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Ladder-Type Oligo(p-phenylene)s with D-π-A Architectures: Design, Synthesis, Optical Gain Properties and Stabilized Amplified Spontaneous Emission

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General Methods: All reactions were monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 plus at 295 K. The MALDI-TOF mass spectroscopy measurements were carried out with a Bruker mass spectrometer use trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix. Elemental analysis was conducted with a Carlo Erba-1106 instrument. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were done on Shimadzu DSC-60A and DTG-60H equipment, respectively. AFM measurements of surface morphology were conducted on the Bruker ScanAsyst AFM in auto scan (AC) mode. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were measured using a Shimadzu RF-5301PC spectrofluorimeter with a xenon lamp as a light source. The fluorescence quantum yields were determined by full-featured steady state/transient fluorescence spectrometer FLS-920 from Edinburgh Instruments. PL decays were measured with an Edinburgh FLS-920 spectrometer. All fluorescent lifetimes were determined from the data using the Edinburgh Instruments software package. Cyclic voltammetry (CV) was performed on an Eco Chemie's Autolab at room temperature under nitrogen with a scanning rate of 100 mV/s.

1. Synthesis and characterization

Synthesis of (2,5-Dibromo-1,4-phenylene)bis((4-butylphenyl)methanone) (**MA1**). 2,5-Dibromoter phthalic acid (4.00 g, 12.3 mmol) was treated with 40 mL of thionly chloride ($SOCl_2$) and refluxed for 10 h. The excess $SOCl_2$ was removed in vacuum to give 3,6-dibromo-2,5-phenylenendi(carboxylic acid chloride) as a crystalline yellow solid. To a solution of butylbenzene (5.7 mL, 36.9 mmol) and aluminum trichloride (2.47g, 18.5 mmol), a mixture of all products and 30 mL of CH_2Cl_2 were added dropwise. After stirring at room temperature for 2 h, the mixture was poured into ice. The organic layer was washed with 1 M NaOH and water, then dried over Na_2SO_4, and concentrated. The residue was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane (2:3) (by vol) to afford **MA1** 4.92 g (72% yield) as a white crystal. ^{1}H NMR (400

MHz, $CDCl_3$, δ): 7.76 (d, *J* = 8.3 Hz, 4H), 7.58 (s, 2H), 7.32 (d, *J* = 8.3 Hz, 4H), 2.73-2.68 (m, 4H), 1.41-1.35 (m, 4H), 1.24 (t, *J* = 7.0 Hz, 4H), 0.94 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 193.39, 150.57, 143.36, 132.91, 130.50, 129.02, 118.44, 35.89, 33.13, 22.37, 13.90.

Synthesis of (4-Bromo-4'-(diphenylamino)-[1,1'-biphenyl]-2,5-diyl) bis((4-butylphenyl) methanone) (**1**). A mixture of MA1 (2.0 g, 3.6 mmol), *N*,*N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (446 mg, 1.2 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol), 2M K_2CO_3 (15 mL), ethanol (15 mL) and toluene (30 mL) under nitrogen atmosphere was heated to 95 °C for 24 h with good magnetic stirring. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, evaporated to dryness. The residue was purified through silica gel column chromatography with CH_2Cl_2/hexane (2:1) (by vol) affording **1** (0.56 g, 65% yield) of a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.87-7.69 (m, 3H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.43 (s, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.23-7.12 (m, 6H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 6.9 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 6H), 2.75-2.59 (m, 4H), 1.60 (s, 4H), 1.36 (d, *J* = 17.5 Hz, 4H), 0.93 (d, *J* = 7.4 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 196.58, 195.03, 150.18, 149.08, 147.76, 147.28, 142.63, 141.27, 139.76, 134.39, 133.43, 133.13, 131.92, 130.55, 130.14, 129.75, 129.56, 129.22, 128.89, 128.28, 124.42, 123.17, 123.13, 117.91, 35.88, 35.76, 33.15, 22.37, 22.33, 13.90. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{46}H_{42}BrNO_2$, 720.74; found 719.963.

Synthesis of 7-Bromo-9,9-dimethyl-N,N-diphenyl-9H-fluoren-2-amine (**NPhFBr**). To a mixture of 2,7- dibromo-9,9-dimethyl-9H-fluorene (6.00 g, 17.0 mmol), diphenylamine (1.92 g, 11.4 mmol), CuI (0.108 g, 0.57 mmol), sodium tert-butoxide (1.63 g, 17.0 mmol), and L(-)-proline (0.264 g, 2.3 mmol) was added degassed 1,4-dioxane (80 mL). The solution was heated to 110 °C and stirred at this temperature for 48 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into 150 mL of brine. The solution was extracted with CH_2Cl_2. The organic layer was washed with brine and water, then dried over anhydrous Na_2SO_4. After the solvent was removed, the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:10) (by vol) as the eluent to afford **NPhFBr** (2.92 g, 58% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54-7.38 (m, 5H), 7.28 (s, 1H), 7.24 (s, 1H), 7.14 (t, J = 1.5 Hz, 5H), 7.07-6.97 (m, 4H), 1.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.61, 154.72, 147.88, 147.80, 138.08, 132.81, 130.07, 129.29, 126.02, 124.26, 123.20, 122.85, 120.74, 120.71, 120.09, 118.22, 47.07, 26.96.

Synthesis of 9,9-Dimethyl-N,N-diphenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-amine (**NPhFBSZ**). To a mixture of 5 (2.92 g, 6.64 mmol), bis(pinacolato) diborane (2.03 g, 8.0 mmol), and KOAc (1.88 g, 19.2 mmol), degassed 1, 4-dioxane (30 mL) was added under a flow of nitrogen atmosphere. Afterward, $Pd(dppf_2)_2$ (0.25 g, 0.33 mmol) was added. The solution was heated to 100 °C and stirred at this temperature overnight under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into ice water. The solution was extracted with CH_2Cl_2. The organic layer was washed with brine and water, then dried over anhydrous Na_2SO_4. After the solvent was removed, the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:3) (by vol) as the eluent to afford **NPhFBSZ** (2.52 g, 78% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.83 (s, 1H), 7.79 (d, J = 0.9 Hz, 1H), 7.65-7.57 (m, 2H), 7.28 (s, 1H), 7.27 (s, 1H), 7.24 (s, 2H), 7.19 (d, J = 2.0 Hz, 1H), 7.16-7.12 (m, 4H), 7.05-7.00 (m, 3H), 1.42 (s, 6H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.79, 152.68, 147.94, 142.07, 134.00, 133.71, 129.25, 128.61, 124.25, 123.05, 122.76, 121.07, 118.76, 118.28, 83.70, 46.84, 27.03, 24.95.

Synthesis of (2-Bromo-5-(7-(diphenylamino)-9,9-dimethyl-9H-fluoren-2-yl)-1,4-phenylene) bis((4-butylphenyl)methanone) (**2**). A mixture of NPhFBSZ (1.26 g, 2.59 mmol), MA1 (4.32 g, 7.77 mmol), $Pd(PPh_3)_4$ (149 mg, 0.13 mmol), 2M K_2CO_3 (15 mL), and toluene (30 mL) under nitrogen atmosphere were heated to 95 °C for 24 h with good magnetic stirring. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, evaporated to dryness. The residue was purified through silica gel column chromatography with CH_2Cl_2/hexane (1:2) (by vol) affording **2**

(1.28 g, 59% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.87-7.78 (m, 3H), 7.56-7.47 (m, 3H), 7.43 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.25-7.15 (m, 6H), 7.09 (d, J = 7.5 Hz, 5H), 6.98 (d, J = 7.1 Hz, 6H), 2.70 (t, J = 7.6 Hz, 2H), 2.52 (t, J = 7.3 Hz, 2H), 1.69-1.58 (m, 2H), 1.41 (d, J = 28.8, 7.0 Hz, 4H), 1.23 (s, 6H), 1.14 (d, J = 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H), 0.78 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 196.65, 195.15, 155.26, 153.64, 150.22, 149.19, 147.87, 147.70, 142.66, 141.53, 140.45, 138.84, 136.34, 133.96, 133.43, 133.02, 130.60, 130.11, 129.75, 129.35, 129.26, 128.95, 128.35, 127.89, 124.23, 123.32, 123.06, 122.83, 120.98, 120.79, 119.47, 118.18, 118.12, 117.81, 46.74, 35.91, 35.59, 33.18, 32.97, 26.74, 22.39, 22.01, 13.95, 13.81. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{55}H_{50}BrNO_2$: 836.89; found: 836.84.

Synthesis of (4,4''-Dibromo-[1,1':4',1''-terphenyl]-2,2'',5,5''-tetrayl)tetrakis((4-butylphenyl) meth- anone) (**MA2**). A mixture of MA1 (842 mg, 1.5 mmol), 1, 4-benzenediboronic pinacol ester (50 mg, 0.15 mmol), KOH (84 mg, 1.5 mmol), THF (12 mL) in a 35 mL pressurized vessel was carefully degassed before and after the addition of $Pd(PPh_3)_4$ (8 mg, 0.008 mmol). The vessel was then sealed and heated in the CEM Discover system. The initial microwave power was set at 100 W. After the set temperature of 120 °C was reached, the microwave power regulated itself to keep that temperature for 10 min before cooling to room temperature. The mixture was subsequently diluted with CH_2Cl_2, washed with aqueous HCl (1M), and then with a saturated solution of brine and water, dried over anhydrous Na_2SO_4. After the solvent was removed, the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (3:1) (by vol) as the eluent to afford **MA2** (98 mg, 63% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78 (d, J = 7.6 Hz, 4H), 7.67 (s, 2H), 7.56 (d, J = 7.7 Hz, 4H), 7.34-7.28 (m, 6H), 7.12 (d, J = 12.5 Hz, 8H), 2.70 (t, J = 7.3 Hz, 4H), 2.58 (t, J = 7.3 Hz, 4H), 1.63 (d, J = 7.0 Hz, 4H), 1.54 (d, J = 12.4 Hz, 4H), 1.33 (d, J = 44.3 Hz, 8H), 0.91 (d, J = 7.1 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 195.71, 194.78, 150.28, 149.66, 142.50, 141.41, 139.33, 137.90, 134.05, 133.27, 132.73, 130.50, 130.16, 130.06, 128.93, 128.91, 128.58, 118.29, 35.89, 35.69, 33.15, 33.03, 22.38, 22.27, 13.91, 13.84.

Synthesis of (4-bromo-4'''-(diphenylamino)-[1,1':4',1'':4'',1'''-quaterphenyl]-2,2'',5,5''-tetrayl) tetrakis((4-butylphenyl)methanone) (**3**). A mixture of MA2 (1.66 g, 1.62 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzene (200 mg, 0.54 mmol), $Pd(PPh_3)_4$ (31 mg, 0.03 mmol), 2M K_2CO_3 (10 mL) and toluene (25 mL) under nitrogen atmosphere was heated to 95 °C for 24 h with good magnetic stirring. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, evaporated to dryness. The residue was purified through silica gel column chromatography with CH_2Cl_2/ethyl acetate (10:1) (by vol) as the eluent to afford **3** (0.45 g, 70% yield) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$, δ) 7.79 (d, J = 8.1 Hz, 2H), 7.69 (s, 1H), 7.62 (d, J = 8.2 Hz, 3H), 7.56 (d, J = 2.3 Hz, 3H), 7.50 (d, J = 11.3 Hz, 2H), 7.31 (d, J = 7.7 Hz, 4H), 7.24-7.03 (m, 16H), 6.99 (t, J = 7.3 Hz, 2H), 6.89 (d, J = 7.7 Hz, 3H), 6.84 (d, J = 8.5 Hz, 2H), 2.72-2.55 (m, 8H), 1.69-1.49 (m, 8H), 1.44-1.19 (m, 8H), 0.96-0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 198.00, 197.38, 195.94, 194.86, 150.25, 149.61, 149.31, 148.81, 147.50, 147.35, 142.45, 141.46, 140.76, 140.44, 139.44, 139.32, 138.74, 138.69, 137.49, 134.72, 134.57, 134.05, 133.30, 132.75, 132.67, 130.53, 130.25, 130.14, 129.86, 129.19, 129.06, 128.94, 128.85, 128.56, 128.49, 128.33, 128.20, 124.34, 123.23, 123.04, 118.25, 35.89, 35.76, 35.71, 35.69, 33.18, 33.16, 33.07, 33.02, 22.39, 22.34, 22.28, 13.92, 13.86, 13.84. MS (MALDI-TOF, *m/z*): $[M]^+$ Calcd for $C_{80}H_{74}BrNO_4$: 1193.35; found: 1193.50.

