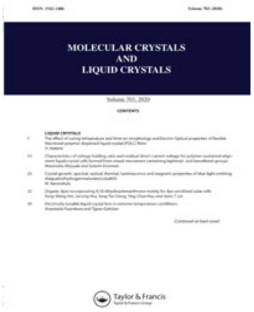

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Organic dyes incorporating 9,10-dihydrophenanthrene moiety for dye-sensitized solar cells

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ABSTRACT
A series of new dipolar organic dyes containing 9,10-dihydrophenanthrene has been synthesized as sensitizers for the application in dye-sensitized solar cells. These new materials containing less rigid π–linker as sensitizers exhibit good performance with conversion efficiencies ranging from 1.58% to 6.21% reaching 11∼83% of the ruthenium dye N719-based cell under the same condition.

KEYWORDS
D-π-A; 9,10-dihydrophenanthrene; dye-sensitized solar cells; organic photosensitizers

Introduction

Dye-sensitized solar cells (DSSCs) have attracted intensive attention due to their relatively high power conversion efficiency and low-cost converting of solar energy to clean electricity [1]. The photosensitizers clearly play a crucial role in DSSCs. Photosensitizers can be categorized into three classes: ruthenium (Ru)-based organometallic dyes, zinc-porphyrins sensitizers and metal-free organic sensitizers composed of donor–π–bridge acceptors (D–π–A). To date, the best cell efficiencies of the ruthenium complexes, Zn-porphyrins and metal-free organic dyes have achieved 11.8% [2], 13.0% [3] and 13.0% [4], respectively. However, the high cost and limited availability of ruthenium resources as well as the complex synthetic procedures and purification difficulty for zinc-porphyrin dyes restrict their further practical application in DSSCs.

Recently, metal-free organic sensitizers have been intensively investigated owing to their low cost, high molar extinction coefficients and good flexibility of molecular design [5–7]. Generally, metal-free organic dyes are adopted as a representative donor-π-bridge-acceptor (D-π-A) architecture, which promotes an efficient photoinduced intramolecular charge transfer (ICT) properties [8–10].

We have been interested in the development of new dipolar organic dyes featuring donor-to-accepter configuration bridged by different rigid spacers for solar cell applications [11]. Incorporating a rigid spacer into D-π-A structure, such as fluorene, facilitated effective intramolecular charge separation and led to high conversion efficiencies. On the contrary, a more rigid spacer is expected to favor electron recombination after electron injection from the dye to the conduction band of TiO_2. We therefore decided

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to develop sensitizers incorporating a less rigid congener of fluorene, 9,10-dihydrophenanthrene in the spacer. Herein, we report a new series of dyes with a 9,10-dihydrophenanthrene entity in the conjugated spacer. DSSCs using these dyes as the sensitizers will be also discussed.

Experimental

Unless otherwise specified, all the reactions were performed under nitrogen atmosphere using standard Schlenk techniques. All solvents and chemicals were commercially available and used without further purification (unless specially mentioned), and all reactions dealing with air- or moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. Structural analysis was conducted with ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300-MHz or 400-MHz spectrometer. Absorption spectra were recorded on a Cary 50 probe UV-Vis spectrophotometer. Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Cyclic voltammetric (CV) was used to investigate the electrochemical characteristics of these dyes (Model: CHI-621B).

DP-1: ^{1}H NMR (400 MHz, THF-d$_8$): δ 8.36 (s, 1H), 7.85 (d, $J = 4.0$ Hz, 1H), 7.81 (d, $J = 4.0$ Hz, 1H), 7.73 – 7.65 (m, 2H), 7.61 (s, 1H), 7.58 (d, $J = 9.3$ Hz, 1H), 7.27 – 7.23 (m, 4H), 7.11 – 7.09 (m, 4H), 7.03 – 6.95 (m, 4H), 2.79 – 2.76 (m, 2H), 2.52 – 2.48 (m, 2H). ^{13}C NMR (THF-d$_8$): δ 154.61, 148.81, 148.71, 146.65, 140.19, 139.70, 138.61, 136.72, 132.12, 130.14, 129.13, 126.68, 125.85, 125.76, 125.47, 124.97, 124.72, 123.95, 123.54, 122.96, 68.72, 67.23, 67.01, 30.68, 29.85, 29.74, 25.36, 25.16, 24.96. MS (FAB): m/z 524.16 (calcd [M]+).

