Supporting Information

Hydrogen-bonded effects on supramolecular blue phase liquid crystal dimeric complexes

Chong-Lun Wei,[†] Te-Cheng Chen,[†] Putikam Raghunath,[‡] Ming-Chang Lin[‡] and Hong-Cheu Lin[*,†]

[†]Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan

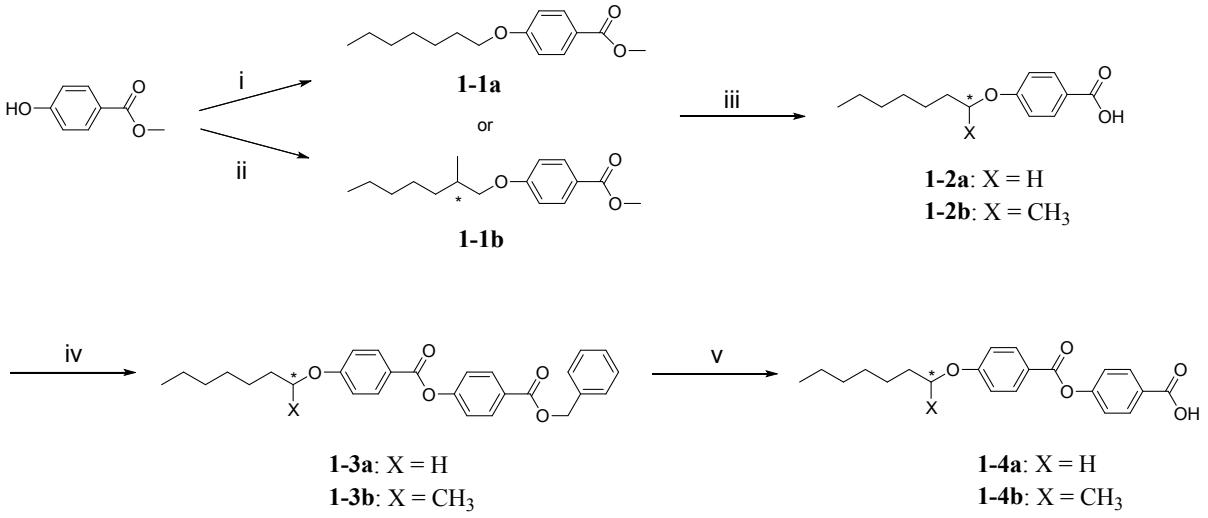
[‡]Center for Interdisciplinary Molecular Science, Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

---

Table of Contents:

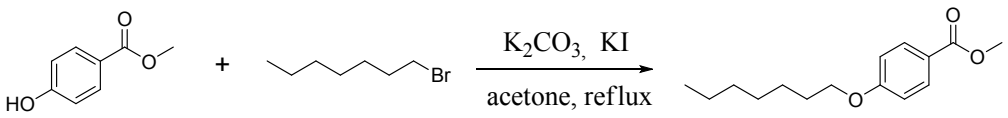
Preparation of materials.

Scheme S1



Reagents and conditions: (i) 1-bromoheptane, K_2CO_3, KI, acetone, reflux, 24 h; (ii) (S)-(+)-2-octanol, DIAD, PPh3, THF, 0 °C, 15 min, then r.t., overnight; (iii) KOH, MeOH, reflux, overnight, then HCl aqueous; (iv) benzyl 4-hydroxybenoate, DCC, DMAP, DCM, r.t., overnight; (v) H2, 10% Pd-C, THF, r.t., 10 h.

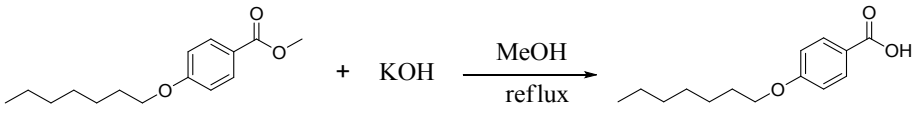
Synthesis of methyl 4-(heptyloxy)benzoate (1-1a)



A mixture of methyl 4-hydroxybenzoate (5.0 g, 32.9 mmol), 1-bromoheptane (7.07 g, 39.5 mmol), K_2CO_3 (6.82 g, 49.4 mmol), and potassium iodide (0.05 g) in dry acetone (200 mL) was stirred and refluxed under nitrogen temperature for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was taken up in water and extracted with ethyl acetate. Then, the organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 40:1 v/v) to afford compound **1-1a** as a white solid in 93% yield.

^{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), 1.77-1.24 (m, 10H), 0.86 (t, *J* = 6.3Hz, 3H).

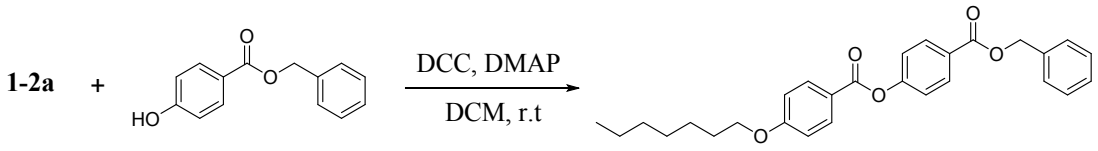
Synthesis of 4-(heptyloxy)benzoic acid (1-2a)



To a stirred solution of **1-1a** (3.68 g, 15.6 mmol) in ethanol (80 mL), an aqueous solution 10 mL of potassium hydroxide (2.5 g, 44.7 mmol) was added dropwise and heated to reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure, and acidified with 6 N HCl. The precipitated product was collected by filtration and recrystallization from ethanol/H_2O (3:1 v/v) to afford compound **1-2a** as a white solid in 95% yield.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.85 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 4.01 (t, J = 6.3 Hz, 2H), 1.74-1.66 (m, 10H), 0.84 (t, J = 6.3Hz, 3H).

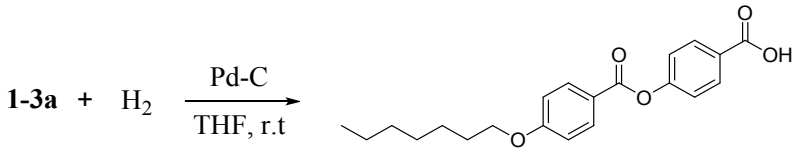
Synthesis of benzyl 4-((4-(heptyloxy)benzoyl)oxy)benzoate (1-3a)



To a stirred solution of **1-2a** (3.0 g, 12.7 mmol), benzyl 4-hydroxybenoate (2.42 g, 10.6 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.13 g, 1.06 mmol) in dry dichloromethane (100 mL), *N*,*N*-dicyclohexylcarbodiimide (DCC) (2.79 g, 13.8 mmol) was added and the reaction mixture stirred at room temperature overnight under nitrogen. The resulting precipitate of dicyclohexylurea (DCU) was filtered off and washed with an excess of dichloromethane (20 mL). The solvent was evaporated and the crude product was purified by silica gel chromatography (*n*-hexane/dichloromethane = 1:1 v/v) to afford compound **1-3** as a white solid in 85% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (m, 4H), 7.41 (m, 5H), 7.27 (m, 2H), 6.94 (d, J = 8.4 Hz, 2H) , 5.36 (s, 2H), 4.10 (t, J = 6.3 Hz, 2H), 1.70-1.61 (m, 2H), 1.41-1.25 (m, 8H), 0.86 (t, J = 6.3 Hz, 3H).

