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Review

Low-cost dyes based on methylthiophene for high-performance dye-sensitized solar cells

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1. Introduction

The search for novel dves in the context of dve-sensitized solar cells (DSSCs) has gained much impetus since the first report in 1991 by O'Regan et al. [1]. As a key part of DSSCs, dyes play a crucial role in high solar-to-electricity conversion efficiency (η) and have been studied in depth by many researchers. There are two kinds of dyes, namely, metal-complex and metal-free types. Important metalcomplex dyes are ruthenium complexes, such as N3/N719 [2,3] and others [4], including C101 [5,6] and CYC-B1 [7], which display solarto-electricity conversion efficiencies of 11.3% under AM 1.5 irradiation. In view of the limited availability and environmental issues associated with ruthenium dyes, metal-free dyes are considered to be an alternative for use in DSSCs because they have high molar absorption coefficients and can be prepared more easily and economically. Several metal-free dyes have been reported as sensitizers in DSSCs in recent years, representatives including coumarin- [8,9], indoline- [10-12], oligoene- [13,14], merocyanine-

ABSTRACT

Three donor–acceptor, π -conjugated (D– π –A) dyes containing methylthiophene or vinylene methylthiophene as π -conjugated spacer were utilised in dye-sensitized nanocrystalline TiO₂ solar cells. The relationship between the structure of the dyes and their photophysical, electrochemical and photovoltaic properties was investigated systematically. The vinyl unit, introduced as the π -conjugated spacer, leads to unfavorable back-electron transfer and decrease of the open-circuit voltage. A dye-sensitized solar cell based on 2-cyano-3-(5-(4-(diphenylamino)phenyl)-4-methylthiophenyl-2-yl) acrylic acid displayed the most efficient solar-to-electricity conversion efficiency of the dyes with a maximum η value of 8.27% ($V_{oc} = 0.72 \text{ V}, J_{sc} = 15.76 \text{ mA cm}^{-2}, \text{FF} = 0.73$) under simulated AM 1.5 G solar irradiation (100 mW cm}^{-2}). © 2010 Elsevier Ltd. All rights reserved.

> [15], hemicyanine- [16,17], phenothiazine- [18], phthalocyanine-[19,20], tetrahydroquinoline- [21], dimethylfluorene- [22], carbazole- [23], and triphenylamine-based compounds [24–27]. Most of these dyes show impressive η values in the range of 5–10.3%.

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The donor– $(\pi$ -spacer)–acceptor (D– π –A) structural system is the basis of metal-free dyes owing to its effective photoinduced intramolecular charge transfer properties. The photoelectric properties of such dyes can be finely tuned by alternating independently or matching different groups within the D $-\pi$ -A structure. In order to possess broad and intense spectral absorption in the visible light region, one strategy for optimizing dye structure is to introduce more π -conjugation segments between the donor and acceptor, thereby forming a D $-\pi$ $-\pi$ -A structure [21,28,29]. However, this may induce the recombination of the injected electrons with triiodide ions, $\pi - \pi^*$ stacking and intermolecular aggregation at the semiconductor surface [29,30], resulting in lower photovoltaic performance. Another strategy is to incorporate a bis-donor moiety into the framework, this resulting in various dyes of D–D– π –A structure having been studied [27,31–35]. Compared with D– π –A dyes, D–D– π –A compounds not only have much stronger electron-donating ability but also greater steric hindrance, which can prevent unfavorable dye aggregation [31]. However, D–D– π –A dyes do not always show better photovoltaic performances than their D– π –A counterparts [27,32] because two donor moieties

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that posses steric hindrance can twist the structure and thereby reduce coplanarity between the electron donor and electron acceptor, resulting in lower light harvesting and charge transfer ability [32]. Moreover, the synthesis of both $D-\pi-\pi-A$ and $D-D-\pi-A$ dyes is usually more complicated and expensive than that of $D-\pi-A$ dyes.

The present researchers have employed triphenylamine dyes based on π -conjugated hexylthiophene for DSSCs, and the effects of the length of the π -conjugated unit and the structure of the electron donor unit on photocurrent characteristics were studied [36,37]. In this paper, low-cost methylthiophene is used instead of hexylthiophene in the synthesis of D– π –A dyes. To evaluate the effect, on solar cell performance, of the spacers between the electron-donating moieties and π -conjugated methylthiophene, both methylthiophene and vinylene methylthiophene were used as π -conjugated spacer (Fig. 1).

