Supplementary Information

Anilino-Carbazole-Based D-π-D’-π-D blue light material coordinated exciplex for achieving white light dynamic regulation

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Contents

1. Experimental section

1.1 Materials

All the drugs shown in this experiment can be used directly. The reagents are not specifically labeled for direct use, except for toluene, which requires redistillation.

Petroleum ether, dichloromethane, tetrahydrofuran, ethyl acetate, N, N-dimethylformamide, ethanol, and toluene were all purchased from Tianjin Damao Chemical Reagent Factory. Carbazole, p-fluoronitrobenzene, potassium carbonate, stannous chloride dihydrate, sodium hydroxide, and tri (dibenzyl acetone) palladium were all purchased from Sa En Chemical Technology Shanghai Co., Ltd. 9,9-dioctyl-2,7-dibromofluorene, p-methoxyaniline, 4,4 '- dimethoxydiphenylamine, sodium tert butanol, and tert butyl phosphine tetrafluoroborate were all purchased from Zhengzhou Alpha Chemical Co., Ltd.

1.2 Test and Characterization Methods

All synthesized molecules were structurally confirmed using ^{1}H NMR and ^{13}C NMR on a Bruker Avance 600 MHz NMR spectrometer, and the solvents used for the tests were deuterium dimethyl sulfoxide (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 analysized 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.

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.

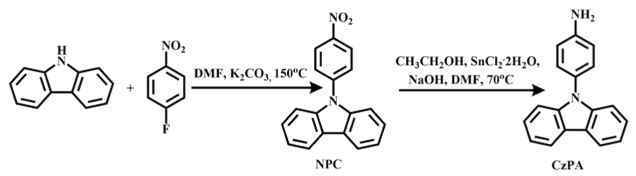
Characterization of end-product optoelectronic properties: Electroluminescence (EL) spectra and CIE color coordinates are measured using a spectrophotometer; voltage, brightness, current density and power efficiency are determined using a Keithley 2400 Source Meter and an ST-900M Spot Brightness Meter, 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 (600MHz) 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 and target products

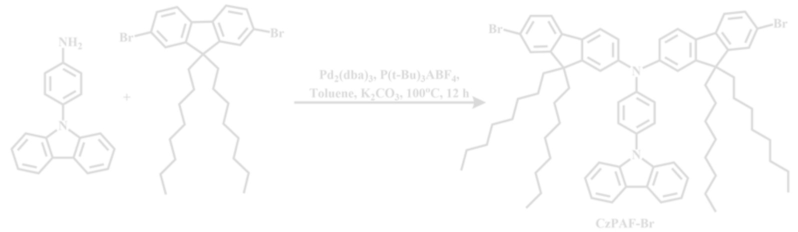
Carbazole (2.00 g, 12.00 mmol), p-fluoronitrobenzene (2.54 g, 18.00 mmol) and anhydrous potassium carbonate (8.29 g, 60.00 mmol) were added to N,N-dimethylformamide (DMF, 120 mL), purged under nitrogen for 15 min, then filled with nitrogen three times, and heated up to 110°C for 12 h. The reaction was cooled down to room temperature with a large amount of deionized water followed by ultrafiltration. The reaction time was 12 h. The reaction was cooled down to room temperature, added a large amount of deionized water and subsequently filtered, and the crude product was recrystallized from toluene. NPC (3.29 g, 95%) was obtained. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.46 (dt, *J* = 1.2 Hz, 7.2 Hz, 8.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H).

NPC (3.29 g, 11.40 mmol), stannous(II) chloride dihydrate (10.29 g, 45.60 mmol) was added to ethanol (100 mL), purged under nitrogen atmosphere for 15 min, then charged and discharged with nitrogen three times, and the reaction was heated up to 80 °C for 3 h under nitrogen atmosphere. Cooled to room temperature, dichloromethane extracted the resulting mixture of organic solvent and water. The organic layer was obtained by drying and filtration using anhydrous magnesium sulfate, followed by distillation under reduced pressure to remove the solvent. Further purification was carried out by placing the crude product in a silica gel column with hexane/ethyl acetate (8:1) as eluent and eluting the product to give the end product CzPA (2.65 g, 90%). ^{1}H NMR (600 MHz, C_2D_6OS) δ 8.20 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.11 (m, 6H), 6.82 (dt, *J* =8.4 Hz, 1.8 Hz, 2H), 5.43 (s, 2H).



