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Squaraine-Arylamine Sensitizers for Highly Efficient p-Type Dye-Sensitized Solar Cells

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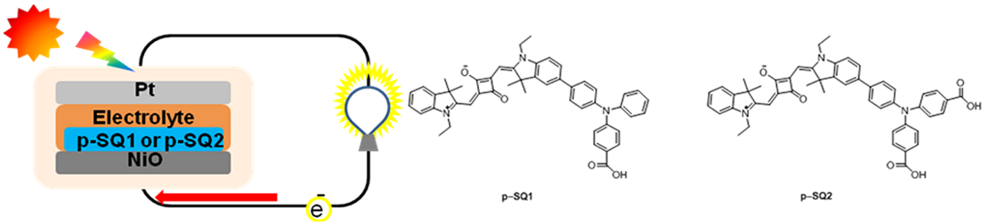
ABSTRACT



New near-IR (NIR) squaraine dyes (p-SQ1 and p-SQ2) containing one and two anchoring groups were synthesized and used as the sensitizers of p-type DSSCs. The dye (0.113%) with two anchoring groups (p-SQ2) shows better performance than the dye (0.053%) with only one anchoring group (p-SQ1). Cosensitized p-type DSSCs using two dyes with complementary absorption were tested. They have broadened IPCE spectra and good cell performance.

Dye-sensitized solar cells (DSSCs) have attracted considerable attention since the first report by Grätzel et al. in 1991.[1] Although the power conversion efficiency (PCE) of n-type DSSCs based on metal-containing dyes such as ruthenium[2] and Zn-porphyrin complexes[3] have achieved 11% and 12.3% under AM 1.5 illumination, these dyes are either expensive or complex in synthetic procedures. Therefore, metal-free sensitizers are promising alternatives due to their low cost, high molar absorption coefficients, and design flexibility. So far, the best PCE of organic dyes has achieved 10%.[4]

To improve the PCE of DSSCs, the sensitizers should have broader and intense absorption spectra. A convenient approach is using cosensitized systems in which different dyes which absorb in the complementary spectral region are adsorbed on the TiO_2 of n-type DSSCs.[5] An alternative approach first reported by Lindquist et al. includes using tandem cells which combine an n-type semiconductor as the photoanode and a p-type semiconductor such as NiO[6] as the photocathode.[7] With such a device design, dyes absorbing in different spectral regions are adsorbed on different electrodes. Theoretical calculation predicts that an efficiency up to 43% is possible for tandem cells.[8] Compared with n-type DSSCs, research on p-type DSSCs is still in its infancy.[9] In 2008, Sun et al. developed triphenylamine-based dyes with different acceptors for p-type DSSCs, and the PCEs ranged from 0.03% to

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(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

(2) (a) Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 10720. (b) Chen, C.-Y.; Wang, M.; Li, J.-Y.; Pootrakulchote, N.; Albabaei, L.; Ngoc-le, C.-h.; Decoppet, J.-D.; Tsai, J.-H.; Grätzel, C.; Wu, C.-G.; Zakeeruddin, S. M.; Grätzel, M. *ACS Nano* **2009**, *3*, 3103.

(3) (a) Bessho, T.; Zakeeruddin, S. M.; Yeh, C.-Y.; Diau, E. W.-G.; Grätzel, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6646. (b) Yella, A.; Lee, H. W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W. G.; Yeh, C. Y.; Zakeeruddin, S. M.; Grätzel, M. *Science* **2011**, *334*, 629.

(4) Zheng, W.; Cao, Y.; Bai, Y.; Wang, Y.; Shi, Y.; Zhang, M.; Wang, F.; Pan, C.; Wang, P. *Chem. Mater.* **2010**, *22*, 1915.

(5) Yum, J.-H.; Baranoff, E.; Wenger, S.; Nazeeruddin, M. K.; Grätzel, M. *Energy Environ. Sci.* **2011**, *4*, 842.

