

Supporting Information for

Synthesis and Physical Properties of the Conjugated Dendrons

Bearing Twisted Acenes Used in Solution-Processing of Organic

Light-Emitting Diodes

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Experimental Section

Materials and Characterization:

NMR spectra were measured on Bruker 600 MHz spectrometer using CDCl_3 as a solvent without any internal standard. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF. UV-vis and fluorescence spectra were carried out on Shimadzu UV-2550 and RF5300PC spectrometer. Cyclic voltammograms were measured on CHI 630 A electrochemical analyzer with a standard three-electrode cell in a 0.1 M tetrabutylammonium hexafluorophosphate solution dissolved in CH_2Cl_2 in nitrogen atmosphere at a rate of 0.1 V s^{-1} .

Device Fabrication and Measurement

The general procedure was presented as follows. Indium-tin oxide (ITO)-coated glass substrates were pre-cleaned and treated by UV ozone for 15 min. PEDOT: PSS (Baytron PVP CH 8000) aqueous solution was spin-coated onto the ITO substrate and baked at 110°C for 30 min. Then the substrates were transferred to glove box, where the emitting layers (10 mg/mL) were spin-coated onto the PEDOT:PSS layer from chloroform solution and annealed at 100°C for 30 min. In evaporation chamber, TPBi (Nichem Fine Technology Co. Ltd.) was evaporated at an evaporation rate of 2 Hz/s under a pressure of $1.1 \times 10^{-3} \text{ Pa}$ and the LiF/Al bilayer cathode was evaporated at evaporation rates of 0.1 and 10~15 Hz/s for LiF and Al (Sigma- aldrich), respectively, under a pressure of $1.1 \times 10^{-3} \text{ Pa}$. The current-luminance-voltage characteristics were measured by a Keithley source measurement unit (Keithley 2400 and Keithley 2000)

with a calibrated silicon photodiode. The electroluminescent spectra were carried out with a PR650 Spectrophotometer.

Synthesis

Compound

1,4-di(2-(5,12-diphenyl-6:7,10:11-bis(4'-tert-butylbenzo)tetracene))benzene (**DPPh**).

A mixture of compound **1** (250 mg, 0.39 mmol), 1,4-benzenediboronic acid (**2**, 20 mg, 0.12 mmol), Pd(PPh₃)₄ (52 mg, 0.045 mmol) and Na₂CO₃ (437 mg, 4 mmol) in THF/H₂O (40 mL/4mL, v/v, 10:1) was stirred in 60 °C for 5 days in nitrogen atmosphere. The mixture solution was cooled to room temperature and brine was added. After extracted with methylene chloride (50 mL × 4), the organic phase was collected, dried with sodium sulfate and further concentrated in reduced pressure. The as-obtained residue was purified through silica gel column chromatography with petroleum ether firstly and then methylene chloride/petroleum ether (v/v, 1:20) to give compound **DPPh** (yellow solid, 41 mg, 28%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 8.17 (m, 4H), 8.14 (d, 2H), 7.95 (s, 1H), 7.94 (s, 1H), 7.85 (m, 8H), 7.77 (d, 1H), 7.76 (d, *J* = 6.0 MHz, 1H), 7.71 (s, 4H), 7.66-7.63 (m, 8H), 7.59-7.57 (m, 8H), 7.50-7.48 (m, 4H), 1.13 (s, 36H). ¹³C NMR (150 MHz, CDCl₃, 298 K): δ = 147.29, 147.27, 142.66, 142.60, 140.05, 137.23, 136.43, 135.98, 132.50, 132.42, 132.34, 131.36, 130.32, 130.24, 129.63, 129.60, 129.38, 129.33, 127.71, 127.64, 127.61, 126.92, 124.99, 124.44, 123.89, 122.28, 122.24, 34.77, 31.40. MS (MALDI-TOF): Calc. for C₉₄H₇₈: [M] 1206.61, found: [M+1] 1207.6.

Compound

1,3-di(2-(5,12-diphenyl-6:7,10:11-bis(4'-tert-butylbenzo)tetracene))benzene (**DMPH**).

A mixture of compound **1** (254 mg, 0.39 mmol), 1,3-benzenediboronic acid (**3**, 22 mg, 0.13 mmol), Pd(PPh₃)₄ (52 mg, 0.045 mmol) and Na₂CO₃ (432 mg, 4 mmol) in THF/H₂O (40 mL/4mL, v/v, 10:1) was stirred in 65 °C for 5 days in nitrogen atmosphere. After cooling to room temperature, brine was added and then the solution was extracted with methylene chloride (50 mL × 3). The organic phase was collected, dried with sodium sulfate and further concentrated in reduced pressure. The crude product was purified through silica gel column chromatography with methylene chloride/petroleum ether (v/v, 3.5:100) to give compound **DMPH** (yellow solid, 70 mg, 44%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 8.20 (d, *J* = 6.0 MHz, 2H), 8.19 (d, *J* = 6.0 MHz, 2H), 8.16 (d, *J* = 6.0 MHz, 2H), 7.97 (d, *J* = 12.0 MHz, 2H), 7.91 (s, 1H), 7.86 (d, *J* = 6.0 MHz, 8H), 7.76 (d, 1 H), 7.75 (d, *J* = 6.0 MHz, 1H), 7.66 (d, *J* = 6.0 MHz, 8H), 7.60 (t, 6H), 7.54 (t, 4H), 7.52-7.49 (m, 3H), 7.44 (t, 2H), 1.14 (s, 18H), 1.13 (s, 18H). ¹³C NMR (150 MHz, CDCl₃, 298 K): δ = 147.30, 147.28, 142.80, 142.68, 142.59, 141.80, 137.77, 136.49, 135.99, 132.50, 132.45, 132.33, 131.41, 130.35, 129.64, 129.36, 127.68, 127.57, 126.95, 126.30, 124.78, 123.95, 123.92, 122.30, 122.28, 34.79, 31.41. MS (MALDI-TOF): Calc. for C₉₄H₇₈: [M] 1206.61, found: [M+1] 1207.5.

Compound

1,3,5-tri(2-(5,12-diphenyl-6:7,10:11-bis(4'-tert-butylbenzo)tetracene))benzene

(**TPPh**). A mixture of compound **4** (692 mg, 0.3 mmol), 1,3,5-tribromobenzene (**5**, 19

mg, 0.06 mmol), Pd(PPh₃)₄ (60 mg, 0.05 mmol) and Na₂CO₃ (416 mg, 4 mmol) in THF/H₂O (40 mL/4mL, v/v, 10:1) was stirred in 65 °C for 5 days in nitrogen atmosphere. After the solution was cooled to room temperature, brine was added. The mixture solution was then extracted with methylene chloride (50 mL × 3) and the organic phase was collected, dried with sodium sulfate. After the organic phase was concentrated in reduced pressure, the as-prepared residue was purified through silica gel column chromatography with using methylene chloride/petroleum ether (v/v, 11:100) to afford compound **TPPh** (yellow solid, 68 mg, 64%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 8.24 (s, 3H), 8.20 (s, 6H), 8.01 (d, *J* = 6.0 MHz, 3 H), 7.87-7.85 (m, 15H), 7.78 (dd, *J*¹ = 6.0 MHz, *J*² = 12.0 MHz, 3H), 7.69-7.61 (m, 18H), 7.54-7.50 (m, 9H), 7.40 (t, 3H), 1.15-1.13 (d, 54H). ¹³C NMR (150 MHz, CDCl₃, 298 K): δ = 147.32, 147.29, 142.70, 142.68, 142.51, 142.45, 137.77, 136.53, 135.99, 132.49, 132.47, 132.32, 131.48, 129.99, 129.63, 129.35, 127.77, 127.63, 127.58, 126.94, 125.44, 125.27, 124.87, 123.94, 122.30, 34.79, 34.78, 31.42, 31.39. MS (MALDI-TOF): Calc. for C₁₃₈H₁₁₄: [M+1] 1770.89, found: [M+1] 1771.7.

