

**Tuning Optical Properties of Gold Nanoparticles via Photoactive Liquid
Crystalline Azo Ligands**

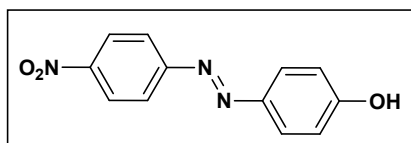
Sachin Ashok Bhat,^a D. S. Shankar Rao,^a S. Krishna Prasad,^a Channabasaveshwar. V. Yelamggad^{a*}

Email: Yelamaggad@cens.res.in

^a*Centre for Nano and Soft Matter Sciences, Bengaluru-560013, India.*

Synthesis and characterization of (E)-4-((4-nitrophenyl)diazenyl)phenol (1.2)

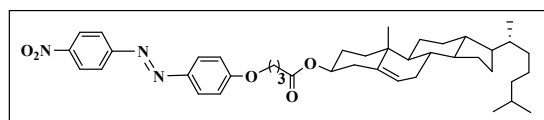
4-nitroaniline (1 eq) was dissolved in 30 ml of distilled water and 5% hydrochloric acid (5 ml) was added to that dropwise. The solution was cooled to -5°C and sodium nitrate (200 mg) solution was added slowly and the mixture was stirred rapidly. Phenol (1.2 eq) was taken in 20 ml alkaline solution (2% NaOH) to which the diazotized solution was added dropwise and stirred vigorously until a thick solid precipitate separates. The reaction mixture was neutralized with the help of dil. Hydrochloric acid and extracted with DCM repeatedly and washed with water and dried on Na_2SO_4 . The crude product obtained was purified using column chromatography using 60-120 silica mesh and DCM:Hexanes mixture as the eluant.



$R_f = 0.52$ in DCM; a reddish yellow solid; yield: 75%; IR (KBr Pellet): ν_{max} in cm^{-1} : 3521, 2945, 1620, 1463, 1348, 1250, 1130, 1003, 848; $^1\text{H NMR}$ (400MHz, CDCl_3): δ 8.42 (d, $J = 8$ Hz, 2H, Ar), 7.90 (d, 2H, $J = 8$ Hz, Ar), 7.62 (d, $J = 8$ Hz, 2H, Ar), 7.01 (d, $J = 8$ Hz, 2H, Ar); Anal. calcd for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_3$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.68; H, 4.10; N, 17.01.

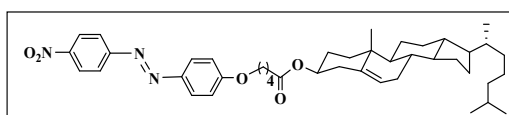
Synthesis and characterization of Cholesteryl (4-((E)-(4-nitrophenyl)diazenyl)phenoxy)alkanoate (1.3a-c)

A mixture of cholesteryl ω -bromoalkanoates (**1.1a-c**) (1 equiv.), (E)-4-((4-nitrophenyl)diazenyl)phenol (1.2 equiv.) and anhyd. K_2CO_3 (1.5 equiv.) in dry DMF (20 ml) was degassed and stirred at 85°C for 12 h under nitrogen atmosphere. The hot reaction mixture was filtered through celite bed and the filtrate was concentrated and poured into water. The solid separated was collected by filtration. It was purified by recrystallization from CH_2Cl_2 -ethanol (1:9) to yield yellow solid. (Yield: 82% - 85%)



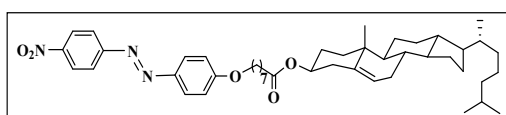
1.3a: Cholesteryl (4-((E)-(4-nitrophenyl)diazenyl)phenoxy)butanoate: $R_f = 0.78$ in 30% CH_2Cl_2 : Hexanes; a yellow solid; yield: 82 %; IR (KBr Pellet): ν_{max} in cm^{-1} : 3430, 2930, 1728, 1601, 1522, 1459, 1339, 1253,

1139, 1027; ^1H NMR (400MHz, CDCl_3): δ 8.37 (d, $J = 8$ Hz, 2H,Ar),7.99-7.95 (m, 4H, Ar), 7.03 (d, $J = 4$ Hz, 2H,Ar), 5.38 (brd, $J = 3.6$ Hz, 1H, 1 \times olefinic), 4.65-4.61 (m, 1H, 1 \times CHOCO), 4.14 (t, 2H, $J=6.0$ Hz, 1 \times OCH_2), 2.31 (m, 4H, 2 \times allylic CH_2 , $-\text{COOCH}$) and 2.17-0.67 (m, 41H, 6 \times CH, 10 \times CH_2 , 5 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): 172.4, 162.6, 156.1, 148.3, 146.9, 139.6, 125.6, 124.7, 123.1, 122.8, 114.9, 67.3, 56.7, 56.2, 50.1, 39.5, 35.8, 31.9, 31.8, 28.3, 28.0, 23.9, 22.8, 22.6, 19.3, 18.8, 11.9; Anal. calcd for $\text{C}_{42}\text{H}_{57}\text{N}_3\text{O}_5$: C, 73.76; H, 8.40; N, 6.14. Found: C, 73.43; H, 8.17; N,6.02.



1.3b:Cholesteryl (4-((E)-(4-nitrophenyl)diazenyl)phenoxy)pentanoate: $R_f = 0.77$ in 30% CH_2Cl_2 : Hexanes; a white solid; yield: 83

% ; IR (KBr Pellet): ν_{max} in cm^{-1} : 3447, 2932, 2860, 1728, 1601, 1463, 1347, 1253, 1170, 1018; ^1H NMR (400MHz, CDCl_3): δ 8.37 (d, $J = 8$ Hz, 2H,Ar),7.99 – 7.95 (m, 4H, Ar), 7.03 (d, $J = 8$ Hz, 2H,Ar), 5.38 (brd, $J = 3.6$ Hz, 1H, 1 \times olefinic), 4.63-4.62 (m, 1H, 1 \times CHOCO), 4.10 (t, 2H, $J=6.0$ Hz, 1 \times OCH_2), 2.40-2.30 (m, 4H, 2 \times allylic CH_2 , $-\text{COOCH}$) and 1.98-0.67 (m, 43H, 6 \times CH, 11 \times CH_2 , 5 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): 172.5, 162.7, 156.1, 148.3, 147.0, 139.7, 125.7, 124.8, 123.2, 122.8, 115.0, 67.4, 56.8, 56.2, 50.1, 39.6, 35.9, 31.9, 28.3, 28.1, 23.9, 22.9, 22.6, 19.4, 18.8, 11.9; Anal. calcd for $\text{C}_{43}\text{H}_{59}\text{N}_3\text{O}_5$: C, 74.00; H, 8.52; N, 6.02. Found: C, 74.32; H, 8.84; N, 6.18.

