

Supporting Information

Donor engineering to regulate fluorescence of symmetrical structure based on fluorene-bridged for white light emission

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1. Experimental section

1.1 Materials

The reagents used in this experiment were purchased from Tianjin Damao Chemical Reagent Factory. Potassium tert-butoxide, p-methoxyaniline, and 4,4'-dimethoxydianiline were purchased from Zhengzhou Alpha Chemical Co., Ltd. and 9,9-dioctyl-2,7-dibromofluorene was purchased from Sarn Chemical Technology Co. Trifluoroacetic acid, sodium tert-butoxide and palladium acetate were purchased from Sahn Chemical Technology Shanghai Co. The reagents, except toluene, which needs to be redistilled, were not specially labelled and can be used directly.

1.2 Test and Characterization Methods

Determination of the structure of the molecules: All synthesized molecules were structurally confirmed using ^1H NMR and ^{13}C NMR, and the solvents used for the tests were deuterium dimethyl sulfoxide ($\text{DMSO-}d_6$) or deuterium chloroform (CDCl_3). The concentration of the solution was 0.5 mg/mL for hydrogen spectra and 20 mg/mL for

carbon spectra, and the molecules were analysed for specific elements using an elemental analyzer, the Vario EL III.

To test the thermal stability of the molecules: the materials were tested using Thermal Gravimetry Analysis (TGA) under nitrogen atmosphere, after placing the materials, the temperature was increased at a constant rate (10 °C /min) over a range of 100 ~ 800 °C, and thermogravimetric curves were obtained. T_d was obtained at 5% weight loss of the material; the thermal analyzer was used under nitrogen atmosphere with the same heating rate (10 °C/min), and after putting the material in, it was heated from room temperature to 300 °C, after which it was cooled down to room temperature and heated up to 300 °C again with the same rate to get the Differential Scanning Calorimetry (DSC) curve of the material to determine the Glass Transition Temperature (T_g) of the compound.

Simulation of molecular configuration: The Gaussian Gaussian 09 software was used to optimize the final products by Density Functional Theory (DFT) on the 6-31G(d) basis group using the B3LYP algorithm to optimize the ground state structure and frontier orbital electron distribution of the target molecules.

The photophysical properties of the molecules were tested: the Ultraviolet-visible (UV-vis) absorption spectra of the compounds were tested by a UV spectrometer at room temperature; the Photoluminescence (PL) spectra of the compounds were tested by a steady-state fluorescence spectrometer, also at room temperature; the transient fluorescence spectra of the compounds and the steady-state fluorescence spectra of the compounds were tested by a steady-state fluorescence spectrometer. The transient

fluorescence spectra and photoluminescence quantum yields of the compounds were tested using an Edinburgh FLS 980 transient fluorescence spectrometer and integrating sphere, respectively.

Testing the electrochemical properties of the molecules: Cyclic Voltammetry (CV) curves of the compounds were tested on an electrochemical workstation under nitrogen atmosphere. The electrolyte was prepared as an acetonitrile solution of tetrabutylammonium perchlorate at a concentration of 0.1 M. Ferrocenium (Fc^+) was chosen as the internal standard, and the reference, auxiliary and working electrodes were chosen to be calomel, platinum wire and glassy carbon electrodes, respectively, and the CV curves of the final products were measured by the electrochemical workstation.

Characterization of end-product optoelectronic properties: Electroluminescence (EL) spectra and CIE color coordinates are measured using a spectrophotometer; voltage, brightness, current density and power efficiency are determined using a Keithley 2400 Source Meter and an ST-900M Spot Brightness Meter, For OLED devices, ITO conductive glass is generally used as the substrate, and the washing procedure of the substrate is as follows: firstly, use the decontamination powder, then use detergent and acetone to wash again, and then put it into the oven for drying, and finally, use the UV lamp to directly illuminate the substrate for 25 min; the purity of the qualified materials and the ITO glass are placed in the instrument, and then vacuumed, according to the reasonable conditions. The purity qualified material and ITO glass are placed in the apparatus, vacuumed, and the layers are vapor-deposited in

accordance with the appropriate thickness according to the reasonable device structure in order to obtain the OLED device.

