Electronic Supporting Information

Efficient Blue Thermally Activated Delayed Fluorescent Emitters Based on Boranaphtho[3,2,1-de]anthracene Acceptor

Ranran Pei,[a] He Liu,[a]* Changjiang Zhou,[b] Jingsheng Miao,[a]* Chuluo Yang.[a]*

R Pei, Dr. H. Liu, Dr. J. Miao, Prof. C. Yang

[a] College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, P. R. China.

E-mail: liuhe001@szu.edu.cn, jingshengmiao@szu.edu.cn, clyang@szu.edu.cn

Dr. C. Zhou

[b] College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

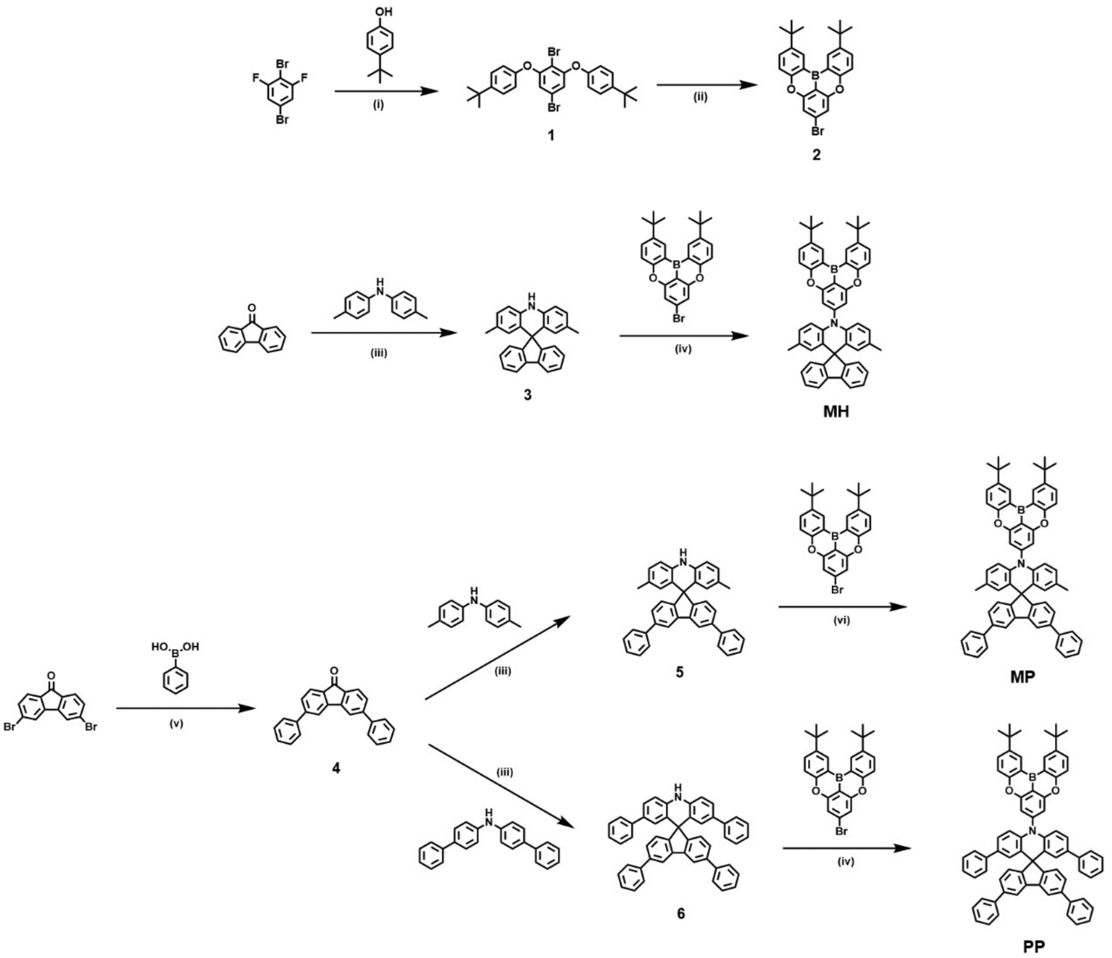
General information

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere. All the chemicals were purchased from commercial sources and used as received unless stated otherwise. Toluene was refluxed over Na and distilled under dry argon. Synthesized compounds were subject to purification by temperature gradient sublimation in high vacuum before used in subsequent studies. The 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra were recorded on a Bruker Ascend spectrometer using $CDCl_3$ or DMSO-d^6 as solvent and tetramethylsilane (TMS) as an internal reference. Mass analyses were recorded by Bruker autoflex MALDI-TOF mass spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-3100 recording spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. Phosphorescence spectra of thin films were conducted at 77 K. Thermogravimetric analysis (TGA) was recorded on a TA Q50 instrument under nitrogen atmosphere at a heating rate of 10 ^{o}C/min from 50 ^{o}C to 800 ^{o}C. The temperature of degradation (T_d) was correlated to a 5% weight loss. Differential Scanning Calorimetry were carried out on a TA Q200. The glass transition temperature (T_g) was determined from the second heating scan at a heating rate of 10 ^{o}C min^{-1} from 60 to 300 ^{o}C. Cyclic voltammetry (CV) was carried out in nitrogen-purged *N*, *N'*-dimethylformamide at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode with ferroceniumferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV/s. Formal potentials were calculated as the average of cyclic voltammetric anodic and cathodic peaks. The HOMO energy levels of the compounds were calculated according to the formula: $-[4.8 + (E_{\mathrm{onset(ox/red)}} - E_{\mathrm{1/2(Fc/Fc+)}})]$ eV. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. The PL lifetimes were measured by PicoQuant Fluotime300. The samples were placed in a vacuum cryostat chamber. The solid state absolute PLQYs were measured on a Quantaurus-QY measurement system (C9920-02, Hamamatsu Photonics) equipped with a calibrated integrating sphere in the host of PPF (10 wt%) and all the samples were excited at 360 nm. During the PLQY measurements, the integrating sphere was purged with pure and dry argon to maintain an inert environment. The ground state molecular structures were optimized at the B3LYP/def2-SVP level of theory; and the excited state were investigated by time-dependent DFT (TDDFT) at PBE0/def2-SVP level. In addition, the overlaps between the hole and electron density distributions in the S_1 and T_1 states were estimated by the Multiwfn code.[1]

Device Fabrication

Patterned ITO glass substrates were cleaned sequentially with acetone, deionized water and isopropyl alcohol in an ultrasonic cleaner, then dried with N_2 flow and finally transferred into a vacuum chamber for deposition. Both 8-hydroxyquinolinolato-lithium (Liq) as electron injection layer and aluminum (Al) as cathode layer were deposited by thermal evaporation at 5×10^{-5} Pa. Additionally, the organic layers were deposited at the rates of 0.2-3 Å/s. After the organic film deposition, Liq and Al layer were deposited with rates of 0.1 and 3 Å/s, respectively. The emitting area of the device is about 0.09 cm^2. The current density-voltage-luminance (*J-V-L*), *L-EQE* curves and electroluminescence spectra were measured using a Keithley 2400 source meter and an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan).

Synthesis



(i) Cs_2CO_3, DMF, 110 °C,12 h

(ii) *n*-BuLi, BBr_3, DIPEA, DCB, 180 °C, 12 h

(iii) $TsOH{\cdot}H_2O$, 170 - 200 °C, 30 min

(iv) $Pd_2(dba)_3$, $^tBu_3PHBF_4$, tBuONa, Xylene, 110°C, 12 h

(v) $Pd(PPh_3)_4$, K_2CO_3, Toluene/H_2O , 95 °C, 12h

(vi) $Pd(OAc)_2$, $^tBu_3PHBF_4$, $Cs_2(CO)_3$, Toluene, 85 °C, 12 h

Scheme S1. synthetic route of **MH**, **MP** and **PP**.

Synthesis of 4,4'-((2,5-dibromo-1,3-phenylene)bis(oxy))bis(tert-butylbenzene) **(1)**

5.4 g (20 mmol) 2,5-dibromo-1,3-difluorobenzene, 3g (22 mmol) 4-(tert-butyl)phenol, 16.3g (50 mmol) Cs_2CO_3 and 50 ml *N,N*-Dimethylformamide were loaded in a 250 ml three-necked round bottom flask. The flask was then evacuated and backfilled with nitrogen, this evacuation and backfill procedure was repeated twice and then refluxed and stirred at 110°C for 12 h. 70 ml water were added to the flask and the flesh pink precipitate was filtered off followed by washed with water and dried at 60°C overnight. (7 g, Yield: 65.8%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.01 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.76 (s, 2H, Ar-H), 1.37 (s, 18H, CH_3).

