

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

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Ruthenium dye-based dye-sensitized solar cells (DSSCs) have received great deal of attraction from chemists and material scientists because of their over 10% of photon to current conversion efficiency.¹ The high cost and much synthetic efforts of ruthenium dyes, nevertheless, has often been reported as problematic.²

Recently, organic dye-based DSSCs whose photon to current conversion efficiency approximates near 9% are suggested as an alternative.³ Organic dyes have several advantages compared to Ru dyes for DSSCs.⁴ For instance, organic dyes have larger absorption coefficients than Ru-based dyes which is attributed to an intramolecular π - π transition, that leads to an effective light harvesting properties. Organic dyes vary in structure and can be easily modified for molecular design, essential features for tuning the absorption characteristics of DSSCs. In addition, the use of organic dyes as DSSCs eliminates the requirement of large quantities of heavy metals which is an advantage considering escalating costs for metals and their limited availability.

Generally, organic dyes consist of three parts: electron-donor, electron-acceptor, and spacer as a linker between the two. A variety of organic dyes with high efficiency have been synthesized to date,² particularly, when electron donor material contributed to high efficiencies.^{2,5} Arylamine derivatives are reported as the electron donors mainly because these compounds make it easy to produce holes and to stabilize the complex through modification of the geometric structure in excited state.⁶ However, the synthesis of organic dyes with carbazole substituted electron donors and the performance of DSSC has been rarely done in spite of the similar properties of carbazole derivatives to those of arylamine in organic electronics.⁷ In addition, studies on increasing the efficiency of DSSC by controlling the spacer has been rarely explored, contrasting to the number of studies regarding increased efficiency of DSSC by varying the electron donors and/or acceptors.⁸

The previous studies suggest that including a thiophene-substituted spacer shows a comparatively large value of molar extinction coefficient in the absorption spectra.⁹ Moreover, additional studies on spacer control of organic dyes are related to the effect of introduction of steric bulky groups. A bulky group introduced into the molecular frame-

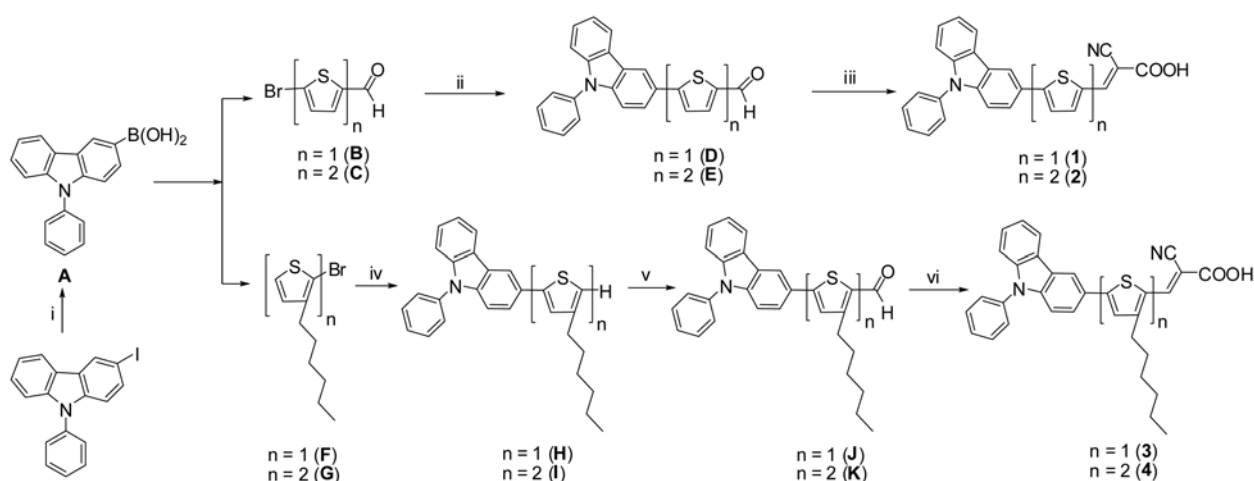
work does not only increase the electron life time (τ_e) of the dyes in the conduction band of TiO₂ but also inhibit dye-aggregation. This results in an increase of open-circuit voltage (V_{oc}). Such an approach was introduced by the Hara group, in which a bulky spacer, such as a hexylthiophene, was incorporated into the organic structure.⁷ We have previously synthesized a system containing thiophene analogs as a spacer,⁸ coupled with a phenyl-carbazole segment as an electron donor. Systematic investigation into the effect of bulky substituent in the spacers on efficiency of the DSSCs was carried out by molecular engineering. In this study, we report the synthesis of four new organic dyes, their photo-physical characteristics and DSSCs performances.