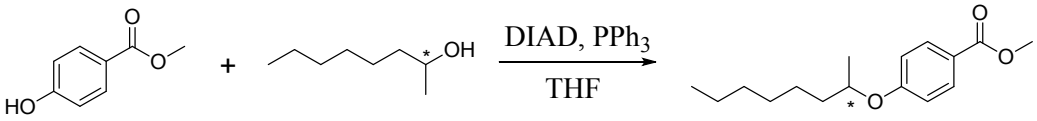
Synthesis of 4-(4-(heptyloxy)benzoyloxy)benzoic acid (1-4a)



To a stirred solution of **1-3a** (2.1 g, 4.5 mmol) in tetrahydrofuran (THF) (80 mL) was added palladium carbon (Pd/C) (0.3 g, 10 wt%). The reaction mixture was stirred at room temperature under hydrogen atmosphere over 10 h. The Pd/C was removed by filtration through Celite and washed with THF. The solvent was evaporated and the crude product recrystallized from ethanol to give compound **1-4a** as a white solid in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (m, 4H), 7.35 (d, J = 8.4 Hz 2H), 6.90 (d, J = 8.4 Hz, 2H), 4.05 (t, J = 6.3 Hz, 2H), 1.70-1.61 (m, 2H), 1.41-1.25 (m, 8H), 0.86 (t, J = 6.3 Hz, 3H). Anal. calcd for $C_{21}H_{24}O_5$: C, 70.77, H, 6.79; found: C, 70.97, H, 6.70 %.

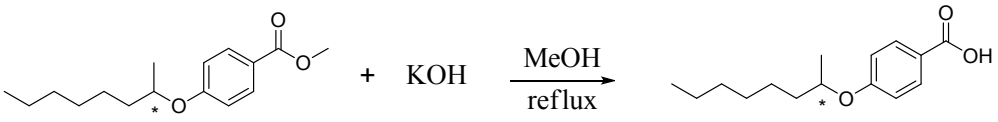
Synthesis of methyl 4-{[(1*R*)-1-methylheptyl]oxy}benzoate (1-1b)



To a solution of methyl 4-hydroxybenzoate (4.0 g, 26.2 mmol), (S)-(+)-2-octanol (3.0 g, 23.0 mmol), and triphenylphosphine (PPh_3) (10.0 g, 38.1 mmol) in dry dichloromethane (20 mL) at 0 °C under nitrogen for 15 min was added dropwise with diisopropyl azodicarboxylate (DIAD) (8.0 g, 39.5 mmol) in dry dichloromethane (10 mL). After the mixture was warmed to room temperature and stirred overnight. The resulting mixture was quenched by water, extracted with dichloromethane, and then dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 40:1 v/v) to afford compound **2-1** as a colorless oil in 75% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.97 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.42 (m, 1H) 3.88 (s, 3H), 1.71-1.57 (m, 2H), 1.42-1.25 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H).

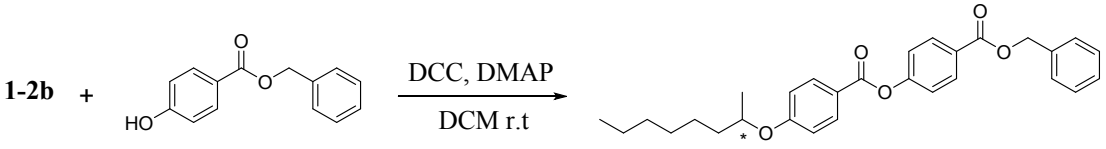
Synthesis of 4-{[(1*R*)-1-methylheptyl]oxy}benzoic acid (1-2b)



The similar manner was followed as that described above for the preparation of **1-2a**. Compound **1-2b** was obtained as a white solid in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 8.4Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.47 (t, 1H), 1.71-1.57 (m, 2H), 1.42-1.25 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H).

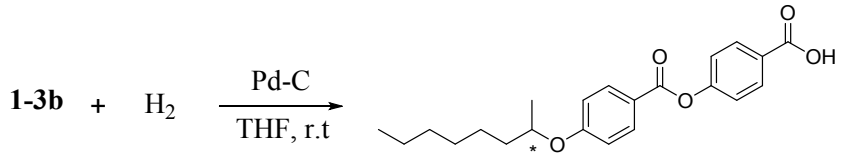
Synthesis of benzyl 4-((4-((1*R*)-1-methylheptyloxy)benzoyl)oxy)benzoate (1-3b)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **1-3b** was obtained as a white solid in 85% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.14 (m, 4H), 7.44-7.32 (m, 5H), 7.27-7.25 (m, 2H), 6.94 (m, 2H), 5.35 (s, 2H), 4.45 (m, 1H), 1.71-1.59 (m, 2H), 1.42-1.25 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H).

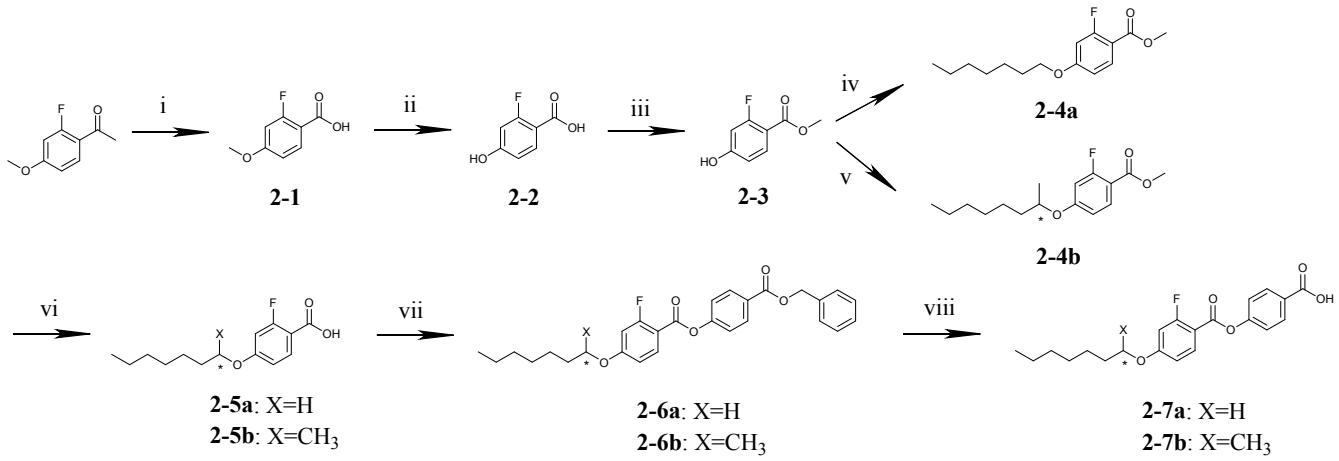
Synthesis of 4-((4-((1*R*)-1-methylheptyloxy)benzoyl)oxy)benzoic acid (1-4b)



The similar manner was followed as that described above for the preparation of **1-4a**. Compound **1-4b** was obtained as a white solid in 94% yield.

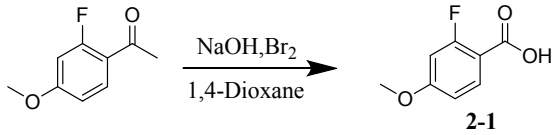
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.13 (m, 4H), 7.32 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.46 (m, 1H), 1.75-1.60 (m, 2H), 1.43-1.27 (m, 11H), 0.86 (t, J = 6.3 Hz, 3H). Anal. calcd for $C_{22}H_{26}O_5$: C, 71.33, H, 7.07; found: C, 71.35, H, 7.00 %.

Scheme S2



Reagent and condition: (i) Br_2, NaOH, 1,4-Dioxane, 0 °C; (ii) BBr_3, DCM, r.t; (iii) Toluene, H_2SO_4, MeOH, 80 °C; (iv) 1-bromoheptane, K_2CO_3, KI, acetone, reflux, 24 h; (v) (S)-(+)-2-octanol, PPh_3, DIAD, THF, 0 °C, 15 min, then r.t., overnight; (vi)KOH, MeOH, Reflux; (vii) DCC, DMAP, DCM, r.t; (viii) H_2, Pd/C, THF, r.t.

