

## Electronic supporting information

# Synthesis of new U-shaped azobenzene liquid crystals for photoswitching properties

Md Lutfur Rahman,<sup>a\*</sup> Shaheen M. Sarkar,<sup>a</sup> Mashitah M. Yusoff,<sup>a</sup> Sandeep Kumar,<sup>b</sup> Carsten Tschierske<sup>c</sup>

<sup>a</sup>Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

<sup>b</sup>Raman Research Institute, Raman Avenue, Sadashivanagar, Bangalore 560080, India

<sup>c</sup>Institute of Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt-Mothes Str. 2, Halle D-06120, Germany

## 1. Experimental

### 1.1 Materials

Ethyl 4-aminobenzoate (Sigma), Sodium nitrite (BDH), phenol (Merck), potassium carbonate (Fluka), 4-bromo-1-butene (Aldrich), 5-bromo-1-pentene (Aldrich), 6-bromo-1-hexene (Aldrich), 7-bromo-1-heptene (Aldrich), 8-bromo-1-octene (Aldrich), resorcinol (Aldrich), catechol (Sigma-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 pentoxide (Merck) and dichloromethane was refluxed over calcium hydride and both were distilled before use. Other solvents and chemicals were used without further purification.

### 1.2 Ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate (1)

Compound **1** was synthesized according to the reported procedure<sup>1</sup> from ethyl 4-aminobenzoate (12.00 g, 0.0727 mol), conc. hydrochloric acid (17 ml), sodium nitrite (5.018 g, 0.0727 mol) and phenol (6.836 g, 0.0727 mol) in 650 ml methanol. Yield: 9.71 g, 51.2% as red crystals and mp 160°C. IR,  $\nu_{\max}/\text{cm}^{-1}$  3324 (OH), 1726 (C=O, ester), 1601, 1482 (C=C, aromatic), 1251, 1140 (C-O), 829 (C-H).  $\delta_{\text{H}}$ (500 MHz; acetone- $d_6$ ; Me<sub>4</sub>Si) 8.16 (2H, d,  $J$  = 8.1 Hz, Ph), 7.91 (2H, d,  $J$  = 6.8 Hz, Ph), 7.87 (2H, d,  $J$  = 7.9 Hz, Ph), 7.01 (2H, d,  $J$  = 8.8 Hz, Ph), 5.61 (1H, s, OH), 4.40 (2H, q,  $J$  = 6.9 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 1.47 (3H, -CH<sub>2</sub>CH<sub>3</sub>).  $\delta_{\text{C}}$ (125 MHz; acetone- $d_6$ ; Me<sub>4</sub>Si) 14.57, 61.42, 116.11, 122.56, 125.53, 130.74, 131.63, 147.17, 155.43, 159.25, 166.52. Elemental Analysis, Found: C, 66.55; H, 5.24; N, 10.24. Calc. for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 66.69; H, 5.22; N, 10.36%.

### 1.3 Ethyl 4-[[4-(but-3-en-1-yloxy)phenyl]diazenyl]benzoate (2a)

Compound **1** (1.80 g, 6.66 mmol) was dissolved in dry acetone (150 ml); 4-bromo-1-butene (1.230 g, 9.10 mmol), potassium carbonate (1.260 g, 9.13 mmol) and a catalytic amount of potassium iodide (20 mg) were added and the mixture was refluxed for 24 h under argon atmosphere. Then, it was poured into ice-cold water and acidified with dilute hydrochloric acid (pH<3). The precipitate was filtered off and crystallized from ethanol/chloroform (2:1). Then the compound was purified on silica gel by column chromatography using dichloromethane/ hexane as an eluant. Solid was recrystallized from ethanol and chloroform (2:1). Yield of **2a**: 1.71 g, 59.4% and exhibit phase transition, Cr 128 SmA 142 I. IR,  $\nu_{\max}/\text{cm}^{-1}$  3072 (=CH<sub>2</sub>), 2924 (CH<sub>2</sub>), 2852 (CH<sub>2</sub>), 1728 (C=O, ester), 1640 (C=C, vinyl), 1601, 1470 (C=C, aromatic), 1248, 1134, 1060 (C-O),

## Electronic supporting information

827 (C-H).  $\delta_{\text{H}}$ (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.20 (2H, d,  $J = 8.6$  Hz, Ph), 7.96 (2H, d,  $J = 9.0$  Hz, Ph), 7.90 (2H, d,  $J = 8.7$  Hz, Ph), 7.05 (2H, d,  $J = 9.1$  Hz, Ph), 5.94 (1H, m, CH=), 5.26 (1H, dd,  $J = 15.6$  Hz, =CH<sub>2</sub>), 5.17 (1H, dd,  $J = 8.7$  Hz, =CH<sub>2</sub>), 4.13 (2H, t,  $J = 6.6$  Hz, OCH<sub>2</sub>-), 3.97 (2H, s, OCH<sub>2</sub>CH<sub>3</sub>), 2.62 (2H, m, -CH<sub>2</sub>-), 1.65 (3H, t, -CH<sub>2</sub>CH<sub>3</sub>).  $\delta_{\text{C}}$ (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 14.44, 26.22, 61.26, 69.14, 115.14, 118.25, 122.44, 125.21, 130.63, 131.61, 132.71, 147.16, 155.35, 161.72, 166.28.

### 1.4 Ethyl 4-[[4-(pent-4-en-1-yloxy)phenyl]diazenyl]benzoate (2b)

Compound **1** (2.60 g, 9.62 mmol), dry acetone 180 ml, 5-bromo-1-pentene (1.980 g, 13.28 mmol), potassium carbonate (1.830 g, 13.3 mmol), potassium iodide 20 mg, refluxed for 24 h. Etherification was carried out by the same method as used for synthesis of **2a**. Yield: 2.20 g, 67.5% and exhibit phase transition, Cr 124 SmA 136 l. IR,  $\nu_{\text{max}}/\text{cm}^{-1}$  3066 (=CH<sub>2</sub>), 2924 (CH<sub>2</sub>), 2852 (CH<sub>2</sub>), 1724 (C=O, ester), 1636 (C=C, vinyl), 1597, 1480 (C=C, aromatic), 1242, 1132, 1054 (C-O), 840 (C-H).  $\delta_{\text{H}}$ (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.20 (d, 2H,  $J = 8.6$  Hz), 7.97 (d, 2H,  $J = 9.0$  Hz), 7.92 (d, 2H,  $J = 8.6$  Hz), 7.05 (d, 2H,  $J = 9.0$  Hz), 5.90 (m, 1H, CH=), 5.12 (dd, 1H,  $J = 15.5$  Hz, =CH<sub>2</sub>), 5.04 (dd, 1H,  $J = 9.2$  Hz, =CH<sub>2</sub>), 4.09 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>-), 3.97 (s, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.30 (m, 2H, -CH<sub>2</sub>-), 1.96 (m, 2H, -CH<sub>2</sub>-), 1.62 (t, 3H, -CH<sub>2</sub>CH<sub>3</sub>).  $\delta_{\text{C}}$ (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 14.42, 26.12, 28.45, 61.27, 69.15, 115.19, 118.84, 122.62, 125.33, 130.56, 131.71, 132.74, 147.35, 155.44, 161.82, 166.28.

