Chem. Mater. **2006,** *18,* 5604−5608

Oligophenylenevinylene-Functionalized Ru(II)-bipyridine Sensitizers for Efficient Dye-Sensitized Nanocrystalline TiO_2 Solar Cells

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Received June 22, 2006. Revised Manuscript Received September 16, 2006

New 4- and 4,4′-oligophenylenevinylene-functionalized Ru(II)-bipyridine sensitizers were synthesized and used in dye-sensitized TiO_2 solar cells (DSSCs) to study their sensitizing properties relative to those of the usual N3 dye. Among those studied, two sensitizers, denoted as D5 and D6, have rendered considerably higher photocurrents and efficiencies for their cells, compared to those of a cell using the conventional N3 dye. The short-circuit photocurrent densities for N3, D5, and D6 are 9.8, 10.8, and 11.7 mA/cm^2, and the efficiencies are 4.1, 4.6, and 4.8%, respectively. The enhanced photocurrents are correlated with the increased molar absorption coefficients of the D5 and D6 dyes over the entire visible spectra region, relative to those of the N3 dye. Corresponding enhancements in IPCE values are attributed to the oligophenylenevinylene groups of D5 and D6 that consist of conjugated double bonds. Analysis of the absorption spectra of the sensitizer-coated TiO_2 films and the desorbed dyes in an aqueous KOH solution indicates that D5 and D6 adhere more strongly to TiO_2 particles than the N3 dye, which is beneficial from the viewpoint of the long-term stability of the DSSCs.

Introduction

Modification of the dye is one of the essential strategies to improve the performance of dye-sensitized solar cells (DSSCs). Several Ru(II) complexes, including N3 ([Ru(dcbpyH$_2$)$_2$(NCS)$_2$]), N719 ((Bu$_4$N)$_2$[Ru(dcbpyH)$_2$(NCS)$_2$]), and N712 ((Bu$_4$N)$_4$[Ru(dcbpy)$_2$(NCS)$_2$]) have been used in DSSCs as efficient sensitizers, where dcbpyH stands for 4,4′-dicarboxy-2,2′-bipyridine.[1] Among them N3 is the most frequently used dye. Efforts have been made to further improve the cell performance achieved with the N3 dye by attaching hydrophobic chains to the pyridine rings, thereby increasing the open-circuit voltage (V_{oc}),[2] and by substituting the NCS ancillary ligands with numerous ligands.[3] Bimetallic coordination compounds such as those with Ru−Re,[4] Ru−Rh,[5] and Ru−Os[6] were also investigated as sensitizers for DSSCs, in which only one metal complex was directly attached to TiO_2 film through its anchoring ligands. Recently, a Ru(II)-bpt-Ru(II) polypyridyl complex, where two N3 dyes were bridged by 3,5-bis(pyridin-2-yl)-1,2,4-triazole (bpt, a very rigid linker) replacing all NCS ligands of N3 dyes, was used as a sensitizer in a DSSC;[7] however, the incident photon to current conversion efficiency (IPCE) was found to be half that obtainable with a mononuclear ruthenium compound as the sensitizer. We reported recently that the linking of N3 with another TiO_2-attached N3 through *trans*-1,2-bis(4-pyridyl)ethylene rendered an enhanced short-circuit photocurrent and thereby conversion efficiency for the pertinent DSSC, relative to those of a cell with only N3 dye.[8]

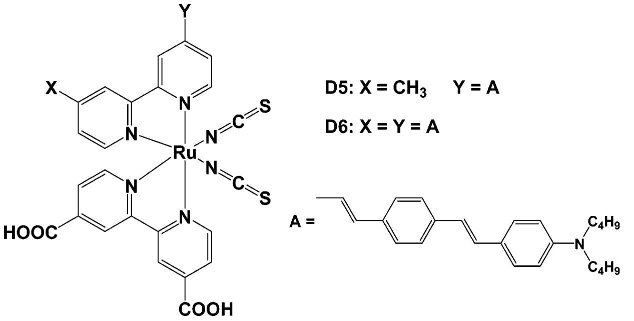

Figure 1. Molecular structures of synthesized D5 and D6.