Scheme 1. Synthetic steps of intermediate product CzPA

CzPA (0.31 g, 1.20 mmol), 9,9-dioctylfluorene (1.63 g, 3.00 mmol), and sodium tert-butoxide (0.58 g, 6.00 mmol) were firstly added into the redistilled toluene (40 mL), and purged under nitrogen atmosphere for 15 min, after which two catalysts, tris(dibenzylideneindenylacetonato)dipalladium (0.04 g, 0.04 mmol) and tri-tert-butylphosphonium tetrafluoroborate (0.04 g, 0.12 mmol), then charged with nitrogen three times, protected by nitrogen, and heated to 110 °C for 12 h. Cooled to ambient temperature, the resulting mixture of organic solvent and water was extracted with dichloromethane and water. The organic layer was obtained by drying and filtration using anhydrous magnesium sulfate, followed by distillation under reduced pressure to remove the solvent. Further purification was carried out by adding the crude product to a silica gel column with the eluent of petroleum ether/ethyl acetate (100:1) and eluting the product to give the final product CzPAF-Br (1.09 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.8 Hz, 4H), 7.45 – 7.41 (m, 8H), 7.34 – 7.27 (m, 4H), 7.26 – 7.21 (m, 2H), 7.14 (d, J = 7.5 Hz, 2H), 1.93 – 1.86 (m, 8H), 1.20 – 1.06 (m, 40H), 0.79 (t, J = 7.2 Hz, 12H), 0.74 – 0.66 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.90, 143.89, 132.93, 131.93, 131.12, 130.64, 129.00, 128.76, 126.23, 123.58, 123.42, 123.33, 123.22, 122.73182, 122.11, 112.64, 58.34, 43.10, 34.68, 32.89, 32.24, 32.13, 26.82, 25.50, 16.92.



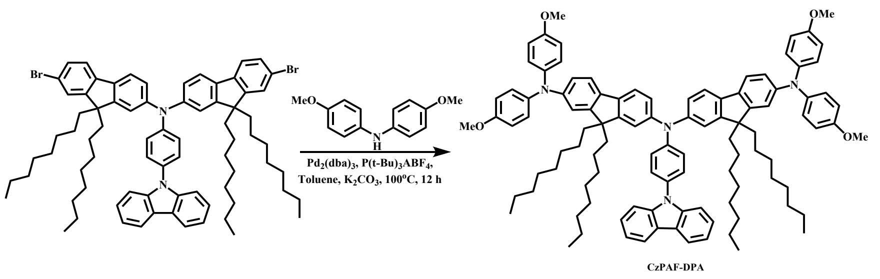
Scheme 2. Synthetic steps of intermediate product CzPAF-Br

Synthesis of N-(4-Methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine

Firstly, 2-bromo-9,9'-dimethylfluorene (0.66 g, 2.40 mmol), 4-methoxyaniline (0.59 g, 4.80 mmol), and sodium tert-butoxide (1.15 g, 12.00 mmol) were added into the redistilled toluene (40 mL), and purged under nitrogen atmosphere for 15 min, after which the catalysts tris(dibenzylideneindenacetone) dipalladium (0.04 g, 0.07 mmol), and tri-tert-butylphosphonium tetrafluoroborate (0.04 g, 0.24 mmol) were added under nitrogen atmosphere, then filled with nitrogen three times. dipalladium (0.04 g, 0.07 mmol), and tri-tert-butylphosphonium tetrafluoroborate (0.04 g, 0.24 mmol), and then filled with nitrogen three times, protected by nitrogen, heated to 100°C, the reaction time was 10 h. Cooled to room temperature, ethyl acetate extraction of the resulting organic solvent and water mixture. The organic layer was obtained by drying and filtration using anhydrous magnesium sulfate, followed by distillation under reduced pressure to remove the solvent. Further purification was carried out by adding the crude product to a silica gel column with the eluent being petroleum ether/ethyl acetate (60:1) and eluting the product to give N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (0.65 g, 85%). ^{1}H 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 CzPAF-DPA

