

Supporting Information

A convenient one-pot synthesis of C(sp²)-C(sp³) linked 3D-Grid via an 'A₂ + B₃' approach

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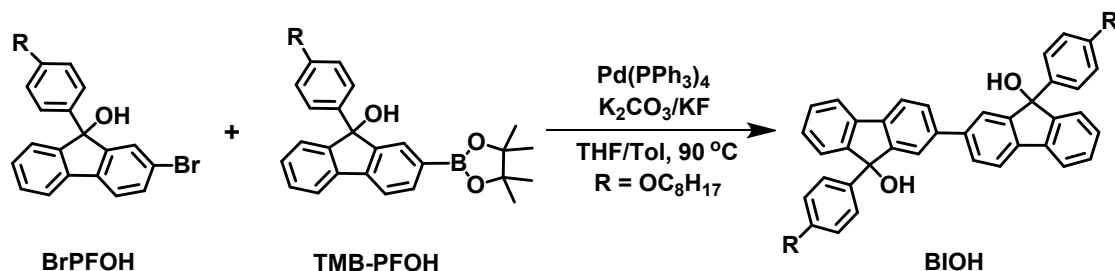
I. General Information of Synthesis

General information: Chemicals. All the solvents and reagents were purchased from commercial suppliers and used without further purification, unless noted otherwise. All products were purchased by flash column chromatography which was carried out with Kanto Silica Gel 60N (40-63 μm). Spectrochemical-grade solvents were used for optical measurements. Tetra(triphenylphosphine)palladium(II), triphenylamine were obtained from Aldrich Chemical Co. Borontrifluoride etherate, potassium carbonate, potassium fluoride, magnesium sulphate were purchased from Sinopharm Chemical Reagent Co, Ltd. Without further purification. Dichloromethane were dried by anhydrous sodium under room temperature. THF and toluene were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. 2-bromo-9-(4-(octyloxy)phenyl)-fluoren-9-ol (**BrFOH**), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(4-(octyloxy)phenyl)-fluoren-9-ol (**FOH-Bpin**) were obtained according to the reported literatures.¹⁻⁵

Characterization. $^1\text{H-NMR}$, $^1\text{H-}^1\text{H COSY}$ and $^{13}\text{C-NMR}$ were recorded at 25 $^\circ\text{C}$ on a Bruker 400 MHz spectrometer in d-CDCl_3 with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GC-MS 2010 PLUS. For the MALDI-TOF MS spectra, the spectra were recorded in reflective mode, and substrates were used. GPC analysis was performed on a HP1100 HPLC system equipped with the 7911GP-502 and GP NXC columns using polystyrenes as the standard and THF as the eluent at a flow rate of 1.0 mL/min at 25 $^\circ\text{C}$. Absorption and emission spectra were measured in CHCl_3 for a concentration of 1×10^{-5} mg/ml in solution and in solid films spin-coated from 10~15 mg/ml in CHCl_3 using a Shimadzu UV-3150 spectrometer and Shimadzu RF-530XPC spectrophotometer, respectively. Cyclic Voltammetry (CV) were conducted at room temperature on the CHI660E system in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag^+) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature and performed on the solution of the sample on a glassy carbon electrode measured in a 0.1 mol/L acetonitrile solution of tetrabutylammonium hexafluorophosphate ($\text{n-Bu}_4\text{N}^+\text{PF}_6^-$) at a sweeping rate of 0.1V/s. According to the redox onset potentials of the CV measurements, the highest occupied molecular orbital (HOMO)/lowest unoccupied energy levels (LUMO) of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): $\text{HOMO/ LUMO} = - (E_{\text{ox/red}} - 0.053 \text{ V}) - 4.8 \text{ eV}$, where the value 0.053 V is the standard potential for ferrocene/ferrocenium vs Ag/Ag^+ . Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H thermogravimetric analyzer under a heating rate of 10 $^\circ\text{C}$ /min. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument at a heating rate of 10 $^\circ\text{C}$ /min.

General procedure for synthesis of compound

Synthesis procedure of BIOH.



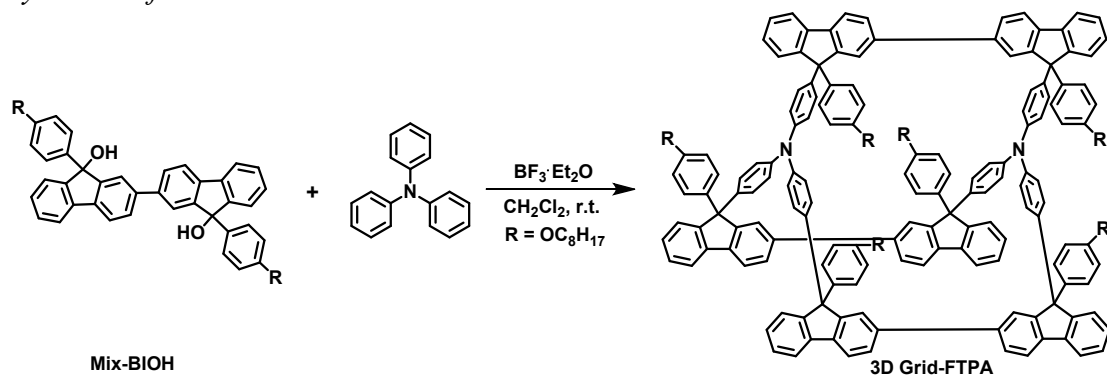
In a three-necked schlenk flask (100 mL), **BrFOH** (5.45 g, 11.71 mmol), **FOH-Bpin** (5.00 g, 9.76 mmol), Pd(PPh₃)₄ (0.34 g, 0.29 mmol) were added. The flask was evacuated and back-filled with nitrogen atmosphere over three times, after which degassed toluene (17 mL) and K₂CO₃ aqueous solution (2 M, 10 mL) were injected into the flask through syringe. The mixture was heated up to 90 °C and stirred for 24 h. Water (40 mL) was successively added to quench the reaction. And then the mixture was separated and the aqueous phase was extracted with DCM. The combined DCM layers were washed and dried (MgSO₄). After removal of the solvent, the remaining crude product was purified by the column chromatography using PE:EA = 12:1 (v/v) as the eluent to provide a yellow solid compound **BIOH** (6.58 g, 8.54mmol, 87.51%).

Mix-BIOH: ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.64 (t, *J* = 6.9 Hz, 4H), 7.59 – 7.57 (dd, *J* = 9.0, 1.6 Hz, 2H), 7.55 (s, 1H), 7.53 (s, 1H), 7.37 – 7.32 (m, 4H), 7.32 – 7.31 (d, *J* = 4.0 Hz, 2H), 7.30 – 7.29 (t, *J* = 2.8 Hz, 2H), 7.24 – 7.22 (m, 2H), 6.79 – 6.75 (m, 4H), 3.90 – 3.85 (t, *J* = 6.7 Hz, 4H), 2.52 (s, 2H), 1.77 – 1.70 (m, 4H), 1.42 – 1.40 (m, 4H), 1.30 – 1.28 (m, 16H), 0.9 – 0.8 (m, 6H).

Rac-BIOH: ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.65 (t, *J* = 7.6 Hz, 4H), 7.61 – 7.58 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.55 (s, 2H), 7.38 – 7.33 (dd, *J* = 14.7, 7.4 Hz, 4H), 7.33 – 7.32 (d, *J* = 4.0 Hz, 2H), 7.30 – 7.29 (d, *J* = 4.0 Hz, 2H), 7.25 – 7.23 (d, *J* = 7.7 Hz, 2H), 6.79 – 6.76 (d, *J* = 8.8 Hz, 4H), 3.90 – 3.86 (t, *J* = 6.5 Hz, 4H), 2.49 (s, 2H), 1.76 – 1.69 (m, 4H), 1.42 – 1.38 (m, 4H), 1.32 – 1.36 (m, 16H), 0.88 – 0.85 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 151.3, 150.9, 141.1, 139.1, 138.8, 134.8, 129.1, 128.4, 128.0, 126.6, 124.7, 123.3, 120.4, 120.1, 114.2, 83.42, 67.9, 31.8, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1. MALDI-TOF-MS [-OH]: *m/z* calcd for C₅₄H₅₈O₄: 770.43; found: 752.19, 769.16.

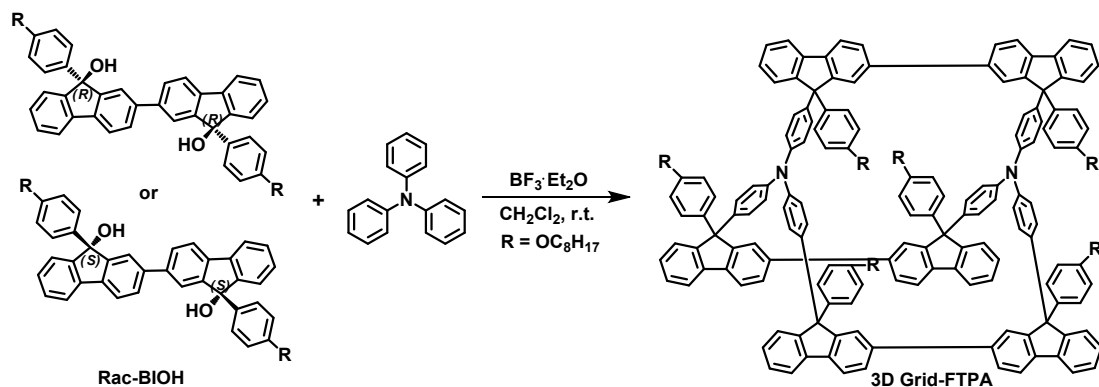
Meso-BIOH: ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.66 (t, *J* = 8.0 Hz, 4H), 7.59 – 7.56 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.53 (s, 2H), 7.38 – 7.33 (m, 4H), 7.32 – 7.31 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.30 (d, *J* = 4.0 Hz, 2H), 7.25 – 7.23 (dd, *J* = 7.4, 1.0 Hz, 2H), 6.81 – 6.77 (m, 4H), 3.92 – 3.88 (t, *J* = 6.5 Hz, 4H), 2.44 (s, 2H), 1.77 – 1.70 (m, 4H), 1.44 – 1.38 (m, 4H), 1.29 – 1.25 (m, 16H), 0.89 – 0.85 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 151.3, 150.9, 141.3, 139.0, 138.8, 134.9, 129.0, 128.4, 128.1, 126.6, 124.7, 123.3, 120.4, 120.1, 114.2, 83.4, 68.0, 31.8, 29.4, 29.3, 29.3, 26.1, 22.7, 14.1. MALDI-TOF-MS [-OH]: *m/z* calcd for C₅₄H₅₈O₄: 770.43; found: 752.56, 769.55.

Synthesis of 3D-Grid-FTPA in Route I.



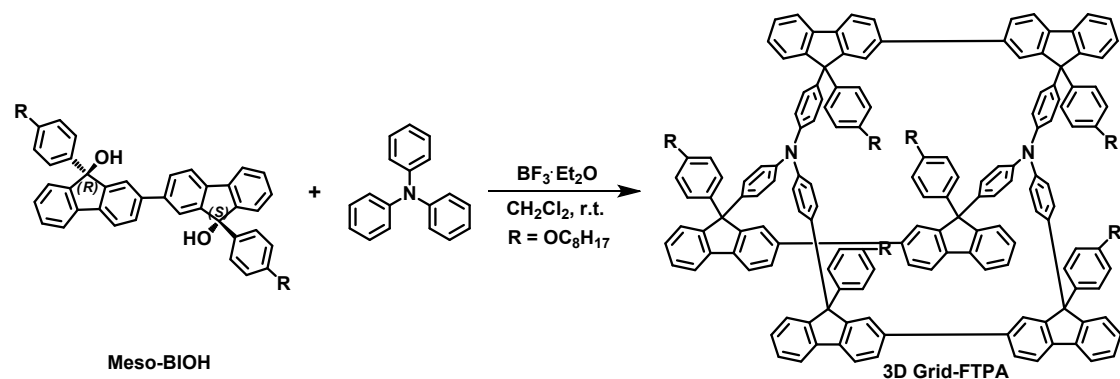
A 3:2 mixture solution of compound **Mix-BIOH** (150 mg, 0.19 mmol) and triphenylamine (31.83 mg, 0.13 mmol) in DCM (300 mL) was added dropwise a solution of boron trifluoride-diethyl ether complex (1.17 mL, 1 mol/L) in DCM (600 mL). The reaction mixture was stirred at r.t. (25 °C) for 8 h. Ethanol (15 mL) and water (25 mL) was successively added to quench the reaction. Then the mixture was separated and the aqueous phase was extracted with DCM. The combined DCM layers were washed and dried (MgSO₄). After removal of the solvent, the reaction mixtures was deposited by ethanol subsequently extracted by ethyl acetate. The remaining crude product was purified by the column chromatography using PE:DCM = 6:1 (v/v) as the eluent to provide a white solid compound **3D-Grid-FTPA** (71.36 mg, 0.027 mmol, 40.8%).

