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Enhanced Performance of the Dye-Sensitized Solar Cells with Phenothiazine-Based Dyes Containing Double D−A Branches

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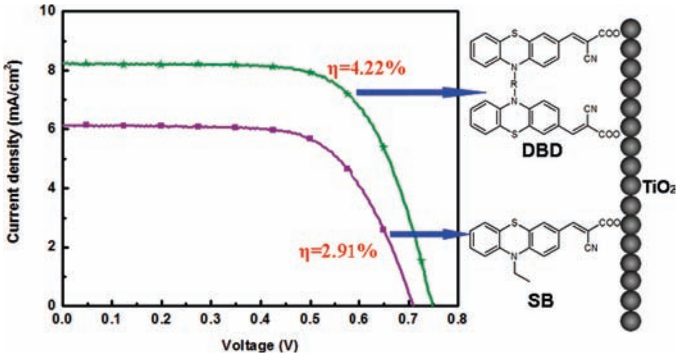
ABSTRACT



Double donor−acceptor (D−A) branched dyes (DBD) with a phenothiazine unit as electron donor and a 2-cyanoacrylic acid unit as electron acceptor were synthesized and used as sensitizers for solar cells (DSSCs). The conversion efficiency of the DSSCs amounts up to 4.22% (2.91% for the single D−A branched dye) under AM 1.5 G irradiation. The results show that the performance of DSSCs can be effectively enhanced by the cooperation of two donor−acceptor containing branches in one molecule of the dyes.

Dye-sensitized solar cells (DSSCs) which emerged as a new generation of photovoltaic devices[1] have attracted significant attention and have been studied extensively because of their high efficiency, low cost, and facile fabrication.[2] Although Ru-based complexes hold the record of validated efficiency of over 11%,[3] they have encountered problems such as limited resources and difficult purification. On the other hand, metal-free organic dyes have been developed for DSSCs. Their advantages are due to their high molar absorption coefficients, simple syntheses, low costs, and variable structure adjustabilities.[4] Moreover, encouraging efficiencies up to 10% have been reported.[5]

It is well-known that the sensitizers play a critical role for the cell performance. A major factor is the adsorbed amount of dye on the TiO_2 surface. The higher the amount of adsorbed dye, the higher the overall yield (η) of the DSSCs provided that the formation of aggregates is not a

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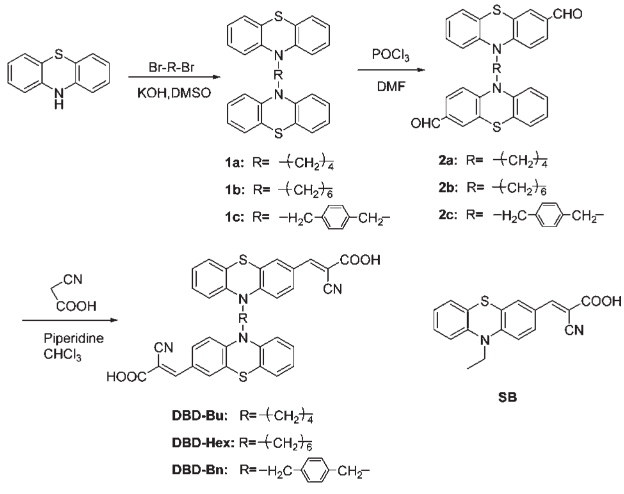
restricting factor. Nevertheless, there is a maximum of adsorbed amount of dye on a limited TiO_2 surface.

The light-harvesting unit is the effective part of the dye. If the light-harvesting units increase, η of DSSCs should increase. In the presently applied dyes, there is normally only one light-harvesting unit per molecule.

On the basis of the above considerations, we designed and synthesized three double D−A branched dyes (DBD) which contained two separate light-harvesting units in one molecule. In addition, the corresponding single D−A branched dye, coded SB, was synthesized for a comparison. Thus, if the TiO_2 surface of the DSSCs would adsorb the same number of DBD and SB molecules, the light-harvesting units might be doubled in DSSCs with DBD compared to that with SB. Even when the TiO_2 surface adsorbs somewhat less DBD molecules, the number of light-harvesting units can be enhanced, provided that the intramolecular distance of the chromophores is smaller than their average intermolecular distance.