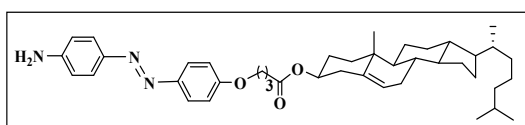


1.3c: Cholesteryl (4-((E)-(4-nitrophenyl)diazenyl)phenoxy)octanoate: $R_f = 0.77$ in 30% CH_2Cl_2 : Hexanes; a yellow solid; yield: 85

% ; IR (KBr Pellet): ν_{max} in cm^{-1} : 3445, 2937, 1733, 1601, 1522, 1465, 1342, 1257, 1140, 1106, 1003; ^1H NMR (400MHz, CDCl_3): δ 8.37 (d, $J = 8$ Hz, 2H, Ar), 7.99 (m, 4H, Ar), 7.03 (d, $J = 8$ Hz, 2H, Ar) 5.37 (brd, $J = 4$ Hz, 1H, 1 \times olefinic), 4.63-4.61 (m, 1H, 1 \times CHOCO), 4.08 (t, $J = 6$ Hz, 2H, 1 \times OCH_2), and 2.32-0.67 (m, 53H, 6 \times CH, 16 \times CH_2 , 5 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): 173.0, 162.8, 156.1, 148.3, 146.9, 139.6, 125.6, 124.7, 123.1, 122.7, 114.9, 68.2, 56.7, 56.2, 50.1, 39.6, 35.8, 31.9, 31.9, 28.2, 28.0, 23.9, 22.8, 22.5, 19.3, 18.7, 11.8; Anal. calcd for $\text{C}_{46}\text{H}_{65}\text{N}_3\text{O}_5$: C, 74.66; H, 8.85, N, 5.68. Found: C, 74.16; H, 8.51, N, 5.42.

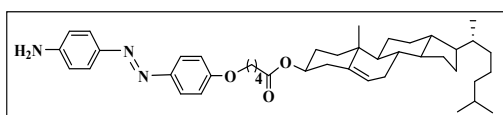
Synthesis and characterization of cholesteryl (4-((E)-(4-aminophenyl)diazenyl)phenoxy)alkanoate (*An-LCL*):

A mixture of cholesteryl (4-((E)-(4-nitrophenyl)diazenyl)phenoxy)alkanoate (**1.3a-c**) (1 equiv.) was dissolved in tetrahydrofuran (THF). To this mixture an aqueous solution of Sodium hydrogen sulfate (NaHS) (3 equiv) was added. The reaction mixture was refluxed under N₂ environment for 24 hrs. The reaction mixture was cooled, solvent was evaporated and the mixture was added to water. Further it was extracted with DCM and washed with water and dried over anhydrous Na₂SO₄. Solvent was evaporated and crude compound was purified using basic alumina column chromatography with dichloromethane (DCM) as eluant. (yield: 87% - 92%)



A3-LCL: Cholesteryl (4-((E)-(4-aminophenyl)diazenyl)phenoxy)butanoate: $R_f = 0.45$ in 30% CH₂Cl₂ : Hexanes; a yellow solid;

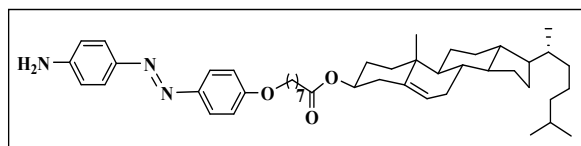
yield: 87 %; IR (KBr Pellet): ν_{\max} in cm⁻¹; 3447, 3356, 2932, 1707, 1608, 1498, 1463, 1251, 1150, 1015; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, $J = 8$ Hz, 2H, Ar), 7.77 (d, $J = 8$ Hz, 2H, Ar), 6.97 (d, 2H, $J = 8$ Hz, Ar), 6.74 (d, 2H, $J = 8$ Hz, Ar), 5.37 (brs, 1H, 1 \times olefinic), 4.63 - 4.60 (m, 1H, 1 \times CHOCO), 4.04-3.98 (m, 2H, 1 \times OCH₂), 2.34 - 2.30 (m, 4H, 1 \times allylic CH₂, -COOCH), 2.01-0.68 (m, 41H, 6 \times CH, 10 \times CH₂, 5 \times CH₃); ¹³C NMR (100 MHz, CDCl₃): 172.8, 152.1, 140.1, 139.7, 122.7, 116.4, 115.7, 67.5, 56.7, 56.1, 50.0, 39.5, 36.2, 35.8, 31.9, 31.3, 28.3, 28.1, 24.9, 23.9, 22.9, 22.6, 19.4, 18.7, 11.9; Anal. calcd for C₄₂H₅₉N₃O₃: C, 77.14; H, 9.09; N, 6.43. Found: C, 77.63; H, 9.23; N, 6.60.



A4-LCL: Cholesteryl (4-((E)-(4-aminophenyl)diazenyl)phenoxy)pentanoate: $R_f = 0.51$ in 30% CH₂Cl₂ : Hexanes; a yellow solid;

yield: 92 %; IR (KBr Pellet): ν_{\max} in cm⁻¹: 3449, 3360, 2930, 2863, 1705, 1601, 1501, 1465, 1378, 1258, 1151, 1020; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, $J = 8$ Hz, 2H, Ar), 7.77 (d, $J = 8$ Hz, 2H, Ar), 6.97 (d, 2H, $J = 4$ Hz, Ar), 6.74 (d, 2H, $J = 4$ Hz, Ar), 5.37 (brs, 1H, 1 \times olefinic), 4.62-4.61 (m, 1H, 1 \times CHOCO), 4.03-4.01 (m, 2H, 1 \times OCH₂), 2.32-2.27 (m, 4H, allylic CH₂, -COOCH), 2.01-0.67 (m, 43H, 6 \times CH, 11 \times CH₂, 5 \times CH₃); ¹³C NMR (100

MHz, CDCl₃): 173.3, 152.2, 139.9, 139.7, 122.6, 116.4, 115.7, 68.3, 56.7, 56.4, 56.3, 54.2, 50.0, 42.3, 39.5, 35.8, 35.5, 29.1, 28.1, 25.7, 22.9, 22.6, 19.4, 18.7, 18.7, 12.3, 12.1, 11.9; Anal. calcd for C₄₃H₆₁N₃O₃: C, 77.32; H, 9.21; N, 6.29. Found: C, 77.60, H, 9.42; N, 6.47.



A7-LCL: Cholesteryl (4-((E)-(4-aminophenyl)diazenyl)phenoxy)octanoate: R_f = 0.48 in 30% CH₂Cl₂ : Hexanes; a yellow

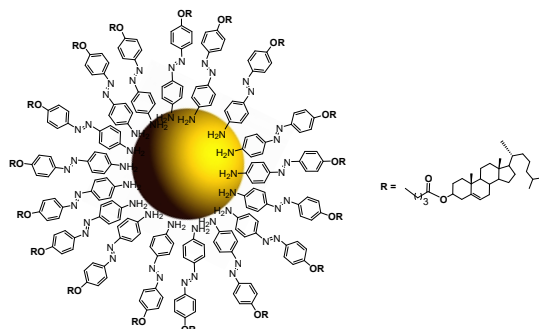
solid; yield: 90 %; IR (KBr Pellet): ν_{\max} in cm⁻¹: 3481, 3374, 2936, 2863, 1723, 1632, 1598, 1501, 1466, 1381, 1253, 1174, 1142, 1107; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 8 Hz, 2H, Ar), 7.77 (d, J = 8 Hz, 2H, Ar), 6.97 (d, J = 4 Hz, 2H, Ar), 6.74 (d, J = 4 Hz, 2H, Ar), 5.37 (brs, 1H, 1 \times olefinic), 4.62-4.61 (m, 1H, 1 \times CHOCO), 4.03-3.98 (m, 2H, 1 \times OCH₂), 2.32-0.67 (m, 53H, 6 \times CH, 16 \times CH₂, 5 \times CH₃); ¹³C NMR (100 MHz, CDCl₃): 172.2, 159.7, 147.9, 146.1, 140.7, 138.7, 123.6, 123.0, 121.5, 113.7, 113.6, 72.7, 67.1, 55.6, 55.1, 49.0, 41.3, 38.5, 35.6, 34.7, 30.8, 27.9, 27.2, 27.0, 24.8, 22.8, 21.80, 21.5, 18.3, 17.7, 10.8; Anal. calcd for C₄₆H₆₇N₃O₃: C, 77.81; H, 9.51; N, 5.92. Found: C, 77.43, H, 9.78; N, 6.23.

