ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

Multiresponsive Luminescent Dicyanodistyrylbenzenes and their Photochemistry in Solution and in Bulk

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Content list:

1. Experimental section

Materials and General Techniques. All chemical reagents were purchased from Aldrich and were used as received. Dichloromethane (DCM) and tetrahydrofurane (THF) were purchased from Scharlab and dried using a Pure Solv system from Innovative Technology, Inc. Compounds were synthesized by following the synthetic procedures described in Scheme 1. Compounds **4**, **5** and **6** were prepared according to procedures already reported in the literature [1] and the characterization data are in agreement with those previously reported; experimental details for them are not included. All compounds that contain the dicyanodistyrylbenzene unit are photosensitive and, for this reason, care was taken to avoid exposure to ambient light during their synthesis and purification.

^{1}H NMR spectra were recorded on spectrometers operating at 300.13 MHz (ARX-300 and AV-300) and at 75.47 MHz for ^{13}C NMR spectra. Chemical shifts are given in ppm relative to TMS. Elemental analysis was performed on a PERKIN-ELMER 240C CHNS elemental analyzer. FT-IR spectra were obtained with a THERMONICOLET Avatar 360 using KBr pellets. Mass spectrometry studies (MALDI^{+}) were performed with a Microflex (MALDI-ToF) apparatus. Mesophase identification was based on microscopic examination of the textures with samples sandwiched between two glass plates. NIKON and OLYMPUS BH-2 polarizing microscopes equipped with a LINKAM THMS600 hot stage were used. The temperatures and enthalpies of the phase transitions were determined by calorimetric measurements with a DSC TA Instrument Q-20 system at a heating/cooling rate of 10 ºC min^{-1}. Thermogravimetric analysis (TGA) was performed using a TA Q5000IR instrument at a heating rate of 10 ºC min^{-1} under a nitrogen flow. Molecular dimensions were estimated by molecular modeling

1. (a) Gimeno, N.; Ros, M. B.; Serrano, J. L.; de la Fuente, M. R., Hydrogen-bonded banana liquid crystals. *Angewandte Chemie-International Edition* **2004,** *43*, 5235-5238; (b) Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C., Molecular design of nonchiral bent-core liquid crystals with antiferroelectric properties. *Journal of the American Chemical Society* **2000,** *122*, 1593-1601; (c) Muhammad, K.; Hameed, S.; Tan, J.; Liu, R., Facile synthesis and mesomorphic properties of 4-hydroxybutyl 4-(4-alkoxybenzoyloxy) benzoate mesogens. *Liq. Cryst.* **2011,** *38*, 333-348; (d) Laursen, B.; Denieul, M.-P.; Skrydstrup, T., Formal total synthesis of the PKC inhibitor, balanol: preparation of the fully protected benzophenone fragment. *Tetrahedron* **2002,** *58*, 2231-2238.

(ChemSketch3D). The X-ray investigations on non-oriented samples were carried out in Lindemann capillary tubes (diameter 0.9 mm) using a PINHOLE (ANTON-PAAR) film camera in order to confirm the liquid crystal phases.

Solid solutions of cyanostilbene molecules were prepared by adding a solution of cyanostilbene bent core molecules to a solution of PMMA in DCM and stirred to form a homogeneous mixture. The concentration of the molecules was kept below 0.01% (w/w). The solution was then drop casted on a fused silica substrate to form a solid solution of these molecules in the PMMA matrix.

Absorption and fluorescence measurements in solution were carried out using ATI-Unicam UV4-200 and PERKIN-ELMER LS50B instruments, respectively. Fluorescence emission in the solid state was measured on a Horiba FluoroLog 3 Spectrophotometer, equipped with double monochromators in the emission and excitation sides. Fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) technique. The excitation source was a 405 nm picosecond pulsed diode laser (LDH-D-C-405, PicoQuant) driven by a PDL828 driver (PicoQuant) with FWHM 70 ps. The emission was dispersed across wavelengths using an Acton SP2500 spectrometer (as mentioned above) and detected by a blue sensitive, low dark current photomultiplier (PMA 06, PicoQuant), which covers a spectral range from 220 to 650 nm (transit time spread 50 ps, FWHM). A HydraHarp-400 TCSPC event timer with 1 ps time resolution was used to measure the fluorescence decays. The PL quantum efficiencies of solutions and in condensed phases were measured in an absolute quantum yield measurement system (Hamamatsu C9920) with a detection range from 300 nm to 950 nm and bandwidth from 2 nm to 5 nm (FWHM).

Synthesis of the bent-core compounds and their dicyanodistyrylbenzene precursors:

Compound 1: [2] 4-Hydroxybenzaldehyde (2.00 g, 16.4 mmol) and 1,4-phenylenediacetonitrile (1.03 g, 6.6 mmol) were disolved in 1-propanol (18 mL) and acetic acid (0.79 mL). The solution was heated at reflux under an argon atmosphere and piperidine (0.97 mL) was slowly added. After 24 h the reaction mixture was cooled to room temperature and the solid was filtered and washed with 1-propanol and then with methanol (yellow solid, 87% yield). M.p. (ºC): 288 (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.93 (s, 2H), 7.91-7.84 (m, 4H), 7.79 (s, 4 H), 6.96-6.87 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 160.3, 143.2, 134.4, 131.7, 126.0, 124.8, 118.5, 116.0, 105.1; IR, ν (KBr, cm^{-1}): 3450-3100, 2225, 1610, 1589, 1516, 1442, 1280, 1266, 1173.

Compound 2: Compound **1** (2.00 g, 5.5 mmol) and anhydrous potassium carbonate (0.77 g, 5.5 mmol) were stirred in dry N,N-dimethylformamide (DMF) (90 mL). The solution was heated at 120 ºC, under argon atmosphere, and 1-bromotetradecane (1.3 mL, 1.62 g, 4.4 mmol) was slowly added. After 20 h the reaction mixture was cooled to room temperature and poured into 2.5 mL of HCl (10 % w/w). The mixture was extracted with DCM and the organic fraction was washed with water, saturated brine, and dried over anhydrous magnesium sulfate. After evaporating the solvent, a mixture of compound **2** and **DCS14** was obtained, which was separated by column chromatography using a polarity gradient from DCM/hexane (7/3) to DCM to DCM/ethyl acetate (9.75/0.25) followed by two recrystallizations from ethyl acetate. Compound **2** was obtained in 56% yield. M.p. (ºC): 175 (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.95-7.82 (m, 4H), 7.71 (s, 4H), 7.51 (s, 2H), 7.03-6.89 (m, 4H), 4.03 (t, J = 6.2 Hz, 2H), 1.53-1.13 (m, 24 H), 0.88 (t, J = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 160.7, 159.8, 142.3, 141.7, 134.7, 134.3, 131.1, 125.6, 125.5, 124.4, 118.0, 115.7, 114.4, 67.7, 31.3, 29.1, 29.1, 29.0, 29.0, 28.9, 28.8, 28.7, 28.5, 25.4, 22.1, 13.6; IR, ν (KBr, cm^{-1}): 3550-3100, 2918, 2850, 2214, 1594, 1517, 1471, 1286, 1181.

