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Electronic Supplementary Information

Multi-Carbazole Encapsulation as A Simple Strategy for Constructing Solution-Processed, Non-Doped Thermally Activated Delayed Fluorescence Emitters

Jiajia Luo,† Shaolong Gong,† Yu Gu, Tianheng Chen, Yifan Li, Cheng Zhong, Guohua Xie and Chuluo Yang*

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan, 430072, People's Republic of China

General information:

All the solvents and reagents were purchased form commercial sources and used as received. *Trans*-1,2-diaminocyclohexane was purified by potassium sodium alloy backflow under argon. ^{1}H NMR and ^{13}C NMR spectra were recorded on a MERCURYVX300 spectrometer. MALDI-TOF (matrix-assisted laser-desorption/ionization time-of-flight) mass spectra were performed on a Bruker BIFLEX III TOF mass spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2700 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. The temperature of degradation (T_d) was correlated to a 5% weight loss. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium–ferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV s^{-1}. Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks. 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 was measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation source. Absolute PLQYs were obtained using a Quantaurus-QY measurement system (C11347-11, Hamamatsu Photonics) and all the samples were excited at 310 nm.

Devices Fabrication and Characterization:

The ITO substrates were degreased in acetone, ethanol and deionized water consecutively in an ultrasonic bath before UV-ozone treatment for 10 minutes. A layer of 40 nm thick PEDOT:PSS was spin-coated onto the ITO substrate and then baked at 110 ^{o}C for 10 minutes. Another baking at 110 ^{o}C for 10 minutes was conducted before spin-coating the light emitting TADF materials (chlorobenzene as a solvent). To enhance the electron injection into the emitting layer, a layer of TPBI was thermally deposited onto the TADF materials. After the evaporation of the composite Liq/Al cathode, all the devices were encapsulated with UV-curable resin. The current-voltage-luminance characteristics and the EL spectra were measured simultaneously by a customized software controlling a PR735 spectrascan spectrometer and a Keithley 2400 source measurement unit. The power efficiency and the external quantum efficiency were calculated by assuming a Lambertion emission profile.

Synthesis of materials:

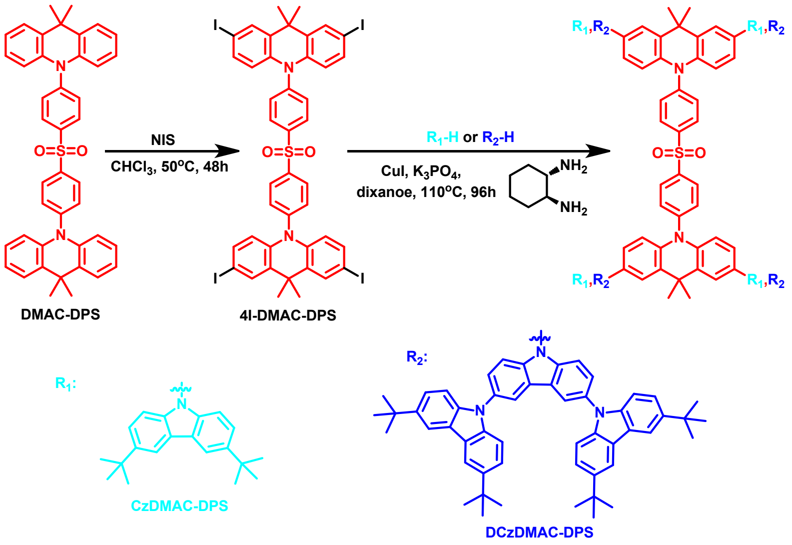
10,10'-(Sulfonylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (**DMAC-DPS**) was synthesized according to the literature methods.[1]