### 1.5 Ethyl 4-[[4-(hex-5-en-1-yloxy)phenyl]diazenyl]benzoate (2c)

Compound **1** (2.20 g, 8.14 mmol), dry acetone 170 ml, 6-bromo-1-hexene (1.652 g, 10.14 mmol), potassium carbonate (1.401 g, 10.14 mmol), potassium iodide 20 mg, refluxed for 24 h. Etherification was carried out by the same method as used for synthesis of **2a**. Yield: 2.01 g, 77.1% and exhibit phase transition, Cr 125 SmA 140 l. IR,  $\nu_{\text{max}}/\text{cm}^{-1}$  3076 (=CH<sub>2</sub>), 2928 (CH<sub>2</sub>), 2850 (CH<sub>2</sub>), 1724 (C=O, ester), 1642 (C=C, vinyl), 1601, 1462 (C=C, aromatic), 1251, 1130, 1042 (C-O), 825 (C-H).  $\delta_{\text{H}}$ (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.20 (d, 2H,  $J = 8.6$  Hz), 7.97 (d, 2H,  $J = 8.9$  Hz), 7.92 (d, 2H,  $J = 8.6$  Hz), 7.04 (d, 2H,  $J = 8.9$  Hz), 5.86 (m, 1H, CH=), 5.09 (dd, 1H,  $J = 15.3$  Hz, =CH<sub>2</sub>), 5.00 (dd, 1H,  $J = 8.4$  Hz, =CH<sub>2</sub>), 4.08 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>-), 3.97 (s, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.18 (m, 2H, -CH<sub>2</sub>-), 1.87 (m, 2H, -CH<sub>2</sub>-), 1.64 (m, 2H, -CH<sub>2</sub>-), 1.61 (t, 3H, -CH<sub>2</sub>CH<sub>3</sub>).  $\delta_{\text{C}}$ (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 14.41, 25.45, 27.12, 28.18, 61.25, 69.15, 115.18, 118.11, 122.39, 125.26, 130.59, 131.62, 132.69, 147.26, 155.32, 161.82, 166.27.

### 1.6 Ethyl 4-[[4-(hept-6-en-1-yloxy)phenyl]diazenyl]benzoate (2d)

Compound **1b** (1.10 g, 4.07 mmol), dry acetone 100 ml, 7-bromo-1-heptene (0.897 g, 5.07 mmol), potassium carbonate (0.700 g, 5.07 mmol), potassium iodide 20 mg, refluxed for 24 h. Etherification was carried out by the same method as used for synthesis of **2a**. Yield: 0.83 g, 55.5% and exhibit phase transition, Cr 115 SmA 128 l. IR,  $\nu_{\text{max}}/\text{cm}^{-1}$  3072 (=CH<sub>2</sub>), 2924 (CH<sub>2</sub>), 2852 (CH<sub>2</sub>), 1724 (C=O, ester), 1646 (C=C, vinyl), 1601, 1472 (C=C, aromatic), 1243, 1136, 1050 (C-O), 830 (C-H).  $\delta_{\text{H}}$ (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.20 (d, 2H,  $J = 8.6$  Hz), 7.98 (d, 2H,  $J = 11.9$  Hz), 7.92 (d, 2H,  $J = 8.5$  Hz), 7.04 (d, 2H,  $J = 9.2$  Hz), 5.86 (m, 1H, CH=), 5.06 (dd, 1H,  $J = 12.3$  Hz, =CH<sub>2</sub>), 4.98 (dd, 1H,  $J = 8.2$  Hz, =CH<sub>2</sub>), 4.07 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>-), 3.97 (s, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.13 (m, 2H, -CH<sub>2</sub>-), 1.87 (m, 2H, -CH<sub>2</sub>-), 1.55 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 1.57 (t, 3H, -CH<sub>2</sub>CH<sub>3</sub>).  $\delta_{\text{C}}$ (125 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 14.44, 22.98, 25.45, 26.12, 29.12, 61.24, 69.15, 115.55, 118.54, 122.45, 125.34, 130.55, 131.71, 132.68, 147.23, 155.43, 161.82, 166.27.

## Electronic supporting information

### 1.7 Ethyl 4-[[4-(oct-7-en-1-yloxy)phenyl]diazanyl]benzoate (2e)

Compound **1** (1.10 g, 4.07 mmol), dry acetone 100 ml, 8-bromo-1-octene (0.968 g, 5.07 mmol), potassium carbonate (0.700 g, 5.07 mmol), potassium iodide 20 mg, refluxed for 24 h. Etherification was carried out by the same method as used for synthesis of **2a**. Yield: 0.84 g, 54.5% and exhibit phase transition, Cr 120 SmA 133 I. IR,  $\nu_{\max}/\text{cm}^{-1}$  3077 (=CH<sub>2</sub>), 2928 (CH<sub>2</sub>), 2854 (CH<sub>2</sub>), 1724 (C=O, ester), 1642 (C=C, vinyl), 1601, 1470 (C=C, aromatic), 1251, 1134, 1052 (C-O), 825 (C-H).  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.18 (d, 2H, *J* = 8.5 Hz), 7.98 (d, 2H, *J* = 8.8 Hz), 7.91 (d, 2H, *J* = 8.5 Hz), 7.02 (d, 2H, *J* = 8.6 Hz), 5.86 (m, 1H, CH=), 5.06 (dd, 1H, *J* = 13.2 Hz, =CH<sub>2</sub>), 5.01 (dd, 1H, *J* = 9.5 Hz, =CH<sub>2</sub>), 4.07 (t, 2H, *J* = 6.7 Hz, OCH<sub>2</sub>-), 3.97 (s, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.18 (m, 2H, -CH<sub>2</sub>-), 1.88 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 1.57 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 1.49 (t, 3H, -CH<sub>2</sub>CH<sub>3</sub>).  $\delta_{\text{C}}$ (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 14.44, 20.44, 25.56, 26.68, 29.68, 30.15, 62.22, 69.18, 116.23, 118.24, 122.88, 125.32, 130.68, 131.67, 132.79, 147.25, 155.38, 161.77, 166.22.