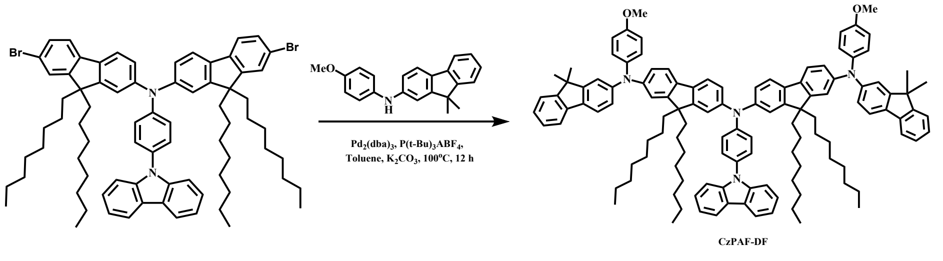
CzPAF-Br (0.72 g, 0.60 mmol), 4,4′-dimethoxydiphenylamine (0.34 g, 1.50 mmol), and sodium tert-butoxide (0.29 g, 3.00 mmol) were firstly added into the redistilled toluene (20 mL), and purged under nitrogen atmosphere for 15 min, after which the catalysts tris(dibenzylidene indanone) dipalladium (0.02 g, 0.02 mmol), tri-tert-butylphosphonium tetrafluoroborate (0.02 g, 0.06 mmol), and then filled with nitrogen three times, protected by nitrogen, heated to 100 °C, the reaction time was 12 h. Cooled to room temperature, dichloromethane extracted the resulting organic solvent and water mixture. The organic layer was obtained by drying and filtration using anhydrous magnesium sulfate, 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 the eluent of petroleum ether/ethyl acetate (45:1) and eluting the product to give the final product CzPAF-DPA (0.42 g, 62%). ^{1}H NMR (600 MHz, acetone-d_6) δ 8.21 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 6.0 Hz, 2H), 7.48-7.42 (m, 6H), 7.33 (dd, J = 9.0, 15.0 Hz, 4H), 7.28 (dt, J =1.2 Hz, 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.05-7.03 (m, 10H), 6.87 (dd, J= 2.4 Hz, 8.4 Hz, 10H), 3.79 (s, 12H), 1.91-1.81 (m, 8H), 1.23-1.11 (m, 40H), 0.79 (t, J = 6.6 Hz, 20H). ^{13}C NMR (150 MHz, acetone-d_6) δ: 157.0, 153.0, 149.2, 147.0, 142.5, 142.2, 138.4, 135.4, 128.8, 127.0, 125.1, 124.4, 123.9, 121.7, 124.4, 121.0, 120.9, 120.8, 117.4, 115.8, 110.8, 56.0, 41.2, 30.3, 30.2, 30.1, 29.9, 29.8, 14.7. Elemental Analysis: C, 83.83; H, 8.12; N, 3.76; O, 4.29. Found: C, 83.84; H, 8.07; N, 3.70; O, 4.39.



