

Supporting Information

Triphenylene Trimeric Discotic Liquid Crystals: Synthesis, Columnar Mesophase and Photophysical Properties

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Table of Contents

1. Materials and Methods.....	S2
2. Synthesis and Characterization	S3
3. TGA Curves and DSC Curves	S11
4. UV-vis Absorption Spectrum and Fluorescence Spectrum	S12
5. POM Textures	S13
6. XRD Pattern.....	S15
7. NMR Spectrum	S17
8. HRMS Spectrum.....	S27
9. DFT Computational Studies	S30

1. Materials and Methods

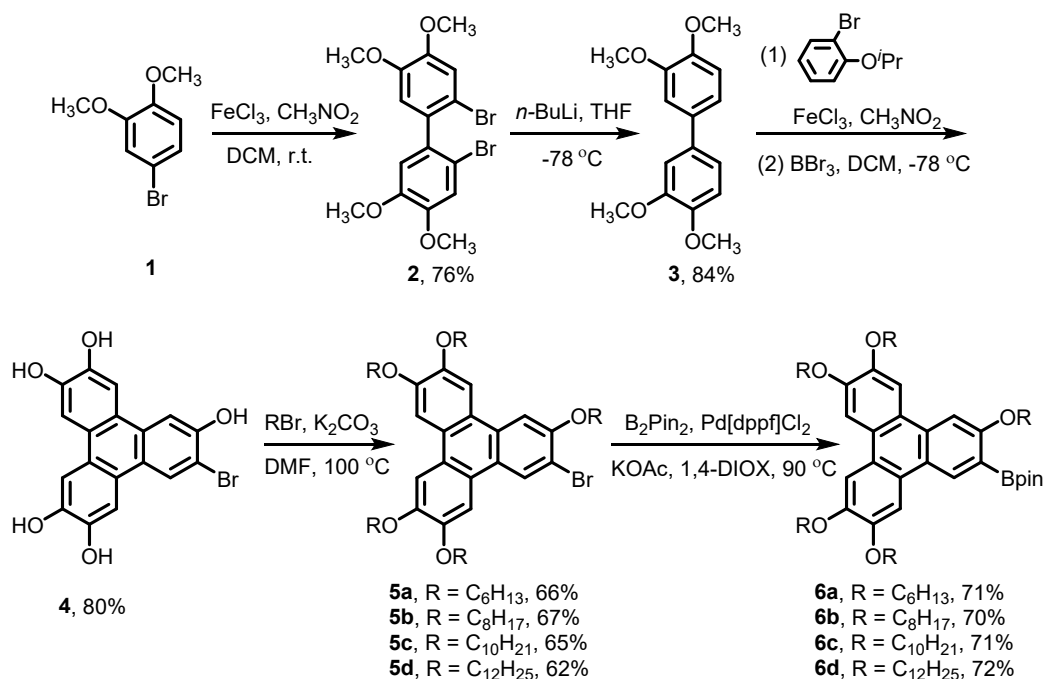
The purity of the reagents used was analytically pure (AR). The solvents were purified by traditional methods and then used. The other reagents were not further purified before use.

^1H NMR spectra were measured at America Bruker Advance 400 MHz. ^{13}C NMR spectra were measured at America Bruker Advance 600 MHz. High-resolution mass spectra (HRMS) spectra were recorded at the Fourier Transform ion cyclotron resonance mass spectrometer (7.0T FTICR-MS) instrument made by IonSpec with MALDI as the ion source. Elemental analyses (EA) were performed on EA3000 (company: Italy Eurovector).

Thermal gravimetric analysis (TGA) was measured on America TA Discovery TGA Q500 instrument with a heating rate of 10 °C/min in the N_2 atmosphere. Differential scanning calorimetry (DSC) was tested on America TA Discovery DSC Q100 instrument with a heating or cooling rate of 10 °C/min in the N_2 atmosphere. Liquid crystalline optical textures were observed by Polarized Optical Microscope (POM) on Olympus BH2 Polarized Optical Microscope (POM) equipped with a MettlerFP82 hot-stages of which temperatures were controlled by XPR-201 and MettlerFP90. Temperature-variation SAXS experiments on Rigaku Smartlab with TCU 110 temperature controller were used to confirm the structure of the mesophases, while the sample temperature was controlled within ± 1 K and the X-ray sources ($\text{Cu K}\alpha$, $\lambda = 0.154$ nm) were provided by 40 kW ceramic tubes as well as a scanning speed of 10 °C/min. UV-vis absorption spectra were recorded on an America PE Lambda 950 at room temperature. Fluorescence spectra were measured on HORIBA Fluoromax-4p, and the quantum efficiencies were measured by HORIB-F-3029 Integrating Sphere, HORIBA, Kyoto, Japan.

2. Synthesis and Characterization

2.1 Synthesis of Intermediate



Scheme S1. Preparation of the pentylalkoxy-substituted triphenyleneboronic esters 6.

Synthesis of 2,2'-dibromo-3,3',4,4'-tetramethoxy-1,1'-biphenyl (2)

To a stirred solution of 4-bromo-1,2-dimethoxybenzene (10.00 g, 4.60 mmol) in CH₂Cl₂ (20 mL), a solution of FeCl₃ (15.00 g, 9.20 mmol) in CH₃NO₂ (5 mL) was added slowly. The resulting solution was stirred at room temperature until completed conversion of the substrate. Methanol was slowly dropwise added to the reaction system at -40 °C until the solution was yellow, extracted with dichloromethane (DCM) and distilled water, dried with anhydrous magnesium sulfate for the organic phase, filtered, concentrated to remove the solvent, and recrystallization with ethanol and ethyl acetate to obtain white solid compound 2 (7.51 g, 76% yield).

¹H NMR (CDCl₃, 400 MHz) δ 7.10 (s, 2H, ArH), 6.75 (s, 2H, ArH), 3.90 (s, 6H, OCH₃), 3.85 (s, 6H, OCH₃).

Synthesis of 3,3',4,4'-tetramethoxy-1,1'-biphenyl (3)

Compound 2 (16.00 g, 38.00 mmol) was weighed in a round bottom flask, and the tetrahydrofuran (THF, 100 mL) was added under the protection of nitrogen. The *n*-BuLi

(50 mL, 125.00 mmol, 2.50 mol/L) was slowly injected into the flask in a constant temperature reaction bath at -78 °C, then the mixture was stirred for 24 h. Methanol was slowly added dropwise to the flask until the solution was milky white, and then distilled water (50 mL) was added and stirred for 5 min, then extracted with DCM, and the organic phase was dried with anhydrous magnesium sulfate, filtered, concentrated under reduced pressure to remove the solvent, and recrystallization with methanol. Filtration gave the product as a yellow solid compound **3** (8.40 g, 84% yield).

¹H NMR (CDCl₃, 400 MHz) δ 7.16 – 7.02 (m, 4H, ArH), 6.91 (d, J = 8.2 Hz, 2H, ArH), 3.92 (d, J = 14.5 Hz, 12H, OCH₃).

Synthesis of 11-bromotriphenylene-2,3,6,7,10-pentaol (**4**)

Compound **3** (2.00 g, 7.2 mmol), 1-bromo-2-propoxybenzene (2.40 g, 10.00 mmol), and FeCl₃ (7.00 g, 21.90 mmol) were weighed into a 250 mL round bottom flask, 10 mL of CH₃NO₂ and 130 mL of DCM were added to dissolve, stirred at room temperature. After the reaction is finished, keep it in an ice water bath, and pour the reaction solution into the beaker slowly, Distilled water was added to precipitate the solid. The solid were dried, weighed and dissolved with dried DCM (100 mL) in a schlenk tube, BBr₃ (3.20 mL, 18.76 mol) was slowly added under the protection of nitrogen at -78 °C. The resulting solution was stirred for 12 h. The reaction mixture was slowly poured into the distilled water in a beaker at 0 °C, distilled water was added sequentially to precipitate the solid. Filtration gave dark blue solid **4** (2.58 g, 81% yield).

¹H NMR (DMSO-d₆, TMS, 400 MHz) δ 10.42 (s, 1H, OH), 8.40 (d, J = 3.9 Hz, 1H, ArH), 7.82 (d, J = 4.1 Hz, 1H, ArH), 7.76 (d, J = 4.5 Hz, 1H, ArH), 7.68 (d, J = 4.3 Hz, 1H, ArH), 7.64 (t, J = 5.3 Hz, 2H, ArH), 3.56 (d, J = 18.6 Hz, 4H, OH).

Synthesis of compound **5a**

Compound **4** (1.90 g, 4.90 mol), 1-bromohexane (4.90 g, 29.80 mmol), K₂CO₃ (13.7 g, 100.00 mmol), DMF (80 mL) were added in a round bottom flask, the reaction solution was refluxed at 100 °C for 24 h. The reaction solution was slowly poured into the distilled water in a beaker at 0 °C, then dilute hydrochloric acid was added dropwise to adjust the pH to acidic. The crude product was filtered and purified by silica gel column chromatography (eluent: V_{DCM}: V_{PE} = 1 : 3). Finally recrystallization with ethyl acetate and ethanol to obtain a white solid compound **5a** (2.61 g, 66% yield).

$^1\text{H NMR}$ (CDCl_3 , TMS, 400 MHz) δ : 8.57 (s, 1H, ArH), 7.83 (s, 1H, ArH), 7.77 (d, $J = 7.4$ Hz, 4H, ArH), 4.26-4.19 (m, 10H, OCH_2), 1.99-1.89 (m, 10H, CH_2), 1.57 (s, 10H, CH_2), 1.39 (s, 20H, CH_2), 0.98 – 0.87 (m, 15H, CH_3).

Synthesis of compound 5b

Compound 4 (2.00 g, 5.20 mmol), 1-bromooctane (6.25 g, 31.20 mmol), K_2CO_3 (13.70 g, 100.00 mmol), DMF (90 mL) were added in a round bottom flask, the reaction solution was refluxed at 100 °C for 24 h. The reaction solution was slowly poured into the distilled water in a beaker at 0 °C, then dilute hydrochloric acid was added dropwise to adjust the pH to acidic. Silica gel column chromatography (eluent: $V_{\text{DCM}} : V_{\text{PE}} = 1 : 3$) was used for separation and purification, and recrystallization with ethyl acetate and ethanol to obtain light yellow solid compound 5b (3.21 g, 68% yield).

$^1\text{H NMR}$ (CDCl_3 , TMS, 400 MHz) δ : 8.58 (s, 1H, ArH), 7.85 (s, 1H, ArH), 7.79 (d, $J = 7.1$ Hz, 4H, ArH), 4.27 – 4.20 (m, 10H, OCH_2), 1.99-1.90 (m, 10H, CH_2), 1.58 (dd, $J = 14.5, 8.6$ Hz, 10H, CH_2), 1.45-1.29 (m, 40H, CH_2), 0.90 (dd, $J = 6.9, 5.4$ Hz, 15H, CH_3).

Synthesis of compound 5c

Compound 4 (1.80 g, 4.70 mmol), 1-bromodecane (6.20 g, 31.00 mmol), K_2CO_3 (13.70 g, 100.00 mmol), DMF (90 mL) were added in a round bottom flask, the reaction solution was refluxed at 100 °C for 24 h. The reaction solution was slowly poured into the distilled water in a beaker at 0 °C, then dilute hydrochloric acid was added dropwise to adjust the pH to acidic. Silica gel column chromatography (eluent: $V_{\text{DCM}} : V_{\text{PE}} = 1 : 3$) was used for separation and purification, and recrystallization with ethyl acetate and ethanol to obtain light yellow solid compound 5c (3.33 g, 65% yield).

$^1\text{H NMR}$ (CDCl_3 , TMS, 400 MHz) δ : 8.57 (s, 1H, ArH), 7.84 (s, 1H, ArH), 7.78 (d, $J = 7.1$ Hz, 4H, ArH), 4.30 – 4.17 (m, 10H, OCH_2), 1.94 (m, 10H, CH_2), 1.58 (d, $J = 8.4$ Hz, 10H, CH_2), 1.47 – 1.24 (m, 60H, CH_2), 0.88 (t, $J = 6.6$ Hz, 15H, CH_3).

Synthesis of compound 5d

Compound 4 (2.00 g, 5.20 mmol), 1-bromododecane (7.70 g, 31.00 mmol), K_2CO_3 (13.70 g, 100.00 mmol), DMF (100 mL) were added in a round bottom flask, the reaction solution was refluxed at 100 °C for 24 h. The reaction solution was slowly poured into the distilled water in a beaker at 0 °C, then dilute hydrochloric acid was

added dropwise to adjust the pH to acidic. Silica gel column chromatography (eluent: $V_{\text{DCM}} : V_{\text{PE}} = 1 : 3$) was used for separation and purification, and recrystallization with ethyl acetate and ethanol to obtain a light yellow solid compound for **5d** (4.10 g, 62% yield).

$^1\text{H NMR}$ (CDCl_3 , TMS, 400 MHz) δ : 8.59 (s, 1H, ArH), 7.85 (s, 1H, ArH), 7.79 (d, $J = 6.9$ Hz, 4H, ArH), 4.27-4.20 (m, 10H, OCH_2), 2.00 – 1.89 (m, 10H, CH_2), 1.63-1.55 (m, 10H, CH_2), 1.46-1.22 (m, 80H, CH_2), 0.88 (t, $J = 6.8$ Hz, 15H, CH_3).

Synthesis of compound **6a**

Under protection of nitrogen, compound **5a** (0.32 g, 0.40 mmol), B_2Pin_2 (0.25 g, 1.00 mmol), KOAc (0.13 g, 1.30 mmol), $\text{Pd}[\text{dppf}]\text{Cl}_2$ (36.5 mg, 0.04 mmol), 1,4-dioxane (10 mL) were added in a reaction tube. The resulting solution was stirred at 90 °C for 24 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: $V_{\text{DCM}} : V_{\text{PE}} = 2 : 1$), and finally recrystallization with ethyl acetate and ethanol to obtain white solid compound **6a** (0.28 g, 71% yield).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.97 (s, 1H, ArH), 8.04 (d, $J = 5.9$ Hz, 1H, ArH), 7.90 (s, 1H, ArH), 7.82 (s, 2H, ArH), 7.76 (d, $J = 17.4$ Hz, 1H, ArH), 4.24 (s, 10H), 1.94 (s, 10H, OCH_2), 1.58 (s, 10H, CH_2), 1.50 – 1.41 (m, 12H, CH_3), 1.40 (s, 20H, CH_2), 0.94 (s, 15H, CH_3).

Synthesis of compound **6b**

Under protection of nitrogen, compound **5b** (0.47 g, 0.50 mmol), B_2Pin_2 (0.28 g, 1.10 mmol), $\text{Pd}[\text{dppf}]\text{Cl}_2$ (40.9 mg, 0.05 mmol), KOAc (0.15 g, 1.50 mmol) were added in a reaction tube. The resulting solution was stirred at 90 °C for 24 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO_4 and concentrated in vacuo. Separation and purification were performed using silica gel column chromatography (eluent: $V_{\text{DCM}} : V_{\text{PE}} = 2 : 1$), and finally recrystallization with ethyl acetate and ethanol to obtain white solid compound **6b** (0.35 g, 70% yield).