### 1.8 4-[[4-(But-3-en-1-yloxy)phenyl]diazanyl]benzoic acid (3a)

Compound **2a** (1.600 g, 4.92 mmol) was dissolved in 250 ml of methanol. A solution of potassium hydroxide (0.800 g, 14.26 mmol) in water (10 ml) was added and the solution was refluxed for 4 h. The mixture was poured into ice-cold water (400 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 **3a**. The compound was purified on silica gel by column chromatography using dichloromethane/ hexane as an eluant. Solid was recrystallized from ethanol and chloroform (2:1). Yield: 1.12 g, 57% and mp 236 °C. IR,  $\nu_{\max}/\text{cm}^{-1}$  3076 (=CH<sub>2</sub>), 2924 (CH<sub>2</sub>), 2862 (CH<sub>2</sub>), 1684 (C=O, acid), 1642 (C=C, vinyl), 1601, 1466 (C=C, aromatic), 1244, 1132, 1064 (C-O), 826 (C-H).  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.26 (d, 2H, *J* = 8.7 Hz), 7.99 (d, 2H, *J* = 9.0 Hz), 7.95 (d, 2H, *J* = 8.7 Hz), 7.06 (d, 2H, *J* = 9.0 Hz), 5.96 (m, 1H, CH=), 5.24 (dd, 1H, *J* = 15.5 Hz, =CH<sub>2</sub>), 5.16 (dd, 1H, *J* = 9.8 Hz, =CH<sub>2</sub>), 4.15 (t, 2H, *J* = 6.7 Hz, OCH<sub>2</sub>-), 2.63 (m, 2H, -CH<sub>2</sub>-).  $\delta_{\text{C}}$ (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 26.23, 69.13, 115.18, 118.25, 122.41, 125.24, 130.64, 131.66, 132.73, 147.23, 155.38, 161.69, 167.11.

### 1.9 4-[[4-(Pent-4-en-1-yloxy)phenyl]diazanyl]benzoic acid (3b)

The hydrolysis of **2b** was carried out according to the method described for **3a**. Yield of **3b**: 1.64 g, 83% and mp 229 °C. IR,  $\nu_{\max}/\text{cm}^{-1}$  3076 (=CH<sub>2</sub>), 2932 (CH<sub>2</sub>), 2862 (CH<sub>2</sub>), 1684 ( $\nu$ C=O, acid), 1646 (C=C, vinyl), 1601, 1502 (C=C, aromatic), 1262, 1142, 1011 (C-O), 832 (C-H).  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.25 (d, 2H, *J* = 8.4 Hz), 7.98 (d, 2H, *J* = 9.0 Hz), 7.94 (d, 2H, *J* = 8.5 Hz), 7.03 (d, 2H, *J* = 8.9 Hz), 5.88 (m, 1H, CH=), 5.06 (dd, 1H, *J* = 17.8 Hz, =CH<sub>2</sub>), 5.01 (dd, 1H, *J* = 8.9 Hz, =CH<sub>2</sub>), 4.09 (t, 2H, *J* = 6.5 Hz, OCH<sub>2</sub>-), 2.06 (m, 2H, -CH<sub>2</sub>-), 1.70 (m, 2H, -CH<sub>2</sub>-).  $\delta_{\text{C}}$ (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 26.19, 28.35, 69.22, 115.23, 118.75, 122.65, 125.41, 130.48, 131.83, 132.66, 147.45, 155.56, 161.77, 167.21.

### 1.10 4-[[4-(Hex-5-en-1-yloxy)phenyl]diazanyl]benzoic acid (3c)

The hydrolysis of **2c** was carried out according to the method described for **3a**. Yield of **3c**: 1.57 g, 83.7% and mp 232 °C. IR,  $\nu_{\max}/\text{cm}^{-1}$  3072 (=CH<sub>2</sub>), 2925 (CH<sub>2</sub>), 2860 (CH<sub>2</sub>), 1684 ( $\nu$ C=O, acid), 1647 (C=C, vinyl), 1600, 1504 (C=C, aromatic), 1268, 1142, 1015 (C-O), 826 (C-H).  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.25 (d, 2H, *J* = 8.5 Hz), 7.98 (d, 2H, *J* = 9.0 Hz), 7.94 (d, 2H, *J* = 8.5 Hz), 7.05 (d, 2H, *J* = 8.9 Hz), 5.89 (m, 1H, CH=), 5.13 (dd, 1H, *J* = 15.5 Hz, =CH<sub>2</sub>), 5.06 (dd, 1H, *J* = 8.5 Hz, =CH<sub>2</sub>), 4.10 (t, 2H, *J* = 6.5 Hz, OCH<sub>2</sub>-), 2.29 (m, 2H, -CH<sub>2</sub>-), 1.96 (m, 2H,

## Electronic supporting information

-CH<sub>2</sub>-), 1.70 (m, 2H, -CH<sub>2</sub>-).  $\delta_C$ (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 25.41, 27.23, 28.23, 69.15, 115.33, 118.45, 122.42, 125.31, 130.61, 131.55, 132.72, 147.13, 155.23, 161.67, 167.16.

