Supporting information

New SmCG Phases in a Hydrogen-Bonded Bent-Core Liquid Crystal Featuring a Branched Siloxane Terminal Group

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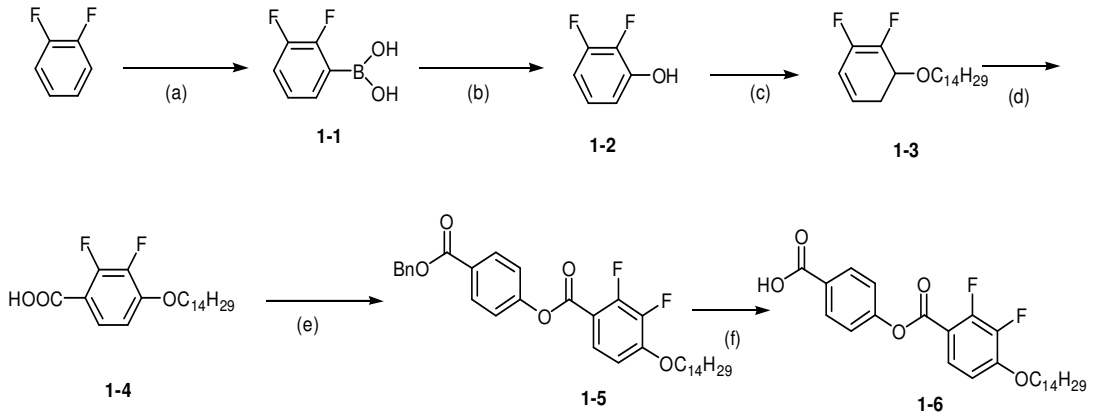
Synthesis



Scheme S1. Reagents and conditions: (a) (i) *n*-BuLi, THF, -78 °C, (ii) triisopropyl borate, (iii) 10% HCl; (b) 30% H_2O_2, ether, reflux, 2 h; (c) K_2CO_3, KI, acetone, reflux, 48 h; (d) (i) *n*-BuLi, PMDTA, THF, -78 °C, (ii) $CO_{2(s)}$, (iii) 10% HCl; (e) DCC, DMAP, CH_2Cl_2, r.t., 16 h; (f) H_2, 10% Pd-C, THF.

Synthesis of 2,3-Difluorophenylboronic acid (1-1)

Into a 250 ml round bottom two-neck flask, 1,2-difluorobenzene (3.00 g, 11.4 mmol) were mixed in dry THF (50 mL) homogeneously under nitrogen and cooled to -78 °C. Then, 5 ml (12.5 mmol) of n-butyl lithium (2.5 M in hexane) was injected to the previous solution slowly and stirred at the same temperature for 1 h. Trimethyl borate (8.3 ml, 17.1 mmol) was added to the reaction mixture and then warmed up to room temperature slowly and stirred overnight. The reaction mixture was

quenched with 4N HCl (100 ml) and extracted with dichloromethane (300 ml). After being washed with water (300 ml) and brine (100 ml), the organic layer extract was dried with $MgSO_4$, and the solvent removed under reduced pressure. The residue was recrystallized from hexane to afford 2.72 g (77%) of compound **1-1** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.15 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H).

Synthesis of 2,3-Difluorophenol (1-2)

Into a 500 ml round bottom flask, 2.73 g (17.1 mmole) of 2,3 difluorophenylboronic acid was dissolved in diethyl ether. 10 ml of Hydrogen peroxide (30 wt% in water) was added dropwise to a stirred solution and the reaction was refluxed for 1 h and then cooled to room temperature. The crude product was extracted with diethyl ether (100 ml) and washed with 10% aqueous ammonium ferrous sulphate solution (200ml) and brine (100 ml), and then dried with $MgSO_4$. After the solvent being removed under reduced pressure, the purification via vacuum distillation afforded 2.15 g (94%) of compound **1-2** as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.15 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H).

Synthesis of Tetradodecyloxy-2,3-difluorobenzene (1-3)

A mixture of 2,3-difluorophenol (2.04 g, 15.3 mmol), 4-bromotetradodecane (3.82 g, 13.9 mmol), K_2CO_3 (4.21 g, 30.7 mmol), and potassium iodide (0.05 g) was stirred at reflux temperature in 200 ml of acetone overnight. After cooling to room temperature, the solvent was removed under reduced pressure. Then, water was added and the mixture was extracted with dichloromethane (200 ml) and brine (100 ml), and dried with $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (*n*-hexane) to afford 4.23 g (93%) of compound **1-3** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.95 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.98 (t, *J* = 6.3 Hz, 2H), 31.77 (m, 2H), 1.29−1.31 (m, 22H), 0.86 (t, *J* = 6.3 Hz, 3H).

Synthesis of 4-Tetradodecyloxy-2,3-difluoro benzoic acid (1-4)

Under nitrogen atmosphere, a solution of **1-3** (4.02 g, 12 mmol) and PMDTA (2.1 ml, 12 mmol) in THF (100 ml) was cooled to -78 °C. Afterward, 5.71 ml (14.4 mmol) n-butyl lithium (2.5 M in hexane) was added dropwise, and stirred at -78 °C for 1 h. Solid CO_2 (5.00 g, 0.11 mol) was subsequently added to the mixture to react, and warmed up to room temperature and stirred overnight. The residue was acidified to pH = 2 with diluted HCl and then extracted with dichloromethane. The organic phase was washed with water (300 ml) and brine (100 ml), dried with $MgSO_4$. The solvent was evaporated and the crude product was crystallized from hexane to afford 3.11 g (70 %) of compound **1-4** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 12.59 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 4.01 (t, *J* = 6.3 Hz, 2H), 1.74–1.66 (m, 2H), 1.34–1.16 (m, 22H), 0.84 (t, *J* = 6.3 Hz, 3H).

