Supporting Information for

Synthesis and Self-Assembly of Coil-Rod-Coil Molecules with Lateral Methyl and Ethyl Groups in the Center of the Rod Segment

Lirong Tian,[1] Ke-Li Zhong,[1] Yuanjuan Liu,[1] Zhegang Huang,[2] Long Yi Jin[1]* and Linda S. Hirst [3]*

[1]Key Laboratory for Organism Resources of the Changbai Mountain and Functional Molecules, Ministry of Education and Department of Chemistry, College of Science, Yanbian University, No. 977 Gongyuan Road, Yanji 133002, People's Republic of China

[2] Department of Chemistry, Yonsei University, Seoul 120-749, Korea

[3] School of Natural Sciences, University of California, Merced, CA 95343

Correspondence to: L. Y. Jin (E-mail: lyjin@ybu.edu.cn)

or L. S. Hirst (E-mail: lhirst@ucmerced.edu)

Experimental

Synthesis of 4-chloro-3-methylphenyl acetate and 4-chloro-3-ethylphenyl acetate

4-chloro-3-methylphenyl acetate and 4-chloro-3-ethylphenyl acetate were synthesized using the same procedure. A representative example is described for 4-Chloro- 3-ethylphenyl Acetate, 4-Chloro-3-ethylphenol (4.7g, 0.03mol), acetic anhydride (3.4 mL, 0.036 mol) and a few drops of H_2SO_4 were stirred at 60 °C for 2 h, cooled to room temperature, poured into H_2O (20mL), stirred (1h), then extracted with Et_2O.The organic phase was dried ($MgSO_4$), concentrated, and Purified by column chromatography(silica gel PE/CH_2Cl_2 4:1) to give a colorless liquid (5.5g, 92%) ^{1}H-NMR(300Hz, $CDCl_3$, ppm): 7.32(d, *J* = 8.5 Hz, 1 H), 6.96(d, 1 H, *J* = 2.5 Hz), 6.87(dd,1 H, *J* =8.5, 2.5 Hz), 2.56(q, 2H), 2.35 (s, 3 H), 2.27(s, 3 H, CH_3).

Synthesis of 2,2'-dimethyl-4,4'-dihydroxybiphenyl and 2,2'-diethyl-4,4'-dihydroxy biphenyl

2,2'-dimethyl-4,4'-dihydroxybiphenyl and 2,2'-diethyl-4,4'-dihydroxybiphenyl were synthesized using the same procedure. A representative example is described for 2,2'-diethyl-4,4'-dihydroxybiphenyl. DMAc (15mL) was added to a 100 mL flask containing $NiCl_2$ (0.15 g, 1.16 mmol), PPh_3 (1.52 g, 5.8 mmol), Zn (2.19 g, 33.52 mmol), and 2,2′-bipyridine (0.18g,1.16mmol). The mixture was heated to 65 °C, 4-chloro- 3-ethylphenyl acetate (4.44g, 22.36 mmol) was added dropwise, and the reaction was stirred at 70 °C for 4 h. The mixture was filtered, poured into a solution of NaOH (50g /500 ml of H_2O), stirred overnight at room temperature, washed with Et_2O (30mL), then, acidified with concentrated HCl to pH =1. The resulting precipitate was collected by filtration, washed with water, dried($MgSO_4$), and Purification by column chromatography (silica gel CH_2Cl_2) to give colorless crystals (1.07g, 40%).^{1}H-NMR（300 Hz, $CDCl_3$, δ,ppm): 7.19(d, 2H, J=8.55Hz), 6.73(d, 2H, J=3Hz), 6.62(dd, 2H, J=3Hz, 8.55Hz), 4.70 (s, 2H, OH)，2.70(q, 4H, J= 7.5 Hz), 1.25(t, 6H, J=7.5Hz)。

