Electronic Supplementary Information

Liquid crystalline dihydroazulene photoswitches

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Synthesis – Experimentals S5
NMR Spectra S10
UV-Vis Data S98
DSC Thermograms S106
Conversion of 3g to the corresponding VHF in the nematic phase (1H-NMR) S108
**Synthesis – Experimental**

4-((5-Bromopentyl)oxy)benzonitrile (7a): A mixture consisting of 4-cyanophenol 6 (9.35 g, 78.5 mmol), 1,5-dibromopentane 5a (27 mL, 198 mmol) and K$_2$CO$_3$ (16.70 g, 121 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution of petroleum spirit to toluene) to afford 7a (14.92 g, 71%) as a white solid. R$_f$=0.50 (toluene). M.p. = 54.0-55.9 °C.

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.3 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H), 1.97-1.91 (m, 2H), 1.87-1.81 (m, 2H), 1.67-1.60 (m, 2H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 162.4, 134.1, 119.4, 115.3, 104.0, 68.1, 33.6, 32.5, 28.3, 24.8 ppm. MS (ESP +ve): m/z = 290 [(M+Na)$^+$]. Analysis calcld (%) for C$_{12}$H$_{14}$BrNO (268.15): C 55.33, H 5.72, N 4.96; found: C 55.66, H 5.72, N 5.13.

4-((6-Bromohexyl)oxy)benzonitrile (7b): A mixture consisting of 4-cyanophenol 6 (3.50 g, 29.4 mmol), 1,6-dibromohexane 5b (10 mL, 65.0 mmol) and K$_2$CO$_3$ (8.51 g, 61.6 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution of petroleum spirit to toluene) to afford 7b (5.75 g, 69%) as a white solid. R$_f$=0.50 (toluene). M.p. = 44.0-46.5 °C.

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.57 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.43 (t, J = 6.6 Hz, 2H), 1.90 (p, J = 6.6 Hz, 2H), 1.82 (p, J = 6.6 Hz, 2H), 1.53-1.50 (m, 4H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.9, 68.3, 33.8, 32.7, 29.0, 28.0, 25.3 ppm. MS (ESP +ve): m/z = 282 [(M+Na)$^+$]. Analysis calcld (%) for C$_{13}$H$_{18}$BrNO (282.18): C 55.33, H 5.72, N 4.96; found: C 55.66, H 5.72, N 4.98.

4-((8-Bromoocetyl)oxy)benzonitrile (7c): A mixture consisting of 4-cyanophenol 6 (5.49 g, 46.1 mmol), 1,8-dibromoocotane 5c (25.95 g, 95.4 mmol) and K$_2$CO$_3$ (9.40 g, 68.0 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution; petroleum spirit to toluene) to afford 7c (9.92 g, 69%) as a white solid. R$_f$=0.50 (toluene). M.p. = 68.5-69.8 °C.

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.89-1.84 (m, 2H), 1.82-1.77 (m, 2H), 1.49-1.42 (m, 4H), 1.39-1.33 (m, 4H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 162.5, 134.1, 119.4, 115.3, 103.8, 68.5, 34.1, 32.9, 29.2, 29.1, 28.8, 28.2, 26.0 ppm. MS (ESP +ve): m/z = 310 [(M+H)$^+$]. Analysis calcld (%) for C$_{15}$H$_{20}$BrNO (310.24): C 58.07, H 6.50, N 4.51; found: C 58.26, H 6.53, N 4.51.

4-((9-Bromononyl)oxy)benzonitrile (7d): A mixture consisting of 4-cyanophenol 6 (5.17 g, 43.4 mmol), 1,9-dibromononane 5d (24.71 g, 86.4 mmol) and K$_2$CO$_3$ (8.97 g, 64.9 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution; petroleum spirit to toluene) to afford 7d (9.98 g, 71%) as a white solid. R$_f$=0.50 (toluene). M.p. = 64.1-65.7 °C.
1H NMR (500 MHz, CDCl₃): δ = 7.55 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 3.98 (t, J = 6.5 Hz, 2H), 3.39 (t, J = 6.5 Hz, 2H), 1.86-1.75 (m, 4H), 1.46-1.39 (m, 4H), 1.36-1.29 (m, 6H) ppm. 13C NMR (125 MHz, CDCl₃): δ = 162.5, 134.0, 119.4, 115.2, 103.7, 68.4, 34.1, 32.8, 29.3, 29.2, 29.0, 28.7, 28.2, 25.9 ppm. MS (ESP +ve): m/z = 324 [(M+H)+]. Analysis calcd (%) for C₂₆H₂₃NO₃: C 74.7, 74.6, 74.5; H 6.8, 6.7, 6.7; O 3.9, 3.9, 3.9.

