Supporting Information for

Luminescent liquid crystals bearing aggregation-induced emission active tetraphenylthiophene fluorophore

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General considerations

2,3,4,5-Tetrabromothiophene, (3,4-dimethoxyphenyl)boronic acid, (4-methoxyphenyl)boronic acid, tetrakis(triphenylphosphine)palladium, methyl gallate, boron tribromide, 1-bromododecane, 1-bromodecane, 1-bromooctane, 4-dimethylaminopyridine (DMAP), diisopropylcarbodiimide (DIC), 1,4-dioxane, methyl alcohol, ethanol, hydrochloric acid, potassium hydroxide, potassium carbonate, sodium chloride, magnesium sulfate, sodium sulfate were purchased from Aladdin Inc (Shanghai). Prior to use, dichloromethane (DCM) and acetone were distilled from CaH_2 under nitrogen. Tetrahydrofuran (THF) was distilled from sodium-benzophenoneketyl under nitrogen. Other chemical reagents were used as received without further purification. All non-aqueous reactions were conducted in oven-dried glassware, under a dry nitrogen atmosphere. All flash chromatography were performed by using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm). Distilled water was used in all the experiments.

In order to confirm the synthesized compounds, nuclear magnetic resonance (NMR) experiments of all compounds were performed. All ^{1}H spectra and ^{13}C NMR spectra were obtained using either a Bruker HW600 MHz spectrometer (AVANCE AV-600) or a Bruker HW300 MHz spectrometer (AVANCE AV-300) to determine molecular structure, with deuterated chloroform ($CDCl_3$, internal reference 7.26 ppm) or Dimethyl sulfoxide-d (DMSO-d, internal reference 2.54 ppm) as solvents, with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were measured using a Maldi-Tof MS (Bruker microflex mass spectrometer) with HPLC grade THF as the solvent and HCCA as the test matrix.

Thermogravimetric analysis (TGA) was carried out by using Perkin-Elmer TGA7 under nitrogen atmosphere at a heating rate of 10 °C/ min from 25 to 800 °C, and with the flow rate of 100 mL/min. The thermotropic liquid crystalline properties of compounds were investigated by variable-temperature polarized optical microscope (POM) and differential scanning calorimetry (DSC). Polarized optical microscope (POM) observations of the liquid crystalline textures of the compounds were performed on an Olympus BX53P microscope equipped with a Mettler PF82HT hot stage. The images were captured using a Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) at a heating rate of 10 °C/min under a nitrogen atmosphere from -50 °C to 120 °C. X-ray scattering experiments were performed with a

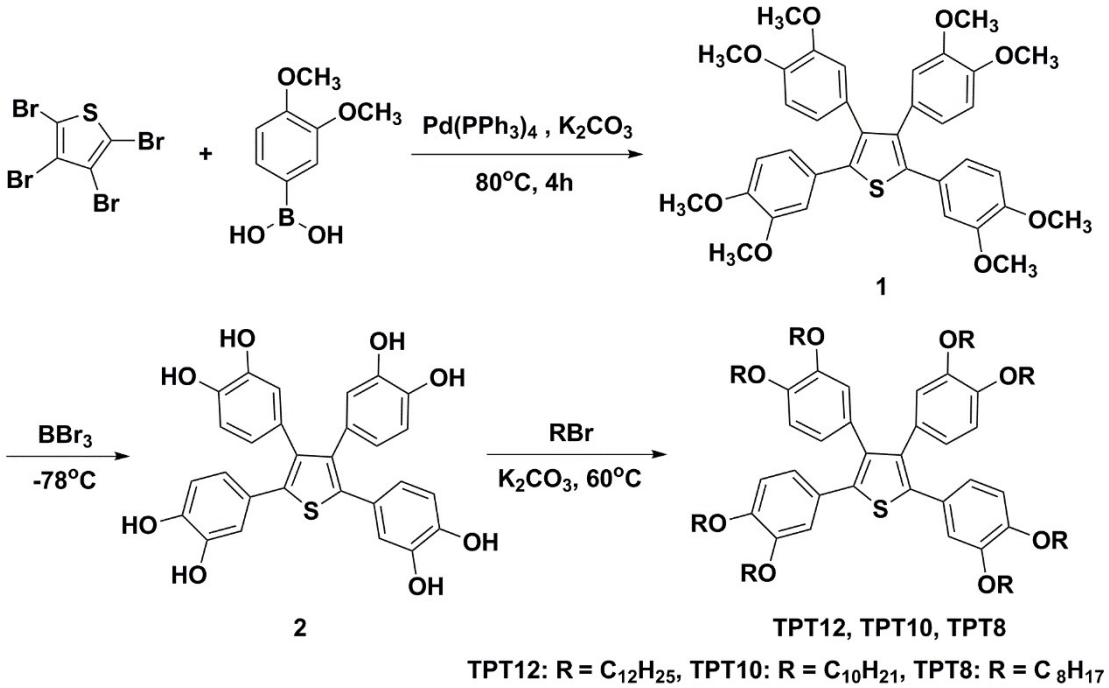
high-flux small angle X-ray scattering (SAXS) instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system and a temperature control unit (Anton Paar TCS300). At each single steady temperature, small angle X-ray scattering was simultaneously recorded on an imaging-plate (IP), which extended to high-angle range (the q range covered by the IP was from 0.06 to 29 nm^{-1}, $q = 4\pi(\sin\theta)/\lambda$, where the wavelength λ is 0.1542 nm of Cu-Kα radiation and 2θ is the scattering angle) at 40 kV and 40 mA for 30 min.

UV-vis spectra were recorded on a UV-2600 ultraviolet-visible spectrophotometer (UV/VIS spectrometer) with the wavelength ranging from 190 nm to 1100 nm. Fluorescence emission spectra were performed on Horiba Scientific Fluoromax spectrofluorometer 4 with the excitation wavelength ranging from 220 to 660 nm and the emission wavelength ranging from 290 to 850 nm.

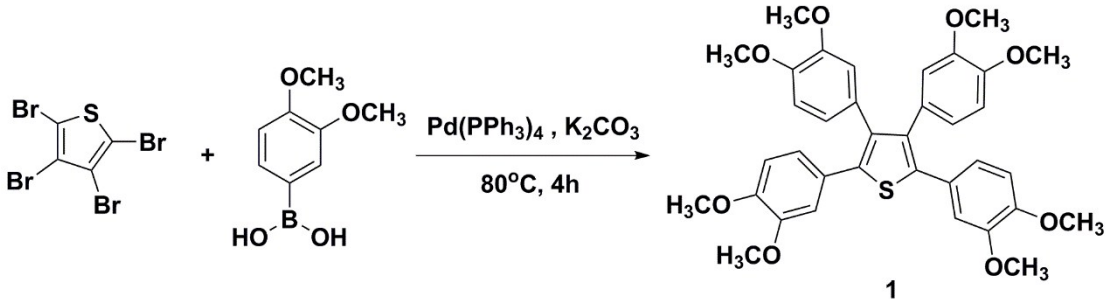
Cyclic Voltammetry experiments were conducted by using a CHI620E (Shanghai Chenhua Corporation). Electrochemical workstation. Gelation property was measured by the ‘‘stable to inversion of a test tube’’ method. The morphologies of the specimens were observed by field emission scanning electron microscopy (FE-SEM, Navo Nano SEM450).

Detailed experimental procedures:

I. Synthesis and characterization of TPTn (n=12, 10, 8)



Scheme S1 Synthetic routes of compound **TPTn (n=12, 10, 8)**



2,3,4,5-Tetrakis(3,4-dimethoxyphenyl)thiophene (1).

2,3,4,5-Tetrabromothiophene (400 mg, 1.0 mmol) and tetra(triphenylphosphorus) palladium (700 mg, 0.6 mmol) were dissolved in 1,4-dioxane (20 mL) in a 100 mL round-bottom flask equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature. 3,4-Dimethoxyphenyl boric acid (1100 mg, 6.0 mmol) and aqueous potassium carbonate solution (2 M, 3.0 mL) were then added into the above reaction solution. The resulting mixture was stirred at 80 °C for 18 h under nitrogen atmosphere. After cooling to room temperature, the solution was concentrated by rotary evaporation. The crude mixture was extracted with CH_2Cl_2 and distilled

water (v:v=1:1) for three times (60 mL× 3). The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was subjected to purification by flash column chromatography (petroleum ether : ethyl acetate = 5/1) to give the desired product **1** (565 mg, yield: 90.0 %) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.92 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 2.0 Hz, 2H), 6.68 (d, *J* = 8.3 Hz, 2H), 6.59 (m, 2H), 6.52 (d, *J* = 1.9 Hz, 2H), 3.87 (s, 6H), 3.82 (s, 6H), 3.59 (s, 6H), 3.52 (s, 6H).

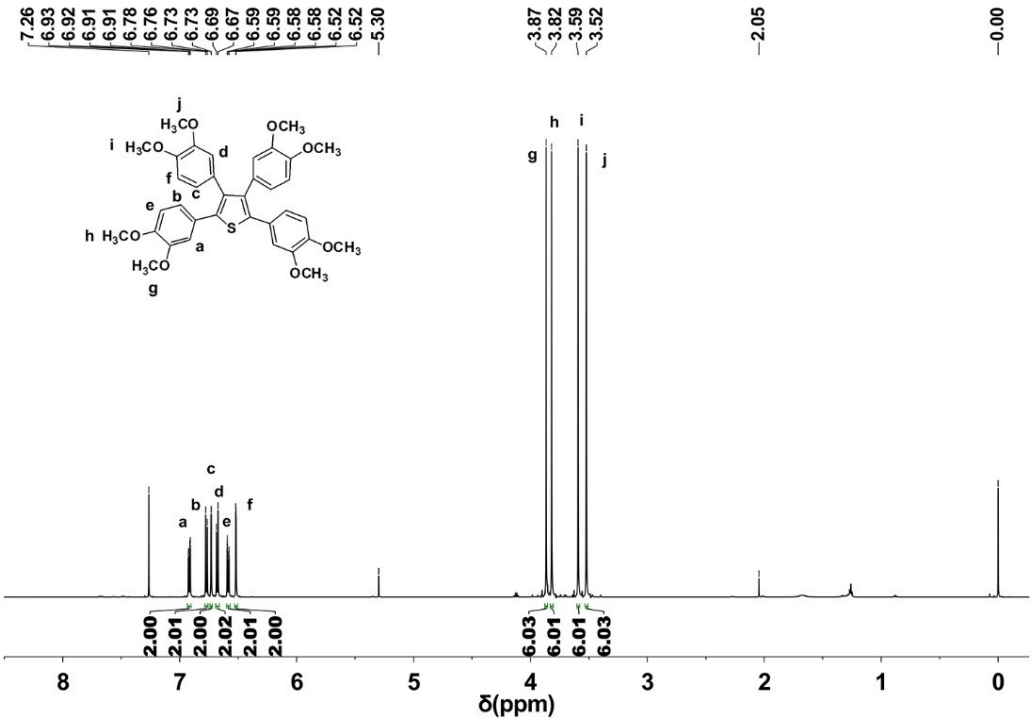
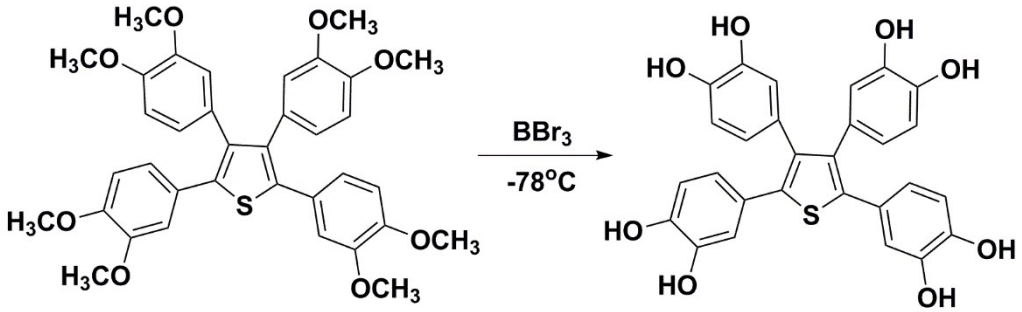


Figure S1. ^{1}H NMR spectrum of Compound **1**



1 2

2,3,4,5-Tetrakis(3,4-dihydroxyphenyl)thiophene (2).

Compound **1** (565 mg, 0.9 mmol) was dissolved in 60 mL anhydrous CH_2Cl_2 in a 250 mL three-necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel. Under nitrogen atmosphere, the resulting solution was cooled to -78 °C. Boron tribromide (3.60 g, 14.4 mmol) was diluted with 10 mL anhydrous dichloromethane, which was slowly injected into the above three-necked flask with a needle tube. After stirring at -78 °C for 1 h, the reaction mixture was heated to 0 °C and stirred for another 3 h at 0 °C. Afterwards the reaction mixture was cooled to -78 °C and quenched by adding 50 mL methanol dropwise. The reaction solution was cooled to room temperature, stirred for 5 h and concentrated by rotary evaporation. The resulting solution was added with 10 mL deionized water and stirred at 70 °C for 2 h. After filtration, the solid product was collected and subjected to cryodesiccation to provide the desired product **2** (455 mg, yield: 98.0 %) as white solid powder. ^{1}H NMR (600 MHz，DMSO-d) δ: 8.96 (s, 2H), 8.87 (s, 2H), 8.68 (s, 2H), 8.62 (s, 2H), 6.62 (d, J = 2.2 Hz, 2H), 6.57 (d, J = 8.2 Hz, 2H), 6.50 (d, J = 8.1 Hz, 2H), 6.43 (m, 2H), 6.31 (d, J = 2.0 Hz, 2H), 6.18 (m, 2H).

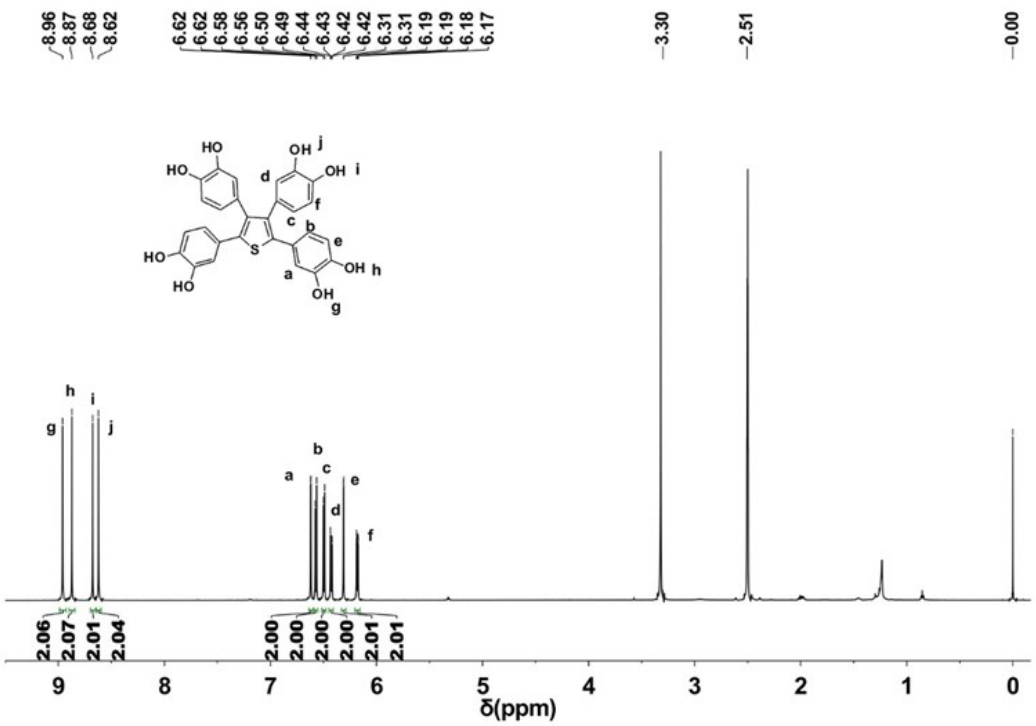
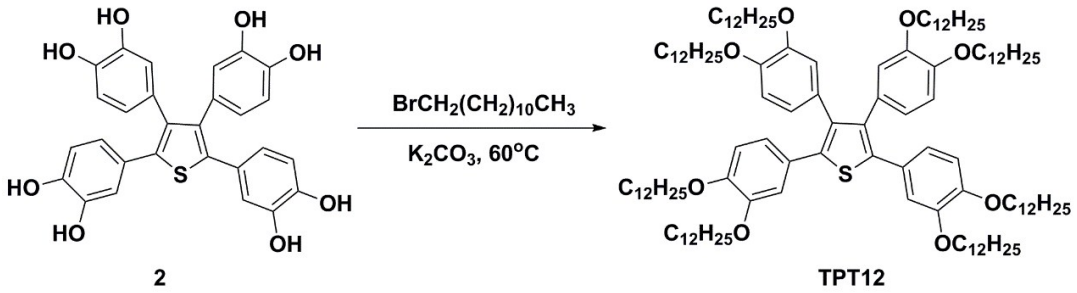


Figure S2. ^{1}H NMR spectrum of Compound **2**.