Synthesis of compounds 3, 4 and 5

Compounds **3**, **4** and **5** were synthesized using the same procedure. A representative example is described for **3**. A mixture of poly(ethylene glycol) methyl ether (Mw=350) (3.5g, 10mmol) dissolved in dry dichloromethane (20mL) was put into a two-necked flask. Toluene-*p*-sulfonyl chloride (TsCl, 3.82g, 204mmol) dissolved in dry dichloromethane (30ml) and pyridine (8ml) was added two-necked flask. The reaction mixture was further stirred for

12h at room temperature. The resulting solution was dissolved in ice water (45ml) and acidified with concentrated HCl to a pH=1, then, extracted with dichloromethane. The organic solution was dried ($MgSO_4$) and filtered. The solvent was removed in a rotary evaporator and the crude product was purified by column chromatography on silica gel using ethyl acetate, as eluent to yield 4.5g of colorless liquid (89%).^{1}H NMR(300MHz, $CDCl_3$, δ, ppm): 7.79(d, 2Ar-H, *o* to SO_3, *J*=8.2Hz), 7.33(d, 2Ar-H, *o* to CH_3, *J*=8.2Hz), 4.14(t, 2H, $OCH_2CH_2OSO_2$), 3.52-3.68(m, 26H, -OCH_2CH_2O- and $OCH_2CH_2OSO_2$), 3.24(s, 3H, OCH_3), 2.43 (s, 3H, CH_3Phenyl).

Compound 4 Yield 90% . ^{1}H NMR(300MHz, $CDCl_3$, δ, ppm): 7.79(d, 2Ar-H, *o* to SO_3, *J*=8.2Hz), 7.33(d, 2Ar-H, *o* to CH_3, *J*=8.2Hz), 4.14(t, 2H, $OCH_2CH_2OSO_2$), 3.52-3.68(m, 46H, -OCH_2CH_2O- and $OCH_2CH_2OSO_2$), 3.24(s, 3H, OCH_3),2.43 (s, 3H, CH_3Phenyl). **Compound 5** Yield 85%. ^{1}H NMR(300MHz, $CDCl_3$, δ, ppm): 7.79(d, 2Ar-H, *o* to SO_3, *J*=8.2Hz), 7.33(d, 2Ar-H, *o* to CH_3, *J*=8.2Hz), 4.14(t, 2H, $OCH_2CH_2OSO_2$), 3.52-3.68(m, 66H, -OCH_2CH_2O- and $OCH_2CH_2OSO_2$), 3.24(s, 3H, OCH_3), 2.43 (s, 3H, CH_3Phenyl).

Synthesis of compounds 6,7 and 8

Compounds **6**, **7** and **8** were synthesized using the same procedure. A representative example is described for compound **6**. Excess K_2CO_3 and 4,4'-biphenol (5.95g, 32mmol) were dissolved in absolute ethyl alcohol (100mL). Compound **3** (4.05g, 8mmol) dissolved in absolute EtOH (30 ml) was added by drops into the above mixture for 4 h under reflux conditions. The mixture was further refluxed for 20h. The solvent was removed in a rotary evaporator. 50mL distilled water was added into the resulting mixture, extracted with ethyl acetate. Dried over anhydrous magnesium sulfate and filtered. After the solvent was removed in a rotary evaporator, the crude product was purified by silica gel chromatography on silica gel using CH_2Cl_2, CH_2Cl_2:MeOH (20:1 v/v) as eluent to yield 4.0g of a yellow ropy liquid (96%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm) 7.37-7.47 (m, 4Ar-H, *m* to phenyl-OH, *m* to CH_2Ophenyl), 6.88-6.96(m, 4Ar-H, *o* to phenyl-OH, *o* to CH_2Ophenyl), 6.65(m, 1H, O*H*), 4.15(t, 2H, phenylOC$H_2$$CH_2$O, *J*=5.0Hz), 3.87(t, 2H, phenylOCH_2CH_2O, *J*=5.0Hz), 3.54-3.74(m, 24H, -OCH_2 CH_2O-), 3.37(s, 3H, OCH_3).