4-((10-Bromodecyl)oxy)benzonitrile (7e); A mixture consisting of 4-cyanophenol 6 (4.97 g, 41.7 mmol), 1,10-dibromodecane 5e (30.68 g, 102 mmol) and K₂CO₃ (9.20 g, 66.6 mmol) in acetone (200 mL) was heated to reflux point for 16 h. The contents of the vessel were allowed to cool to rt and filtered. The solvent was removed from the filtrate and the crude residue was subjected to column chromatography (gradient elution; petroleum spirit to toluene) to afford 7e (11.00 g, 78%) as a white solid. Rf=0.50 (toluene). M.p. = 73.2-74.7 °C. 1H NMR (500 MHz, CDCl₃): δ = 7.57 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.88-1.77 (m, 4H), 1.48-1.40 (m, 4H), 1.36-1.28 (m, 8H) ppm. 13C NMR (125 MHz, CDCl₃): δ = 162.6, 134.1, 119.5, 115.3, 103.8, 68.5, 34.2, 32.9, 29.5, 29.5, 29.4, 29.1, 28.9, 28.3, 26.1 ppm. MS (ESP +ve): m/z = 360 [(M+Na)+]. Analysis calcd (%) for C₁₇H₁₄BrNO (338.29): C 60.36, H 7.15, N 4.14; found: C 60.53, H 7.19, N 4.15.

4-((5-(4-Acetylenoxy)pentyl)oxy)benzonitrile (9a); A mixture consisting of 4-hydroxyacetophenone 8 (2.69 g, 19.8 mmol), 7a (4.48 g, 16.7 mmol) and K₂CO₃ (2.98 g, 21.6 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH₂Cl₂ (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO₂ column (CH₂Cl₂) to afford 9a (4.42 g, 82%) as a white solid. Rf=0.39. M.p. = 100.8-102.8 °C. 1H NMR (500 MHz, CDCl₃): δ = 7.96 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.06 (t, J = 6.2 Hz, 2H), 4.04 (t, J = 6.3 Hz, 2H), 2.55 (s, 3H), 1.92-1.87 (m, 4H), 1.70-1.64 (m, 2H) ppm. 13C NMR (125 MHz, CDCl₃): δ = 196.9, 163.0, 162.4, 134.1, 130.7, 130.4, 119.4, 115.3, 114.2, 104.0, 68.2, 68.0, 29.0, 28.9, 26.5, 22.8 ppm. HRMS (MALDI +ve) calcd for C₂₀H₂₂NO₃ [(M+H)+]: m/z = 324.1594; exp 324.1595. Analysis calcd (%) for C₂₀H₂₂NO₃ (323.39): C 74.28, H 6.55, N 4.33; found: C 74.09, H 6.28, N 4.27.

4-((6-(4-Acetlenylenoxy)hexyl)oxy)benzonitrile (9b); A mixture consisting of 4-hydroxyacetophenone 8 (2.26 g, 16.6 mmol), 7b (4.00 g, 14.2 mmol) and K₂CO₃ (4.27 g, 30.9 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH₂Cl₂ (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO₂ column (CH₂Cl₂) to afford 9b (4.26 g, 89%) as a white solid. Rf=0.33. M.p. = 99.5-101.3 °C. 1H NMR (500 MHz, CDCl₃): δ = 7.92 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.55 (s, 3H), 1.87-1.82 (m, 4H), 1.57-1.55 (m, 4H) ppm. 13C NMR (125 MHz, CDCl₃): δ = 196.9, 163.1, 162.5, 134.1, 130.7, 130.4, 119.4, 115.3, 114.2, 103.9, 68.3, 68.1, 29.2, 29.1, 26.5, 25.9, 25.9 ppm. HRMS (MALDI +ve) calcd for C₂₁H₂₃NO₃ [(M+H)+]: m/z = 338.1751; exp 338.1751. Analysis calcd (%) for C₂₁H₂₃NO₃ (337.42): C 74.75, H 6.87, N 4.15; found: C 74.60, H 6.73, N 3.99.
4-((8-(4-Acetylphenoxy)octyl)oxy)benzonitrile (9c): A mixture consisting of 4-hydroxyacetophenone 8 (2.61 g, 19.2 mmol), 7c (4.94 g, 15.9 mmol) and K$_2$CO$_3$ (4.75 g, 34.4 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH$_2$Cl$_2$ (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO$_2$ column (CH$_2$Cl$_2$) to afford 9c (3.64 g, 63%) as a white solid. R$_f$=0.35. M.p. = 91.1-92.3 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.92 (d, J = 8.9 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.55 (s, 3H), 1.84-1.78 (m, 4H), 1.50-1.45 (m, 4H), 1.41-1.38 (m, 4H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 196.9, 163.2, 162.5, 134.1, 130.7, 130.3, 119.4, 115.3, 114.2, 103.8, 68.5, 68.3, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.0 ppm. HRMS (MALDI +ve) calcd for C$_{29}$H$_{29}$NO$_3$Na ([M+Na]$^+$): m/z = 388.1883; exp 388.1884. Analysis calcd (%) for C$_{29}$H$_{29}$NO$_3$: C 75.59, H 7.45, N 3.83; found: C 75.51, H 7.28, N 3.78.