DP-2: ^{1}H NMR (400 MHz, acetone-d$_6$): δ 8.03 (s, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.79 – 7.72 (m, 5H), 7.35 – 7.31 (m, 4H), 7.13 – 7.07 (m, 6H), 6.97 – 6.94 (m, 2H), 4.84 (s, 2H), 2.94 – 2.92 (m, 2H), 2.82 – 2.80 (m, 2H). ^{13}C NMR (THF-d$_8$): 193.0, 167.4, 167.2, 153.6, 148.7, 139.6, 138.6, 137.7, 137.3, 136.4, 132.2, 130.4, 130.1, 129.9, 129.1, 126.5, 126.3, 125.7, 125.6, 125.5, 124.7, 123.9, 123.6, 122.9, 120.7, 45.4, 29.9, 29.8. MS (FAB): m/z 630.11 (calcd [M]+).

DP-3: ^{1}H NMR (400 MHz, THF-d$_8$): δ 8.34 (s, 1H), 7.82 – 7.80 (m, 1H), 7.76 – 7.74 (m, 1H), 7.72 – 7.68 (m, 2H), 7.30 – 7.23 (m, 4H), 7.09 (d, $J = 8.0$ Hz, 4H), 7.02 – 6.94 (m, 4H), 4.46 – 4.43 (m, 4H), 2.89 – 2.77 (m, 2H), 2.75 – 2.51 (m, 2H). ^{13}C NMR (THF-d$_8$): δ 164.35, 148.73, 141.08, 139.73, 139.24, 138.15, 135.99, 131.03, 130.13, 129.30, 127.06, 126.55, 125.72, 125.45, 124.29, 123.90, 123.60, 123.01, 110.70, 95.67, 29.83. MS (FAB): m/z 582.16 (calcd [M]+).

DP-4: ^{1}H NMR (400 MHz, acetone-d$_6$): δ 8.43 (s, 1H), 7.97 (d, $J = 4.1$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.77 – 7.72 (m, 7H), 7.40 – 7.38 (m, 2H), 7.35 (dd, $J = 7.3$, 1.3 Hz, 1H), 7.31 (dd, $J = 3.9$, 1.5 Hz, 2H), 7.29 (dd, $J = 6.0$, 1.2 Hz, 1H), 7.25 (d, $J = 1.2$ Hz, 2H), 7.16 (dd, $J = 8.1$, 2.1 Hz, 2H), 7.08 (dd, $J = 2.1$, 8.4 Hz, 1H), 7.05 (d, $J = 2.1$ Hz, 1H), 2.95 – 2.80 (m, 4H), 2.02 – 1.82 (m, 8H), 0.34 (t, $J = 7.3$ Hz, 12H). ^{13}C NMR (THF-d$_8$): δ 164.13, 154.67, 152.08, 150.49, 149.13, 148.14, 146.67, 142.45, 140.22, 139.61, 138.54, 138.12, 136.77, 135.96, 132.06, 128.92, 127.82, 127.30, 126.70, 125.86, 125.72, 124.95, 124.69, 124.51, 123.53, 123.42, 122.68, 121.33,