Synthesis of 3D-Grid-FTPA in Route II.



A mixture solution of compound **Rac-BIOH** (150 mg, 0.19 mmol) and triphenylamine (31.83 mg, 0.13 mmol) in DCM (300 mL) was added dropwise a solution of boron trifluoride-diethyl ether complex (1.17 mL, 1 mol/L) in DCM (600 mL). The reaction mixture was stirred at r.t. (25 °C) for 8 h. Ethanol (15 mL) and water (25 mL) was successively added to quench the reaction. Then the mixture was separated and the aqueous phase was extracted with DCM. The combined DCM layers were washed and dried (MgSO₄). After removal of the solvent, the reaction mixtures was deposited by ethanol subsequently extracted by ethyl acetate. The remaining crude product was purified by the column chromatography using PE:DCM = 6:1 (v/v) as the eluent to provide a white solid compound **3D-Grid-FTPA**. (93.37 mg, 0.072 mmol, 55.1%).

Synthesis of 3D-Grid-FTPA in Route III.



A mixture solution of compound **Meso-BIOH** (150 mg, 0.19 mmol) and triphenylamine (31.83 mg, 0.13 mmol) in DCM (300 mL) was added dropwise a solution of boron trifluoride-diethyl ether complex (1.17 mL, 1 mol/L) in DCM (600 mL). The reaction mixture was stirred at r.t. (25 °C) for 8 h. Ethanol (15 mL) and water (25 mL) was successively added to quench the reaction. Then the mixture was separated and the aqueous phase was extracted with DCM. The combined DCM layers were washed and dried (MgSO_4). After removal of the solvent, the reaction mixtures was deposited by ethanol subsequently extracted by ethyl acetate. The remaining crude product was purified by the column chromatography using PE:DCM = 6:1 (v/v) as the eluent to provide a white solid compound **3D-Grid-FTPA**. (54.92 mg, 0.021 mmol, 31.4%).

Un-Grid-FTPA: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 – 7.77 (t, $J = 6.8$ Hz, 4H), 7.59 – 7.57 (m, 4H), 7.45 – 7.43 (d, $J = 7.4$ Hz, 2H), 7.39 – 7.35 (t, $J = 7.1$ Hz, 2H), 7.31–7.28 (t, $J = 7.5$ Hz, 2H), 7.23 – 7.21 (m, 4H), 7.19 – 7.15 (m, 8H), 7.12 – 7.09 (m, 4H), 7.09 – 7.07 (d, $J = 2.0$ Hz, 4H), 7.07 – 7.05 (d, $J = 7.2$ Hz, 4H), 7.00 – 6.88 (m, 8H), 6.80 – 6.73 (dd, $J = 16.2, 8.9$ Hz, 4H), 3.91 – 3.86 (m, 4H), 1.78 – 1.71 (m, 4H), 1.31 – 1.29 (m, 20H), 0.91 – 0.88 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.0, 157.9, 152.4, 152.1, 147.7, 146.3, 146.3, 141.0, 139.8, 139.6, 139.3, 137.8, 129.2, 128.9, 127.7, 127.4, 126.7, 126.2, 124.9, 124.4, 124.4, 123.3, 123.2, 122.8, 122.8, 120.3, 120.2, 114.2, 67.9, 64.5, 31.9, 29.4, 29.4, 29.3, 26.1, 22.7, 14.2. MALDI-TOF-MS: m/z calcd for $\text{C}_{90}\text{H}_{84}\text{N}_2\text{O}_2$: 1224.65; found: 1224.18.

2D-Grid-FTPA-1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 – 7.75 (m, 4H), 7.75 – 7.73 (m, 4H), 7.63 – 7.60 (dd, $J = 8.0, 3.4$ Hz, 2H), 7.57 – 7.55 (d, $J = 8.0$, 1H), 7.42 – 7.28 (m, 11H), 7.23 – 7.19 (m, 4H), 7.12 – 7.09 (m, 6H), 7.05 – 7.01 (t, $J = 8.7$ Hz, 6H), 6.98 – 6.91 (dd, $J = 17.2, 8.3$ Hz, 12H), 6.89 – 6.83 (m, 6H), 6.76 – 6.67 (m, 8H), 6.62 – 6.60 (d, $J = 8.1$ Hz, 2H), 6.46 – 6.44 (d, $J = 8.6$ Hz, 2H), 3.88 – 3.78 (m, 8H), 1.79 – 1.67 (m, 8H), 1.42 – 1.37 (m, 8H), 1.29 – 1.26 (m, 32H), 0.90 – 0.83 (m, 12H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.1, 158.0, 157.9, 157.9, 153.0, 152.5, 152.3, 152.3, 152.2, 151.9, 151.8, 149.3, 149.3, 147.8, 147.4, 146.8, 146.2, 146.1, 146.1, 145.7, 145.6, 142.4, 141.6, 141.4, 140.9, 140.9, 139.9, 139.8, 139.8, 139.6, 139.5, 139.5, 139.3, 139.3, 139.2, 139.0, 139.0, 138.9, 138.2, 138.1, 137.9, 137.8, 137.5, 136.6, 129.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 127.9, 127.7, 127.7, 127.6, 127.5, 127.4,

126.6, 126.5, 126.4, 126.3, 126.3, 126.2, 126.2, 126.1, 126.0, 125.8, 125.7, 125.6, 125.0, 124.6, 124.5, 124.1, 123.7, 123.7, 123.6, 123.2, 122.7, 122.4, 120.5, 120.3, 120.2, 120.2, 120.1, 119.5, 119.2, 119.0, 114.4, 114.2, 114.1, 68.1, 67.9, 64.5, 64.3, 35.1, 34.6, 33.9, 32.1, 31.9, 31.6, 31.6, 30.3, 30.2, 29.8, 29.5, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.1, 26.2, 26.1, 22.8, 22.8, 14.3, 14.2, 1.2. MALDI-TOF-MS: m/z calcd for: m/z calcd for $C_{144}H_{138}N_2O_4$: 1959.07; found: 1958.96.

3D Grid-FTPA-1: 1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (d, J = 7.9 Hz, 2H), 7.76 – 7.74 (d, J = 7.7 Hz, 2H), 7.69 – 7.68 (d, J = 7.4 Hz, 2H), 7.65-7.63 (dd, J = 8.0, 2.5 Hz, 6H), 7.61 – 7.49 (m, 6H), 7.49 – 7.43 (m, 4H), 7.37 – 7.36 (d, J = 4.0 Hz, 2H), 7.35 – 7.34 (d, J = 4.0 Hz, 2H), 7.34 – 7.31 (m, 3.9 Hz, 6H), 7.30 – 7.27 (m, 4H), 7.25 – 7.24 (m, 4H), 7.24 – 7.22 (d, J = 8.0 Hz, 3H), 7.20 – 7.19 (d, J = 1.9 Hz, 3H), 7.17 – 7.16 (d, J = 2.7 Hz, 2H), 7.12 – 7.10 (d, J = 8.7 Hz, 3H), 7.00 – 6.98 (d, J = 8.8 Hz, 3H), 6.97 – 6.94 (d, J = 9.1 Hz, 3H), 6.94 – 6.88 (m, 6H), 6.84 – 6.81 (d, J = 9.4 Hz, 3H), 6.81 – 6.78 (m, 6H), 6.76 – 6.75 (d, J = 2.7 Hz, 3H), 6.74 – 6.71 (dd, J = 8.4, 4.5 Hz, 6H), 6.69 – 6.67 (d, J = 8.7 Hz, 6H), 6.64 – 6.62 (d, J = 8.9 Hz, 3H), 3.93 – 3.82 (m, 12H), 1.77 – 1.72 (m, 12H), 1.45 – 1.43 (m, 12H), 1.26 – 1.24 (m, 48H), 0.90 – 0.89 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 152.8, 152.4, 152.2, 146.0, 145.5, 141.8, 140.8, 139.87, 139.10, 138.95, 137.7, 136.9, 129.6, 129.3, 129.2, 128.8, 128.7, 128.5, 127.8, 127.6, 127.3, 126.6, 126.3, 126.2, 126.0, 124.8, 123.7, 123.6, 120.8, 120.3, 120.1, 114.2, 114.1, 76.9, 68.0, 68.0, 64.7, 64.3, 32.0, 31.9, 31.9, 31.9, 31.5, 30.3, 29.8, 29.5, 29.4, 29.3, 29.3, 26.2, 26.1, 26.1, 22.7, 14.2, 1.5, 1.2, 1.1. MALDI-TOF-MS: m/z calcd for $C_{198}H_{192}N_2O_6$: 2695.48; found: 2695.99.

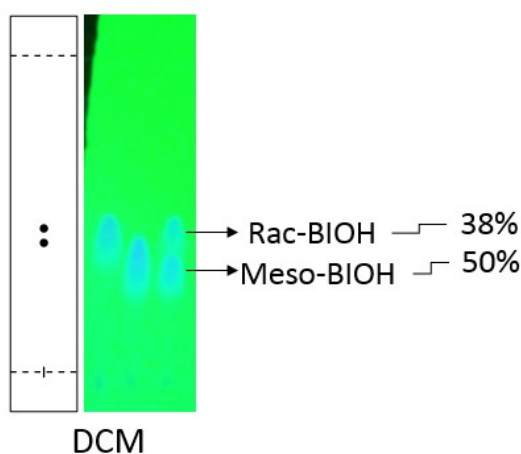


Figure S1. TLC photographs of **BIOH** under the UV lamp with irradiation wavelength of 254 nm and 365nm (using dichloromethane as developing solvent). Right: mixed compound, left and middle: the separated compounds.