Synthesis of 7-bromo-2,12-tert-butyl-5,9-dioxa-13b-boranaphtho[3,2,1] anthracene **(2)**

In a two-neck flask, intermediate 1 (7 g, 13.2 mmol) was dissolved in 50 ml dehydrated 1,2-dichlorobenzene and stirred at 0 °C under nitrogen atmosphere. The mixture was cooled to 0 °C for 10 minutes. Then 2.4 M *n*-BuLi (9.1 ml, 14.5 mmol) was injected slowly to the mixture dropwise and the mixture was stirring at 0 °C for 2 h. After that, the BBr_3 (1.5 ml, 15.8 mmol) was added to the mixture, and stirred at room temperature for 20 minutes. Then 2 ml dehydrated *N, N*-Diisopropylethylamine was added to the mixture at 0 °C. The mixture was stirred for 12 h at 180 °C. 2 ml *N, N*-diisopropylethylamine were used to quench the reaction. After removing of the solvent, the mixture was applied to a silica gel column using petroleum as eluent to give the product as white power. (1.6 g, Yield: 26.5%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.72 (d, 2H, J = 2.4 Hz, Ar-H), 7.80-7.77 (dd, J = 8.8 Hz, J = 2.4 Hz, 2H, Ar-H), 7.47 (d, J = 8.8 Hz, 2H, Ar-H), 7.36 (s, 2H, Ar-H), 1.48 (s, 18H, CH_3).

Synthesis of 2,7-dimethyl-10H-spiro[acridine-9,9'-fluorene] **(3)**

A 100 ml three neck flask with a magnetic stir bar was charged with *p*-Toluenesulfonic acid monohydrate (0.17 g, 0.9 mmol) and di-*p*-tolylamine (1.8 g, 9 mmol) under nitrogen atmosphere. The mixture was heated to 120 °C and continually stirred for 15 min; then 9H-fluoren-9-one (0.54 g, 3 mmol) was quickly added with vigorous stirring. The resulting solution was heated to 200 °C for 30 minutes[1]. After being cooling down, it was diluted with 30 mL of dichloromethane, then the solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica using petroleum ether/ethyl acetate (100/3 to 50/1, v/v) as eluent, followed by recrystallization from CH_2Cl_2/CH_3OH for three times to yield the pure product as yellow solid (551 mg, Yield: 51.2 %). ^1H NMR (500 MHz, DMSO-d_6, δ): 8.99 (s, 1H, N-H), 7.91 (d, J = 7.5 Hz, 2H, Ar-H), 7.41-7.32 (m, 2H, Ar-H), 7.23 (t, J = 7.4 Hz, 2H, Ar-H), 7.17 (d, J = 7.5 Hz, 2H, Ar-H), 6.88-6.84 (m, 4H, Ar-H), 5.89 (s, 2H, Ar-H), 1.88 (s, 6H, CH_3)

Synthesis of 3,6-diphenyl-9H-fluoren-9-one **(4)**

A flask was charged with 3,6-dibromo-9H-fluoren-9-one (3.4 g, 10 mmol), phenylboronic acid (2.7 g, 22 mmol), $Pd(PPh_3)_4$ (57.6 g, 0.05 mmol), K_2CO_3 (4.1g, 30 mmol), H_2O (15 ml) and toluene (15 ml). The reaction mixture was stirred at 95 °C for 12 h under nitrogen atmosphere. After cooled down to room temperature, the mixture was poured into 20 ml water, extracted with CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. After removal of solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane(10/3, v/v), then evaporated to obtain the pure product as yellow solid (3 g, Yield: 90.4%). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.79 (s, 2H, Ar-H), 7.77 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.68-7.65 (m, 4H), 7.54-7.47 (m, 6H, Ar-H), 7.45-7.40 (m, 2H, Ar-H).

Synthesis of 2,7-dimethyl-3',6'-diphenyl-10H-spiro[acridine-9,9'-fluorene] **(5)**

2,7-dimethyl-3',6'-diphenyl-10H-spiro[acridine-9,9'-fluorene] was synthesized use the same reaction conduction with intermediate 3 between di-*p*-tolylamine and 9H-fluoren-9-one. The compound was yellow powder (Yield 49%).^1H NMR (500 MHz, DMSO-d_6, δ): 9.06 (s, 1H, N-H), 8.45 (d, J = 1.8 Hz, 2H, Ar-H), 7.87 -7.78 (m, 4H, Ar-H), 7.60-7.57 (m, 2H, Ar-H), 7.53-7.48 (m, 4H, Ar-H), 7.42 – 7.37 (m, 2H, Ar-H), 7.28 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.93-6.86 (m, 4H, Ar-H), 6.03 (d, *J* = 2.0 Hz, 2H, Ar-H), 1.91 (s, 6H,CH_3).

Synthesis of 2,3',6',7-tetraphenyl-10H-spiro[acridine-9,9'-fluorene] **(6)**

2,3',6',7-tetraphenyl-10H-spiro[acridine-9,9'-fluorene] was synthesized use the same reaction conduction with intermediate 3 between di-*p*-tolylamine and 9H-fluoren-9-one. The compound was yellow powder (Yield 45%).^1H NMR (500 MHz, DMSO-d_6, δ): 9.67 (s, 1H, N-H), 8.52 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.85 (d, *J* = 9.0 Hz, 4H, Ar-H), 7.65-7.63 (dd, *J* = 10.0 Hz, *J* = 2.5 Hz, 2H, Ar-H), 7.52-7.39 (m, 10H, Ar-H), 7.25(t, *J* = 9.5 Hz, 4H, Ar-H), 7.18-7.12 (m, 8H, Ar-H), 6.52 (d, *J* = 2.5 Hz, 2H, Ar-H).

Synthesis of ***MH***

A mixture of intermediate 3 (359 mg, 1 mmol), intermediate 2 (507 mg, 1.1 mmol),

$Pd_2(dba)_3$ (46 mg, 0.05 mmol), $^tBu_3PHBF_4$ (37 mg, 0.13 mmol) and tBuONa (190 mg, 2 mmol) in xylene (5 ml) was stirred at 110 °C under nitrogen for 12 h. After cooling to room temperature, the mixture was washed with brine and the organic phase was dried with anhydrous sodium sulfate. After removing of the solvent, the mixture was applied to a silica gel column using petroleum ether/ethyl acetate (50/1 to 100/1, v/v) as eluent to give the pure product as yellow powder(358 mg, Yield: 48.4%).^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.82 (s, 2H, Ar-H), 7.82-7.78 (m, 4H, Ar-H), 7.40-7.31 (m, 4H, Ar-H), 7.42-7.37 (m, 4H, Ar-H), 7.31-7.27 (m, 2H, Ar-H), 6.73-6.71 (dd, J = 8.8 Hz, J = 2.0 Hz, 2H, Ar-H), 6.43 (d, J = 8.8 Hz, 2H, Ar-H), 6.62 (s, 2H, Ar-H), 1.95 (s, 6H, CH_3), 1.48 (s, 18H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 147.51, 145.47, 139.35, 139.06, 131.86, 130.38, 129.77, 128.49, 128.12, 127.89, 127.63, 127.57, 125.94, 124.84, 121.80, 119.92, 118.17, 114.80, 111.11, 57.00, 34.68, 31.64, 20.50. MALDI-TOF-MS(M): m/z 740.7 $[M+H]^+$. Anal. calcd for $C_{30}H_{24}N_4$(%): C 86.06, H 6.22, N 1.62; found: C 86.55, H 5.92, N 1.89.