10,10'-(Sulfonylbis(4,1-phenylene))bis(2,7-diiodo-9,9-dimethyl-9,10-dihydroacridine)(**4I-DMAC-DPS**): *N*-Iodosuccinimide (23.6 g, 10.5 mmol) in dry chloroform (50 mL) was dropped to a solution of DMAC-DPS (6.32 g, 10 mmol) in dry chloroform (100 mL). The mixture was away from light and stirred at 50 °C for 48 hours. After that, the reaction mixture was slowly cooled to room temperature, washed by sodium thiosulfate solution (3 x 50 mL) for three times. The mixture was extracted with CH_2Cl_2 and the organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (silica, hexane/CH_2Cl_2 v/v: 3:1) to give a greyish-green powder (7.61 g, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] 8.28 (d, *J* = 8.1 Hz, 4H), 7.60 (d, *J* = 1.8 Hz, 4H), 7.52 (d, *J* = 8.1 Hz, 4H), 7.28 (d, *J* = 9.0 Hz, 4H), 5.99 (d, *J* = 8.7 Hz, 4H), 1.63 (s, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ [ppm] 145.57, 140.87, 139.51, 135.32, 134.20, 133.09, 131.53, 130.83, 116.54, 84.44, 35.98, 30.88, 30.63. MS (MALDI-TOF): *m/z* 1120.89 $[M-CH_3]^+$. Anal. Calcd for $C_{43}H_{32}I_4N_2O$ (%): C, 44.66; H, 2.95; N, 2.46. Found: C, 44.68, H, 2.95, N, 2.41.

10,10'-(Sulfonylbis(4,1-phenylene))bis(2,7-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)-9,9-dimethyl-9,10-dihydroacridine) (**CzDMAC-DPS**): A mixture of 4I-DMAC-DPS (1.14 g, 1 mmol), 3,6-di-*tert*-butyl-9*H*-carbazole (2.23 g, 8 mmol), CuI (152 mg, 0.8 mmol), K_3PO_4 (12.7 g, 60 mmol) and (±)-*trans*-1,2-diaminocyclohexane (1.37 g, 12 mmol) in 10 mL dry dioxane was stirred at 110 °C under argon for 96 hours. Then the reaction mixture was cooled to room temperature, poured into water (100 mL) and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified to column chromatography (silica, hexane/CH_2Cl_2 v/v: 3:1) to give a bluish-green powder (1.0 g, 58%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] 8.23 (d, *J* = 8.7 Hz, 4H), 8.13 (d, *J* = 1.5 Hz, 8H), 7.81 (d, *J* = 8.4 Hz, 4H), 7.64 (d, *J* = 2.1 Hz, 4H), 7.44 (dd, J_1 = 1.8 Hz,

J_2 = 8.4 Hz 8H), 7.29 (s, 4H), 7.22 (d, *J* = 11.1 Hz, 8H), 6.55 (d, *J* = 9.0 Hz, 4H), 1.73 (s, 12H), 1.45 (s, 72H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ [ppm] 142.55, 140.61, 140.08, 131.23, 130.80, 125.98, 123.79, 123.50, 123.08, 119.39, 116.18, 110.90, 109.01, 34.67, 32.13, 31.94, 31.86, 31.56, 31.30. MS (MALDI-TOF): *m/z* 1725.85 $[M-CH_3]^+$. Anal. Calcd for $C_{123}H_{128}N_6O$ (%): C, 82.85, H, 7.33; N, 4.61. Found: C, 82.94, H, 7.42, N, 4.61.

