Electronic Supplementary Information

High efficiency and stable dye-sensitized solar cells with an organic chromophore featuring a binary conjugated spacer

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Experimental details

1. Materials

All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Lithium diisopropylamide, and tetrabutylammonium hexafluorophosphate were purchased from Aldrich. Guanidinium thiocyanate, 2-cyanoacetic acid, ethyl mercapoacetate, and 3α,7α-dihyroxy-5β-cholic acid were purchased from Fluka. 1-Ethyl-3-methylimidazolium tetracyanoborate and 400-nm-sized TiO_2 anatase particles were received as gifts from Dyesol. The synthesis of 1,3-dimethylimidazolium iodide and 1-ethyl-3-methylimidazolium iodide was described in our previous paper.[S1] *N*,*N*-Bis(4-hexyloxyphenyl)-4-bromoaniline,[S2] (thieno[3,2-*b*]thiophen-2-yl)boronic acid,[S3,S4] and 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene,[S5] were synthesized according to the corresponding literature methods.

2. Synthesis

2-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-3,4-(ethylenedioxy)thiophene (1). A mixture of *N*,*N*-bis(4-hexyloxyphenyl)-4-bromoaniline (3.2 g, 6.1 mmol), 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (3.4 g, 7.95 mmol), $Pd(PPh_3)_4$ (0.7 g, 0.61 mmol) and 50 mL of anhydrous toluene was refluxed for 20 h under Ar. After removing solvent with a rotoevaporator, the residue was purified on a silica gel column with dichloromethane/hexane (1/2, *v*/*v*) as eluent to obtain **1** (3.0 g, 83.3%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, J=7.2 Hz, 6H), 1.31 (m, 8H), 1.41 (m, 4H), 1.71 (m, 4H), 3.92 (t, J=6.4 Hz, 4H), 4.21 (m, 2H), 4.25 (m, 2H), 6.48 (s, 1H), 6.77 (d, *J*=8.8 Hz, 2H), 6.88 (d, *J*=8.8 Hz 4H), 6.97 (d, *J*=8.8 Hz, 4H), 7.43 (d, *J*=8.8 Hz, 2H).

2-{2-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-3,4-(ethylenedioxy)thiophene-5-yl}thieno[3,2-*b*]thiophene (3). A solution of *N*-bromosuccinimide (0.8 g, 4.5 mmol) in DMF (5 mL) was added dropwise to a stirred solution of compound **1** (2.4 g, 4.1 mmol) in DMF (30 mL) at 0 °C. After stirring the solution for 10 min at 0 °C, water (50 mL) was added, and the aqueous layer was extracted with ethyl acetate (50 mL). The organic layer was dried over anhydrous sodium sulfate and the solvent was removed with a rotoevaporator. The residue was purified on a silica gel column with ethyl acetate/petroleum ether (1/10, *v*/*v*) as eluent to obtain **2** (2.6 g, 96%). The compound **2** (1.3 g, 1.96 mmol), (thieno[3,2-*b*]thiophen-2-yl)boronic acid (0.72 g 3.91 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.20 mmol) were dispersed in a mixture of THF (70 mL) and 2 M potassium carbonate aqueous solution (6.9 mL). After the reaction was performed at 70 °C for 12 h under Ar the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with a sodium carbonate aqueous solution and water, and subsequently dried over anhydrous sodium sulfate. The solvent was removed with a rotoevaporator and the residue was purified on a silica gel column with ethyl acetate/petroleum ether (1/10, *v*/*v*) as eluent to obtain **3** (0.7 g, 50%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, *J*=7.2 Hz, 6H), 1.31 (m, 8H), 1.41 (m, 4H), 1.71 (m, 4H), 3.93 (t, *J*=6.4 Hz, 4H), 4.37 (m, 2H), 4.42 (m, 2H), 6.78 (d, *J*=8.8 Hz, 2H), 6.89 (d, *J*=8.8 Hz, 4H), 7.01 (d, *J*=8.8 Hz, 4H), 7.40 (d, *J*=5.2 Hz, 1H), 7.47 (d, *J*=8.8 Hz, 2H), 7.54 (s, 1H), 7.60 (d, *J*=5.2 Hz, 1H).