[2] Holm, M. J.; Zienty, F. B.; Terpstra, M. A., Condensation of aromatic and heterocyclic aldehydes with benzenediacetonitriles. *J. Chem. Eng. Data* **1968,** *13*, 70-74.

DCS14: M.p. (ºC): See Table 1; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.94-7.86 (m, 4H), 7.71 (s, 4H), 7.51 (s, 2H), 7.02-6.93 (m, 4H), 4.03 (t, *J* = 6.6 Hz, 2H), 1.88-1.74 (m, 2H), 1.53-1.21 (m, 22 H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 161.5, 142.4, 135.3, 131.5, 126.4, 126.2, 118.5, 115.1, 107.5, 68.4, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.2, 22.8, 14.3; IR, ν (KBr, cm^{-1}): 2955, 2870, 2216, 1608, 1593, 1518, 1465, 1256, 1182.

Compound 3: An experimental procedure similar to that used for the synthesis of compound **2** was followed, using in this case compound **1** (0.60 g, 1.6 mmol), anhydrous potassium carbonate (0.24 g, 1.6 mmol), 1-bromobutane (0.14 mL, 0.18 g, 1.3 mmol) and DMF (30 mL). A mixture of compound **3** and **DCS4** was obtained, which were purified in the same way as for compound **2** (58% yield). M.p. (ºC): 220 (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.94-7.85 (m, 4H), 7.72 (s, 4H), 7.52 (s, 2H), 7.02-6.90 (m, 4H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.87-1.70 (m, 2H), 1.59-1.46 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 161.5, 158.2, 142.5, 135.4, 131.8, 126.4, 126.2, 118.5, 116.2, 115.1, 107.9, 107.5, 68.13, 31.3, 19.4, 14.0; IR, ν (KBr, cm^{-1}): 3550-3100, 2956, 2850, 2214, 1608, 1591, 1517, 1441, 1259, 1178.

DCS4: M.p. (ºC): See Table 1; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.94-7.86 (m, 4H), 7.71 (s, 4H), 7.52 (s, 2H), 7.02-6.93 (m, 4H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.88-1.74 (m, 2H), 1.61-1.44 (m, 2 H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 161.5, 142.4, 135.3, 131.5, 126.4, 126.2, 118.5, 115.1, 107.6, 68.1, 31.3, 19.4, 14.0; IR, ν (KBr, cm^{-1}): 2956, 2870, 2216, 1608, 1593, 1518, 1466, 1256, 1182.

Compound 7:

Step 1: The carboxylic acid **5** (3.95 g, 8.7 mmol), compound **4** (2.00 g, 8.7 mmol) and 4-dimethylaminopyridine (DMAP) (0.10 g, 0.9 mmol) were dissolved in DCM (60 ml) and cooled at 0 ºC under inert atmosphere. Then, N,N'-Dicyclohexylcarbodiimide (DCC) (1.81 g, 8.7 mmol) was added, and the mixture was stirred for 30 minutes and then allowed to warm up to room temperature. The mixture was stirred for 24 h, filtered off through Celite® and the filtrate was evaporated to give a white solid. The solid was purified by column chromatography using DCM/hexane (9/1) as eluent to give the benzylic ester compound in 91% yield. M.p. (ºC): 82; ^{1}H NMR (300 MHz, $CDCl_3$), δ

(ppm): 8.34-8.26 (m, 2H), 8.22-8.14 (m, 2H), 8.03 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.94 (t, *J* = 1.9 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.48-7.31 (m, 8H), 7.07-6.97 (m, 2H), 5.40 (s, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 1.90-1.76 (m, 2H), 1.58-1.19 (m, 22H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 165.6, 164.4, 164.4, 164.0, 155.7, 151.0, 135.9, 132.5, 132.0, 131.9, 129.7, 128.8, 128.5, 128.4, 128.4, 127.4, 126.7, 126.6, 123.2, 122.3, 121.0, 114.6, 68.5, 67.1, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.2, 26.1, 22.8, 14.3; IR, ν (KBr, cm^{-1}): 2920, 2848, 1741, 1713, 1603, 1510, 1469, 1445, 1248, 1197.

Step 2: The compound obtained in the previous step (2.40 g, 3.6 mmol) was dissolved in ethanol (100 mL) and cyclohexene (50 mL). The mixture was heated at reflux under an argon atmosphere and then $Pd(OH)_2/C$ (20% w/w) (0.30 g) was added. After 24 hours, the mixture was filtered off through Celite® and the filtrate was evaporated to give a white solid. Compound **7** was purified by recrystallization from ethanol (92 % yield). M.p. (ºC): 170-171; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.35-8.24 (m, 2H), 8.21-8.10 (m, 2H), 8.04 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.97 (t, *J* = 1.9 Hz, 1H), 7.59 (7.94 (t, *J* = 7.9 Hz, 1H), 7.50 (ddd, *J* = 8.1, 2.4, 1.5 Hz, 1H), 7.46-7.33 (m, 2H), 7.05-6.94 (m, 2H), 4.06 (t, *J* = 6.5 Hz, 2H), 1.91-1.76 (m, 2H), 1.54-1.16 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 170.4, 164.4, 164.3, 164.1, 155.8, 151.2, 132.6, 132.0, 131.01, 129.8, 127.9, 127.4, 126.7, 123.7, 122.3, 121.2, 114.7, 68.6, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.3, 26.2, 22.8, 14.2; IR, ν (KBr, cm^{-1}): 3200-2500, 2920, 2851, 1745, 1729, 1689, 1605, 1511, 1453, 1308, 1253, 1203, 1168.

Compound 8:

Step 1: An experimental procedure similar to that used for the synthesis of compound **7** was followed, using in this case compound **6** (0.96 g, 3.1 mmol), compound **4** (0.70 g, 3.1 mmol), DMAP (0.09 g, 0.7 mmol), DCC (0.73 g, 3.7 mmol) and DCM (60 mL). The mixture was stirred for 25 h, filtered off through Celite® and the filtrate was evaporated to give a white solid. The solid was purified by recrystallization from ethanol to give compound **8** in 81% yield. M.p. (ºC): Cr 96 I; I 77 N 55 SmA 32 Cr; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.35-8.26 (m, 2H), 8.23-8.13 (m, 2H), 8.03 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.94 (t, *J* = 1.9 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.51-7.32 (m, 8H), 7.05-6.98 (m, 2H), 5.40 (s, 2H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.92-1.77 (m, 2H), 1.63-1.47 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 165.6, 164.4, 164.4, 164.0, 155.7, 151.0, 135.9, 132.5, 132.0, 131.9, 129.6, 128.7, 128.5, 128.4, 127.4,

126.7, 126.6, 123.2, 122.3, 121.0, 114.5, 68.2, 67.1, 31.2, 19.3, 13.9; IR, ν (KBr, cm^{-1}): 2937, 2873, 1734, 1722, 1607, 1512, 1294, 1273, 1257, 1191, 1164.

