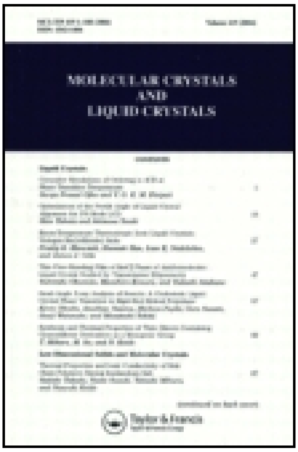

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Synthesis and Photovoltaic Properties of Organic Photosensitizers Based on Phenothiazine Chromophore for Application of Dye-Sensitized Solar Cells

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We developed organic dye containing the multi-chromophororic system in a molecule by connecting two individual chromophores with alkyl chain directly forusein DSSCs. Each of chromophore contains phenothiazine moiety as an electron donor and various electron acceptor/anchor to identify the effects of the number of electron acceptor and the kind of electron acceptor on the performance of DSSCs. The molecular structure having multi-chromophoric system containing cyanoacrylic acid moieties provided about 10% higher J_{sc} value than their counter parts of single-chromophore type.

Keywords Dye-sensitized solar cells; multi-chromophoric system; organic photosensitizers; phenothiazinechromophore; photovoltaic performances

Introduction

The improvement of solar energy-to-electricity conversion efficiency has continued to be an important research area of solar cell. Among them, dye-sensitized solar cells (DSSCs) have attracted much attention of many research groups because of their benefits, for instance, of low-cost fabrication with decently high efficiencies compared to conventional p-n junction solar cells [1,2].

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A typical DSSC is constructed with the photosensitizer absorbed wide band gap oxide semiconductor electrode such as TiO_2, electrolyte containing I^-/I_3^- redox couples, and Pt as a counter electrode. The photosensitizer initiates the overall operation of DSSC with electrons excited by the absorption of photons. The Ru-dyes coded N3 and N719 have been used as photosensitizers to achieve high photo conversion efficiencies up to 11% under AM 1.5 irradiation [3,4]. Although the power conversion efficiencies achieved with the metal-free organic dyes used in DSSCs are considerably lower than those achieved with Ru-based dyes, they are suitable for use as photosensitizers, because metal-free organic dyes are environment-friendly and have high molar extinction coefficients, customization of their molecular design, and appropriate tuning of their molecular energy levels is possible [5]. Several efficient organic dyes based on phenothiazine/phenoxazine [6] and thiophene [7] have been reported which suggested that smartly designed metal-free organic dyes was highly competitive candidates for use as photo sensitizers in DSSCs.

We had reported that organic dyes of double-electron acceptor type as photosensitizers for DSSC turned out more efficient compared to those of single-electron acceptor type due to the increase of their electron extraction paths from electron donor and the higher molar extinction coefficients [6(a)]. In this work, we have studied on the synthesis and characterization of the organic dyes containing different number of chromophoresin which two chromophores were connected with an alkyl bridge. The photo voltaic properties of the solar cells composed of organic dyes containing multi-chromophoresin a molecule were measured with I-V curves, incident photon-to-current (IPCE) efficiencies, and impedance analysis and evaluated by comparison with that of ruthenium dye (N3).

Experimental

Materials and Synthesis. All commercially available starting materials and solvents were purchased from Aldrich, TCI, and ACROS Co. and used without further purification unless otherwise stated. The synthetic procedures were followed in the literature method [8]. Structural analysis was conducted with ^1H NMR spectra were recorded on Bruker Advance NMR 300 Hz spectrometer using DMSO-d_6. The redox properties of three dyes were examined using cyclic voltammetry (Model: CV-BAS-Epsilon).

10-Hexyl-phenothiazine (1). ^1H NMR (300 MHz, $CDCl_3$): δ 7.20 (d, J = 7.5 Hz, 2H), 7.15 (t, J = 7.5 Hz, 2H), 7.0 (d, J = 8.1 Hz, 2H), 6.93 (t, J = 7.3 Hz, 2H), 3.85 (t, J = 6.9 Hz, 2H), 1.71–0.79 (m, 11H).

3,7-Dibromo-10-hexyl-phenothiazine (2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.36 (m, J = 6.6 Hz, 4H), 6.96 (d, J = 9 Hz, 2H), 3.82 (t, J = 6.9 Hz, 2H), 1.63–0.82 (m, 11H).

10-Hexyl-3,7-di(thiophen-2-yl)-phenothiazine(3). ^1H NMR (300 MHz, DMSO): δ 7.48 (d, 2H), 7.43 (m, 4H), 7.114 (d, J = 5.1 Hz, 2H), 7.10 (t, J = 4.3 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 3.89 (t, J = 6.9 Hz, 2H), 1.72–0.83 (m, 11H).

