**New pyrimidine-based photo-switchable bent-core liquid crystals**

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Experimental

Materials

Sodium nitrite (BDH), ethyl 4-aminobenzoate (Fluka), urea (BDH), phenol (Merck), potassium carbonate (Fluka), allyl bromide (Aldrich), 4-bromo-1-butene (Aldrich), 5-bromo-1-penetene(Aldrich), 6-bromo-1-hexene (Aldrich), 7-bromo-1-heptene (Aldrich), 8-bromo-1-octene (Aldrich), 2,6-pyrimidinediol (Aldrich), 1,3-dicyclohexylcarbodiimide (DCC) (Fluka) and 4-(N,N-dimethylamino)pyridine (DMAP) (Fluka) and silica gel-60 (Merck) were used as received. Acetone was refluxed over phosphorus pentaoxide (Merck) and dichloromethane was refluxed over calcium hydride and both were distilled before use.

**Ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate (1)**

Compound **1** was prepared following the reported procedure [1, 2] from ethyl 4-aminobenzoate (10.18 g, 0.0616 mol), conc. hydrochloric acid (14 ml), sodium nitrite (4.257 g, 0.0616 mol) and phenol (5.79 g, 0.0616 mol) in 600 ml methanol. Yield: 8.01 g (50.7%) as red crystals, m.p. 160 °C. IR, νmax/cm-1 3322 (OH), 1724 (C=O, ester), 1604, 1480 (C=C, aromatic), 1249, 1142 (C-O), 828 (C-H). δH(500 MHz; acetone-d6; Me4Si) 8.16 (d, 2H, *J* = 8.0 Hz), 7.90 (d, 2H, *J* = 6.8Hz), 7.88 (d, 2H, *J* = 7.8 Hz), 7.0 (d, 2H, *J* = 8.9 Hz), 5.57 (s, 1H, OH), 4.42 (q, 2H, *J* = 6.9 Hz, -*CH2*CH3), 1.47 (3H, -CH2*CH3*). δC(125 MHz; acetone-d6; Me4Si) 14.58, 61.40, 116.10, 122.59, 125.58, 130.70, 131.62, 147.19, 155.41, 159.21, 166.41.

**Ethyl 4-{2-[4-(but-3-enyloxy)phenyl]diazenyl}benzoate (2b)**

Compound **1** (1.20 g, 4.44 mmol) was dissolved in dry acetone (100 ml), 4-bromo-1-butene (0.820 g, 6.07 mmol), potassium carbonate (0.840 g, 6.08 mmol) and a catalytic amount of potassium iodide (20 mg) were added and the mixture was refluxed for 24 h under argon atmosphere. Afterwards, it was poured into ice-cold water and acidified with dilute hydrochloric acid (pH<3). The precipitate was filtered off and was crystallized from methanol/chloroform (10:2). Yield of **2b**: 0.820 g (57 IR, νmax/cm-1 3070 (=CH2), 2924 (CH2), 2854 (CH2), 1728 (C=O, ester), 1642 (C=C, vinyl), 1601, 1472 (C=C, aromatic), 1248, 1132, 1064 (C-O), 828 (C-H). δH(500 MHz; CDCl3; Me4Si)8.18 (d, 2H, *J* = 8.6 Hz), 7.96 (d, 2H, *J* = 6.9 Hz), 7.93 (d, 2H, *J* = 6.8 Hz), 7.05 (d, 2H, *J* = 6.8 Hz), 5.95 (m, 1H, CH=), 5.21 (d, 1H, *J*= 16.2 Hz, =CH2), 5.16 (d, 1H, *J*= 10.1 Hz, =CH2), 4.14 (t, 2H, *J* = 6.9 Hz, OCH2-), 3.98 (q, 2H, O*CH2*CH3), 2.62 (m, 2H, -CH2-)*,* 1.61 (t, 3H, -CH2*CH3*). δC(125 MHz; CDCl3; Me4Si) 14.43, 25.45, 61.24, 69.15, 115.13, 118.24, 122.41, 125.22, 130.62, 131.66, 132.70, 147.15, 155.39, 161.71, 166.23.