$^1\text{H NMR}$ (CDCl_3 , TMS, 400 MHz) δ 8.95 (d, $J = 14.3$ Hz, 1H, ArH), 8.06 (d, $J = 7.9$ Hz, 1H, ArH), 7.90 (s, 1H, ArH), 7.82 (d, $J = 2.8$ Hz, 2H, ArH), 7.76 (d, $J = 8.8$ Hz, 1H, ArH), 4.27 (m, 10H, OCH_2), 1.95 (q, $J = 7.2$ Hz, 10H, CH_2), 1.64 – 1.51 (m, 10H,

CH₂), 1.42 (t, $J = 7.3$ Hz, 12H, CH₃), 1.36 – 1.24 (m, 40H, CH₂), 0.89 (t, $J = 6.6$ Hz, 15H, CH₃).

Synthesis of compound 6c

Under protection of nitrogen, compound **5c** (1.09 g, 1.00 mmol), B₂Pin₂ (0.51 g, 2.00 mmol), Pd[dppf]Cl₂ (40.8 mg, 0.05 mmol), KOAc (0.30 g, 3.00 mmol) were added in a reaction tube. The resulting solution was stirred at 90 °C for 24 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. Separation and purification were performed using silica gel column chromatography (eluent: V_{DCM} : V_{PE} = 2 : 1), and white solid compound **6c** (0.80 g, 71% yield) was obtained by recrystallization with ethyl acetate and ethanol.

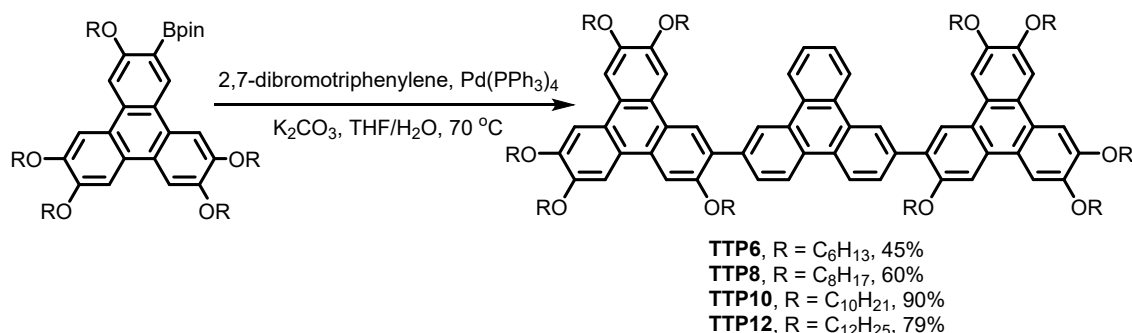
¹H NMR (CDCl₃, TMS, 400 MHz) δ 8.97 (s, 1H, ArH), 8.05 (s, 1H, ArH), 7.89 (s, 1H, ArH), 7.82 (s, 2H, ArH), 7.77 (s, 1H, ArH), 4.33 – 4.22 (m, 10H, OCH₂), 1.95 (dd, $J = 14.3, 6.7$ Hz, 10H, CH₂), 1.62 – 1.55 (m, 10H, CH₂), 1.43 (d, $J = 7.6$ Hz, 12H, CH₃), 1.34 (d, $J = 39.4$ Hz, 60H, CH₂), 0.89 (t, $J = 6.5$ Hz, 15H, CH₃).

Synthesis of compound 6d

Under protection of nitrogen, compound **5d** (0.55 g, 0.45 mmol), B₂Pin₂ (0.25 g, 0.98 mmol), Pd[dppf]Cl₂ (36.5 mg, 0.04 mmol), KOAc (0.13 g, 1.34 mmol) were added in a reaction tube. The resulting solution was stirred at 90 °C for 24 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. Separation and purification were performed using silica gel column chromatography (eluent: V_{DCM} : V_{PE} = 2 : 1), was used for separation and purification, and white solid compound **6d** (0.41 g, 72% yield) was obtained by recrystallization with ethyl acetate and ethanol.

¹H NMR (CDCl₃, TMS, 400 MHz) δ 8.38 (d, $J = 9.2$ Hz, 1H, ArH), 7.91 (s, 2H, ArH), 7.86 (d, $J = 2.5$ Hz, 1H, ArH), 7.82 (s, 2H, ArH), 4.21 (m, 10H, OCH₂), 1.92 (q, $J = 8.7, 8.1$ Hz, 10H, CH₂), 1.55 (s, 10H, CH₂), 1.50 – 1.38 (m, 12H, CH₃), 1.27 (d, $J = 5.0$ Hz, 80H, CH₂), 0.88 (t, $J = 6.6$ Hz, 15H, CH₃).

2.2 Synthesis of Target Molecule



Scheme S2 Synthesis of compound **TTPn**.

Synthesis of compound **TTP6**

Under protection of nitrogen, compound **6a** (0.34 g, 0.40 mmol), 2,7-Dibromotriphenylene (70.0 mg, 0.18 mmol), K₂CO₃ (0.50 g, 3.62 mmol), Pd(PPh₃)₄ (35.0 mg, 0.03 mmol), and THF/H₂O (2/1, 10 mL) were added in a reaction tube. The resulting solution was stirred at 70 °C for 48 h. The reaction mixture was cooled to room temperature washed with saturated brine and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: V_{DCM} : V_{PE} = 1 : 2), and finally recrystallization with ethyl acetate and ethanol to obtain yellow solid **TTP6** (0.14 g, 45% yield).

¹H NMR (CDCl₃, TMS, 400 MHz) δ 9.05 (s, 2H, ArH), 8.85 – 8.76 (m, 4H, ArH), 8.57 (s, 2H, ArH), 8.09 – 7.95 (m, 8H, ArH), 7.88 (s, 4H, ArH), 7.70 (dd, *J* = 6.1, 3.0 Hz, 2H, ArH), 4.39 – 4.12 (m, 20H, OCH₂), 1.93 (m, 20H, CH₂), 1.62 – 1.24 (m, 60H, CH₂), 1.01 – 0.76 (m, 30H, CH₃). ¹³C NMR (CDCl₃, TMS, 151 MHz) δ 155.16, 149.38, 148.91, 148.85, 137.65, 130.62, 129.75, 129.64, 129.26, 127.18, 125.70, 124.92, 124.73, 124.08, 123.55, 123.22, 122.97, 107.92, 107.60, 106.97, 106.77, 105.12, 69.91, 69.87, 69.54, 69.50, 68.89, 31.80, 31.77, 31.70, 31.62, 29.54, 29.49, 29.45, 26.03, 25.97, 25.95, 25.93, 25.86, 22.73, 22.65, 22.59, 14.12, 14.05, 14.01. **HRMS** (MALDI) calculate for C₁₁₄H₁₅₂O₁₀ [M]⁺ 1682.1419, found 1682.1420. **Elemental Analysis** (C₁₁₄H₁₅₂O₁₀, MW 1682.46, %): calculate C 81.38%, H 9.11%; found C 80.83%, H 8.91%.

Synthesis of compound TTP8

Under protection of nitrogen, compound **6b** (0.33 g, 0.33 mmol), 2,7-dibromobenzophene (58.0 mg, 0.40 mmol), K₂CO₃ (0.30 g, 2.25 mmol), and Pd(PPh₃)₄ (35.0 mg, 0.03 mmol), and THF/H₂O (2/1, 10 mL) were added in a reaction tube. The resulting solution was stirred at 70 °C for 48 h. The reaction mixture was cooled to room temperature washed with saturated brine and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: V_{DCM} : V_{PE} = 1 : 2), and finally recrystallization with ethyl acetate and ethanol to obtain light yellow solid **TTP8** (0.18 g, 60% yield).

¹H NMR (CDCl₃, TMS 400 MHz) δ 9.05 (s, 2H), 8.86 – 8.76 (m, 4H), 8.57 (s, 2H), 8.08 – 7.94 (m, 8H), 7.88 (s, 4H), 7.69 (dd, *J* = 6.2, 3.2 Hz, 2H), 4.24 (d, *J* = 26.7 Hz, 20H), 2.03 – 1.80 (m, 20H), 1.63 – 1.15 (m, 100H), 0.96 – 0.69 (m, 30H). ¹³C NMR (CDCl₃, TMS, 151 MHz), δ 147.85, 136.58, 129.62, 128.59, 128.18, 126.13, 124.64, 123.67, 122.49, 122.16, 121.91, 106.91, 105.94, 105.71, 104.14, 68.86, 68.50, 68.43, 67.89, 30.86, 30.79, 30.76, 28.68, 28.51, 28.44, 28.36, 28.27, 28.23, 25.34, 25.24, 25.21, 25.14, 21.69, 21.64, 21.61, 13.11, 13.05. HRMS (MALDI) calculate for C₁₃₄H₁₉₂O₁₀ [M]⁺ 1962.4549, found 1962.4547. **Elemental Analysis** (C₁₃₄H₁₉₂O₁₀, MW 1963.00, %): calculate C 81.99%, H 9.86%; found C 82.04%, H 9.40%.

Synthesis of compound TTP10

Under protection of nitrogen, compound **6c** (0.33 g, 0.37 mmol), 2,7-Dibromotriphenylene (58.0 mg, 0.15 mmol), K₂CO₃ (0.3 g, 2.25 mmol), and Pd(PPh₃)₄ (35.0 mg, 0.03 mmol), and THF/H₂O (2/1, 10 mL) were added in a reaction tube. The resulting solution was stirred at 70 °C for 48 h. The reaction mixture was cooled to room temperature washed with saturated brine and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: V_{DCM} : V_{PE} = 1 : 2), and finally recrystallization with ethyl acetate and ethanol to obtain light yellow solid **TTP10** (0.28 g, 90% yield).

¹H NMR (CDCl₃, TMS 400 MHz) δ 9.06 (s, 2H, ArH), 8.85 – 8.78 (m, 4H, ArH), 8.57 (s, 2H, ArH), 8.08 – 7.96 (m, 8H, ArH), 7.88 (s, 4H, ArH), 7.69 (dd, *J* = 6.3, 3.2 Hz, 2H, ArH), 4.36 – 4.14 (m, 20H, OCH₂), 2.02 – 1.84 (m, 20H, CH₂), 1.63 – 1.15 (m,

140H, CH₂), 0.95 – 0.78 (m, 30H, CH₃). ¹³C NMR (CDCl₃, TMS, 151 MHz) δ 148.92, 129.25, 127.20, 125.72, 124.74, 123.56, 123.23, 122.98, 108.02, 107.03, 106.81, 105.17, 69.93, 69.57, 69.49, 68.92, 31.99, 31.94, 31.91, 29.77, 29.70, 29.68, 29.61, 29.57, 29.54, 29.45, 29.39, 29.36, 26.38, 26.29, 26.26, 26.19, 22.75, 22.71, 14.17, 14.14. **HRMS** (MALDI) calculate for C₁₅₄H₂₃₂O₁₀ [M]⁺ 2242.7679, found 2242.7670. **Elemental Analysis** (C₁₅₄H₂₃₂O₁₀, MW 2243.54, %): calculate C 82.45%, H 10.42%; found C 82.86%, H 10.33%.

Synthesis of compound TTP12

Under protection of nitrogen, compound **6d** (0.42 g, 0.33 mmol), 2,7-Dibromotriphenylene (58.0 mg, 0.15 mmol), K₂CO₃ (0.30 g, 2.25 mmol), and Pd(PPh₃)₄ (35.0 mg, 0.03 mmol), and THF/H₂O (2/1, 10 mL) were added in a reaction tube. The resulting solution was stirred at 70 °C for 48 h. The reaction mixture was cooled to room temperature washed with saturated brine and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: V_{DCM} : V_{PE} = 1 : 2), and finally recrystallization with ethyl acetate and ethanol to obtain light yellow solid **TTP12** (0.28 g, 79% yield).

¹H NMR (CDCl₃, TMS 400 MHz) δ 9.06 (s, 2H, ArH), 8.85 – 8.78 (m, 4H, ArH), 8.57 (s, 2H, ArH), 8.08 – 7.96 (m, 8H, ArH), 7.88 (s, 4H, ArH), 7.69 (dd, *J* = 6.1, 3.1 Hz, 2H, ArH), 4.34 – 4.17 (m, 20H, OCH₂), 2.02 – 1.83 (m, 20H, CH₂), 1.69 – 1.08 (m, 180H, CH₂), 0.95 – 0.79 (m, 30H, CH₃). ¹³C NMR (CDCl₃, TMS, 151 MHz) δ 154.14, 147.87, 128.19, 126.14, 123.90, 123.68, 122.19, 121.93, 106.97, 105.98, 105.77, 104.12, 68.88, 68.52, 68.45, 67.87, 30.93, 30.88, 30.85, 28.71, 28.68, 28.64, 28.62, 28.58, 28.56, 28.53, 28.51, 28.48, 28.41, 28.39, 28.33, 28.30, 25.33, 25.24, 25.21, 25.15, 21.69, 21.65, 13.11, 13.08. **HRMS** (MALDI) calculate for C₁₇₄H₂₇₂O₁₀ [M]⁺ 2523.0809, found 2523.0807. **Elemental Analysis** (C₁₇₄H₂₇₂O₁₀, MW 2524.08, %): calculate C 82.80%, H 10.86%; found C 82.36%, H 10.94%.

3. TGA Curves and DSC Curves

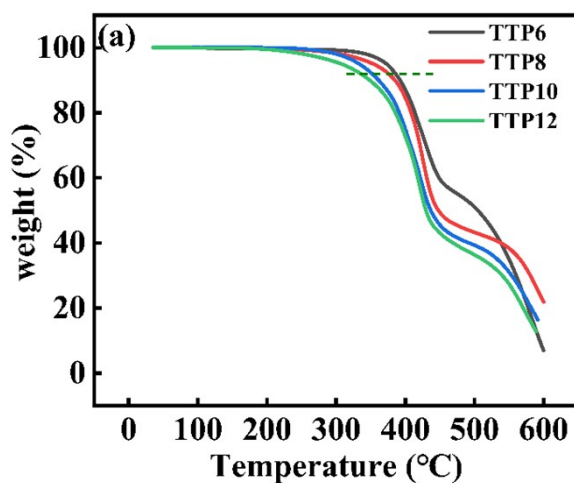
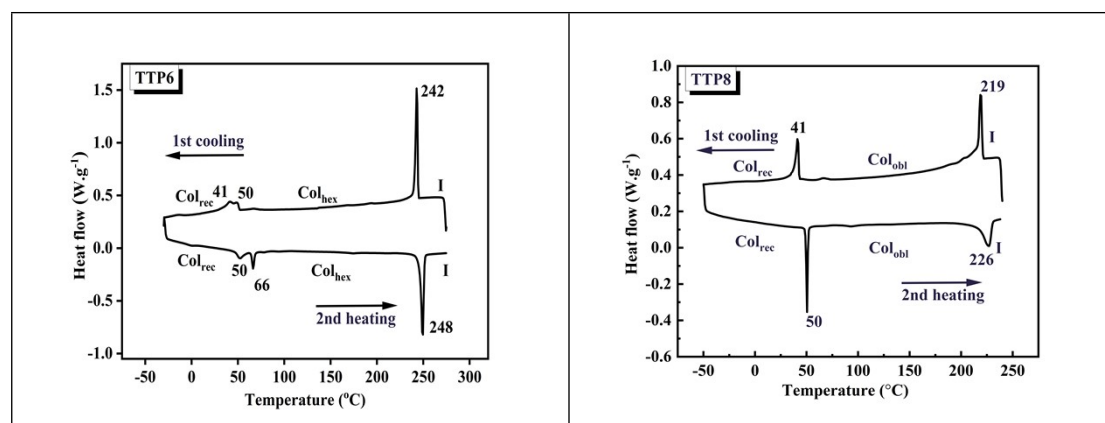


Figure S1. TGA Curves of TTPn.