9',9'',9''',9''''-(10,10'-(Sulfonylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine-10,7,2-triyl))tetrakis(3,3'',6,6''-tetra-tert-butyl-9'H-9,3':6',9''-tercarbazole) (**DCzDMAC-DPS**)：A similar procedure to Cz-DMAC-DPS was followed, but with 3,3'',6,6''-tetra-*tert*-butyl-9'*H*-9,3':6',9''-tercarbazole (5.77 g, 8 mmol) to replace 3,6-di-tert-butyl-9*H*-carbazole. After filtration and evaporation of the solvent, the residue was purified to column chromatography (silica, hexane/CH_2Cl_2 v/v: 3:1) to give a pale blue powder (1.8 g, 51%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] 8.53 (d, *J* = 6.6 Hz, 4H), 8.24 (s, 8H), 8.15 (s, 16H), 7.90-7.79 (m, 12H), 7.59-7.51 (m, 16H), 7.43 (d, *J* = 6.3 Hz 16H), 7.31 (d, *J* = 8.4 Hz, 16H), 6.68 (d, *J* = 9.0 Hz, 4H), 1.76 (s, 12H), 1.46 (s, 144H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ [ppm] 142.57, 140.66, 139.41, 138.78, 132.06, 131.66, 130.95, 125.09, 124.37, 123.48, 123.09, 116.21, 115.66, 108.94, 36.78, 34.64, 32.72, 32.42, 32.37, 32.11, 31.83, 31.53, 31.26. MS (MALDI-TOF): *m/z* 3494.83 $[M-CH_3]^+$. Anal. Calcd for $C_{251}H_{248}N_{14}O$ (%): C, 83.29, H, 7.42; N, 5.09. Found: C, 83.48, H, 7.40, N, 5.16.



Scheme S1. The synthetic routes of TADF materials.

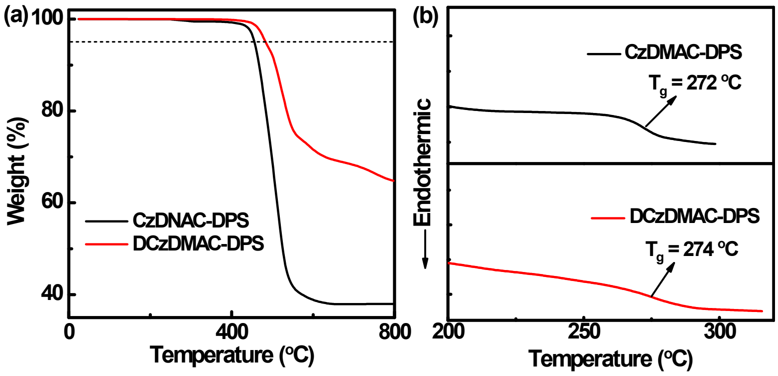


Fig. S1 (a) TGA traces of CzDMAC-DPS and DCzDMAC-DPS recorded at a heating rate of 10 °C min^{-1}. (b) DSC traces of CzDMAC-DPS and DCzDMAC-DPS recorded at a heating rate of 10 °C min^{-1}.

Table S1. The photophysical and electrochemical data of CzDMAC-DPS and DCzDMAC-DPS.

Compound	λ_{abs} [nm][a]	ε_{CT} [M^{-1} cm^{-1}][b]	$\lambda_{em,max}$ [nm][a]	$\lambda_{em,max}$ [nm][c]	HOMO/LUMO [eV][d]	S_1 [eV]	T_1 [eV]	ΔE_{ST} [eV]	Φ_{PL}[e] [%]
CzDMAC-DPS	240/299/349	8.96 × 10^4	492	498	-5.24/-2.31	2.95	2.86	0.09	67.5
DCzDMAC-DPS	240/299/349	6.03 × 10^4	464	484	-5.18/-2.09	3.07	2.87	0.20	48.2

[a] Measured in neat films. [b] Molar extinction coefficient of CT in toluene. [c] Measured in toluene. [d] The HOMO levels are determined from the half wave potential oxidation potentials. The LUMO levels were obtained from the HOMO value add up the optical band gap. [e] PLQYs in film without oxygen.

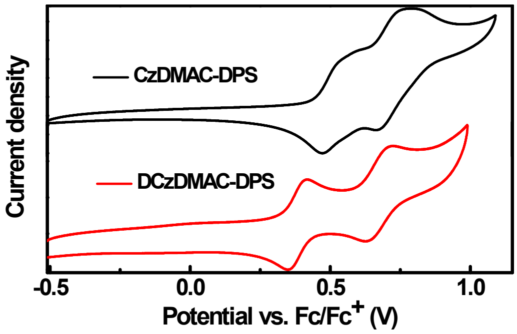


Fig. S2 Cyclic voltammograms of CzDMAC-DPS and DCzDMAC-DPS in CH_2Cl_2 for oxidation.

