Supporting Information

A Bolaamphiphilic Sexithiophene with Liquid Crystalline Triangular Honeycomb Phase

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1. General

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Tetrahydrofuran (THF) was distilled from sodium prior to use. Commercially available chemicals were used as received. 3-Decylthiophene **2**[1b] and 3-decyl-2-bromothiophene **3**[2] were synthesized as reported previously. Thin-layer chromatography was performed on aluminum plates precoated with 5735 silica gel 60 PF254 (Merck). Column chromatography was performed on Merck silica gel 60 (230-400 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded

on a Bruker-DRX-500 spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer.

2. Syntheses and analytical data

See Scheme 1 in the main text for the general synthesis scheme and compound numbers.

2-Bromo-5-(4-methoxyphenyl)thiophene 6. A mixture of **5** (1.45 g, 6 mmol), 4-methoxybenzene boronic acid (866.4 mg, 5.7 mmol), $Pd(PPh_3)_4$ (15 mg), ethyleneglycol dimethyl ether (5 mL), and K_2CO_3 solution (2 M, 5 mL) was refluxed for 6 h under an argon atmosphere. After staying overnight at RT, the reaction mixture was extracted with $CHCl_3$ (3×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (petroleum ether). Yield: 969 mg, 64%; white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.43 (d, J = 8.8, 2 H, 2 Ar**H**), 6.99-6.98 (d, J = 3.9, 1 H, Ar**H**), 6.94-6.93 (d, J = 3.8, 1 H, Ar**H**), 6.90-6.89 (d, J = 8.8, 2 H, 2 Ar**H**), 3.83 (s, 3 H, OC**H**$_3$).

3-Decyl-5'-(4-methoxyphenyl)-2,2'-bithiophene 7. Compounds **7** were prepared as outlined by Zimmer *et al.*[3] Accordingly, 2-bromo-3-decylthiophene (**3**) (970.6 mg, 3.2 mmol) was dissolved in dry THF (20 mL). Magnesium turnings (960 mg, 40 mmol) were covered by this solution (3 mL). After the reaction had started, the remaining solution was added dropwise, maintaining the temperature below 60 °C. Stirring was continued under reflux for 1 h, and then the mixture was cooled to RT, and added dropwise to a mixture of **6** (861.3 mg, 3.2 mmol) and $Ni(dppp)Cl_2$ (60 mg) in THF (35 mL) at 0°C, maintaining the temperature of the solution below 5 °C. Stirring of the mixture was continued for additional 15 h under reflux, and the reaction mixture was cooled to RT, quenched with crushed ice (50 g), and HCl (50 mL, 2 M) was added until the precipitate was dissolved. Diethyl ether (100 mL) was

added, the organic layer was separated and the aqueous layer was extracted with diethyl ether (3×100 mL). The combined ether solutions were dried over anhydrous Na_2SO_4, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (eluent: petroleum ether). Yield: 937.5 mg, 71%; yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.8, 2 H, 2 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.05-7.04 (d, J = 3.8, 1 H, Ar**H**), 6.94-6.91 (m, 3 H, 3 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.79-2.76 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.68-1.62 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.25 (m, 14 H, 7 C**H**$_2$), 0.89-0.86 (t, J = 6.9, 3 H, C**H**$_3$).

5-Bromo-3-decyl-5'-(4-methoxyphenyl)-2,2'-bithiophene 8. The synthesis of compounds **8** was carried out according to a modified procedure. [S1] At 30 °C under an argon atmosphere, *N*-bromo succine imide (NBS, 400.5 mg, 2.25 mmol) was added slowly to a stirred solution of **7** (928.5 mg, 2.25 mmol) dissolved in dry THF (20 mL). The mixture was stirred overnight at 30 °C and then quenched with water, the organic layer was separated, and the water layer was extracted with chloroform (3×10 mL). The combined chloroform extracts were dried over anhydrous magnesium sulfate, the solvent was removed in *vacuo* and the residue was purified by column chromatography (petroleum ether). Yield: 984.3 mg, 89%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56-7.54 (d, J = 8.4, 2 H, 2 Ar**H**), 7.16-7.15 (d, J = 3.6, 1 H, Ar**H**), 7.02-7.01 (d, J = 3.5, 1 H, Ar**H**), 6.96-6.94 (d, J = 8.4, 2 H, 2 Ar**H**), 6.92 (s, 1 H, Ar**H**), 3.87 (s, 3 H, OC**H**$_3$), 2.76-2.72 (t, J = 7.8, 2 H, ArC**H**$_2$), 1.65-1.58 (m, 2 H, ArCH$_2$C**H**$_2$), 1.37-1.28 (m, 14 H, 7 C**H**$_2$), 0.92-0.89 (t, J = 6.3, 3 H, C**H**$_3$).