Compound 7. A mixture of compound **4** (267 mg, 0.41 mmol) and (trimethylsilyl)acetylene (**6**, 61 mg, 0.62 mmol) were dissolved in dry THF/Et₃N solution. CuI (4 mg, 0.02 mmol), PPh₃ (13 mg, 0.04 mmol) and Pd(PPh₃)₂Cl (16 mg, 0.02 mmol) were added successively. The mixture solution was stirred at 65 °C for 10 h under nitrogen atmosphere. After cooling to room temperature, the brine was added and then the solution was extracted with methylene chloride (20 mL × 3). The organic phase was collected, dried with anhydrous sodium sulfate and the solvent was

removed in reduced pressure. The crude product was further purified through column chromatography using methylene chloride/petroleum ether (v/v, 1:15) to afford the intermediate (light yellow solid, 225 mg, 83%). The intermediate (201 mg, 0.3 mmol) and tetrabutylammonium fluoride (79 mg, 0.3 mmol) were stirred at room temperature for 0.5 h. Methylene chloride and brine were added, and then the organic phase was collected. After the organic solvent was removed, the as-formed residue was further purified through column chromatography using methylene chloride/petroleum ether (v/v, 1:15) to give compound **7** (light yellow solid, 153 mg, 86%). ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 8.14 (dd, J^1 = 6.0 MHz, J^2 = 12.0 MHz, 2H), 8.04 (s, 1H), 7.85 (s, 4H), 7.80 (d, J = 6.0 MHz, 1H), 7.57-7.54 (m, 8H), 7.48 (d, J = 12.0 MHz, 3H), 3.14 (s, 1H), 1.11 (s, 18H). ¹³C NMR (150 MHz, CDCl₃, 298 K): δ = 147.34, 147.33, 142.33, 142.09, 136.00, 135.99, 132.41, 132.36, 131.27, 130.77, 130.34, 129.44, 129.38, 129.37, 129.35, 128.01, 127.73, 127.70, 127.68, 127.63, 126.99, 126.96, 126.93, 123.95, 123.91, 122.55, 122.48, 118.88, 84.57, 77.76, 34.78, 31.40, 31.39. MS (MALDI-TOF): Calc. for C₄₆H₃₈: [M] 590.30, found: [M] 590.4.

Compound **DPyA (8)**. A mixture of compound **7** (204 mg, 0.34 mmol), **1** (263 mg, 0.41 mmol), PPh₃ (7 mg, 0.027 mmol), CuI (14 mg, 0.073 mmol) and PdCl₂(PPh₃)₂ (15 mg, 0.021 mmol) in dry THF/Et₃N (30 mL/10mL, v/v, 3:1) was stirred in 65 °C for 10 h under nitrogen atmosphere. After cooling to room temperature, brine was added and then the mixture solution was extracted with methylene chloride (30 mL × 3). The organic phase was collected, dried with anhydrous sodium sulfate and further

concentrated in reduced pressure. The crude product was purified through silica gel column chromatography with methylene chloride/petroleum ether (v/v, 70:4) to give compound **DPyA** (yellow solid, 181 mg, 46%). ^1H NMR (600 MHz, CDCl_3 , 298 K): δ = 8.14 (dd, 4H), 8.08 (s, 2H), 7.85 (s, 8H), 7.83-7.80 (t, 2H), 7.62-7.56 (m, 17H), 7.48-7.47 (m, 5H), 1.12 (d, 36H). ^{13}C NMR (150 MHz, CDCl_3 , 298 K): δ = 147.40, 147.37, 147.33, 142.41, 142.25, 142.29, 141.97, 136.07, 132.37, 131.71, 131.55, 131.15, 130.69, 130.58, 130.36, 129.51, 129.34, 127.76, 127.70, 127.64, 126.98, 126.96, 124.00, 123.96, 123.94, 122.67, 122.56, 122.45, 120.26, 118.55, 91.43, 83.29, 74.92, 34.80, 31.43. MS (MALDI-TOF): Calc. for $\text{C}_{90}\text{H}_{74}$: [M] 1155.55, found: [M] 1155.9, [M+Na $^+$] 1178.9.

Compound

1,2,3,4,5,6-hexa(2-(5,12-diphenyl-6:7,10:11-bis(4'-tert-butylbenzo)tetracene))benzene (**HPPh**). **DPyA** (222 mg, 0.91 mmol) was firstly dissolved in 1,4-dioxane (20 mL) in nitrogen atmosphere and then $\text{Co}_2(\text{CO})_8$ (6.5 mg, 0.02 mmol) was added to the solution. The mixture was stirred and refluxed for 48 h. After cooling room temperature, brine was added and the reaction mixture was extracted with methylene chloride (20 mL \times 3). The organic phase was collected, dried with anhydrous sodium sulfate and further removed in reduced pressure. The as-prepared residue was further purified through column chromatography (silica gel) with methylene chloride/petroleum ether (v/v, 70:4) to afford **HPPh** (light yellow solid, 20 mg, 9%). MS (MALDI-TOF): Calc. for $\text{C}_{270}\text{H}_{222}$: [M] 3466.65, found: [M] 3466.5.