(6) (a) Gibson, E. A.; Smeigh, A. L.; Pleux, L. L.; Fortage, J.; Boschloo, G.; Blart, E.; Pellegrin, Y.; Odobel, F.; Hagfeldt, A.; Hammarström, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 4402. (b) Odobel, F.; Pleux, L. L.; Pellegrin, Y.; Blart, E. *Acc. Chem. Res.* **2010**, *43*, 1063.

(7) (a) He, J.; Lindström, H.; Hagfeldt, A.; Lindquist, S.-E. *J. Phys. Chem. B* **1999**, *103* (42), 8940. (b) He, J.; Lindström, H.; Hagfeldt, A.; Lindquist, S.-E. *Sol. Energy Mater. Sol. Cells* **2002**, *62*, 265.

(8) Green, M. A. *Third Generation Photovoltaics: Advanced Solar Energy Conversion*; Springer-Verlag: Berlin, Heidelberg, 2003.

(9) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Peterssen, H. *Chem. Rev.* **2011**, *110*, 6595.

(10) (a) Qin, P.; Zhu, H.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *J. Am. Chem. Soc.* **2008**, *130*, 8570. (b) Qin, P.; Wiberg, J.; Gibson, E. A.; Linder, M.; Li, L.; Brinck, T.; Hagfeldt, A.; Albinsson, B.; Sun., L. *J. Phys. Chem. C* **2010**, *114*, 4738.

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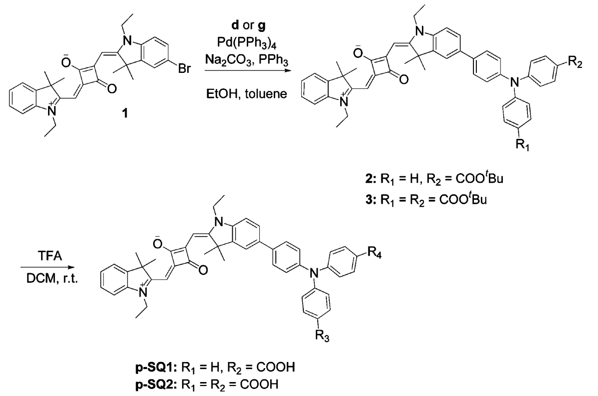
Scheme 1. Synthesis of the Dyes



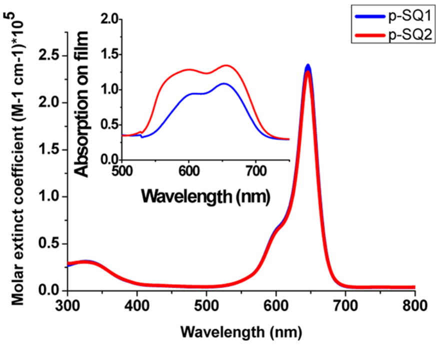


Figure 1. Absorption spectra of the squaraine dyes in EtOH (10^{-5} mol/L). Insert: absorption spectra on NiO films (~0.5 μm).

0.15%.[10] Later Bach[11] reported arylamine dyes containing perylene monoimide (PMI) acceptors and oligothiophene spacers with PCEs ranging from 0.09% to 0.41%. Recently, we also reported arylamine dyes for p-type DSSCs and found that dyes with two anchoring groups more effectively injected holes and suppressed dark currents compared to dyes with only one anchoring group.[12] So far the best efficiency of p-type DSSCs is about one order lower than that of n-type DSSCs due to the slow hole mobility of the NiO electrode, fast charge recombination, and nonideal nature of the redox mediator, iodide. As ~50% of solar light is in the red to near-IR (NIR) region, dyes capable of absorbing light intensely in this region should be beneficial for light harvesting. Therefore, we set out to develop squaraine dyes for p-type DSSCs because they normally exhibit strong absorption in the red−NIR region (700−850 nm). This characteristic renders squaraine dyes useful in many applications, e.g., organic field-effect trainsistors,[13] chemosensors,[14] and bioimaging.[15] Though there have been examples of bulk-heterojunction solar cells[16] and n-type DSSCs[17] based on squaraine dyes, there is no report of squaric acid dyes for p-type DSSCs. Herein we report new squaraine dyes for p-type DSSCs with one or two anchoring groups. Cosensitized p-type DSSC cells based on one of the new dyes will also be reported.

