

## 1. Methods

### 1.1. General Techniques

Miscellaneous solvents were purchased from Fisher Scientific dried by sequential percolation through columns of activated alumina and copper Q5 catalyst prior to use. Alkene terminated 4-alkoxy-4'-cyanobiphenyls, <sup>1</sup> and ((trimethylsilyl)methyl)dimethylsilane were synthesised according to precedent. <sup>2</sup> Low sulphur toluene was prepared according to Mandle *et. al.* <sup>3</sup> The liquid crystalline material **9** ([2SiC]11OCB; 4-(12,12,14,14-tetramethyl-12,14-disila-pentadecyloxy)-4'-cyanobiphenyl) was prepared as described previously. <sup>3</sup> Unless otherwise noted, miscellaneous chemicals were purchased from commercial suppliers and used as received.

Reactions were monitored by thin layer chromatography (TLC) using an appropriate solvent system. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using UV light at wavelengths of both 254 nm and 365 nm. Column chromatography was performed using flash grade silica from Fluorochem (40 - 63µm particle size). Yields refer to chromatographically (TLC) and spectroscopically (<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR and <sup>29</sup>Si{<sup>1</sup>H} NMR) homogenous material.

### 1.2. Nuclear Magnetic Resonance

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (<sup>1</sup>H), 100.5 MHz (<sup>13</sup>C{<sup>1</sup>H}) and 76.4 MHz (<sup>29</sup>Si{<sup>1</sup>H}) as solutions in deuterated chloroform. Spectra were referenced to the residual protic solvent for <sup>1</sup>H (7.26 ppm), or to the resonance of CDCl<sub>3</sub> for <sup>13</sup>C{<sup>1</sup>H} (77.16 ppm).

### 1.3. Mass Spectrometry

Mass spectra were recorded on a Bruker compact time of flight mass spectrometer with both ESI and APCI sources, and we extend our gratitude to Mr. Karl Heaton of the University of York for obtaining MS data.

### 1.4. Polarised Optical Microscopy

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Photomicrographs were captured *via* an InfinityX-21 MP digital camera mounted atop the microscope.

### 1.5. Differential Scanning Calorimetry.

Differential scanning calorimetry was performed on a Mettler DSC822<sup>e</sup> fitted with an autosampler operating with Mettler Star<sup>e</sup> software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg<sup>-1</sup>) under an atmosphere of dry nitrogen.

### 1.6. X-ray scattering

Small angle X-ray diffraction was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was copper Kα (λ = 0.154056 nm) from a 1 µS microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample,

allowing simultaneous collection of small and wide angle scattering data. Samples were filled into 1mm capillary tubes and aligned with a pair of 1T magnets. Diffraction patterns were collected as a function of temperature on cooling. Background subtraction, radial integration and processing of raw X-ray scattering data contained within Bruker .gfrm files was performed in Matlab using scripts and functions developed in house.

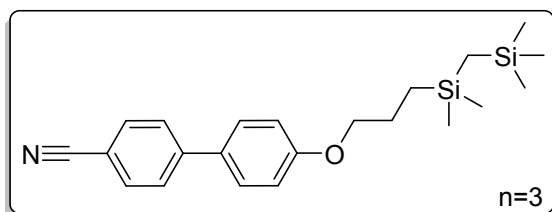
### **1.7. Computational Chemistry**

Quantum chemical calculations were performed using the Gaussian 09 revision D01;<sup>4</sup> this work was undertaken on ARC4, part of the High Performance Computing facilities at the University of Leeds, UK.

### **1.8. Standard Hydrosilylation Protocol**

An oven dried Schlenk tube was cooled under an atmosphere of dry nitrogen gas and charged with alkene (1 mmol), ((trimethylsilyl)methyl)dimethylsilane (1.1 mmol) and toluene (5 ml). The suspension was stirred until homogenous (< 5 min) and Karstedt's catalyst (20  $\mu$ l) added in one portion. The reaction was stirred until complete consumption of the alkene (TLC). The reaction solution was concentrated *in vacuo* and purified by flash chromatography over silica gel with a hexane/DCM gradient, affording the title compounds as viscous liquid crystals.

