# Supporting Information

**for**

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# Photoresponsive Glass-Forming Butadiene-Based Chiral Liquid Crystals with Circularly Polarized Photoluminescence

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## Experimental Section

**Synthesis of (4-methoxyphenyl)methanol (2):** The solvents were dried according to the procedures reported in the literature[1]. Anisol is weighed (500 mg) and dissolved in dry ethanol (10 mL), cooled to 0 ºC. Stirred for 5 minutes. Sodiumborohydride (277 mg) was added slowly, stirred for 20 minutes in room temperature. Excess sodiumborohydride was quenched by adding water and the product was extracted using ether, and dried over anhydrous sodium sulphate. Yield: 91 %. IR $\nu_{max}$ (KBr): 1510, 2401, 3419 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300MHz) δ (ppm): 3.59(s, 3H, methoxy), 4.42 (s, 2H, bezylic), 6.34-6.69(m, 2H, aromatic), 7.07-7.27(m, 2H, aromatic).

**Synthesis of 1-(bromomethyl)-4-methoxybenzene (3):** 500 mg of (**2**) was dissolved in dry Dichloromethane (20 mL) and cooled the solution to -10 ºC. $PBr_3$ (in dichloromethane) was added slowly and stirred for 20 minutes. Excess $PBr_3$ was quenched by adding sodium bicarbonate solution. The organic layer was extracted using diethyl ether and dried over anhydrous sodiumsulphate. Yield: 89 % .IR $\nu_{max}$ (KBr): 1226, 1710, 3020 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300MHz) δ (ppm): 3.80 (s, 3H, methoxy), 4.51 (s, 2H, benzylic), 6.84-6.87 (d, 2H, aromatic), 7.30-7.33 (d, 2H, aromatic).

**Synthesis of diethyl 4-methoxybenzylphosphonate (4): A** mixture of compound **3** (650 mg) and triethylphosphite (1.3 mL) was heated at 100 ºC for 24 h and the excess triethylphosphite was distilled out under reduced pressure. The product obtained was purified by column chromatography using silica (100-200 mesh), and 30 % ethyl acetate - hexane as the eluent. Yield: 92 %. IR $\nu_{max}$ (KBr): 1219, 3018, 3684 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.12-1.26 (t, 6H, aliphatic), 4.11-4.31 (q, -$OCH_2$-), 6.83-7.10 (d, 2H, aromatic), 7.19-7.28 (d, 2H, aromatic).

**Synthesis of (1*E*,3*E*)-1,4-bis(4-methoxyphenyl)buta-1,3-diene (5):** Reagent 4 (700 mg) and potassium t-butoxide (6 eq.) were stirred in dry DMF (8 mL) and cooled to 0 ºC and stirred for 4 minutes. 4-methoxycinnamldehyde (dissolved in dry DMF) was added to the reaction mixture slowly and stirred the mixture for 12 h. Poured the reaction mixture into ice water. The product was filtered and purified by column chromatography over silica, using 5 % ethyl acetate - hexane as the eluent. Yield: 73 %. IR $\nu_{max}$ (KBr): 1219, 3018, 3684cm$^{-1}$. $^{1}$H NMR ($CDCl_3$, 300MHz) δ (ppm): 3.82 (s, 6H, methoxy), 6.56-6.62 (d, 2H, aromatic), 6.78-6.88 (m, 6H, aromatic, olefinic), 7.35-7.39 (d, 2H, aromatic). $^{13}$C NMR ($CDCl_3$, 75MHz), δ (ppm): 54.1, 125.9, 129.1, 150.2, 112.7, 170.0.

**Synthesis of 4,4'-((1*E*,3*E*)-buta-1,3-diene-1,4-diyl)diphenol (6): T**he reagents **5** (150 mg) and KOH (25 eq, 853 mg) in triethyleneglycol (12 mL) were refluxed at 210 ºC for 12 h. Then the reaction mixture was poured in to ice water and neutralized using 6N HCl. Product got precipitated. Filtered the product and purified by column chromatography over silica (100-200 mesh), using 40 % ethyl acetate - hexane as the eluent.[2] Yield: 89 % IR $\nu_{max}$ (KBr): 1219, 3018, 3684 cm$^{-1}$. $^{1}$H NMR ($CDCl_3$, 300MHz) δ (ppm): 6.56-6.62 (d, 2H, aromatic), 6.78-6.88(m, 6H, aromatic, olefinic), 7, 35-7.39 (d, 2H, aromatic). 9.06 (broad, hydroxyl). $^{13}$C NMR (Acetone-$d_6$, 75 MHz), δ (ppm): 116.4, 127.3, 128.4, 130.5, 137.1, 157.9.