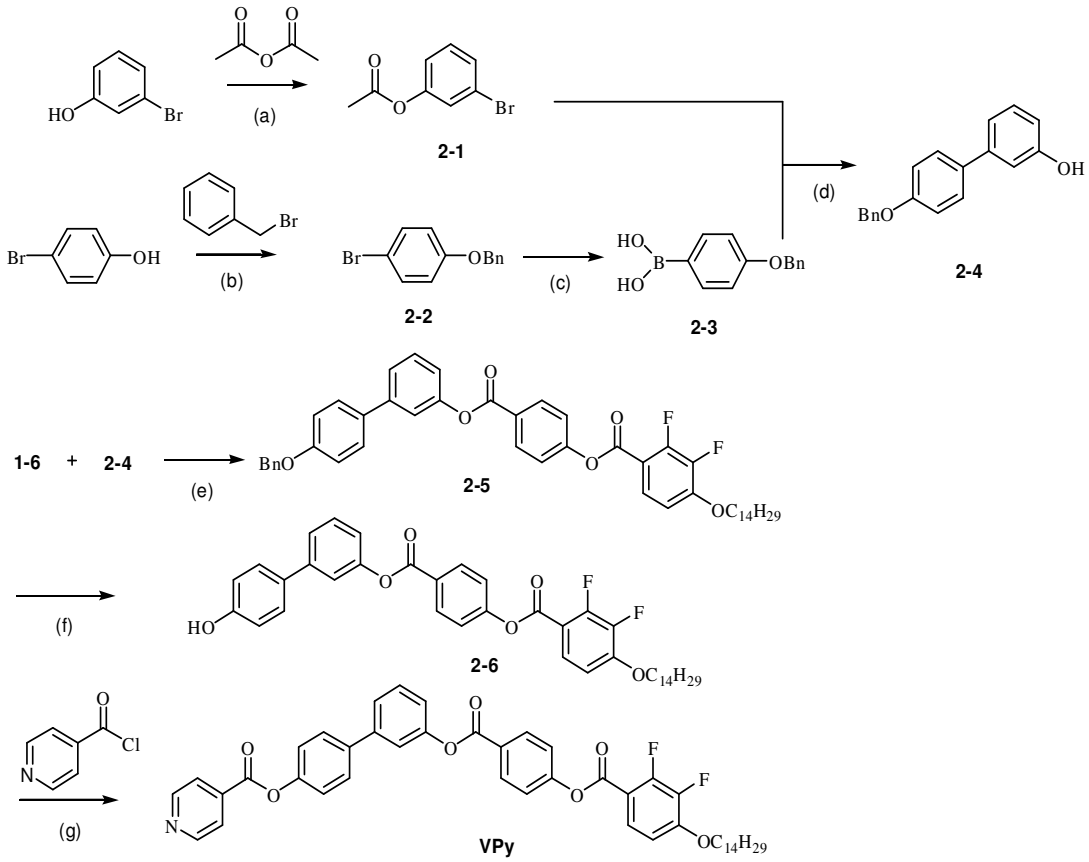
Synthesis of 4-(Benzyloxycarbonyl)phenyl 4-(tetradodecyloxy) 2,3-difluorobenzoate (1-5)

In a 500 ml round bottom flask, **1-4** (3.02 g, 8 mmole), N,N-dicyclohexylcarbodiimide (DCC) (2.5g, 12 mmole), 4-(N,Ndimethylamino) pyridine (DMAP) (50.0 mg, 0.04 mg), and benzyl 4-hydroxybenoate (2.22 g, 9.6 mmole) were mixed in dry THF (100 ml) under nitrogen and the mixture was stirred overnight at ambient temperature. The precipitated dicyclohexylurea (DCU) was filtered off and washed with an excess of DCM (20 ml). The filtrate was extracted with water/DCM and the organic liquid layer was dried over anhydrous $MgSO_4$. The purification was poured on column chromatography and eluted with mixture of hexane/CH_2Cl_2 = 1/2. The solvent was removed by a rotavap to afford **1-5** (3.8 g, 82%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.15 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.46–7.37 (m, 5H), 6.89 (d, *J* = 8.7 Hz, 1H), 5.28 (s, 2H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.80 (m, 2H),
1.28 (m, 22H), 0.86 (t, *J* = 6.3 Hz, 3H).

Synthesis of 4-(Benzyloxycarbonyl)phenyl 4-(dodecyloxy)-2,3-difluorobenzoic acid (1-6)

Compounds **1-5** (3.5 g, 6 mmole) and Pd/C (10 wt%) catalyst were stirred in THF under hydrogen

at room temperature. The catalyst was removed by filtration through Celite and washed with THF. The solvent was removed by evaporation under reduced pressure and the crude product recrystallized by THF/hexane to give **1-6** (2.8 g, 95%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 12.05 (s, 1H), 8.17 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.7 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.7 Hz, 1H), 4.07 (t, J = 6.6 Hz, 2H), 1.78−1.68 (m, 2H), 1.38−1.26 (m, 22H), 0.88 (t, J = 6.6 Hz, 3H).