Table S1 Thermal decomposition loss temperature of compound TTPn.

Compounds	TTP6	TTP8	TTP10	TTP12
$T_{dec}/^{\circ}\text{C}$ (1% loss)	316	270	286	230
$T_{dec}/^{\circ}\text{C}$ (2% loss)	343	307	310	261
$T_{dec}/^{\circ}\text{C}$ (5% loss)	373	353	342	316

T_{dec} is to maintain a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen, measuring the temperature when 1%, 2%, and 5% weight loss is detected.



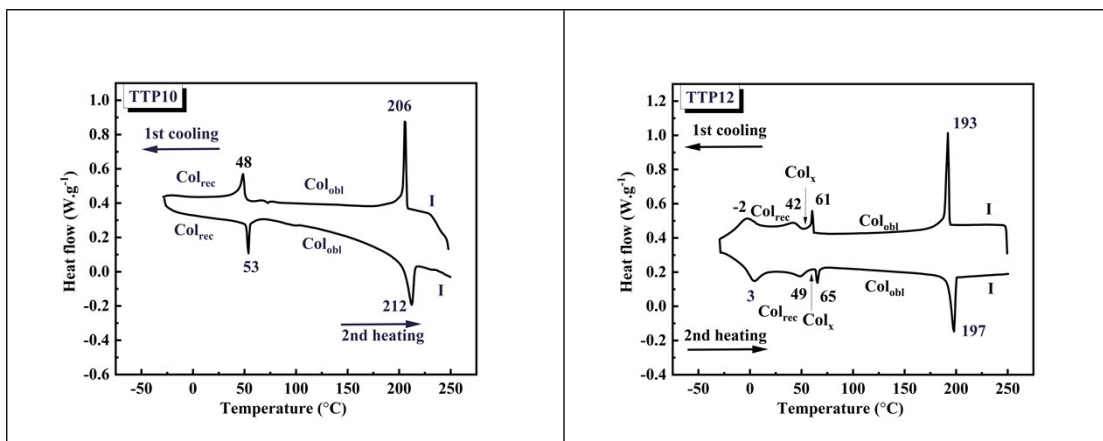


Figure S2 DSC of TTPn.

4. UV-vis Absorption Spectrum and Fluorescence Spectrum

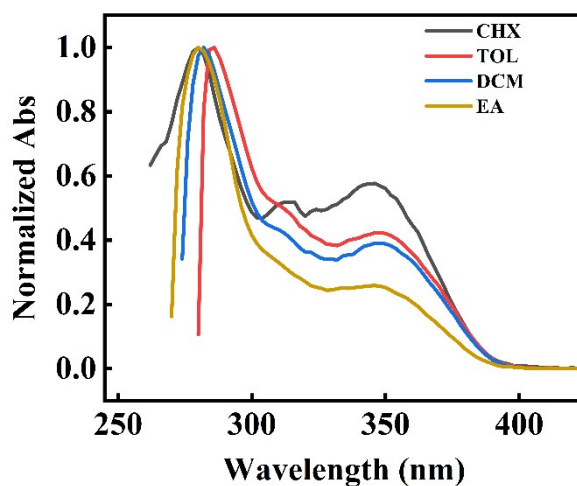


Figure S3 UV-vis absorption spectrum of TTP8 in different solvents ($c = 1 \times 10^{-5}$ mol/L).

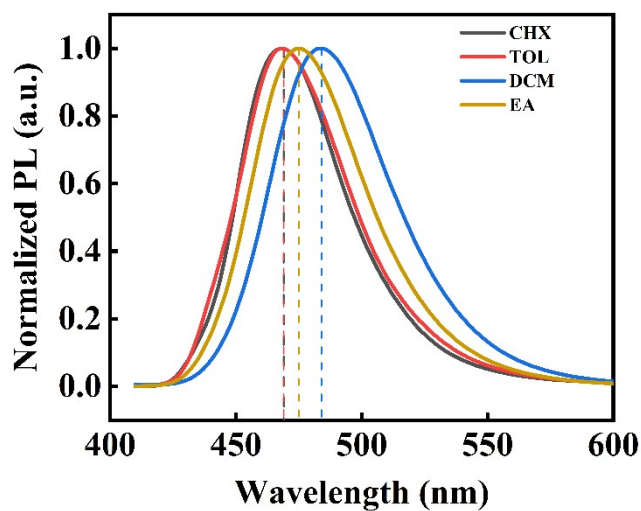
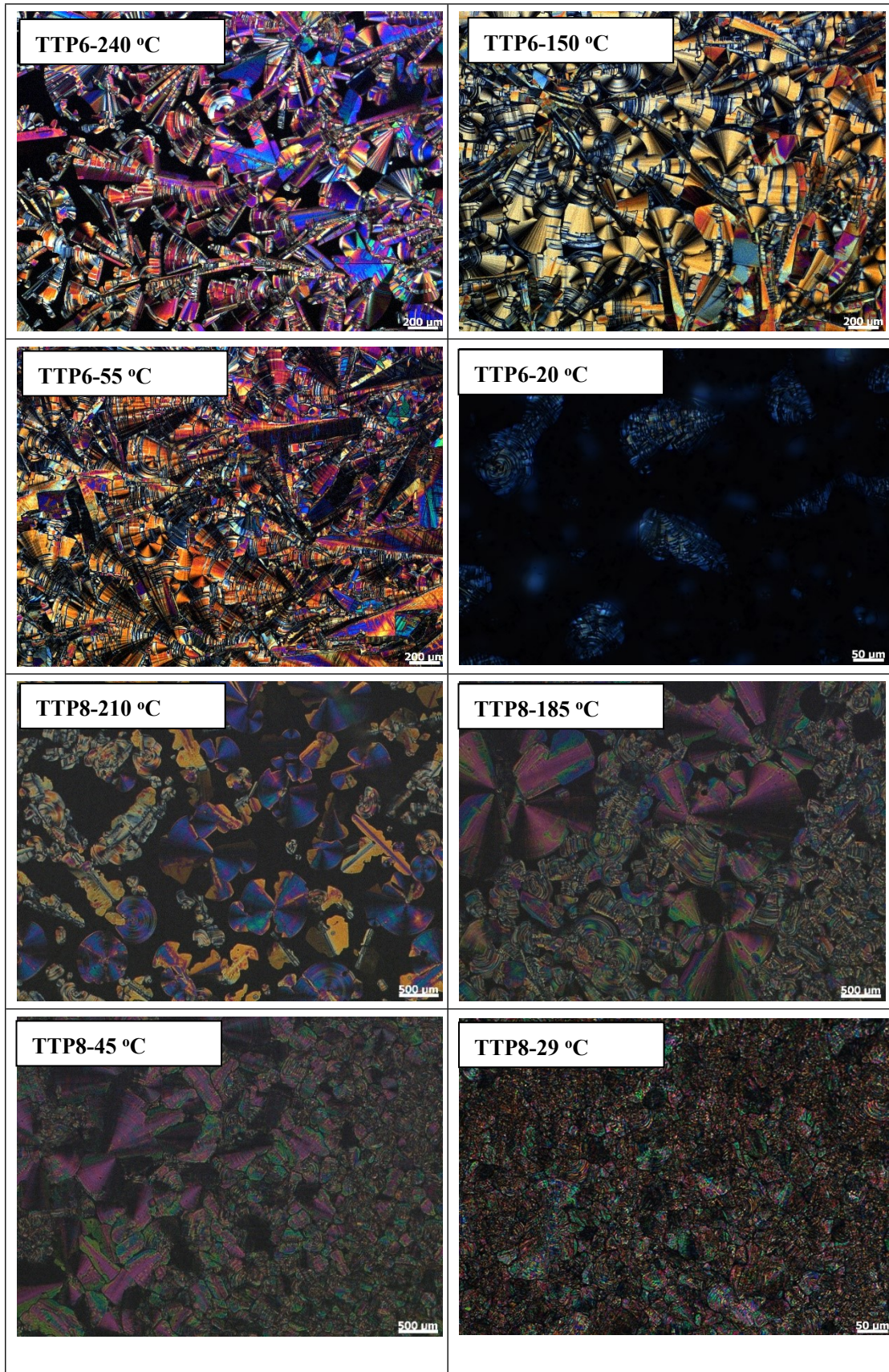


Figure S4 Fluorescence spectrum of TTP8 in different solvents ($c = 1 \times 10^{-5}$ mol/L).

5. POM Textures



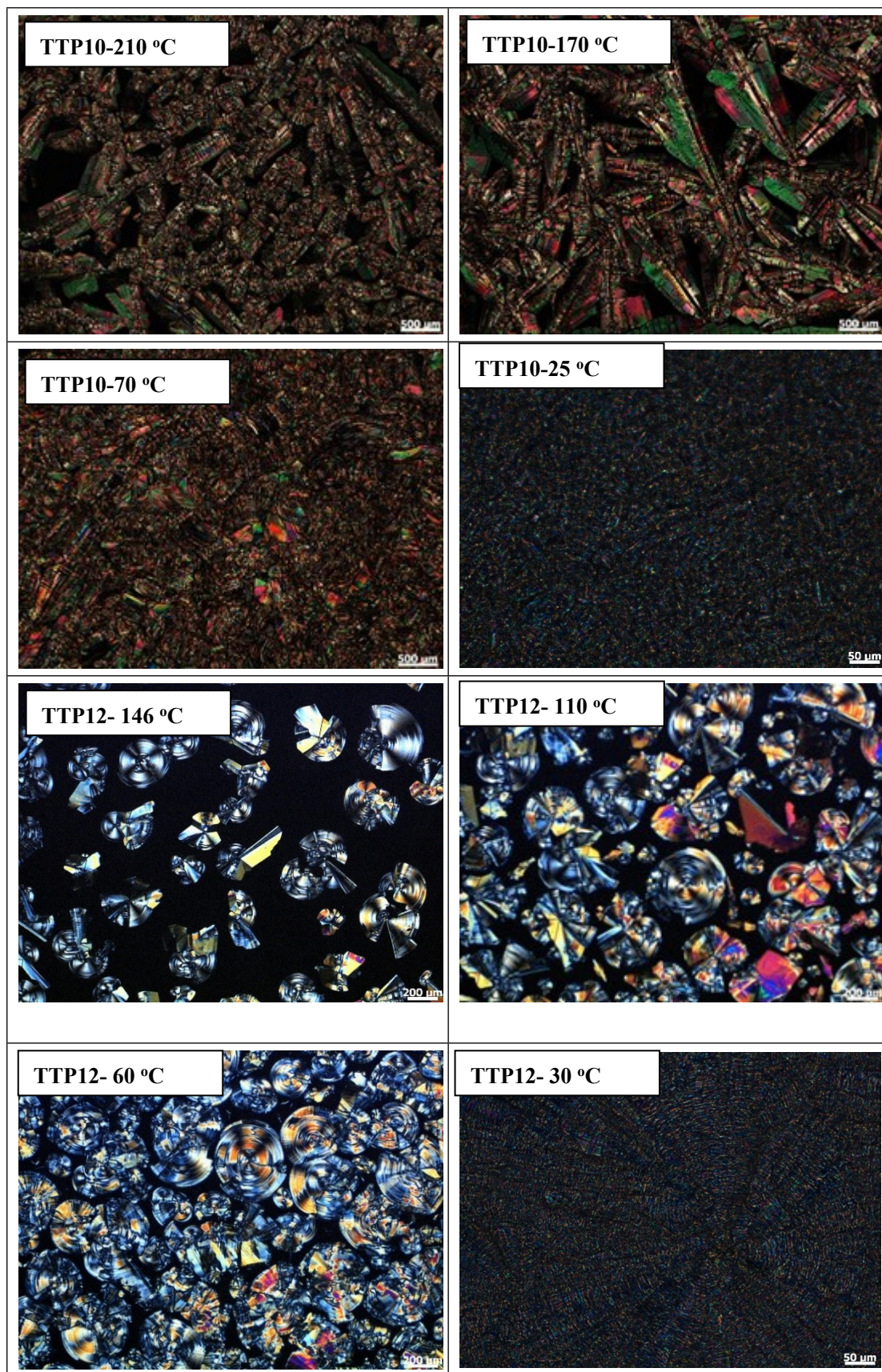


Figure S5 POM textures of TTPn at different temperatures.

6. XRD Pattern

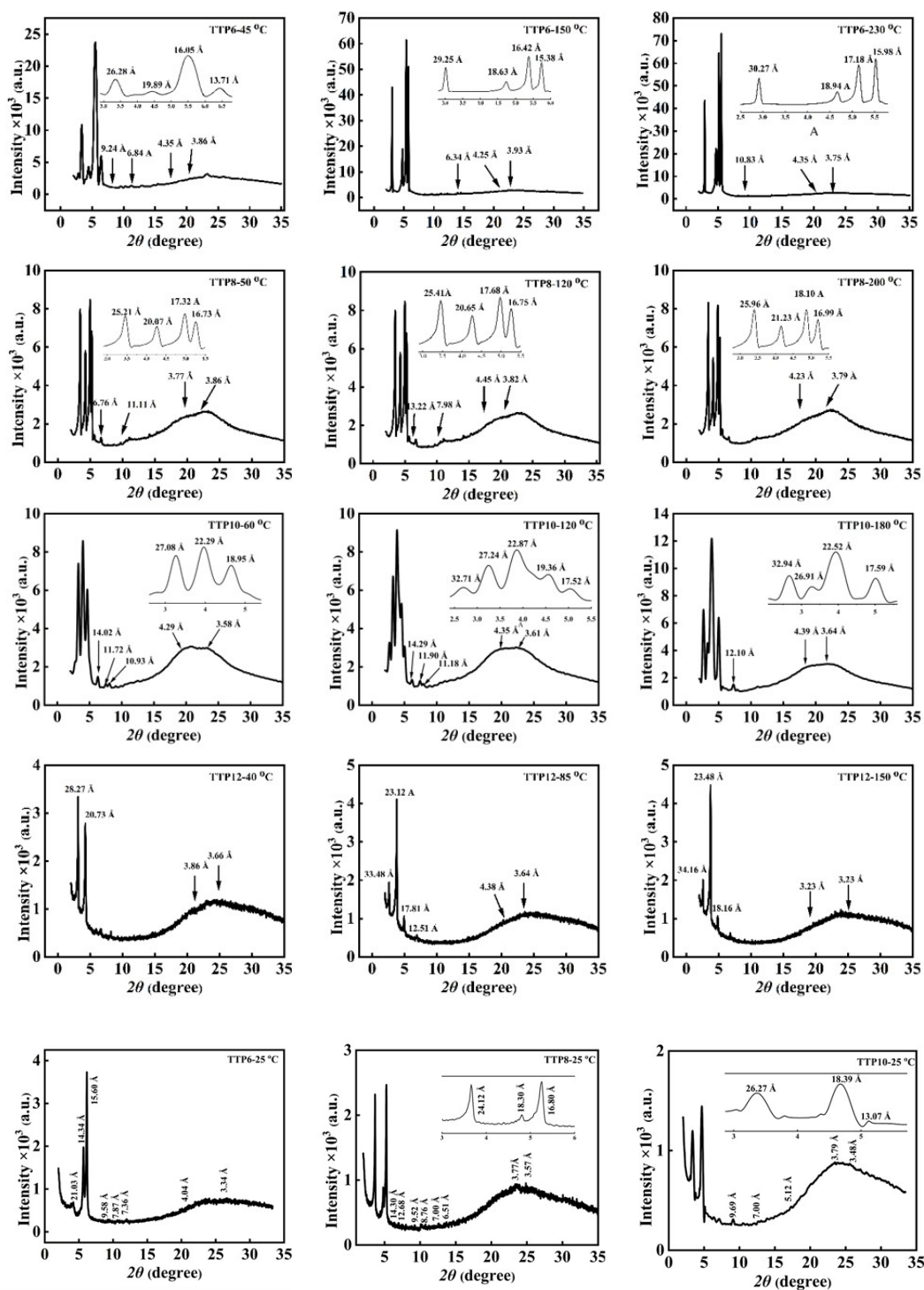


Figure S6 XRD patterns of the mesophases of TTPn (record on cooling) .