General procedures for the synthesis of 4, 5 and 6 through Suzuki reaction: A mixture of the corresponding bromides (**1**, **2**, or **3**), (1.0 equiv.), (4-fluorophenyl)boronic acid (1.2 equiv.), $Pd(PPh_3)_4$ (0.02 equiv.), $NaHCO_3$ (8 equiv.), TBAB (0.5 equiv.), was added into a solution of degassed THF (28 mL for 1 mmol **1**, **2**, or **3**) and H_2O (14 mL for 1 mmol **1**, **2**, or **3**). The solution was heated to reflux for 48 h under nitrogen atmosphere. After cooling to room temperature, the solution was extracted with CH_2Cl_2. The organic layer was washed with brine and H_2O, and then dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvents, the resulting product was purified by flash chromatography on a silica gel column with hexane/dichloromethane to afford the target (**4, 5** or **6**) as a yellow powder.

Compound 4: yellow powder; yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.64 (d, *J* = 8.3 Hz, 2H), 7.61-7.59 (m, 4H), 7.32-7.29 (m, 2H), 7.23-7.18 (m, 4H), 7.17-7.11 (m, 6H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.94-6.85 (m, 8H), 2.67-2.57 (m, 4H), 1.60-1.55 (m, 4H), 1.31 (d, *J* = 13.2,, 4H), 0.91 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 198.03, 197.71, 163.63, 161.17, 149.30, 148.82, 147.54, 147.39, 140.86, 140.57, 139.47, 138.35, 135.19, 135.15, 134.79, 134.54, 132.71, 130.69, 130.60, 130.32, 130.21, 130.18, 129.91, 129.54, 129.20, 128.49, 128.20, 124.36, 123.27, 123.06, 115.49, 115.28, 35.75, 35.71, 33.18, 33.08, 29.71, 22.33, 22.23, 13.91, 13.87. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{52}H_{46}FNO_2$: 735.94; found: 735.42.

Compound 5: yellow powder; yield 83%. ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.65 (d, *J* = 12.5, Hz, 4H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.0, 5.4 Hz, 2H), 7.33-7.28 (m, 3H), 7.23 (d, *J* = 7.5 Hz, 3H), 7.14-7.08 (m, 7H), 7.02 (d, *J* = 7.8 Hz, 4H), 6.98-6.90 (m, 4H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.58-1.53 (m, 4H), 1.44 (d, *J* = 7.6 Hz, 2H), 1.34-1.28 (m, 6H), 1.17-1.12 (m, 2H), 0.90 (s, 3H), 0.78 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 198.12, 197.90, 163.68, 161.21, 155.30, 153.60, 149.31, 148.94, 147.92, 147.62, 140.87, 140.22, 138.64, 138.49, 137.06, 135.24, 135.21, 134.53, 134.37, 133.25, 130.75, 130.67, 130.25, 130.21, 130.17, 129.78, 129.26, 128.52, 128.29, 128.05, 124.20, 123.54, 123.14, 122.79, 120.77, 119.45, 118.29, 115.54, 115.33, 46.76, 35.72, 35.58, 33.09, 32.99, 29.74, 26.79, 22.23, 22.01, 13.91, 13.82. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{61}H_{54}FNO_2$: 852.11; found: 852.09.

Compound 6: yellow powder; yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.64-7.57 (m, 8H), 7.51 (t, *J* = 8.3 Hz, 4H), 7.27 (d, *J* = 6.2 Hz, 4H), 7.19 (t, *J* = 7.1 Hz, 8H), 7.12 (t, *J* = 7.8 Hz, 10H), 6.99 (t, *J* = 6.8 Hz, 2H), 6.92-6.83 (m, 7H), 2.64-2.58 (m, 8H), 1.58 (s, 8H), 1.33-1.25 (m, 8H), 0.93-0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 198.00, 197.51, 197.46, 197.37, 163.65, 161.19, 149.34, 149.32, 149.26, 148.78, 147.49, 147.37, 140.79, 140.76, 140.64, 140.44, 139.28, 139.14, 138.79, 138.53, 138.49, 138.14, 135.03, 134.78, 134.62, 134.47, 134.42, 132.74, 130.67, 130.59, 130.38, 130.23, 130.17, 130.03, 129.93, 129.88, 129.18, 129.01, 128.51, 128.47, 128.19, 124.34, 123.24, 123.03, 115.49, 115.28, 35.75, 35.69, 33.17, 33.05, 33.02, 22.34, 22.27, 22.23, 13.91, 13.87, 13.83. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{86}H_{78}FNO_4$: 1208.54; found: 1208.43.

General procedures for the synthesis of 7, 8 and 9 through Suzuki reaction:. A mixture of the corresponding bromides (**1**, **2**, or **3**), (1.0 equiv.), (4'-fluoro-[1,1'-biphenyl]-4-yl)boronic acid (1.2 equiv.), $Pd(PPh_3)_4$ (0.02 equiv.), $NaHCO_3$ (8 equiv.), TBAB (0.5 equiv.), was added into a solution of degassed THF (28 mL for 1 mmol **1**, **2**, or **3**) and H_2O (14 mL for 1 mmol **1**, **2**, or **3**). The solution was heated to reflux for 48 h under nitrogen atmosphere. After cooling to room temperature, the solution was extracted with CH_2Cl_2. The organic layer was washed with brine and H_2O, and then dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvents, the resulting product was purified by flash chromatography on a silica gel column with hexane/dichloromethane to afford the target (**7**, **8** or **9**) as a yellow powder.

Compound 7: yellow powder; yield 83%. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.71(s, 1H) – 7.68 (d, J = 2.5 Hz, 2H), 7.61 (t, J = 4.1 Hz, 3H), 7.48-7.46 (m, 2H), 7.41 (s, 4H), 7.22-7.13 (m, 10H), 7.08 (t, J = 8.7 Hz, 2H), 7.00 (t, J = 7.4 Hz, 2H), 6.96-6.83 (m, 6H), 2.68-2.56 (m, 4H), 1.56 (s, 4H), 1.33-1.26 (m, 4H), 0.91-0.84 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 198.11, 197.79, 163.75, 161.30, 149.23, 148.82, 147.52, 147.40, 140.82, 140.60, 139.40, 139.37, 139.00, 138.09, 136.57, 136.54, 134.84, 134.67, 132.80, 130.40, 130.33, 130.21, 129.93, 129.65, 129.46, 129.21, 128.59, 128.51, 128.47, 126.95, 124.37, 123.28, 123.06, 115.72, 115.51, 35.77, 35.72, 33.19, 33.15, 22.35, 22.25, 13.92, 13.86. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{58}H_{50}FNO_2$: 812.02; found: 812.10.

Compound 8: yellow powder; yield 85%. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, J = 9.1 Hz, 4H), 7.60 (d, J = 8.2 Hz, 2H), 7.48-7.40 (m, 7H), 7.30 (d, J = 2.6 Hz, 2H), 7.24 (d, J = 7.5 Hz, 5H), 7.15-6.94 (m, 14H), 2.55 (m, 4H), 1.59-1.32 (m, 10H), 1.26 (s, 4H), 0.85-0.78 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 198.20, 197.98, 167.74, 161.31, 155.29, 153.58, 149.23, 148.93, 147.91, 147.58, 140.87, 140.81, 140.11, 139.40, 139.11, 138.59, 138.11, 137.11, 136.57, 136.53, 134.63, 134.39, 133.26, 132.35, 130.94, 130.34, 130.17, 129.85, 129.50, 129.25, 128.87, 128.60, 128.52, 128.48, 128.28, 128.03, 126.97, 124.18, 123.87, 123.53, 123.12, 122.77, 120.74, 119.43, 118.28, 115.73, 115.52, 65.60, 46.75, 35.72, 35.58, 33.14, 32.99, 30.61, 26.94, 26.78, 22.23, 22.01, 19.22, 13.87, 13.80, 13.77. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{67}H_{58}FNO_2$: 928.18; found: 928.03.

Compound 9: yellow powder; yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.67 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 5.2 Hz, 4H), 7.58 (d, J = 6.2 Hz, 3H), 7.53 (s, 1H),7.51 (d, J = 3.9 Hz, 2H), 7.46-7.42 (m, 2H), 7.38 (d, J = 2.6 Hz, 4H), 7.23-7.16 (m, 9H), 7.15-7.11 (m, 11H), 7.06 (d, J = 8.7 Hz, 2H), 6.99 (t, J = 7.3 Hz, 2H), 6.90 (d, J = 7.9 Hz, 4H), 6.85 (d, J = 8.7 Hz, 2H), 2.66-2.56 (m, 8H), 1.55 (d, J = 8.1 Hz, 8H), 1.33-1.24 (m, 8H), 0.92-0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 198.01, 197.58, 197.49, 197.43, 163.75, 161.30, 149.30, 149.26, 148.78, 147.49, 147.38, 140.79, 140.77, 140.60, 140.44, 139.44, 139.28, 139.17, 139.08, 138.81, 138.46, 138.22, 137.97, 136.53, 136.49, 134.78, 134.63, 134.56, 134.53, 132.75, 130.28, 130.24, 130.20, 130.16, 129.88, 129.44, 129.18, 129.02, 128.58, 128.49, 128.20, 126.93, 124.34, 123.24, 123.03, 115.71, 115.50, 35.76, 35.72, 35.69, 33.17, 33.13, 33.05, 33.03, 22.34, 22.28, 22.27, 22.24, 13.91, 13.85. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{92}H_{82}FNO_4$: 1284.67; found: 1284.65.

Synthesis of (n)L-F/(n)L-Ph-F (n=2,3): To a solution of 1-bromo-4-butylbenzene (20 equiv.) in dry THF (60 mL for 1 mmol **4**, **5**, **7** or **8**) at -78°C was added *n*-BuLi (20 equiv., 2.5 M in hexane) slowly under nitrogen atmosphere. After stirring at -78 °C for 1 h, a mixture of corresponding compound (1 equiv.) (**4, 5, 7** or **8**) in dry THF (5 mL) was added. The reaction was then allowed to warm up to room temperature and stirred overnight. The reaction mixture was quenched with ice-water, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and evaporated to dryness. After the solvent was removed, the residue was purified through silica gel column chromatography, affording a yellow oil. The yellow oil was dissolved into dry dichloromethane (20 mL) and 0.2 mL of $BF_3{\cdot}Et_2O$ was added as catalyst. The mixture was stirred for 30 min at room temperature. Methanol (50 mL) was added to destroy the catalyst. The mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine. The CH_2Cl_2 solvent was removed under reduced pressure.

The residue was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane to afford **(n)L-F/(n)L-Ph-F (n=2,3)**.

Compound 2L-F: Light yellow powder; yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.63 (s, 2H), 7.58-7.55 (m, 1H), 7.49 (d, J = 8.3 Hz, 1H), 7.21-7.08 (m, 14H), 7.03 (t, J = 9.7 Hz, 13H), 6.97-6.95 (m,3H), 2.59-2.54 (m, 8H), 1.58 (d, J = 7.9 Hz, 8H), 1.38-1.32 (m, , 8H), 0.92 (t, J = 6.4 , 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 163.74, 161.30, 154.22, 154.15, 153.45, 151.40, 151.14, 147.71, 147.30, 143.22, 142.90, 141.44, 141.17, 139.68, 138.38, 136.33, 136.31, 134.81, 129.16, 128.37, 128.23, 128.16, 124.06, 123.32, 122.71, 122.03, 120.68, 117.63, 117.32, 114.63, 114.40, 113.65, 113.42, 64.67, 35.28, 33.61, 33.58, 29.78, 22.54, 22.53, 14.05. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{72}H_{70}FN$: 968.33; found: 968.23. Anal. Calcd for $C_{72}H_{70}FN$: C 89.31, H 7.29, N 1.45. Found: C 89.38, H 7.23, N 1.46.

Compound 3L-F: Light yellow powder; yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.74 (s, 1H), 7.65 (d, J = 14.0 Hz, 2H), 7.59 (s, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.26-7.15 (m, 14H), 7.12-7.03 (m, 13H), 7.02-6.97 (m, 4H), 2.59-2.54 (m, 8H), 1.56 (s, 8H), 1.43 (s, 6H), 1.39-1.32 (m, 8H), 0.94-0.89 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 163.74, 161.30, 155.52, 154.29, 154.22, 153.28, 151.93, 151.60, 151.29, 148.02, 147.22, 143.58, 142.90, 141.43, 141.18, 140.17, 138.85, 138.78, 136.30, 136.28, 134.37, 129.22, 128.37, 128.31, 128.24, 128.20, 123.99, 123.55, 122.59, 121.07, 120.99, 120.56, 118.84, 117.55, 117.35, 117.25, 114.63, 114.40, 114.20, 114.13, 113.63, 113.39, 64.76, 64.74, 64.39, 46.57, 35.27, 33.56, 33.55, 29.75, 27.36, 22.55, 22.54, 14.01. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{81}H_{78}FN$: 1084.52; found: 1084.28. Anal. Calcd for $C_{81}H_{78}FN$: C 89.71, H 7.25, N 1.29. Found: C 89.62, H 7.21, N 1.25.

