

Supporting Information

Highly Efficient and Stable Organic Sensitizers with Duplex Starburst Triphenylamine and Carbazole Donors for Liquid and Quasi-solid-state Dye-sensitized Solar Cells

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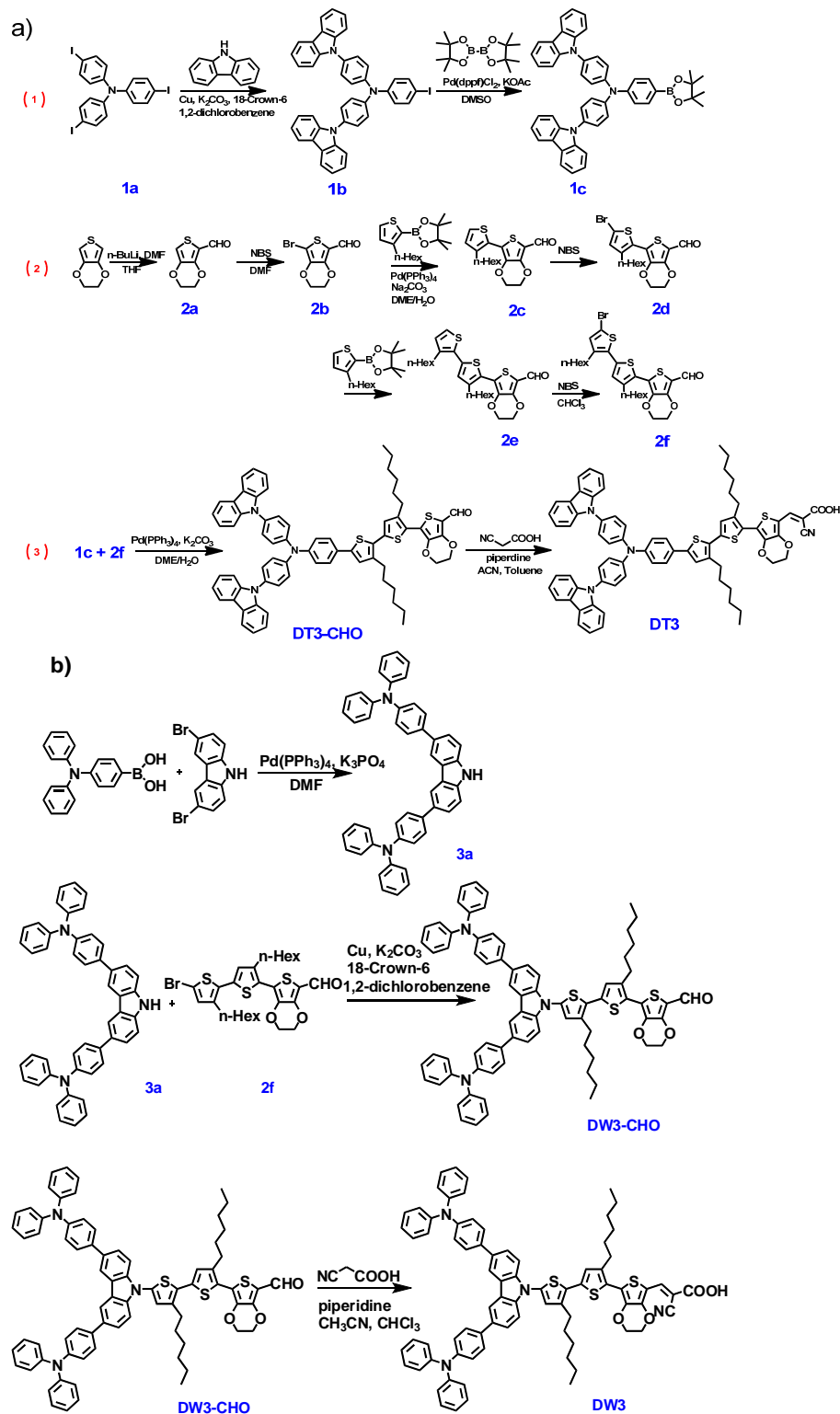
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Table of Contents

- 1. Synthetic procedure and characterization data.**
- 2. Computational method**
- 3. Dye-loading measurements.**
- 4. Figure S1 Absorption spectra of two dyes DT3 and DW3 on TiO₂.**
- 5. Table S1 Selected calculated singlet excited-state transitions for DW3 and DT3.**
- 6. Table S2 The resistance and Lifetime deduced from the EIS studies of DW3 and DT3.**

1. Synthetic procedure and characterization data



Scheme S1 Graphical synthetic routes of **DT3** and **DW3**.

The intermediates **2c-2f** and **3a** were synthesized according to the procedures listed below.

