Supporting Information

Synthesis of Alkyl-functionalized Organic Dyes and Their Application to Dye Sensitized Solar Cells (DSSCs)

Eunji Lee, Narae Jung, Jinho Kim, Chan Im,[†] Yongil Seo, Hyonseok Hwang, and Youngjin Kang^{*}

Division of Science Education & Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea *E-mail: kangy@kangwon.ac.kr

[†]Department of Chemistry, Konkuk University, Seoul 143-701, Korea Received August 28, 2011, Accepted November 2, 2011

Materials and Characterization. All reagents were purchased from commercial sources and without further purification unless otherwise noted. All solvent were freshly distilled from appropriate drying agents prior to use. Conventional Schlenk techniques were used, and reactions were carried out under Ar unless otherwise noted. ¹H NMR Spectra were recorded with a Bruker avance 300 MHz or 600 MHz spectrometer instrument. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-Visible spectrometer and a Perkin LS fluorescence spectrometer, respectively. Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.). A three-electrode system was used and consisted of a gold disk, working electrode and a platinum wire electrode. Redox potentials of dyes on TiO2 were measured in CH3CN with 0.1 M (n-C₄H₉)₄NPF₆ with a scan rate of 50 mV s⁻¹.

Cell Fabrication. FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min, rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM TiCl₄ (aqueous) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by doctor blade printing TiO₂ paste (Solaronix, Ti-Nanoxide T/SP) and then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min .The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA), a paste for the scattering layer containing 400 nm sized anatase particles (CCIC, PST-400C) was deposited by doctor blade printing and then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The resulting layer was composed of 10 µm thickness of transparent layer and 4 µm thickness of scattering layer. The TiO₂ electrodes were treated again by TiCl₄ at 70 °C for 30 min and sintered at 500 °C for 30 min. The TiO_2 electrodes were immersed into the 1-4 (0.3 mM in EtOH containing 10 mM 3a,7a-dihydroxy-5b-cholic acid (Cheno)) and kept at room temperature for 12 h. The FTO plate (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) for counter electrodes cleaned with ultrasonic bath in H_2O , acetone and 0.1 M HCl(aq), subsequently. Counter electrodes were prepared by coating with a drop of H₂PtCl₆ solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate and heating at 400 °C for 15 min. The dye adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell by heating at 80 °C with a hotmelt ionomer film (Surlyn SX 1170-25, Solaronix) as a spacer between the electrodes. A drop of electrolyte solution (electrolyte of 0.6 M DMPImI, 0.05 M iodine, 0.1 M LiI, and 0.5 M tert-butylpyridine in acetonitrile) was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness).

Characterization of DSSC. The cells were measured using 1000W xenon light source, whose power of an AM 1.5 Oriel solar simulator was calibrated by using KG5 filtered Si reference solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV measurements).

Synthesis of Starting Materials (D ~ K)

9-(*N*-**phenylcarbazol-3-yl)thiophen-2-carboxaldehyde** (**D**). To a solution of compound **A** (0.5 g, 1.74 mmol), Pd(PPh₃)₄ (0.101 g, 0.087mmol) and 5-Bromothiophen-2carboxaldehyde (0.207 mL, 1.74 mmol) in dry toluene (25 mL) was added 2 M-Na₂CO₃ (8.7 ml, 17.4 mmol). The reaction mixture was refluxed for 12 h. After cooling the organic layer was extracted with CH₂Cl₂, and washed with H₂O, dried with MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂, R_f = 0.85) to yield compound **D** (47%). ¹H-NMR (CDCl₃, 300 MHz) 9.80 (1H, s), 8.28 (1H, s), 8.04 (1H, d), 7.59 (1H, d), 7.55 (1H, m), 7.49 (2H, m), 7.37 (3H, m), 7.27 (4H, m), 7.20 (1H, m)

9-(N-phenylcarbazol-3-yl)-5-formyl-2,2'-bithiophene

(E). The synthesis of compound E was carried out in a similar manner to that of **D**. The crude product was purified by column chromatography (CH₂Cl₂, $R_f = 0.69$) to yield compound E (77%). ¹H-NMR(CDCl₃, 300 MHz) δ 9.8 (1H,

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s), 8.3 (1H, s), 8.13 (1H, d), 7.55 (6H, m), 7.43 (1H, m), 7.35 (4H, m), 7.27 (2H, m), 7.23 (1H, m).

3-(3-hexylthiophen-2-yl)-9-phenyl-9H-carbazole (H). To a solution of compound A (0.63g, 2.19 mmol), Pd(PPh₃)₄ (0.20 g, 0.18 mmol) and 2-bromo-3-hexylthiophene(0.57 mL, 2.85 mmol) in dry THF (30 mL) was added 2 M-K₂CO₃ (10.97 mL, 21.94 mmol). The reaction mixture was refluxed for 68 h. After cooling the organic layer was extracted with CH_2Cl_2 , and washed with H_2O , dried with MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (Hexane, $R_f = 0.33$) to yield compound H (69%). ¹H-NMR (CDCl₃, 300 MHz) δ 8.11 (d, J = 0.56 Hz, 1H), 8.08 (d, J = 7.73 Hz, 1H), 7.58-7.51 (m, 4H), 7.44-7.35 (m, 5H), 7.26-7.20 (m, 1H), 7.16 (s, 1H), 6.95 (d, *J* = 5.2 Hz, 1H), 2.66-2.61 (t, *J* = 7.85 Hz, 2H), 1.60-1.52 (m, 2H), 1.27-1.15 (m, 6H), 0.78-0.74 (t, J = 6.69 Hz, 3H).