Compound 2L-Ph-F: Light yellow powder; yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71-7.68 (m, 2H), 7.66 (s, 1H), 7.54 (s, 1H), 7.52 (s, 1H), 7.50-7.46 (m, 3H), 7.19 (t, J = 8.8 Hz, 9H), 7.12 (d, J = 8.3 Hz, 4H), 7.08-7.02 (m, 13H), 6.96 (t, J = 8.2 Hz, 3H), 2.61-2.51 (m, 8H), 1.60-1.53 (m, 8H), 1.38-1.33 (m, 8H), 0.94-0.89 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 163.59, 161.14, 153.43, 152.69, 151.74, 151.01, 143.28, 143.18, 141.21, 141.11, 140.03, 139.61, 139.13, 138.76, 137.58, 137.55, 134.83, 129.11, 128.71, 128.63, 128.25, 128.19, 126.26, 124.68, 124.01, 123.28, 122.65, 121.99, 120.66, 120.29, 117.94, 117.32, 115.61, 115.40, 64.75, 64.59, 35.22, 33.56, 33.52, 22.52, 22.47, 13.99. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{78}H_{74}FN$: 1044.43; found: 1044.00. Anal. Calcd for $C_{78}H_{74}FN$: C 89.70, H 7.14, N 1.34. Found: C 89.78, H 7.09, N 1.33.

Compound 3L-Ph-F: Light yellow powder; yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.76 (d, *J* = 6.9 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.66 (s, 1H), 7.60 (s, 1H), 7.54(s, 1H),7.51-7.49 (m, 4H), 7.24 (d, *J* = 8.2 Hz, 12H), 7.16 (s, 1H), 7.12-7.05 (m, 14H), 6.99 (d, *J* = 7.4 Hz, 3H), 2.59-2.54 (m, 8H), 1.57 (d, *J* = 7.5 Hz, 8H), 1.44 (s, 6H), 1.39-1.33 (m, 8H), 0.92 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 163.60, 161.15, 155.52, 153.27, 152.79, 151.85, 151.67, 151.63, 148.00, 147.20, 143.59, 143.33, 141.22, 141.15, 140.58, 139.60, 139.20, 138.91, 138.84, 137.58, 137.55, 134.37, 129.20, 128.72, 128.64, 128.32, 128.29, 128.22, 126.28, 124.69, 123.97, 123.61, 123.54, 122.56, 120.54, 120.37, 118.83, 117.90, 117.38, 117.23, 115.62, 115.41, 114.22, 64.79, 64.37, 46.56, 35.25, 33.54, 33.53, 29.73, 27.35, 22.54, 13.99. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{87}H_{82}FN$: 1160.59; found: 1159.36. Anal. Calcd for $C_{87}H_{82}FN$: C 90.03, H 7.12, N 1.21. Found: C 89.94, H 7.18, N 1.23.

Synthesis of (n)L-F/(n)L-Ph-F (n=4): To a solution of 1-bromo-4-butylbenzene (20 equiv.) in dry THF (80 mL for 1 mmol **6** or **9**) at -78°C was added *n*-BuLi (40 equiv., 2.5 M in hexane) slowly under nitrogen atmosphere. After stirring at -78 °C for 1 h, a mixture of corresponding compound (1 equiv.) (**6** or **9**) in dry THF (5 mL) was added. The reaction was then allowed to warm up to room temperature and stirred overnight. The reaction mixture was quenched with ice-water, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$ and evaporated to dryness. After the solvent was removed, the residue was purified through silica gel column chromatography, affording a yellow oil. The yellow oil was dissolved into dry dichloromethane (20 mL) and 0.2 mL of $BF_3{\cdot}Et_2O$ was added as catalyst. The mixture was stirred for 30 min at room temperature. Methanol (50 mL) was added to destroy the catalyst. The mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine. The CH_2Cl_2 solvent was removed under reduced pressure. The residue was chromatographically purified on silica gel eluting with CH_2Cl_2/hexane to afford **(n)L-F/(n)L-Ph-F (n=4)**.

Compound 4L-F: Yellow powder; yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.61 (s, 1H), 7.57 (m, 5H), 7.48 (d, J = 8.2 Hz, 1H), 7.20-7.14 (m, 13H), 7.13-6.99 (m, 30H), 6.95 (m, 4H), 2.55 (t, J = 7.7 Hz, 16H), 1.60-1.53 (m, 16H), 1.35 (m, 16H), 0.91 (t, J = 7.2 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 163.71, 161.27, 154.37, 154.30, 153.55, 152.02, 151.64, 147.65, 147.10, 143.44, 143.14, 142.77, 141.37, 141.24, 140.93, 140.33, 140.04, 139.76, 139.40, 136.13, 134.88, 129.09, 128.30, 123.93, 123.33, 122.58, 122.05, 121.03, 120.59, 118.02, 117.46, 117.26, 117.24, 114.34, 113.57, 113.34, 64.69, 64.26, 35.25, 33.49, 22.54, 14.01. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{126}H_{126}FN$: 1673.35; found: 1673.18. Anal. Calcd for $C_{126}H_{126}FN$: C 90.44, H 7.59, N 0.84. Found: C 90.50, H 7.52, N 0.85.

Compound 4L-Ph-F: Yellow powder; yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.69 (d, J = 8.4 Hz, 2H), 7.61-7.59 (m, 4H), 7.56 (s, 1H), 7.51-7.44 (m, 5H), 7.22-7.15 (m, 17H), 7.11-7.00 (m, 26H), 6.98-6.92 (m, 3H), 2.56 (t, J = 7.5 Hz, 16H), 1.59-1.55 (m, 16H), 1.38-1.33 (m, 16H), 0.92 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 163.57, 161.12, 153.55, 152.87, 152.03, 151.95, 151.68, 151.61, 151.44, 150.78, 147.64, 147.09, 143.44, 143.21, 143.13, 141.16, 141.12, 141.09, 141.02, 140.45, 140.33, 139.89, 139.68, 139.44, 139.41, 139.31, 139.18, 137.56, 137.52, 134.88, 129.07, 128.42, 128.29, 128.23, 128.19, 126.21, 124.66, 123.92, 123.32, 122.57, 122.04, 120.58, 120.36, 117.81, 117.69, 117.56, 117.23, 115.60, 115.39, 64.78, 64.62, 64.24, 35.23, 33.46, 22.55, 22.49, 13.99. MS (MALDI-TOF, *m/z*) $[M]^+$ Calcd for $C_{132}H_{130}FN$: 1749.45; found: 1749.26. Anal. Calcd for $C_{132}H_{130}FN$: C 90.62, H 7.49, N, 0.80. Found: C 90.71, H 7.44, N 0.83.

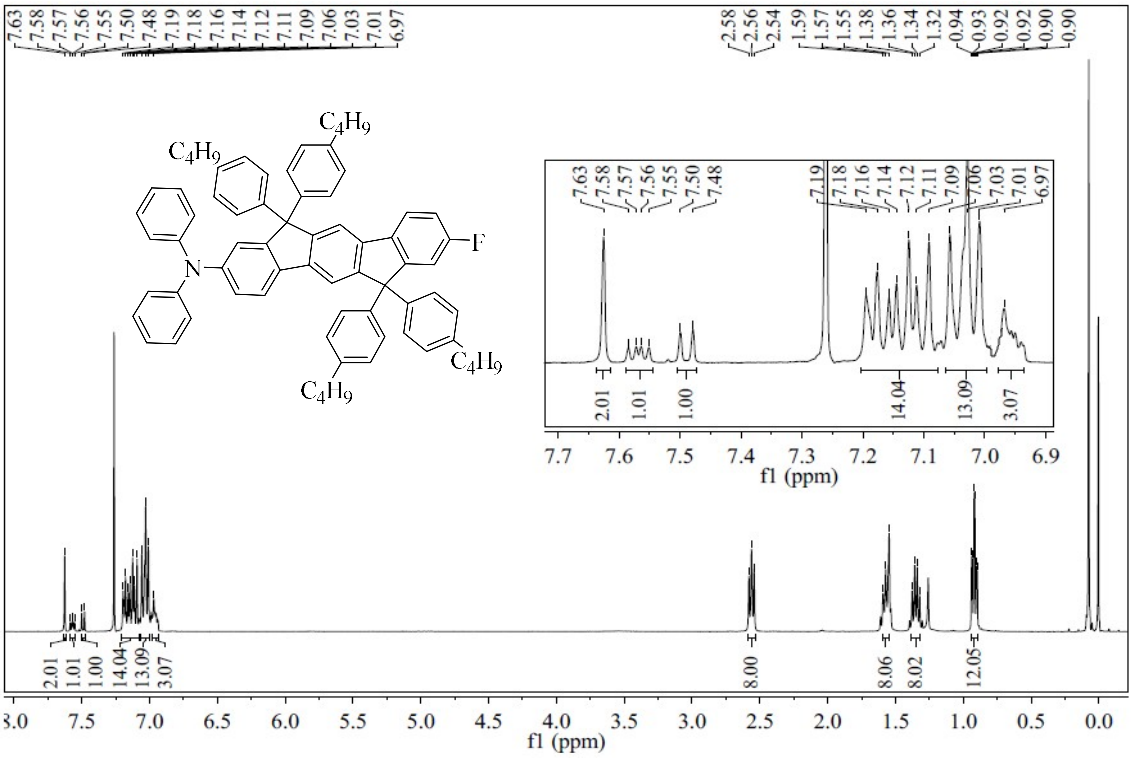


Fig. S1 ^{1}H NMR spectra of 2L-F.

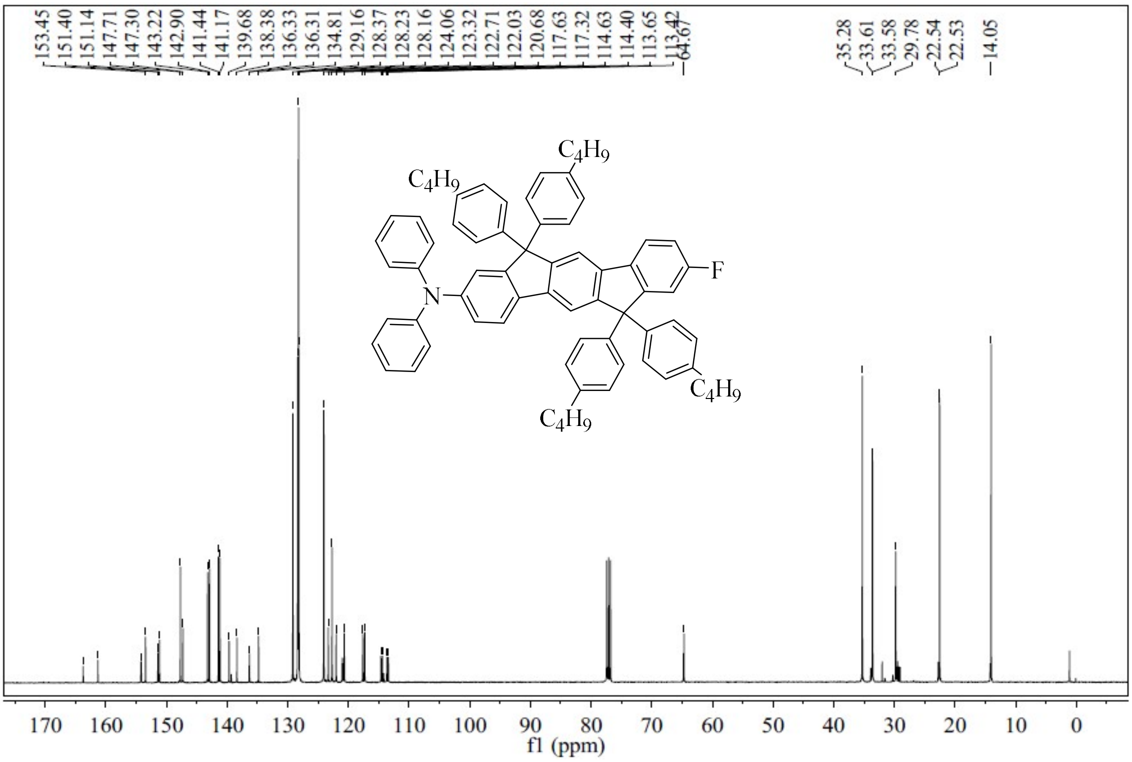


Fig. S2 ^{13}C NMR spectra of 2L-F.