Synthesis of **2c**

The mixture **2b** (500 mg, 2.0 mmol), 2-(3-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (768 mg, 2.6 mmol), Pd(PPh₃)₄ (148 mg, 0.12 mmol) was added to a Schlenk flask under nitrogen atmosphere, and then degassed dimethoxyethane (24 mL) and 2 M degassed anhydrous Na₂CO₃ solution (360 mg, 3.4 mmol, 1.7 mL) was added. The reaction mixture was then refluxed at 90 °C. After completion of the reaction as monitored by TLC, the mixture was cooled and evaporated to dryness. The residue was dissolved in ethyl acetate and the organic content was washed with water and brine. The combined organic extracts were subsequently dried over anhydrous MgSO₄, filtered and evaporated to afford a crude product which was further purified by silica-gel column chromatography using petroleum ether and ethyl acetate as the eluant (3:1, v/v) to yield 615 mg yellow solid. Yield: 91%. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 9.93 (s, 1H), 7.34 (d, *J* = 5.2 Hz, 1H), 6.95 (d, *J* = 5.2 Hz, 1H), 4.37 (tdd, *J* = 6.7, 4.1, 2.6 Hz, 5H), 2.81-2.74 (m, 2H), 1.69-1.56 (m, 2H), 1.39-1.26 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 179.6, 148.3, 142.9, 137.4, 129.7, 126.7, 126.1, 122.6, 116.3, 65.2, 64.6, 31.7, 30.4, 29.8, 29.3, 22.6, 14.1; MALDI-TOF: *m/z* 336.454 ([M⁺]).

Synthesis of **2d**

The mixture of **2c** (159 mg, 0.47 mmol) and NBS (84 mg, 0.47 mmol) in CHCl₃ (10 mL) was stirred at room temperature for 10 h, and then evaporated to dryness. The residue was dissolved in ethyl acetate and the organic content was washed with water and brine. The combined organic extracts were subsequently dried over anhydrous MgSO₄, filtered and evaporated to afford a crude product which was further purified by silica-gel column chromatography using petroleum ether and ethyl acetate as the eluant (3:1, v/v) to yield 177 mg yellow solid. Yield: 90%. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.40 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.89 (dd, *J* = 10.5, 6.3 Hz, 3H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.83-1.70 (m, 2H), 1.57-1.41 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 159.1, 146.0,

130.7, 126.9, 126.3, 122.1, 115.0, 110.1, 67.8, 31.3, 19.2, 13.8; MALDI-TOF: m/z 310.031 ($[M]^+$).

Synthesis of 2e

The mixture of **2d** (495 mg, 1.5 mmol), 2-(3-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (563 mg, 1.9 mmol), Pd(PPh₃)₄ (110 mg, 0.088 mmol) was added to a Schlenk flask under nitrogen atmosphere, and then degassed dimethoxyethane (18 mL) and 2 M degassed anhydrous Na₂CO₃ solution (276 mg, 2.6 mmol, 1.3 mL) was added. The reaction mixture was then refluxed at 90 °C. After completion of the reaction as monitored by TLC, the mixture was cooled and evaporated to dryness. The residue was dissolved in ethyl acetate and the organic content was washed with water and brine. The combined organic extracts were subsequently dried over anhydrous MgSO₄, filtered and evaporated to afford a crude product which was further purified by silica-gel column chromatography using petroleum ether and ethyl acetate as the eluant (5:1, v/v) to yield 592 mg yellow solid. Yield: 80%. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 9.94 (s, 1H), 7.18 (d, $J = 5.2$ Hz, 1H), 6.96 (s, 1H), 6.93 (d, $J = 5.2$ Hz, 1H), 4.39 (dd, $J = 11.1, 5.2$ Hz, 4H), 2.78 (dd, $J = 16.2, 9.4$ Hz, 4H), 1.75 - 1.58 (m, 4H), 1.44-1.21 (m, 12H), 0.94-0.82 (m, 6H) ; ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 179.5, 148.3, 143.1, 140.1, 137.4, 137.3, 130.2, 130.1, 128.3, 126.0, 124.1, 122.5, 116.1, 65.2, 64.7, 31.7, 31.6, 30.7, 30.3, 30.1, 29.3, 29.37, 29.2, 22.6, 14.1; MALDI-TOF: m/z 502.147 ($[M]^+$).

Synthesis of 2f

The mixture of **2e** (282 mg, 0.56 mmol) and NBS (100 mg, 0.56 mmol) in CHCl₃ (10 mL) was stirred at room temperature for 10 h, and then evaporated to dryness. The residue was dissolved in ethyl acetate and the organic content was washed with water and brine. The combined organic extracts were subsequently dried over anhydrous MgSO₄, filtered and evaporated to afford a crude product which was further purified by silica-gel column chromatography using petroleum ether and ethyl acetate as the eluant (5:1, v/v) to yield 294 mg yellow solid. Yield: 90%. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 9.94 (s, 1H), 6.90 (s, 1H), 6.89 (s, 1H), 4.40 (dd, $J = 11.8, 4.6$ Hz, 5H), 2.83-2.74 (m, 2H), 2.74-2.65 (m, 2H), 1.75-1.60 (m, 4H), 1.45-1.18 (m,

12H), 0.88 (M, 6H); ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm): 179.6, 148.2, 143.1, 140.7, 137.4, 135.9, 132.8, 131.7, 128.6, 126.6, 122.1, 116.3, 110.9, 65.2, 64.7, 31.7, 31.6, 30.5, 30.3, 30.0, 29.3, 29.1, 22.6, 14.1; MALDI-TOF: m/z 578.895 ($[\text{M}]^+$).

