Electronic Supplementary Information (ESI) for

Pyrene-Centered Cyanophenyl End-Capped Starbursts: Design, Synthesis, Stabilized Blue Electroluminescence and Lasing Properties

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1. Synthesis and characterization

4-(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)benzo-nitrile (3): A mixture of compound **1** (14.8 g, 0.03 mol), **2** (1.47 g, 0.01 mol), and $Pd(PPh_3)_4$ (0.02 equiv.) was carefully degassed in the dark before and after the addition of toluene (50 mL) and an aqueous 2M K_2CO_3 (4.0 equiv.) solution. This mixture was stirred at 95 ^oC for 24 h under an atmosphere of nitrogen. Upon cooling, the organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine (300 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents, the resulting product was purified by flash chromatography on a silica gel column with hexane/dichloromethane (80:20) to afford a white solid. Yield: 70%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 5H), 7.59 (s, 2H), 7.51 (d, J = 11.4 Hz, 3H), 1.99 (s, 4H), 1.06 (s, 12H), 0.77 (s, 6H), 0.64 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 151.4, 145.9, 140.7, 139.2, 138.3, 132.6, 130.2, 127.7, 126.4, 126.2, 121.6, 121.5, 121.4, 120.3, 119.0, 110.7, 55.6, 40.2, 31.4, 29.6, 23.7, 22.5, 13.9.

General procedures for the synthesis of oligofluorene boronates 4, 6 and 8 through Miyaura reaction: A mixture of the corresponding oligofluorene bromides (**3**, **5**, or **7**) (1.0 equiv.), bis(pinacolato)diboron (1.6 equiv.), KOAc (3.0 equiv.) and $Pd(dppf)_2Cl_2$ (0.02 equiv) was added in nitrogen atmosphere. 1,4-dioxane (20 mL) was added into the mixture and heated to reflux with continuous stirring at 100 ^oC in the dark for 24 h under the protection of nitrogen. After cooling to room temperature, the organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine (200 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents, the resulting product was purified by flash chromatography on a silica gel column with hexane/dichloromethane (60:40) to afford oligofluorene boronates (**4**, **6** or **8**).

Compound 4: Pale-yellow solid; yield 63%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, J = 17.6, 9.0 Hz, 3H), 7.76 (s, 5H), 7.57 (d, J = 10.4 Hz, 2H), 2.04 (d, J = 6.9 Hz, 4H), 1.41 (s, 12H), 1.07 (dd, J = 16.4, 9.4 Hz, 12H), 0.75 (t, J = 6.8 Hz, 6H), 0.63 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 150.2, 146.1, 143.2, 141.6, 138.3, 133.9, 132.6, 128.9, 127.7, 126.2, 121.5, 120.7, 119.3, 119.0, 110.6, 83.8, 55.3, 40.2, 31.4, 29.6, 24.9, 23.7, 22.5, 14.0.

Compound 6: Pale-yellow solid; yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.79 (m, 6H), 7.79–7.75 (m, 5H), 7.70–7.67 (m, 2H), 7.66–7.61 (m, 3H), 7.60–7.58 (m, 1H), 2.13–2.03 (m, 8H), 1.41 (s, 12H), 1.16–1.03 (m, 26H), 0.79–0.75 (m, 12H), 0.75–0.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 152.1, 151.8, 150.2, 146.1, 143.7, 141.6, 141.1, 140.8, 140.3, 139.4, 137.8, 133.8, 132.6, 128.9, 127.7, 126.3, 126.3, 126.1, 121.6, 121.5, 120.4, 120.3, 119.0, 110.5, 83.7, 55.4, 55.2, 40.3, 31.4, 29.6, 24.9, 23.8, 22.5, 14.0.

Compound 8: Pale-yellow solid; yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.85 (m, 7H), 7.83–7.78 (m, 5H), 7.76–7.69 (m, 8H), 7.65–7.62 (m, 2H), 2.20–2.06 (m, 12H), 1.45 (s, 12H), 1.16 (dt, J = 18.5, 8.1 Hz, 36H), 0.87 (d, J = 8.9 Hz, 4H), 0.81 (dd, J = 6.9, 3.5 Hz, 18H), 0.79 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 152.1, 151.9, 151.8, 150.2, 146.1, 143.8, 141.6, 141.2, 141.0, 140.6, 140.3, 140.2, 140.0, 139.4, 137.8, 133.9, 132.6, 128.9, 127.7, 126.4, 126.3, 126.2, 126.1, 121.5, 120.4, 120.1, 119.1, 110.6, 83.7, 55.3, 40.4, 31.5, 29.7, 25.0, 23.8, 22.6, 14.1.

General procedures for the synthesis of oligofluorene bromides 5 and 7 through Suzuki reaction: A mixture of oligofluorene boronates (1.0 equiv.), 1 (3.0 equiv.), and Pd $(PPh_3)_4$ (0.02 equiv.) was added to an air-free two-phase mixture of toluene (50 mL) and an aqueous 2M K_2CO_3 (2.0 equiv.) solution. The resulting mixture was intensively stirred under a nitrogen atmosphere at 95 ^{o}C in the dark for 48 h. The organic layer was separated and the aqueous phase was extracted

with dichloromethane. The organic layers were combined and washed with brine (250 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue went through silica-gel column with hexane/ dichloromethane (66:34) to afford oligofluorene bromides (**5** or **7**).