Synthesis of 2-fluoro-4-methoxybenzoic acid, 2-1

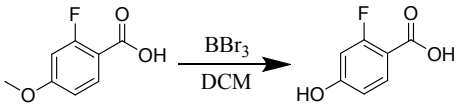


2-1

Into a 500 ml round bottom flask 2-fluoro-4-methoxyacetophenone (5 g, 29.8 mmol) were stirred and dissolved in 1,4-Dioxane. After dropping NaOH (3.57 g, 89.3 mmol) aqueous slowly and dropping Bromine (4.75 g, 29.8 mmol) under ice bath at room temperature. The reaction was extracted with water / DCM and water layer was acidified to pH = 3 with diluted HCl and the residue was washed by DI water to give white solid of **3-1**, yield 90 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：7.9 (d, 1H, Ar-H), 7.83-7.78 (dd, *J* = 7.5, 2.2 Hz 1H, Ar-H), 7.02 (t, *J* = 6.1 Hz 1H, Ar-H), 3.97 (s, 3H, -OCH_3).

Synthesis of 2-fluoro-4-hydroxybenzoic acid, 2-2

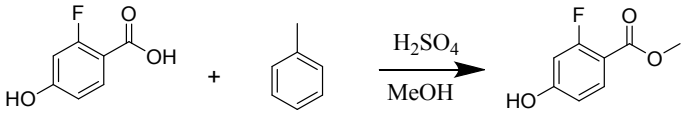


2-2

Into a 250 ml round bottom two-neck flask **2-1** (4.9 g, 28.8 mmol) were mixed in dry CH_2Cl_2 (30 mL) under nitrogen and cooled to -78 °C. Then BBr_3 (14.4 g, 57.6 mmol) was injected to the previous solution slowly and the temperature of the reaction go to room temperature for 12 hrs. The reaction mixture was quenched with 2N NaOH until the solution became clear and the residue solvent was neutralized by HCl. The mixture was extracted with water / ethyl acetate and organic liquid layer was dried over anhydrous $MgSO_4$. Removal of the solvent by evaporation under reduced pressure to give white solid of **2-2**, yield 99 %.

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm)：12.74 (s, 1H, Ar-COOH), 10.74 (s, 1H, Ar-OH), 7.62-7.58 (m, 1H, Ar-H), 7.01 (t, *J* = 8.4 Hz 2H, Ar-H).

Synthesis of methyl 2-fluoro-4-hydroxybenzoate, 2-3

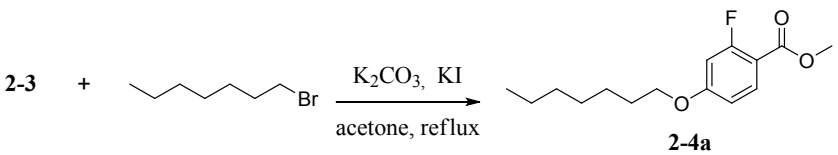


2-3

Into a 500 ml round bottom flask compound **2-2** (5 g, 32 mmol), H_2SO_4 (7 ml) and MeOH (250 ml) were reflux at 90 °C. The reaction was removed the solvent by evaporation under reduced pressure and then extracted by water / ethyl acetate. The organic liquid layer was dried over anhydrous $MgSO_4$. The residue was purified by column chromatography (n-hexane / ethyl acetate) to give a white solid of **2-3**, yield 80 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：7.76 (d, *J* = 8.2 Hz 1H, Ar-H), 7.74 (s, 1H, Ar-H), 7.06 (d, *J* = 8.1 Hz 1H, Ar-H), 6.10 (s, 1H, Ar-OH), 3.91 (s, 3H, -OCH_3).

Synthesis of methyl 2-fluoro-4-(heptyloxy)benzoate, 2-4a

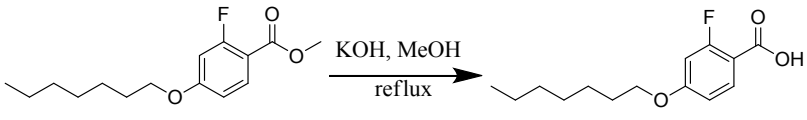


2-4a

Into a 500 ml round bottom compound **2-3** (1.5 g, 8.8 mmol), K_2CO_3 (2.36 g, 17.1 mmol) and potassium iodide (0.05 g) were stirred at reflux temperature in 200 ml of acetone and dropped 1-bromohexane (1.9 g, 10.6 mmol) slowly for overnight. After cooling to room temperature, the solvent was removed under reduced pressure. Then, the mixture was extracted with water / DCM and organic liquid layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (n-hexane/ ethyl acetate) to give a white solid of **2-4a**, yield 75%.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：7.86 (t, *J* = 8.7 Hz 1H, Ar-H), 6.69 (dd, 1H, Ar-H), 6.61 (dd, 1H, Ar-H), 3.97 (t, *J* = 6.3 Hz 2H, -OCH2-), 3.87 (s, 3H, -OCH3), 1.77 (m, 2H, -CH_2-), 1.45-1.20 (m, 8H, -CH_2-), 0.87 (t, *J* = 6.3 Hz 3H, -CH_3).

Synthesis of 2-fluoro-4-(heptyloxy)benzoic acid, 2-5a

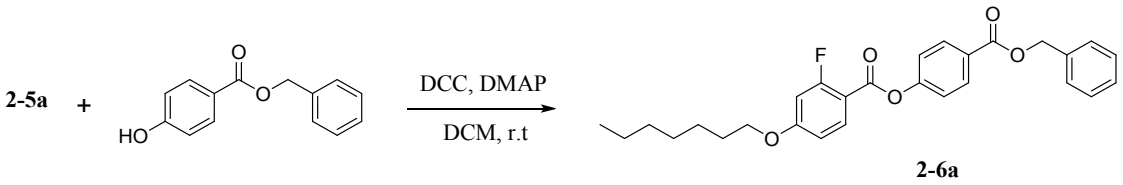


2-5a

Into a 500 ml round bottom two-neck flask compound **2-4a** (2 g, 11.2 mmol) and KOH (3.0 g, 53.1 mmol) were stirred with MeOH under reflux at 90 ^{O}C. After removal of the solvent by evaporation under reduced pressure and the residue was acidified to pH= 3 to give white solid of **2-5a**, yield 85 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：11.02 (s, 1H, Ar-COOH), 8.01 (d, *J* = 8.4 Hz 1H, Ar-H), 7.35 (d, *J* = 8.7 Hz 1H, Ar-H), 6.92 (d, *J* = 9.0 Hz 1H, Ar-H), 3.97 (t, *J* = 6.3 Hz 2H, -OCH2-), 1.77 (m, 2H, -CH_2-), 1.45-1.20 (m, 8H, -CH_2-), 0.87 (t, *J* = 6.3 Hz 3H, -CH_3).

Synthesis of 4-((benzyloxy)carbonyl)phenyl 2-fluoro-4-(heptyloxy)benzoate, 2-6a

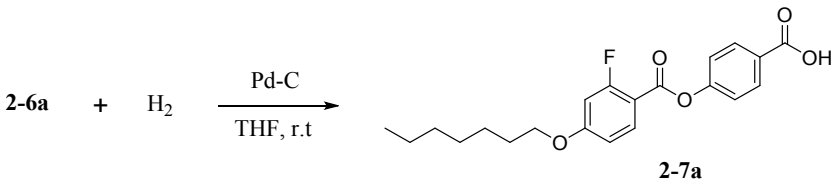


2-6a

Into a 500 ml round bottom two-neck flask compound **2-5a** (2 g, 7.86 mmol), benzyl 4-hydroxybenzoate (2.1 g, 7.3 mmol), DMAP (0.04 g, 0.32 mmol) and DCC (3.68 g, 17.8 mmol) were mixed with DCM and the mixture was stirred at room temperature. The precipitated DCU was filtered off and washed with an excess of DCM (40 ml). The filtrate was extracted with water / DCM and organic liquid layer was dried over anhydrous $MgSO_4$, and removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography (n-hexane / DCM) to give a light yellow solid of **2-6a**, yield 78 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：8.11 (d, *J* = 9.6 Hz 2H, Ar-H), 8.01 (t, *J* = 8.4 Hz 1H, Ar-H), 7.44-7.34 (m, 4H, Ar-H), 7.32-7.22 (m, 3H, Ar-H), 6.74 (dd, 1H, Ar-H), 6.65 (dd, 1H, Ar-H), 6.70 (dd, 2H, Ar-H), 5.35(s, 1H, -CH_2Ph), 4.01 (t, *J* = 6.0 Hz 2H, -OCH_2-), 1.77 (q, 2H, -CH_2-), 1.50-1.31 (m, 8H, -CH_2-), 1.02 (t, *J* = 6.0 Hz 3H, -CH_3).