**Ethyl 4-{2-[4-(pent-4-enyloxy)phenyl]diazenyl}benzoate (2c)**

Compound **1** (1.30 g, 4.81 mmol), dry acetone 100 ml, 5-bromo-1-pentene (0.990 g, 6.64 mmol), potassium carbonate (0.919 g, 6.65 mmol), potassium iodide 20 mg, refluxed for 24 h. Work-up procedure was followed by the same method as used for synthesis of **2a**.Yield: 1.05 g (64.5%). IR, νmax/cm-1 3065 (=CH2), 2924 (CH2), 2854 (CH2), 1724 (C=O, ester), 1639 (C=C, vinyl), 1599, 1486 (C=C, aromatic), 1246, 1130, 1054 (C-O), 839 (C-H). δH(500 MHz; CDCl3; Me4Si)8.18 (d, 2H, *J* = 8.6 Hz), 7.95 (d, 2H, *J* = 6.9 Hz), 7.92 (d, 2H, *J* = 6.9 Hz), 7.04 (d, 2H,*J* = 8.8 Hz), 5.86 (m, 1H, CH=), 5.10 (d, 1H, *J* = 16.2 Hz, =CH2), 5.03 (d, 1H, *J* = 10.1 Hz, =CH2), 4.08 (t, 2H, *J* = 4.9 Hz, OCH2-), 3.97 (q, 2H, O*CH2*CH3), 2.17 (m, 2H, -CH2-)*,* 1.86 (m, 2H, -CH2-)*,* 1.61 (t, 3H, -CH2*CH3*).

**Ethyl 4-{2-[4-(hex-5-enyloxy)phenyl]diazenyl}benzoate (2d)**

Compound **1** (1.00 g, 3.70 mmol), dry acetone 100 ml, 6-bromo-1-hexene (0.826 g, 5.07mmol), potassium carbonate (0.700 g, 5.07 mmol), potassium iodide 20 mg, refluxed for 24 h. Work-up procedure was followed by the same method as used for synthesis of **2a**. Yield: 1.02g (78.3%). IR, νmax/cm-1 3077 (=CH2), 2924 (CH2), 2852 (CH2), 1724 (C=O, ester), 1644 (C=C, vinyl), 1600, 1466 (C=C, aromatic), 1250, 1133, 1045 (C-O), 824 (C-H). δH(500 MHz; CDCl3; Me4Si)8.19 (d, 2H, *J* = 8.7 Hz), 7.96 (d, 2H, *J* = 6.9 Hz), 7.92 (d, 2H, *J* = 6.8 Hz), 7.03 (d, 2H, *J* = 8.8 Hz), 5.90 (m, 1H, CH=), 5.13 (d, 1H, *J*= 16.0 Hz, =CH2), 5.05 (d, 1H, *J* = 10.6 Hz, =CH2), 4.10 (t, 2H, *J* = 4.9 Hz, OCH2-), 3.98 (q, 2H, O*CH2*CH3), 2.31 (m, 2H, -CH2-)*,* 1.96 (m, 4H, -CH2CH2-)*,* 1.62 (t, 3H, -CH2*CH3*).

**Ethyl 4-{2-[4-(hept-6-enyloxy)phenyl]diazenyl}benzoate (2e)**

Compound **1** (1.20 g, 4.44 mmol), dry acetone 100 ml, 7-bromo-1-heptene (0.840 g, 6.08 mmol), potassium carbonate (0.840 g, 6.08 mmol), potassium iodide 20 mg, refluxed for 24 h. Work-up procedure was followed by the same method as used for synthesis of **2a**.Yield: 0.90 g (55.3 %). IR, νmax/cm-1 3070 (=CH2), 2924 (CH2), 2855 (CH2), 1725 (C=O, ester), 1648 (C=C, vinyl), 1601, 1476 (C=C, aromatic), 1247, 1137, 1053 (C-O), 833 (C-H). δH(500 MHz; CDCl3; Me4Si)8.19 (d, 2H, *J* = 8.7 Hz), 7.97 (d, 2H, *J* = 6.7 Hz), 7.92 (d, 2H, *J* = 6.9 Hz), 7.03 (d, 2H, *J* = 8.4 Hz), 5.85 (m, 1H, CH=), 5.04 (d, 1H, *J*= 15.2 Hz, =CH2), 5.00 (d, 1H, *J* = 10.1 Hz, =CH2), 4.08 (t, 2H, *J* = 4.9 Hz, OCH2-), 3.98 (q, 2H, O*CH2*CH3), 2.14 (m, 2H, -CH2-)*,* 1.86 (m, 2H, -CH2)*,* 1.56 (m, 4H, -CH2CH2-)*,* 1.48 (t, 3H, -CH2*CH3*).