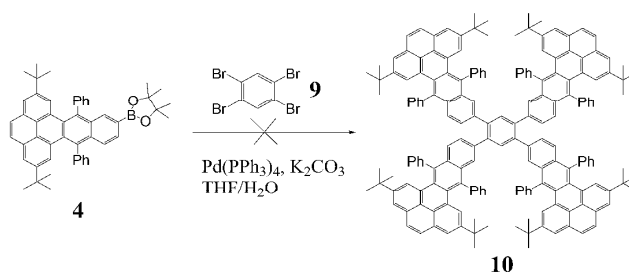


Figure S1 the synthetic procedure to compound **10**

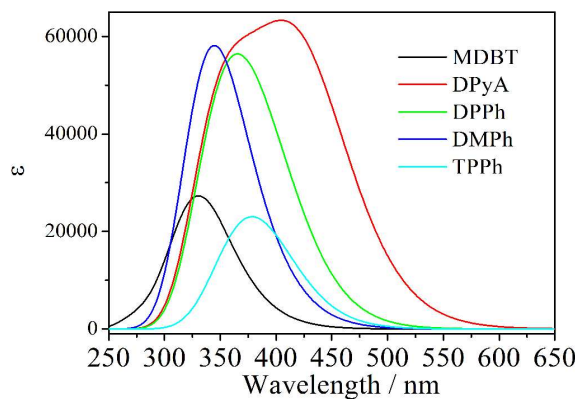


Figure S2 the simulated UV-Vis absorption spectra of compounds **MDBT** to **DPyA**

Table S1. Physical Properties of MDBT-HPPh

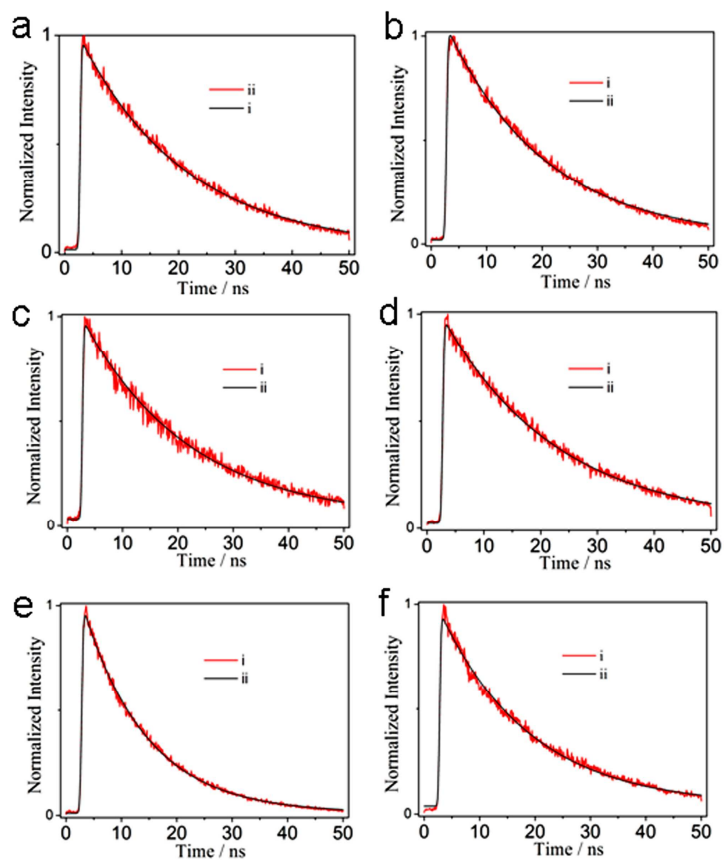
Comp.	Absorption/film (nm)	Emission/ film(nm)	Φ_f	τ [ns]	K_r [10^7 s^{-1}]	K_{nr} [10^7 s^{-1}]
MDBT	334/340	437/467	0.25	18.8	1.33	39.9
DPPh	355/355	448/483	0.47	18.0	2.61	29.4
DMPPh	348/352	445/469	0.42	19.3	2.18	21.8
TPPh	352/353	447/470	0.49	20.2	2.43	25.2
DPyA	359/360	456/483	0.67	11.5	5.83	28.7
HPPh	352/357	449/535	0.21	16.3	1.29	48.5

Table S2 CV data and thermal properties

Comp.	HOMO	HOMO (calculation)	LUMO	LUMO (calculation)	E_g	T_d (5% weight loss, $^{\circ}\text{C}$)
MDBT	-5.32	-5.33	-2.0	-1.50	3.32	370
DPPh	-5.17	-5.20	-2.29	-1.68	2.88	462
DMPPh	-5.26	-5.28	-2.01	-1.61	3.25	241
TPPh	-5.26	-5.27	-2.26	-1.62	3.00	232
DPyA	-5.31	-5.12	-2.54	-1.88	2.77	444
HPPh	-5.29		-2.27		2.92	277

Table S3 Device performances of compounds **DPPh-TPPh**

Device	V_{on} (V)	PE_{max} lm/w	LE_{max} cd/A	EQE %	100cd/m ²		1000 cd/m ²	
					PE	LE	PE	LE
DPPh	4.6	1.32	2.02	0.78	1.10	1.97	0.50	1.26
DMPH	5.4	1.30	2.23	1.06	0.79	1.46	0.16	0.51
TPPh	5.2	1.09	1.80	1.07	0.91	1.63	0.87	0.33

**Figure S3** Fluorescence decay of compounds (a) **MDBT**, (b) **DPPh**, (c) **DMPH**, (d) **TPPh**, (e) **DPyA** and (f) **HPPh** in methylene chloride, (i) experimental result, (ii) simulation line.

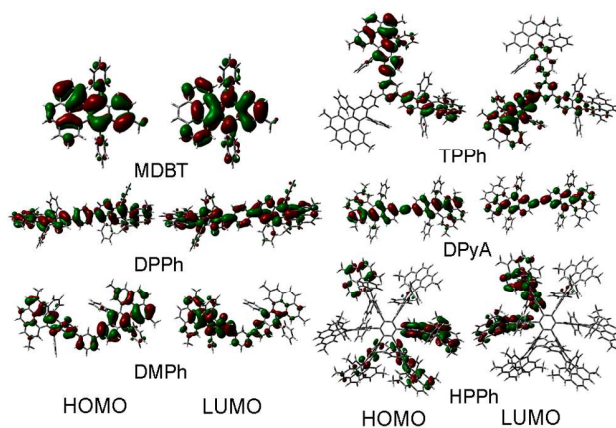


Figure S4 The frontier molecular orbitals (HOMO and LUMO) of compounds **MDBT-HPPh** obtained through DFT calculations at the B3LYP/6-31G*