Synthesis of ***MP***

A mixture of intermediate 5 (512 mg, 1 mmol), intermediate 2 (507 mg, 1.1 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $^tBu_3PHBF_4$ (37 mg, 0.13 mmol) and $Cs_2(CO)_3$ (651 mg, 2 mmol) in toluene (5 ml) was stirred at 85 °C under nitrogen for 12 h. After cooling to room temperature, the mixture was washed with brine and the organic phase was dried with anhydrous sodium sulfate. After removing of the solvent, the mixture was applied to a silica gel column using petroleum ether/ ethyl acetate (50/1 to 100/1, v/v) as eluent to give the pure product as yellow powder (464 mg, Yield: 52.2%). ^{1}H NMR

(400 MHz, $CDCl_3$, δ): 8.82 (d, *J* = 2.4 Hz, 2H, Ar-H) , 8.10 (s, 2H, , Ar-H), 7.84-7.81 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H, Ar-H), 7.74 (d, *J* = 7.2 Hz, 4H, Ar-H), 7.57-7.54 (m, 6H, Ar-H), 7.49 (t, *J* = 1.2 Hz, 4H, Ar-H), 7.40-7.36 (m, 4H, Ar-H), 6.77-6.75 (dd, *J* = 8.4 Hz, *J* = 2 Hz, 2H, Ar-H), 6.46 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.34 (d, *J* = 2.4 Hz, 2H, Ar-H), 2.00 (s, 6H, CH_3), 1.52 (s, 18H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 159.51, 158.84, 155.67, 147.42, 145.45, 141.35, 140.76, 139.80, 139.06, 131.84, 130.36, 129.89, 128.85, 128.20, 127.85, 127.34, 127.30, 126.10, 124.71, 121.77, 118.61, 118.13, 114.85, 111.04, 56.61, 34.65, 31.60, 20.51. MALDI-TOF-MS(M): m/z 892.5 $[M+H]^+$. Anal. calcd for $C_{30}H_{24}N_4$(%): C 87.44, H 6.05, N 1.35; found: C 87.44, H 5.80, N 1.56.

Synthesis of ***PP***

PP was synthesized use the same reaction conduction with BNO-Me between intermediate 6 and intermediate 2. The compound was yellow powder (Yield 43%). ^1H NMR (400 MHz, CD_2Cl_2, δ): 8.95 (d, *J* = 2.8 Hz, 2H, Ar-H), 8.25 (d, *J* = 1.6 Hz, 2H, Ar-H), 7.95-7.92 (dd, *J*= 8.8 Hz, J_2= 2.4 Hz, 2H, Ar-H), 7.84-7.82 (m, 4H, Ar-H), 7.75-7.65 (m, 6H, Ar-H), 7.59-7.54 (m, 6H, Ar-H), 7.45 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.34-7.25 (m, 10H, Ar-H), 7.21-7.17 (m, 2H, Ar-H), 6.90 (d, *J* = 2.0 Hz, 2H, Ar-H), 6.78 (d, *J* = 8.8 Hz, 2H, Ar-H), 1.60 (s, 18H, CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2, δ): 159.76, 158.84, 155.56, 146.61, 145.76, 141.15, 141.10, 140.42, 140.24, 139.93, 133.77, 132.14, 130.49, 128.85, 128.55, 127.81, 127.43, 127.26, 126.54, 126.24, 126.14, 126.02, 125.85, 125.38, 121.66, 119.00, 118.02, 115.66, 115.05, 110.86, 56.73, 34.58, 31.33. MALDI-TOF-MS(M): m/z 1018.4 $[M+H]^+$. Anal. calcd for $C_{30}H_{24}N_4$(%): C

88.58, H 5.71, N 1.18; found: C 89.09, H 5.49, N 1.38.

Exciton Lifetime and Rate Constant

The rate constants of ISC (k_{ISC}) and RISC (k_{RISC}) of three emitters based on the following equations:

$$k_p = \frac{1}{\tau_p} \tag{1}$$

$$k_d = \frac{1}{\tau_d} \tag{2}$$

$$k_{r,s} = \Phi_p k_p + \Phi_d k_d \approx \Phi_p k_p \tag{3}$$

$$k_{RISC} \approx \frac{k_p k_d \Phi}{k_{r,s}} \tag{4}$$

$$k_{ISC} \approx \frac{k_p k_d \Phi_d}{k_{RISC} \Phi_p} \tag{5}$$

In this study, the prompt PLQY (Φ_{p}) and delayed PLQY (Φ_{d}) were determined by using the total PLQY and the integrated intensity ratio between prompt and delayed components which was calculated from transient photoluminescence measurements. The intensity ratio between prompt ($\mathrm{r_p}$) and delayed ($\mathrm{r_d}$) components were determined using two fluorescent lifetimes (τ_{p}, τ_{d}) and fitting parameter ($\mathrm{A_p}$, $\mathrm{A_d}$) as follow.

$$I\,(t) = A_p e^{-\frac{t}{\tau_p}} + A_d e^{-\frac{t}{\tau_d}} \tag{6}$$

$$r_p = \frac{A_p \tau_p}{A_p \tau_p + A_d \tau_d} \tag{7}$$

$$r_d = \frac{A_d \tau_d}{A_p \tau_p + A_d \tau_d} \tag{8}$$

Then, the prompt PLQY (Φ_{p}) and delayed PLQY (Φ_{d}) were determined using ratio

(r_p, r_d) and total PLQY.

$$\Phi_{total} = \Phi_p + \Phi_d \tag{9}$$

$$\Phi_p = r_p \Phi_{total} \tag{10}$$

$$\Phi_d = r_d \Phi_{total} \tag{11}$$

Supplementary Figures

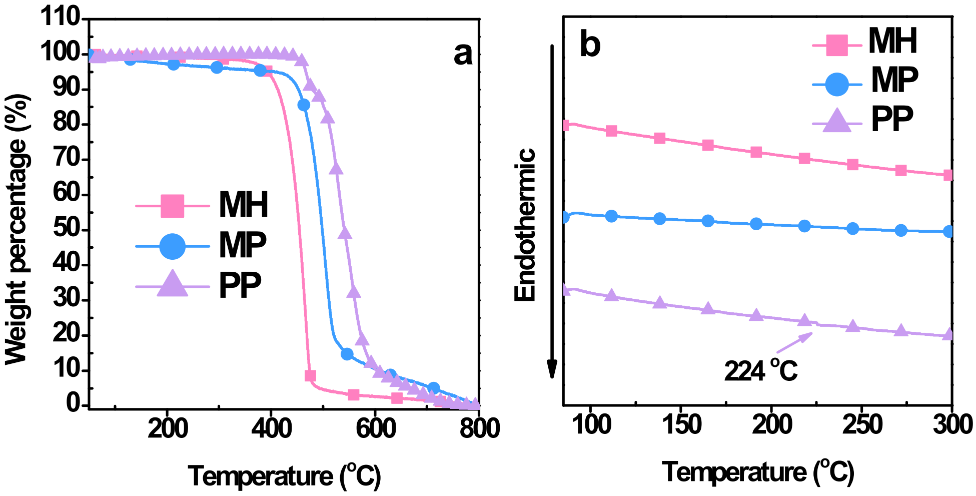


Figure S1. (a) TGA and (b) DSC curves of MH, MP and PP recorded under N_2 with a heating rate of 10 K/min.