A recent work by Grätzel’s group has revealed that the use of K-19 as the amphiphilic bipyridyl ruthenium complex is promising.[9] The dye has an alkoxystyryl group in its ligand

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(1) Nazeeruddin, M. K.; Humphry-Baker, R.; Liska, P.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 8981.

(2) (a) Lagref, J.-J.; Nazeeruddin, M. K.; Grätzel, M. *Synth. Met.* **2003**, *138*, 333. (b) Wang, P.; Zakeeruddin, S. M.; Moser, J.-E.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 13280.

(3) Polo, A. S.; Itokazu, M. K.; Murakami Iha, N. Y. *Coord. Chem. Rev.* **2004**, *248*, 1343.

(4) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Meyer, G. J. *Inorg. Chem.* **1997**, *36*, 2.

(5) Kleverlaan, C. J.; Indelli, M. T.; Bignozzi, C. A.; Pavanin, L.; Scandola, F.; Hasselman, G. M.; Meyer, G. J. *J. Am. Chem. Soc.* **2000**, *122*, 2840.

(6) Kleverlaan, C.; Alebbi, M.; Argazzi, R.; Bignozzi, C. A.; Hasselman, G. M.; Meyer, G. J. *Inorg. Chem.* **2000**, *39*, 1342.

(7) Lees, A. C.; Kleverlaan, C. J.; Bionozzi, C. A.; Vos, J. G. *Inorg. Chem.* **2001**, *40*, 5343.

(8) Jang, S.-R.; Vittal, R.; Lee, J.; Jeong, N.; Kim, K.-J. *Chem. Commun.* **2006**, *103*.

(9) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 808.

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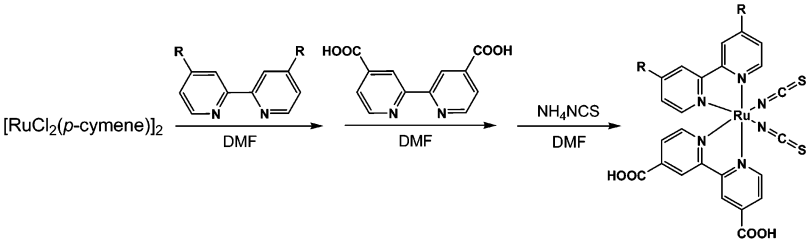
Scheme 1. Synthetic Route To Produce D5 and D6



and this ligand was reported to enhance the harvesting of solar light. On the other hand, Arakawa's group has synthesized novel conjugated organic dyes that have *N*,*N*-dimethylaniline moieties as the electron donors and achieved a remarkably high efficiency of 6.8%.[10] The search for new dyes is challenging for enhancing the conversion efficiency up to the level of that for practical applications of DSSCs. Judicious tuning of the LUMO and HOMO levels of a dye for maintaining sufficient thermodynamic driving forces for both electron transfer and dye regeneration processes, panchromatic sensitization of TiO_2 particles over the whole visible range extending up to a threshold wavelength of about 920 nm for light-harvesting efficiency, and increasing of the molar absorption coefficient of a dye for its enhanced solar light absorption, are the specific strategies to be pursued in the molecular designing of dyes.

In line with the continuation of the efforts in this direction for improving the solar energy conversion efficiency, we synthesized a new type of the ruthenium sensitizer, consisting of both styryl and *N*-butylamino moieties as electron-donating groups. The general idea is to utilize styryl or methine groups for extending the π-conjugated backbone, instead of pyridyl groups, in the *trans*-1,2-bis(4-pyridyl)-ethylene linker that successfully linked two N3 molecules for an improved DSSC, as was reported earlier by us.[8] Investigation on dyes also envisages the aspect of increasing their optical cross section, which is beneficial for the harvesting of solar light and durability of the pertinent solar cells.