5,5′-(10-Hexyl-phenothiazine)dithiophene-2-carbaldehyde (4). ^1H NMR (300 MHz, DMSO): δ 9.88 (s, 2H), 8.01 (d, J = 3.9 Hz, 2H), 7.70 (d, J = 3.9 Hz, 2H), 7.63 (m, 4H), 7.12 (d, J = 8.7 Hz, 2H), 3.89 (t, J = 6.9 Hz, 2H), 1.72–0.83 (m, 11H).

(DYE 1) (5). ^{1}H NMR (300 MHz, DMSO): δ 8.12 (s, 2H), 7.74 (d, J = 3.9 Hz, 2H), 7.59 (d, J = 3.9 Hz, 2H), 7.54 (m, 4H), 7.10 (d, J = 8.1 Hz, 2H), 3.93 (t, J = 6.9 Hz, 2H), 1.71–0.81 (m, 11H).

(DYE 2) (6). ^{1}H NMR (300 MHz, DMSO): δ 8.10 (s, 2H), 7.76 (d, J = 4.2 Hz, 2H), 7.60 (d, J = 3.9 Hz, 2H), 7.59 (m, 4H), 7.06 (d, J = 8.4 Hz, 2H), 4.64 (s, 4H), 3.94 (t, J = 7.1 Hz, 2H), 1.70–0.84 (m, 11H).

(DYE 3) (7). ^{1}H NMR (300 MHz, DMSO): δ 8.91 (s, 2H), 8.20 (d, J = 3.9, 2H), 7.96 (d, J = 7.8 Hz, 4H), 7.79 (d, J = 4.2 Hz, 2H), 7.69 (m, 4H), 7.50 (t, J = 8.1 Hz, 4H), 7.26 (t, J = 6.9 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 4.01 (t, J = 8.3 Hz, 2H), 1.74–0.85 (m, 11H).

1,6-Bis(phenothiazine)hexane (8). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (d, J = 7.5 Hz, 4H), 7.13 (t, J = 7.5 Hz, 4H), 6.95 (d, J = 8.1 Hz, 4H), 6.90 (t, J = 7.3 Hz,4H), 3.81 (t, J = 6.9 Hz,4H), 1.63–1.17 (m, 8H).

1,6-Bis(3,7-dibromo-phenothiazine)hexane (9). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, J = 6.6 Hz, 4H), 6.90 (d, J = 8.4 Hz, 4H), 3.77 (t, J = 6.9 Hz, 4H), 1.59–1.11 (m, 8H).

1,6-Bis(3,7-di(thiophene)-phenothiazine)hexane (10). ^{1}H NMR (300 MHz, DMSO): δ 7.48 (d, 4H), 7.46 (m, 8H), 7.39 (d, J = 5.1 Hz, 4H), 7.10 (t, J = 4.3 Hz, 4H), 7.01 (d, J = 8.4 Hz, 4H), 3.87 (t, J = 6.9 Hz, 4H), 1.7–1.45 (m, 8H).

1,6-Bis(phenothiazino-3,7-dithiophene-2-carbaldehyde) (11). ^{1}H NMR (300 MHz, DMSO): δ 9.86 (s, 4H), 7.97 (d, J = 3.9 Hz, 4H), 7.63 (d, J = 3.6 Hz, 4H), 7.55 (m, 8H), 7.06 (d, J = 8.1 Hz, 4H), 3.90 (t, J = 6.9 Hz, 4H), 1.69–1.45 (m, 8H).

(DYE 4) (12). ^{1}H NMR (300 MHz, DMSO): δ 8.13 (s, 4H), 7.74 (d, J = 3.9 Hz, 4H), 7.56 (d, J = 3.9 Hz, 4H), 7.48 (m, 8H), 7.07 (d, J = 8.1 Hz, 4H), 3.90 (t, J = 6.9 Hz, 4H), 1.70–1.46 (m, 8H).

(DYE 5) (13). ^{1}H NMR (300 MHz, DMSO): δ 7.98 (s, 4H), 7.69 (d, J = 4.2 Hz, 4H), 7.57 (d, J = 3.9 Hz, 4H), 7.48 (m, 8H), 7.05 (d, J = 8.4 Hz, 4H), 4.60 (s, 8H), 4.11 (t, J = 7.1 Hz, 4H), 1.75–7.50 (m, 8H).

