Supporting Information

Light Induced Generation of Stable Blue Phase in Photoresponsive Diphenylbutadiene Based Mesogen

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General Experimental Methods:

HPLC analysis was carried out on a Shimadzu HPLC applying the following conditions: Shimadzu System Controller SCL10AVP; Shimadzu LC-6AD pump; Shimadzu SPD- 6AV UV-vis spectrophotometer detector set at 317 nm; Rheodyne injection valve with 20 mL (analytical) and 200 mL (preparative) sample loops; Shimadzu CLC-Sil (4.6 mm X 25 cm) analytical column packed with totally porous, spherical silica particles (5 mm particle diameter, 100 Å pore diameter) with chemically modified surfaces; Prep-Sil (20mm X 25 cm) preparative columns packed with totally porous, irregular-shaped silica particles (15 mm particle diameter, 100 Å pore diameter) with chemically modified surfaces; hexane/ethyl acetate (98:2) as the mobile phase at a flow rate of 2 $mLmin^{-1}$ for analytical and 20 $mLmin^{-1}$ for preparative runs. Phase transitions were observed using a Leica DM 2500P+DFC 490 polarized-light optical microscope, equipped with a Mettler (FP82) (Linkam TP9o temperature programmer) heating and freezing stage. Absorption spectra were recorded on a Shimadzu UV-3101PC UV-vis-NIR spectrophotometer. ^1H NMR spectra were recorded on Bruker DPX 300 MHz spectrometer using tetramethylsilane as the internal standard. Differential scanning calorimetric studies were performed using a PerkinElmer Pyris 6 DSC Instrument. X-Ray diffraction patterns were measured using a Rigaku diffractometer (Type

4037) with graded d-space elliptical side-by-side multilayer optics, monochromated Cu K_α radiation (40 kV, 30 mA) and imaging plate (R-Axis IV). The samples were put in quartz capillary tubes (1.5 mm diameter, 0.01 mm wall thickness) and positioned on a hot stage. The samples were heated to their isotropic phase, cooled to the mesophase and then exposed to a radiation beam of 150 mm camera length.

Synthesis and Characterization:

1-(p-Cyanophenyl)-4-(p-hydroxyphenyl) buta-1-E, 3-E, diene (**BCOH**) was dissolved in dry DMF and the solution was treated with a base, K_2CO_3. The corresponding chiral alkyl bromides were added to this solution and the mixture was heated at 100 °C for 12 hrs. The reaction mixture was cooled, precipitated by adding to ice cold water and filtered. The filtered solid was then dissolved in CH_2Cl_2, dried over anhydrous Na_2SO_4 and purified by column chromatography to get the solid chiral butadiene in good yields. The products were then purified by recycling HPLC. The characterization details are provided below.

1; IRν_{max} (KBr): 3013, 2965, 2924, 2874, 2220, 1597, 1570, 1508, 1472, 1456, 1379, 1304, 1256, 1175, 1109, 1018, 997, 852, 824, 808 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.95-0.97 (m, 3H, CH_3), 1.21-1.41 (m, 3H, aliphatic), 1.61-1.86 (m, 8H, aliphatic), 1.99-2.04 (m, 2H, (CH_2), 3.99-4.04 (m, 2H, (OCH_2), 5.08-5.12 (t, 1H, vinylic), 6.56-6.61 (d, 1H, vinylic), 6.68-6.89 (m, 3H, 2 aromatic, 1vinylic,), 6.99-7.08 (dd, 1H, vinylic, J =15.5 Hz), 7.37-7.40 (d, 2H, aromatic), 7.47-7.49 (d, 2H, aromatic), 7.58-7.60 (d, 2H, aromatic). ^{13}C ($CDCl_3$, 75 MHz), δ (ppm) 17.65, 19.51, 25.41, 25.71, 36.04, 37.08, 66.33, 109.92, 114.76, 119.15, 124.59, 126.11, 126.44, 127.95, 129.22, 132.38, 133.19, 135.25, 142.10, 159.34.; MS (FAB^+) m/z 385 (M^+, $C_{27}H_{31}NO$).

