Supporting Information

A D–π–A–π-A sensitizer for high efficiency dye-sensitized solar cells

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1. Computational Detail

The ground-state geometries of **C311** and **C321** have been optimized in the gas phase by DFT, using the hybrid B3LYP [1] function with 6-311G** basis set. Frequency calculations at the same level were performed to confirm each stationary point to be a true energy minimum. Performed on the optimized ground-state geometries, the electronic absorption spectra of dyes were calculated with the time dependent density functional theory (TD-DFT) method using the 6-311G** level. Different with function used in the geometry optimization, MPW1K[2] function has been used in the computation of absorption spectra. The effects of the respective solvents were added using the polarizable continuum model of solvation (CPCM). The calculations for isolated dyes were performed with the Gaussian 09 program

package[3]. To model the TiO_2 anatase (101) surface, a $(TiO_2)_{38}$ cluster which nicely reproduce the main electronic characteristics was used. The dye-absorbed geometries were optimized in the gas phase using the Dmol[3] package based on density functional theory (DFT) employing the generalized gradient approximation (GGA)[4] with the Perdew-Burke-Ernzerhof (PBE)[5] functional with DNP basis set. The electronic structure of the combined system subsequently calculated at DFT/B3LYP level of theory using the SVP basis set in CH3CN solution. Electron injection time evaluated from an orbital broadening model derived from the Newns-Anderson approach[6], involving calculation of the energetic broadening (Δ) of the absorbate LUMO level, $\tau_{inj} = 658/\Delta$. The long hexyloxy chains were replaced with methoxy-substituents to reduce the computation cost of the dye-TiO_2 complex.

2. Synthesis

4-(Hexyloxy)iodobenzene (1)：

p-iodophenol (15 g, 68 mmol) and 1-bromohexane (11.3 g, 68 mmol) were dissolved in DMSO (50 ml). potassium hydroxide (15.2 g, 272 mmol) was added to the flask,the misture was stirred at room temperature for 30 minutes, The reaction was quenched by the addition of water (150 mL) and extracted with dichloromethane (3 × 70 mL), washed with water (2 × 50 mL) and dried over $MgSO_4$, the solvent was removed in vacuo. The compound 1 was used for the next reaction as obtained, with no further purifications. Yield: 20.1 g, (97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, J= 8.8 Hz, 2H) , 6.68 (d, J= 8.8 Hz, 2H), 3.90 (t, 2H), 1.79-1.72 (m, 2H), 1.47-1.40 (m, 2H), 1.35-1.30 (m, 4H), 0.92-0.88 (t, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 159.1. 138.3, 117.0, 82.5, 68.2, 31.7, 29.2, 25.8, 22.7, 14.2.

N,N-bis-(4-hexoxylphenyl)aniline (2)：

To a mixture of Compound 1 (19.2 g, 63 mmol), Aniline (2.65 g, 28.5 mmol), copper powder (1.8 g, 28 mmol), 18-crown-6 (100 mg) and K_2CO_3 (44.85 g, 315 mmol) were heated to reflux under argon atmosphere for 48 h. After cooling to room temperature, the reaction mixture was

dissolved in dichloromethane (3 × 150 mL), washed with water (2 × 200 mL) and dried over $MgSO_4$, the solvent was removed in vacuo. The crude product was purified by column chromatography (hexane/ dichloromethane) gave compound 2 (10.68 g, 38 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 - 7.15(m, 2H), 7.07 (d, J = 2.4 Hz, 4H), 6.97 (d, J = 7.6 Hz, 2H), 6.89- 6.81 (m , 5H), 3.94 (t, J = 6.4 Hz, 4H), 1.83 - 1.76 (m, 4H), 1.52 – 1.45 (m, 4H), 1.38 – 1.35 (m, 8H), 0.94 (t, J = 6.8 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 155.4, 148.9, 141.0, 129.0, 126.5, 120.9, 120.5, 115.3, 68.3, 31.7, 29.5, 25.9, 22.8, 14.2.