Preparation and characterization of liquid crystal-gold nanoparticles (*An*-LCNPs)

To dichloromethane (DCM) (~ 15 ml) placed in a sample bottle, an aqueous solution of hydrogen tetrachloroaurate(III) (HAuCl₄.3H₂O) (10.2 mg, 30 μ mol) dissolved in deionized water (~ 8 ml) at room temperature (RT) was added; the top aqueous phase of the liquid bilayer appears pale-yellow due to the presence of Au(III) ions. To the resultant liquid bilayer was added a solution of tetraoctylammonium bromide (TOAB) (27.3 mg, 50 μ mol) dissolved a minimum quantity DCM and the mixture was hand-swirled vigorously; here, the organic phase (DCM) gains intense yellow colour owing to the presence of Au(III) ions. To a well-settled liquid bilayer, a solution of chosen liquid crystal ligand (**A3-LCL**, Qty. 110.2 mg; or **A4-LCL**, Qty. 113.7 mg, or **A7-LCL**, Qty. 120.4 mg) (180 μ mol, 6 equivalent) dissolved in minimum quantity of DCM was slowly added drop-wise while hand-swirling; after completion of addition the mixture was continued to hand-swirl for a while; the colour of organic layer appears to be deep-red implying the instant interaction between the ALC and GNPs resulting into the formation of *An*-LCNPs. The bilayer was allowed to settle and the organic layer separated and collected was thoroughly washed with deionized water repeatedly. The solvent was evaporated under high vacuum and the dark-greenish mass

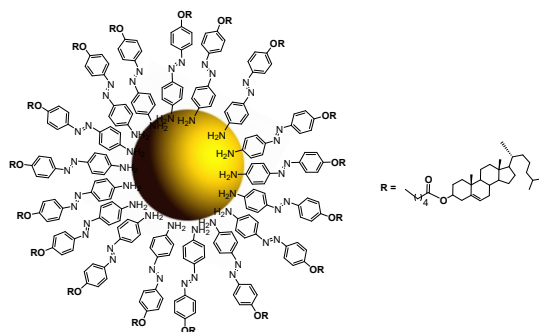
obtained was dissolved in hot ethanol and reprecipitated and collected via centrifugation. (Yield: 28% - 35%)

A3-LCNP: **GNPs** coated withcholesteryl (4-((E)-(4-aminophenyl)diazenyl)phenoxy)butanoate



Reddish black solid; yield: 35 %; IR (KBr Pellet): ν_{\max} in cm^{-1} : 3442, 2936, 2862, 1732, 1600, 1500, 1465, 1374, 1256, 1176, 1107, 1053; ^1H NMR (400 MHz, CDCl_3): δ 8.21-7.80 (m, 4H, Ar), 6.89 - 6.62 (m, 4H, Ar), 5.36 (brs, 1H, 1 \times olefinic), 4.62 (m, 1H, 1 \times CHOCO), 4.13-4.01 (m, 2H, 1 \times OCH_2), 2.52-0.68 (m, 45H, 6 \times CH, 12 \times CH_2 , 5 \times CH_3); ^{13}C NMR (100 MHz, CDCl_3): 172.5, 140.8, 139.5, 129.4, 125.9, 124.0, 122.7, 121.7, 114.7, 114.5, 114.4, 76.7, 71.8, 56.8, 56.7, 56.2, 56.1, 50.1, 50.0, 42.3, 39.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 24.3, 23.8, 22.5, 18.7, 13.7, 11.8; Elemental analysis: Weight %; C, 77.14; H, 9.09; N, 6.43. Found: C, 77.57; H, 9.37; N, 6.60.

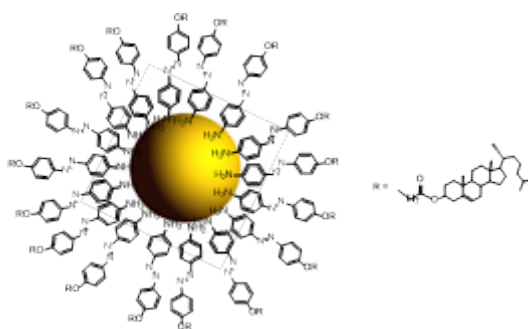
A4-LCNP: **GNPs** coated withcholesteryl (4-((E)-(4-aminophenyl)diazenyl)phenoxy)pentanoate



Reddish black solid; yield: 32 %; IR (KBr Pellet): ν_{\max} in cm^{-1} : 3356, 2950, 2864, 1731, 1674, 1511, 1470, 1479, 1376, 1250, 1172, 1056, 825; ^1H NMR (400 MHz, CDCl_3): δ 7.86-

7.80 (m, 4H, Ar), 6.98-6.93 (m, 4H, Ar), 5.36 (brs, 1H, 1 × olefinic), 4.63-4.61 (m, 1H, 1 × CHOCO), 4.09-4.06 (m, 2H, 1 × OCH₂), 2.75-0.68 (m, 47H, 6 × CH, 13 × CH₂, 5 × CH₃); ¹³C NMR (100 MHz, CDCl₃): 172.8, 140.8, 139.7, 126.0, 125.6, 122.8, 122.7, 122.7, 121.80, 114.7, 114.4, 76.8, 71.8, 59.2, 56.8, 56.7, 56.2, 56.2, 56.1, 50.1, 50.0, 42.3, 42.3, 39.8, 39.79, 37.5, 36.2, 35.8, 31.9, 31.8, 31.7, 28.3, 28.1, 27.8, 24.3, 23.9, 22.9, 22.6, 21.1, 19.4, 19.3, 13.8, 13.7, 11.9, 11.8, 11.7; Elemental analysis: Weight % ;C, 77.14; H, 9.09; N, 6.43. Found: C, 77.63; H, 9.23; N, 6.60.

