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Organic Dyes Incorporating Low-Band-Gap Chromophores for Dye-Sensitized Solar Cells

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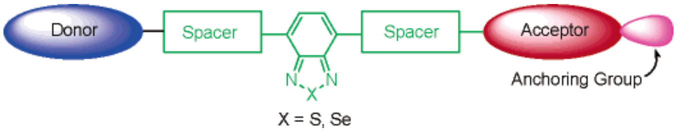
ABSTRACT



Versatile dyes based on benzothiadiazole and benzoselenadiazole chromophores have been developed that perform efficiently in dye-sensitized solar cells. Power conversion efficiency of 3.77% is realized for a dye in which charge recombination is probably hindered by the nonplanar charge-separated structure.

The demand for energy conservation triggered the search for alternate renewable energy sources.[1] A practical solution is the adoption of light-harvesting biological concepts. This biomimetic strategy has been recently translated into technological advances such as solar cells.[2,3] Although silicon-based semiconductors[4] dominated solar cell applications for decades, recent demonstration of dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 by Grätzel et al. opened up the opportunity for organic and organometallic dyes in this area.[5,6] A dye with excellent light-absorbing capability in the red and near-IR region, photostability, and redox stability is presumed to be attractive for the functioning of DSSCs.

Coumarin-,[7] indoline-,[8] cyanine-,[9a] and hemicyanine-based[9b,c] dyes have been used for the construction of DSSCs recently. Though benzothiadiazole-based polymers[10,11] have been widely employed in photovoltaic applications, to the best of our knowledge, small molecules containing benzothiadiazole or benzoselenadiazole structural motifs have not been exploited for DSSCs. In this letter, we report a series

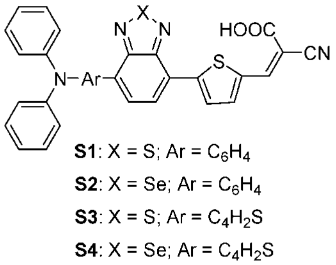


Figure 1. Structure of the dyes.

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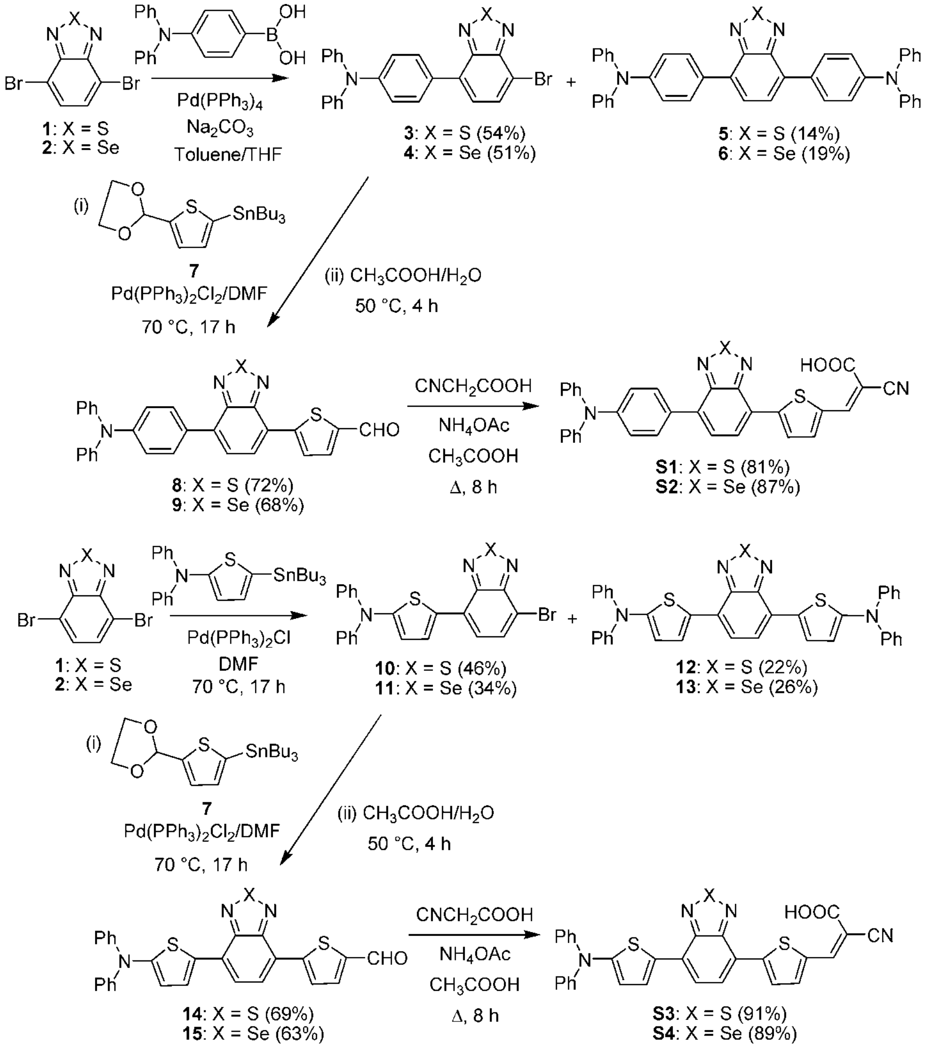
Scheme 1. Synthesis of the Dyes



