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Journal Name

COMMUNICATION

Eugenic Metal-free Sensitizers with Double Anchors for High Performance Dye-Sensitized Solar Cells

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A series of new phenothiazine-based dyes (HL5–HL7) with double acceptors/anchors have been synthesized and used as the sensitizers for highly efficient dye-sensitized solar cells (DSSCs). Among them, HL7-based cell exhibits the best efficiency of 8.32% exceeding the N719-based cell (7.35%) by ~13%.

Dye-sensitized solar cells (DSSCs) have attracted considerable interest in both academic and industrial communities since the innovative report by Grätzel et al. in 1991,[1] due to their easy fabrication and low cost. There are three major types of organic sensitizers for DSSCs application: zinc porphyrins, ruthenium complexes and metal-free dyes. The highest cell efficiencies (AM 1.5) of single dye-based DSSCs are 13.0%,[2] 11.5%[3] and 10.65%,[4] for zinc porphyrin dyes, ruthenium dyes and metal-free dyes, respectively. Several recent reports witnessed that metal-free organic sensitizers could have cell efficiencies competitive with that of N719-based DSSC.[5]

Dyes with two pinched D-π-A segments represent an alternative approach of molecular tuning for dark current suppression: with appropriate design, they can more effectively suppress the dark current compared to their congeners with single D-π-A segment (A also functions as the anchor) due to more compact packing of the dye molecules in the former.[6] In contrast, dyes with two acceptors, D(-π-A)$_2$, may[7,6b] or may not[8] exhibit more efficient dark current suppression than their D-π-A congeners. An interesting feature with these D(-π-A)$_2$ dyes are that they not only exhibit better light harvesting, but also provide more electron extraction paths compared to the congeners with only one anchor. Consequently, photocurrent can be increased.[9] Phenothiazine is a fairly strong donor and there have been some reports of high performance DSSCs based on phenothiazine sensitizers,[10] including the one exhibiting efficiency surpassing N719.[5d] Previously we took advantage of easy introduction of functional groups at the C-3 and C-7 sites of a phenothiazine and developed D(-π-A)$_2$ dyes where D was the

phenothiazine entity.[7a] Compared to the congener containing only one anchor, the charge transfer band of these dyes is considerably more intense and shifts to a longer wavelength. The highest cell efficiency was comparable with that of the N719-based standard cell. We also found that dark current suppression and dye aggregation could be alleviated via introduction of long alkyl chain at the conjugated spacer. Though the short-circuit currents of the cells rivaled that of the standard cell, the open-circuit voltages were smaller than that of N719-based cell by ~0.1 V. More efficient suppression of dark current should be beneficial to further raising the voltage. In order to tackle this issue without negative perturbation of the conjugated skeleton, we decided to replace the alkyl substituent at the nitrogen atom of phenothiazine with a 2,6-alkoxyl substituted phenyl ring, an approach successfully used in porphyrin systems.[11] Herein we report new phenothiazine-based sensitizers with double anchors which exhibit efficiencies surpassing that of N719-based cell.

The structures of new phenothiazine-based dyes are shown in Fig. 1, and the synthetic routes of the compounds are depicted in Scheme S1.
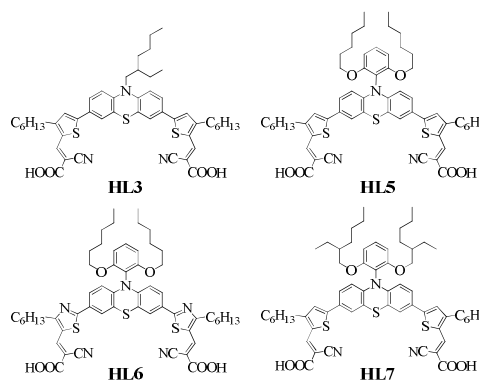

Fig. 1 The structure of the dyes.