4-((9-(4-Acetylphenoxy)nonyl)oxy)benzonitrile (9d): A mixture consisting of 4-hydroxyacetophenone 8 (2.47 g, 18.1 mmol), 7d (4.96 g, 15.3 mmol) and K$_2$CO$_3$ (5.20 g, 37.6 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH$_2$Cl$_2$ (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO$_2$ column (CH$_2$Cl$_2$) to afford 9d (5.54 g, 95%) as a white solid. R$_f$=0.35. M.p. = 86.4-87.2 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.92 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.55 (s, 3H), 1.83-1.77 (m, 4H), 1.49-1.43 (m, 4H), 1.39-1.35 (m, 6H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 196.9, 163.2, 162.6, 134.1, 130.7, 130.3, 119.5, 115.3, 114.3, 103.8, 68.5, 68.3, 29.6, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.1 ppm. HRMS (MALDI +ve) calcd for C$_{24}$H$_{30}$N$_2$O$_2$ ([M+H]$^+$): m/z = 380.2220; exp 380.2221. Analysis calcd (%) for C$_{24}$H$_{30}$N$_2$O$_2$: C 75.96, H 7.70, N 3.69; found: C 75.82, H 7.68, N 3.55.

4-((10-(4-Acetylphenoxy)decyl)oxy)benzonitrile (9e): A mixture consisting of 4-hydroxyacetophenone 8 (2.51 g, 18.4 mmol), 7e (5.16 g, 15.3 mmol) and K$_2$CO$_3$ (5.10 g, 36.9 mmol) in acetone (100 mL) was heated to reflux point for 24 h. The contents of the vessel were allowed to cool to rt, diluted with CH$_2$Cl$_2$ (200 mL) and filtered. The solvent was removed from the filtrate and the crude residue was passed through a short SiO$_2$ column (CH$_2$Cl$_2$) to afford 9e (5.12 g, 85%) as a white solid. R$_f$=0.40. M.p. = 71.5-73.5 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.92 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.99 (d, J = 6.5 Hz, 2H), 2.55 (s, 3H), 1.83-1.76 (m, 4H), 1.48-1.42 (m, 4H), 1.37-1.32 (m, 8H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ = 196.9, 163.2, 162.6, 134.1, 130.7, 130.3, 119.4, 115.3, 114.2, 103.8, 68.5, 68.4, 29.6, 29.4, 29.4, 29.2, 29.1, 26.5, 26.1, 26.1 ppm. 1C masked. HRMS (MALDI +ve) calcd for C$_{25}$H$_{32}$NO$_3$ ([M+H]$^+$): m/z = 394.2377; exp 394.2377. Analysis calcd (%) for C$_{25}$H$_{31}$NO$_3$: C 76.30, H 7.94, N 3.56; found: C 76.29, H 7.90, N 3.52.

2-(1-((5-(4-Cyanophenoxy)pentyl)oxy)phenyl)ethylidene)malononitrile (13a): A biphasic mixture of 9a (2.27 g, 7.02 mmol), malononitrile (1.66 g, 25.1 mmol), NH$_4$OAc (2.20 g, 28.5 mmol) in toluene (100 mL) and AcOH (4 mL) was heated using a Dean-Stark
apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over MgSO₄, filtered and the solvent removed in vacuo. The residue was recrystallized from CH₂Cl₂/MeOH to give 13a (2.02 g, 77%), as a yellowish solid. Rf=0.65 (CH₂Cl₂). M.p. = 83.2-84.9, 95.6-100.3 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H) 6.97 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.06 (t, J = 6.2 Hz, 2H), 4.04 (t, J = 6.2 Hz, 2H), 2.61 (s, 3H), 1.92-1.87 (m, 4H), 1.79-1.64 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 174.4, 162.7, 162.4, 134.1, 130.0, 127.9, 119.4, 115.3, 115.0, 113.8, 113.5, 104.0, 82.0, 28.9, 28.8, 23.9, 22.8 ppm, 1C masked. HRMS (MALDI +ve) calcd for C₂₃H₂₂N₃O₂ ([M+H]⁺): m/z = 372.1707; exp 372.1707. Analysis calcd (%) for C₂₃H₂₂N₃O₂: 74.78, 6.01, 10.90; found: C 74.75, H 5.73, N 10.81.