Compound 5: Light yellow solid; yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 2.6 Hz, 1H), 7.82 (d, J = 2.6 Hz, 1H), 7.78 (d, J = 1.5 Hz, 4H), 7.76 (s, 1H), 7.67 (ddd, J = 7.8, 4.8, 1.5 Hz, 2H), 7.63 (s, 1H), 7.61 (dt, J = 8.0, 3.1 Hz, 4H), 7.52–7.47 (m, 2H), 2.12–1.98 (m, 8H), 1.17–1.07 (m, 26H), 0.78 (dd, J = 9.6, 5.2 Hz, 12H), 0.75–0.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 152.1, 151.9, 151.1, 146.1, 141.5, 140.9, 140.8, 139.7, 139.5, 139.3, 137.8, 132.6, 130.0, 127.7, 126.3, 126.2, 121.5, 121.5, 121.4, 121.1, 121.0, 120.4, 120.3, 120.0, 119.1, 110.6, 55.4, 40.3, 31.6, 29.6, 23.7, 22.6, 14.0.

Compound 7: Light yellow solid; yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, J = 7.8, 2.5 Hz, 4H), 7.78 (t, J = 1.8 Hz, 4H), 7.76 (d, J = 3.7 Hz, 1H), 7.71–7.66 (m, 3H), 7.65 (s, 3H), 7.64–7.59 (m, 4H), 7.58 (s, 1H), 7.51–7.47 (m, 2H), 2.14–1.98 (m, 12H), 1.15–1.06 (m, 36H), 0.91–0.85 (m, 4H), 0.78 (dd, J = 9.4, 4.6 Hz, 18H), 0.74 (dd, J = 12.7, 4.7 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 152.1, 151.9, 151.8, 151.1, 146.1, 141.5, 141.1, 141.0, 140.4, 140.3, 140.1, 140.0, 139.8, 139.4, 139.2, 137.8, 132.6, 130.0, 127.7, 126.3, 126.2, 121.5, 121.4, 121.1, 120.9, 120.3, 120.0, 119.1, 110.5, 55.5, 55.4, 55.3, 40.3, 31.6, 31.4, 29.6, 23.8, 22.6, 14.0.

General procedures for the synthesis of T*n* (*n* = 1, 2, 3): A solution of 9 (1.0 equiv., 0.10 mmol), 4, 6, or 8 (8.0 equiv.) and Cs_2CO_3 (16 equiv.) in THF (3-5 mL) in a 10 mL pressurized vessel was carefully degassed before and after the addition of $Pd(PPh_3)_4$ (0.6 equiv.). 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 150 ^{o}C was reached, the microwave power regulated itself to

keep that temperature for 25 min before cooling to room temperature. The mixture was subsequently diluted with CH_2Cl_2 and then washed with aqueous HCl (1 mL) and a saturated solution of brine, and dried over Na_2SO_4, and evaporated. The resulting residue was purified with column chromatography using hexane/CH_2Cl_2 as eluent to give the final product. The temperature of the reaction was monitored by using a calibrated infrared temperature control mounted under the reaction vessel. A load cell, connected to the vessel through the septum, controlled the pressure.

Compound T1: Yellow solid; yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 3H), 8.20 (s, 2H), 7.93 (s, 4H), 7.89 (d, J = 7.9 Hz, 4H), 7.79 (d, J = 3.1 Hz, 17H), 7.74 (d, J = 7.8 Hz, 8H), 7.63 (d, J = 16.8 Hz, 8H), 2.09 (s, 16H), 1.08 (s, 50H), 0.83 (d, J = 6.4 Hz, 16H), 0.68 (d, J = 6.3 Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 151.4, 146.1, 141.5, 140.3, 139.6, 138.0, 137.7, 132.6, 129.7, 129.3, 128.4, 127.7, 126.4, 126.2, 125.4, 125.3, 121.6, 120.4, 119.9, 119.0, 110.6, 55.5, 40.2, 31.4, 29.6, 23.9, 22.5, 13.9. MALDI-TOF-MS (m/z): calcd for $C_{144}H_{150}N_4$, exact mass: 1937.20; Found: 1937.8 (M^+). Anal. Calcd for $C_{144}H_{150}N_4$: C 89.21, H 7.90 N 2.89. Found: C 89.28, H 7.82, N 2.90.

Compound T2: Kelly solid; yield 45%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 4H), 8.22 (s, 2H), 7.94 (d, J = 8.1 Hz, 4H), 7.89 (d, J = 7.9 Hz, 4H), 7.85 (s, 4H), 7.83 (s, 4H), 7.80 (s, 2H), 7.78 (s, 16H), 7.75 (d, J = 2.6 Hz, 8H), 7.72 (s, 4H), 7.70 (s, 4H), 7.67 (d, J = 3.9 Hz, 6H), 7.62 (s, 2H), 7.60 (s, 2H), 7.58 (s, 4H), 2.11 (d, J = 6.3 Hz, 32H), 1.12 (d, J = 12.2 Hz, 96H), 0.90 (s, 8H), 0.76 (t, J = 6.9 Hz, 48H), 0.71 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 151.8, 151.4, 146.1, 145.7, 141.5, 141.1, 140.4, 140.2, 140.0, 139.9, 139.4, 137.9, 137.8, 132.6, 129.6, 128.4, 127.7, 126.3, 126.2, 125.4, 125.3, 123.3, 121.5, 120.2, 110.5, 55.4, 40.3, 31.4, 29.6, 23.8, 22.5, 14.0. MALDI-TOF-MS (m/z): calcd for $C_{244}H_{278}N_4$, exact mass: 3264.19; Found: 3265.7 (M^+). Anal.