The prototype molecular structure of p-type dyes has a donor-spacer-acceptor skeleton, and the anchoring groups for adsorbing on the photocathode (e.g., NiO) surface are tethered at the donor and farther away from the acceptor. The new squaraine dyes and their synthetic protocol of the compounds are illustrated in Schemes 1, S1, and S2 (see Supporting Information (SI)). Compound **1** was prepared according to the published procedures.[17g] A Pd-catalyzed Suzuki coupling[18] reaction between **1** and appropriate Suzuki reagents, prepared in situ from triphenylamine derivatives with carboxylic ester as the protection group of carboxylic acid, afforded **2** and **3**. Treatment of **2** and **3** with trifluoroacetic acid provided the desired products, **p-SQ1** and **p-SQ2**.

The absorption spectra of the dyes in EtOH are shown in Figure 1, and the relevant data are summarized in Table 1. Both dyes show a very intense band at 646 nm with the molar extinction coefficient exceeding 200 000 $M^{-1}cm^{-1}$. This band is ascribed to a squaraine-centered π−π* electron transition with minimal charge transfer character from the arylamine to the squaraine (see computation, vide infra). Small Stokes shifts (~30 nm) of the emission spectra (Figure S1) for the two dyes is ascribed to the dominance of the squaraine-centered π−π* transition in the $S_0 \rightarrow S_1$ transition (vide infra). The broadened absorption spectra feature upon adsorption on NiO (Figure 1) is attributed to the aggregation of the dye molecules.[19]

The results of density functional calculations at the B3LYP/6-31G* level of the dyes are included in Table S1 (see SI). The dihedral angles between successive units of the molecules are shown in Figure S2. The twist angle between the planar bis(indoline) squaraine segment and the arylamine is ~36° for both dyes. The computed frontier orbitals of the compounds and their corresponding energy states are included in Figures S3 and S4 (see SI), respectively.

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(11) Nattestad, A.; Mozer, A. J.; Fischer, M. K. R.; Cheng, Y.-B.; Mishra, A.; Bäuerle, P.; Bach, U. *Nat. Mater.* **2010**, *9*, 31.

(12) Yen, Y.-S.; Chen, W.-T.; Hsu, C.-Y.; Chou, H.-H.; Lin, J. T.; Yeh., M.-C. *Org. Lett.* **2011**, *13*, 4930.

(13) Smits, E. C. P.; Setayesh, S.; Anthopoulos, T. D.; Buechel, M.; Nijssen, W.; Coehoorn, R.; Blom, P. W. M.; de Boer, B.; de Leeuw, D. M. *Adv. Mater.* **2007**, *19*, 734.

(14) Yan, Z. Q.; Guang, S. Y.; Xu, H. Y.; Liu, X. Y. *Analyst* **2011**, *136*, 1916.

(15) Gassensmith, J. J.; Braumes, J. M.; Smith, B. D. *Chem. Commun.* **2009**, 6329.

(16) Bagnis, D.; Beverina, L.; Huang, H.; Silvestri, F.; Yao, Y.; Yan, H.; Pagani, G. A.; Marks, T. J.; Facchetti, A. *J. Am. Chem. Soc.* **2010**, *132*, 4074.

