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# Molecular engineering of cyclopentadithiophene-containing organic dyes for dye-sensitized solar cell: Experimental results *vs* theoretical calculation



PIGMENTS

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#### ABSTRACT

Four donor–conjugated spacer–acceptor  $(D-\pi-A)$  organic dyes containing cyclopentadithiophene unit as a part of the conjugated spacer are prepared and studied to investigate the effects of the conjugated spacer and donor on the short-circuit current and conversion efficiency of the corresponding DSSCs. Theoretical calculations reveal that a shorter conjugated spacer or a stronger donor leads to more effective electron injection upon photo excitation. Therefore,  $D-\pi-A$  typed dye with longer conjugated spacer may have higher absorption coefficient and longer  $\lambda_{max}$ . Nevertheless, it may also have lower effective electron injection upon photo excitation. Calculation data also show that cyclopentadithiophene although is a good moiety for extending the conjugation length of the organic dyes, it also acts as an electron sink, decreasing the effective electron injection. The transition probability calculated with the electron density difference analyses combining with the experimental absorption and photovoltaic performance data provides a useful protocol for designing organic photosensitizers for DSSCs at the electronic and structural levels.

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#### 1. Introduction

Global warming and finite fossil fuels have made renewable energy to be an active research topic. The Sun, providing a huge amount of energy  $(3.78 \times 10^{24} \text{ J per year})$  [1] to the earth, is one of the best resources of the renewable energy. The most convenient way to use solar energy is convert it into electricity *via* photovoltaic devices. Dye-sensitized solar cells (DSSCs) have been regarded as one of the most promising candidates for the photovoltaic application by virtue of their low manufacturing cost and impressive conversion efficiency [2]. DSSCs based on ruthenium sensitizers currently achieve a remarkable conversion efficiency over 11% [3] and the stability was also demonstrated [4]. Recently the efficiency of DSSC based on zinc porphyrin dye and Co(II)/Co(III) electrolyte reaches more than 12% [5]. Since the sensitizer is a vital

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component of DSSC devices, molecular engineering of the sensitizers to achieve high photovoltaic performance is an extensive research topic [6–8].

In general the efficiency of DSSCs based on organic dyes is lower than that of those sensitized with ruthenium complexes. Nevertheless, organic dyes have the advantages of high molar absorption coefficient, variety of the structure, environmentally-friendly property and essentially unlimited resources. Therefore, various organic dyes for DSSCs, such as coumarin- [9], cyanine- [10], hemicyanine- [11], triarylamine- [12], thiophene- [13], oligoene- [14], porphyrin- [15], and perylene [16]-based molecules have been developed, and up to 10% efficiency has been attained [17]. The structure of the  $(D-\pi-A)$  organic dyes employed in the DSSCs typically consists of an electron donor, an anchoring acceptor, and a  $\pi$ -conjugated spacer for tuning the spectral coverage. Remarkable progress has been made, and the structure-related photovoltaic performance has also been reviewed [18]. The conjugated spacer in the sensitizers is widely recognized as an important parameter for the performance of the D $-\pi$ -A organic dye. It is valuable to be able to predict their performance before the dye molecules are prepared and their performance is explored. Therefore a great number of work

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focuses on the theoretical calculations using density functional theory (DFT) and time-dependent DFT (TD-DFT), complementing experiments, to study the structure, electronic absorption spectra, energy levels of the sensitizers both in solution [19–24] and on  $TiO_2$  clusters [25–29]. The results provide useful information to expedite the development of appropriate dyes for DSSCs.

This article reports the photovoltaic performance of a series new  $D-\pi-A$  organic dves containing cvclopentadithiophene moiety as a part of the conjugated spacer. It was known that dithiophene is generally used as a linker for high-efficiency  $D-\pi-A$  photosensitizers. Compared to dithiophene, cyclopentadithiophene (CPDT) unit has a more rigid conjugation structure, higher absorption coefficient [30] and better charge mobility [31] as well as facile structure modification. Therefore CPDT has been generally used as a monomer for the low band-gap polymer [32–35]. Furthermore, cyclopentadithiophene moiety may act as a photon absorber where the charge separation occurs, and migrates to the opposite directions by the presence of the donor and acceptor units at each side, increasing the separation of the excitons. Nevertheless, cyclopentadithiophene is not generally employed in the high-efficient organic dyes. Therefore, knowing the parameters which determine the photovoltaic performance of cyclopentadithiophenecontaining organic dyes is the focus of this article.