In this paper, we report the synthesis of promising 4- and 4,4′-oligophenylnevinylene-functionalized Ru(II)-bipyridine sensitizers, denoted respectively as D5 and D6, the former featuring an extended oligophenylenevinylene π-conjugated backbone with a *N*,*N*-dibutylamino moiety and the latter with two such backbones (Figure 1). The synthetic route to produce D5 and D6 utilizing a double Wadsworth-Emmons reaction[11,12] is shown in Scheme 1. Synthetic details and analytical data are provided in the Supporting Information. These extended conjugation dyes were successfully employed in DSSCs, as evidenced by the higher photovoltaic performances of their pertinent cells, relative to that of a cell using N3 dye. Though similar compounds with and without Ru (and other) metal centers were synthesized previously,[11,12] they were not used as sensitizers in DSSCs. In addition, four new Ru(II)-bipyridine sensitizers that contain *N*,*N*-dimethylaniline moieties at the end of their π-conjugated backbones were also synthesized according to the procedure given by Hara et al.[10]

Each of these synthesized sensitizers has higher molar absorptivities than those of N3 over the visible region. Photovoltaic properties of DSSCs with these newly developed sensitizers are compared with those of a cell with the standard N3 dye.

Experimental Section

DSSCs were fabricated using TiO_2 films made from Dyesol titania paste (Dyesol Ltd., Australia). In each case the Dyesol paste was coated on the titanium(IV) isopropoxide pretreated FTO glass (using a doctor blade technique). The paste on the FTO was then annealed at 450 °C for 30 min to produce a 13 μm thick nanocrystalline TiO_2 film, unless otherwise specified. The annealed film thus obtained was impregnated with 0.5 mM Ru(II) sensitizer in DMF for 24 h at room temperature. Each dye-coated film was soaked in DMF for 3 h to remove unattached dye molecules, and then in absolute ethanol for 2 d to remove DMF. The resulting sensitizer-coated TiO_2 film was washed with ethanol and then used to fabricate the DSSC, according to the procedure reported elsewhere.[13]

The redox electrolyte solution for a DSSC consisted of 0.05 M I_2, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-hexylimidazolium iodide, and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile. The DSSCs were characterized for their photoelectrochemical characteristics using a Keithley M 236 source measure unit. A 300 W Xe lamp with an AM 1.5 filter (Oriel) was used to illuminate the working electrode of 0.4×0.4 cm^2 at the light intensity of 1 sun (100 mW/cm^2). The light intensity was adjusted using a Si solar cell. IPCE values were measured using a system by PV Measurement, Inc. An HP 8453A diode array spectrophotometer was used for measuring the absorption spectra of the sensitizers in solutions and on TiO_2 films.

Results and Discussion

Figure 2 compares the photocurrent−voltage ($J-V$) curves of three DSSCs fabricated with TiO_2 films, anchored with N3, D5, and D6 sensitizers. The corresponding short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and solar-to-electricity conversion efficiency (η) values are summarized in Table 1. Analysis of the $J-V$ curves indicates that the newly developed D5 and D6 yield higher photocurrents than N3, whereas the V_{oc}'s are essentially the same. As a result of mainly the J_{sc} enhancement, the overall solar energy conversion efficiencies of the cells

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[10] Hara, K.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *Chem. Commun.* **2003**, *252*.

[11] Maury, O.; Viau, L.; Sénéchal, K.; Corre, B.; Guégan, J.-P.; Renouard, T.; Ledoux, I.; Zyss, J.; Le Bozec, H. *Chem. Eur. J.* **2004**, *10*, 4454.

[12] Viau, L.; Maury, O.; Le Bozec, H. *Tetrahedron Lett.* **2004**, *45*, 125.

[13] Kang, M. G.; Kim, K. M.; Ryu, K. S.; Chang, S. H.; Park, N.-G.; Hong, J. S.; Kim, K.-J. *J. Electrochem. Soc.* **2004**, *151*, E257.