Step 2: The compound obtained in the previous step (2.40 g, 3.6 mmol) was dissolved in ethanol (100 mL) and cyclohexene (50 mL). The mixture was heated at reflux under an argon atmosphere and then $Pd(OH)_2/C$ (20% w/w) (0.30 g) was added. After 24 hours, the mixture was filtered off through Celite® and the filtrate was evaporated to give a white solid. The compound **8** was purified by recrystallization from ethanol (96% yield). M.p. (ºC): 197; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.28-8.18 (m, 2H), 8.16-8.06 (m, 2H), 7.94 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.86 (t, *J* = 1.9 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.37 (ddd, *J* = 8.2, 2.5, 1.4 Hz, 1H), 7.41-7.28 (m, 2H), 7.00-6.89 (m, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 1.86-1.68 (m, 2H), 1.56-1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 167.7, 164.4, 163.9, 155.5, 150.8, 132.7, 132.4, 131.8, 129.4, 127.4, 126.6, 126.1, 123.2, 122.2, 120.9, 116.3, 114.4, 68.1, 31.1, 19.2, 13.8; IR, ν (KBr, cm^{-1}): 3400-2400, 2958, 2947, 2877, 1740, 1706, 1608, 1590, 1413, 1221, 1170.

Compound B14-DCS14: The carboxylic acid **7** (0.25 g, 0.4 mmol) was dissolved in dry THF (60 mL) under an argon atmosphere at room temperature, then, oxalyl chloride (0.09 mL, 0.13 g, 1.0 mmol) and two drops of DMF were added. After 12 hours the solvent was evaporated. The freshly synthesized acid chloride was dissolved in THF (20 mL) and the solution was added over a solution of compound **2** (0.21 g, 0.4 mmol) and trimethylamine (0.07 mL, 0.5 mmol) in dry THF (40 mL) under an argon atmosphere. After stirring for 24 hours, the orange solid was washed with ethanol followed by a recrystallization from ethyl acetate and then from toluene (70 % yield). M.p. (ºC): See Table 1; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.35-8.26 (m, 2H), 8.21-8.12 (m, 3H), 8.09 (t, *J* = 2.0 Hz, 1H), 8.05-7.97 (m, 2H), 7.96-7.86 (m, 2H), 7.75 (s, 4H), 7.68-7.49 (m, 4H), 7.46-7.33 (m, 4H), 7.03-6.95 (m, 4H), 4.07 (t, *J* = 6.5 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.89-1.75 (m, 4H), 1.65-1.14 (m, 44H), 0.89(t, *J* = 6.7Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 164.4, 164.1, 164.0, 161.6, 155.9, 152.9, 151.3, 142.7, 141.4, 136.1, 134.7, 132.6, 132.1, 131.6, 131.6, 131.0, 131.0, 130.0, 128.0, 127.6, 126.7, 126.6, 126.5, 126.2, 123.8, 122.6, 122.4, 121.2, 118.4, 117.7, 115.2, 114.7, 111.2, 107.5, 68.6, 68.5, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 29.3, 29.3, 26.2, 26.2, 22.8, 14.2; IR, ν (KBr, cm^{-1}): 2918, 2850, 2216, 1737, 1606, 1509, 1471, 1446, 1256, 1172; MS (MALDI$^+$) m/z: 1139.7 $[M+Na]^+$; Elemental analysis: Calcd. for $C_{73}H_{84}N_2O_8$: C 78.46, H 6.82, N 2.51; found C 78.13, H 6.72, N 2.73.

Compound B14-DCS4: The synthetic method was similar to that used for the synthesis of compound **B14-DCS14**, using compound **7** (0.30 g, 0.5 mmol), oxalyl chloride (0.10 mL, 0.14 g, 1.0 mmol), two drops of DMF and dry dichloromethane (DCM) (40 mL). After 12 hours the solvent was evaporated. The freshly synthesized acid chloride was dissolved in DCM (15 mL) and the solution was added over a solution of compound **3** (0.18 g, 0.4 mmol) and trimethylamine (0.08 mL, 0.6 mmol) in dry DCM (35 mL) under an argon atmosphere. After 24 hours, the orange solid was washed with ethanol and purified by column chromatography using DCM/hexane 9:1 as eluent followed by a recrystallization from ethyl acetate and then from toluene (62% yield). M.p. (ºC): See Table 1; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.35-8.27 (m, 2H), 8.20-8.12 (m, 3H), 8.09 (t, *J* = 2.0 Hz, 1H), 8.08-7.98 (m, 2H), 7.95-7.88 (m, 2H), 7.75 (s, 4H), 7.67-7.51 (m, 4H), 7.44-7.34 (m, 4H), 7.03-6.94 (m, 4H), 4.11-3.99 (m, 4H), 1.91-1.74 (m, 4H), 1.59-1.20 (m, 24H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 164.4, 164.0, 164.0, 161.6, 155.8, 152.6, 151.2, 142.7, 141.4, 136.0, 134.7, 132.6, 132.1, 131.6, 131.5, 131.0, 130.9, 130.0, 128.0, 127.6, 126.7, 126.5, 126.5, 126.2, 123.8, 122.6, 122.4, 121.1, 118.4, 117.8, 115.1, 114.6, 111.1, 107.4, 68.6, 68.1, 32.1, 31.3, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.3, 26.1, 22.9, 19.4, 14.3, 14.0; IR, ν (KBr, cm^{-1}): 2917, 2851, 2215, 1735, 1605, 1508, 1472, 1445, 1255, 1161; MS (MALDI^{+}) m/z: 999.5 $[M+Na]^{+}$; Elemental analysis: Calcd. for $C_{63}H_{64}N_2O_8$: C 77.43, H 6.60, N 2.87; found C 77.15, H 6.39, N 3.04.