Table S2 Summary of liquid crystal phase state data for **TTPn** at room temperatures.

Compd.	$2\theta_{\text{exp}}$ (°)	d_{exp} (Å)	d_{cal} (Å)	I (%)	hk	Lattice parameters
TTP6 (25 °C)	4.198	21.03	21.03	15.0	30	a = 63.08 b = 32.20 $A_{\text{rec}} = 2031.33$
	5.66	15.60	15.60	74.8	12	
	6.16	14.34	14.34	100.0	22	
	9.214	9.58	9.56	2.2	33	
	11.22	7.87	7.80	2.9	24	
	12.005	7.36	7.52	2.8	34	
	21.954	4.04	-	1.5	h_{ch}	
	26.671	3.34	-	4.7	h_{π}	
	3.66	24.12	23.85	71.6	30	
	4.802	18.39	18.39	49.0	12	
TTP8 (25 °C)	5.255	16.80	16.80	100.0	22	a = 71.54 b = 38.06 $A_{\text{rec}} = 2722.70$
	6.18	14.30	14.31	1.8	50	
	6.963	12.68	12.69	1.6	03	
	9.282	9.52	9.51	1.2	04	
	10.085	8.76	8.84	5.9	34	
	12.624	7.00	7.00	2.9	45	
	13.592	6.51	6.72	2.8	55	
	23.563	3.77	-	11.9	h_{ch}	
	24.862	3.58	-	1.6	h_{π}	
	3.36	26.27	26.27	50.8	11	
TTP10 (25 °C)	4.68	18.39	18.39	100.0	12	a = 31.69 b = 46.98 $A_{\text{rec}} = 1489.79$
	5.173	13.07	13.14	8.4	22	
	9.119	9.69	9.63	4.3	32	
	12.64	7.00	7.02	0.1	35	
	17.3	5.12	5.25	0.2	55	
	23.46	3.79	-	0.2	h_{ch}	
	25.54	3.48	-	0.2	h_{π}	

Compd.	$2\theta_{\text{exp}}^{[a]}$ (°)	$d_{\text{exp}}^{[b]}$ (Å)	$d_{\text{cal}}^{[c]}$ (Å)	$I^{[d]}$ (%)	$hk^{[e]}$	Lattice parameters ^[f]
TTP12 (25 °C)	3.16	27.94	27.94	9.6	01	a = 29.98 b = 27.94 A _{rec} = 837.59
	4.32	20.44	20.44	100.0	11	
	6.64	13.30	13.21	2.1	21	
	8.3	10.64	10.22	9.9	22	
	12.3	7.19	7.24	1.3	41	
	20.74	4.28	-	0.1	h_{ch}	
	25.584	3.48	-	0.3	h_{π}	

Annotation: $2\theta_{\text{exp}}$: diffraction angles corresponding to each peak by experiment; D_{exp} : distance corresponding to each peak by experiment; d_{cal} : distance corresponding to each peak by calculation; I : relative intensity of the reflections; hk : Miller indices of columnar lattice reflection; h_{ch} : average distance between alkyl chains; h_{π} : average distance of π - π stacking of molecules; a , b , γ : columnar lattice parameters; A : lattice area; Z : number of molecules stacked per lattice, in this case $Z = 2$.

7. NMR Spectrum

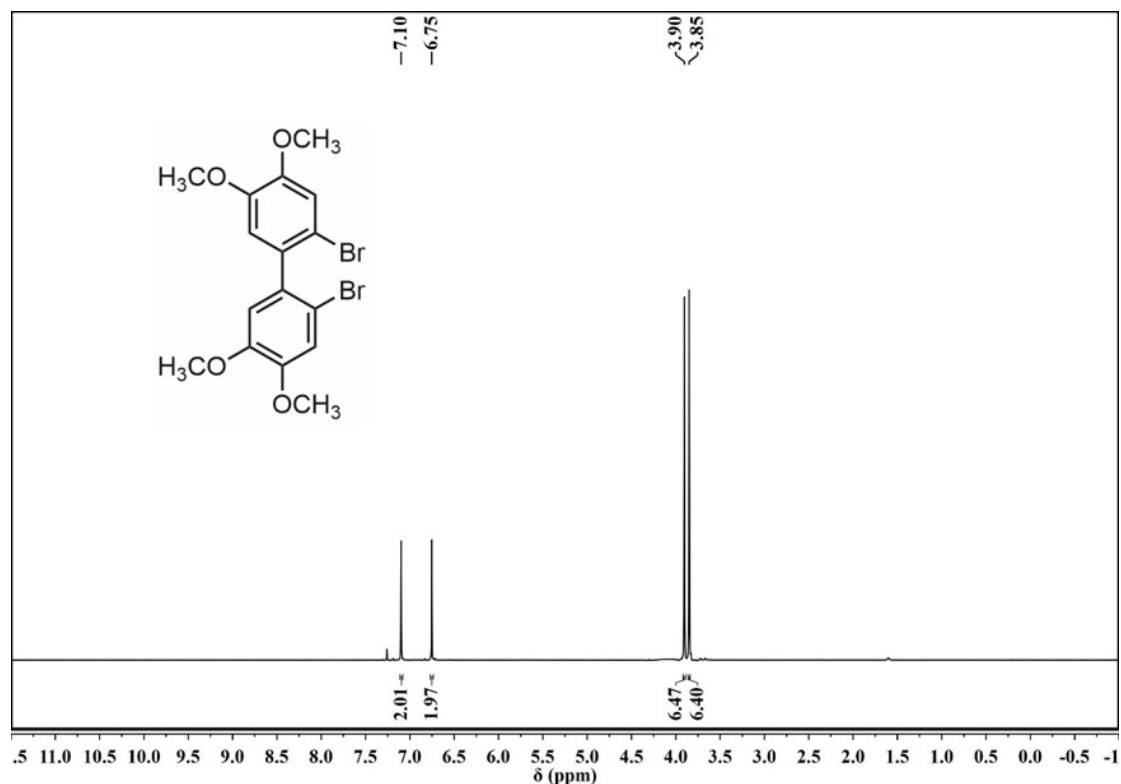


Figure S7 ¹H NMR (CDCl₃, 400 MHz) spectrum of **2**.

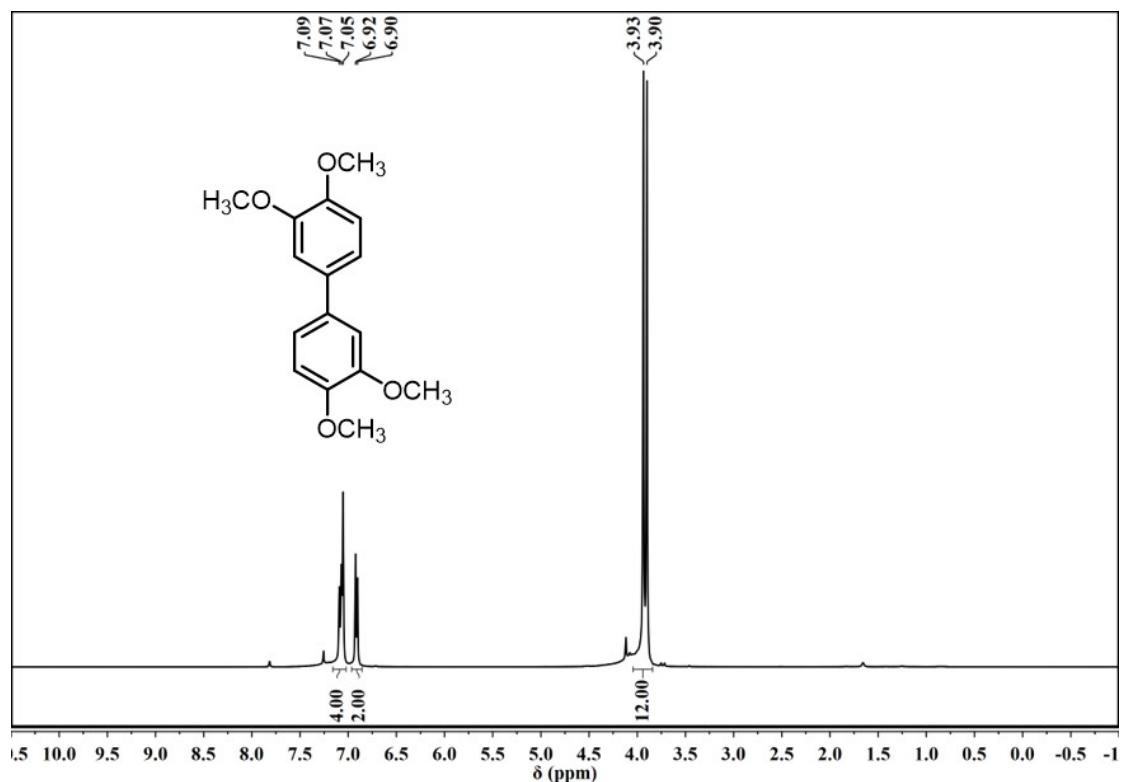


Figure S8 ^1H NMR (CDCl_3 , 400 MHz) spectrum of **3**.

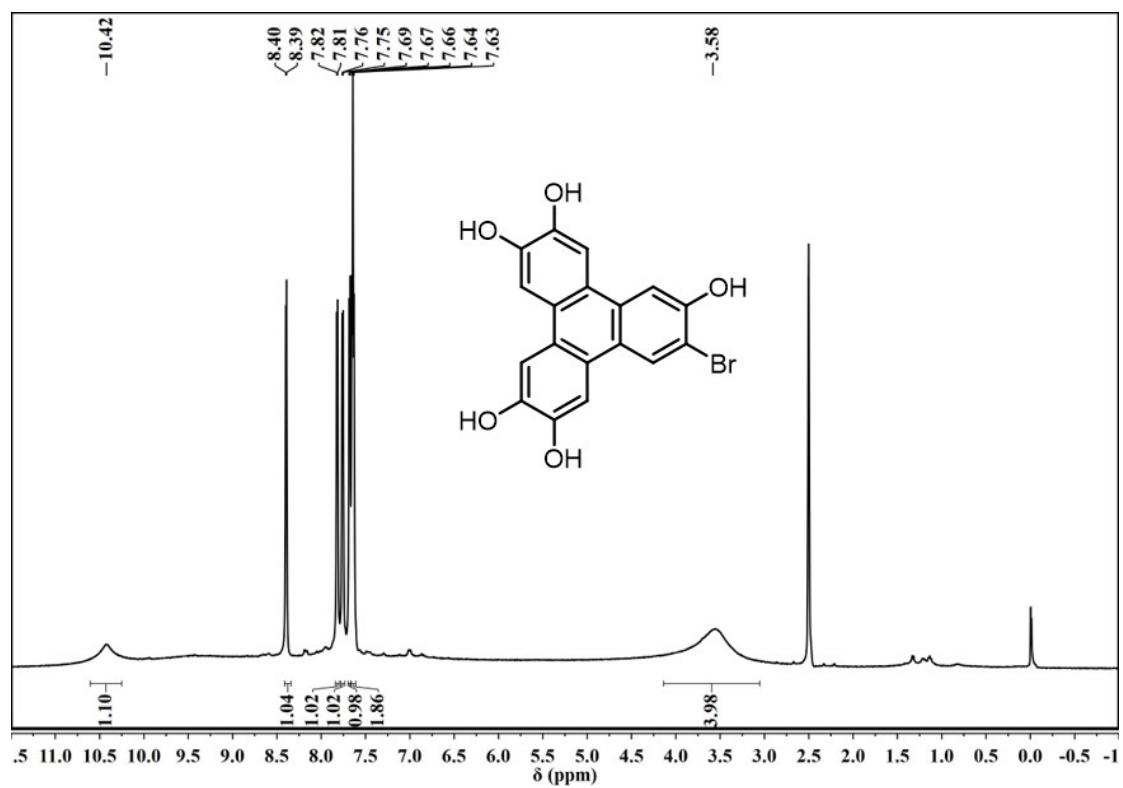


Figure S9 ^1H NMR (DMSO , 400 MHz) spectrum of **4**.

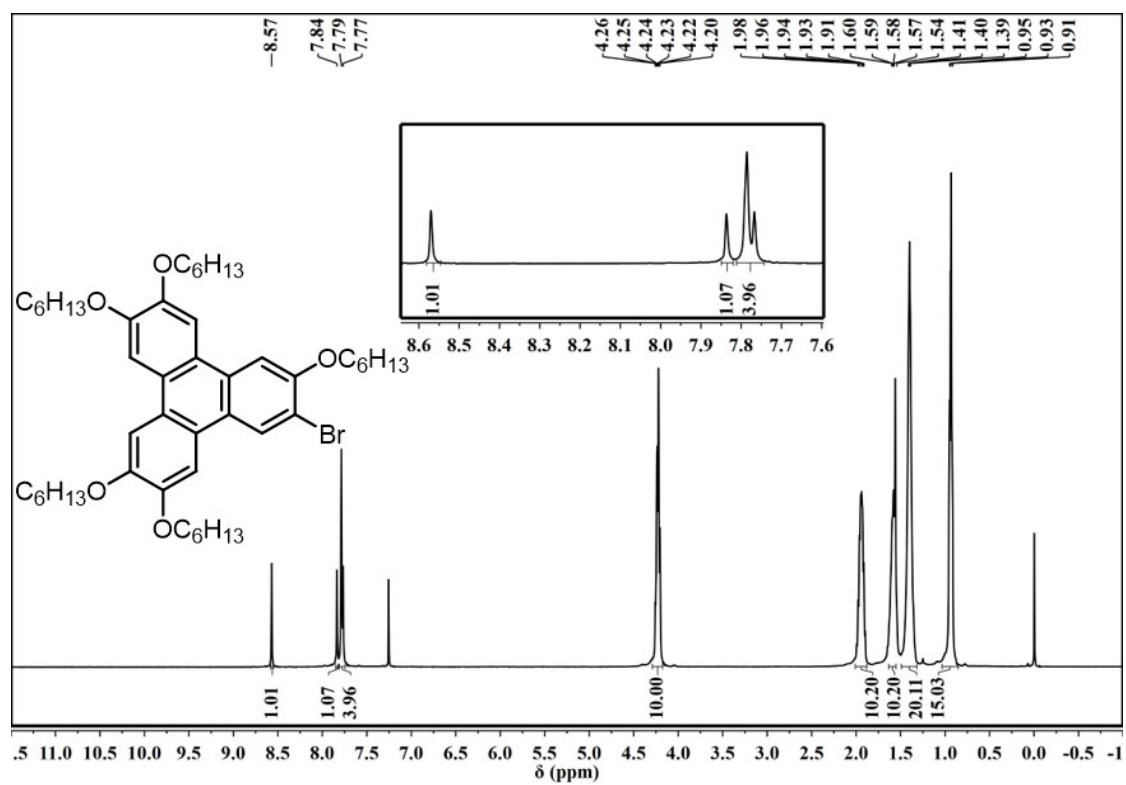


Figure S10 $^1\text{H NMR}$ (CDCl₃, 400 MHz) spectrum of **5a**.