**Ethyl 4-{2-[4-(oct-7-enyloxy)phenyl]diazenyl}benzoate (2f)**

Compound **1**(1.20 g, 4.44 mmol), dry acetone 100 ml, 8-bromo-1-octene (1.161 g, 6.07 mmol), potassium carbonate (0.840 g, 6.08 mmol), potassium iodide 20 mg, refluxed for 24 h. Work-up procedure was followed by the same method as used for synthesis of **2a**.Yield: 0.91 g (54 IR, νmax/cm-1 3076 (=CH2), 2929 (CH2), 2856 (CH2), 1725 (C=O, ester), 1645 (C=C, vinyl), 1600, 1477 (C=C, aromatic), 1250, 1137, 1056 (C-O), 825 (C-H). δH(500 MHz; CDCl3; Me4Si)8.18 (d, 2H, *J* = 8.6 Hz), 7.98 (d, 2H, *J* = 6.9 Hz), 7.91 (d, 2H, *J* = 6.9 Hz), 7.02 (d, 2H, *J* = 8.5 Hz), 5.86 (m, 1H, CH=), 5.05 (d, 1H, *J*= 16.1 Hz, =CH2), 5.01 (d, 1H, *J* = 10.2 Hz, =CH2), 4.07 (t, 2H, *J* = 4.8 Hz, OCH2-), 3.98 (q, 2H, O*CH2*CH3), 2.18 (m, 2H, -CH2-)*,* 1.88 (m, 4H, -CH2CH2-)*,* 1.57 (m, 4H, -CH2CH2-)*,* 1.49 (t, 3H, -CH2*CH3*).

**4-{2-[4-(but-3-enyloxy)phenyl]diazenyl}benzoic acid (3b)**

Compound **2a** (0.800 g, 2.46 mmol) was dissolved in 150 ml of methanol. A solution of potassium hydroxide (0.400 g, 7.13mmol) in water (10 ml) was added and the solution was refluxed for 4 h. The mixture was poured into ice-cold water (200 ml) and the precipitate was acidified with conc. hydrochloric acid (10 ml). The precipitate was filtered off, washed with water and crystallized from ethanol/chloroform (2:1) to give compound **3a**. Yield: 0.55 g (56.4%). IR, νmax/cm-1 3075 (=CH2), 2925 (CH2), 2860 (CH2), 1684 (C=O, acid), 1644 (C=C, vinyl), 1599, 1466 (C=C, aromatic), 1249, 1136, 1064 (C-O), 829 (C-H). δH(500 MHz; CDCl3; Me4Si)8.24 (d, 2H, *J* = 8.5 Hz), 7.97 (d, 2H, *J* = 7.9 Hz), 7.95 (d, 2H, *J* = 6.9 Hz), 7.07 (d, 2H, *J* = 8.6 Hz), 5.96 (m, 1H, CH=), 5.25 (d, 1H, *J* = 16.1 Hz, =CH2), 5.18 (d, 1H, *J* = 10.3 Hz, =CH2), 4.15 (t, 2H,*J* = 4.9 Hz, OCH2-), 2.63 (m, 2H, -CH2δC(125 MHz; CDCl3; Me4Si) 25.91, 69.13, 115.18, 118.25, 122.41, 125.24, 130.64, 131.66, 132.73, 147.23, 155.38, 161.69, 166.98.

**4-{2-[4-(pent-4-enyloxy)phenyl]diazenyl}benzoic acid (3c)**

The hydrolysis of **2b** was carried out according to the method described for **3a**. Yield of **3b**: 0.80 g (82.5%). IR, νmax/cm-1 3074 (=CH2), 2935 (CH2), 2866 (CH2), 1684 (νC=O, acid), 1651 (C=C, vinyl), 1602, 1504 (C=C, aromatic), 1268, 1142, 1015 (C-O), 836 (C-H). δH(500 MHz; CDCl3; Me4Si)8.24 (d, 2H, *J* = 8.7 Hz), 7.98 (d, 2H, *J* = 7.5 Hz), 7.94 (d, 2H, *J* = 6.8 Hz), 7.05 (d, 2H, *J* = 8.9 Hz), 5.94 (m, 1H, CH=), 5.10 (d, 1H, *J* = 15.6 Hz, =CH2), 5.01 (d, 1H, *J* = 10.4 Hz, =CH2), 4.09 (t, 2H,*J* = 4.8 Hz, OCH2-), 2.06 (m, 2H, -CH2), 1.70 (m, 2H, -CH2-).