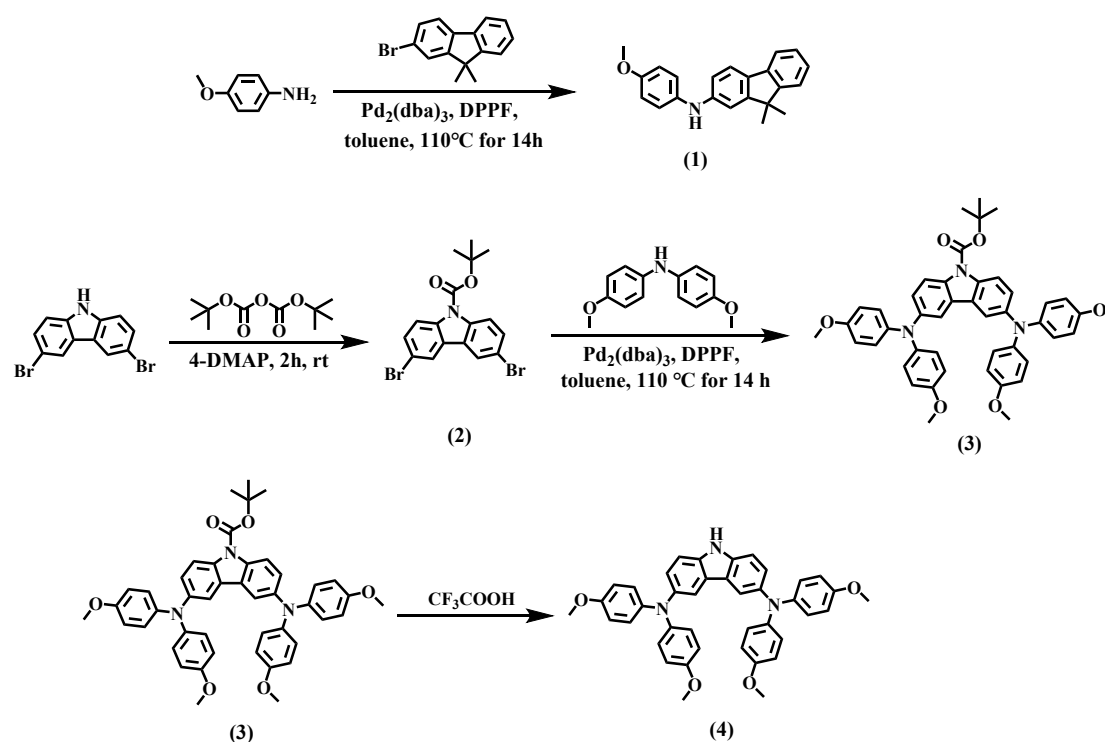
In addition to the above steps in the use of instruments other than those mentioned in the label, the rest of the main experimental instruments are as follows: electronic balance (Botelle-Torrie Instruments ME1040E/02), collector-type constant-temperature heating magnetic stirrer (Hangzhou Ruijia Precision Instruments DF-101S), rotary evaporator (Shanghai Yarong Biochemical Instruments RE-2000A), NMR spectrometer (Bruker DR (400MHz) type), fluorescence spectroscopy (Bruker DR), and the NMR spectroscopy (Bruker DR (400MHz) type). MHz), fluorescence spectrometer (Horiba Fluoru Max-4 spectrophotometer), UV-visible spectrometer (U.S. Hitachi U-3900), thermogravimetric analyzer (TGA) (Germany, the NETZSCH 209F3), Differential Scanning Calorimetry (DSC) (the U.S. company TA DSC Q100 V9.4), electrochemical workstations (Shanghai Chenhua electrochemical workstation CHI600E type), high vacuum evaporation and plating equipment (Shenyang Kecheng Vacuum Technology Co., Ltd.), spectral scanning colorimeter (Photo Research PR655 spectral scanning colorimeter), spin coating instrument (Chenat Technology KW-4A).

1.3 Synthesis of compounds

Two molecules were synthesized with 9,9-dioctylfluorene as a π -bridge and the donors were chosen as *N*-(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine as well as *N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine respectively. D- π -D type small molecules were synthesized by Buchwald-Hartwig amination reaction

and named **FFA** and **FCzA**, respectively. The synthetic route is shown in Scheme 1 and Scheme 2.

The synthesis of both donor moieties *N*-(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine and *N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine was carried out as described in the literature^[1-3].



Scheme 1. Synthetic steps of intermediate products

Synthesis of intermediate (1) *N*-(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine

Firstly, 2-bromo-9,9'-dimethylfluorene (1.04 g, 3.81 mmol), 4-methoxyaniline (0.99 g, 8.04 mmol) and sodium tert-butoxide (1.92 g, 20.00 mmol) were added to re-evaporated toluene (80 mL), and purged under nitrogen atmosphere for 15 min, and then catalysts tris(dibenzylideneindanone)dipalladium(II) (0.06 g, 0.06 mmol) and tri-

tert-butylphosphonium tetrafluoroborate (0.06 g, 0.20 mmol) were added under nitrogen atmosphere, and then the catalyst was heated up to 110 °C under nitrogen protection for 10 h. Subsequently, it was cooled down to ambient temperature, and the resulting mixture of organic solvent and water was extracted with dichloromethane. The organic layer was dried and filtered using anhydrous magnesium sulphate, followed by distillation under reduced pressure to remove the solvent to give the donor *N*-(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine. Further purification was carried out by adding the crude product to a chromatographic column with the eluent petroleum ether/ethyl acetate (60:1) and eluting the product to give the intermediate (1) (1.08 g, 85%). ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.02 (s, 1H), 7.60 (dd, *J* = 16.2, 7.8 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 6.0 Hz, 1H), 7.20-7.14 (m, 1H), 7.09 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.93-6.87 (m, 3H), 3.72 (s, 3H), 1.38 (s, 6H).