Scheme S2. Reagents and conditions: (a) CH_2Cl_2, r.t., overnight; (b) K_2CO_3, KI, acetone, reflux, 48 h (c) (i) *n*-BuLi, THF, -78 °C, (ii) triisopropyl borate, (iii) 10% HCl; (d) $Pd(PPh_3)_4$, K_2CO_3, EtOH/toluene (1:3, v/v), 90 °C, 5 h; (e) DCC, DMAP, CH_2Cl_2, r.t., 16 h; (f) H_2, 10% Pd-C, THF; (g) Et_3N, CH_2Cl_2, r.t., 5 h.

Synthesis of 3-Bromophenyl acetate (2-1)

Into a 500 ml round bottom flask, 3-bromophenol (10.00 g, 58 mmole) and acetic anhydride (5.43 g, 52.7 mmole) were stirred in dichloromethane at ambient temperature. The solvent was removed by

evaporation under reduced pressure, and eluted with mixture of hexane/EtOAc = 1/20 by column chromatography to give **2-1** (10.52 g, 93%) as a white liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.45 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.32 (t, *J* = 6.3 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 2.41 (s, 3H).

Synthesis of 1-(Benzyloxy)-4-bromobenzene (2-2)

The similar step for the synthesis of compound **1-3** was employed to obtain **2-2** as a white solid. Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.52 (d, *J* = 8.7 Hz, 2H), 7.46–7.38 (m, 5H), 6.98 (d, *J* = 9.0 Hz, 2H), 5.16 (s, 2H).

Synthesis of 4-(Benzyloxy)phenylboronic acid (2-3)

The similar step for the synthesis of compound **1-1** was carried out to yield compound **2-3** as a white solid. Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.15 (d, 2H), 7.55–7.33 (m, 5H), 7.07 (d, 2H), 5.14 (s, 2H).

Synthesis of 4'-(Benzyloxy)biphenyl-3-ol (2-4)

Into a 500ml round bottom flask, **2-1** (3.11 g, 14.5 mmol), **2-3 (**3.00 g, 13.2 mmol), K_2CO_3 (2.37 g, 17.2 mmol), and $Pd(PPh_3)_4$ (0.17 g, 0.2 mmol) were stirred to react in EtOH/toluene of 280 mL (1:3, v/v) under nitrogen at 80 °C for 5 h. After cooling to room temperature, the solvent was evaporated. The residue was dissolved in dichloromethane and washed with water for several times. After drying over anhydrous $MgSO_4$, the solvent was evaporated. The residue was purified by silica gel column chromatography with dichloromethane as an eluent and followed by recrystallization from hexane/dichloromethane (1/1) to give **2-4** (2.42 g, 65%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.30-7.52 (m, 5H), 7.27 (d, J = 4.8 Hz, 1H), 7.11-7.14 (d, J = 8.4 Hz, 2H), 7.01-7.05 (d, J = 8.4 Hz, 2H), 6.75-6.79 (m, 3H), 5.11 (s, 2H), 4.74 (s, 1H).

Synthesis of 4-((4'-(Benzyloxy)biphenyl-3-yloxy)carbonyl) phenyl 2,3-difluoro-4-

(tetradecyloxy)benzoate (2-5)

The similar step for the synthesis of compound **1-5** was proceeded to achieve compound **2-5** as a white solid. Yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.29 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.74 (s, 1H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.55−7.33 (m, 10H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 5.20 (s, 2H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.80−1.76 (m, 2H), 1.43−1.28 (m, 22H), 0.86 (t, *J* = 6.3 Hz, 3H).

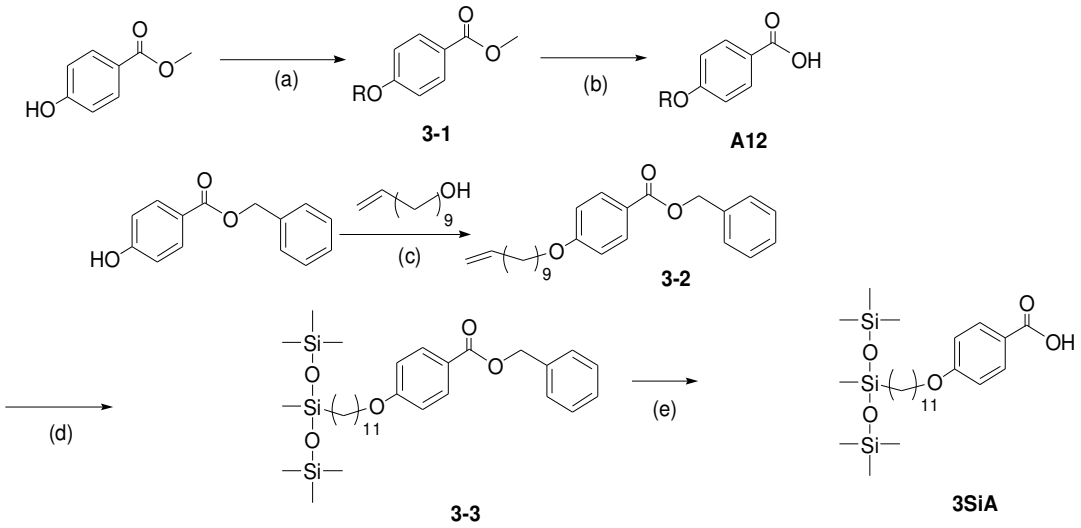
Synthesis of 4-((4'-Hydroxybiphenyl-3-yloxy)carbonyl) phenyl 2,3-difluoro-4- (tetradecyloxy) benzoate (2-6)

The similar step for the synthesis of compounds **1-7** was carried out to acquire **2-6** as a white solid. Yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.29 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.62−7.52 (m, 5H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 1H), 6.89−6.85 (m, 3H), 5.35 (s, 1H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.80−1.76 (m, 2H), 1.43−1.28 (m, 22H), 0.86 (t, *J* = 6.3 Hz, 3H).