3,4'-Didecyl-5''-(4-methoxyphenyl)-2,2':5',2''-terthiophene 9. Compound **9** was synthesized in an analogues way as **7** from **3** (606.6 mg, 2.0 mmol) and **8** (983 mg, 2.0 mmol)**.** Yield: 965.2 mg, 76%; pale yellow solid. ^{1}H NMR ($CDCl_3$, 500MHz): δ = 7.54-7.53 (d, J = 8.2, 2 H, 2 Ar**H**), 7.16-7.15 (m , 2 H, 2 Ar**H**), 7.07-7.06 (m, 1 H, **Ar**H), 6.93-6.91 (m, 4 H, 4 Ar**H**), 3.84 (s, 3 H, OC**H**$_3$), 2.85-2.75 (m, 4 H, 2 ArC**H**$_2$), 1.76-1.64 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.47-1.20 (m, 28 H, 14 C**H**$_2$), 0.92-0.82 (m, 6 H, 2 C**H**$_3$).

4-[3',3''-Dialkyl-(2,2':5',2''-terthiophene)-5-yl]phenol 10. Compound **9** (635 mg, 1 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to -78°C, BBr_3 (0.1 mL, 1.1 mmol) was added and the solution was stirred at RT under TCL control. As soon as the reaction was completed (7-13 h), ice-water (10 mL) was carefully added, the mixture was extracted with $CHCl_3$ (3×15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (eluent: petroleum ether / ethyl acetate V / V = 7 / 1). The obtained product was used directly for the next step.

5''-(4-Allyloxyphenyl)-3,4'-didecyl-2,2':5',2''-terthiophene 11. Allyl bromide (0.13 mL, 1.5 mmol) was added to a mixture of **10** (621 mg, 1 mmol) an K_2CO_3 (414 mg, 3 mmol) in dry CH_3CN (10 mL) under an argon atmosphere. The mixture was refluxed for 2 h and then CH_3CN was evaporated in *vacuo*. Water and ethyl acetate were added to the residue. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×10 mL), the combined extracts were washed with H_2O (3×10 mL), dried over anhydrous Na_2SO_4, and the solvent was removed in *vacuo*. The crude product was purified by chromatography (eluent: petroleum ether). Yield: 542 mg, 82%; pale yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.6, 2 H, 2 Ar**H**), 7.17-7.16 (m , 2 H, 2 Ar**H**), 7.08-7.07 (d, J = 3.7, 1 H, Ar**H**), 6.95-6.93 (m , 4 H, 4 Ar**H**), 6.12-6.04 (m, 1 H, C**H**=), 5.46-5.42 (d, J = 17.3, 1 H, C$\mathbf{H}_2$=), 5.33-5.31 (d, J = 10.5, 1 H, C$\mathbf{H}_2$=), 4.58-4.57 (d, 2 H, ArOC$\mathbf{H}_2$), 2.80-2.77 (t, J = 7.1, 4 H, 2 ArC$\mathbf{H}_2$), 1.68-1.63 (m, 4 H, 2 ArCH$_2$C$\mathbf{H}_2$), 1.36-1.25 (m, 28 H, 14 C$\mathbf{H}_2$), 0.87-0.86 (t, J = 6.1, 6 H, 2 C$\mathbf{H}_3$).

3-{4-[3',3''-Decyl-(2,2':5',2''-terthiophene)-5-yl]phenoxy}propane-1,2-diol 12. Compound **11** (529 mg, 0.8 mmol) and NMMNO (0.6 mL, 60% solution in water) were dissolved in acetone (xx mL). Osmium tetroxide (0.7 mL, 0.004 M solution in *tert*-butanol) was added, and the solution was stirred for 24 h at RT. Afterwards, sat. aq. Na_2SO_3 (5 mL) was added, and the mixture was stirred for 30 min at RT. The

mixture was filtered. Ethyl acetate (30 mL) and 10% H_2SO_4 (5 mL) were added into the liquid and the organic layer was separated, washed with sat. aq. $NaHCO_3$ (50 mL) and H_2O (50 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. Purification of the product was done by chromatography (eluent: petroleum ether / ethyl acetate V / V = 1 / 2). Yield: 439.3 mg, 79%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56-7.54 (d, J = 8.6, 2 H, 2 Ar**H**), 7.17-7.16 (m, 2 H, 2 Ar**H**), 7.08-7.07 (d, J = 3.8, 1 H, Ar**H**), 6.95-6.93 (m, 4 H, 4 Ar**H**), 4.15-4.08 (m, 3 H, ArOC**H**$_2$, C**H**OH), 4.19-3.77 (m, 2 H, C**H**$_2$OH), 2.80-2.77 (t, J = 6.9, 4 H, 2 ArC**H**$_2$), 1.68-1.62 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.36-1.24 (m, 28 H, 14 C**H**$_2$), 0.89-0.86 (t, J = 5.6, 6 H, 2 C**H**$_3$).