Scheme 3. Synthetic steps of target product CzPAF-DPA

Synthesis of CzPAF-DF

CzPAF-Br (0.72 g, 0.60 mmol), N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine 0.47 g, 1.50 mmol), and sodium tert-butoxide (0.29 g, 3.00 mmol) were firstly added into the redistilled toluene (20 mL), and purged under the atmosphere of nitrogen for 15 min, and then the catalyst tris(dibenzylideneindeneacetone)dipalladium (0.02 g, 0.02 mmol) and tri-tert-butylphosphonium tetrafluoroborate (0.02 g, 0.06 mmol) were added under nitrogen atmosphere, and then nitrogen was charged three times, and the temperature was raised to 110°C under nitrogen atmosphere for 10 h. The reaction was cooled down to ambient temperature, and the mixture of organic solvent and water was extracted with dichloromethane and water. The organic layer was obtained by drying and filtration using anhydrous magnesium sulfate, followed by distillation under reduced pressure to remove the solvent. Further purification was carried out by adding the crude product to a silica gel column with the eluent of petroleum ether/ethyl acetate (35:1) and eluting the product to give the end product CzPAF-DF (0.49 g, 50%). ^{1}H NMR (600 MHz, C_2D_6OS) δ 8.21 (dt, *J* = 7.8 Hz, 1.2 Hz, 2H), 7.88 (dt, *J* = 10.2 Hz, 3.6 Hz, 1H), 7.96 (dd, *J* = 6.0 Hz, 3.0 Hz, 1H), 7.69 (d, *J* = 6.6 Hz, 4H), 7.61 (d, *J* = 3.6 Hz, 2H), 7.49 – 7.41 (m, 8H), 7.36 (d, *J* = 9 Hz, 4H), 7.32 – 7.1320 (m, 12H), 7.13 (d, *J* = 9 Hz, 4H), 7.00 – 6.91 (m, 8H), 3.81 (s, 6H), 1.94 – 1.84 (m, 8H), 1.41 (s, 12H), 1.18 – 1.07 (m, 40H), 0.84 – 0.79 (m, 8H), 0.77 (t, *J* = 6.6 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.30, 146.52, 145.41, 145.15, 143.47, 139.58, 135.56, 135.53, 134.73, 130.78, 128.19728, 127.81, 127.16, 124.88, 123.59, 123.14, 123.09, 122.68, 122.29, 122.19, 121.34, 120.81, 120.32, 119.37, 114.46, 112.59, 112.45, 80.62, 74.97, 55.40, 34.18, 32.61, 29.74, 29.60, 29.50, 26.79, 23.91, 21.80, 14.16



Scheme 4. Synthetic steps of target product CzPAF-DF

2. NMR spectra of products and intermediates

Figure S1. ^{1}H NMR spectrum of NPC

Figure S2. ^{1}H NMR spectrum of CzPA

Figure S3. ^{1}H NMR spectrum of CzPAF-Br

Figure S4. ^{13}C NMR spectrum of CzPAF-Br

Figure S5. ^{1}H NMR spectrum of CzPAF-DPA

Figure S6. ^{13}C NMR spectrum of CzPAF-DPA.

Figure S7. ^{1}H NMR spectrum of CzPAF-DF

Figure S8. ^{13}C NMR spectrum of CzPAF-DF

3. CV spectra

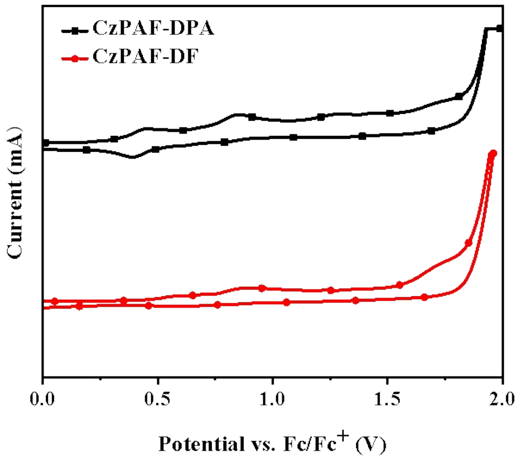


Figure S9. CV curves of CzPAF-DPA and CzPAF-DF

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

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

Table S1. Electroluminescence performances of devices

Devices	λ [nm]	V_{on} [a] [V]	$L_{\max}$ [cd/m^2]	$CE_{\max}$ [cd/A]	$PE_{\max}$ [lm/W]	$EQE_{\max}$ [%]	**CIE (x, y)**
CzPAF-DPA	424/496	4.8	320.8	0.25	0.13	0.13	(0.24,0.29)
CzPAF-DF	428/500	3.3	670.1	0.66	0.39	0.14	(0.23,0.28)

[a] V_{on} 为 1 cd/m^2 的电压

4. PL spectra of target products doped with electron transfer layer

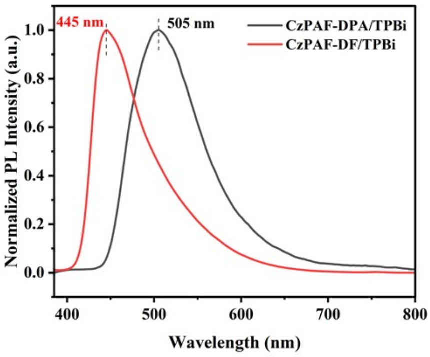


Figure S10. The PL spectra of CzPAF-DPA and CzPAF-DF doped with TPBi