Fig. 2a shows the UV-vis absorption spectra of organic dyes in THF, and the corresponding data are summarized in Table 1. The spectrum of **HL-7** at different concentrations and the absorption vs. dye concentration plot are shown in Fig. S1. Two distinct bands were observed for these compounds. Based on theoretical computations (vide infra), the band at shorter wavelength (band I) is attributed to aromatic $\pi-\pi^*$ transition, and the band of longer wavelength (band II) is assigned to the intramolecular donor to acceptor charge transfer (ICT) transition with $\pi-\pi^*$ character. Although **HL5−HL7** have a large dihedral angle (~86°) between the 2,6-disubstituted phenyl ring and phenothiazine moiety (vide infra), their ICT bands have impressively longer wavelengths (by ~40 nm) compared with that of **HL3**[7a] (Fig. 2a) which has a 2-ethylhexyl chain instead of phenyl ring at the phenothiazine entity. Replacement of the thiophene ring with a thiazole ring leads to red shifting of the λ_{abs} value by 5 nm, which is consistent with the trend observed in other dipolar compounds.[12] Blue shift of the ICT band (Fig. 2b) of the dyes adsorbed on TiO$_2$ film relative to that in the solution can be ascribed to the deprotonation of carboxylic acid.[13] Bis(*n*-hexyloxy)phenyl or bis(2-ethylhexyloxy)phenyl entity certainly is more effective than 2-ethylhexyl in suppressing dye aggregation when adsorbed on TiO$_2$ film: **HL3** has prominent blue shift of the spectrum upon addition of 30 mM of CDCA, whereas nearly no change was observed for **HL5** or **HL7** (Fig. S2). This implies that a phenyl entity with two hexyloxy substituents at the ortho positions is still not sufficient for enveloping the dyes from J-aggregation when the molecule has a more planar conjugated skeleton (vide infra).
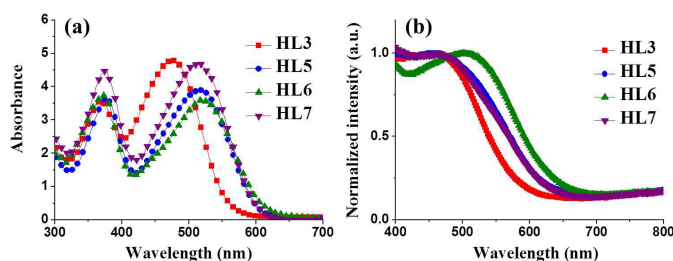

Fig. 2 Absorption spectra of **HL** dye in THF (10 μM) (a) and on the TiO$_2$ film (b).

The electrochemical properties of the organic dyes were measured by cyclic voltammetry (CV) in THF solutions with ferrocene/ferrocenium as the internal reference (Fig. S3), and the relevant data are listed in Table 1. The **HL** dye with a 2,6-disubstituted phenyl entity at the phenothiazine (**HL5** and **HL7**) have more negative first oxidation potentials compared with their congeners containing a 2-ethylhexyl substituent (**HL3**), which is consistent with the longer wavelength ICT band of the former (vide supra).

Table 1. Optical and electrochemical data of the dyes.

dye	λ_{abs} ($\varepsilon \times 10^4 M^{-1}cm^{-1}$)[a] [nm]	λ (TiO$_2$) [nm]	E_{ox}[b] [V]	E_{0-0}^{*c} [V]
HL3	475 (4.79), 369 (3.56)	456	1.10	-1.09
HL5	516 (3.90), 377 (3.65)	444	1.04	-1.06
HL6	520 (3.78), 374 (3.94)	508	1.17	-0.90
HL7	518 (4.68), 376 (4.19)	450	1.05	-1.06

[a] Recorded in THF solution at 298 K; [b] Recorded in THF solutions using ferrocene/ferrocenium (+212 mV relative to the Ag/AgNO$_3$ nonaqueous reference electrode) as the internal reference. E_{ox} = $1/2(E_{pa}+E_{pc})$, $\Delta E_p = E_{pa}-E_{pc}$, where E_{pa} and E_{pc} are peak anodic and cathodic potential, respectively. Oxidation potential was reported relative to ferrocene (+212 mV relative to the Ag/AgNO$_3$

nonaqueous reference electrode; [c] E_{0-0}^*: The excited state oxidation potential vs. NHE.

