# **Electronic Supplementary Information**

# *Ortho*-fluorination of azophenols increases the mesophase stability of photoresponsive hydrogen-bonded liquid crystals

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## 1. Materials and Methods

All Commercially available compounds including **A** and solvents were used without further purification as received from suppliers. <sup>1</sup>H-, <sup>19</sup>F-, and <sup>13</sup>C-NMR-Spectra of the compounds were collected in deuterated solvent (DMSO<sub>d6</sub>) at room temperature, using a *Varian* Mercury 300 MHz. Mass spectra were obtained with a *Bruker* amazon SL (LRMS) or a MaXis 4G Q-TOF-mass spectrometer (HRMS). IR-spectra were recorded with a *Jasco* FT/IR-430 Spectrometer. DSC data were collected using a DSC 3+/700/866/Argon from *Mettler Toledo* equipped with an intra cooler. The Samples were measured in 40 µL standard almunium crucibles with a heating and cooling rate of 5 K/min. Polarized optical microscopy (POM) images were taken on a *Zeiss* Axio Scope.A1 microscope, a *Linkam* hot stage, and an *Axiocam 305 color* microscope camera. The light-responsive properties of the LCs were studied using an *Agilent* Cary 60 spectrophotometer and a large custom-built cavity that allows the installation of a temperature-controlled sample stage and the photoexcitation of the studied sample. A *Linkam* LinkPad was used for controlling the sample temperature and a *Prior Scientific* Lumen-1600 was used as the photoexcitation source.

## 2. Synthetic Procedures

## (E)-4-((4-butylphenyl)diazenyl)-3,5-difluorophenol (B-4):



To a cooled solution (0 °C) of 4-butylaniline (6.70 mmol, 1.0 g) and hydrochloric acid in acetone:water (1:1) was added a cold (0 °C) aqueous solution of sodium nitrite (7.10 mmol, 0.49 g) and allowed to stand at 0 °C for 15 minutes. In a separate flask, an aqueous solution of 3,5-difluorophenl (7.21 mmol, 0.938 g), sodium hydroxide (7.16 mmol, 0.286 g) and sodium carbonate (11.18 mmol, 1.1 g) was prepared and cooled to 0°C. The first mixture of diazonium salt was slowly added to the phenolic mixture and the combined reaction mixture was allowed to stir for 30 minutes. The reaction mixture was diluted with ethyl acetate and washed with water three times. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 20% ethyl acetate/80% hexane v/v to yield compound **B-4** (1.33 g, 68%) as an orange-yellow solid. <sup>1</sup>H NMR (300 MHz, DMSO<sub>d6</sub>, TMS):  $\delta$  = 7.68

(d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 12.0 Hz, 2H), 2.64 (t, *J* = 7.92 Hz, 2H), 1.62-1.52 (m, 2H), 1.36-1.24 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (75 MHz, DMSO<sub>d6</sub>, TMS):  $\delta$  = 160.85 (t, *J* = 15 Hz), 156.8 (dd, <sup>1</sup>*J*<sub>CF</sub> = 248 Hz; <sup>2</sup>*J*<sub>CF</sub> = 7.5 Hz), 151.19, 146.33, 129.26, 123.41 (t, J = 7.5 Hz), 122.08, 100.11 (m), 34.67, 32.89, 21.75, 13.76. <sup>19</sup>F NMR (282 MHz, DMSO<sub>d6</sub>):  $\delta$  = -119.47 (d, *J* = 11.2 Hz). HRMS: *m*/*z* calcd for C<sub>16</sub>H<sub>16</sub>F<sub>2</sub>N<sub>2</sub>O: 291.1309; found: 291.1322 [M+H]<sup>+</sup>.