2-(1-(4-((6-(4-Cyanophenoxy)hexyl)oxy)phenyl)ethylidene)malononitrile (13b); A biphasic mixture of 9b (2.57 g, 7.62 mmol), malononitrile (1.85 g, 28.0 mmol), NH₄OAc (3.40 g, 44.1 mmol) in toluene (100 mL) and AcOH (4 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over MgSO₄, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH₂Cl₂) to give 13b (2.42 g, 82%), as a white solid. Rf=0.61 (CH₂Cl₂). M.p. = 62.5-64.5 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H) 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 4.02 (t, J = 6.3 Hz, 2H), 2.61 (s, 3H), 1.86-1.83 (m, 4H), 1.57-1.54 (m, 4H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 174.4, 162.8, 162.5, 134.1, 130.0, 127.9, 119.4, 115.3, 115.0, 113.8, 113.5, 103.9, 82.0, 68.3, 29.1, 29.1, 25.9, 25.9, 23.9, 22.8 ppm, 1C masked. HRMS (MALDI +ve) calcd for C₂₃H₂₄N₃O₂ ([M+H]⁺): m/z = 386.1858; exp 386.1864. Analysis calcd (%) for C₂₃H₂₄N₃O₂: 74.78, H 6.01, N 10.90; found: C 74.75, H 5.73, N 10.81.

2-(1-(4-((8-(4-Cyanophenoxy)octyl)oxy)phenyl)ethylidene)malononitrile (13c); A biphasic mixture of 9c (2.53 g, 6.92 mmol), malononitrile (1.56 g, 23.6 mmol), NH₄OAc (2.88 g, 37.4 mmol) in toluene (100 mL) and AcOH (4 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over MgSO₄, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH₂Cl₂) to give 13c (2.02 g, 71%), as a white solid. Rf=0.62 (CH₂Cl₂). M.p. = 67.0-67.7 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.64 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H) 7.00 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.64 (s, 3H), 1.87-1.81 (m, 4H), 1.54-1.48 (m, 4H), 1.46-1.41 ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 119.5, 115.2, 114.9, 113.9, 113.6, 103.7, 81.8, 68.4, 29.4, 29.1, 29.1, 26.0, 26.0, 24.0 ppm. HRMS (MALDI +ve) calcd for C₂₅H₂₈N₃O₂ ([M+H]⁺): m/z = 414.2176; exp 414.2177. Analysis calcd (%) for C₂₅H₂₈N₃O₂: 75.52, H 6.58, N 10.16; found: C 75.13, H 6.29, N 10.19.
2-(1-4-((9-(4-Cyanophenoxy)nonyl)oxy)phenyl)ethylidene)malononitrile (13d); A biphasic mixture of 9d (3.11 g, 8.19 mmol), malononitrile (2.47 g, 37.4 mmol), NH₄OAc (6.15 g, 79.8 mmol) in toluene (100 mL) and AcOH (7 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase was washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over MgSO₄, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH₂Cl₂) to give 13d (3.08 g, 88%), as a white solid. Rᵣ=0.68 (CH₂Cl₂). M.p. = 87.1-88.1 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.61 (s, 3H), 1.83-1.77 (m, 4H), 1.49-1.43 (m, 4H), 1.39-1.35 (m, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 119.5, 115.3, 115.0, 113.9, 113.6, 103.7, 81.8, 68.5, 68.5, 29.6, 29.4, 29.1, 29.1, 26.1, 26.0, 23.9 ppm, 1C masked. HRMS (MALDI +ve) calcd for C₂₇H₂₉N₂O₂Na ([M+Na]⁺): m/z = 450.2157; exp 450.2153. Analysis calcd (%) for C₂₇H₂₉N₂O₂ (427.55): C 75.85, H 6.84, N 9.83; found: C 75.50, H 6.81, N 9.80.