II. MALDI-TOF-MS of compounds.

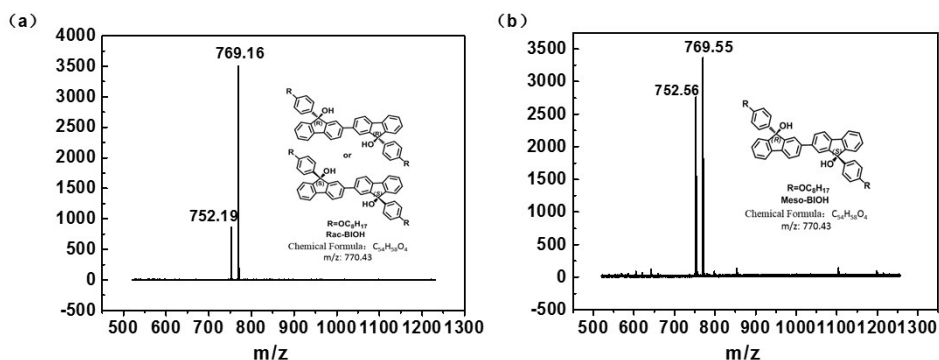
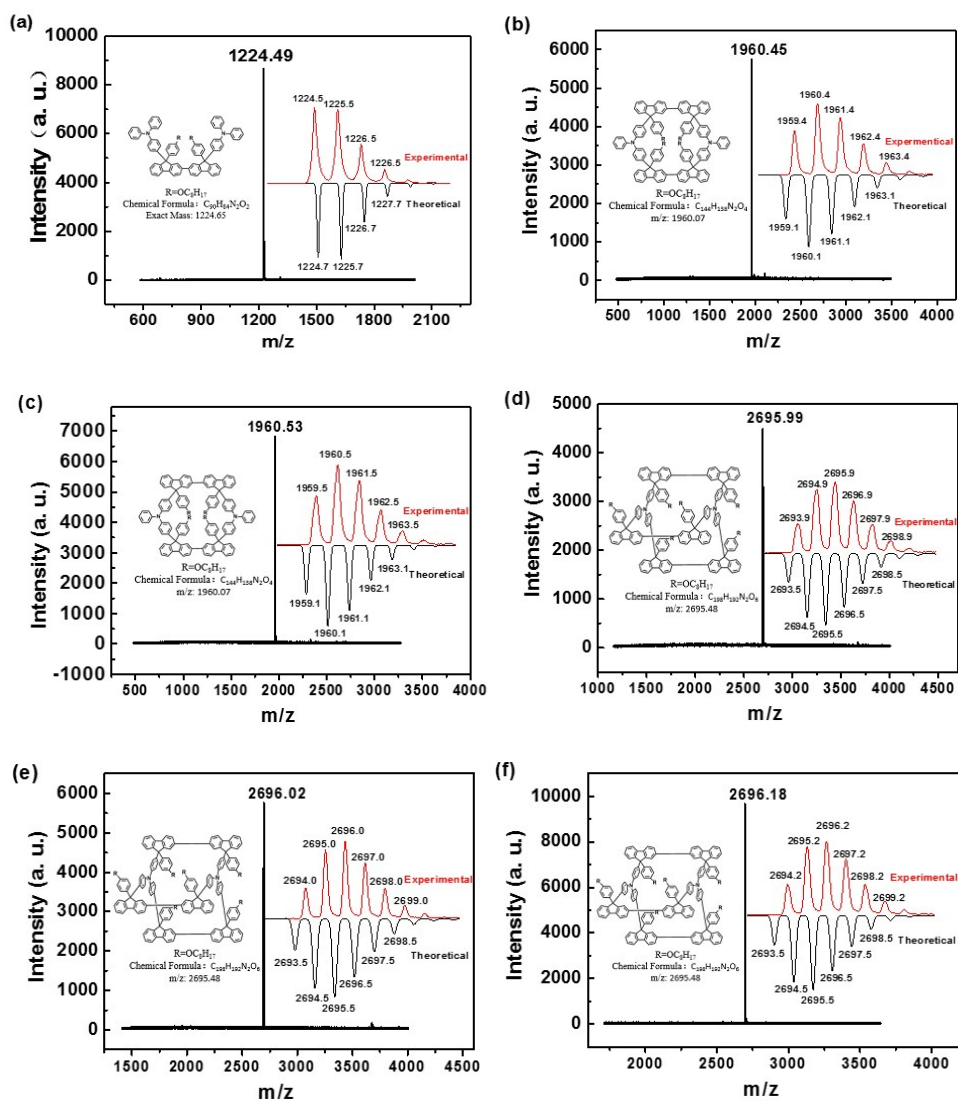


Figure S2. MALDI-TOF-MS spectra of (a) Rac-BIOH and (b) Meso-BIOH.



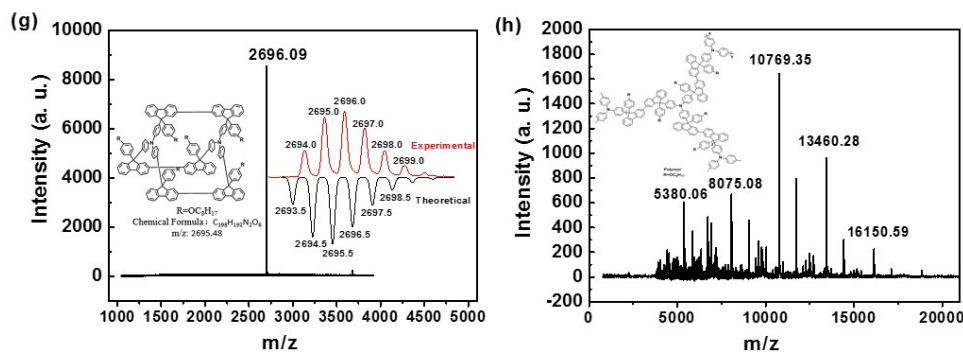


Figure S3. MALDI-TOF-MS spectra of each spot in route III. (a) DTPAF, (b) 2D-Grid-FTPA-1, (c) 2D-Grid-FTPA-2, (d) 3D-Grid-FTPA-1, (e) 3D-Grid-FTPA-2, (f) 3D-Grid-FTPA-3, (g) 3D-Grid-FTPA-4, (h) Polymer III (the spectra were recorded in linear mode).

III. GPC spectrum of Polymers

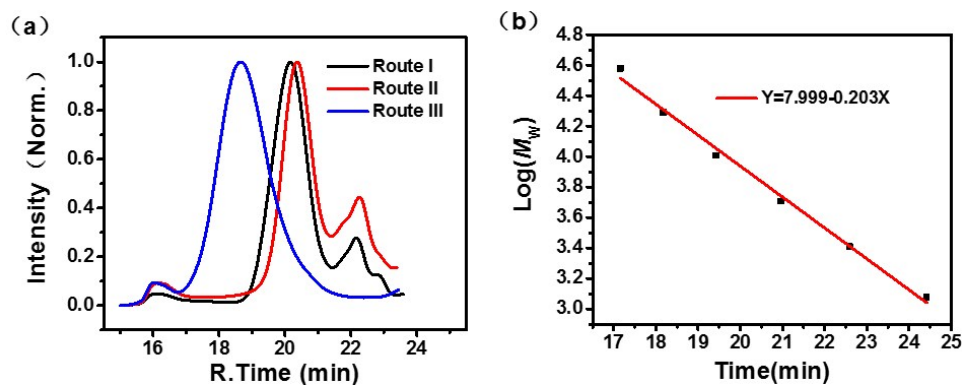


Figure S4. (a) GPC spectrum of polymers in three routes. (b) standard curve determined by GPC in THF using polystyrene standards.

Table S1. Molecular weights of polymers.

Polymer	M_n	M_w	PDI
I	6846, 3405	7137, 3439	1.04, 1.01
II	6193, 3254	6386, 3323	1.03, 1.02
III	12191	15098	1.24

IV. The structure of configurational isomers of BIOH, 2D-Grid-FTPFA and 3D-Grid-FTPFA.

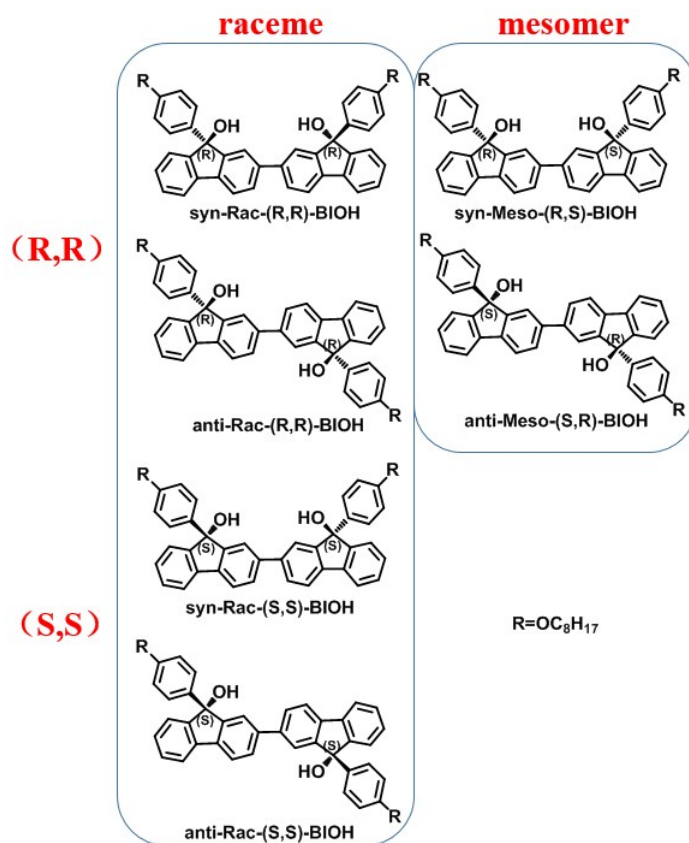


Figure S5. The structure of configurational isomers of BIOH regarded A2-type building block where the syn or anti refer to the conformers with bifluorene of either same or different side.

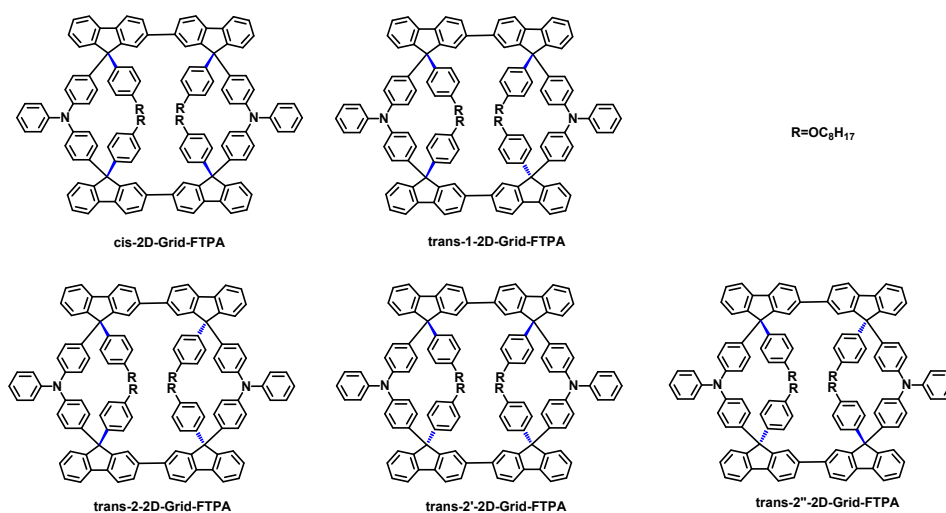


Figure S6. The structure of configurational isomers of 2D-Grid-FTPFA.

