

## Electronic Supplementary Information for

### Zwitterionic pyridinium derivatives of [*closo*-1-CB<sub>9</sub>H<sub>10</sub>]<sup>+</sup> and [*closo*-1-CB<sub>11</sub>H<sub>12</sub>]<sup>+</sup> as high Δε additives to a nematic host

Jacek Pecyna,<sup>a</sup> Damian Pocięcha,<sup>b</sup> and Piotr Kaszyński\*<sup>a,c</sup>

<sup>a</sup> Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA, Tel: 1-615-322-3458; E-mail: piotr.kaszynski@vanderbilt.edu.

<sup>b</sup> Department of Chemistry, University of Warsaw, Zwirki i Wigury 101, 02-089 Warsaw, Poland.

<sup>c</sup> Faculty of Chemistry, University of Łódź, Tamka 12, 91403 Łódź, Poland.

#### Table of content

1. Synthetic details	.....S2
2. Enantiomeric Excess	.....S7
3. Powder XRD measurements	.....S7
4. Electronic absorption spectra	.....S8
5. Binary mixtures	.....S9
• Binary mixtures preparation	.....S9
• Thermal analysis	.....S9
• Dielectric measurements	.....S11
6. Background for calculations in the nematic phase	.....S12
7. Quantum mechanical calculations	.....S13
8. Archive for DFT calculations	.....S17
9. References	.....S19

## 1. Additional synthetic details

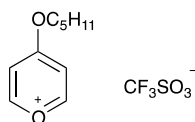
### 1-Amino-12-hexyl-1-carba-*closo*-dodecaborane (**4[6]**).<sup>1</sup>



A solution of dry  $\text{ZnCl}_2$  (1.46 g, 10.7 mmol) in anhydrous THF (50 mL) under Ar was treated with  $\text{C}_6\text{H}_{13}\text{MgBr}$  (5.4 mL, 10.7 mmol, 2.0 M in  $\text{Et}_2\text{O}$ ) at 0 °C forming a white, thick slurry which was stirred for 20 min. Anhydrous NMP (25 mL),  $\text{Pd}_2\text{dba}_3$  (16 mg, 2 mol %), and  $[\text{HPCy}_3]^+ [\text{BF}_4]^-$  (27 mg, 8 mol %) were added and the reaction mixture turn dark brown, but slowly faded to red/orange. After 15 minutes, iodo amine **8** (320 mg, 0.894 mmol) was added and the reaction mixture was refluxed at 90 °C for 72 hr. The reaction was cooled to room temperature, washed with saturated  $\text{NH}_4\text{Cl}$ , and the solvents were removed *in vacuo*. The solution was extracted with  $\text{Et}_2\text{O}$  (3x100 mL).  $\text{Et}_2\text{O}$  was dried and evaporated to leave brown residue. Excess alcohol and NMP were removed under reduced pressure to leave brown liquid. The crude material was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ , 3:1) to give 102 mg of the desired material as brown solid. The solid was treated with 10% HCl and extracted into  $\text{Et}_2\text{O}$  [ $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 400 MHz)  $\delta$  0.66 (br t,  $J = 6.6$  Hz, 2H), 0.86 (t,  $J = 7.1$  Hz, 3H), 1.0-2.8 (br m, 10H), 1.09-1.28 (m, 8H), 5.8 (br s, 3H);  $\{^1\text{H}\}^{11}\text{B}$  NMR ( $\text{CD}_3\text{CN}$ , 128 MHz)  $\delta$  -15.1 (5B), -12.4 (5B), 0.94 (1B)]. The  $\text{Et}_2\text{O}$  layers were combined and solvent evaporated. The residue was washed several times with boiling  $\text{H}_2\text{O}$ . The water washes were combined, the pH of the solution was adjusted slightly above 7 with 10% KOH and excess  $\text{NMe}_4\text{OH}\cdot 5\text{H}_2\text{O}$  (1.5 eq) was added resulting in white precipitation. The solution was extracted with  $\text{CH}_2\text{Cl}_2$ , the organic layers combined, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to give 98 mg (35% yield) of the product as yellowish viscous oil. Analytical sample of **4[6]** was prepared by recrystallization from  $\text{EtOH}/\text{H}_2\text{O}$ : mp 165 °C;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 400 MHz)  $\delta$  0.40 (br s, 2H), 0.86 (t,  $J = 7.0$  Hz, 3H), 1.0-2.8 (br m, 10H), 1.09-1.28 (m, 10H), 3.08 (s, 12H);  $\{^1\text{H}\}^{11}\text{B}$  NMR ( $\text{CD}_3\text{CN}$ , 128 MHz)  $\delta$  -13.2 (10B), -3.5 (1B). Anal. Calcd. for  $\text{C}_{11}\text{H}_{37}\text{N}_2\text{B}_{11}$ : C, 41.77; H, 11.79; N, 8.86. Found: C, 41.59; H, 11.37; N, 8.06%.

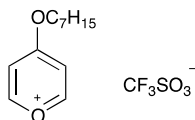
**[closo-1-CB<sub>11</sub>H<sub>10</sub>-1-NH<sub>2</sub>-12-C<sub>5</sub>H<sub>11</sub>]<sup>+</sup>[NMe<sub>4</sub>]<sup>-</sup> (4[5])** and **[closo-1-CB<sub>11</sub>H<sub>10</sub>-1-NH<sub>2</sub>-12-C<sub>10</sub>H<sub>21</sub>]<sup>+</sup>[NMe<sub>4</sub>]<sup>-</sup> (4[10])** were obtained by reacting iodo amine **8** with appropriate Grignard reagents following the procedure for **4[6]**.<sup>2</sup> Their preparation is described elsewhere.<sup>1</sup>

#### 4-Pentyloxyppyrylium triflate (5a).



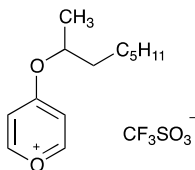
The compound was prepared in about 80% purity by Method A. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.90 (t, *J* = 7.1 Hz, 3H), 1.33-1.48 (m, 4H), 1.92 (quint, *J* = 6.5 Hz, 2H), 4.60 (t, *J* = 6.5 Hz, 2H), 7.74 (d, *J* = 5.8 Hz, 2H), 9.15 (d, *J* = 5.8 Hz, 2H). Major impurity: 7.32 (d, *J* = 6.0 Hz) and 8.72 (d, *J* = 6.0 Hz) in a 1:1 ratio.

#### 4-Heptyloxyppyrylium triflate (5b).



The compound was prepared in about 85% purity by Method A. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz) δ 0.91 (t, *J* = 6.8 Hz, 3H), 1.27-1.41 (m, 6H), 1.43-1.51 (m, 2H), 1.90 (quint, *J* = 7.2 Hz, 2H), 4.58 (t, *J* = 6.6 Hz, 2H), 8.63 (d, *J* = 6.0 Hz, 2H), 9.07 (d, *J* = 5.9 Hz, 2H). Major impurity: 7.53 (d, *J* = 5.9 Hz) and 8.93 (d, *J* = 5.9 Hz) in a 1:1 ratio.