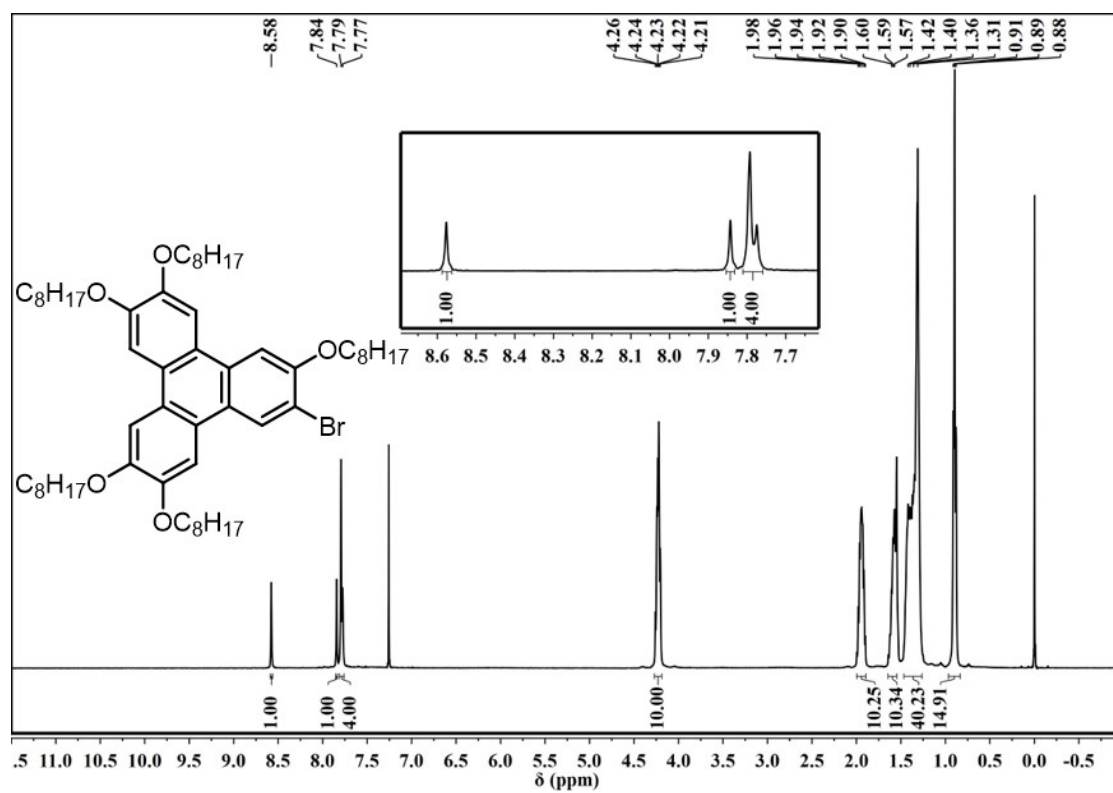


Figure S11 $^1\text{H NMR}$ (CDCl₃, 400 MHz) spectrum of **5b**.

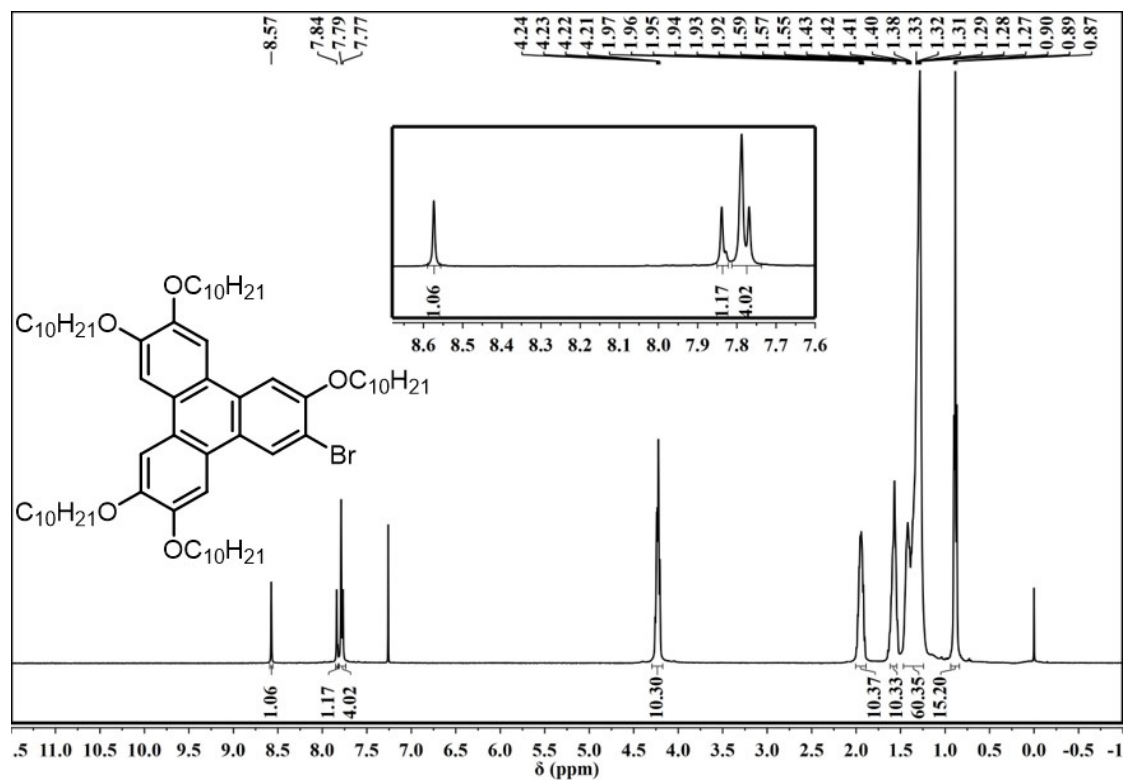


Figure S12 ¹H NMR (CDCl₃, 400 MHz) spectrum of **5c**.

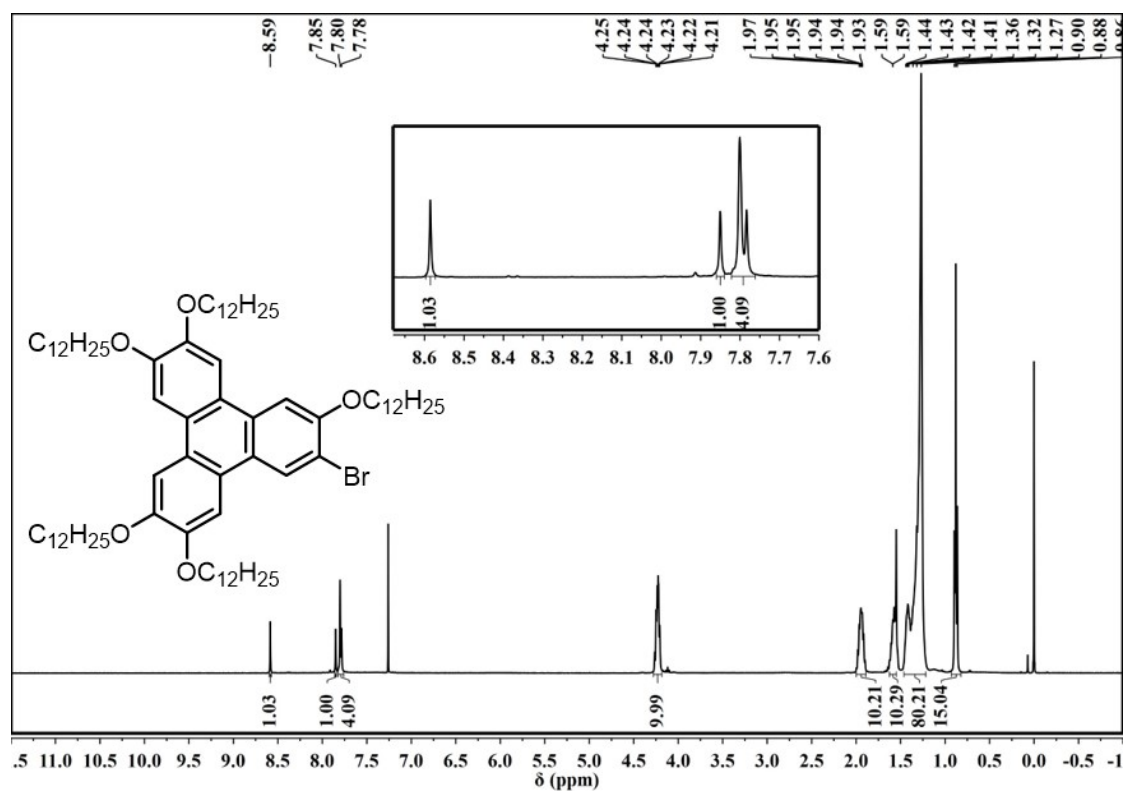


Figure S13 ¹H NMR (CDCl₃, 400 MHz) spectrum of **5d**.

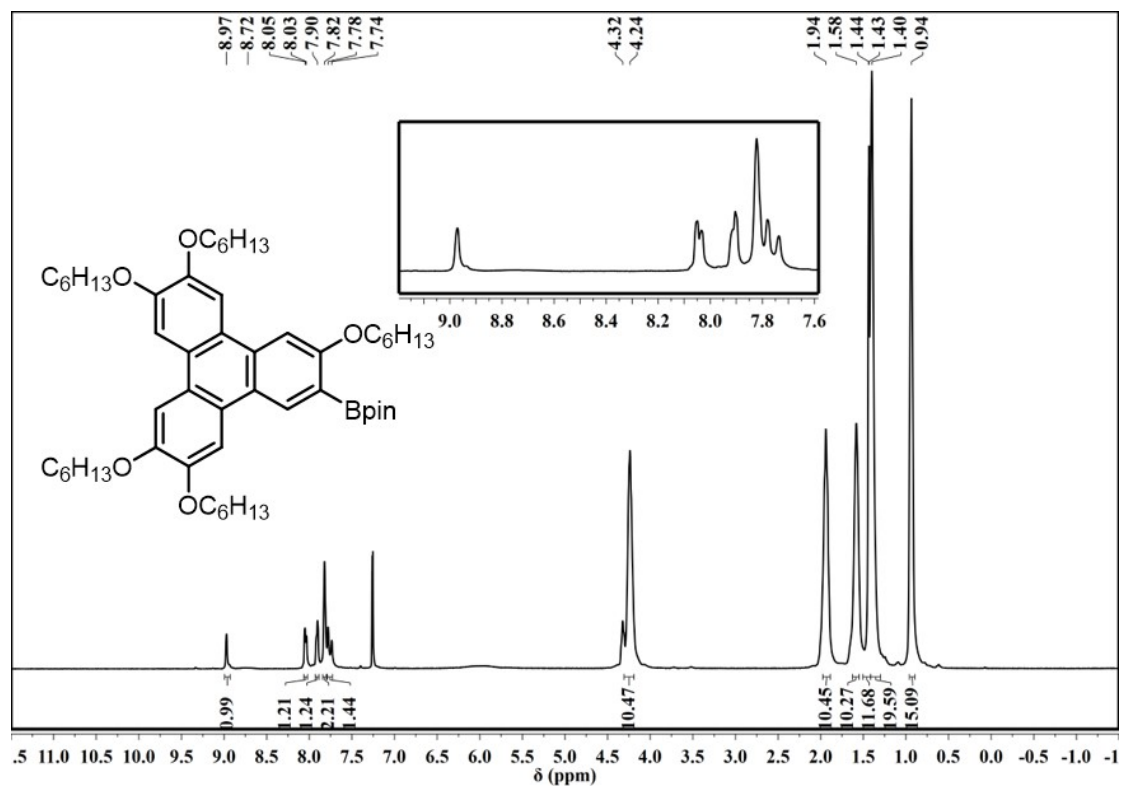


Figure S14 ¹H NMR (CDCl₃, 400 MHz) spectrum of **6a**.

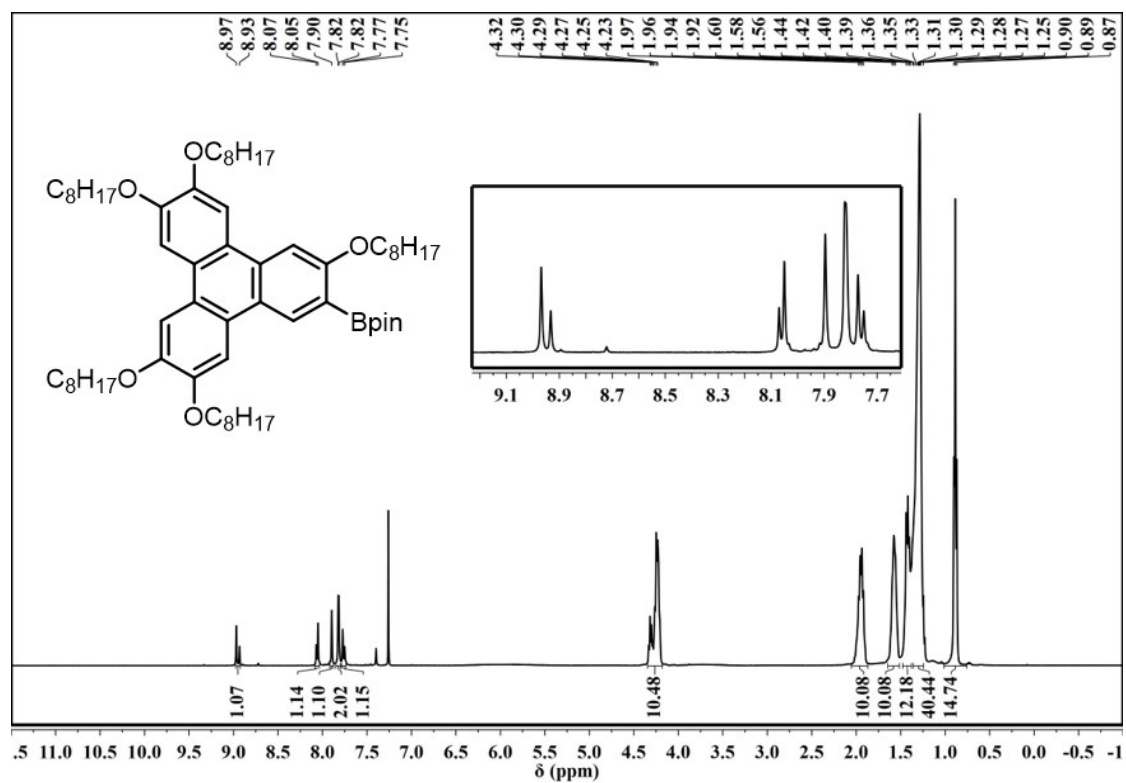


Figure S15 ¹H NMR (CDCl₃, 400 MHz) spectrum of **6b**.