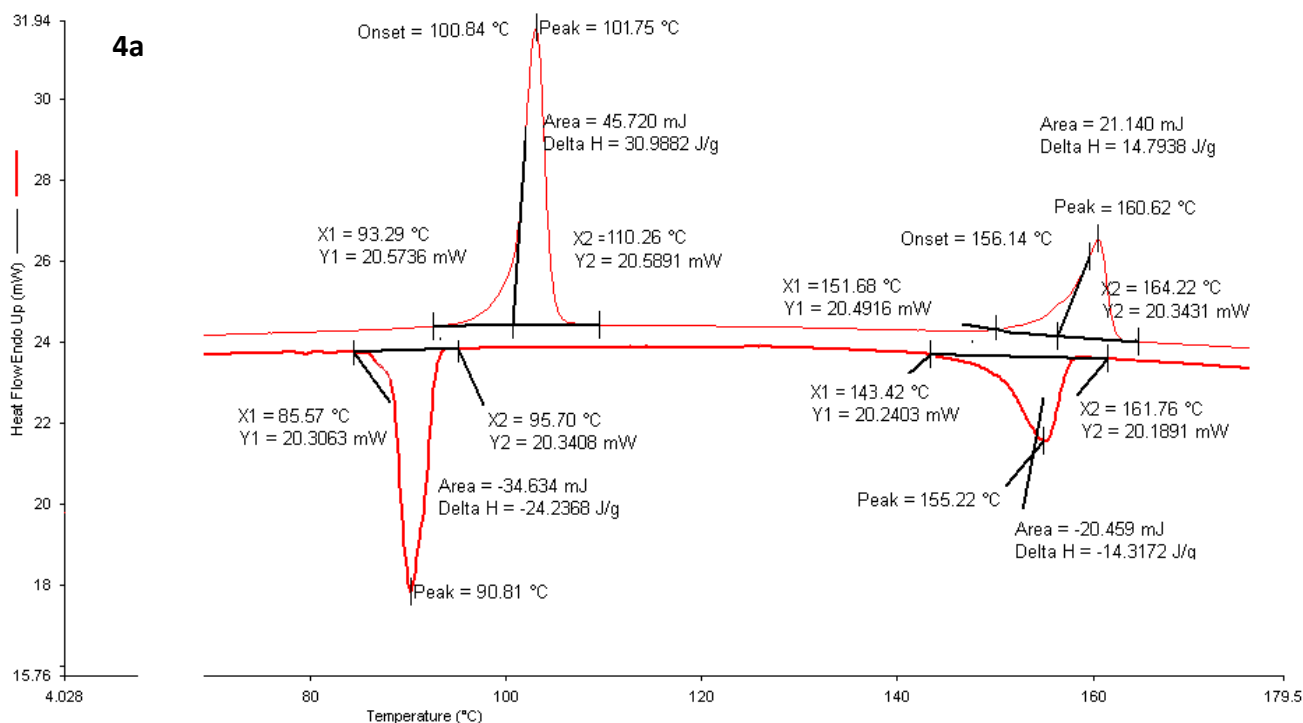
### 1.11 4-[[4-(Hept-6-en-1-yloxy)phenyl]diazanyl]benzoic acid (3d)

The hydrolysis of **2d** was carried out according to the method described for **3a**. Yield of **3d**: 1.16 g, 66.1 and mp 222 °C. IR,  $\nu_{\max}/\text{cm}^{-1}$  3062 (=CH<sub>2</sub>), 2922 (CH<sub>2</sub>), 2854 (CH<sub>2</sub>), 1684 ( $\nu\text{C}=\text{O}$ , acid), 1650 (C=C, vinyl), 1603, 1507 (C=C, aromatic), 1262, 1140, 1012 (C-O), 830 (C-H).  $\delta_H$ (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.26 (d, 2H,  $J = 8.5$  Hz), 7.98 (d, 2H,  $J = 7.1$  Hz), 7.95 (d, 2H,  $J = 7.7$  Hz), 7.05 (d, 2H,  $J = 9.0$  Hz), 5.85 (m, 1H, CH=), 5.03 (dd, 1H,  $J = 13.6$  Hz, =CH<sub>2</sub>), 4.98 (dd, 1H,  $J = 8.2$  Hz, =CH<sub>2</sub>), 4.08 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>-), 2.14 (m, 2H, -CH<sub>2</sub>-), 1.87 (m, 2H, -CH<sub>2</sub>-), 1.52 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-).  $\delta_C$ (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 22.97, 25.56, 26.59, 29.02, 69.24, 115.65, 118.44, 122.33, 125.35, 130.55, 131.67, 132.47, 147.26, 155.43, 161.69, 166.21.

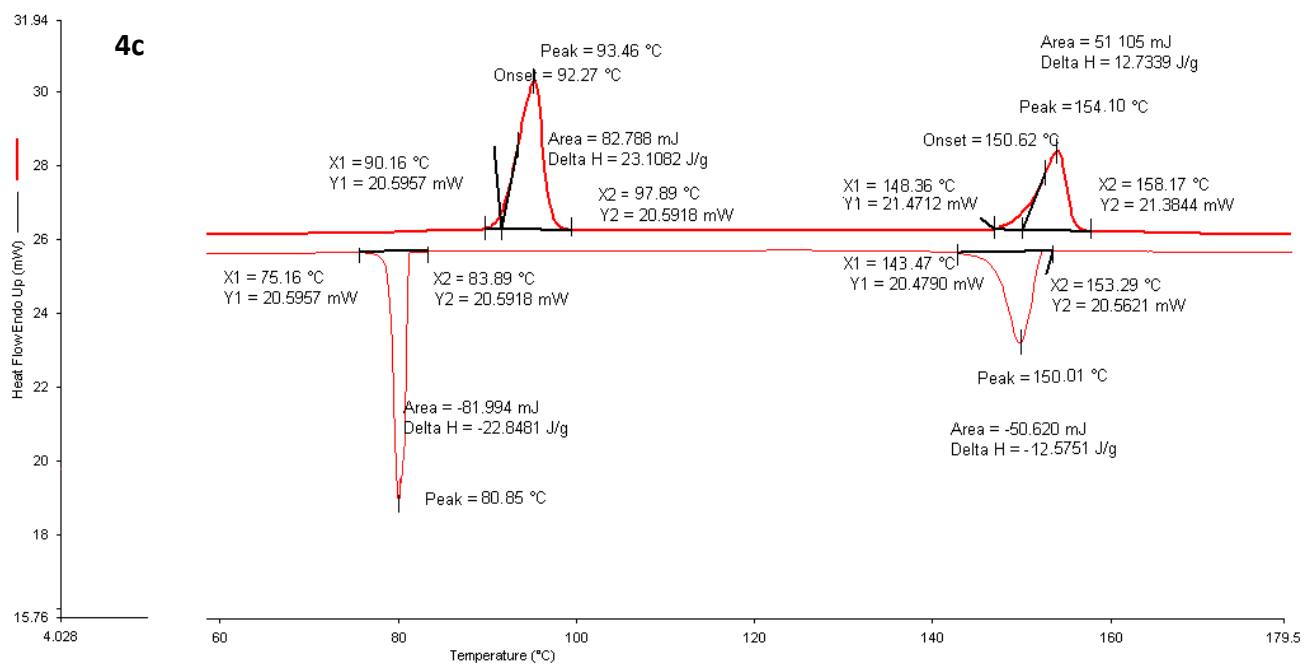
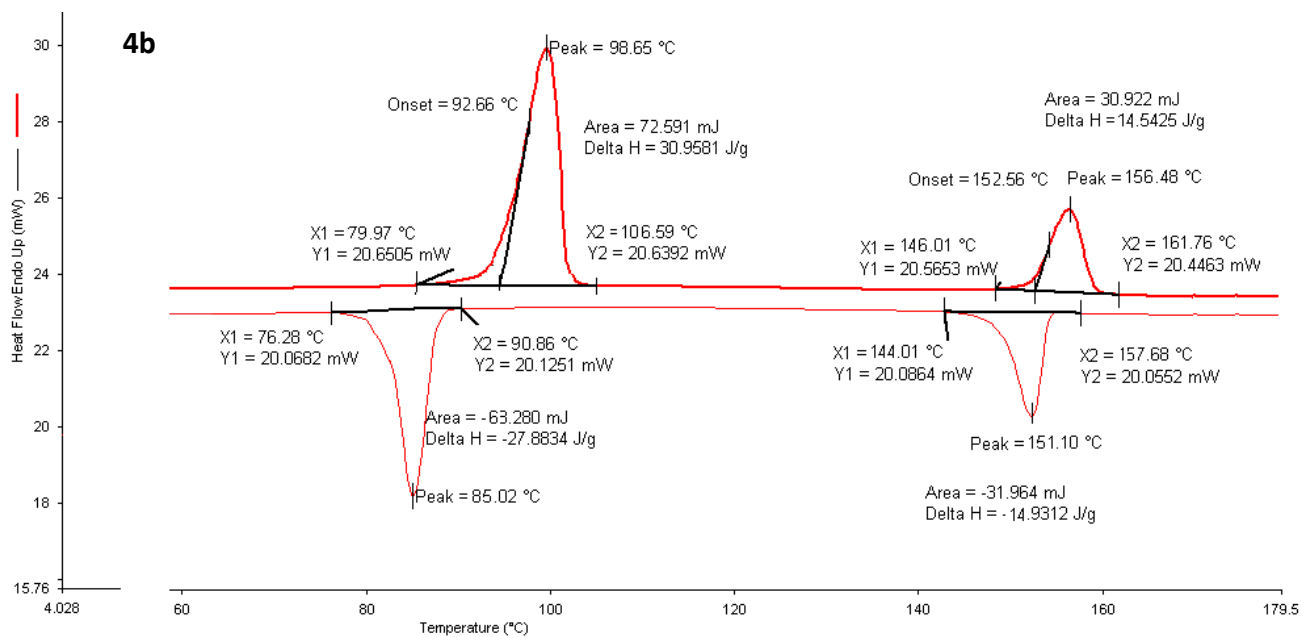
### 1.12 4-[[4-(Oct-7-en-1-yloxy)phenyl]diazanyl]benzoic acid (3e)