4-Bromo-N,N-bis(4-hexoxylphenyl)aniline (3)

The Compound 2 (7 g, 15.7mmol) was dissolved in THF (100 ml), the reaction mixture was cooled to 0 ºC, NBS (2.79 g, 15.7 mmol) was added in one portion. After stirring the solution at 0 °C for 3 h. The reaction was quenched by the addition of water (50 mL) and extracted with dichloromethane (2 × 70 mL), the organic layer was dried over $MgSO_4$, the solvent was removed in vacuo. The crude product was purified by column chromatography (hexane/ dichloromethane) gave compound 3 (2.88 g, 35%). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 155.9, 132.0, 129.9, 126.9, 125.9, 122.7, 121.1, 120.2, 119.9, 117.9, 115.8, 115.7, 115.5, 68.6, 31.9, 29.7, 26.1, 22.9, 14.4.

4-Bromo-7-(4-formylphenyl)-2,1,3-benzothiadiazole (4).

4,7-Dibromo-2,1,3-Benzothidiazole (1.5 g, 5.1mmol), 4-formylphenylboronic acid (765 mg, 5.1mmol) and tetrakis(triphenylphosphine)palladium(115 mg, 0.1mmol) were dissolved under argon in dry Toluene (50 ml), the mixture was heated to reflux under argon atmosphere for 1 h, ethanol (12 mL) and aqueous 2 M sodium carbonate solution(20 mL) were added to the mixture then refluxed for 3 h. After cooling to room temperature, the reaction mixture was dissolved in dichloromethane (2 × 100 mL), washed with water (2 × 20 mL) and dried over $MgSO_4$, the solvent was removed in vacuo. and the crude product was purified by column chromatography (hexane/ dichloromethane) gave compound 4 (450 mg, 29%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.12 (s, 1H), 8.10(d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 191.7, 153.9, 152.8, 142.4, 136.1, 132.5, 132.2, 130.4, 130.0, 129.8, 128.9, 114.7.

4-Bromo-7-bromomethylbenzo-2,1,3-thiadiazole (5)

4-Bromo-7-methylbenzo-2,1,3-thiadiazole (4.8 g, 21mmol), benzoyl peroxide (15 mg), 33%

HBr in AcOH (1mL) and NBS (3.7 g, 21mmol) were dissolved in CCl_4 (150ml), the mixture was stirred at room temperature for 30 minutes, The reaction was quenched by addition of water and extracted with DCM. The combined organic extract was dried over anhydrous MgSO4 and filtered, The crude product was purified by column chromatography (hexane/ dichloromethane) gave compound 5 (5.45 g, 85%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83(d, J = 7.6 Hz, 1H), 7.55(d, J = 7.6 Hz, 1H), 4.94(s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 153.5, 152.9, 131.9, 130.3, 129.8, 114.8, 27.7.

4-Bromo-7-hydroxymethylbenzo-2,1,3-thiadiazole (6)

The compound 5 (5 g, 16 mmol) was dissolved in a mixture of dioxane/water (100 mL, 1:1 v/v), K_2CO_3 (6.72 g, 48 mmol) was added to the mixture then refluxed for 1 h, the solvents were removed in vacuo. The residue was acidified with 20% aqueous HCl and extracted with dichloromethane. The organic layer was dried over $MgSO_4$, the solvent was removed in vacuo. The crude product was purified by column chromatography (hexane/ dichloromethane) gave compound 6 (2.02 g, 51%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84(d, J = 7.2 Hz, 1H), 7.49(d, J = 7.2 Hz, 1H), 5.14(d, J = 5.6 Hz, 2H), 2.58(t, J = 6.4 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 153.5, 153.1, 133.2, 132.0, 126.9, 113.2, 61.8.

7-Bromobenzo[1,2,5]thiadiazole-4-carbaldehyde (7)

The compound 6 (1.5 g, 6 mmol) was dissolved in chloroform, Manganese dioxide (2.09 g, 24 mmol) added to the mixture, the mixture was stirred at room temperature for 15 h, the reaction mixture was filtered, the solvent was removed in vacuo. The crude product was purified by column chromatography (hexane/ dichloromethane) gave compound 7 (1.28 g, 85%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.78 (s, 1H), 8.11(d, J = 7.6 Hz, 1H), 8.06(d, J = 7.6 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 188.4, 154.1, 152.4, 132.2, 131.7, 126.9, 121.9.

