Supporting Information

NIR Light-Directing Self-Organized 3D Photonic Superstructures Loaded with Anisotropic Plasmonic Hybrid Nanorods

Ling Wang, Karla G. Gutierrez-Cuevas, Hari Krishna Bisoyi, Jie Xiang, Gautam Singh, Rafael S. Zola, Satyendra Kumar, Oleg D. Lavrentovich, Augustine Urbas, and Quan Li*

*aLiquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, OH 44242, USA; bDepartment of Physics, Kent State University, Kent, Ohio 44242, United States; cDepartamento de Física, Universidade Tecnológica Federal do Paraná-Apucarana, PR 86812-460, Brazil; and dMaterials and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Dayton, Ohio 45433, United States

*Email: qli1@kent.edu

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1. Experimental materials and methods

All chemicals and solvents were purchased from commercial supplies and used without further purification. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$. $^1$H NMR (400 MHz) spectra were recorded on a Bruker 400 spectrometer and $^{13}$C NMR (200 MHz) spectra were recorded on a Varian 200 spectrometer. Chemical shifts are in $\delta$ units (ppm) with the residual solvent peak. NMR splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (230-400 mesh). Mass spectrum was taken by Mass Spectrometry & Proteomics Facility of Ohio State University. Textures of liquid crystals were observed by using optical polarizing microscope (Leitz or Nikon or Olympus BX51). The Mettler Hotstage (FP82HT) attached with temperature controller (FP90) was used to control the temperature of the sample with thermal stability of $\pm0.1^\circ$C. The continuous-wave 808 nm NIR laser (Ningbo Lasever Inc.) with the power of 2 W was used as the excitation source in our experiment.

For the X-ray diffraction (XRD) measurements, the mesogenic surfactant 5 was filled into a quartz capillary of 1 mm diameter. After that, it was flame sealed. The capillary sample was placed between a pair of rare earth permanent magnets inside the Linkam hot stage equipped with temperature controller (HFSX350-CAP) with temperature stability of $\pm0.1^\circ$C. XRD measurements were carried out by using the Rigaku Screen Machine with microfocus sealed X-ray tube with Copper anode ($\lambda=1.541870\text{Å}$). The diffraction patterns were recorded by using high resolution Mercury 3 CCD detector positioned 76.47 mm away from the capillary sample. The 2D diffraction patterns were analyzed by using FIT2D software after subtracting the background measured with an empty capillary in the sample position or isotropic scattering. The data was calibrated against silver behenate or silicon standards traceable to the National Institute of Standards and Technology.

2. Synthesis and characterizations of mesogenic surfactant 5

The mesogenic surfactant 5 was synthesized according to the procedure in Scheme S1.
Scheme S1. Synthetic route for mesogenic surfactant 5. Reaction conditions: (a) LiAlH₄, THF, reflux; (b) Br(CH₂)₉Br, K₂CO₃, KI, CH₂Cl₂, reflux; (c) PPh₃, DIAD, THF, reflux; (d) KSAc, CHCl₃: DMF, RT and (e) Tetrabutylammonium cyanide, MeOH: CHCl₃, 50 °C.

2.1 Synthesis of 4′-pentyl-biphenyl benzyl alcohol 1

In a one neck 100 mL round bottom flask, 1.050 g (3.91 mmol) of 4′-pentyl--biphenyl carboxylic acid and 60 mL of anhydrous THF were added. The mixture was cooled for 15 minutes with an ice bath. Then, 0.272 g (7.78 mmol) of LiAlH₄ was slowly added in small portions; the reaction mixture was maintained under reflux and continuous stirring for 5 hours in N₂ atmosphere. When the reaction was finished, the mixture was quenched to 0 °C with an ice bath and then methanol was slowly added to decompose the excess of hydride. After the mixture was acidified to pH < 5 with diluted HCl, the organic phase was extracted with diethyl ether for 3 times. The solution was dried with MgSO₄ and the solvent removed by rotate evaporation. The residue obtained was purified through column using dichloromethane as eluent to obtain as white crystals intermediate 1.¹ Yield: 93%, ¹H NMR (CDCl₃, 400 MHz) δ: 0.94 (t, J = 6.95, 3H, CH₃-CH₂-), 1.38 (m, 4H, -CH₂-), 1.45 (m, 2H, -CH₂-CH₂-Ar-), 2.67
(t, J = 7.84 Hz, 2H, -CH$_2$-CH$_2$-Ar), 4.76 (s, 2H, Ar-CH$_2$-OH), 7.24 (m, 2H, Ar-H), 7.44 (m, 2H, Ar-H), 7.53 (m, 2H, Ar-H), 7.61 (m, 2H, Ar-H); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 13.20, 21.73, 30.34, 30.72, 34.74, 64.31, 126.07, 126.31, 126.61, 128.01, 137.27, 138.71, 139.79, 141.37.