2. Experimental section

2.1. Materials and reagents

All starting materials were purchased from commercial suppliers (Pacific ChemSource and Alfa Aesar) and were of analytical grade. THF and toluene were dried and distilled over sodium and benzophenone. DMF, CHCl₃, CH₃CN and POCl₃ were dried over by accustomed methods and distilled before use. All other solvents and chemicals used in this work were analytical grade and used without further purification. All chromatographic separations were carried out on silica gel (200–300 mesh).

2.2. Analytical measurements

¹H NMR and ¹³C NMR spectra were measured with Bruker Advance 400 instrument. UV–vis spectra of the dyes were measured on a Perkin–Elmer Lamada 25 spectrometer. The PL spectra were obtained using Perkin–Elmer LS-50 luminescence spectrometer. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode cell and an electrochemistry workstation (CHI830B, Chenhua Shanghai). The working electrode was a glassy carbon electrode, the auxiliary electrode was a Pt wire, and saturated calomel electrode (SCE) was used as reference electrode. Tetrabutylammonium perchlorate (TBAP) 0.1 M was used as supporting electrolyte in dry acetonitrile. Ferrocene was added to each sample solution and used as an



Fig. 1. Molecular structures of the dyes TD1, TD2, and TD3.

internal potential reference at the end of the experiments. The potentials of dyes versus NHE were calibrated by addition of 0.63 V to the potentials versus Fc^+/Fc [38].

2.3. General procedure for preparation and test of solar cells

Fluorine-doped, SnO₂ conducting glass (FTO) was cleaned and immersed in an aqueous 40 mmol L^{-1} TiCl₄ solution at 70 °C for 30 min, then washed with water and ethanol and finally sintered at 450 °C for 30 min. 20–30 nm TiO₂ colloid was prepared from 12 g P25 (Degussa AG, Germany) following the literature procedure [2] and was added to 3.6 mL 0.1% magnesium acetate solution [39]. 200 nm TiO₂ colloid comprised 4.7% 200-nm-sized TiO₂ and 9.5% ethyl cellulose in n-butanol. Firstly, 20-30 nm TiO₂ colloid was coated on the FTO glass using a sliding glass rod method to obtain a TiO₂ film of 10–15 µm thickness after drying. Subsequently, the 200 nm TiO₂ colloid was coated on the electrode using the same method, resulting in a TiO₂ light-scattering layer of 4-6 µm thickness. The double-layer TiO2-coated FTO glass was sintered at 450 °C for 30 min, treated with TiCl₄ solution and calcined at 450 °C for 30 min. After cooling to 100 °C, the TiO₂ electrodes were soaked in a mixture of 0.5 mmol L^{-1} dye and 1.0 mmol L^{-1} coadsorbent (chenodeoxycholic acid, CDCA), and kept at room temperature in the dark for 24 h; the ensuing dye-adsorbed TiO₂ electrode was washed with ethanol and dried. A drop of electrolyte solution was deposited on the surface of the electrode and a Pt foil counter electrode was clipped onto the top of the TiO₂ electrode so as to comprise a dye-sensitized solar cell for photovoltaic performance measurements. The electrolyte consisted of 0.5 mol L^{-1} LiI, 0.05 mol L^{-1} I₂, and 0.5 mol L^{-1} 4-*tert*-butylpyridine (TBP) in 3methoxypropionitrile and the irradiated area of the cell was 0.196 cm². Photocurrent–voltage curves were measured using a Keithley 2602 Source meter under 100 mW cm⁻² irradiation using a 500 W Xe lamp equipped with a global AM 1.5 filter for solar spectrum simulation; the incident light intensity was calibrated using a standard Si solar cell. The measurement of monochromatic incident photon-to-current conversion efficiencies (IPCE) was performed using a Zolix DCS300PA Data acquisition system.