Synthesis of 3a

The mixture 3,6-dibromocarbazole (488 mg, 1.5 mmol), 4-(diphenylamino) phenylboronic acid (954 mg, 3.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (69 mg, 0.06 mmol) was added to a Schlenk flask under nitrogen atmosphere, and then degassed DMF (9 mL) and K_3PO_4 (1.1 g, 4.5 mmol) was added. The reaction mixture was then refluxed at 100 °C. After completion of the reaction as monitored by TLC, the mixture was cooled and evaporated to dryness. The residue was dissolved in ethyl acetate and the organic content was washed with water and brine. The combined organic extracts were subsequently dried over anhydrous MgSO_4 , filtered and evaporated to afford a crude product which was further purified by silica-gel column chromatography using petroleum ether and dichloromethane as the eluant (2:1, v/v) to yield 736 mg white solid. Yield: 75%. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.35 (s, 2H), 8.12 (s, 1H), 7.71 (dd, $J = 8.4$ Hz, 1.8, 2H), 7.65-7.63 (m, 4H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.32 (dt, $J = 7.3$ Hz, 1.7 Hz, 8H), 7.24-7.22 (m, 4H), 7.20 (dd, $J = 8.6$ Hz, 1.1 Hz, 8H), 7.07 (dd, $J = 10.4$ Hz, 4.2 Hz, 4H). ^{13}C NMR (100 MHz, DMSO) δ (ppm): 147.87, 146.51, 136.38, 129.27, 127.94, 124.49, 124.23, 122.73, 118.41, 110.87, 58.49, 29.73, 26.95, 18.46. **ESI-MS**: m/z 652.961 ($[\text{M}-\text{H}]^-$).

2. Computational method

Density Functional theory (DFT) at the hybrid Becke, three-parameter and Lee-Yang (B3LYP) level and the CPCM solvent model were used to optimize the geometries of the model compounds. For all the atoms (C, H, O, N and S), the 6-31G* basis set was used. All the calculations were carried out with the Gaussian09 software package.

3. Dye-loading measurements.

The dye loading on TiO_2 films was measured by desorbing the dye into 0.05 M $(\text{NH}_4)_4\text{NOH}$ in ethanol solution, and the resultant solutions were diluted to the same concentration and their UV-*vis* absorption spectra were recorded. The dye-adsorbed amount was calculated from the different concentration of each solution before and

after TiO₂ film immersion.

4. Figure S1

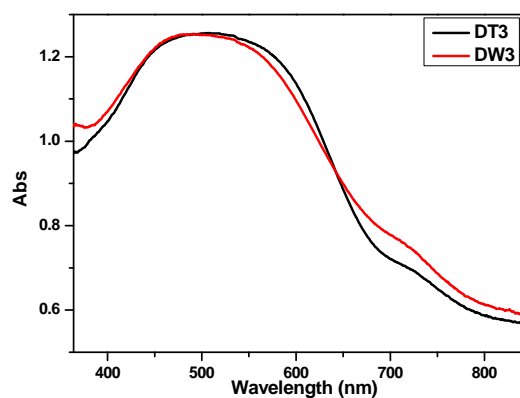


Figure S1 Absorption spectra of two dyes **DT3** and **DW3** on TiO₂.

5. Table S1

Table S1 Selected calculated singlet excited-state transitions for **DW3** and **DT3**.

Dye	State	Composition ^a	Calc.(eV, nm)	f	Exp.(eV, nm)
DW3	S ₁	63% H-2 →L	2.81(442)	1.7284	2.53(490)
	S ₂	53% H →L+3	4.02(308)	1.3818	3.66(339)
DT3	S ₁	47% H →L	2.78(446)	1.8476	2.42(512)
	S ₂	56% H →L+5	4.08(304)	0.8494	3.99(311)

a : H=HOMO, H-1=HOMO-1, H-2=HOMO-2, L=LUMO

6. Table S2

Table S2 The resistance and Lifetime deduced from the EIS studies of **DW3** and **DT3**.

Dye	Left semicircle		Right semicircle			
	R _{pt} (ohm)	R _{pt} Error%	R _r (ohm)	CPE-T(μF)	Lifetime(ms)	R _r Error%
DT3	4.819	4.78%	225.1	1.338E-3	301.2	0.5375
DW3	1.809	7.16%	202.3	1.098E-3	242.1	0.5807