We selected phenothiazine as an electron donor D on the basis of the following reasons: (1) the heterocyclic compound contains electron-releasing nitrogen and sulfur heteroatoms; (2) the phenothiazine ring is nonplanar and therefore can impede the molecular aggregation and the formation of intermolecular excimers.[6] Moreover, the use of alkyl bridges in the molecular design is not only beneficial to suppress dye aggregation, but also can help to suppress the dark current upon reducing the recombination of conduction-band electrons with I_3^-.

Scheme 1. Synthesis of DBD Dyes



Three double-branched dyes (DBD-Bu, DBD-Hex and DBD-Bn) were obtained in desired yields as illustrated in Scheme 1. The three synthetic steps correspond to well-known reactions such as N-alkylation, Vilsmeier−Haack formylation, and Knoevenagel condensation. The comparison compound SB was prepared according to the literature procedure.[7] The detailed synthetic procedures of these dyes are described in the Supporting Information.

The cyanoacrylic acid side chain represents the acceptor part A of the DA compounds. Since their LUMO is mainly located at the acceptor substructure, which is directly adsorbed to the TiO_2 surface, an easy electron transfer is provided.

Originally, 10-alkyl-2-cyano-3-(10*H*-phenothiazin-3-yl)-acrylic acids and their esters were studied in context with synthetic aspects[8] or with applications as sensitizers in colored photographic layers[9] or as light stabilizers for polymers.[10] In recent years, the main interest in these DA systems has been focused on their light-harvesting effect in solar cells DSSCs.[7,11]

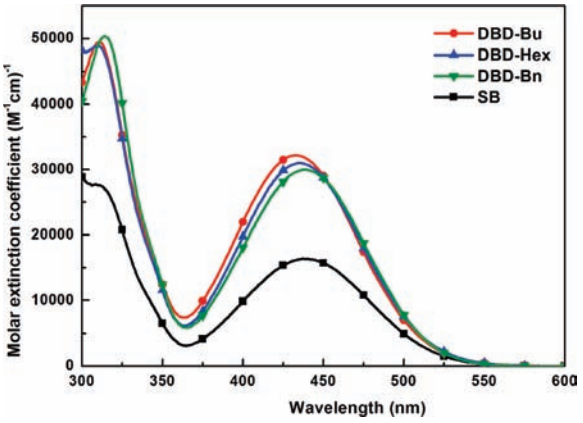


Figure 1. Absorption spectra of **DBD** dyes and **SB** in THF.

Table 1. Absorption and Fluorescence Properties of the Dyes[a]

dye	λ_{max}, nm ($\varepsilon \times 10^{-4}$, $M^{-1}\,cm^{-1}$)	λ_{em}, nm
DBD-Bu	433 (3.2), 310 (4.9)	589
DBD-Hex	435 (3.1), 310 (4.9)	583
DBD-Bn	439 (3.0), 314 (5.0)	577
SB	439 (1.6), 300 (2.9)	586

[a] THF solution (2×10^{-5} M).

The absorption spectra of the dyes in THF solution are displayed in Figure 1, and the corresponding data are presented in Table 1. All of the dyes have an intense absorption band at 430−450 nm which is attributed to the $\pi-\pi^*$ transition with charge-transfer character D→A. The molar extinction coefficients of the DBD dyes are

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Table 2. Performance Parameters of DSSCs[a]: Open-Circuit Photovoltage V_{oc}, Short-Circuit Photocurrent Density J_{SC}, Fill Factor ff, Solar Energy-to-Electricity Conversion Efficiency η, and Specific Dye Loading

dye	V_{OC} (mV)	J_{SC} (mA/cm^2)	ff	η (%)	dye amount (10^{-7} mol cm^{-2})
DBD-Bu	740	7.86	0.71	4.13	2.33
DBD-Hex	750	8.27	0.68	4.22	2.25
DBD-Bn	740	6.98	0.69	3.56	2.16
SB	709	6.13	0.67	2.91	2.44
N719	734	12.64	0.62	5.75	-

[a] Active area: 0.237 cm^2; electrolyte: 0.05 M I_2, 0.5 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile solution.

nearly twice as high as that of SB because of the two donor–acceptor units.