2.4. Synthesis

Pinacol(4-(N,N-diphenylamino)phenyl)boronate (1), 2-bromo-3-methyl-thiophene (2) and 5-bromo-4-methylthiophene-2-carbaldehyde (3) were synthesized according to the methods reported in the literature [36,40]. The synthetic routes to the three dyes are shown in Fig. 2.

2.4.1. 5-[2-(4-Diphenylaminophenyl)]-4-methylthiophene-2carbaldehyde (**4**)

Under an argon atmosphere, 1 (0.63 g, 1.69 mmol), 3 (0.47 g, 2.29 mmol), aqueous K_2CO_3 (2 mol L^{-1} , 2 mL) and DMF (18 mL) were placed in a 100 mL three-necked flask, and the mixture was heated to 60 °C. Pd(PPh₃)₄ was added quickly and the mixture was stirred at 100 °C for 36 h. The solution was extracted with dichloromethane after it cooled to room temperature and the combined organic layer was washed with water and brine several times, dried over anhydrous MgSO₄, filtered and evaporated. The crude product was purified by column chromatography on silica gel with hexane/dichloromethane (1:1, v:v) as eluent to obtain a yellow solid. Yield: 0.34 g (54%). ¹H NMR (CDCl₃, 400 MHz, δ / ppm): 9.81 (s, 1H), 7.57 (s, 1H), 7.35–7.25 (m, 6H), 7.16–7.24 (d, 4H), 7.09–7.06 (t, 4H), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 182.5, 149.0, 148.4, 147.2, 140.2, 139.9, 134.0, 129.7, 129.5, 126.6, 125.3, 124.1, 122.2, 15.3.



Fig. 2. Synthetic routes for the three new dyes. Reaction conditions: (a) (I) THF, -78 °C, n-BuLi, 3 h; (II) 2-isopoxyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C for 3 h then to rt, 12 h. (b) NBS, THF/Acetic acid, rt. (c) DMF, POCl₃, 60–70 °C, 8 h. (d) DMF, K₂CO₃, Pd[P(Ph)₃]₄, 100 °C, 36 h. (e) CNCH₂COOH, piperidine, MeCN, 90 °C, 10 h. (f) HCl, HCHO, -5 to -10 °C, 2 h. (g) PO(OCH₂CH₃)₃, 140 °C, 6 h. (h) t-BuOK, THF, rt, 24 h. (i) n-BuLi, -40 °C, DMF.

2.4.2. 2-Cyano-3-(5-(4-(diphenylamino)phenyl)-4methylthiophenyl-2-yl) acrylic acid (**TD1**)

In a 100 mL three-necked flask, a mixture of **4** (0.29 g, 0.79 mmol), cyanoacetic acid (0.13 g, 1.56 mmol), piperidine (0.2 mL), and CH₃CN (30 mL) was refluxed for 12 h under an Ar atmosphere. After cooling to room temperature, the reaction product was poured into a mixture of distilled water and 2.0 mol L⁻¹ HCl aqueous solution and extracted with chloroform. The organic layer was washed with water and dried over anhydrous MgSO₄. After removal of solvent, the crude product was purified by column chromatography over silica gel with a dichloromethane/ methanol mixture (10:1, v:v) as eluent to obtain a dark purple solid. Yield: 0.21 g (62%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.25 (s, 1H), 7.64 (s, 1H), 7.31–7.25 (m, 8H), 7.15–7.05 (m, 6H), 2.36 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 149.9, 147.0, 144.1, 136.2, 132.7, 129.5, 129.4, 125.1, 123.8, 123.4, 122.0, 121.6, 120.0, 119.8, 29.7.

2.4.3. 2-(Chloromethyl)-3-methylthiophene (5)

Hydrochloric acid (35%, 10 mL, 113.9 mmol), formaldehyde (37%, 40 mL, 402.1 mmol) and 3-methylthiophene (7.04 g, 71.8 mmol) were placed in a 100 mL three-neck flask and kept at -5 °C to -10 °C. The stirred reaction mixture was added gaseous HCl over 2 h and the ensuing mixture was poured into 75 mL water and extracted with ether. The organic layer was washed with water and dried over anhydrous MgSO₄. After removal of solvent, 2-(chloromethyl)-3-hexyl-thiophene was obtained as yellow oil and used without further purification.