Calcd for $C_{244}H_{278}N_4$: C 89.71, H 8.58 N 1.72. Found: C 89.76, H 8.52, N 1.72.

Compound T3: Light yellow solid; yield 42%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 4H), 8.24 (s, 2H), 7.95 (d, J = 8.0 Hz, 4H), 7.90 (d, J = 7.9 Hz, 4H), 7.86 – 7.83 (m, 18H), 7.79 (t, J = 5.2 Hz, 16H), 7.75 (d, J = 4.2 Hz, 8H), 7.71 (dd, J = 9.9, 4.6 Hz, 24H), 7.66 (s, 8H), 7.63 (d, J = 1.2 Hz, 2H), 7.60 (s, 2H), 7.58 (s, 4H), 2.12 (s, 48H), 1.11 (d, J = 11.8 Hz, 144H), 0.90 (d, J = 8.9 Hz, 12H), 0.84 (s, 12H), 0.78 (dd, J =11.9, 6.8 Hz, 72H), 0.72 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 151.9, 151.8, 151.4, 146.1, 141.5, 141.1, 140.6, 140.3, 140.2, 140.1, 139.9, 139.8, 139.8, 139.4, 137.7, 132.6, 127.6, 126.2, 126.2, 121.5, 120.2, 119.9, 110.4, 55.4, 55.3, 40.3, 31.4, 31.4, 29.6, 23.8, 22.5, 14.04, 14.02. MALDI-TOF-MS (m/z): calcd for $C_{344}H_{406}N_4$, exact mass: 4593.19; Found: 4596.0 (M^+). Anal. Calcd for $C_{344}H_{406}N_4$: C 89.88, H 8.90 N 1.22. Found: C 89.93, H 8.83, N 1.25.

2. MALDI-TOF , ^{1}H NMR spectra and ^{13}C NMR spectra of T*n* (*n* = 1, 2, 3)

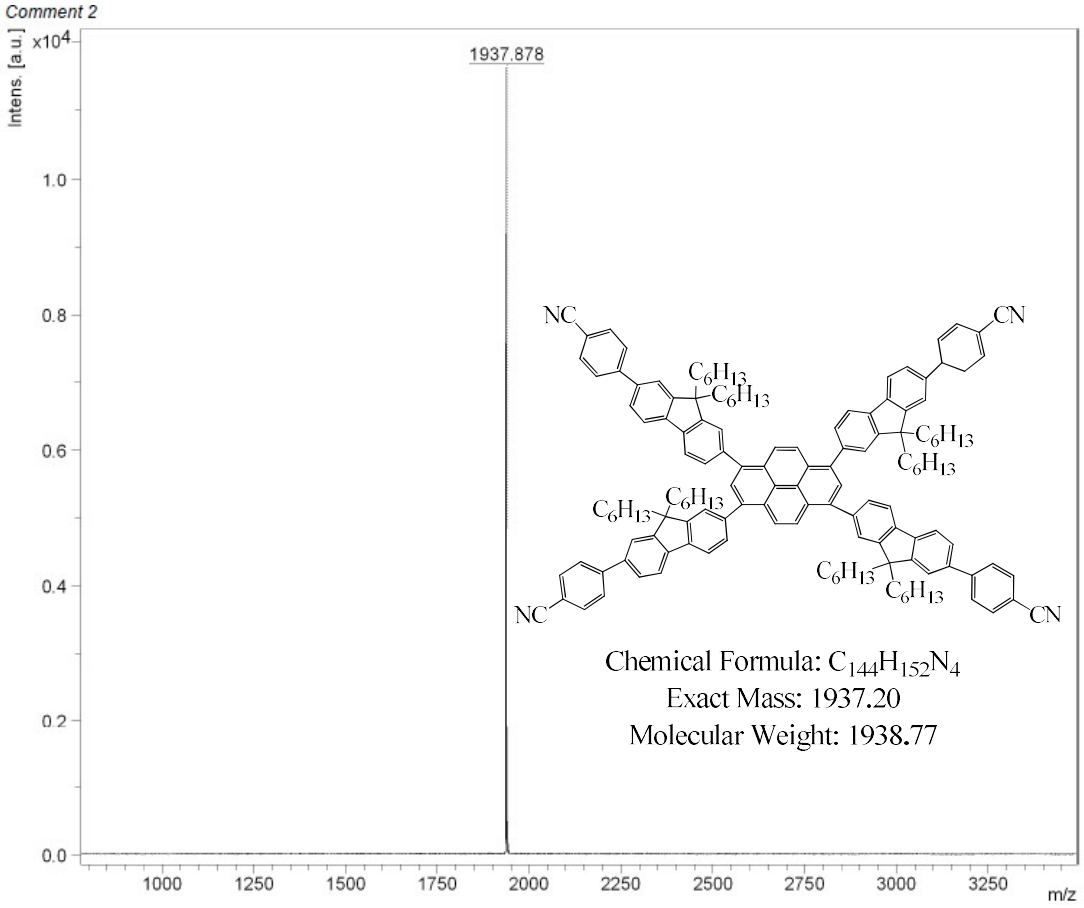

Fig. S1 MADIL-TOF spectra of **T1**.