The DSSCs were fabricated using these organic dyes as the sensitizers and nanocrystalline anatase TiO$_2$ as the photoanode. In addition to N719, **HL3** dye was also used as the reference for comparison. The device performance parameters under simulated AM 1.5 illumination are collected in Table 2. Fig. 3a shows the photocurrent-voltage (*J-V*) plots under illumination and in the dark, and the incident photon-to-current conversion efficiencies (IPCE) of the cells are shown in Fig. 3b. It is intriguing that the efficiencies of **HL5−HL7** surpass that of N719 (7.35%), and the efficiency of **HL7** (8.32%) is ~13% higher than that of N719-based standard cell fabricated and measured under similar conditions. By comparison of **HL5** (or **HL7**) with **HL3**, it is obvious that 2,6-disubstituted phenyl unit plays an important role for the high performance of DSSCs. Its contribution to the cell efficiency is manifold: (1) the higher J_{sc} value due to red shifting of the absorption spectra; (2) low tendency of dye aggregation due to better encapsulation effect of the phenothiazine core, similar to that observed for porphyrin dyes;[11] (3) more effective suppression of the dark current (Fig. 3a). The higher V_{oc} for **HL7** than for **HL5** is consistent with more efficient dark current suppression in the former (vide infra) and suggests that the branched alkoxyphenyl entity can more effectively block the electrolyte from approaching the TiO$_2$ surface.
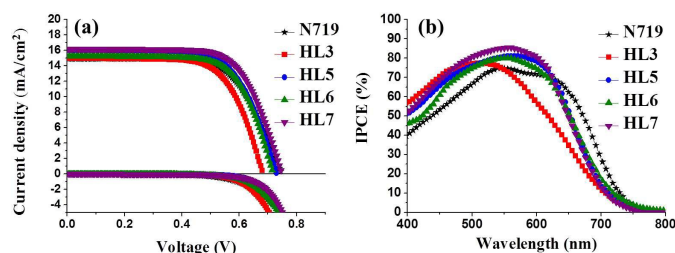

Fig. 3 (a) *J-V* curves of DSSCs based on the dyes measured under AM 1.5 illumination and in the dark. (b) IPCE spectra of DSSCs.

More effective suppression of the dark current (Fig. 3a) by **HL5−HL7** is also supported by electrochemical impedance spectra (EIS) in the dark (**Fig. 4a**). In the Nyquist plots, the electron recombination resistance (R_{rec}) decreases in the order of **HL7** > **HL5** > **HL6** > **HL3**, indicating that the electron recombination rate decreases in the same order. Better dark current suppression leads to higher V_{oc} values: **HL5−HL7** vs. **HL3**.

Table 2. Photovoltaic parameters for DSSCs of the dyes.

dye	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	η [%]	dye loading [mol cm^{-2}]
HL3	0.68	14.95	0.68	6.91	4.98×10^{-7}
HL5[a]	0.73 ± 0.005	16.08 ± 0.33	0.66 ± 0.005	7.80 ± 0.04	6.10×10^{-7}
HL6[a]	0.72 ± 0.005	15.21 ± 0.34	0.68 ± 0.005	7.43 ± 0.05	5.88×10^{-7}
HL7[a]	0.75 ± 0.005	16.23 ± 0.41	0.68 ± 0.02	8.32 ± 0.13	6.06×10^{-7}
N719	0.75	14.96	0.66	7.35	

[a] Based on five measurements.

Further support of the argument comes from intensity-modulated photovoltage spectroscopy (IMVS). Fig. 4b shows the recombination electron lifetime as a function of charge density at open circuit. At a fixed charge density (Q), the electron lifetime for **HL5**, **HL6** and

HL7 is larger than that for **HL3** by 5.9-, 3.1-fold and 12.8-fold, respectively. Bis(2-ethylhexyloxy)phenyl substituent can more effectively suppress dark current than its bis(hexyloxy)phenyl congener therefore finds further supports from both EIS and IMVS results, and this illustrates that a small tuning of the molecular structure can lead to significant change of the cell performance.
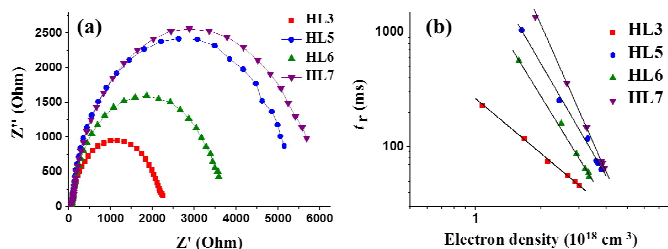

Fig. 4 (a) ESI (Nyquist plots) of DSSCs measured in the dark under -0.55 V bias. (b) Electron lifetime against the electron density of DSSCs based on IMVS studies.