Result and Discussion

Four novel carbazole based organic dyes **1-4** (see Scheme 1), have been synthesized for the present study. Dyes **1-4** were obtained in good yields via two step processes that involved first a Suzuki cross-coupling of **A** with corresponding bromoformylthiophene (**B-C**), or bromohexylthiophene (**F-G**), followed by Knoevenagel condensation with cyanoacetic acid in the presence of a catalytic amount of piperidine in acetonitrile/chloroform, as shown in Scheme 1. The molecular structures of dyes **1-4**, were confirmed using various spectroscopic methods, such as NMR, mass and elemental analysis (see supporting information). Compounds **1** and **2** are slightly soluble in THF, CH₂Cl₂ and DMSO, while compounds **3** and **4** have good solubility in a variety of organic solvents.

Figure 1 shows the absorption and emission spectra of **1-4** measured in THF at ambient temperature. The UV-vis spectra of all dyes exhibit intense absorption bands at longer wavelength regions, and their maximum values (λ_{max}) are observed at 408-443 nm, as shown in Table 1. The absorption patterns for all compounds are similar, but molar extinction coefficients vary significantly.

As expected, the longer the π -conjugation within the spacer (increased number of thiophenes) the more red-shifted the absorption spectra. Interestingly, with the same number of thiophenes, additional hexyl substituents enhanced the molar extinction coefficient and shifted to longer



Scheme 1. Reagent and conditions: i) 2.5 M *n*-BuLi, B(OMe)₃, -78 °C; rt, 15 h; 1 M-HCl, 1 h. ii) & iv) Pd(PPh₃)₄, Aliquat[®] 336, 2 M-K₂CO₃, reflux, 68 h, THF. iii) & vi) cyanoacetic acid, piperidine, CH₃CN, 110 °C, 15 h. v) POCl₃, DMF, 0 °C, 10 min; 80 °C, 5 h.

Table 1. Optical, redox, and DSSC performance parameters of the dyes

Dye	λ_{abs}^a [nm] (ϵ [M ⁻¹ cm ⁻¹])	E_{ox}^b [V]	E_{0-0}^c [V]	E_{LUMO}^d [V]	J_{sc} [mAcm ⁻²]	V_{oc} [V]	ff	η^e [%]
1	238 (16100),	1.44	2.67	-1.23	8.2	0.64	0.68	3.01
	280 (10100)							
	408 (12400)							
2	236 (20900),	1.29	2.57	-1.28	11.30	0.63	0.67	4.78
	262 (17100)							
	427 (16400)							
3	241 (26600),	1.56	2.67	-1.11	7.70	0.71	0.73	4.07
	285 (16500)							
	408 (20400)							
4	240 (46000)	1.49	2.32	-0.83	12.2	0.71	0.72	6.25
	293 (28900)							
	443 (29800)							
JK-2	364 (44000)	14.9	0.70	0.72	7.63			
	452(39000)							

^aThe absorption spectra were measured in THF solution. ^bThe redox potentials of the dyes on TiO₂ were measured in CH₃CN with 0.1 M (N-C₄H₉)₄NPF₆ at a scan rate of 50 mVs⁻¹ (vs. NHE). ^c E_{0-0} was determined from the intersection of the absorption and emission spectra in THF. ^d E_{LUMO} was calculated by $E_{\text{ox}}-E_{0-0}$. ^eThe performances of the DSSCs were measured using a working area of 0.18 cm². Electrolyte: 0.6 M DMPImI, 0.05 M I₂, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in CH₃CN.

wavelength. This indicates considerable effects of bulky hexyl substituent upon electronic transition.

We performed a series of theoretical calculations to find out the origin of the absorption spectrum. For compound **4**, the HOMO originated mainly from the π orbitals of thiophene compared to less contribution of the π orbitals of carbazole that is used as a spacer. In contrast, LUMO was generated primarily by the π^* orbitals of electron acceptors (Figure 1). This result demonstrates very effective charge separation. Consequently, the observed absorption appears to be originated from $\pi-\pi^*$ transition between carbazole/thiophene and cyano group. In the view of harvesting the solar energy and obtaining large photocurrent, the absorption

spectra of these carbazole based dyes (**1-4**) seem highly desirable.