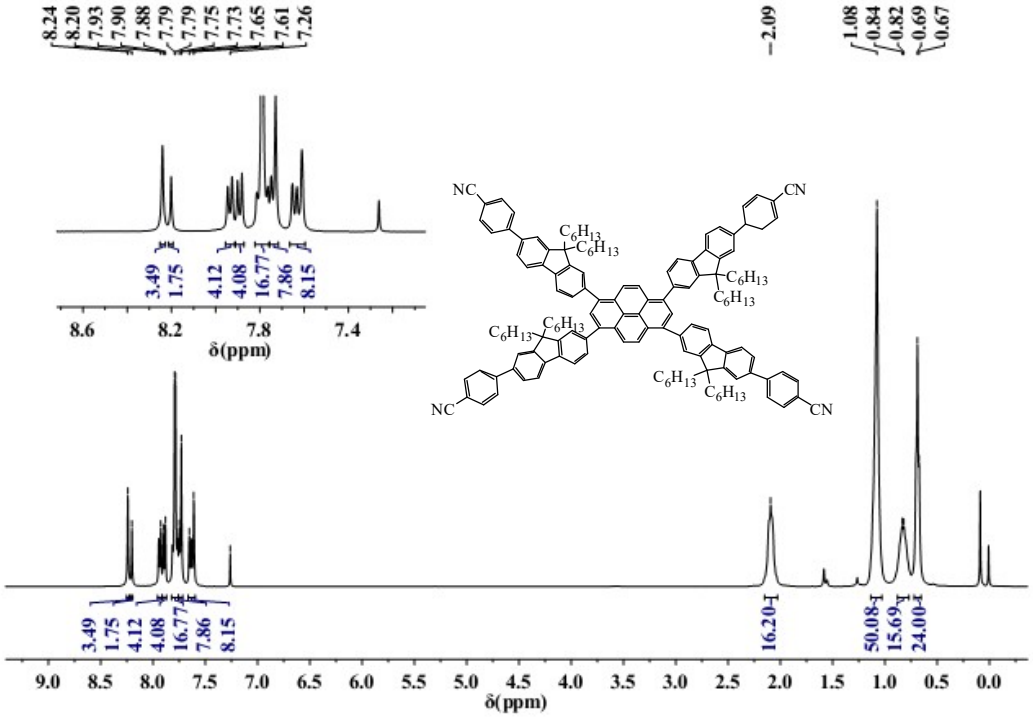

Fig. S2 ^{1}H NMR spectra of **T1** in $CDCl_3$.

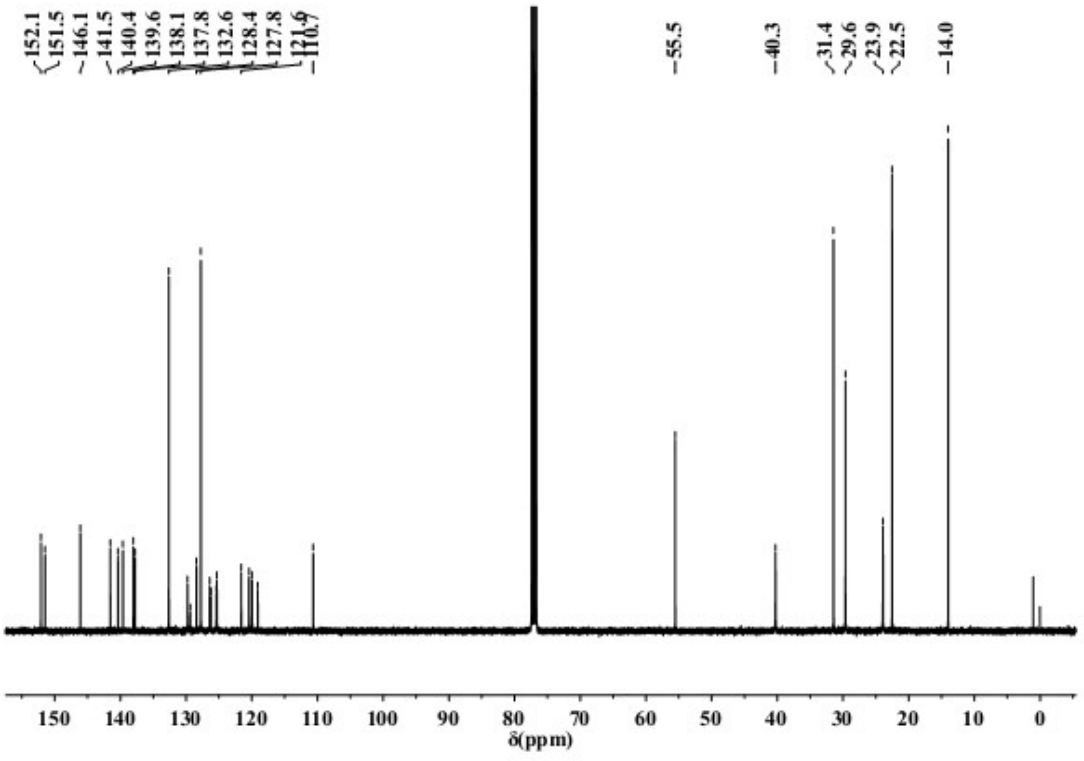

Fig. S3 ^{13}C NMR spectra of **T1** in $CDCl_3$.