Charge extraction technique was used to estimate E_c, and the correlation between V_{oc} and charge density (Q) is shown in Fig. S4. At fixed Q, the V_{oc} value of **HL6**, **HL7** and **HL5** exhibits a downward shift relative to **HL3** by 12, 26 and 30 mV, respectively. Apparently, efficient dark current suppression (vide supra) well compensates for the V_{oc} drop due to the lower E_c of TiO$_2$. It is known that the protons released from the carboxylic acid upon dye adsorption can induce a downward shift of the conduction-band edge for both Ru dyes[14] and metal-free dyes.[15] Consequently, more protons released for the di-anchor dye than the mono-anchor dye upon dye adsorption tend to lower the conduction band edge (E_c) of TiO$_2$ and are detrimental to the V_{oc} value.[7a] Conversion of the carboxylic acid anchor to carboxylate was attempted to further boost the V_{oc} value and the cell efficiency. We were not able to isolate the deprotonated species, as reported for a carboxylic acid[16a] or a hydroxyl anchor.[16b] In order to remove the proton adsorbed on the TiO$_2$ surface, the **HL5**-adsorbed TiO$_2$ photoanode was therefore dipped briefly (30−35 sec.) in solution containing a mixture of acetonitrile and Et$_3$N before assembling the DSSCs. Compared with **HL5** without Et$_3$N treatment, the E_c of the TiO$_2$ after Et$_3$N treatment exhibited slight upward shift (Fig. S5a). Besides, Et$_3$N treatment was found to increase the charge recombination resistance (Fig. S5b) and reduce the dark current, possibly the ammonium cation formed helped with blocking the exposed TiO$_2$ surface from exposing to the electrolytes. Accordingly, the efficiency of the cell was improved from 7.72 to 8.07% due to slight increment of the V_{oc} value (from 0.725 to 0.75 V). We also evaluated the relative stability towards dye-leaching between the dye with two anchors (**HL7**) and the dye with only one anchor (**HL1**),[7a] using the method reported by Calmante.[17] Photoanodes adsorbed with **HL1**[7] and **HL7** were dipped in different vessels containing the KOH solution, and the solution was monitored with UV-vis absorption spectra, as shown in Fig. S6. The rate of dye desorption is higher for **HL1**, suggesting that dye with two anchors is more robust towards leaching. We also replaced both thiophene rings in **HL5** with 4,4-diethyl-4*H*-cyclopenta[2,1-b;3,4-b']dithiophene entities, and the dye obtained had impressively high molar extinction coefficient of 81370 M^{-1}cm^{-1} at 539 nm. There was significant dye aggregation and the cell efficiency only reached 7.18% after addition of CDCA co-adsorbent. Further improvement of cell performance needs more subtle structural modification of the dye and will be the subject of future study.

Density functional (DFT) as well as time-dependent DFT calculations at B3LYP/6-31G* level using Q-Chem4.0 software were carried out on the dyes, and the results for the time-dependent approach are summarized in Table S1. The ground-state intramolecular dihedral angles (Fig. S7) between the phenothiazine and the neighbouring thiophene or thiazole-containing segments range from 0.1 to 22.7°, which allows efficient charge transfer from phenothiazine to the acceptor. Frontier orbitals of the dyes are shown in Fig. S8. The HOMO in these compounds is mainly distributed from phenothiazine to the conjugated spacer, while the LUMO and LUMO+1 are largely distributed from 2-cyano acrylic acid to the spacer. The lowest energy transition (S0 → S1) is ~100% of HOMO → LUMO transition for all compounds, while the S0 → S2 transitions mainly stem from HOMO → LUMO+1 transition. The charge transfer character in these two transitions is evident, and both transitions are believed to contribute to the ICT band in the absorption spectra (Fig. 2). The S0 → S3 transition for **HL3** is mainly stemmed from HOMO-1 → LUMO, while that for the other three dyes mainly comes from HOMO-2 → LUMO transition. Obviously the transition exhibits more π−π* character. The LUMO in all the dyes has contribution from the two anchors, indicating that both anchors can be used for electron injection pathway.

Conclusions

We have synthesized new phenothiazine-based organic dyes containing a 2,6-bis(alkoxy)phen-1-yl substituent at the nitrogen atom of the phenothiazine and two 2-cyanoacrylic acids as the acceptors as well as anchors. In addition to inheriting good characteristics of double anchors, these new dyes have several additional advantages compared with the congeners containing a 2-ethylhexyl substituent at the nitrogen atom of the phenothiazine: red shift of the absorption spectra, better suppression of dye aggregation and dark current. Consequently, better performance was found in DSSCs of the new dyes. The cell efficiencies of the new dyes outperform that of N719-based standard cell by 6−13%.

Notes and references

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