## 2. Chemical Characterisation



1; [2SiC]3OCB

Yield = 65.8%

<sup>1</sup>H NMR (400 MHz)  $\delta$  = 7.69 (d,  $J$  = 8.4 Hz, 2H); 7.64 (d,  $J$  = 8.3 Hz, 2H); 7.53 (d,  $J$  = 8.5 Hz, 2H); 6.99 (d,  $J$  = 8.6 Hz, 2H); 3.96 (t,  $J$  = 6.9 Hz, 2H); 1.86 – 1.75 (m, 2H); 0.65 – 0.58 (m, 2H); 0.05 (s, 6H); 0.04 (s, 9H); -0.23 – -0.26 (m, 2H).

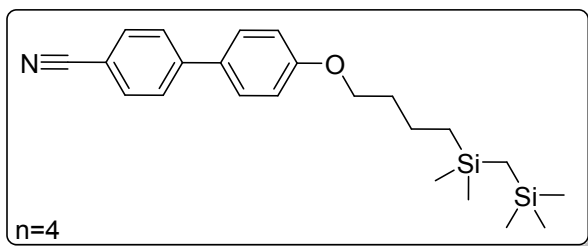
<sup>13</sup>C NMR (101 MHz)  $\delta$  = 159.91, 145.44, 132.71, 131.38, 128.47, 127.21, 119.28, 115.21, 110.16, 77.16, 71.02, 24.03, 13.90, 2.62, 1.54, -0.53.

<sup>29</sup>Si NMR (79 MHz)  $\delta$  = 2.70, 0.91.

DSC:

Transition Temperatures			$\text{j g}^{-1}$		kJ mol	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
14.5	-31.4	34.0	11.02	-7.6	4.2	-2.9

Meas. m/z: 382.203177 (Calcd. m/z: 382.201694 C<sub>22</sub>H<sub>32</sub>NOSi<sub>2</sub> err: 3.9ppm [M+H])



**2; [2SiC]4OCB**

Yield = 67.5%

$^1\text{H}$  NMR (400 MHz)  $\delta$  = 7.69 (d,  $J$  = 8.5 Hz, 2H), 7.64 (d,  $J$  = 8.6 Hz, 2H), 7.53 (d,  $J$  = 8.7 Hz, 2H), 7.00 (d,  $J$  = 8.8 Hz, 2H), 4.02 (t,  $J$  = 6.4 Hz, 2H), 1.93 – 1.74 (m, 2H), 1.54 – 1.37 (m, 2H), 0.69 – 0.50 (m, 2H), 0.06 – -0.03 (m, 15H), -0.22 – -0.34 (m, 2H).

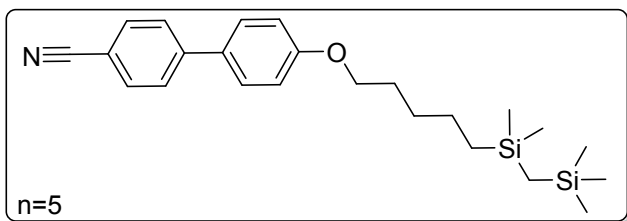
$^{13}\text{C}$  NMR (101 MHz)  $\delta$  = 159.97, 145.44, 132.71, 131.37, 128.45, 127.21, 119.28, 115.22, 110.14, 67.96, 33.13, 20.65, 17.84, 2.66, 1.55, -0.47.

$^{29}\text{Si}$  NMR (79 MHz)  $\delta$  = 2.15, 0.89.

DSC:

Transition Temperatures			$\text{j g}^{-1}$		kJ mol	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
	-28.2	21.1		-7.1	0.0	-2.8

Meas.  $m/z$ : 396.222265 (Calcd.  $m/z$ : 396.217344  $\text{C}_{23}\text{H}_{34}\text{NOSi}_2$  err: -12.4ppm [M+H])



### 3; [2SiC]5OCB

Yield = 57.7%

$^1\text{H}$  NMR (400 MHz)  $\delta$  = 7.69 (d,  $J$  = 8.7 Hz, 2H); 7.64 (d,  $J$  = 8.3 Hz, 2H); 7.53 (d,  $J$  = 8.6 Hz, 2H), 6.99 (d,  $J$  = 8.6 Hz, 2H), 4.00 (t,  $J$  = 6.5 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.49 (dq,  $J$  = 14.0, 6.9 Hz, 2H), 1.42 – 1.30 (m, 2H), 0.58 – 0.47 (m, 2H), 0.01 (d,  $J$  = 5.6 Hz, 14H), -0.25 – -0.32 (m, 2H).