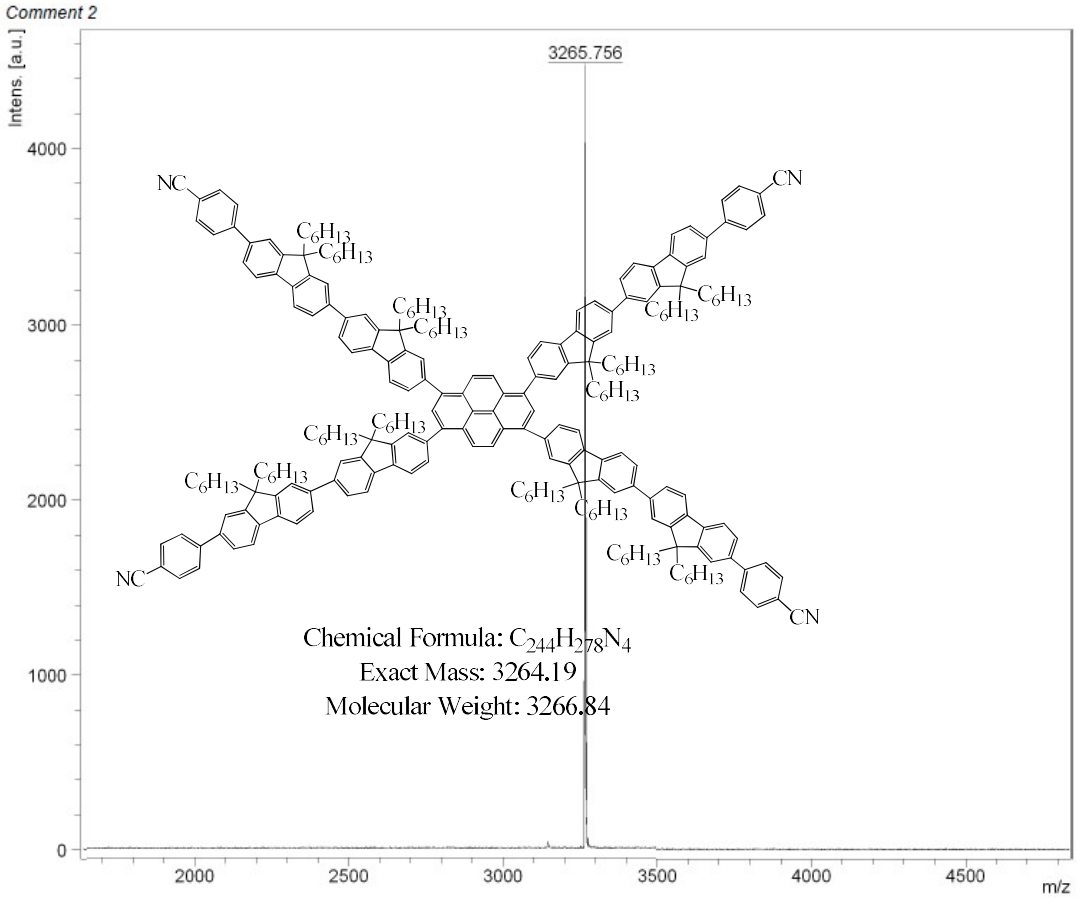

Fig. S4 MADIL-TOF spectra of **T2**.

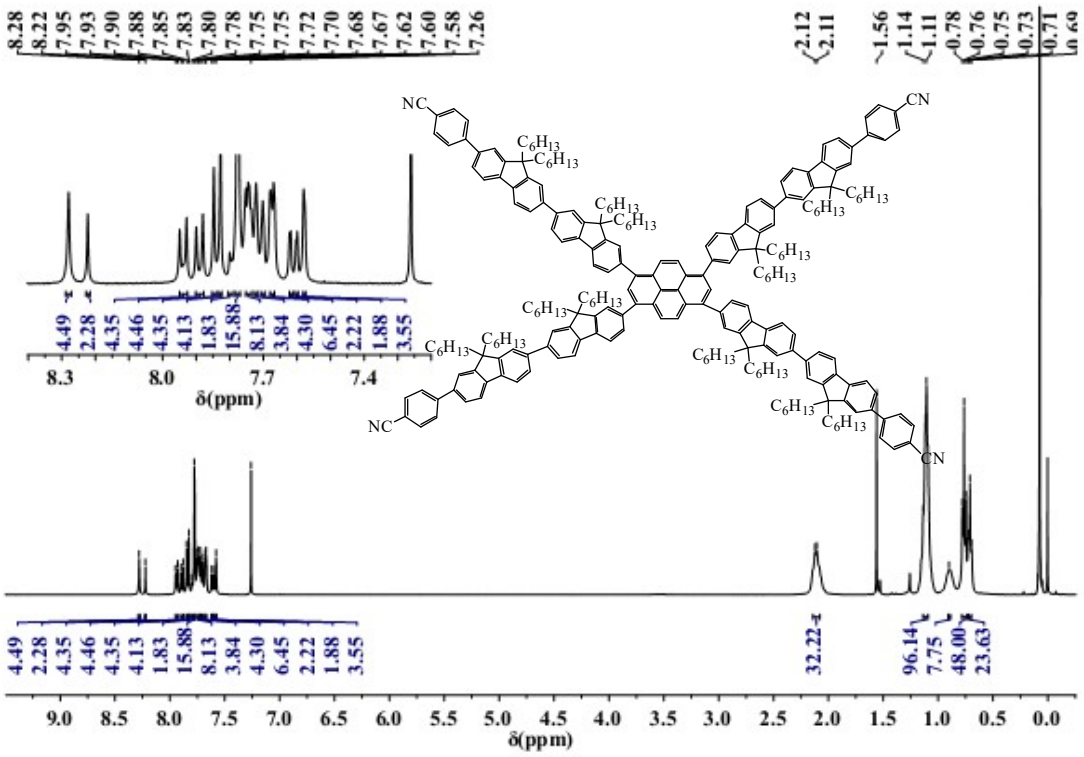

Fig. S5 ^{1}H NMR spectra of **T2** in $CDCl_3$.