2,3,4,5-Tetrakis(3,4-bis(dodecyloxy)phenyl)thiophene (TPT12).

Compound **2** (100 mg, 0.2 mmol), potassium carbonate (430 mg, 3.1 mmol) and 80 mL acetone were added into a 250 mL three-necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel. Under nitrogen atmosphere, the reaction mixture was stirred at room temperature for 30 min and heated to 60 °C. A solution of 1-bromododecane (1.100 g, 4.6 mmol) in acetone (20 mL) was added into the above flask through a constant pressure funnel. The reaction mixture was heated to reflux for 40 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with CH_2Cl_2 and distilled water (v:v=1:1) for three times (60 mL× 3). The coalescent organic

phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether : dichloromethane = 10 : 1) to give the desired product **TPT12** (99 mg, yield: 28.0 %) as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.85 (m, 2H), 6.72 (m, 4H), 6.63 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 10.5 Hz, 4H), 3.95 (t, J = 6.6 Hz, 4H), 3.88 (t, J = 6.7 Hz, 4H), 3.66 (t, J = 6.6 Hz, 4H), 3.60 (t, J = 6.7 Hz, 4H), 1.77 (m, 8H), 1.64 (m, 4H), 1.57 (m, 4H), 1.43 (m, 8H), 1.26 (s, 136H), 0.88 (t, J = 6.7 Hz, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.53, 148.45, 148.30, 147.84, 138.54, 137.18, 129.64, 127.31, 123.39, 121.37, 116.89, 114.71, 113.32, 69.17, 68.87, 31.93, 39.68, 29.44, 29.13, 29.07, 26.11, 26.04, 22.68, 14.07. Maldi-Tof MS: *m/z* calculated for $C_{124}H_{212}O_8S$ $[M + H]^+$: 1862.590, found: 1862.857.

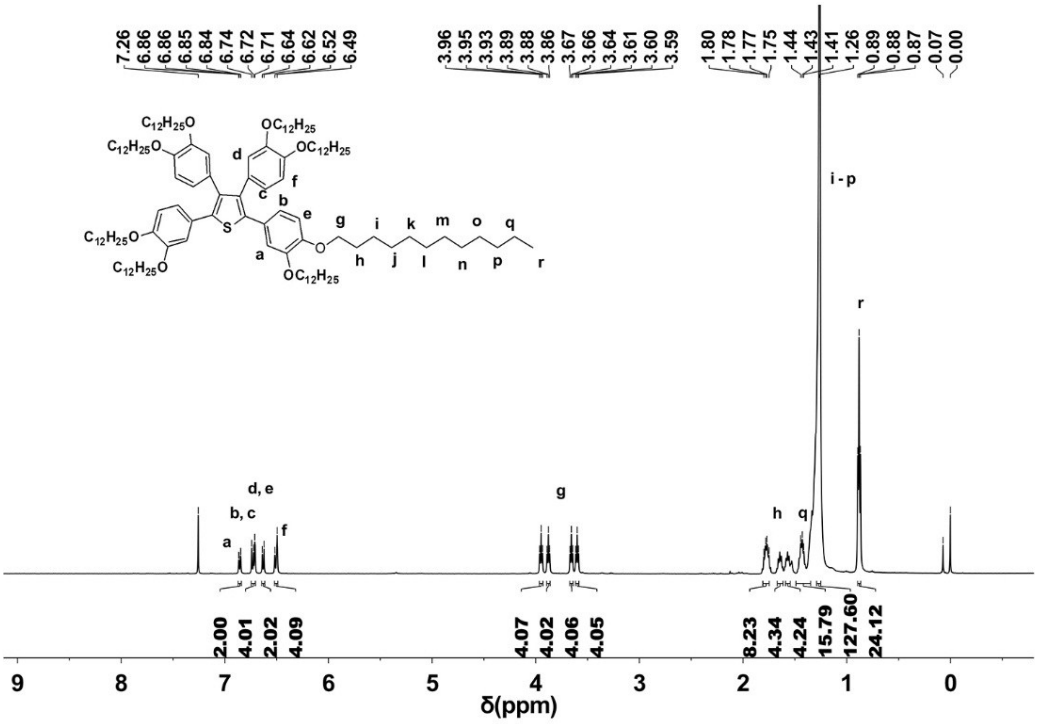


Figure S3. ^{1}H NMR spectrum of Compound **TPT12**.

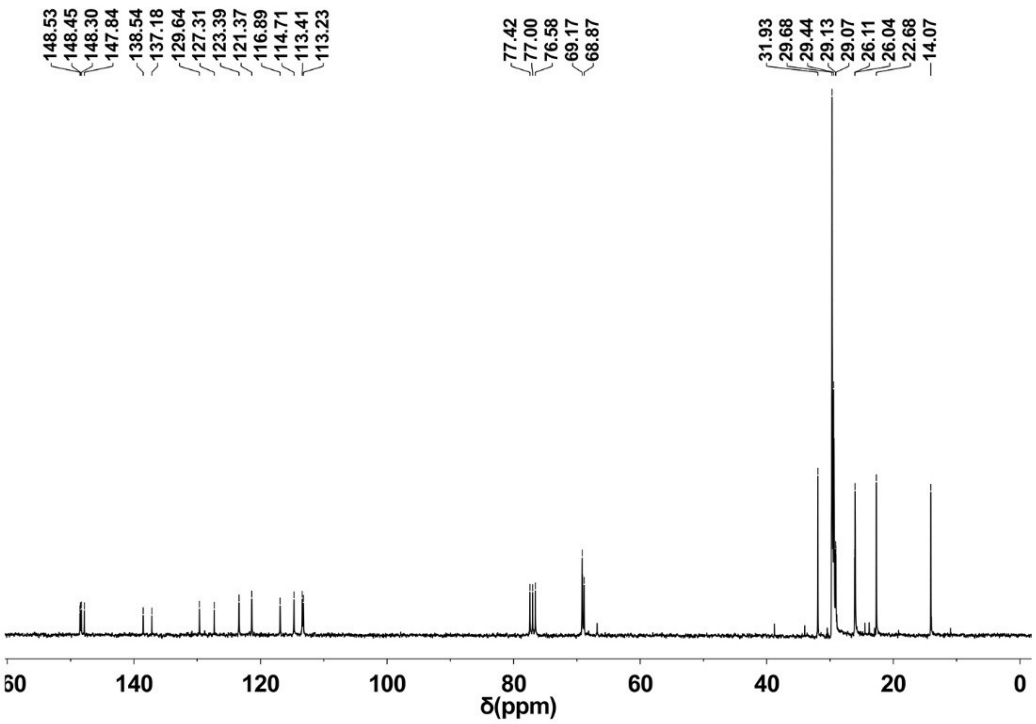


Figure S4. ^{13}C NMR spectrum of Compound **TPT12**.

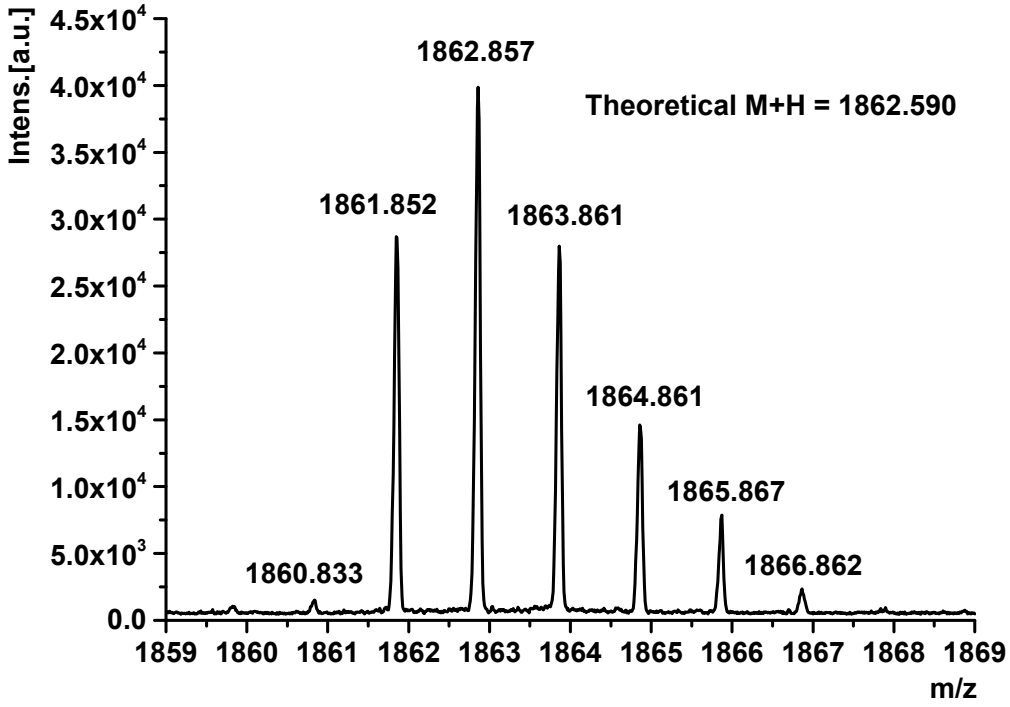
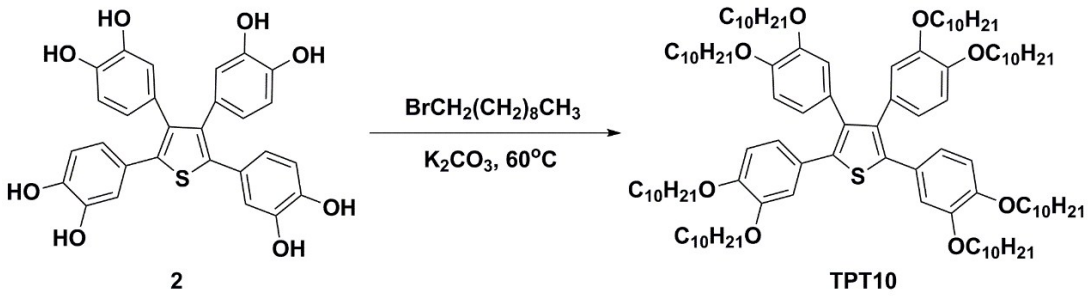


Figure S5. Maldi-Tof mass spectrum of Compound **TPT12**.



2,3,4,5-Tetrakis(3,4-bis(decyloxy)phenyl)thiophene (TPT10).

Compound **2** (100 mg, 0.2 mmol), potassium carbonate (430 mg, 3.1 mmol) and 80 mL acetone were added into a 250 mL three-necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel. Under nitrogen atmosphere, the reaction mixture was stirred at room temperature for 30 min and heated to 60 °C. A solution of 1-bromodecane (1.000 g，4.6 mmol) in acetone (20 mL) was added into the above flask through a constant pressure funnel. The reaction mixture was heated to reflux for 40 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with CH_2Cl_2 and distilled water (v:v=1:1) for three times (60 mL× 3). The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether : dichloromethane = 10 : 1) to give the desired product **TPT10** (93.4 mg, yield: 30.0 %) as a light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.86 (m, 2H), 6.72 (m, 4H), 6.63 (d, *J* = 8.2 Hz, 2H), 6.50 (m, 4H), 3.95 (t, *J* = 6.7 Hz, 4H), 3.88 (t, *J* = 6.7 Hz, 4H), 3.65 (t, *J* = 6.7 Hz, 4H), 3.60 (t, *J* = 6.7 Hz, 4H), 1.78 (m, 8H), 1.65 (m, 4H), 1.57 (m, 4H), 1.44 (d, *J* = 7.9 Hz, 8H), 1.27 (s, 104H), 0.88 (t, *J* = 7.2 Hz, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.47, 148.38, 148.25, 147.79, 138.53, 137.18, 129.49, 127.26, 123.36, 121.35, 116.77, 114.61, 113.29, 113.11, 69.13, 69.06, 68.83, 31.94, 29.75, 29.09, 29.63, 29.43, 29.31, 29.11, 26.11, 26.03, 22.70, 14.10. Maldi-Tof MS: *m/z* calculated for $C_{108}H_{180}O_8S$ $[M + H]^+$: 1638.339, found: 1638.207.

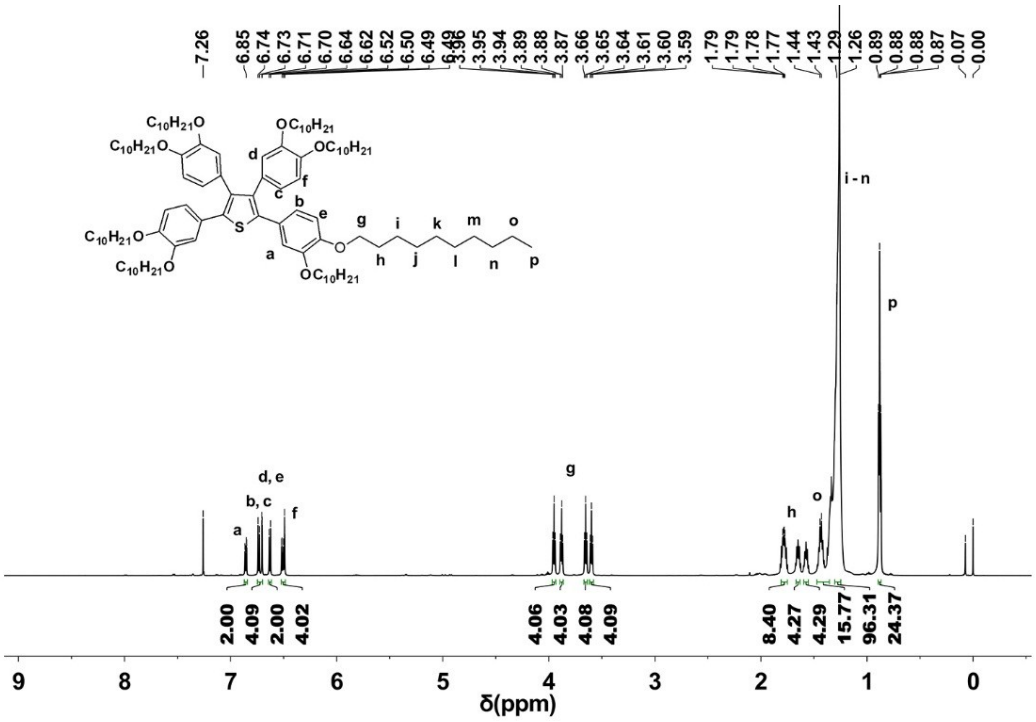


Figure S6. [1]H NMR spectrum of Compound **TPT10**.