Synthesis of 4-((2-fluoro-4-(heptyloxy)benzoyl)oxy)benzoic acid, 2-7a

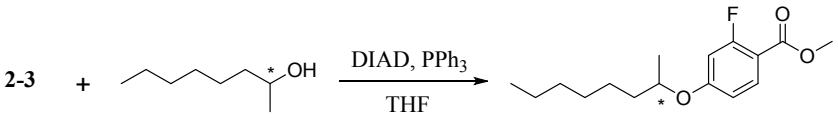


2-7a

Into a 500 ml round bottom two-neck flask compound **2-6a** (2.8 g, 5.8 mmol) and 10 % Pd/C (0.1 g) catalyst were stirred in THF (150 ml) under hydrogen at room temperature for overnight. 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 light yellow solid of **2-7a**, yield 88 %. Anal. calcd for $C_{21}H_{23}FO_5$: C, 67.37, H, 6.19; found: C, 67.49, H, 6.10 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：11.01 (s, 1H, Ar-COOH), 8.17 (d, *J* = 9.6 Hz 2H, Ar-H), 8.04 (t, *J* = 8.4 Hz 1H, Ar-H), 7.33 (d, *J* = 8.7 Hz 2H, Ar-H), 6.77 (dd, 1H, Ar-H), 6.68 (dd, 1H, Ar-H), 4.03 (t, *J* = 6.0 Hz 2H, -OCH_2-), 1.86 (t, 2H, -CH_2-), 1.47-1.27 (m, 8H, -CH_2-), 0.86 (t, *J* = 6.3 Hz 3H, -CH_3)

Synthesis of (S)-methyl 2-fluoro-4-(octan-2-yloxy)benzoate, 2-4b

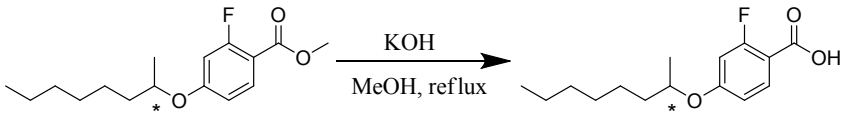


2-4b

Into a 500 ml round bottom two-neck flask compound **2-3** (5 g, 29.4 mmol) and PPh_3 (8.89 g, 33.8 mmol) were under vacuum for 1 hr and dry THF were injected under nitrogen. After 10 minutes, injecting (S)-(+)-2-octanol (4.6 g, 35.2 mmol) and the mixture were stirred for 15 minutes and injected DIAD (8.9 g, 44 mmol). Removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography (n-hexane / DCM) to give a light yellow solid of **2-4b**, yield 85 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：7.92 (s, 1H, Ar-H), 7.25 (d, *J* = 8.7 Hz 1H, Ar-H), 6.87 (d, *J* = 9.0 Hz 1H, Ar-H), 4.30 (m, 1H, -OCH-), 3.84 (s, 3H, -OCH_3), 1.71 (m, 1H, -CH_2-), 1.57 (m, 1H, -CH_2-), 1.42-1.25 (m, 11H, -CH_2CH_3), 0.83 (t, *J* = 6.3 Hz 3H, -CH_3).

Synthesis of (S)-2-fluoro-4-(octan-2-yloxy)benzoic acid, 2-5b

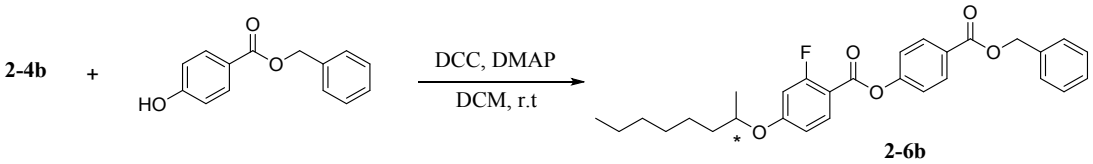


2-5b

Into a 500 ml round bottom two-neck flask compound **2-4b** (5 g, 17.7 mmol) and KOH (3.0 g, 53.1 mmol) were stirred with MeOH under reflux at 90 ^{O}C. After removal of the solvent by evaporation under reduced pressure and the residue was acidified to pH = 3 to give light yellow solid of **2-5b**, yield 82 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：11.01 (s, 1H, Ar-COOH), 8.02 (d, *J* = 6.5 Hz 1H, Ar-H), 7.35 (d, *J* = 9.6 Hz 1H, Ar-H), 6.97 (d, *J* = 6.9 Hz 1H, Ar-H), 4.40 (s, 1H, -OCH-), 1.70 (m, 1H, -CH_2-), 1.61 (m, 1H, -CH_2-), 1.41-1.26 (m, 11H, -CH_2CH_3), 0.86 (t, *J* = 6.3 Hz 3H, -CH_3).

Synthesis of (S)-benzyl 4-((4-(octan-2-yloxy)benzoyl)oxy)benzoate, 2-6b

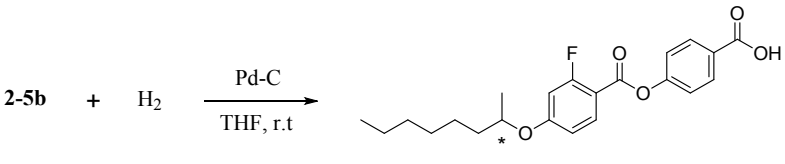


2-6b

Into a 500 ml round bottom two-neck flask compound **2-5b** (1.0 g, 3.7 mmol), benzyl 4-hydroxybenzoate (0.8 g, 3.5 mmol), DMAP (0.02 g, 0.16 mmol) and DCC (1.5 g, 7.4 mmol) were mixed with DCM and the mixture was stirred at room temperature. The precipitated DCU was filtered off and washed with an excess of DCM (40 ml). The filtrate was extracted with water / DCM and organic liquid layer was dried over anhydrous $MgSO_4$, and removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography (n-hexane / DCM) to give a white solid of **2-6b**, yield 80 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：8.13 (d, *J* = 9.6 Hz 2H, Ar-H), 8.02 (t, *J* = 8.4 Hz 1H, Ar-H), 7.45-7.30 (m, 5H, Ar-H), 7.29-7.25 (m, 2H, Ar-H), 6.74 (dd, 1H, Ar-H), 6.66 (dd, 1H, Ar-H), 5.37 (s, 1H, -O$\underline{CH_2}$Ph), 4.40 (m, 1H,-OCH-), 1.70 (m, 1H, -CH_2-), 1.61 (m, 1H, -CH_2-), 1.41-1.26 (m,11H, -CH_2CH_3), 0.86 (t, *J* = 6.3 Hz 3H, -CH_3).