A7-LCNP: GNPs coated withcholesteryl (4-((aminophenyl)diazenyl)phenoxy)octanoate



Reddish black solid; yield: 30 %; IR (KBr Pellet): ν_{\max} in cm⁻¹: 3448, 2920, 2862, 1728, 1597, 1497, 1250, 1165, 1023, 840; ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.75 (m, 4H, Ar), 6.97-6.73 (m, 4H, Ar), 5.37 (brs, 1H, 1 × olefinic), 4.62-4.61 (m, 1H, 1 × CHOCO), 4.03-4.00 (m, 2H, 1 × OCH₂), 2.32-0.67 (m, 53H, 6 × CH, 16 × CH₂, 5 × CH₃); ¹³C NMR (100 MHz, CDCl₃): 173.3, 160.8, 148.9, 147.1, 145.7, 139.8, 124.7, 124.1, 122.7, 114.8, 114.7, 73.8, 68.2, 56.7, 56.2, 50.1, 42.3, 39.8, 39.6, 38.2, 37.1, 36.3, 35.9, 34.7, 31.9, 29.2, 38.1, 28.3, 28.1, 27.9, 25.0, 24.3, 23.9, 22.9, 22.6, 22.1, 19.4, 18.7, 11.9; Elemental analysis: Weight %;C, 77.81; H, 9.51; N, 5.92. Found: C, 77.43, H, 9.78; N, 6.23.

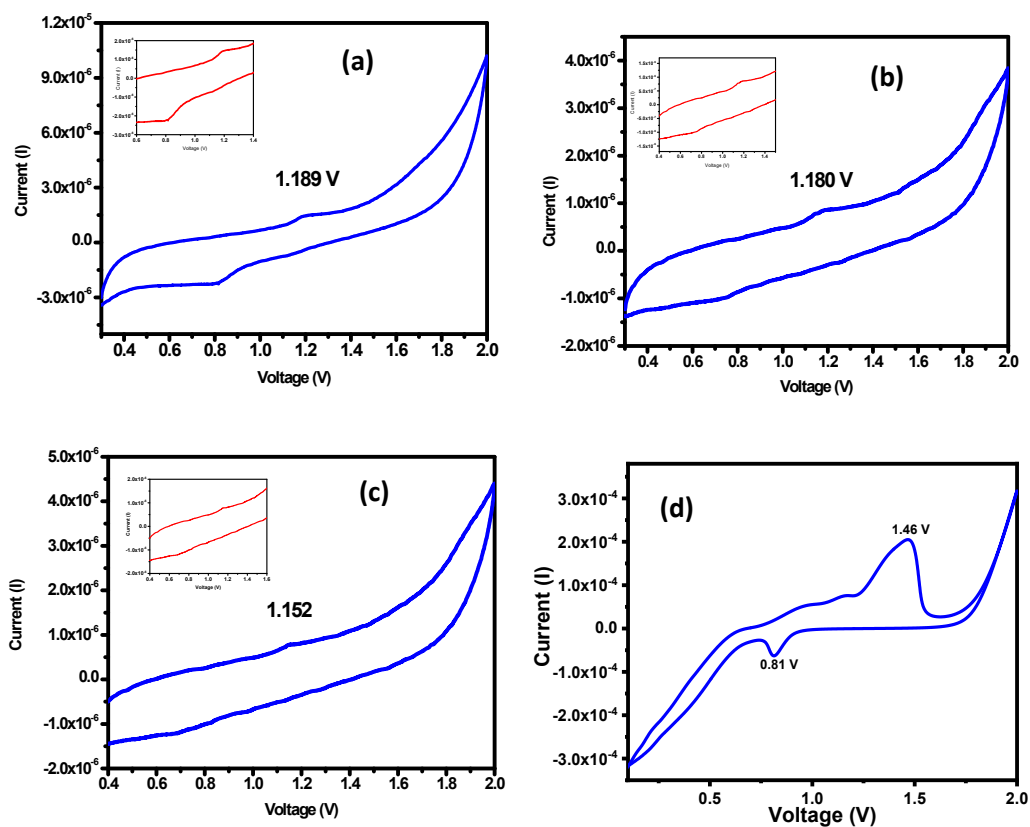


Figure S01. Cyclic voltammograms of azo ligands and H₂AuCl₄: (a) A3-LCL, (b) A4-LCL, (c) A7-LCL (insets show the expanded regions) (*V*/s Ag/AgCl electrodes, in 0.1 M tetrabutyl ammonium hexafluorophosphate electrolyte in acetonitrile), and (d) Aqueous solution of H₂AuCl₄ showing the oxidation and reduction peaks.

Table S01. The oxidation & reduction potentials of HAuCl_4 and **A*n*-LCLs**

Compds.	E_{ox} (Oxidation potential)	E_{red} (Reduction potential)
HAuCl_4	1.47 V [Au(0) to Au(I)]	0.8V [Au(III) to Au(0)]
A3-LCL	1.18 V	-----
A4-LCL	1.18 V	-----
A7-LCL	1.15 V	-----

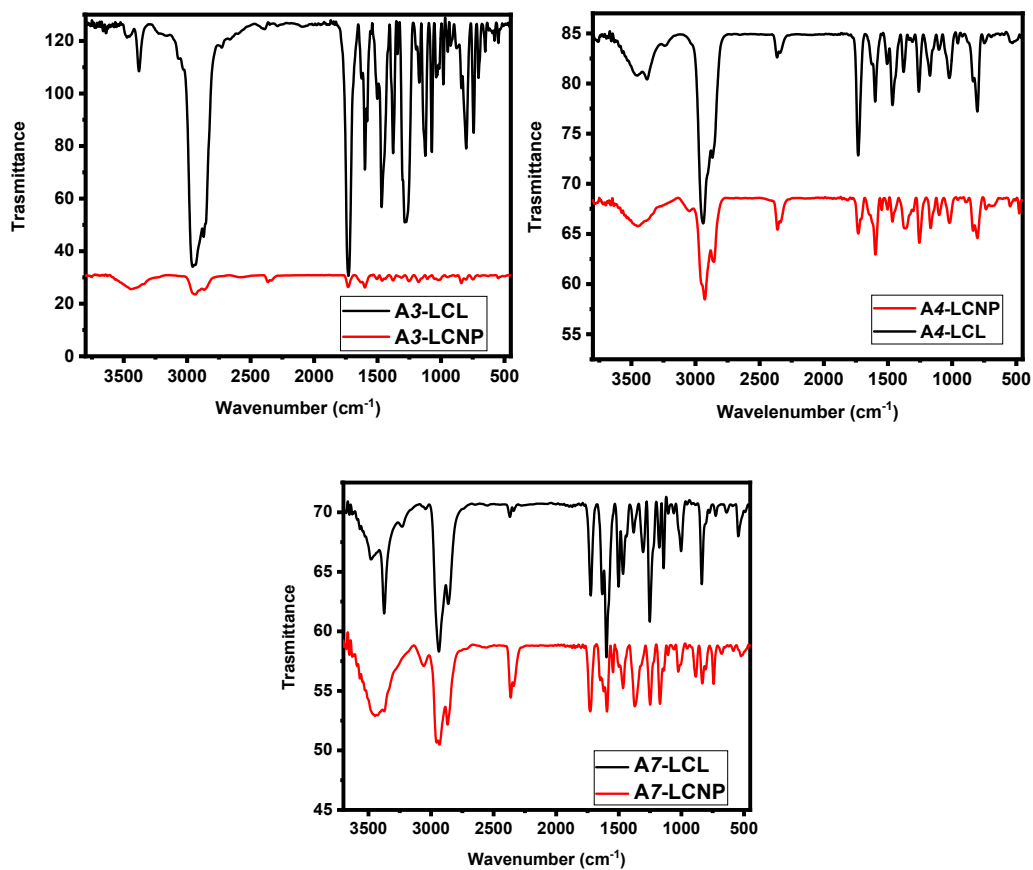


Figure S02. FTIR spectra of drop-coated film (over NaCl cell) of *An*-LCLs (black traces) and *An*-LCNPs (red traces).