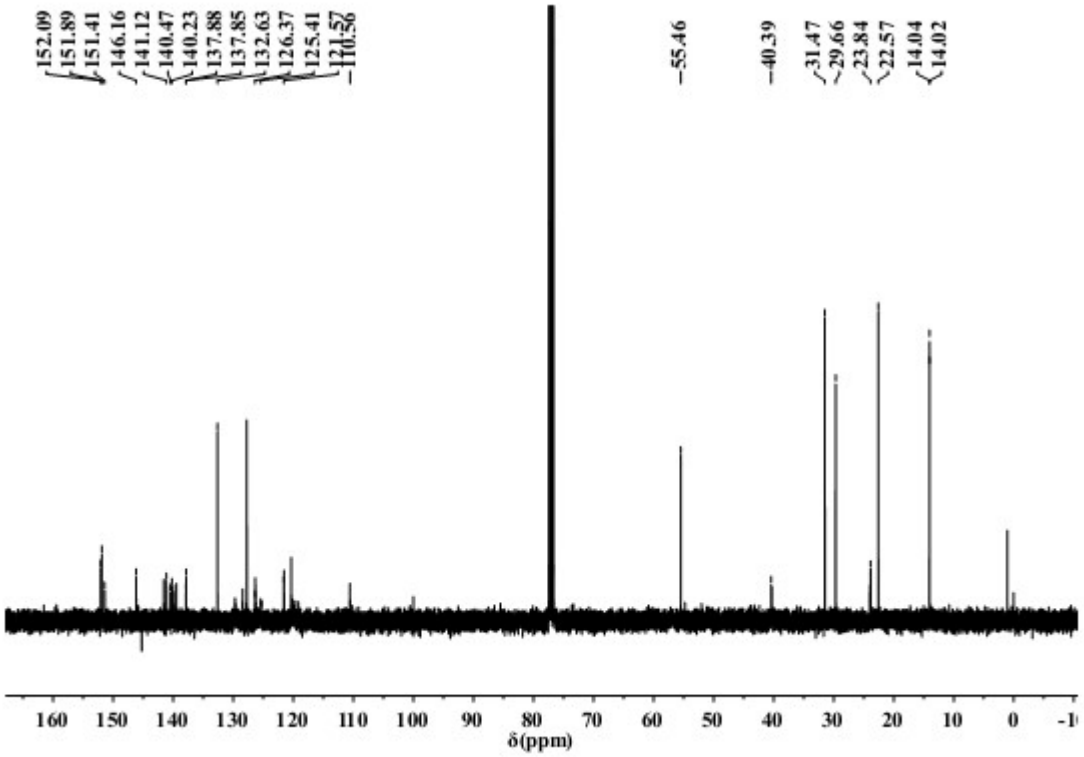

Fig. S6 ^{13}C NMR spectra of **T2** in $CDCl_3$.