(17) (a) Takechi, K.; Sudeep, P. K.; Kamat, P. V. *J. Phys. Chem. B* **2006**, *110*, 16169. (b) Burke, A.; Schmidt-Mende, L.; Ito, S.; Grätzel, M. *Chem. Commun.* **2007**, 234. (c) Choi, H.; Kim, J.-J.; Song, K.; Ko, J.; Nazeeruddin, M. K.; Grätzel, M. *J. Mater. Chem.* **2010**, *20*, 3280. (d) Paek, S.; Choi, H.; Kim, C.; Cho, N.; So, S.; Song, K.; Nazeeruddin, M. K.; Ko, J. *Chem. Commun.* **2011**, *47*, 2874. (e) Li, J.-Y.; Chen, C.-Y.; Lee, C.-P.; Chen, S.-C.; Lin, T.-H.; Tsai, H.-H.; K.-C.; Ho, K.-C.; Wu, C.-G. *Org. Lett.* **2010**, *12*, 5454. (f) Yan, Z.; Guang, S.; Su, X.; Xu, H. *J. Phys. Chem. C* **2012**, *116*, 8894. (g) Shi, Y.; Hill, R. B. M.; Yum, J.-H.; Dualeh, A.; Barlow, S.; Grätzel, M.; Marder, S. R.; Nazeeruddin, M. K. *Angew. Chem., Int. Ed.* **2011**, *50*, 6619. (h) Funabiki, K.; Mase, H.; Saito, Y.; Otsuka, A.; Hibino, A.; Tanaka, N.; Miura, H.; Himori, Y.; Yoshida, T.; Kubota, Y.; Matsui, M. *Org. Lett.* **2012**, *14*, 1246.

(18) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(19) Cornil, J.; Beljonee, D.; Calbert, J.-P.; Brédas, J.-L. *Adv. Mater.* **2001**, *13*, 1053.

Table 1. Electrooptical and Electrochemical Parameters of the Dyes

dyes	λ_{abs} ($\varepsilon \times 10^{-5}$ M^{-1} cm^{-1})[a] nm	λ_{em}[a] nm	$E_{0\text{-}0}$[b] eV	λ_{NiO}[c] nm	E_{ox}[d] mV	HOMO/ LUMO eV	E_{0-0^*}[e] V
p-SQ1	324 (0.31), 646 (2.40)	675	1.87	662	336	5.44/3.57	−0.83
p-SQ2	328 (0.31), 646 (2.32)	679	1.87	663	350	5.45/3.58	−0.82

[a] Recorded in EtOH at 298 K. [b] $E_{0\text{-}0} = 1240/\lambda_{opt}$. [c] Recorded in NiO film dependent on EtOH at 298 K. [d] Oxidation potential reported is referenced to the potential of ferrocene (E_{ox} = 212 mV vs Ag/AgNO$_3$) which was used as an internal reference. Scan rate: 100 mV/s. $E_{ox} = 1/2(E_{pa} + E_{pc})$. [e] vs NHE.

Table 2. DSSC Performance Parameters and Dye Loading of the Dyes

dyes	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)	dye loading (10^{-7} mol/cm^2)
P1 (THF)	2.31	0.132	0.331	0.101	1.29
P1 (EtOH)	2.88	0.140	0.330	0.133	1.58
p-SQ1 (EtOH)	1.22	0.117	0.371	0.053	1.07
p-SQ2 (EtOH)	1.92	0.140	0.420	0.113	1.98

Both the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the dyes are mainly composed of the bis(indoline) squaraine moiety, and the HOMO has a minor contribution from the arylamine moiety (vide infra). Consequently, **p-SQ1** and **p-SQ2** have nearly the same HOMO (**p-SQ1**: −4.50 eV; **p-SQ2**: −4.53 eV) and LUMO (**p-SQ1**: −2.28 eV; **p-SQ2**: −2.31 eV) levels. Accordingly, they also have very high oscillator strength (*f*): **p-SQ1**, 1.83; **p-SQ2**: 1.82. This and the small changes of Mulliken charge (Figure S5 and Table S1) of arylamine in the $S_0 \rightarrow S_1$ transition (**p-SQ1**, 0.03; **p-SQ2**: 0.01) imply unfavorable hole injection from the excited dye to the NiO. Thus, the squaraine dyes in this study are different from the dyes we reported earlier,[12] in which the HOMOs of the dyes have a significant contribution from the arylamine.