3-(3',4-dihexyl-2,2'-bithiophen-5-yl)-9-phenyl-9*H***-carbazole (I). The synthesis of compound I was carried out in a similar manner to that of H**. The crude product was purified by column chromatography (CH₂Cl₂, $R_f = 0.24$) to yield compound I (50%). ¹H-NMR (CDCl₃, 300 MHz) δ 8.21 (d, J = 1.41 Hz, 1H), 8.16 (d, J = 7.72 Hz, 1H), 7.65-7.57 (m, 4H), 7.53-7.41 (m, 5H), 7.33-7.28 (m, 1H), 7.16 (d, J = 5.19 Hz, 1H), 7.03 (s, 1H), 6.94 (d, J = 5.2 Hz, 1H), 2.85-2.69 (dt, J = 7.83 Hz, J = 7.82 Hz, 4H), 1.73-1.53 (m, 4H), 1.43-1.24 (m, 12H), 0.91-0.82 (dt, J = 6.95 Hz, J = 5.97 Hz, 6H).

4-hexyl-5-(9-phenyl-9H-carbazol-3-yl)thiophene-2-carbaldehyde (J). To a cold solution of H (0.29g, 0.71 mmol) in dry DMF (5 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.15 mL of POCl₃ in DMF (0.5 mL). The mixture was stirred at 80 °C for 5 h, and quenched with 10% aqueous solution of NaOAc (30 mL) after cooling, and extracted with EtOAc three times. The combined organic layer was washed with H2O, dried over MgSO4, and evaporated under reduced pressure. The crude product was purified by column chromatography (Dichloromethane/ Hexane = 1:1, $R_f = 0.35$) to obtain J (52%).¹H-NMR $(CDCl_3, 300 \text{ MHz}) \delta 9.88 \text{ (s, 1H)}, 8.23 \text{ (d, } J = 0.89 \text{ Hz}, 1\text{H}),$ 8.16 (d, J = 7.73 Hz, 1H), 7.70 (s, 1H), 7.67-7.57 (m, 4H), 7.53-7.44 (m, 5H), 7.36-7.31 (m, 1H), 2.78-2.73 (t, J = 7.84 Hz, 2H), 1.72-1.62 (m, 2H), 1.38-1.24 (m, 6H), 0.91-0.82 (t, J = 8.04 Hz, 3H).

3,4'-dihexyl-5'-(9-phenyl-9*H***-carbazol-3-yl)-2,2'-bithiophene-5-carbaldehyde (K).** The synthesis of compound **K** was carried out in a similar manner to that of **J**. The crude product was purified by column chromatography (CH₂Cl₂/ Hexane = 1:1, R_f = 0.34) to yield compound **K** (47%). ¹H-NMR (CDCl₃, 300 MHz) δ 9.83 (s, 1H), 8.21 (d, *J* = 1.09 Hz, 1H), 8.17 (d, *J* = 7.73 Hz, 1H), 7.66-7.58 (m, 5H), 7.53-7.42 (m, 5H), 7.35-7.30 (m, 1H), 7.22 (s, 1H), 2.89-2.70 (dt, *J* = 7.83 Hz, *J* = 7.81 Hz, 4H), 1.77-1.62 (m, 4H), 1.45-1.26 (m, 12H), 0.92-0.82 (dt, *J* = 7.40 Hz, *J* = 6.95 Hz, 6H).



Figure S1. ¹H-NMR of C.



Figure S2. ¹H-NMR of D.



Figure S3. ¹H-NMR of 1.



Figure S4. MALDI-TOF of 1.



Figure S5. ¹H-NMR of E.

Notes



Figure S6. ¹H-NMR of 2.



Figure S7. MALDI-TOF of 2.



Figure S8. ¹H-NMR of H.



Figure S9. ¹H-NMR of I.

Notes



Figure S10. ¹H-NMR of J.



Figure S11. ¹H-NMR of K.



Figure S16. MALDI-TOF of 4.



Figure S17. ¹³C-NMR of 4.

Notes

Computational methods

The geometry optimizations in the ground state of **1-4** were carried out at the density functional theory (DFT) level with the B3LYP exchange–correlation functional and a 6-

31* basis set. The molecular orbitals were obtained at the same level of calculations. All the calculations were performed using the Gaussian 03 package¹ and visualizations were made possible by GaussView 5^{2} .



Figure S18. Isodensity surface plots of the HOMO and LUMO of 1-4 (isodensity value = 0.02 a.u.).



Figure S19. IPCE spectra.

References

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