Synthesis of 3'-(4-(2,3-Difluoro-4-(tetradecyloxy)benzoyloxy)benzoyloxy) biphenyl-4-yl isonicotinate (VPy)

A mixture of **2-6** (3.00 g, 4 mmole), isonicotinoyl chloride hydrochloride (0.70 g, 4.7 mmole), and triethylamine (8 mmole) was dissolved in 300 ml dry dichloromethane (DCM) under nitrogen for 8 h at room temperature. After work up, the solvent was extracted with water/DCM (3/1 vol.) and the organic liquid layer was dried over anhydrous $MgSO_4$. After removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography and recrystallized from THF/hexane to give **Vpy** as a white solid (2.30 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.89 (d, 2H, Ar-H), 8.29 (d, *J* = 8.3 Hz, 2H, Ar-H), 8.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.86 (m, 1H, Ar-H), 7.67(d, *J* = 8.2 Hz, 2H, Ar-H), 7.53 (d, 4.7 Hz, 2H, Ar-H), 7.46 (s, 1H, Ar-H), 7.42 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.23-7.19 (m, 1H, Ar-H), 6.82-6.89 (m, 1H, Ar-H), 4.10 (t, *J* = 6.3 Hz, 2H, OCH_2), 1.80−1.76 (m, 2H, OCH_2CH_2), 1.43−1.28 (m, 22H, CH_2),

0.86 (t, J = 6.3 Hz, 3H, CH_2CH_3). Anal. Calcd for $C_{46}H_{47}F_2NO_7$: C, 72.33; H, 6.20; N, 1.83. Found: C, 71.51; H, 6.09; N, 1.90 . MS (FAB^+) *m/z*: 763.33 (M^+); found, 764 (M^+).



Scheme S3. Reagents and conditions: (a) K_2CO_3, KI, acetone, reflux, 16 h; (b) KOH, EtOH, 24 h; (c) DIAD, PPh_3, THF, 0 °C, 1 h, then 24 h, r.t.; (d) 1,1,1,3,5,5,5-heptamethyltrisiloxane, Pt(0) cat., toluene, 70 °C, overnight; (e) H_2, 10% Pd-C, THF.

Synthesis of Methyl 4-(dodecyloxy) benzoate (3-1)

The similar step for the synthesis of compound **1-3** was carried out to obtain **3-1** as a white solid. Yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.95 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 3.98 (t, J = 6.3 Hz, 2H), 3.86 (s, 3H), 1.77 (m, 2H), 1.29−1.31 (m, 18H), 0.86 (t, J = 6.3 Hz, 3H).

Synthesis of 4-(Dodecyloxy) benzoic acid (A12)

Into a 500 ml flask, **3-1** (5.00 g, 15.6 mmole) and KOH (2.60 g, 46.8 mmole) in 200 ml ethanol were dissolved, and the mixture was refluxed overnight. After cooling to room temperature, the mixture was acidified with 6N HCl solution, and extracted with EA twice. The solvent was removed by evaporation under reduced pressure and the crude product recrystallized by THF/hexane to give a white solid of **A12** (4.40 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 12.59 (s, 1H, Ar-COOH), 7.85 (d, J = 8.7 Hz, 2H, Ar-H), 6.98 (d, J = 8.7 Hz, 2H, Ar-H), 4.01 (t, J =

6.3 Hz, 2H, OCH_2), 1.74−1.66 (m, 2H, OCH_2CH_2), 1.34−1.16 (m, 18H, OCH_2), 0.84 (t, J = 6.3 Hz, 3H, CH_2CH_3). Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.44; H, 9.52. MS (FAB^+) m/z: 306.44 (M^+); found, 306 (M^+).

Synthesis of Benzyl 4-(undec-10-enyloxy) benzoate (3-2)