The amount of the dyes adsorbed on TiO_2 decreases in the order of SB > DBD-Bu > DBD-Hex > DBD-Bn (Table 2). The dye adsorption is directly related to the structure and the molecular size of the dyes. SB exhibits the highest loading on the TiO_2 surface because it has the smallest size.

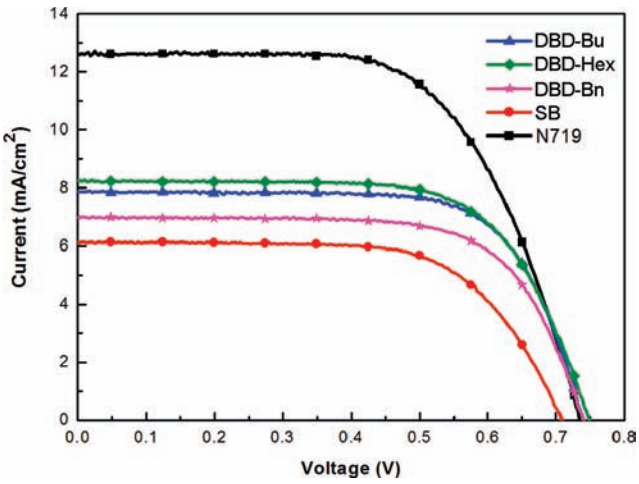

Figure 2. *J*–*V* curves of the DSSCs.

Figure 2 illustrates the current–voltage (*J*–*V*) curves plotted for the DSSCs.

The performance statistics of our DSSCs fabricated with the dyes as sensitizers under AM 1.5 illumination are listed in Table 2. DBD-Bu and DBD-Hex exhibited impressive photovoltaic performances. The maximum η (4.22%) of DSSC sensitized with DBD-Hex reached ~70% of the N719-based DSSC[12] (5.75%) fabricated and measured under similar conditions. N719 (ditetrabutylammonium cis-bis(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)) is one of the best dyes for DSSC and becomes a well-reproducible standard control to evaluate the performance of new DSSC.[12] The short-circuit current densities J_{SC} and the overall yields η for the four dyes decrease in the order DBD-Hex > DBD-Bu > DBD-Bn > SB. This result may be rationalized by the following reasons: (1) SB loaded the highest molar dye amount on TiO_2 (2.44×10^{-7} mol cm^{-2}), but the least amount of D–A units (2.44×10^{-7} mol cm^{-2}, which is smaller than that of DBD, for example, $2 \times 2.16 \times 10^{-7}$ mol cm^{-2} for DBD-Bn), because each molecule SB contains only one D–A unit while one molecule DBD contains two D–A units; (2) the number of light-harvesting units adsorbed on TiO_2 determined the

Table 3. Photovoltaic Performance of DSSCs with DBD-Hex in Different Solutions[a]

dye	solvent	V_{OC} (mV)	J_{SC} (mA/cm^2)	ff	η (%)
DBD-Hex	DMF/CH_2Cl_2[b]	740	7.40	0.68	3.74
	DMF/EtOH[b]	736	8.25	0.69	4.18
	THF/CH_2Cl_2[b]	742	8.87	0.69	4.56
	THF/EtOH[b]	757	7.42	0.70	3.92
	THF/CH_3CN[b]	745	9.29	0.68	4.75
	THF	750	8.27	0.68	4.22

[a] Active area: 0.237 cm^2; electrolyte: 0.05 M I_2, 0.5 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile solution. [b] Dye bath: mixed solvent (1:4, v/v).

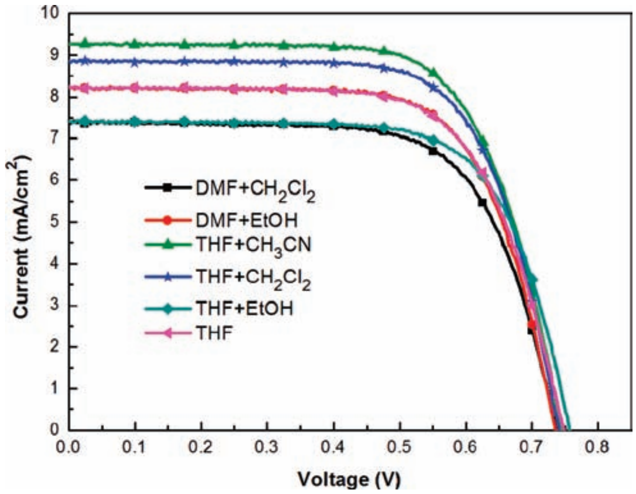

Figure 3. *J*–*V* curves of the DSSCs with DBD-Hex in different solutions.