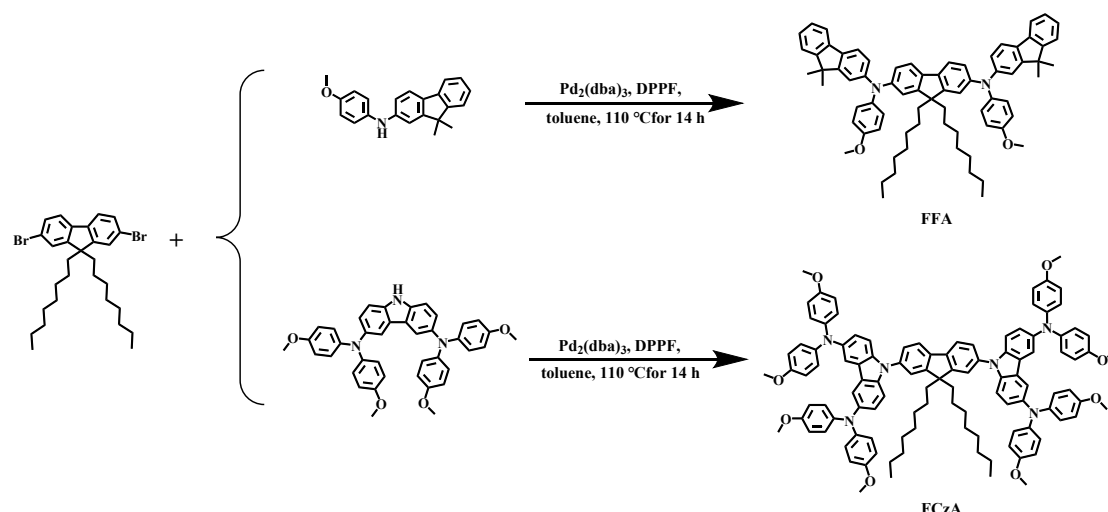
Synthesis of intermediate (4) *N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine

To tetrahydrofuran (20 mL) were added 3,6-dibromocarbazole (4.00 g, 12.31 mmol), di-tert-butyl dicarbonate (4.00 g, 18.40 mmol), and *N*-(4-pyridyl)dimethylamine (0.30 g, 2.4 mmol), stirred well, and then the mixture was heated to 66 °C under nitrogen protection for 4 h. The reaction was then cooled to room temperature and the solvent was removed using reduced pressure distillation. Further purification was carried out by column chromatography, and the crude product was added to a silica gel column, the eluent was petroleum ether/ethyl acetate (50:1), and the product was eluted to give the intermediate (2) (4.40 g, 90%). ¹H NMR (400 MHz,

CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 2H), 7.90 (s, 2H), 7.53 (d, $J = 12.6$ Hz, 2H), 1.76 (s, 9H).

To anhydrous toluene (80 mL) was added 4,4'-dimethoxydianiline (4.80 g, 20.00 mmol), Intermediate 1 (4.00 g, 9.40 mmol) and potassium tert-butoxide (3.20 g, 28.00 mmol). The reaction was purged under nitrogen for 15 min, after which tri-tert-butylphosphonium tetrafluoroborate (0.10 g, 0.38 mmol) and tris(dibenzylideneindanone)dipalladium (0.10 g, 0.38 mmol) were added under nitrogen, and the reaction was heated to 110 °C for 6 h. The reaction was then cooled down to ambient temperature, and the solvent was removed under reduced pressure to give a crude product which was then purified by addition to a silica gel column. The crude product was further purified by adding the product onto a silica gel column with the eluent of petroleum ether/dichloromethane (15:1) and eluting the product to give the intermediate (3) (5.30 g, 80%). ^1H NMR (600 MHz, CDCl_3) δ 8.19 (s, 2H), 7.46 (s, 2H), 7.24-7.12 (m, 2H), 6.93 (s, 16H), 3.80 (s, 12H), 1.73 (s, 10H).

Intermediate 2 (8.00 g, 11.34 mmol) was added to dichloromethane (50 mL), dissolved and poured into 180 g of trifluoroacetic acid, and stirred at room temperature for 1 h. At the end of the stirring period, the trifluoroacetic acid was neutralized with saturated aqueous sodium bicarbonate solution and aqueous sodium hydroxide solution, then extracted with dichloromethane, and the solvent was removed by distillation under reduced pressure, and then recrystallized from toluene to give the following products Intermediate (4) (6.20 g, 88.6%). ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 11.16 (s, 1H), 7.63 (s, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.06 (dd, $J = 8.4, 1.8$ Hz, 2H), 6.88-6.76 (m, 16H), 3.68 (s, 12H).



Scheme 2. Synthetic steps of FFA and FCzA

Synthesis of the end product FFA (*N*²,*N*⁷-bis(9,9-dimethyl-9*H*-fluoren-2-yl)-*N*²,*N*⁷-bis(4-methoxyphenyl)-9,9-dioctyl-9*H*-fluorene-2,7-diamine)