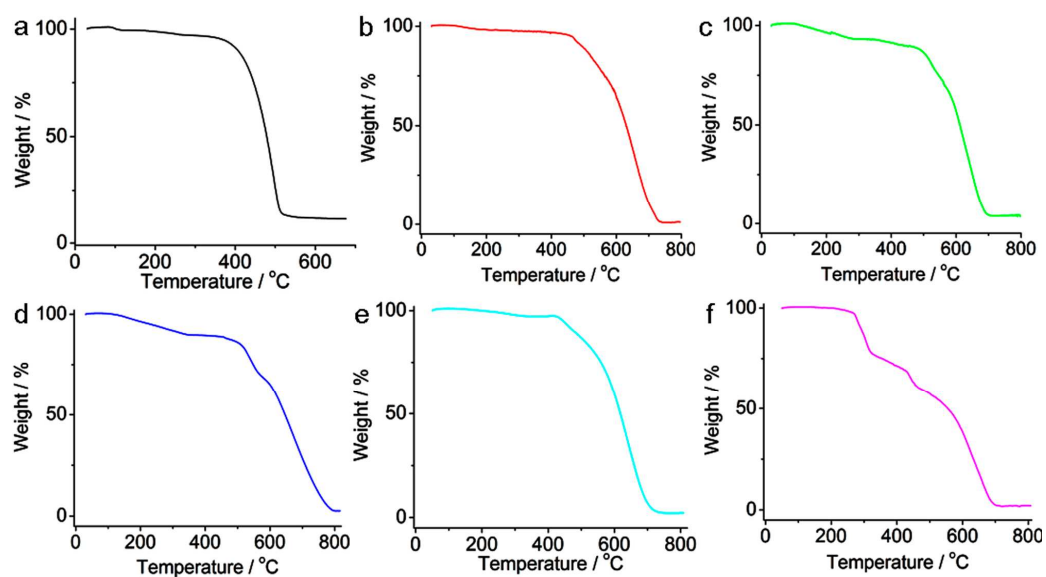
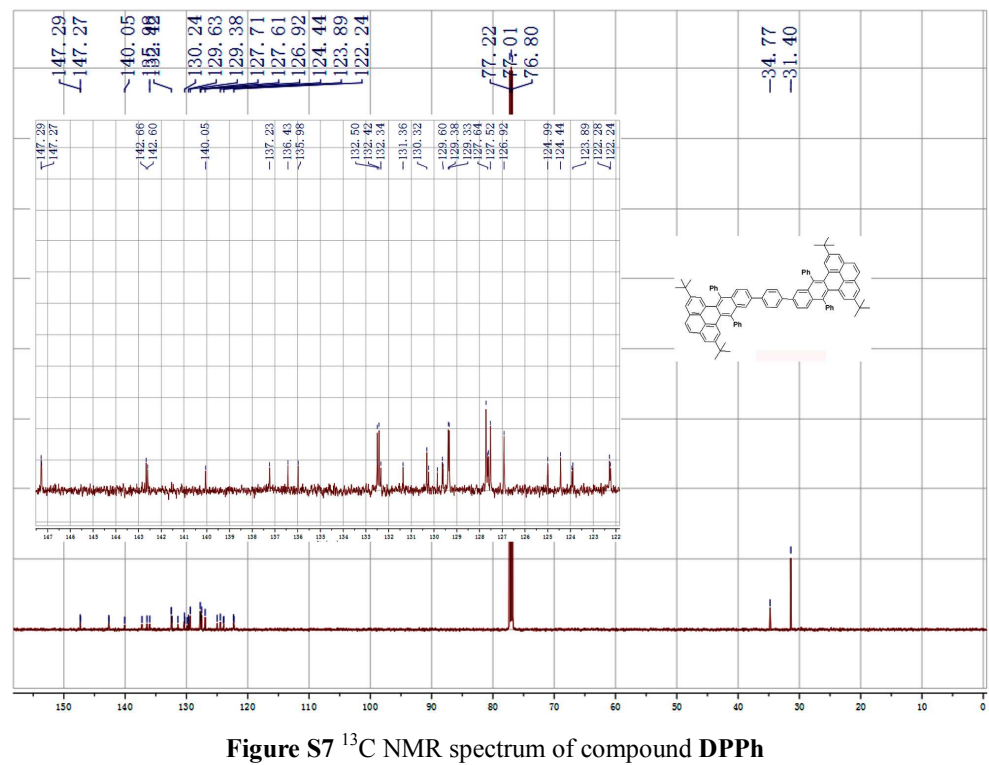
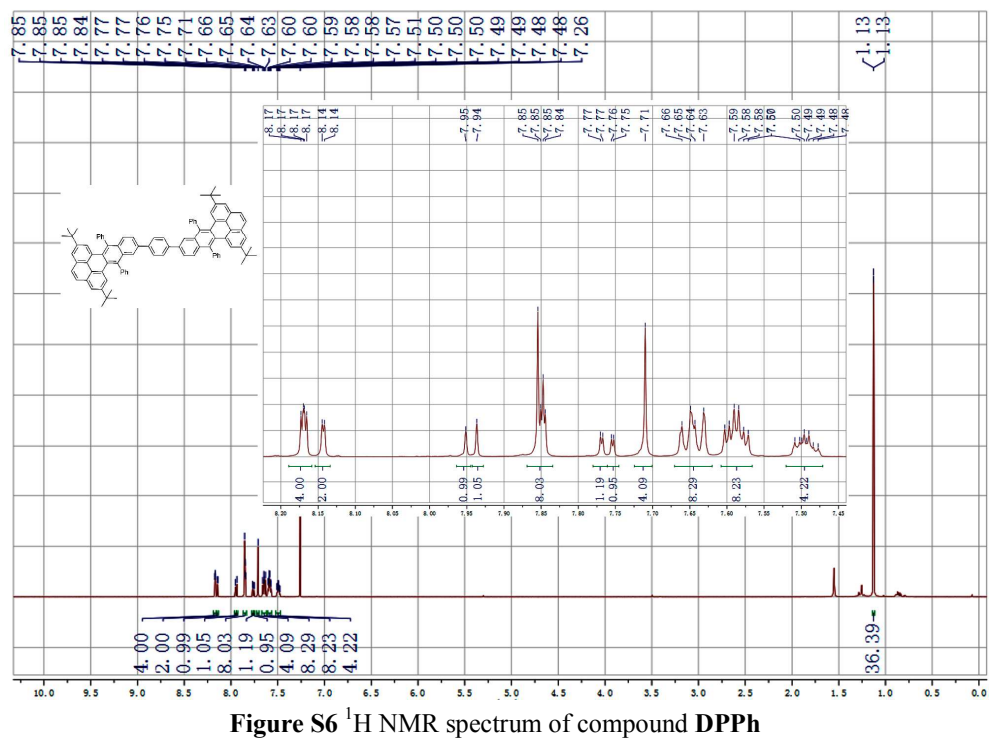


Figure S5 TGA data of (a) **MDBT**, (b) **DPPh**, (c) **DMPH**, (d) **TPPh**, (e) **DPyA**, (f) **HPPh** under nitrogen at a heating rate of 10 degree/min.