#### 2. Experimental

#### 2.1. Materials

All reagents were obtained from the commercial resources and used as received unless specified. Solvents were dried over sodium or CaH<sub>2</sub> before use. Unless otherwise specified, all reactions were performed under an Ar atmosphere using the standard Schlenk techniques. All chromatographic separations were carried out on the silica gel (60M, 240–400 mesh) column. The structures of dyes and their intermediates were identified with <sup>1</sup>H NMR spectra. The structure of the final products was further confirmed by IR, <sup>13</sup>C NMR spectra, FAB-MS and elemental analysis.

#### 2.2. Physicochemical studies

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker 300 MHz NMR spectrometer in CDCl<sub>3</sub> or [D<sub>6</sub>]DMSO. FAB-MS spectra were obtained using the JMS-700 HRMS. UV/Vis spectra of dyes in THF and adsorbed on TiO<sub>2</sub> (4  $\mu$ m thickness) films were measured using a Cary 300 Bio spectrometer. Photoluminescence spectra (in THF solutions, Figure S1, ESI) were obtained using a Hitachi F-4500 spectrophotometer in the laboratory atmosphere at room temperature. Cyclic voltammetric measurement was performed in a single-compartment, three-electrode cell with an ITO glass working electrode and a Pt wire counter electrode. The reference electrode was Ag/Ag<sup>+</sup> and the supporting electrolyte was 0.1 M LiClO<sub>4</sub> in THF using an Autolab system (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands), the scan rate is 50 mV  $s^{-1}$  and the ferrocene/ ferrocinium redox couple was used as an external calibration standard. Elemental analysis was carried out with a Heraeus CHN-O–S Rapid-F002 analysis system. The thickness of TiO<sub>2</sub> film was measured by a profile-meter (Dektak3, Veeco/Sloan Instruments Inc., USA).

#### 2.3. Synthesis of W-series dyes

The detailed synthesis and characterization of all intermediates and the IR spectra as well as <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figures S2– S10) of these four metal free dyes can be found in the electronic supporting information (ESI). 2.3.1. Synthesis of 3,6-di-tert-butyl-9-9H-carbazole-2-thiophen-4,4-dimethyl-2H-cyclo-penta[2,1-b;3,4-b']dithiophene-2-acrylic acid (W-1)

(W-1) was prepared by refluxing the mixture of 3,6-di-tertbutvl-9-9H-carbazole-2-thiophen-4,4-dimethyl-2H-cyclopenta [2.1-b:3.4-b']di-thiophene-2-car-boxaldehvde (1.0 g. 1.7 mmol, see ESI), NH4OAc (0.20 g, 2.6 mmol), and CNCH2COOH (0.22 g, 2.6 mmol) in CH<sub>3</sub>COOH (50 mL) for 6 h under Ar. CHCl<sub>3</sub> was used to extract the product, after recrystallization, W-1 dye was obtained as a red solid, mp = 285 °C (decomposed). IR (1679 cm<sup>-1</sup> (C=O); 2213 cm<sup>-1</sup> (C $\equiv$ N), see Figure S2, ESI). <sup>1</sup>H NMR (Figure S3 (ESI), 300 MHz,  $\delta_{\rm H}$ /ppm in DMSO-d<sub>6</sub>): 1.45 (18H, s), 1.60 (6H, s), 7.48 (1H, d, 3.8 Hz), 7.60 (5H, m), 7.73 (1H, s), 8.10 (1H, s), 8.41 (2H, s), 8.52 (1H, s). <sup>13</sup>C NMR (Figure S4 (ESI), 300 MHz,  $\delta_H$ /ppm in DMSO-d<sub>6</sub>): 24.41, 31.75, 34.56, 44.99, 109.53, 116.88, 117.28, 118.81, 123.17, 123.48, 124.14, 125.40, 132.35, 132.96, 134.17, 136.63, 137.53, 139.20, 141.85, 143.71, 146.58, 147.00, 160.63, 164.08, 165.95. MS: m/z 660 ( $[M]^{\pm}$ ); HRAB-MS found: m/z 660.3426. Elemental analysis: calcd. for C<sub>39</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>.H<sub>2</sub>O: C, 69.02; H, 5.60; N, 4.13; S, 14.16%. Found: C, 68.48; H, 5.73; N, 4.17; S, 14.10%.