of organic donor−acceptor compounds (Figure 1) that contain diphenylamine donors and cyano acrylic acid acceptors bridged by a benzothiadiazole or benzoselenadiazole fragment. The carboxylic acid group is introduced so that it will function as an anchoring group toward nanocrystalline TiO_2 in the solar cell setup. We believe that the low-band-gap chromophores will function as a photon sink where charge separation occurs, and their migration in opposite directions is facilitated by the presence of donor and acceptor units. In benzo(thia/selena)diazole-based fluorophores, the low-energy absorption is predominantly charge transfer in nature, and the same is true with the low-lying excited state also.[12] This will ensure and enhance the possibility of charge separation and migration in such systems.

The dyes were obtained in moderate yields in three steps as illustrated in Scheme 1. In the first step, the donor is

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Table 1. Electrooptical Parameters of the Dyes[a]

dye	λ_{abs}/nm ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1})	$E_{1/2}$ (ox) (ΔE_p)/mV	$E_{1/2}$ (red) (ΔE_p)/mV	HOMO, eV	LUMO, eV	band gap, eV
S1	491 (27.5), 388 (16.3), 309 (28.4)	581 (91)	−1718 (90)	5.381	3.260	2.121
S2	502 (6.30), 351 (15.6)	556 (77)	−1630 (96)	5.356	3.338	2.018
S3	541 (24.4), 398 (20.1), 312 (21.0)	322 (85)	−1660 (106)	5.122	3.256	1.866
S4	544 (13.2), 363 (26.5)	263 (107)	−1556 (138)	5.063	3.290	1.773

[a] Absorption and electrochemical data were collected in tetrahydrofuran solutions. Scan rate, 100 mV/sec; electrolyte, (n-C_4H_9)$_4$NPF$_6$; ΔE_p is the separation between the anodic and cathodic peaks. Potentials are quoted with reference to the internal ferrocene standard ($E_{1/2}$ = +265 mV vs Ag/AgNO$_3$).

attached to the core either by Stille[13] or Suzuki[14] coupling reactions. These reactions produced the disubstituted side products as well. However monocapped compounds can be easily separated by column chromatography. In the next step, this bromo-exposed intermediate was reacted with (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributyl stannane under Stille coupling conditions, and subsequent cleavage of the 1,3-dioxalane protecting group in aqueous acetic acid produced the free aldehydes. These aldehydes, on reaction with cyanoacetic acid in the presence of ammonium acetate catalyst in acetic acid, produced the required dyes. The dyes are dark red or black in the solid state and freely dissolve in tetrahydrofuran to produce a red or violet solution.

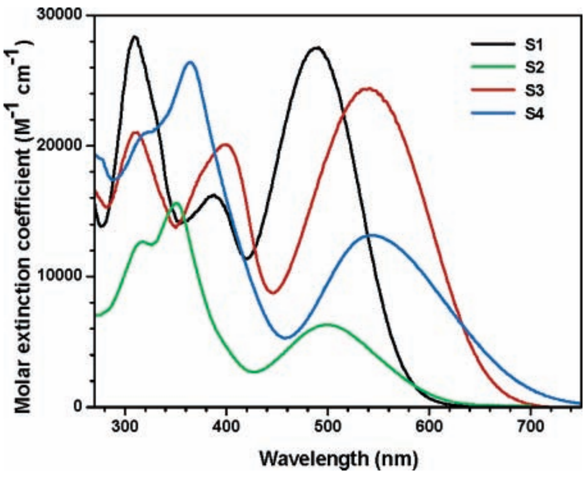

Figure 2. Absorption spectra of dyes **S1**−**S4** recorded in THF.

The absorption spectra recorded for the tetrahydrofuran solution of the dyes are displayed in Figure 2. All the dyes exhibit three transitions and cover a broad range (250−700 nm) of spectra (Figure 2 and Table 1). For the similar structural architecture, the benzoselenadiazole derivatives (**S2** and **S4**) display red-shifted absorption when compared to the benzothiadiazole analogues (**S1** and **S3**). However, the benzoselenathiadiazole derivatives possess less optical density for the CT transition. Another effect due to the linking aromatic segment was also noticed, i.e., the thiophene-linked compounds (**S3** and **S4**) show bathochromic shift for the charge-transfer band when compared to the phenylene-linked derivatives (**S1** and **S2**). The drop in the extinction coefficient of the CT absorption in the benzoselenadiazole derivatives (**S2** and **S4**) is more pronounced for the phenylene-conjugated derivative **S2** (4.37 times when compared to **S1**) than for the thiophene-linked analogue **S4** (1.85 times when compared to **S3**). These observations are attributed to the larger size and smaller electronegativity of Se when compared to S. These factors will lead to less electron density on Se and thus diminished aromaticity for benzoselenadiazole when compared to benzothiadiazole.[15] Similarly, the increased donor property and coplanar arrangement of thiophene with the core substantially compensate the drop in transition probablity for **S4**.