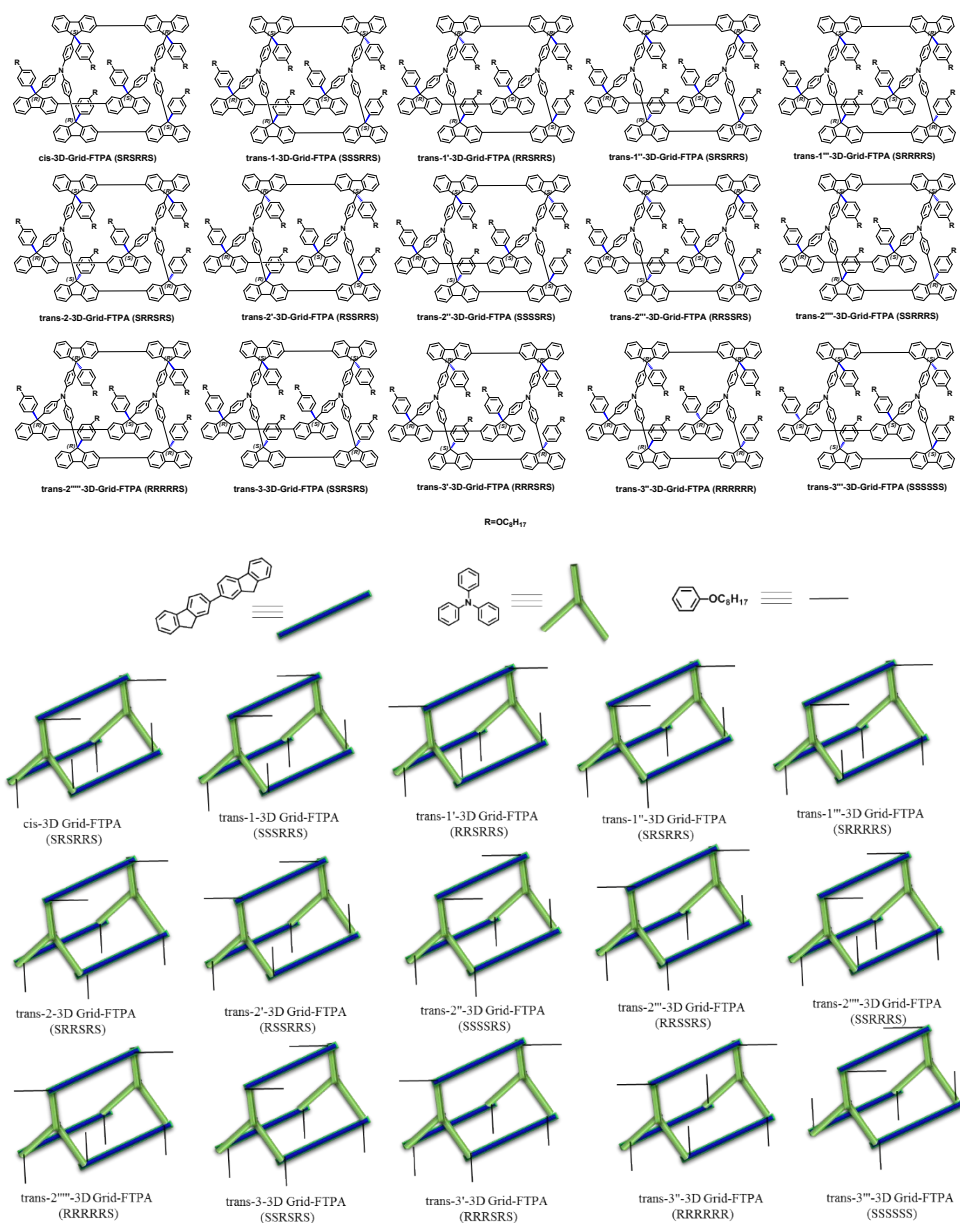


Figure S7. The structure and cartoon representation of configurational isomers of **3D-Grid-FTPAs**.

V. ^1H NMR and ^{13}C NMR analysis of these compounds.

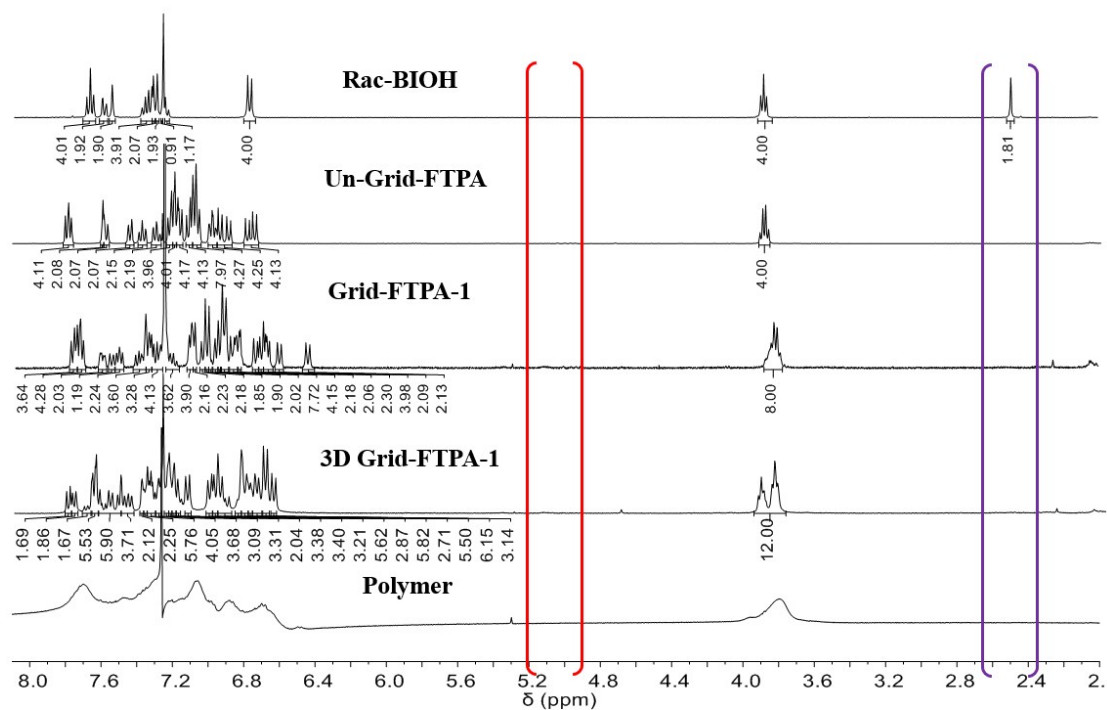


Figure S8. The ^1H NMR spectrum of these compounds.

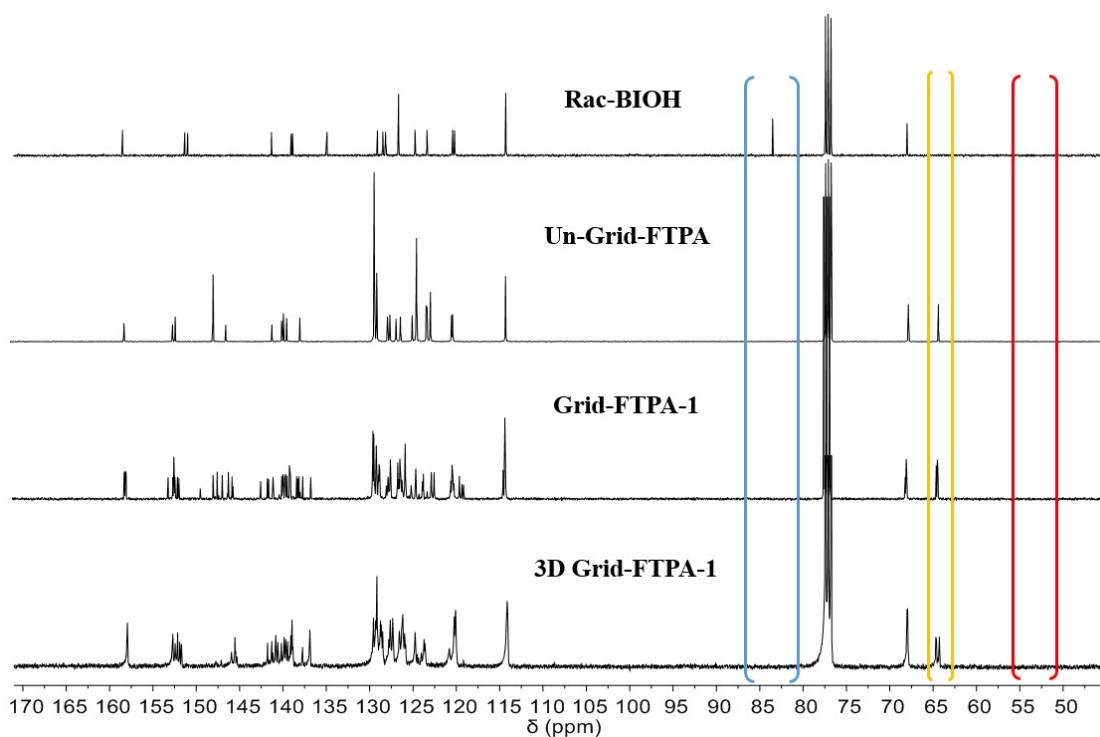


Figure S9. The ^{13}C NMR spectrum of these compounds.

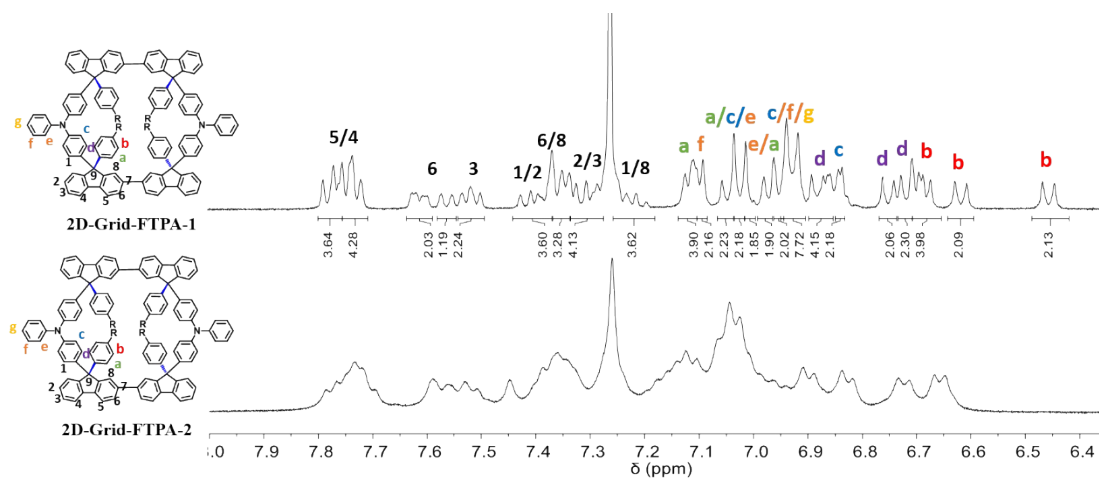


Figure S10. ^1H NMR spectra of 2D-Grid-FTPA-1 and 2D-Grid-FTPA-2 in route I.

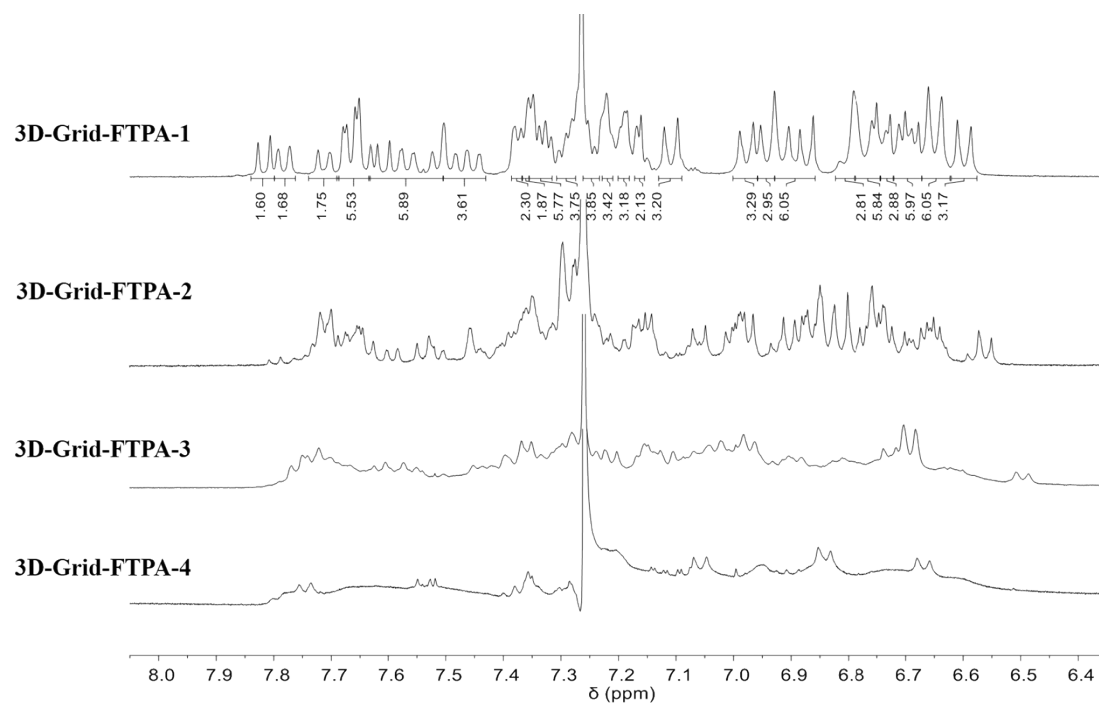


Figure S11. The ^1H NMR spectrum of isomers of 3D-Grid-FTPA in route I.