**4-{2-[4-(hex-5-enyloxy)phenyl]diazenyl}benzoic acid (3d)**

The hydrolysis of **2c** was carried out according to the method described for **3a**. Yield of **3c**: 0.850 g (85.3%). IR, νmax/cm-1 3072 (=CH2), 2925 (CH2), 2860 (CH2), 1684 (νC=O, acid), 1647 (C=C, vinyl), 1600, 1504 (C=C, aromatic), 1268, 1142, 1015 (C-O), 826 (C-H). δH(500 MHz; CDCl3; Me4Si)8.24 (d, 2H, *J* = 8.5 Hz), 7.98 (d, 2H, *J* = 7.6 Hz), 7.94 (d, 2H, *J* = 6.8 Hz), 7.05 (d, 2H, *J* = 8.9 Hz), 5.91 (m, 1H, CH=), 5.10 (d, 1H, *J* = 16.1 Hz, =CH2), 5.04 (d, 1H, *J* = 10.5 Hz, =CH2), 4.10 (t, 2H, *J* = 4.8 Hz, OCH2-), 2.29 (m, 2H, -CH2), 1.95 (m, 4H, -CH2CH2-).

**4-{2-[4-(hept-6-enyloxy)phenyl]diazenyl}benzoic acid (3e)**

The hydrolysis of **2d** was carried out according to the method described for **3a**. Yield of **3d**: 0.57 g (65 IR, νmax/cm-1 3064 (=CH2), 2925 (CH2), 2854 (CH2), 1685 (νC=O, acid), 1653 (C=C, vinyl), 1600, 1508 (C=C, aromatic), 1267, 1140, 1015 (C-O), 832 (C-H). δH(500 MHz; CDCl3; Me4Si)8.26 (d, 2H, *J* = 8.6 Hz), 7.97 (d, 2H, *J* = 7.6 Hz), 7.95 (d, 2H, *J* = 6.9 Hz), 7.05 (d, 2H, *J* = 8.8 Hz), 5.90 (m, 1H, CH=), 5.08 (d, 1H, *J* = 16.2 Hz, =CH2), 5.00 (d, 1H, *J* = 10.3 Hz, =CH2), 4.09 (t, 2H, *J* = 4.7 Hz, OCH2-), 2.14 (m, 2H, -CH2), 1.86 (m, 2H, -CH2-), 1.54 (m, 4H, -CH2CH2-).

**4-{2-[4-(oct-7-enyloxy)phenyl]diazenyl}benzoic acid (3f)**

The hydrolysis of **2e** was carried out according to the method described for **3a**. Yield of **3e**: 0.58 g (66.8%). IR, νmax/cm-1 3080 (=CH2), 2928 (CH2), 2852 (CH2), 1684 (νC=O, acid), 1624 (C=C, vinyl), 1602, 1507 (C=C, aromatic), 1260, 1143, 1012 (C-O), 827 (C-H). δH(500 MHz; CDCl3; Me4Si)8.21 (d, 2H, *J* = 8.5 Hz), 7.98 (d, 2H, *J* = 7.9 Hz), 7.92 (d, 2H, *J* = 6.8 Hz), 7.05 (d, 2H, *J* = 8.6 Hz), 5.88 (m, 1H, CH=), 5.05 (d, 1H, *J* = 16.5 Hz, =CH2), 5.01 (d, 1H, *J* = 10.6 Hz, =CH2), 4.08 (t, 2H,*J* = 4.7 Hz, OCH2-), 2.10 (m, 2H, -CH2), 1.87 (m, 2H, -CH2-), 1.51 (m, 2H, -CH2-), 1.45 (m, 4H, -CH2CH2-).