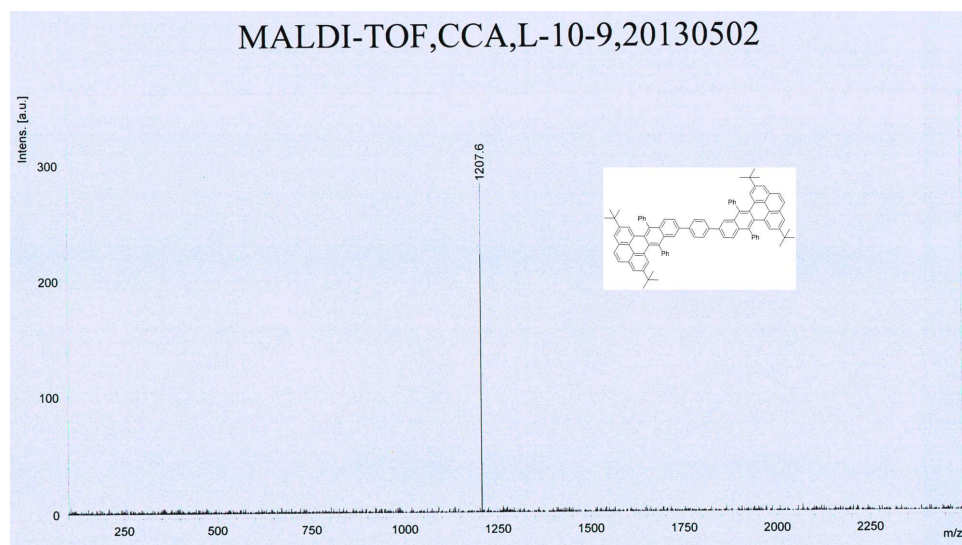


Figure S8 MALDI-TOF mass spectrum of compound **DPPh**

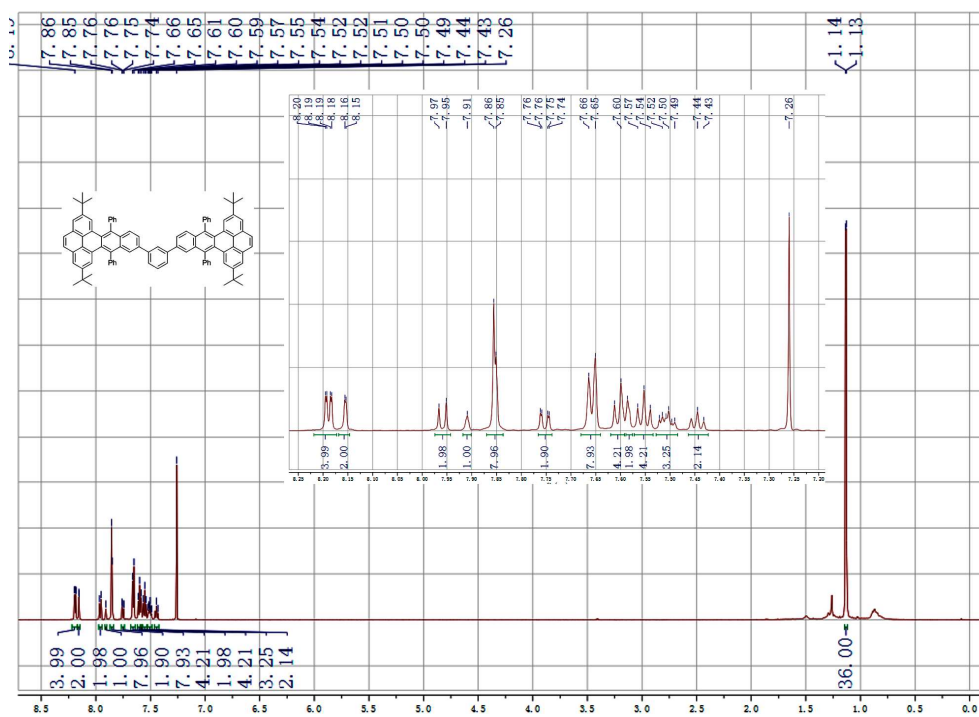


Figure S9 ^1H NMR spectrum of compound **DMPH**

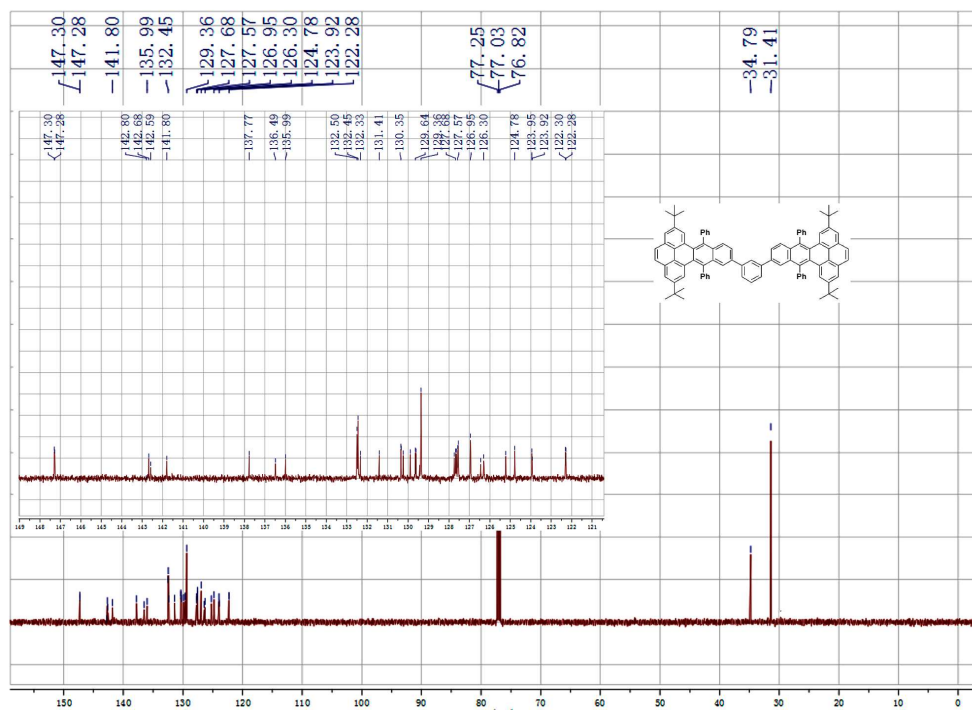


Figure S10 ^{13}C NMR spectrum of compound DMPh

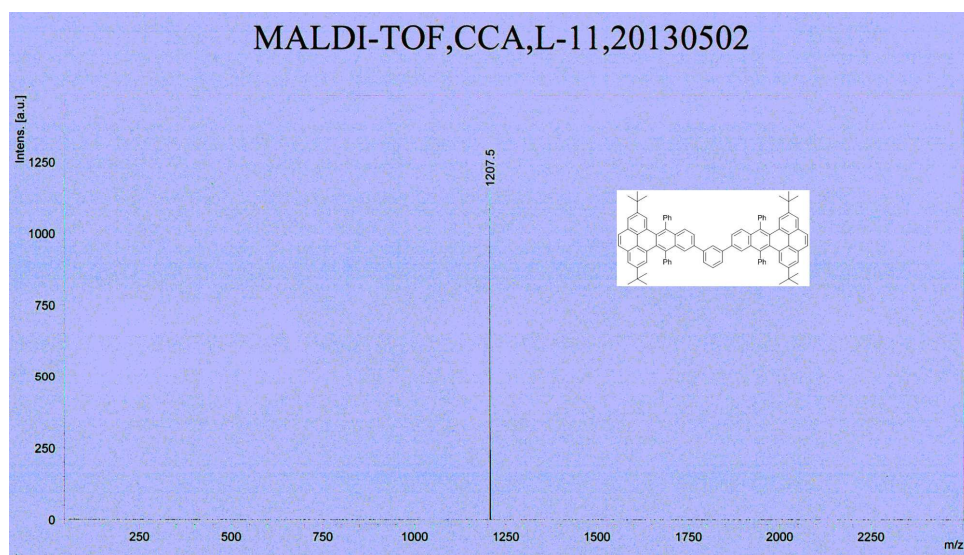