2; IRν_{max} (KBr): 3013, 2953, 2926, 2849, 2870, 2220, 1597, 1570, 1508, 1470, 1383, 1306, 1256, 1177, 1016, 995, 852, 831, 808 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.87-0.96 (m, 9H, $(CH_3)_2$), 1.15-1.82 (m, 10H, aliphatic), 3.97-4.02 (m, 2H, (OCH_2), 6.54-6.59 (d, 1H, vinylic), 6.66-6.87 (m, 3H, 2 aromatic, 1vinylic,), 6.97-7.05 (dd, 1H, vinylic, J =15.40 Hz), 7.34-7.37 (d, 2H, aromatic), 7.45-7.48 (d, 2H, aromatic), 7.57-7.63 (d, 2H, aromatic). ^{13}C ($CDCl_3$, 75 MHz), δ (ppm) 19.73, 22.69, 22.79, 24.72, 28.03, 29.90, 36.22, 37.35, 39.30, 66.35, 96.19, 103.20, 113.35, 118.94, 126.10, 126.47, 127.99, 129.22, 129.37, 131.99, 132.39, 132.11, 135.40, 142.11, 159; MS (FAB^+) m/z 388 (M^+, $C_{27}H_{33}NO$).

3; IRν_{max} (KBr): 3010, 2965, 2928, 2876, 2222, 1595, 1506, 1568, 1464, 1413, 1304, 1258, 1175, 1111, 991, 964, 852, 833, 806, 773; cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.93-1.03 (m, 6H, CH_3), 1.25-1.32 (m, 2H, (CH), 1.84-1.90 (m, 1H, (CH), 3.72-3.86 (m, 2H, (OCH_2), 6.56-6.61 (d, 1H, vinylic), 6.68-6.89 (m, 3H, 2 aromatic, 1vinylic,), 6.99-7.08 (dd, 1H, vinylic, J =15.5 Hz), 7.37-7.40 (d, 2H, aromatic), 7.46-7.49 (d, 2H, aromatic), 7.57-7.60 (d, 2H, aromatic). ^{13}C ($CDCl_3$, 75 MHz), δ (ppm) 11.28, 16.50, 26.11, 34.68, 72.96, 114.82, 126.46, 127.95, 129. 43, 132.39, 133.23, 135.30, 142.15, 159.59.; MS (FAB^+) m/z 317 (M^+, $C_{22}H_{23}NO$).

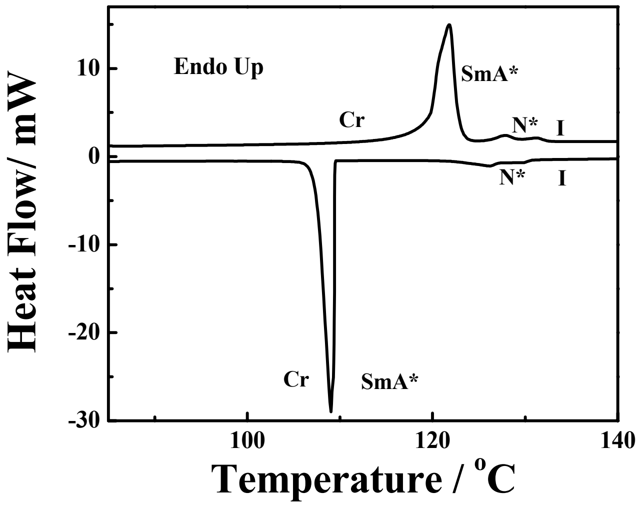

Figure S1. DSC thermogram of the compound **1** at a heating rate of 2 °C/ min.