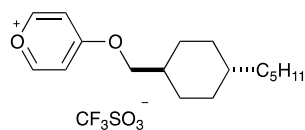
#### 4-(2-octyloxy)ppyrylium triflate (5c).



The compound was prepared in about 25% purity by Method C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.83 (t, *J* = 6.8 Hz, 3H), 1.20-1.42 (m, 8H), 1.46 (d, *J* = 6.1 Hz, 3H), 1.69-1.76 (m, 1H),

1.79-1.88 (m, 1H), 5.17 (sextet,  $J = 6.1$  Hz, 1H), 7.71 (d,  $J = 5.8$  Hz, 2H), 9.12 (d,  $J = 5.8$  Hz, 2H). Major impurity: 6.69 (d,  $J = 6.2$  Hz) and 8.08 (d,  $J = 6.1$  Hz) in a 1:1 ratio.

#### 4-((*trans*-4-Pentylcyclohexyl)methoxy)pyrylium triflate (5d).



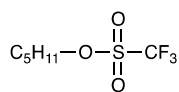
The compound was prepared in about 60% purity by Method B.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.87 (t,  $J = 6.7$  Hz, 3H), 0.90-1.00 (m, 4H), 1.15-1.30 (m, 9H), 1.69-1.84 (m, 5H), 4.40 (d,  $J = 6.3$  Hz, 2H), 7.71 (d,  $J = 5.9$  Hz, 2H), 9.14 (d,  $J = 5.9$  Hz, 2H). Major impurity: 6.95 (d,  $J = 5.4$  Hz) and 8.30 (d,  $J = 5.1$  Hz) in a 1:1 ratio.

#### General methods for preparation of alkyl triflates 6.

**Method A.** Following a general method for alkyl triflates,<sup>3</sup> to a vigorously stirred solution of triflic anhydride (1.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) at 0 °C, a solution of pyridine (1 mmol) and primary alcohol (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added dropwise over a 15-min period and the mixture was stirred for an additional 1 hr at 0 °C. The solution was washed with ice-cold  $\text{H}_2\text{O}$ , dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to dryness to give the appropriate alkyl triflate **6** as a colorless liquid that quickly began to darken. The resulting mixture was filtered through a cotton plug and used without further purification.

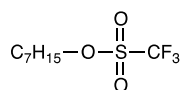
**Method B.** To a vigorously stirred mixture of a secondary alcohol (1 mmol) and pyridine (1 mmol) at -78 °C in  $\text{CH}_2\text{Cl}_2$  (25 mL) was added dropwise triflic anhydride (1 mmol). The mixture was stirred for 10 minutes at -78 °C and then kept at 0 °C until the alcohol was consumed (by TLC). The mixture was washed with ice-cold water, dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent was removed *in vacuo* at 0 °C. The resulting triflate **6** was kept at 0 °C and quickly used in the next step.

#### 1-Pentyl triflate (6a).<sup>4,5</sup>



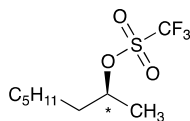
The compound was prepared by Method A as a colorless liquid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.93 (t,  $J = 7.1$  Hz, 3H), 1.33-1.46 (m, 4H), 1.84 (quint,  $J = 6.6$  Hz, 2H), 4.54 (t,  $J = 6.5$  Hz, 2H).

### 1-Heptyl triflate (6b).<sup>6</sup>



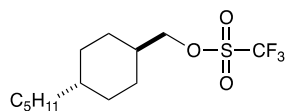
The compound was prepared by Method A as a colorless liquid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.89 (t,  $J = 7.0$  Hz, 3H), 1.26-1.46 (m, 8H), 1.83 (quint,  $J = 6.6$  Hz, 2H), 4.54 (t,  $J = 6.5$  Hz, 2H).

### (S)-2-octyl triflate (6c).



The compound was prepared by Method B as a colorless liquid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.89 (t,  $J = 7.0$  Hz, 3H), 1.24-1.47 (m, 8H), 1.51 (d,  $J = 6.3$  Hz, 3H), 1.63-1.74 (m, 1H), 1.78-1.87 (m, 1H), 5.07 (sext,  $J = 6.3$  Hz, 1H).

### (trans-4-Pentylcyclohexyl)methyl triflate (6d).



The compound was prepared by Method A as a colorless liquid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  0.88 (t,  $J = 6.6$  Hz, 3H), 0.90-1.09 (m, 4H), 1.15-1.34 (m, 9H), 1.70-1.77 (m, 1H), 1.80-1.83 (br d,  $J = 10.6$  Hz, 4H), 4.33 (d,  $J = 6.3$  Hz, 2H).

### Preparation of [closo-1-CB<sub>11</sub>H<sub>10</sub>-1-NH<sub>2</sub>-12-I]<sup>-</sup>[NMe<sub>4</sub>]<sup>+</sup> (8).<sup>1</sup>



A suspension of [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-COOH-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> (**9**,<sup>7</sup> 1.108 g) [<sup>11</sup>B NMR (CD<sub>3</sub>CN, 128 MHz): δ -11.6 (5B), -13.6 (5B), -16.6 (1B)] in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was treated with (COCl)<sub>2</sub> (0.952 g, 7.50 mmol). Vigorous bubbling of CO and CO<sub>2</sub> was observed, followed by the dissolution of the substrate and the formation of a slightly yellow solution. The solution was stirred for 45 min at room temperature and the solvent was removed *in vacuo* to give 1.16 g of crude [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-COCl-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> as a slightly yellow solid: <sup>11</sup>B NMR (CD<sub>3</sub>CN, 128 MHz) δ -11.0 (5B), -13.1 (5B), -15.4 (1B).

Crude [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-COCl-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> (1.16 g, 2.51 mmol) was dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and added via a syringe to solid anhydrous ZnCl<sub>2</sub> (34 mg, 0.25 mmol) under Ar atmosphere. The reaction was cooled to 0 °C and Me<sub>3</sub>SiN<sub>3</sub> (374 mg, 3.25 mmol) was added. The reaction mixture was stirred at 0 °C for 30 minutes, after which it was warmed to room temperature and stirred for 4 hr. The reaction mixture was poured into ice-cold H<sub>2</sub>O (15 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered and the solvent was removed *in vacuo* giving 1.19 g of [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-CON<sub>3</sub>-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> as a slightly yellow crystalline solid: <sup>11</sup>B NMR (CD<sub>3</sub>CN, 128 MHz) δ -11.2 (5B), -13.6 (5B), -16.0.

Crude [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-CON<sub>3</sub>-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> (1.19 g, 2.54 mmol) was dissolved in anhydrous CH<sub>3</sub>CN (20 mL) and refluxed for 2 hr. The reaction was cooled to room temperature, the solvent removed and the residue dried *in vacuo* giving 1.15 g of crude [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-NCO-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> as a slightly yellow solid: <sup>11</sup>B NMR (CD<sub>3</sub>CN, 128 MHz) δ -12.4 (10B), -20.2 (1B).