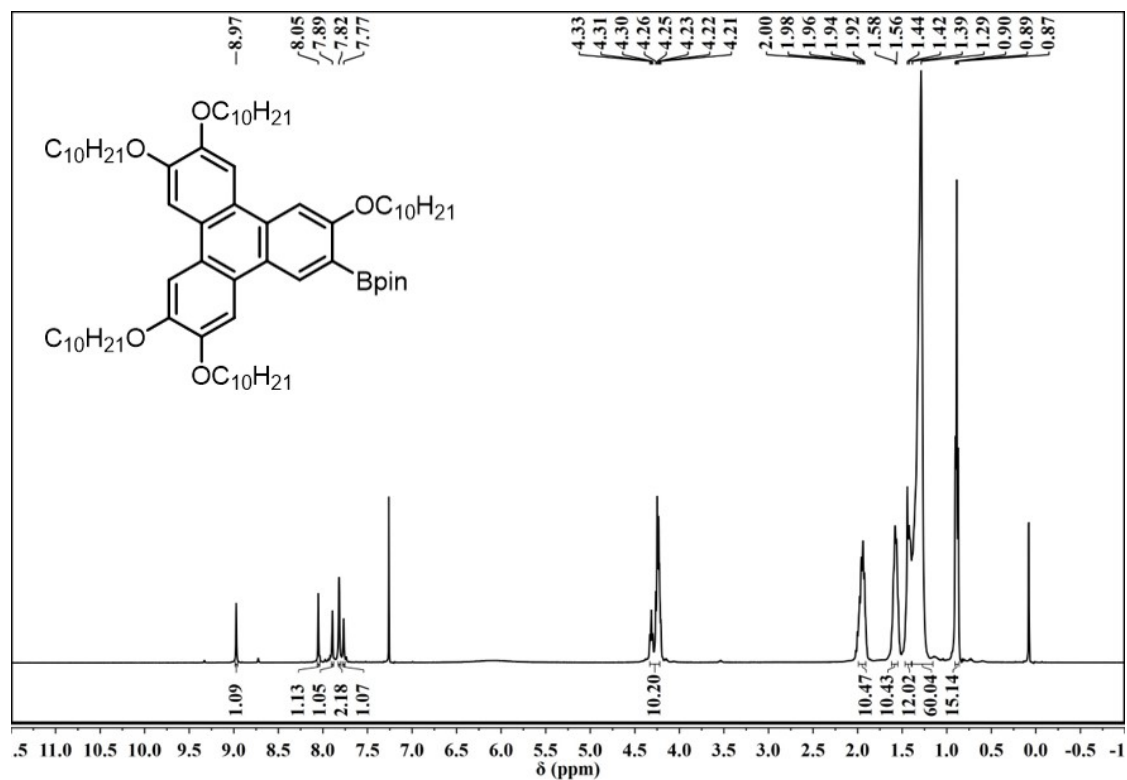


Figure S16 ^1H NMR (CDCl_3 , 400 MHz) spectrum of **6c**.

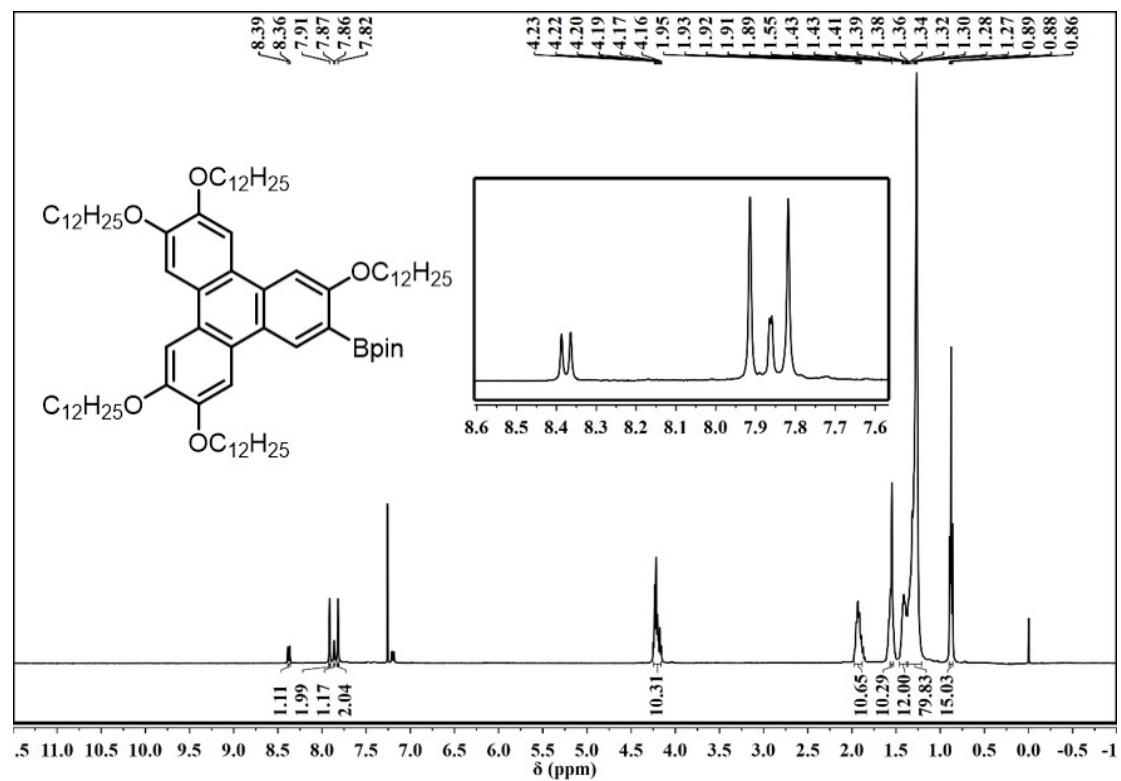


Figure S17 ^1H NMR (CDCl_3 , 400 MHz) spectrum of **6d**.

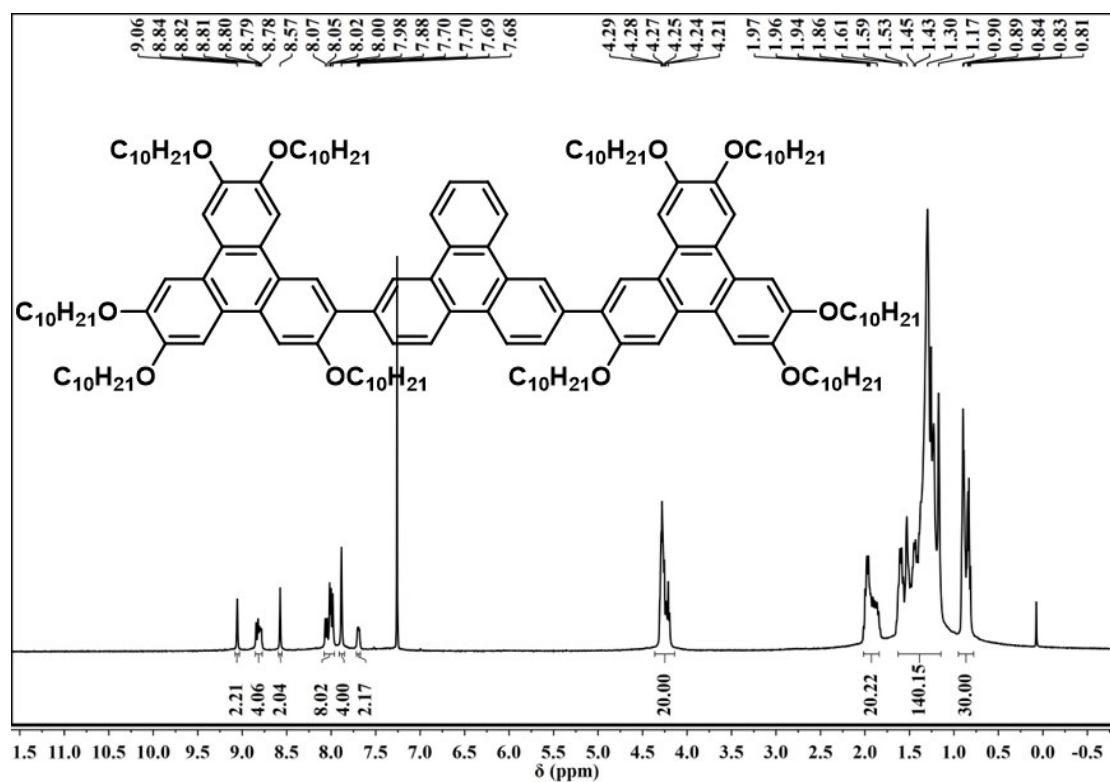


Figure S20 $^1\text{H NMR}$ (CDCl₃, 400 MHz) spectrum of TTP10.

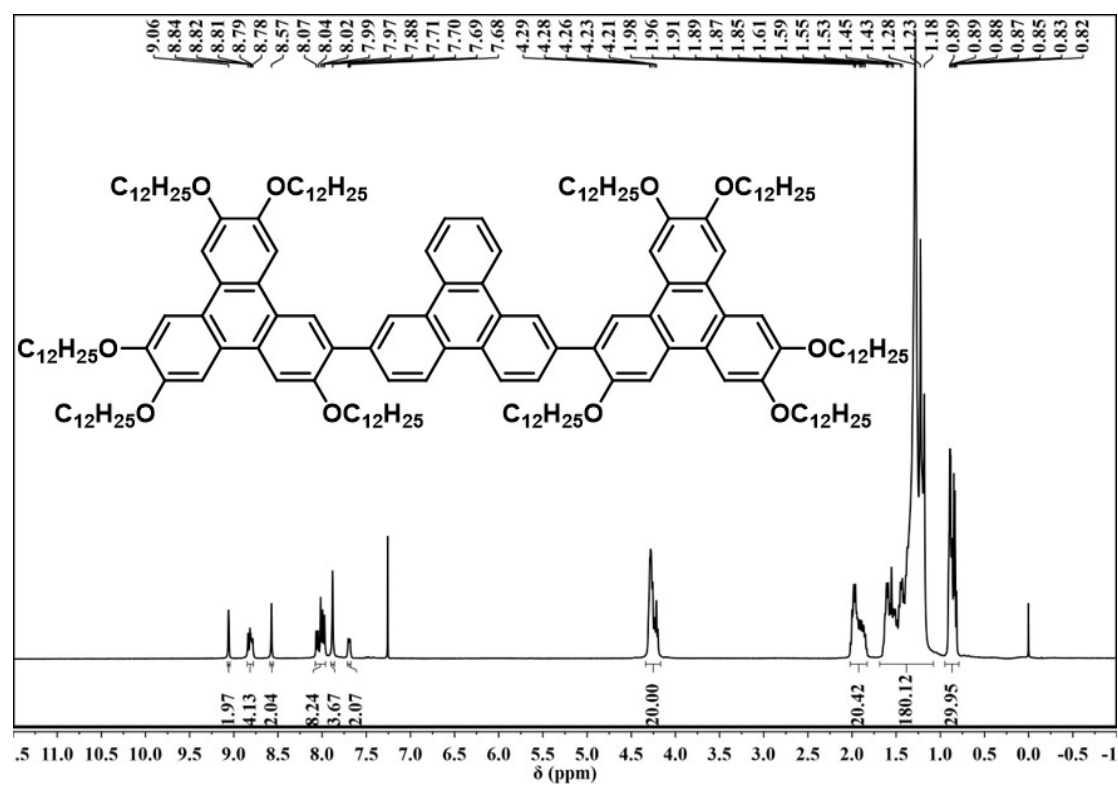


Figure S21 $^1\text{H NMR}$ (CDCl₃, 400 MHz) spectrum of TTP12.

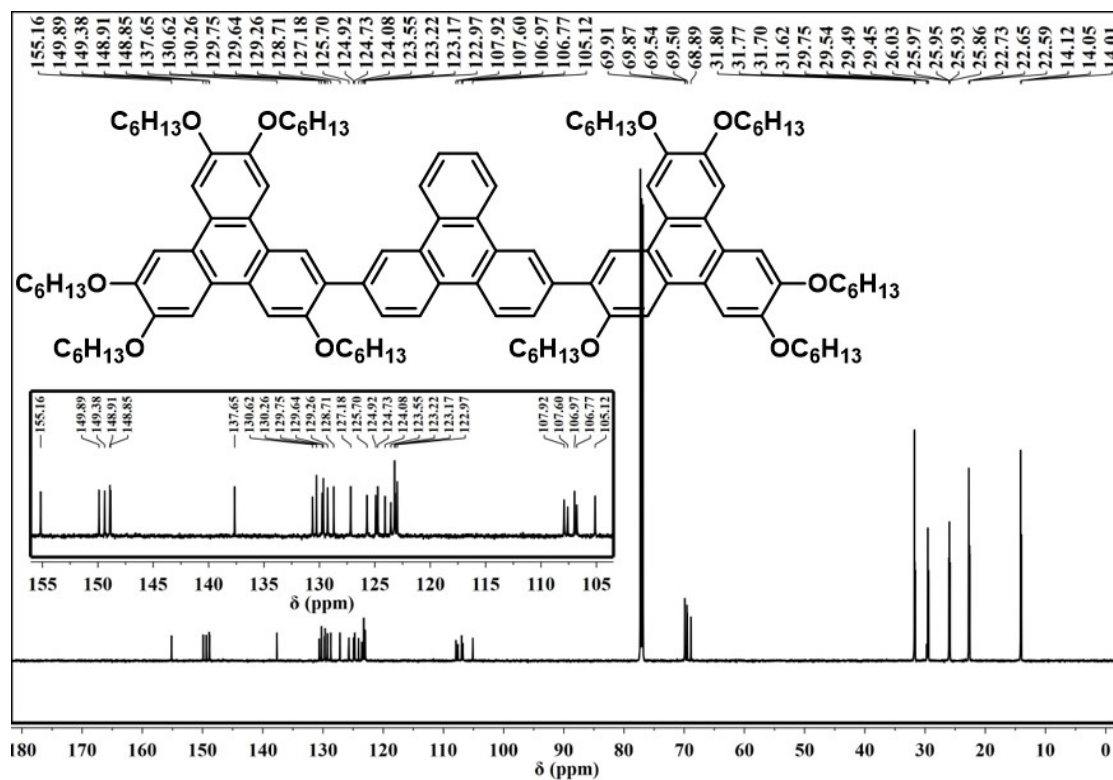


Figure S22 ^{13}C NMR (CDCl₃, 151 MHz) spectrum of TTP6.