2.4.4. 2-(Methylphosphonate acid ethyl ester)-3methylthiophene (**6**)

Compound **5** (4 g, 27.4 mmol) and triethyl phosphite (4.98 g, 30 mmol) were placed in a flask and the ensuing mixture was stirred for 6 h at 140 °C. Excess triethyl phosphite was distilled under vacuum and a sticky yellow coloured oil was obtained. The crude product was purified on silica gel chromatography using a petroleum ether/ethyl acetate mixture (2:1, v:v) as eluent to obtain a yellow viscous oil. Yield: 5.7 g (84%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.04 (d, 1H), 6.79 (d, 1H), 4.15–4.01 (q, 4H), 3.33–3.25 (d, 2H), 2.19 (s, 3H), 1.36–1.24 (t, 6H).

2.4.5. 2-(4-Diphenylaminostyryl)-3-methylthiophene (9)

4-(Diphenylamino)-benzaldehyde **7** (1.54 g, 5.63 mmol) and **6** (1.44 g, 5.82 mmol) were dissolved in 15 mL of fresh dried THF and t-BuOK (0.39 g, 3.48 mmol) dissolved in 10 mL THF was added dropwise under a N₂ atmosphere. After reacting for 24 h at room temperature, the reaction mixture was poured into water and extracted twice with chloroform. The combined organic extracts were washed three times with water, dried over anhydrous MgSO₄, evaporated under vacuum, and purified with column chromatography on silica gel with petroleum ether/dichloromethane mixture (10:1, v:v) as eluent to obtain a yellow viscous oil. Yield: 1.71 g (83%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.35–7.33 (d, 2H), 7.27–7.23 (m, 4H), 7.13–7.01 (m, 10H), 6.82–6.78 (m, 2H), 2.29 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 147.6, 147.2, 136.8, 135.0, 131.6, 130.8, 129.3, 127.4, 127.1, 124.5, 123.7, 123.0, 14.0.

2.4.6. 2-[2-[p-(Di-p-tolylamino)phenyl]vinyl]-3methylthiophene (**10**)

The synthetic procedure for **10** was similar to that for **9**, except that 4-(di-p-tolylamino)benzaldehyde **8** (1.03 g, 5.15 mmol) was used instead of **7**. The crude product was purified by column chromatography over silica gel with petroleum ether/dichloromethane mixture (10:1, v:v) as eluent to obtain a yellow viscous oil. Yield: 1.32 g (81%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.32 (d, 2H), 7.11–6.98 (m, 12H), 6.82–6.78 (d, 2H). 2.32 (s, 1H), 2.30 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 147.7, 145.2, 137.0, 134.8, 132.7, 130.8, 130.7, 130.0, 127.6, 127.0, 124.8, 122.5, 122.3, 118.4, 20.9, 14.0.

2.4.7. 5-(4-(Diphenylamino)styryl)-4-methylthiophene-2carbaldehyde (**11**)

Compound **9** (1.5 g, 4.08 mmol) was dissolved in THF (35 mL) and the solution was cooled to -40 °C under a nitrogen atmosphere. n-Butyllithium (3 mL, 2.5 mol L⁻¹ in hexane solution) was added dropwise over 25 min and the mixture was stirred at -40 °C for 1 h. After cooling to room temperature DMF (1.2 mL, 15.5 mmol) was added dropwise; after 2.5 h, the ensuing solution was poured into a saturated aqueous solution of ammonium chloride and extracted with dichloromethane. The organic layer was dried over

anhydrous MgSO₄ and evaporated, then the residue was purified with column chromatography on silica gel with petroleum ether/ dichloromethane mixture (3:1, v:v) as eluent to obtain a red viscous oil. Yield: 1.13 g (72%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 9.78 (s, 1H), 7.47 (s, 1H), 7.37-7.35 (d, 2H), 7.28-7.25 (m, 4H), 7.12-6.96 (m, 10H), 2.32 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 182.4, 148.4, 147.6, 147.2, 139.8, 139.0, 135.8, 132.1, 129.9, 129.4, 127.8, 124.9, 123.5, 122.8, 117.4, 14.0,