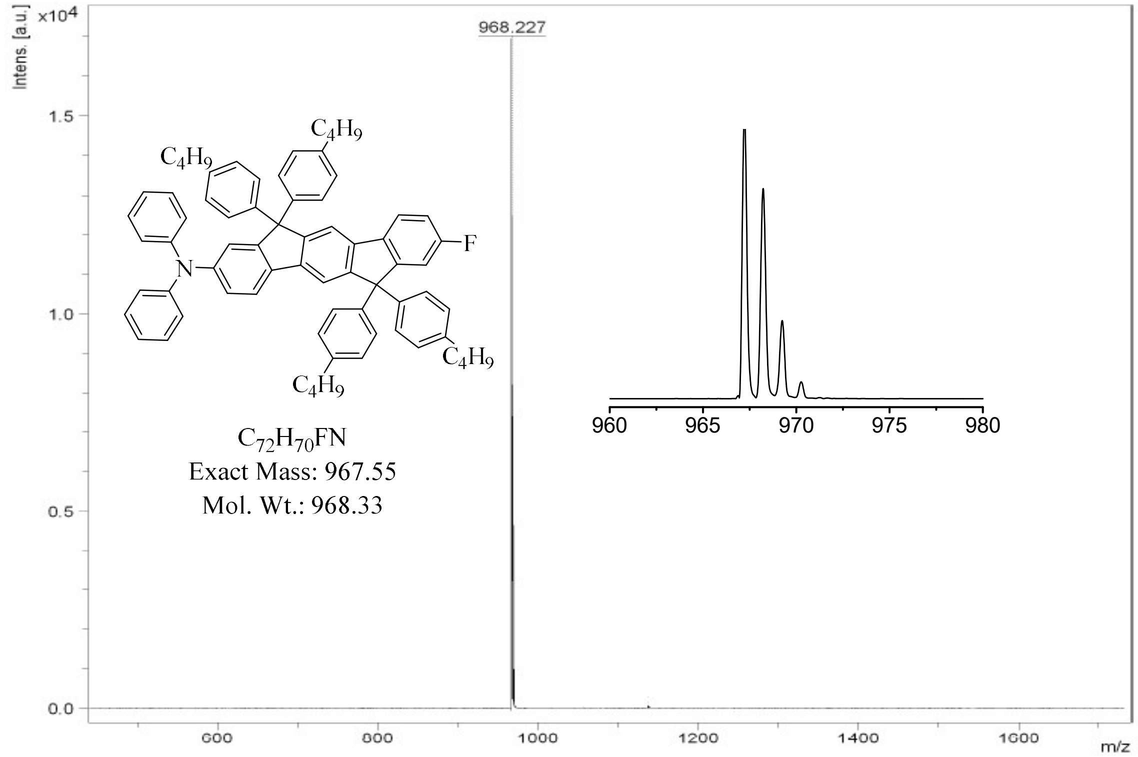


Fig. S3 MADIL-TOF spectra of 2L-F.

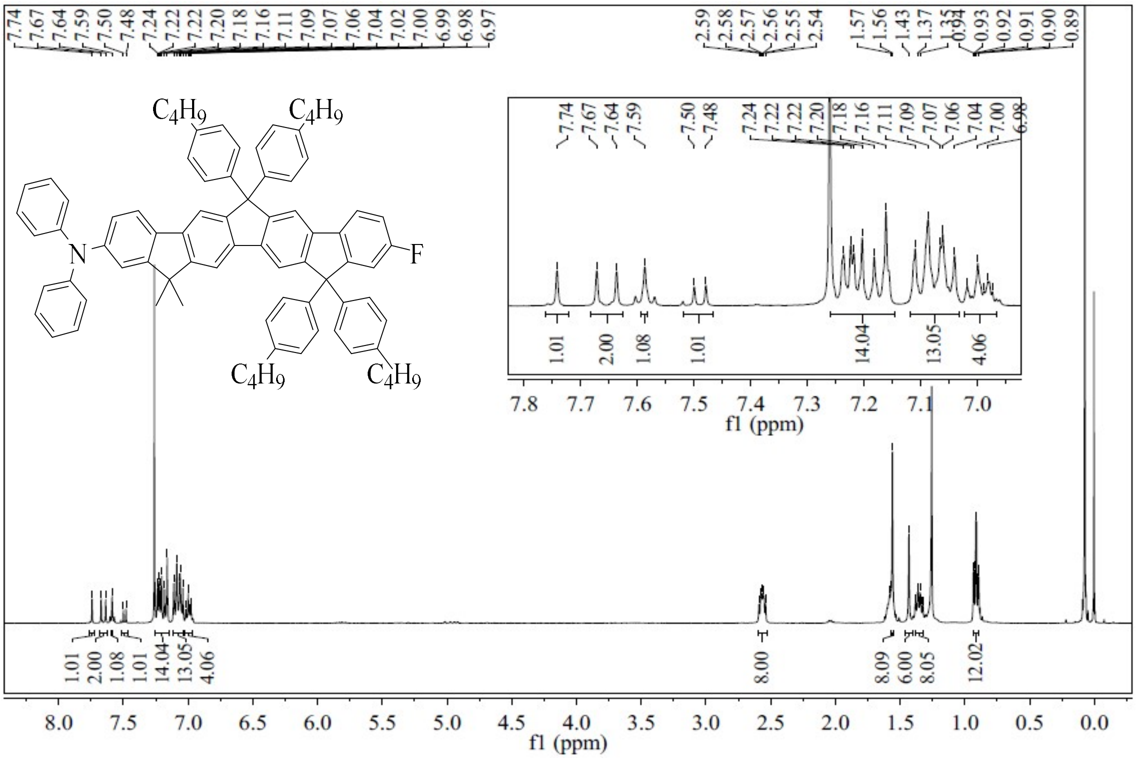


Fig. S4 ^{1}H NMR spectra of 3L-F.

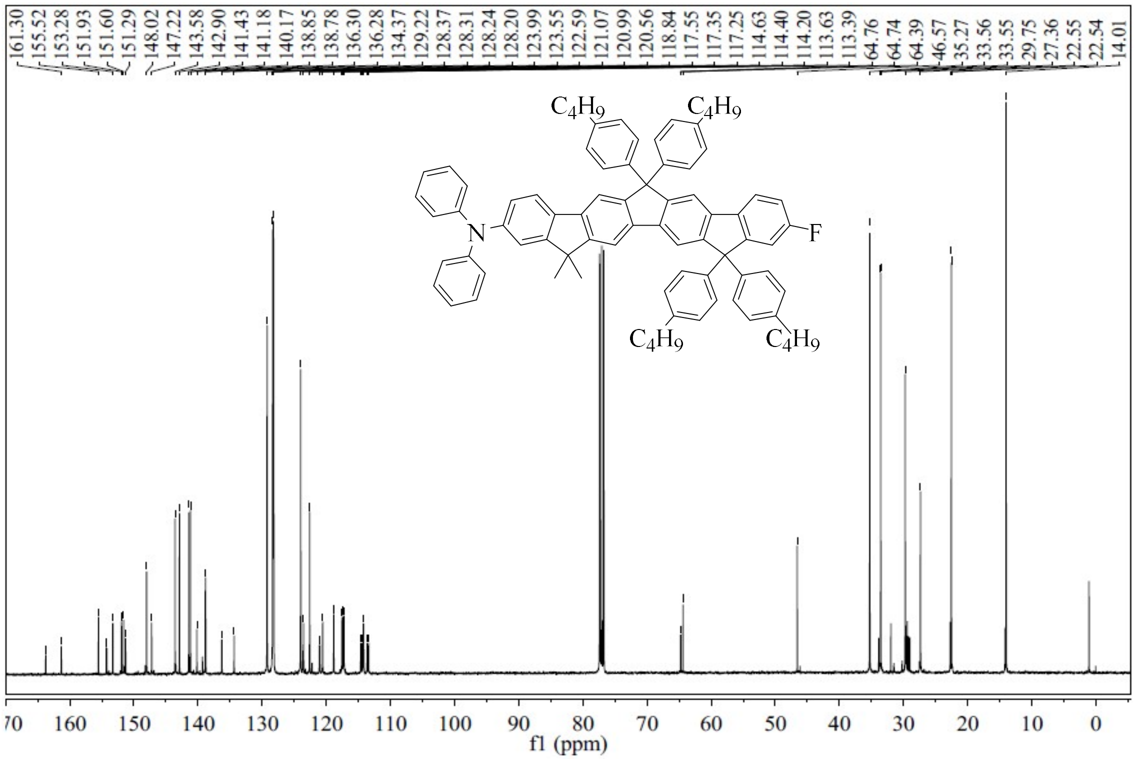


Fig. S5 ^{13}C NMR spectra of 3L-F.

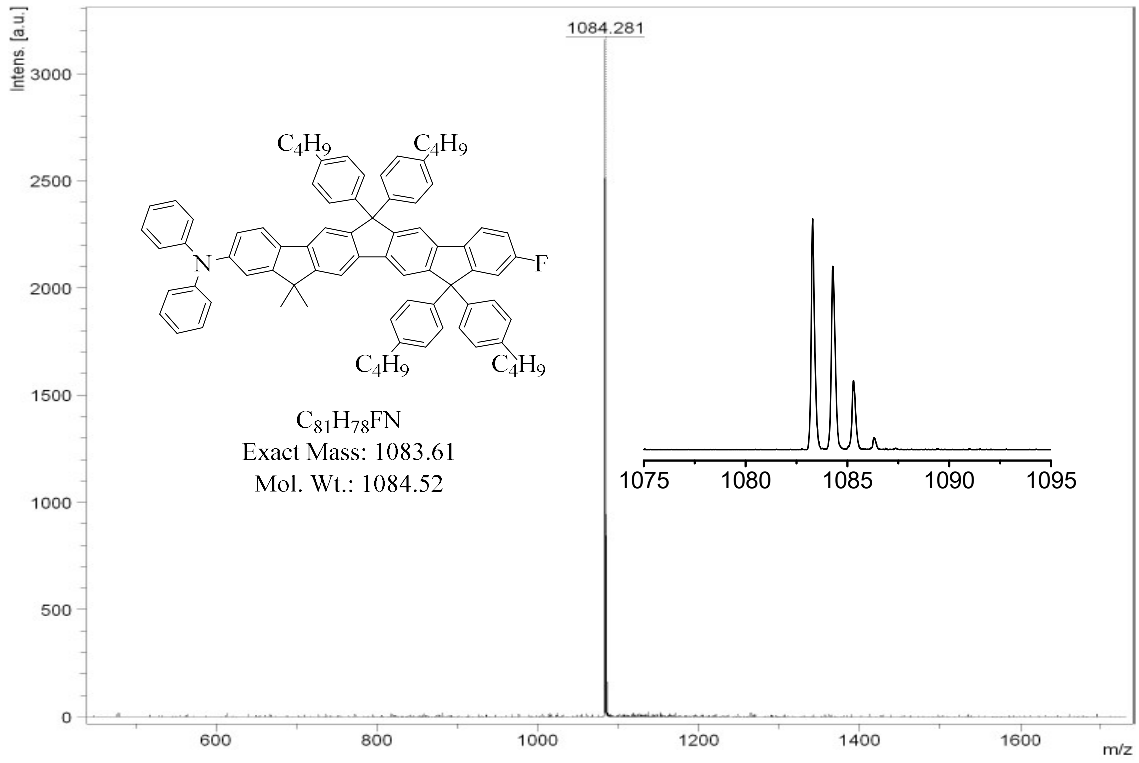


Fig. S6 MADIL-TOF spectra of 3L-F.

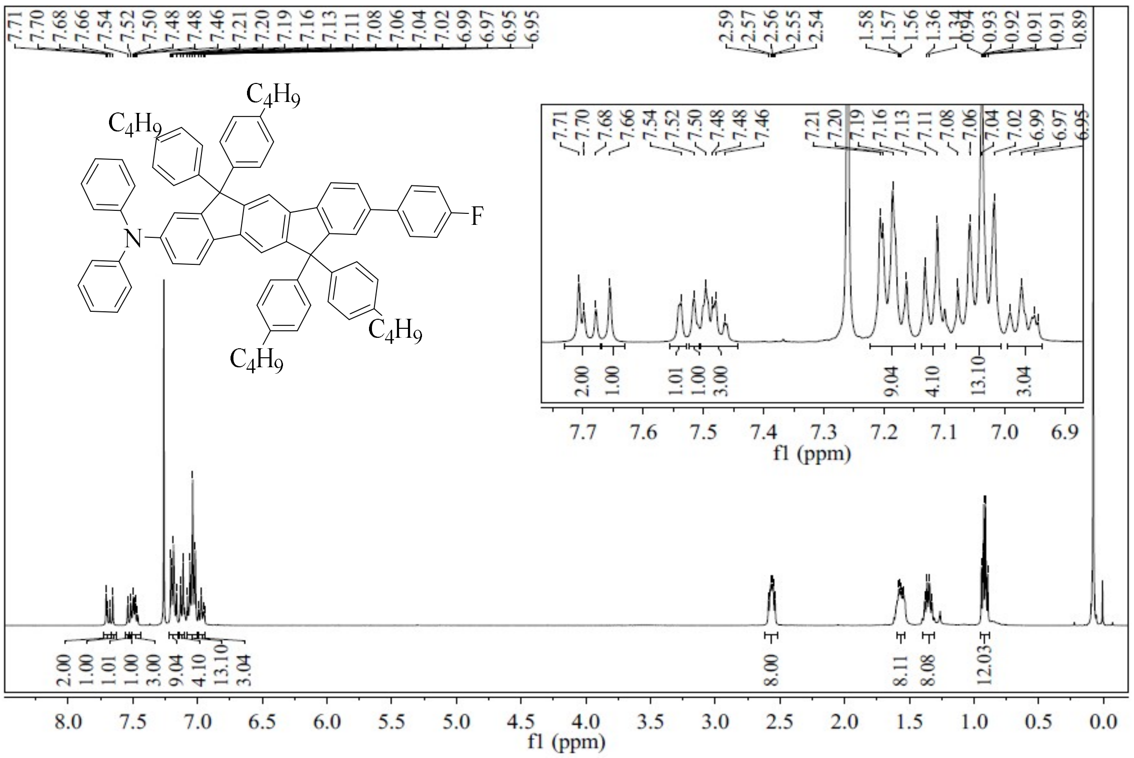


Fig. S7 ^{1}H NMR spectra of 2L-Ph-F.

