Supporting Information

Supramolecular self-assembly of thiol functionalized pentaalkynylbenzene-decorated gold nanoparticles exhibiting a room temperature discotic nematic liquid crystal phase

Monika Gupta,^a Subhransu Sekhar Mohapatra,^b Surajit Dhara^b and Santanu Kumar Pal^{*a}

^{a.} Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector-81, Knowledge City, Manauli-140306, India.

^{b.} School of Physics, University of Hyderabad, Hyderabad-500046, India

*Corresponding author: Tel.: +91-172-2240266; fax: +91-172-2240266; E-mail:

skpal@iisermohali.ac.in ; santanupal.20@gmaill.com

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1. Experimental Section

1.1. Materials and Reagents

Chemicals and solvents were all of AR quality and were used without further purification. Pentabromophenol, 1-ethynyl-4-pentylbenzene, copper iodide, bis(triphenylphosphine) palladium (II) dichloride, triphenylphosphine, triethylamine, dibromohexane, dibromooctane, dibromodecane, dibromododecane, potassium carbonate, potassium iodide, potassium thioacetate, methanol, butanone, dimethylformamide and dichloromethane were all purchased from Sigma–Aldrich (Bangalore, India). Column chromatographic separations were performed on silica gel (60-120, 100-200 & 230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254).

1.2. Synthesis and characterization of target compounds (5a-d)

Synthesis of compound 2 has been described in the earlier reports.²⁶ For the synthesis of compound 3, compound 2 (1 equivalent) was dissolved in DMF followed by the addition of potassium thioacetate (3 equivalents). The reaction mixture was stirred at room-temperature for 8 hours. After completion of reaction, the mixture was poured into water and the organic layer was extracted with dichloromethane. The compound was then purified through column chromatography over silica gel. For the synthesis of compound 4, five-fold sonogashira coupling of compound 3 was carried out following the earlier reported procedures. For the synthesis of thiols 5, compound 4 was dissolved in 1:1 mixture of methanol and dichloromethane. To the above solution, a pinch of potassium carbonate was added. The reaction mixture was stirred at room-temperature for 4-5 hours. The mixture was then poured into water and extracted with dichloromethane. The organic layer was washed with brine & dried over anhydrous sodium sulphate. The dichloromethane was removed by rotary evaporation and the resulting residue was purified by column chromatography over silica gel (230-400) using hexane & ethyl acetate as eluent.

The synthesized compounds **4a-d** and **5a-d** were characterized by ¹H NMR, ¹³C NMR, IR, UV-Vis and mass spectrometry as shown below:

Compound 4a

FT-IR (cm⁻¹): 3079.7, 3031.3, 2958.8, 2929.1, 2857.5, 2206.1, 1690.7, 1606.1, 1512.4, 1463.7, 1423.9, 1377.2, 1348.0, 1308.1, 1262.0, 1200.0, 1177.0, 1139.0, 1107.9, 1082.8, 1019.4, 961.7, 852.3, 812.9, 728.0, 629.4, 530.2

UV-vis (nm): 236, 263, 338, 380, 418.

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.55 (m, 10H), 7.21 (m, 10H), 4.38 (t, 2H, *J* = 4, 8 Hz), 2.83 (t, 2H, *J* = 8, 4 Hz), 2.66 (m, 10H), 2.34 (s, 3H), 1.94 (p, 2H, *J* = 8, 8, 8, 4 Hz), 1.64 (m, 14H), 1.42 (m, 24H), 0.94 (m, 15H).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 196.00, 160.16, 144.05, 143.97, 143.74, 131.79, 131.67, 131.58, 128.77, 128.60, 124.13, 120.69, 120.46, 120.09, 99.58, 99.39, 97.35, 87.07, 86.59, 84.04, 74.51, 36.00, 31.52, 30.99, 30.66, 30.45, 29.49, 29.12, 28.80, 25.96, 22.58, 14.08.