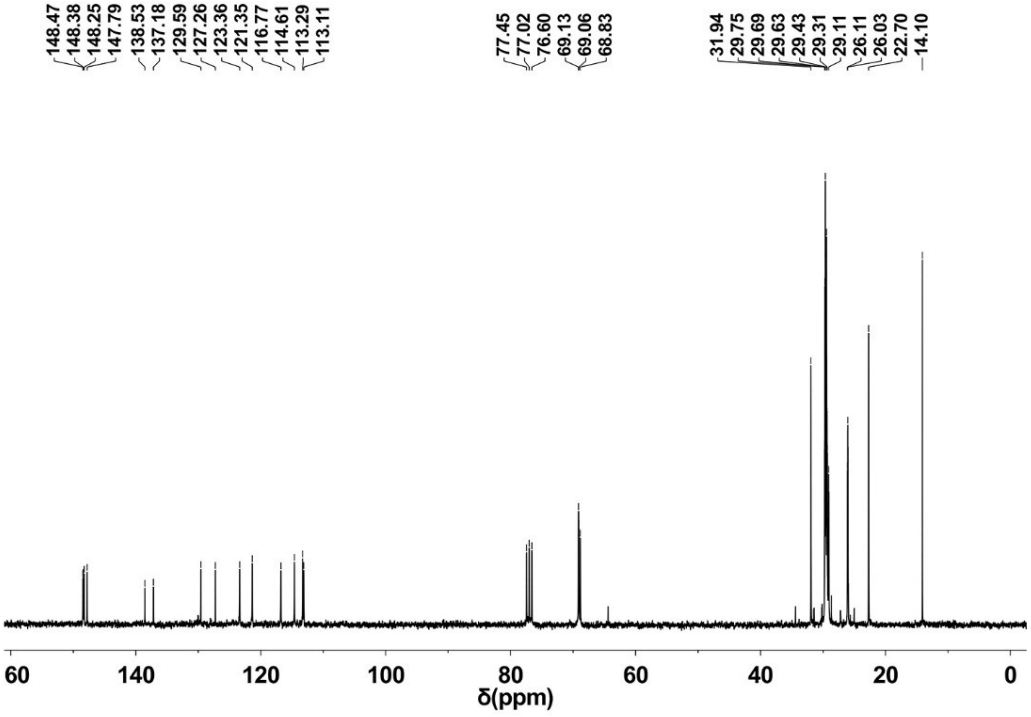


Figure S7. [13]C NMR spectrum of Compound **TPT10**.

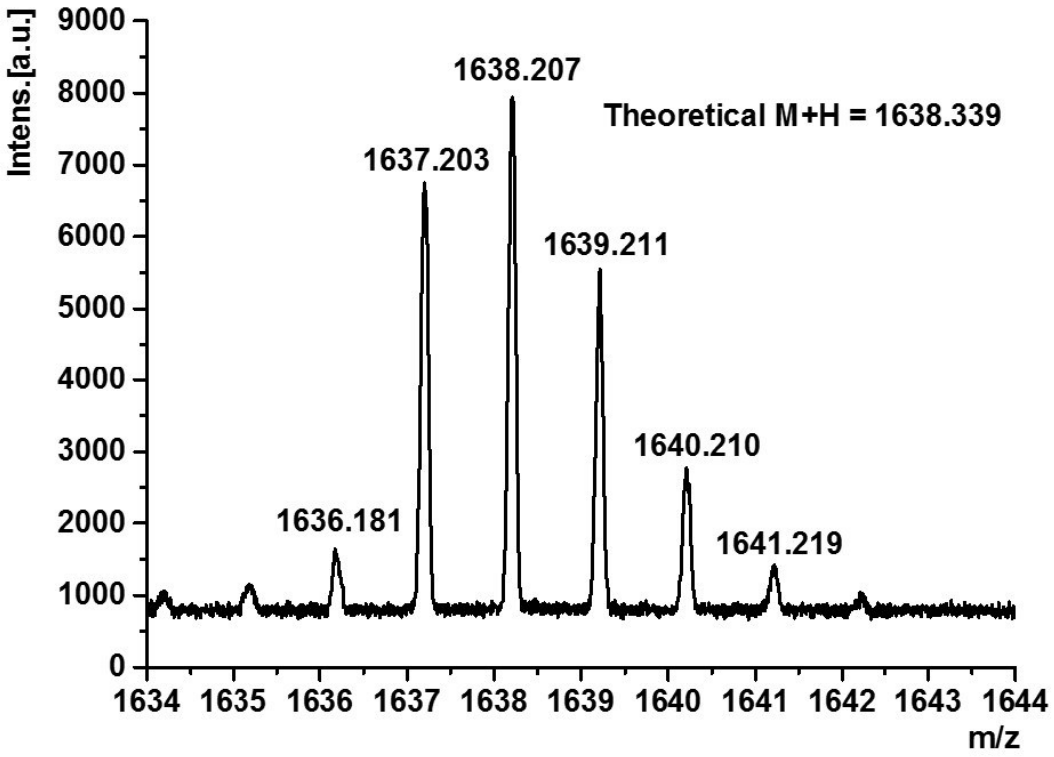
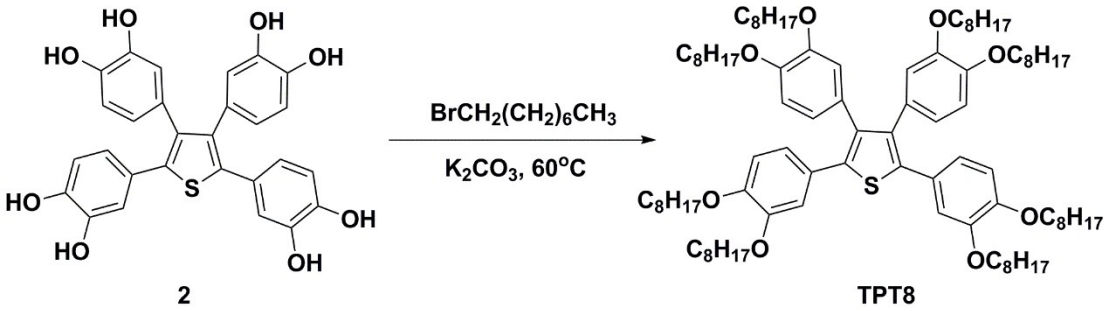


Figure S8. Maldi-Tof mass spectrum of Compound **TPT10**.



2,3,4,5-Tetrakis(3,4-bis(octyloxy)phenyl)thiophene (TPT8).

Compound **2** (100 mg, 0.2 mmol), potassium carbonate (430 mg, 3.1 mmol) and 80 mL acetone were added into a 250 mL three-necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel. Under nitrogen atmosphere, the reaction mixture was stirred at room temperature for 30 min and heated to 60 °C. A solution of 1-bromooctane (888 mg, 4.6 mmol) in acetone (20 mL) was added into the above flask through a constant pressure funnel. The reaction mixture was heated to reflux for 40 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with CH_2Cl_2 and distilled water (v:v=1:1) for three times (60 mL× 3). The coalescent organic phase

was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether : dichloromethane = 10 : 1) to give the desired product **TPT8** (80.6 mg, yield: 30.0 %) as a light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.85 (m, 2H), 6.72 (m, 4H), 6.63 (d, *J* = 8.2 Hz, 2H), 6.50 (m, 4H), 3.95 (t, *J* = 6.7 Hz, 4H), 3.88 (t, *J* = 6.8 Hz, 4H), 3.66 (t, *J* = 6.7 Hz, 4H), 3.60 (t, *J* = 6.8 Hz, 4H), 1.79 (m, 8H), 1.65 (m, 4H), 1.57 (m, 4H), 1.44 (m, 8H), 1.26 (s, 72H), 0.88 (t, *J* = 7.2, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.46, 148.38, 148.25, 147.78, 138.54, 137.18, 129.58, 127.26, 123.35, 121.36, 116.75, 114.90, 113.28, 113.10, 69.10, 68.83, 31.85, 29.47, 29.39, 29.30, 29.10, 29.04, 26.09, 25.99, 22.67, 14.07. Maldi-Tof MS: *m/z* calculated for $C_{92}H_{148}O_8S$ $[M+H]^+$: 1414.089, found: 1414.308.

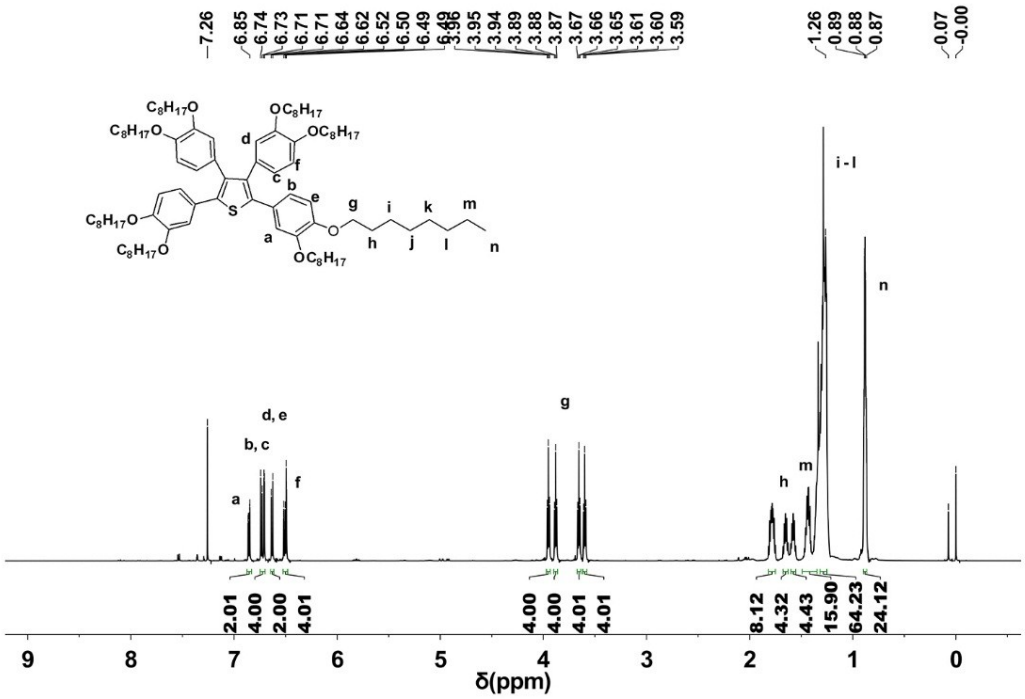


Figure S9. ^{1}H NMR spectrum of Compound **TPT8**.

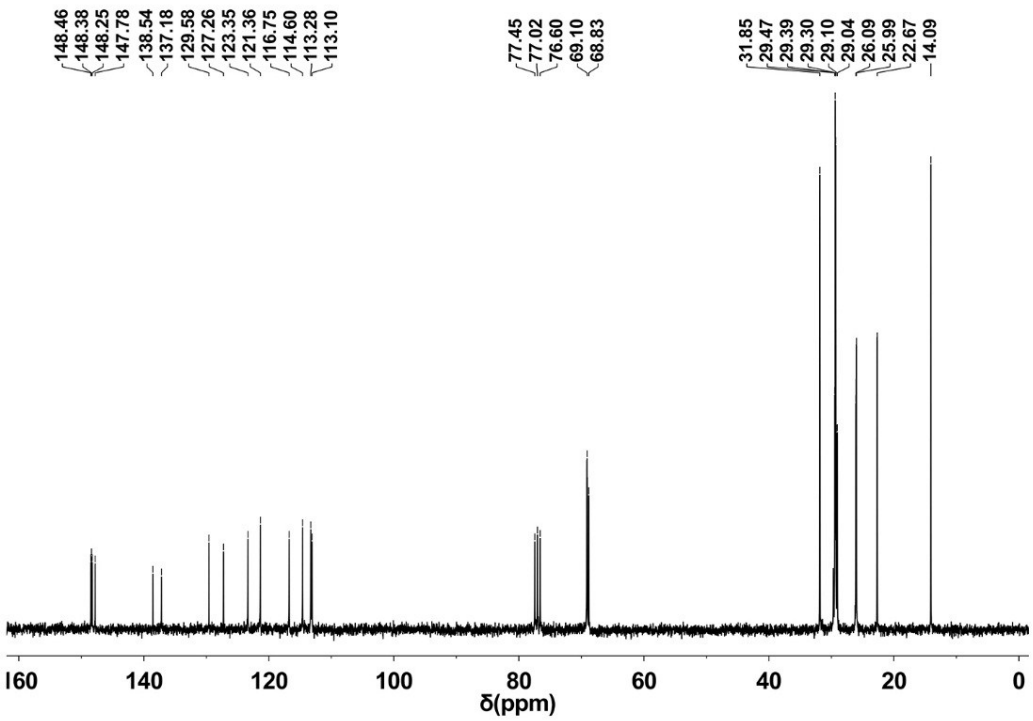


Figure S10. ^{13}C NMR spectrum of Compound **TPT8**.