**2,6-Pyrimidine bis[4-{[4-(allyl-en-1-yloxy)phenyl]diazenyl}benzoate] (4a)**

Compound **3a** (0.290 g, 1.02 mmol) and 2,6-pyrimidinediol (0.0570 g, 0.510 mmol) was dissolved in 50 ml of dry dichloromethane. Then DCC (0.226 g, 1.10 mmol) and DMAP (0.013 g, 0.11 mmol) were added and the mixture was stirred for 48 h. The precipitate was removed by filtration and the solvent was removed. The product was dissolved in dichloromethane and water. The organic phase was washed with diluted acetic acid and water and the solvent was removed under reduced pressure. The compound was purified on silica gel by column chromatography using dichloromethane/ hexane as an eluant. Solid was recrystallized from ethanol and chloroform to get the target compound **4a**. Yield: 0.112 g, 34%. IR, νmax/cm-1 3090 (=CH2), 2923 (CH2), 2858 (CH2), 1749 (C=O ester), 1642 (C=C, vinyl), 1594, 1496 (C=C, aromatic), 1248, 1129, 1052 (C-O), 852 (CH, aromatic). ) δH(500 MHz; CDCl3; Me4Si) 8.30 (4H, d, *J* = 8.9 Hz, Ph), 8.02 (1H, d, Py), 7.97 (4H, d, *J* = 6.8 Hz, Ph), 7.92 (4H, d, *J* = 6.9 Hz, Ph), 7.03 (4H, d, *J* = 5.6 Hz, Ph), 6.95 (1H, t, Py), 6.07 (2H, m, CH=), 5.46 (2H, dd, *J* = 17.2 Hz, =CH2), 5.32 (2H, dd, *J* = 10.3 Hz, =CH2), 4.63 (4H, t, *J* = 6.5 Hz, OCH2-). δC(125 MHz; CDCl3; Me4Si) 69.19, 115.11, 115.21, 122.31, 122.91, 124.15, 125.48, 131.76, 132.64, 138.55, 147.17, 156.42, 161.92, 165.55, 168.67. Elemental Analysis, Found: C, 67.16; H, 4.22; N, 13.02. Calc. for C36H28N6O6: C, 67.49; H, 4.40; N, 13.11%.

**2,6-Pyrimidine** **bis[4-{[4-(but-3-en-1-yloxy)phenyl]diazenyl}benzoate] (4b)**

Compound **3b** (0.2960 g, 1.00 mmol), 2,6-pyrimidinediol (0.0560 g, 0.50 mmol), 75 ml of dry dichloromethane, DMAP (14.6 mg, 0.012 mmol) and DCC (0.2480 g, 1.20 mmol) were stirred for 48 h. Yield of **4b**: 0.1350 g, 41%. IR, νmax/cm-1 3078 (=CH2), 2932 (CH2), 2850 (CH2), 1712 (C=O, ester), 1642 (C=C, vinyl), 1601, 1458 (C=C, aromatic), 1277, 1142, 1007 (C-O), 839 (C-H). δH(500 MHz; CDCl3; Me4Si) 8.24 (4H, d, *J* = 8.6 Hz, Ph), 8.02 (1H, d, Py), 9.97 (4H, d, *J* = 5.6 Hz, Ph) 7.92 (4H, d, *J* = 5.7 Hz, Ph), 7.05 (4H, d, *J* = 9.0 Hz, Ph), 6.91 (1H, t, Py), 5.91 (2H, m, CH=), 5.14 (2H, dd, *J* = 15.3 Hz, =CH2), 5.11 (2H, dd, *J* = 9.8 Hz, =CH2), 4.10 (4H, t, *J* = 6.5 Hz, OCH2-), 2.31 (4H, m, -CH2-). δC(125 MHz; CDCl3; Me4Si) 26.17, 68.79, 114.18, 114.68, 122.59, 122.67, 124.49, 125.38, 130.72, 130.88, 138.89, 146.72, 155.62, 162.43, 165.67, 168.78. Elemental Analysis, Found: C, 68.12; H, 4.70; N, 12.36. Calc. for C38H32N6O6: C, 68.25; H, 4.82; N, 12.56%.