Synthesis of (S)-4-((4-(octan-2-yloxy)benzoyl)oxy)benzoic acid, 2-7b

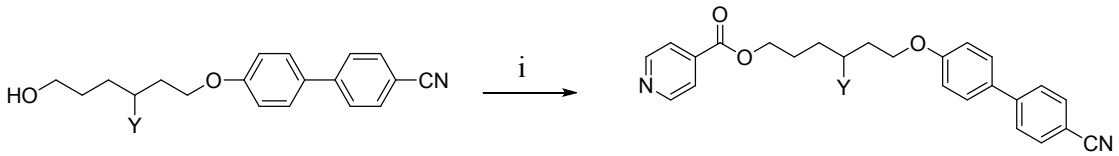


2-7b

Into a 500 ml round bottom two-neck flask compound **2** (2.0 g, 4.3mmol) and 10 % Pd/C (0.2 g) catalyst were stirred in THF (200 ml) under hydrogen at room temperature for overnight. 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 light yellow solid of **2-7b**, yield 89 %.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)：11.01 (s, 1H, Ar-COOH), 8.06 (d, 2H, Ar-H), 8.02 (t, *J* = 8.4 Hz 1H, Ar-H), 7.32 (m, 2H, Ar-H), 6.97 (dd, *J* = 9.0 Hz 1H, Ar-H), 6.74 (dd, *J* = 9.0 Hz 1H, Ar-H), 6.68 (dd, *J* = 9.0 Hz 1H, Ar-H), 4.43 (m, 1H, -OCH-), 1.70 (m, 1H, -CH_2-), 1.61 (m, 1H, -CH_2-), 1.41-1.26 (m, 11H, -CH_2CH_3), 0.86 (t, *J* = 6.3 Hz 3H, -CH_3). Anal. calcd for $C_{22}H_{25}FO_5$: C, 68.03, H, 6.49; found: C, 68.33, H, 6.41 %.

Scheme S3



3-1a: Y = H
3-1b: Y = CH_3

3-2a: Y = H
3-2b: Y = CH_3

Reagents and conditions: (i) isonicotinoyl chloride hydrochloride, Et3N, DCM.

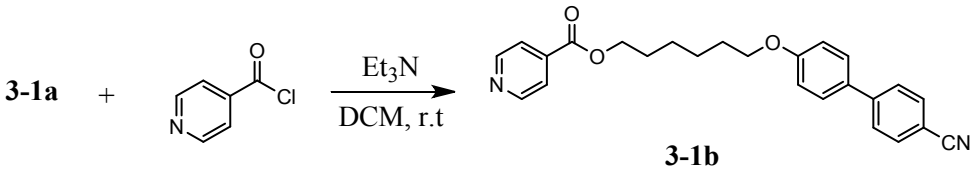
Synthesis of 6-[(4-cyano-4'-biphenylyl)oxy]hexanol (3-1a)

The synthetic procedure of compound **3-1a** has been reported in reference 33 (see supporting information Scheme S2).

Synthesis of (S)-6-[(4-cyano-4'-biphenylyl)oxy]-4-methylhexanol (3-1b)

The synthetic procedure of compound **3-1b** has been reported in reference 33 (see supporting information Scheme S2).

Synthesis of 6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl isonicotinate (3-2a)



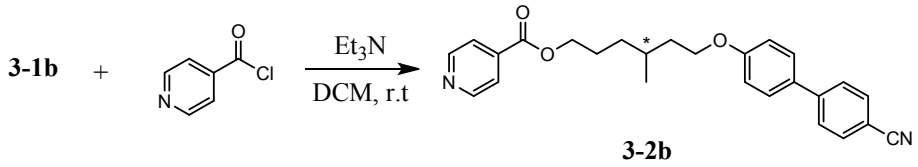
3-1b

A mixture of **3-1a** (2g, 6.78 mmol), isonicotinoyl chloride hydrochloride (1.44 g, 8.15 mmol) and triethylamine (2.36 ml) was dissolved in dry dichloromethane (DCM) under nitrogen for 8 h at room temperature. After work up, the solvent was extracted with water/DCM and organic liquid layer was dried over anhydrous magnesium sulphate. After removal of the solvent by

evaporation under reduced pressure, the residue was purified by column chromatography and recrystallized from THF/hexane to afford compound **3-2a** as a white solid in 70% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.96 (d, J=4.21Hz, 2H, Ar-H), 7.81 (d, 4.2Hz, 2H, Ar-H), 7.66 (q, J=8.9Hz, 4H, Ar-H), 7.41 (d, J=8.8Hz, 2H, Ar-H), 7.02 (d, J=8.9Hz, 2H, Ar-H), 4.43 (t, J=6.3Hz, 2H, -OCH_2), 4.11 (t, J=6.4Hz, 2H, -OCH_2), 1.82 (m, 4H, -CH_2), 1.61 (m, 4H, -CH_2-). Anal. calcd for $C_{25}H_{24}N_2O_3$: C, 74.98, H, 6.04, N, 7.00; found: C, 74.97, H, 6.29, N, 7.01 %.

Synthesis of (S)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)-4-methylhexyl isonicotinate (3-2b)



3-2b

The similar manner was followed as that described above for the preparation of **3-1b**. Compound **3-2b** was obtained as a light yellow solid in 63% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.77 (d, J=4.2Hz, 2H, Ar-H), 7.91 (m, 6H, Ar-H), 7.69 (d, J=8.8Hz, 2H, Ar-H), 7.02 (d, J=8.9Hz, 2H, Ar-H), 4.41 (t, J=6.3Hz, 2H, -OCH_2), 4.01(t, J=6.4Hz, 2H, -OCH_2), 1.82-1.21 (m, 7H, -CH_2), 1.13 (d, J=6.3Hz, 3H, -CH_3). Anal. calcd for $C_{26}H_{26}N_2O_3$: C, 75.34, H, 6.32, N, 6.76; found: C, 75.09, H, 6.44, N, 6.69 %.