To estimate the feasibility of electron transfer from the excited state of the dye to the conduction band of TiO₂ electrode, we carried out cyclic voltammetry experiment in order to determine the redox potential. The redox potentials of dyes **1-4** were measured in CH₃CN with 0.1 M tetrabutylammoniumhexafluorophosphate. TiO₂ films coated with the sensitizers were used as working electrodes. All dyes adsorbed on TiO₂ films show an irreversible single oxidation (Table 1). The oxidation potentials (vs NHE) are observed at 1.44 V for **1**, 1.56 V for **3** and 1.49 V for **4** respectively. In addition, the oxidation wave patterns are very similar for **1**, **3** and **4**. However, compound **2** adsorbed on TiO₂ films show a smaller oxidation (1.29 V) than in **1**, **3** and **4**. These irreversible processes can be assigned to the oxidation of *N*-phenylcarbazole and thiophene group. Compound **2** shows low oxidation potential because of its coplanarity with two thiophene rings. The ground state structure of **2** possesses an 5.32° twist between two thiophene units based on DFT calculation. (See supporting information) Compound **4**, however, has a similar oxidation potential to compound **1** and/or compound **3** because the coplanarity with both thiophene rings is disrupted by the bulky hexyl group, introduced to thiophene (dihedral angle for **4**: 12.81°). Accordingly, a lower oxidation potential of **2** relative to **4** derives from more delocalization over an entire conjugated system. The LUMO energies of dyes **1-4** calculated from the oxidation potentials and the E_{0-0} determined from the intersection of absorption and emission spectra, are listed in Table 1. The LUMO energies of **1**, **2**, **3** and **4** are -1.23 V, -1.28 V, -1.11 V and -0.83 V (vs NHE), respectively. The LUMO energies for **1**, **2** and **3** are much higher than that of **MK-2** (-0.84 V), 2-cyano-3-[5'''-(9-Ethyl-9*H*-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']-quaterthiophenyl-5-yl] acrylic acid, which contains four hexyl-thiophene unit as a spacer.⁶ This increment of LUMO energies are originated from the lack of thiophene in the spacers. However, compound **4** shows much lower LUMO energy

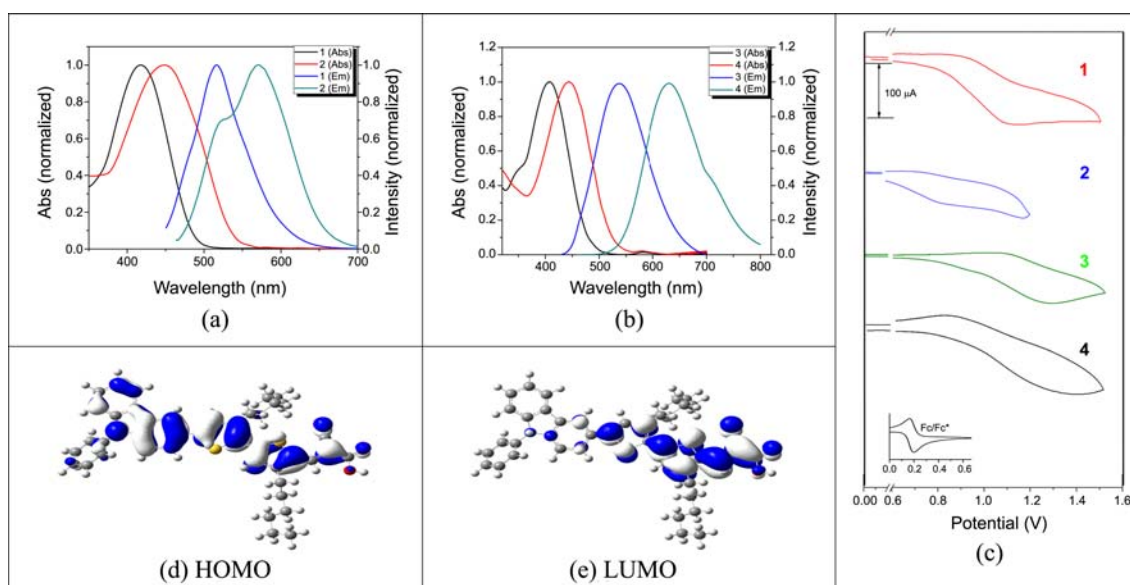


Figure 1. (a) Absorption and emission spectra of **1** and **2** in THF at ambient temperature. (b) Absorption and emission spectra of **3** and **4** in THF at ambient temperature. (c) Cyclic voltammetry of **1-4** dye attached to a nanocrystalline TiO₂ film deposited on conducting FTO glass. (d) & (e) Electron density of HOMO and LUMO in **4** as a representative.

compared to those of other three compounds. Such a low-lying LUMO for **4** permits the electron in the excited state of the dye to be effectively injected into the conduction band of TiO₂ (−0.5 V vs NHE).