2-(1-4-((10-(4-Cyanophenoxy)decyl)oxy)phenyl)ethylidene)malononitrile (13e); A biphasic mixture of 9e (3.01 g, 7.65 mmol), malononitrile (2.39 g, 36.2 mmol), NH₄OAc (4.95 g, 64.2 mmol) in toluene (100 mL) and AcOH (6 mL) was heated using a Dean-Stark apparatus for 3 h. The vessel was cooled, diluted with toluene (100 mL) and decanted into a separatory funnel and water (100 mL) was added. The phases were separated and the organic phase was washed with water (3 x 100 mL) and brine (100 mL). The organic phase was dried over MgSO₄, filtered and the solvent removed in vacuo. The residue was purified by flash column chromatography (CH₂Cl₂) to give 13e (2.80 g, 83%), as a white solid. Rᵣ=0.65 (CH₂Cl₂). M.p. = 62.6-63.8 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.60 (d, J = 8.9 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.61 (s, 3H), 1.83-1.77 (m, 4H), 1.47-1.43 (m, 4H), 1.37-1.31 (m, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 174.2, 162.8, 162.5, 134.1, 130.0, 127.7, 199.5, 115.3, 115.0, 113.9, 113.6, 103.7, 81.8, 68.5, 68.5, 29.6, 29.4, 29.1, 29.1, 26.1, 26.0, 23.9 ppm, 2Cs masked. HRMS (MALDI +ve) calcd for C₂₈H₃₂N₂O₂ ([M+H]⁺): m/z = 442.2489; exp 442.2491. Analysis calcd (%) for C₂₈H₃₂N₂O₂ (441.58): C, 76.16; H, 7.08; N, 9.52; found: C 76.30, H 7.07, N 9.50.

2-(1-4'-(Octyloxy)-[1,1'-biphenyl]-4-yl)ethylidene)malononitrile (13f); A mixture of 9f (5.57 g, 17.2 mmol), malononitrile (3.55 g, 53.7 mmol) and NH₄OAc (4.69 g, 60.8 mmol) in toluene (300 mL) and AcOH (6.5 mL, 113 mmol) was equipped with a Dean-Stark trap and heated to reflux point for 5 h. Additional malononitrile (2.13 g, 32.2 mmol), NH₄OAc (2.26 g, 29.3 mmol) and glacial AcOH (3.2 mL, 56 mmol) were added and the mixture heated an additional 2 h. A third portion of malononitrile (2.18 g, 33.0 mmol), NH₄OAc (2.39 g, 31.0 mmol) and glacial AcOH (3.2 mL, 56 mmol) was added and the mixture heated an additional 3 h. The contents of the vessel were allowed to cool to rt, washed with water (4 x 250 mL) and brine (1 x 250 mL), dried over MgSO₄ and filtered. The solvent was removed under reduced pressure and the crude residue was crystallized from CH₂Cl₂/heptane to give pure 13f (4.60 g, 70%) as a white solid. Rᵣ=0.56 (toluene). M.p. = 58.6–59.4 °C. ¹H NMR
(500 MHz, CDCl₃): δ = 7.68 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 2.67 (s, 3H), 1.84–1.78 (m, 2H), 1.51–1.45 (m, 2H), 1.40–1.26 (m, 8H), 0.90 (t, J = 6.9 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 174.7, 159.9, 145.2, 133.8, 131.5, 128.4, 128.3, 127.1, 115.2, 113.2, 83.8, 68.3, 32.0, 29.5, 29.4, 29.4, 26.2, 24.1, 22.8, 14.3 ppm. HRMS (MALDI +ve) calcd for C₂₅H₂₂N₂O [(M+Na)⁺]: m/z = 395.2094; exp 395.2102. Analysis calcd (%) for C₂₅H₂₆N₂O (372.51): C 80.61, H 7.58, N 7.52; found: C 80.67, H 7.67, N 7.38.

2-(1-(2',3'-difluoro-4'-octyloxy)-[1,1'-biphenyl]-4-yl)ethylidene)malononitrile (13g); A mixture of 9g (4.62 g, 12.8 mmol), malononitrile (2.38 g, 36.0 mmol) and NH₂OAc (3.39 g, 44.0 mmol) in toluene (300 mL) and AcOH (4.8 mL, 84 mmol) was equipped with a Dean-Stark trap and heated to reflux point for 3 h. Additional malononitrile (2.76 g, 41.8 mmol) and AcOH (4.8 mL, 84 mmol) were added and the mixture was refluxed for a further 2 h. TLC analysis indicated the presence of 9g and therefore additional malononitrile (1.89 g, 28.6 mmol), NH₂OAc (1.98 g, 25.7 mmol) and AcOH (2.52 g, 2.4 mL, 41.9 mmol) were added and the reaction mixture was refluxed for 2 h. The reaction mixture was allowed to cool to rt, washed with water (4 x 250 mL), dried over MgSO₄ and filtered. The solvent was removed in vacuo and the residue crystallized from CH₂Cl₂/heptane to give 13g (3.75 g, 72%) as a white solid. Rₐ=0.61 (toluene). M.p. = 59.5–60.4 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.65 (apparent s, 4H), 7.16–7.10 (ddd, J = 8.7, 8.2, 2.4, 1H), 6.83 (ddd, J = 9.1, 7.5, 1.8 Hz, 1H), 4.09 (t, J = 6.6 Hz, 2H), 2.68 (s, 3H), 1.92–1.81 (m, 2H), 1.54–1.44 (m, 2H), 1.42–1.22 (m, 8H), 0.89 (t, J = 6.8, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 174.7, 149.1 (dd, J = 250, 11.4 Hz), 149.0 (dd, J = 8.1, 3.1 Hz), 141.9 (dd, J = 248.2, 14.8 Hz), 139.3, 134.9, 129.4, 129.4, 127.9, 123.8, 123.7, 123.7, 121.2, 121.1, 113.1, 112.9, 109.9, 84.7, 70.1, 31.9, 29.4, 29.4, 29.3, 26.0, 24.3, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for C₂₅H₂₇F₂N₂O [(M+H)⁺]: m/z = 409.2086; exp 409.2095. Analysis calcd (%) for C₂₅H₂₆F₂N₂O (408.49): C 73.51, H 6.42, N 6.86; found: C 73.33, H 6.30, N 6.78.