Figure S11 MALDI-TOF mass spectrum of compound DMPh

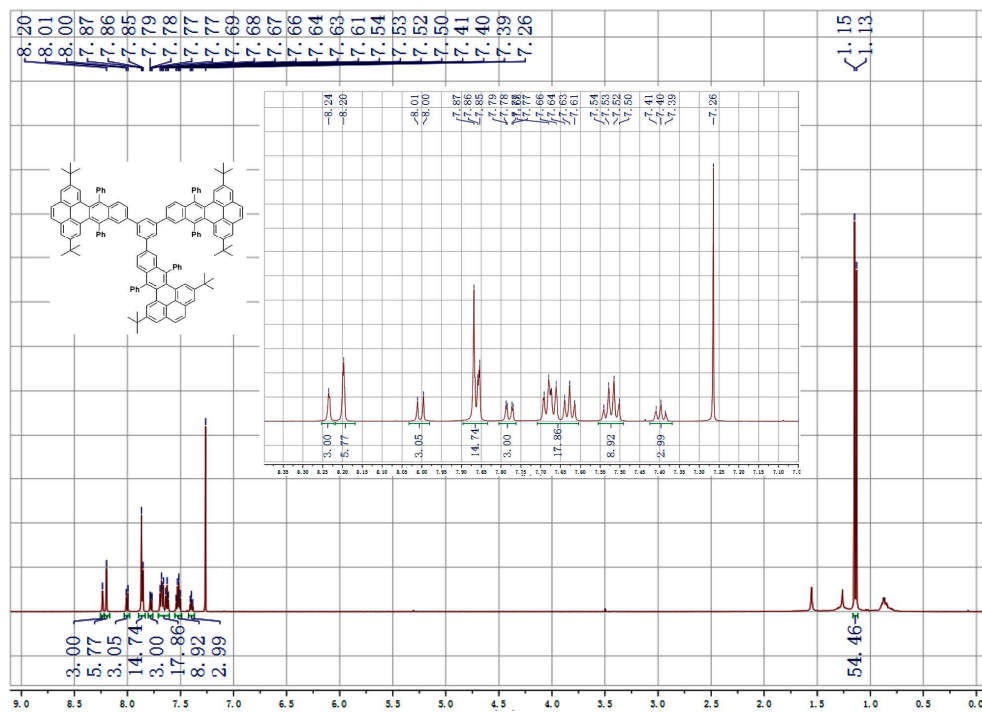


Figure S12 ¹H NMR spectrum of compound TPPh

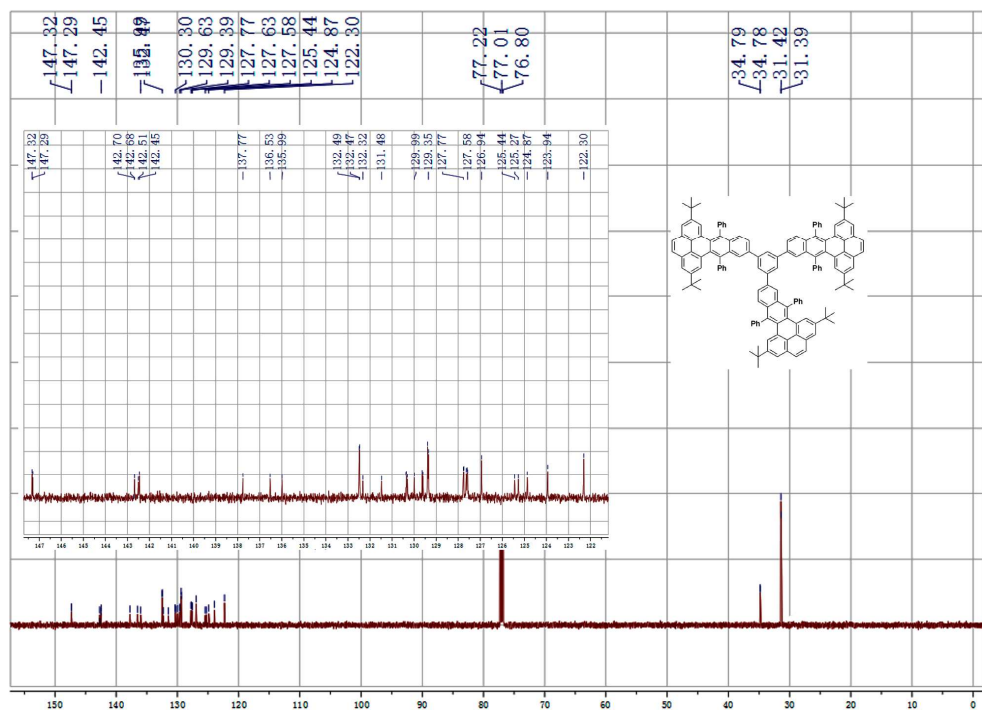


Figure S13 ¹³C NMR spectrum of compound TPPh

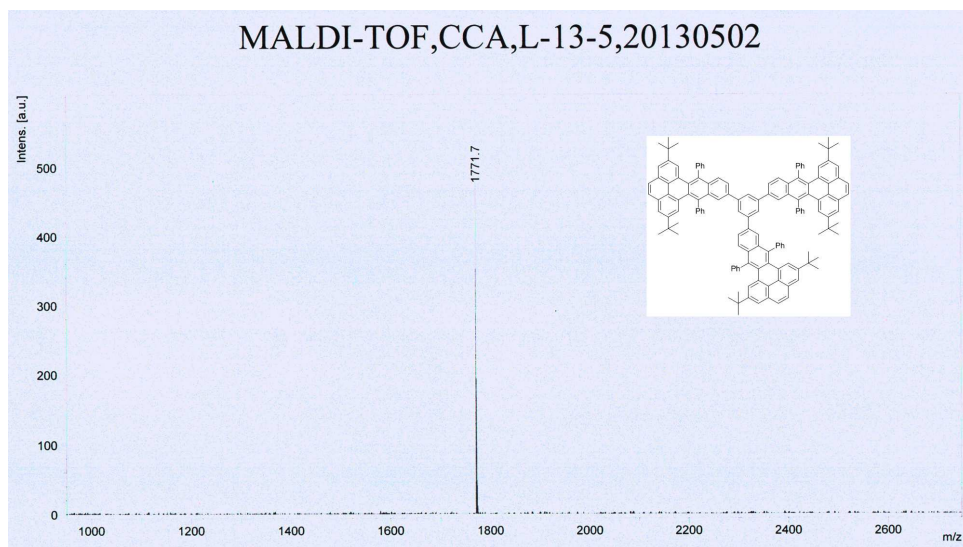


Figure S14 MALDI-TOF mass spectrum of compound **TPPh**

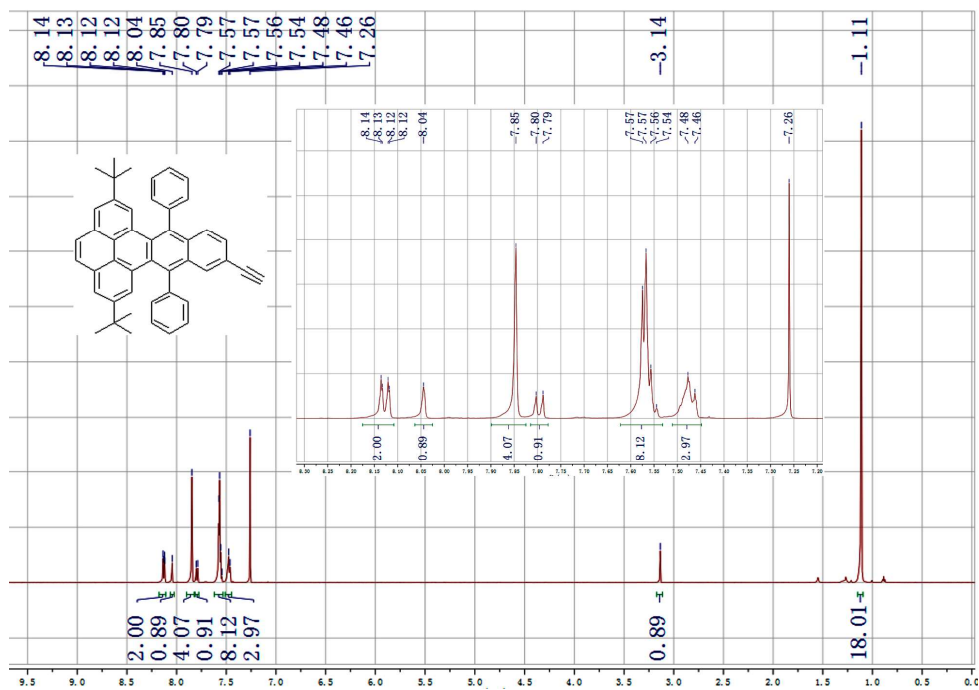


