

# **Improved photovoltaic performance of star-shaped molecules with triphenylamine core by tuning substituted position of carbazolyl at terminal**

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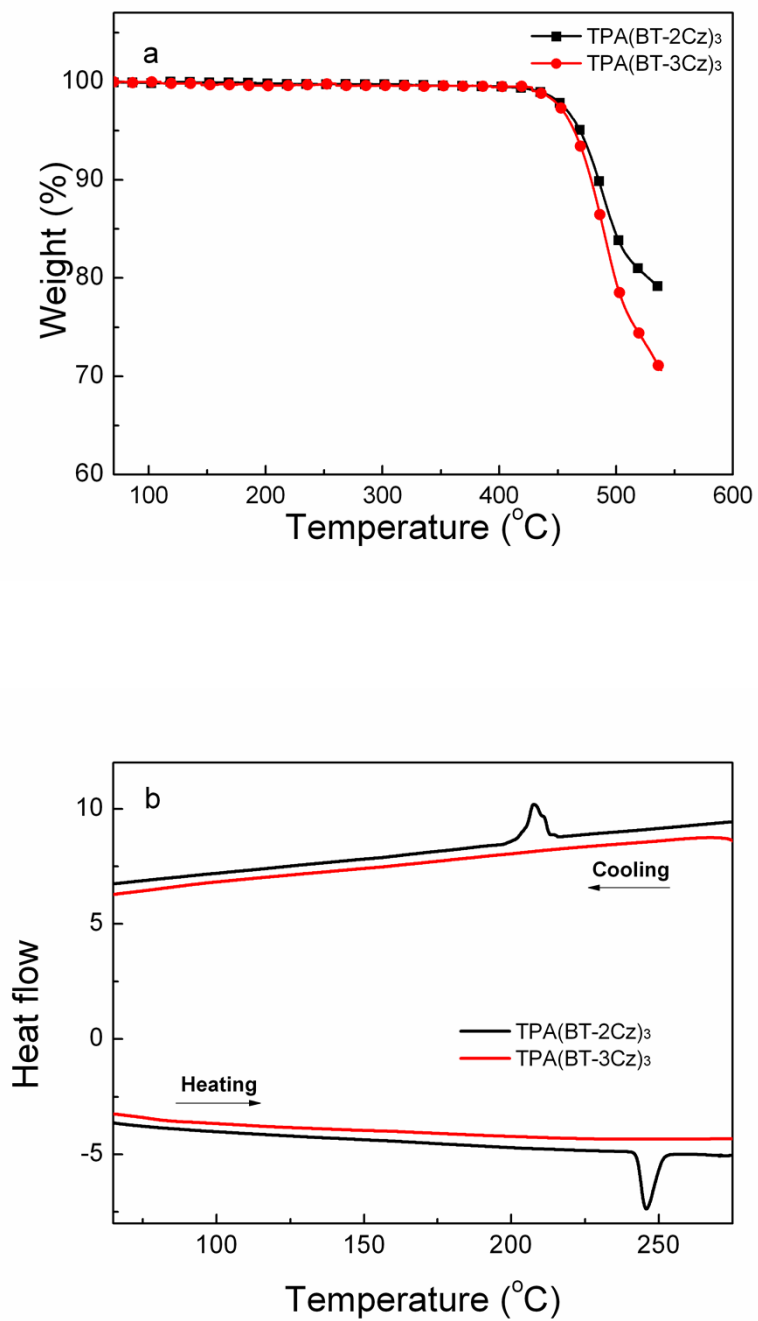
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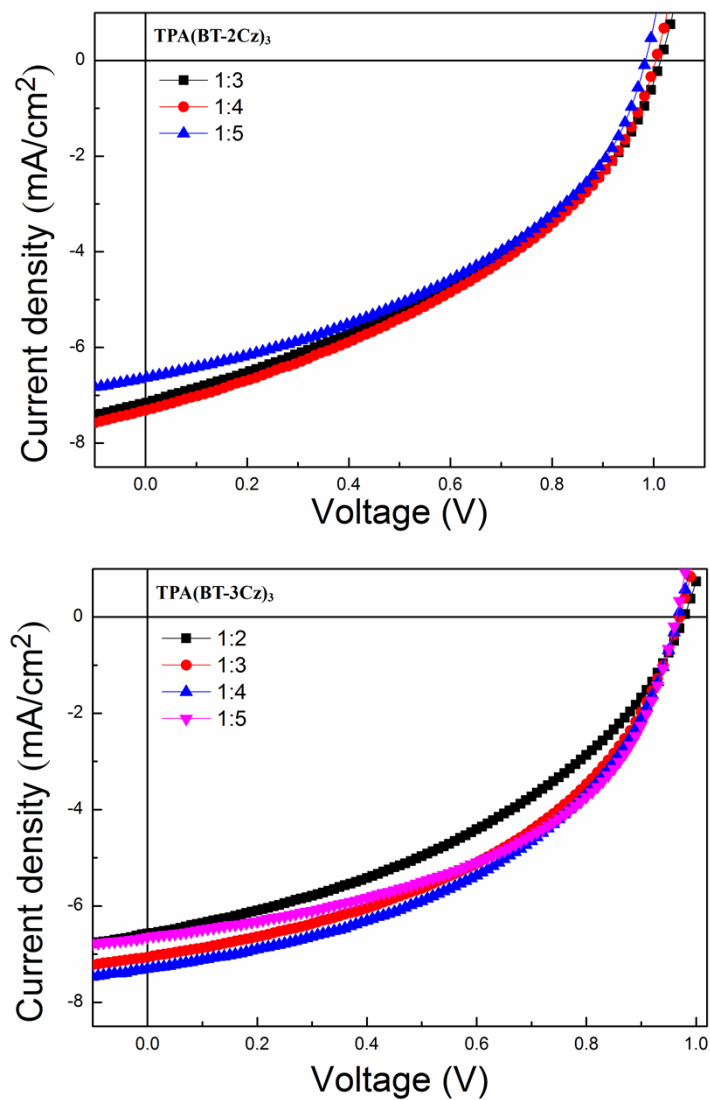