## 2.3.2. Synthesis of 3,6-di-tert-butyl-9-[5-(thiophen-2-yl)thiophen-2-yl]-9H-carbazole-4,4-dimethyl-2H-cyclopenta[2,1-b;3,4-b'] dithiophene-2-acrylic acid (W-2)

The preparation procedures of W-2 dyes are the same as those for synthesizing W-1 dye except 3,6-di-tert-butyl-9-[5-(thiophen-2-yl)thiophen-2-yl]-9H-carbazole instead of 3,6-di-tert-butyl-9-(thiophen-2-yl)-9H-carbazole (2.93 g, 6.8 mmol, see ESI) was used to react with Me<sub>3</sub>SnCl (1.5 M. 3 mL). 3.6-di-tert-butyl-9-[5-(thiophen-2-yl)thiophen-2-yl]-9H-carbazole was prepared by Stille coupling between 3,6-di-tert-butyl-9-[5(trimethylstannanyl)-thiophen-2-yl]-9H-carbazole and 2-bromothiohene. W-2 dye was isolated as a dark green solid, mp = 300 °C (decomposed). IR (1679 cm<sup>-1</sup> (C=0); 2213 cm<sup>-1</sup> (C≡N), see Figure S2, ESI). <sup>1</sup>H NMR spectrum was displayed in Figure S5 (ESI). <sup>1</sup>H NMR (300 MHz,  $\delta_{\rm H}$ / ppm in DMSO-d<sub>6</sub>): 1.51 (18H, s), 1.57 (6H, s), 7.50 (8H, m), 7.71 (1H, s), 8.06 (1H, s), 8.39 (2H, s), 8.47 (1H, s). <sup>13</sup>C NMR (Figure S6, 300 MHz, δ<sub>H</sub>/ppm in DMSO-d<sub>6</sub>): 24.87, 32.21, 35.01, 45.50, 109.99, 117.27, 119.08, 119.18, 123.59, 123.86, 124.63, 125.59, 125.92, 126.03, 130.60, 133.54, 133.91, 135.62, 136.52, 137.69, 137.84, 139.72, 140.93, 144.02, 144.18, 161.05, 165.28, 165.55. MS: *m*/*z* 742 ([M]<sup>±</sup>); LRFAB-MS found: m/z 742.2990. Elemental analysis: calcd. for C43H38N2O2S4.0.5H2O: C, 68.71; H, 5.19; N, 3.72; S, 17.04%. Found: C, 68.69; H, 5.04; N, 3.27; S, 17.05%.

## 2.3.3. Synthesis of 3,6-di-tert-butyl-9-(3-octylthiophen-2-yl)-9H-carbazole-4,4-dimethyl-H-cyclopenta[2,1-b;3,4-b']di-thiophene-2-acrylic acid (W-3)

The preparation procedures of W-3 dye is the same as those for the synthesis of W-1 dye except 2-bromo-3-octylthiophene instead of 2-bromothiophene was used to react with 3,6-ditert butylcarbazole. W-3 dye was isolated as a red solid,  $mp = 240 \degree C$ (decomposed). IR (1679 cm<sup>-1</sup> (C=0); 2213 cm<sup>-1</sup> (C=N), see Figure S2, ESI).<sup>1</sup>H NMR spectrum was displayed in Figure S7 (ESI).<sup>1</sup>H NMR (300 MHz,  $\delta_{\rm H}$ /ppm in DMSO-d<sub>6</sub>): 0.81 (3H, t, 7.0 Hz), 1.08 (10H, s), 1.48 (18H, s), 1.51 (8H, s), 2.33 (2H, t, 7.2 Hz), 7.23 (1H, s), 7.26 (1H, s), 7.59 (3H, m), 7.71 (1H, s), 8.09 (1H, s), 8.38 (2H, s), 851 (1H, s). <sup>13</sup>C NMR (Figure S8 (ESI), 300 MHz,  $\delta_{\rm H}$ /ppm in DMSO-d<sub>6</sub>): 14.04, 22.54, 24.94, 27.61, 29.04, 29.08, 29.79, 31.70, 31.99, 34.75, 45.66, 92.65, 109.63, 116.27, 116.70, 117.57, 123.54, 123.89, 124.56, 130.84, 132.59, 133.09, 134.98, 136.43, 140.57, 142.17, 143.55, 144.28, 148.05, 149.53, 161.30, 166.51, 169.01. MS: *m*/*z* 772 ([M]<sup>±</sup>); LRFAB-MS found: *m*/*z* 772.4457. Elemental analysis: calcd. for C<sub>47</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>.0.5H<sub>2</sub>O: C, 72.21; H, 6.91; N, 3.59; S, 12.29%. Found: C, 72.62; H, 6.86; N, 3.55; S, 12.55%.