Tributyl(3,4-ethylenedioxythien-2-yl)stannane (8)

Tributyl(3,4-ethylenedioxythienyl-2)stannane (10 g, 70 mmol) was dissolved in dry THF (200 ml) at −78°C under argon, n-butyllithium (30 mL, 75 mmol, 2.5 M in hexane) was added dropwise. After stirring for 1 h, tributyltin chloride (27.7 g, 85 mmol) was added slowly to it over 1 h, then the reaction mixture was stirred at room temperature for 4 h. After removing the THF solvent, the residue was dissolved in PE and filtered. The solvent was removed in vacuo. The compound was used for the next reaction as obtained, with no further purifications. Yield: 30 g

(99%). MALDI-TOF (m/z): 432.9 [M^+].

2-{4-[N,N-Bis(4-hexyloxyphenyl)amino]phenyl}-3,4-(ethylenedioxy)thiophene (9)

The compound 3(1.92 g, 3.7 mmol), the compound 8(2.36 g, 5.5 mmol) and Bis(triphenylphosphine)palladium(II) chloride (260 mg, 0.37 mmol) were dissolved under argon in dry toluene (50 ml), the mixture was heated at 100°C under argon atmosphere for 12 h. After cooling to room temperature, the reaction mixture was dissolved in dichloromethane (3 ×50 mL), washed with water (2 × 20 mL) and dried over $MgSO_4$, the solvent was removed in vacuo. The crude product was purified by column chromatography (hexane/ dichloromethane) gave compound 9(680 mg, 31%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52(d, J = 8.8 Hz, 2H), 7.06(d, J = 8.8 Hz, 2H), 6.94(d, J = 8.8 Hz, 2H), 6.83(d, J = 8.8 Hz, 4H), 6.22(s, 1H), 4.29(m, 2H), 4.24(m, 2H), 3.95(t, J = 6.4 Hz, 4H), 1.82(m, 4H), 1.51(m, 4H), 1.38(m, 8H), 0.94(t, J = 7.2 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ:155.7, 147.7, 142.5, 140.9, 127.0, 126.7, 125.6, 120.9, 118.1, 115.5, 96.5, 68.6, 65.0, 64.8, 31.9, 29.6, 26.0, 22.9, 14.3. MALDI-TOF (m/z): 586.2 [M^+].

4-[5-tributylstannyl-3,4-ethylenedioxythiophene-2-yl]-N,N-bis(4-hexyloxyphenyl)aniline (10)

The compound 10 was synthesized by the same method as the compound8. using 9(600 mg, 1.2 mmol) instead of Tributyl(3,4-ethylenedioxythienyl-2)stannane to gave compound 10. MALDI-TOF (m/z): 876.9 [M^+].