The hydrolysis of **2e** was carried out according to the method described for **3a**. Yield of **3e**: 1.17 g, 67.3% and mp 226 °C. IR,  $\nu_{\max}/\text{cm}^{-1}$  3081 (=CH<sub>2</sub>), 2924 (CH<sub>2</sub>), 2852 (CH<sub>2</sub>), 1684 ( $\nu\text{C}=\text{O}$ , acid), 1629 (C=C, vinyl), 1602, 1502 (C=C, aromatic), 1261, 1142, 1011 (C-O), 825 (C-H).  $\delta_H$ (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.20 (d, 2H,  $J = 8.8$  Hz), 7.97 (d, 2H,  $J = 8.9$  Hz), 7.92 (d, 2H,  $J = 8.7$  Hz), 7.04 (d, 2H,  $J = 9.0$  Hz), 5.85 (m, 1H, CH=), 5.05 (dd, 1H,  $J = 13.6$  Hz, =CH<sub>2</sub>), 4.96 (dd, 1H,  $J = 8.2$  Hz, =CH<sub>2</sub>), 4.08 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>-), 2.11 (m, 2H, -CH<sub>2</sub>-), 1.87 (m, 2H, -CH<sub>2</sub>-), 1.51 (m, 2H, -CH<sub>2</sub>-), 1.44 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-).  $\delta_C$ (125 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 21.50, 25.86, 26.12, 29.67, 29.65, 30.34, 69.88, 115.66, 118.34, 122.78, 125.33, 130.68, 131.69, 132.89, 147.27, 155.48, 161.78, 167.73