4-{4-[3',3''-Didecyl-(2,2':5',2''-terthiophene)-5-yl]phenoxymethyl}-2,2-dimethyl-1,3-dioxolane 13. Compound **12** (417 mg, 0.6 mmol) was dissolved in 2,2-dimethoxypropane (5 mL). After addition of pyridium p-toluenesolfonate (50 mg), the mixture was stirred at RT until the reaction was complete. The solvent was evaporated and the residue was taken up in ethyl acetate (100 mL). The solution was washed with sat. aq. $NaHCO_3$ (50 mL), H_2O (50 mL) and brine (50 mL) and the organic layer was dried with anhydrous Na_2SO_4. Purification of the product was done by chromatography (eluent: petroleum ether / ethyl acetate V / V = 20 / 1). Yield: 348.5 mg, 79%; yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 8.6, 2 H, 2 Ar**H**), 7.16-7.15 (m, 2 H, 2 Ar**H**), 7.08-7.07 (d, J = 3.7, 1 H, Ar**H**), 6.95-6.93 (m, 4 H, 4 Ar**H**), 4.52-4.48 (m, 1 H, ArOC**H**$_2$), 4.20-3.91 (m, 4 H, ArOC**H**$_2$, C**H**O, C**H**$_2$O), 2.80-2.77 (t, J = 7.4, 4 H, 2 ArC**H**$_2$), 1.68-1.65 (m, 4 H, 2 ArCH$_2$C**H**$_2$), 1.48 (s, 3 H, OCC**H**$_3$), 1.42 (s, 3 H, OCC**H**$_3$), 1.41-1.38 (m, 28 H, 14 C**H**$_2$), 0.89-0.86 (m, 6 H, 2 C**H**$_3$).

Bisacetonide **14**. Under an argon atmosphere, **13** (294 mg, 0.4 mmol) was dissolved in anhydrous THF (10 mL) and cooled to -60 °C, then *n*-BuLi (1.6 M in *n*-hexane, 0.4 mL, 0.6 mmol) was added dropwise and the solution was stirred for 30 min, and then warmed to -40 °C Powdered anhydrous $CuCl_2$ (81 mg, 0.6 mmol) was added in

one portion. The mixture was warmed to RT and stirred for 12 h. The mixture was poured slowly into water (20 mL) containing 10 mL of 1 M HCl and extracted with diethyl ether (3×15 mL). The combined organic phase was washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate V / V = 10 / 1). Yield: 231.9 mg, 79%; orange solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55-7.53 (d, J = 7.9, 4 H, 4 Ar**H**), 7.17-7.14 (m, 2 H, 2 Ar**H**), 7.10-7.08 (m, 2 H, 2 Ar**H**), 6.99-6.93 (m, 8 H, 8 Ar**H**), 4.51-3.81 (m, 10 H, 2 ArOC**H**$_2$, 2 OC**H**, 2 OC**H**$_2$), 2.79-2.75 (m, 8 H, 4 ArC**H**$_2$), 1.68-1.62 (m, 8 H, 4 ArCH$_2$C**H**$_2$), 1.48 (s, 6 H, 2 OCC**H**$_3$), 1.42 (s, 6 H, 2 OCC**H**$_3$), 1.36-1.24 (m, 56 H, 28 C**H**$_2$), 0.88-0.86 (m, 12 H, 4 C**H**$_3$).