Compound 7 Yield 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm) 7.37-7.47 (m, 4Ar-H, *m* to phenyl-OH, *m* to CH_2Ophenyl), 6.88-6.96(m, 4Ar-H, *o* to phenyl-OH, *o* to CH_2Ophenyl), 6.65(m, 1H, O*H*), 4.15(t, 2H, phenylOC$H_2$$CH_2$O, *J*=5.0Hz), 3.87(t, 2H, phenylOCH_2CH_2O, *J*=5.0Hz), 3.54-3.74(m, 44H, -OCH_2 CH_2O-), 3.37(s, 3H, OCH_3).

Compound 8 Yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm) 7.37-7.47(m, 4Ar-H, *m* to phenyl-OH, *m* to CH_2O-phenyl), 6.88-6.96(m, 4Ar-H, *o* to phenyl-OH, *o* to CH_2Ophenyl), 6.65(m, 1H, O*H*), 4.15(t, 2H, phenylOC$H_2$$CH_2$O, *J*=5.0Hz), 3.87(t, 2H, phenyl CH_2CH_2O, *J*=5.0Hz), 3.54-3.74(m, 64H, -OCH_2 CH_2O-), 3.37(s, 3H, OCH_3).

Synthesis of compounds 9, 10 and 11

Compounds **9**, **10** and **11** were synthesized using the same procedure. A representative example is described for **9**. Excess K_2CO_3 and 4,4'-bis(bromomethyl)biphenyl (5.25g, 15.44mmol) were dissolved in acetone (100 ml) . Compound **6** (4.0g, 7.72 mmol) was added by drops into the above mixture for 3h under reflux conditions. The mixture was further refluxed for 21 h, filtered and concentrated by evaporation, then separated by chromatography on silica gel (CH_2Cl_2, EA, CH_2Cl_2:CH_3OH=20:1 as eluent). The desired compound was separated as the most polar fraction to yield 4.20 g of a wax-like white solid (70%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm) 7.45-7.62(m, 12Ar-H, *o* to OCH_2phenyl, *m* to OCH_2phenyl, *o* to CH_2Br, *m* to CH_2Br, *m* to CH_2Ophenyl and *m* to phenylO$CH_2$$CH_2$O), 6.95-7.06(dd, 4Ar-H, *o* to CH_2Ophenyl, *o* to phenylO$CH_2$$CH_2$O, *J*=8.5Hz), 5.14(s, 2H, OCH_2phenyl), 4.55(s, 2H, CH_2Br), 4.15(t, 2H, phenylOC*H*$_2$CH$_2$O), 3.88(t, 2H, phenylOCH$_2$C*H*$_2$O), 3.56-3.73(m, 24H, -OC*H*$_2$ C*H*$_2$O-), 3.37(s, 3H, OC*H*$_3$).

Compound 10 Yield 80%. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm) 7.46-7.63(m, 12Ar-H, *o* to OCH$_2$phenyl, *m* to OCH$_2$phenyl, *o* to CH$_2$Br, *m* to CH$_2$Br, *m* to CH$_2$Ophenyl and *m* to phenylOCH$_2$CH$_2$O), 6.96-7.04(dd, 4Ar-H, *o* to CH$_2$Ophenyl, *o* to phenylOCH$_2$CH$_2$O, *J*=8.5Hz), 5.15(s, 2H, OC*H*$_2$phenyl), 4.56(s, 2H, C*H*$_2$Br), 4.16(t, 2H, phenylOC*H*$_2$CH$_2$O), 3.87(t, 2H, phenylOCH$_2$C*H*$_2$O), 3.54-3.71(m, 44H, -OC*H*$_2$ C*H*$_2$O-), 3.39(s, 3H, OC*H*$_3$).