A solution of anhydrous *tert*-butanol (10 mL), anhydrous CH<sub>3</sub>CN (15 mL) and crude [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-NCO-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> (1.15 g, 2.61 mmol) was stirred at 85 °C for 3 hr, after which solvents were removed, leaving 1.08 g of crude [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-NHBoc-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> as a yellow solid. The crude solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and passed through a silica gel plug buffered with 1% NEt<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. Elution with a buffered CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> solution (1% NEt<sub>3</sub>, 20% CH<sub>3</sub>CN, 79% CH<sub>2</sub>Cl<sub>2</sub>) afforded 0.431 g (45% yield) contaminated with the deprotected iodo amine **8**: <sup>11</sup>B NMR (CD<sub>3</sub>CN, 128 MHz) δ -12.7 (10B), -21.8 (1B).

A suspension of [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-NHBoc-12-I]<sup>-</sup>[NEt<sub>4</sub>]<sup>+</sup> (0.431 g, 0.838 mmol) in a 1:3 mixture of concentrated HCl in CH<sub>3</sub>OH (50 mL) was stirred overnight at room temperature. Water

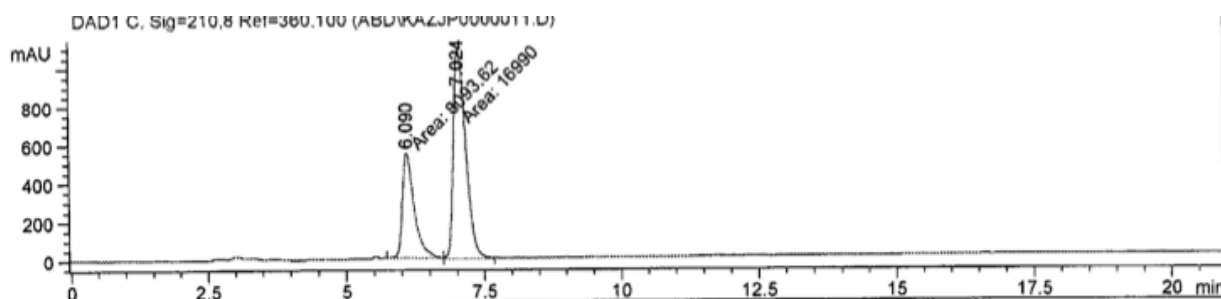
was added (30 ml) and CH<sub>3</sub>OH was removed *in vacuo*. Concentrated HCl was added (10 mL) and [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-NH<sub>3</sub>-12-I] was extracted into Et<sub>2</sub>O (3 x 25 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated in *vacuo* to give 0.25 g of oily residue. The oil was treated with aqueous solution of NMe<sub>4</sub>OH to give (0.32 g) of crude [*closo*-1-CB<sub>11</sub>H<sub>10</sub>-1-NH<sub>2</sub>-12-I][NMe<sub>4</sub>]<sup>+</sup> (**8**) which was recrystallized from aqueous EtOH and dried in *vacuo*. Analytical data are consistent with those obtained by different route: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 128 MHz) δ -12.7 (10B), -23.0 (1B).

## 2. Enantiomeric Excess

A solution of compound **1[6]c** in EtOH (1 mg / 1 mL) was analyzed using a reversed phase AD-H Chiral column and 15% EtOH in hexane as the eluent. The resulting two signals in the chromatogram (Fig. S1) were integrated and *ee* was calculated from the formula:

$$ee = 100\% * (\text{areaI} - \text{areaII}) / (\text{areaI} + \text{areaII}).$$

The structural relationship of the two compounds showing as separate signals in the chromatogram was confirmed by analysis of their UV spectra.



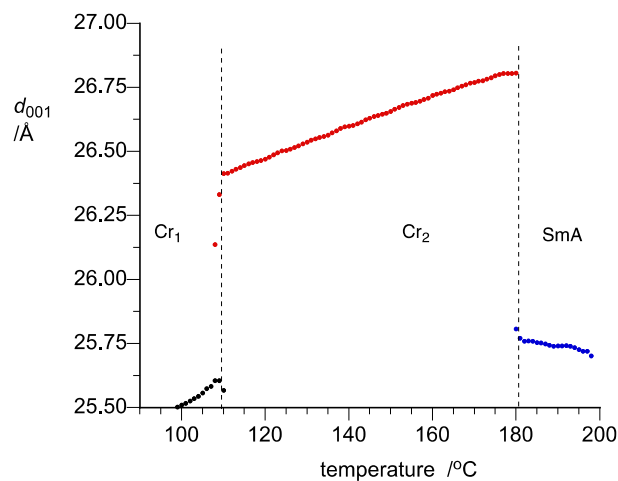
**Fig. S1.** A chromatogram for **1[6]c**.

## 3. Powder XRD measurements

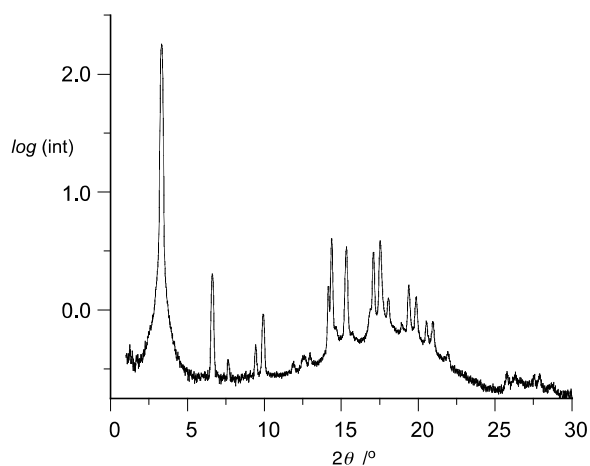
X-ray diffraction experiments were performed with Bruker D8 GADDS (Cu K $\alpha$  radiation, Göbel mirror, point collimator, Vantec 2000 area detector) equipped with a modified Linkam heating stage and with Bruker D8 Discover system (Cu K $\alpha$  radiation, Göbel mirror, scintillation counter, Anton Parr DCS350 heating stage). Samples were prepared in a form of a thin film or a droplet on heated surface. The X-ray beam was incident nearly parallel to sample surface, and resulting XRD patterns were recorded as a function of temperature on cooling.

XRD data was analyzed using program TOPAS 3 (Bruker). The asymmetric wide angle signal in diffractogram of **2[10]b** was fitted with two functions type PV (pseudo-Voigt).

Thermal expansion coefficients were obtained from the data in a temperature range 196–183 °C for SmA phase and 120–170 °C for the Cr<sub>2</sub> phase (Fig. S2).