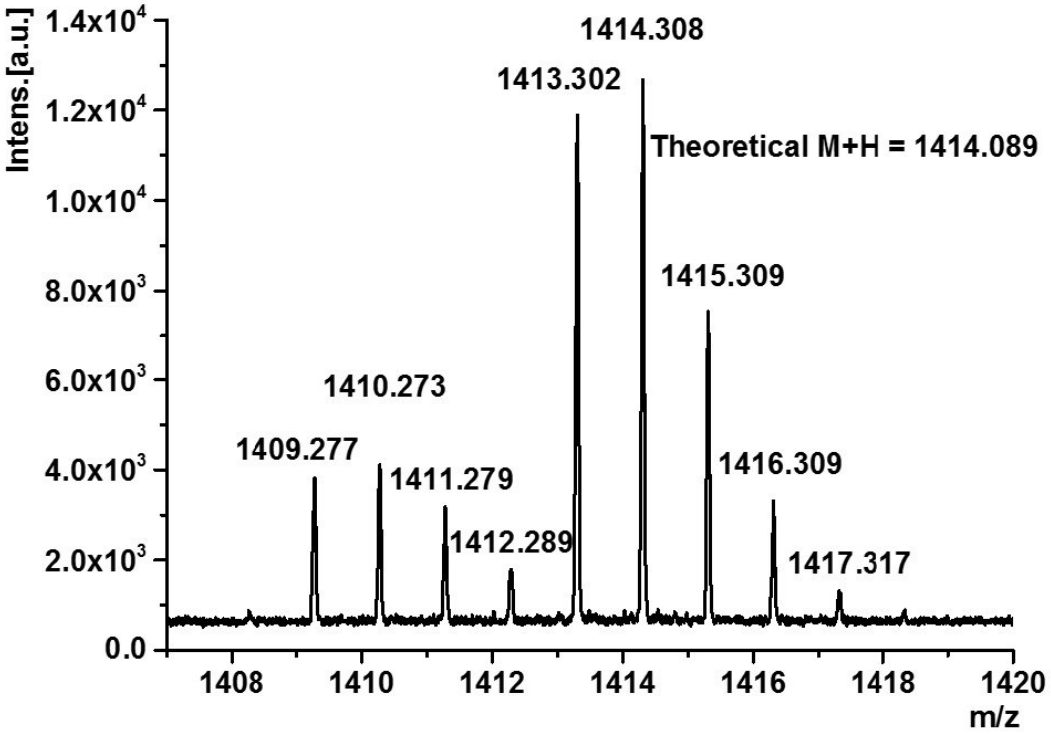
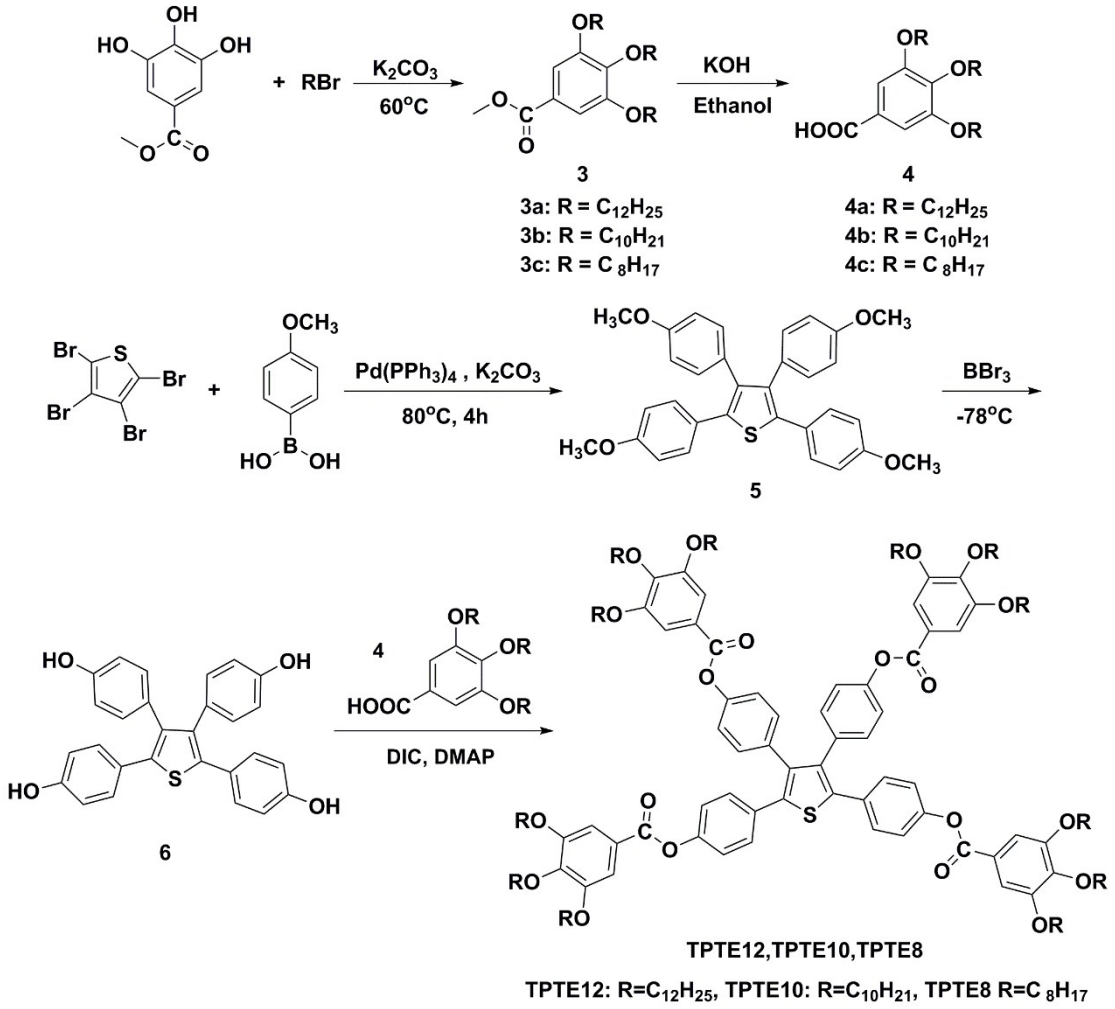
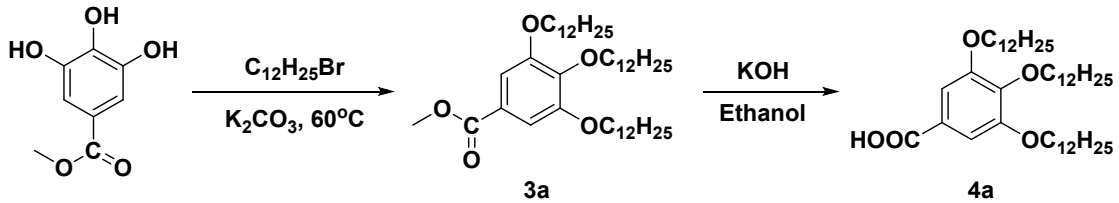


Figure S11. Maldi-Tof mass spectrum of Compound **TPT8**.

II. Synthesis and characterization of TPTEn (n=12, 10, 8)



Scheme S2. Synthetic routes of compound **TPTEn (n=12, 10, 8)**



3,4,5-Tris(dodecyloxy)-benzoic acid (4a).

3,4,5-Tris(dodecyloxy)methyl benzoate **(3a)**: methyl gallate (10.00 g, 54.3 mmol), potassium carbonate (45.00 g, 325.8 mmol) and 250 mL acetone were added into a 500 mL three-neck flask equipped with a nitrogen inlet tube and a constant pressure funnel. Under nitrogen atmosphere, the

resulting solution was heated to 60 °C. A solution of 1-bromododecane (121.8 g, 488.7 mmol) in acetone (10 mL) was added into the above flask by a constant pressure funnel, the reaction mixture was stirred and heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with ether and distilled water (v:v = 1:1) for three times (60 mL× 3), washed with 200 mL distilled water and 50 mL saturated sodium chloride aqueous solution, successively. The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound which was purified by flash column chromatography (petroleum ether : ethyl acetate = 10:1) to give the desired product **3a** (35.40 g, yield: 95.0 %) as a light yellow oily liquid.

3,4,5-Tris-dodecyloxy-benzoic acid **(4a)**: Compound **3a** (35.40 g, 51.5 mmol), potassium hydroxide (23.10 g, 411.8 mmol), 200 mL ethanol and 200 mL distilled water were added into a 1000 mL three-necked flask. The reaction mixture was heated to reflux at 80 °C for 15 h. After cooling to room temperature, the resulting mixture was acidified by diluted HCl solution to pH = 2, and then the white precipitates appeared and were filtered. The precipitate was washed with 80 mL deionized water and dried over anhydrous magnesium sulfate ($MgSO_4$) overnight. The crude compound was recrystallized from methanol for three times to provide the desired product **4a** (17.70 g, yield: 51.0 %) as a white solid. ^{1}H NMR (600MHz, $CDCl_3$) δ: 7.33 (s, 2H), 4.04 (m, 6H), 1.81 (m, 6H), 1.47 (m, 6H), 1.29 (m, 48H), 0.88 (t, J = 7.0 Hz, 9H).

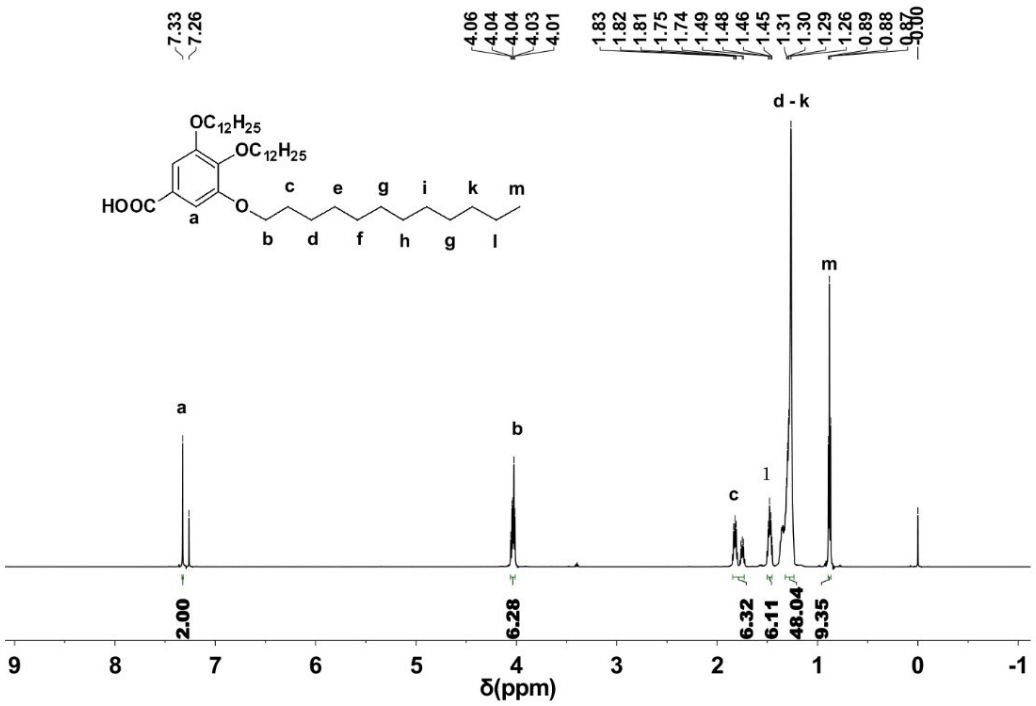
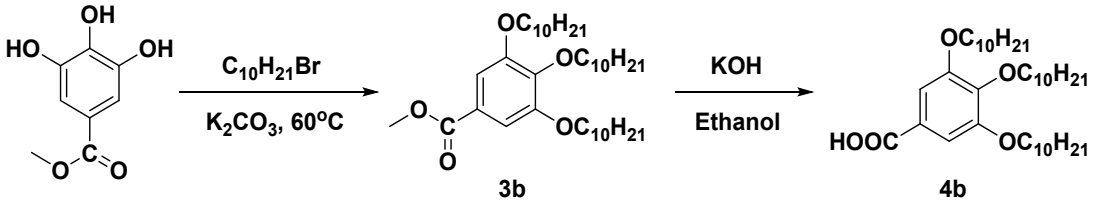


Figure S12. ^{1}H NMR spectrum of Compound **4a**.



3,4,5-Tris(decyloxy)benzoic acid (4b).

3,4,5-Tris(decyloxy) methyl benzoate **(3b)**: methyl gallate (10.00 g, 54.3 mmol), potassium carbonate (45.00 g, 325.8 mmol) and 250 mL acetone were added into a 500 mL three-neck flask equipped with a nitrogen inlet tube and a constant pressure funnel. Under nitrogen atmosphere, the resulting solution was heated to 60 °C. A solution of 1-bromodecane (108.1g, 488.7 mmol) in acetone (10 mL) was added into the above flask through a constant pressure funnel, the reaction mixture was stirred and heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with dichloromethane and distilled water (v:v=1:1) for three times (60 mL× 3), washed with 200 mL distilled water and 50 mL saturated sodium chloride aqueous solution, successively. The coalescent organic phase was dried over anhydrous magnesium sulfate

($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether: dichloromethane = 5:1) to give the desired product **3b** (29.5 g, yield: 90.0 %) as colorless oily liquid.

3,4,5-Tris(decyloxy)benzoic acid **(4b)**: Compound **3b** (29.50 g, 48.8 mmol), potassium hydroxide(21.90 g, 390.4 mmol), 200 mL ethanol and 200 mL distilled water were added into a 1000 mL three-necked flask. The reaction mixture was heated to reflux at 80 °C for 15 h. After cooling to room temperature, the resulting mixture was acidified by diluted HCl solution to pH = 2, and then the white precipitates appeared and were filtered. The precipitate was washed with 80 mL deionized water and dried over anhydrous magnesium sulfate ($MgSO_4$) overnight. The crude compound was recrystallized from acetone for three times to provide the desired product **4b** (14.4 g, yield: 50.0 %) as a white solid. ^{1}H NMR (600MHz, $CDCl_3$) δ: 7.32 (s, 2H), 4.04 (m, 6H), 1.81 (m, 6H), 1.48 (m, 6H), 1.29 (m, 36H), 0.88 (t, J = 6.7 Hz, 9H).

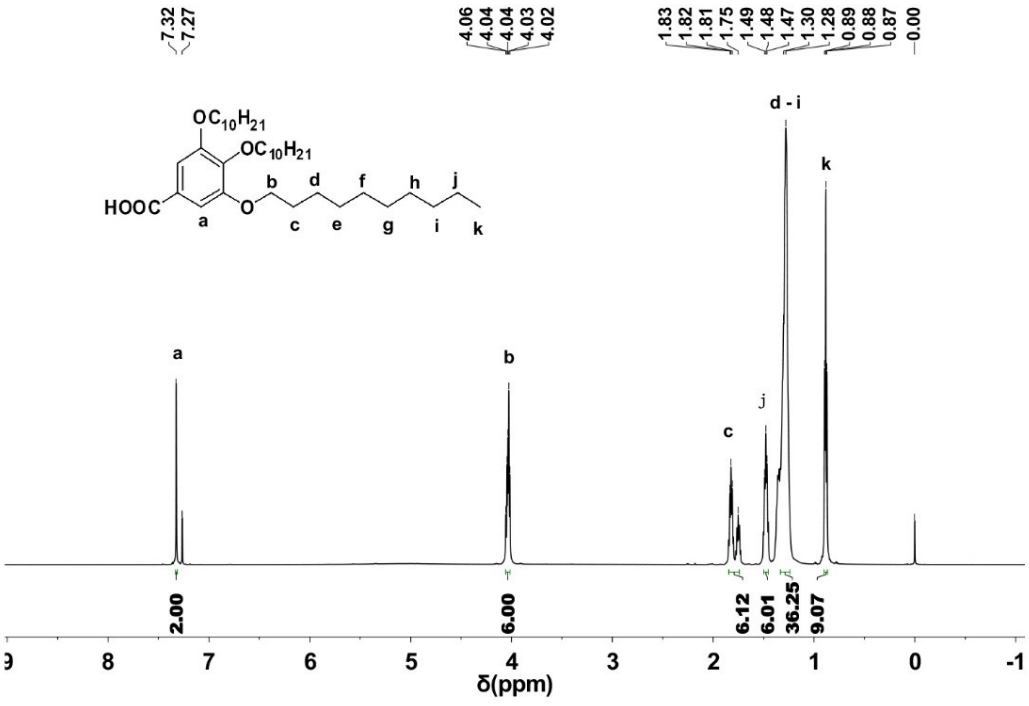
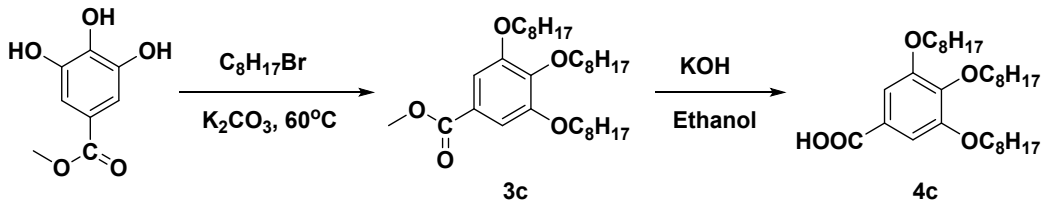


Figure S13. ^{1}H NMR spectrum of Compound **4b**.



3,4,5-Tris(octyloxy)benzoic acid (4c).

3,4,5-Tris(octyloxy)methyl benzoate **(3c)**: methyl gallate (10.0 g, 54.3 mmol), potassium carbonate (45.0 g, 325.8 mmol) and 250 mL acetone were added into a 500 mL three-neck flask equipped with a nitrogen inlet tube and a constant pressure funnel. Under nitrogen atmosphere, the resulting solution was heated to 60 °C. A solution of 1-bromooctane (94.4 g, 488.7 mmol) in acetone (10 mL) was added into the above flask by a constant pressure funnel, the reaction mixture was stirred and heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with dichloromethane and distilled water (v:v=1:1) for three times (60 mL× 3), washed with 200 mL distilled water and 50 mL saturated sodium chloride aqueous solution, successively. The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether: ethyl acetate = 5:1) to give the desired product **3c** (25.7 g, yield: 91.0 %) as colorless oily liquid.