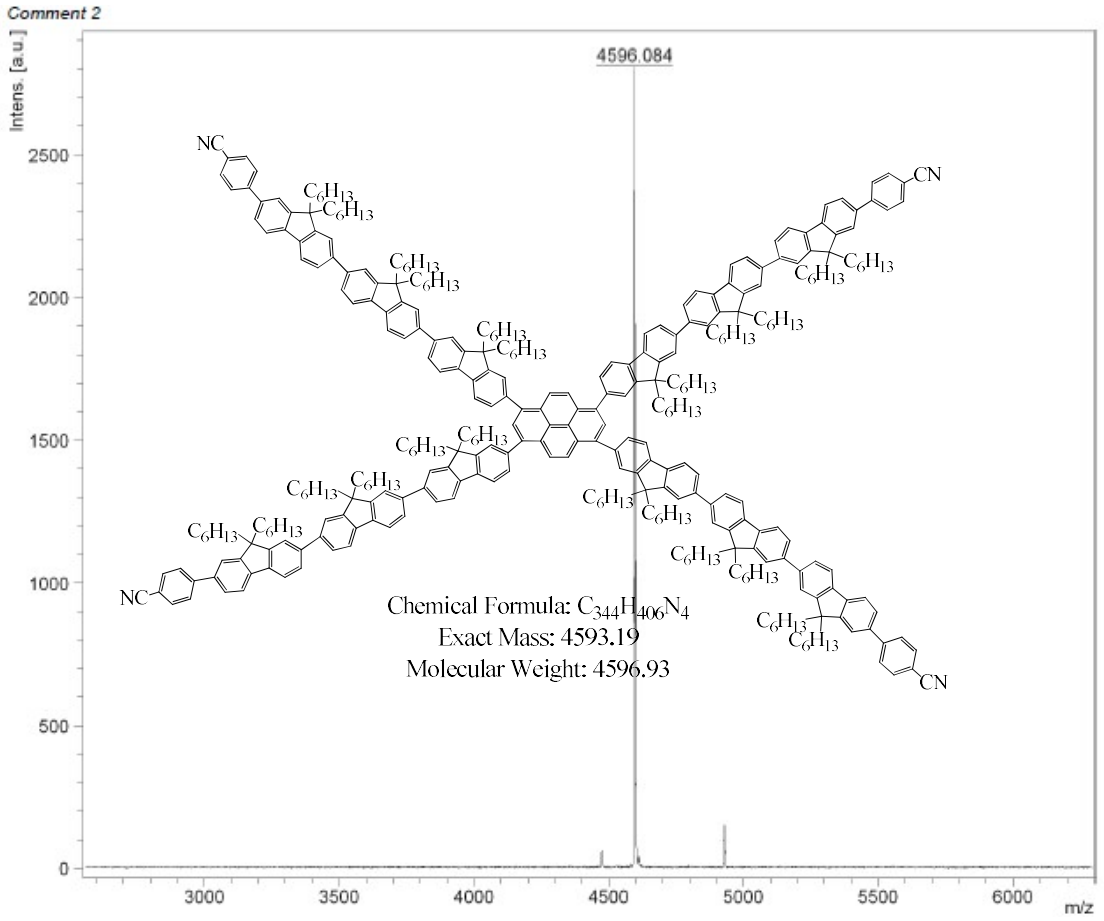

Fig. S7 MADIL-TOF spectra of **T3**.

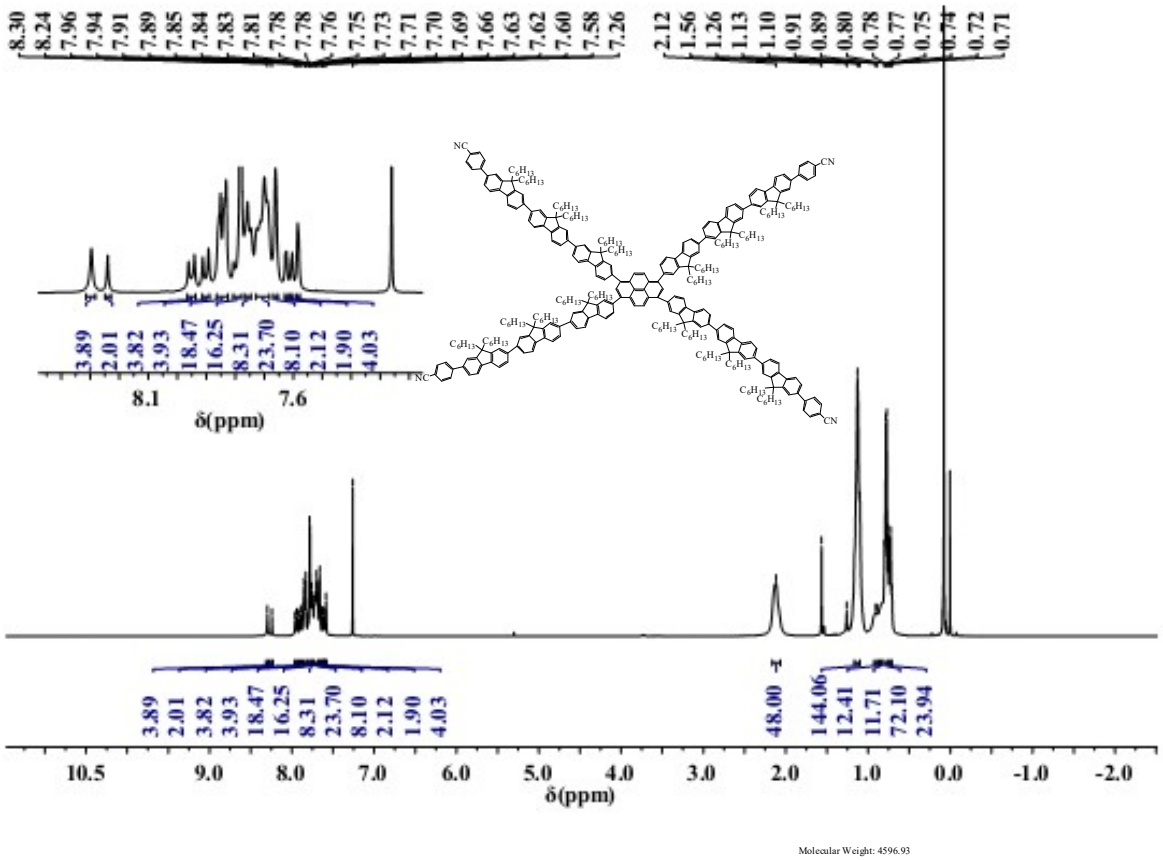

Fig. S8 ^{1}H NMR spectra of **T3** in $CDCl_3$.