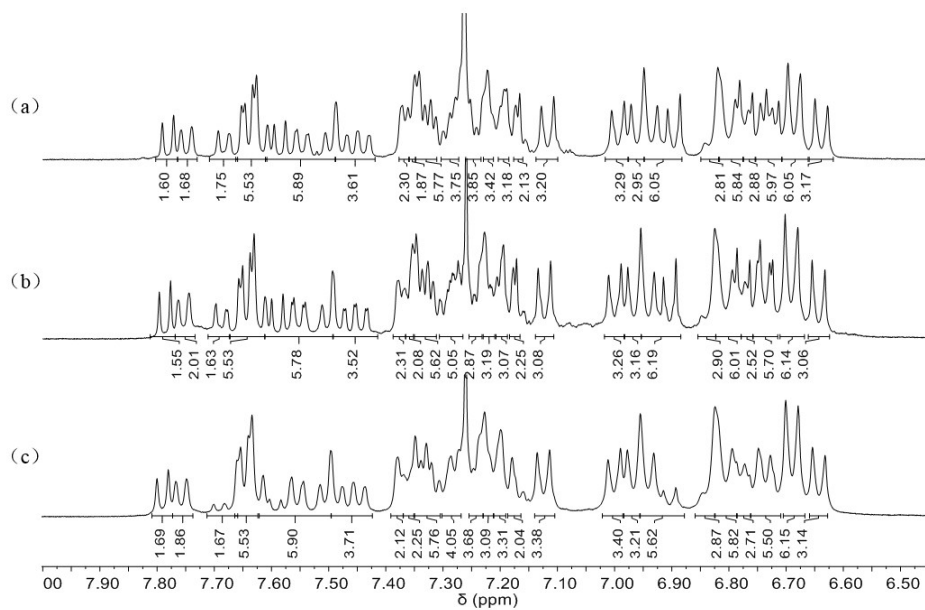


Figure S12. The ^1H NMR spectra of the **3D-Grid-FTPA-1** in (a) route I, (b) route II, (c) route III.

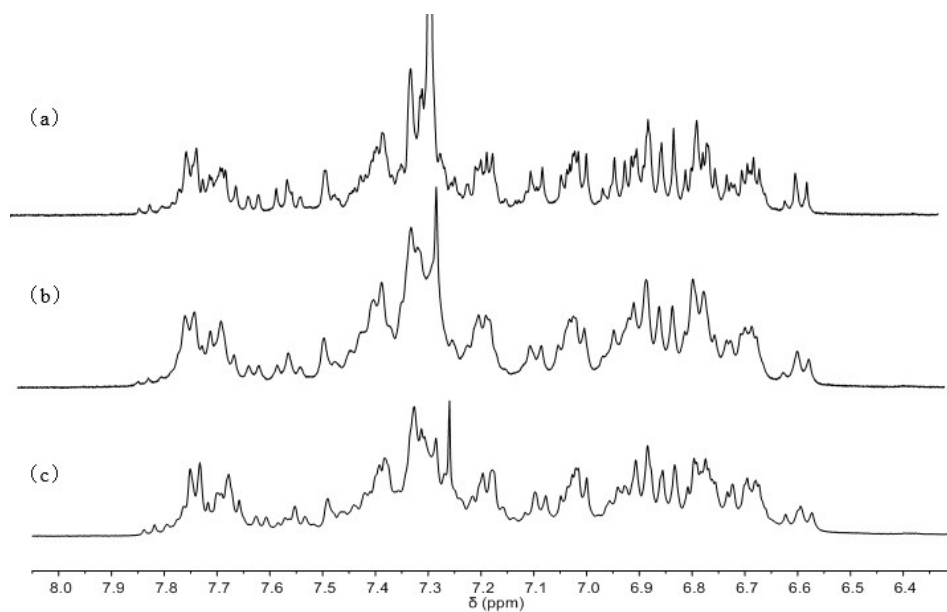


Figure S13. The ^1H NMR spectra of the **3D-Grid-FTPA-2** in TLC in (a) route I, (b) route II, (c) route III.

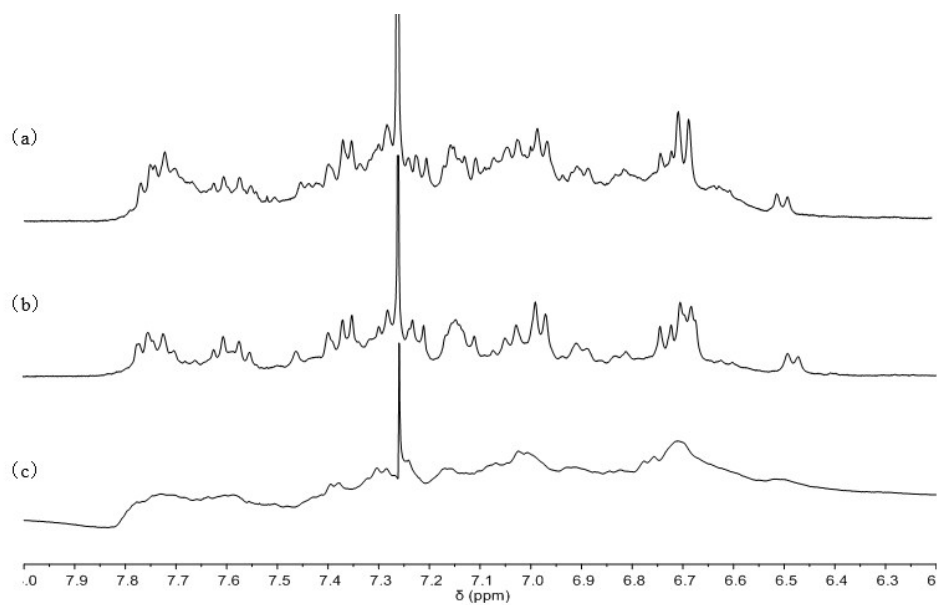


Figure S14. The ^1H NMR spectra of the **3D-Grid-FTPA-3** in TLC in (a) route I, (b) route II, (c) route III.

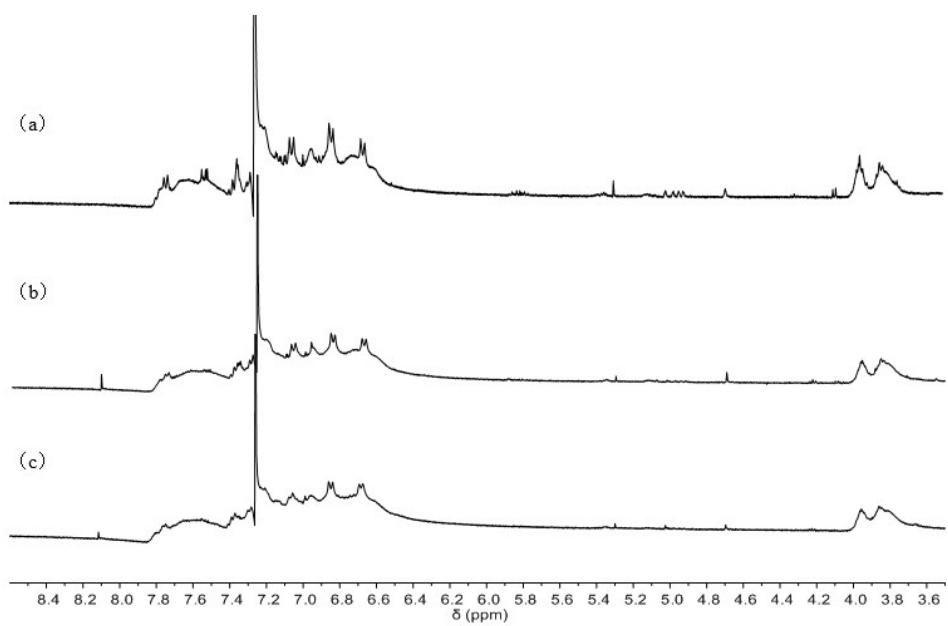


Figure S15. ^1H NMR spectra of the **3D-Grid-FTPA-4** in TLC in (a) route I, (b) route II, (c) route III.

VI. ^1H - ^1H COSY spectra of these compounds.

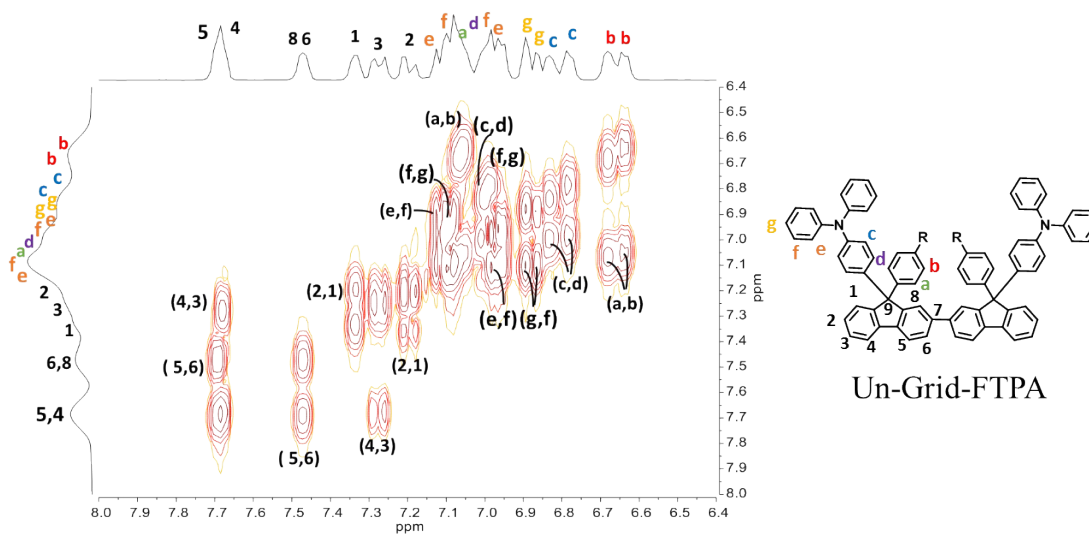


Figure S16. ^1H - ^1H COSY spectra (400MHz, CDCl_3 , 298K) of Un-Grid-FTP.

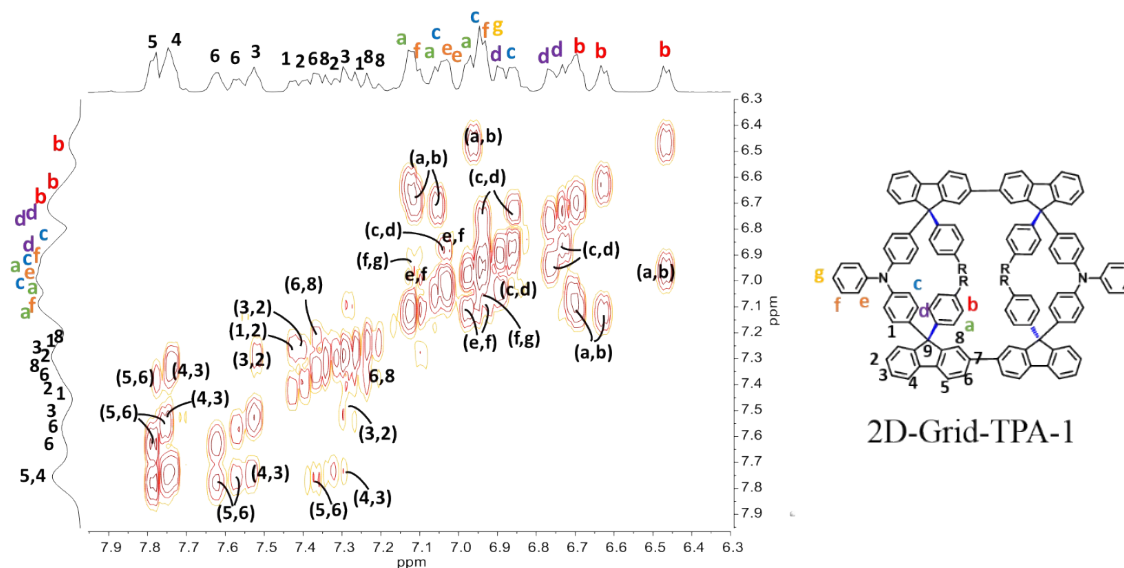


Figure S17. ^1H - ^1H COSY spectra (400MHz, CDCl_3 , 298K) of 2D-Grid-TPA-1.