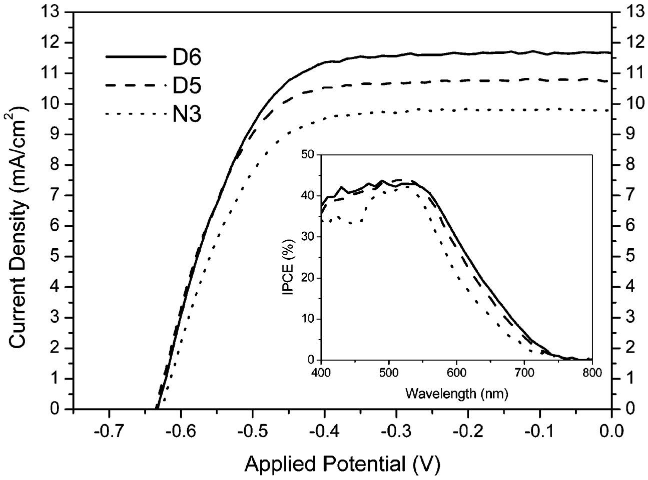

Figure 2. $J-V$ curves of DSSCs prepared with TiO_2 films impregnated with D6, D5, and N3 in DMF. Light intensity was 100 mW/cm^2. The inset shows corresponding IPCE spectra.

Table 1. Photovoltaic Parameters of the Dye-Sensitized Solar Cells with Different Sensitizers[a,b]

sensitizer	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
N3	9.80	0.63	0.66	4.1
D5	10.8	0.63	0.68	4.6
D6	11.7	0.63	0.66	4.8
D13	3.39	0.58	0.70	1.4
D14	4.43	0.58	0.67	1.7
D15	3.79	0.58	0.66	1.5
D16	2.36	0.54	0.56	0.72

[a] Each electrolyte consisted of 0.05 M I_2, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-hexylimidazolium iodide, and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile. [b] Measured under an illumination of AM 1.5 solar light (100 mW/cm^2).

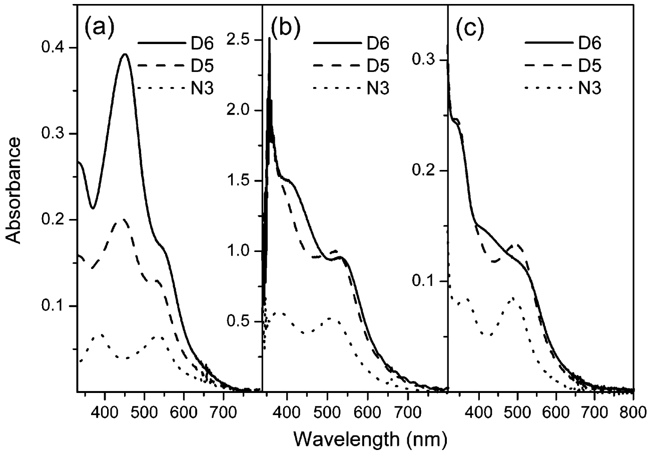

Figure 3. Absorption spectra of (a) 5.0×10^{-6} M each of N3, D5, and D6 in DMF, (b) 7 μm thick TiO_2 films coated each with 0.5 mM N3, D5, and D6 in DMF, and (c) desorbed N3, D5, and D6 from their corresponding TiO_2 films into aqueous 10 mM KOH for 3 d.

Table 2. Absorption Peaks and Molar Absorption Coefficients of the Synthesized Sensitizers[a]

sensitizer	λ_{max} (nm) (ϵ_{max} (10^4 M^{-1} cm^{-1}))
N3	385 (1.36), 533 (1.33)
D5	441 (4.03), 527 (2.60)
D6	449 (7.85), 539 (3.43)
D13	453 (1.61)
D14	463 (1.99), 532 (1.76)
D15	452 (2.16)
D16	471 (4.54), 555 (2.67)

[a] Measured in DMF.

with D5 and D6 dyes have increased to 4.6% and 4.8%, respectively, relative to 4.1% efficiency of the cell with N3 dye.