2.3.4. Synthesis of 2-cyano-{5-[4-(diphenylamino)phenyl]-2thienyl]-4,4-dimethyl-2H-cyclopenta[2,1-b;3,4-b']di-thiophene-2acrylic acid (W-4)

Under 5-[4-(diphenylamino)phenyl]-2-thiophen-4,4-Ar. dimethyl-2H-cyclopenta [2,1-b; 3,4-b']di-thiophene-2-carboxaldehyde (0.7 g, 1.1 mmol), NH<sub>4</sub>OAc (0.14 g, 1.8 mmol), CNCH<sub>2</sub>COOH (0.16 g, 1.9 mmol) and CH<sub>3</sub>COOH (50 mL) were mixed and refluxed for 6 h. The product was extracted with CHCl<sub>3</sub>, after recrystallization from dichloromethane/hexane, W-4 dye was isolated as a dark green solid, mp = 280 °C (decomposed). IR (1679 cm<sup>-1</sup> (C=O); 2213 cm<sup>-1</sup> (C $\equiv$ N) see Figure S2, ESI). <sup>1</sup>H NMR (Figure S9, 300 MHz,  $\delta_{\rm H}$ /ppm in DMSO-d<sub>6</sub>): 1.58 (6H, s), 7.14 (8H, m), 7.40 (6H, m), 7.66 (3H, m), 8.06 (1H, s), 8.48 (1H, s). <sup>13</sup>C NMR (Figure S10, 300 MHz,  $\delta_{H}$ / ppm in DMSO-d<sub>6</sub>): 24.41, 30.64, 44.95, 118.17, 122.78, 123.56, 124.00, 124.42, 125.64, 126.36, 126.87, 129.64, 132.13, 132.43, 135.03, 136.48, 139.20, 142.34, 142.85, 146.72, 147.10, 160.49, 164.12, 166.09, 206.48. MS: *m*/*z* 626 ([M]<sup>±</sup>); LRFAB-MS found: *m*/*z* 626.2602. Elemental analysis: calcd. for C<sub>37</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>.H<sub>2</sub>O: C, 68.94; H, 4.35; N, 4.34; S, 14.91%. Found: C, 68.91; H, 4.24; N, 4.00; S, 15.45%.

## 2.4. Fabrication and characterization of W-series dyes sensitized DSSCs

The procedure for the fabrication and characterization of DSSCs is the same as what we reported previously [36]. The characteristic current density–voltage (J–V) curves of the cells under the illumination of AM 1.5G simulated sunlight (Yamashita Denso Corporation, YSS-50A, 100 mW cm<sup>-2</sup>) were obtained by applying external potential bias to the cell and measuring the photocurrent output with a Keithley model 2400 digital source meter (Keithley, USA). Incident photon to electron conversion efficiency (IPCE) spectra were recorded with a custom-designed instrument provided by Enlitech Co., Taiwan, in which a 300 W Xenon lamp was focused through a Gemini-180 double monochromator to produce the excitation beam and Keithley 2400 Source Meter (Keithley) was used to record the current.

#### 2.5. Computational methods

The ground-state molecular geometries were optimized by the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional and 6-31G (d, p) basis set, as implemented in the Gaussian 09 program [37]. The Conductor-like Polarizable Continuum Model (C-PCM) [38] was used to account for THF solvation effect. For the convenience of the calculations, the long alkyl chain was replaced by a methyl group. Tetramethylammonium (TMA) was used to model the counter ion. The time-dependent DFT (TD-DFT) calculations were performed to calculate the UV-Vis spectra. To account for the charge transfer excitations, the coulomb-attenuating method (CAM) [39] was applied (calculated at TD-CAM-B3LYP/6-31G(d,p) level) to calculate the UV-Vis spectra of the sensitizers based on their optimized geometries calculated at B3LYP/6-31G(d,p) level. Electron density difference map (EDDM) of the electronic transitions was calculated using the Gaussum program (version 2.5.5) [40].

We employed damped Car–Parrinello [41] molecular dynamics to optimize the structure of dye-(TiO<sub>2</sub>)<sub>38</sub> system using CPMD program [42]. Damped Car–Parrinello [41] molecular dynamics was performed in a vacuum, using the PBE functional [43] in conjunction with PBE-consistent ultra soft pseudopotentials [44] with a cut-off of 25 Ry. The (TiO<sub>2</sub>)<sub>38</sub> cluster has an Anatase (101) surface. The dye-(TiO<sub>2</sub>)<sub>38</sub> system was centered in a periodically repeated orthorhombic box and the system was separated by a vacancy ~ 10.0 Å wide. The calculated UV–Vis spectra of the free deprotonated dyes in THF were similar to the experimental spectra of the dye adsorbed on TiO<sub>2</sub> thin film indicating that the adsorbed dyes were mainly in the deprotonated form. Therefore, we used deprotonated dye to model the dye-(TiO<sub>2</sub>)<sub>38</sub> system [45]. The dye molecules were adsorbed on (TiO<sub>2</sub>)<sub>38</sub> cluster *via* its two oxygen atoms of the carboxylic acid group in a bidentate manner because the bidentate adsorption mode is more stable than the monodentate adsorption mode [46,47]. The optimized geometries of the dye-(TiO<sub>2</sub>)<sub>38</sub> from the Car–Parrinello [41] damped molecular dynamics calculations were used for TD-DFT calculations to determine the lowest excitation energies calculated at TD-CAM-B3LYP/6– 31G(d,p) level using Gaussian 09 program [37].