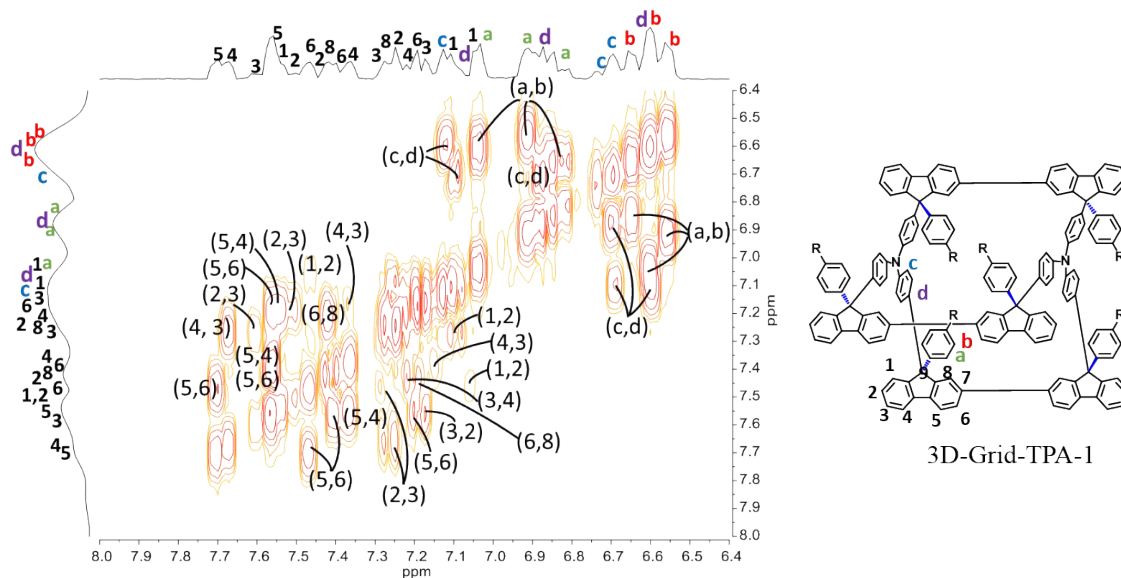


Figure S18. ^1H - ^1H COSY spectra of the 3D-Grid-FTPA-1.

VII. Electrochemical Characterization.

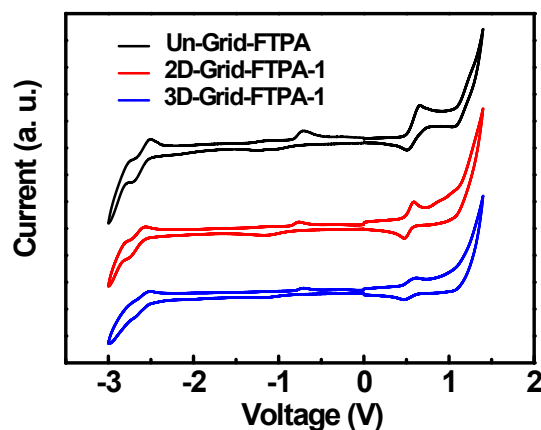


Figure S19. CV curves of Un-Grid-FTPA, 2D-Grid-FTPA-1 and 3D-Grid-FTPA-1.

VIII. Thermal Analysis.

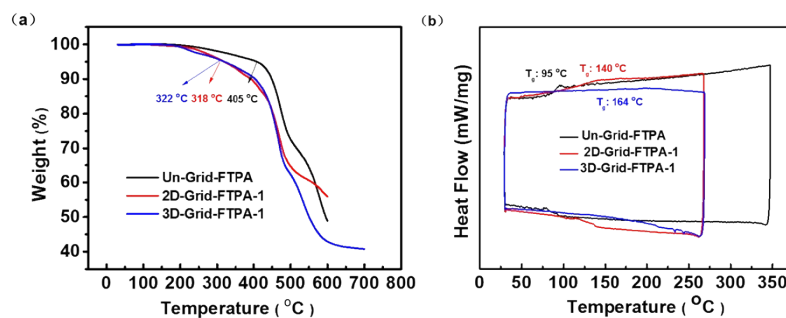
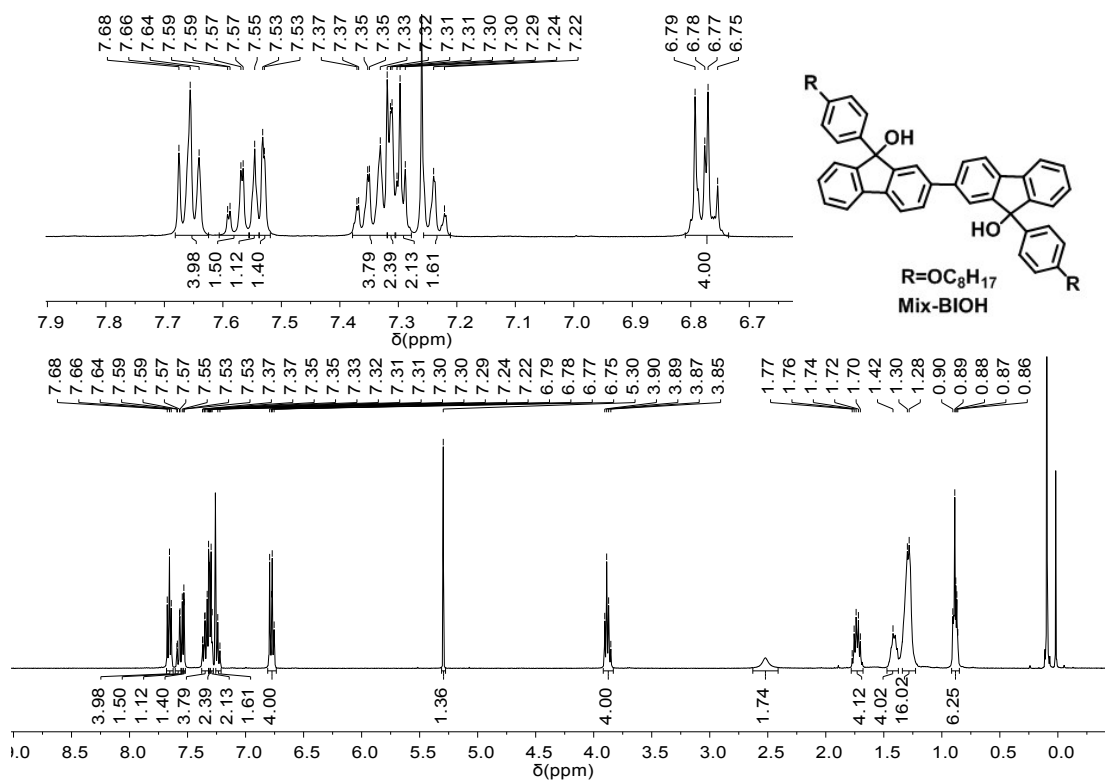
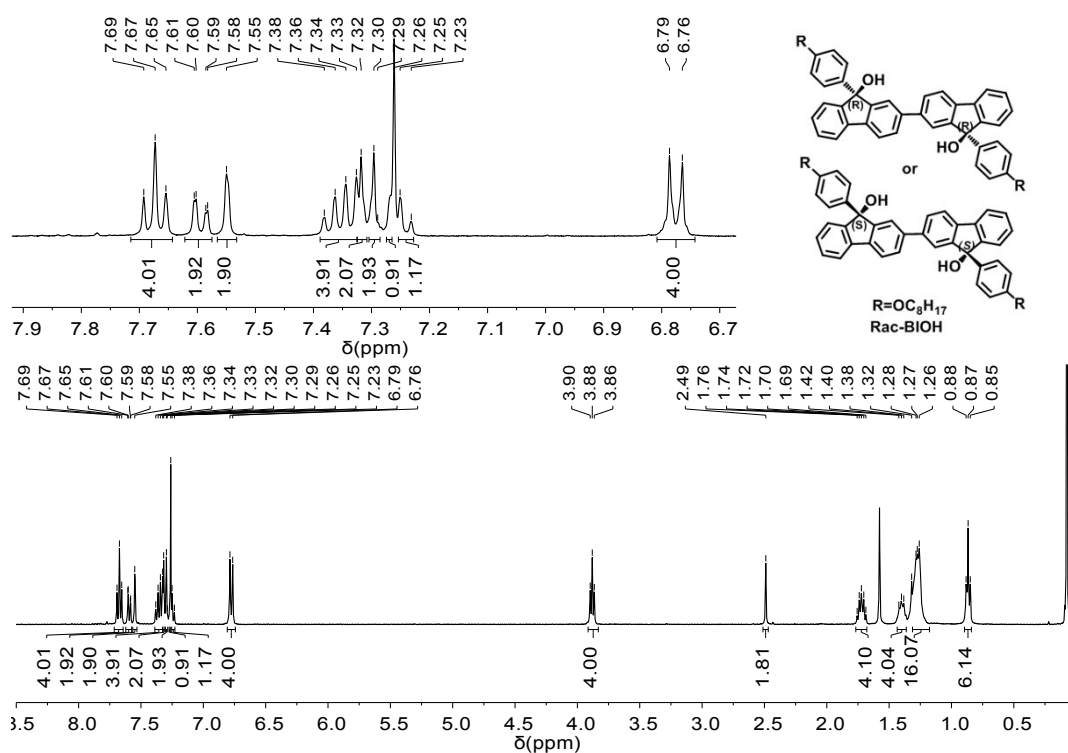


Figure S20. (a) TGA and (b) DSC of Un-Grid-FTPA, 2D-Grid-FTPA-1 and 3D-Grid-FTPA-1.

IX. ^1H and ^{13}C -NMR spectra of these compounds.

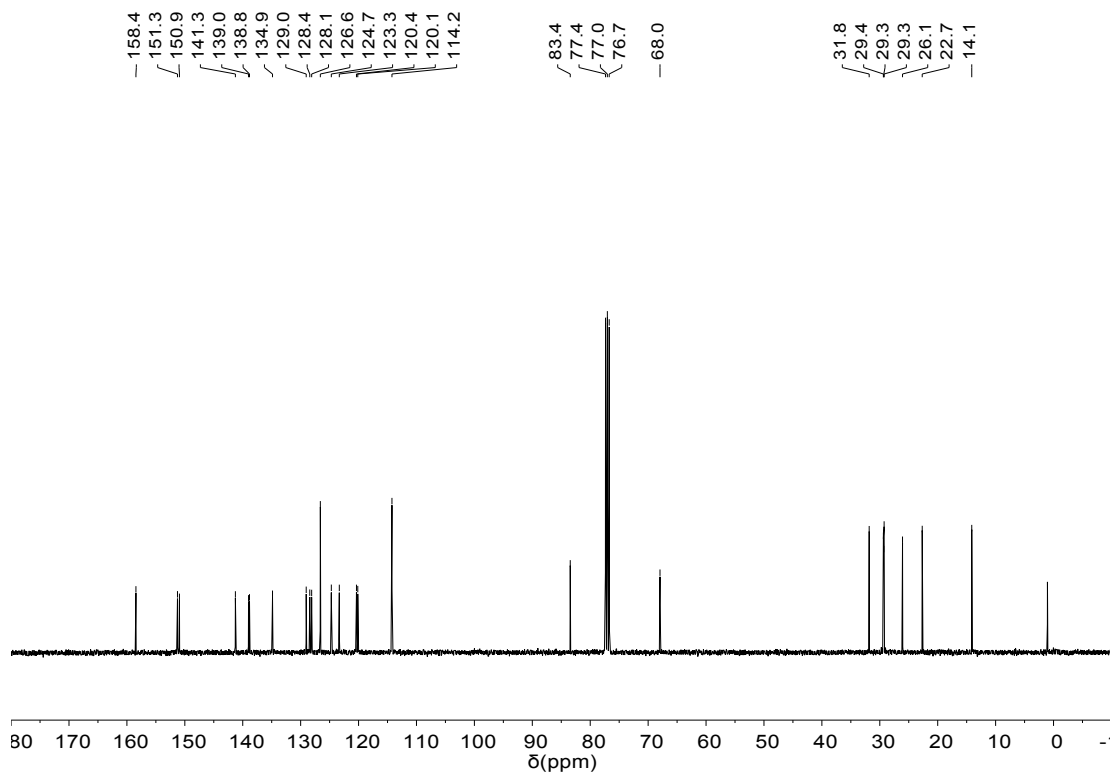


^1H NMR spectra of 9,9'-bis(4-(octyloxy)phenyl)-9*H*,9'*H*-[2,2'-bifluorene]-9,9'-diol (Mix-BIOH).