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Table 4. Photovoltaic Performance of DSSCs Based on DBD-Hex Sensitized in Different Solutions[a]

solvent	[CDCA]	V_{OC} (mV)	J_{SC} (mA/cm^2)	ff	η (%)	dye amount, 10^{-7} (mol cm^{-2})
THF	0	750	8.27	0.68	4.22	2.25
THF	saturated	740	7.80	0.69	4.09	2.03
THF/CH_3CN[b]	0	750	9.32	0.68	4.73	2.86
THF/CH_3CN[b]	saturated	722	8.07	0.70	3.94	1.93

[a] DSSCs had an active area of 0.237 cm^2 and an electrolyte composed of 0.05 M I_2, 0.5 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile solution. [b] Dye bath: mixed solvent (1:4, v/v).

η of DSSC; (3) alkyl groups acted as a barrier preventing hydrophilic I_3^- ions from approaching to the TiO_2 surface, thereby retarding electron leakage to the redox electrolyte. The latter effect accounted for the significant improvement (~30 mV) of DBD dyes compared to SB in the V_{OC} value. The η values of DBD-Bu, DBD-Hex, and DBD-Bn are 4.13%, 4.22%, and 3.56%, respectively, which is consistent with the result of J_{SC}. The more rigid Bn linker between the chromophores is less suitable than the flexible alkyl chains Bu and Hex, although both spacers have almost the same length.

It has been verified that different dye baths for semiconductor sensitization have a crucial effect on the performance of the DSSCs due to the different amount of adsorbed dye.[13] As an attempt to improve the performance of the DSSCs based on DBD-Hex, we optimized the solvent of the dye baths. Considering the solubility of DBD-Hex, we chose mixed solvents with DMF and THF as better solvents. The results are summarized in Table 3 and the corresponding $J-V$ curves are shown in Figure 3. When a THF/CH_3CN solution of DBD-Hex was used, the DSSC reached the maximum η value of 4.75%.

It has been reported that chenodeoxycholic acid (CDCA) can enhance the performance of the DSSCs because CDCA can reduce the aggregation of the dyes on the TiO_2 surface.[14] We studied the performance of the DSSCs in different solvents in the presence of CDCA in concentrations at 0 and a saturated solution. The results are collected in Table 4, and the corresponding $J-V$ curves are shown in Figure 4. CDCA did not improve the device's performance, in contrast, it decreased the power conversion efficiency. A possible explanation is that the amount of dye adsorbed on the TiO_2 surface was reduced by the coadsorption of CDCA, resulting in a loss of active light-harvesting. We take this result as a hint that these phenothiazine dyes did not aggregate on the TiO_2 surface.

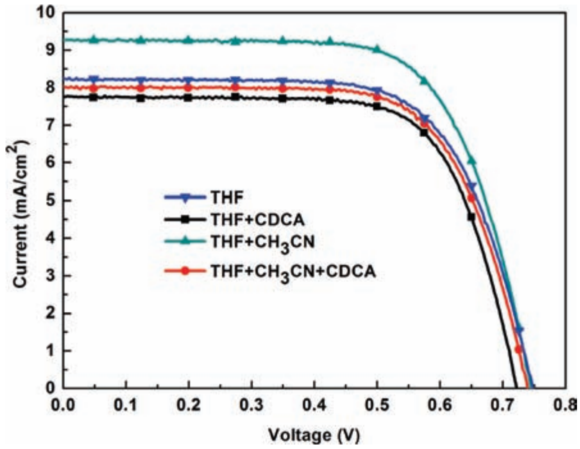

Figure 4. $J-V$ curves of the DSSCs based on DBD-Hex as sensitizer in different solutions in the presence or absence of CDCA.

In summary, a new class of dyes which contained double D−A branches were developed and successfully used as sensitizers of DSSCs. The conversion efficiency η of these DSSCs was effectively enhanced compared to the corresponding single D−A phenothiazine dye, which reached ~70% of N719-based DSSCs. This design opens up the promising possibility to prepare double or more D−A branched dyes for an enhanced light-current conversion.

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

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