MS (MALDI): *m*/*z* for C₇₉H₉₀O₂S 1102.6662; found 1102.7709.

Compound 4b

FT-IR (cm⁻¹): 3029.6, 2929.1, 2856.9, 2206.5, 1692.9, 1606.2, 1512.3, 1463.7, 1423.6, 1377.6, 1348.2, 1301.2, 1262.7, 1200.6, 1179.1, 1134.6, 1111.7, 1082.8, 1019.4, 957.3, 845.8, 814.4, 729.8, 627.8, 530.6.

UV-vis (nm): 236, 263, 338, 381, 418.

¹H NMR (400 MHz, CDCl₃, *δ* in ppm): 7.56 (m, 10H), 7.20 (m, 10H), 4.38 (t, 2H, *J* = 4, 8 Hz), 2.85 (t, 2H, *J* = 8 Hz), 2.66 (m, 10H), 2.34 (s, 3H), 1.94 (p, 2H, *J* = 4, 8, 8, 8 Hz), 1.66 (p, 12H, *J* = 8, 8, 4, 8 Hz), 1.54 (p, 2H, J = 4, 8, 8, 8 Hz), 1.35 (m, 26H), 0.93 (t, 15H, J = 8, 4 Hz).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 196.07, 160.22, 144.04, 143.94, 143.73, 131.78, 131.67, 131.59, 128.75, 128.56, 124.08, 120.69, 120.51, 120.10, 99.54, 99.38, 97.31, 87.08, 86.60, 84.07, 74.72, 35.99, 31.52, 31.01, 30.98, 30.67, 30.57, 29.17, 29.14, 28.84, 26.32, 22.58, 14.09.

MS (MALDI): *m*/*z* for C₈₁H₉₄O₂S 1130.6975; found 1130.7202.

Compound 4c

FT-IR (cm⁻¹): 3083.1, 3026.9, 2958.8, 2928.4, 2856.0, 2207.8, 1693.2, 1601.7, 1512.2, 1463.8, 1424.6, 1380.7, 1348.2, 1262.4, 1202.6, 1180.4, 1134.0, 1084.5, 1019.7, 965.8, 837.9, 817.7, 731.4, 626.6, 550.8, 534.6.

UV-vis (nm): 236, 260, 338, 382, 419.

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.54 (m, 10H), 7.20 (t, 10H, *J* = 8 Hz), 4.38 (t, 2H, J = 4, 8 Hz), 2.87 (t, 2H, *J* = 8 Hz), 2.65 (t, 10H, *J* = 8, 4 Hz), 2.34 (s, 3H), 1.94 (p, 2H, J = 4, 8, 8, 4 Hz), 1.66 (m, 12H), 1.54 (m, 2H), 1.31 (m, 28H), 0.93 (t, 15H, J = 8 Hz).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 196.12, 166.66, 144.03, 143.92, 131.78, 131.66, 131.60, 128.74, 128.56, 124.06, 120.46, 120.11, 99.53, 87.07, 84.07, 74.79, 35.99, 31.50, 31.01, 30.66, 29.53, 29.49, 29.19, 28.87, 26.36, 22.58, 14.08.

MS (MALDI): *m*/*z* for C₈₃H₉₈O₂S 1158.7288; found 1158.7325.

Compound 4d

FT-IR (cm⁻¹): 3027.0, 2958.8, 2928.0, 2855.6, 2207.8, 1693.6, 1608.6, 1512.3, 1463.7, 1424.6, 1377.2, 1348.5, 1261.7, 1202.6, 1177.0, 1134.0, 1107.9, 1085.6, 1019.8, 954.3, 837.9, 724.5, 626.6, 531.6.

UV-vis (nm): 236, 263, 338, 381, 419.