Figure S15 ^1H NMR spectrum of compound **7**

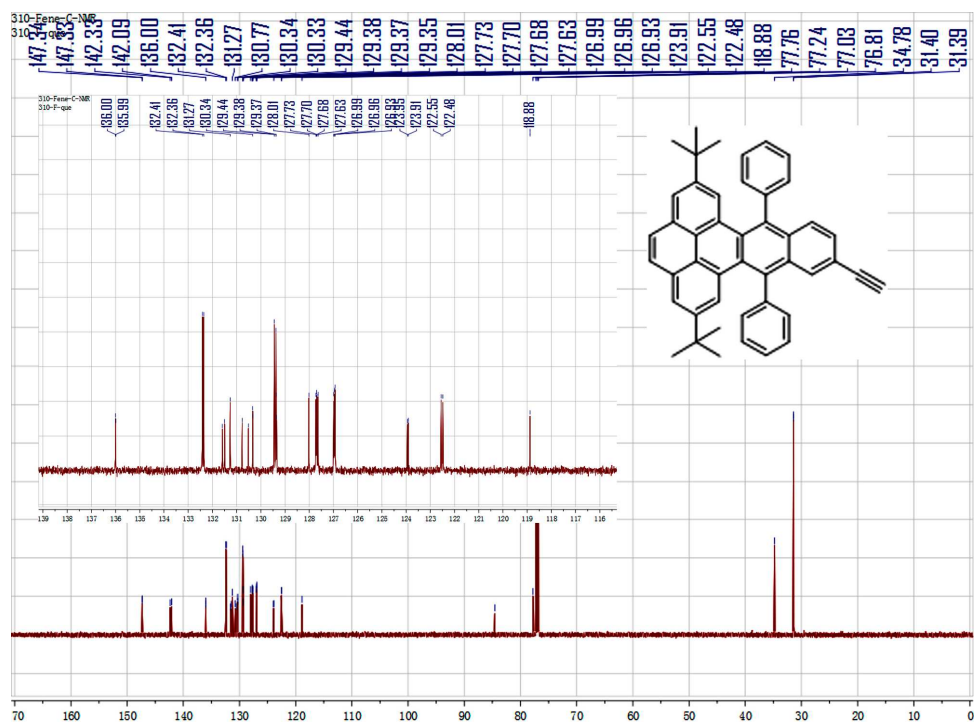


Figure S16 ^{13}C NMR spectrum of compound 7

MALDI-TOF,CCA,PY-2,20130325

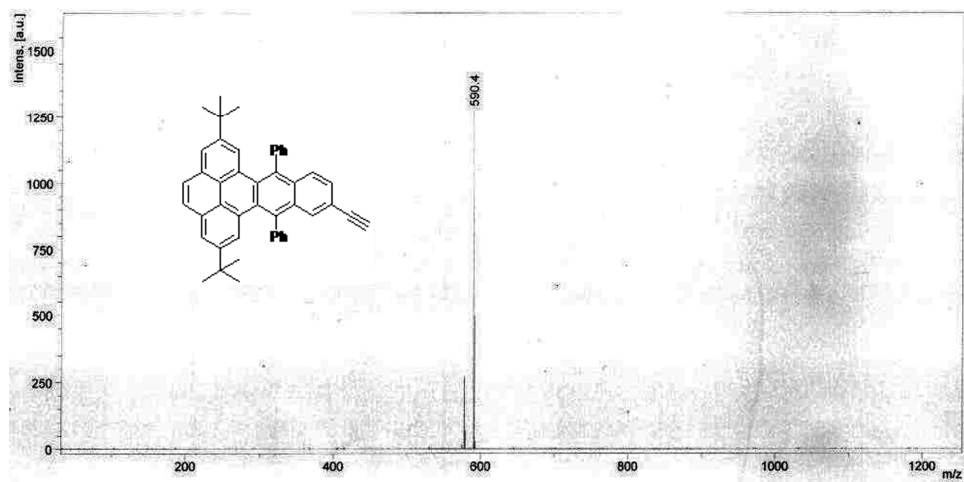


Figure S17 MALDI-TOF mass spectrum of compound 7

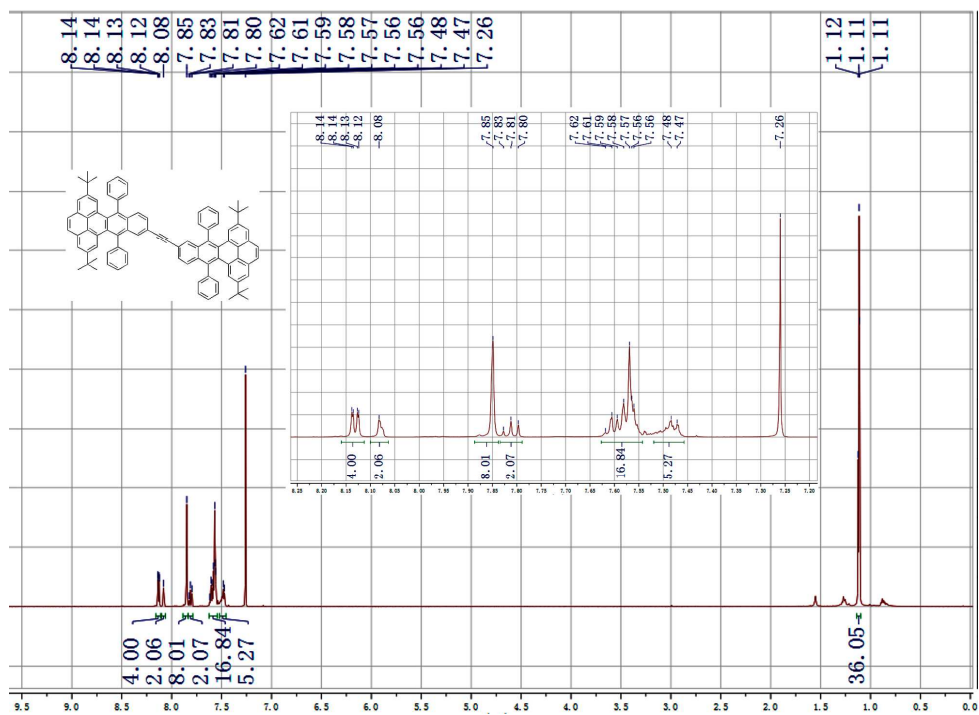


Figure S18 ^1H NMR spectrum of compound DPyA