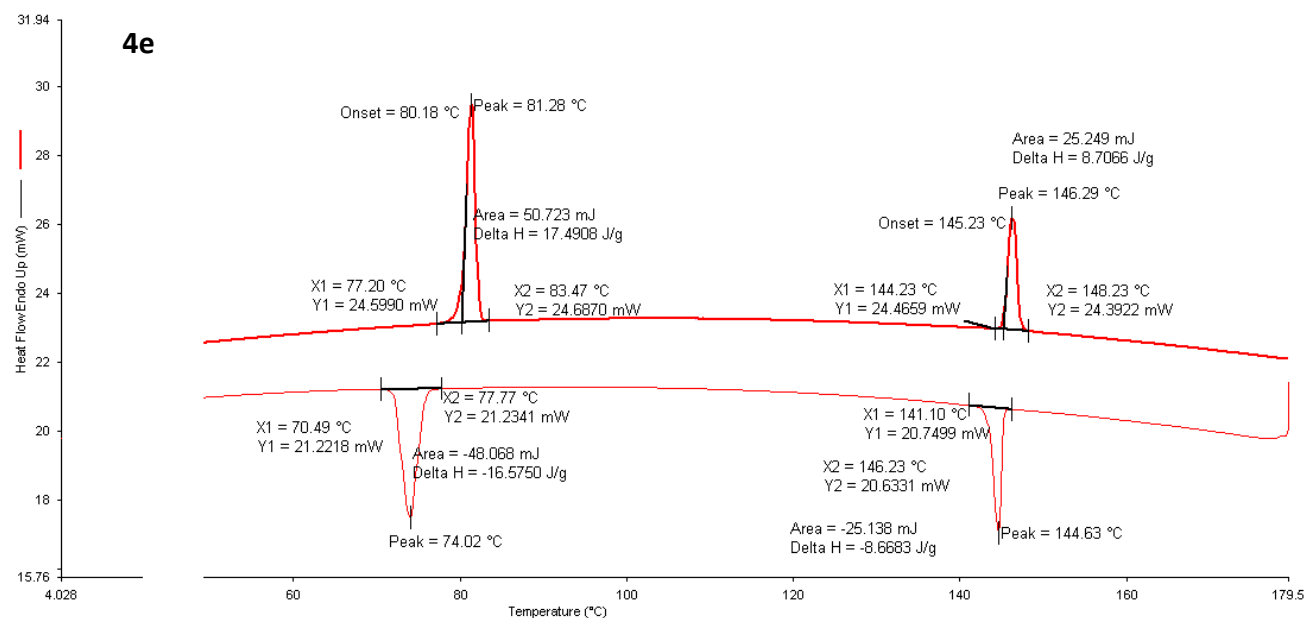
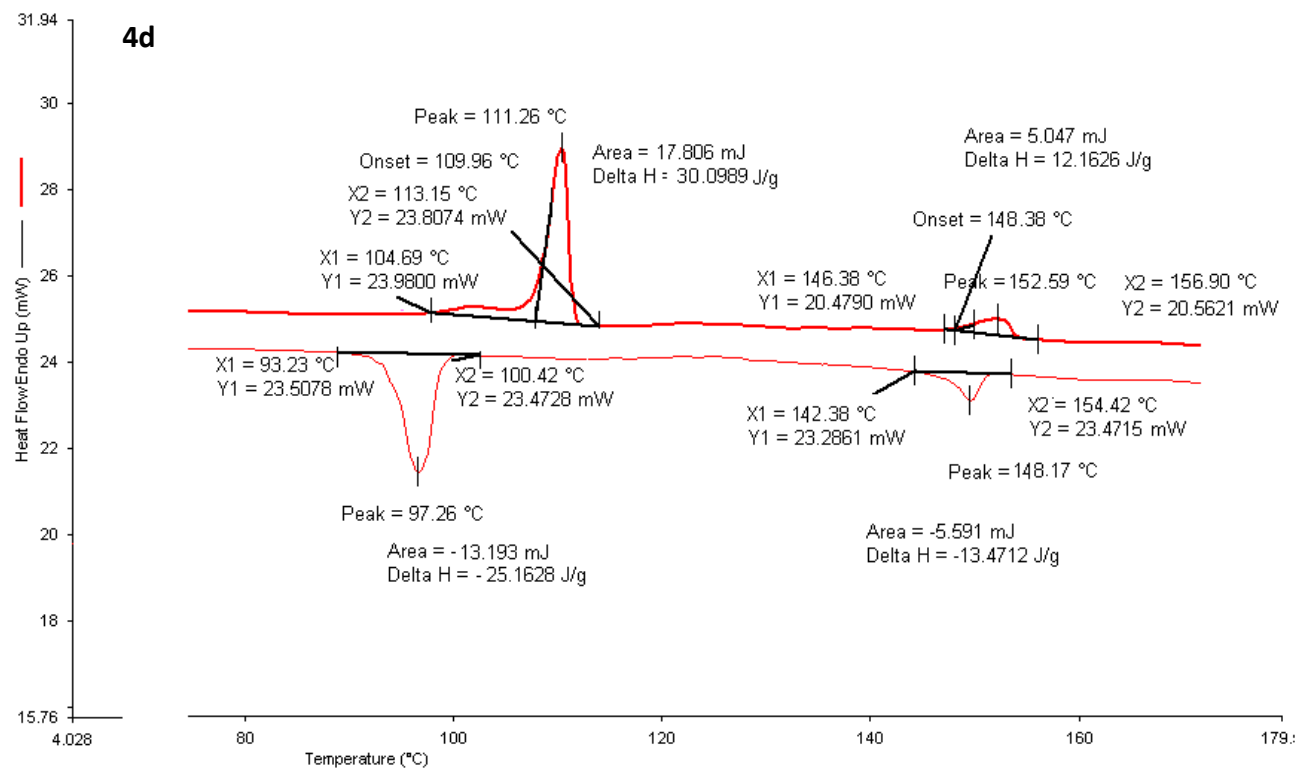
## 2.1 DSC for representative compounds



# Electronic supporting information



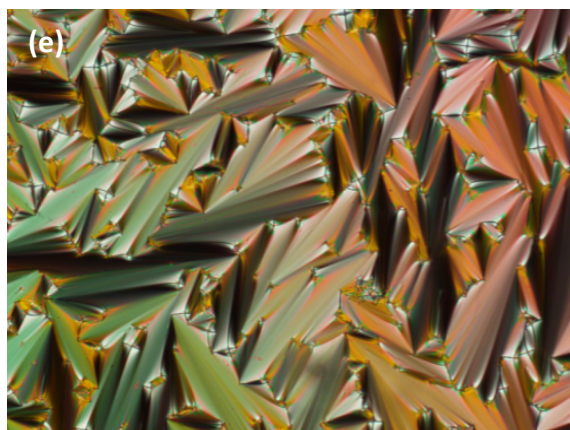
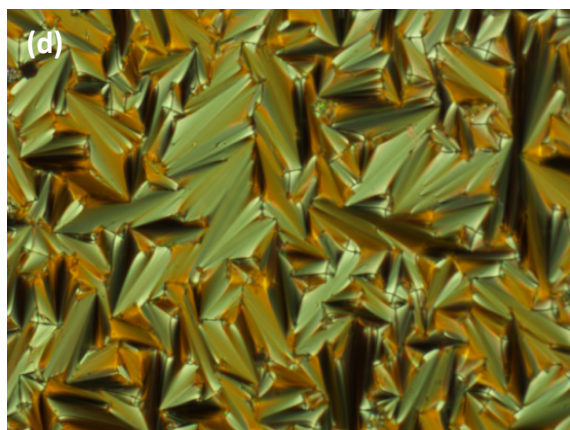
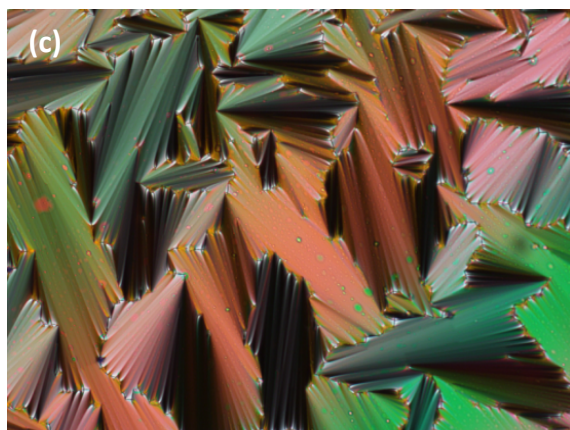
## Electronic supporting information