Compound 11 Yield 75%. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm) 7.47-7.62(m, 12Ar-H, *o* to OCH$_2$phenyl, *m* to OCH$_2$phenyl, *o* to CH$_2$Br, *m* to CH$_2$Br, *m* to CH$_2$Ophenyl and *m* to phenylOCH$_2$CH$_2$O), 6.96-7.04(dd, 4Ar-H, *o* to CH$_2$Ophenyl, *o* to phenylOCH$_2$CH$_2$O, *J*=8.5Hz), 5.14(s, 2H, OC*H*$_2$phenyl), 4.55(s, 2H, C*H*$_2$Br), 4.16(t, 2H, phenylOC*H*$_2$CH$_2$O), 3.87(t, 2H, phenylOCH$_2$C*H*$_2$O), 3.55-3.72(m, 64H, -OC*H*$_2$ C*H*$_2$O-), 3.37(s, 3H, OC*H*$_3$).

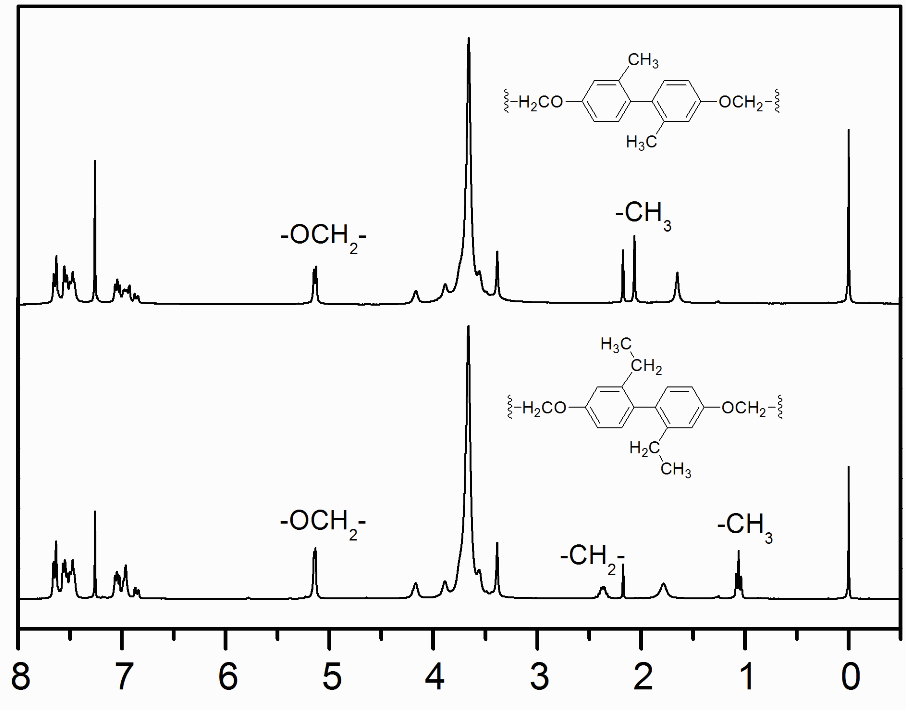

Figure S1. Representative ^{1}H-NMR spectra of molecules **1b** and **2b** in CDCl$_3$ (ppm)