Firstly, 9,9-dioctyl-2,7-dibromofluorene (0.88 g, 1.60 mmol), *N*-(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine (1.26 g, 4.00 mmol) and potassium tert-butoxide (0.56 g, 5.00 mmol) were added to re-evaporated toluene (30 mL), which was purged under nitrogen atmosphere for 15 min. Two catalysts, tri-tert-butylphosphonium tetrafluoroborate (0.04 g, 0.24 mmol) and tris(dibenzylideneindeneacetone)dipalladium (0.04 g, 0.24 mmol) were added under nitrogen atmosphere and charged with nitrogen three times, and then protected by nitrogen, the reaction was heated to 110 °C for 16 h. The reaction was cooled down to ambient temperature, and the organic solvents were extracted by methylene chloride to obtain the mixture of organic solvents and water. The organic layer was dried and filtered using anhydrous magnesium sulphate, followed by distillation under reduced pressure to remove the solvent. Further purification was carried out by placing the crude product on a silica gel column with petroleum ether/dichloromethane (2:1) as eluent

and eluting the product to give the final product **FFA** (1.22 g, 75%). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 7.65 (d, $J = 7.2$ Hz, 2H), 7.59 (dd, $J = 13.8, 8.4$ Hz, 4H), 7.46 (d, $J = 7.8$ Hz, 2H), 7.28 (t, $J = 7.8$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 2H), 7.08 (dd, $J = 30.0, 13.2$ Hz, 8H), 6.92 (d, $J = 9.0$ Hz, 4H), 6.85 (dd, $J = 22.8, 7.2$ Hz, 4H), 3.75 (s, 6H), 1.32 (s, 12H), 1.24-0.92 (m, 25H), 0.80 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 155.87, 151.66, 148.78, 136.70, 132.06, 125.60, 122.65, 117.03, 55.68, 50.01, 33.92, 30.41, 29.01, 27.31, 23.73, 14.41.

Synthesis of the end product FCzA (9,9'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(N^3,N^3,N^6,N^6 -tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine))

Firstly, 9,9-dioctyl-2,7-dibromofluorene (0.16 g, 0.26 mmol), N^3,N^3,N^6,N^6 -tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine (0.42 g, 0.68 mmol) and potassium tert-butoxide (0.10 g, 0.86 mmol) were added to re-evaporated toluene (10 mL), and the mixture was purged under nitrogen atmosphere for 15 min. After that, two catalysts, tri-tert-butylphosphonium tetrafluoroborate (0.02 g, 0.10 mmol) and tris(dibenzylideneindenylacetone)dipalladium (0.02 g, 0.10 mmol) were added under nitrogen atmosphere and nitrogen was charged three times, and the temperature was raised to 110 °C under nitrogen atmosphere for 16 h. The reaction was cooled down to ambient temperature, and the organic solvent and water mixture were extracted with dichloromethane. and water mixture was extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulphate and filtered, followed by distillation under reduced pressure to remove the solvent. Further purification was carried out by placing the crude product on a silica gel column with petroleum

ether/dichloromethane (2:1) as eluent and eluting the product to give the final product **FCzA** (0.36 g, 70%). ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.71 (s, 4H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 4H), 7.19 - 7.12 (m, 2H), 7.07 - 7.02 (m, 4H), 6.85 (d, *J* = 9.0 Hz, 16H), 6.79 (d, *J* = 8.4 Hz, 16H), 3.67 (s, 24H), 2.02 (s, 4H), 1.23 (s, 2H), 0.98 (s, 22H), 0.61 (t, *J* = 6.6 Hz, 7H). ¹³C NMR (101 MHz, CDCl₃) δ 151.71, 123.34, 119.91, 113.11, 109.50, 54.47, 30.65, 28.95, 28.28, 28.10, 25.87, 23.07, 21.48, 12.98.

