### **Supplemental Data**

## 3-Cyano Thiophene based $\pi$ -Conjugated Mesogens: XRD and <sup>13</sup>C NMR Investigations

G. Pratap<sup>†⊥</sup>, Deepshika Malkar<sup>§</sup>, E. Varathan<sup>‡⊥</sup>, Nitin P. Lobo<sup>‡⊥</sup>, Arun Roy<sup>§\*</sup> and T. Narasimhaswamy<sup>†⊥\*</sup>

 <sup>†</sup>Polymer Science and Technology, <sup>‡</sup>Inorganic and Physical Chemistry, CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India
<sup>§</sup>Soft Condensed Matter, Raman Research Institute, Bangalore, 560080, India
<sup>⊥</sup>Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bhavan, New Delhi, 110001, India

## **Experimental Section**

Synthesis of 4- bromo-4'- (octyloxy) biphenyl (1) The reaction is carried out in oven-dried glassware. In a 250 ml round bottom flask 10g 4'-bromobiphenyl-4-ol and 3.86g (moles)  $K_2CO_3$  were taken and dissolved in 100 ml DMF. The mixture was stirred and heated to 90 °C followed by dropwise addition of 25 ml of 1-bromooctane. The temperature of the mixture was maintained at 90° C for 5h. Then the reaction mixture was poured into 1L distilled water and transferred to a separating funnel and extracted with chloroform. The chloroform layer was washed using 5% NaOH solution and distilled water, and the organic layer was dried over anhydrous sodium sulfate. Upon evaporation white solid is obtained and is further purified by recrystallization from acetonitrile. Yield:80%.

synthesis of 2,5-bis(4'-(octyloxy)-[1,1'-biphenyl]-4-yl)thiophene-3-carbonitrile: (PCN8) To a degassed mixture of 4- bromo-4'- (octyloxy) biphenyl (4.14 g, 18 mmol), 3- cyanothiophene(1g, 3.08 mmol), K<sub>2</sub>CO<sub>3</sub> (6 mmol, 0.81g), Pd(OAc)<sub>2</sub> (6 mol %, 0.178 mmol, 40 mg), PCy<sub>3</sub>.HBF<sub>4</sub> (12 mol %, 0.358 mmol, 132 mg), pivalic acid (30 mol %, 0.90 mmol, 92 mg), 8 ml of dry N,N-dimethyl acetamide was added via syringe. The reaction mixture was then vigorously stirred at 110°C for 12 h under argon. The solution was then cooled to room temperature and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times). The organics layer was dried over MgSO4 and evaporated under reduced pressure and then eluted with hexane /ethyl acetate (9: 1). The solid obtained was recrystallization from 1-propanol. [1,2] Yield: 76%, m.p.:91.1 °C.

**FT-IR** (**cm**<sup>-1</sup>):2926, 2858, 1606, 1494, 1468, 1392, 1286, 1249, 1177, 1122, 1029, 997, 819, 721, 628; <sup>1</sup>H NMR (400 MHz, CDCl3):δ 7.85 (d, J = 8.2 Hz, 2H), 7.66-7.53 (m, 10H), 7.45(s, 1H), 7.00-6.97(dd, 4H), 4.02-3.99 (m, 4H), 1.85 – 1.79 (m, 4H), 1.56 – 1.30 (m, 24H),

0.91 – 0.88 (t, J = 6.7 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl3):δ159.31, 159.19, 152.06, 143.67, 142.22, 141.32, 132.28, 132.16, 130.58, 129.61, 128.08, 127.96, 127.82, 127.28, 126.20, 125.37, 116.02, 114.98, 106.33, 68.19, 31.84, 29.38, 29.30, 29.25, 26.08, 22.67, 14.09.