Using the four dyes, we made DSSCs to investigate photovoltaic properties. For denotative comparison, we fabricated one more DSSC as a reference with **JK-2**, {3-5'-[N,N-bis(9,9-dimethyl fluorene-2-yl)phenyl]2,2'-bithiophene-5-yl}-2-cyanoacrylic acid, as a standard material which is well known to be a highly effective organic dye. Under standard global AM (Air Mass) 1.5 solar conditions, a compound **4** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 12.2 mA/cm², an open circuit voltage (V_{oc}) of 0.71 V, and a fill factor of 0.72, corresponding to an overall conversion efficiency η , derived from the equation $J_{sc} \cdot V_{oc} \cdot ff / \text{light intensity}$, of 6.25% (See Figure 2). This conversion efficiency marks well over 80% of the value for a **JK-2** based DSSC (7.63%).

By contrast, the conversion efficiencies of **1**, **2** and **3** based DSSCs are 3.01%, 4.78% and 4.07%, respectively, which are lower than that of **JK-2** sensitized cell under the same condition (J_{sc} : 8.2 mA/cm², V_{oc} : 0.64 V, ff : 0.68 for **1**; J_{sc} : 11.3 mA/cm², V_{oc} : 0.63 V, ff : 0.67 for **2**; J_{sc} : 7.70 mA/cm², V_{oc} : 0.71 V, ff : 0.73 for **3**). The increased J_{sc} of compound **4** based DSSC has most likely originated from a larger absorption coefficient and lengthening π -conjugation compared to those of compound **1**, **2** and **3**. It is noteworthy that the V_{oc} for a DSSC with **4** sensitizer containing bulky spacer, is much higher than those for **1** and **2**. The V_{oc} values between compounds of **1** and **2** and those between compounds of **3** and **4** appear nearly the same in each case. Compared to compounds **1** and **2**, compounds **3** and **4** showed increased value of V_{oc} by more than 10%, in which the bulky substituents are introduced, demonstrating a considerable impact

of bulky substituents on V_{oc} values.

Generally, the V_{oc} values have close relation to electron life time of organic dyes. The electron life time becomes lengthened either when the advancement of electrolyte I₃[−] toward the surface of TiO₂ is perturbed or when the reorganization energy of dyes are decreased. Studies report that this increased electron life time is designated by the increased V_{oc} values.

Although there is a little difference of HOMO energy in compound **1** and **2**, the V_{oc} values of both compounds are almost the same. This result is most likely due to the same dark current of two compounds. Further experimentation, therefore, is necessary to prove our expectation of the longer electron life time of the compounds **3** and **4** compared to that of the compounds **1** and **2**. What apparent, however, is that compounds with hexyl group contributes to a considerable increase of V_{oc} values.

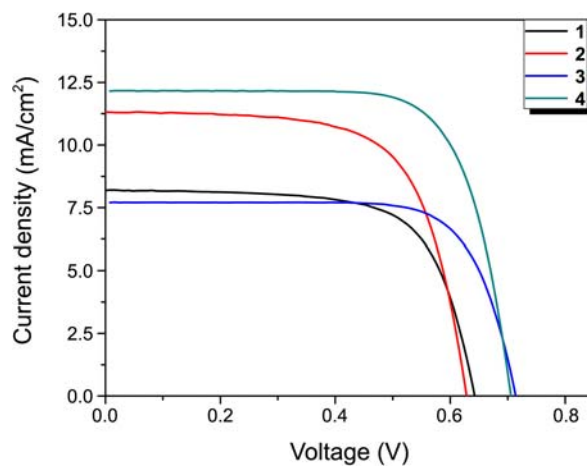


Figure 2. A photocurrent voltage curve obtained with a DSSC based on **1** (black line), **2** (red line), **3** (blue line) and **4** (green line) under AM 1.5 radiation.