**Fig. S2.** *d* spacing for **2[10]b** as a function of temperature obtained on cooling.



**Fig. S3.** XRD pattern for **2[10]b** at 170 °C (the Cr<sub>2</sub> phase)

#### 4. Electronic absorption spectra

UV-vis spectra for **1[6]c** and **2[6]c** were recorded in spectroscopic grade MeCN at concentration in a range of 1–10 × 10<sup>-5</sup> M. Extinction coefficients were obtained by fitting the maximum absorbance at 282 nm for **1[6]c** and 264 nm for **2[6]c** against concentration in agreement with Beer's law.



## 5. Binary mixtures

Binary mixtures preparation. Solutions of the pyridinium derivatives in appropriate host (15-20 mg of the host) were prepared in an open vial. The mixture of the compound and host in  $\text{CH}_2\text{Cl}_2$  was heated for 2 hr at 60 °C to remove the solvent. The binary mixtures were analyzed by polarized optical microscopy (POM) to ensure that the mixtures were homogenous. The mixtures were then allowed to stand for 2 hr at room temperature.

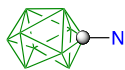
Thermal analysis  $T_{\text{NI}}$  for each homogenous mixture was determined by DSC as the peak of the transition using small samples (0.5 - 1 mg) and a heating rate of 5  $\text{K}\cdot\text{min}^{-1}$ . The results are shown in Tables S1-S3. The virtual N-I transition temperatures,  $[T_{\text{NI}}]$ , were determined for **1[6]c** and **1[6]d** by extrapolation from the single concentration. For compound **2[10]b** the  $[T_{\text{NI}}]$  was obtained by line extrapolation of the data for peak of the transition to pure substance ( $x = 1$ ) and the result is shown in Fig. S4. To minimize the error, the intercept in the fitting function was set as the peak  $T_{\text{NI}}$  for the pure host.

**Table S2.**  $T_{\text{NI}}$  for solution of **1[6]c** in ClEster.



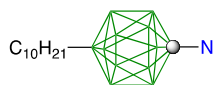
$T_{\text{NI}}/\text{°C}$	Mole fraction, $x$			
	0.00 (host)	0.01697	0.03883	-
Onset		39.02	38.32	-
Peak	46.36	40.50	39.59	-

**Table S2.**  $T_{NI}$  for solution of **1[6]d** in ClEster.



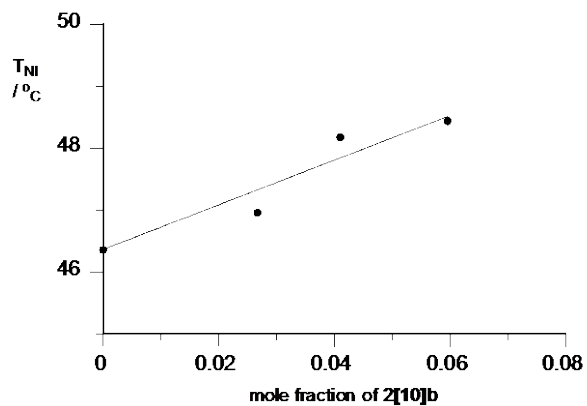
$T_{NI}/^{\circ}\text{C}$	Mole fraction, $x$			
	0.00 (host)	0.0078	0.0178	–
Onset		40.04	40.13	–
Peak	46.36	41.99	42.22	–

**Table S3.**  $T_{NI}$  for solution of **2[10]b** in ClEster.



$T_{NI}/^{\circ}\text{C}$	Mole fraction, $x$			
	0.00 (host)	0.02676	0.04102	0.05961
Onset		46.38	47.67	47.60
Peak	46.36	46.96	48.18	48.44

$[T_{NI}] = 82 \pm 4 \text{ }^{\circ}\text{C}$ ,  $r^2 = 0.91$



**Fig. S4.** Nematic-isotropic transition temperature ( $T_{NI}$ ) as a function of mole fraction of **2[10]b** in **ClEster**.

Dielectric measurements Dielectric parameters for compounds **1[6]** and **2[10]** in low concentration solutions in **ClEster** host were measured in two different cells: 4  $\mu\text{m}$  and 10  $\mu\text{m}$  supplied by LC Vision, Inc.

**Table S4.** Dielectric parameters for **1[6]c** in **ClEster** at 25 °C.



Parameter	Mole fraction, $x$			
	0.00 (host)	0.0170 (4 $\mu\text{m}$ )	0.0374 (10 $\mu\text{m}$ )	–
$\epsilon_{\parallel}$	2.86±0.01	4.39±0.02	4.58±0.01	–
$\epsilon_{\perp}$	3.42±0.01	3.73±0.02	3.81±0.01	–
$\Delta\epsilon$	-0.56±0.01	0.66±0.01	0.77±0.01	–

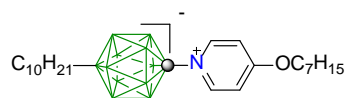
**Table S5.** Dielectric parameters for **1[6]d** in **ClEster** at 25 °C.



Parameter	Mole fraction, $x$			
	0.00 (host)	0.0271 (4 $\mu\text{m}$ )	0.0271 (10 $\mu\text{m}$ )	–
$\epsilon_{\parallel}$	2.86±0.01	3.94±0.01	4.59±0.01	–
$\epsilon_{\perp}$	3.42±0.01	3.48±0.01	3.69±0.01	–

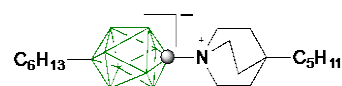
$\Delta\varepsilon$	$-0.56\pm 0.01$	$0.46\pm 0.01$	$0.91\pm 0.01$	–
---------------------	-----------------	----------------	----------------	---

**Table S6.** Dielectric parameters for **2[10]d** in **ClEster** at 25 °C measured in 10  $\mu\text{m}$  cells..



Parameter	Mole fraction, $x$				
	0.00 (host)	0.0267 (4 $\mu\text{m}$ )	0.0296 (10 $\mu\text{m}$ )	0.0371 (10 $\mu\text{m}$ )	0.0649 (10 $\mu\text{m}$ )
$\varepsilon_{\parallel}$	$2.86\pm 0.01$	$4.80\pm 0.02$	$4.54\pm 0.05$	$4.64\pm 0.03$	$5.15\pm 0.03$
$\varepsilon_{\perp}$	$3.42\pm 0.01$	$3.66\pm 0.01$	$3.62\pm 0.04$	$3.73\pm 0.03$	$3.86\pm 0.03$
$\Delta\varepsilon$	$-0.56\pm 0.01$	$1.13\pm 0.02$	$0.91\pm 0.01$	$0.91\pm 0.01$	$1.29\pm 0.01$

**Table S5.** Dielectric parameters for **1-Quin** in **ClEster** at 25 °C measured in 10  $\mu\text{m}$  cells..



Parameter	Mole fraction, $x$			
	0.00 (host)	0.0234 (10 $\mu\text{m}$ )	–	–
$\varepsilon_{\parallel}$	$2.86\pm 0.01$	$4.06\pm 0.01$	–	–
$\varepsilon_{\perp}$	$3.42\pm 0.01$	$3.60\pm 0.01$	–	–
$\Delta\varepsilon$	$-0.56\pm 0.01$	$0.46\pm 0.01$	–	–