#### 3. Results and discussion

#### 3.1. Synthesis and optical properties of W-series dyes

W-1-W-4 dyes were synthesized according to Schemes 1 and 2. Two types of donor: triphenyl amine and carbazole are used as a donor moiety. Cyanoacetic acid is used as an anchor and acceptor. The conjugated spacer is a combination of (oligo) thiophene and cyclopentadithiophene moieties. A palladium catalyzed Stille coupling reaction [48] is used to connect the conjugated spacer, donor and acceptor. Cyclopentadithiophene reacts with n-butyl lithium and DMF in THF to produce the aldehyde group, which is used for the production of the anchoring/donor group. The aldehyde then reacts with the cyanoacetic acid by Knoevenagel reaction using ammonium acetate/ acetic acid as a catalyst to produce the final products. W-1 and W-3 dves are deep red color, whereas W-2 and W-4 dves are dark green powders (the detailed preparation and characterization of all intermediates can be found in the Electronic Supporting Information (ESI)). All dyes exhibit fairly good thermal stability: TGA data (shown in Fig. 1) reveal that they all can stable up to 200 °C under nitrogen atmosphere.

All dyes are soluble in THF (tetrahydrofuran) with the absorption coefficient higher than 60,000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> at their  $\lambda_{max}$ (see Fig. 2a and the optical data are summarized in Table 1). The general feature of the absorption spectra for W-series dyes (except W-4) consists one broad band in the visible region and a weak absorption band in the UV region which correspond to the  $\pi - \pi^*$ transitions (or intramolecular charge transfer) for the molecule and dialkylcyclopentadithiophene unit, respectively. The broad absorption in the visible region for the intramolecular  $\pi - \pi^*$  charge transfer transition is a typical behavior for organic dyes with a D- $\pi-A$  architecture. It was found that  $\lambda_{max}$  of the dyes depends on the conjugated spacer and the strength of the donor. The  $\lambda_{max}$  of the dye with a triphenyl amine donor (W-4) are red-shifted compared to that with a carbazole donor (W-1) and dye with a longer conjugation spacer has a longer  $\lambda_{max}$ . However, when a long side chain was added in the thiophene ring (*i.e.* W-3), the  $\lambda_{\text{max}}$  of the dye was slightly blue-shifted by 5 nm (see Table 1). This is probably because of the conformation of W-3 is not as planar as W-1, due to the steric effect of the large octyl group.

The absorption spectra of the W-series dyes adsorbed on TiO<sub>2</sub> thin films are displayed in Fig. 2b and the related data are also listed in Table 1. Compared to the spectra of the corresponding dyes in THF, the absorption spectra of the dyes adsorbed on TiO<sub>2</sub> are slightly broader, and at the same time,  $\lambda_{max}$  blue-shifts by 30–47 nm. The broadening of the absorption peak can be attributed to the interaction between the carboxylate group and TiO<sub>2</sub> surface or the molecular conformation of the dyes adsorbed on TiO<sub>2</sub> may not be totally the same. The blue-shift in  $\lambda_{max}$  suggests that there is an H-aggregation of the dyes or the dye molecules are deprotonated (carboxylate is a weaker acceptor compared to carboxylic acid) when adsorbed on TiO<sub>2</sub> [49].



Scheme 1. Synthetic procedures for the preparation of W-1, W-2, and W-3 dyes.

## 3.2. Electro-optical properties and photovoltaic performance of the W-series dye

The oxidation potential and energy level of the frontier orbitals for the W-series dyes listed in Table 2 are determined by cyclic

voltammetry (see Figure S11, ESI) and the band gap energy,  $E_{0-0}$ , defined by the intersection of the absorption and emission spectra, see Figure S1, ESI. As depicted in Table 2, based on W-1, adding one more thiophene unit to the dye (*i.e.* W-2) does slightly drive up the HOMO level, but keeps the LUMO level almost the same, therefore



Scheme 2. Synthetic procedures for the preparation of W-4 dye.