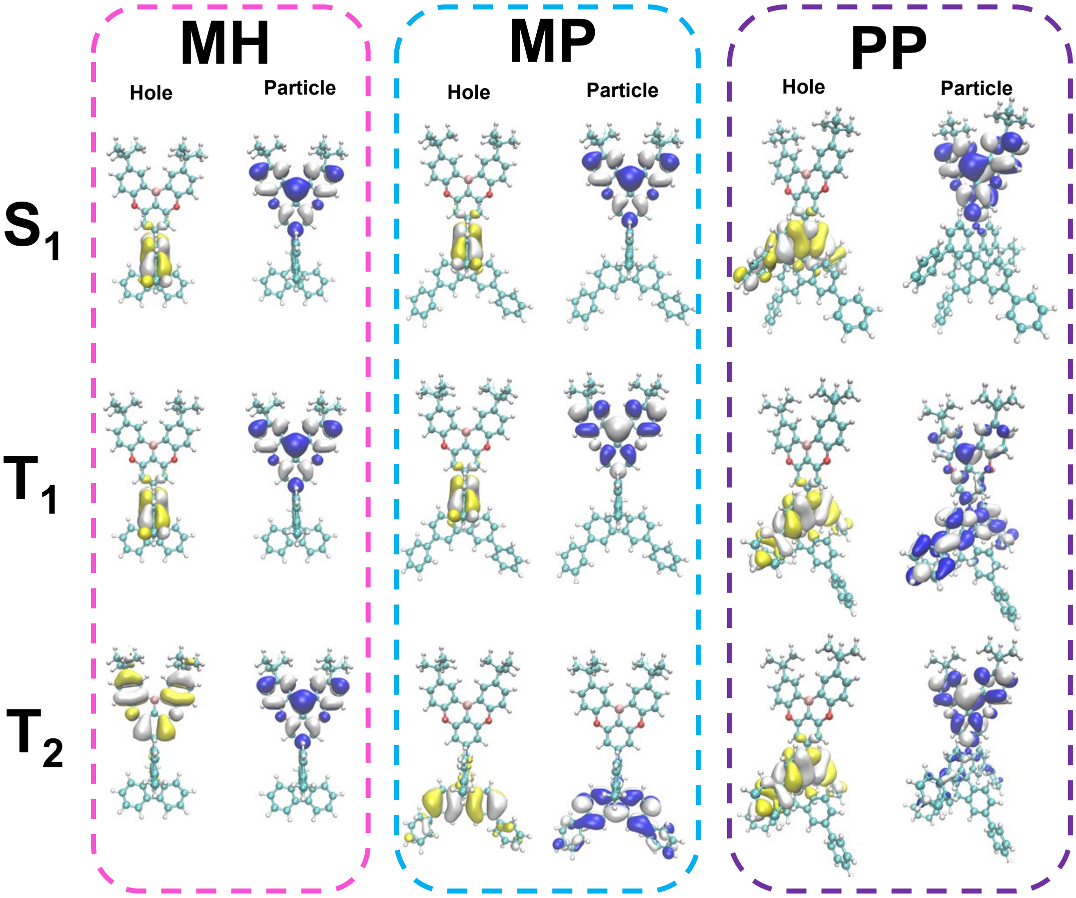


Figure S2. Natural transition orbitals analysis of MH, MP and PP.

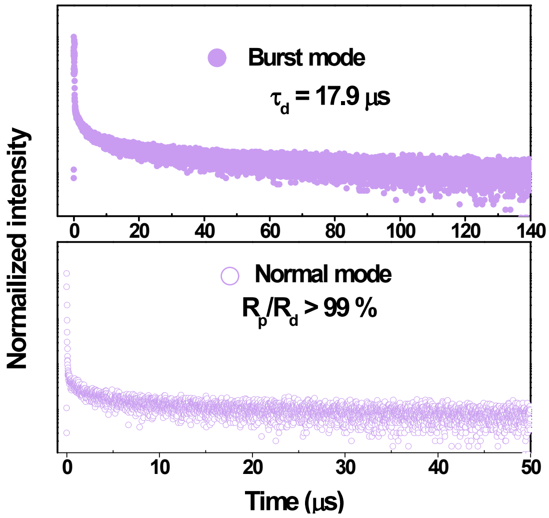


Figure S3. Transient PL decay of PP in doped films (10 wt% in PPF) under normal and burst mode.

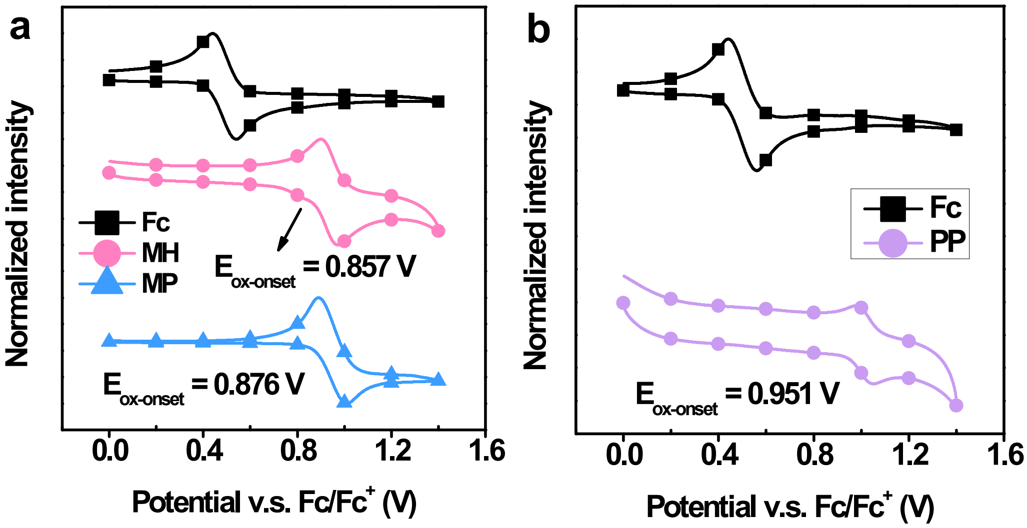


Figure S4. CV profiles of a) MH, MP and b) PP recorded under the scanning speed of 100 mV/s.

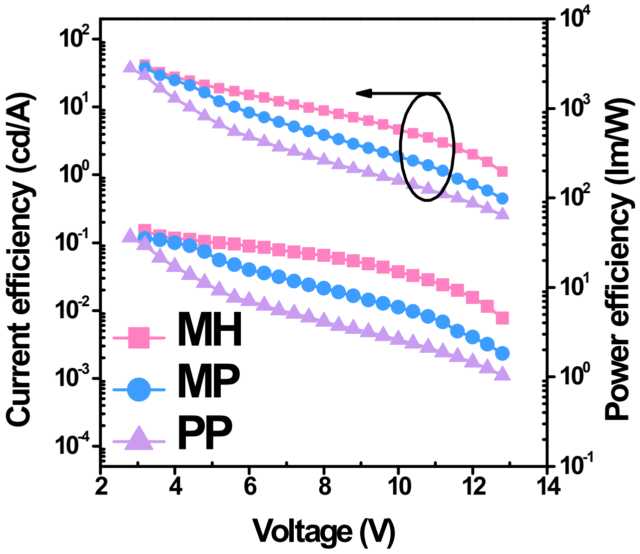


Figure S5. Device performances of MH, MP and PP.

Table S1. EL performance of MH, MP and PP.

Emitters	Current efficiency^a (cd/A)	Power efficiency^a (lm/W)
MH	42.2	42.9
MP	38.2	35.0
PP	37.6	36.2

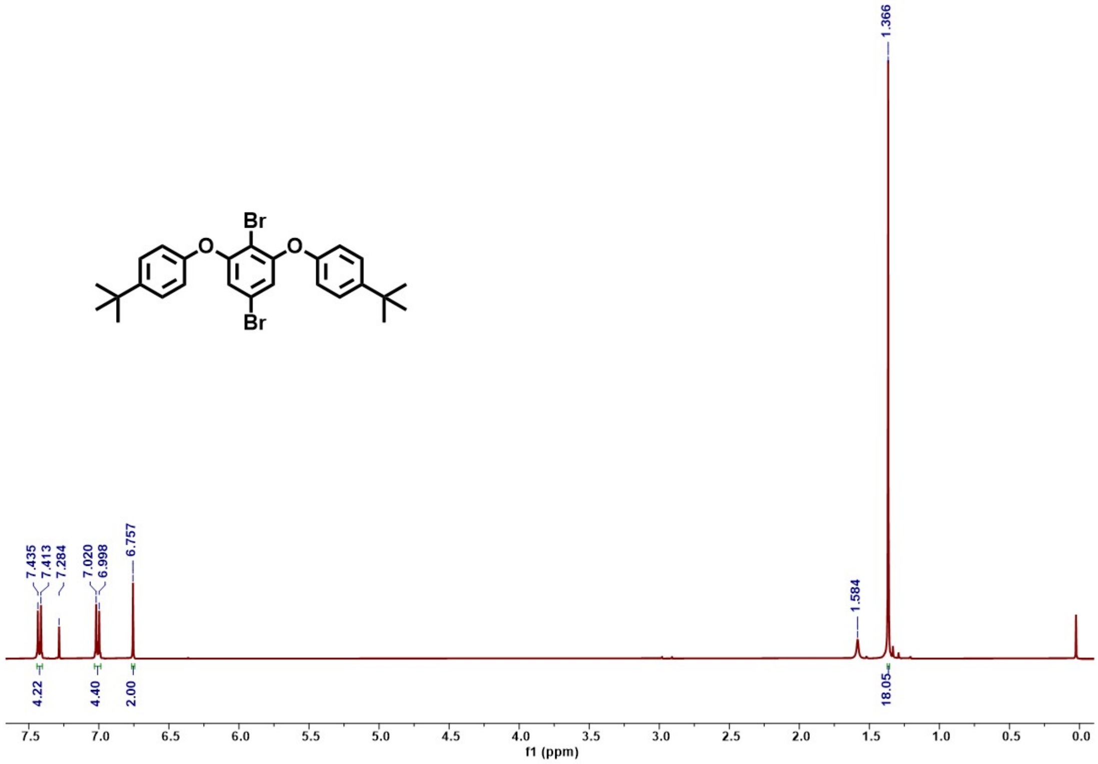
[a] The maximum value of current efficiency and power efficiency of devices based on MH, MP and PP