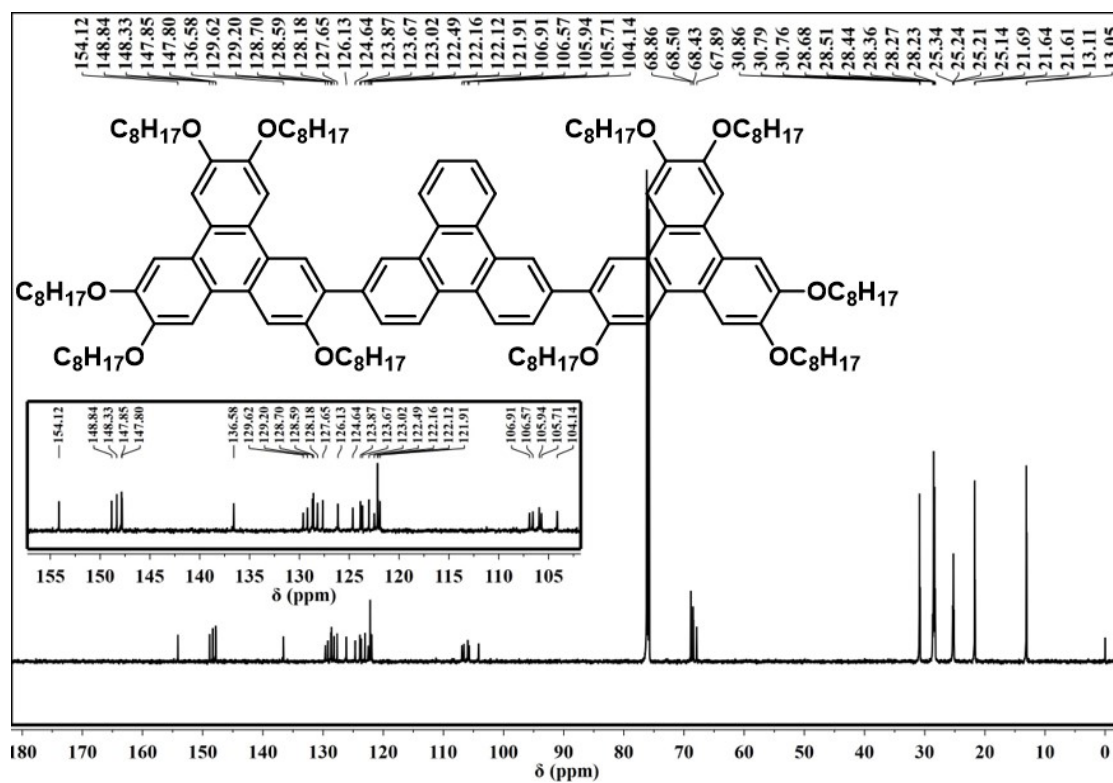


Figure S23 ^{13}C NMR (CDCl₃, 151 MHz) spectrum of TTP8.

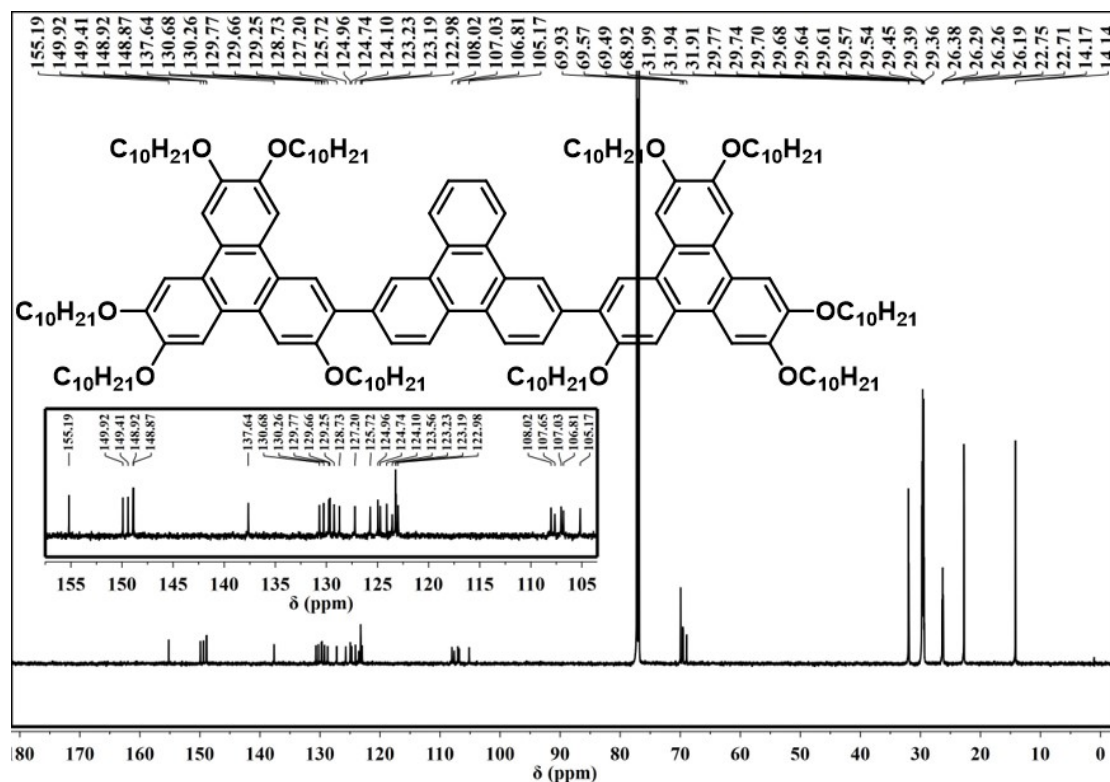


Figure S24 ¹³C NMR (CDCl₃, 151 MHz) spectrum of TTP10.

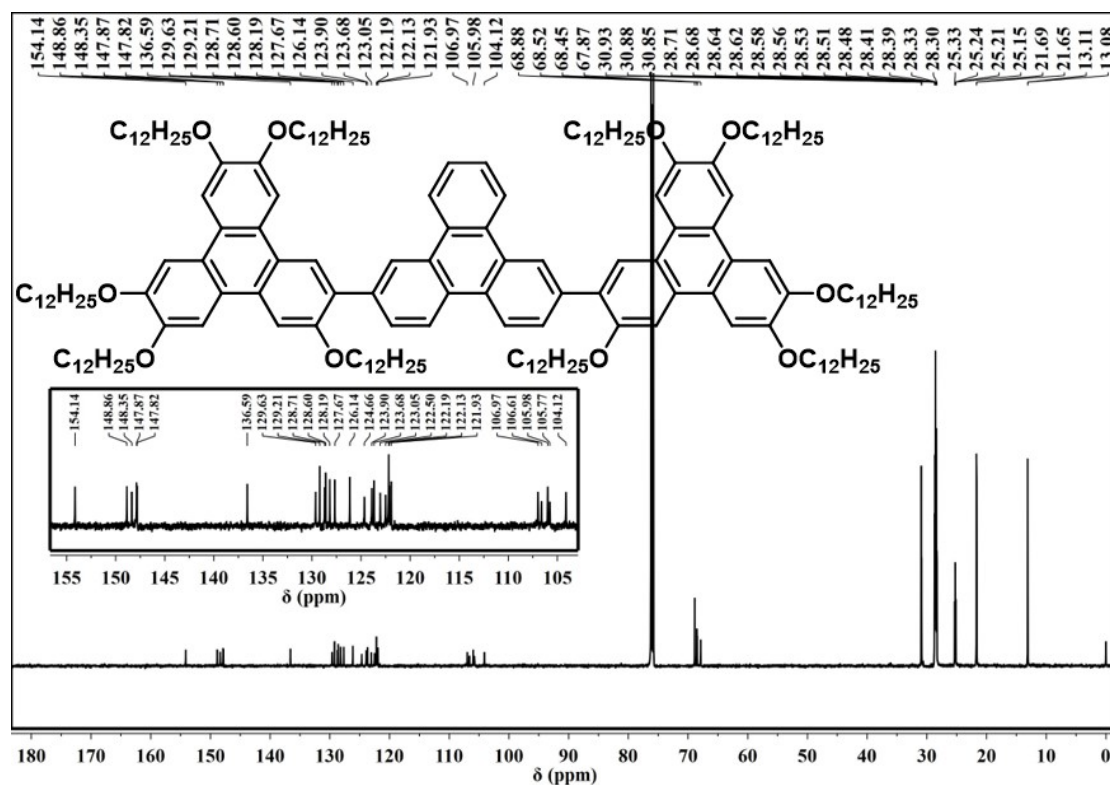


Figure S25 ¹³C NMR (CDCl₃, 151 MHz) spectrum of TTP12.

8. HRMS Spectrum

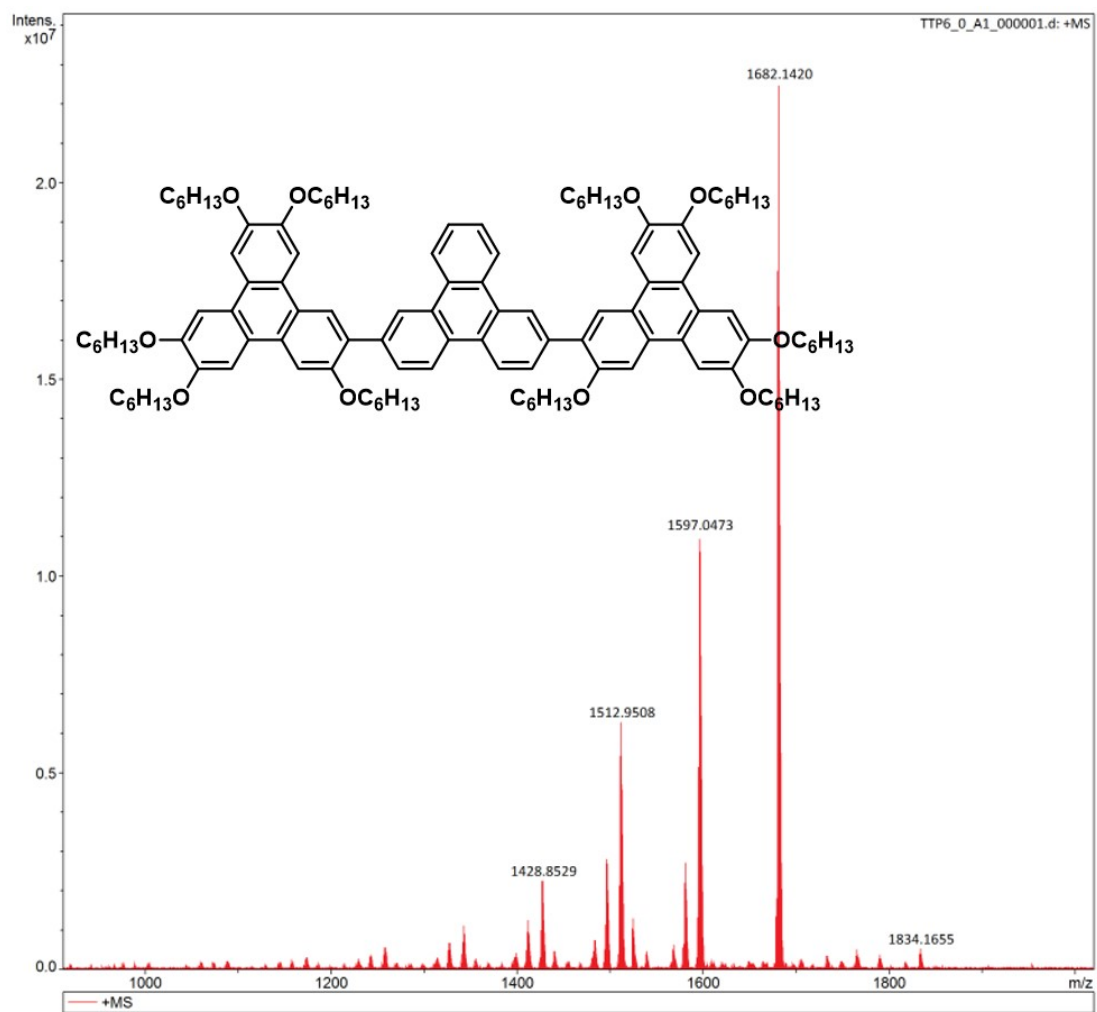


Figure S26 HRMS of TTP6.

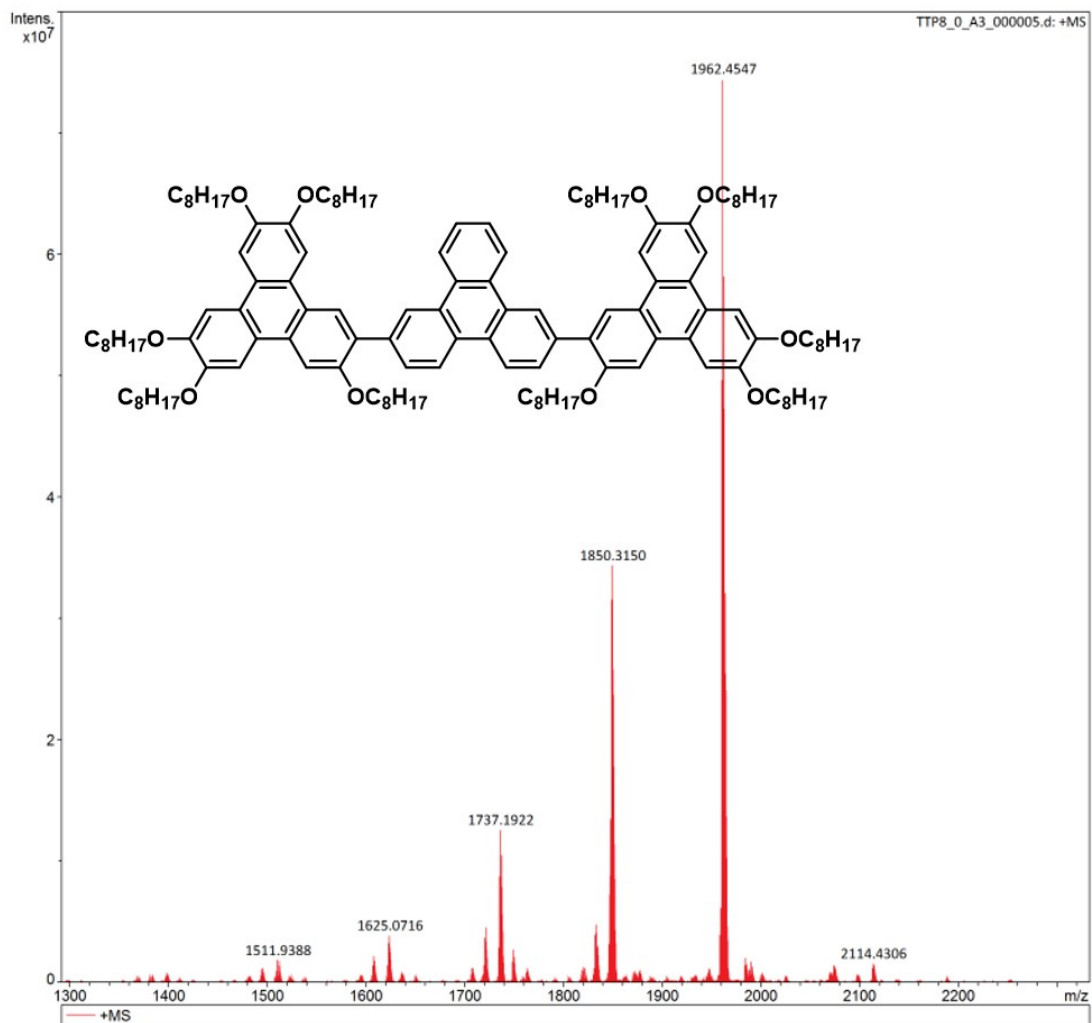


Figure S27 HRMS of TTP8.