2-{2-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-3,4-(ethylenedioxy)thiophene-5-yl}thieno[3,2-*b*]thiophen-5-carbaldehyde (4). The compound **3** (0.7 g, 0.97 mmol) and DMF (0.75 mL, 9.7 mol) were dissolved in 1,2-dichloroethane (10 mL). After cooling the solution to 0 °C, phosphorus oxychloride (0.13 mL, 1.4 mmol) was added dropwise. The reaction was kept at 70 °C for 6 h under Ar. After cooling to room temperature, 20 mL water was added into the reaction mixture, followed by neutralizing with sodium acetate. The mixture was extracted with dichloromethane, and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed with a rotoevaporator and the residue was purified on a silica gel column with ethyl acetate/petroleum ether (1/5, *v*/*v*) as eluent to obtain **4** (0.32 g, 43%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, *J*=7.2 Hz, 6H), 1.31 (m, 8H), 1.42 (m, 4H), 1.71 (m, 4H), 3.94 (t, *J*=7.2 Hz, 4H), 4.40 (m, 2H), 4.47 (m, 2H), 6.78 (d, *J*=8.8 Hz, 2H), 6.90 (d, *J*=8.8 Hz, 4H), 7.01 (d, *J*=8.8 Hz, 4H), 7.51 (d, *J*=8.8 Hz, 2H), 7.71 (s, 1H), 7.65 (s, 1H), 8.32 (s, 1H), 9.92 (s, 1H).

3-{2-{2-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-3,4-(ethylenedioxy)thiophene-5-yl}thieno[3,2-*b*]thiophen-5-yl}-2-cyano-acrylic acid (C217). The compound **4** (0.32 g, 0.43 mmol), cyanoacetic acid (0.11 g, 1.28 mmol), and piperidine (0.02 mL, 2.15 mmol) were added to 10 mL chloroform. The mixture was refluxed for 15 h. Then 20 mL water was added. The solution was acidified with 20% aqueous HCl and extracted with chloroform. The organic phase was dried over anhydrous sodium sulfate. The solvent was removed with a rotary evaporator and the residue was purified on a silica gel column with chloroform as eluent to obtain the crude product. The crude product was dissolved in chloroform and washed with aqueous HCl solution. The removal of solvent under reduced pressure gave **C217** (200 mg, 57%). IR (KBr) v/cm^{-1}: 1714 (COOH), 2214 (CN). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, *J*=6.8 Hz, 6H), 1.31 (m, 8H), 1.42 (m, 4H), 1.70 (m, 4H), 3.94 (t, *J*=6.4 Hz, 4H), 4.40 (m, 2H), 4.48 (m, 2H), 6.78 (d, *J*=9.2 Hz, 2H), 6.90 (d, *J*=9.2 Hz, 4H), 7.01 (d, *J*=9.2 Hz, 4H), 7.51 (d, *J*=9.2 Hz, 2H), 7.70 (s, 1H), 8.25 (s, 1H), 8.51 (s, 1H), 13.63 (s, 1H). ESI-MS *m*/*z* calcd. for ($C_{46}H_{46}N_2O_6S_3$): 817.0. Found: 818.3.

3. Computation

All calculations were performed in the Gaussian 03 program package. Without any symmetry constraints, the structure of the C217 sensitizer was optimized by using density functional theory (DFT) method combined with Becke's three-parameter hybrid functional[S6] and Lee-Yang-Parr's gradient corrected correlation functional.[S7] In particular, 6-31G(d) basis set was applied for all atoms. The optimized model was then incorporated into the ZINDO/S method to calculate the vertical electronic transition properties. The results were treated with the SWizard program (http://www.sg-chem.net/swizard/) to calculate the absorption profile as a sum of the Gaussian band using the following equation.[S8]

$$\varepsilon(\omega) = 2.174 \times 10^9 \sum_I \frac{f_I}{\Delta_{1/2,I}} \exp\left(-2.773 \frac{(\omega - \omega_I)^2}{\Delta_{1/2,I}^2} \right) \qquad (1)$$

Where ε is the molar extinction coefficient given in units of M^{-1} cm^{-1}, the energy ω of all allowed transitions included in equation 1 is expressed in cm^{-1}, f_I denotes the oscillator strength, and the half-bandwidths $\Delta_{1/2}$ is assumed to be 3000 cm^{-1}.

4. UV-Vis and Voltammetric Measurements

Electronic absorption spectra were performed on a UNICO WFZ UV-2802PC/PCS spectrometer. A computer controlled CHI660C electrochemical workstation was used for square-wave voltammetric measurements in combination with a mini three-electrode electrochemical cell equipped with a 5 μm radium Pt ultramicroelectrode as working electrode. A Pt wire and a silver wire were used as counter and quasi-reference electrodes, respectively.