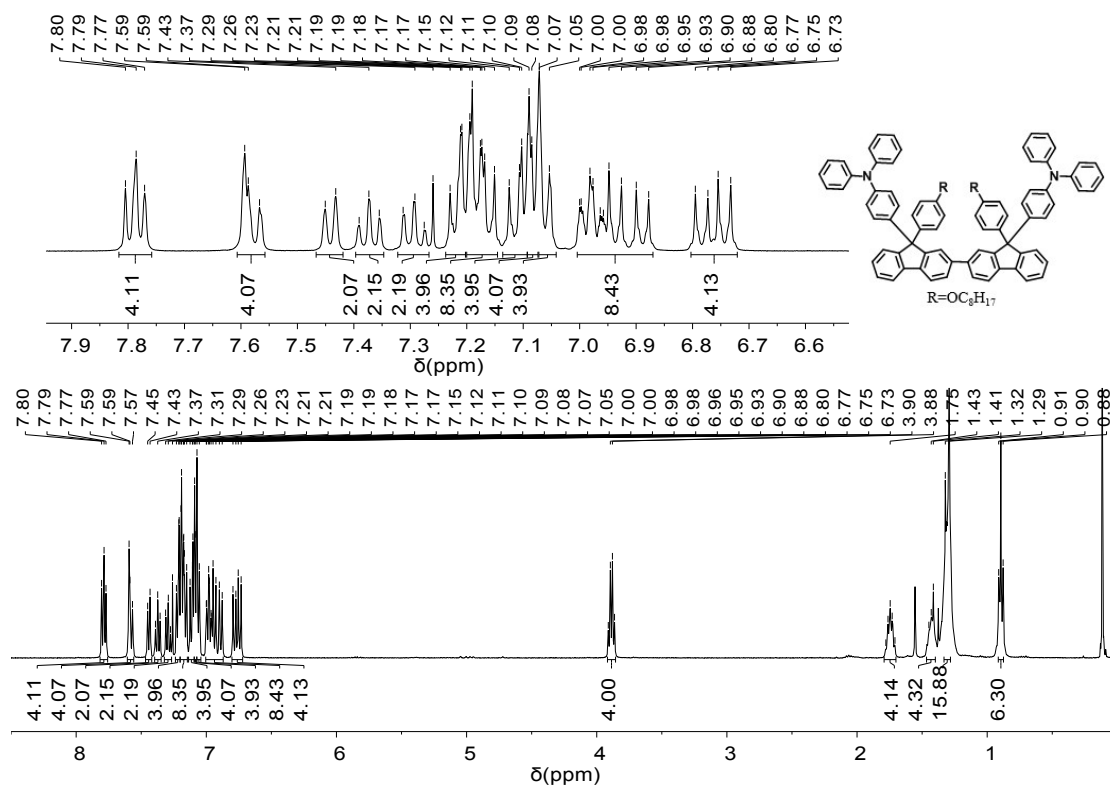


^1H NMR spectra of 9,9'-bis(4-(octyloxy)phenyl)-9*H*,9'*H*-[2,2'-bifluorene]-9,9'-diol (Rac-BIOH).

(Meso-BIOH).

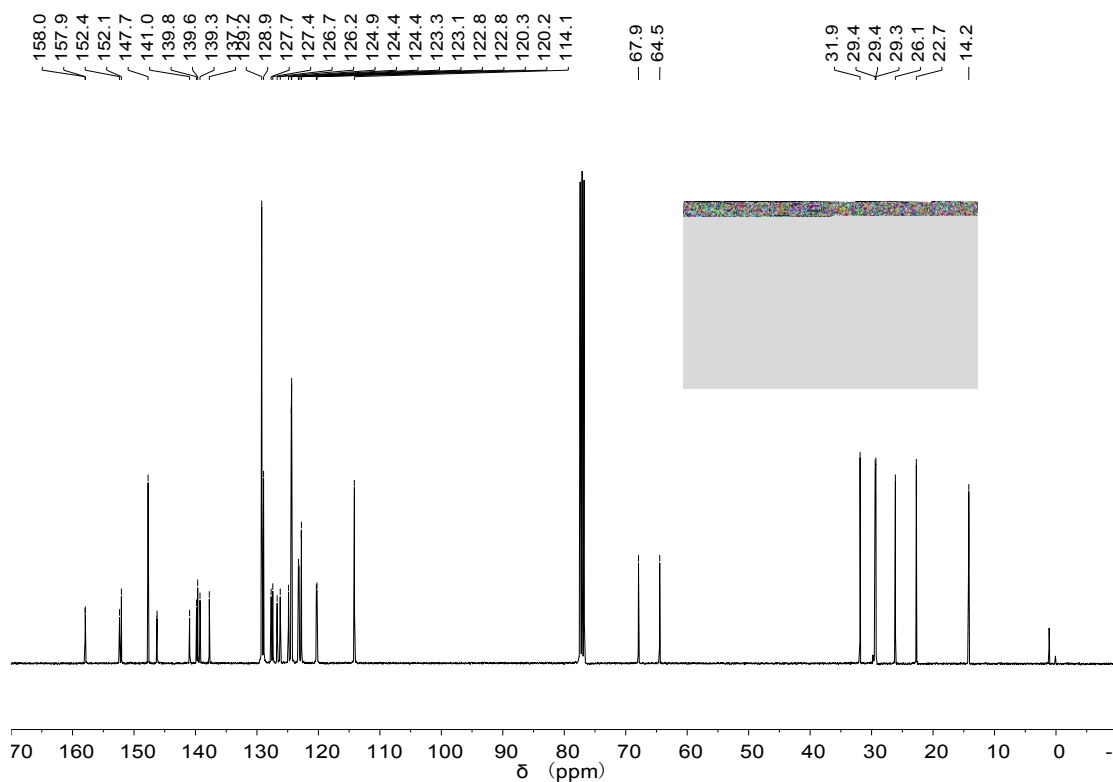


^{13}C NMR spectra of 9,9'-bis(4-(octyloxy)phenyl)-9H,9'H-[2,2'-bifluorene]-9,9'-diol (Meso-BIOH).

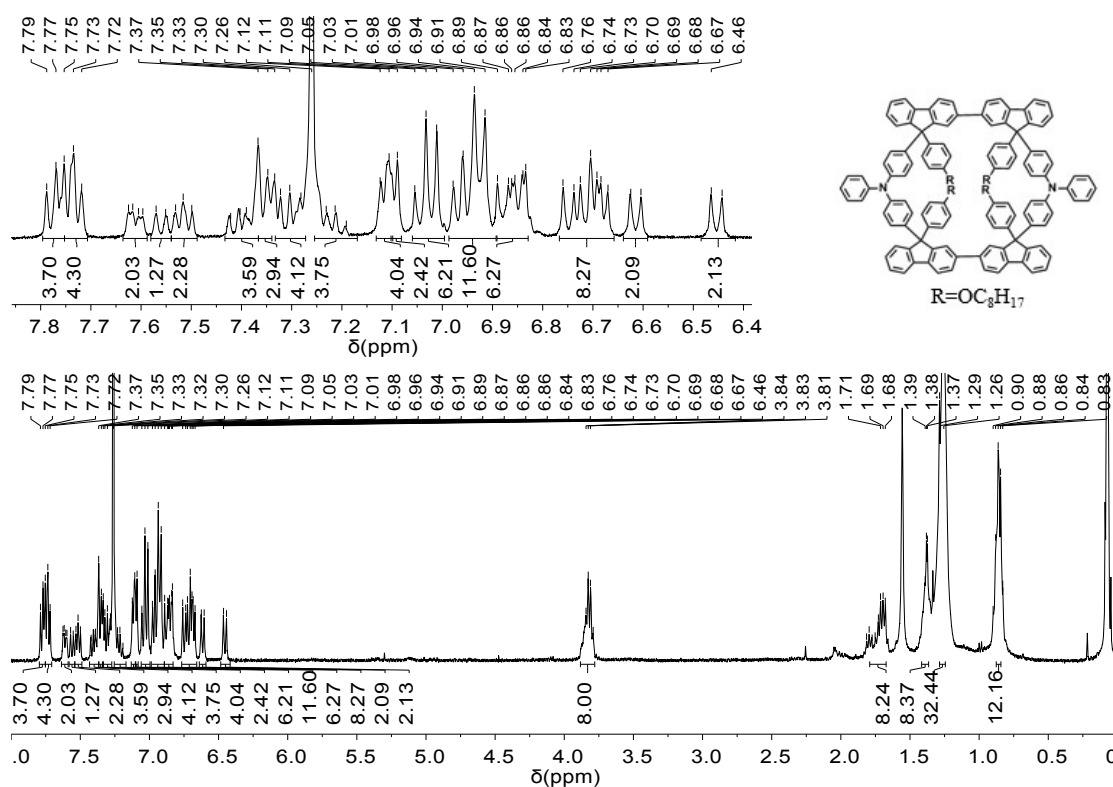


^1H NMR spectra of 4,4'-(9,9'-bis(4-(octyloxy)phenyl)-9H,9'H-[2,2'-bifluorene]-9,9'-

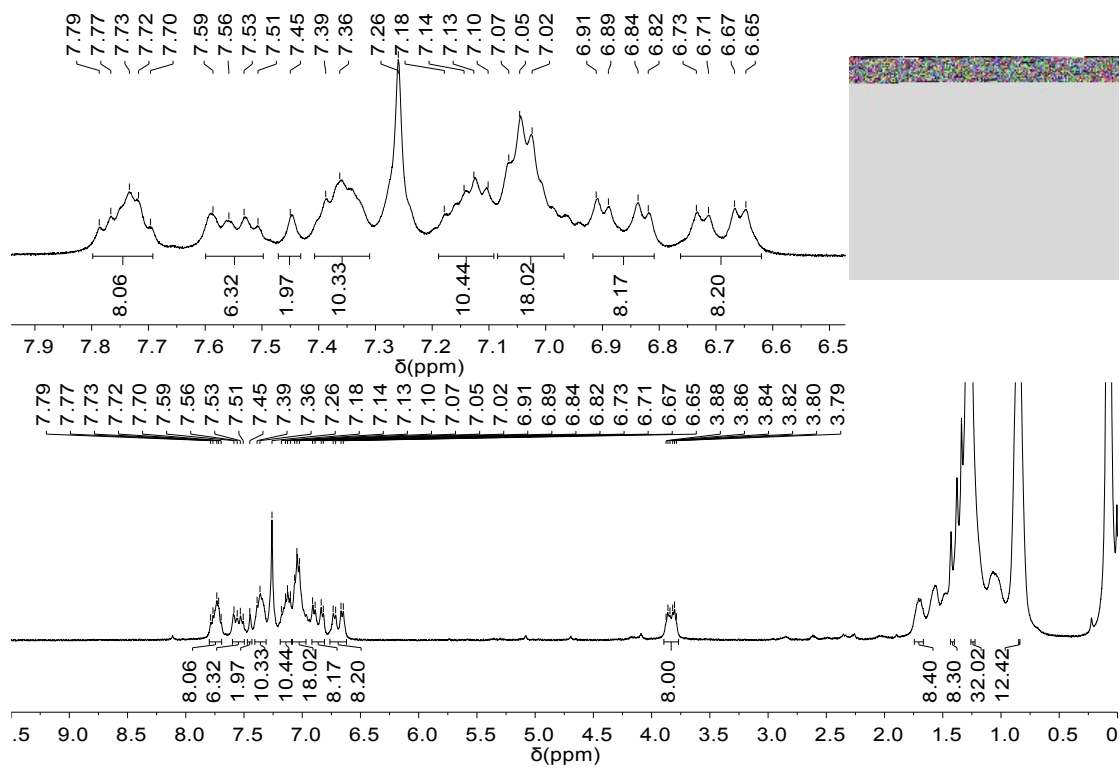
diyl)bis(N,N-diphenylaniline) (Un-Grid-FTPA).