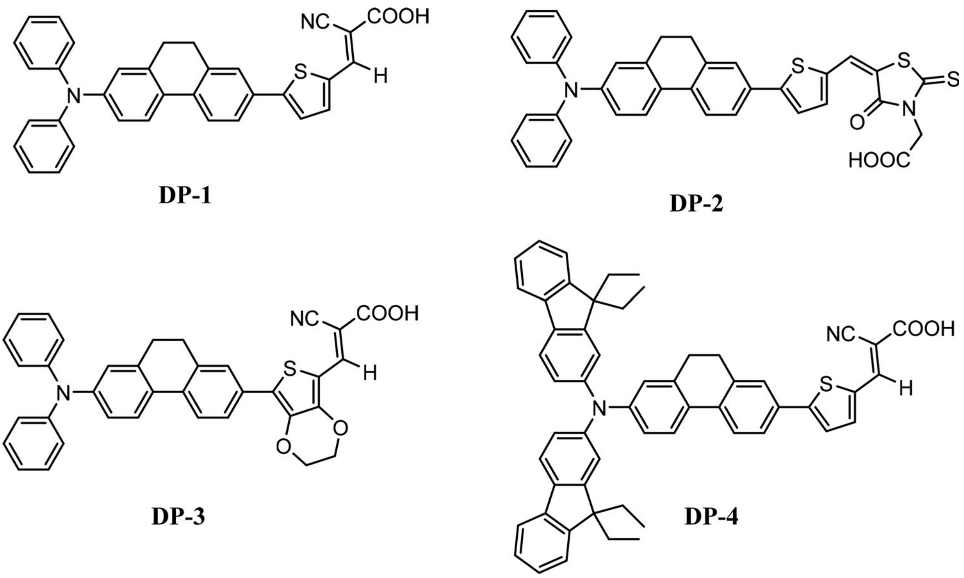


Figure 1. Structure of the dyes.

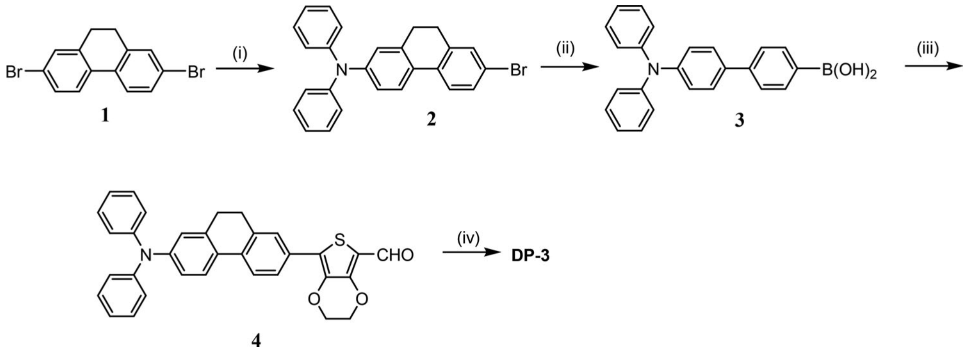
120.16, 119.99, 116.70, 99.70, 68.58, 56.99, 33.49, 29.95, 29.76, 9.00. MS (FAB): m/z 812.34 (calcd [M]+).

Assembly of DSSCs

The photoanode used was the TiO_2 thin film (15 μm of 20 nm particles as the absorbing layer and 6 μm of 400 nm particles as the scattering layer) coated on fluorine-doped tin oxide (FTO, 15Ω/square) glass substrate [12] with a dimension of $0.5 \times 0.5\,cm^2$. A platinized FTO produced by thermopyrolysis of H_2PtCl_6 was used as the counter electrode. The TiO_2 thin film was dipped into the THF solution containing 3×10^{-4} M of dye sensitizers for at least 12 h. After rinsing with CH_3CN, the photoanode adhered with a polyester tape of 30 μm in thickness and with a square aperture of $0.36\,cm^2$ was placed on the top of the counter electrode and the two were tightly clipped them together to form a cell. Electrolyte was then injected into the void space of the cell, which was then sealed with the Torr Seal® cement (Varian, MA, USA). The electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I_2), and 0.5 M 4-*tert*-butylpyridine dissolved in acetonitrile.

Results and discussion

The structures of the new dyes are shown in Fig. 1. The new organic dyes were synthesized by similar procedures, and only the synthetic route of **DP-3** was illustrated in Scheme 1. **DP-1** was prepared according to published procedure for comparison purposes [13]. **Two** was obtained from $Pd(dba)_2$ catalyzed Buchwald-Hartwig cross-coupling reactions of **one** with the diphenylamine. The Suzuki-Miyaura cross-coupling reaction of **3** with 7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde



Scheme 1. Synthesis routes for DP-3. (i) $Pd(dba)_2$, diphenylamine, *t*-BuONa, DPPF, toluene (ii) (a) n-BuLi, (b) $B(OMe)_3$, (c) 2 N HCl (iii) 7-bromo-2,3-dihydrothieno[3,4-b][1, 4]dioxine-5-carbaldehyde, $Pd(PPh_3)_4$, 2 M Na_2CO_3 (iv) cyanoacetic acid, NH_4OAc, acetic acid.

afforded **4**. Finally, **Dp-3** was obtained by Knoevenagel condensation of **four** with cyanoacetic acid in the acetic acid in the presence of ammonium acetate.