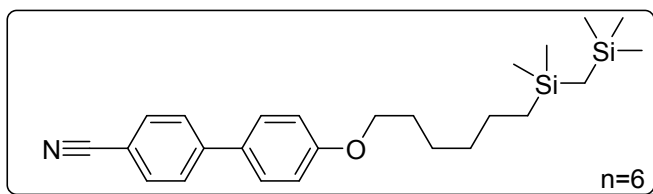
$^{13}\text{C}$  NMR (101 MHz)  $\delta$  = 159.94, 145.43, 132.71, 131.37, 128.45, 127.21, 119.28, 115.21, 110.14, 77.16, 68.32, 30.12, 29.09, 23.95, 18.06, 2.70, 1.55, 1.31, 0.57, -0.45.

$^{29}\text{Si}$  NMR (79 MHz)  $\delta$  = 2.03, 0.88.

DSC:

Transition Temperatures			$\text{j g}^{-1}$		kJ mol	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
4.3	-31.1	51.3	30.1	-9.0	12.3	-3.7

Meas.  $m/z$ : 410.237376 (Calcd.  $m/z$ : 410.232994  $\text{C}_{24}\text{H}_{36}\text{NOSi}_2$  err: -10.7ppm [M+H])



#### 4; [2SiC]6OCB

Yield = 51.5%

$^1\text{H}$  NMR (400 MHz)  $\delta$  = 7.69 (d,  $J$  = 8.6 Hz, 2H), 7.64 (d,  $J$  = 8.3 Hz, 2H), 7.53 (d,  $J$  = 8.7 Hz, 2H), 6.99 (d,  $J$  = 9.0 Hz, 2H), 4.01 (t,  $J$  = 6.5 Hz, 2H), 1.89 – 1.75 (m, 2H), 1.48 (dt,  $J$  = 15.0, 6.7 Hz, 2H), 1.43 – 1.35 (m, 2H), 1.35 – 1.28 (m, 2H), 0.62 – 0.35 (m, 2H), 0.03 – -0.03 (m, 14H), -0.25 – -0.35 (m, 2H).

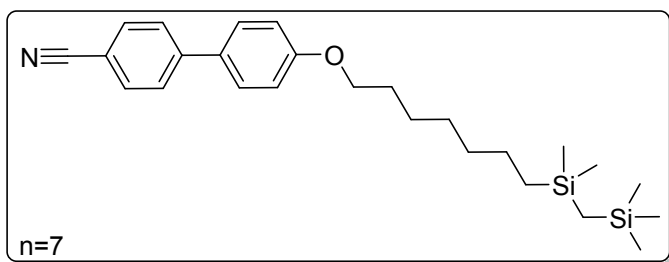
$^{13}\text{C}$  NMR (101 MHz)  $\delta$  = 159.94, 145.43, 132.71, 131.37, 128.46, 127.21, 119.28, 115.21, 110.15, 68.33, 33.53, 29.30, 25.88, 24.04, 18.06, 2.69, 1.55, -0.44.

$^{29}\text{Si}$  NMR (79 MHz)  $\delta$  = 2.01, 0.87.

DSC:

Transition Temperatures			$\text{j g}^{-1}$		$\text{kJ mol}^{-1}$	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
	-36.4	46.0		-9.1	0.0	-3.8

Meas.  $m/z$ : 424.253130 (Calcd.  $m/z$ : 424.248644  $\text{C}_{25}\text{H}_{38}\text{NOSi}_2$  err: -10.6ppm [M+H])



5; [2SiC]7OCB

Yield = 62.9%

$^1\text{H}$  NMR (400 MHz)  $\delta$  = 7.69 (d,  $J$  = 8.5 Hz, 2H), 7.64 (d,  $J$  = 8.5 Hz, 2H), 7.53 (d,  $J$  = 8.8 Hz, 2H), 6.99 (d,  $J$  = 8.7 Hz, 2H), 4.01 (t,  $J$  = 6.5 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.45 (dt,  $J$  = 15.6, 7.7 Hz, 2H), 1.41 – 1.23 (m, 6H), 0.54 – 0.44 (m, 2H), 0.03 – -0.04 (m, 15H), -0.26 – -0.33 (m, 2H).