Fig. 1. TGA of the W-series dyes.



Table 1

The optical data of W-series dyes.

-	-		
Dye	λ <sub>max</sub> in THF (nm)	$\epsilon$ at $\lambda_{max}$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}$ adsorbed on TiO <sub>2</sub> (nm)
W-1	490	65,157	450
W-2	501	71,446	466
W-3	485	62,232	455
W-4	505	84,006	458

the  $E_{0-0}$  energy decreases. Adding an octyl group to the thiophene ring (*i.e.* W-3) increases the oxidation potential and band-gap energy ( $E_{0-0}$ ) simultaneously, probably due to the steric effect of the octyl chain making W-3 dye less planar (effectively a shorter conjugation pathway). Nevertheless, LUMO for all dyes (-1.12 to -1.32 V vs NHE) is higher than TiO<sub>2</sub> conduction band edge (-0.5 V vs NHE), which provides a sufficient thermodynamic driving force (0.62–0.82 V) for the electron injection [50]. HOMO for the W-series dyes falls to 0.90–1.20 V (vs NHE) which is more positive than the redox potential (0.4 V vs NHE) of the iodide/triiodide couple used in DSSC, facilitating the dye regeneration. The frontier orbital energy levels of the W-series dyes match the requirement for a dye to be used in DSSCs.

Preliminary photovoltaic performance tests are carried out and the resulting I-V curves and IPCE plots are shown in Fig. 3. The photovoltaic parameters are summarized in Table 3 and the detailed DSSC device fabrication and photovoltaic performance measurements can be found in the ESI. As listed in Table 3, DSSC based on the W-4 dye has the highest efficiency of 5.0%, which is 75% of that for N719 (the structure was also shown in Scheme 2) sensitized device fabricated using the same fabrication procedures. The good photovoltaic performance of the W-4 dye may be attributed to its high absorption coefficient and the absorption profile matches better with the AM 1.5G Sunlight, as well as its structure has a strong triphenyl amine donor, results in higher short-circuit current  $(I_{sc})$ . Furthermore, the quantity of the dye molecules adsorbed on the practical TiO<sub>2</sub> electrode (displayed in Table 3) is also an important parameter for the photovoltaic performance of a DSSC. The values can be estimated by desorbing the dye molecules from the practical TiO<sub>2</sub> electrode using a basic solution as reported [51]. It was found that, except for W-3, a similar amount of molecules is adsorbed on TiO<sub>2</sub> electrode. The fact that a fewer W-3 molecules adsorbed on TiO<sub>2</sub> is due to W-3 has large octyl chains on the thiophene ring, which occupies a larger TiO<sub>2</sub> surface.

The energy levels of the frontier orbitals and  $E_{0-0}$  energy for W-2 are close to those for W-4 (see Table 2) but the conversion efficiency of W-2 based DSSC is much lower. This may be attributed to the difference in the donor group (triphenyl amine for W-4 dye *vs* carbazole for W-2 dye) or the higher absorption intensity of W-4 self-assembled on TiO<sub>2</sub> (see Fig. 2b). On the other hand, compared to W-2, W-1 has the same donor (carbazole), a similar number of molecules adsorbed on TiO<sub>2</sub> and lower absorption coefficient. Nevertheless, the conversion of a W-1 sensitized device is higher than for a W-2 based device. The aggregation (see Fig. 2b) of W-2 dye when adsorbed on TiO<sub>2</sub> may be the reason for its low efficiency.

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Dye	<i>E</i> (D <sup>+</sup> /D) <sup>a</sup> ( <i>vs</i> NHE)	$E_{0-0}^{b}$ (eV)	HOMO (V vs NHE)	LUMO (V vs NHE)
W-1	0.49	2.26	0.98	-1.28
W-2	0.41	2.22	0.90	-1.32
W-3	0.61	2.32	1.20	-1.12
W-4	0.41	2.21	0.90	-1.31

<sup>a</sup> HOMO (V vs NHE) =  $E_{ox} - E_{fc/fc+} + 0.63$ .

<sup>b</sup>  $E_{0-0}$  was defined by the intersection of the absorption and emission spectra.

Fig. 2. UV/Vis absorption spectra of the W-series dyes (a) in THF, (b) adsorbed on  $\text{TiO}_2.$ 



Fig. 3. (a) I-V curves, (b) IPCE plots of DSSCs sensitized with the W-series dyes.