Synthesis of 2,5-Bis(4-butoxyphenyl)thiophene-3-carbonitrile(PMB10):To a degassed mixture of 4- bromo-4'- (decyloxy)phenyl (4.14 g, 18 mmol ), 3-cyanothiophene(1g, 3.08 mmol), K<sub>2</sub>CO<sub>3</sub> (2 equiv, 6 mmol, 0.81g), Pd(OAc)<sub>2</sub> (6 mol%, 0.178 mmol, 40 mg), PCy<sub>3</sub>.HBF<sub>4</sub> (12 mol%, 0.358 mmol, 132 mg), pivalic acid (30 mol%, 0.90 mmol, 92 mg), 8 ml of dry N,N-dimethylacetamide was added via syringe. The reaction mixture was then vigorously stirred at 110°C for 12 h under argon. The solution was then cooled to room temperature and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times). The organic layer was dried over MgSO4 and evaporated under reduced pressure followed by eluting with hexane /ethyl acetate (9: 1). The recrystallization from 1-propanol afforded as light blue color solid. Yield: 76%, m.p:86.8°C; <sup>1</sup>H NMR (400 MHz, CDCl3):  $\delta$  7.72 – 7.69 (d, J = 8.7 Hz, 1H), 7.47-7.45 (d, J = 8.5 Hz, 1H), 7.23(s, 1H), 6.97-6.90(dd, 4H), 4.00-3.95 (m, 4H), 1.83 – 1.77 (m, 4H), 1.47 – 1.32 (m, 30H), 0.90 – 0.87 (t, J = 6.7 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl3): $\delta$  160.34, 159.65, 151.78, 143.07, 128.78, 127.09, 124.99, 124.07, 123.91, 116.28, 115.12, 105.27, 68.23, 31.92, 29.60, 29.41, 29.34, 29.23, 29.20, 26.04, 22.70, 14.12.

**Dioctyl-4,4'-(3-cyanothiophene-2,5-diyl)dibenzoate(PBO2):** The octyl 4-bromobenzoate was prepared by earlier reported procedure.[3,4] <sup>1</sup>H NMR (400 MHz, CDCl3):  $\delta$  8.16 – 8.10 (d, J = 8.4 Hz, 1H), 7.90-7.87 (d, J = 8.3 Hz, 1H), 7.68-7.65(d, 2H), 7.57(s, 1H), 4.37-4.32(m, 4H), 1.80 – 1.77 (m, 4H), 1.47 – 1.30 (m, 20H), 0.91 – 0.88 (t, J = 6.7 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl3): $\delta$  165.84, 165.75, 151.72, 143.85, 135.97, 135.00, 131.66, 130.84, 130.56, 130.51, 127.41, 127.11, 125.67, 115.21, 107.91, 65.54, 31.79, 29.25, 29.19, 28.72, 26.04, 22.64, 14.08. The synthetic protocol (direct arylation) followed for PMB10 is also used for the preparation of PBO2. m.p:77.1°C <sup>1</sup>H NMR (500 MHz, )  $\delta$  7.52 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 1.79 (dt, *J* = 14.4, 6.6 Hz, 2H), 1.50 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl3): $\delta$  159.05, 139.85, 132.28, 131.77, 128.27, 128.22, 127.92, 120.72, 114.96, 68.18, 31.60, 29.26, 22.61, 14.02.

	PBO2				PMB10			
C. N.	Solution (ppm)	78 °C			C = 1+	85°C		
		CS	AIS	DOF	Solution (nnm)	CS	AIS	DOF
		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
1	165.8	206.1	40.3	1.19	160.3	213.5	53.2	1.02
2	135.9	196.9	61.0	1.25	115.2	140.0	24.8	2.04
3	130.5	165.5	35.0	1.85	128.8	149.5	20.7	2.31
4	127.4	153.1	25.7	2.04	125.0	185.6	60.6	0.87
5	131.6	189.0	57.4	1.06	151.8	176.4	24.6	0.89
6	151.7	212.6	60.9	1.18	105.3	132.8	27.5	1.01
7	107.9	139.2	31.3	1.10	116.3	111.6	-4.7	0.85
8	115.2	103.1	-12.1	1.30	124.1	154.8	30.7	2.49
9	127.1	162.5	35.4	2.59	143.1	207.4	64.3	1.04
10	143.8	214.6	70.8	1.23	123.9	185.6	61.7	0.87
11	130.8	188.4	57.6	0.85	127.1	152.3	25.2	1.45
12	125.6	156.4	30.8	1.31	115.2	139.3	24.1	1.26
13	130.5	165.5	35.0	1.33	159.7	213.5	53.9	1.02
14	135.0	195.0	60.0	0.86				
15	165.7	206.1	40.4	1.19				