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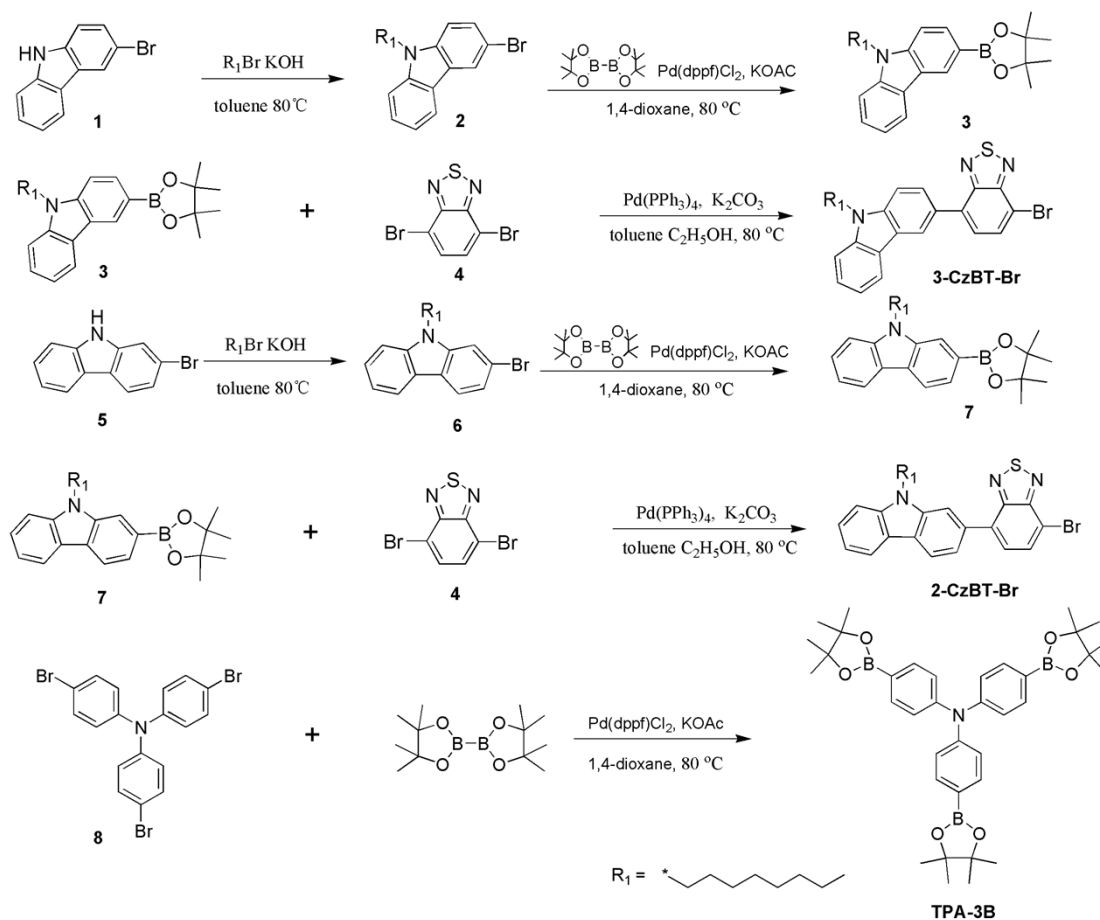
**Fig. S1.** TGA (a) and DSC (b) curves of TPA(BT-2Cz)<sub>3</sub> and TPA(BT-3Cz)<sub>3</sub> at a heating rate of 10 °C/min under an inert atmosphere.