The absorption spectra of the dyes in THF solutions are shown in Fig. 2. All of the dyes exhibited two prominent transition bands in THF, the one below 400 nm is attributed to the $\pi-\pi^*$ transition of the conjugate molecules and the other ranging from $410-450$ nm is attributed to the more delocalized $\pi-\pi^*$ transition possibly with intramolecular charge transfer character. Rhodanine-3-acetic acid derivative **DP-2** leads, as expected, to the most pronounced bathochromic shift both in the absorption because of the greater conjugation of the 4-oxo-2-thioxothiazolidine ring compared with the cyanoacetic group. In consistence with Ko's observation [14], **DP-4** with the strongest electron donor, bis-diethylfluorenylamine, has the largest λ_{abs} value compared to that of **DP-1**. When the dyes were absorbed on TiO_2 surface(Fig. 2b), the absorption spectra of these dyes are broadened and slightly blue-shifted to that of in solutions, indicating deprotonation of the carboxylic acid [15,16] or H-aggregation of the dyes on TiO_2 surface [17,18].

Photovoltaic devices

The photovoltaic performance statistics under a solar condition (AM 1.5) illumination are collected in Table 1. Fig. 3a shows the photocurrent-voltage (J-V) curves of the cells. The incident photon-to-current conversion efficiencies (IPCE) of the dyes on TiO_2 are plotted in Fig. 3b. Except for **DP-2**, the incident photon-to-current conversion efficiencies (IPCE) of the dyes exceed 65% in the 400 to 500 nm region. The importance of light-harvesting to the cell efficiency is also supported by the high conversion efficiency of DSSC based on **DP-4** in spite of the relatively shorter τ_R value. Comparison of the devices with dyes **DP-1** and **DP-2** shows that the photovoltaic performances are significantly declined upon replacing cyanoacetic acid with rhodanine-3-acetic acid, with the power conversion efficiency of the solar cell based on cyanoacetic dye **DP-1** being three times higher than that of rhodanine dye **DP-2**. It was due to lack of conjugation between the rhodanine ring and the carboxyl anchoring group for organic dyes [19].

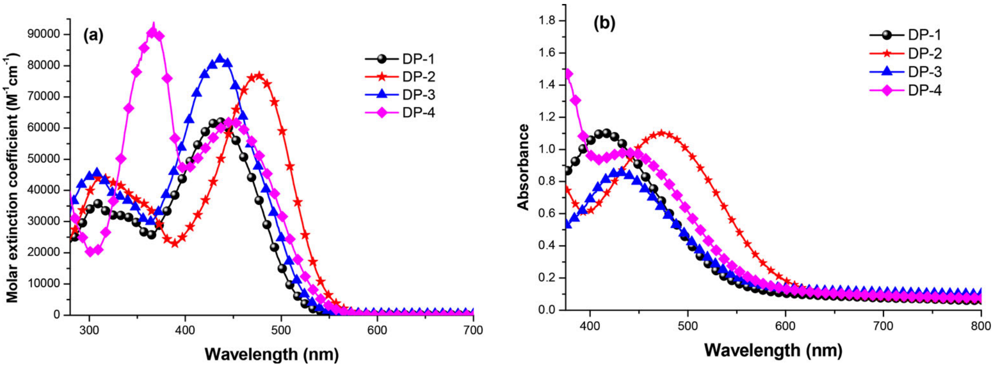


Figure 2. Absorption of the dyes (a) in the THF solution (b) absorbed on TiO_2 film.

Table 1. Performance parameters of DSSCs constructed using the dyes.

Dye	V_{OC} (V)	J_{SC} (mA/cm^2)	η (%)	FF	τ_R(ms)^a
DP-1	0.65	12.69	5.29	0.64	9.1
DP-2	0.54	4.63	1.58	0.64	7.7
DP-3	0.67	11.92	5.33	0.67	6.4
DP-4	0.68	14.24	6.21	0.65	4.1
N719	0.72	15.64	7.43	0.66	8.9

Experiments were conducted using TiO_2 photoelectrodes with approximately 18 μm thickness and 0.25 cm^2 working area on the FTO (15 Ω/sq.) substrates.

[a] τ_R is lifetime of an electron measured by transient photovoltage for DSSCs constructed using the dyes.