**Table S1**:<sup>13</sup>C NMR Data for the Core Unit of PBO2 and PMB10 Mesogens in Solution and smectic A Phase<sup>a</sup>

<sup>a</sup>CS: chemical shift; AIS: alignment induced shift; DOF: dipolar oscillation frequencies

C	0.1.4	100 °C			195℃		
C. N.	Solution (ppm)	CS	AIS	DC <sup>b</sup>	CS	AIS	DC <sup>b</sup>
		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
1	159.3	223.6	64.3	1.13	215.9	56.6	1.05
2	114.9	142.1	27.2	2.18	138.6	23.7	1.94
				1.70			1.53
3	128.0	154.1	26.1	2.47	149.7	21.7	2.15
				1.53			1.38
4	129.6	201.6	72.0	1.10	193.5	63.9	1.00
5	141.3	216.6	75.3	0.92	209.2	67.9	0.83
6	127.2	152.0	24.8	2.34	148.1	20.9	2.02
0				1.50			1.38
7	127.8	1541	26.2	2.47	140.7	21.9	2.15
/		154.1	26.3	1.53	149.7		1.38
8	130.5	194.3	63.8	0.90	188.8	58.3	0.79
9	152.0	194.9	42.9	1.07	186.6	34.6	0.81
10	106.3	137.4	31.1	1.51	134.2	27.9	1.34
11	116.0	117.6	1.6	1.20	114.3	-1.7	1.09
12	2 125.3	163.0	37.7	2.79	157.3	32.0	2.47
12				0.47			0.39
13	143.6	213.4	69.8	1.10	205.5	61.9	0.98
14	132.1	196.3	64.2	0.86	188.8	56.7	0.79
15	126.2	2 152.0	27.5	1.63	148.4	22.2	1.55
15				1.50			1.38
16	127.2	1527	26.5	1.53	149.7	22.5	1.32
10		153.7		1.53			1.32
17	142.2	207.5	65.3	0.87	200.0	57.8	0.77
18	132.2	205.2	73.0	1.08	196.9	64.7	0.97
19	127.9	154.8	26.9	1.52	150.7	22.8	1.34
				1.52			1.34
20	114.9	1.9 140.9	26.0	1.50	137.0	22.1	1.36
				1.50			1.36
21	159.1	223.6	64.5	1.13	215.9	56.8	1.03

**Table S2**:<sup>13</sup>C NMR Data for the Core Unit of PCN8 Mesogen in Solution and smectic C phase<sup>a</sup>

<sup>a</sup>CS: chemical shift; AIS: alignment induced shift; DC: dipolar couplings.

<sup>b</sup>The first entry values are coupling from directly bonded C–H pairs; the second entry values are from indirectly bonded C–H pairs.

Model systems	States	Absorption (nm)	Energy (eV)	Oscillator strength (f)	Dominant contribution <sup><i>a</i></sup> (%)	Exp. (nm)
Т	$egin{array}{c} \mathbf{S}_1 \ \mathbf{S}_2 \ \mathbf{S}_9 \end{array}$	390 299 262	3.18 4.44 4.72	2.0450 0.0529 0.4573	$H \rightarrow L (99\%)$ $H \rightarrow L+1(93\%)$ $H-1 \rightarrow L+1(97\%)$	310
PCN14	$egin{array}{c} \mathbf{S}_1 \ \mathbf{S}_3 \ \mathbf{S}_8 \end{array}$	406 308 280	3.05 4.01 4.42	1.5642 0.3033 0.3318	H→L (99%) H→L +1(95%) H-1→L+1 (84%)	375
HT8	$\begin{array}{c} S_1\\S_9\\S_{10}\end{array}$	365 265 262	3.39 4.67 4.72	1.9110 0.4743 0.1055	H→L (99%) H-1→L+1(84%) H-3→L+1(81%)	344

**Table S3:** Summary of the Excited State Electronic Transitions obtained from TD-DFT calculations at the B3LYP/6-31G\* level.