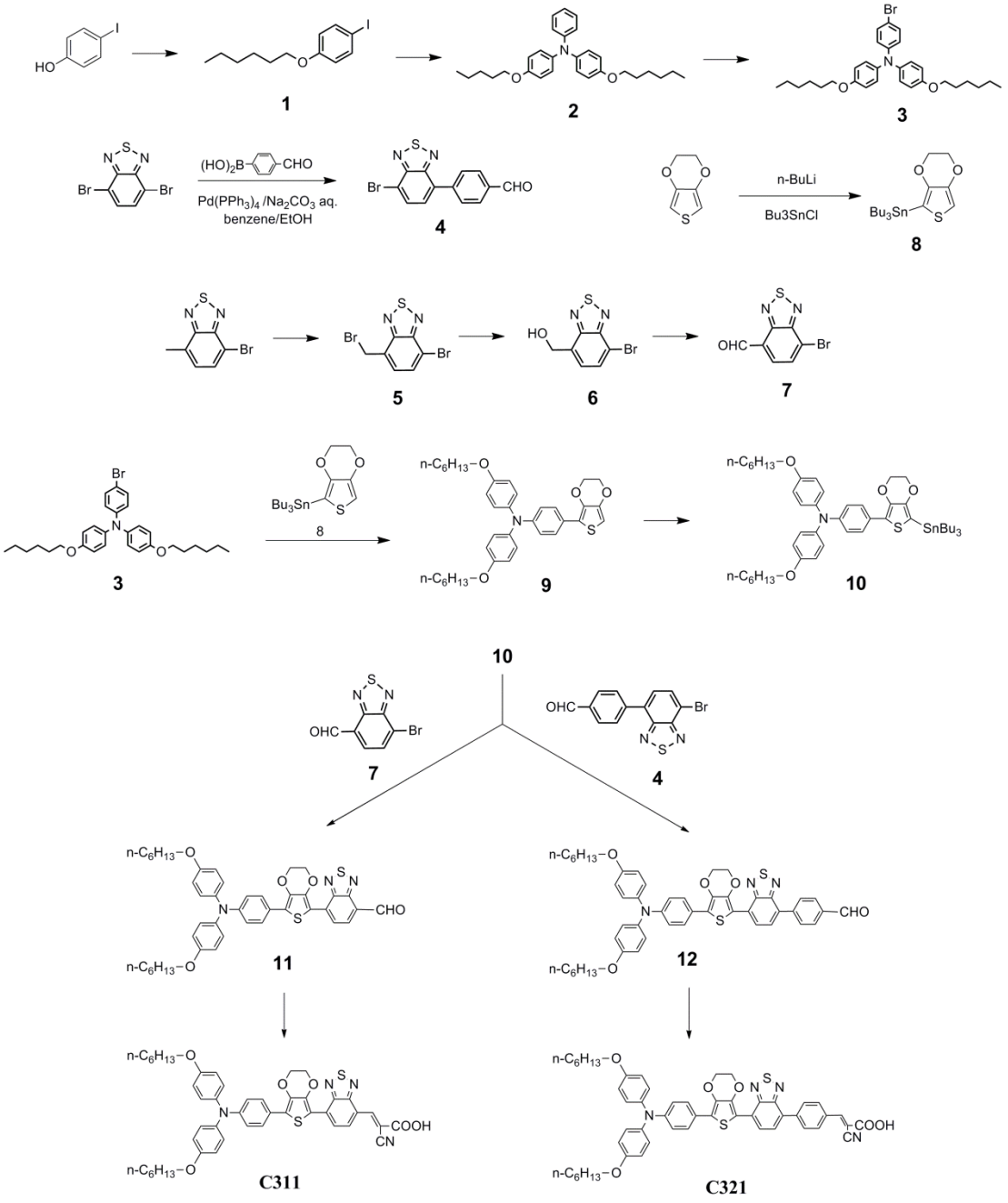
7-{4-[N,N-Bis(4-hexyloxyphenyl)-4-aminophenyl]-3,4-ethylenedioxythiophene-2-yl}benzo[1,2,5]thiadiazole-4-carbaldehyde (11)

The compound 11 was synthesized by the same method as the compound 9. using 7(109 mg, 0.45 mmol) and 10(300 mg, 0.34 mmol) instead of 3 and 8 to gave compound 11(185 mg, 73%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.54(s, 1H), 8.58(d, J = 8.0 Hz, 1H), 8.30(d, J = 8.0 Hz, 1H), 7.63(d, J = 8.8 Hz, 2H), 7.05(d, J = 8.8 Hz, 4H), 6.93(d, J = 8.8 Hz, 4H), 6.83(d, J = 8.8 Hz, 2H), 4.56 (m, 2H), 4.44(m, 2H), 3.96(t, J = 6.4 Hz, 4H), 1.74(m, 4H), 1.44(m, 4H), 1.33(m, 8H), 0.90(t, J = 7.2 Hz, 6H). 13C NMR (400 MHz, CDCl3) δ: 188.4, 155.8, 153.6, 152.3, 148.5, 143.8, 137.2, 132.5, 127.4, 123.5, 119.9, 115.4, 68.3, 65.2, 64.3, 31.9, 31.6, 29.7, 29.3, 25.8, 22.6, 14.0. MALDI-TOF (m/z): 747.7 [M^+].