2.2 Synthesis of the intermediate 2
In a 100 mL round bottom flask, 2.030 g (0.0184 mol) of hydroquinone was mixed with 5.19 g (0.0181 mol) of 1,9-dibromononane, 2.17 g (0.0157 mol) of potassium carbonate and 13 mg (0.078 mmol) of potassium iodide in 60 mL of acetone. The reaction mixture was stirred and refluxed for 24 hours in N$_2$ atmosphere. After reaction the mixture was filtrated and acetone was removed by rotate evaporation. The remaining solid was dissolved in dichloromethane and filtrated to remove the excess of hydroquinone. The resulting mixture was further concentrated using a rotate evaporator and purified by silica gel column and dichloromethane as eluent. Yield: 23%, $^1$H NMR (CDCl$_3$, 400 MHz) δ: 1.18 (m, 10H), 1.62 (tt, J = 6.72, J = 6.91 Hz, 2H, -CH$_2$-CH$_2$-Br), 1.87 (tt, J = 6.72, J = 7.86, 2H, -CH$_2$-CH$_2$-O-), 3.43 (t, J = 6.83 Hz, 2H, -CH$_2$-CH$_2$-Br), 3.91 (t, J = 6.50 Hz, 2H, -O-CH$_2$-CH$_2$), 4.23 (s, 1H, -OH), 6.60 (m, 4H, Ar-H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 25.14, 27.29, 27.83, 28.40, 28.49, 31.95, 33.21, 67.93, 114.82, 115.17, 148.53, 152.41.

2.3 Synthesis of the intermediate 3
In a 100 mL round bottom flask, 0.509 g (2 mmol) of 1, 0.62 g (1.97 mmol) of intermediate 2 and 0.511 g (1.95 mmol) of triphenylphosphine (PPh$_3$) in 25 mL of anhydrous THF were added. The solution was cooled to 0 °C with an ice bath and 0.41 g (2 mmol) of DIAD were further added to the mixture, and then the reaction mixture was stirred and refluxed overnight in N$_2$ atmosphere. After reaction was completed THF was removed by rotate evaporation and the concentrated mixture was suspended in 100 mL of hexane/diethyl ether, filtered over a silica gel bed and eluted with diethyl ether in order to remove triphenylphosphine oxide, this procedure was repeated three times and solvent was removed by rotate evaporation. The product was purified using silica gel-column and dichloromethane as eluent. Yield: 52 %, $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.9 (t, J = 6.50 Hz, 3H, CH$_3$-CH$_2$-), 1.20-1.80 (m, 20H, Br-CH$_2$-(CH$_2$)$_4$-CH$_2$-O-, CH$_3$-(CH$_2$)$_3$-CH$_2$-), 2.60 (t, J = 8.38 Hz, 2H, CH$_3$-(CH$_2$)$_3$-CH$_2$-), 3.40 (t, J = 6.79 Hz, 2H, Br-CH$_2$-), 3.90 (t, J = 6.79 Hz, 2H, -CH$_2$-CH$_2$-O-Ar), 5.0 (s, 2H, Ar-CH$_2$-O-Ar), 6.80 (m, 4H, Ar-H), 7.20 (m, 2H, Ar-H), 7.50 (m, 4H, Ar-H), 7.60 (m, 2H, Ar-H); $^{13}$C NMR (CDCl$_3$, 50 MHz) δ: 13.19, 21.71, 25.17, 27.30, 27.84, 28.43, 28.50, 28.87, 30.32, 30.71,
31.96, 33.13, 34.74, 67.73, 69.68, 114.58, 15.03, 126.08, 126.28, 127.09, 128.00, 135.16, 137.29, 139.98, 141.38, 152.07, 152.70. HRMS calcd for \([C_{33}H_{43}BrO_2Na]^+\) 575.2324, found = 575.2331.