6T/10. A mixture of **14** (220.2 mg, 0.3 mmol) and 10% HCl (1 ml) in MeOH (10 mL) was heated under reflux for 6 h. After cooling to RT, the solvent was evaporated and $NaHCO_3$ solution (20 mL) was added. The residue was filtered and washed with water (3×20 mL). The product was purified by repeated crystallization from ethyl acetate/CH_3OH (10:5)**.** Yield: 131.2 mg, 63%; red solid. ^{1}H NMR (DMSO, 500 MHz): δ = 7.58-7.56 (d, J = 8.5, 4 H, 4 Ar**H**), 7.34-7.33 (d, J = 3.6, 2 H, 2 Ar**H**), 7.15-7.13 (m, 4 H, 4 ArH), 7.04 (s, 2 H, 2 Ar**H**), 7.01-6.99 (d, J = 8.6, 4 H, 4 Ar**H**), 4.08-3.50 (m, 10 H, 2 ArOC**H**$_2$, 2 C**H**OH , 2 C**H**$_2$OH), 2.78-2.71 (m, 8 H, 4 ArC**H**$_2$), 1.65-1.62 (m, 8 H, 4 ArCH$_2$C**H**$_2$), 1.36-1.24 (m, 56 H, 28 C**H**$_2$), 0.84-0.81(t, J = 6.1, 12 H, 4 C**H**$_3$); ^{13}C-NMR (DMSO, 125 MHz): δ = 158.18 (2C), 143.32 (4C), 139.79(4C), 139.14 (4C), 133.31 (4C), 127.97 (4C), 126.19 (4C), 126.12 (4C), 121.95 (2C), 114.53 (4C), 69.79(2 C), 68.88(2 C), 62.87(2 C), 31.05-22.02, 13.65 (multicarbons in alkyl chain). Elemental analysis calcd (%) for $C_{82}H_{114}O_6S_6$ (1388.17): C 70.95, H 8.28; Found: C 70.69, H 8.09.

3. XRD Data

Table S1. Crystallographic data of the $Col_{hex}/p6mm$ phase of compound **6T/10** at different temperatures.[a]

T/°C	$2\theta_{obs}$/°	d_{obs}/nm	*hk/n*	d_{calc}/ nm	d_{obs}-d_{calc}	a_{hex}/ nm	n_{cell}	n_{wall}	ρ_{calc}/ g cm^{-3}
140	2.5319	3.49	10	3.49	0.00	4.03	2.95	0.98	1.08
	4.3621	2.03	11	2.01	0.02				
	5.0570	1.75	20	1.74	0.01				
	19.3470	0.46	diffuse						
120	2.4816	3.56	10	3.56	0.00	4.11	3.00	1.00	1.05
	4.2819	2.06	11	2.06	0.00				
	4.9139	1.80	20	1.78	0.02				
	19.5610	0.45	diffuse						
100	2.4300	3.64	10	3.64	0.00	4.20	3.13	1.04	1.05
	4.1936	2.11	11	2.10	0.01				
	4.8147	1.84	20	1.82	0.02				
	19.7420	0.45	diffuse						
80	2.3833	3.71	10	3.71	0.00	4.28	3.25	1.08	1.05
	4.1115	2.15	11	2.14	0.01				
	4.7263	1.87	20	1.85	0.02				
	19.9100	0.45	diffuse						
60	2.3479	3.76	10	3.76	0.00	4.34	3.27	1.09	1.03
	4.0586	2.18	11	2.17	0.01				
	4.6673	1.89	20	1.88	0.01				
	6.9283	1.28	30	1.25	0.03				
	20.1480	0.44	diffuse						
40	2.3280	3.79	10	3.79	0.00	4.38	3.33	1.11	1.03
	4.0285	2.19	11	2.19	0.00				
	4.6250	1.91	20	1.90	0.01				
	6.8777	1.29	30	1.27	0.02				
	20.3330	0.44	diffuse						

[a] The XRD patterns were recorded with CuK_α radiation; the exposure time was 60 min; θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated d spacing; *hk*: assigned indices for the Col_{hex} phase; n_{cell} = number of molecules in the unit cell, calculated using a_{hex} and assuming a height h corresponding to the maximum of the diffuse wide angle scattering; the molecular volume was calculated using the crystal volume increments of Immirzi;[4] n_{wall} = average thickness of the cylinder walls given by the average number of sexithiophene units arranged side by side in the walls separating two adjacent cylinder cores; ρ_{calc}/gcm^{-3} was calculated using the following equation: $\rho = n_{cell}/\ (a_{hex}^2/2)\sqrt{3}h(N_A/M)$, where h = *0.45 nm*

(maximum of the diffuse wide angle scattering), N_A = Avogadro constant, (N_A = 6.02 x 10^{23}) and M = molecular mass =1388.17 g/mol.

4. References

1.(a) T. A. Chen, X. M. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233-244; (b) R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem*., 1993, **58**, 904-912.

2. X. H. Cheng, X. Dong, G. H. Wei, M. Prehm and C. Tschierske, *Angew. Chem.,* 2009, **121**, 8158-8161; *Angew. Chem. Int. Ed.*, 2009, **48**, 8014-8017.

3. C. V. Pham, H. B. Mark, and H. Zimmer, *Synth. Commun.,* 1986, **16**, 689-696.

4. A. Immirzi and B. Perini, *Acta Cryst. Sect. A.,* 1977, **33**, 216-218