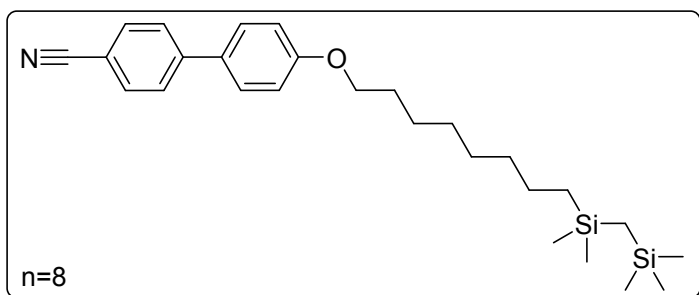
$^{13}\text{C}$  NMR (101 MHz)  $\delta$  = 159.94, 145.44, 132.71, 131.37, 128.46, 127.21, 119.28, 115.21, 110.14, 68.30, 33.74, 29.39, 29.25, 26.11, 24.04, 18.09, 2.70, 1.55, -0.43.

$^{29}\text{Si}$  NMR (79 MHz)  $\delta$  = 1.98, 0.85.

DSC

Transition Temperatures			$\text{j g}^{-1}$		kJ mol	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
25.7		60.1	13.4	10.9	5.9	4.8

Meas.  $m/z$ : 438.268063 (Calcd.  $m/z$ : 438.264294  $\text{C}_{26}\text{H}_{40}\text{NOSi}_2$  err: -8.6ppm [M+H])



**6; [2SiC]8OCB**

Yield = 49.1 %

$^1\text{H}$  NMR (400 MHz)  $\delta$  = 7.72 – 7.67 (m, 2H), 7.66 – 7.62 (m, 2H), 7.55 – 7.50 (m, 2H), 7.02 – 6.96 (m, 2H), 4.01 (t,  $J$  = 6.5 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.53 – 1.42 (m, 2H), 1.40 – 1.24 (m, 8H), 0.54 – 0.43 (m, 2H), 0.09 – -0.05 (m, 15H), -0.25 – -0.34 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz)  $\delta$  = 159.93, 145.41, 132.69, 131.35, 128.44, 127.19, 119.27, 115.20, 110.13, 68.30, 33.77, 29.47, 29.44, 29.35, 26.20, 24.09, 18.09, 2.69, 1.55, 1.31, -0.43.

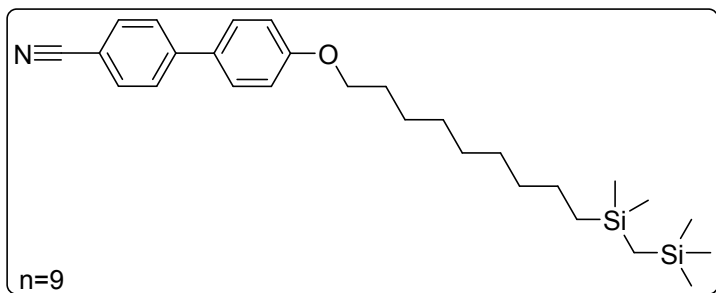
$^{29}\text{Si}$  NMR (79 MHz)  $\delta$  = 2.00, 0.86.

DSC:

Transition Temperatures			$\text{j g}^{-1}$		kJ mol	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
26.4	-43.7	54.3	36.7	8.8	16.6	4.0

Meas.  $m/z$ : 452.272015 (Calcd.  $m/z$ : 452.279944  $\text{C}_{27}\text{H}_{42}\text{NOSi}_2$  err: 17.5ppm [M+H])





**7; [2SiC]9OCB**

Yield = 48.2%

$^1\text{H}$  NMR (400 MHz)  $\delta$  = 7.71 – 7.67 (m, 2H), 7.64 (d,  $J$  = 8.4 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.01 – 6.96 (m, 2H), 4.01 (t,  $J$  = 6.5 Hz, 2H), 1.94 – 1.72 (m, 2H), 1.47 (dt,  $J$  = 14.9, 6.8 Hz, 2H), 1.39 – 1.24 (m, 10H), 0.56 – 0.44 (m, 2H), 0.06 – -0.06 (m, 15H), -0.27 – -0.32 (m, 2H).

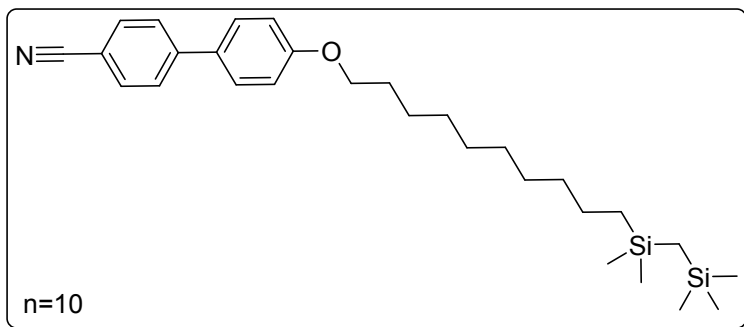
$^{13}\text{C}$  NMR (101 MHz)  $\delta$  = 159.94, 145.44, 132.71, 131.37, 128.46, 127.21, 119.29, 115.21, 110.14, 68.32, 33.84, 29.67, 29.57, 29.47, 29.37, 26.17, 24.11, 18.11, 2.70, 1.55, -0.43.