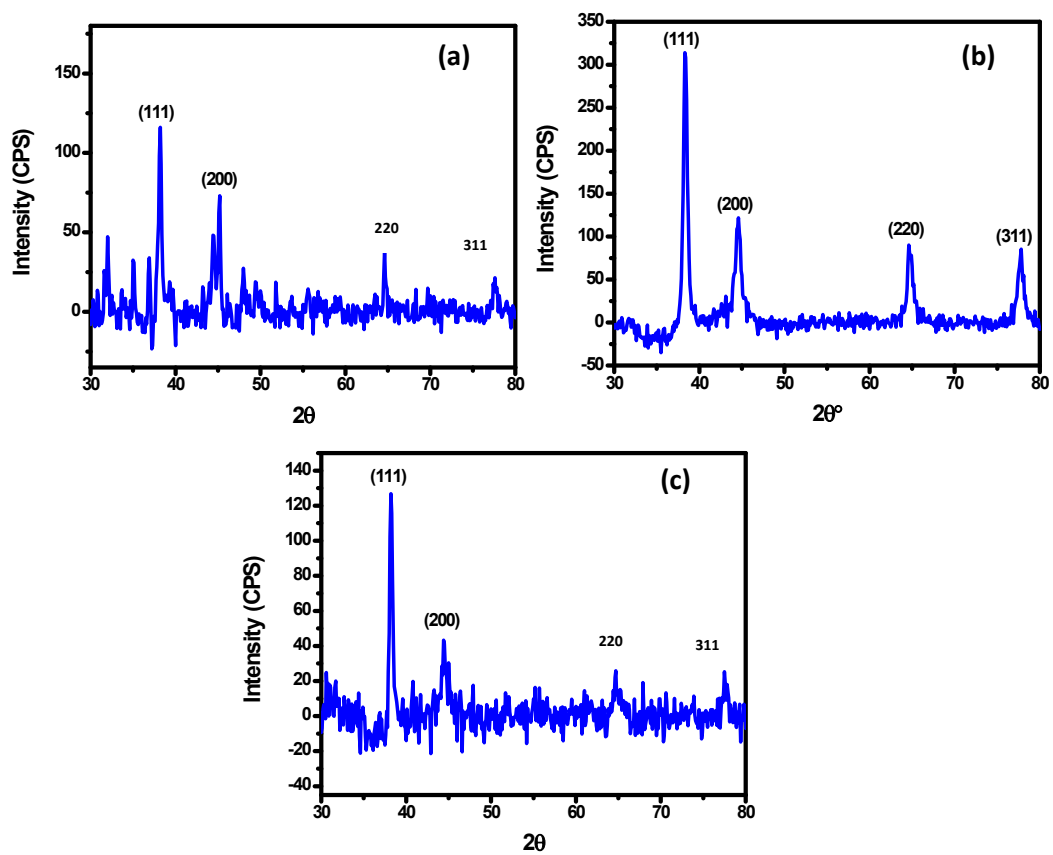


Figure S03. Powder XRD profiles of as-prepared A3-LCNP(a), A4-LCNP(b), and A7-LCNP(c)

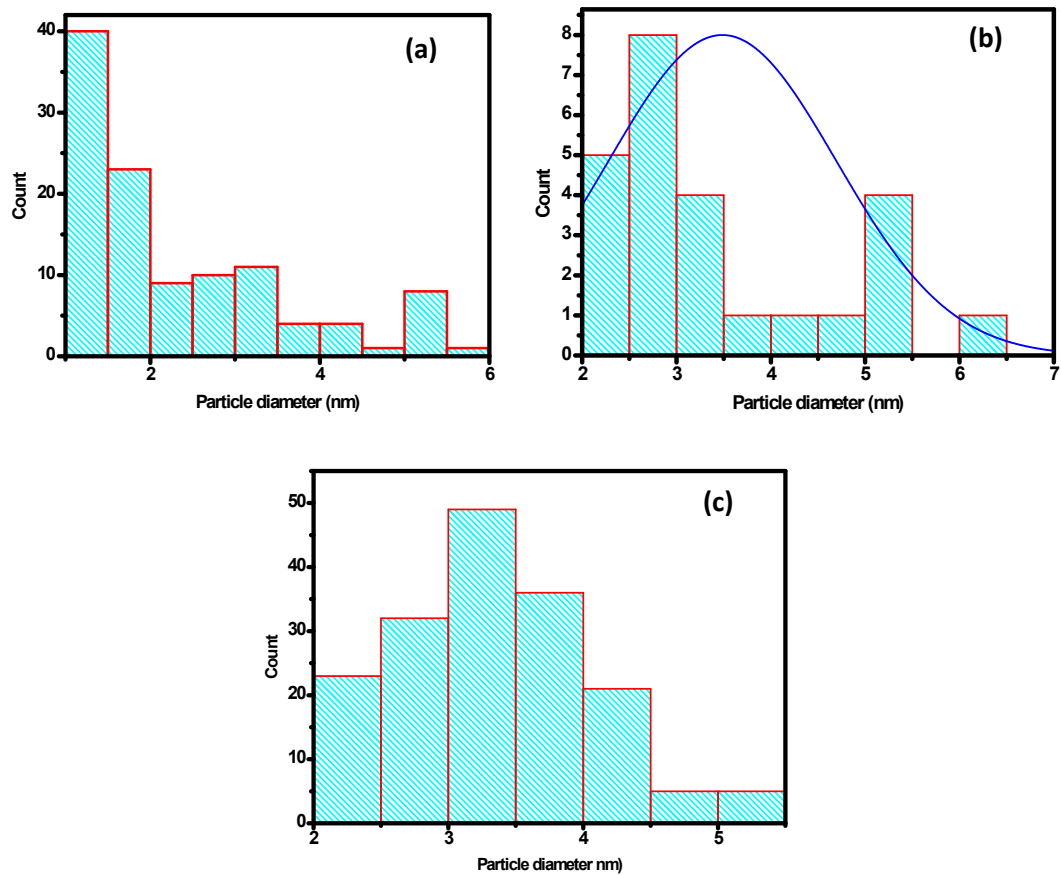


Figure S04. Histograms depicting the size distribution of (a) A3-LCNP, (b) A4-LCNP, and (c) A7-LCNP.