2.4 Synthesis of the intermediate 4

0.5702 g (1 mmol) of compound 3, 0.2366 g (2 mmol) of potassium thioacetate were added into a round bottom 100 mL flask. A mixture of 65 mL of CHCl₃: DMF 1:1 was further added and stirred at room temperature in inert atmosphere for four days. After reaction was finished, the mixture was dissolved in dichloromethane and washed with water. The organic phase was dried with Na₂SO₄ and filtered. Dichloromethane was removed using rotate evaporation and the product was purified using silica column with a mixture of CH₂Cl₂ and hexane as eluent. Product was obtained as white solid. Yield: 85%. ¹H NMR (CDCl₃, 400 MHz) δ: 0.90 (t, \(J = 7.14\), 3H, CH₃-CH₂-), 1.20-1.77 (m, 20H, S-CH₂-(CH₂)₇-CH₂-O-, CH₃-(CH₂)₃-CH₂-), 2.30 (s, 3H, CH₃-CO-S-), 2.45 (m, 2H, -CH₂-Ar-), 2.85 (t, \(J = 7.45\), 2H, -CH₂-S-CO-), 3.87 (t, J=6.73, 2H, -CH₂-CH₂-O-), 5.01 (s, 2H, -Ar-CH₂-O-Ar), 6.81 (m, 2H, Ar-H), 6.89 (m, 2H, Ar-H), 7.22, (m, 2H, Ar-H)-7.40-7.60 (m, 6H); ¹³C NMR (CDCl₃, 50 MHz) δ: 14.015, 22.54, 26.00, 28.76, 29.01, 29.13, 29.29, 29.36, 29.47, 31.15, 31.54, 35.57, 68.58, 70.66, 115.41, 115.83, 126.91, 127.11, 127.92, 128.83, 135.99, 138.12, 140.82, 142.21, 152.88, 153.52. HRMS calcd for [C₃₅H₄₆O₃SNa]⁺ 569.3060, found 569.3077.

Figure S1. Mass spectra of intermediate 4.
2.4 Synthesis of mesogenic surfactant 5

In a 50 mL round bottom flask, 0.2392 g (0.44 mmol) of 4, 0.2350 g (0.87 mmol) of tetrabutylammonium cyanide and a mixture of CHCl$_3$ and MeOH (40 mL) were added. The mixture was stirred and heated at 50 °C for 24 hours. After reaction was finished the reaction mixture was extracted with CHCl$_3$ three times. The organic phase was washed with a diluted solution of ammonium chloride and the organic layer was separated. Further, the organic phase was dried with MgSO$_4$, filtrated and solvent was removed by rotary evaporation. The product was purified using silica gel column using CHCl$_3$ as eluent to obtain a white solid. Yield: 72 %, $^1$H NMR (CDCl$_3$, 400 MHz) δ: 0.91 (t, J = 6.71Hz, 3H, CH$_3$-CH$_2$-), 1.25-0.80 (m, 20H, SH-CH$_2$-(CH$_2$)$_7$-CH$_2$-O-, CH$_3$-(CH$_2$)$_3$CH$_2$-), 2.66 (m, 4H, CH$_3$-(CH$_2$)$_3$CH$_2$-Ar, SH-CH$_2$-), 3.90 (t, J = 6.75 Hz, -CH$_2$-CH$_2$-O-, 2H), 5.04 (s, -Ar-CH$_2$-O-Ar, 2H), 6.80-6.95 (m, Ar-H, 4H), 7.24 (m, Ar-H, 2H), 7.50 (m, Ar-H, 4H), 7.62 (m, Ar-H, 2H) ; $^{13}$C NMR (CDCl$_3$, 100 MHz) δ: 14.05, 22.57, 26.06, 28.51, 29.18, 29.22, 29.35, 29.40, 29.44, 31.19, 31.57, 35.60, 39.19, 68.61, 70.53, 126.95, 127.14, 127.96, 128.86, 136.01, 138.14, 140.84, 142.24, 152.90, 153.54.