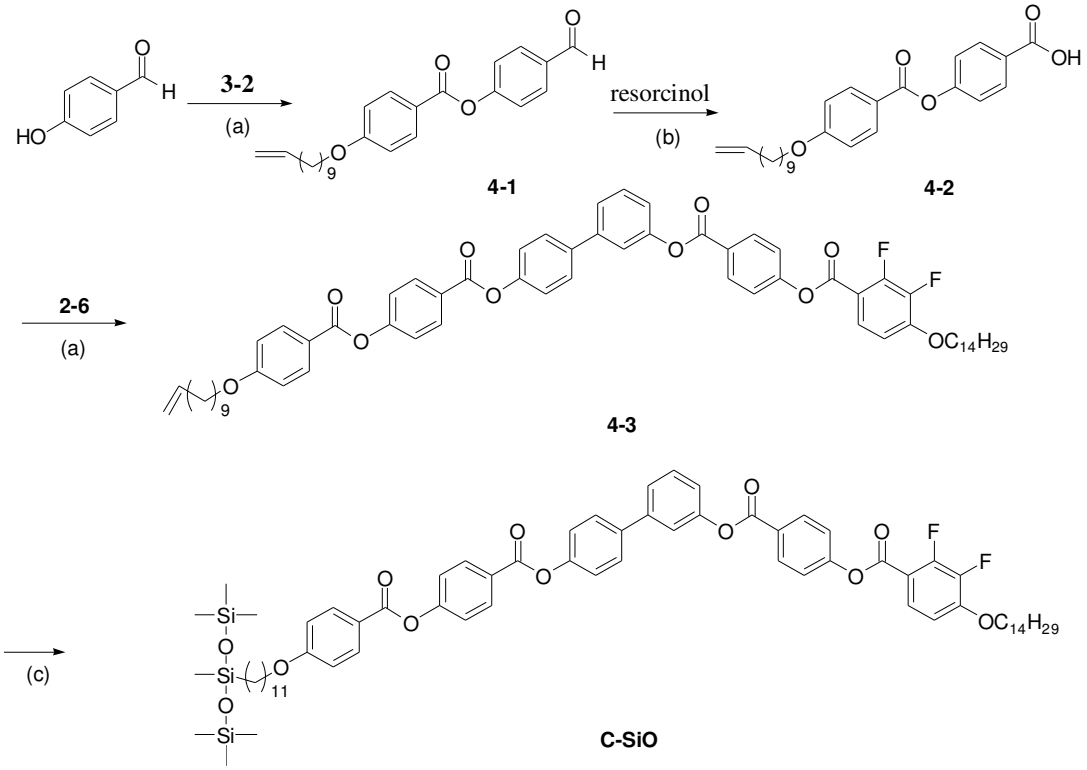
Into a 500 ml flask, benzyl 4-hydroxybenzoate (10.00 g, 43.8 mmol), triphenyl phosphine (13.78 g, 52.6 mmol) in dry THF (200 mL) were mixed under nitrogen and cooled to ice bath. Then, diisopropyl azodicarboxylate (DIAD) (13.28 g, 65.7 mmol) was injected and the mixture became muddy. After that, 10-undecen-1-ol (8.95 g, 52.6 mmole) was injected at the same condition. The mixture was warmed to ambient temperature and stirred overnight. After work up, the solvent was extracted with water/DCM (3/1 vol.) and the organic liquid layer was dried over anhydrous $MgSO_4$. After removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography (hexane/DCM = 1/1) to give **3-2** as a light yellow liquid (15.32 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46−7.37 (m, 5H), 7.14 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 5.82−5.74 (m, 1H), 5.27 (s, 2H), 5.07−5.02 (m, 2H), 4.06−4.28 (t, J = 6.0 Hz, 2H), 2.28−2.19 (m, 2H), 1.76−1.71 (m, 2H), 1.47−1.43 (m, 2H), 1.47−1.43 (m, 10H).

Synthesis of Benzyl 4-(heptamethyltrisiloxyl) undecyloxybenzoate (3-3)

To a 100 mL round-bottomed flask, **3-2** (1.2 g, 3.2 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.75 g, 7.9 mmol), and Karstedt's catalyst (0.34 mL, 0.034 mmol ,3 wt% (0.1 M) solution in xylene) in 25 mL of toluene were added. The mixture was stirred overnight at room temperature. The solvent was removed under vacuum to give a black residue purified by column chromatography (DCM) to give **3-3** as a white solid (1.32 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.05 (d, J = 9.0 Hz, 2H), 7.4 (m, 5H), 6.95 (d, J = 8.5 Hz, 2H), 5.3 (s, 2H), 3.95 (t, J = 6.0 Hz, 2H), 1.75(m, 2H), 1.52−1.32(m, 16H), 0.46 (t, J = 7.8 Hz, 2H), 0.05 (s, 18H), 0.01 (s, 3H).

Synthesis of 4-(Heptamethyltrisiloxyl) undecyloxybenzoic acid (3SiA)

The similar step for the synthesis of compound **1-6** was carried out to get **3SiA** as a white solid. Yield: 91%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.05 (d, *J* = 9.0 Hz, 2H), 7.40 (m, 5H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.3 (s, 2H), 3.95 (t, *J* = 6.0 Hz, 2H), 1.75(m, 2H), 1.52−1.32(m, 16H), 0.46 (t, *J* = 7.8 Hz), 0.05 (s, 18H), 0.01 (s, 3H). Anal. Calcd for $C_{25}H_{48}O_5Si_3$: C, 58.54; H, 9.43. Found: C, 58.59; H, 9.41. MS (FAB$^+$) *m*/*z*: calcd, 512.28; found, 512 (M^+).



Scheme S4. Reagents and conditions: (a) DCC, DMAP, CH_2Cl_2, r.t., 16 h; (b) $NaClO_2$, $NaH_2PO_4{\cdot}H_2O$, THF/*t*-BuOH (3:2, v/v), r.t., overnight; (c) 1,1,1,3,5,5,5-heptamethyltrisiloxane, Pt(0) cat., toluene, 70 °C, overnight.

Synthesis of 4-Formylphenyl 4-(undec-10-enyloxy) benzoate (4-1)

The similar step for the synthesis of compound **1-5** was carried out to produce **4-1** as a white solid. Yield: 78%. ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 10.02 (s, 1H), 8.14 (d, *J* =9.0 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* =9.0 Hz, 2H), 5.83-5.77 (m, 1H), 5.02-4.92 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 3H), 2.20-2.17 (m, 2H), 1.85-1.78 (m, 2H), 1.48-1.26 (m, 12H).