Table S02.The particle size and number of gold atoms in the GNPs

S.No	GNPs	Particle Size (nm)	Total Au atoms	Surface Au atoms
1	A3-LCNP	1.8	137	102
2	A4-LCNP	3.5	1191	428
3	A7-LCNP	3.3	1296	453

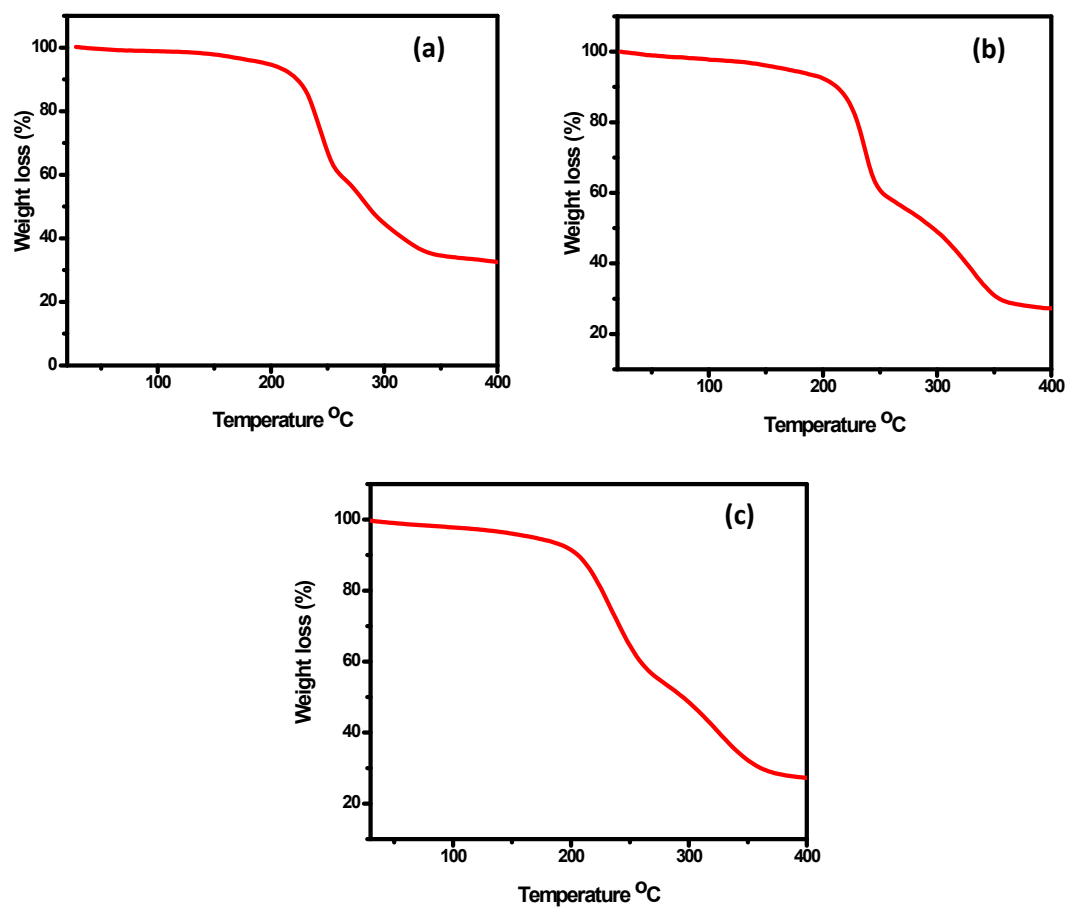


Figure S05. TGA traces of A3-LCNP (a), A4-LCNP (b), and A7-LCNP (c). These traces indicate that the *An*-LCNPs are stable at least up to 220 °C.

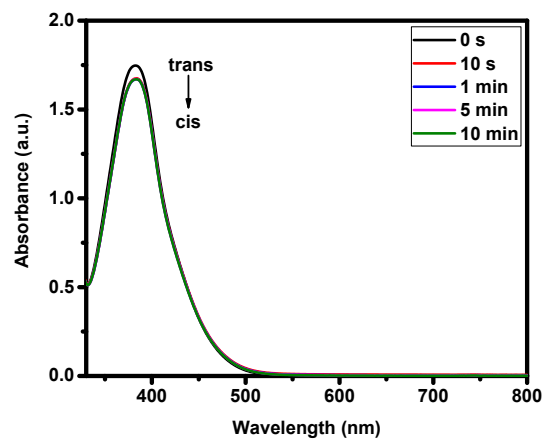


Figure S06. Time-dependent UV-Vis spectra of A7-LCL

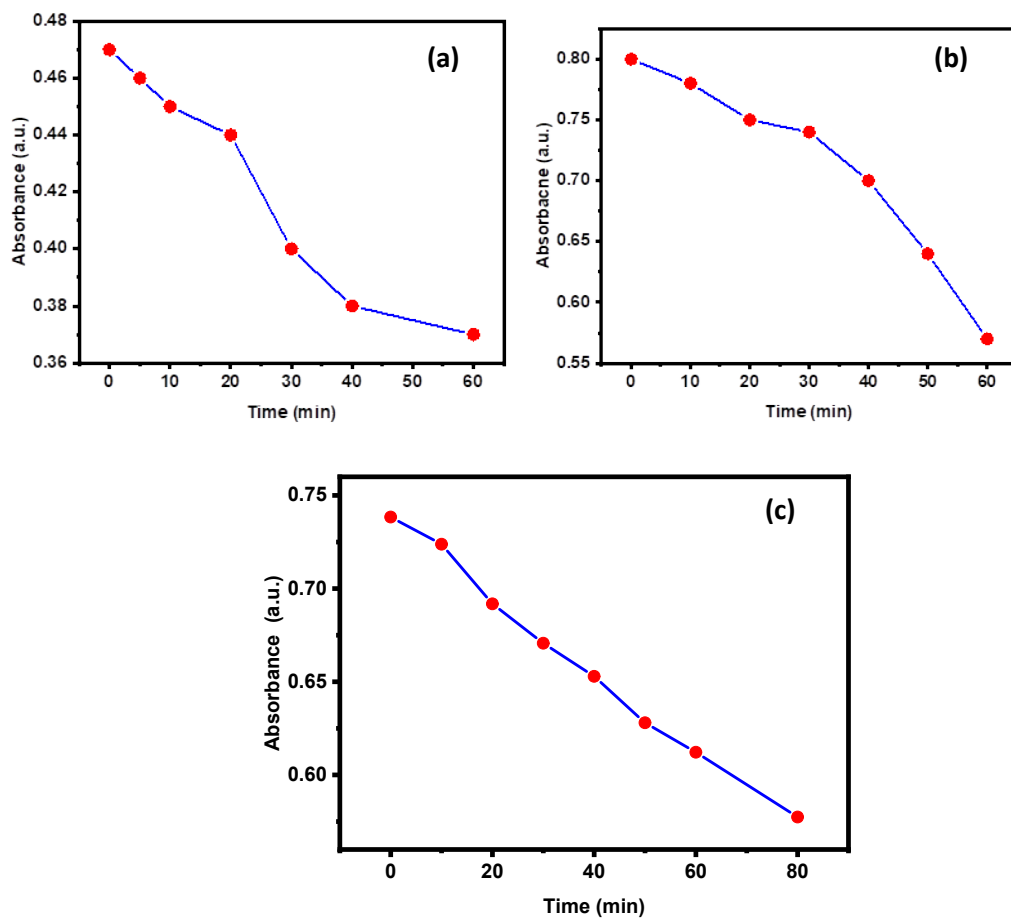


Figure S07. The profiles showing the variation in the absorption peak intensity as a function of exposure time with the light of 365nm. (a) A3-LCNP, (b) A4-LCNP, & (c) A7-LCNP.