## 6. Background for calculations in the nematic phase

The equations derived from the Maier-Meier theory<sup>9</sup> used in this work were adopted from literature<sup>10</sup> and had the following form:

$$\Delta\varepsilon = \frac{NFh}{\varepsilon_0} \left\{ \Delta\alpha - \frac{F\mu_{eff}^2}{2k_B T} (1 - 3\cos^2\beta) \right\} S \quad (1)$$

$$\varepsilon_{\parallel} = 1 + \frac{NFh}{\varepsilon_0} \left\{ \bar{\alpha} + \frac{2}{3} \Delta\alpha S + \frac{F\mu_{eff}^2}{3k_B T} \left[ 1 - (1 - 3\cos^2 \beta) S \right] \right\} \quad (2)$$

$$\varepsilon_{\perp} = 1 + \frac{NFh}{\varepsilon_0} \left\{ \bar{\alpha} + \frac{1}{3} \Delta\alpha S + \frac{F\mu_{eff}^2}{3k_B T} \left[ 1 - (1 - 3\cos^2 \beta) S \right] \right\} \quad (3)$$

All quantities were in SI units as defined in the ESI in previous publications.<sup>11</sup>

Field parameters  $F = 1.2090$  and  $h = 1.28754$  in equations 1-3 were assumed to be of pure host, **ClEster**, and obtained from literature dielectric and optical data<sup>12</sup> according to equation 4 and 5. Permittivity  $\varepsilon_s$  was assumed to be experimental average permittivity ( $\varepsilon = 3.07$ ) for the pure host, **ClEster**.

$$F = \frac{1}{1 - \alpha \cdot f} \quad \text{where } f = \frac{2(\varepsilon_s - 1)}{2\varepsilon_s + 1} \cdot \frac{N}{3\varepsilon_0} \quad (4)$$

$$h = \frac{3\varepsilon_s}{(2\varepsilon_s + 1)} \quad (5)$$

Number density  $N$  used in all calculations was obtained for each additive assuming density of the liquid to be  $1000 \text{ kg} \cdot \text{m}^{-3}$ .

## 7. Results of quantum mechanical calculations

B3LYP/6-31G(d,p) in vacuum

### Dipole moment components and polarizability tensors for selected molecules in vacuum

All molecules are in Gaussian standard orientation with their long molecular axes oriented along the x axis. Dipole moments in Debye and polarizability in au ( $1\text{\AA}^3 = 0.1482 \text{ au}$ )

#### **1[6]b**

Dipole moment (field-independent basis, Debye):

X= -18.1719    Y= 1.9841    Z= 0.1473    Tot= 18.2805

Exact polarizability: 527.733    12.233    271.109    0.853    -2.557    231.411

#### **2[6]b**

Dipole moment (field-independent basis, Debye):

X= -18.1273    Y= -1.8980    Z= -0.2514    Tot= 18.2281

Exact polarizability: 513.575    6.870    285.654    0.575    -2.720    250.112

#### **1-Sulf**

Dipole moment (field-independent basis, Debye):

X= 14.3783    Y= 1.0547    Z= 2.2309    Tot= 14.5885

Exact polarizability: 437.478 2.589 250.632 7.877 5.079 254.336

### 1-Quin

Dipole moment (field-independent basis, Debye):

X= 15.1515 Y= 2.7897 Z= 0.0065 Tot= 15.4062

Exact polarizability: 432.278 5.453 257.396 -0.435 -0.245 249.024

**Table S7.** Calculated molecular parameters for selected compounds in vacuum.<sup>a</sup>

	$\mu_{  }$ /D	$\mu_{\perp}$ /D	$\mu$ /D	$\beta^{\square}$ /°	$\Delta\alpha$ /Å <sup>3</sup>	$\alpha_{\text{avrg}}$ /Å <sup>3</sup>
<b>1[6]b</b>	18.2	2.0	18.3	6.3	41.0	50.9
<b>2[6]b</b>	18.1	1.9	18.2	6.0	36.4	51.8
<b>1-Sulf</b>	14.4	2.5	14.6	9.7	27.4	46.6
<b>1-Quin</b>	15.2	2.8	15.4	10.4	26.5	46.4

<sup>a</sup> Vacuum dipole moments and polarizabilities obtained at the B3LYP/6-31G(d,p) level of theory. Polarizability values calculated from diagonal polarizability tensors were converted from a.u. to Å<sup>3</sup> using the factor 0.1482. <sup>b</sup> Angle between the net dipole vector  $\mu$  and  $\mu_{||}$ .

B3LYP/6-31G(d,p)// B3LYP/6-31G(d,p) with PCM

### Dipole moment components and polarizability tensors for selected molecules in CIEster dielectric medium

All molecules are in Gaussian standard orientation with their long molecular axes oriented along the x axis. Dipole moments in Debye and polarizability in au ( $1\text{Å}^3 = 0.1482\text{ au}$ ).

#### 1[6]b

Dipole moment (field-independent basis, Debye):

X= -20.1791 Y= -2.3542 Z= -0.1742 Tot= 20.3167

Exact polarizability: 551.381 13.075 327.035 1.156 -3.660 276.749

#### 2[6]b

Dipole moment (field-independent basis, Debye):

X= -20.0273 Y= -2.2408 Z= -0.2946 Tot= 20.1544

Exact polarizability: 548.816 8.304 346.624 0.818 -3.905 300.736

#### 1-Sulf

Dipole moment (field-independent basis, Debye):

X= 16.1039 Y= 1.1720 Z= 2.7095 Tot= 16.3722

Exact polarizability: 471.668 3.522 300.573 9.564 6.459 307.605

#### 1-Quin

Dipole moment (field-independent basis, Debye):

X= 16.7704 Y= 3.3147 Z= 0.0004 Tot= 17.0949

Exact polarizability: 464.778 7.201 310.761 -0.616 -0.232 302.458

B3LYP/6-31G(d,p) // B3LYP/6-31G(d,p) TD-DFT with PCM

Calculated electronic transition in MeCN dielectric medium

**1[6]b**

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 4.0164 eV 308.69 nm f=0.2479 <S\*\*2>=0.000  
107 ->108 0.70374

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1101.81732722

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.0546 eV 305.78 nm f=0.0004 <S\*\*2>=0.000  
106 ->108 0.70330

Excited State 3: Singlet-A 4.5880 eV 270.23 nm f=0.0037 <S\*\*2>=0.000  
99 ->108 0.11388  
107 ->109 0.68994

Excited State 4: Singlet-A 4.7669 eV 260.09 nm f=0.0001 <S\*\*2>=0.000  
106 ->109 0.70514

Excited State 5: Singlet-A 4.8536 eV 255.45 nm f=0.0008 <S\*\*2>=0.000  
104 ->108 -0.46181  
105 ->108 0.52379