Synthesis of 4-(4-(Udec-10-enyloxy)benzoyloxy) benzoic acid (4-2)

Into a 500 ml flask, **4-1** (4.00 g, 10.2 mmole) and resorcinol (1.44 g, 4.9 mmole) in 300 ml

THF/*t*-BuOH (3:2, v/v) were added. Then, the aqueous solution of $NaClO_2$ (5.5 g, 6.1 mmol) and $NaH_2PO_4 \cdot H_2O$ (4.2 g, 3.1 mmol) was added to the previous flask stepwise. The mixture was stirred overnight at room temperature. After work up, the solvent was removed under vacuum. The residue was acidified to pH = 2 with diluted HCl and then extracted with dichloromethane. After removal of the solvent by evaporation under reduced pressure, the white solid of **4-2** was obtained. Yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 11.59 (s, 1H), 8.28−8.15 (m, 4H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.82−5.74 (m, 1H), 5.07−5.02 (m, 2H), 4.06 (t, *J* = 6.3 Hz, 2H), 2.19−2.10 (m, 2H), 1.76−1.71 (m, 2H), 1.47−1.43 (m, 2H), 1.29−1.23 (m, 12H).

Synthesis of Compound 4-3

The similar step for the synthesis of compound **1-5** was carried out to yield **4-3** as a white solid. Yield: 68%. ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 8.33-8.29 (m, 4H), 8.16 (d, *J* = 9.0 Hz, 2H), 7.87 (m, 1H), 7.67 (d, 8.7 Hz, 2H), 7.52 (d, 4.8 Hz, 2H), 7.46 (s, 1H), 7.42-7.37 (m, 4H), 7.31 (d, 8.4 Hz, 2H), 7.23-7.19 (m, 1H), 7.69 (d, 9.0 Hz, 2H), 6.84 (t, 8.4 Hz, 1H), 5.02-4.92 (m, 1H), 4.14 (t, 6.6 Hz, 2H), 4.05 (t, 6.6 Hz, 2H), 2.06-1.96 (m, 2H), 1.92- 1.72 (m, 6H), 1.64-1.26 (m, 32H), 0.88 (t, 6.9 Hz, 3H).

Synthesis of Compound C-SiO

The similar step for the synthesis of compound **3-3** was followed to obtain **C-SiO** as a white solid. Yield: 81%. 1H NMR (300 MHz, CDCl3) δ (ppm): 8.33-8.28 (m, 4H), 8.16 (d, *J* = 9.0 Hz, 2H), 7.89-7.83 (m, 1H), 7.67 (d, 8.7 Hz, 2H), 7.52 (d, 4.8 Hz, 2H), 7.46 (s, 1H), 7.42-7.37 (m, 4H), 7.31 (d, 8.4 Hz, 2H), 7.23-7.19 (m, 1H), 7.69 (d, 9.0 Hz, 2H), 6.84 (t, 8.4 Hz, 1H), 4.14 (t, 6.6 Hz, 2H), 4.05 (t, 6.6 Hz, 2H), 2.00-1.80 (m, 8H), 1.49-1.12 (m, 32H), 0.88 (t, 6.9 Hz, 3H), 0.46 (t, *J* = 7.8 Hz, 2H), 0.05 (s, 18H), 0.01 (s, 3H). Anal. Calcd for $C_{70}H_{90}F_2O_{12}Si_3$: C, 67.49; H, 7.28. Found: C, 67.45; H, 7.20. MS (FAB$^+$) *m*/*z*: calcd, 1244.57; found, 1244 (M^+).

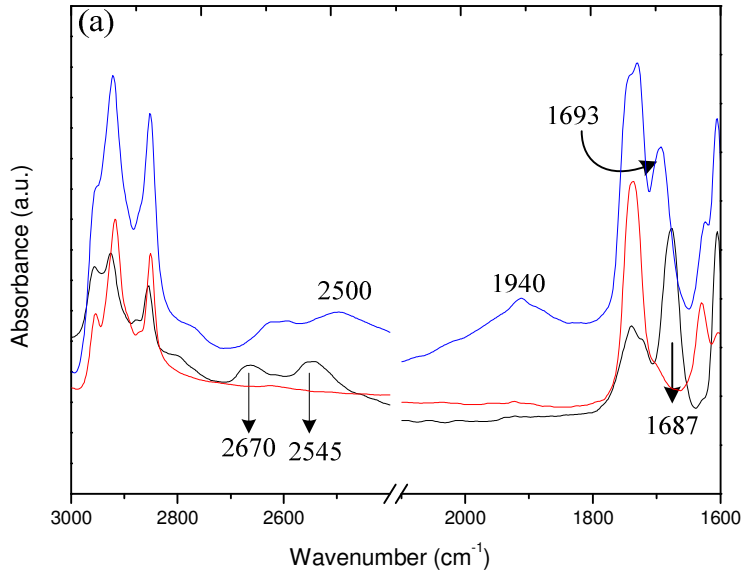


Figure S1. FT-IR spectra of H-bonded complex **H-SiO** (blue) and its composed moieties **3SiA** (black) and **VPy** (red).