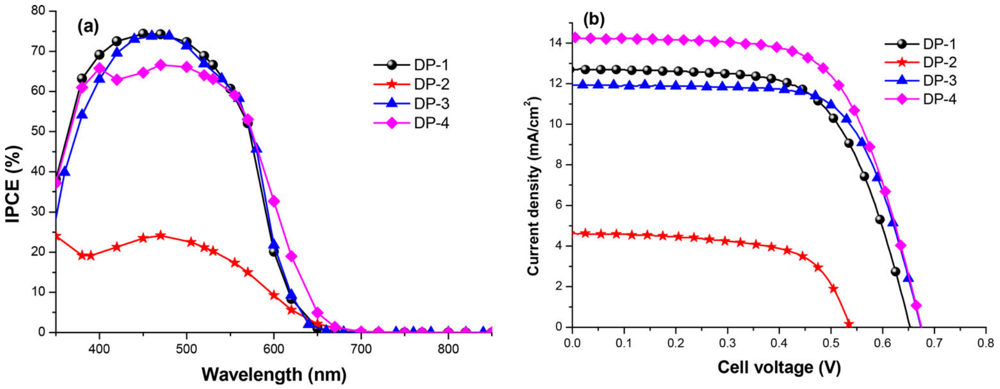


Figure 3. (a) Incident photon-to-current conversion efficiency spectra s and (b) current density – voltage curve for the DSSCs.

The electrochemical impedance spectroscopy of the DSSCs was further used to analyze the resistance of the DSSCs. Fig. 4a shows the Nyquist plots of DSSCs with different dyes under dark condition by applying a voltage of −0.50 V. The radius of the larger semicircle decreases in the order **DP-3** > **DP-4** > **DP-2** > **DP-1**, indicating increases electron recombination rate in the order of **DP-3** < **DP-4** < **DP-2** < **DP-1**. Its means that the electron recombination from the conduction band to electrolyte occurs more difficulty. The Bode phase plots are also shown in Fig. 4b. The difference in Bode phase plots occurs in the lower frequency lying in the range of $1-10^2$ Hz means a longer electron recombination lifetime if regeneration of the oxidized sensitizer is assumed

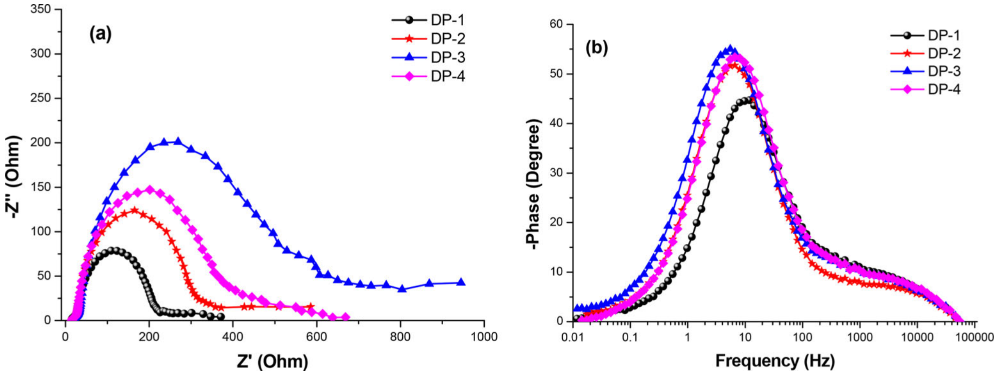


Figure 4. Electrochemical impedance spectra of DSSC for dyes measured in the dark: (a) Nyquist and (b) Bode plots.

to be fast. This results approximately are in agreement with the observed shifted in the V_{OC} values.

Conclusions

We have synthesized dipolar compounds containing arylamine unit bridged by 9,10-dihydrophenanthrene conjugated spacer. DSSCs using these sensitizers exhibited efficiencies ranging from 11–82% under one sun (AM 1.5) illumination. We have also studied that rhodanine-3-acetic acid is not a good anchoring group because of the broken conjugation between the acceptor and anchor from the intervening methylene group. The bis-diethylfluorenyl amino-containing dye **DP-4** has the best cell performance, and the conversion efficiency reaches 6.20%, which is approximately 83% of the standard cell based on N719.

Funding

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