The cyclic voltammograms and the electrochemical data of the dyes are presented in Figure S6 and Table 1, respectively. Only one quasi-reversible redox wave attributable to the oxidation of the bis(indoline) squaraine moiety (vide supra) was observed for the dyes. The two dyes have very similar oxidations (ΔE = 14 mV) because they have similar HOMO features (vide supra). In comparison, the dye with two carboxylic acid groups is oxidized at a significantly higher potential (ΔE > 60 mV) than that with only one carboxylic acid group in our earlier report.[12] The HOMO energy levels of the dyes were calculated from the oxidation potential and by comparison with ferrocene (5.1 eV).[20] The HOMO/LUMO gap for both dyes (1.87 eV) was estimated from the intersection of the normalized absorption and emission spectra. The data were then used to obtain the LUMO (LUMO = HOMO − E_{0-0}) energy levels (Table 1). No discernible reduction wave due to the reduction of the dyes prevents us from estimating the ability of hole injection[6b] from the excited dye to the NiO. The LUMO levels of dyes (**p-SQ1**: −0.83 V; **p-SQ2**: −0.82 V) are higher than that of the I^-/I_3^- redox system (0.44 V vs NHE), suggesting that the reduced dyes can efficiently reduce the oxidized electrolyte. p-Type DSSCs were fabricated with the use of **p-SQ** dyes and nanostructured NiO. The cells had an effective area of 0.25 cm^2, and the electrolyte used was composed of I_2 (0.1 M)/LiI (1.0 M)/*tert*-butylpyridine (TBP, 0.5 M) in CH_3CN. The device performance statistics under AM 1.5 illumination are collected in Table 2. Due to the lower solubility of **p-SQ** dyes in THF, ethanol was used as the dipping solvent for the cell fabrication. Figures 2 and 3 show the photocurrent−voltage (*J*−*V*), dark currents, and the incident photon-to-current conversion efficiencies (IPCEs) of the cells. The short-circuit photocurrent density (J_{SC}), open circuit voltage (V_{OC}), and fill factor (FF) of the device are in the range of 1.22−1.92 mA cm^{-2}, 0.117−0.140 V, and 0.371−0.420, respectively, corresponding to an overall conversion efficiency of 0.053−0.113%. The performance is comparable to that of the dye reported by Sun (**P1**) (Figure S7) (η = 0.101% in THF, η = 0.135% in ethanol) fabricated and measured under similar conditions. It is important to note that the DSSCs in ethanol conditions show better PCEs than in THF, likely due to the higher dye loading density (Table 2). In view of the unfavorable hole injection of the dyes (vide supra), we speculate that hole injection may take place also via hopping, in which two anchoring groups may have an advantage.

The cell of **p-SQ2** exhibited a higher short-circuit photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (FF) than that of **p-SQ1**. Consequently, the former had a higher conversion efficiency than the latter (**p-SQ1**: 0.053%; **p-SQ2**: 0.113%). The higher dye loading density of **p-SQ2** (1.98×10^{-7} mol/cm^2) than **p-SQ1** (1.07×10^{-7} mol/cm^2) is believed to have important contributions to the significantly higher current density of **p-SQ2** (1.92 mA cm^{-2}) than **p-SQ1** (1.22 mA cm^{-2}). Better dark current suppression

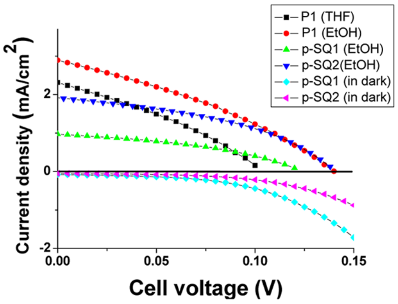

Figure 2. Current density−voltage curves of **P1**, **p-SQ1**, **p-SQ2** and dark-current characteristics of **p-SQ1**, **p-SQ2** dissolved in EtOH under AM 1.5 solar simulator of 100 mW cm^{-2}. Cell area = 0.25 cm^2.

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(20) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. *Adv. Mater.* **2011**, *23*, 2367.