Reference

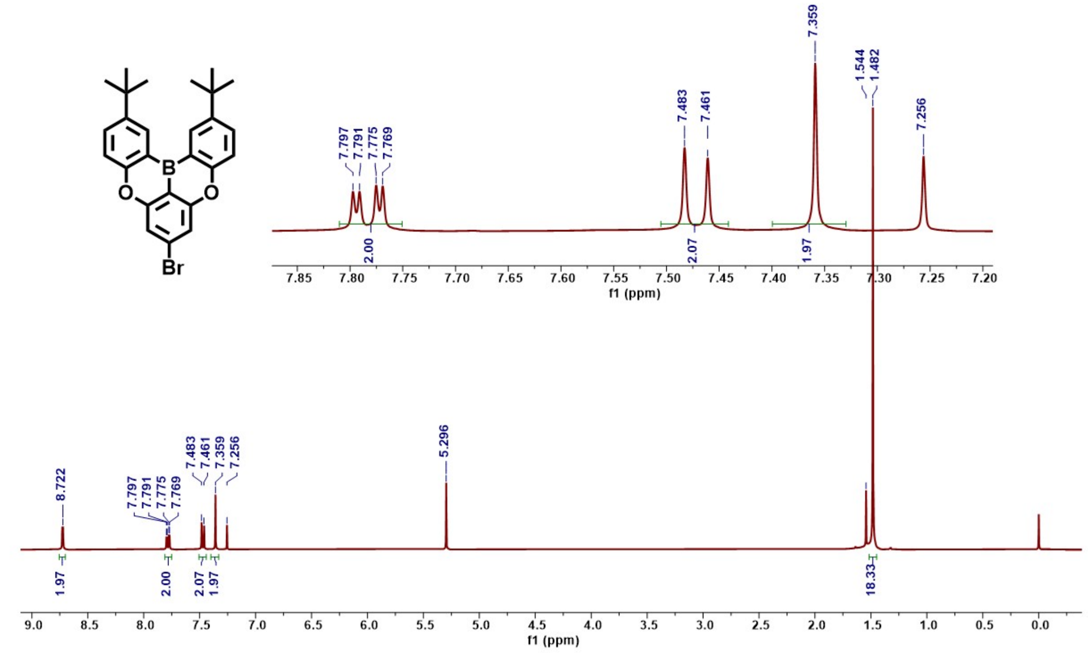
[1] T. Lu, F. Chen, J. Comput. Chem. 33 (2012), 580-592.

NMR spectra

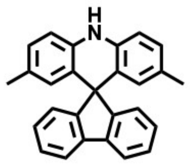
^{1}H NMR spectra of **1** ($CDCl_3$)

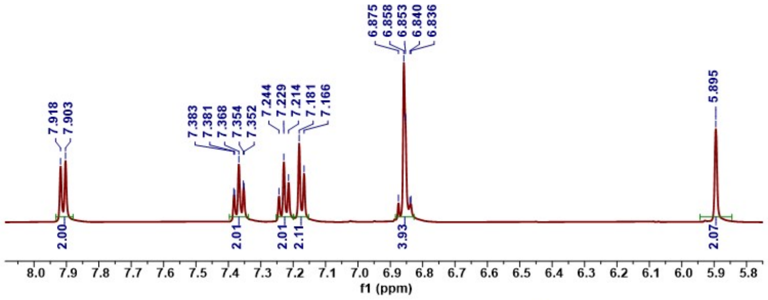


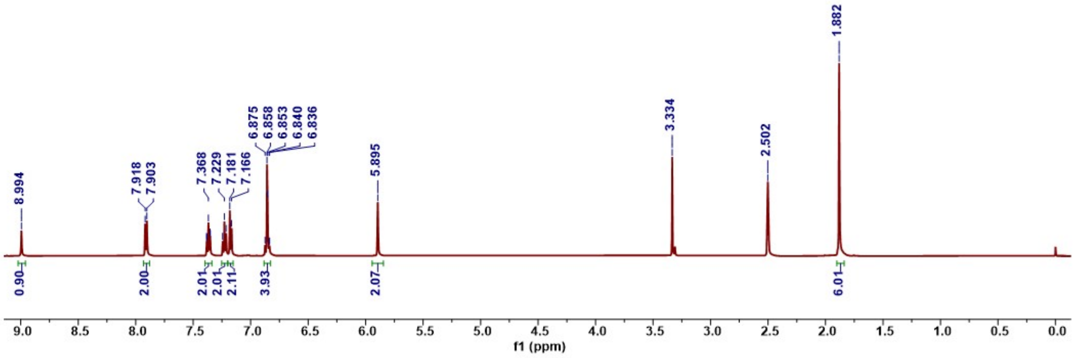
^{1}H NMR spectra of **2** ($CDCl_3$)



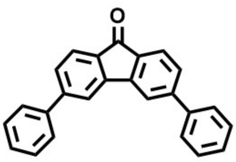
^{1}H NMR spectra of **3** (DMSO-d_6)