(DYE 6) (14). ^{1}H NMR (300 MHz, DMSO): δ 8.78 (s, 4H), 8.04 (d, J = 3.9, 4H), 7.92 (d, J = 7.8 Hz, 8H), 7.69 (d, J = 4.2 Hz, 4H), 7.60 (m, 8H), 7.44 (t, J = 8.1 Hz, 8H), 7.22 (t, J = 6.9 Hz, 4H), 7.11 (d, J = 8.7 Hz, 4H), 3.94 (t, J = 8.3 Hz, Hz, 4H), 1.73–1.51 (m, 8H).

Assembly of DSSCs. The TiO_2 paste was coated on the pre-cleaned FTO (TEC8, Pilkington, 8 Ω/□, Thickness of 2.3 mm) coated glass substrate using doctor-blade, and sintered at 500°C for 30 min. The other TiO_2 paste was re-coated over the sintered layer using ca. 250 nm size of TiO_2 particle as scattering layer, and then sintered again at 500°C for 30 min. The prepared TiO_2 film was dipped in 0.04 M of $TiCl_4$ aqueous solution at 70°C for 30 min. For dye adsorption, the annealed TiO_2 electrodes were immersed in dye solution (0.5 mM of dye in DMF; TPA series, N3/N719) at 50°C for 3 hours. The dye-adsorbed TiO_2 electrode and Pt counter electrode were assembled using 60 μm-thick Surlyn

(Dupont 1702) as a bonding agent. A liquid electrolyte was introduced through a pre-punctured hole on the counter electrode.

Results and Discussion

Synthesis and Electo-optical Properties of Organic Dyes

Hitherto, it was known that the multi-anchors/acceptors with cyanoacrylic acid moieties inorganic dyes exhibit a strong electron-withdrawing capability and abundant electronic coupling at the interface of the TiO_2 particles, leading to efficient electron injection from the LUMO level of the dye to the conduction band of the TiO_2[6(c)]. In the further pursuit of these objectives, we synthesized organic dyes containing different number of chromophores in a molecule as shown in Figure 1. In the case of **DYE 4~DYE 6**, two chromophores were connected with an alkyl bridge so that the organic dye contains four anchors/acceptors in a molecule. Organic dyes with a single electron acceptor with thiophene bridge in a molecule were also synthesized for comparison purposes in **DYE 1~DYE 3**.

The absorption spectra of the dyes were recorded in the DMSO solution and on the TiO_2 film state (B) are shown in Figure 1. In the solution state, λ_{max} of multi-chromophores were well corresponded to single-chromophoric dyes, respectively. The dye absorption band on the TiO_2 film can be shifted due to dye aggregation through molecular π-π stacking [9] It is noteworthy that the absorption spectra of **DYE 3** and **DYE 6** on the TiO_2 film state show significant red-shift ($\Delta\lambda_{max} = 50\,nm$) to compare with those in their solution state, due to the J-type aggregation on the TiO_2 surface. Furthermore, in the case of **DYE 2** and **DYE 5**, the absorption showed blue-shift in 10 nm and 65 nm on TiO_2 surface compare with those of solution state, due to the H-type aggregation, respectively. It is interesting that the same chromophore produces same spectral shift on the TiO_2 surface, thus they may have similar aggregation property on their solid state. The aggregation

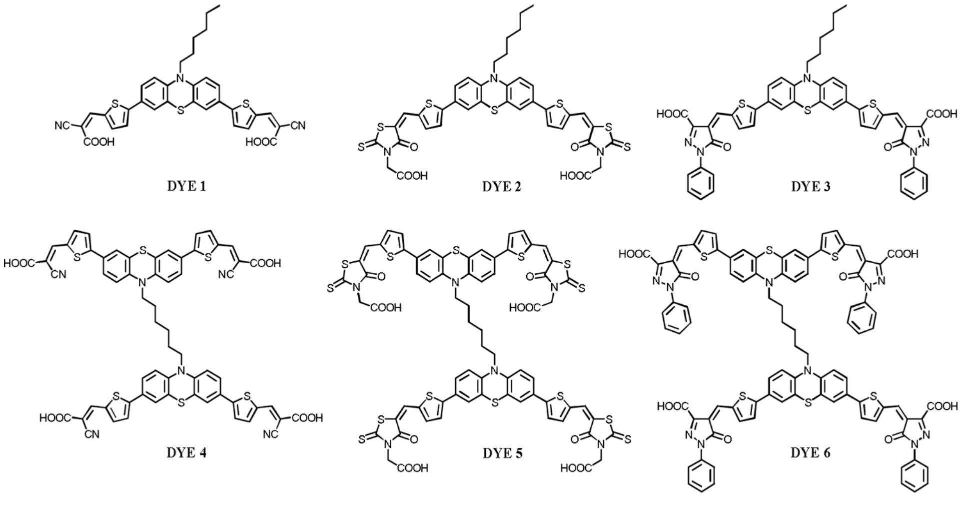

Figure 1. Chemical structures of organic dyes.

