Electronic Supplementary Information

Enhanced electroluminescence based on thermally activated delayed fluorescence from a carbazole-triazine derivatives

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1. Synthesis of 3-(2'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-2-yl)-9-phenyl-9*H*-carbazole (PhCzTAZ)

Scheme S1 outlines the synthesis of PhCzTAZ.



Scheme S1. Synthesis of PhCzTAZ.

Synthesis of 3-(2'-bromobiphenyl-2-yl)-9-phenyl-9*H*-carbazole (1)

A two-neck flask charged with 2-bromo-2'-iodobiphenyl 1 (15.2g, 42.3 mmol), 9-phenyl-3- (4, 4, 5, 5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H carbazole 2 (14.9g, 40.3 mmol), Pd(PPh₃)₄ (1.86g, 1.61 mmol), Ba(OH)₂. 8H₂O (44.5g, 141 mmol) was vacuumed and refilled with argon. The flask was then added degassed 1,4-dioxane (120mL) and water (30 mL), and refluxed for 48 h. The mixture was cooled to room temperature, and 10% aq. HCl was added until the solution was neutralized. And then was extracted with ethyl acetate (100 mL \times 2). The combined organic layer was washed with brine and dried over MgSO₄. The solution was concentrated to obtain the crude residue which was purified on a silica gel column using CH₂Cl₂/hexanes (1:10) as eluent to give a white solid **1**. (12.6 g, yield: 67%) ¹H NMR (CDCl₃, 400 MHz): δ [ppm]8.00 (d, J = 7.6 Hz, 1H), 7.96 (s, 1H), 7.49-7.61 (m, 7H), 7.43 (t, J = 8 Hz, 2H), 7.35-7.38 (m, 3H), 7.25-7.27 (m, 1H), 7.18-7.22 (m, 2H), 7.10-7.17 (m, 2H), 7.00-7.05 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 142.21, 141.11, 140.55, 139.38, 139.18, 137.17, 132.58, 132.08, 131.82, 130.40, 130.14, 129.37, 127.94, 127.75, 127.34, 126.93, 126.57, 126.41, 126.04, 125.46, 123.60, 123.08, 122.65, 120.84, 119.81, 119.57, 109.54, 108.70; MS (m/z, FAB⁺) 473.1 (83), 475.1 (90) [M⁺]; HRMS (m/z, FAB⁺) Calcd for C₃₀H₂₀⁷⁹BrN 473.0779, found: 473.0782; Calcd for C₃₀H₂₀⁸¹BrN 475.0759, found: 475.0773.

Synthesis of 3-(2'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-2-yl)-9-phenyl-9*H*-carbazole (PhCzTAZ)

n-Butyllithium (1 mL, 1.6 M in hexanes, 1.60 mmol) was slowly added into a solution of 3-(2'bromobiphenyl-2-yl)-9-phenyl-9H-carbazole (0.5 g, 1.06 mmol) in anhydrous THF (50 mL) at -78 $^{\circ}$ C under argon atmosphere. The solution was then stirred for 1 h and warmed to -70 $^{\circ}$ C. A solution of 2-chloro-4,6-diphenyl-1,3,5-triazine (0.45g, 1.70 mmol) in anhydrous THF (3 mL) was added into the reaction solution in one portion, and was stirred under room temperature for another 12 h. The reaction mixture was quenched with saturated NH₄Cl aqueous solution, then extracted with ethyl acetate. The organic layer was further extract with H₂O and brine, then dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography (silica, hexanes/ethyl acetate = 40/1, then 20/1). The residue was further recrystallized from CH₂Cl₂/MeOH solution to give white crystal **PhCzTAZ** (0.35g, yield: 53%). ¹H NMR (CD₂Cl₂, 400 MHz): δ [ppm] 8.09 (dd, J = 8, 1.2 Hz, 4H), 8.00 (d, J = 7.6 Hz, 1H), 7.74 (dd, J = 7.2, 1.2 Hz, 1H), 7.54-7.64 (m, 4H), 7.43-7.50 (m, 6H), 7.33-7.42 (m, 7H), 7.28 (td, J = 8.4, 1.2 Hz, 1H, 7.14-7.19 (m, 4H), 6.92 (d, J = 8.8 Hz, 1H), 6.77 (dd, J = 8.4, 1.6 Hz, 1H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ173.71, 171.38, 143.16, 141.87, 141.49, 141.31, 139.73, 137.98, 137.25, 136.52, 133.25, 133.01, 132.55, 131.49, 131.24, 130.97, 130.75, 130.17, 129.12, 128.79, 127.97, 127.84, 127.73, 127.61, 127.19, 126.26, 123.75, 123.67, 121.65, 120.42, 120.31, 110.12, 109.25; MS (m/z, FAB⁺) 626.2 (66), 627.2 (66) [M⁺]; HRMS (m/z, FAB⁺) Calcd for $C_{45}H_{30}N_4$ 626.2470, found:626.2474.

2. Experimental details

Optical properties of **CzT** solutions were tested in $1.5 \cdot 10^{-5}$ concentration solutions. The **CzT**: DPEPO (100 nm) co-deposited films were fabricated by thermal deposition. The film thickness was monitored in-situ by an oscillating quartz thickness monitor during thermal deposition process. Absorption and fluorescence spectra were measured in air using UV2550 (SHIMAZU) and PF6500 (JASCO). Temperature dependence of PL properties was measured using Optistat DN2 cryostat (Oxford Instruments) and PF6500 spectrometer. PL quantum efficiency was measured using Quantaurus QY measurement system (HAMAMATSU Co.). Fluorescence decay transients were measured using Quantaurus Tau measurement system (HAMAMATSU Co.). External quantum efficiency, luminance and luminous efficacy of OLED were measured using an integrating sphere with a multichannel spectrometer (PMA-12, HAMAMATSU Co.) and Keithley 2400 as a voltage source.

3. Determination method of ϕ_{PR} and ϕ_{DEL}

In this study, ϕ_{PR} and ϕ_{DEL} were determined by using total PL quantum efficiency (ϕ_{PL}) and the ratio between prompt and delayed components which was calculated from transient PL measurements. The intensity ratio between prompt (r_1) and delayed (r_2) components were determined using emission life time (τ_1 , τ_2) and fitting parameter (A₁, A₂) as follow.

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$
$$r_1 = \frac{A_1 \tau_1}{A_1 \tau_1 + A_2 \tau_2}$$
$$r_2 = \frac{A_2 \tau_2}{A_1 \tau_1 + A_2 \tau_2}$$

Then, ϕ_{PR} and ϕ_{DEL} were determined using intensity ratio (r_1, r_2) and total emission quantum yield

$$\phi_{PL} = \phi_{PR} + \phi_{DEL}$$

 $\phi_{PR} = r_1 \phi_{PL}$
 $\phi_{DEL} = r_2 \phi_L$



Figure S1. ¹H NMR spectra of compound **1**.



Figure S2. ¹³C NMR spectra of compound **1**.

6. ¹H NMR spectra of compound **PhCzTAZ**





Figure S3. ¹H NMR spectra of compound PhCzTAZ