2-(1-(2,3-difluoro-4-octyloxy)phenyl)ethylidene)malononitrile (13h); A mixture consisting of 9h (5.84 g, 20.6 mmol), malononitrile (3.83 g, 57.9 mmol) and NH₂OAc (5.44 g, 70.6 mmol) in toluene (250 mL) and AcOH (7.75 mL, 135 mmol) was heated using a Dean-Stark apparatus for 1 h. The reaction was not determined to be complete by TLC and malononitrile (3.98 g 60.3 mmol), NH₂OAc (5.32 g, 69.0 mmol) and AcOH (7.75 mL, 135 mmol) were added to the vessel and the mixture was refluxed for a further 2 h. Extra malononitrile (3.71 g, 56.2 mmol), NH₂OAc (5.45 g, 70.7 mmol) and AcOH (7.75 mL, 135 mmol) were again added and the reaction mixture was heated for 2 h and allowed to cool to rt. The reaction mixture was washed with water (4 x 240 mL) and brine (1 x 250 mL), dried with MgSO₄, filtered and concentrated under reduced pressure to the give pure 13h (6.79 g, 99%) as an off-white solid. Rₐ=0.62 (toluene); M.p. = 59.1–60.5 °C; ¹H NMR (500 MHz, CDCl₃): δ = 7.13 (ddd, J = 9.9, 7.6, 2.2 Hz, 1H), 6.82 (ddd, J = 9.9, 7.2, 1.8 Hz, 1H), 4.09 (t, J = 6.5 Hz, 2H), 2.61 (d, J = 1.6 Hz, 3H), 1.92–1.74 (m, 2H), 1.50–1.39 (m, 2H), 1.41–1.19 (m, 8H), 0.94–0.76 (m, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 170.3 (dd, J = 2.5, 1.5 Hz), 151.9 (dd, J = 8.1, 3.7 Hz), 148.5 (dd, J = 254.3, 12.1 Hz), 141.6, (dd, J = 251.7, 13.8 Hz), 123.2 (dd, J = 4.5, 3.2 Hz), 117.4 (d, J = 10.6 Hz), 112.2, 112.1, 109.3 (dd, J = 3.1, 1.3 Hz),
organics were washed with water (100 mL), dried over MgSO₄ and AcOH (32.0 mL, 559 mmol) was heated using a Dean-Stark apparatus for 3 h. The vessel was allowed to cool to rt and the reaction mixture washed with water (5 x 200 mL), dried over MgSO₄, filtered and concentrated under vacuum to give 13i (24.16 g; 100%) as a white solid. Rf=0.65 (toluene). M.p. = 51.5–52.0 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.50 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 2.66 (t, J = 7.7 Hz, 2H), 2.63 (s, 3H), 1.66–1.1.60 (m, 2H), 1.35–1.27 (m, 10H), 0.88 (t, J = 7.1 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 175.3, 148.5, 133.3, 129.3, 127.7, 113.3, 113.2, 83.7, 36.1, 32.0, 31.2, 29.5, 29.4, 29.3, 24.2, 22.8, 14.2 ppm. HRMS (MALDI +ve) calcd for C₁₉H₂₂N₂Na ([M+Na]⁺): m/z: 355.1592, found m/z = 355.1600.