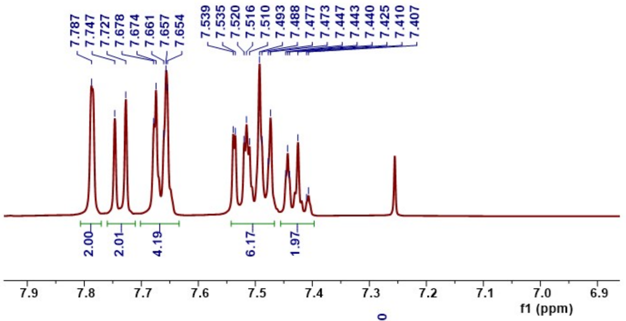


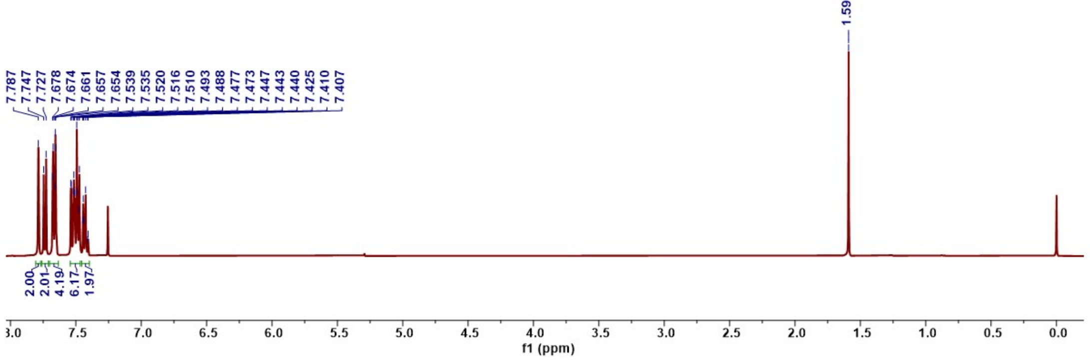




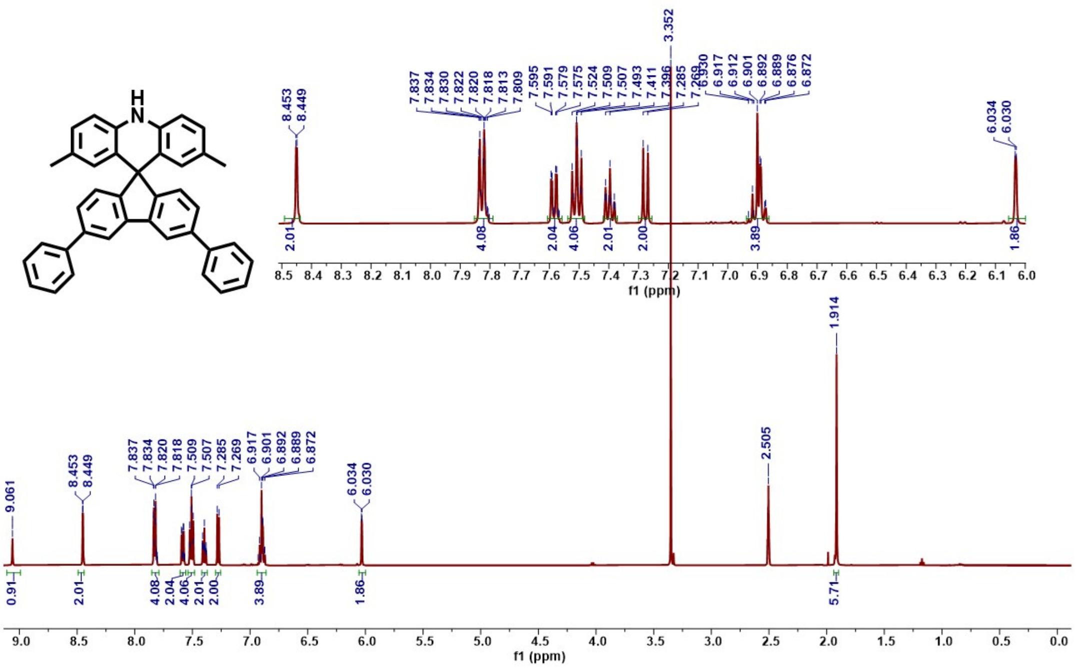
^{1}H NMR spectra of **4** (CDCl$_3$)



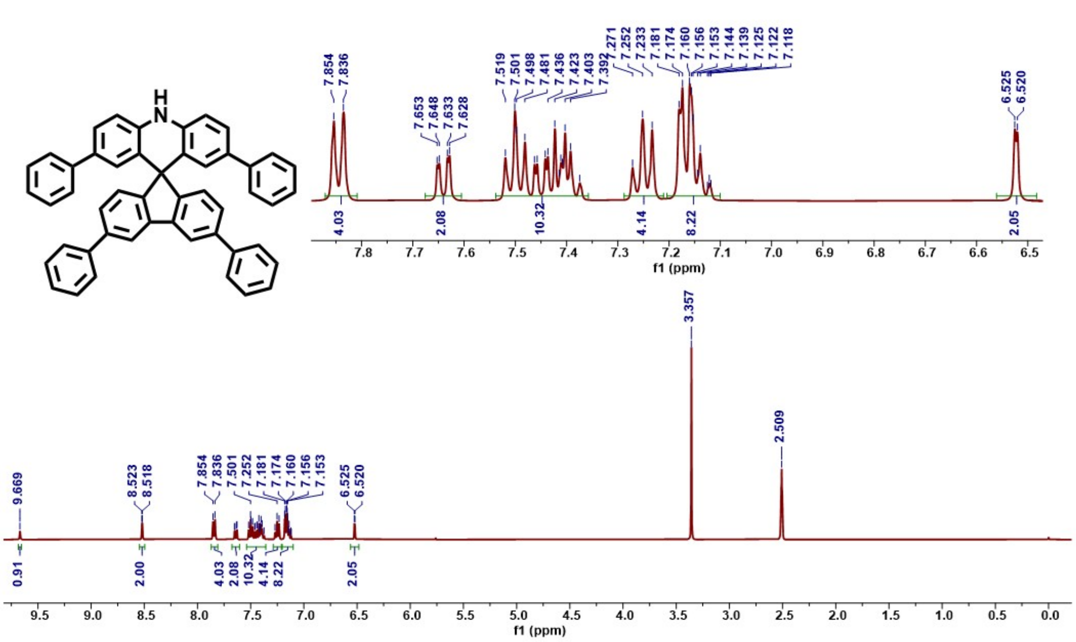




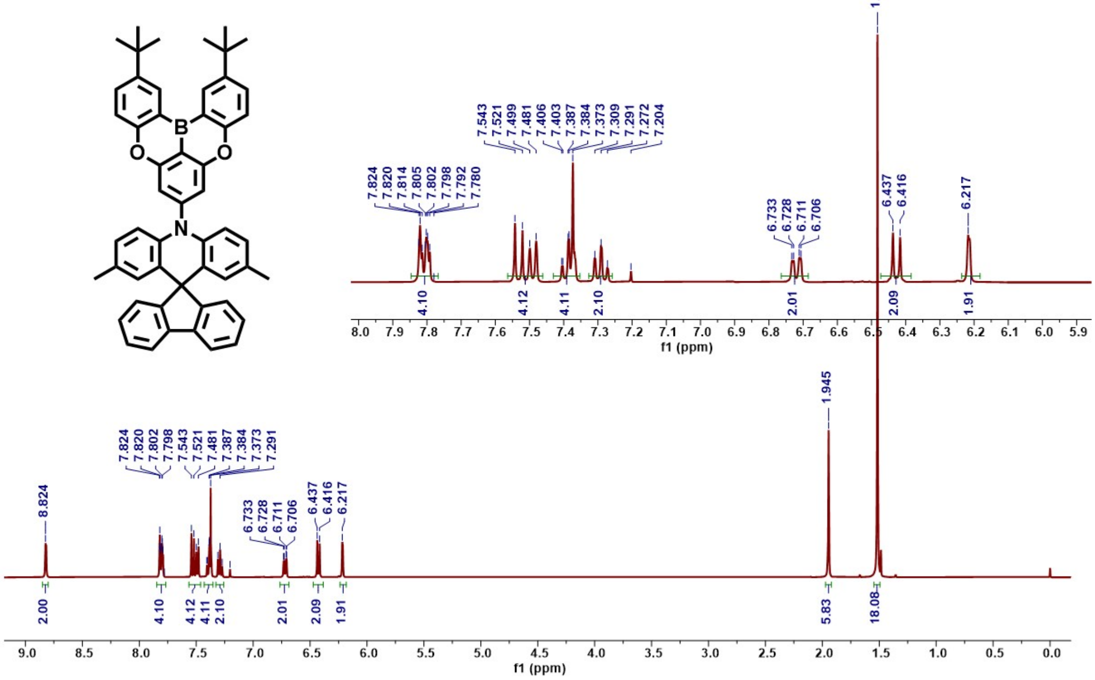
^{1}H NMR spectra of **5** (DMSO-d_6)



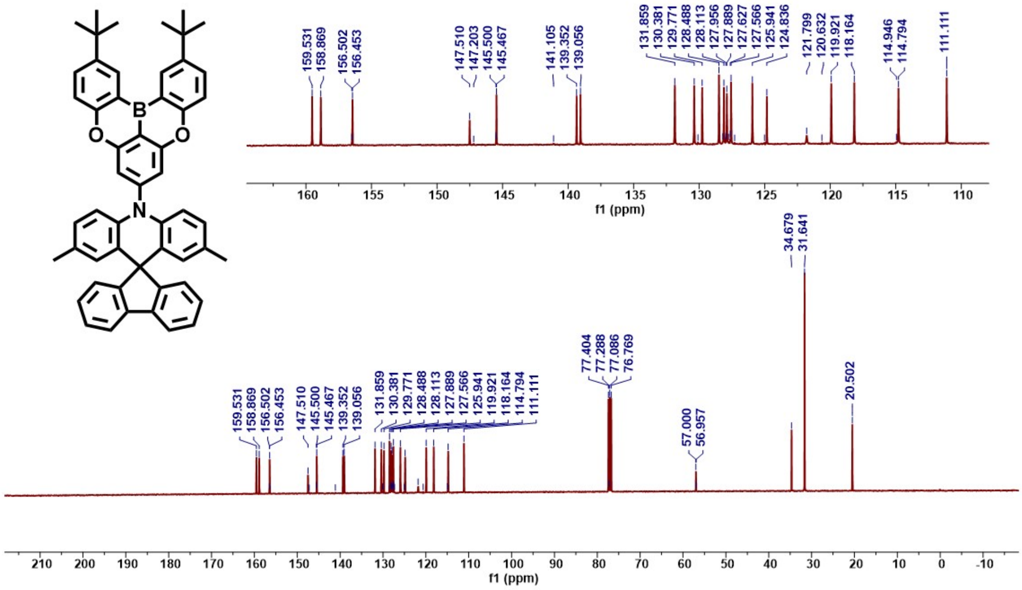
^{1}H NMR spectra of **6** (DMSO-d_6)