Compound B4-DCS4: The synthetic method was similar to that used for the synthesis of compound **B14-DCS14**, using compound **8** (0.30 g, 0.7 mmol), oxalyl chloride (0.13 mL, 0.19 g, 1.38 mmol), two drops of DMF and dry THF (40 mL). After 12 hours the solvent was evaporated. The freshly synthesized acid chloride was dissolved in THF (20 mL) and the solution was added over a solution of compound **3** (0.24 g, 0.6 mmol) and trimethylamine (0.11 mL, 0.8 mmol) in dry THF (40 mL) under argon atmosphere. After 24 hours, the orange solid was washed with ethanol and purified by column chromatography using DCM/hexane 9:1 as eluent followed by a recrystallization from ethyl acetate and then from toluene (73% yield). M.p. (ºC): See Table 1; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.35-8.27 (m, 2H), 8.21-8.12 (m, 3H), 8.09 (t, *J* = 2.0 Hz, 1H), 8.05-7.98 (m, 2H), 7.95-7.88 (m, 2H), 7.75 (s, 4H), 7.69-7.51 (m, 4H), 7.44-7.33 (m, 4H), 6.99 (m, 4H), 4.07 (t, *J* = 6.7 Hz, 2H), 4.05 (t, *J* = 6.7 Hz, 2H), 1.88-1.73 (m, 4H), 1.61-1.44 (m, 4H), 1.01 (t, *J* = 7.4, 3H), 1.00 (t, *J* = 7.4, 3H); ^{13}C NMR (75 MHz,

$CDCl_3$), δ (ppm): 164.4, 164.0, 164.0, 161.5, 155.8, 152.6, 151.2, 142.7, 141.4, 135.9, 134.6, 132.6, 132.0, 131.6, 131.5, 130.9, 130.9, 130.0, 128.0, 127.6, 126.7, 126.5, 126.4, 126.1, 123.8, 122.5, 122.4, 121.0, 118.4, 117.7, 115.1, 114.6, 111.0, 107.4, 68.2, 68.1, 31.3, 31.3, 19.3, 14.0; IR, ν (KBr, cm^{-1}): 2956, 2932, 2871, 2215, 1735, 1604, 1508, 1473, 1446, 1253, 1160.; MS (MALDI$^+$) m/z: 859.1 $[M+Na]^+$; Elemental analysis: Calcd. for $C_{53}H_{44}N_2O_8$: C 76.06, H 5.30, N 3.35; found C 76.05, H 5.55, N 3.54.

2. NMR spectra of the bent-core compounds.

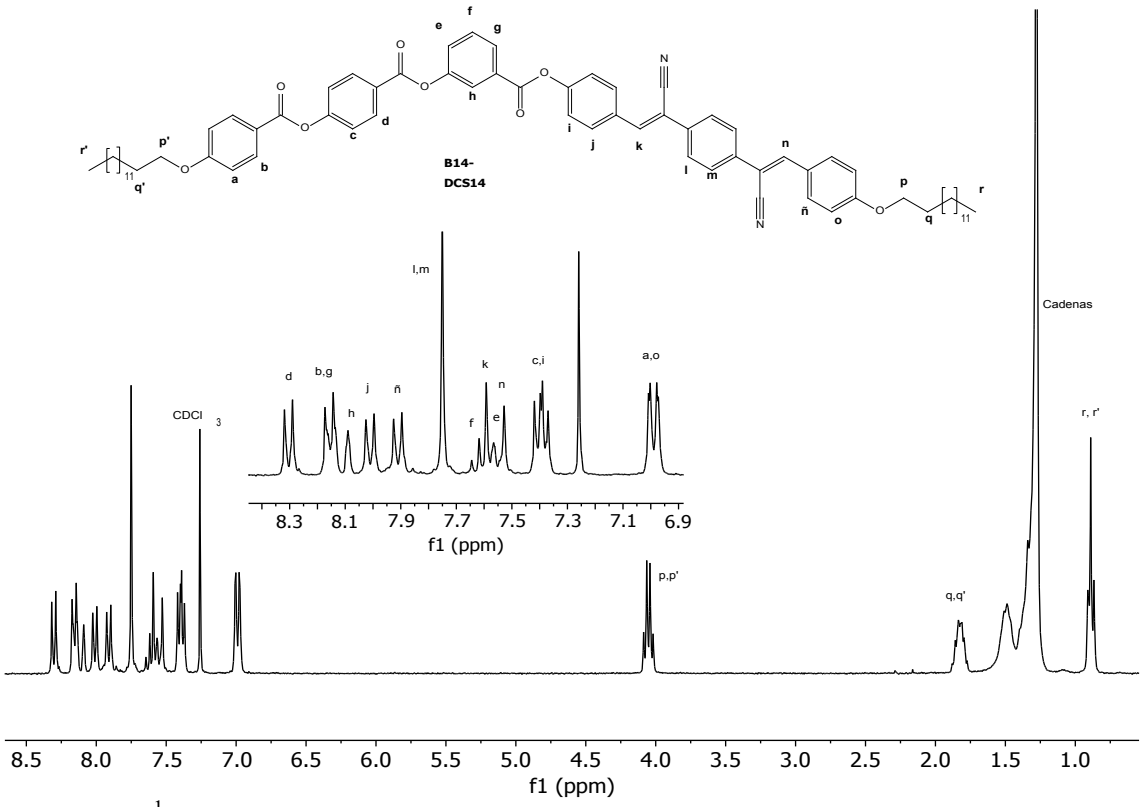

Figure S1. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **B14-DCS14**.