XRD investigations

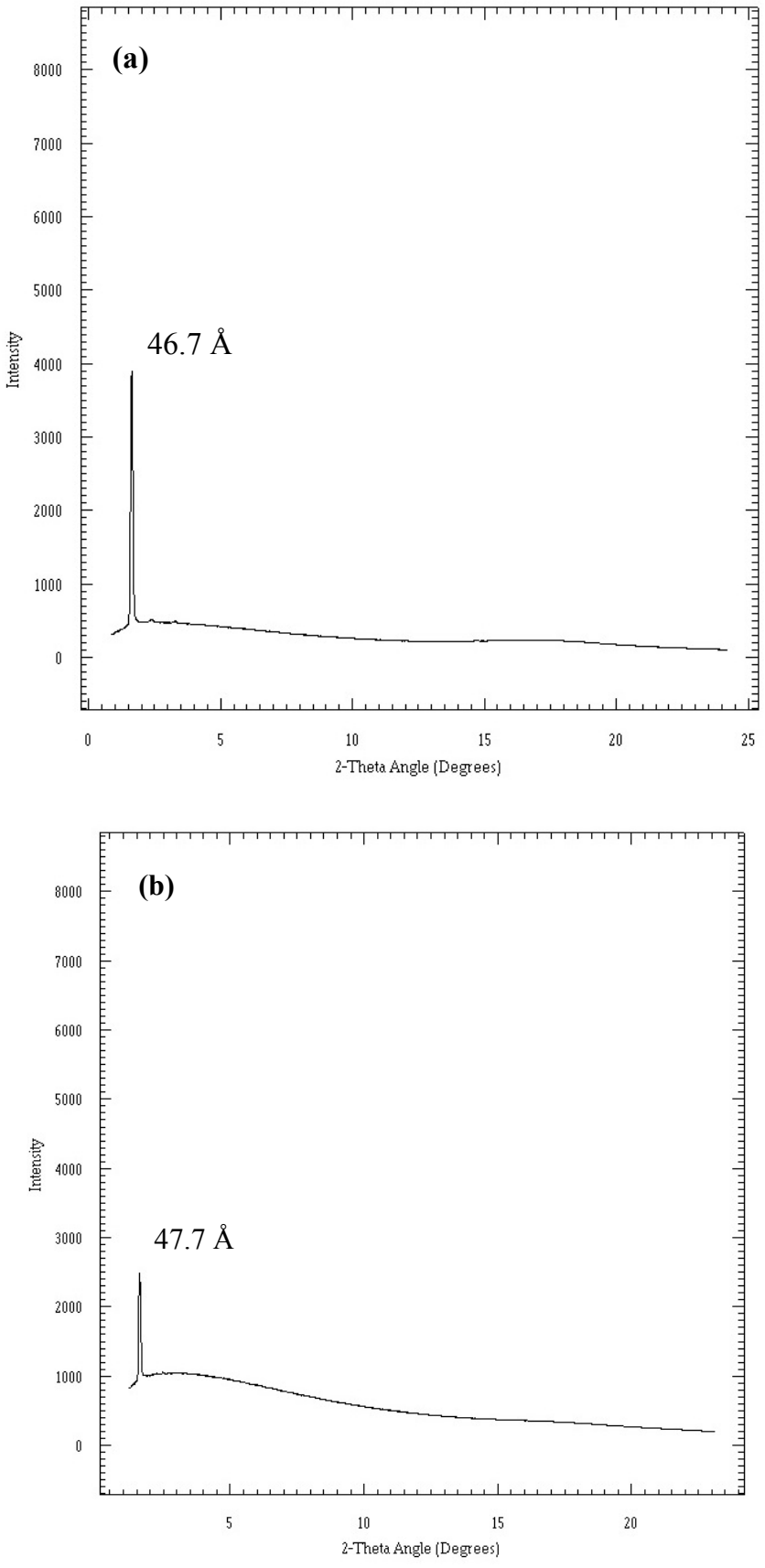


Fig. S1 Powder XRD Analyses of complexes (a) **AF*/P** (1:1 mol.) at 50.2 °C, (b) **A*/P*** (1:1 mol.) at 52.1 °C.

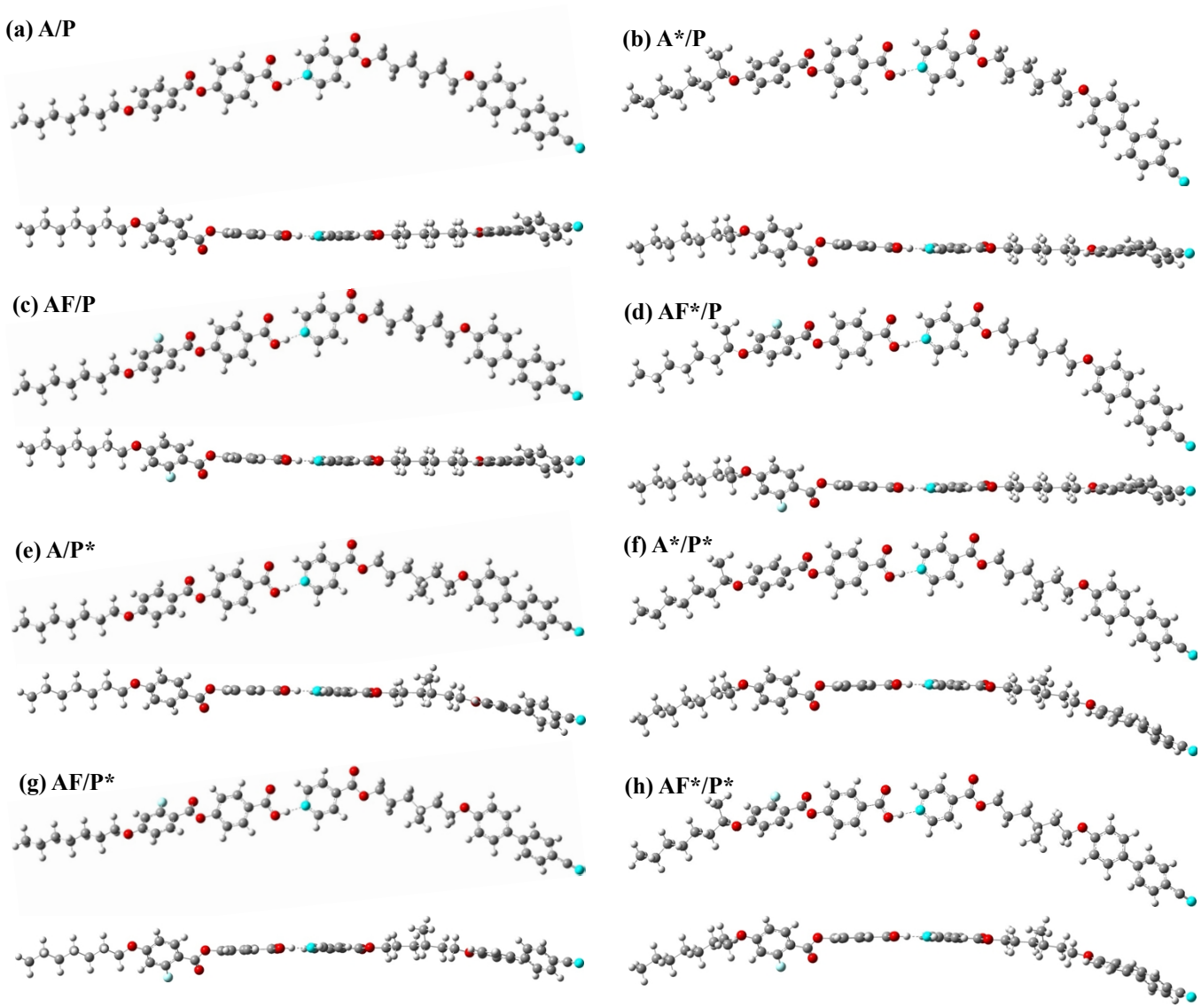


Fig. S2 Molecular models of the lowest energy conformations of complexes **D/P** and **D/P*** (where **D** = **A**, **A***, **AF** and **AF***). At molar ratio of H-acceptors and H-donors is 1:1.