2.4.8. 5-[p-(Di-p-tolylamino)styryl]-4-methylthiophene-2carbaldehyde (12)

The synthetic procedure for **12** was similar to that for **11**, except that 10 (0.89 g, 2.25 mmol) was used instead of 9. The crude product was purified by column chromatography over silica gel with petroleum ether/dichloromethane mixture (3:1, v:v) as eluent to obtain a red viscous oil. Yield: 0.66 g (63%). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 9.77 (s, 1H), 7.46 (s, 1H), 7.33-7.31 (d, 2H), 7.09-6.95 (m, 14H), 2.31 (s, 1H,), 2.29 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 182.3, 148.8, 147.8, 144.7, 139.7, 138.8, 135.5, 133.3, 132.3, 130.0, 129.0, 127.7, 125.1, 121.6, 116.9, 20.8, 13.9.

2.4.9. 3-(5-(4-(Diphenylamino)styryl)-4-methylthiophen-2-yl)-2cyanoacrylic acid (**TD2**)

The synthetic procedure for TD2 was similar to that for TD1, Yield 76%, a red solid. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.22 (s, 1H), 7.52 (s, 1H), 7.39-7.37 (d, 2H), 7.29-7.26 (m, 2H), 7.14-7.10 (m, 12H), 2.34 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 149.5, 147.1, 137.9, 133.2, 129.7, 129.4, 129.3, 129.3, 128.0, 125.1, 125.0, 124.5, 123.7. 123.1. 122.5. 121.5. 29.7.

2.4.10. 3-(5-(4-(Di-p-tolylamino)styryl)-4-hexylthiophen-2-yl)-2cyanoacrylic acid (TD3)

The synthetic procedure for TD3 was similar to that for TD1, Yield 78%, a dark purple solid. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.22 (s, 1H), 7.52 (s, 1H), 7.36–7.34 (d, 2H), 7.11–6.96 (m, 12H), 2.34 (s, 6H), 2.33 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 149.7, 147.1, 144.5, 136.3, 133.5, 131.1, 130.1, 129.0, 128.0, 126.9, 125.3, 121.2, 116.2, 29.7, 20.9.

3. Results and discussion

3.1. Synthesis

The molecular structures of the three dyes are shown in Fig. 1. All of these dyes have been prepared according to several classical reactions, which involve the Suzuki coupling reaction [41], Wittig-Horner reaction [37] and Knoevenagel condensation reaction [40]. The synthetic strategies are showed in Fig. 2. Suzuki coupling of triphenylamine boronic acid pinacol ester 1 and brominated methylthiophene aldehydes 3 with tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) as the catalyst in a biphasic mixture of K₂CO₃ and DMF afforded 5-[2-(4-Diphenylaminophenyl)]-4methylthiophene-2-carbaldehyde 4. Subsequently, Knoevenagel condensation reactions with cyanoacetic acid in the presence of piperidine gave the target dye TD1 in 62% yield. 2-(Chloromethyl)-3methylthiophene 5 was synthesized from 3-methylthiophene in the presence of formaldehyde and hydrochloric acid, and then reacted with triethyl phosphite to obtain intermediate 6. Wittig-Horner reaction of 6 and 4-(diphenylamino) benzaldehyde or 4-(di-p-tolylamino)benzaldehyde give the corresponding intermediates 9, 10, respectively. Then compounds 9, 10 were subjected to formylation reaction in the presence of n-BuLi and DMF, affording aldehydes 11, 12 [42]. The final Knoevenagel condensation reactions of 11, 12 with cyanoacetic acid gave the target dyes TD2 and TD3 in the



Fig. 3. Absorption and emission spectra of the dyes in $CHCl_3$ solutions (10^{-5} mol L^{-1}).

presence of piperidine. The chemical structures of all dyes were characterized with ¹H NMR and ¹³C NMR spectroscopy.