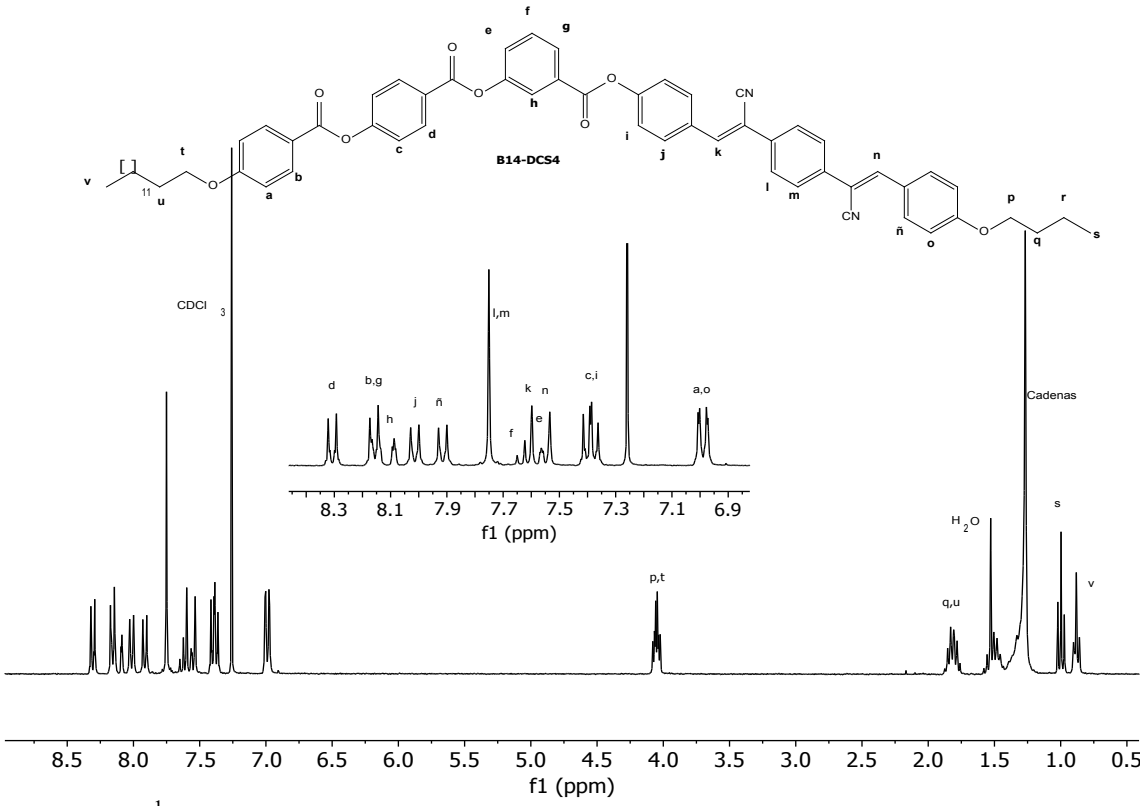

Figure S2. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **B14-DCS4**.

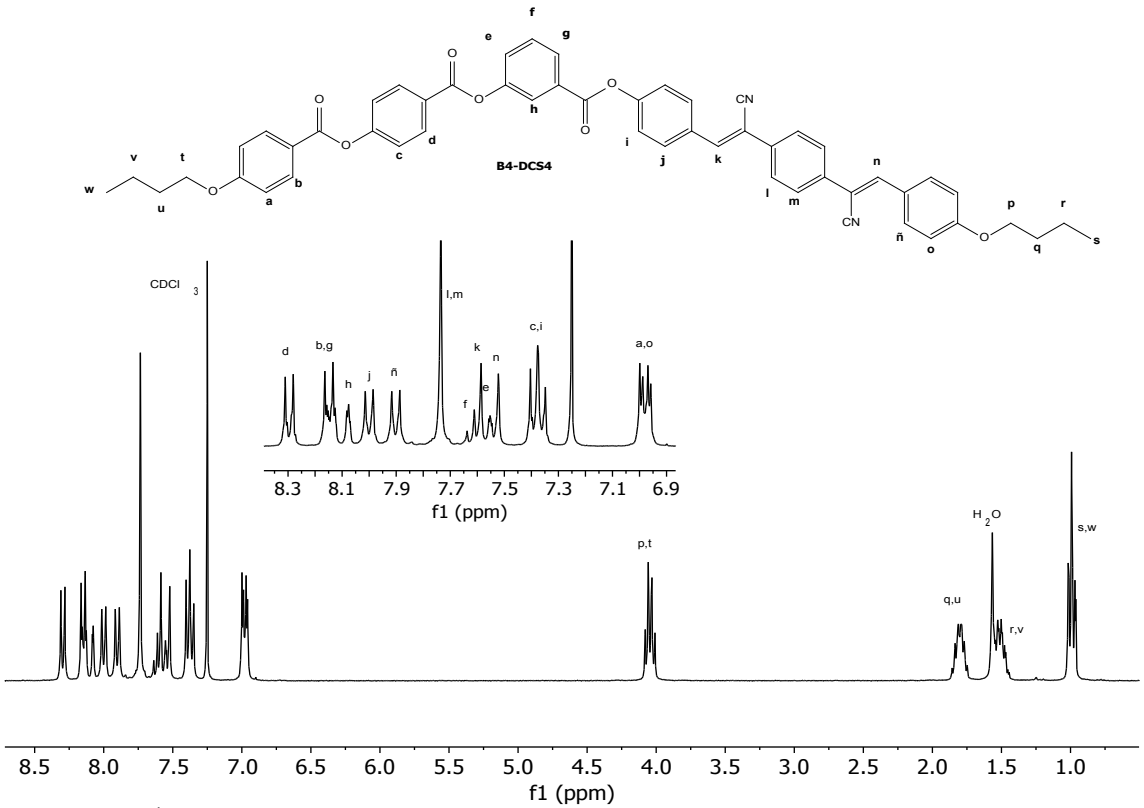

Figure S3. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **B4-DCS4**.

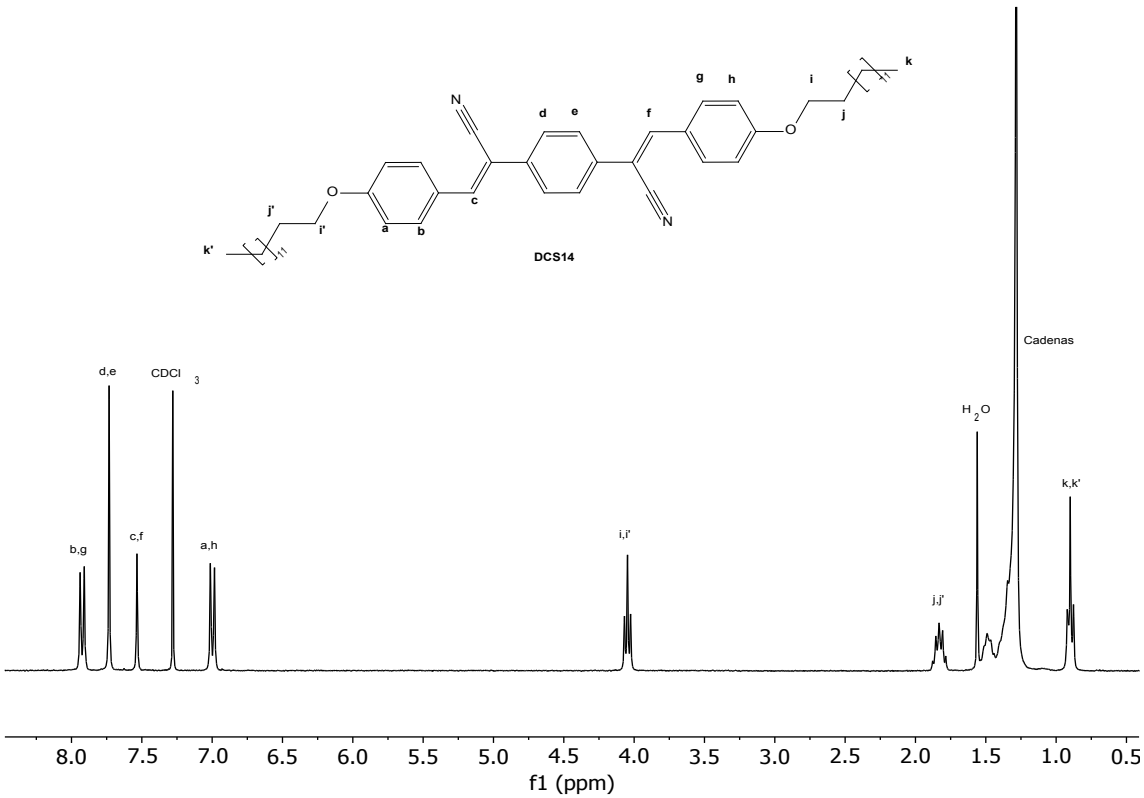

Figure S4. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **DCS14**.