The J_{sc} enhancements can be correlated with the increased molar absorption coefficients of the newly synthesized sensitizers over the entire visible spectral region, compared with those of N3 as shown by the corresponding curves in Figure 3a. The values of the absorption peaks and their molar absorption coefficients are given in Table 2. The J_{sc} values of N3, D5, and D6 are consistent with the IPCE values, as shown in the inset of Figure 2, where the cells prepared using D5 and D6 show consistently higher IPCE values over the visible region, compared to those of N3. These enhanced IPCE values imply that the new sensitizers act as more efficient electron donors to the conduction bands of their TiO_2 films upon excitation, obviously owing to the chains of the oligophenylenevinylene groups in D5 and D6, consisting of conjugated double bonds.

Contrary to the J_{sc} increase, the near invariance of V_{oc} of the cells with the three sensitizers (Figure 2) suggests that the alkyl chains of oligophenylenevinylene groups with *N*,*N*-dibutylamino moieties in D5 and D6 are ineffective for inducing self-organization near the surfaces of their TiO_2 nanoparticles, in a fashion facilitating the V_{oc} increase. That is to say, the rigid, long alkyl chains of oligophenylenevinylene groups bonded to the 4- and 4,4′-positions of D5 and D6 respectively could not form hydrophobic layers around their corresponding TiO_2 particles. The formation of such a layer can reduce the back electron transfer from the conduction band of TiO_2 to the I_3^- ions in the electrolyte solution and thereby can increase the V_{oc}; the basis for this assumption lies on the reports as was reported by Lagref et al. and Wang et al. that formation of hydrophobic layers with long, saturated hydrocarbon chains such as those with $C_{16}H_{33}$ and $C_{13}H_{27}$ can increase the V_{oc}.[2] Furthermore, a shift in the Fermi level of TiO_2, which would have changed V_{oc}s for D5 and D6, cannot be expected because the proton concentration on their TiO_2 surfaces remain most likely the same as that in the case of N3 owing to the large distance between their tertiary amine groups and their corresponding TiO_2 surfaces.

Figures 3a, 3b, and 3c show respectively UV−vis absorption spectra of the three sensitizers in DMF, the dye-coated TiO_2 films (thickness: 7 μm), and the same sensitizers desorbed from their TiO_2 films (0.5×0.5 cm^2) into 3.5 mL of aqueous 10 mM KOH. Analysis of the spectral behavior in Figure 3a (solution spectra) and Figure 3b (film spectra) near the 530 nm region reveals that the ratio of the absorption of D5 to N3 in DMF is the same as the ratio of the absorption of D5 to N3 on the TiO_2 surfaces. This observation implies that the moles of D5 adsorbed to the TiO_2 film are nearly the same as those of the adsorbed N3 to the TiO_2 film. A similar way of comparing the spectra of D6 and N3 in Figures 3a and 3b reveals that the moles of the adsorbed D6 are about 73% of those of the adsorbed N3. The relative moles of the adsorbed sensitizers was confirmed by ICP emission spectrometry. The lesser adsorption of D6 is thought to be due to the presence of an additional bulky oligophenylenevinylene group, compared to the single group in D5. This type of geometrical constraints for the dyes to occupy sites on the TiO_2 particles are explained in a recent report by Bandara and Weerasinghe[14] by calculating the number of molecules of a dye per nm^2 of TiO_2 surface and the number of sites available for the dye to occupy 1 nm^2 of TiO_2 surface, in which the authors have taken into account the molecular size of the dyes. It is remarkable to observe a higher J_{sc} of 11.7 mA/cm^2 with D6 compared to 9.8 mA/cm^2 with N3, although the surface coverage of D6 on TiO_2 film is less than that of N3 by 27%. This result is understood to be due to the fact that the molar absorptivities of D6 are much higher than those of N3 over the entire visible region (Figure 3a and Table 2). Introduction of the 4- and 4,4′-oligophenylenevinylene groups (with reference to N3) for the D5 and D6 dyes, respectively, tune the HOMO and LUMO levels of the dyes and, consequently, their absorption properties relative to those of N3.[15]