![Figure S2. $^1$H NMR of thiol 5 in CDCl$_3$](image)

2.5 Liquid crystalline properties of mesogenic surfactant 5

Visual observation of liquid crystalline transitions and optical textures under cross-polarised light were made using a polarized light microscope (POM). Figure S3 illustrates the POM textures of mesogenic surfactant 5 in a 10 μm thick cell with homogenous surface anchoring at a cooling rate of 3.0 °C/min. When cooling down from isotropic phase, a smectic phase was observed at the temperature of 140 °C. As the temperature was further decreased to 75 °C, the phase completely changed into crystal phase.
The detailed phase behaviors were fully confirmed by variable-temperature XRD measurements. The capillary sample was heated well above to the isotropic phase and then cooled down slowly under the presence of external magnetic field. The temperature-dependent two dimensional XRD patterns are shown in Figure S4. The sample remains isotropic above 140°C as scattering remains isotropic at both wide angle (W.A.) and small angle (S.A.) regions. However, scattering at S.A. region is not clearly visible due to its very low scattering intensity (I vs q scan is shown in Figure S5(a)). In general, the d spacing corresponding to S.A. and W.A. regions provides the average length and breadth of the molecule (or intermolecular separation), respectively. So, in case of smectics, the S.A. reflection peak corresponds to the layer spacing and W.A. to intermolecular separation. In the conventional smectic phases (such as SmA and SmC), reflections from S.A. are sharper than nematic (N) phase but W.A. reflection remains diffuse in nature as in N phase and which confirms that molecules are still random inside the layer, i.e., liquid like ordering. If molecules inside the smectic layers get ordered then W.A. reflection will be sharper due to increase in the in-plane ordering. Upon cooling of the sample from isotropic phase, at ~140°C, very sharp reflections (i.e., rings) at S.A. and W.A. are developed and which belongs to powder like sample (i.e., Sample is not aligned by external magnetic field). However, the observed 2D pattern is typical for unoriented SmB phase. The layer spacing corresponding to S.A. reflection (~35.6Å) is very close to the calculated molecular length (~33.4Å) and the estimated tilt is ~90°, which confirms that molecules (i.e., long molecular axes) are perpendicular to layer planes. The further lowering of temperature enhances only the scattering intensity of both reflections (S.A. and W.A., only peak position of W.A. shifting towards higher q as shown in Figure S5). Finally the sample crystallizes at 80°C as several reflections at both S.A. and W.A. are developed. As seen from I versus q scans in Figure S5,
the peak postion of S.A. reflection remains more or less identical except scattering intensity variation with temperature. However, the peak position of W.A. reflection significantly shifts towards higher $q$ range. In other words, the lateral separation between molecules inside the smectic layer significantly decreases, i.e., the molecules are getting closer to each other and hence dense packing. In general, one used to get only one very sharp W.A. reflection peak in case of hexagonal lattice. So, the present phase is SmB in which molecules are hexagonally packed within the smectic layers. The d spacings (Å) at 80°C (Crystalline phase) are: (i) S.A.: 31.93, 15.91, 10.62, 7.36, 5.91, 5.72 and (ii) W.A.: 4.81, 4.56, 4.5, 4.4, 4.13, and 4.0. The temperature-dependent d spacing (corresponding to first S.A. reflection) graph in Figure S5(d) shows that it remains more or less constant in the SmB phase. But it does decrease when sample goes from SmB to Crystalline phase. In summary, the phase sequence of mesogenic surfactant 5 is Iso. 140°C SmB 80°C Cr.

![Figure S4. 2D XRD Patterns of the mesogenic surfactant 5 as a function of temperature.](image)
Figure S5. (a-c): Scattering intensity (I) versus scattering vector (q) scans of mesogenic surfactant 5 at different temperatures; (d) the temperature-dependent layer spacing (d spacing).

3. Synthesis of mesogen-functionalized gold nanorods (M-GNRs)

3.1 Synthesis of CTAB-GNRs: The CTAB coated GNRs were freshly prepared by the seed-mediated growth method. For the seed preparation, specifically, 0.5 mL of an aqueous 0.01 M solution of HAuCl$_4$ was added to CTAB solution (15 mL, 0.1 M) in a vial. A bright brown-yellow color appeared. Then, 1.20 mL of 0.01 M aqueous NaBH$_4$ solution was added, followed by rapid inversion mixing for 2 minutes. The solution developed a pale brown-yellow color. Then, the vial was kept in a water bath maintained at 25 °C for future use. For nanorods growth, 9.5 mL of 0.1 M CTAB solution in water was added to a tube, 0.40 mL of 0.01 M HAuCl$_4$ and 0.06 mL of 0.01 M AgNO$_3$ aqueous solutions were added in this order and mixed by inversion. Then, 0.06 mL of 0.1 M of ascorbic acid solution was added and the resulting mixture at this stage becomes colorless. The seed solution (0.02 mL) was added to the above mixture tube, and the tube was slowly mixed for 10 seconds and left to sit still in the water bath at 25-30 °C for 3 h. The final solution turned purple within minutes after the tube was left undisturbed.