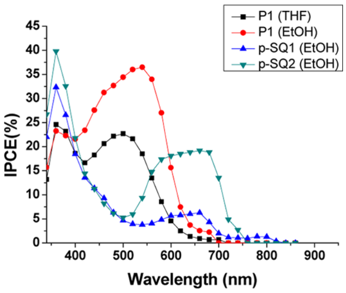

Figure 3. IPCE plots of **P1**, **p-SQ1**, and **p-SQ2**.

by **p-SQ2** may also be important (vide infra). The two carboxylic acid groups in **p-SQ2** may be favorable for more upright anchoring and therefore more compact packing of the molecules on the NiO surface. Similar to our previous observations,[12] the dye with two anchoring groups exhibited a higher V_{OC}: **p-SQ1**, 0.117 V; **p-SQ2**, 0.140 V. This outcome may be attributed to more effective coverage of the naked NiO surface by dye molecules from exposure to the electrolyte, i.e., suppression of dark current. The smaller dark current in the DSSC of **p-SQ2** was further supported by the dark current measurements (Figure 2).

Electrochemical impedance was measured under a bias of −0.15 V in the dark, and the Nyquist plots of DSSCs with the dyes are shown in Figure S8a. The second semicircle can be used to derive the charge recombination resistance on the NiO surface. The higher resistance in the DSSC of **p-SQ2** (**p-SQ1**: 136 Ω; **p-SQ2**: 188 Ω) provides further support for its lower dark current. The electrochemical impedance measurement under illumination was also tested, and the Nyquist plots of DSSCs are shown in Figure S8b. Upon illumination of 100 mW cm^{-2} light under open circuit conditions, the radius of the intermediate frequency semicircle in the Nyquist plot represents the electron transport resistance. No significant difference in the electron transport resistance (R_{ct}) was found between the cells of **p-SQ1** (156 Ω) and **p-SQ2** (148 Ω).

Similar to other squaraine dyes, the dyes in this study have somewhat narrower absorption bands which limit light harvesting efficiency. A dye (**P1**) developed by Sun[10a] has complementary absorption with **p-SQ2**. Therefore, cosensitized p-type DSSCs using **p-SQ2** with **P1** were tested. The performance data are presented in Table 3. The UV absorption spectra on NiO and IPCE plots are shown in Figures S9 and 4, respectively. Though we found no apparent improvement in the cosensitized systems, the IPCE spectra clearly indicated that both dyes had a significant contribution to the current density at various dye ratios, which is consistent with the UV absorption spectra of the dye film. It is encouraging that the efficiency

Table 3. Cosensitized System Performance Parameters of **P1** and **p-SQ2**

dyes in vol. ratio	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
P1:p-SQ2 = 10:0	2.88	0.140	0.330	0.133
P1:p-SQ2 = 8:2	2.78	0.142	0.324	0.128
P1:p-SQ2 = 6:4	2.72	0.147	0.305	0.122
P1:p-SQ2 = 4:6	2.90	0.154	0.302	0.135
P1:p-SQ2 = 2:8	2.48	0.145	0.327	0.118
P1:p-SQ2 = 0:10	1.92	0.140	0.420	0.113

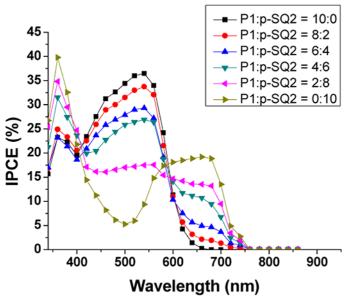

Figure 4. IPCE plots of cosensitizer system based on **P1** and **p-SQ2**.

was retained upon introduction of the second sensitizer in view of the fact that thin NiO film (~1.5 μm) was used.

In summary, we have synthesized two NIR squaraine dyes (SQ) with high molar extinction coefficients. They can be used as the sensitizers of p-type DSSCs. The dye with two anchoring groups has better cell performance than that with only one anchoring group due to its more compact packing on the NiO surface and more effective suppression of the dark current. High open-circuit voltage (0.140 V) and conversion efficiency (0.113%) were achieved with one of the cells using ethanol as the dipping solvent. Cosensitized p-type DSSCs were reported for the first time. The cell exhibited a broader IPCE spectrum and high cell performance with the use of a second dye having an absorption spectrum complementary with the SQ dye. Development of sensitizers with improved absorption at a shorter wavelength region and improved hole injection is currently ongoing.

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Supporting Information Available. Synthetic procedures for new compounds and other physical properties. These materials are available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.