Conclusions

Four carbazole-based organic dyes have been synthesized to investigate the effect of bulky substituents on the efficiency of DSSCs. The efficiency of compound **4** with two hexylthiophene in a spacer marked over 80% of the efficiency of **JK-2**. The introduction of a bulky substituent increased V_{oc} values more than 10% than other cases. Consequently, the combination of carbazole and a spacer with proper bulky substituent could achieve a highly efficient DSSC, which currently being investigated in our laboratory.

Experimental Section

Materials and Characterization. The several of π -conjugating thiophene spacers and key starting material, (9-phenyl-9*H*-carbazol-3-yl)boronic acid, were prepared as described in literature.¹⁰ The synthetic details of intermediates (**D**, **E**, **H**, **I**, **J** and **K**) are described in supporting information.

General Synthesis of 1, 2, 3 and 4. A mixture of corresponding aldehyde (0.247 mmol) and cyanoacetic acid (0.04 g, 0.496 mmol) was vacuum dried and MeCN (30 mL) and piperidine (0.008 mL, 0.074 mmol) were added. The mixture was refluxed for 15 hrs. After cooling the reaction mixture, all volatiles were removed in vacuo. The pure products were obtained by column chromatography (silica) in 80-90% yield.

2-Cyano-3-(5-(9-phenyl-9*H*-carbazol-3-yl)thiophen-2-yl)acrylic Acid (1). Eluent: EtOH, $R_f = 0.83$; Yield: 86%, yellow solid. ¹H-NMR (DMSO-*d*₆, 300 MHz) δ 8.7 (1H, s), 8.4 (1H, $J = 7.61$ Hz, d), 8.1 (1H, s), 7.8-7.3 (11H, m), 6.9 (1H, s). ¹³C-NMR (DMSO-*d*₆, 100 MHz) δ 165.7, 151.9, 141.6, 141.1, 140.6, 139.6, 137.0, 136.8, 135.5, 130.6, 128.3, 127.2, 127.0, 125.6, 125.2, 124.9, 123.9, 123.7, 122.9, 121.4, 120.9, 119.5, 118.9, 118.3, 110.7, 108.1. Mass (m/z): 420 [M^+]. Anal. Calcd for C₂₆H₁₆N₂O₂S: C, 74.27; H, 3.84. Found: C, 74.32; H, 3.87.

2-Cyano-3-(5'-(9-phenyl-9*H*-carbazol-3-yl)-[2,2'-bithiophen]-5-yl)acrylic Acid (2). Eluent: EtOH, $R_f = 0.77$; Yield: 95%, orange solid. ¹H-NMR (DMSO-*d*₆, 300 MHz) δ 8.7 (1H, $J = 1.29$ Hz, d), 8.4 (1H, $J = 7.64$ Hz, d), 8.1 (1H, s), 7.8 (1H, $J = 7.61$ Hz, d), 7.75-7.28 (12H, m), 6.8 (1H, s). ¹³C-NMR (DMSO-*d*₆, 100 MHz) δ 151.8, 145.7, 141.2, 140.2, 139.5, 136.9, 133.9, 133.5, 132.5, 132.4, 131.8, 130.6, 129.1, 129.0, 128.3, 128.2, 127.4, 127.1, 127.0, 125.7, 125.2, 124.4, 123.7, 123.0, 121.4, 120.8, 119.3, 117.9, 110.6, 110.1. Mass (m/z): 502 [M^+]. Anal. Calcd for C₃₀H₁₈N₂O₂S₂: C, 71.69; H, 3.61. Found: C, 71.65; H, 3.63.

2-Cyano-3-(4-hexyl-5-(9-phenyl-9*H*-carbazol-3-yl)thiophen-2-yl)acrylic Acid (3). Eluent: CHCl₃/EtOH (1/1: v/v), $R_f = 0.35$. Yield: 81%, orange solid, ¹H-NMR (DMSO-*d*₆, 300 MHz) δ 8.35-8.30 (dd, $J = 0.99$ Hz, $J = 4.55$ Hz, 2H), 8.14 (s, 1H), 7.73-7.63 (m, 5H), 7.59-7.38 (m, 5H), 7.33-7.28 (t, $J = 7.31$ Hz, 1H), 2.71-2.66 (t, $J = 7.64$ Hz, 2H), 1.60-1.53 (m, 2H), 1.34-1.16 (m, 6H), 0.76-0.72 (t, $J = 6.41$ Hz, 3H) ¹³C-NMR (DMSO-*d*₆, 150 MHz) δ 164.5, 144.6, 141.5, 141.1, 140.3, 139.2, 138.0, 137.0, 135.0, 130.7, 129.1,

128.4, 127.7, 127.3, 127.2, 125.5, 123.5, 122.9, 121.4, 120.9, 119.6, 110.5, 110.3, 31.3, 30.6, 30.5, 30.3, 28.9, 28.3, 28.1, 22.4, 14.3. Mass (m/z): 504 [M^+]. Anal. Calcd for C₃₂H₂₈N₂O₂S: C, 76.16; H, 5.59. Found: C, 76.14; H, 5.57.