3.2. Optical properties

The UV-vis absorption spectra and fluorescence emission spectra of the dyes in diluted CHCl₃ solution $(10^{-5} \text{ mol } L^{-1})$ are shown in Fig. 3, and the corresponding data are collected in Table 1. In CHCl₃ solution, all the dyes give two distinct absorption bands: one relatively weak band is in the near-UV region (280-311 nm) corresponding to the $\pi - \pi^*$ electron transitions of the conjugated molecules, and the other is a strong absorption band in the visible region (460–540 nm) that can be attributed to an intramolecular charge transfer (ICT) between the donating units and the cyanoacrylic acid anchoring moiety [43]. It can be seen that the maximum absorption of TD2 and TD3 is obviously red-shifted in comparison with that of **TD1**, which is due to the extension of π -conjugated system by introduction of vinyl unit in the π -spacer part. On the other hand, the spectrum of TD3 is red-shifted in comparison with that of **TD2** since di(*p*-tolyl)phenylamine moiety is a stronger electrondonating unit than triphenylamine moiety. As depicted in Table 1, the molar extinction coefficients ϵ (>2.3 \times 10⁴ mol⁻¹ L cm⁻¹) of three as-synthesized dyes are higher than that of the standard N719 dye $(1.4 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1})$ [42], which indicates the dyes have a better ability of light harvesting. Fig. 3 also shows the emission spectra of the three as-synthesized dyes, we can see that the maximum emission wavelength of the dyes in CHCl₃ solution is in the order of **TD3** > **TD2** > **TD1**, which is consistent with that of the maximum absorption.

When the dyes are adsorbed on TiO₂ surface, the absorption spectra of these dyes are broadened and blue-shifted more or less as compared to that in solutions (Fig. 4), The similar phenomenon was also observed for other organic dyes [9,13]. The trend may be

Table 1	
Maximum absorption and emission data of the as-synthesized of	dyes. ^a

Dye	$\lambda_{abs}^{a}/nm (\epsilon/mol^{-1} L cm^{-1})$			$\lambda_{\max}^{\mathbf{b}}/\mathbf{nm}$	λ _{em} ^c /nm
TD1	466(22 000)	308(21 000)	-	460	625
TD2	517(23 000)	310(16 000)	279(14 000)	485	684
TD3	535(34 000)	311(18 000)	280(18 000)	504	708

 ε is the extinction coefficient at λ_{abs} of maximum absorption.

^a Maximum absorption in CHCl₃ solution (10⁻⁵ mol L⁻¹).

^b Maximum absorption on TiO₂ film.

 $^{\rm c}\,$ Maximum emission of the dyes in CHCl_3 solution (10^{-5} mol L^{-1}).



Fig. 4. Absorption spectra of the dyes on TiO₂ film.

ascribed to H-type aggregation of the dyes on the TiO₂ surface [29]. According to the data collected in Table 1, the blue-shift values of **TD1**, **TD2** and **TD3** are 6, 32, 31 nm, respectively. It can be seen that **TD2** and **TD3** have a much higher blue-shift values compared to **TD1**, which indicates that they have a stronger tendency to form aggregation state on TiO₂ surface. This stronger tendency of aggregation should be attributed to the differences of electron spacer parts of the dyes. In our early study, triphenylamine dyes with a vinyl bridge unit in the π -spacer part could present considerable coplanar character [37]. It means that the coplanar structure of **TD2** and **TD3** dyes, linked by vinyl unit between the donor moiety and the spacer part, could lead to the stronger tendency to form aggregation state on TiO₂ surface comparing with **TD1**.

3.3. Electrochemical properties

To evaluate the thermodynamic possibility of electron transfer from the excited dye molecule to the conductive band of TiO₂, cyclic voltammetry (CV) was performed. The first oxidation potential vs. NHE (E_{ox}), which corresponds to the highest occupied molecular orbital (HOMO vs. NHE), was calibrated by addition of 0.63 V to the



Fig. 5. Cyclic voltammograms of the three as-synthesized dyes: working electrode, Pt ring; auxiliary electrode, Pt wires; reference electrode, Hg/Hg_2Cl_2 ; scanning rate is 100 mV s⁻¹. The ferrocene (Fc) is the internal standard.