2-(1-(4-Octylphenyl)ethylidene)malononitrile (13i); A biphasic mixture consisting of 9i (20.02 g, 86.16 mmol), malononitrile (15.39 g, 233.0 mmol) and NH₂OAc (22.03 g, 285.8 mmol) in toluene (250 mL) and AcOH (32.0 mL, 559 mmol) was heated using a Dean-Stark apparatus for 3 h. The vessel was allowed to cool to rt and the reaction mixture washed with water (ca. 50 g), dried over MgSO₄, filtered and extracted with Et₂O (3 x 75 mL). The combined organics were washed with water (ca. 50 g) and extracted with Et₂O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over MgSO₄, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave 14a (1.66 g, 95%) as a white solid. Rf=0.41. M.p. = 29.1-30.5 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.57 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 4.01 (t, J = 6.3 Hz, 2H), 3.32 (t, J = 6.7 Hz, 2H), 1.84 (p, J = 6.3 Hz, 2H), 1.68 (p, J = 6.7 Hz, 2H), 1.65–1.51 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 162.4, 134.1, 119.4, 115.3, 104.0, 68.1, 51.4, 28.7, 28.7, 23.5 ppm. HRMS (ESP +ve) calcd for C₁₂H₁⁴N₂ONa ([M+Na]⁺): m/z = 323.1060; exp 323.1060.

4-((5-Azidopentyl)oxy)benzonitrile (14a); To a solution of 7a (2.04 g, 7.61 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN₃ (876 mg, 13.5 mmol) and the contents of the reaction vessel were heated to 50 °C for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et₂O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over MgSO₄, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave 14b (870 mg, 88%) as a white solid. Rf=0.42. M.p. = 37.4-40.5 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.29 (t, J = 6.8 Hz, 2H), 1.82 (p, J = 6.4 Hz, 2H), 1.64 (p, J = 6.8 Hz, 2H), 1.57–1.42 (m, 4H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 162.5, 134.1, 119.4, 115.3, 103.9, 68.3, 51.5, 29.0, 28.9, 26.6, 25.7 ppm. HRMS (ESP +ve) calcd for C₁₃H₁₆N₄O₃Na ([M+Na]⁺): m/z = 267.1217; exp 267.1216.

4-((6-Azidohexyl)oxy)benzonitrile (14b); To a solution of 7b (1.14 g, 4.04 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN₃ (550 mg, 8.46 mmol) and the contents of the vessel allowed to stir at 50 °C for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et₂O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over MgSO₄, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave 14c (1.56 g, 5.03 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN₃ (512 mg, 7.88 mmol) and the contents of the vessel were allowed to stir at 50 °C for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et₂O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over MgSO₄, filtered and the volatiles...
removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) afforded 14c (966 mg, 71%) as a white solid. Rf=0.44. M.p. = 33.9-36.5 °C. 1H NMR (500 MHz, CDCl3): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.26 (t, J = 6.6 Hz, 2H), 1.80 (p, J = 6.5 Hz, 2H), 1.63–1.56 (m, 2H), 1.53–1.16 (m, 8H) ppm. 13C NMR (125 MHz, CDCl3): δ = 162.5, 134.1, 119.4, 115.3, 103.8, 68.5, 51.6, 29.3, 29.2, 29.1, 28.9, 26.8, 26.0 ppm. HRMS (ESP +ve) calcd for C15H20N4ONa ([M+Na]+): m/z = 295.1529; exp 295.1530.

4-((9-Azidononyl)oxy)benzonitrile (14d); To a solution of 7d (3.35 g, 10.3 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN3 (1.01 g, 15.5 mmol) and the contents of the vessel allowed to stir at 50 °C for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et2O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over MgSO4, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave 14d (2.52 g, 85%) as a white solid. Rf=0.49. M.p. = 42.5-43.2 °C. 1H NMR (500 MHz, CDCl3): δ = 7.57 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.26 (t, J = 6.8 Hz, 2H), 1.79 (t, J = 6.56 Hz, 2H), 1.60 (t, J = 6.8 Hz, 2H), 1.51–1.25 (m, 10H) ppm. 13C NMR (125 MHz, CDCl3): δ = 162.5, 134.1, 119.5, 115.3, 103.8, 68.5, 51.6, 29.5, 29.3, 29.2, 29.1, 29.0, 26.8, 26.0 ppm. HRMS (ESP +ve) calcd for C16H22N4ONa ([M+Na]+): m/z = 309.1687; exp 309.1686.

4-((10-Azidodecyl)oxy)benzonitrile (14e); To a solution of 7f (3.40 g, 10.1 mmol) in DMSO (20 mL), under an argon atmosphere, was added NaN3 (982 mg, 15.1 mmol) and the contents of the vessel allowed to stir at 50 °C for 2 h. The cooled reaction mixture was poured into ice-water (ca. 50 g) and extracted with Et2O (3 x 75 mL). The combined organics were washed with water (100 mL), dried over MgSO4, filtered and the volatiles removed in vacuo. Purification by flash column chromatography (1% EtOAc/toluene) gave 14f (2.68 g, 89%) as a white solid. Rf=0.49. M.p. = 46.7-47.7 °C. 1H NMR (500 MHz, CDCl3): δ = 7.57 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 3.26 (t, J = 6.9 Hz, 2H), 1.80 (p, J = 6.6 Hz, 2H), 1.60 (p, J = 6.9 Hz, 2H), 1.48–1.31 (m, 12H) ppm. 13C NMR (125 MHz, CDCl3): δ = 162.4, 134.0, 119.3, 115.2, 103.7, 68.4, 51.5, 29.4, 29.4, 29.3, 29.1, 29.0, 28.8, 26.7, 25.9 ppm. HRMS (ESP +ve) calcd for C17H24N4ONa ([M+Na]+): m/z = 323.1842; exp 323.1842.
NMR Spectra