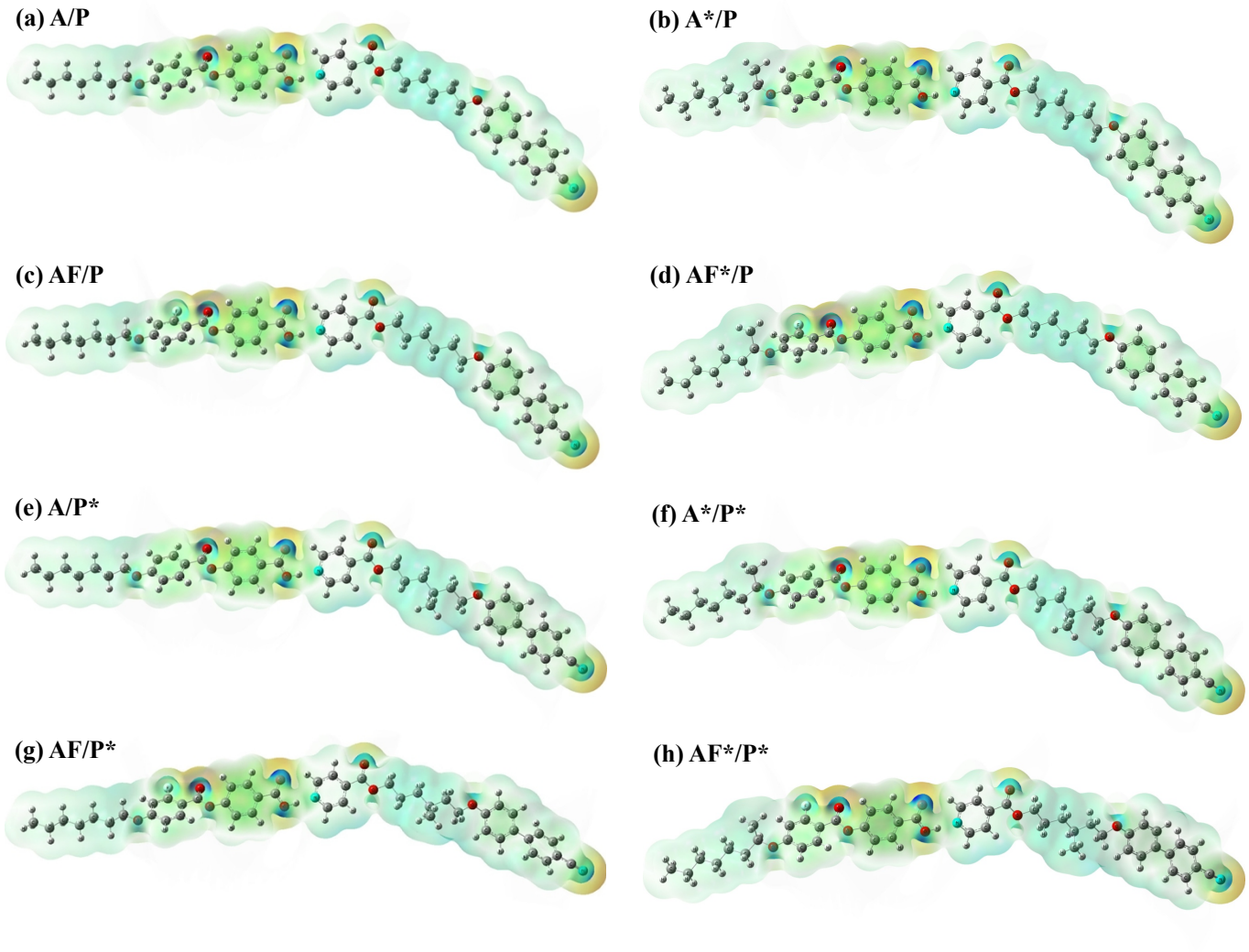


Fig. S3 Molecular electrostatic potential mapped on the electron density of the lowest energy structure for complexes **D/P** and **D/P*** (where **D** = **A**, **A***, **AF** and **AF***). At molar ratio of H-acceptors and H-donors is 1:1.

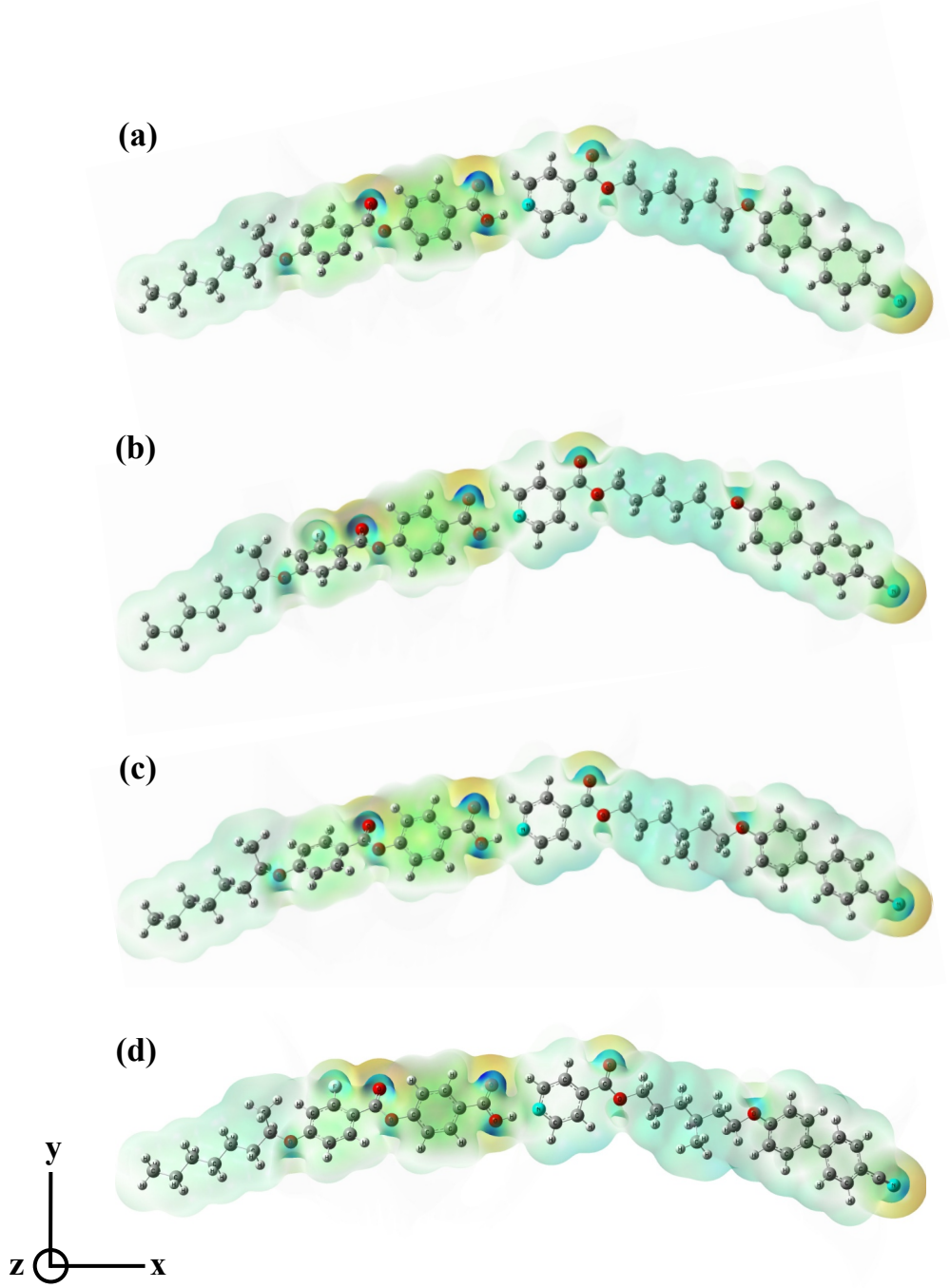


Fig. S4 Molecular electrostatic potential mapped on the electron density of the lowest energy diad liquid crystal structures: (a) **A*/P** (1:1 mol.), (b) **AF*/P** (1:1 mol.), (c) **A*/P*** (1:1 mol.) and (d) **AF*/P*** (1:1 mol.). The electron density was visualized continuously increases from red (electron-rich) > orange > yellow > green > blue (electron-poor).

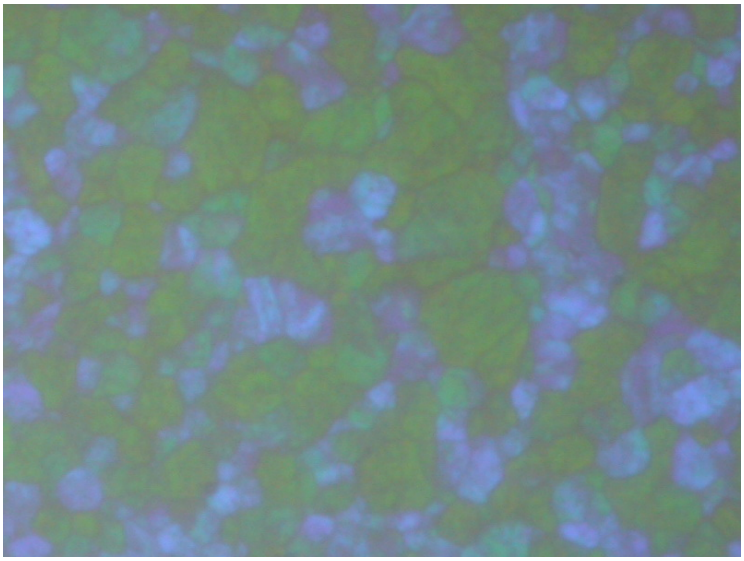


Fig. S5 An expended POM texture shows the phase transition process of the asymmetric H-bonded dimeric complex **A*/P** (3:1 mol.). On cooling rate 0.5 °Cmin^{-1}. The blue phase I (platelet textures with different colors and fine stripes) at 102.8°C.

Table S1 XRD data of complexes **A/P**, **A*/P**, **AF/P**, **AF*/P**, **A/P***, **A*/P*** and **AF/P*** (1:1 mol.)