3,4,5-Tris(octyloxy)benzoic acid **(4c)**: Compound **3c** (25.7 g, 49.4 mmol), potassium hydroxide (22.2 g, 395.2 mmol), 200 mL ethanol and 200 mL distilled water were added into a 1000 mL three-necked flask. The reaction mixture was heated to reflux at 80 °C for 15 h. After cooling to room temperature, the resulting mixture was acidified by diluted HCl solution to pH = 2, and then the white precipitates appeared and were filtered. The precipitate was then washed with 80 mL deionized water and dried over anhydrous magnesium sulfate ($MgSO_4$) overnight. The crude compound was recrystallized from acetone for three times to provide the desired product **4c** (11.30 g, yield: 45.0 %) as a white solid. ^{1}H NMR (600MHz, $CDCl_3$) δ: 7.33 (s, 2H), 4.04 (m, 6H), 1.81 (m, 6H), 1.48 (m, 6H), 1.29 (m, 24H), 0.89 (t, J = 8.4 Hz, 9H).

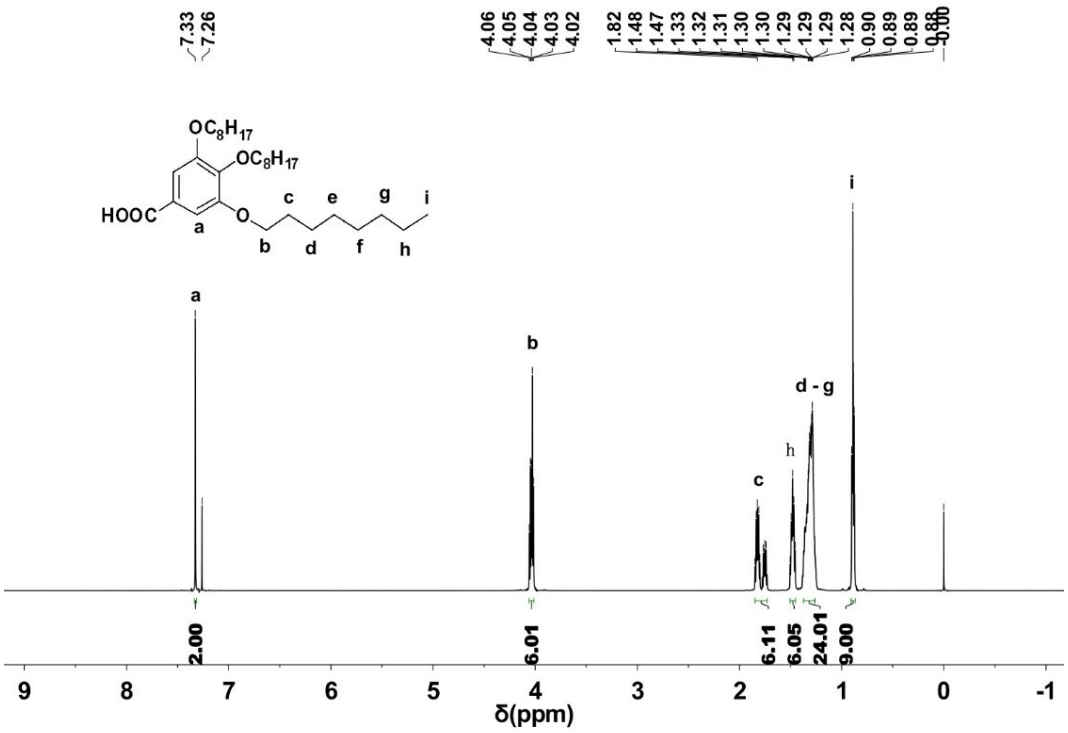
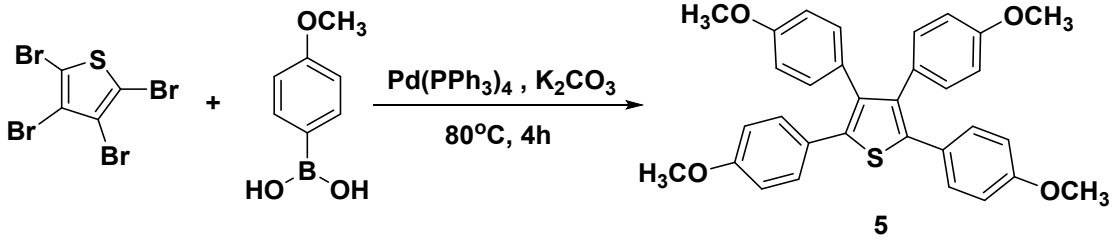


Figure S14. ^{1}H NMR spectrum of Compound **4c**.



2,3,4,5-Tetrakis(4-methoxyphenyl)thiophene (5).

2,3,4,5-Tetrabromothiophene (400 mg, 1.0 mmol) and tetra(triphenylphosphorus) palladium (700 mg, 0.6 mmol) were dissolved in 1,4-dioxane (20 mL) in a 100 mL round-bottom flask equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature for 30 min. 4-Methoxyphenyl boronic acid (912 mg, 6.0 mmol) and potassium carbonate solution aqueous solution (2.0 M, 3.0 mL) were then added into the above reaction solution. The resulting mixture was stirred at 80 °C for 18 h under nitrogen atmosphere. After cooling to room temperature, the solution was concentrated by rotary evaporation. The crude mixture was extracted with CH_2Cl_2

and distilled water (v:v=1:1) for three times (60 mL× 3). The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was subjected to purification by flash column chromatography (petroleum ether : ethyl acetate = 5 : 1) to give the desired product **5** (417 mg, yield: 82.0 %) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.15 (d, *J* = 8.8 Hz, 4H), 6.86 (d, *J* = 8.7 Hz, 4H), 6.76 (d, *J* = 8.8 Hz, 4H), 6.67 (d, *J* = 8.7 Hz, 4H), 3.78 (s, 6H), 3.75 (s, 6H).

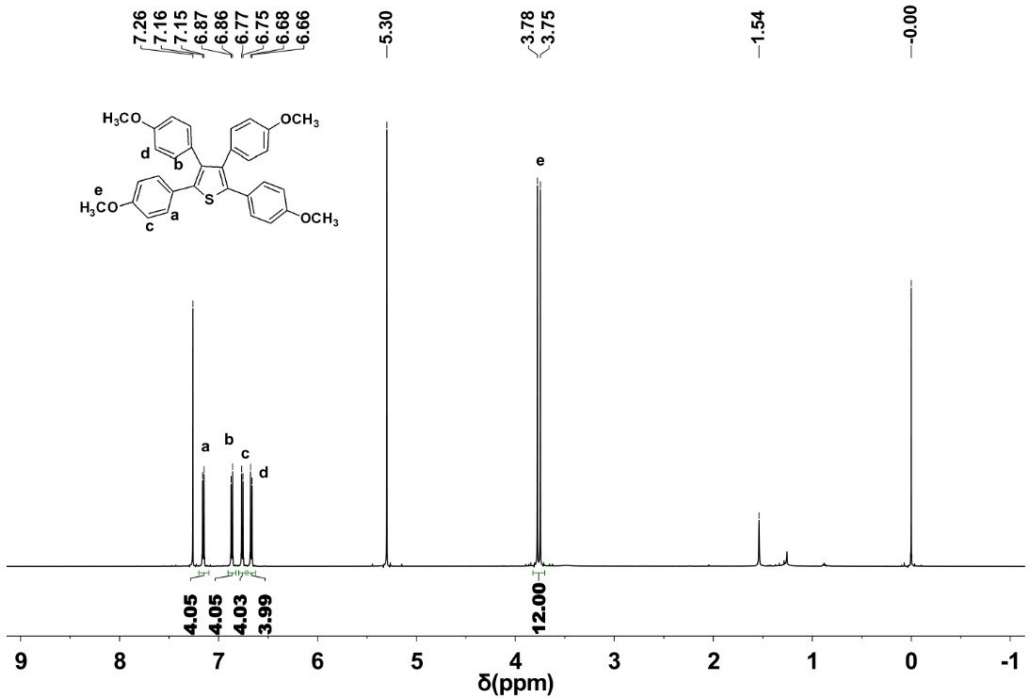
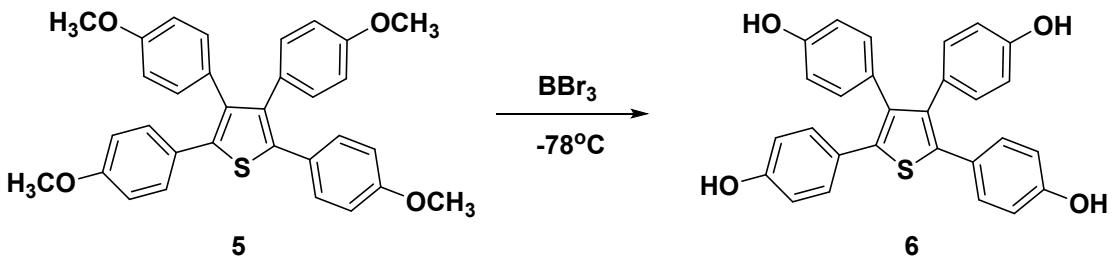


Figure S15. ^{1}H NMR spectrum of Compound **5**.



2,3,4,5-Tetrakis(4-monohydroxyphenyl)thiophene (6).

Compound **5** (417 mg, 0.8 mmol) was dissolved in 50 mL anhydrous CH_2Cl_2 in a 250 mL three-

necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel. Under nitrogen atmosphere, the resulting solution was cooled to -78 °C. Boron tribromide (1.600 g, 6.6 mmol) diluted in 10 mL anhydrous dichloromethane, was slowly injected into the above three-necked flask through a needle tube. After stirring at -78 °C for 1 h, the reaction mixture was heated to 0 °C and stirred for another 3 h at 0 °C. Afterwards the reaction mixture was cooled to -78 °C and quenched by adding 40 mL methanol dropwise. The reaction solution was stirred at room temperature for 5 h and then concentrated by rotary evaporation. The resulting solution was added with 10 mL deionized water and stirred at 70 °C for 2 h. After filtration, the solid product was collected and subjected to cryodesiccation to provide the desired product **6** (404 mg, yield: 97.0 %) as a white solid powder. ^{1}H NMR (600 MHz, DMSO-d) δ: 9.54 (s, 2H), 9.29 (s, 2H), 6.98 (d, J = 8.7 Hz, 4H), 6.72 (d, J = 8.5 Hz, 4H), 6.63 (d, J = 8.7 Hz, 4H), 6.53 (d, J = 8.4 Hz, 4H).

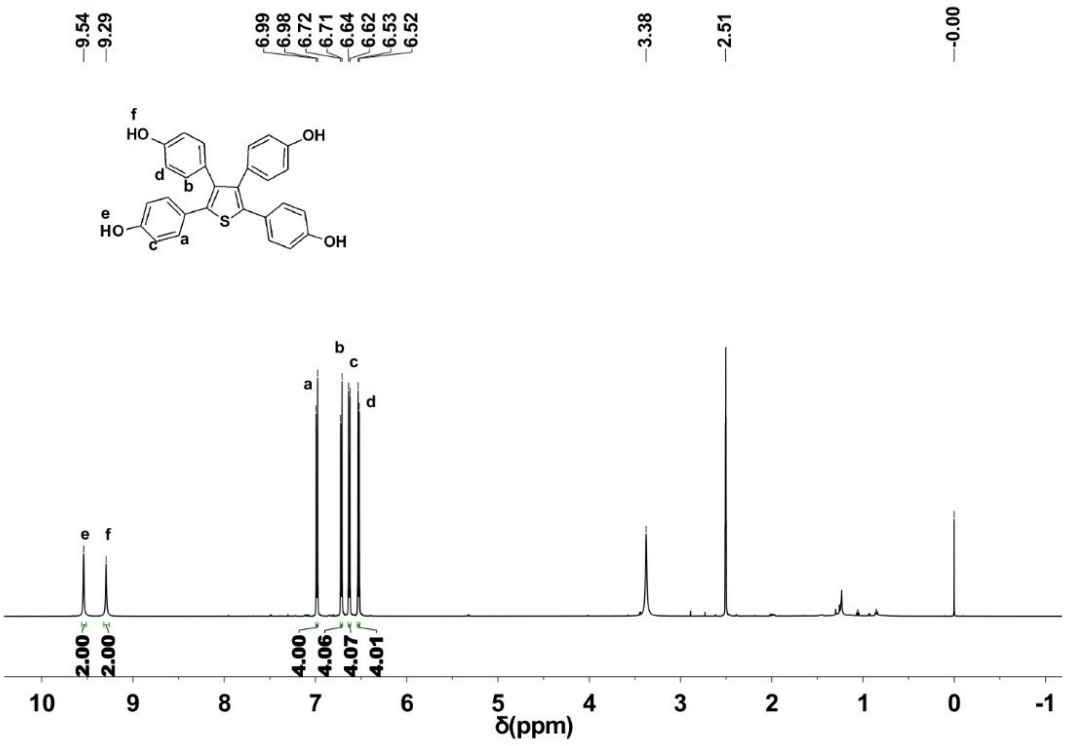
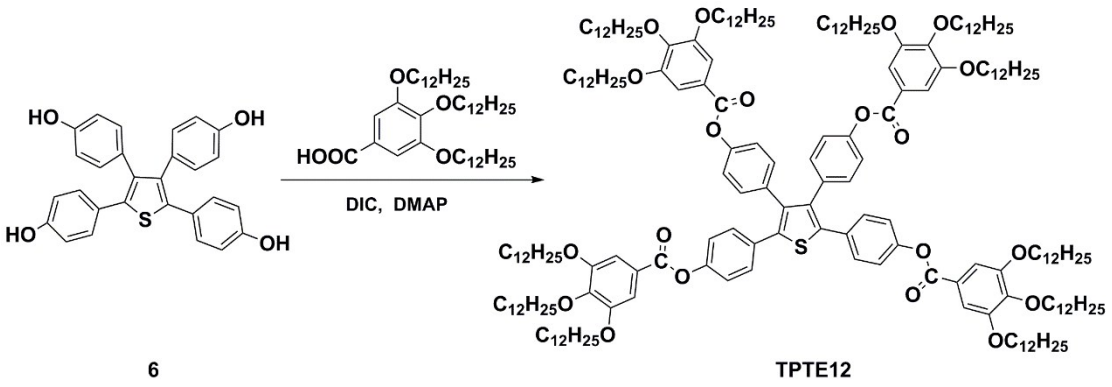


Figure S16. ^{1}H NMR spectrum of Compound **6**.



Thiophene-2,3,4,5-tetrayltetrakis(benzene-4,1-diyl)tetrakis(3,4,5-tris(dodecyloxy)benzoate) (TPTE12).

Compound **6 (**181 mg, 0.4 mmol), 3,4,5-tris(dodecyloxy)-benzoic acid **4a** (2.200 g, 3.2 mmol), 4-dimethylaminopyridine (195 mg, 1.6 mmol), 25 mL anhydrous tetrahydrofuran and N,N-diisopropylcarbodiimide (202 mg, 1.6 mmol) were successively added into a 100 mL three-necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel. Under nitrogen atmosphere, the reaction mixture was heated to reflux at 70 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with CH_2Cl_2 and distilled water (v:v=1:1) for three times (60 mL× 3). The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether : dichloromethane = 10 : 1) to give the desired product **TPTE12** (259 mg，yield: 21.0 %) as a light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 8.6 Hz, 8H), 7.32 (d, *J* = 8.3 Hz, 4H), 7.12 (d, *J* = 8.4 Hz, 4H), 7.05 (m, 8H), 4.04 (m, 24H), 1.82 (m, 24H), 1.48 (m, 24H), 1.29 (m, 192H), 0.88 (t, *J* = 7.2 Hz, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.90, 152.97, 150.39, 149.98, 143.00, 138.48, 138.29, 133.57, 131.88, 131.57, 130.36, 123.74, 121.86, 121.55, 108.48, 73.58, 69.26, 31.94, 30.36, 29.74, 29.70, 29.64, 29.41, 29.37, 27.32, 26.10, 22.69, 14.10. Maldi-Tof MS: *m/z* calculated for $C_{200}H_{324}O_{20}S$ $[M+Na]^{23+}$: 3103.409, found: 3103.231.