2. NMR spectra of products and intermediates

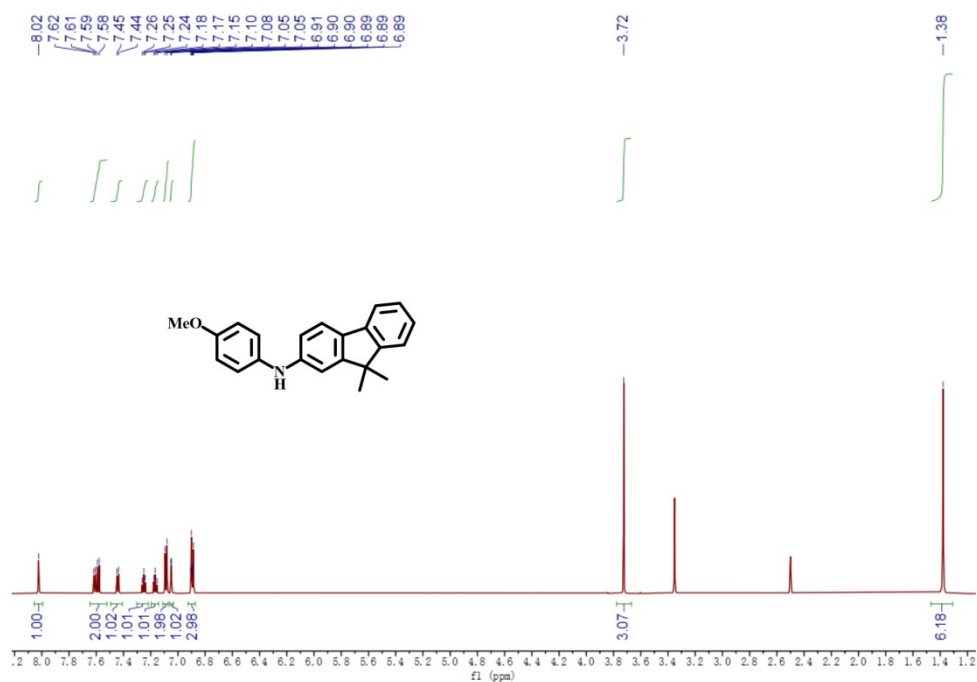


Figure S1. ¹H NMR spectrum of intermediate product 1

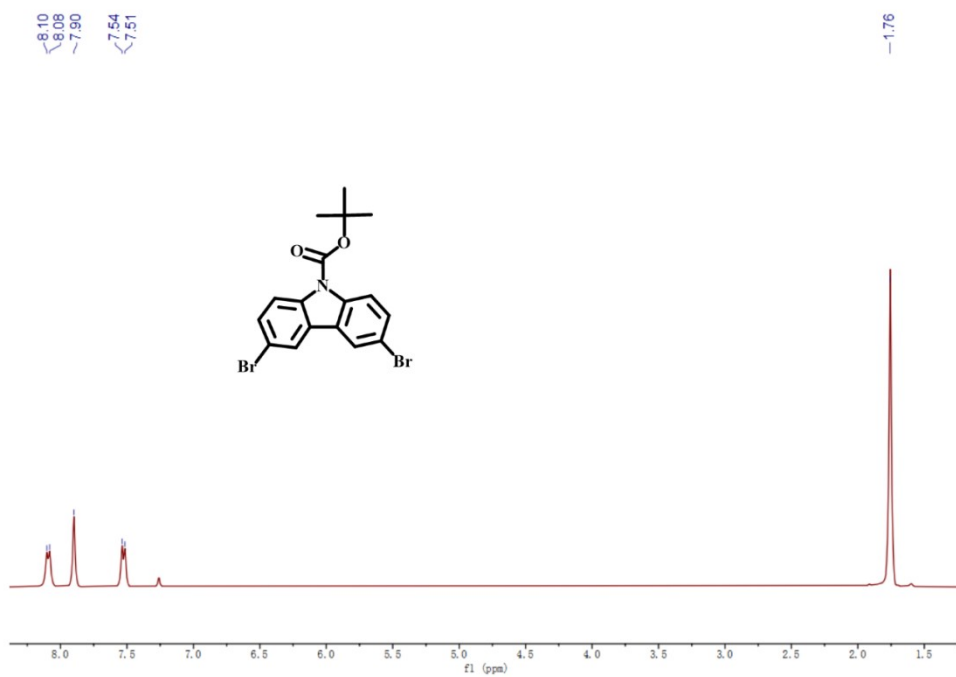


Figure S2. ¹H NMR spectrum of intermediate product 2

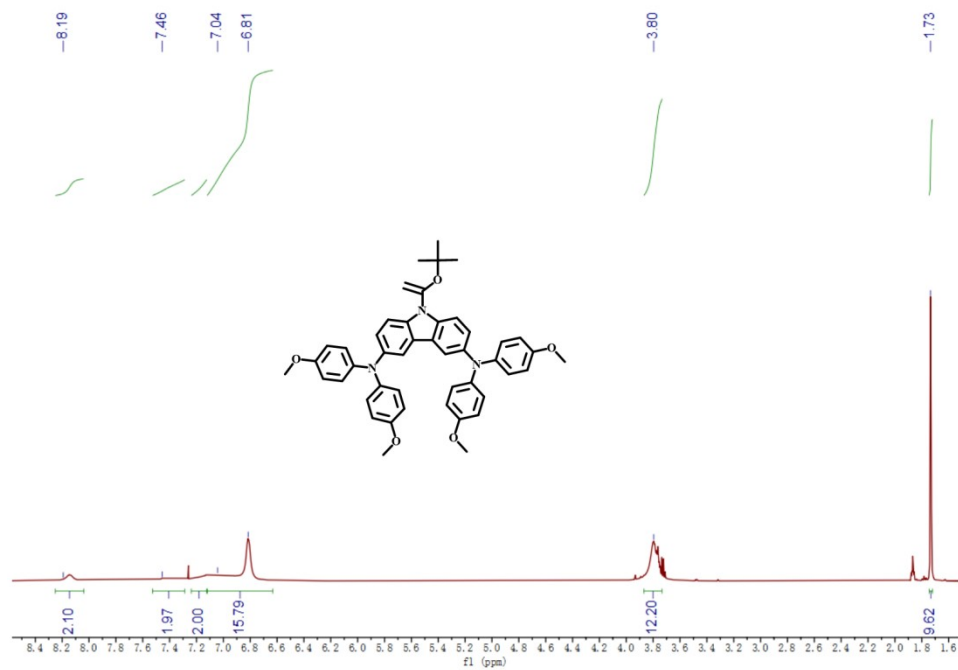


Figure S3. ^1H NMR spectrum of intermediate product 3

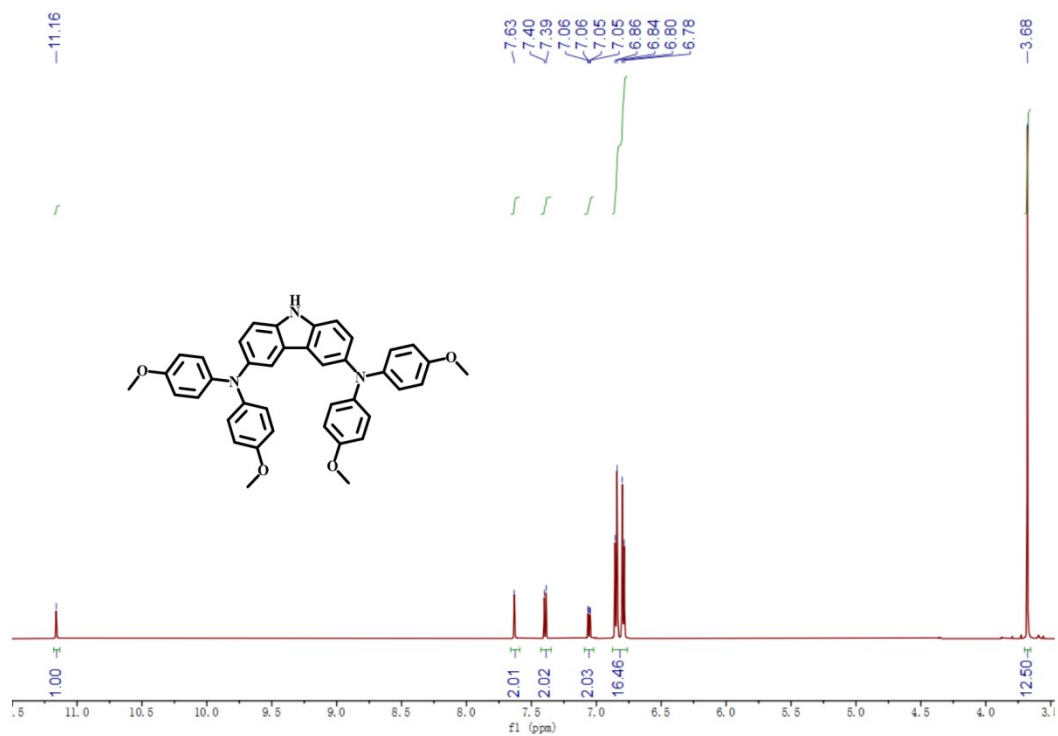


Figure S4. ^1H NMR spectrum of intermediate product 4

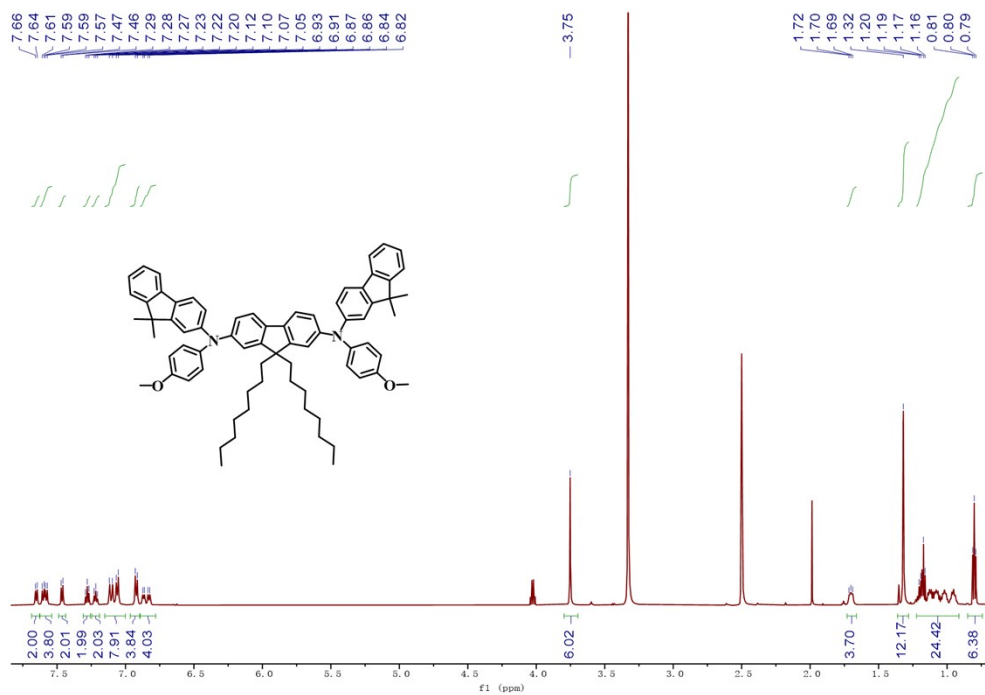


Figure S5. ^1H NMR spectrum of FFA

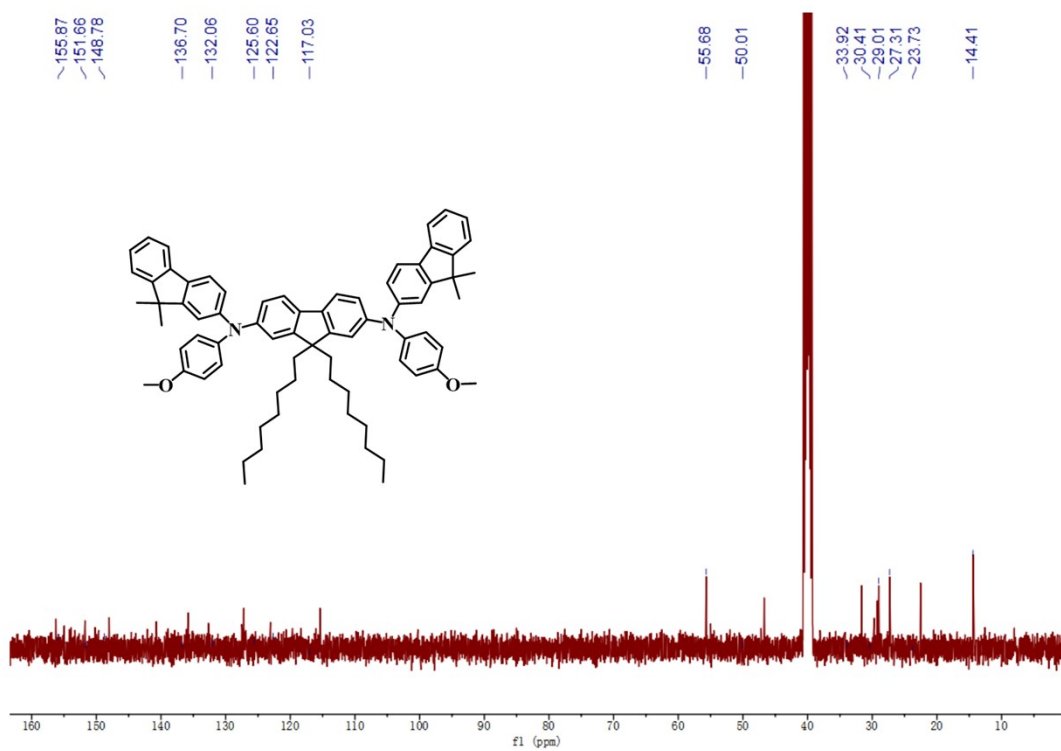


Figure S6. ^{13}C NMR spectrum of FFA

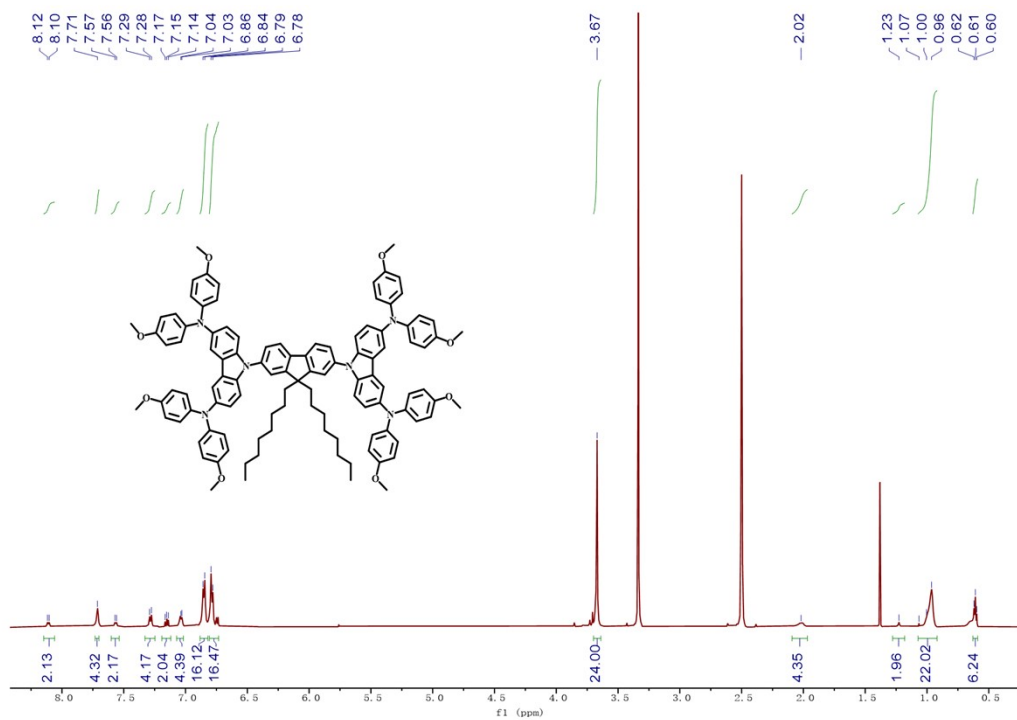


Figure S7. ¹H NMR spectrum of FCzA

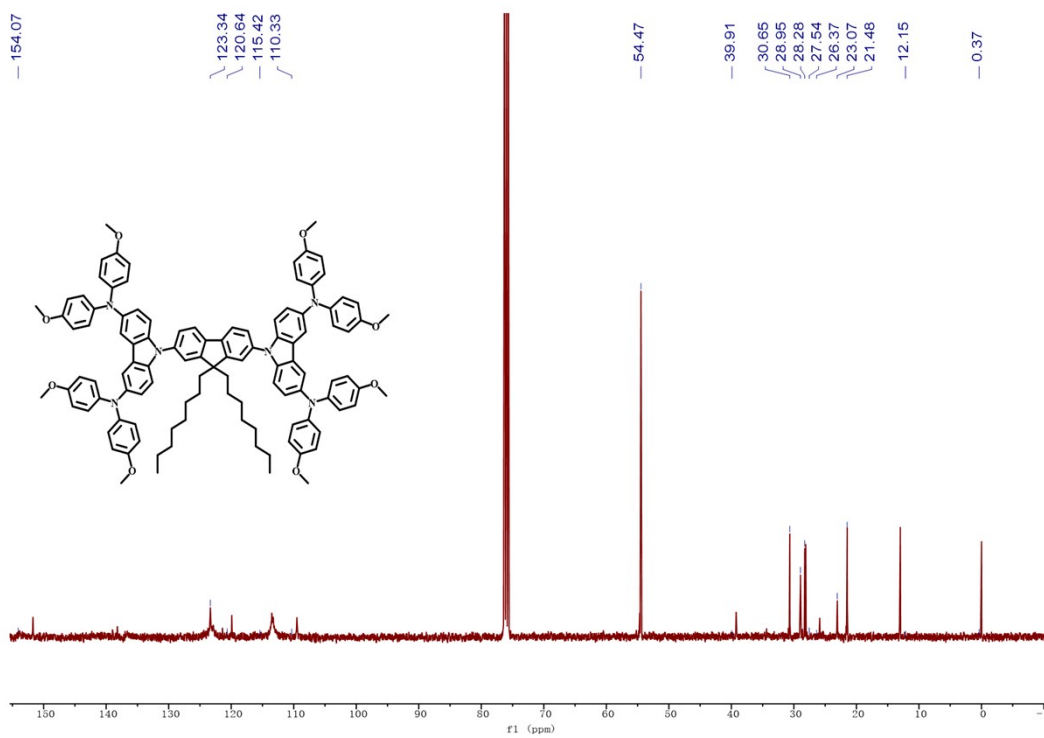


Figure S8. ¹³C NMR spectrum of FCzA