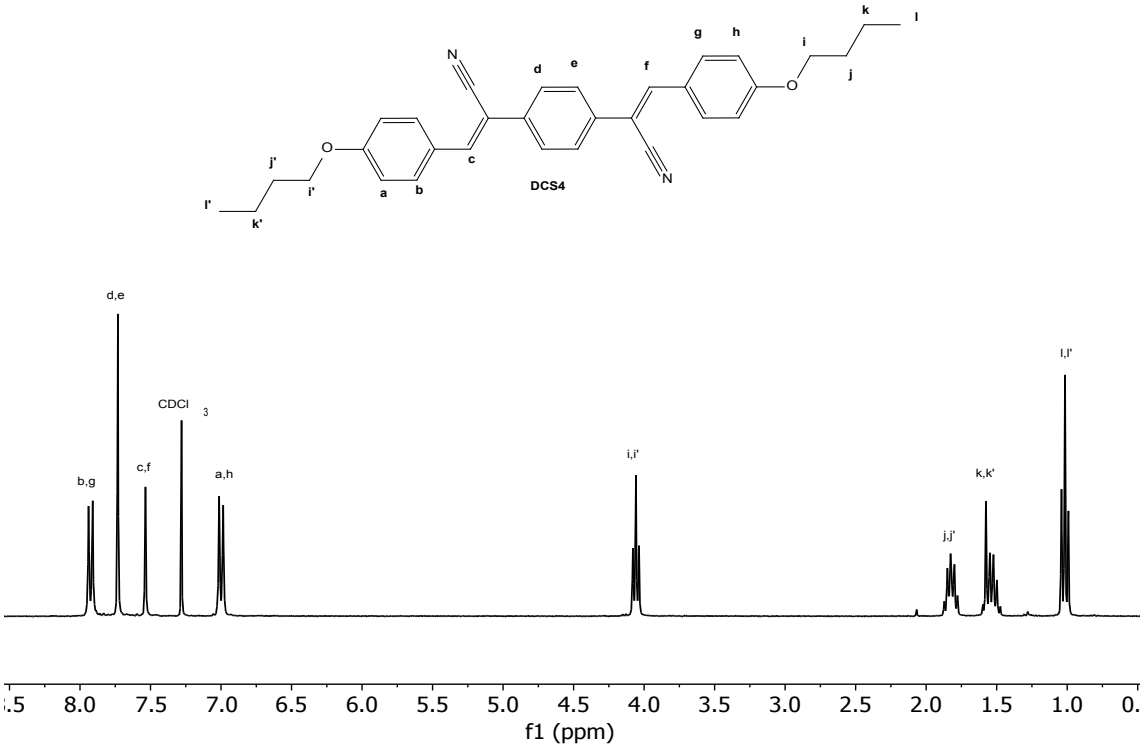

Figure S5. ^{1}H NMR (300 MHz) in $CDCl_3$ at 25 ºC of **DCS4**.

3. DSC thermograms

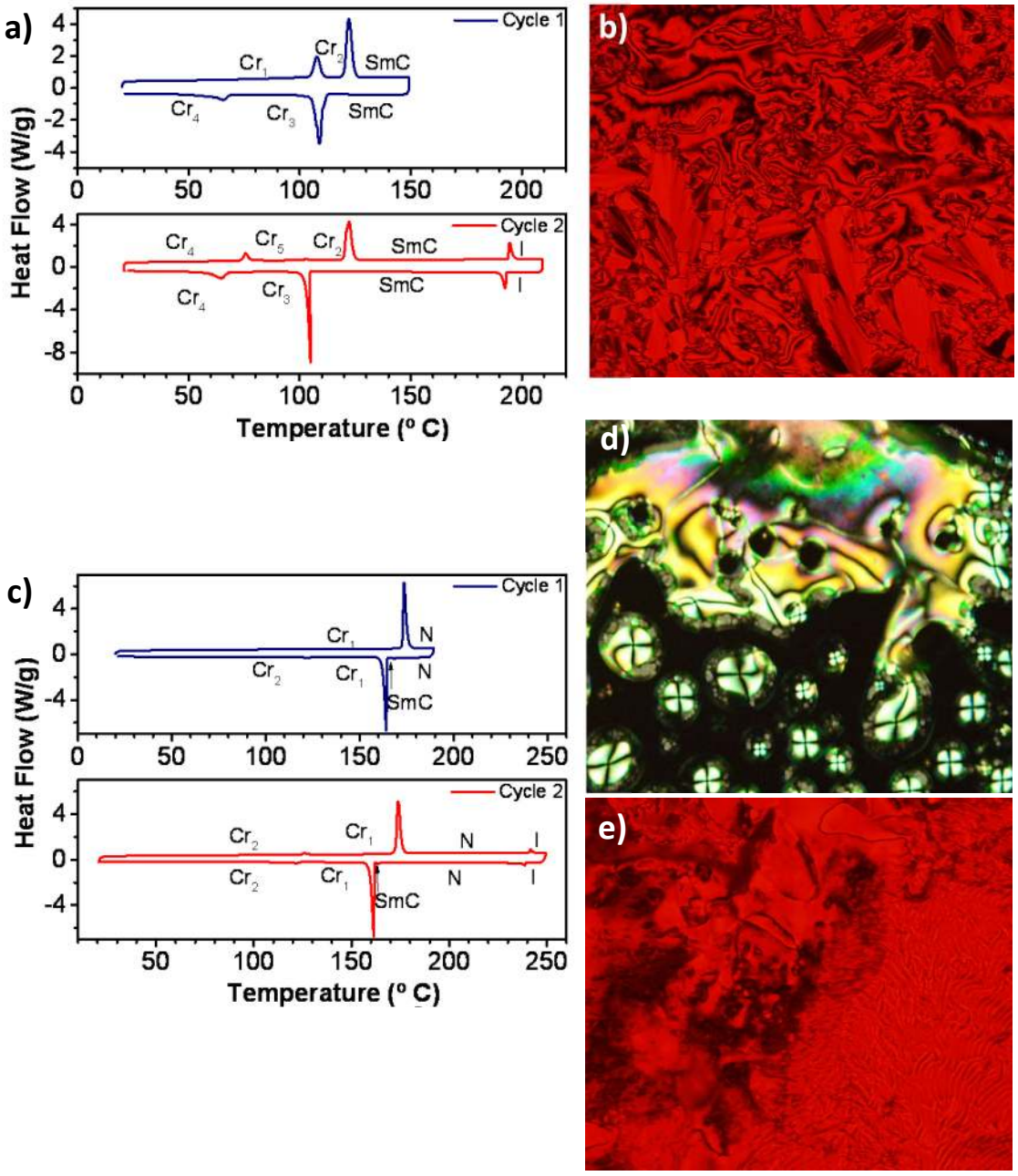

Figure S6. DSC thermograms, first and second heating/cooling cycles of: a) **DCS14** and c) **DCS4**; POM textures of: b) **DCS14** at 192 ºC (SmC phase); d) **DCS4** at 188 ºC (N phase); and e) **DCS4** at 168 ºC (transition N to SmC)

4. X-ray diffraction studies

Table S1: XRD data.