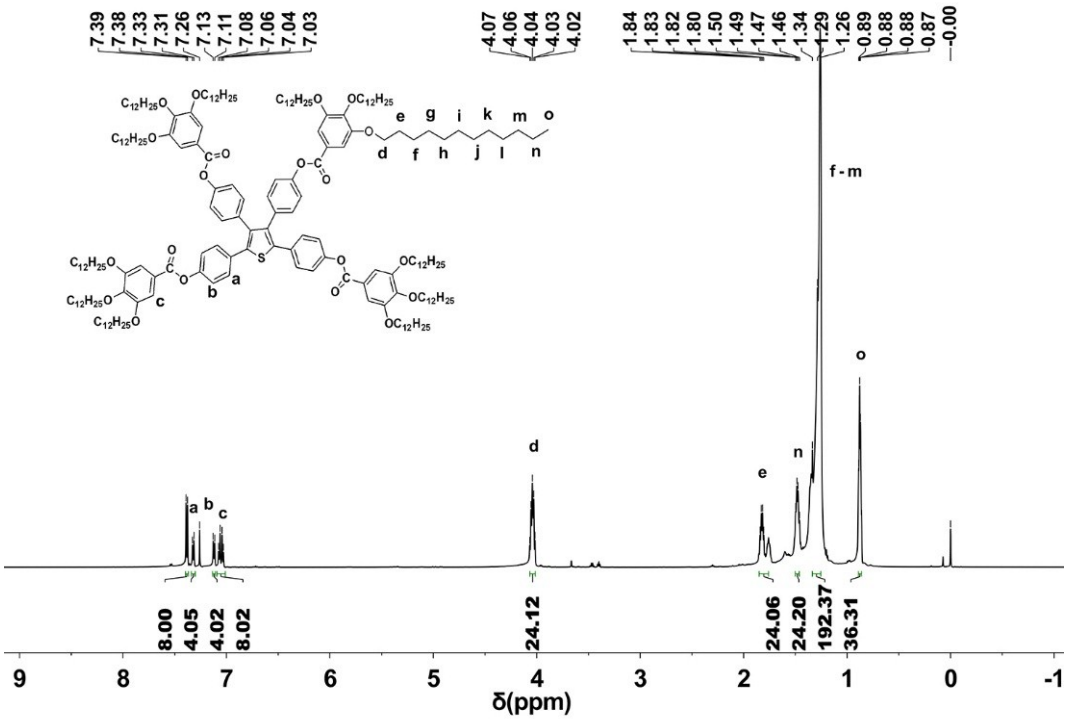


Figure S17. [1]H NMR spectrum of Compound **TPTE12**.

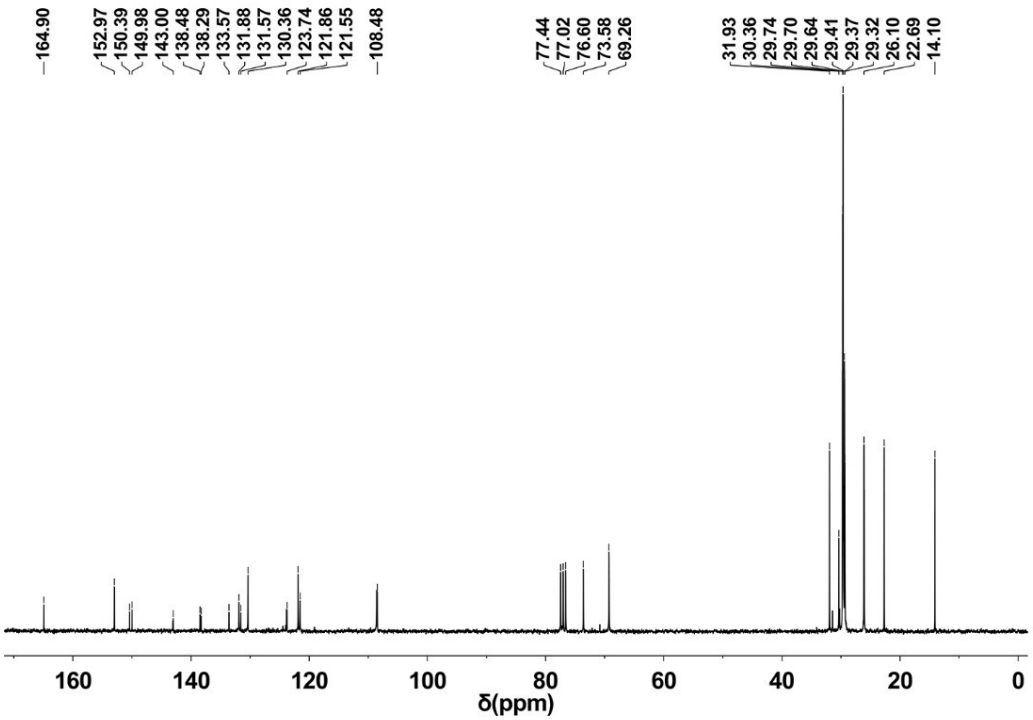


Figure S18. [13]C NMR spectrum of Compound **TPTE12**.

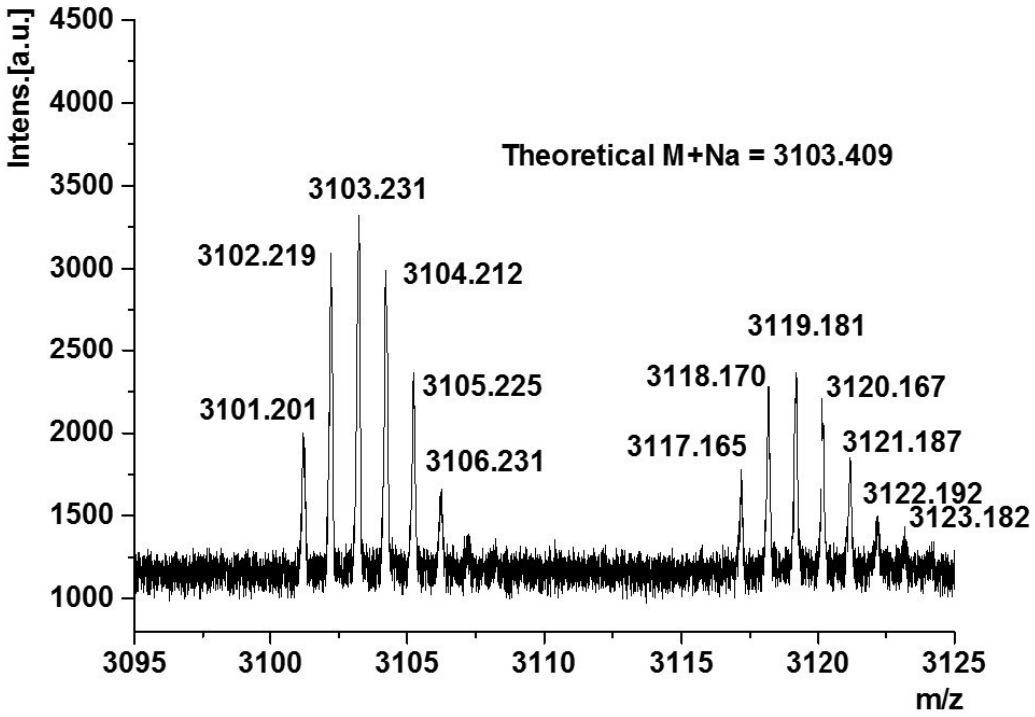
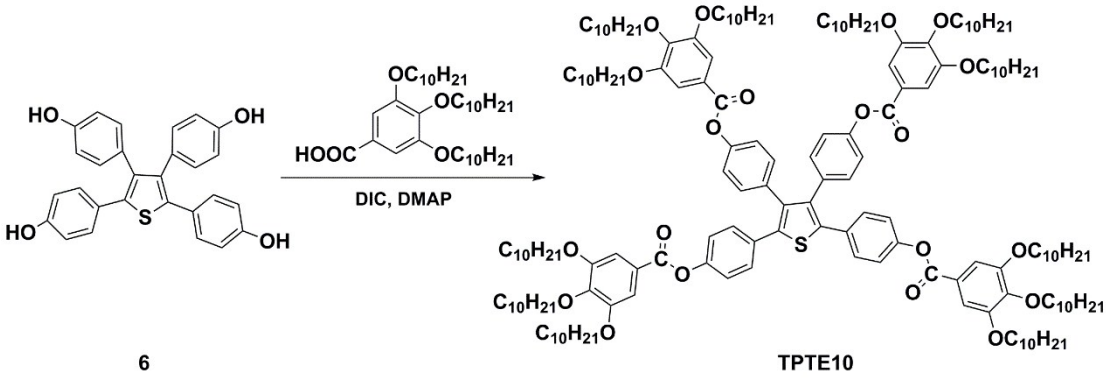


Figure S19. Maldi-Tof mass spectrum of Compound **TPTE12**.



Thiophene-2,3,4,5-tetrayltetrakis(benzene-4,1-diyl) tetrakis(3,4,5-tris(decyloxy)benzoate) (TPTE10).

Compound **6** (181 mg, 0.4 mmol), 3,4,5-tris(decyloxy)benzoic acid **4b** (1.900 g, 3.2 mmol), 4-dimethylaminopyridine (195 mg, 1.6 mmol), 25 mL anhydrous tetrahydroufuran and N,N-diisopropylcarbodiimide (202 mg, 1.6 mmol) were added into a 100 mL three-necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel successively. Under nitrogen atmosphere, the reaction mixture was heated to reflux at 70 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary

evaporation. The resulting compound was extracted with CH_2Cl_2 and distilled water (v:v=1:1) for three times (60 mL× 3). The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether : dichloromethane = 10 : 1) to give the desired product **TPTE10** (209 mg , yield: 19.0 %) as a light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ : 7.39 (d, *J* = 8.5 Hz, 8H), 7.32 (d, *J* = 8.2 Hz, 4H), 7.12 (d, *J* = 8.3 Hz, 4H), 7.06 (m, 8H), 4.04 (m, 24H), 1.80 (m, 24H), 1.48 (m, 24H), 1.29 (m, 144H), 0.88 (t, *J* = 7.2 Hz, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ : 166.18, 154.29, 151.73, 151.33, 144.48, 139.81, 139.60, 134.90, 133.19, 132.88, 131.66, 125.07, 123.15, 122.85, 109.95, 109.88, 78.76, 78.33, 77.91, 74.88, 70.60, 33.21, 31.67, 30.92, 30.88, 30.69, 30.63, 27.40, 23.98, 15.38. Maldi-Tof MS: *m/z* calculated for $C_{176}H_{276}O_{20}S$ $[M+Na]^{23+}$: 2766.029, found: 2766.628.

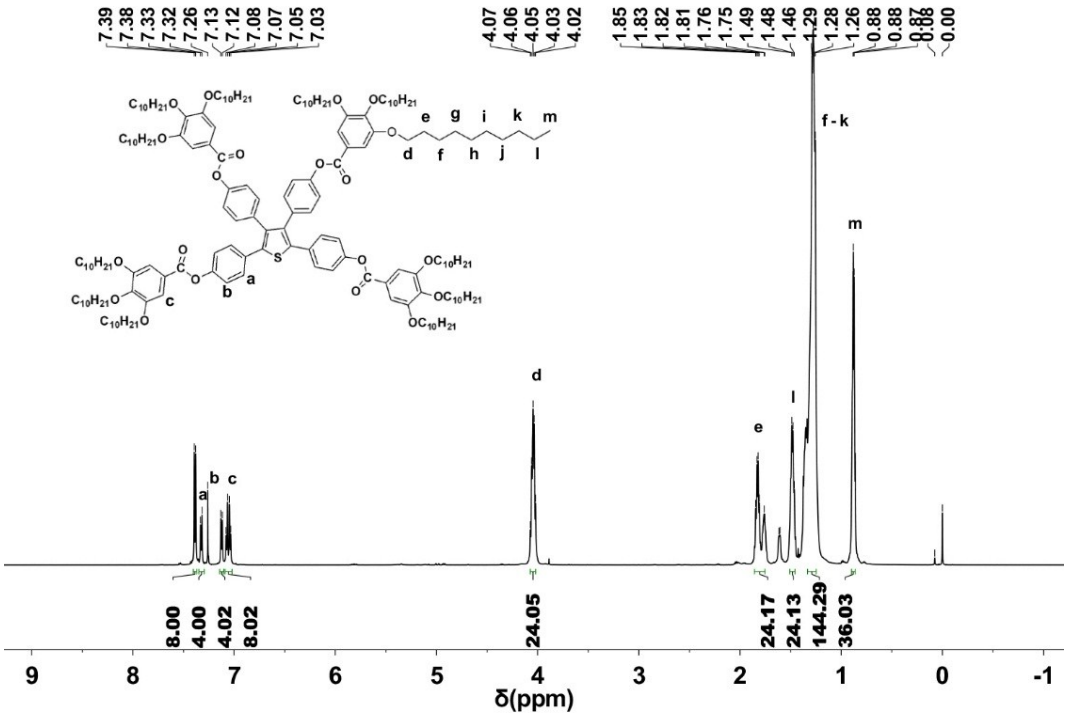


Figure S20. ^{1}H NMR spectrum of Compound **TPTE10**.

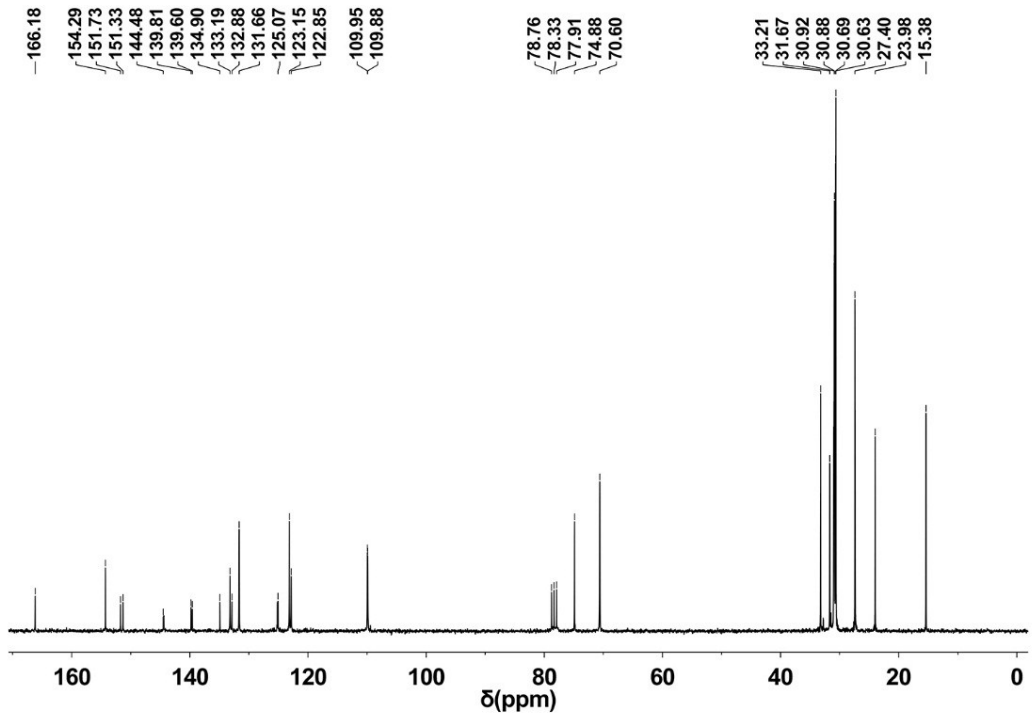


Figure S21. ^{13}C NMR spectrum of Compound **TPTE10**.