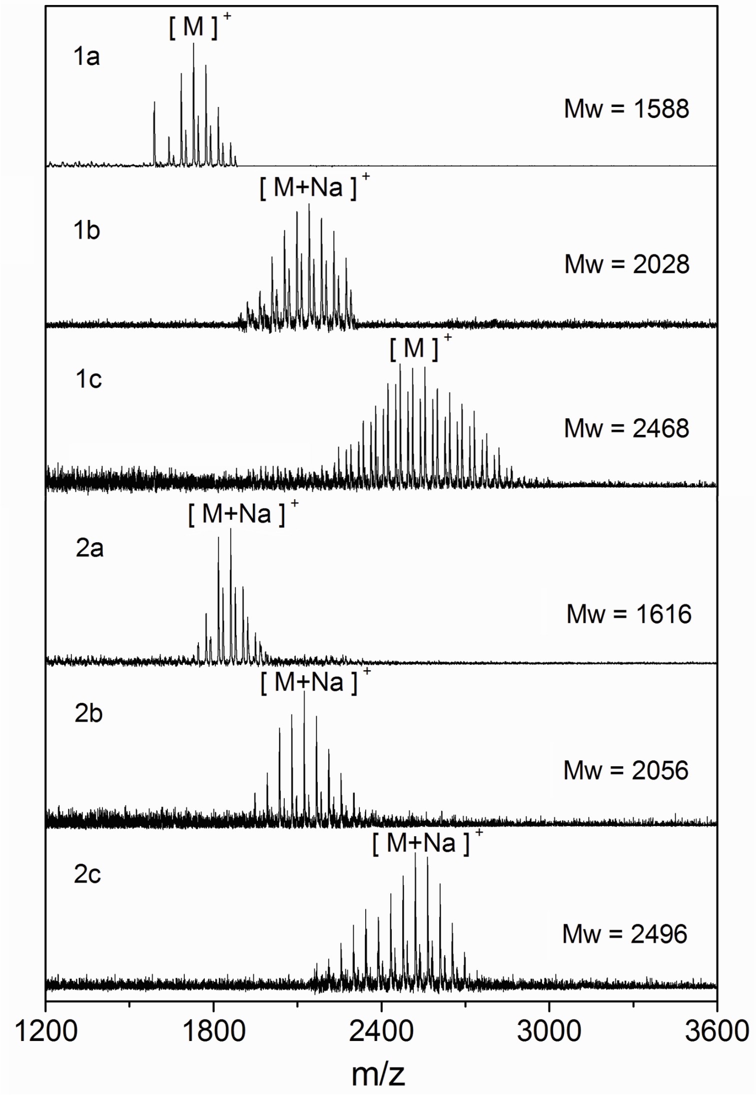

Figure S2. MALDI-TOF-MS spectra for molecules **1a-1c** and **2a-2c**(matrix: CHCA).