3. Additional data for simulation calculation and CV spectra

Figure S9. The singlet and triplet energy diagrams of FFA(a) and FCzA(b)

Table S1. Photophysical performances of FFA and FCzA in different solvents

Solvents	$f(\epsilon, n)$	FFA			FCzA		
		$\nu_a^a)$ (nm)	$\nu_f^b)$ (nm)	FWHM (nm)	$\nu_a^a)$ (nm)	$\nu_f^b)$ (nm)	FWHM (nm)
Hexane	0.0012	399	414	22	375	435	42
Toluene	0.012	402	421	29	376	447	45
1,4-Dioxane	0.021	400	422	31	369	445	48
Triethylamine	0.048	399	420	30	374	439	44
Chloroform	0.149	400	428	42	371	446	50
Ethyl acetate	0.2	397	422	34	370	447	51
Tetrahydrofuran	0.21	401	424	34	373	458	58
Dichloromethane	0.217	400	428	38	371	462	77
Dimethyl formamide	0.276	398	428	41	367	464	77
Acetonitrile	0.305	394	426	44	365	465	81

^{a)} absorption peak level, ^{b)} emission peak level.

$$E_g = \frac{1240}{\lambda_{\text{edge}}} \quad (\text{eq.S1})$$

$$E_{\text{HOMO}} = -E_{\text{ox}} - 4.5 \text{ eV} \quad (\text{eq.S2})$$

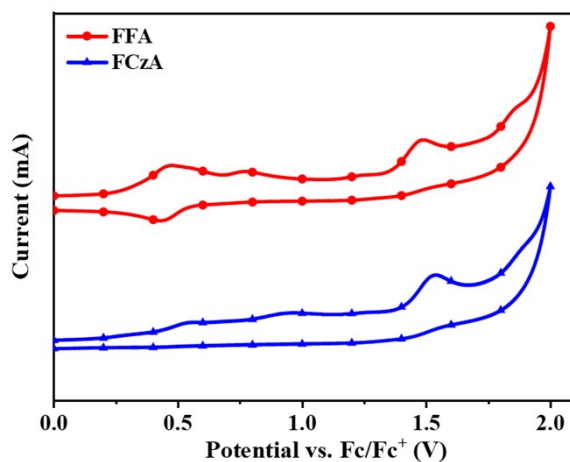


Figure S10. CV curves of FFA and FCzA

4. Current density-voltage-luminance (J-V-L) curves and current efficiency and power efficiency and brightness (CE-L-PE) curves

Figures S11 (b) and (c) show the *CE-L-PE* curves and the *EQE-L* curves, and all of the devices show good performance, with the maximum current efficiency (CE_{\max}) of device II being 0.42 cd/A and the power efficiency (PE_{\max}) being 0.24 lm/W. The FFA based device I is the most efficient device in terms of current and power efficiency, with the maximum current efficiency of 0.42 cd/A and the power efficiency of 0.24 lm/W. The FFA based device I is the most efficient device in terms of current and power efficiency. FFA, device I shows the best EL performance with a CE_{\max} of 3.47 cd/A and a PE_{\max} of 3.03 lm/W. Devices b and c have the best external quantum efficiency (EQE) values of 1.17% and 0.17%, respectively. In addition, devices based on both compounds show a small efficiency roll-off.

Figure S11. EL spectra of FFA (a) and FCzA (b) at different voltages

Figure S12. EL performance of FFA and FCzA based devices: (a) *J-V-L* curves, (b) *CE-L-PE* curves, (c) *EQE-L*

References

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