Compound	Mesophase (T / °C)	d (Å)	Miller index	Parameters (Å)
DCS14	SmC (150 °C)	37.9	001	c = 37.9
DCS4	N (190 °C)	Diffuse peak (25.3)	-	-

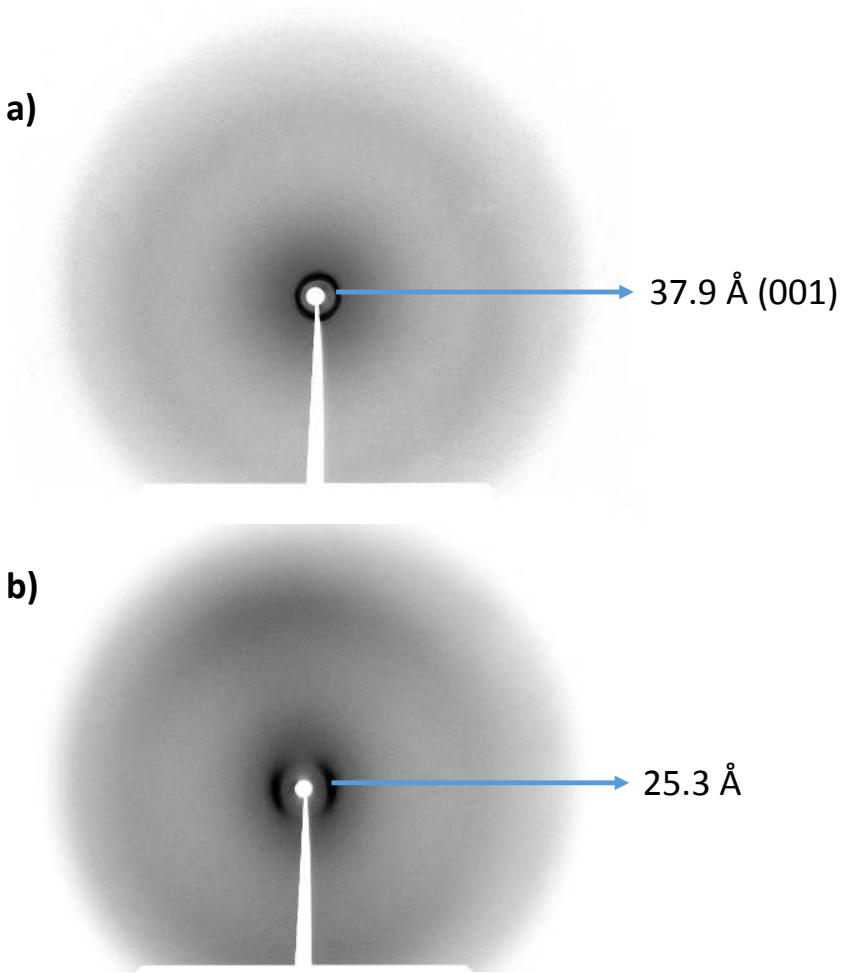

Figure S7. XRD patterns of the representative mesophases of the rod-like dicyanodistyrylbenzenes: a) **DCS14**, SmC phase at 150 ºC; b) **DCS4**, N phase at 190 ºC.

5. Thermogravimetric analysis

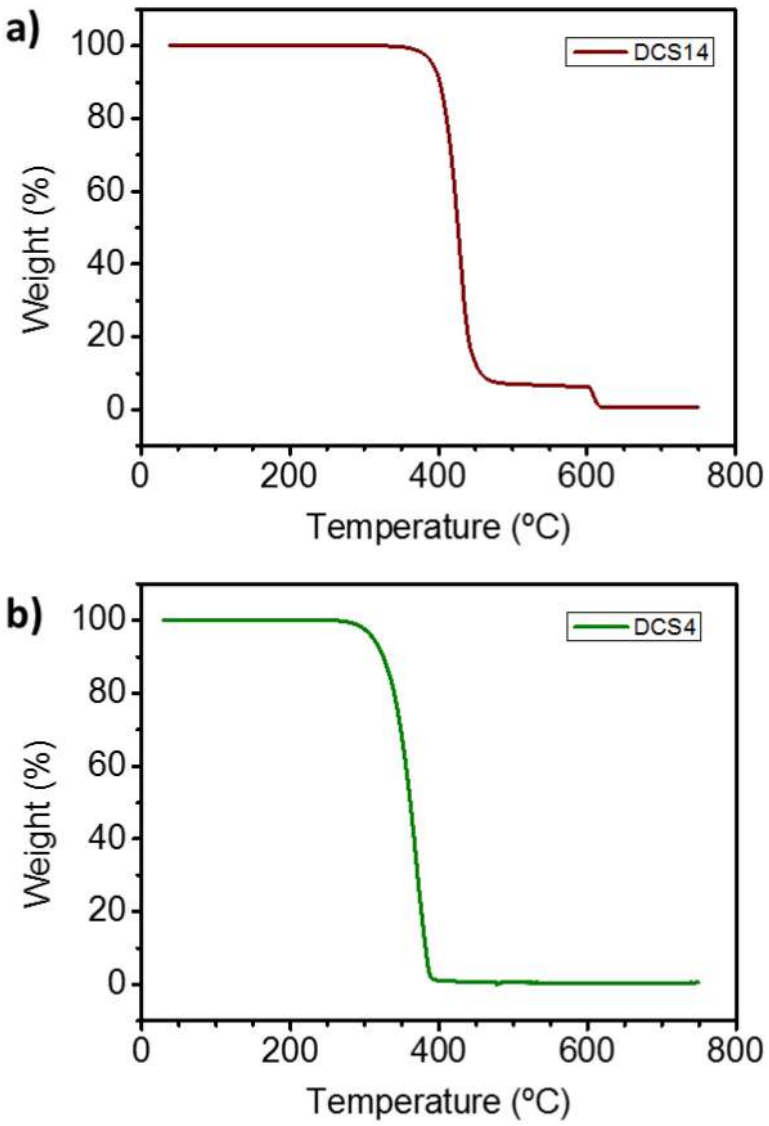

Figure S8. Thermogravimetric analysis of the rod-like dicyanodistyrylbenzenes: a) **DCS14**; b) **DCS4**.