**Synthesis of DCBC Series:** Dissolve reagent **6** (100 mg) in acetonitrile. Add $K_2CO_3$ heated at 60 ºC for 10 minute. Add **7** dissolved in acetonitrile slowly and heated up to 80 ºC for 12 h. Then poured in to ice water and filtered the product. Purified by column chromatography over silica (100-200 mesh) using 5 % ethyl acetate - hexane as the eluent. Yield: 35 %. Recycling preparative HPLC using chloroform as the eluent does further purification.

**DCBC1:** IR $\nu_{max}$ (KBr): 2947, 2899, 2847, 1755, 1506, 1464, 1439, 1371, 1315, 1254, 1225, 1171, 1049, 1011, 989, 970, 949, 843 $cm^{-1}$. $^{1}H$ NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.69 – 2.50 (m, 43H, cholesterol and aliphatic protons), 4.59 (m, 1H, -OCH), 5.43 (m, 1H, vinylic), 6.62-6.91 (m, 2H, olefinic), 7.03-7.19 (m, 3H, 2 aromatic, olifenic), 7.42-7.52 (m, 2H, aromatic); $^{13}C$ NMR ($CDCl_3$, 75 MHz), δ (ppm); 11.86, 18.71, 19.28, 21.06, 22.56, 22.81, 23.83, 24.28, 27.65, 28.01, 28.22, 31.85, 31.91, 35.79, 36.19, 36.56, 36.84, 37.94, 39.52, 39.72, 42.32, 50.00, 56.14, 56.69, 78.93, 121.31, 123.20, 127.28, 127.41, 127.91, 129.34, 131.88, 135.14, 139.14, 150.57, 152.87. MALDI - TOF: m/z - 1061($M^+$). Anal. calcd. for $C_{72}H_{102}O_6$: C- 81.31, H – 9.67, Found: C - 81.23, H – 9.59. $[\alpha]_D$ -31.2

**DCBC8:** IR $\nu_{max}$ (KBr): 2945, 2903, 2868, 1740, 1601, 1506, 1468, 1375, 1315, 1250, 1202, 1175, 1111, 1030, 987, 949, 845, 797, 774, 744 $cm^{-1}$; $^{1}H$ NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.88 – 2.41 (m, 43H, cholesterol and aliphatic protons), 3.94-3.99 (t, 2H, $OCH_2$), 4.09-4.14 (t, 2H, $OCH_2$), 4.49 (m, 1H, OCH), 5.40 (m, 1H, vinylic), 6.54-6.59 (d, 1H, 1 olefinic), 6.78-6.91 (m, 3H, 2 aromatic, olefinic), 7.33-7.36 (m, 2H, aromatic); $^{13}C$ NMR ($CDCl_3$, 75 MHz), δ (ppm): 18.69, 19.24, 21.02, 22.54, 22.80, 23.81, 24.26, 25.67, 27.69, 28.00, 28.21, 29.19, 29.68, 31.82. 35.77, 36.16, 36.52, 36.84, 38.03, 39.49, 39.70, 42.98, 56.11, 56.67, 114.67, 122.92, 127.43, 131.28, 139.40. MALDI - TOF: M/Z 1318.2($M^+$). Anal. calcd. for $C_{96}H_{150}O_8$: C- 80.07, H – 10.23. Found: C - 80.11, H – 10.09, $[\alpha]_D$ -33.6

**DCBC12:** IR $\nu_{max}$ (KBr): 2932, 2853, 1740, 1603, 1510, 1468, 1398, 1371, 1254, 1175, 1134, 1111, 1028, 986, 949, 847, 798, 725 $cm^{-1}$; $^{1}H$ NMR ($CDCl_3$, 300MHz) δ (ppm) 0.67-2.4 (m, 55H, cholesterol and aliphatic protons), 3.94-3.98 (t, 2H, $OCH_2$), 4.09 - 4.13 (t, 2H, $OCH_2$), 4.09 - 4.14 (t, 2H, $OCH_2$), 4.47-4.49 (m, 1H, OCH), 5.38 - 5.40 (m, 1H, vinylic), 6.78-6.87 (m, 3H, 2 aromatic, 1 olefin), 7.33-7.36 (m, 2H, 2 aromatic); $^{13}C$ ($CDCl_3$, 75MHz), δ (ppm); 18.72, 19.23, 21.00, 22.53, 22.79, 23.80, 25.62, 25.89, 27.98, 28.62, 29.08, 29.15, 31.81, 31.87, 35.75, 36.83, 38.03, 39.48, 49.97, 56.11, 56.66, 67.76, 67.99, 78.32 109.96, 114.76, 119.12, 114.76, 119.12, 122.87, 126.12, 126.45, 127.96, 129.22,