**Fig. S2. Current density-voltage characteristics of the TPA(BT-2Cz)<sub>3</sub> and TPA(BT-3Cz)<sub>3</sub> based OSCs at different D/A ratios under the illumination of AM 1.5 G 100 mW/cm<sup>2</sup>.**



## Synthesis of the compounds



### Synthesis of 3-bromo-9-octylcarbazole ( 2 )

To a solution of 3-bromo-9H-carbazole (2.16 g, 8.78 mmol) in degassed NaOH (20 mL, wt 50%) and toluene (100 mL) was added 1-bromooctane (1.86 g, 9.64 mmol). The mixture was then heated to 80 °C and stirred for 16 h under the atmosphere of nitrogen. After cooled down to room temperature (RT), the resulting mixture was poured into 50 mL water, then extracted with dichloromethane (DCM) three times (30 mL  $\times$  3) and washed with water (100 mL  $\times$  3). The combined organic layer was dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>) and after the filtration, the residue was purified by column chromatography on silica gel using petroleum ether (PE) as eluent

to give compound **2** as light yellow oil (2.2 g, yield 70.00%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, δ<sub>ppm</sub>): 8.20 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.1 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 9.0 Hz, 2H), 4.25 (t, *J* = 9.2 Hz, 2H), 1.99–1.75 (m, 2H), 1.38–1.1 (br, 10H), 0.84 (t, *J* = 8.0 Hz, 3H).

### Synthesis of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-octylcarbazole (**3**)

To a solution of 3-bromo-9-octylcarbazole (**2**) in 60 mL dry 1,4-dioxane was added bis(pinacolato)diboron (3.12 g, 12.28 mmol), potassium acetate (4.81 g, 49.12 mmol) and [1,10-bis(diphenylphosphino)-ferrocene]dichloropalladium (30 mg, 0.18 mmol) under the atmosphere of nitrogen. The mixture was then heated to 80 °C and stirred for 24 h. After that, the mixture was extracted with DCM and the combined organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was then removed off and the residue was passed through a flash silica gel column using DCM-PE (*V/V*=1:5~1:3) as the eluent to give compound **3** as yellow oil (2.50 g, yield 70.22%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, δ<sub>ppm</sub>): 8.73 (s, 1H), 8.27 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.4, 4H), 4.43 (t, *J* = 7.2 Hz, 2H), 2.01–1.88 (m, 2H), 1.50–1.35 (br, 12H), 1.35–1.10 (m, 10H), 0.86 (t, *J* = 9.7 Hz, 3H).