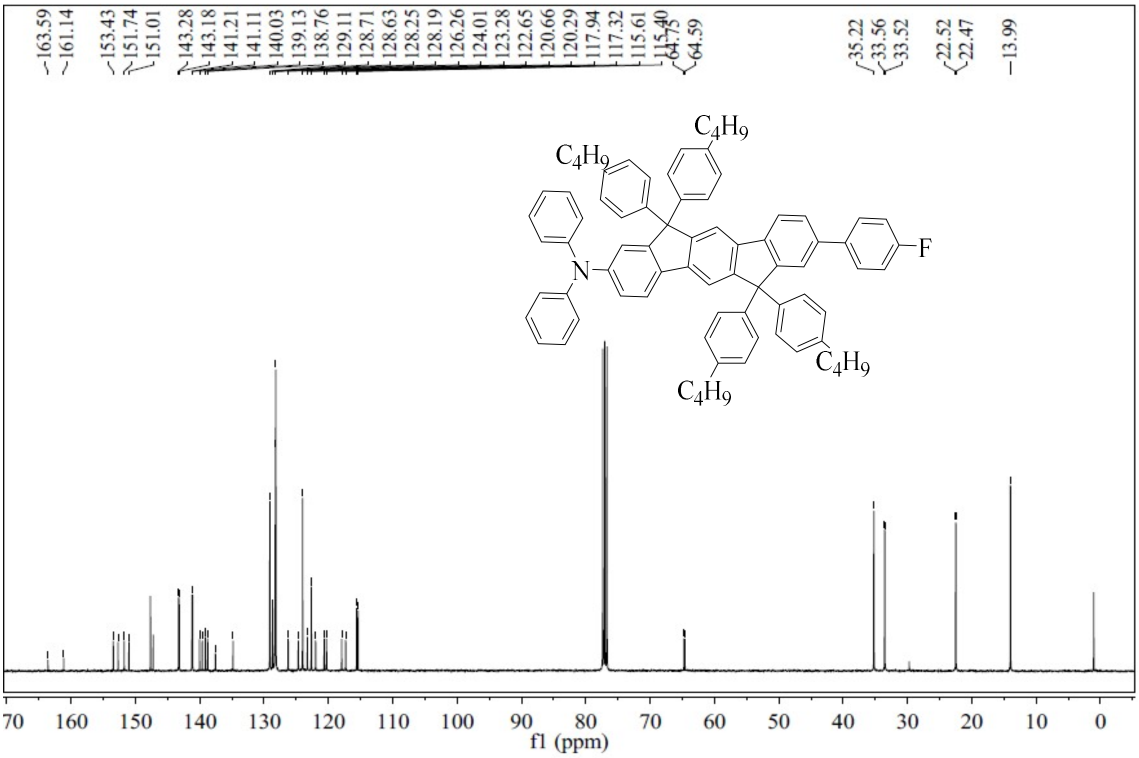


Fig. S8 ^{13}C NMR spectra of 2L-Ph-F.

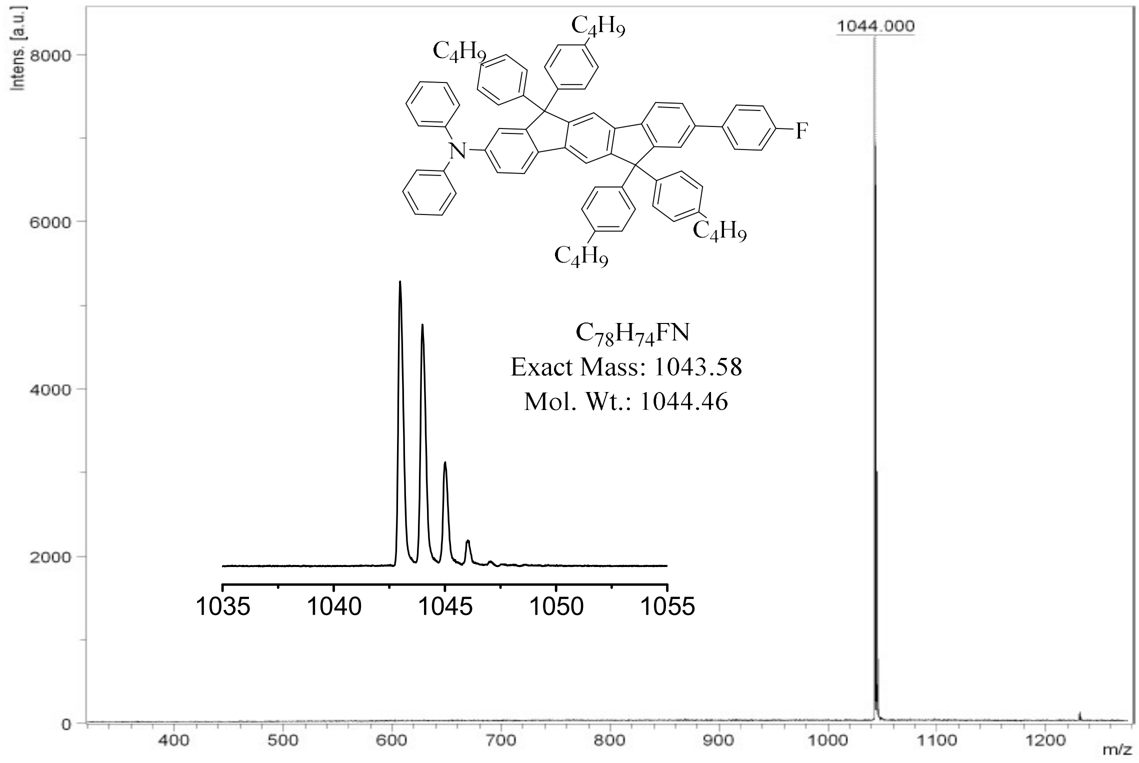


Fig. S9 MADIL-TOF spectra of 2L-Ph-F.

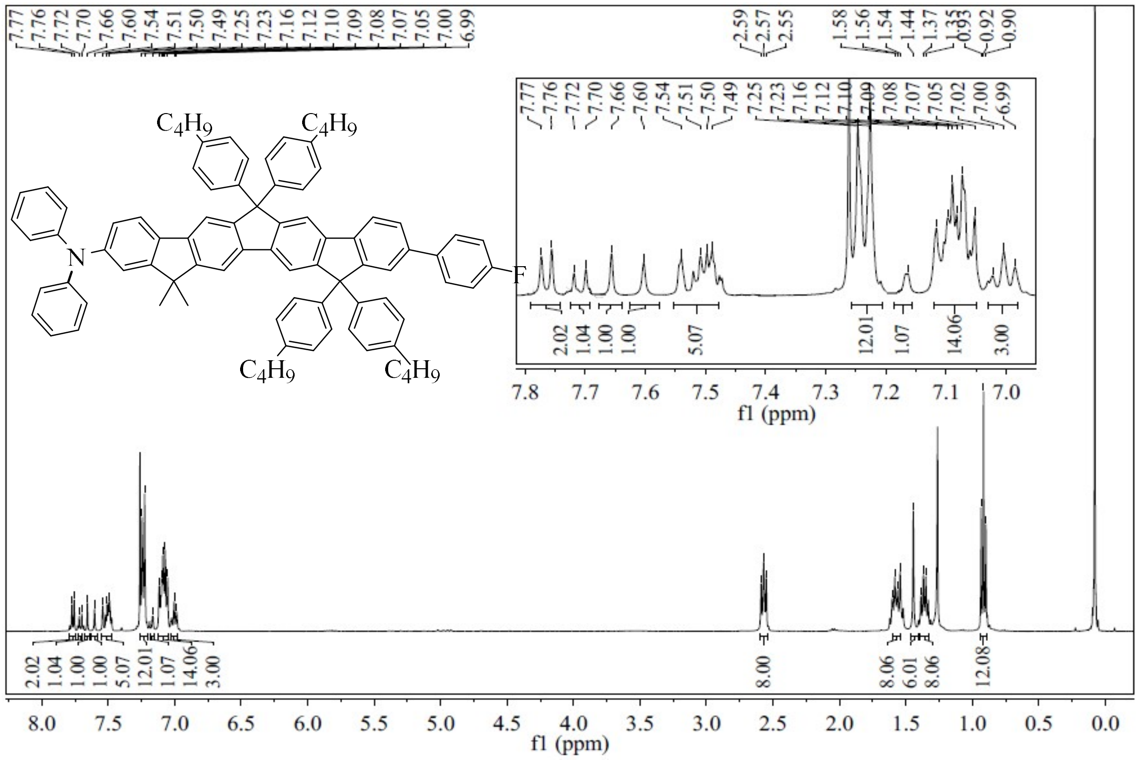


Fig. S10 ^{1}H NMR spectra of 3L-Ph-F.

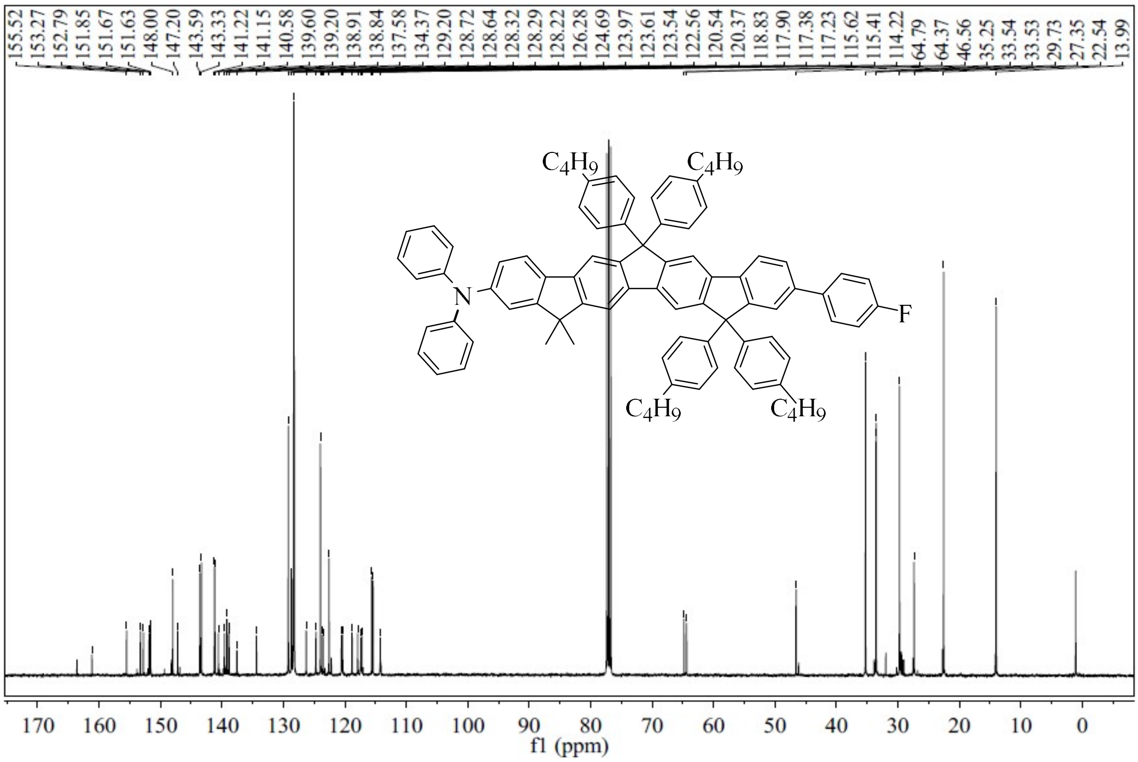


Fig. S11 ^{13}C NMR spectra of 3L-Ph-F.