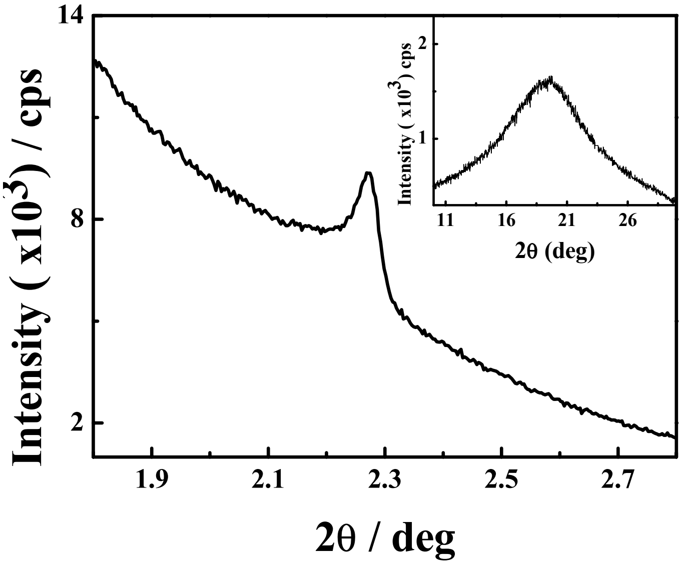

Figure S2. Small angle XRD pattern of the compound **1** at 118 °C. Inset shows the diffuse peak in the wide angle region, corresponding to liquid like ordering. The combination of the sharp peak at low angles and a broad one at wide angles gives evidence of the smectic structure.

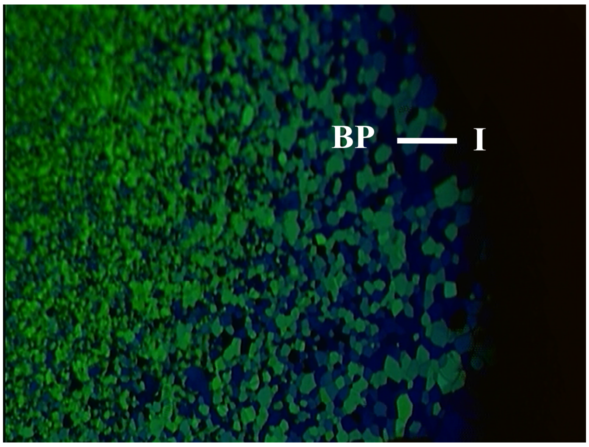

Figure S3. Polarized Optical Image of the compound **1** at the Blue phase-Isotropic boundary state at 128 ºC.

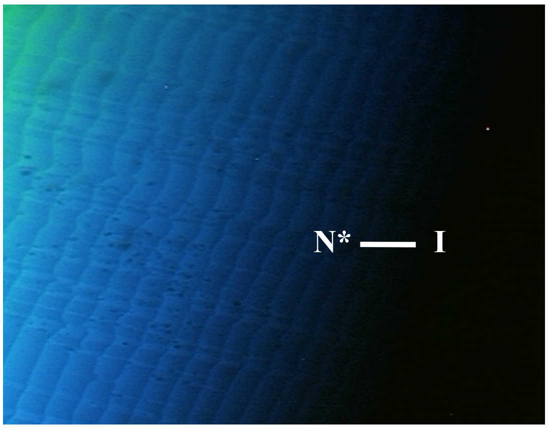

Figure S4. POM Image of the compound **1** in a wedge-cell at the N*- Isotropic boundary state at 130.5 °C.

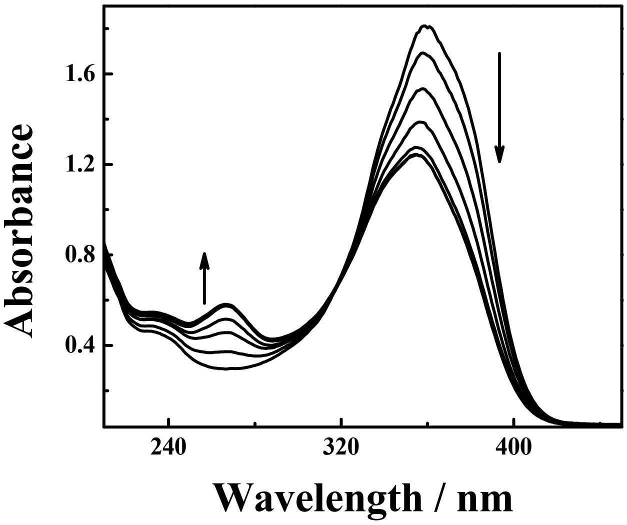

Figure 3. Changes in absorption spectra of compound **1** in acetonitrile on photolysis using 360 nm.