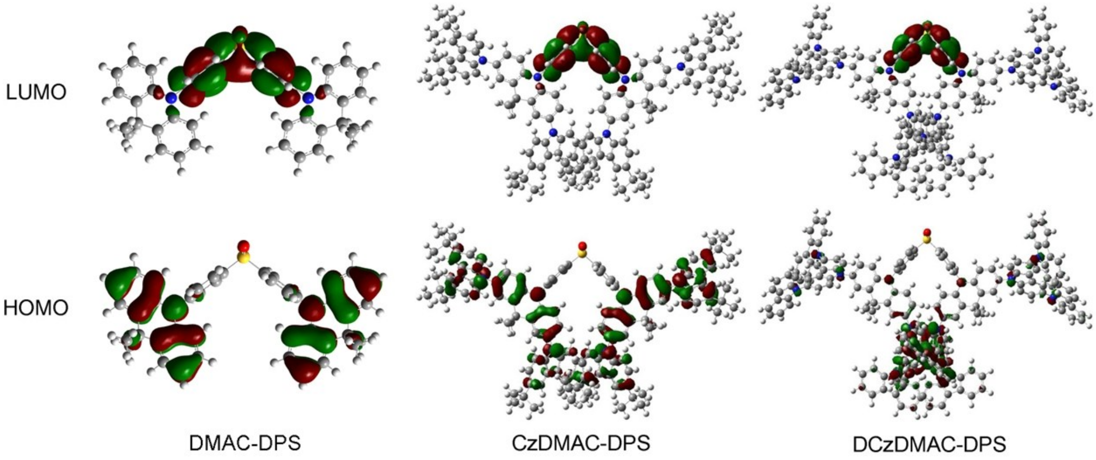


Fig. S3 HOMO and LUMO distributions of DMAC-DPS, CzDMAC-DPS and DCzDMAC-DPS obtained by density functional theory calculations [B3LYP; 6-31G(d)].

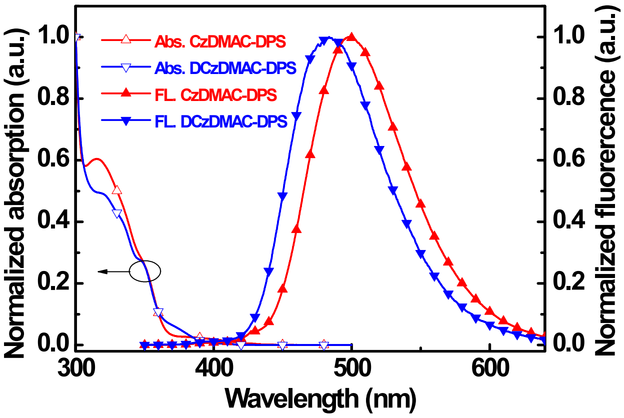


Fig. S4 PL spectra of CzDMAC-DPS and DCzDMAC-DPS in toluene.

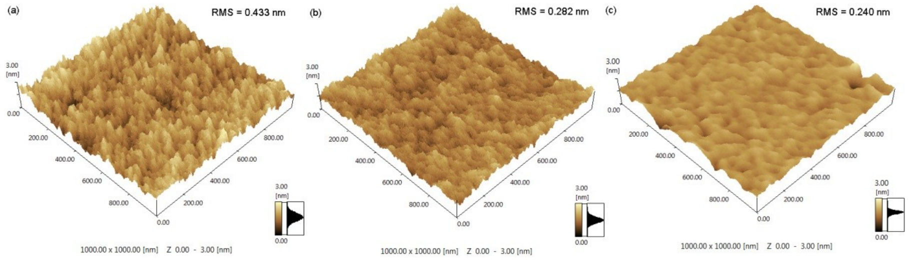


Fig. S5 AFM topographic images of the solution-processed (a) DMAC-DPS, (b) CzDMAC-DPS and (c) DCzDMAC-DPS films.

Reference:

1 Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka, C. Adachi, *Nature Photon.* 2014, **8**, 326.