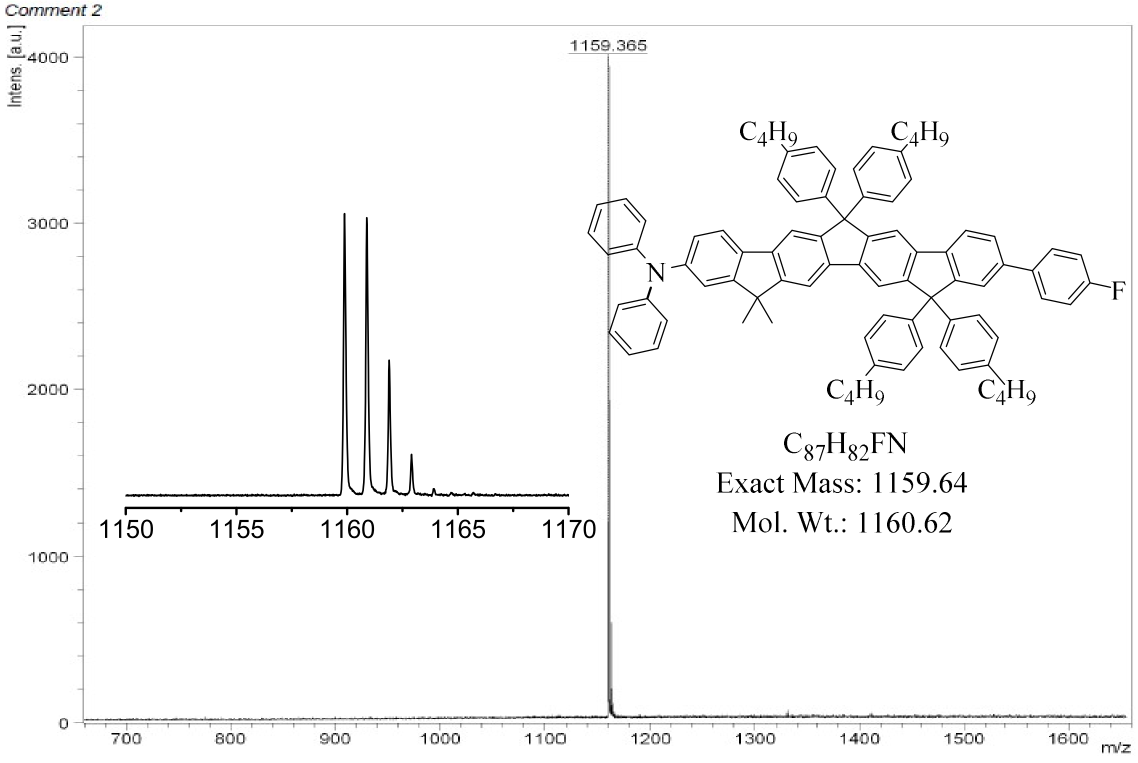


Fig. S12 MADIL-TOF spectra of 3L-Ph-F.

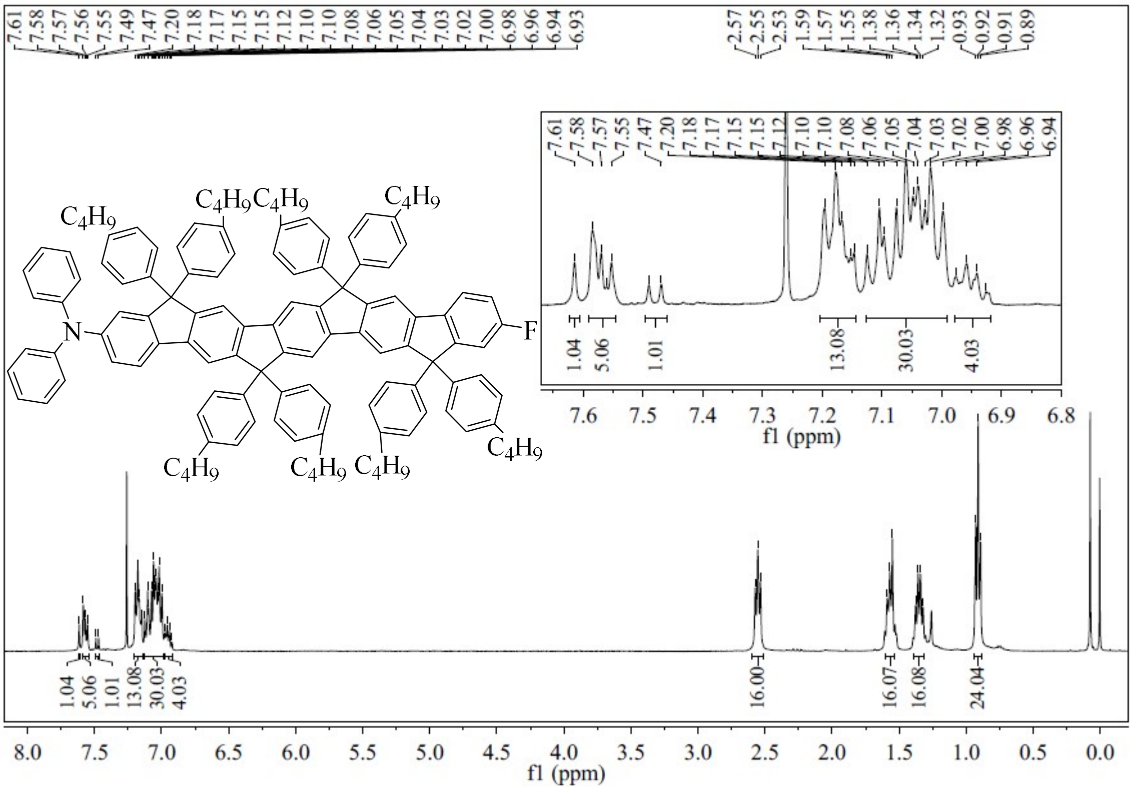


Fig. S13 ^{1}H NMR spectra of 4L-F.

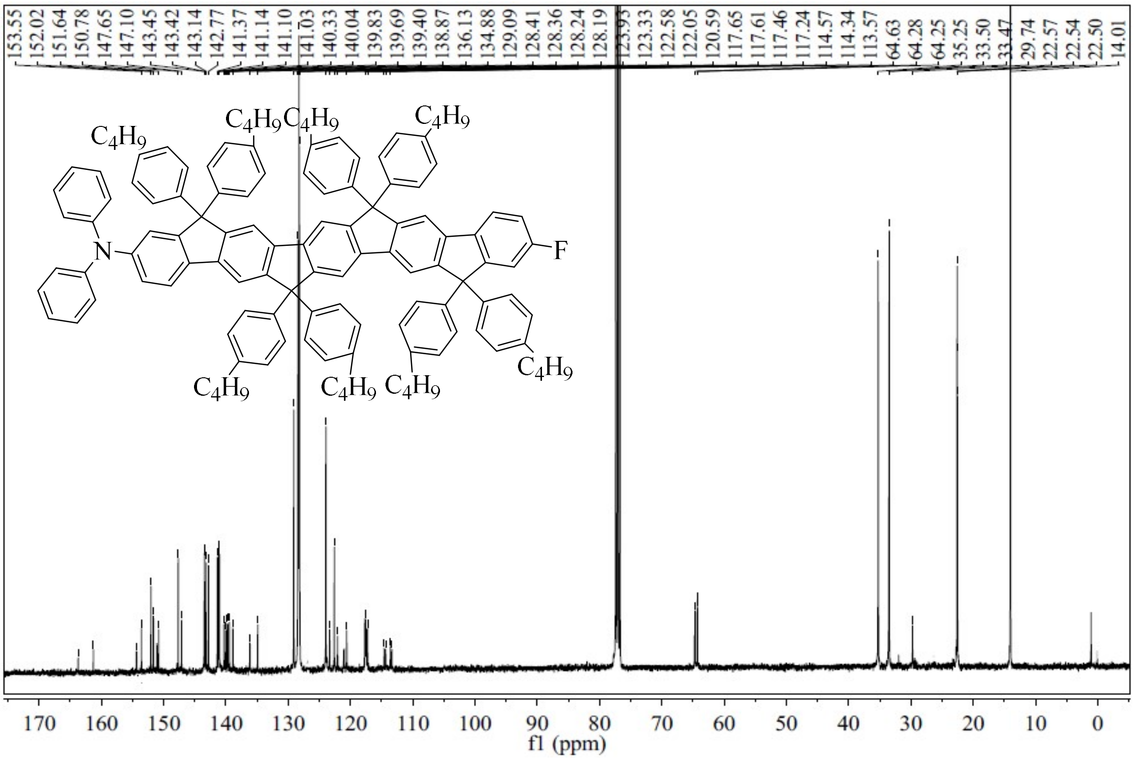


Fig. S14 ^{13}C NMR spectra of 4L-F.

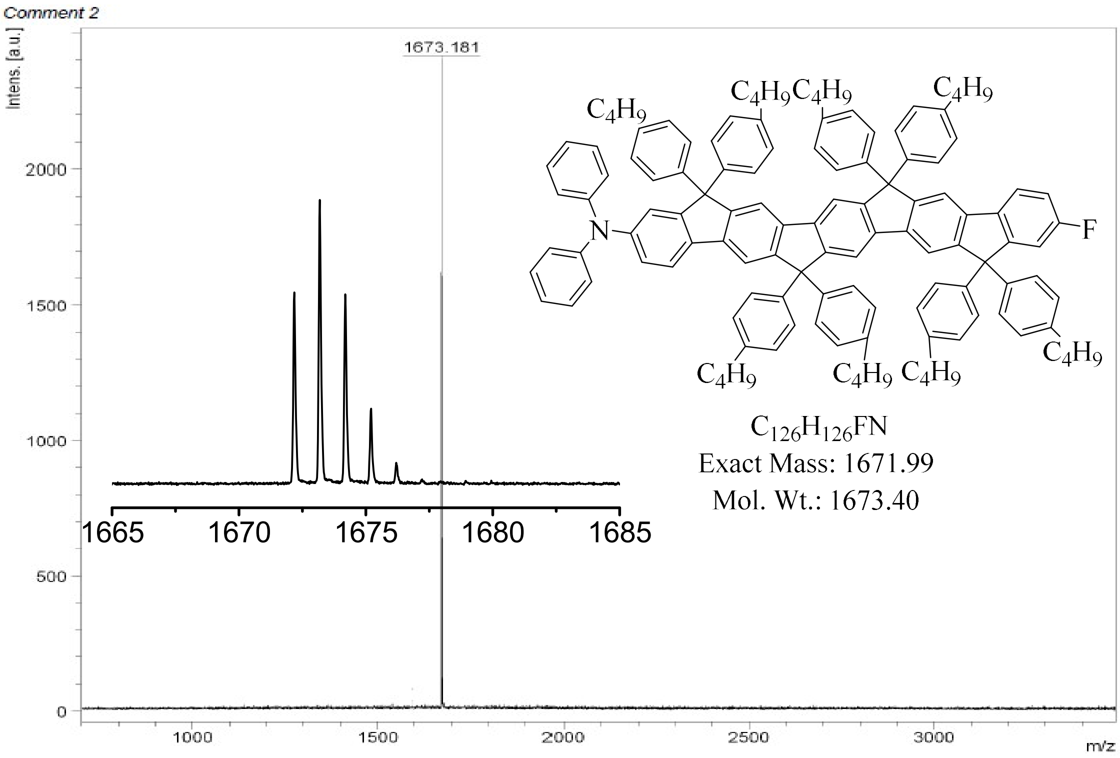


Fig. S15 MADIL-TOF spectra of 4L-F.