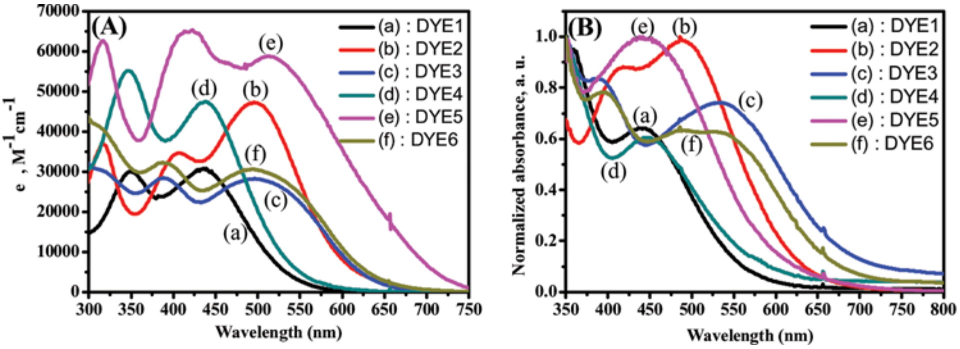

Figure 2. (A) Absorption spectra of the organic dyes in the DMF solution (B) Normalized absorption spectra of the organic dyes that were adsorbed onto the TiO_2 films.

properties of multi-chromophoric system of organic dyes are now in progress in details.

Photovoltaic Performances of the DSSCs with Organic Dyes

The photovoltaic properties of DSSCs prepared frommulti-chromophoresare shown in Figure 3 and summarized for comparison in Table 1. The dye, **DYE 4** containing cyanoacrylic acidas the multi-chromophoric dye showed better photo voltaic performance to compare with that of single-chromophoric dye in J_{sc} value as shown in Table 1 which results were well consistent with the incident photon-to-current efficiency (IPCE) spectra of the DSSCs as shown in Figure 3(B). However, the electron injection efficiency of **DYE 2** (**DYE 5**) and **DYE 3** (**DYE 6**) may be very loweven though they have longer wavelength absorption properties than that of **DYE 1** as shown in IPCE results (Fig. 3(b)). Furthermore, in case of **DYE 5** and **DYE 6**, they

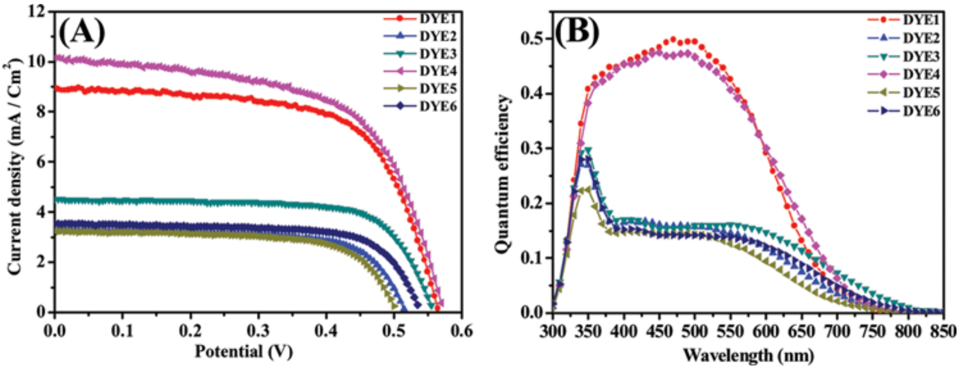

Figure 3. (A) Current density-voltage characteristics for DSSCs containing organic dyes under illumination of simulated solar light (AM 1.5, 100 mW/cm^2). (B) IPCE curves for DSSCs based on organic dyes. *Sample condition : Blocking layer, TiO_2 paste : B32, Organic Dye 0.5 mM – PMII(0.7 M) + LiI (0.2 M) + I_2 (0.05 M) + TBP (0.5 M) in ACN/VN 85:15 – Pt electrode solution (7 mM), 60 µm surlyn, Dr. blade (2 T).