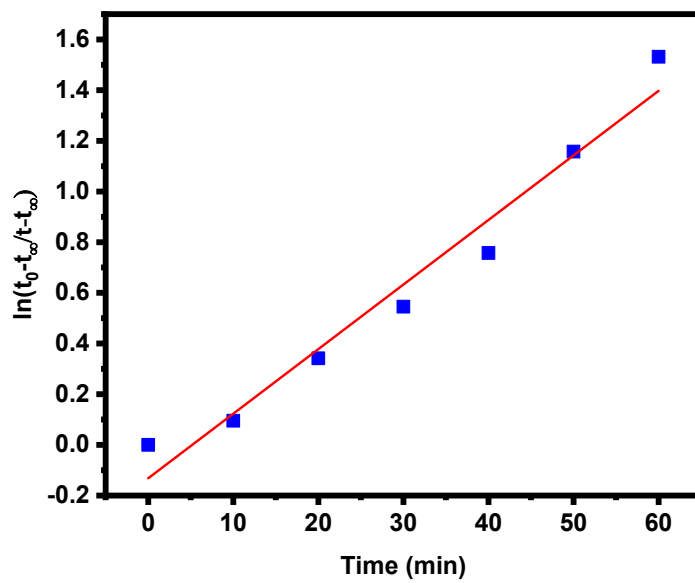


Figure S08: First-order-plots for the effect of *trans-cis* photo isomerization of A7-LCNP

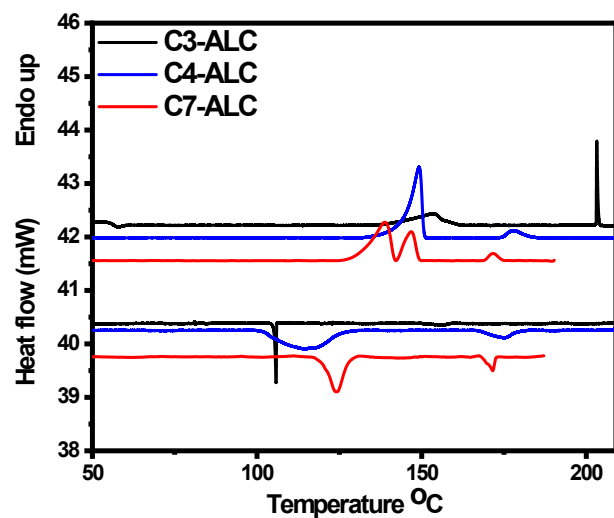


Figure S09. DSC thermograms registered during the first heating-cooling cycles of amine ligands (*An-LCLs*).

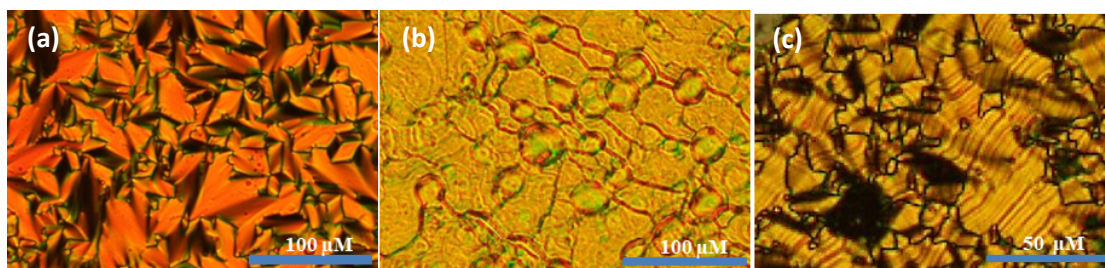


Figure S10. Microphotographs of the textures observed under POM for the mesophases of the ligands; (a) the *pseudofocal conic* texture of the N* phase of A4-LCL(160 °C); (b) the *oily streak* texture observed upon shearing the N* mesophase of the ligand A4-LCL(160 °C); (c) the *focal conic fan* textures with *chiral lines* of SmC* phase observed for A3-LCL(110 °C)

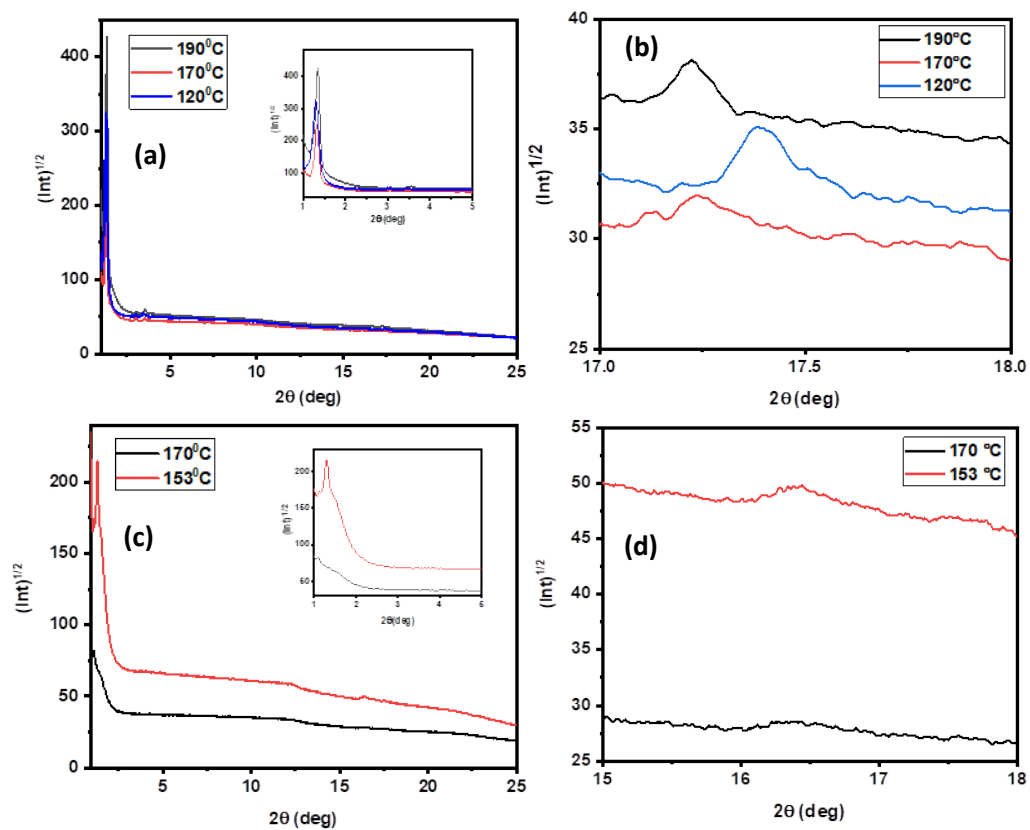


Figure S11: 1D intensity v/s 2θ profiles of the **An-LCNPs** as a function of temperature in the LmX* phase: (a) **A3-LCNP**; (b) **A4-LCNP** and (c) **A7-LCNP**; (d)-(f) show the wide-angle region of the corresponding **An-LCNPs** containing broad peaks.