**2,6-Pyrimidine** **bis[4-{[4-(pent-4-en-1-yloxy)phenyl]diazenyl}benzoate] (4c)**

Compound **3c** (0.3100 g, 1.00 mmol), 2,6-pyrimidinediol (0.0560 g, 0.50 mmol), 75 ml of dry dichloromethane, DMAP (14.6 mg, 0.012 mmol) and DCC (0.2480 g, 1.20 mmol) were stirred for 48 h. Yield of **4c**: 0.1480 g, 43%. IR, νmax/cm-1 3076 (=CH2), 2942 (CH2), 2868 (CH2), 1713 (C=O, ester), 1641 (C=C, vinyl), 1604, 1470 (C=C, aromatic), 1277, 1142, 1006 (C-O), 837 (C-H). δH(500 MHz; CDCl3; Me4Si) 8.21 (4H, d, *J* = 8.6 Hz, Ph), 8.01 (1H, d, Py), 7.96 (4H, d, *J* = 5.5 Hz, Ph) 7.91 (4H, d, *J* = 5.8 Hz, Ph), 7.05 (4H, d, *J* = 9.0 Hz, Ph), 6.92 (1H, t, Py), 5.91 (2H, m, CH=), 5.14 (2H, dd, *J* = 15.2 Hz, =CH2), 5.10 (2H, dd, *J* = 9.8 Hz, =CH2), 4.09 (4H, t, *J* = 6.4 Hz, OCH2-), 2.32 (4H, m, -CH2-), 1.96 (4H, m, -CH2-). δC(125 MHz; CDCl3; Me4Si) 25.77, 28.22, 68.59, 114.28, 114.78, 122.55, 122.65, 124.59, 125.34, 130.71, 130.87, 138.93, 146.76, 155.66, 162.23, 165.69, 168.79. Elemental Analysis, Found: C, 68.81; H, 5.11; N, 11.96. Calc. for C40H36N6O6: C, 68.95; H, 5.20; N, 12.06%.

**2,6-Pyrimidine** **bis[4-{[4-(hex-5-en-1-yloxy)phenyl]diazenyl}benzoate] (4d)**

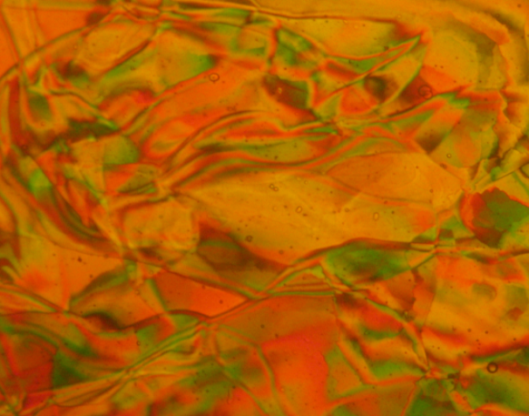
Compound **3d** (0.3240 g, 1.00 mmol), 2,6-pyrimidinediol (0.0560 g, 0.50 mmol), 75 ml of dry dichloromethane, DMAP (14.6 mg, 0.012 mmol) and DCC (0.2480 g, 1.20 mmol) were stirred for 48 h. Yield of **4d**: 0.1521 g, 42%. IR, νmax/cm-1 3078 (=CH2), 2940 (CH2), 2873 (CH2), 1711 (C=O, ester), 1641 (C=C, vinyl), 1601, 1473 (C=C, aromatic), 1279, 1143, 1025 (C-O), 838 (C-H). δH(500 MHz; CDCl3; Me4Si) 8.21 (4H, d, *J* = 8.7 Hz, Ph), 8.01 (1H, d, Py), 7.98 (4H, d, *J* = 5.8 Hz, Ph) 7.91 (4H, d, *J* = 6.8 Hz, Ph), 7.05 (4H, d, *J* = 7.9 Hz, Ph), 6.94 (1H, t, Py), 5.87 (2H, m, CH=), 5.10 (2H, dd, *J* = 16.1 Hz, =CH2), 5.02 (2H, dd, *J* = 13.8 Hz, =CH2), 4.10 (4H, t, *J* = 6.5 Hz, OCH2-), 2.19 (4H, m, -CH2), 1.92 (4H, m, -CH2-), 1.63 (4H, m, -CH2-). δC(125 MHz; CDCl3; Me4Si) 25.73, 28.12, 29.19, 68.39, 114.18, 114.68, 122.45, 122.47, 124.39, 125.29, 130.65, 130.77, 138.92, 146.66, 155.46, 162.13, 165.67, 168.69. Elemental Analysis, Found: C, 69.55; H, 5.39; N, 11.44. Calc. for C42H40N6O6: C, 69.59; H, 5.56; N, 11.59%.