(E)-3,5-difluoro-4-((4-hexylphenyl)diazenyl)phenol (B-6):



To a cooled solution (0 °C) of 4-hexylaniline (11.2 mmol, 2.0 g) and hydrochloric acid in acetone:water (1:1) was added a cold (0 °C) aqueous solution of sodium nitrite (12.0 mmol, 0.82 g) and allowed to stand at 0 °C for 15 minutes. In a separate flask, an aqueous solution of 3,5-difluorophenl (12.14 mmol, 1.60 g), sodium hydroxide (12.12 mmol, 0.485 g) and sodium carbonate (18.87 mmol, 2.0 g) was prepared and cooled to 0°C. The first mixture of diazonium salt was slowly added to the phenolic mixture and the combined reaction mixture was allowed to stir for 30 minutes. The reaction mixture was diluted with ethyl acetate and washed with water three times. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 20% ethyl acetate/80% hexane v/v to yield compound **B-6** (2.60 g, 72%) as orange-yellow solid. <sup>1</sup>H NMR (300 MHz, DMSO<sub>d6</sub>, TMS):  $\delta$  = 7.68 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 6.64 (d, J = 12.0 Hz, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.59-1.52 (m, 2H), 1.25 (s, 6H), 0.83 (t, J = 7.02 Hz, 3H). <sup>13</sup>C NMR (75 MHz, DMSO<sub>d6</sub>, TMS):  $\delta$  = 160.85 (t, J = 15 Hz), 156.8 (dd, <sup>1</sup> $J_{CF}$  = 248 Hz; <sup>2</sup> $J_{CF}$  = 7.5 Hz), 151.22, 146.36, 129.23, 123.41 (t, J = 7.5 Hz), 122.08, 100.11 (m), 35.02, 31.11, 30.72, 28.33, 22.07, 13.93. <sup>19</sup>F NMR (282 MHz, DMSO<sub>d6</sub>):  $\delta$  = -119.06 (d, J = 10.90 Hz) (m). HRMS: *m/z* calcd for C<sub>18</sub>H<sub>20</sub>F<sub>2</sub>N<sub>2</sub>O: 319.1622; found: 319.1636 [M+H]<sup>+</sup>.





#### 3. Formation and characterization of the supramolecular assemblies

Our supramolecular complexes were prepared by weighting separately one equivalent of the appropriate hydrogen-bond-donor (**A**, **B-4** or **B-6**) and one equivalent of the appropriate stilbazole. The hydrogen-bond-donors and acceptors were then dissolved in chloroform and the respective solution were combined. The

solvent was removed under high vacuum and the complexes were collected after scrupulous grinding. A collection of the DSC data is presented in **Table S1**.

Table	S1.	Transition	temperatures	for	the	mesomorphic	complexes	reported	in	the	present	paper,	as
determ	nined	by DSC.											

Complex		Transition	Peak temperature (°C)	Enthalpy change (J/g)
		Cr-N	68.0	32.00
D 4-64 4	Heating	N-Cr	72.0	-55.00
D-4•31-1		Cr-I	100.1	64.80
	Cooling	I-N	65.8	-1.04
	Heating	Cr-N	64.4	31.53
D 4-04-0		N-I	87.4	0.71
B-4•31-2	Qaalima	I-N	81.4	-0.53
	Cooling	N-SmA	21.8	-0.027
	Heating	Cr-N	86.1	39.50
		N-I	91.9	0.40
B-4•St-4	Cooling	I-N	86.2	-0.69
		N-SmA	77.8	-0.79
		SmA-Cr	6.0	-10.22
	11	Cr-SmA	75.5	13.17
D 4-04-0	Heating	SmA-I	106.4	7.63
B-4•31-0	0	I-SmA	86.0	-3.21
	Cooling	SmA-Cr	17.4	-15.98
	l la afin a	Cr-SmA	65.0	39.16
B-4•St-12	пеаціпу	SmA-I	113.3	9.43
	Cooling	I-SmA	97.2	-5.06
	Llaating	Cr-N	62.4	46.40
D 6-84 4	пеаціпу	N-I	82.1	1.00
D-0-31-1	Cooling	I-N	74.6	-0.68
		N-SmA	41.0	-0.38
	Hoating	Cr-N	88.1	41.17
	пеашу	N-I	98.5	0.95
B-6•St-2	Cooling	I-N	93.2	-0.84
		N-SmA	75.9	-0.32
		SmA-Cr	51.9	-25.79
	Llooting	Cr-SmA	90.9	55.42
R Goet A	Tieating	SmA-I	100.1	3.72
D-0-31-4	Cooling	I-SmA	93.1	-3.78
		SmA-Cr	13.5	-17.86
	Hoating	Cr-SmA	70.9	31.06
B-6.St-8	Tieating	SmA-I	113.1	8.32
D-0-31-0	Cooling	I-SmA	93.5	-3.65
	Cooling	SmA-Cr	24.9	-16.74
	Hosting	Cr-SmA	63.2	36.00
B_6.9+_12		SmA-I	118.1	11.23
D-0-31-12	Cooling	I-SmA	103.3	-5.87
	Cooling	SmA-Cr	19.0	-24.91