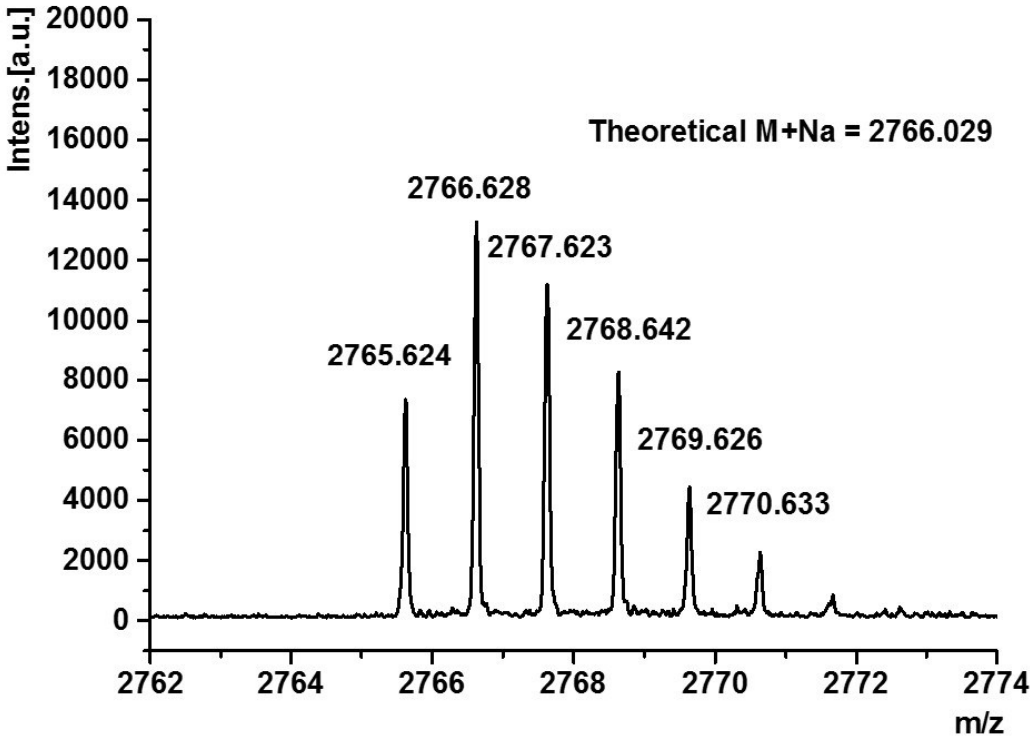
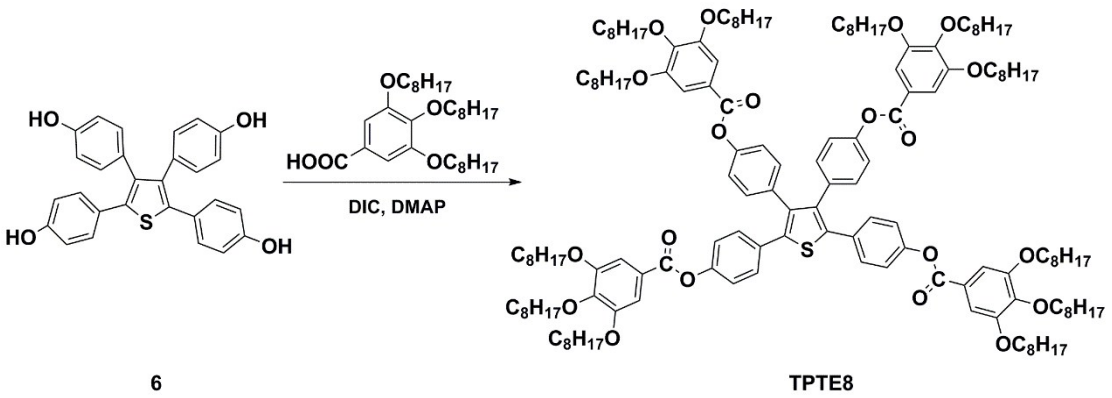


Figure S22. Maldi-Tof mass spectrum of Compound **TPTE10**.



6 TPTE8

Thiophene-2,3,4,5-tetrayltetrakis(benzene-4,1-diyl)tetrakis(3,4,5-tris(octyloxy)benzoate) (TPTE8).

Compound **6** (181 mg, 0.4 mmol), 3,4,5-tris(octyloxy)benzoic acid **4c** (1.600 g, 3.2 mmol), 4-dimethylaminopyridine (195 mg, 1.6 mmol), 25 mL anhydrous tetrahydroufuran and N,N-diisopropylcarbodiimide (202 mg, 1.6 mmol) were added into a 100 mL three-necked flask equipped with a nitrogen inlet tuber and a constant pressure funnel successively. Under nitrogen atmosphere, the reaction mixture was heated to reflux at 70 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated by rotary evaporation. The resulting compound was extracted with CH_2Cl_2 and distilled water (v:v=1:1) for three times (60 mL× 3). The coalescent organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$) overnight, and then filtered. The filtrate was concentrated by rotary evaporation to give the crude compound, which was purified by flash column chromatography (petroleum ether : dichloromethane = 10 : 1) to give the desired product **TPTE8** (173 mg, yield: 18.0 %) as a light yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.5 Hz, 8H), 7.32 (d, *J* = 8.6 Hz, 4H), 7.12 (d, *J* = 8.6 Hz, 4H), 7.06 (m, 8H), 4.04 (m, 24H), 1.80 (m, 24H), 1.48 (m, 24H), 1.29 (m, 96H), 0.88 (t, *J* = 7.2 Hz, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.19, 154.28, 151.72, 151.32, 144.47, 139.81, 139.59, 134.90, 133.18, 132.88, 131.66, 125.07, 123.15, 122.84, 109.95, 109.88, 78.75, 78.32, 77.90, 74.89, 70.60, 33.20, 33.12, 31.66, 30.99, 30.80, 30.63, 30.56, 27.38, 23.95, 15.36. Maldi-Tof MS: *m/z* calculated for $C_{152}H_{228}O_{20}S$ $[M+Na]^{23+}$: 2430.659, found: 2430.202.

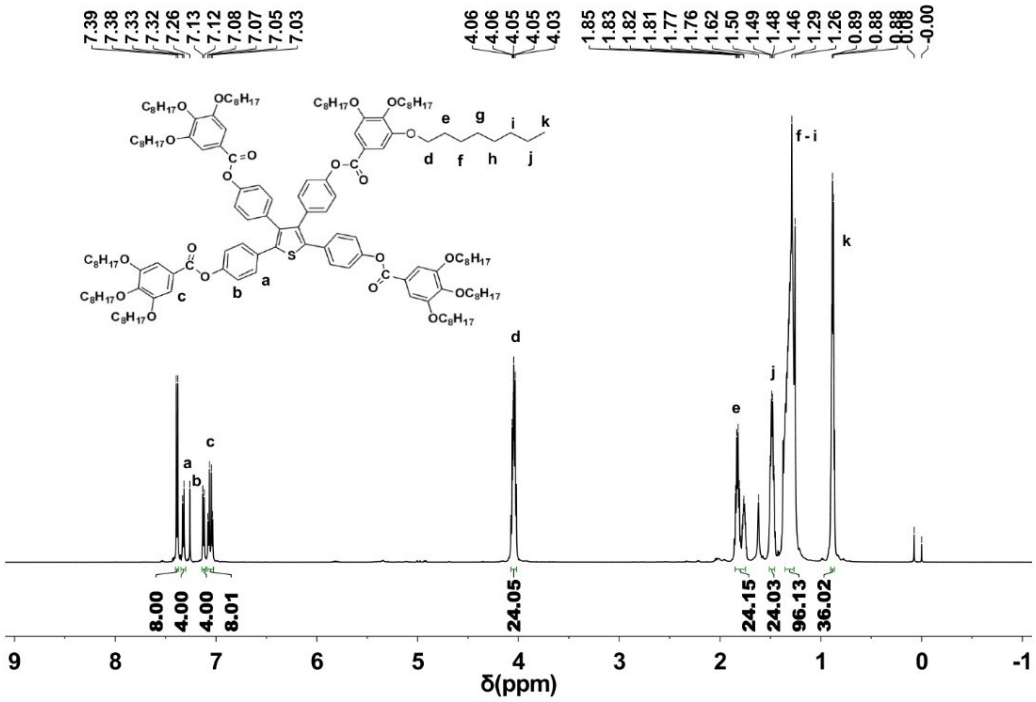


Figure S23. [1]H NMR spectrum of Compound **TPTE8**.

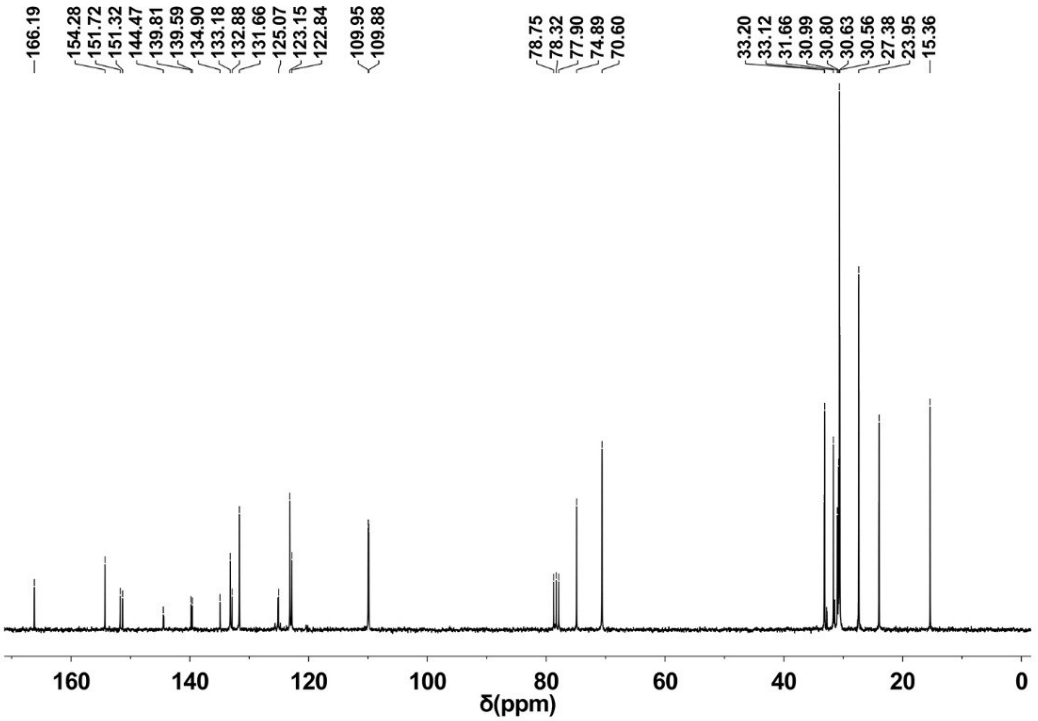


Figure S24. [13]C NMR spectrum of Compound **TPTE8**.

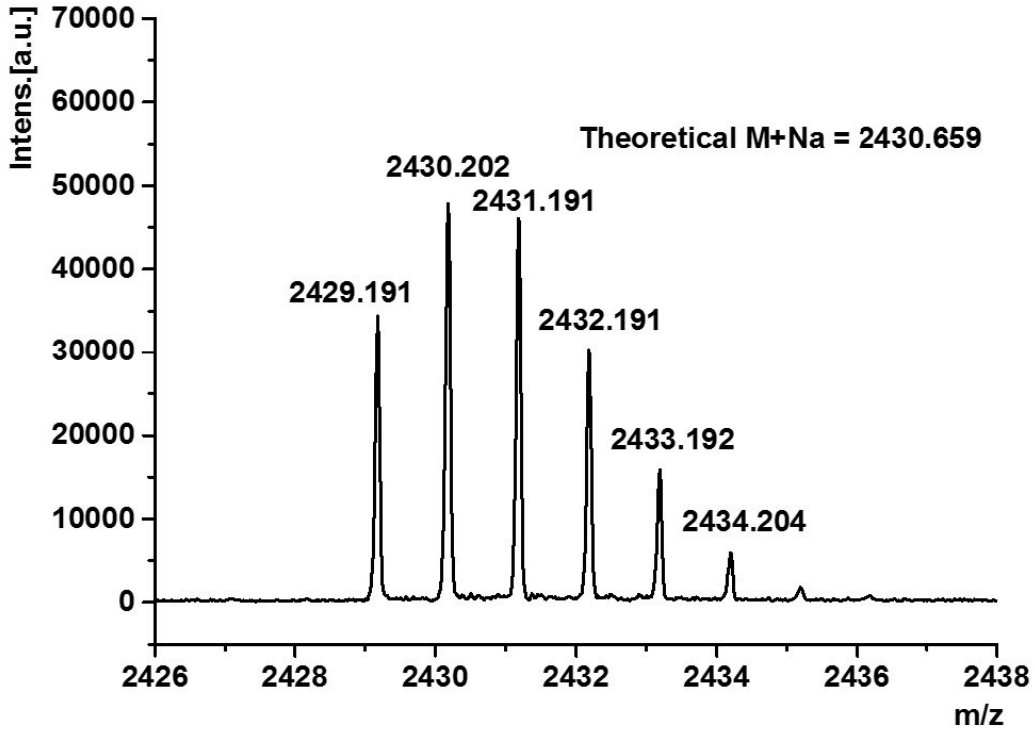


Figure S25. Maldi-Tof mass spectrum of Compound **TPTE8**.

III. Mesomorphic properties of TPTn and TPTEn (n=10, 8)

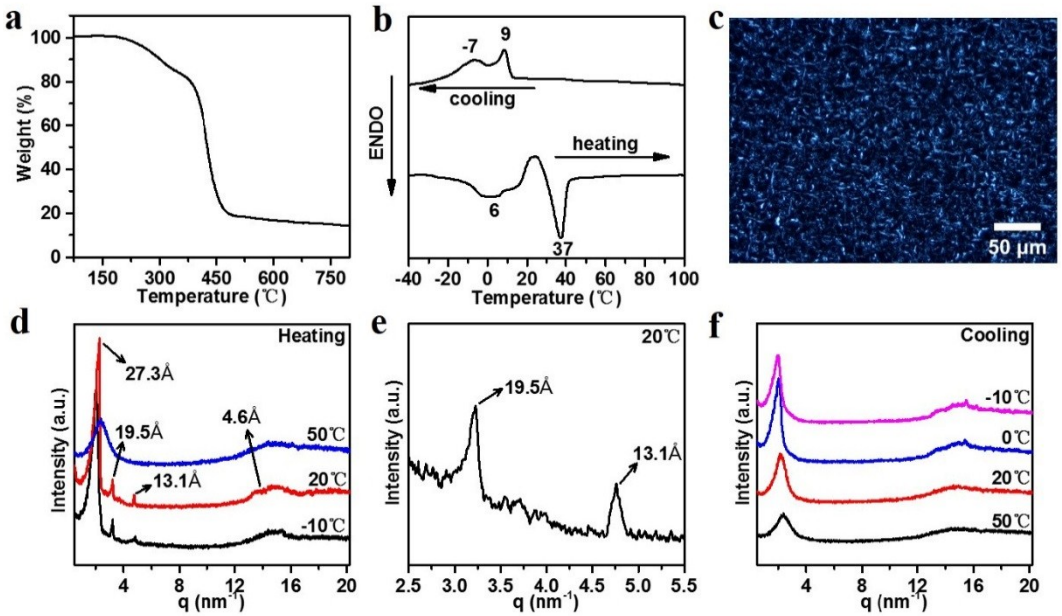


Figure S26. (a) TGA curve of **TPT10**. (b) DSC thermogram of **TPT10** with a heating/cooling rate of 10 °C /min. (c) POM image of **TPT10** recorded at 24 °C. (d) WAXS patterns of **TPT10** recorded on heating process. (e) Partial enlarged small-angle region of WAXS pattern of **TPT10** on heating process recorded at 20 °C. (f) WAXS patterns of **TPT10** recorded on cooling process.