Excited State 6: Singlet-A 4.9196 eV 252.02 nm f=0.0002 <S\*\*2>=0.000  
103 ->108 0.66756  
104 ->108 -0.19010

Excited State 7: Singlet-A 5.0933 eV 243.43 nm f=0.0003 <S\*\*2>=0.000  
103 ->108 0.17099  
104 ->108 0.49545  
105 ->108 0.46878

Excited State 8: Singlet-A 5.2501 eV 236.16 nm f=0.4446 <S\*\*2>=0.000  
99 ->109 0.12253  
102 ->108 0.67039  
103 ->109 -0.10200

Excited State 9: Singlet-A 5.4041 eV 229.42 nm f=0.0000 <S\*\*2>=0.000  
107 ->110 0.69719

Excited State 10: Singlet-A 5.4988 eV 225.47 nm f=0.0272 <S\*\*2>=0.000  
99 ->108 -0.37311  
102 ->109 0.53344  
103 ->109 0.12975  
107 ->109 0.10797

**2[6]b**

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 4.7745 eV 259.68 nm f=0.1555  
<S\*\*2>=0.000  
112 ->114 -0.17631  
113 ->114 0.66664

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1152.76925703  
Copying the excited state density for this state as the 1-particle RhoCI  
density.

Excited State 2: Singlet-A 4.7894 eV 258.87 nm f=0.0276  
<S\*\*2>=0.000  
111 ->114 0.21861  
112 ->114 0.65087  
113 ->114 0.14868

Excited State 3: Singlet-A 5.0074 eV 247.60 nm f=0.0021  
<S\*\*2>=0.000  
109 ->114 -0.17564  
111 ->114 0.64357  
112 ->114 -0.17811  
113 ->114 -0.13995

Excited State 4: Singlet-A 5.0481 eV 245.61 nm f=0.0129  
<S\*\*2>=0.000  
108 ->114 -0.28229  
109 ->114 -0.19533  
110 ->114 0.60224

Excited State 5: Singlet-A 5.0569 eV 245.18 nm f=0.0023  
<S\*\*2>=0.000  
109 ->114 0.64730  
110 ->114 0.20085  
111 ->114 0.15428

Excited State 6: Singlet-A 5.2195 eV 237.54 nm f=0.0248  
<S\*\*2>=0.000  
103 ->114 0.23430  
105 ->114 0.14107  
107 ->114 0.27800  
108 ->114 0.14694  
108 ->115 -0.16543  
110 ->114 0.14294  
110 ->115 -0.11962  
112 ->115 -0.30862  
113 ->115 0.39669

Excited State 7: Singlet-A 5.3064 eV 233.65 nm f=0.4083  
<S\*\*2>=0.000  
103 ->115 0.11790  
107 ->114 -0.15636  
108 ->114 0.59768  
110 ->114 0.24441  
113 ->115 -0.10697

Excited State 8: Singlet-A 5.3804 eV 230.44 nm f=0.0156  
<S\*\*2>=0.000  
103 ->114 -0.14918  
107 ->114 0.61347  
112 ->115 0.15295  
113 ->115 -0.22645



Excited State	9:	Singlet-A	5.3975 eV	229.71 nm	f=0.0005
<S**2>=0.000					
106	->114	0.69200			
Excited State	10:	Singlet-A	5.4768 eV	226.38 nm	f=0.0002
<S**2>=0.000					
111	->115	0.21836			
112	->115	0.53351			
113	->115	0.39869			

## 8. Archive for DFT calculations

### 1[6]b

```
1\1\GINC-OCTOPUS\FOpt\RB3LYP\6-31G(d,p)\C19H40B9N1O1\PIOTR\23-Apr-2013
\0\#P B3LYP/6-31G(d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle) fche
ck\10-hexyl-CB9-1-(4-heptyloxyppyridine), C1\0,1\B,0.3322175806,-0.04
2049143,-0.0485731575\B,0.0914582288,-0.0367224471,1.7836361309\B,1.91
84386502,0.1099017716,2.0228365983\B,2.1569204045,0.1058604239,0.19069
38517\B,1.037348004,1.1400148623,0.9747077713\C,0.9238356877,2.7286086
824,0.9721490869\C,-0.1601365643,3.3123078119,0.0483921272\C,-0.246959
7844,4.8435067813,0.0894709901\H,-0.3801780768,0.2950045856,-0.9405523
138\H,-0.8255983608,0.303775118,2.4626527299\H,2.5646302096,0.58232806
54,2.9047123698\H,3.0114824639,0.5713285867,-0.4953694779\H,1.89552399
04,3.1613780567,0.6925448709\H,0.7365379287,3.0781499077,1.9979077605\
H,0.0263607453,2.9897891584,-0.9850425096\H,-1.1373864219,2.8885991146
,0.3186766491\H,0.7294616249,5.26923246,-0.1849917639\C,-1.3285222156,
5.4264980481,-0.8282795343\H,-0.4356033173,5.1683183117,1.1233323956\C
,-1.4152907615,6.9572005822,-0.7882275155\C,-2.501764209,7.5288189055,
-1.7043580247\H,-2.3249130101,7.2506798116,-2.7498142468\H,-3.49227752
81,7.1495229992,-1.4275837604\H,-2.5388194673,8.6223558489,-1.65345374
69\H,-1.600657665,7.2816664991,0.2450164525\H,-0.4411135903,7.38198523
37,-1.0669587638\H,-1.1411502984,5.1023292407,-1.8623398242\H,-2.30525
11685,5.0023801101,-0.5532945055\C,0.8359156547,-5.9325764484,0.130364
4804\C,2.3504352858,-5.790789145,2.0053550367\B,1.4121390849,-1.453610
7769,-0.2982939393\B,-0.0579630806,-1.5539964718,0.8357340211\B,1.0720
202947,-1.4451057781,2.3112862473\B,2.5417341961,-1.3439582348,1.17673
78445\C,0.7446683735,-4.5628430768,0.1337303815\C,2.2162909683,-4.4181
660234,1.9566163182\N,1.4288400719,-3.8109307466,1.038536916\C,1.31450
96108,-2.3698077989,1.0185541592\C,1.6514978871,-6.5836281224,1.077330
026\O,1.6933734817,-7.9149088938,1.0138586058\C,2.5178296928,-8.654439
7409,1.9446815749\C,2.3677495564,-10.1313338784,1.6209201679\C,3.22288
64772,-11.0135568661,2.5405056259\C,3.0811888056,-12.5093966588,2.2313
265433\C,3.9406653654,-13.4010426364,3.1352438473\C,3.7998481447,-14.8
971424843,2.8284345642\C,4.6647218701,-15.7816255388,3.7311291501\H,5.
7275492966,-15.5366728628,3.6252283683\H,4.3997543609,-15.6509810073,4
.7864014018\H,4.5424908276,-16.841523541,3.4870465938\H,2.7458174009,-
15.1890429363,2.9296137391\H,4.0643256655,-15.0766826709,1.7775733426\
H,4.9959202863,-13.1090228556,3.0367347956\H,3.6731754647,-13.21998094
71,4.1860975654\H,2.0260449543,-12.800351995,2.3285182054\H,3.35049842
94,-12.6884119289,1.1810898453\H,4.278853743,-10.7232778422,2.44948692
08\H,2.9446301532,-10.8320783309,3.588049791\H,1.3100871416,-10.405996
6322,1.7096105218\H,2.6511493573,-10.2916860926,0.5740073642\H,3.55946
40113,-8.3271884371,1.8357968617\H,2.1862982951,-8.4350056542,2.967319
7439\H,0.2850951979,-6.5161243476,-0.5967667195\H,2.9933320538,-6.2205
839099,2.7610165199\H,1.5933822167,-1.9996173406,-1.3396396212\H,-1.06
```