<sup>a</sup>H denotes HOMO and L denotes LUMO



**Figure S1**: Pulse sequence for SAMPI-4 experiment, belongs to the family of CP based SLF techniques provides the 2D correlation spectrum between <sup>13</sup>C chemical shift (in F2 dimension) with the associated <sup>13</sup>C-<sup>1</sup>H dipolar frequency (F1 dimension). Experiment starts with a cross-polarization (CP) block with a polarization inversion for a contact time  $\tau$ , then the evolution of high resolution heteronuclear <sup>13</sup>C-<sup>1</sup>H dipolar couplings monitored under the absence of homonuclear<sup>1</sup>H-<sup>1</sup>H dipolar couplings (suppressed by "magic sandwich" pulses) during the t<sub>1</sub> period and finally <sup>13</sup>C signals are acquired by employing SPINAL-64 heteronuclear decoupling pulse scheme during t<sub>2</sub> period. Here the darker boxes represent 90° pulses.



**Figure S2**: Pulse sequence for 2D Proton Encoded Local Field (PELF) experiment. BLEW-48[5] homonuclear decoupling sequence employed during  $t_1$  period to suppress the homonuclear <sup>1</sup>H-<sup>1</sup>H dipolar couplings and SPINAL-64 scheme is applied during  $t_2$  period heteronuclear decoupling sequence to acquire <sup>13</sup>C signals. CP step with a contact time,  $\tau$  was used to transfer proton magnetization to carbon. Here, thin and thick rectangular darker boxes represent 90° and 180° pulses, respectively.



Figure S3: <sup>1</sup>H NMR Spectrum of Mesogen PBO2



Figure S4: <sup>13</sup>C NMR Spectrum of Mesogen PBO2



Figure S5: <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of Mesogen PMB10



Figure S6: <sup>1</sup>H-<sup>13</sup>C HSQC NMR Spectrum of Mesogen PMB10



Figure S7: <sup>1</sup>H-<sup>13</sup>C HMBC NMR Spectrum of Mesogen PMB10



Figure S8: <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of Mesogen PBO2



Figure S9: <sup>1</sup>H-<sup>13</sup>C HSQC NMR Spectrum of Mesogen PBO2



Figure S10: <sup>1</sup>H-<sup>13</sup>C HMBC NMR Spectrum of Mesogen PBO2



Figure S11: <sup>1</sup>H-<sup>1</sup>H COSY NMR Spectrum of Mesogen PCN8



Figure S12: <sup>1</sup>H-<sup>13</sup>C HSQC NMR Spectrum of Mesogen PCN8



Figure S13: <sup>1</sup>H-<sup>13</sup>C HMBC NMR Spectrum of Mesogen PCN8



Figure S14: DSC Heating and Cooling Scans of (A) PCN8, (B) PBO2 and (C) PMB10



Figure S15: Powder X-ray diffraction profiles of PCN8 at different temperatures



**Figure S16:** (A) XRD intensity profile in the de Vries SmA phase at 74 <sup>o</sup>C and (B) variation of layer spacing with temperature for the compound PBO2. Solid line is guide to the eye.



Figure S17: Powder X-ray diffraction profile of PMB10 in the SmA phase at 85 °C.



Figure S18: Optimized geometry at B3LYP/6-31G\* level of theory



**Figure S19:** 1D solution <sup>1</sup>H decoupled <sup>13</sup>C spectra of (A) PMB10, (B) PBO2 and (C) PCN8 mesogens.



**Figure S20:** 2D SAMPI-4 spectra of mesogens (A) PMB10 in smectic A at 85 °C and (B) PBO2 in smectic A at 78 °C.



**Figure S21:** Schematic representation for bent-angle between local para axes of phenyl rings with respect to long axis passing through thiophene ring (marked Z) for mesogen PMB10.