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.56 (m, 10H), 7.21 (m, 10H), 4.39 (t, 2H, J = 4, 8 Hz), 2.88 (t, 2H, J = 8, 4 Hz), 2.66 (t, 10H, J = 8 Hz), 2.34 (s, 3H), 1.95 (p, 2H, J = 4, 8, 8, 8 Hz), 1.63 (m, 14H), 1.33 (m, 30H), 0.94 (t, 15H, J = 4, 8 Hz).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 196.12, 160.26, 144.03, 143.91, 131.79, 131.67, 131.61, 128.74, 128.57, 128.55, 124.08, 120.71, 120.54, 120.13, 99.53, 99.38, 97.31, 87.10, 86.62, 84.10, 74.81, 36.01, 31.52, 31.01, 30.98, 29.67, 29.55, 29.20, 28.90, 26.41, 22.59, 140.09.

MS (MALDI): *m*/*z* for C₈₅H₁₀₂O₂S 1186.7601; found 1186.7948.

Compound 5a

FT-IR (cm⁻¹): 3031.3, 2955.4, 2928.6, 2856.9, 2207.8, 1605.1, 1512.4, 1463.5, 1424.9, 1377.2, 1347.2, 1304.7, 1266.7, 1204.5, 1177, 1114.8, 1084.1, 1019.8, 966.2, 838.0, 821.2, 731.4, 552.1, 531.1.

UV-vis (nm): 237, 263, 338, 382, 417.

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.53 (m, 10H), 7.19 (t, 10H, *J* = 8 Hz), 4.37 (t, 2H, *J* = 4, 8 Hz), 2.64 (m, 12H), 1.94 (p, 2H, *J* = 4, 8, 8, 4), 1.65 (m, 14H), 1.49 (q, 2H, *J* = 8 Hz), 1.36 (m, 20H), 0.92 (m, 15H).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 160.14, 143.98, 131.79, 131.67, 131.57, 128.77, 128.58, 128.50, 120.49, 120.08, 99.59, 99.36, 97.32, 87.09, 84.05, 38.97, 35.99, 31.50, 30.96, 29.21, 28.54, 26.09, 22.51, 14.07.

MS (MALDI): *m*/*z* for C₇₇H₈₈OS 1060.6556; found 1060.6500.

Compound 5b

FT-IR (cm⁻¹): 3031.3, 2928.1, 2856.3, 2208.2, 1605.1, 1512.5, 1463.5, 1424.4, 1379.5, 1347.5, 1302.5, 1262.1, 1203.4, 1181.4, 1115.4, 1082.6, 1019.9, 975.9, 837.7, 816.4, 726.5, 551.8, 530.2.

UV-vis (nm): 236, 262, 335, 382, 419.

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.54 (m, 10H), 7.20 (m, 10H), 4.38 (t, 2H, J = 8, 4 Hz), 2.64 (m, 12H), 1.94 (m, 2H), 1.66 (m, 14H), 1.37 (m, 26H), 0.93 (m, 15H).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 162.18, 143.92, 143.69, 131.79, 131.67, 131.59, 128.77, 128.55, 124.09, 120.54, 120.49, 120.10, 99.51, 99.37, 87.11, 86.64, 84.10, 52.62, 39.11, 36.00, 31.50, 30.99, 30.96, 30.61, 29.55, 29.29, 28.59, 26.37, 22.57, 14.07.

MS (MALDI): *m*/*z* for C₇₉H₉₂OS 1088.6869; found 1088.6685.

Compound 5c

FT-IR (cm⁻¹): 3027.0, 2955.1, 2928.0, 2855.7, 2207.9, 1606.5, 1512.4, 1463.7, 1424.2, 1380.7, 1347.4, 1300.6, 1262.8, 1202.8, 1180.4, 1111.3, 1082.9, 1019.7, 968.9, 837.4, 821.2, 728.0, 552.0, 531.1.

UV-vis (nm): 234, 263, 328, 379, 420.