6. Absorption and fluorescence studies

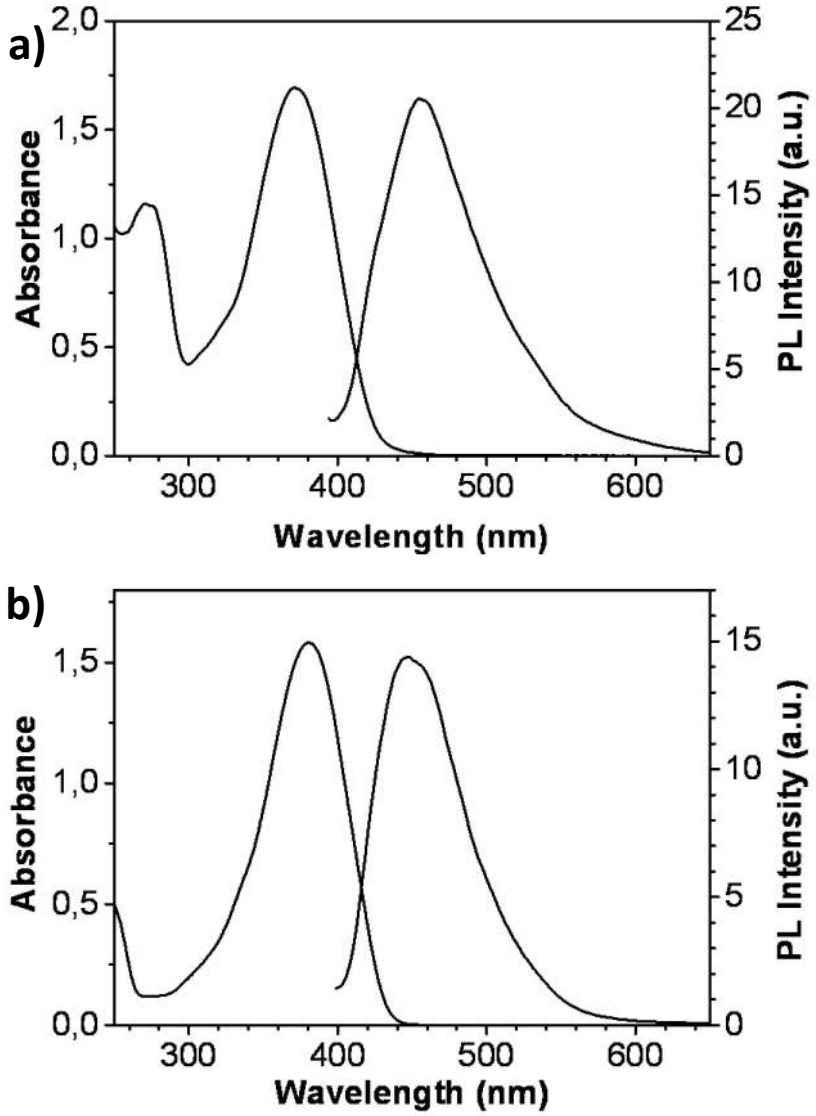

Figure S9. Absorption and fluorescence spectra in DCM of: a) **B14-DCS14** (2.78 x 10^{-5} M and 1.39 x 10^{-6} M, respectively); b) **B4-DCS4** (2.69 x 10^{-5} M and 1.62 x 10^{-6} M, respectively).

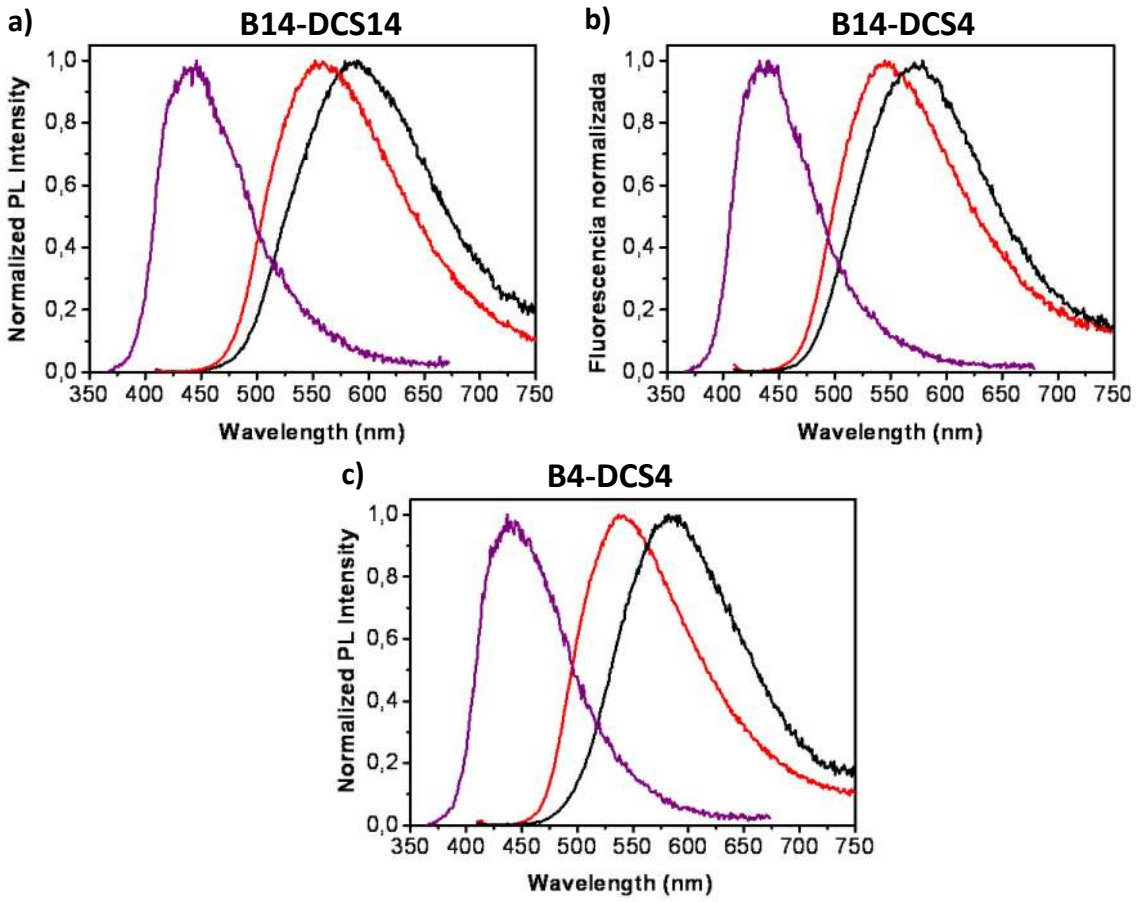

Figure S10. Fluorescence spectra in different solid phases of: a) **B14-DCS14**; b) **B14-DCS4**; c) **B4-DCS4.** Black: as-obtained solid, Red: processed solid, Violet: PMMA film.