**Figure S22:** (A) Expanded region of <sup>1</sup>H NMR of PBO2, (B) selective NOE irradiation of 7.6 ppm singlet and (C) selective irradiation of doublet at 7.7 ppm



Figure S23: Contour plots of FMOs at B3LYP/6-31G\* level of theory

# **Orientational Order Parameter from <sup>13</sup>C-<sup>1</sup>H dipolar couplings**

Generally, the 2D SAMPI-4 experiment provides  ${}^{13}C{}^{-1}H$  dipolar oscillation frequencies. However, the  ${}^{13}C{}^{-1}H$  dipolar couplings need to be extracted from these experimental  ${}^{13}C{}^{-1}H$  dipolar oscillation frequencies as explained in earlier reports.[6-15] The  ${}^{13}C{}^{-1}H$  dipolar couplings are related to orientational order parameters by using following equation[16,17]

$$D_{CH} = K \left[ S_{zz} \left( 3 \cos^2 \theta_z - 1 \right) / 2 + \left( S_{xx} - S_{yy} \right) \left( \cos^2 \theta_x - \cos^2 \theta_y \right) / 2 + S_{xz} \left( \cos \theta_x \cos \theta_z \right) \right]$$
(1)

where  $K = -h\gamma_H\gamma_C/4\pi^2 r^3_{CH}$ , with *h* is the Planck constant,  $\gamma_H$  and  $\gamma_C$  are the gyromagnetic ratios of <sup>1</sup>H and <sup>13</sup>C nuclei respectively,  $r_{CH}$  is the inter nuclear distance between them,  $\theta_x$ ,  $\theta_y$ and  $\theta_z$  are the angles formed by  $r_{CH}$  with the respective coordinate axes of the molecular fragment (phenyl or thiophene). Due to the phenyl ring  $\pi$  flips, the D<sub>2</sub> symmetry is assumed for the phenyl ring and accordingly, two order parameters, i.e.,  $S_{zz}$  and  $S_{xx}$ – $S_{yy}$ , are sufficient. Here, the C<sub>2</sub> axis of phenyl ring is taken as z-axis while y-axis is the in-plane axis perpendicular to z. During fitting, the standard bond distances  $r_{CH}$ =1.1 Å for the *C*–*H* bond





and  $r_{CC}=1.4$  Å for C-C bond are used. To get the best fit, the C-C-H bond angles are also slightly varied around  $120^{\circ}$ .[18]

For the thiophene ring, on the other hand, owing to the asymmetry because of 2,3,5-tri substitution, three order parameters i.e.,  $S_{zz}$ ,  $S_{xx}$ - $S_{yy}$  and  $S_{xz}$  are essential for an arbitrary choice of the axis system.[10,19] Model of thiophenes belongs to three mesogens with the coordinate system used for obtaining the orientational order parameters from experimental dipolar couplings depicted above. The bond angles and bond distances are taken from the energy minimized structure of thiophene for three mesogens.

Initially, for PMB10/ PBO2/PCN8 mesogens the z-axis is considered along the C4-C5/C5-C6/C8-C9 bond with the expectation that the order along this direction is likely to be the largest. The quality of the fit is improved by varying the z-axis by an angle  $\beta$  around 18°. It indicates that the z-axis is almost collinear to C6-C8, C7-C9 and C10-C12 bond respectively, for PMB10, PBO2 and PCN8 mesogens. Addition of the third order parameter, namely, S<sub>xz</sub>, did not improve the results significantly hence, only two order parameters S<sub>zz</sub> and S<sub>xx</sub>-S<sub>yy</sub> are retained.