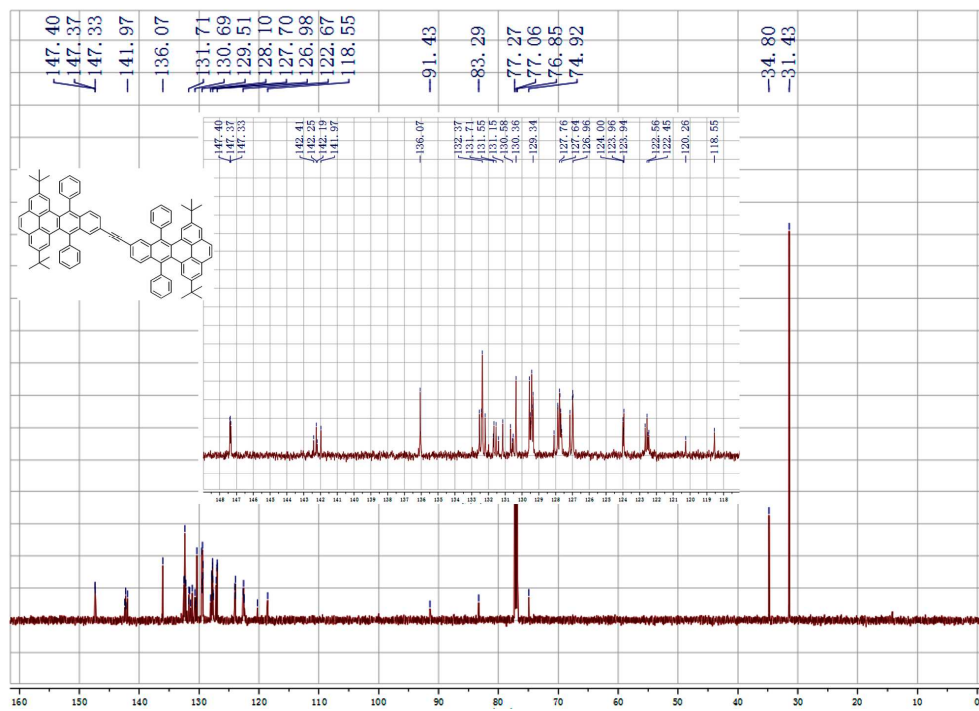


Figure S19 ^{13}C NMR spectrum of compound DPyA

MALDI-TOF,CCA,PY-3,20130325

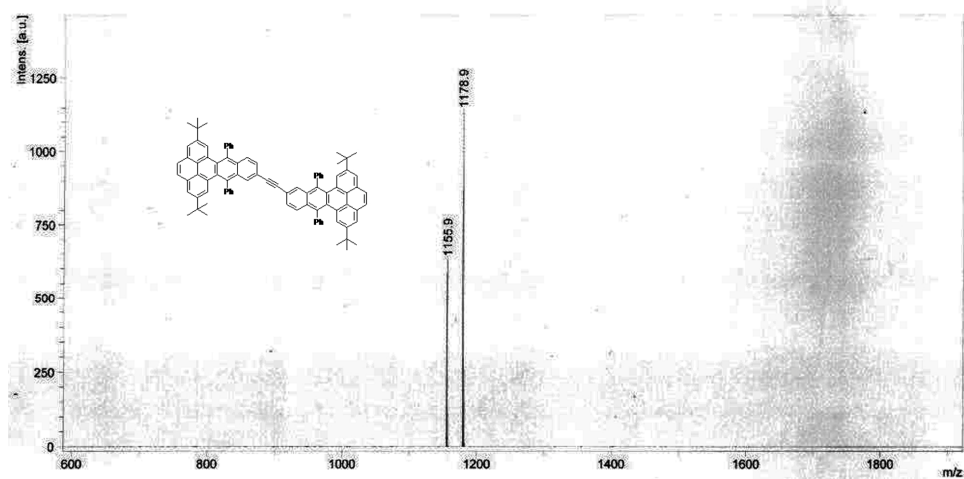


Figure S20 MALDI-TOF spectrum of compound DPyA

MALDI-TOF,CCA,PY-4,2013-03-04

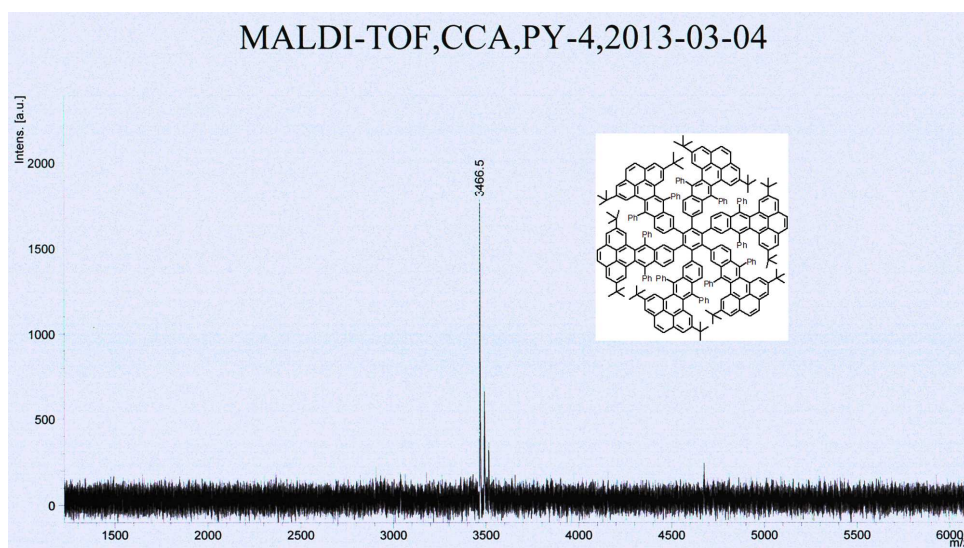


Figure S21 MALDI-TOF spectrum of compound HPPh