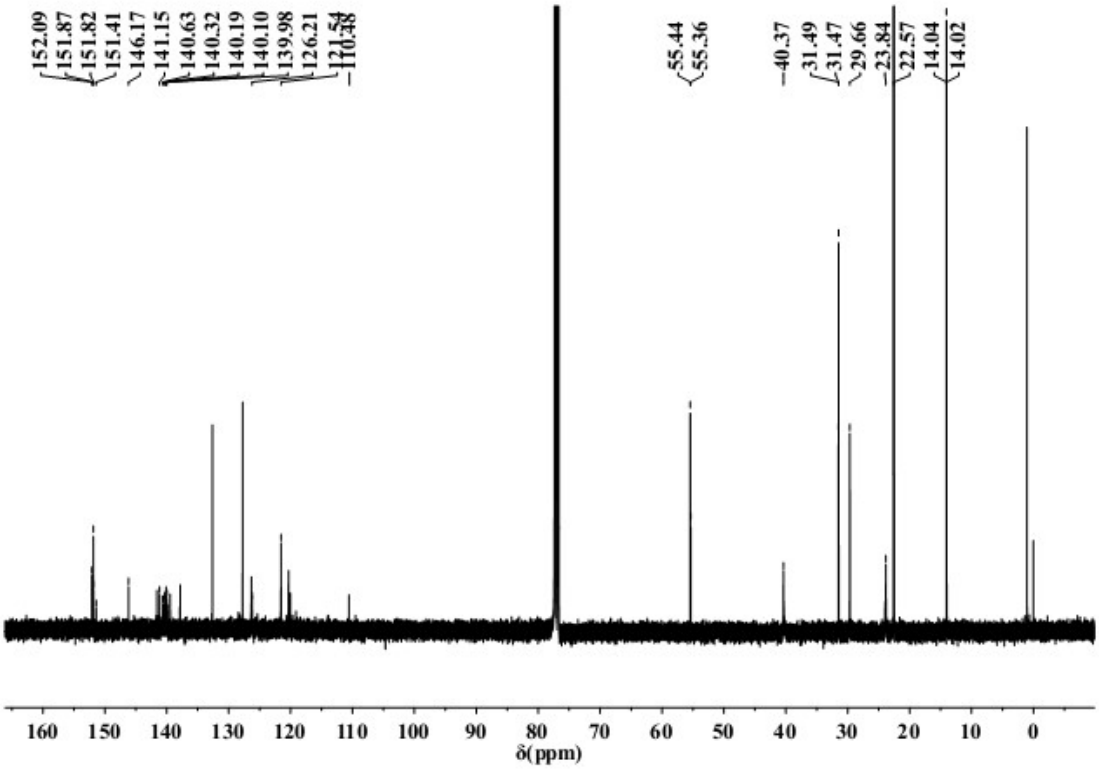

Fig. S9 ^{13}C NMR spectra of **T3** in $CDCl_3$.

3. Thermal and morphological properties

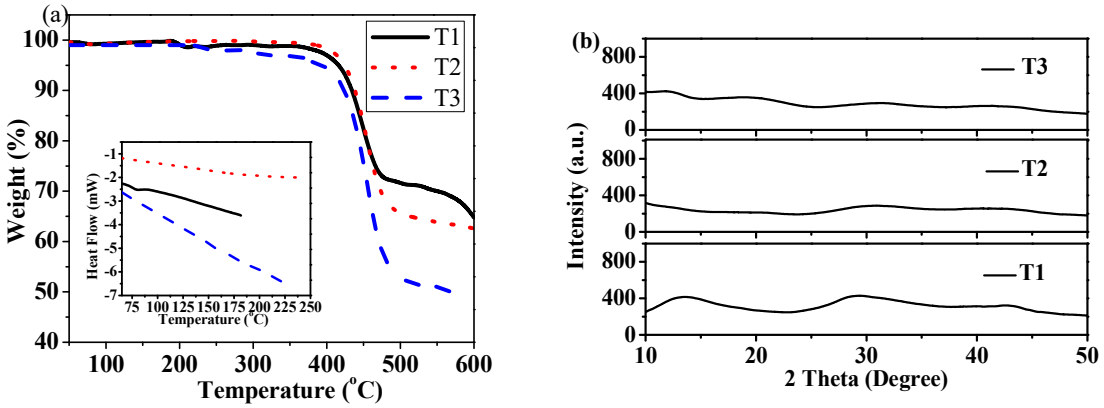

Fig. S10 (a) TGA thermograms and DSC traces (inset) of **T1-T3** at a heating rate of 10 °C min^{-1}; (b) XRD patterns of **T1-T3.**

4. Electrochemical properties

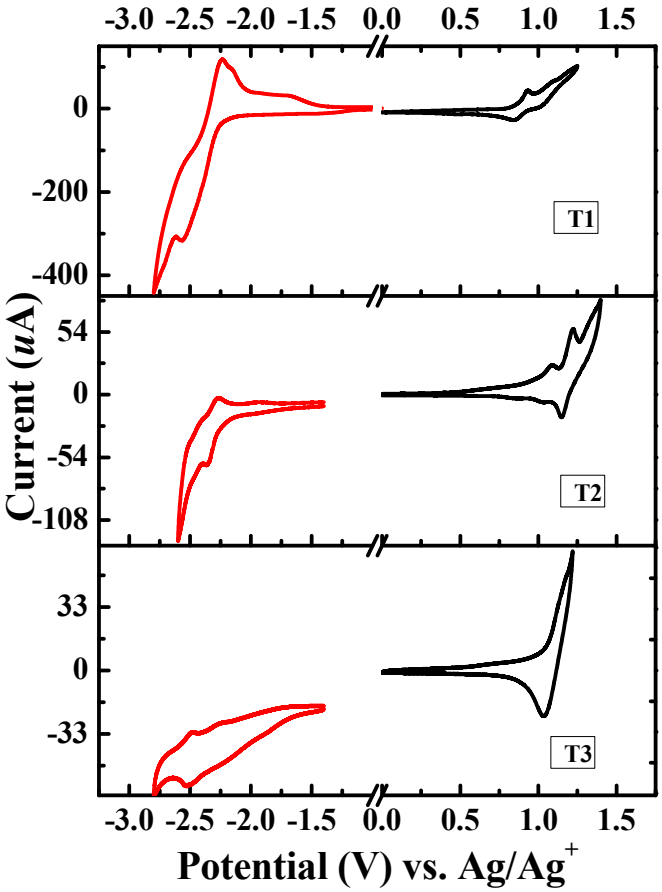

Fig. S11 Cyclic voltammetry (CV) curves of **T1-T3.**