The aggregation of W-2 is due to its long molecular axis and planar conformation. We try to reduce the aggregation of W-2 dye by adding more (30 mM) co-adsorbent (Chenodeoxycholic acid) in the dye solution, but the efficiency of the corresponding device decreases due to the completing adsorption between the dye molecule and co-adsorbent.

Interestingly, as mentioned in the previous paragraph that higher conversion efficiency of W-4 sensitized DSSC (compared to W-2 based device) is due to the higher absorption intensity (combining the effect of the absorption coefficient and dye loading) of W-4 dye adsorbed on TiO<sub>2</sub>. On the other hand, comparing W-1 and W-2 dyes we found that W-2 dye adsorbed on TiO<sub>2</sub> has higher absorption intensity but worse photovoltaic performance of the corresponding device. This may be due to the fact that W-2 dye has a higher HOMO energy level, therefore dye regeneration is more difficult even the LUMO level of W-2 dye is higher than W-1 dye, which may be benefit for electron injection from dye to TiO<sub>2</sub>. These results reveal that it is hard to predict the photovoltaic performance of a dye simply by one of its physicochemical properties or molecular architecture. Therefore, instead of using various spectroscopic methods to identify what are the major parameters for determining the photovoltaic performance of a D $-\pi$ -A organic dye (especially those containing cyclopentadithiophene unit), we used the theoretical calculation to probe the electronic state of the dyes adsorbed on TiO<sub>2</sub> before and after photo excitation to understand how to design high efficiency organic dyes.

### 3.3. Calculated ground state molecular geometry and electron localization of the frontier orbitals of W-series dyes

Fig. 4 displays the selected structural parameters of W-1–W-4 molecules in their protonated and deprotonated states in THF. These structural parameters are the bond lengths and dihedral angles of the two adjacent rigid aromatic rings, which are more sensitive to the chemical environments and will influence the degree of  $\pi$ -conjugation of the dye molecule. Furthermore, the degree of  $\pi$ -conjugation also affects the absorption spectra and coupling strength between the donor and acceptor moieties, which consequently affects the probability of the electron transfer upon photo

 Table 3

 The photovoltaic performance and dye loading of W-series dyes sensitized DSCs.

Dye	$V_{\rm oc}\left({\rm V} ight)$	$J_{\rm sc}~({\rm mA/cm^2})$	FF	η (%)	Dye loading (mole/cm <sup>2</sup> )
W-1	0.66	10.52	0.69	4.78	$0.95 \times 10^{-8}$
W-2	0.62	9.74	0.71	4.33	$0.94  imes 10^{-8}$
W-3	0.66	7.21	0.71	3.38	$0.40 \times 10^{-8}$
W-4	0.66	11.91	0.69	5.39	$0.88 \times 10^{-8}$
N719	0.66	17.37	0.60	6.7	$1.81 \times 10^{-8}$

excitation. For convenience of the discussion, herein we abbreviate these two structural parameters with referring to their two adjacent rings. For example, the dihedral angle between the phenyl ring on the TPA unit and thiophene ring (T) is abbreviated as  $\tau$ (TPA-T) and the length of the bond connecting these two adjacent rings is abbreviated as *d*(TPA–T); N-arylcarbazole and cyclopentadithiophene rings are abbreviated as NCAR and CPDT, respectively. Regardless of the molecular state, the electron donating groups, NCAR and TPA are non-planar with its neighboring thiophene ring. For example, the  $\tau$ (NCAR–T) dihedral angles in W-1, W-2, and W-3 were in the range of  $60^{\circ}-85^{\circ}$ ;  $\tau$ (TPA-T) dihedral angles in W-4 are in the range of  $17^{\circ} \sim 18^{\circ}$ . These calculation results indicate that the terminal electron donating groups, NCAR and TPA, are only partially conjugated with the molecular backbone. For the dihedral angle between the conjugated spacer and acceptor such as  $\tau(T-T)$  and  $\tau(T-CPDT)$ , the dihedral angles indicated a certain degree of non-planarity but they are less twisted than those of the donor-spacer. On the other hand, the anchoring groups generally remain nearly planar with its neighboring CPDT rings.