$^{29}\text{Si}$  NMR (79 MHz)  $\delta$  = 1.96, 0.84.

DSC:

Transition Temperatures			$\text{j g}^{-1}$		$\text{kJ mol}^{-1}$	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
16.5	-22.3	64.9	20.9	-8.5	9.7	-3.9

Meas.  $m/z$ : 466.2704 (Calcd.  $m/z$ : 466.2956  $\text{C}_{28}\text{H}_{44}\text{NOSi}_2$  err: 46ppm [M+H])



**8; [2SiC]10OCB**

Yield = 44.3%

$^1\text{H}$  NMR (400 MHz)  $\delta$  = 7.72 – 7.66 (m, 2H), 7.66 – 7.61 (m, 2H), 7.55 – 7.50 (m, 2H), 7.02 – 6.96 (m, 2H), 4.01 (t,  $J$  = 6.6 Hz, 2H), 1.87 – 1.76 (m, 2H), 1.49 (m, 2H), 1.40 – 1.21 (m, 12H), 0.53 – 0.43 (m, 2H), 0.06 – -0.06 (m, 15H), -0.25 – -0.34 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz)  $\delta$  = 159.94, 145.42, 132.70, 131.36, 128.45, 127.20, 119.27, 115.21, 110.14, 68.31, 33.86, 29.75, 29.69, 29.53, 29.36, 26.18, 24.11, 18.10, 2.70, 1.55, -0.43.

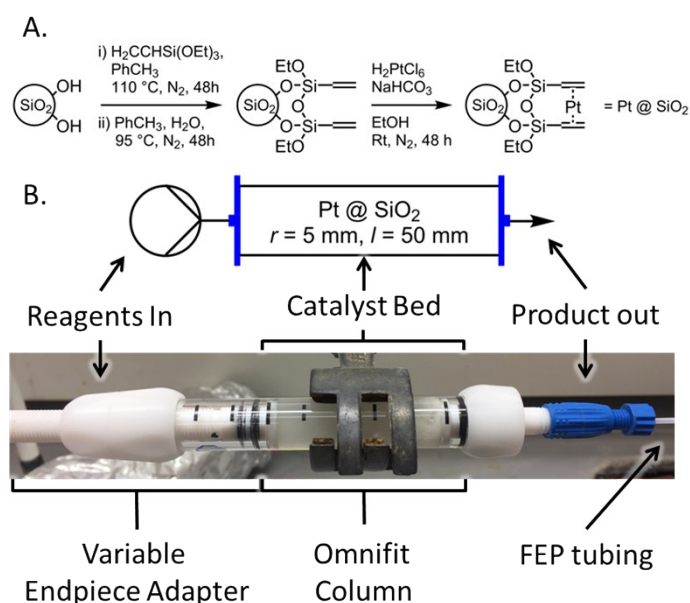
$^{29}\text{Si}$  NMR (79 MHz)  $\delta$  = 1.98, 0.85.

DSC:

Transition Temperatures			$\text{j g}^{-1}$		kJ mol	
<i>MP</i>	<i>tg</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>	<i>MP</i>	<i>SmA-Iso</i>
34.6		61.1	47.6	11.2	22.8	5.4

Meas.  $m/z$ : 480.309462 (Calcd.  $m/z$ : 480.311245  $\text{C}_{29}\text{H}_{46}\text{NOSi}_2$  err: -3.7ppm [M+H])

### 3. Continuous Flow Hydrosilylation



**Figure SI-1:** (a) Scheme 1, showing the synthesis of the catalyst Pt @ SiO<sub>2</sub> used in this work. (b) Top, diagram of the flow reactor. Bottom, photograph of the assembled reactor: the flow direction is from left to right through 0.89 mm I.D. fluorinated ethylene propylene (FEP) tubing, the Omnifit column (and therefore catalyst bed) is cylindrical, having a radius of 5 mm, a length of  $\approx$  50 mm and therefore a volume of  $\approx$  4 cm<sup>3</sup>.