16853779,-2.1799392903,0.7070231755\H,0.9760884995,-1.9878916159,3.365  
8461893\H,3.63068743,-1.8025246635,1.3187502704\H,0.1357251741,-4.0089  
346484,-0.5672215709\H,2.7287890807,-3.7565849332,2.6416253981\\Versio  
n=EM64L-G09RevC.01\State=1-A\HF=-1101.9397579\RMSD=6.035e-09\RMSF=3.43  
1e-06\Dipole=1.0573847,-7.0842532,0.6494791\Quadrupole=0.4134545,-2.25  
87608,1.8453063,-2.8360622,3.6090979,-2.6504184\PG=C01 [X(C19H40B9N1O1  
)]\@

## 2[6]b

1\1\GINC-OCTOPUS\FOpt\RB3LYP\6-31G(d,p)\C19H42B11N1O1\PIOTR\14-Aug-201  
3\0\#P B3LYP/6-31G(d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle) fch  
eck #P freq(noraman)\12-hexyl-CB11-1-(4-heptyloxypyridine), C1\0,1\B  
,0.007007,-0.123844,-0.068871\B,-0.055191,-0.052751,1.719652\B,1.72004  
3,-0.14444,-0.560572\B,1.617457,-0.025344,2.330096\B,2.717953,-0.08253  
9,0.921119\B,2.396014,-1.537317,1.867083\B,2.46073,-1.612963,0.078121\  
B,0.679241,-1.52848,2.364604\B,-0.312263,-1.57858,0.8761\B,0.78256,-1.  
646361,-0.537502\B,1.201757,0.875152,0.828718\C,1.205431,-2.382961,0.9  
61316\N,1.24442,-3.864844,1.009358\C,0.102863,-4.596851,0.893944\C,0.1  
21371,-5.968955,0.922764\C,1.343389,-6.652839,1.071949\O,1.288699,-7.9  
82684,1.089464\C,2.507146,-8.752138,1.234349\C,2.13198,-10.223825,1.20  
0006\C,3.360686,-11.132624,1.342153\C,3.007669,-12.624874,1.302175\C,4  
.229362,-13.540776,1.442694\C,2.514832,-5.883724,1.187528\C,2.4287,-4.  
507852,1.149957\C,1.245424,2.480476,0.750342\C,-0.087439,3.214837,0.97  
3805\C,0.02706,4.739989,0.851389\C,-1.299758,5.48081,1.057001\C,-1.180  
197,7.005314,0.939496\C,-2.511428,7.737185,1.135557\C,3.881943,-15.033  
907,1.398509\C,5.107316,-15.94181,1.538584\H,-2.936726,7.527735,2.1239  
21\H,-2.392027,8.822512,1.048699\H,-3.249401,7.423323,0.388215\H,-0.45  
1207,7.368334,1.677007\H,-0.764678,7.26021,-0.045163\H,-2.035362,5.118  
88,0.323921\H,-1.710187,5.225904,2.04494\H,0.764233,5.10702,1.580632\H  
,0.433295,4.993935,-0.138743\H,-0.833242,2.851228,0.253648\H,-0.485542  
,2.963484,1.96611\H,1.977386,2.853677,1.480983\H,1.644934,2.773709,-0.  
231217\H,-0.851339,0.333694,-0.751807\H,-0.960891,0.451866,2.299307\H,  
2.093589,0.312437,-1.592291\H,1.920817,0.513383,3.345258\H,3.797947,0.  
413754,0.940624\H,3.166948,-2.174516,2.509204\H,3.268208,-2.311846,-0.  
444382\H,0.346611,-2.179728,3.300155\H,-1.3217,-2.20314,0.871271\H,0.5  
15694,-2.373535,-1.438112\H,-0.807789,-4.027328,0.780569\H,-0.80167,-6  
.527367,0.828888\H,3.188721,-8.496176,0.413767\H,2.984871,-8.483993,2.  
184788\H,1.417466,-10.425092,2.006739\H,1.614342,-10.433069,0.256471\H  
,4.077721,-10.908828,0.540023\H,3.876767,-10.907375,2.285853\H,2.28968  
2,-12.848799,2.103257\H,2.490805,-12.848999,0.358714\H,4.948661,-13.31  
2624,0.64327\H,4.745177,-13.316595,2.387301\H,5.623799,-15.767482,2.48  
9217\H,4.826932,-16.999139,1.502222\H,5.828323,-15.76132,0.733388\H,3.  
163245,-15.26169,2.197241\H,3.366724,-15.257179,0.454508\H,3.491062,-6  
.333636,1.303933\H,3.300973,-3.877693,1.232554\\Version=EM64L-G09RevC.  
01\State=1-A\HF=-1152.9205199\RMSD=9.644e-09\RMSF=3.905e-06\Dipole=0.8  
840949,-7.1115604,0.2722084\Quadrupole=1.9059018,3.2467112,-5.152613,-  
4.2062429,1.1253436,-0.061072\PG=C01 [X(C19H42B11N1O1)]\@

## 2[10]b

1\1\GINC-OCTOPUS\FOpt\RB3LYP\6-31G(d,p)\C23H50B11N1O1\PIOTR\16-Aug-201  
3\0\#P B3LYP/6-31G(d,p) FOpt SCF=Direct Geom=(NoDistance,NoAngle) fch  
eck #P freq(noraman)\12-decyl-CB11-1-(4-heptyloxypyridine), C1\0,1\B  
,0.5284988069,1.6474733479,1.8026657927\B,-0.3960891174,0.1335745417,2  
.0192934849\B,2.1624145187,1.2214182388,1.2242910991\B,0.6629926242,-1  
.2293935584,1.5782841078\B,2.2456554119,-0.5583073661,1.0810521613\B,1  
.0702220367,-1.0729251173,-0.1313480242\B,1.9995385508,0.4437502403,-0