As shown in Figure S26b, **TPT10** presented two enantiotropic phase transitions at 6 °C and 37 °C on the second heating process, which were the melting point and the clearing point of **TPT10**, respectively. **TPT10** appeared a broken focal-conic texture in the range from the room temperature to the clearing point (Figure S26c). The representative WAXS patterns of **TPT10** were shown in Figure S26d-f. During heating, **TPT10** consisted of a sharp and intense scattering peak at d-spacing of 27.3 Å, along with two weak reflections at d-spacing of 19.5 Å and 13.1 Å recorded at 20 °C. These peaks were indexed as 100, 110 and 020, with a reciprocal d-spacing ratio of 1 : √2 : 2.0, which were characteristic reflections of square columnar (Col_s) phase, with the average value of lattice constants of a = 27.0 Å. In addition, **TPT10** showed a broad halo at around 4.6 Å in the wide-angle region, which was in accordance with the liquid-like order of peripheral aliphatic tails in the tetragonal columnar phase.

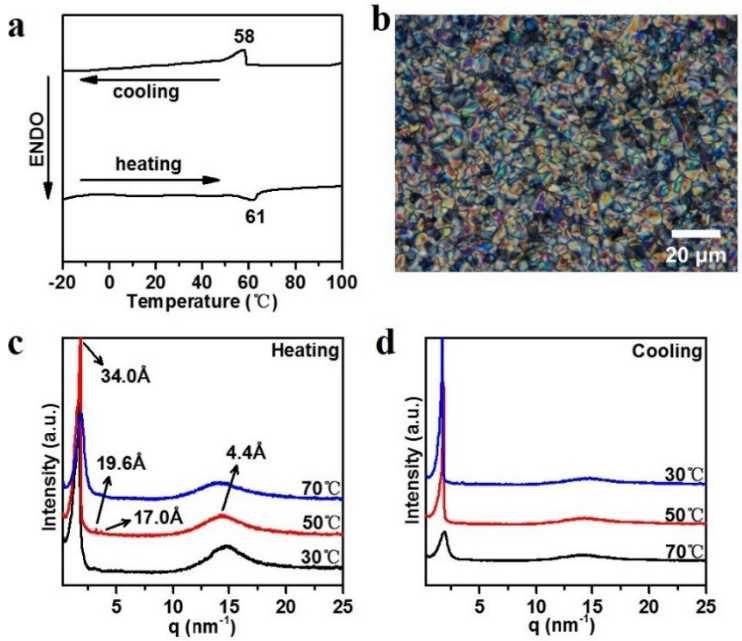


Figure S27. (a) DSC thermogram of **TPTE10** with a heating/cooling rate of 10 °C /min. (b) POM image of **TPTE10** recorded at 45 °C. (c) WAXS patterns of **TPTE10** recorded on heating process. (d) WAXS patterns of **TPTE10** recorded on cooling process.

As illustrated in Figure S27a, the DSC curve of **TPTE10** appeared one phase transition peak with the clearing temperatures at 58 °C on the first cooling process and 61 °C on the second heating process, respectively. Under POM observations, the POM image of **TPTE10** was attributed to a typical focal-conic fan-shaped texture (Figure S27b). The representative WAXS patterns of **TPTE10** at 50 °C recorded on heating process were shown in Figure S27c, which consisted of a sharp and intense scattering peak at d-spacing of 34.0 Å, along with two weak reflections at d-spacing of 19.6 Å and 17.0 Å in the small-angle region, with a reciprocal d-spacing ratio of 1 : √3 : 2. The three peaks were indexed as 100, 110 and 200 reflections, indicating a hexagonal columnar (Col_h) phase. In addition, a broad scattering at around 4.4 Å was observed in the wide-angle region, confirming the liquid-like order of the peripheral alkoxy tails existed.

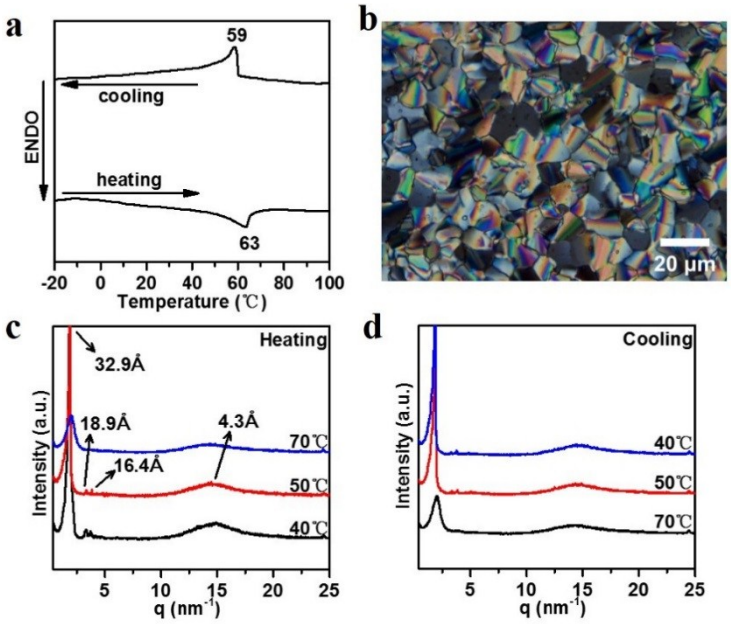


Figure S28. (a) DSC thermogram of **TPTE8** on heating/cooling rate of 10 °C /min. (b) POM image of **TPTE8** recorded at 50 °C. (c) WAXS patterns of **TPTE8** recorded on heating process. (d) WAXS patterns of **TPTE8** recorded on cooling process.

As shown in Figure S28a, the DSC curve of **TPTE8** showed one phase transition peak on the first cooling process (59 °C) and the second heating process (63 °C), respectively. The POM photograph of **TPTE8** exhibited a typical focal-conic fan-shaped texture as shown in Figure S28b. The diffraction pattern of **TPTE8** on heating displayed three reflections in the small-angle region, which consisted of a sharp and intense scattering peak at d-spacing of 32.9 Å, along with two weak reflections at d-spacing of 18.9 Å and 16.4 Å as shown in Figure S28c, with a reciprocal d-spacing ratio of 1 : √3 : 2. The three peaks were indexed as 100, 110 and 200 reflections, indicating a hexagonal columnar (Col_h) phase. In addition, a broad scattering at around 4.3 Å was observed in the wide-angle region, which proved the liquid-like order of the peripheral alkoxy tails.

Ⅳ. UV-vis absorption property of TPTn and TPTEn (n=10, 8)

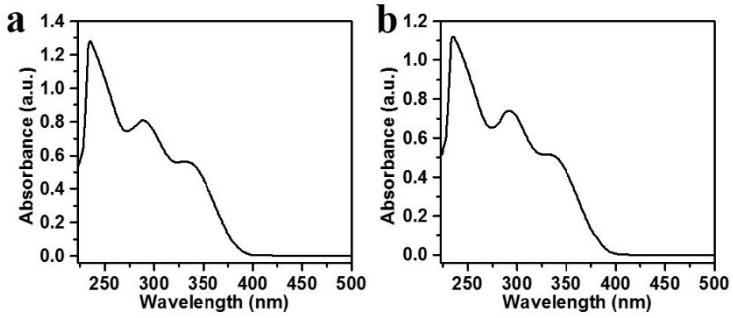


Figure S29. UV-vis spectra of **TPT10** (a) and **TPT8** (b) dissolved in pure THF at r.t. (conc. = 10^{-5} mol/L).

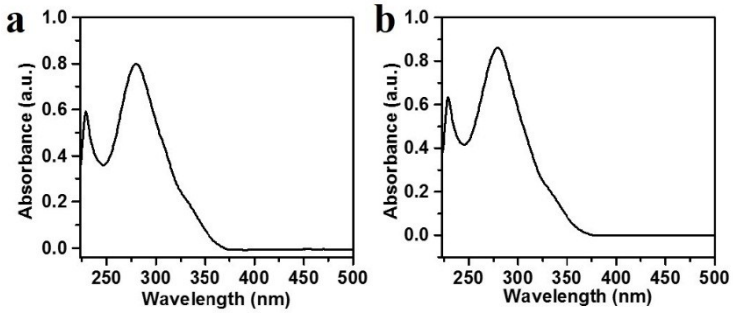


Figure S30. UV-vis spectra of **TPTE10** (a) and **TPTE8** (b) dissolved in pure THF at r.t. (conc. = 10^{-5} mol/L).

Ⅴ. Fluorescence spectra of TPTn and TPTEn (n=10, 8)

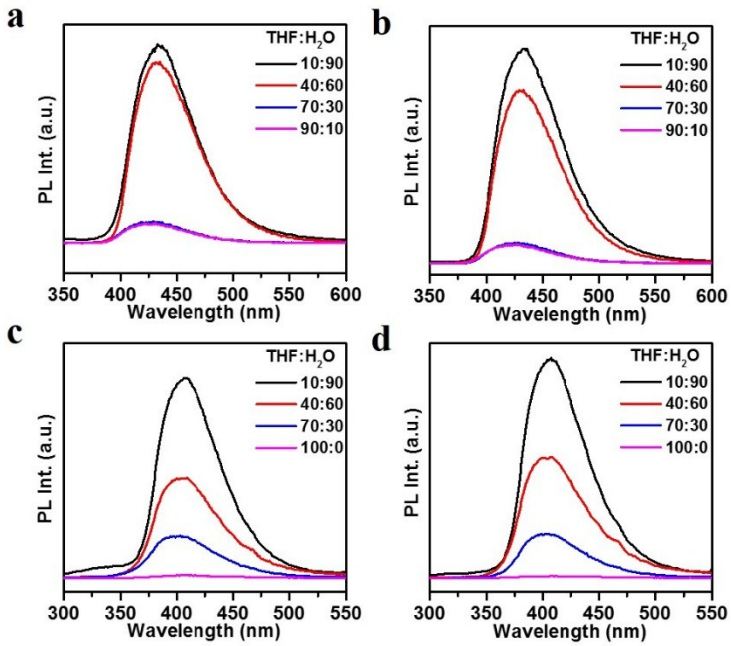


Figure S31. Fluorescence spectra of (a) **TPT10** and (b) **TPT8** in THF/water mixture with different water fractions (conc. = 0.17 mM, λ_{exc} = 330 nm). Fluorescence spectra of (c) **TPTE10** and (d) **TPTE8** in THF/water mixture with different water fractions (conc. = 0.17 mM, λ_{exc} = 280 nm).

Ⅵ. Electrochemical property of TPTn and TPTEn (n=10, 8)

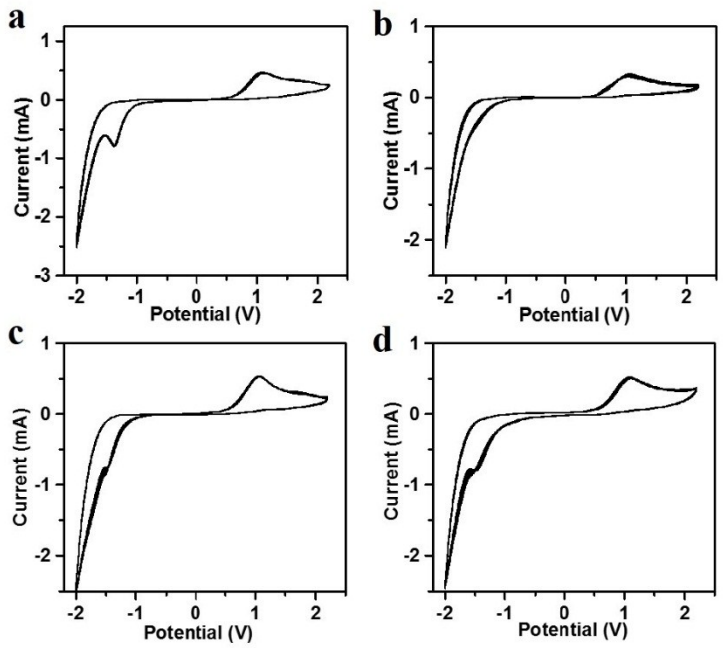


Figure S32. Cyclic voltammetry curves of (a) **TPT10**, (b) **TPT8,** (c) **TPTE10** and (d) **TPTE8** measured in anhydrous dichloromethane (conc. = 10 mg/mL) with a scanning rate of 0.1 V/s at room temperature.

Table S1. Electrochemical properties of **TPTn** and **TPTEn**.

Compound	E_{ox}/eV	E_{red}/eV	E_{HOMO}/eV	E_{LUMO}/eV	ΔEg/eV
TPT10	0.66	-1.05	-5.35	-3.64	1.71
TPT8	0.64	-1.06	-5.33	-3.63	1.70
TPTE10	0.63	-1.27	-5.32	-3.42	1.90
TPTE8	0.64	-1.25	-5.33	-3.44	1.89

Ⅶ. Gelation property

Table S2. Gelation property of **TPT12** and **TPTE12** in various organic solvents

Entry	Solvents	TPT12		TPTE12	
		Phase	(CGC)/mM	Phase	(CGC)/mM
1	DMF	P	-	P	-
2	Methanol	I	-	I	-
3	Ethanol	I	-	I	-
4	Acetone	P	-	P	-
5	THF	S	-	S	-
6	EA	G	32	G	29
7	DCM	S	-	S	-
8	DCM/EA=1/2	G	38	S	-

Note: CGC is the critical gelation concentration measured at room temperature, P = precipitation when cooled from hot solution, I = insoluble, S = soluble at room temperature, G = stable gel (1 month).

Table S3. Gelation property of **TPTn** and **TPTEn** in various organic solvents

Entry	Solvents	TPT10	TPT8	TPTE10	TPTE8
		(CGC)/mM	(CGC)/mM	(CGC)/mM	(CGC)/mM
1	DMF	P	P	P	P
2	Methanol	I	I	I	I
3	Ethanol	I	I	I	I
4	Acetone	P	P	P	P
5	THF	S	S	S	S
6	EA	G(37)	S	S	S
7	DCM	S	S	S	S
8	DCM/EA=1/2	S	S	S	S

Note: CGC is the critical gelation concentration measured at room temperature, P = precipitation when cooled from hot solution, I = insoluble, S = soluble at room temperature, G = stable gel (1 month).

The gelation ability of **TPT10**, **TPT8**, **TPTE10** and **TPTE8** were further tested by the same gelation experimental method, and the experimental results are shown in **Table S3**. When cooled to room temperature, **TPT10** only formed gels in ethyl acetate, and the gel could not stably exist. After a slight shock or a slight increase in temperature, it would return to liquid, which indicated that the gel could not be stable at room temperature. **TPT8**, **TPTE10** and **TPTE8** could not form gels in these above solvents, which may be related to the delicate balance between the rigidity and fluidity required for gelation.[1]

Reference

1. S. K. Pathak, B. Pradhan, M. Gupta, S. K. Pal, A. A. Sudhakar, *Langmuir*, 2016, **32**, 9301-9312.