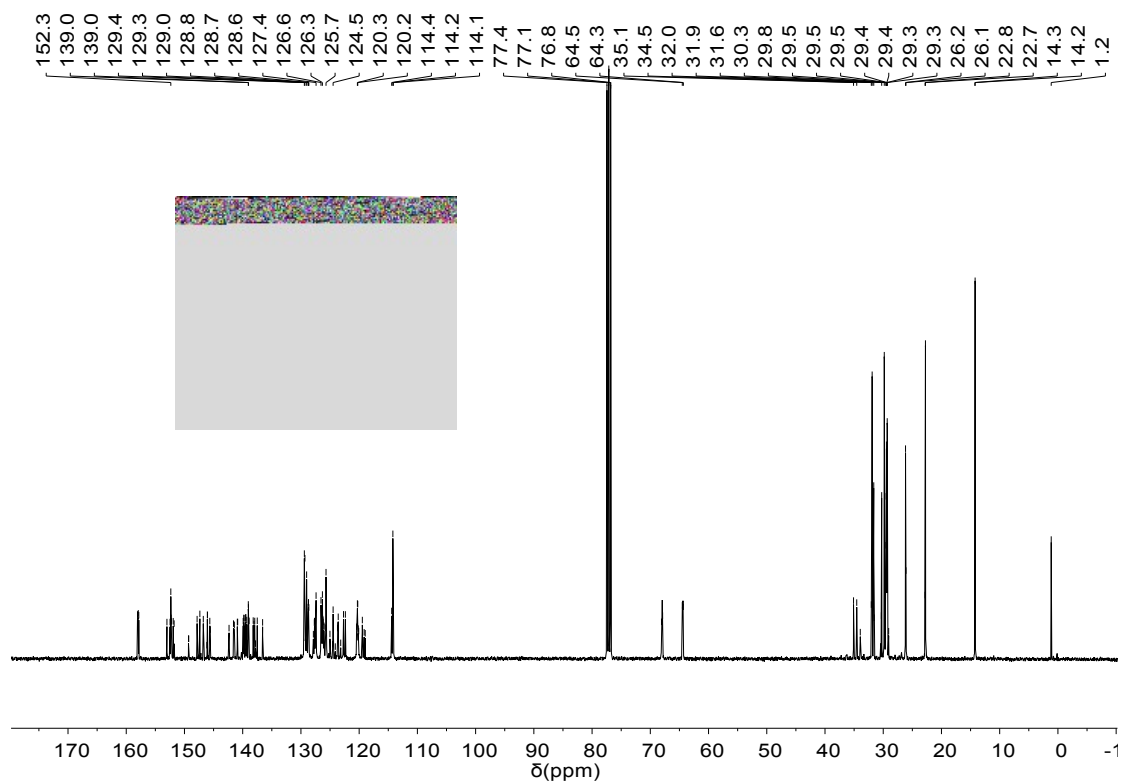
¹³C NMR spectra of 4,4'-(9,9'-bis(4-(octyloxy)phenyl)-9H,9'H-[2,2'-bifluorene]-9,9'-diyl)bis(N,N-diphenylaniline) (Un-Grid-FTPA).



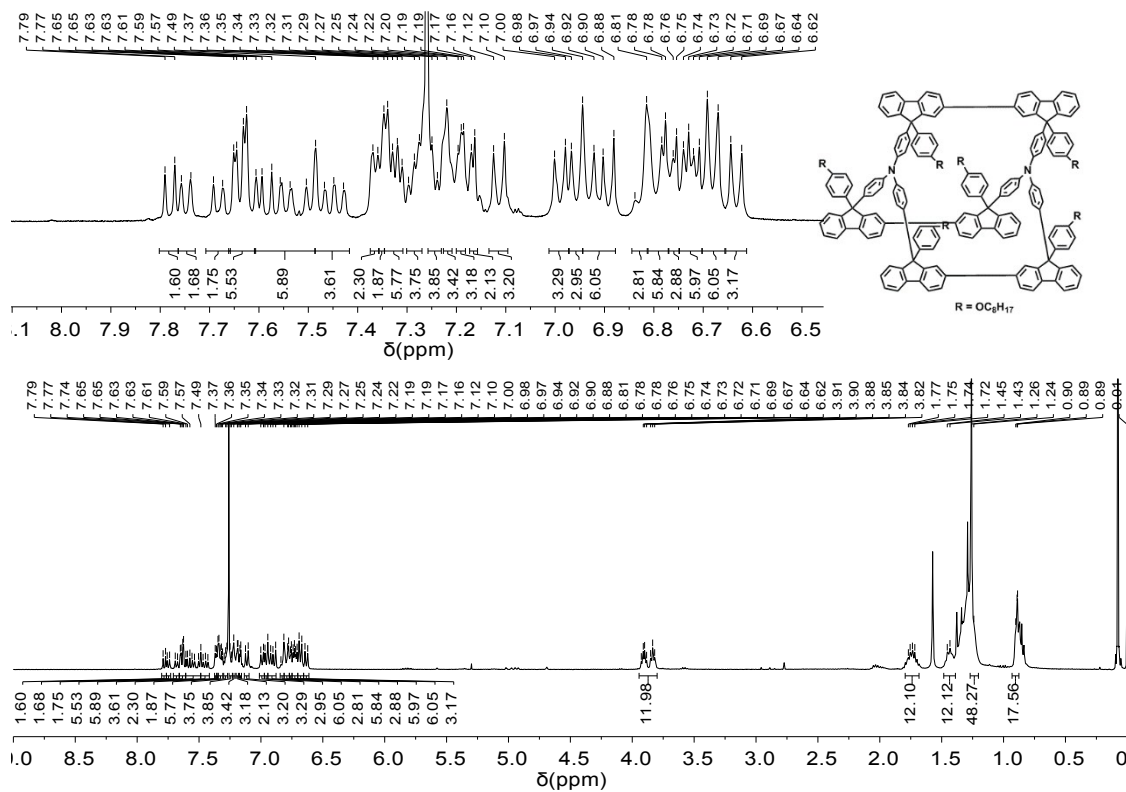
¹H NMR spectra of the 2D-Grid-FTPA-1.



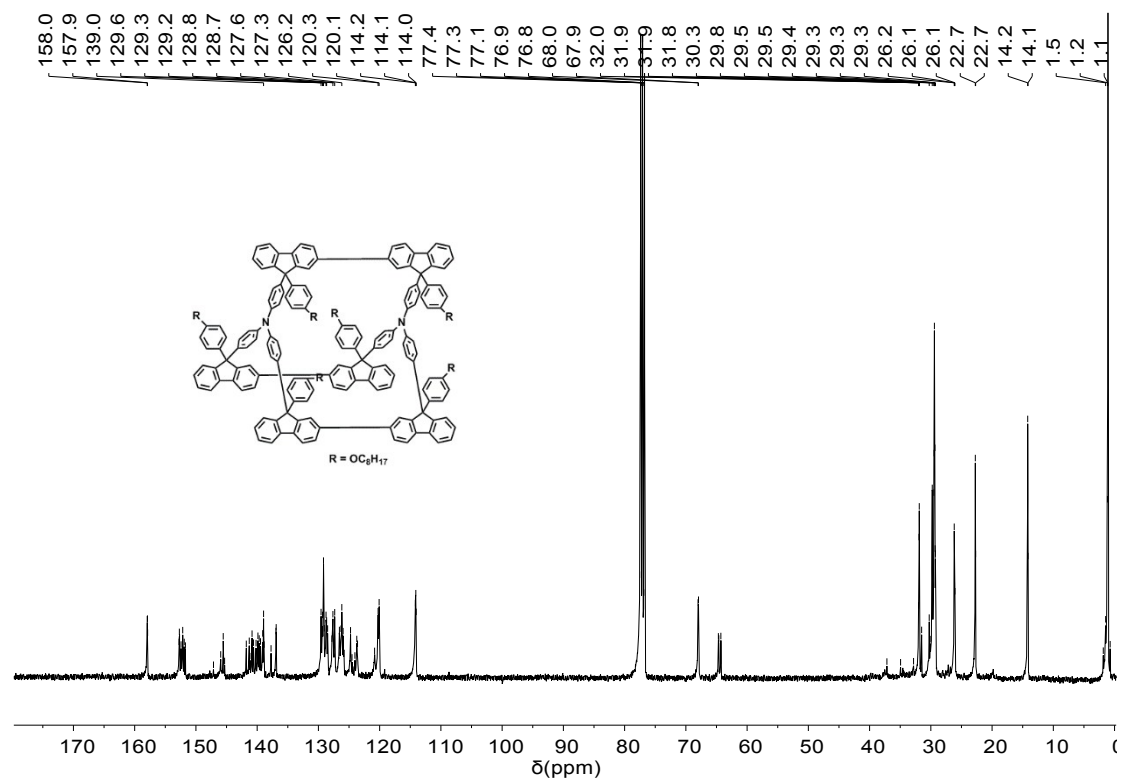
¹H NMR spectra of the 2D-Grid-FTP-2.



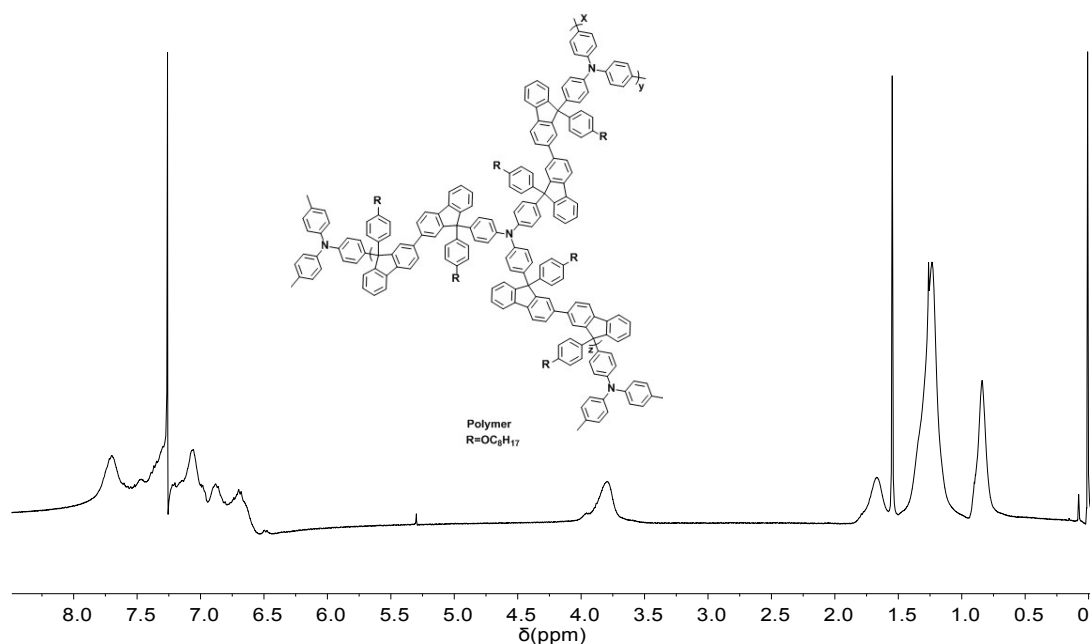
¹³C NMR spectra of 2D-Grid-FTP-1.



¹H NMR spectra of 3D-Grid-FTPA-1.



¹³C NMR spectra of 3D-Grid-FTPA-1.



¹H NMR spectra of the Polymer.

X. References

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