Continuous flow hydrosilylation was achieved using a Karstedt-like platinum-on-silica catalyst ("Pt@SiO<sub>2</sub>") contained in a low pressure Omnifit column (Fig. SI-1).<sup>5,6</sup> A solution of 1,1,3,3-tetramethyldisilabutane and 4'-(11-hydroxyundecyloxy)-4-cyanobiphenyl in low sulphur toluene (0.2 M) was delivered over the catalyst bed at a rate of 0.5 ml min<sup>-1</sup> *via* a syringe pump; removal of volatiles (toluene, 1,1,3,3-disilabutane) gave compound **9** as a colourless, viscous liquid crystal, whose properties and spectra were identical to prior reports.<sup>3</sup>

Yield: >90 %

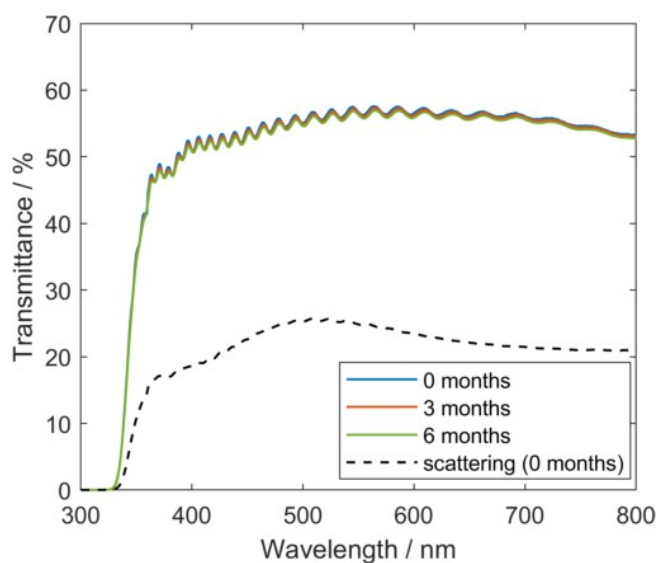
<sup>1</sup>H NMR (400 MHz)  $\delta$  = 7.69 (2H, ddd,  $J$  = 2.1 Hz,  $J$  = 3.2 Hz,  $J$  = 8.5 Hz, ArH), 7.63 (2H, ddd,  $J$  = 2.1 Hz,  $J$  = 3.2 Hz,  $J$  = 8.5 Hz, ArH), 7.53 (2H, ddd,  $J$  = 2.1 Hz,  $J$  = 3.2 Hz,  $J$  = 8.5 Hz, ArH), 6.94 (2H, ddd,  $J$  = 2.1 Hz,  $J$  = 3.2 Hz,  $J$  = 8.5 Hz, ArH), 4.01 (2H, t,  $J$  = 7.0 Hz, ArOCH<sub>2</sub>-CH<sub>2</sub>-), 1.76 - 1.85 (2H, m, -CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>9</sub>Si(CH<sub>3</sub>)<sub>2</sub>), 1.19 - 1.55 (16 H, m, -CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>), 0.45 - 0.53 (2H, m, -CH<sub>2</sub>-CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>-), 0.00 (9H, s, -CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>3</sub>), -0.05 (6H, s, -CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>3</sub>), -0.40 (2H, s, -CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>3</sub>),

<sup>13</sup>C NMR (101 MHz)  $\delta$  = 159.87, 143.36, 132.60, 131.32, 128.37, 127.14, 119.18, 115.12, 110.11, 68.31, 33.84, 29.78, 29.73, 29.65, 29.52, 29.34, 26.17, 24.10, 18.06, 2.67, 1.52, 0.40,

<sup>29</sup>Si NMR (79 MHz)  $\delta$  = 2.01, 0.01

Meas. m/z: 494.329981 (Calcd. m/z: 494.327445 C<sub>30</sub>H<sub>48</sub>NOSi<sub>2</sub> err: -9.3ppm [M+H])

#### 4. Supplemental UV-Vis spectra



**Figure SI-2:** UV-vis spectra of a cell containing compound **4** doped with 0.05 wt%, switched into the clear state at 0 months (i.e. as soon as a spectra could be practically recorded after switching), 3 months and 6 months. For comparison, the scattering state at 0 months is also presented. The maximum difference in % transmittance over the 6 month period studied is less than 0.5 %, indicating that the scattering device is bistable.

#### 5. References

1. R. J. Mandle and J. W. Goodby, *Liq Cryst*, 2017, **44**, 656-665.
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