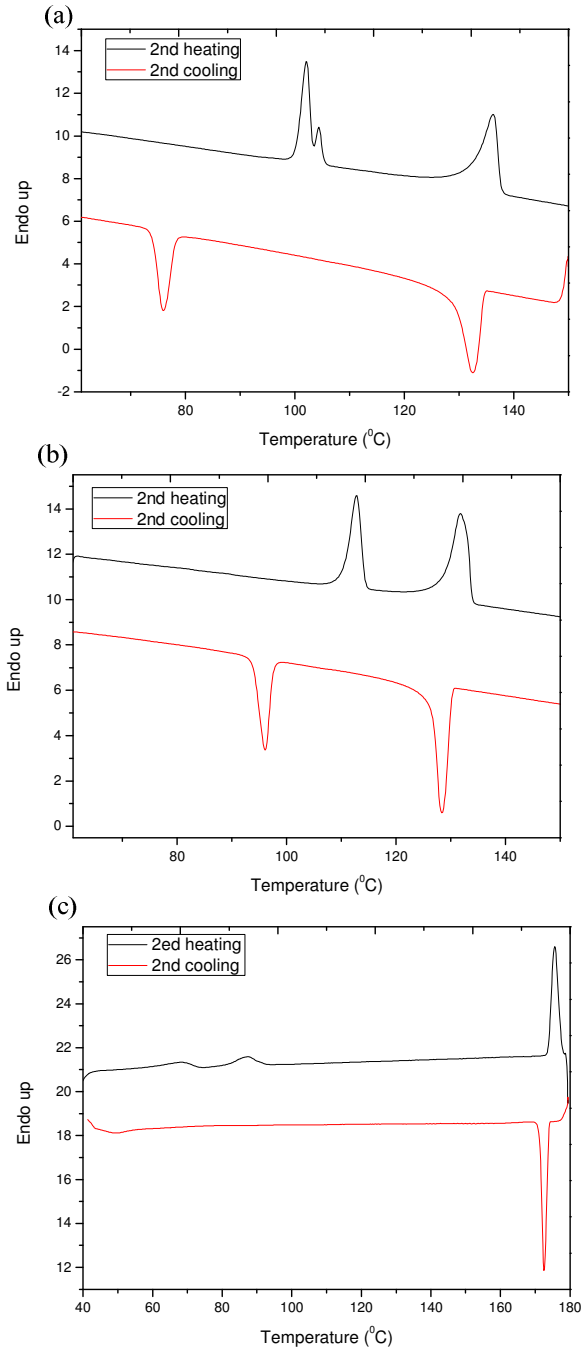


Figure S2. DSC data (upon the second heating and cooling at a rate of 5 °C min^{-1}): (a) H-bonded complex **H-SiO**; (b) H-bonded complex **H-Alk**; (c) covalent-bonded compound **C-SiO**.

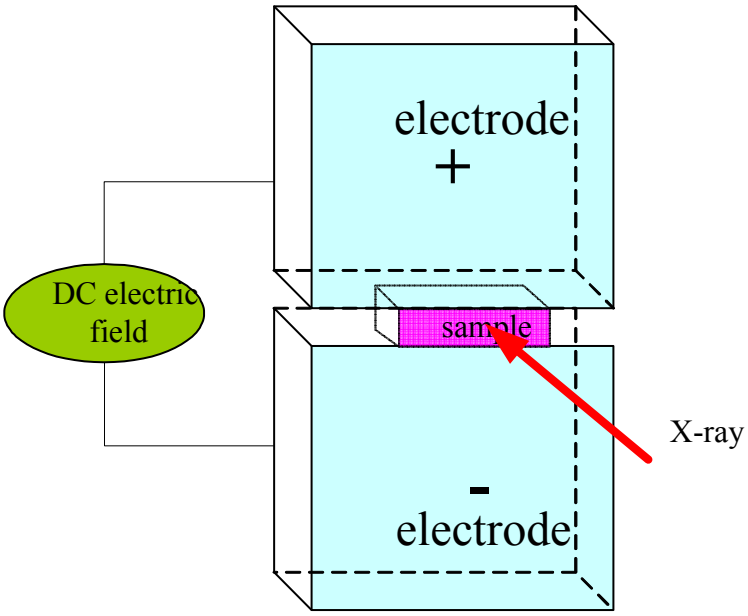


Figure S3. The setup of in-situ SAXS and WAXS measurements under electric fields.

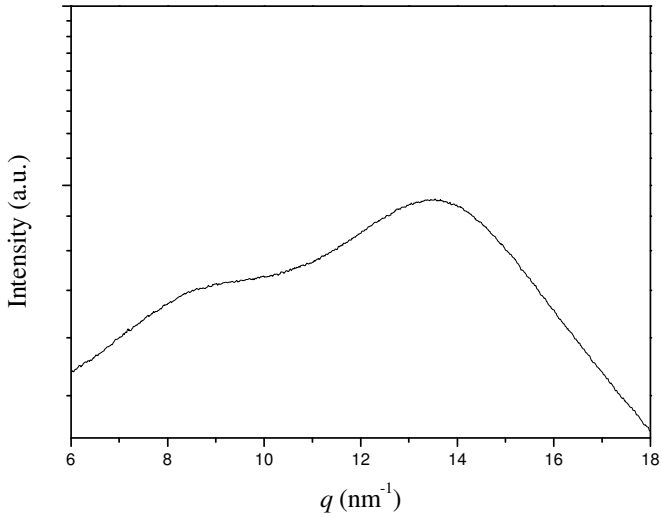


Figure S4. X-ray scattering profile of diffuse scatterings at high-q ranges in H-bonded complex **H-SiO**.