4-{7-{4-[N,N-Bis(4-hexyloxyphenyl)-4-aminophenyl]-3,4-ethylenedioxythiophene-2-yl}benzo[1,2,5]thiadiazole-4-yl} benzaldehyde (12)

The compound 12 was synthesized by the same method as the compound 9. using 4 (143

mg, 0.45 mmol)and 10(300 mg, 0.34 mmol) instead of 3 and 8 to gave compound 12(87 mg, 31%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.09(s, 1H), 8.47(d, J = 8.0 Hz, 1H), 8.17(d, J = 8.0 Hz, 2H), 8.03(d, J = 8.0 Hz, 2H), 7.81(d, J = 8.0 Hz, 1H), 7.68(d, J = 8.8 Hz, 2H), 7.08(d, J = 9.2 Hz, 4H), 6.96(d, J = 8.4 Hz, 2H), 6.84(d, J = 9.2 Hz, 4H), 4.45 (m, 2H), 4.39(m, 2H), 3.96(t, J = 6.4 Hz, 4H), 1.82(m, 4H), 1.49(m, 4H), 1.37(m, 8H), 0.94(t, J = 7.2 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 191.8, 155.6, 153.4, 152.7, 147.9, 143.5, 141.7, 140.5, 137.1, 135.5, 129.9, 129.6, 129.3, 128.9, 127.2, 126.7, 125.4, 124.7, 121.7, 120.3, 115.3, 110.1, 68.3, 64.9, 64.4, 31.6, 29.3, 25.8, 22.6, 14.0. MALDI-TOF (m/z): 823.7 [M^+].



scheme 1

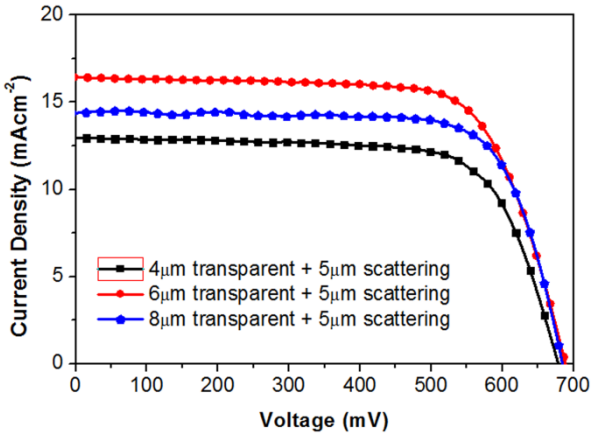


Figure S1. *J-V* curves of the C321 dye based on different thickness of TiO_2 transparent film.

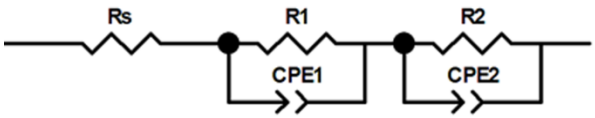


Figure S2. Equivalent circuit employed to fit impedance spectra of DSSCs.

$$n_c = n_0 e^{qv_F/k_B T} \qquad \text{Equation (S1)}$$

V_F is the bias voltage, T is the temperature, k_B is Boltzmann's constant, n_0 is the density of states in the TiO_2 conduction band.

3. Reference

1. A.D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
2 B.J. Lynch, P.L. Fast, M. Harris & D.G. Truhlar, *J. Phys. Chem. A,* 2000, **104**, 4811-4815.
3 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, Gaussian 09: Revision A01; 2009.
4 J.P Perdew & Y. Wang, *Phys. Rev. B,* 1992, **45**, 13244-13249.
5 J.P. Perdew, K. Burke & M. Ernzerhof, Phys. *Rev. Lett.,* 1997, **78**, 1396-1396.
6 D.M. Newns, *Phys. Rev.*, 1969, **178**, 1123-&.