In addition, comparative analysis of the absorption spectra in Figures 3b and 3c reveals that desorption of D5 and D6 from the TiO_2 surfaces into the KOH solution is incomplete, i.e., only 84% and 77%, respectively, contrary to the complete desorption of N3. This incomplete desorption of D5 and D6 could be due to the differences in solubilities of the sensitizers in the aqueous KOH solution and/or due to their binding affinity to the TiO_2 surface. Due to the presence of more hydrophobic ligands at the bipyridine groups in D5 and D6 compared to N3, there could be differences in their solubitities in KOH. To understand further the incomplete desorption, a quantitative analysis is made. With use of the molar absorptivities in Table 2, the moles of N3, D5, and D6 adsorbed to their TiO_2 films of 0.5 cm × 0.5 cm × 13 μm are found to be 2.2×10^{-8}, 2.2×10^{-8}, and 1.6×10^{-8} mol, respectively. From these adsorption values and the above-mentioned desorption values it can be stated that N3 desorbs completely, although its adsorption to the TiO_2 film is far higher than that of D6 to the TiO_2 film. Since small quantities of N3, D5, and D6 (in the order of 10^{-8} mol) desorbs from the TiO_2 films into the large quantity of KOH (3.5×10^{-5} mol) solution, it appears that the differences in solubilities among the three sensitizers play a minor role in the desorption behaviors. Moreover, the desorption process is essentially an acid−base reaction involving the weak acidic sensitizers and the strong base. Thus, we assume that the incomplete desorption of D5 and D6 is more likely due to stronger binding of them to their respective TiO_2 films than that of N3 to its TiO_2 film. This seemingly strong binding of these newly synthesized sensitizers with their TiO_2 particles can be beneficial in terms of long-term stability of the DSSCs.

Removing the middle phenyl groups in the long chains of D5 and D6 and replacing them with methine units (−CH═CH−), thereby expanding the π conjugation, was considered to be a promising design strategy for efficient sensitizers. Based on this concept, we synthesized, referring to the procedure given by Hara et al.,[10] four new Ru(II)-bipyridine sensitizers, D13−D16 (Figure 4), that contain *N*,*N*-dimethylaniline moieties at the end of their π-conjugated backbones. Their UV−vis absorption spectra show higher molar absorptivities than those of N3 over the visible region, which is expected based on the fact that they have very similar chemical structures as those of D5 and D6. Their absorption peak positions and molar absorption coefficients are also listed in Table 2.

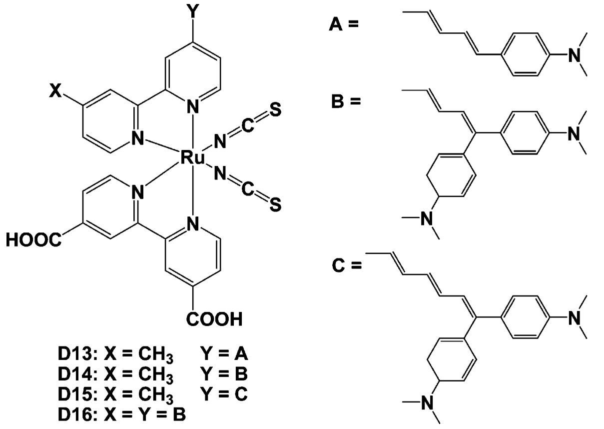

Figure 4. Molecular structures of synthesized D13, D14, D15, and D16.