### Synthesis of 3-(7-bromobenzo[*c*][2,1,3]thiadiazol-4-yl)-9-octylcarbazole (Br-BT-3Cz)

To a mixture of compound **3** (2.5 g, 6.17 mmol) and 4,7-dibromobenzo[*c*][2,1,3]thiadiazole (2.71 g, 9.26 mmol) in a degassed solution of toluene (100 mL), anhydrous ethanol (20 mL) and potassium carbonate aqueous solution (2 M, 15 mL) was added tetrakis(triphenylphosphine)palladium [Pd(PPh<sub>3</sub>)<sub>4</sub>] (212 mg, 0.18 mmol). The

mixture was heated to 80 °C for 24 h under nitrogen. After cooled down to RT, the mixture was poured into water (100 mL) and extracted with DCM three times (3 × 50 mL). Then the combined organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent was removed off by rotary evaporation. After that the residue was passed through a flash silica gel column using DCM- PE (V/V=1:5~1:3) as the eluent to give compound **Br-BT-3Cz** as orange yellow solid. (2.15 g, yield 71.7%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, δ<sub>ppm</sub>): 8.62 (s, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 8.03 (d, *J* = 9.5 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.61–7.41 (m, 3H), 7.34–7.22 (m, 1H), 4.35 (t, *J* = 7.1 Hz, 2H), 2.05–1.79 (t, 2H), 1.48–1.15 (m, 10H), 0.87 (t, *J* = 6.4 Hz, 3H).

#### **Synthesis of 2-bromo-9-octylcarbazole ( 6 )**

Compound **3** was prepared according to the synthetic procedure of compound **2** with a yield of 68.60% as yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, δ<sub>ppm</sub>): 8.06 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.54 (s, 1H), 7.48 (t, *J* = 6.7 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28–7.20 (br, 1H), 4.24 (t, *J* = 6.2 Hz, 2H), 1.97–1.77 (br, 2H), 1.35–1.25 (br, 10H), 1.01–0.75 (br, 3H).

#### **Synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-octylcarbazole ( 7 )**

Compound **4** was prepared according to the synthetic procedure of compound **3** with a yield of 70.60% as light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, δ<sub>ppm</sub>): 8.19-8.02 (br, 2H), 7.88 (s, 1H), 7.69 (d, *J* = 4.6 Hz, 1H), 7.55–7.36 (m, 2H), 7.30–7.13 (m, 1H), 4.47–4.24 (br, 2H), 2.00–1.76 (br, 2H), 1.50–1.30 (br, 12H), 1.30–1.14 (br, 10H), 0.96–0.76 (br, 3H).

### Synthesis of 2-(7-bromobenzo[*c*][2,1,3]thiadiazol-4-yl)-9-octylcarbazole (Br-BT-2Cz)

It was prepared according to the synthetic procedure of compound **Br-BT-3Cz** with a yield of 69.20% as yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, δ<sub>ppm</sub>): 8.22 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 8.00 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.32–7.20 (m, 1H), 4.38 (t, *J* = 7.0 Hz, 2H), 2.10–1.81 (m, 2H), 1.49–1.11 (m, 10H), 0.83 (t, *J* = 6.7 Hz, 3H).

### Synthesis of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine

To a solution of tris(4-bromophenyl)amine (1.0 g, 2.1 mmol), bis(pinacolato)diboron (3.2 g, 12.6 mmol) and potassium acetate (6.15 g, 62.8 mmol) in 60 mL dry 1,4-dioxane were added [1,10-bis(diphenylphosphino)-ferrocene] dichloropalladium (51 mg, 0.06 mmol) under nitrogen. The mixture was then heated to 80 °C for 24 h. After cooled to RT, the mixture was extracted with DCM three times (3×50 mL) and the combined organic layer was dried over anhydrous MgSO<sub>4</sub>. After that the solvent was removed off and the residue was passed through a flash silica gel column using DCM- PE (*V/V*=1:1) as the eluent to give white solid (0.92 g, yield 70.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 6.97 (d, *J* = 8.6 Hz, 6H), 7.68 (d, *J* = 8.2 Hz, 6H), 1.34 (s, 36H).



# NMR and Maldi Toff MS