5. Photovoltaic Characterization

A LS100 solar simulator (Solar Light Com. Inc., USA) was used to give an irradiance of 100 mW cm^{-2} (the equivalent of one sun at AM 1.5G) at the surface of solar cells. The current-voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). This process was fully automated using Labview8.0. A similar data acquisition system was used to control the incident photon-to-collected electron conversion efficiency (IPCE) measurement. Under full computer control, light from a 1000 W xenon lamp was focused through a monochromator onto the photovoltaic cell under test. Photovoltaic performance was measured by using a metal mask with an aperture area of 0.158 cm^2.

S1. Y. Cao, J. Zhang, Y. Bai, R. Li, S. M. Zakeeruddin, M. Grätzel and P. Wang, *J. Phys. Chem. C* 2008, **112**, 13775.

S2. M. Xu, R. Li, N. Pootrakulchote, D. Shi, J. Guo, Z. Yi, S. M. Zakeeruddin, M. Grätzel and P. Wang, *J. Phys. Chem. C*, 2008, **112**, 19770.

S3. D. Prim and G. Kirsch, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2603.

S4. L. S. Fuller, B. Iddon and K. A. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3465.

S5. S. S. Zhu and T. M. Swager *J. Am. Chem. Soc.*, 1997, **119**, 12568.

S6. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

S7. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1998, **37**, 785.

S8. P. J. Hay and W. R. J. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.

Scheme S1. Synthetic route of the C217 dye.

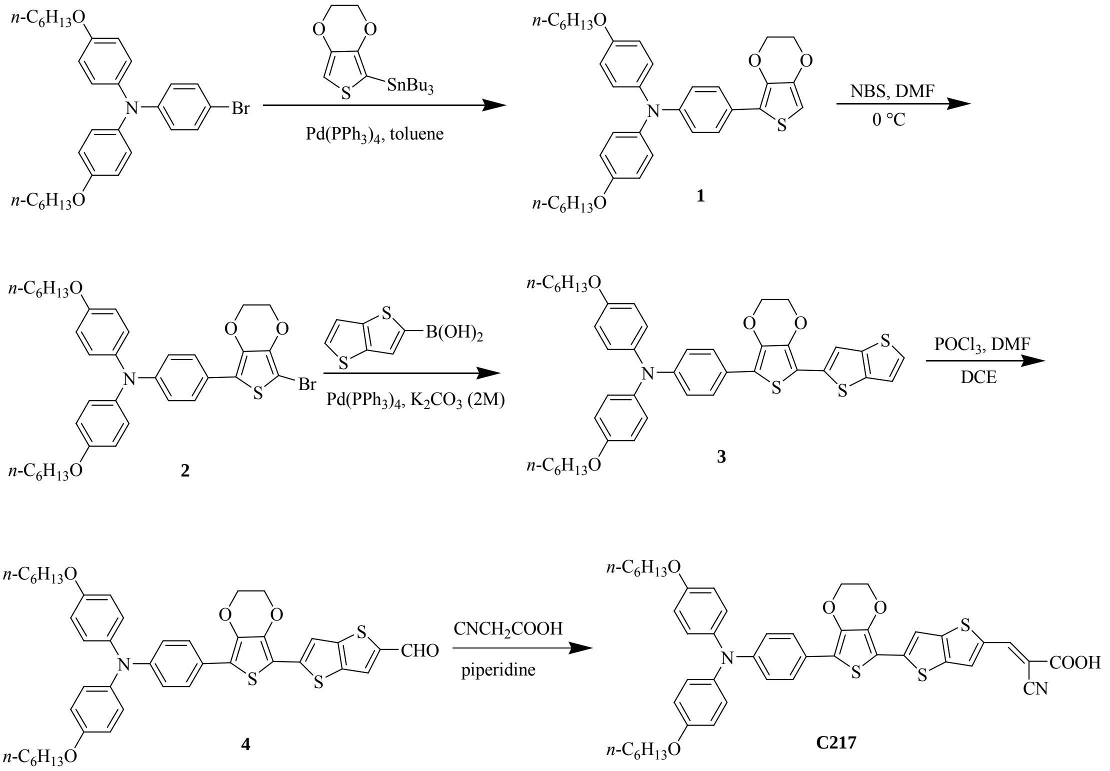

Fig. S1 Calculated transition-involved molecular orbitals of the C217 dye.