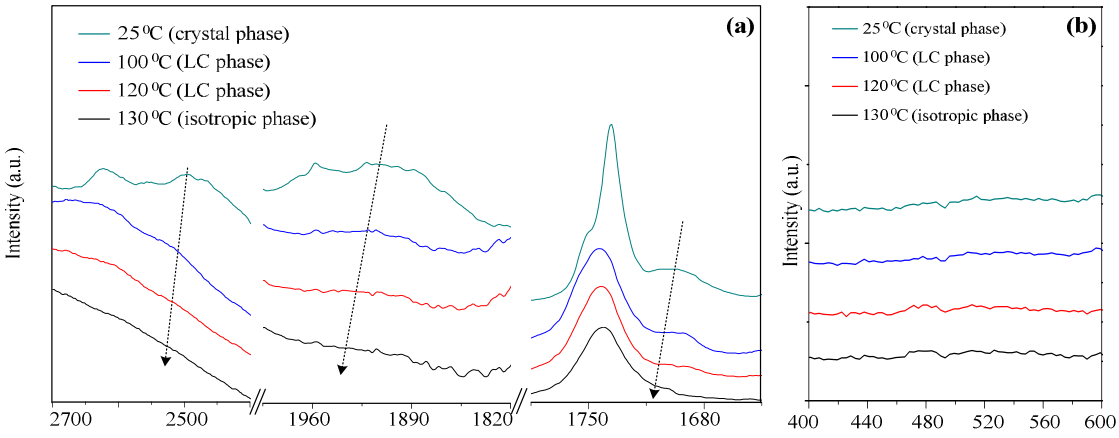


Figure S5. (a) FTIR spectra of the hydrogen-bonded complex **H-Alk** at various temperatures. Two O–H bands appear at 2500 and 1940 cm^{-1}. The C=O band, influenced by the formation of hydrogen bonds between the pyridyl and carboxylic acid groups, appear in the range 1780–1640 cm^{-1}. (b) Temperature-dependent Raman spectra of the hydrogen-bonded complex **H-Alk** at various temperatures (without characteristic peaks for Si–O–Si symmetric stretching bands).

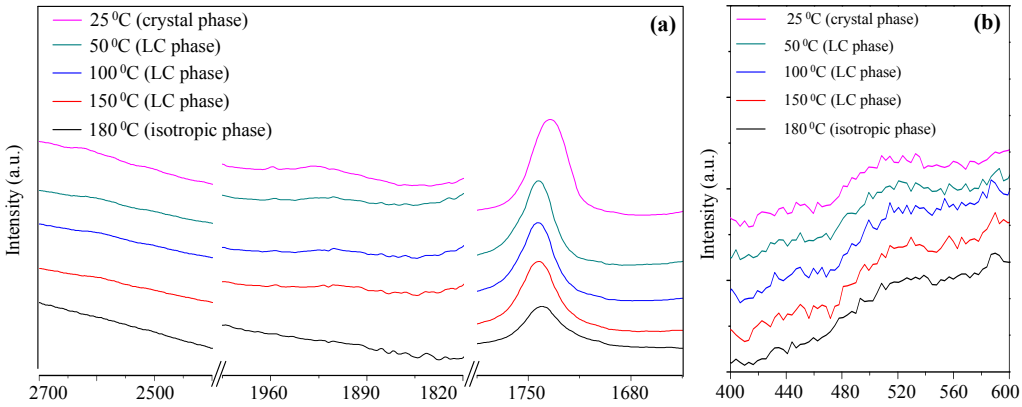


Figure S6. (a) FTIR spectra of compound **C-SiO** at various temperatures. (b) Temperature-dependent Raman spectra of compound **C-SiO** at various temperatures (with characteristic peaks for Si–O–Si symmetric stretching bands).

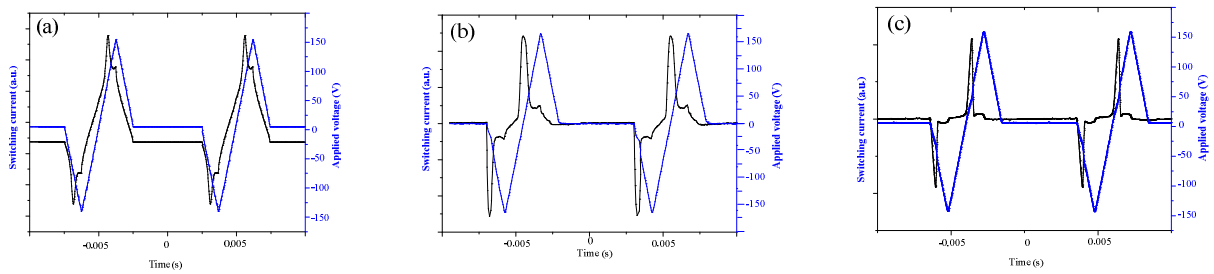


Figure S7. Switching current response curves of the hydrogen-bonded complex **H-SiO** under applied modified triangular waves (Vpp = 300 V; f = 100 Hz; in parallel rubbing cells: thickness, 7.5 μm) at (a) 130 (b) 95 °C for the hydrogen-bonded complex **H-SiO** at (c) 130 °C for the covalent-bonded compound **C-SiO**.

Complete References 3 and 16.

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