Table 1. Photo voltaic Performance of DSSCs and Performances of the mercurochrome and N_3/Organic dye DSSCs and the electron transport properties in their photoanodes determined by impedance analysis. The cell areas are 0.24 cm^2. (Scattering layer; 250 nm, 4 µm + $TiCl_4$)

dyes	J_{sc}/mAcm^{-2}	V_{oc}/V	FF	η/%	R1 (Ω)^a	R2 (Ω)^b	C1	R3 (Ω)^c	C2	τ^d (ms)
N_3	14.6	0.67	0.60	5.9	15.53	4.07	1.15	17.5	0.00135	15.9
DYE 1	8.8	0.57	0.65	3.2	15.67	6.50	6.99	16.5	5.871	1.1
DYE 2	3.2	0.51	0.70	1.2	15.15	6.99	1.17	47.6	2.713	1.6
DYE 3	4.5	0.56	0.71	1.8	16.31	7.48	1.64	32.1	6.261	1.4
DYE 4	9.8	0.57	0.61	3.4	14.86	6.88	7.54	14.6	7.460	1.2
DYE 5	3.1	0.51	0.68	1.1	15.89	6.55	1.19	48.7	2.371	1.5
DYE 6	3.4	0.54	0.71	1.3	14.97	7.83	9.59	40.8	3.789	1.4

[a] R1 is FTO Interface resistance.

[b] R2 is due to the resistance at the interface between the counter electrode and the electrolyte.

[c] R3 is possibly originated from the backward charge transfer from TiO_2 to the electrolyte and the electron conduction in porous TiO_2 film.

[d] τ is life time of an electron in DSSC.

showed strong aggregation properties on the TiO_2 surface which also may diminish the Jsc value in DSSC.

It is generally known the multi-electron anchoring system such as **DYE 4~DYE 6** shows relatively low open circuit voltage (V_{oc}) to compare with that of mono-anchoring system in the DSSC. Nazeeruddin *et al.* [10] had reported that, for photosensitizers containing multi-protonated carboxylic groups, the anchoring groups created a more positive charge on the TiO_2 surface, leading to the increased recombination rate and lower V_{oc} value because the recombination reaction lowers the Fermi level of TiO_2 and decreases the gap between the redox couple of iodine/tri-iodide and the Fermi level. The electron recombination dynamic experiment for the multi-chromophoric dye system was conducted with the impedance analysis as

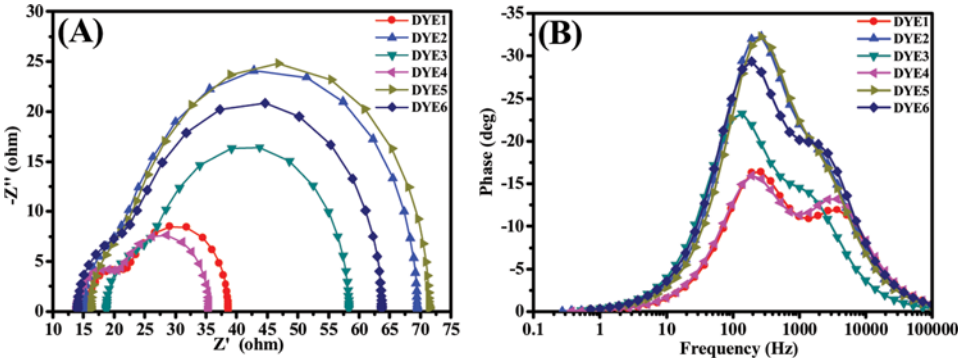

Figure 4. (A) Measured impedance spectrum of DSSC at forward bias applied condition under dark. Fitted curve calculated using circuit shown in the inset. (B) Displays of Bode-phase for DSSC cell.

shown in Figure 4 and summarized in Table 1. The Bode-phase spectrafor DSSCs are also shown in Figure 4(B) to calculate the electron life time in DSSC.

The multi-chromophoric dyes, **DYE 4**~**DYE 6** shows almost same R3 and electron life time values in DSSC to compare with those of single-chromophoric dyes, **DYE 1**~**DYE 3**, respectively which means the recombination kinetics of multi-electron acceptors system are similar with those of mono-chromophoricsystem.

On the other hand, the π-conjugatedorganic dyes tend to π-stack due to thestrong intermolecular interactions between π-electrons. In the case of **DYE 5** and **DYE 6**, it was observed that organic dyes aggregate strongly on the TiO_2 surface as shown in Figure 2 which could diminish the photovoltaic properties in DSSC.

Conclusions

We developed new multi-chromophoric dye system by connecting two chromophores with alkyl chain covalently for use in DSSCs. The solar energy-to-electricity conversion efficiency of 3.4% was achieved in a DSSC containing cyanoacrylic acid as the multi-chromophoric dye which enhanced the J_{sc} value in 10% from that of the mono-electron acceptor system. The dye aggregation of multi-chromophoric system affect photo voltaic properties in DSSC significantly which should be controlled to improve the overall efficiencies of DSSCs.

Acknowledgment

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