Supplementary Material (ESI) for Energy & Environmental Science

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Electronic Supplementary Information

Employ the bisthienothiophen linker to construct an organic chromophore for efficient and stable dye-sensitized solar cells

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1. Materials

All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Lithium diisopropylamide, *n*-butyllithium, 4-bromoaniline, and tetra-*n*-butylammonium 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 Merck and Catalysts & Chemical Ind. Co., respectively. The synthesis of 1,3-dimethylimidazolium iodide and 1-ethyl-3-methylimidazolium iodide were described in our previous paper.[S1] 1-Ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide was prepared according to the reported procedure[S2] and the purity was confirmed by ^{1}H NMR analysis. Thieno[3,2-*b*]thiophen,[S3] (thieno[3,2-*b*]thiophen-2-yl)boronic acid,[S4] and 1-(hexyloxy)-4-iodobenzene[S5] were synthesized according to the corresponding literature methods. 2-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}thieno[3,2-*b*]thiophen and C206 were synthesized in our previous paper.[S6]

2. Synthesis of 2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-5-bromothieno[3,2-*b*]thiophen (1). A solution of *N*-bromosuccinimide (404 mg, 2.27 mmol) in DMF (15 mL) was added dropwise to a stirred solution of 2-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}thieno[3,2-*b*]thiophen (1.15 g, 1.97 mmol) in DMF (40 mL) at 0 °C. After stirring the solution for 1.5 h 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 rotary evaporator. The residue was purified on a silica gel column with dichloromethane/hexane (1/3, *v*/*v*) as eluent to obtain **1** (1.2 g, 92.3%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, *J*=4.8 Hz, 6H), 1.31 (m, 8H), 1.41 (m, 4H), 1.70 (m, 4H), 3.93 (t, *J*=4.4 Hz, 4H), 6.77 (d, *J*=6.0 Hz, 2H), 6.91 (d, *J*=6.0 Hz, 4H), 7.04 (d, *J*=6.0 Hz, 4H), 7.46 (d, *J*=6.0 Hz, 2H), 7.61 (s, 1H), 7.62 (s, 1H).

5-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-2,2'-bi(thieno[3,2-*b*]thiophen) (2). The compound **1** (0.7 g, 1.06 mmol), (thieno[3,2-*b*]thiophen-2-yl)boronic acid (0.29 g 1.6 mmol) and tetrakis(triphenylphosphine)palladium (0.25 g, 0.21 mmol) were dispersed in a mixture of THF (50 mL) and 2 M potassium carbonate aqueous solution (3.7 mL). The reaction was performed at 70 °C for 12 h under Ar and then 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 rotary evaporator and the residue was purified on a silica gel column with dichloromethane/hexane (1/3, *v*/*v*) as eluent to obtain **2** (0.42 g, 55.3%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.89 (t, *J*=4.4 Hz, 6H), 1.31 (m, 8H), 1.41 (m, 4H), 1.70 (m, 4H), 3.94 (t, *J*=4.4 Hz, 4H), 6.78 (d, *J*=5.6 Hz, 2H), 6.92 (d, *J*=6.0 Hz, 4H), 7.04 (d, *J*=6.0 Hz, 4H), 7.45 (d, *J*=3.6 Hz, 1H), 7.50 (d, *J*=5.6 Hz, 2H), 7.68-7.71 (m, 4H).

5'-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-2,2'-bi(thieno[3,2-*b*]thiophen)-5-carbaldehyde (3). The compound **2** (0.42 g, 0.58 mmol) and DMF (0.45 mL, 5.8 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 H_2O 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 rotary evaporator and the residue was purified on a silica gel column with dichloromethane/hexane(1/3, *v*/*v*) as eluent to obtain **3** (0.30 g, 68.2%). ^{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), 1.71 (m, 4H), 3.94 (t, *J*=6.8 Hz, 4H), 6.78 (d, *J*=8.4 Hz, 2H), 6.93 (d, *J*=9.2 Hz, 4H), 7.05 (d, *J*=9.2 Hz, 4H), 7.51 (d, *J*=8.4 Hz, 2H), 7.71 (s, 1H), 7.84 (s, 1H), 7.86 (s, 1H), 8.38 (s, 1H), 9.97 (s, 1H).

3-{5'-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-2,2'-bi(thieno[3,2-*b*]thiophen)-5-yl}-2-cyano-acrylic Acid (C211). The compound **3** (150 mg, 0.2 mmol), cyanoacetic acid (34 mg, 0.4 mmol), and piperidine (0.01 mL, 0.1 mmol) were added to 20 mL chloroform. The mixture was refluxed for 6 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 **C211** (110 mg, 68.8%). IR (KBr) v/cm^{-1}: 1717 (COOH), 2217 (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=6.8 Hz, 4H), 6.77 (d, J=8.4 Hz, 2H), 6.92 (d, J=8.8 Hz, 4H), 7.05 (d, J=8.8 Hz, 4H), 7.50 (d, J=8.4 Hz, 2H), 7.71 (s, 1H), 7.86 (s, 1H), 8.28 (s, 1H), 8.54 (s, 1H), 13.80 (s, 1H). ESI-MS m/z calcd. for ($C_{46}H_{44}N_2O_4S_4$): 817.11. Found: 816.5.