The dyes are redox stable, exhibiting both quasireversible oxidation and reduction couples. Dyes with good redox stability are required for sustaining dye-sensitized solar cells. Benzothiadiazole-based derivatives containing triarylamines have been reported to undergo facile oxidation and reduction.[16] Similarly, in the current derivatives, the oxidation and reduction also originate from the amino and benzothiadiazole/benzoselenadiazole functionality, respectively. Thiophene linker slightly influence the redox potentials. Benzoselenadiazole derivatives display negative shift in oxidation potentials and positive shift in the reduction potentials when compared to the benzothiadiazole derivatives. This results in a substantial reduction in the band gap for the benzoselenadiazole derivatives when compared to the benzothiadiazole analogues (see Table 1).

The dye-sensitized solar cells were constructed using these dyes as a sensitizer for nanocrystalline anatase TiO$_2$. Typical solar cells, with an effective area of 0.25 cm^2, were fabricated with 0.05 M I$_2$/0.5 M LiI/0.5 M *tert*-butyl pyridine in acetonitrile solution as an electrolyte. The device performance statistics under AM 1.5 illumination are collected in Table 2. The incident to photon conversion efficiency data at each wavelength are plotted for **S1**−**S4** in Figure 3. From the data, it is evident that dyes **S1** and **S2** exhibit

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Table 2. Performance Parameters of DSSCs Constructed Using the Dyes[a]

dye	V_{OC}, mV	J_{SC}, mA cm^{-2}	ff	η, %
S1	546	10.44	0.66	3.77
S2	524	8.35	0.67	2.91
S3	517	3.21	0.69	1.15
S4	474	3.57	0.66	1.11
N3	708	11.28	0.66	5.30

[a] Experiments were conducted using TiO_2 photoelectrodes with approximately 14 μm thickness and 0.25 cm^2 working area on the FTO (7 Ω/sq) substrates.

impressive photovoltaic performances. The open-circuit photovoltage and overall yield for the four dyes lie in the order **S1** > **S2** > **S3** ~ **S4**.

The difference in performance between the phenylene-conjugated derivatives (**S1** and **S2**) and thiophene-linked analogues (**S3** and **S4**) probably stems from the difference in the coplanarity of the aromatic segment that bridges the donor and acceptor units. Molecular modeling (SPARTAN, PM3) studies reveal that the phenlylene derivatives (**S1** and **S2**) possess a twisted nonplanar geometry, which will decelerate the recombination of charges in the charge-separated state.[17] Additionally, in the phenylene derivatives (**S1** and **S2**), the reorganization energy required for the decoupled twisted state may be more favorable when compared to the thiophene analogues (**S3** and **S4**).

In summary, we have developed a new class of dyes featuring donor–acceptor architecture that incorporates low-band-gap chromophores. They are successfully adsorbed on nanocrystalline anatase TiO_2 particles, and subsequently efficient dye senstitized solar cells have been fabricated. The performance of these small-molecule-based, dye-sensitized solar cells is better than that fabricated from certain cyanine and hemicyanine dyes.[9] This design opens up the possibility of preparing new dye molecules for DSSCs utilizing low-band-gap building blocks. The approach is unique in that it uses an easily polarizable and electron-deficient bridge between the push–pull chromophores, leading to push–pull–pull architecture that is different from that used previously, which contains a donor and an acceptor bridged through an aromatic or aliphatic linker.

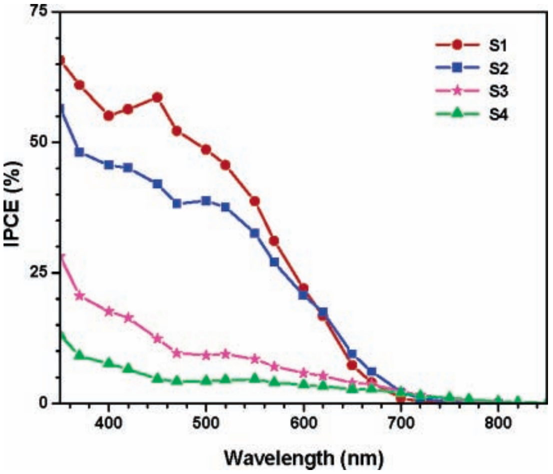

Figure 3. Action spectra for dyes **S1**–**S4**.

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Supporting Information Available: Synthetic procedures and characterization details for the new compounds described in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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