3.2 Synthesis of M-GNRs: The solution of CTAB-GNRs was centrifuged 20 min at 7500 rpm three times to remove the excess of ligand CTAB and other byproducts and re-dispersed in 1.5 mL of water. After, 50 mg of mesogenic surfactant 5 were dissolved in 40 mL of THF and the concentrated solution of CTAB-GNRs was added dropwise to the 5 solution. The
reaction mixture was stirred at room temperature under nitrogen atmosphere for 3 days and centrifuged. To improve better coating GNRs the precipitate was dispersed in 10 mL of CHCl$_3$ and sonicated, then 10 mg of 5 was added into the solution and stirred for 24 hours; this process was repeated two times. The resultant hybrid GNRs were centrifuged and washed with chloroform several times until there was no UV signal in the top layer solution, indicating there were no free thiol molecules. Finally the M-GNR where dried, weighted and a mother solution of 0.2 mg/mL was prepared for further experiments. As illustrated in Figure S6, CTAB-GNRs are only soluble in the top layer of the water phase. After the functionalization with the mesogenic surfactant 5, M-GNRs were found to be soluble in the bottom layer of the organic phase.

Figure S6. Images of solutions of CTAB-GNRs (left) and M-GNRs (right) in water and chloroform.

4. Preparation of M-GNRs/liquid crystal hybrid composites
The BP-exhibiting LC materials (BPLC) were a mixture comprising the following materials: P70-003 (70 wt%, SLICHEM Liquid Crystal Co., Ltd, $\Delta n = 0.156$, $\Delta \varepsilon = 33.6$ at 298 K) and chiral dopant S811 (30 wt%, Merck). The liquid crystalline composites doped with different concentrations of M-GNRs in chloroform solution were prepared by dispersing the M-GNRs into BPLC. In order to achieve good dispersion, the mixtures of BPLC with the M-GNRs were dissolved in chloroform and sonicated for about 30 min. Then, chloroform was evaporated off slowly before the samples were placed in a vacuum system for 24 h at 50 °C.
5. Kossel Diagram in blue phases

It has been theoretically and experimentally verified that the BP II and BP I present in the form of simple cubic (SC) and body-centered cubic (BBC) nanostructures, respectively. According to the Bragg’s law, photonic reflection occurs for a set of planes if they satisfy the following equation: 

\[
\cos \theta = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2na}
\]

where \( \lambda \), \( n \), \( a \) and \( \theta \) denote the wavelength of incidence, refractive index, lattice constant, and the Bragg angle, respectively. \( h, k, l \), called Miller indices, are positive integer numbers and the vector \((h, k, l)\) is defined as the diction normal to \((h, k, l)\) plane. From the view of the equation, if \( \theta = 0^\circ \) and both \( n \) and \( a \) are fixed in the same material and temperature, reflected wavelength mainly are determined by different crystal planes. Different from the traditional periodic crystals, the value of lattice constant herein is in the order of wavelength of visible light, i.e., the periodicity wavelength of cubic BPs are typically in the spectral range of visible light. According to Bravais lattice rules, \( h+k+l \) in BPI, BBC structure, must be an even number, while Bragg reflection occurs for all lattice planes in the BPII, SC structures. In the typical BPs, the bandgap photonic reflections are usually generated by the light diffracted from the (110) and (200) directions of BP I and the (100) direction of BP II.

When the conventional periodic crystals were illuminated with X-ray (X-ray wavelength is \( \sim 0.15 \) nm), the diffraction lines from the Bragg reflection are observed in the focal plane diffraction pattern, i.e., the so-called Kossel lines. However, the illumination source in cubic BPs must be the monochromatic visible light to satisfy the Bragg’s law. In our experiment, monochromatic light is generated with a laser and then made to converge on the sample using a high numerical aperture objective of a microscope. The selectively reflected light can then be collected using the same objective and the Kossel lines are brought to a focus in the back focal plane. Every Kossel line corresponds to Bragg reflection of light at a certain set of planes described by the Miller indices \( h, k, l \). In general, Kossel lines appear as projections of circles onto a plane giving either circles, ellipses or straight lines, depending on the orientation of the corresponding reciprocal lattice vector with respect to the viewing direction. The image created by these lines in the back focal plane is called the Kossel Diagram. With the help of Kossel Diagrams, not only crystal orientation but also types of cubic BPs be identified, because the symmetry of the Kossel Diagram is equal to the symmetry of crystal.
References