**Fig. S1** DSC thermograms of compounds **4a**, **4b**, **4c**, **4d** and **4e**.

## Electronic supporting information

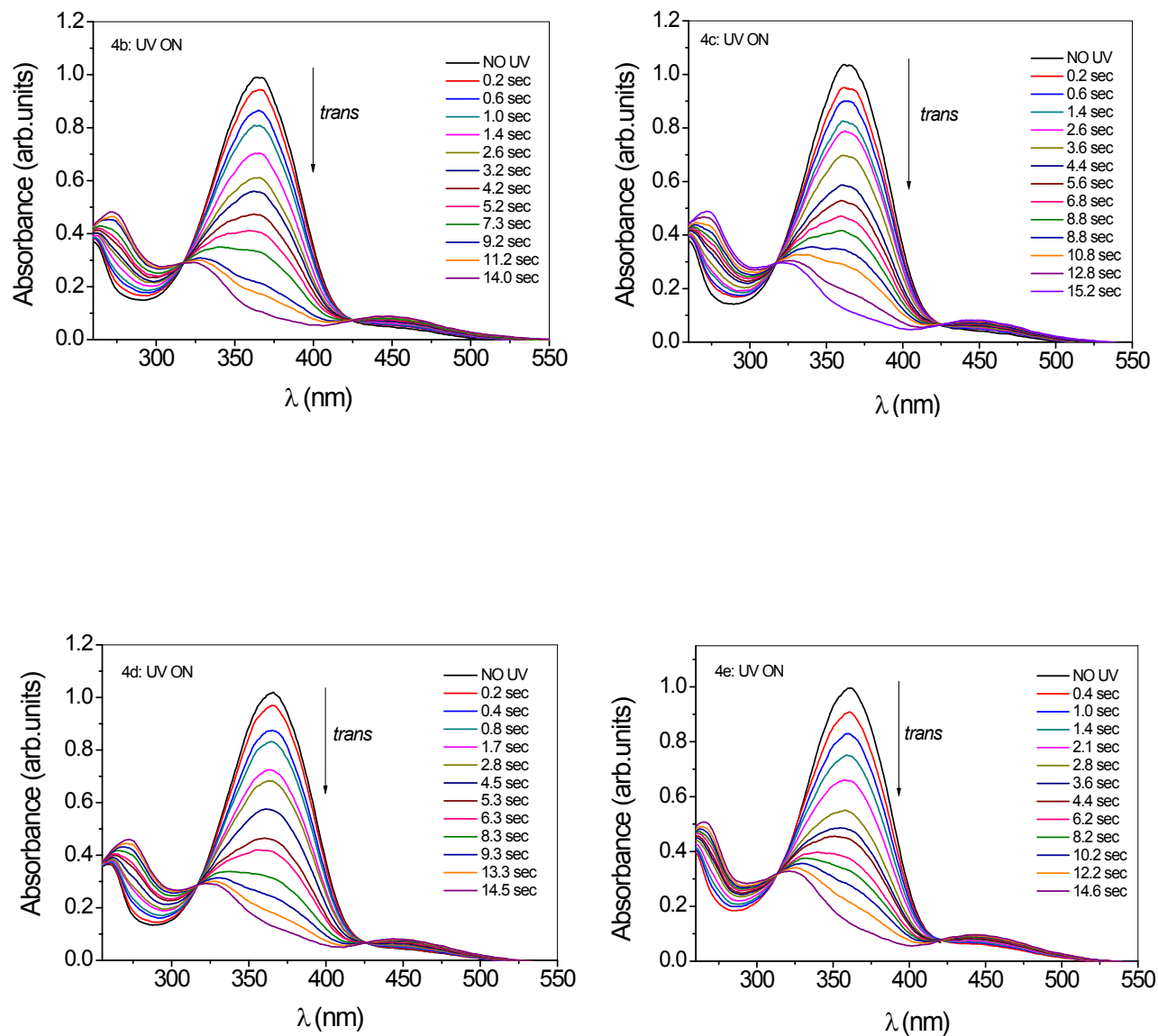
### 2.2 POM study



**Fig. S2** Polarized optical microphotographs of texture: (c) SmA phase at 118°C of **4c**, (d) SmA phase at 114°C of **4d**, SmA phase **4e** at 110°C