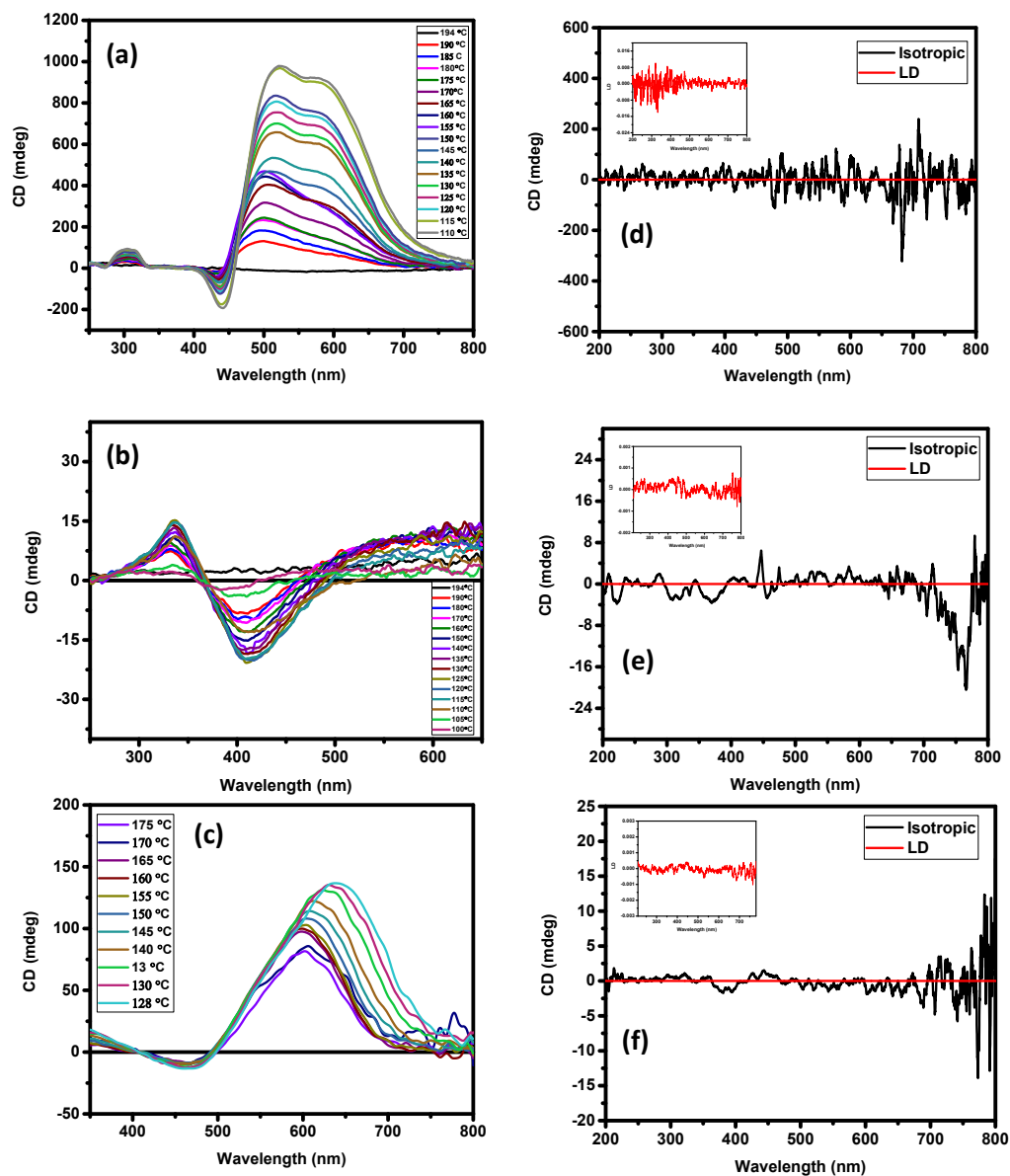


Figure S12. The CD spectra obtained as a function of temperature for the N* phase; (a) A3-LCL, (b) A4-LCL, & (c) A7-LCL. LD (red trace) and CD (black trace) spectra recorded, respectively, in the N* phase and isotropic phase of the samples (d–f).

Table S03. Temperature-dependent CD data for the N* phase of **An-LCLs**

Dimer	Phase	Temperature (°C)	CD	
			λ_{max} (nm)	CD (mdeg)
A3-LCL	N*	190	499, 431	131.2, -16.6
		185	497, 432	182.5, -17.3
		180	501, 431	232.4, -25.4
		175	500, 432	244.5, -26.7
		170	502, 433	317.0, -41.08
		165	508, 432	403.9, -42.4
		160	502, 433	443.4, -43.7
		155	501, 431	462.3, -45.5
		150	512, 436	467.3, -65.7
		145	516, 436	534.0, -69.9
		140	519, 437	657.9, -86.0
		135	518, 436	700.5, -93.6
		130	520, 438	754.5, -101.9
		125	519, 436	806.3, -111.0
		120	519, 439	834.5, -123.7
115	523, 440	968.5, -174.5		
110	523, 440	978.9, -192.9		
A4-LCL	N*	180	406, 331	-8.1, 7.4
		170	402, 332	-9.5, 7.9
		160	410, 332	-10.5, 8.7
		150	410, 331	-12.9, 9.5
		140	410, 335	-13.1, 10.9
		135	409, 336	-15.1, 12.2
		130	413, 335	-16.9, 13.3
		125	414, 335	-18.1, 13.9
		120	414, 337	-18.4, 14.6
		115	413, 338	-19.5, 14.8
110	444, 335	-20.1, 15.2		
A7-LCL	N*	175	603, 445	81.6, -8.5
		170	606, 444	85.8, -8.8
		165	598, 446	97.5, -9.7
		160	599, 445	99.9, -9.9
		155	605, 445	102.7, -10.3
		150	607, 440	107.8, -10.5
		145	608, 441	114.1, -11.3
		140	613, 445	122.2, -12.4
		132	625, 445	130.8, -12.8
		130	632, 440	135.0, -13.0
		128	640, 440	136.6, -13.2

Table S04. Temperature-dependent CD data for the LmX* phase of **A_n-LCNPs**

Dimer	Phase	Temperature (°C)	CD	
			λ_{\max} (nm)	CD (mdeg)
A3-LCNP	LmX*	160	590	970.6
		140	582	1010.7
		120	587	1014.0
		100	580	1134.7
		80	550	1216.0
		60	568	1355.4
		RT	556	1398.4
A4-LCNP	LmX*	180	641, 514	-39.5, 7.5
		170	641, 521	-63.0, 12.6
		160	636, 522	-80.5, 16.6
		140	637, 522	-110.9, 28.1
		130	640, 523	-118.1, 31.2
		120	639, 526	-127.7, 36.8
		115	639, 527	-131.4, 38.2
		100	637, 533	-211.8, 61.4
		95	635, 532	-268.5, 80.29
		90	635, 536	-290.3, 84.3
		85	635, 537	-310.9, 87.1
		80	534, 537	-323.6, 90.5
		RT	635, 535	-328.4, 87.1
A7-LCNP	LmX*	180	624, 477	-45.0, 34.4
		170	619, 471	-62.4, 34.7
		150	618, 477	-82.4, 35.3
		140	618, 474	-95.1, 36.8
		110	619, 473	-101.9, 38.5
		90	618, 477	-103.7, 38.7
		RT	617, 475	-112.1, 40.3