132.38, 133.21, 135.27, 139.38, 142.12, 154.66, 156.35. MALDI - TOF: M/Z 1430.2 ($M^+$). Anal. calcd. for $C_{96}H_{150}O_8$: C- 80.51, H – 10.56. Found: C - 80.6, H – 10.59. $[\alpha]_D$ -34.1

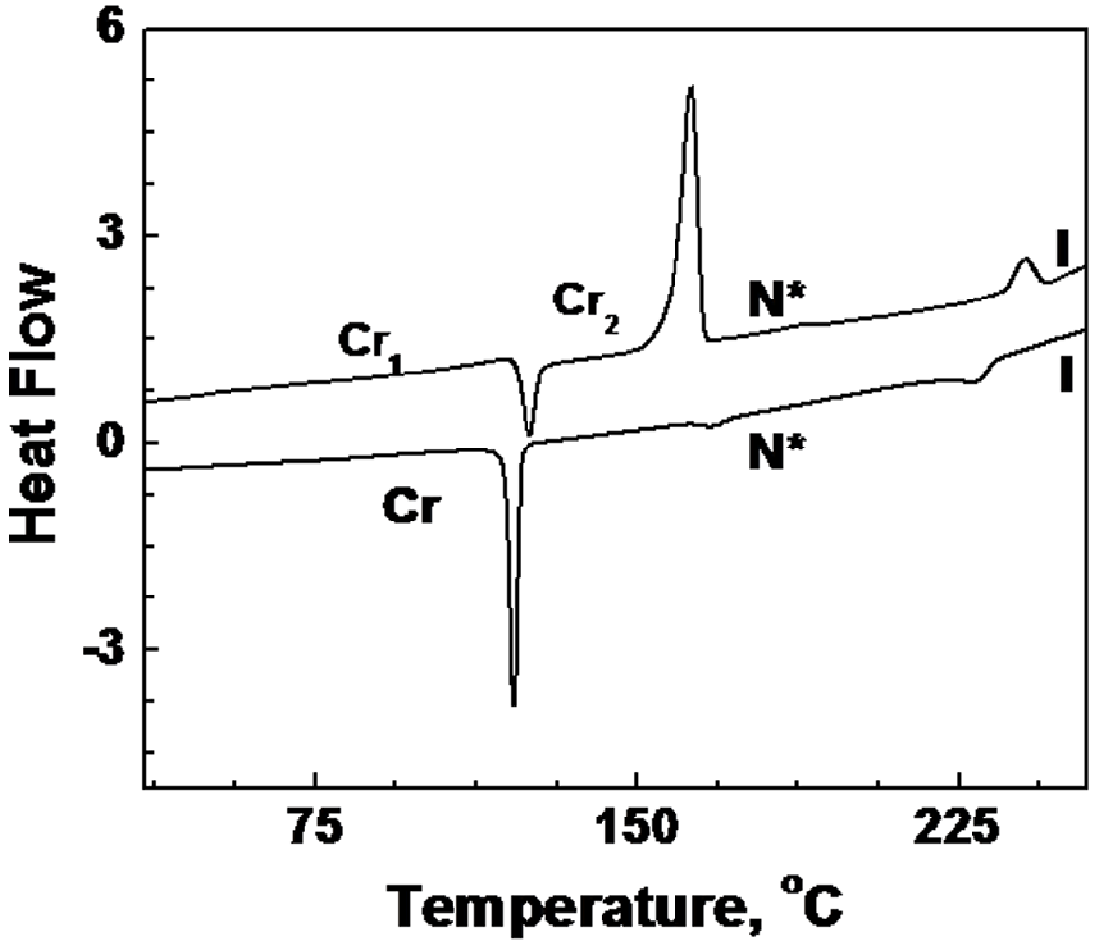


**Figure S1**. DSC trace of DCBC8 in the cooling/heating cycles, rate 5 ° C per minute.

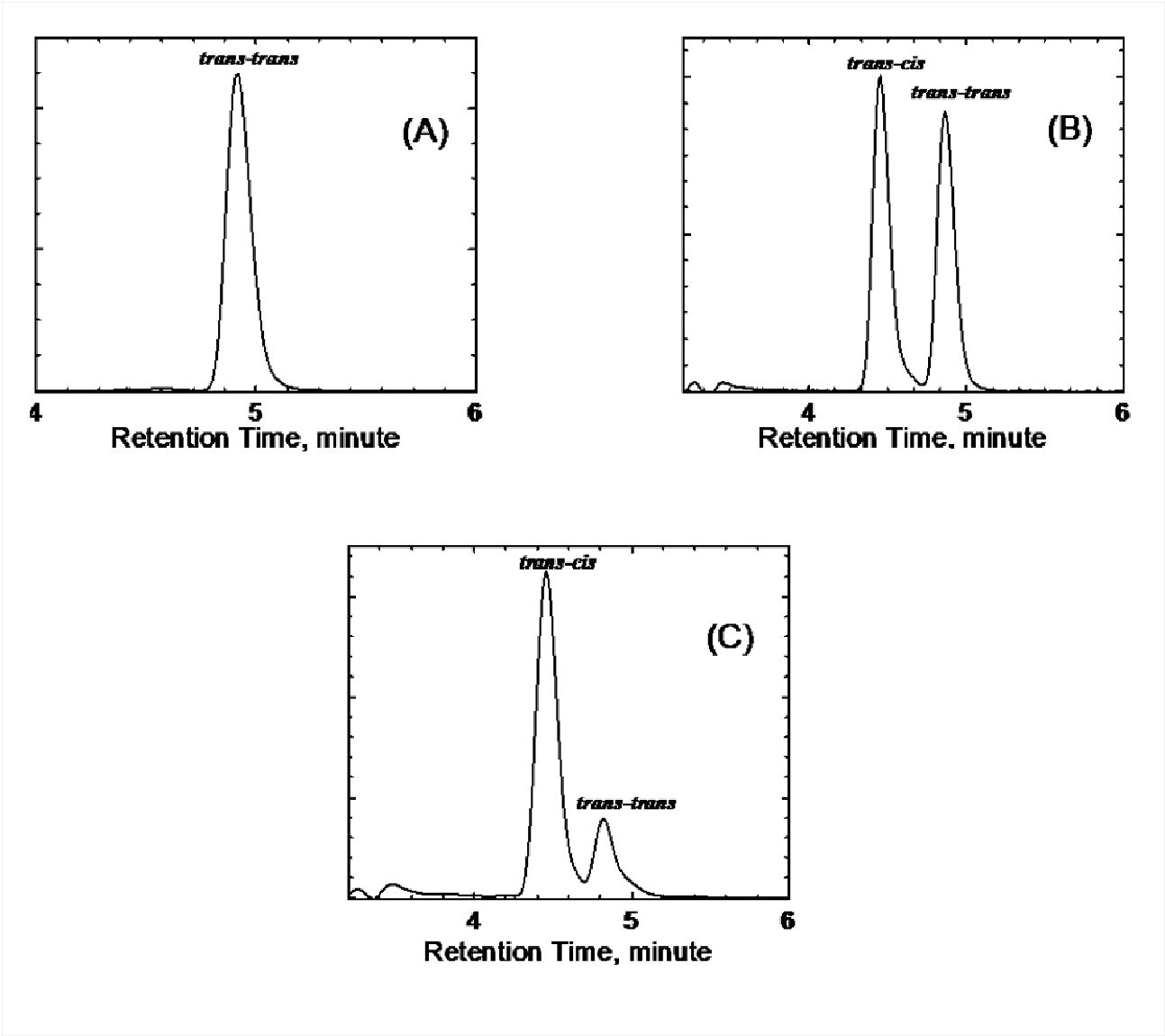


**Figure S 2**. HPLC traces of DCBC12 in 5% Ethyl Acetate: Hexane. (A) Before photolysis and (B) after 100 sec photolysis and (C) the photostationary state.

**References:**

[1] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*. Elsevier Science: USA, **2003**.

[2] S. J. Wang, S. C. Tjong, Y. Z. Meng, M. K. Fung, S. T. Lee. A. S. Hay, *Jour. Appl. Poly. Sci.* **2003**, *89*, 1645.