J−*V* studies were performed on the D13−D16 sensitizers, under the same conditions as those in the investigation of D5 and D6. Contrary to our expectations, it was found that the J_{sc}'s and the efficiencies of the cells using D13, D14, D15, and D16 were less than one-half of those of N3 given in Table 1. It is surprising to observe such low J_{sc}'s and efficiencies, although the D13−D16 sensitizers possess similar chemical structures and favorable absorption characteristics as those of D5 and D6. The reason for the low J_{sc}'s and efficiencies in the case of these sensitizers is unclear, but may be attributed to the occurrence of their very fast nonradiative decay from an excited state to the ground state in the presence of π-conjugated backbones with *N*,*N*-dimethylaniline moieties at the end, due to distortion of their Ru(II) complexes immobilized onto TiO_2 surfaces.[15,16] The nonradiative de-excitation reduces the electron injection yield into the conduction band of TiO_2, thereby decreasing the J_{sc} of the corresponding cell. In the absence of middle phenyl groups in the long chains of these sensitizers (cf. D5 and D6), they can aggregate on their TiO_2 surfaces, which is detrimental to the electron injection quantum yield;[10,17,18] this can be another reason for the lower J_{sc}'s observed in the case of these four dyes. The results obtained with these sensitizers clearly indicate that minor changes in the molecular structure of a sensitizer affect crucially the solar energy conversion efficiency of the pertinent cell.

In this study, we focused on the design and synthesis of 4- and 4,4′-oligophenylnevinylene-functionalized Ru(II)-bipyridine sensitizers, and on their behavior with respect to photovoltaic performances of the pertinent solar cells, relative

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(14) Bandara, J.; Weerasinghe, H. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 864.

(15) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Yoshihara, T.; Murai, M.; Kurashige, M.; Ito, S.; Shinpo, A.; Arakawa, H. *Adv. Funct. Mater.* **2005**, *15*, 246.

(16) Rettig, W.; Majens, W.; Lapouyade, R.; Haucke, G. *J. Photochem. Photobiol. A* **1992**, *62*, 415.

(17) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597.

(18) Khazraji, A. C.; Hotchandani, S.; Das, S.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 4693.

to that of a cell using the N3 sensitizer. We have chosen relatively uncomplicated standard conditions to facilitate comparison between the performances of DSSCs using sensitizers D5, D6, and D13−D16 with the performance of a cell using the well-known sensitizer N3. Using a scattering layer of anatase TiO_2 of particles of about 400 nm, adding a co-adsorbent to the dye such as deoxycholic acid, treating the TiO_2 surface with $TiCl_4$ before it is coated with dye, and covering the cell surface with antireflection film will optimize the performance of the cells using D5 and D6 sensitizers. Even though we have observed the fact that the uptake of N3 dye by TiO_2 film from ethanolic N3 solution is twice as large as that from its DMF solution at the same concentration of N3, we could not use ethanol as a solvent for dye adsorption processes, and instead used DMF, because of poor solubilities of D5 and D6 in ethanol. Further experiments are in progress to tune the ancillary COOH ligands with groups consisting of conjugated double bonds and to find new efficient Ru(II) sensitizers.

Conclusions

We have synthesized new efficient dyes, D6 and D5 containing oligophenylenevinylene π-conjugated backbones, each with one *N*,*N*-dibutylamino moiety. D5 and D6 enabled about 12% and 17% enhancements in solar-to-electricity conversion efficiency, respectively, for their DSSCs, compared to the efficiency obtainable with N3 dye. The enhancements are correlated with higher molar absorption coefficients of these sensitizers with respect to those of N3 over the visible spectral region, due to the presence of oligophenylenevinylene groups with *N*,*N*-dibutylamino moieties in these sensitizers. Furthermore, analysis of the absorption spectra of the dye-coated TiO_2 films and the desorbed dyes in an aqueous KOH solution indicates that D5 and D6 sensitizers bond strongly with nanocrystalline TiO_2 particles. When the middle phenyl groups in the long chains of D5 and D6 were removed and replaced with methine units, the J_{sc}'s and conversion efficiencies of the corresponding cells decreased considerably, relative to those of a cell with N3 dye.

Acknowledgment. We acknowledge financial support for this work by the Korea Research Foundation Grant (KRF-2005-015-C00209) and KOSEF (National Research Lab., 2005). Dye synthesis was partially supported by the Innovative Cluster Program of Seoul.

Supporting Information Available: Synthetic schemes leading to the preparation of the dyes used in this study and related analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

CM061447V