Compound 7a
Compound 7b
Compound 7c
Compound 7d
Compound 7e
Compound 9a
Compound 9c
Compound 9e
Compound 9f
Compound 9g
Compound 9h
Compound 13a
Compound 13b
Compound 13c

[Chemical structure diagram]
Compound 13d
Compound 13e
Compound 13g
Compound 13i
Compound 3a
Compound 3d
Compound 3f
APT $^{13}$C NMR
Compound 3h
Compound 3i
Compound 14b
Compound 14c
Compound 14e
Compound 4a
Compound 4b
Compound 4c
Compound 4d
Compound 4J
Compound 17
UV-Vis Absorption Spectra and Decay of VHF Absorbance at $\lambda_{\text{max},\text{VHF}}$ in MeCN at 25°C

Compound 3a

![Compound 3a](image)

Graph showing UV-Vis absorption spectra and decay of absorbance.

Compound 3b

![Compound 3b](image)

Graph showing UV-Vis absorption spectra and decay of absorbance.
Compound 3e

NC-CN

O

O-CN

Wavelength (nm)

ε (10^3 M^-1 cm^-1)

Time (min)

DHA

VHF

Compound 3f

NC-CN

O

O-CN

Wavelength (nm)

ε (10^3 M^-1 cm^-1)

Time (min)

DHA

VHF

Abs
Compound 4b

\[
\text{\( \text{NC-CN-} \)} \quad \text{\( \text{N=N-} \)} \quad \text{\( \text{O-} \)} \quad \text{\( \text{CN} \)}
\]

\[
\begin{array}{c}
200 & 300 & 400 & 500 & 600 & 700 & 800 \\
\hline
0 & 10 & 20 & 30 & 40 & 50 & 60
\end{array}
\]

\[
\begin{array}{c}
\text{Abs} \\
0 & 0.1 & 0.2 & 0.3 & 0.4
\end{array}
\]

\[
\begin{array}{c}
\text{Time (min)} \\
0 & 200 & 400 & 600 & 800 & 1000 & 1200
\end{array}
\]

Compound 4c

\[
\text{\( \text{NC-CN-} \)} \quad \text{\( \text{N=N-} \)} \quad \text{\( \text{O-} \)} \quad \text{\( \text{CN} \)}
\]

\[
\begin{array}{c}
200 & 300 & 400 & 500 & 600 & 700 & 800 \\
\hline
0 & 10 & 20 & 30 & 40 & 50 & 60
\end{array}
\]

\[
\begin{array}{c}
\text{Abs} \\
0 & 0.1 & 0.2 & 0.3 & 0.4
\end{array}
\]

\[
\begin{array}{c}
\text{Time (min)} \\
0 & 200 & 400 & 600 & 800 & 1000
\end{array}
\]
Compound 4d

![Structure of Compound 4d]

Compounds 4d and 4e are shown with their respective UV-visible spectral and absorbance over time plots.

Compound 4e

![Structure of Compound 4e]
Compound 4j

\[ \varepsilon (10^3 \text{M}^{-1} \text{cm}^{-1}) \]

\[ \text{Wavelength (nm)} \]

\[ \text{Time (min)} \]

Abs

DHA  VHF
DSC Thermograms

**Compound 9f**

![Compound 9f structure diagram]

**Compound 9g**

![Compound 9g structure diagram]
Compound 3f

Compound 3g
Conversion of 3g to the corresponding VHF in the nematic phase
– NMR Characterization

Compound 3g (spectrum a) was heated to over the melt and allowed to cool back to 40 °C, where 3g in the nematic phase was exposed to UV irradiation at 365 nm (TLC lamp) for 1 hour, after which time, the sample was dissolved in C₆D₆ (spectrum b) and checked for VHF content. This solvent was chosen in order to retard the back reaction. In addition 3g was treated in the same manner, but instead exposed to the TLC lamp for 24 hours (spectrum c).

- a) Pure 3g in CDCl₃

- b) 3g irradiated at 40 °C in the nematic phase for 1h

- c) 3g irradiated at 40 °C in the nematic phase for 24h