2-Cyano-3-(3,4'-dihexyl-5'-(9-phenyl-9*H*-carbazol-3-yl)-[2,2'-bithiophen]-5-yl)acrylic Acid (4). Eluent: CHCl₃/EtOH = (1/1: v/v), $R_f = 0.29$. Yield : 84%, red solid. ¹H-NMR (DMSO-*d*₆, 300 MHz) δ 8.35-8.31 (dd, $J = 1.31$ Hz, $J = 7.76$ Hz, 2H), 8.12 (s, 1H), 7.73-7.64 (m, 5H), 7.59-7.38 (m, 5H), 7.34-7.29 (t, $J = 7.75$ Hz, 1H), 7.27 (s, 1H), 2.81-2.68 (dt, $J = 7.66$ Hz, $J = 7.63$ Hz, 4H), 1.62-1.60 (m, 4H), 1.37-1.19 (m, 12H), 0.86-0.74 (dt, $J = 6.90$ Hz, $J = 6.73$ Hz, 6H) ¹³C-NMR (DMSO-*d*₆, 150 MHz) δ 164.0, 142.0, 141.1, 140.2, 140.1, 139.8, 139.7, 139.4, 137.0, 134.3 132.4, 130.7, 130.1, 130.0, 128.4, 127.7, 127.2, 127.1, 125.5, 123.6, 123.0, 121.4, 120.8, 119.0, 110.4, 110.3, 31.5, 31.4, 30.6, 30.1, 29.0, 28.9, 28.5, 22.5, 14.4, 14.3. Mass (m/z): 670 [M^+]. Anal. Calcd for C₄₂H₄₂N₂O₂S₂: C, 75.19; H, 6.31. Found: C, 75.13; H, 6.37.

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References

- (a) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382. (b) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W. *Prog. Photovoltaics* **2008**, *16*, 435. (c) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiyama, R.; Koide, N.; Han, L. Y. *Jpn. J. Appl. Phys., Part 2* **2006**, *45*, L638.
- Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595.
- (a) Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Péchy, P.; Takata, M.; Miura, H.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2006**, *18*, 1202. (b) Ito, S.; Miura, H.; Uchida, S.; Takata, M.; Sumioka, K.; Liska, P.; Comte, P.; Péchy, P.; Grätzel, M. *Chem. Commun.* **2008**, 5194. (c) Zhang, G. L.; Bala, H.; Cheng, Y. M.; Shi, D.; Lv, X. J.; Yu, Q. J.; Wang, P. *Chem. Commun.* **2009**, 2198.
- Hara, K.; Tachibana, Y.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2003**, *77*, 89.
- Ooyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, 2903.
- Marinado, T.; Hagberg, D. P.; Hedlund, M.; Edvinsson, T.; Johansson, E. M. J.; Boschloo, G.; Rensmo, H.; Brinck, T.; Sun, L. C.; Hagfeldt, A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 133.
- Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2008**, *130*, 4202.
- Ko, S.; Choi, H.; Kang, M.-S.; Hwang, H.; Ji, H.; Kim, J.; Ko, J.; Kang, Y. *J. Mater. Chem.* **2010**, *20*, 2391.
- Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J. H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701.
- (a) Kong, H.; Chung, D. S.; Kang, I.-N.; Lim, E.; Jung, Y. K.; Park, J.-H.; Park, C. E.; Shim, H.-K. *Bull. Korean Chem. Soc.* **2007**, *28*, 1945. (b) Wrackmeyer, M. S.; Hummert, M.; Hartmann, H.; Riede, M. K.; Leo, K. *Tetrahedron* **2010**, *66*, 8729. (c) Ho, C.-L.; Wong, W.-Y.; Yao, B.; Xie, Z.; Wang, L.; Lin, Z. *J. Organomet. Chem.* **2009**, *694*, 2735.