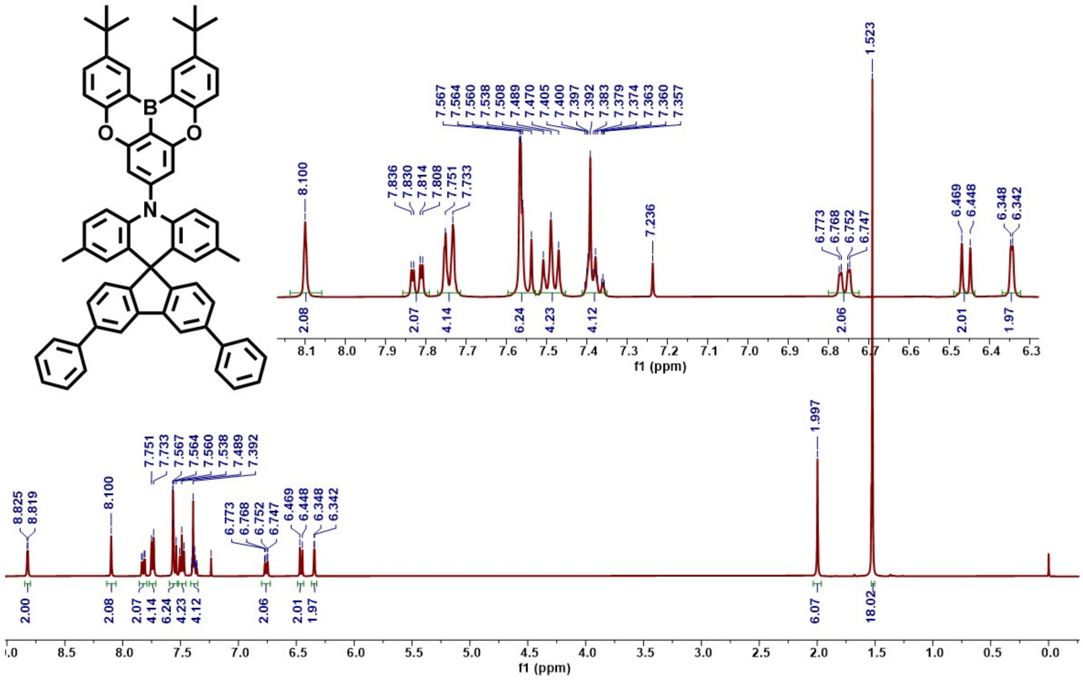
^{1}H NMR spectra of **MH** ($CDCl_3$)



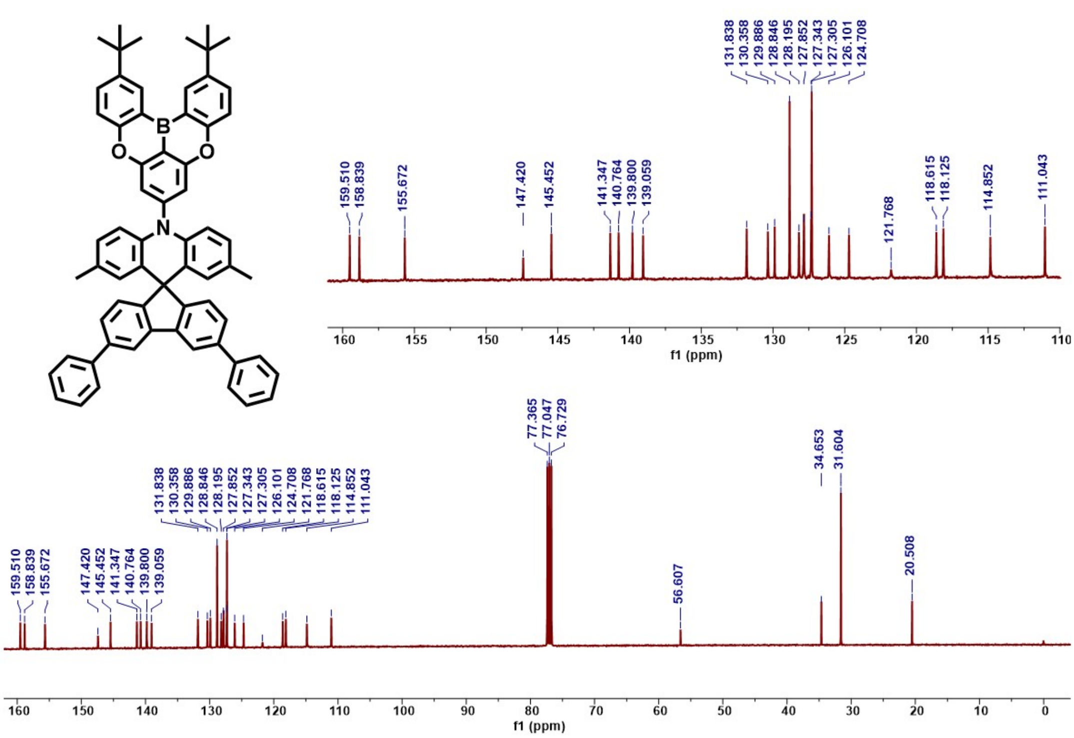
^{13}C NMR spectra of **MH** ($CDCl_3$)



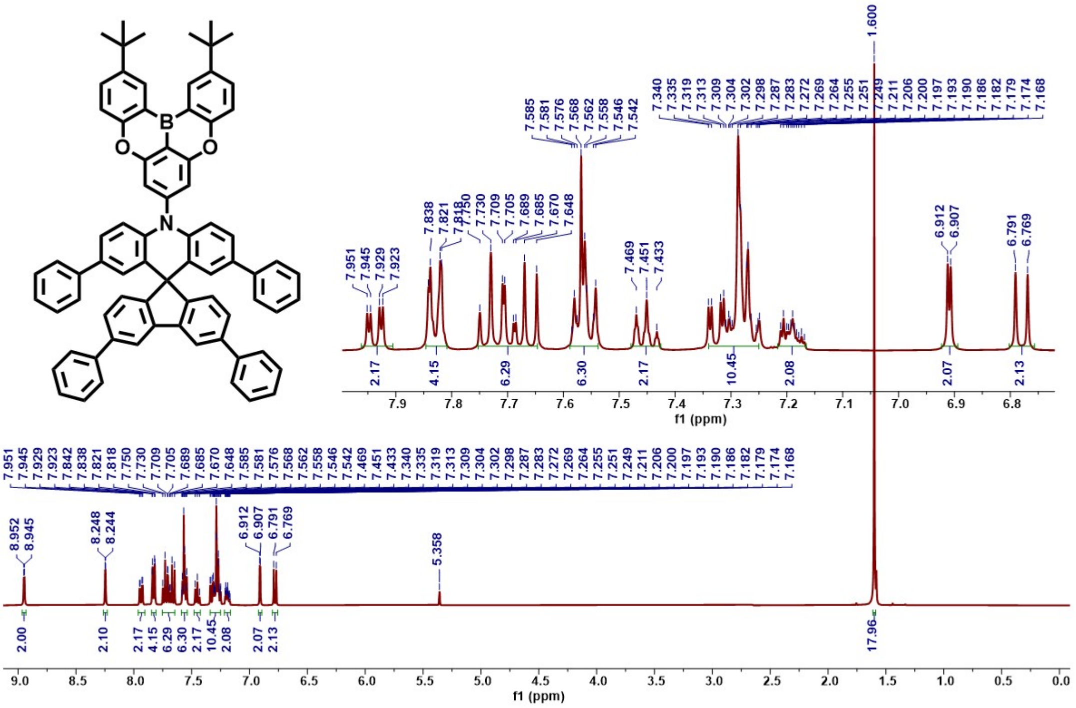
^{1}H NMR spectra of **MP** ($CDCl_3$)