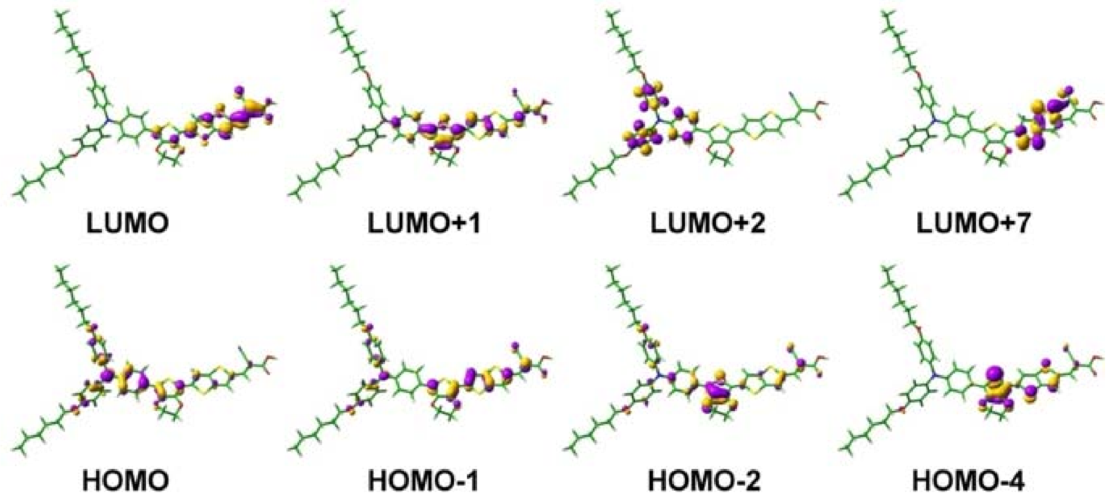

Table S1 Calculated details of electronic transitions with the relative oscillator strengths larger than 0.05 of the C217 dye.

Excitation energy (nm)	**Oscillator strength**	**Transition assignments**
582.6	1.5689	HOMO→LUMO (77%), HOMO-1→LUMO (10%)
401.4	0.2101	HOMO→LUMO+1 (60%), HOMO-1→LUMO (15%), HOMO-2→LUMO (12%)
327.3	0.2084	HOMO→LUMO+2 (45%), HOMO-2→LUMO (15%), HOMO-1→LUMO+1 (11%), HOMO-4→LUMO (5%), HOMO-1→LUMO+7 (5%)

Fig. S2 Calculated electronic transition spectrum of the C217 dye.

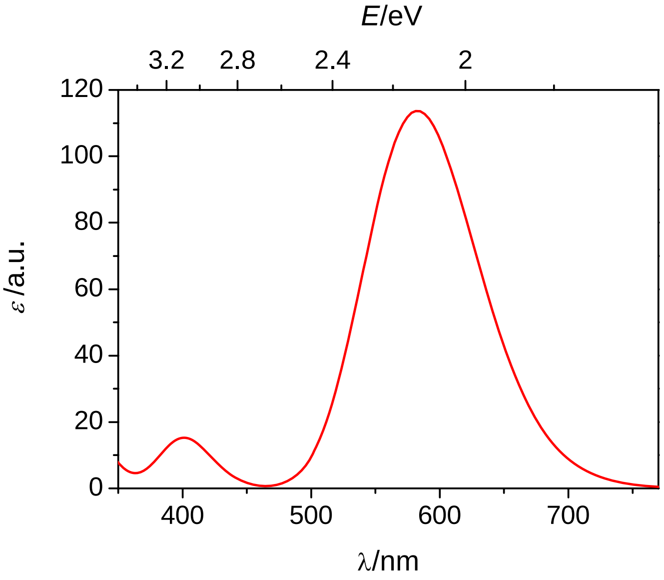

Fig. S3. Detailed photovoltaic parameters of cell B with the C217 dye measured under irradiation of 100 mW cm^{-2} AM1.5G sunlight during successive full sunlight soaking at 60 °C. The solvent-free electrolyte composition is DMII/1-ethyl-3-methylimidazolium iodide/1-ethyl-3-methylimidazolium tetracyanoborate/I_2/*N*-butylbenzimidazole/GNCS (molar ratio: 12/12/16/1.67/3.33/0.67). An antireflection film (λ<380 nm, ARKTOP, ASAHI Glass) is adhered to the DSC photoanode during *J*-*V* measurements.