Table 2	
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Electrochemical data of the as-synthesized dye
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Dye	λ_{int}/nm	E_{0-0}/V	$E_{\rm ox}/V$ vs. NHE	$E_{\rm red}/V$ vs. NHE	$E_{\rm gap}/V$
TD1	553	2.24	1.19	-1.05	0.55
TD2	605	2.04	1.06	-0.98	0.48
TD3	625	1.98	1.01	-0.97	0.47

^a E_{0-0} values were calculated from intersection of the normalized absorption and the emission spectra (λ_{int}): $E_{0-0} = 1240/\lambda_{int}$. The first oxidation potential (vs. NHE), E_{0x} , was measured in acetonitrile and calibrated by addition of 0.63 V to the potential versus Fc/Fc⁺. The reduction potential, E_{red} , was calculated from $E_{ox} - E_{0-0}$. E_{gap} is the energy gap between the E_{red} of dye and the CB level of TiO₂ (-0.5 V vs. NHE).

potential (vs. SCE) versus Fc/Fc^+ by CV (Fig. 5). And the reduction potential vs. NHE (E_{red}), which corresponds to the lowest unoccupied molecular orbital (LUMO vs. NHE), can be obtained from the first oxidation potential and the E_{0-0} value determined from the intersection of absorption and emission spectra, namely, $E_{ox} - E_{0-0}$. Table 2 summarizes the electrochemical properties of the three assynthesized dyes.

To get an efficient charge separation, the LUMO of the dye has to be sufficiently more negative than the conduction-band edge of the TiO₂ (E_{cb} , -0.50 V vs. NHE), and the HOMO has to be more positive than the redox potential of iodine/iodide (0.42 V) to ensure the regeneration of dyes [44]. As shown in Fig. 5, the HOMO levels of TD1, TD2, and TD3 are 1.19, 1.06, and 1.01 V (vs. NHE), respectively. All these HOMO levels are sufficiently more positive than the iodine/iodide redox potential value, indicating that the oxidized dyes formed after electron injection to TiO₂ could accept electrons from iodide ions thermodynamically. From these values, we can find the introduction of the vinyl unit in the π -spacer part lead to the comparatively higher-lying HOMO of the dyes, which decrease the gap between the HOMO level and the redox potential of iodine/ iodide. Simultaneously, it seems that triphenylamine and di(ptolyl)phenylamine have little differences in affecting the HOMO levels of these triphenylamine dyes. On the other hand, the LUMO levels of these as-synthesized dyes range from -0.97 V to -1.05 V, which are more negative than the conduction-band edge of the TiO₂. Therefore, the three dyes can be used as effective sensitizers because the electron injection process from the excited dye molecule to the conduction band of TiO₂ is thermodynamically favorable in DSSCs.

3.4. Photovoltaic performance of DSSCs based on the dyes

The photovoltaic properties of the solar cells constructed from these organic dye-sensitized TiO₂ electrodes were measured under simulated AM 1.5 irradiation (100 mW cm⁻²). The open-circuit photovoltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factor (FF), and solar-to-electricity conversion efficiencies (η) are compared with N719 and listed in Table 3. The incident photon-tocurrent conversion efficiencies (IPCE) and current density–voltage

Photovoltaic performance of DSSCs based on the as-synthesized dyes and N719. ^a	3
	voltaic performance of DSSCs based on the as-synthesized dyes and N719. ^a

Dye	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}\left({\rm V}\right)$	FF	η (%)
TD1	15.76	0.72	0.73	8.27
TD2	16.29	0.66	0.71	7.62
TD3	16.94	0.69	0.67	7.83
N719	17.33	0.76	0.74	9.75

^a Light source: 100 mW cm⁻², AM 1.5 G simulated solar light; working area: 0.196 cm²; Titania paste was prepared from P25 (Degussa AG, Germany) and added 0.1% magnesium acetate solution; 1 mmol L⁻¹ chenodeoxycholic acid (CDCA) was added as a coadsorbent; Dye bath: CH₃CN solution (5 × 10⁻⁴ mol L⁻¹).



Fig. 6. IPCE action spectra for DSSCs based on the three **TD** dye-sensitized transparent TiO_2 films with the electrolyte: 0.5 mol L^{-1} Lil, 0.05 mol L^{-1} I₂ and 0.5 mol L^{-1} 4-tert-butylpyridine (TBP) in 3-methoxypropionitrile.