.3516065241\B,-0.568361816,-0.6489618102,0.4403355005\B,-0.6416770597,  
1.1315100368,0.5883813001\B,0.9371093165,1.8122133632,0.0904349635\B,1  
.3493090187,0.1858267712,2.4500263699\C,0.3064042695,0.3810335968,-0.6  
333844146\N,-0.1289706589,0.4727305336,-2.0482613622\C,-1.1854730109,1  
.2432583336,-2.3976086263\C,-1.5996513924,1.3706308776,-3.7068513223\C  
, -0.9045971532,0.6866726461,-4.7197492534\O,-1.195686052,0.7292327844,  
-6.0179991324\C,-2.3058040635,1.5371393372,-6.4788572236\C,-2.38091708  
58,1.4057099091,-7.9904145367\C,-3.536638391,2.2268685139,-8.578568111  
3\C,-3.631085692,2.1189701956,-10.105851753\C,-4.7870615604,2.93265044  
23,-10.6997058925\C,0.1936195199,-0.109272616,-4.3402882374\C,0.555188  
645,-0.1947810911,-3.0191002046\C,1.8346318028,0.1206060896,3.98135590  
33\C,2.9859861066,-0.8516180272,4.2895021157\C,3.406773116,-0.85713037  
9,5.7649483038\C,4.5512699372,-1.8292976192,6.077337032\C,4.9919469354  
, -1.8124182682,7.5462130537\C,6.131997951,-2.7893899777,7.8594608407\C  
, -4.8836859788,2.8327861104,-12.2271141685\C,-6.0427027511,3.645556871  
7,-12.8113389971\C,6.5828749213,-2.7593668222,9.3249661584\C,7.7189335  
816,-3.7398415434,9.640579332\C,8.1722085894,-3.7057547976,11.10526664  
51\C,9.3048346358,-4.6898363169,11.4128941451\H,6.9913719716,-2.563683  
7348,7.2116894996\H,5.8174940684,-3.8097944582,7.5973050339\H,5.303075  
6024,-0.7936946535,7.8189952651\H,4.1291960817,-2.0449822455,8.1871020  
16\H,4.2464617813,-2.8490777348,5.8013473131\H,5.4140968439,-1.5905659  
368,5.4387559804\H,3.7048976576,0.1598830469,6.0591522827\H,2.53716679  
47,-1.1073172081,6.3902495674\H,2.6976435695,-1.8697661182,3.993130673  
\H,3.8575575347,-0.5983167347,3.6708373493\H,2.133294022,1.1286515368,  
4.3028551992\H,0.976038738,-0.1404759812,4.6166163022\H,0.3166252005,2  
.6155260556,2.4591005491\H,-1.2603357724,0.0343204665,2.8292432549\H,3  
.1184333914,1.8847577197,1.4674181304\H,0.5572680177,-2.3091987104,2.0  
63811798\H,3.2604033302,-1.162057754,1.2086518688\H,1.1826478949,-1.95  
08454631,-0.924191332\H,2.7055569217,0.5591559804,-1.300772795\H,-1.50  
16444739,-1.2305211756,-0.0077210257\H,-1.646116647,1.6979669149,0.304  
6854117\H,0.9552626416,2.7913592295,-0.5824205772\H,-1.681968654,1.750  
3684545,-1.5831460528\H,-2.4522521626,2.0017059031,-3.9165603179\H,-3.  
2265859093,1.1797084004,-6.0015087371\H,-2.1354543714,2.5783854732,-6.  
178699583\H,-1.4271041725,1.7326323862,-8.4208781979\H,-2.5000156283,0  
.3466482461,-8.2474571016\H,-4.4853778359,1.8968401371,-8.1329276311\H  
, -3.4175247995,3.2825758929,-8.2975174919\H,-2.6834745912,2.452067447,  
-10.5513764742\H,-3.745368653,1.063092702,-10.3877488671\H,-5.73442328  
36,2.5972268037,-10.2541130582\H,-4.6744307163,3.9878652977,-10.412614  
5496\H,-5.9428384148,4.7095203057,-12.5687760578\H,-6.0836488845,3.556  
0686514,-13.9013778248\H,-7.0055079047,3.305575487,-12.4135468017\H,-3  
.9377509373,3.1705700198,-12.6715789131\H,-4.9937273687,1.778283931,-1  
2.5140650667\H,0.7540533552,-0.6492269895,-5.093272917\H,1.3905744364,  
-0.7894492391,-2.6829334633\H,5.7229362102,-2.9804524278,9.9735822181\H  
,6.901644671,-1.73974739,9.5851166339\H,7.3999281824,-4.7604822514,9.  
3844368636\H,8.5789749262,-3.5215380765,8.9909759321\H,8.4931820774,-2  
.6865801645,11.3605431024\H,7.3127749514,-3.922706592,11.7543535039\H,  
9.6039456517,-4.6426961715,12.4652528482\H,9.0019120975,-5.7213001115,  
11.1993319859\H,10.191916045,-4.4758766379,10.8056117279\Version=EM64  
L-G09RevC.01\State=1-A\HF=-1310.1865699\RMSD=4.215e-09\RMSF=6.042e-06\  
Dipole=-2.6847529,0.9673891,-6.6306071\Quadrupole=-4.989633,-16.22047,  
21.210103,-8.0898656,23.0010004,-10.966913\PG=C01 [X(C23H50B11N1O1)]\\  
@

## 9. References

- 1 J. Pecyna, B. Ringstrand, S. Pakhomov, A. G. Douglass, P. Kaszynski *in preparation*.

- 2 B. Ringstrand, P. Kaszynski, A. Januszko, V. G. Young, Jr. *J. Mater. Chem.* 2009, **19**, 9204.
- 3 S. Wang, A. Zhang *Org. Prep. Proc. Int.* 2008, **40**, 293.
- 4 C. D. Beard, K. Baum, V. Grakauskas *J. Org. Chem.* 1973, **38**, 3673.
- 5 C. Aubert, J.-P. Bégué *Synthesis* 1985, 759.
- 6 H. Takeuchi, H. Ōya, T. Yanase, K. Itou, T. Adachi, H. Sugiura, N. Hayashi *J. Chem. Soc. Perkin Trans. 2* 1994, 827.
- 7 B. Ringstrand, A. Jankowiak, L. E. Johnson, P. Kaszynski, D. Pocięcha, E. Górecka *J. Mater. Chem.* 2012, **22**, 4874.
- 8 M. A. Fox, J. A. H. MacBride, R. J. Peace, K. Wade *J. Chem. Soc., Dalton Trans.* 1998, 401.
- 9 W. Maier, G. Meier *Z. Naturforsch.* 1961, **16A**, 262.
- 10 S. Urban, in *Physical Properties of Liquid Crystals: Nematics*, (Eds.: D. A. Dunmur, A. Fukuda, and G. R. Luckhurst) IEE, London, **2001**, pp 267-276.
- 11 B. Ringstrand, P. Kaszynski *J. Mater. Chem.* 2011, **21**, 90.
- 12 R. Dabrowski, J. Jadzyn, S. Czerkas, J. Dziaduszek, A. Walczak *Mol. Cryst. Liq. Cryst.* 1999, **332**, 61.