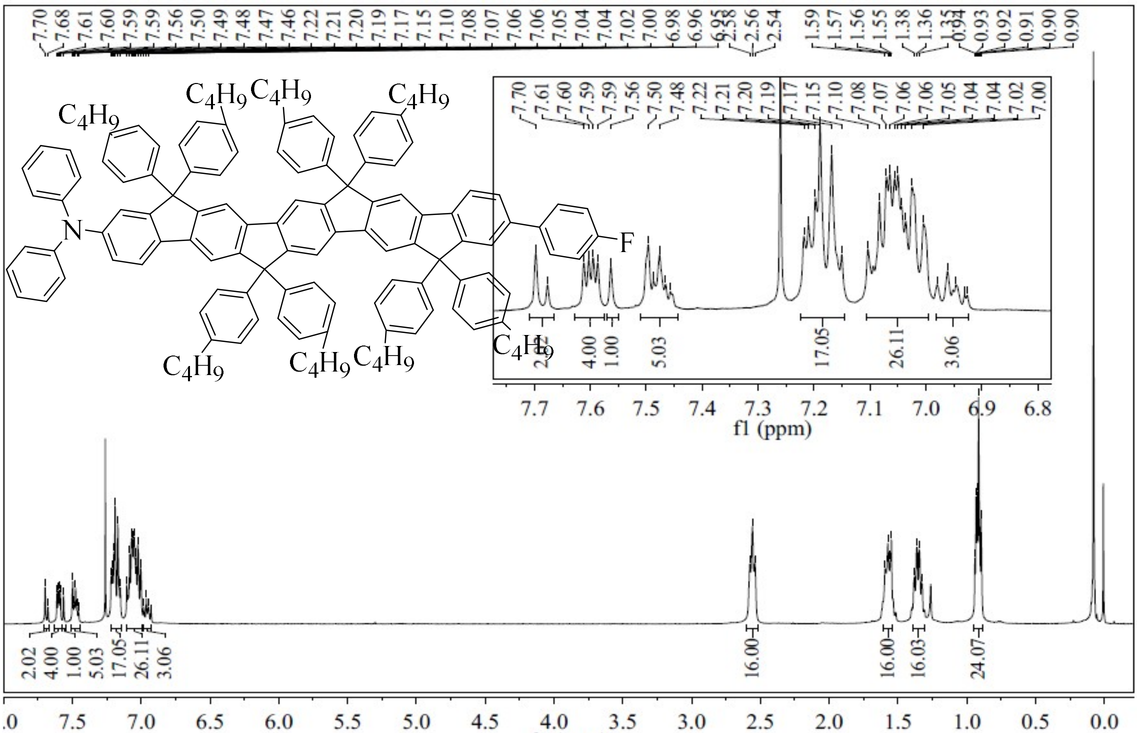


Fig. S16 ^{1}H NMR spectra of 4L-Ph-F.

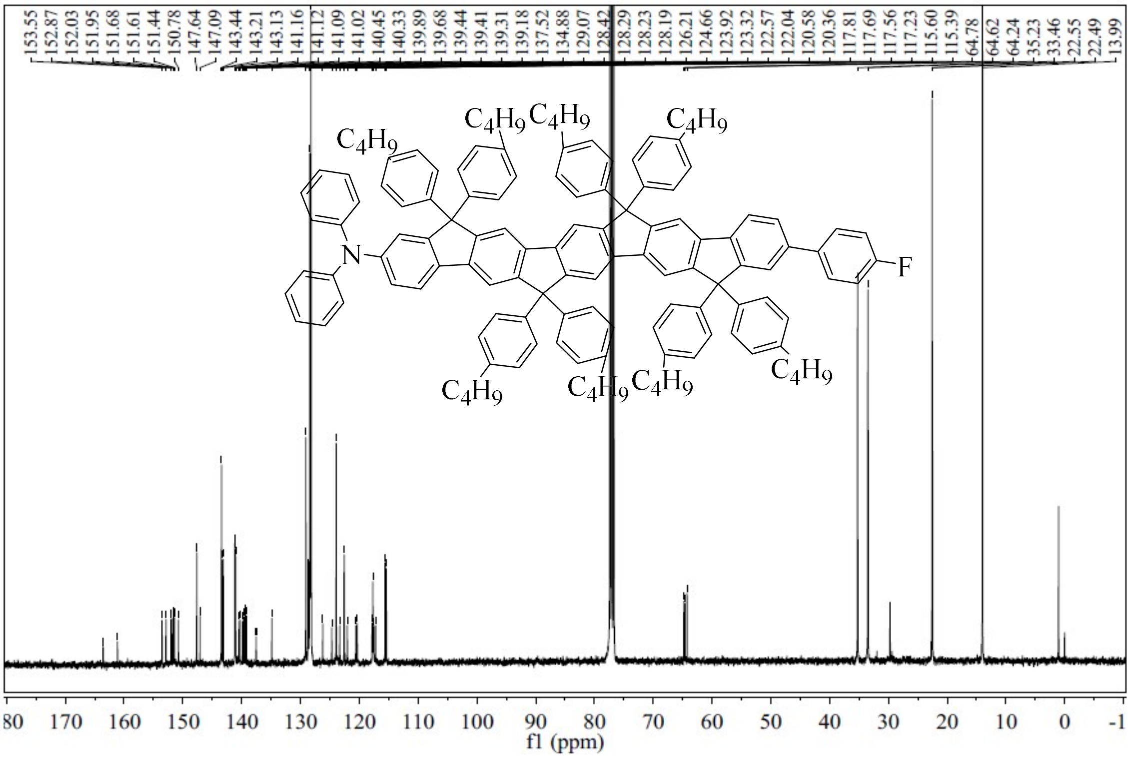


Fig. S17 ^{13}C NMR spectra of 4L-Ph-F.

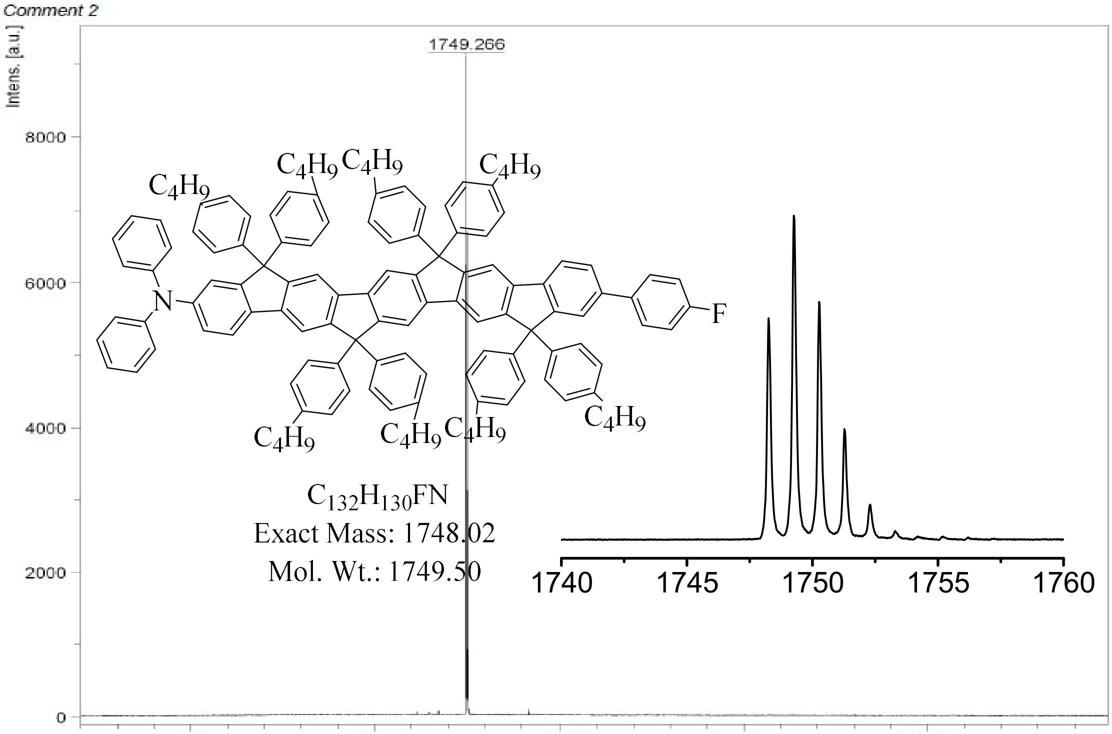


Fig. S18 MADIL-TOF spectra of 4L-Ph-F.

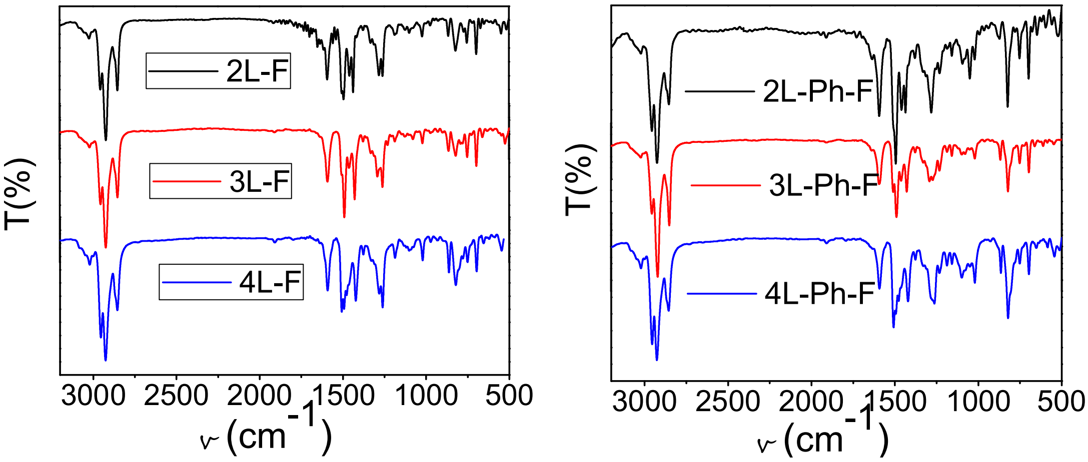


Fig. S19 IR spectroscopy of ladder-type compounds

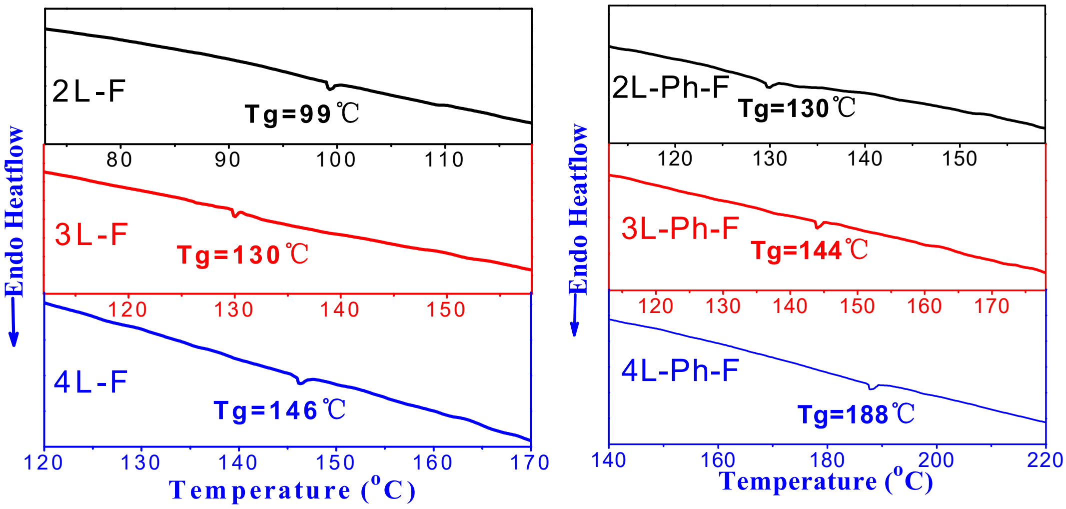


Fig. S20 DSC traces of the ladder-type compounds at a heating rate of 10 °C min^{-1} in N_2 atmosphere.

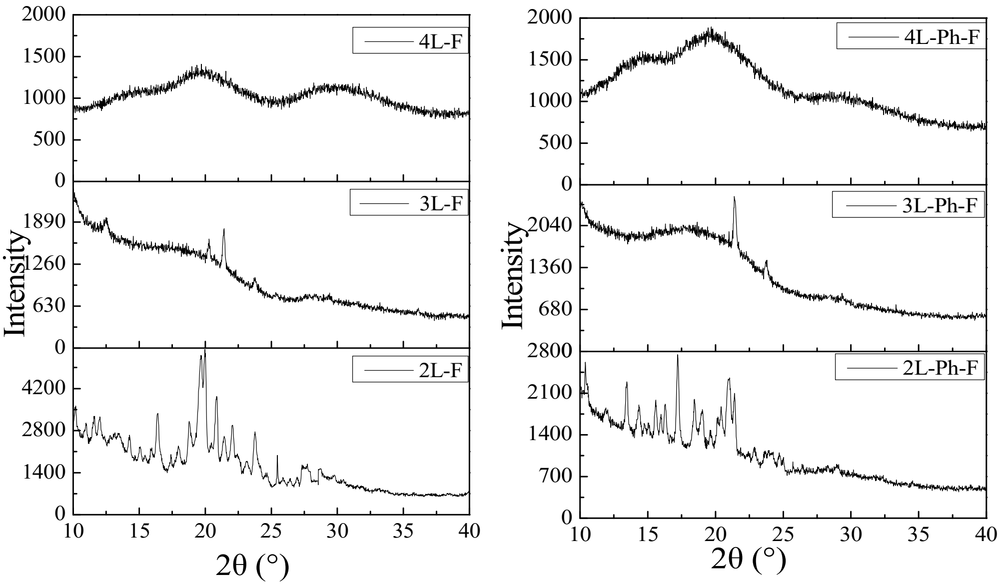


Fig. S21 Powder WAXD patterns of the ladder-type compounds.