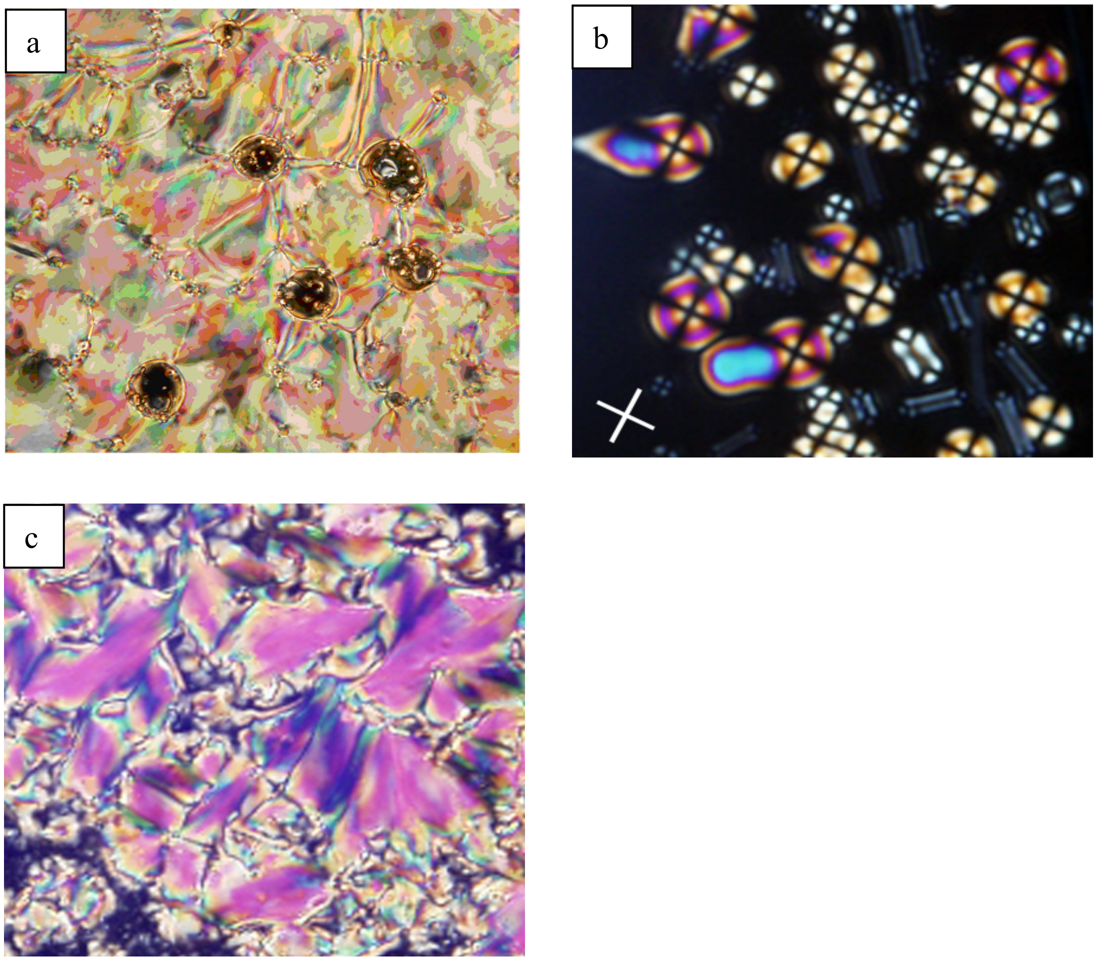

Figure S3. Representative optical polarized micrograph (×40) of the texture exhibited by (a) lamellar structure of **1a**, (b) rectangular columnar structure of **2a** at the transition from the isotropic liquid, (c) the texture of **2a** observed at 160 °C, cooling from the isotropic liquid phase.

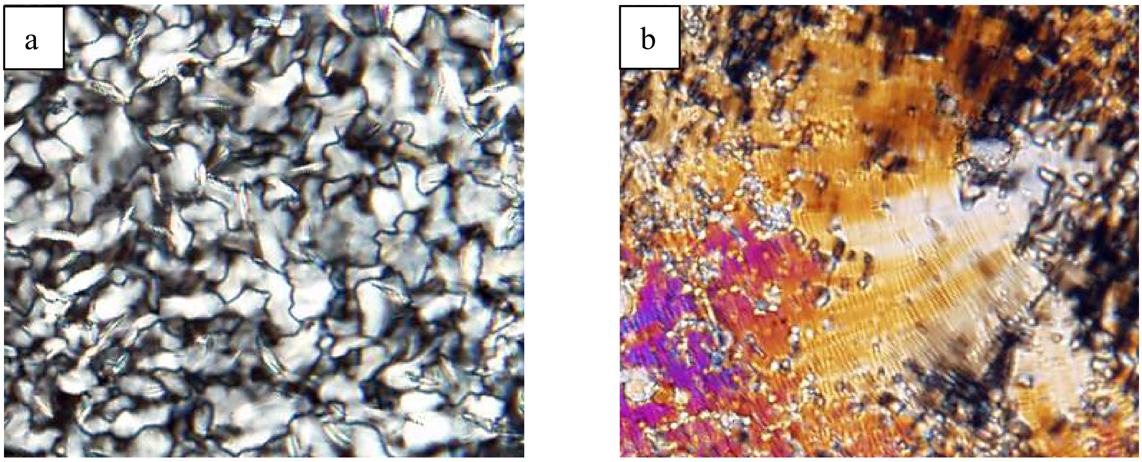

Figure S4. Representative optical polarized micrograph (crossed polarizers, ×40) of the texture exhibited by (a) hexagonal perforated lamellar structure of **1b**, (b) hexagonal perforated lamellar structure of **1c**, in the liquid crystalline phase.