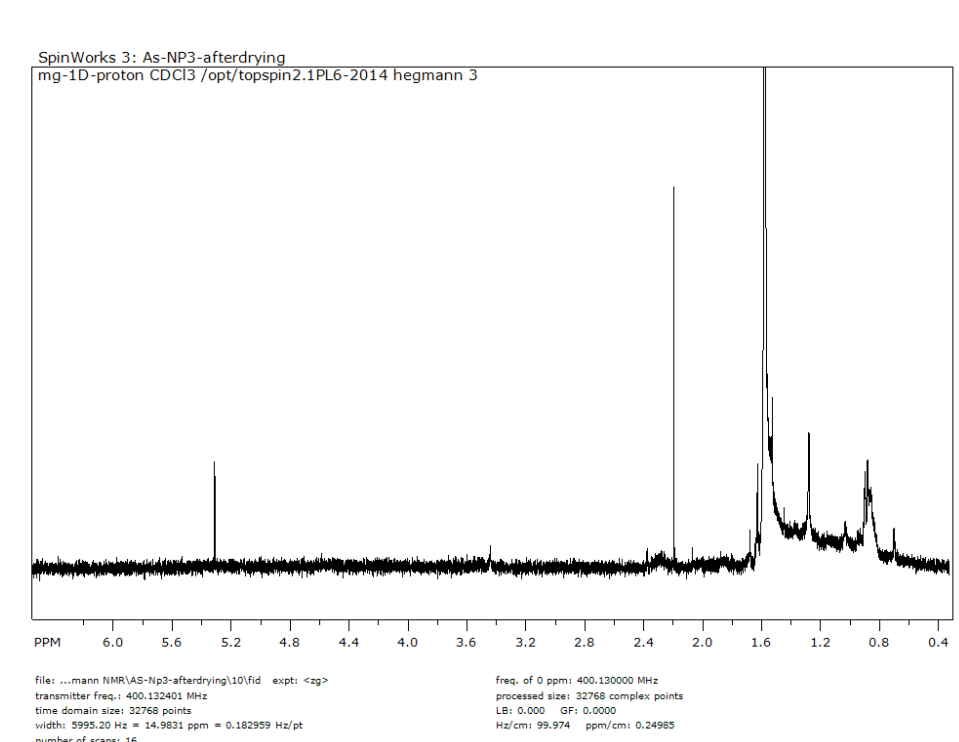


Figure A11. ¹H NMR spectrum of NP₃.