## Electronic supporting information

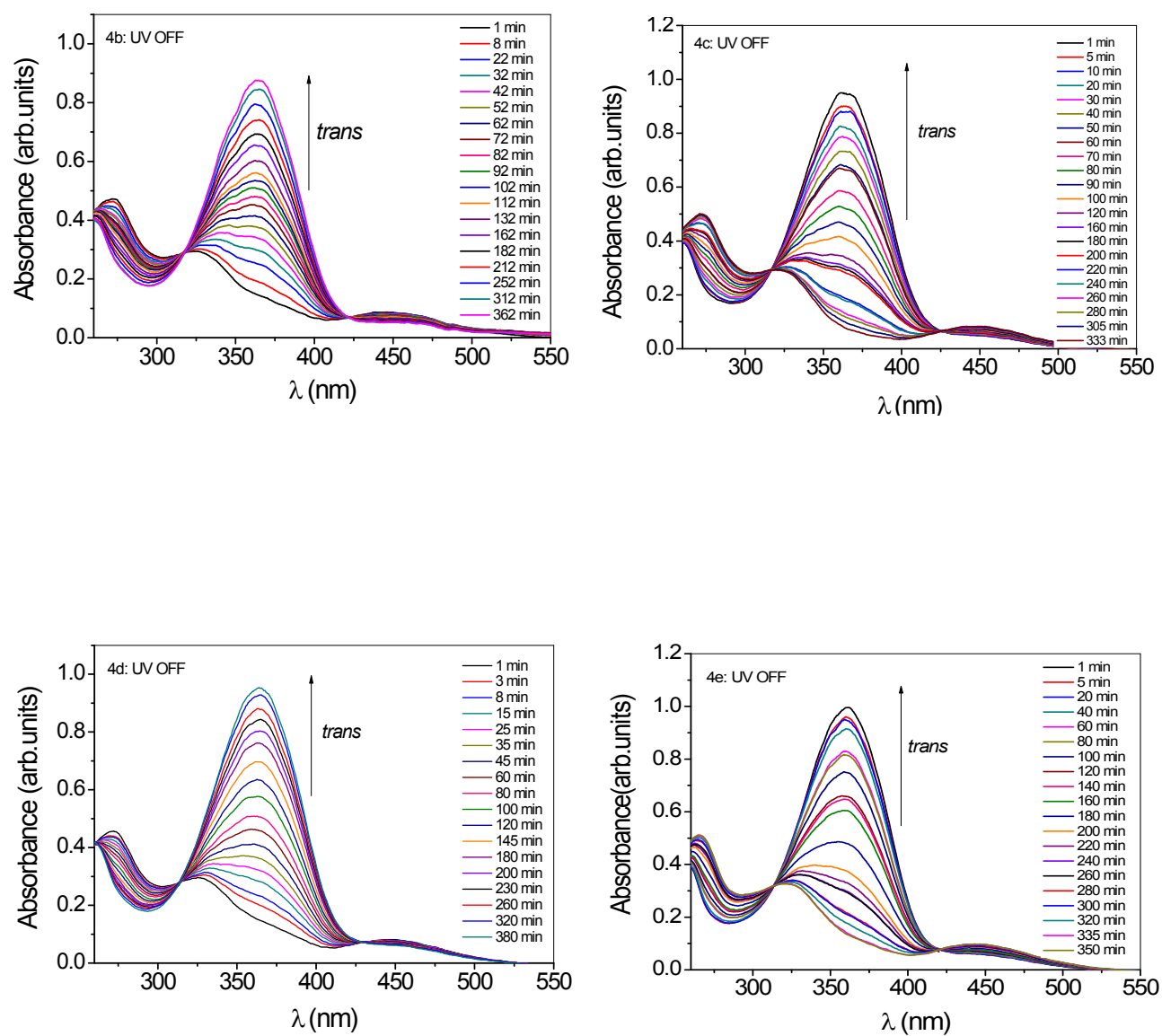
### 2.3 Photoswitching study



**Fig. S3** Absorption spectra of **4b-e** with different exposure time of UV light. Before UV corresponds to the 0 seconds UV light illumination (absence of UV light)

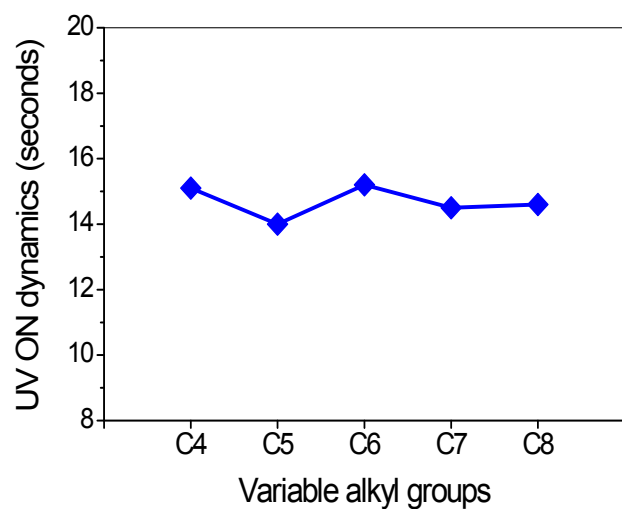


## Electronic supporting information

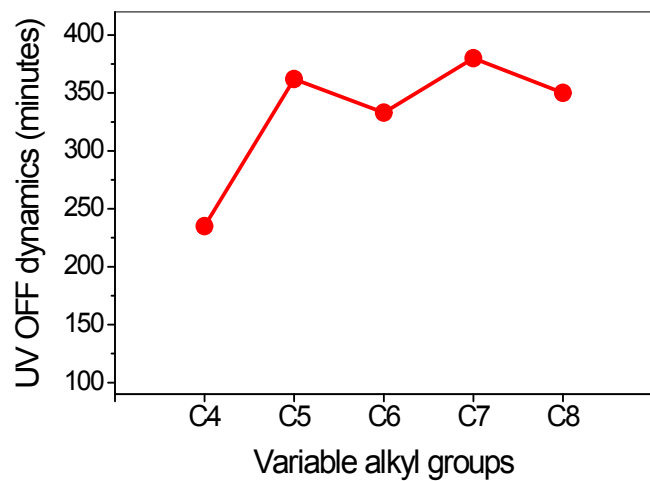


**Fig. S4** Thermal back relaxation process for the compound **4b-e** shows that to relax from cis to trans takes around 380 min. 0 seconds corresponds to the UV off, after illuminating the material for 20 seconds (photo stationary state).

## Electronic supporting information

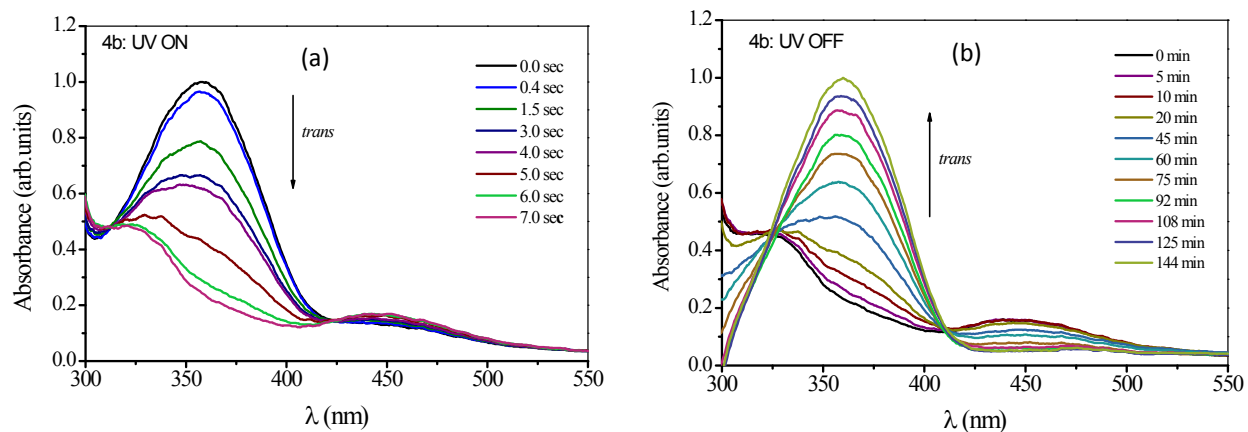


**Fig. S5** Photoisomerization induced odd-even effect of *E* isomers (**4a-e**) showing photoisomerization time (s) versus variable alkyl chains on UV illumination.



**Fig. S6** Photoisomerization induced odd-even effect of *Z* isomers (**4a-e**) showing photoisomerization time (min) versus variable alkyl chains on UV illumination.

## Electronic supporting information



**Fig. S7** (a) Absorption spectra of **4b** (UV light with intensity at 15mW/cm<sup>2</sup>) and (b) Thermal back relaxation process for **4b**.

### References

- S1. M. R. Lutfor, A. Jahimin, K. Sandeep, S. Silong and M. Z. A. Rahman, *Phase Transit.*, 82, 2009, 228-239.
- S2. M. R. Lutfor, G. Hegde, M. Y. Mashitah, M. A. M. Nor Fazli, H. T. Srinivasa and K. Sandeep, *New. J. Chem.*, 37, 2013, 2460-2467.