Complex	Cooling temp. (°C)	Mesophase	d-spacing (Å)	Miller index (a b c)	Molecular length L(Å)
A/P	110.1	SmA	48.1	(001)	47.4
A*/P	88.3	SmA	47.5	(001)	46.7
AF/P	87.4	SmA	47.8	(001)	47.4
AF*/P	55.6	SmA	46.7	(001)	46.7
A/P*	91.2	SmA	48.5	(001)	48.1
A*/P*	52.1	SmA	47.7	(001)	46.5
AF/P*	70.0	SmA	49.1	(001)	48.0

Theoretical simulation

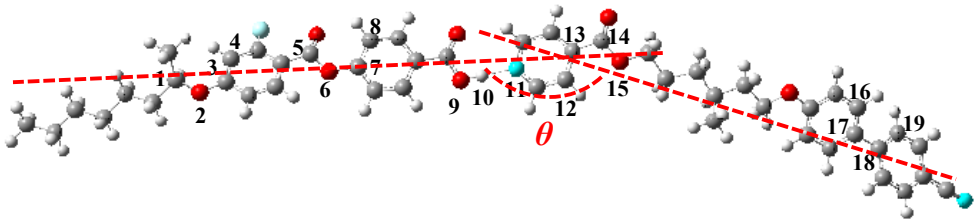


Table S2 Parameters of length, breath, biaxiality, bend angle and dihedral angle for complexes **D/P** and **D/P*** (where **D** = **A**, **A***, **AF** and **AF***)with 1:1 molar ratio of H-acceptors and H-donors

Complex	Hydrogen bond length	Length	Breadth	Breadth	Biaxial parameter	Bent angle	Dihedral angle					HTP
	L (Å)	L (Å)	W1 (Å)	W2 (Å)	W1 /W2	(deg)	1, 2, 3, 4 (deg)	5, 6, 7, 8 (deg)	9, 10, 11 (deg)	12, 13, 14, 15 (deg)	16, 17, 18, 19 (deg)	(μm^{-1})
A/P	1.7	47.4	9.0	3.9	2.31	156.7	-0.2	43.3	178.7	0.0	-32.2	
A*/P	1.7	46.7	9.5	4.9	1.94	152.9	-3.1	44.9	178.3	1.0	-32.3	2.56
AF/P	1.7	47.4	8.9	5.6	1.59	156.7	-0.3	45.2	179.0	0.0	-32.1	
AF*/P	1.7	46.7	9.6	4.9	1.96	150.6	-3.1	45.7	178.5	0.9	-32.1	2.50
A/P*	1.7	48.1	7.8	5.9	1.32	162.0	-0.1	45.5	179.3	-0.5	-32.4	2.44
A*/P*	1.7	46.5	9.3	6.0	1.55	152.5	-1.4	44.8	178.8	2.0	-32.1	2.78
AF/P*	1.7	48.0	8.0	5.9	1.36	160.8	-0.1	46.1	179.0	-1.0	-32.4	
AF*/P*	1.7	46.4	9.4	6.2	1.52	149.9	-1.3	46.6	178.5	1.2	-32.2	2.94
A*-P[a]		41.9	13.2	5.8	2.28	126.5						3.05
A-P*[a]		45.0	10.8	6.4	1.69	141.1						2.97
A*-P*[a]		43.2	12.1	6.5	1.86	132.1						3.22

[a] The analogous covalent diads (see reference 32 in main text).

Table S3 Dipole moments of complexes **D/P** and **D/P*** (where **D** = **A**, **A***, **AF** and **AF***) with 1:1 molar ratio of H-acceptors and H-donors

Complex	X	Y	Z	Total (Debye)
A/P	-5.7	0.6	-0.6	5.8
A*/P	5.9	0.3	1.0	6.0
AF/P	-6.0	1.5	-1.3	6.4
AF*/P	-6.2	1.2	-1.8	6.6
A/P*	6.2	1.0	1.8	6.5
A*/P*	6.1	0.2	2.7	6.7
AF/P*	-6.5	1.7	-2.5	7.2
AF*/P*	-6.5	0.7	-3.5	7.4
A*-P[a]	-12.0	1.0	-2.2	12.3
A-P*[a]	-12.6	1.7	-3.0	13.1
A*-P*[a]	12.7	1.6	3.1	13.2

[a] The analogous covalent diads (see reference 33).

Table S4 Phase transition temperatures (°C) and enthalpies (J/g) of complexes **D/P** and **D/P*** (where **D** = **A**, **A***, **AF** and **AF***) with various molar ratios of H-acceptors and H-donors upon heating

Complex	Molar ratio (H-donor vs. H-acceptor)	Phase transition temperatures (°C) [Enthalpies (J/g)]
A*/P	1 : 1	Cr 107.4 [1.21] SmA 134.8 [3.59] N* 152.9 [0.37] Iso
	2 : 1	Cr 102.3 [1.05] SmA 124.9 [4.31] N* 134.2 [0.59] Iso
	3 : 1	Cr 89.5 [2.31] SmA 97.4 [4.61] N* 109.6 [1.01] Iso
	4 : 1	Cr 124.7 [3.32] N* 153.0 [4.40] Iso
A*/P*	1 : 1	Cr 85.3 [2.97] SmA 92.7 [3.39] N* 120.7 [0.47] Iso
	2 : 1	Cr 87.5 [3.42] SmA 95.6 [2.90] N* 125.1 [0.45] Iso
	3 : 1	Cr 90.1 [2.40] SmA 125.2 [5.51] N* 132.4 [0.73] Iso
	4 : 1	Cr 91.5 [1.32] N* 143.0 [3.12] Iso
AF*/P	1 : 1	Cr 85.1 [0.97] SmA 89.4 [0.33] N* 105.7 [0.56] Iso
	2 : 1	Cr 88.4 [0.45] SmA 91.2 [0.41] N* 107.6 [0.65] Iso
	3 : 1	Cr 91.1 [0.69] SmA 106.5 [0.54] N* 122.7 [0.80] Iso
	4 : 1	Cr 95.6 [0.62] N* 130.9 [0.81] Iso
AF*/P*	1 : 1	Cr 63.1 [1.40] N* 84.4 [0.54] Iso
	2 : 1	Cr 75.6 [0.90] N* 109.8 [0.71] Iso
	3 : 1	Cr 81.3 [1.10] N* 117.1 [0.55] Iso
	4 : 1	Cr 84.1 [1.01] N* 116.0 [0.75] Iso
A/P	1 : 1	Cr 121.7 [3.14] SmA 149.8 [3.11] N 190.1 [4.87] Iso
AF/P	1 : 1	Cr 110.8 [3.55] SmA 152.3 [4.73] N 173.5 [2.41] Iso
A/P*	1 : 1	Cr 118.4 [3.18] SmA 160.1 [4.21] N* 179.2 [3.90] Iso
AF/P*	1 : 1	Cr 102.3 [3.22] SmA 131.5 [3.60] N* 158.8 [4.45] Iso

Table S5 Phase transition temperatures (°C) and enthalpies (J/g) of pure components **P**, **P***, **A**, **A***, **AF** and **AF***

Compound	Phase transition temperatures (°C) [Enthalpies (J/g)]
P	Cr 99.3 [14.68] Iso Iso 67.3 [15.27] Cr
P*	Cr 76.1 [0.52] Iso Iso -5.0 [0.60] Cr
A	Cr 168.1 [6.34] N 227.0 [5.36] Iso Iso 226.0 [5.31] N 160.9 [5.38] Cr
A*	Cr 118.3 [5.43] N* 163.9 [6.53] Iso Iso 162.4 [4.81] N 115.9 [4.89] Cr
AF	Cr 128.3 [11.66] N 218.9 [5.06] Iso Iso 220.9 [4.81] N 105.47 [11.41] Cr
AF*	Cr 106.5 [12.26] N* 147.0 [7.51] Iso Iso 144.0 [3.22] N* 104.3 [16.46] Cr