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.53 (m, 10H), 7.19 (t, 10H, *J* = 8, 4 Hz), 4.37 (t, 2H, *J* = 4, 8 Hz), 2.66 (m, 12H), 1.93 (p, 2H, J = 8, 8, 4, 8 Hz), 1.65 (m, 14H), 1.31 (m, 30H), 0.93 (t, 15H, J = 4, 8 Hz).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 160.23, 144.02, 143.91, 131.78, 131.66, 131.60, 128.74, 128.55, 124.07, 120.70, 120.11, 99.52, 87.08, 84.08, 74.78, 39.13, 36.01, 31.50, 31.01, 30.98, 29.64, 26.40, 22.57, 14.08.

MS (MALDI): *m*/*z* for C₈₁H₉₆OS 1116.7182; found 1116.7401.

Compound 5d

FT-IR (cm⁻¹): 3026.8, 2955.2, 2927.6, 2855.3, 2207.8, 1606.5, 1512.3, 1463.7, 1424.6, 1377.2, 1347.2, 1258.1, 1203.0, 1179.5, 1084.1, 1019.9, 978.7, 837.7, 817.7, 721.9, 552.04.

UV-vis (nm): 235, 263, 338, 381, 418.

¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.56 (t, 10H, J = 8 Hz), 7.20 (t, 10H, J = 8, 4 Hz), 4.39 (t, 2H, J = 4, 8 Hz), 2.68 (m, 12H), 1.95 (p, 2H, J = 4, 8, 8, 4), 1.68 (m, 14H), 1.32 (m, 34H), 0.94 (t, 15H, J = 4, 8 Hz).

¹³C NMR (400 MHz, CDCl₃, δ in ppm): 160.26, 144.01, 143.89, 143.71, 132.33, 132.22, 131.79, 131.67, 131.60, 129.09, 128.75, 128.55, 128.52, 124.07, 120.73, 120.55, 120.50, 120.11, 99.53, 99.38, 97.30, 87.12, 86.64, 84.11, 74.79, 39.17, 36.01, 31.50, 30.99, 30.64, 29.69, 29.29, 28.62, 26.42, 26.19, 22.57, 14.08.

MS (MALDI): *m/z* for C₈₃H₁₀₀OS 1144.7495; found 1144.7487.

2. FT-IR spectra:



Fig. S1 Representative FT-IR spectrum of compound 4d. Other Compounds of this series show similar spectra.



Fig. S2 Representative FT-IR spectrum of compound 5c. Other Compounds of this series show similar spectra.

3. NMR Spectra







Fig. S4 ¹³C NMR spectrum of compound 4a



Fig. S5 ¹H NMR spectrum of compound 4b.



Fig. S6 ¹³C NMR spectrum of compound 4b.



Fig. S7 ¹H NMR spectrum of compound 4c.



Fig. S8 ¹³C NMR spectrum of compound 4c.







Fig. S10 ¹³C NMR spectrum of compound 4d



Fig. S11 ¹H NMR spectrum of compound 5a.



Fig. S12 ¹³C NMR spectrum of compound 5a.



Fig. S13 ¹H NMR spectrum of compound 5b.



Fig. S14 ¹³C NMR spectrum of compound 5b.



Fig. S15 ¹H NMR spectrum of compound 5c.



Fig. S16¹³C NMR spectrum of compound 5c.



Fig. S17 ¹H NMR spectrum of compound 5d.



Fig. S18¹³C NMR spectrum of compound 5d.

4. Photo-physical studies



Fig. S19 UV-vis absorption spectra of compound (a) 4b and (b) 5d in solution (5 μ M in dichloromethane).

Table S1 Thermal behavior of the synthesized compounds 4^{a, b}

Compound	Heating Scan	Cooling Scan
4 a	Cr 80.31 (17.95) N _D 87.37 (0.59) I	I 86.28 (1.91) N _D 54.23 (29.06) Cr
4b	Cr 69.45 (8.85) N _D 74.75 (5.47) I	I 73 N _D 50.61 (26.02) Cr
4c	Cr 33.56 (10.56) N _D 52 I	I 38 N _D -9.47 (7.25) Cr
4d	Cr 44.08 (13.26) N _D 53.14 (16.75) I	I 46 N _D -12.55 (3.48) Cr

[a] Phase transition temperatures (peak) in °C and transition enthalpies in kJmol⁻¹ (in parentheses). [b] Phase assignments: Cr = Crystalline, $N_D =$ discotic nematic, I = isotropic.