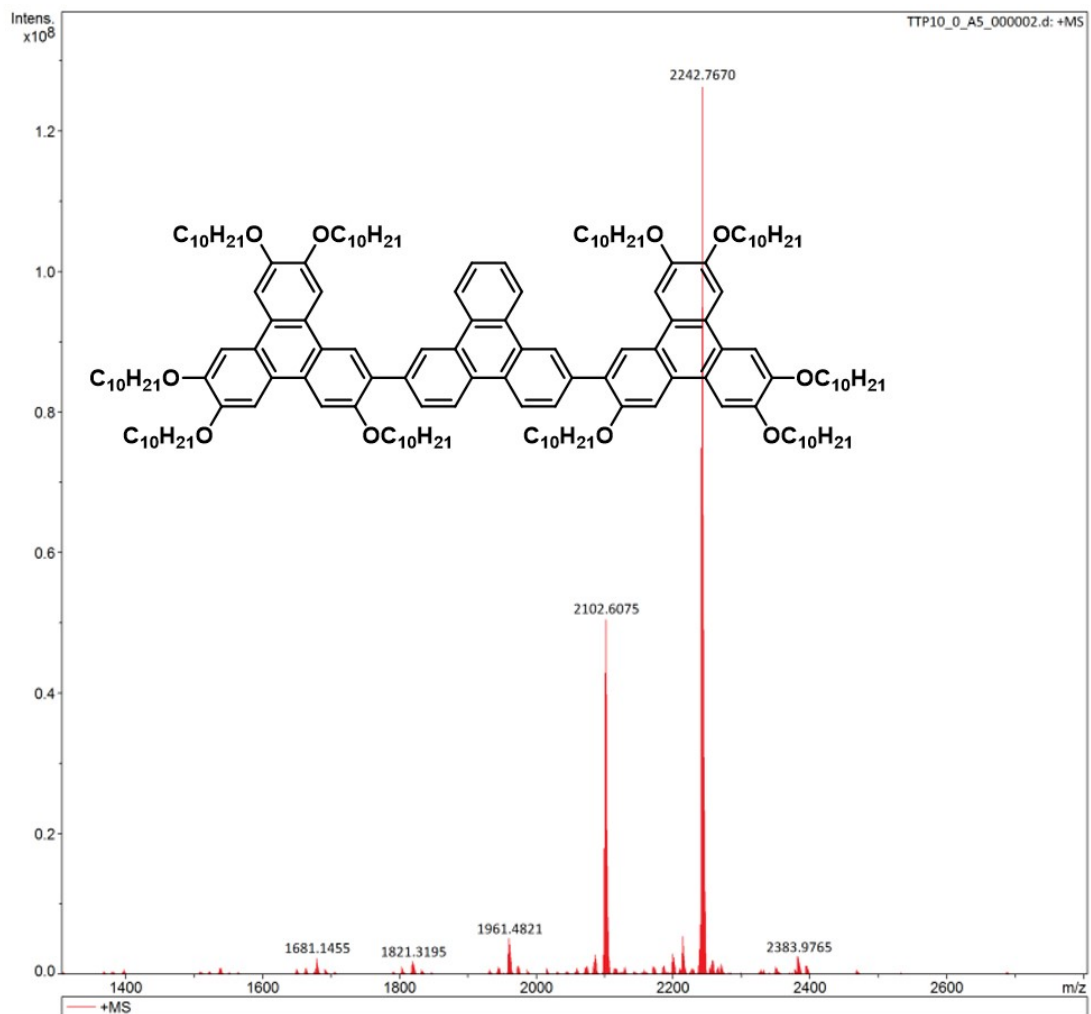


Figure S28 HRMS of TTP10.

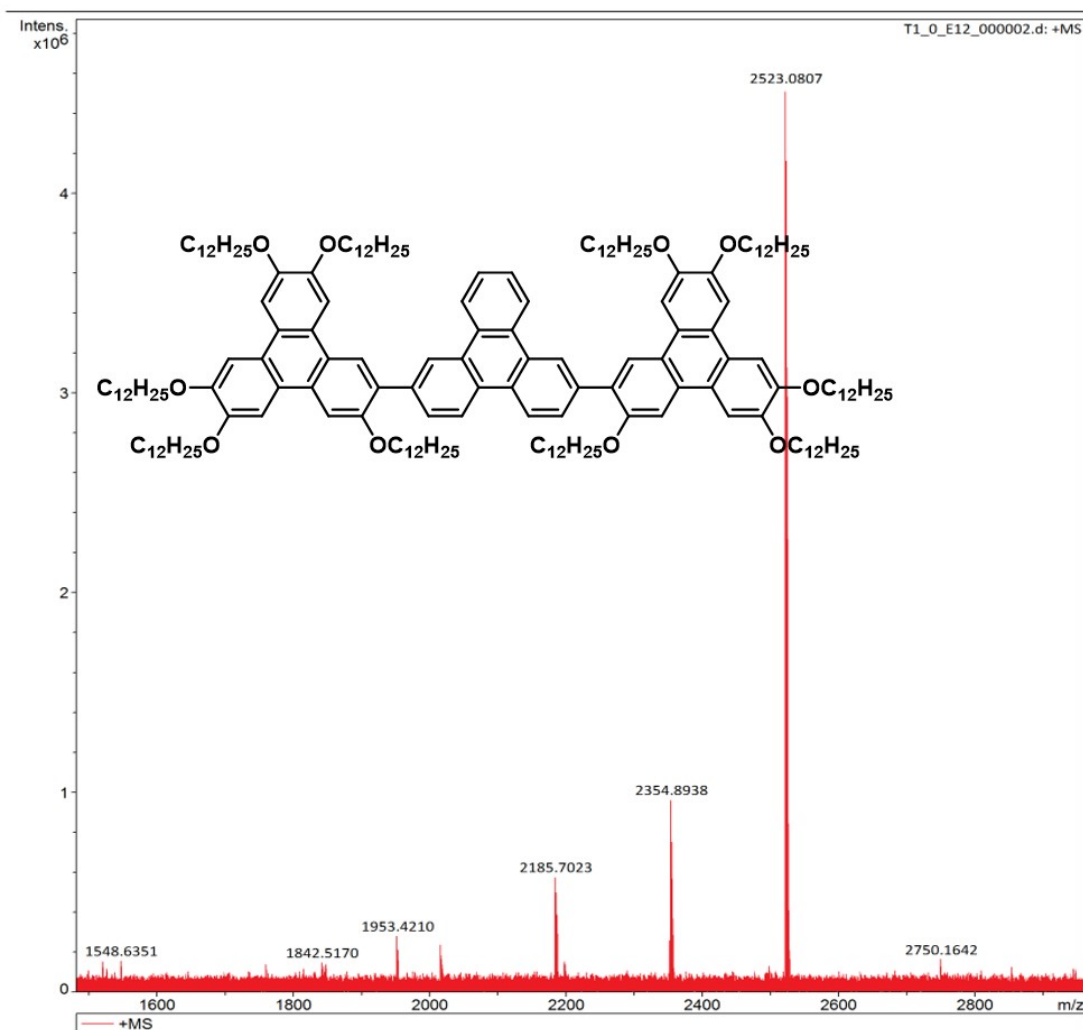


Figure S29 HRMS of TTP12.

9. DFT Computational Studies

General Information for Computation

All calculations were performed with the Gaussian 16 program. Density functional theory calculations using the M06 functional. Geometry optimizations were conducted with the Gaussian 16 software package, B3LYP functional (with d3bj dispersion correction), and 6-311g(d,p) basis set for all other atoms. Single-point energy calculations were conducted with the M06 functional and the 6-311++g(d,p) basis set for all other atoms, along with the SMD THF solvent correction. Thermal corrections were applied to the optimized geometries to provide Gibbs free energies.

Table S3 Optimized molecular structures of **TTP**.

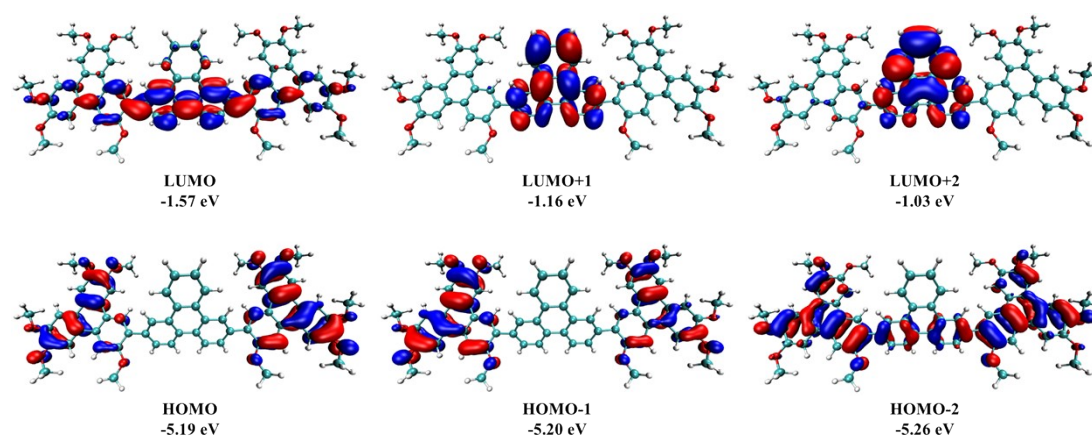
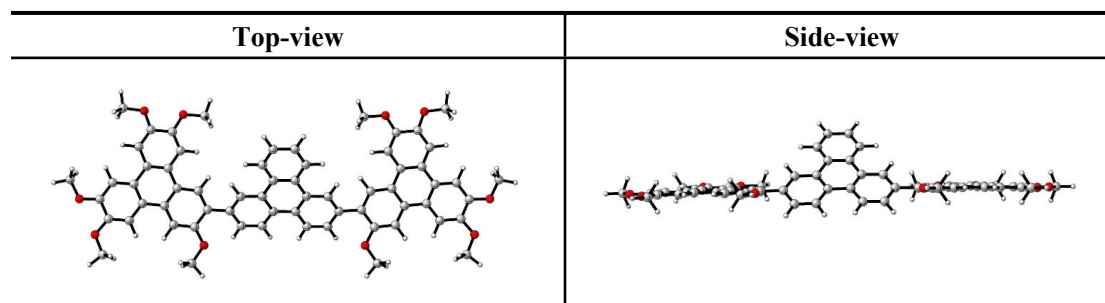


Figure S30 Frontier molecular orbitals and energy levels of **TTP**.

Coordinates and Energies of Stationary Points

C	-7.05584	-0.05494	-0.20613
C	-7.87549	-1.2092	-0.18487
C	-9.32517	-1.06681	-0.20686
C	-9.9077	0.21919	-0.24884
C	-9.06228	1.40668	-0.26946
C	-7.65812	1.27131	-0.24979
C	-9.61642	2.7099	-0.30772
C	-8.83007	3.84164	-0.32746
C	-7.41365	3.70385	-0.30661
C	-6.86193	2.4418	-0.26801
C	-5.65886	-0.23594	-0.18686

C	-5.04469	-1.4762	-0.14423
C	-5.8815	-2.62354	-0.12209
C	-7.25645	-2.47808	-0.1423
C	-10.17626	-2.19879	-0.18621
C	-11.54897	-2.08598	-0.20455
C	-12.13674	-0.79024	-0.24804
C	-11.32001	0.31986	-0.26944
C	1.43987	-0.67731	0.76248
C	0.7342	-1.6056	-0.04265
C	-0.72549	-1.59671	-0.06067
C	-1.43994	-0.68187	0.75198
C	-0.71376	0.25765	1.60939
C	0.70446	0.26616	1.60765
C	-1.39296	1.17258	2.44186
C	-0.71321	2.06825	3.24318
C	0.68618	2.07915	3.2387
C	1.37467	1.19235	2.43496
C	2.84706	-0.69136	0.7345
C	3.57446	-1.5814	-0.0451
C	2.86092	-2.51729	-0.81875
C	1.48336	-2.51963	-0.81459
C	-1.46594	-2.47547	-0.88057
C	-2.84327	-2.4693	-0.9035
C	-3.56579	-1.56444	-0.10161
C	-2.84672	-0.69635	0.70988
C	7.0569	-0.05996	-0.19724
C	7.88233	-1.20808	-0.12624
C	9.3313	-1.05947	-0.15382
C	9.90719	0.22621	-0.25371
C	9.05588	1.40744	-0.32286

C	7.65245	1.26633	-0.29639
C	9.60403	2.7103	-0.41519
C	8.8126	3.83654	-0.48342
C	7.3968	3.69308	-0.45808
C	6.85089	2.43136	-0.36393
C	5.66081	-0.24746	-0.17383
C	5.0532	-1.48823	-0.08217
C	5.89561	-2.62928	-0.00989
C	7.26982	-2.47739	-0.03224
C	10.18843	-2.18481	-0.08348
C	11.5605	-2.06597	-0.11065
C	12.14145	-0.77066	-0.21551
C	11.31879	0.33319	-0.28399
O	-6.70937	4.86256	-0.32628
C	-5.28605	4.77374	-0.31173
O	-9.29472	5.11545	-0.3652
C	-10.70693	5.30697	-0.39402
O	-13.49137	-0.76131	-0.26508
C	-14.12971	0.51353	-0.3016
O	-12.41968	-3.12554	-0.18449
C	-11.8778	-4.44337	-0.13726
O	-5.25292	-3.82765	-0.05659
C	-6.04791	-5.0106	-0.01546
O	6.68693	4.84632	-0.53008
C	5.26397	4.75086	-0.5188
O	9.27206	5.1096	-0.57412
C	10.68363	5.30507	-0.6104
O	13.49588	-0.7355	-0.23931
C	14.12675	0.54012	-0.33276
O	12.43636	-3.09944	-0.04538

C	11.90078	-4.41607	0.06595
O	5.27257	-3.83284	0.10293
C	6.07293	-5.00931	0.19465
H	-10.68735	2.83203	-0.32019
H	-5.78794	2.35294	-0.25014
H	-5.00978	0.62712	-0.22546
H	-7.86779	-3.36535	-0.11383
H	-9.74429	-3.18566	-0.15478
H	-11.78367	1.29222	-0.3037
H	-2.47339	1.18325	2.46452
H	-1.26471	2.75733	3.87235
H	1.23088	2.77712	3.86397
H	2.45493	1.21801	2.45276
H	3.40087	0.00325	1.3489
H	3.39748	-3.23121	-1.42782
H	0.97586	-3.25032	-1.42868
H	-0.9516	-3.17321	-1.52652
H	-3.37251	-3.15514	-1.55013
H	-3.40686	-0.01779	1.33639
H	10.67431	2.83656	-0.43062
H	5.77731	2.33882	-0.34045
H	5.00729	0.60966	-0.25131
H	7.88624	-3.35911	0.03349
H	9.76204	-3.17148	-0.00497
H	11.77659	1.30562	-0.3651
H	-4.92562	5.80095	-0.33369
H	-4.92518	4.28187	0.59774
H	-4.9102	4.2381	-1.18975
H	-10.85885	6.38479	-0.42542
H	-11.15385	4.85147	-1.28399

H	-11.18406	4.89939	0.50352
H	-15.199	0.30817	-0.30503
H	-13.87742	1.11146	0.58039
H	-13.86358	1.06767	-1.20773
H	-12.73461	-5.11529	-0.1253
H	-11.26364	-4.6545	-1.01897
H	-11.28265	-4.59811	0.76884
H	-5.34186	-5.83812	0.03375
H	-6.68985	-5.02882	0.87113
H	-6.66232	-5.1101	-0.91605
H	4.89855	5.77392	-0.59235
H	4.89569	4.17122	-1.37175
H	4.90048	4.30195	0.41156
H	10.83146	6.38122	-0.68679
H	11.16178	4.93711	0.30361
H	11.13262	4.81458	-1.48059
H	15.19723	0.3411	-0.32927
H	13.85601	1.05268	-1.26172
H	13.87222	1.17454	0.52272
H	12.76064	-5.08314	0.10308
H	11.31211	-4.53131	0.98214
H	11.2817	-4.67031	-0.80086
H	5.37056	-5.83725	0.27762
H	6.68889	-5.14389	-0.70036
H	6.71359	-4.98751	1.08213