3. UV-Vis, Emission, FTIR, and Voltammetric Measurements. Electronic absorption spectra were performed on a UNICO WFZ UV-2802PC/PCS spectrometer. Emission spectra were recorded with a PerkinElmer LS55 luminescence spectrometer. The emitted light was detected with a Hamamatsu R928 red-sensitive photomultiplier. The FTIR spectra were measured using a BRUKER Vertex 70 FTIR spectrometer. A computer controlled CHI660C electrochemical workstation was used for square-wave voltammetric measurements in combination with a three-electrode electrochemical cell equipped with a 5 μm radium Pt ultramicroelectrode or platinized FTO as working electrode. A Pt wire and an Ag or Ag/AgCl (saturated KCl) electrode were used as counter and reference electrodes, respectively. Ferrocene was used as internal reference.

4. Photovoltaic Characterization. A 450 W xenon light source (Oriel, 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 spectral output of the lamp was matched in the region of 350−750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra. 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 Wavemetrics software (http://www.wavemetrics.com/). 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 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined by IPCE (λ)=12400($J_{sc}/\lambda\phi$), where λ is the wavelength, J_{sc} is short-circuit photocurrent density (mA cm^{-2}), and ϕ is the incident radiative flux (mW cm^{-2}).

5. Calculations

All calculations were performed in the Gaussian 03 program package. Without any symmetry constraints, the structure of the C211 sensitizer was optimized by using density functional theory (DFT) method combined with Becke's three-parameter hybrid functional[S7] and Lee-Yang-Parr's gradient corrected correlation functional.[S8] 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 was 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.[S9]

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

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}.

References

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. P. Bonhôte, A.-P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.

S3. L. S. Fuller, B. Iddon and K. A. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3465.

S4. D. Prim and G. Kirsch, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2603.

S5. Y. Hiroko, T. Ikuyoshi, O. Kazuchika and E. Takeshi, *Mol. Cryst. Liq. Cryst. A*, 2001, **369**, 47.

S6. 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**, in press.

S7. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

S8. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1998, **37**, 785.

S9. P. J. Hay and W. R. J. Wadt, *J. Chem. Phys*., 1985, **82**, 270.

Fig. S1 Calculated molecular orbitals of the C211 sensitizer.

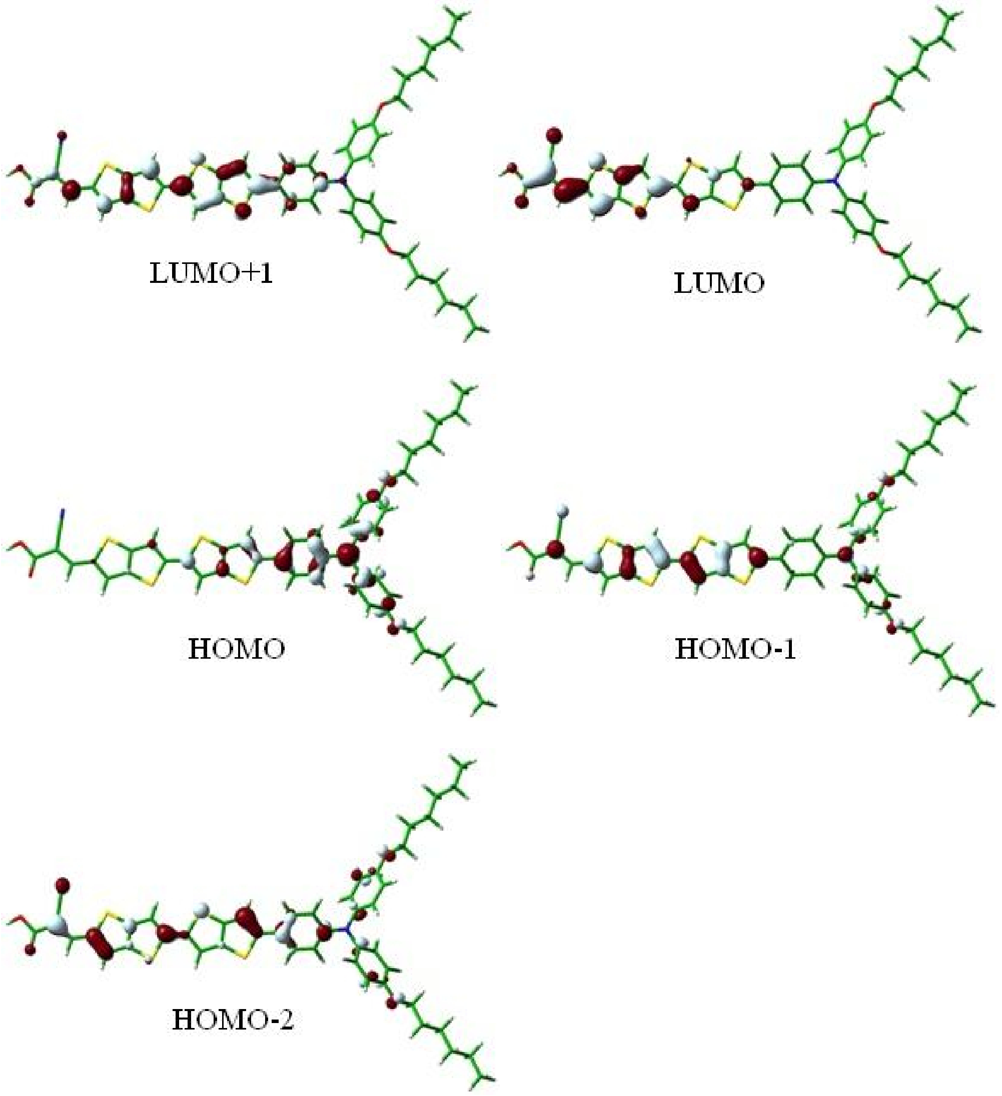

Fig. S2 Calculated electronic transition spectrum of the C211 sensitizer.