(J-V) characteristics of devices based on the three **TD** dyes are shown in Figs. 6 and 7, respectively.

As shown in Fig. 6, the DSSCs based on TD1 show higher IPCE values in the spectra range of 350-495 nm than those of TD2 and TD3, producing a maximum IPCE of $\sim 81\%$ at 443 nm. Nevertheless, the IPCE spectra for DSSCs based on TD2 and TD3 are broader toward the red region than that of TD1, which is in accordance with their absorption spectra on the TiO₂ films (Fig. 4). According to the data in Table 3, η values of 8.27%; 7.62% and 7.83% were obtained by DSSCs based on TD1, TD2 and TD3 dyes, respectively. It's clear that the J_{sc} values of TD2 and TD3 are higher than that of TD1, which is in agreement with the IPCE results (Fig. 6) of the three dyes. The TD1 shows narrower IPCE spectra and lower IPCE values in the red region compared to TD2 and TD3, hence it have a lower I_{sc} value than that of TD2 and TD3. However, the DSSCs based on TD1 show higher solar-to-electricity conversion efficiency because the $V_{\rm oc}$ and FF values of TD1 are obviously higher than those of TD2 and TD3. The lower performances of DSSCs based on TD2 and TD3 may result from the stronger aggregation of TD2 and TD3 on the TiO₂ surface due to the introduction of the vinyl unit into the π -conjugated spacers. Generally, a monolayer of dye molecules



Fig. 7. Current density–voltage (*J*–*V*) characteristics for DSSCs from the three **TD** dyes under illumination of simulated solar light (AM 1.5, 100 mW cm⁻²); The electrolyte used was the same as that Shown in Fig. 6. The dye bath used was CH₃CN.



Fig. 8. *J*–*V* curves obtained with DSSCs based on **TD1**, **TD2**, and **TD3** dyes under dark condition.

adsorbed on the TiO₂ surface is necessary for efficient electron injection from the excited dye to TiO₂. The aggregation could lead to unfavorable back-electron transfer, and decrease of the opencircuit voltage as well as fill factor of the device [45,46]. To confirm this judgment, a dark current test, a technique of testing the capability of the charge recombination, was conducted and the results are shown in Fig. 8 [47]. It is found that the onsets for TD2 and TD3 dyes are similar but evidently lower than TD1 dye. This indicates that the back-electron-transfer process corresponding to the reaction between the conduction-band electrons in the TiO_2 and $I_{\overline{3}}$ in the electrolyte under dark conditions occurs more easily in the DSSCs based on the dyes with vinyl units. The J_{sc} and $V_{\rm oc}$ values of TD3 are increased slightly in comparison with TD2, this can be ascribed to the improvement of the electron-donating ability by substitution of triphenylamine moiety for di(p-tolyl) phenylamine moiety, and this improvement ultimately makes TD3 has a better photovoltaic performance than TD2.

According to the foregoing results and analysis, it seems that the vinyl unit in electron spacer is not a suitable constructional moiety for this series of sensitizers to obtain higher η values, although the vinyl unit could increase the light harvesting capability. Under the same conditions, the η value of the DSSC based on the standard N719 dye is 9.75% ($J_{sc} = 17.33 \text{ mA cm}^{-2}$, $V_{oc} = 0.76 \text{ V}$, FF = 0.74). The result suggests that **TD1** dye is a promising alternative to the traditional metal-organic dyes used in DSSCs.

4. Conlusions

Three triphenylamine dyes based on low-cost methylthiophene as the π -conjugated spacer were designed and synthesized as the dye sensitizers for DSSCs applications. The high photovoltaic performances of the DSSCs based on these as-synthesized dyes were obtained. Though the introduction of vinyl unit in the π -conjugated spacer can obtain red-shifted absorption spectra, it does not give a positive effect on the photovoltaic performance of the DSSCs due to unfavorable back-electron transfer and decrease of the open-circuit voltage. On the basis of optimized conditions, the DSSCs based on these three as-synthesized dyes exhibited the efficiencies ranging from 7.83% to 8.27%, which reached 80–85% with respect to that of an N719-based device. The high conversion efficiency and easy availability of raw materials reveal that these metal-free organic dyes are promising in the development of DSSCs.

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