**2,6-Pyrimidine** **bis[4-{[4-(hept-6-en-1-yloxy)phenyl]diazenyl}benzoate] (4e)**

Compound **3e** (0.1200 g, 0.355 mmol), 2,6-pyrimidinediol (0.0198 g, 0.177 mmol), 50 ml of dry dichloromethane, DMAP (4.8 mg, 0.04 mmol) and DCC (0.0820 g, 0.40 mmol) were stirred for 48 h. Yield of **4d**: 0.0499 g, 38%. IR, νmax/cm-1 3065 (=CH2), 2926 (CH2), 2854 (CH2), 1715 (C=O, ester), 1642 (C=C, vinyl), 1603, 1459 (C=C, aromatic), 1270, 1136, 1035 (C-O), 837 (C-H). δH(500 MHz; CDCl3; Me4Si) 8.26 (4H, d, *J* = 8.7 Hz, Ph), 8.02 (1H, d, Py), 8.0 (4H, d, *J* = 5.4 Hz, Ph) 7.93 (4H, d, *J* = 5.9 Hz, Ph), 7.04 (4H, d, *J* = 9.0 Hz, Ph), 6.92 (1H, t, Py), 5.85 (2H, m, CH=), 5.06 (2H, dd, *J* = 15.3 Hz, =CH2), 4.98 (2H, dd, *J* = 9.8 Hz, =CH2), 4.08 (4H, t, *J* = 6.5 Hz, OCH2-), 2.14 (4H, m, -CH2-), 1.97 (4H, m, -CH2-), 1.86 (4H, m, -CH2-), 1.71 (4H, m, -CH2-). δC(125 MHz; CDCl3; Me4Si) 25.71, 28.22, 29.11, 29.11, 68.37, 114.28, 114.88, 122.35, 122.45, 124.29, 125.29, 130.65, 130.71, 138.89, 146.76, 155.44, 162.23, 165.68, 168.78. Elemental Analysis, Found: 70.02; H, 5.77; N, 11.03. Calc. for C44H44N6O6: C, 70.19; H, 5.89; N, 11.16%.

**2,6-Pyrimidine** **bis[4-{[4-(oct-7-en-1-yloxy)phenyl]diazenyl}benzoate] (4f)**

Compound **3e** (0.1250 g, 0.355 mmol), 2,6-pyrimidinediol (0.0198 g, 0.177 mmol), 50 ml of dry dichloromethane, DMAP (4.8 mg, 0.04 mmol) and DCC (0.0820 g, 0.40 mmol) were stirred for 48 h. Yield of **4e**: 0.0535 g, 39%. IR, νmax/cm-1 3079 (=CH2), 2933 (CH2), 2855 (CH2), 1721 (C=O, ester), 1641 (C=C, vinyl), 1602, 1500 (C=C, aromatic), 1282, 1142, 1028 (C-O), 842 (C-H). δH(500 MHz; CDCl3; Me4Si) 8.20 (4H, d, *J* = 8.7 Hz, Ph), 8.02 (1H, d, Py), 7.97 (4H, d, *J* = 8.7 Hz, Ph) 7.92 (4H, d, *J* = 8.5 Hz, Ph), 7.05 (4H, d, *J* = 8.7 Hz, Ph), 6.91 (1H, t, Py), 5.86 (2H, m, CH=), 5.05 (2H, dd, *J* = 15.5 Hz, =CH2), 4.96 (2H, dd, *J* = 9.7 Hz, =CH2), 4.07 (4H, t, *J* = 6.5 Hz, OCH2-), 2.11 (4H, m, -CH2-), 1.88 (4H, m, -CH2-), 1.72 (4H, m, -CH2-), 1.51 (8H, m, -CH2-). δC(125 MHz; CDCl3; Me4Si) 25.81, 28.80, 29.01, 29.11, 33.70, 68.38, 114.18, 114.80, 122.31, 122.35, 124.39, 125.21, 130.55, 130.60, 138.99, 146.86, 155.41, 162.33, 166.69, 166.77. Elemental Analysis, Found: C, 70.59; H, 6.05; N, 10.61. Calc. for C46H48N6O6: C, 70.74; H, 6.19; N, 10.76%.

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**Fig. S1** POM micrographs by cooling of isotropic melt: **4a** (left)and **4b** (right) crystalline phase

**Fig. S2** UV/visible absorption spectra of **4c-f** in chloroform at conc. 2.25 x 10-5 mol L-1

**References**

S1 M. R. Lutfor, J. Asik, S. Kumar, S. Silong and M. Z. Ab. Rahman. *Phase Transitions*, **82**, 2009, 228–239.

S2 M. R. Lutfor, A. Jahimin, S. Kumar and C. Tschierske, *Liq. Cryst.,* 2008, **35**, 1263-1270.