Fig. S20 DSC thermogram of compound 5d on heating and cooling cycles at the rate of 5 °C/min.



Fig. S21 Optical photomicrograph of compound: **5a** at (a) 60 °C and (b) **5b** at 25 °C respectively (on cooling from isotropic, crossed polarizers, scale bar = $20 \mu m$).



Fig. S22 Optical photomicrograph of compound (a) 4c at 34 °C and (b) 4d at 43 °C (on cooling from isotropic, crossed polarizers).



Fig. S23 DSC thermogram of compound 4b on heating and cooling cycles at the rate of 5 °C/min.



Fig. S24 X-ray diffraction pattern of compounds 4a-d in the nematic phase.

Table S2.	X-ray	reflections	and	corresponding	correlation	lengths	in the	e nematic	phases	of
compound	4a-d .									

Compound	Properties	Small angle peak	Wide angle peak
	d-spacing (Å)	21.00	4.93
4 a	Correlation Length (ξ) (Å)	45.47	8.43
	ξ/d	2.16	1.70
	d-spacing (Å)	21.04	4.94
4b	Correlation Length (ξ) (Å)	43.52	8.83
	ξ/d	2.06	1.78
	d-spacing (Å)	20.70	4.92
4 c	Correlation Length (ξ) (Å)	37.49	8.91
	ξ/d	1.81	1.81
	<i>d</i> -spacing (Å)	20.30	4.94
4d	Correlation Length (ξ) (Å)	29.45	8.96
	ξ/d	1.45	1.81



Fig. S25 The ¹H NMR spectrum of (a) compound 5d and (b) 5d-GNPs.



Fig. S26 The UV-vis spectra of **5d**-GNPs showing characteristic peak at 517 nm for the formation of spherical GNPs.



Fig. S27 DSC thermogram of compound 5d-GNPs on heating and cooling cycles at the rate of 5 $^{\circ}$ C/min.



Fig. S28 TGA curve of **5d**-GNPs. The measurements were performed under a nitrogen atmosphere, with heating and cooling rates of 10 °C/min.

5. Dielectric and Birefringence Studies

For the dielectric and electro-optic measurements the liquid crystal cells were made of two indium-tin-oxide (ITO) coated glass plates with patterned electrodes. These plates were cleaned thoroughly and spin coated with polyimide AL-1254. Subsequently they were cured at 180 °C for 1 hour and rubbed in an antiparallel way. Such cells usually provide planar alignment of the calamitic liquid crystals. However, it gives uniform and homeotropic alignment of the discotic nematic liquid crystal. A typical cell thickness used in the experiment was about 13µm. The empty cell was heated by using a temperature controller (Mettler FP 90) and the sample was filled in the isotropic phase. Birefringence was measured using a phase modulation technique.¹⁻⁴ The sample retardation was measured by using two crossed Glan-Thompson polarizers, Helium-Neon laser ($\lambda = 632.8$ nm), photoelastic modulator (PEM) and a lock-in amplifier.¹⁻⁴ A photodetector collected the light transmitted through the liquid crystal, lock-in amplifier measured the first and second harmonics of the ac signal. Using a function generator (Tektronix-AFG 3102) and voltage amplifier (TEGAM-2350) a sinusoidal voltage of frequency 1 kHz and amplitude up to 23 V was applied. At this high voltage the director was completely reoriented to the homogeneous or planar state. This was further verified by the optical polarising microscope. The birefringence was measured as a function of temperature and voltage. The dielectric constant as a function of voltage was measured using a LCR meter (Agilent, E4980A). All the instruments were interfaced with a computer and a suitable computer program written in Lab View was used to control the experiments.

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