### References

- Liégault B, Lapointe D, Caron L, et al. Establishment of Broadly Applicable Reaction Conditions for the Palladium-Catalyzed Direct Arylation of Heteroatom-Containing Aromatic Compounds. J. Org. Chem. 2009;74:1826–1834.
- 2. Okamoto K, Zhang J, Housekeeper JB, et al. C–H Arylation Reaction: Atom Efficient and Greener Syntheses of  $\pi$ -Conjugated Small Molecules and Macromolecules for Organic Electronic Materials. Macromolecules, 2013;46:8059–8078.
- Cai R, Samulski ET, New thermotropic liquid crystals derived from thiophenes. Liq. Cryst. 1991;9:617-634.

- 4. Kurfurst M, Kozmik V, Svoboda J, et al. Liquid crystalline benzothiophene derivatives. Liq. Cryst. 2008;35:21-31.
- Burum DP, Linder N, Ernst RR, High-power multipulse line narrowing in solid-state NMR. J. Magn. Reson. 1981;44:173–188.
- Nagaraja CS, Ramanathan KV, Determination of Order Parameters of Liquid Crystals: Use of Dipolar Oscillations Enhanced by Lee-Goldburg Decoupling. Liq. Cryst. 1999;26:17–21.
- Gan Z, Spin Dynamics of Polarization Inversion Spin Exchange at the Magic Angle in Multiple Spin Systems. J. Magn. Reson. 2000;143:136–143.
- Kalaivani S, Narasimhaswamy T, Das BB, et al. Phase Characterization and Study of Molecular Order of a Three-Ring Mesogen by <sup>13</sup>C NMR in Smectic C and Nematic Phases. J. Phys. Chem. B 2011;115:11554–11565.
- Lobo NP, Prakash M, Narasimhaswamy T, et al. Determination of <sup>13</sup>C Chemical Shift Anisotropy Tensors and Molecular Order of 4-Hexyloxybenzoic Acid. J. Phys. Chem. A. 2012;116: 7508–7515.
- Lobo NP, Das BB, Narasimhaswamy T, et al. Molecular Topology of Three Ring Nematogens from <sup>13</sup>C-<sup>1</sup>H Dipolar Couplings. RSC Adv. 2014;4:33383–33390.
- Santhosh Kumar Reddy Y, Lobo NP, Sampath S, et al. Morphology, Mesophase, and Molecular Order of 3-Hexyl Thiophene-Based π-Conjugated Mesogens. J. Phys. Chem. C. 2016;120:17960-17971.
- Veeraprakash B, Lobo NP, Narasimhaswamy T, <sup>13</sup>C NMR Studies, Molecular Order, and Mesophase Properties of Thiophene Mesogens. J. Phys. Chem. B. 2015; 119:15063-15074.
- Veeraprakash B, Lobo NP, Narasimhaswamy T, et al. 2-Octyl Thiophene Based Three Ring Mesogens: Solid state <sup>13</sup>C NMR and XRD Investigations. Phys. Chem. Chem. Phys. 2015;17:9936-19947.

- 14. Rajasekhar Reddy K, Varathan E, Lobo NP, et al. Influence of Thiophenes on Molecular Order, Mesophase, and Optical Properties of  $\pi$  Conjugated Mesogens. J. Phys. Chem. C 2016;120:22257-22269.
- Rajasekhar Reddy K, Lobo NP, Narasimhaswamy T, Molecular Order and Mesophase Investigation of Thiophene-Based Forked Mesogens. J. Phys. Chem. B. 2016;120:6897-6909.
- Fung BM, <sup>13</sup>C NMR studies of liquid crystals. Prog.Nucl.Magn.Reson. Spectrosc.2002;41:171-186.
- Emsley JW, Lincon JC. NMR Spectroscopy Using Liquid Crystal Solvents. Oxford (OF): Pergamon; 1975.
- Fung BM, Afzal J, Foss TL et al. Nematic Ordering of 4-n-alkyl-cyanobiphenyls Studied by Carbon-13 NMR with Off-Magic-Angle Spinning. J. Chem. Phys. 1986;85:4808–4814.
- Concistée M, De Luca G, Longeri M, et al. The Structure and Conformations of 2-Thiophenecarboxaldehyde Obtained from Partially Averaged Dipolar Couplings. ChemPhysChem. 2005;6:483–1491.