POM images of the studied complexes in LC phases are depicted in Fig. S1–S5.



Fig. S1. POM images of nematic B-4-St-1 at 71 °C (left) and nematic B-6-St-1 at 68 °C (right) upon heating.



**Fig. S2**. POM images of nematic **B-4-St-2** at 86 °C upon heating (left) and smectic A **B-6-St-2** at 70 °C upon cooling (right).



Fig. S3. POM images of nematic B-4•St-4 at 90 °C (left) and smectic A B-6•St-4 at 91 °C (right) upon heating.



Fig. S4. POM images of smectic A B-4•St-8 at 95 °C (left) and smectic A B-6•St-8 at 70 °C (right) upon heating.



**Fig. S5**. POM images of smectic A **B-4-St-12** at 95 °C (left) and smectic A **B-6-St-12** at 100 °C (right) upon heating.

#### 4. Photochemistry

Cis-lifetimes of A and B-6 were acquired by fitting the kinetic absorbance data with the equation

 $Abs = Abs_{\infty} + (Abs_0 - Abs_{\infty})e^{-kt}$  from which the linear form  $\ln\left(\frac{Abs - Abs_{\infty}}{Abs_0 - Abs_{\infty}}\right) = -kt$  can be derived. The absorbance values as a function of time and the respective linear fits are shown in **Fig. S6–S9** (fitted straight to exponential form for **B-6** in acetonitrile), and the acquired parameters for these experiments are shown in **Table S-2.** Lifetime is the inverse of the constant *k*.



**Fig. S6:** The absorbance as a function of time and a linear exponential fit for the *cis-trans* relaxation of A in toluene.



**Fig S7:** The absorbance as a function of time and a linear exponential fit for the *cis-trans* relaxation of A in acetonitrile.



Fig S8: The absorbance as a function of time and a linear exponential fit for the *cis-trans* relaxation of B-6 in toluene.



Fig. S9: The absorbance and exponential fit of B-6 in acetonitrile.

Table S2: Parameters Abs<sub>0</sub>, Abs<sub>inf</sub>, and k for fitting the lifetime data of **A** and **B-6** in toluene and acetonitrile.

	Abs₀	Abs <sub>inf</sub>	k (s <sup>-1</sup> )
A toluene	0.0250	0.69	0.000412
A acetonitrile	0.0085	0.22	0.9058
B-6 toluene	0.0495	0.85	0.001184
B-6 acetonitrile	0.5740	0.6706	2.050

#### 5. Computational Details

The calculations were performed using Gaussian 16, Revision A.03 (Gaussian, Inc., Wallingford CT, 2016)<sup>1</sup>. Frequency calculations were performed to conform that the obtained geometries were true minima (*i.e.* no imaginary frequencies).



**Fig S10:** The optimized geometry of the complex **A-1•St-1** from two angles, showing the hydrogen bond length.



**Fig S11:** The optimized geometry of the complex **B-1•St-1** from two angles, showing the hydrogen bond length.

#### 6. References

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