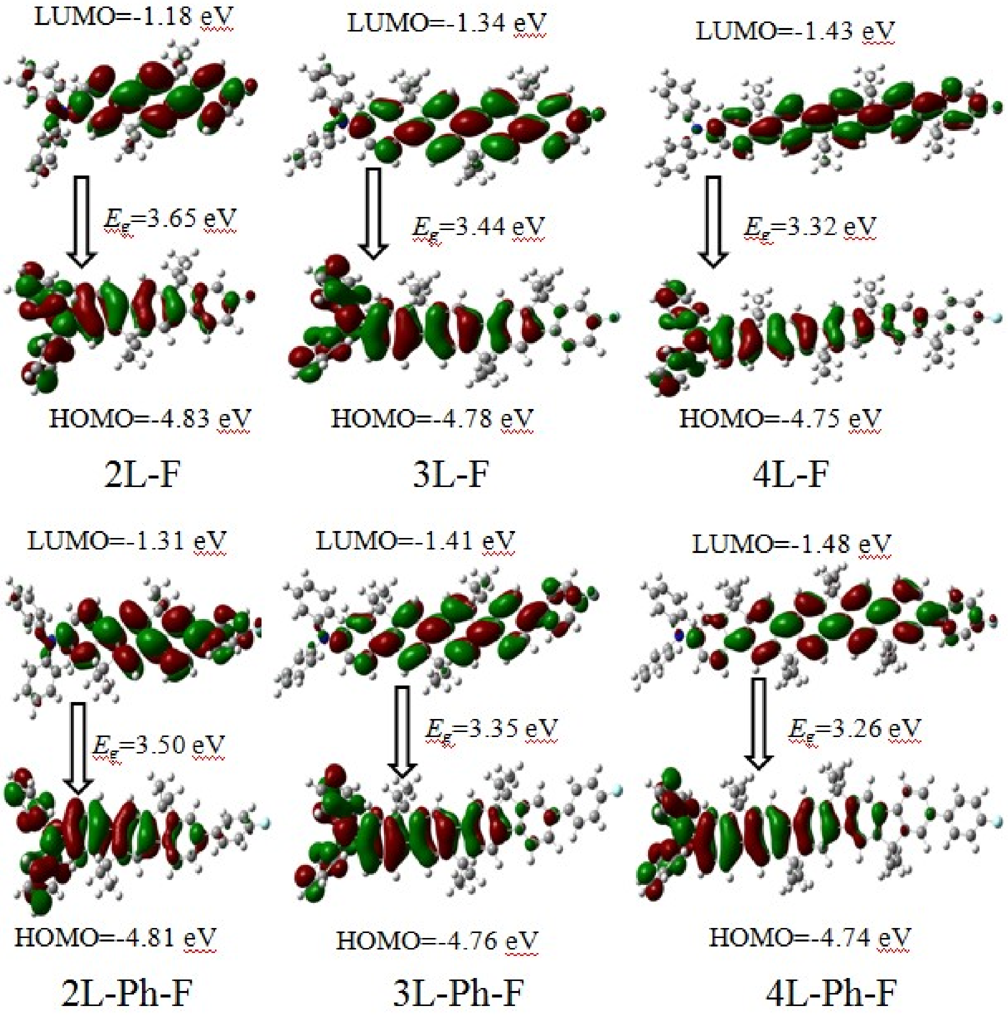
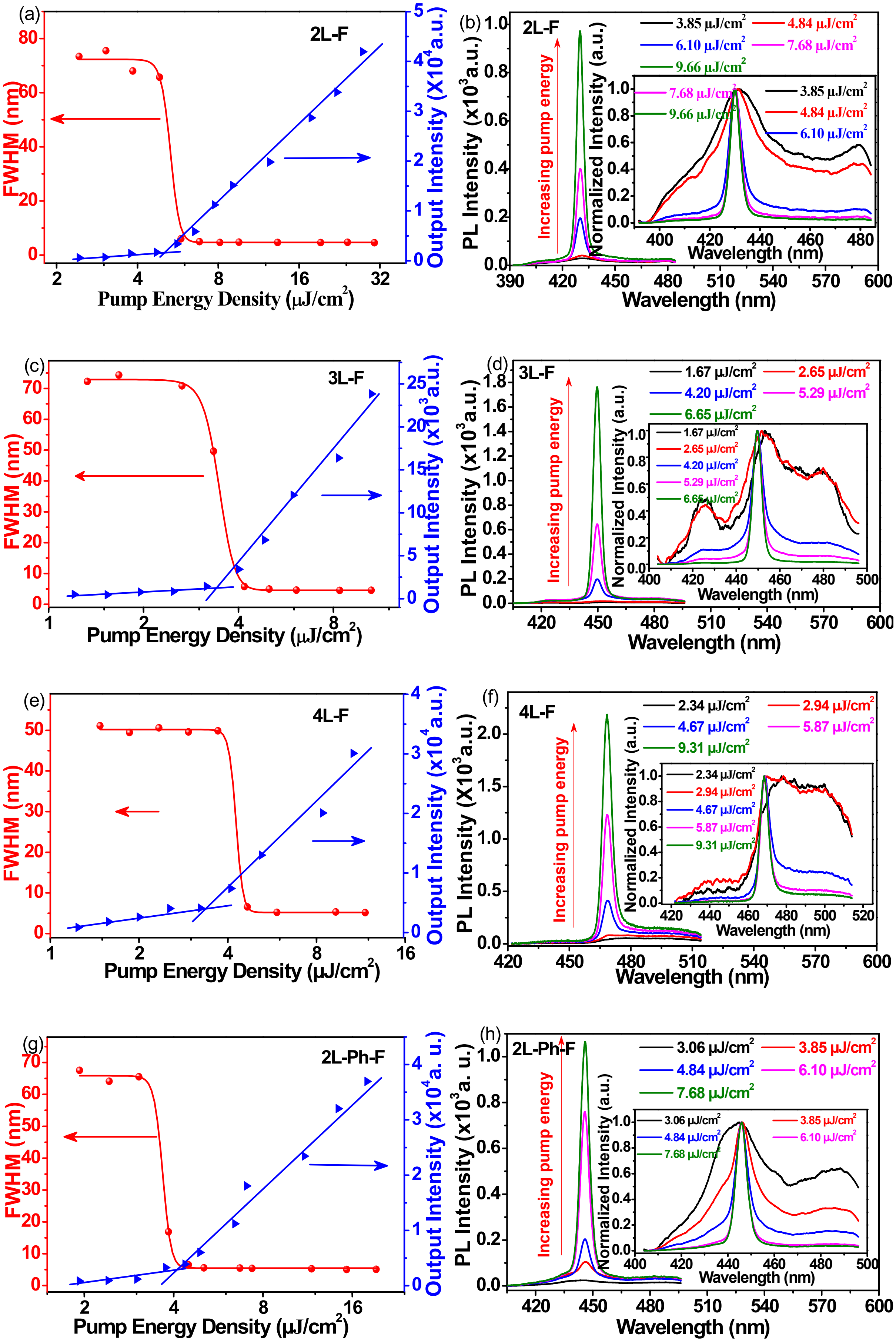


Fig. S22 Optimized molecular geometries and the calculated spatial distributions of the HOMOs and the LUMOs.


(a)
2L-F
FWHM (nm)
Output Intensity (X10^{4}a.u.)
Pump Energy Density (μJ/cm^2)
(b)
2L-F
PL Intensity (x10^{3}a.u.)
Increasing pump energy
Normalized Intensity (a.u.)
Wavelength (nm)
3.85 μJ/cm^2
4.84 μJ/cm^2
6.10 μJ/cm^2
7.68 μJ/cm^2
9.66 μJ/cm^2
(c)
3L-F
FWHM (nm)
Output Intensity (x10^{3}a.u.)
Pump Energy Density (μJ/cm^2)
(d)
3L-F
PL Intensity (x10^{3}a.u.)
Increasing pump energy
Normalized Intensity (a.u.)
Wavelength (nm)
1.67 μJ/cm^2
2.65 μJ/cm^2
4.20 μJ/cm^2
5.29 μJ/cm^2
6.65 μJ/cm^2
(e)
4L-F
FWHM (nm)
Output Intensity (x10^{4}a.u.)
Pump Energy Density (μJ/cm^2)
(f)
4L-F
PL Intensity (X10^{3}a.u.)
Increasing pump energy
Normalized Intensity (a.u.)
Wavelength (nm)
2.34 μJ/cm^2
2.94 μJ/cm^2
4.67 μJ/cm^2
5.87 μJ/cm^2
9.31 μJ/cm^2
(g)
2L-Ph-F
FWHM (nm)
Output Intensity (x10^{4}a. u.)
Pump Energy Density (μJ/cm^2)
(h)
2L-Ph-F
PL Intensity (x10^{3}a. u.)
Increasing pump energy
Normalized Intensity (a.u.)
Wavelength (nm)
3.06 μJ/cm^2
3.85 μJ/cm^2
4.84 μJ/cm^2
6.10 μJ/cm^2
7.68 μJ/cm^2

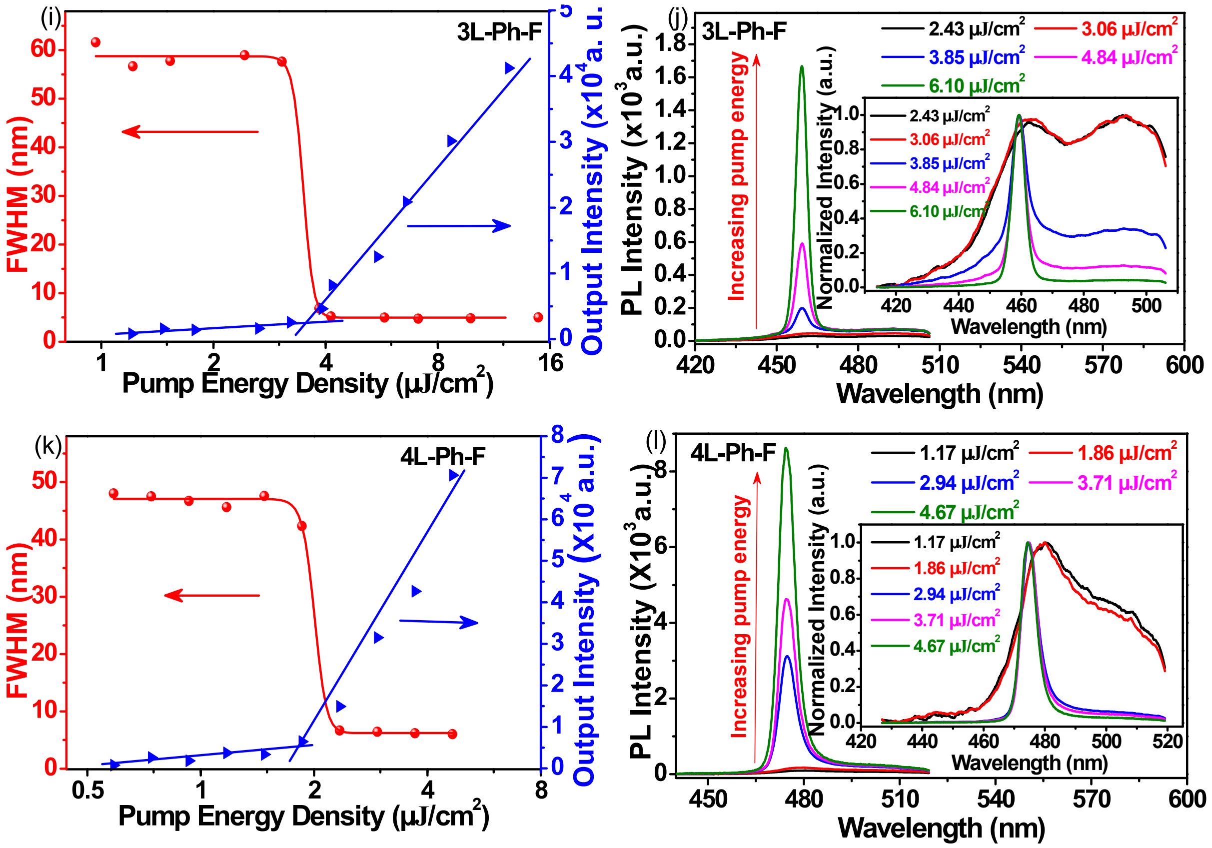


Fig. S23 Dependence of the full-width at half-maximum (FWHM, filled spheres) and the integrated output intensity (filled triangles) of the emission for **(a) 2L-F, (c) 3L-F, (e) 4L-F, (g) 2L-Ph-F, (i) 3L-Ph-F, (k) 4L-Ph-F** at various pump energy densities. The evolution of emission spectra of **(b) 2L-F, (d) 3L-F, (f) 4L-F, (h) 2L-Ph-F, (j) 3L-Ph-F, (l) 4L-Ph-F** neat films for planar waveguides with increasing pump energy. The insets presents the normalized emission spectra.