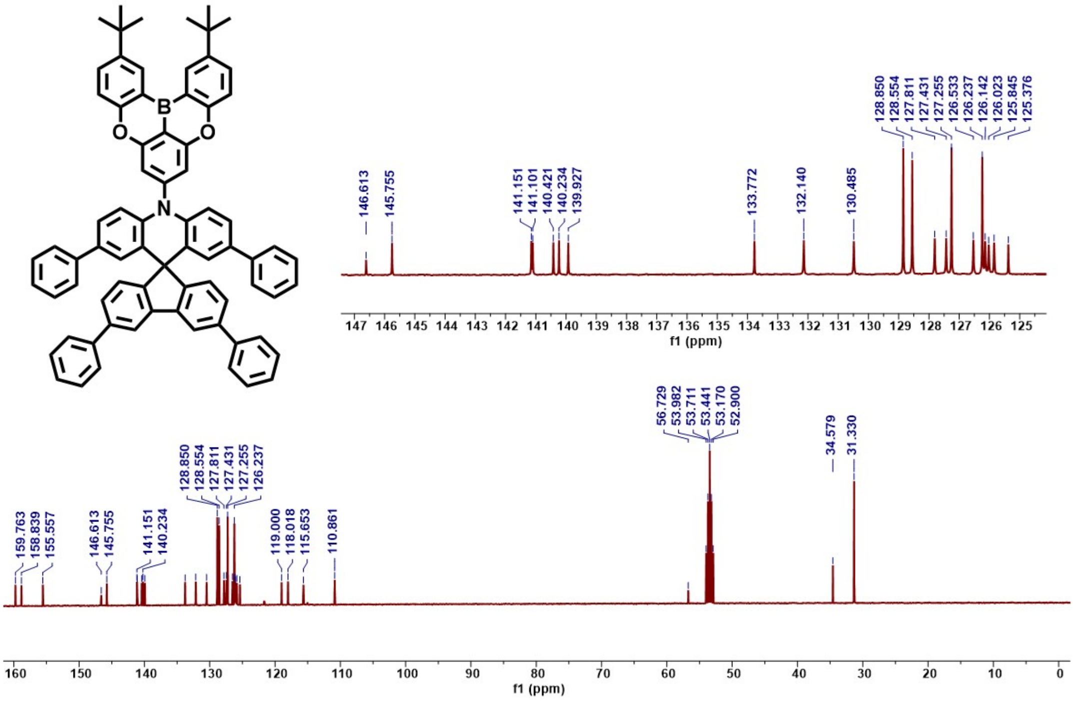
^{13}C NMR spectra of **MP** ($CDCl_3$)



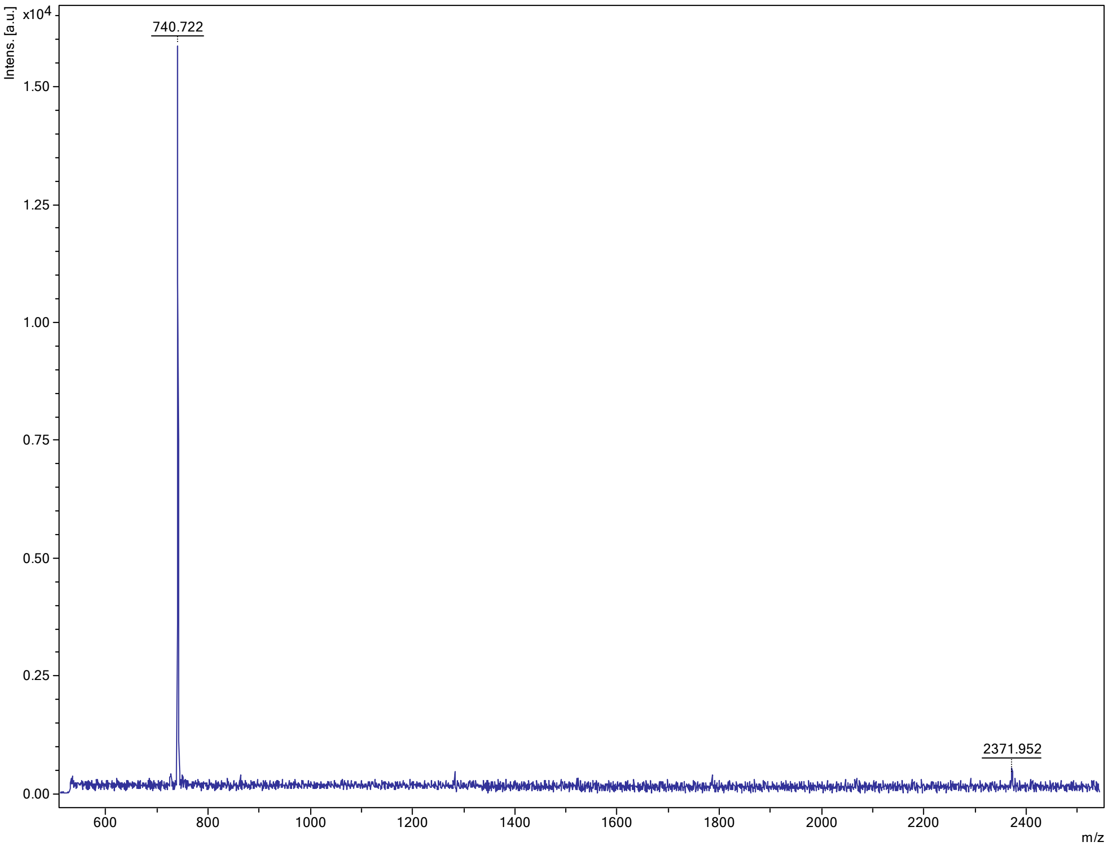
^{1}H NMR spectra of **MP** (CDCl$_2$)



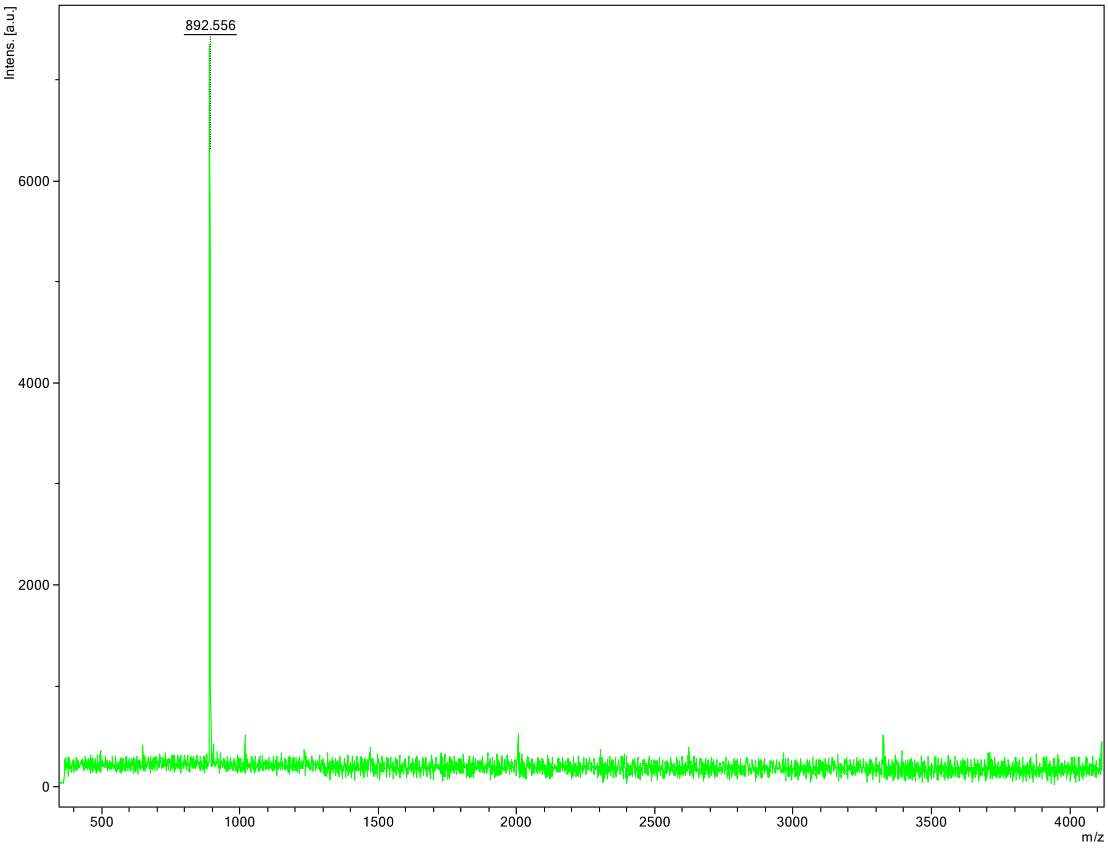
^{13}C NMR spectra of **PP** (CDCl$_2$)



Mass spectrum of MH



Mass spectrum of MP



Mass spectrum of MP