The carbon-carbon bond lengths between two rigid rings depicted in Fig. 4 were in the range of 1.440-1.463 Å. These carbon-carbon bond lengths are shorter than that of a standard carbon-carbon single bond (1.54 Å) and longer than a standard carbon-carbon double bond (1.34 Å). The characteristic carboncarbon partial double bond indicates the existence of the  $\pi$ conjugation between two rigid aromatic rings. Interestingly, the bond lengths of the anchoring groups at the protonated and deprotonated states are different. When the dye molecules are deprotonated, the bonds of the anchoring groups generally elongate. These results suggest that the deprotonated dyes are less conjugated with the molecular framework than their corresponding protonated states. The calculated frontier orbitals of the protonated W-series dyes in THF are displayed in Fig. 5, only HOMO and LUMO orbitals are shown. The distribution of LUMO of all dyes is similar, mainly locating on the CPDT and acceptor/anchor group. The distribution of HOMO (although all are mainly on the conjugated spacer) is different: triphenyl amine donor contributes significantly but little dispensation on carbazole donor. It is hard to predict precisely the effective charge transfer of these W-series dyes simply by the isodensity surface plots of the frontier orbitals. More detailed calculation is needed.

## 3.4. Calculated UV–Vis spectra of the W-series dyes in solution and adsorbed on $TiO_2$

Table 4 lists the computational and experimental electronic absorptions of the W-series dyes in THF. Here, the trends in the experimental UV–Vis spectra and their relationship to the



Fig. 4. Selected molecular geometries for the four studied dye molecules. The bond lengths (Å) are labeled around their corresponding bonds. The dihedral angles (°) are labeled around their corresponding central bonds; their four consecutive atoms are highlighted in bold. The data for dye molecules are arranged, from top to bottom, for the protonated state in THF and the deprotonated state in THF.

#### Table 4

Experimental and computational electronic absorptions of W-series dyes in THF solution.

Dyes	Experiment (in THF)	Calculation (protonated in THF)		Calculation (deprotonated in THF)		
	λ <sub>max</sub>	λ <sub>max</sub>	Deviation	λ <sub>max</sub>	Deviation	
	(nm)	(nm)	from EXP.	(nm)	from EXP.	
W-1	490	484	-6	444	-46	
W-2	501	510	+9	472	-29	
W-3	485	478	-7	444	-41	
W-4	505	514	+9	469	-36	

molecular geometries are discussed first. Only one major absorption for all studied dyes are observed. Relative to W-1 dye, W-3 dye features a less planar structure with its  $\lambda_{max}$  blue-shifted by 5 nm; W-2 dye features a longer  $\pi$ -conjugation length, with its  $\lambda_{max}$  red-



Fig. 5. Isodensity surface plots of the frontier orbitals for the W-series dyes.

shifted 11 nm. On the other hand, W-4 and W-2 dyes have the same spacer and acceptor, but with different donor; compared to W-2 dye,  $\lambda_{max}$  of W-4 dye red-shifted by 4 nm. This result indicates that TPA is more conjugated as a conjugated spacer than N-arylcarbazole, as evidenced by the smaller  $\tau$ (TPA–T) in W-4 dye (*ca.* 18°) than  $\tau$ (NCAR–T) in W-1 dye (*ca.* 60°).

The degree of protonation of the dye molecules in solution is important because it affects the adsorption of the dyes on TiO<sub>2</sub> anode. Table 4 summarizes the calculated electronic absorptions for the W-series dyes in THF at their protonated and deprotonated states. The calculated electronic absorptions of the dye molecules at their protonated states in THF agree well with the experimental observations; the smallest absolute deviation from the experimental value is 6 nm blue-shift for W-1 dye and the largest absolute deviation was a 9 nm red-shift for W-2 and W-4 dyes. In contrast, the calculated values of  $\lambda_{max}$  for the W-series molecules in THF based on their deprotonated state deviate widely from the experimental data; all absolute deviations are greater than 20 nm, with the largest absolute deviation up to 46 nm occurring for W-1 dye. Based on the calculated UV-Vis spectra, the W-series dyes may adopt protonated states in THF solution. Interestingly, the calculated values of  $\lambda_{max}$  for the W-series dyes in their deprotonated states in THF agree well with the experimental  $\lambda_{max}$  of dyes adsorbed on TiO<sub>2</sub>, consistent with what is well-known that dye adsorbed on TiO<sub>2</sub> is in a deprotonated form.

#### 3.5. Calculated UV–Vis spectra of W-series dyes adsorbed on TiO<sub>2</sub>

The experimental electronic transitions of the dye molecules adsorbed on TiO<sub>2</sub> thin film are all blue-shifted by 30–47 nm with respect to their corresponding spectra taken in THF solutions. This is a general phenomenon for the sensitizers containing cyanoacetic acid acceptors [52–55]. The calculated electronic transitions of the dye molecules adsorbed on (TiO<sub>2</sub>)<sub>38</sub> clusters are listed in Table 5. We assume that the dye molecules are in their deprotonated states and adsorbed on (TiO<sub>2</sub>)<sub>38</sub> cluster in a bidentate manner. The calculated  $\lambda_{max}$  values for the dyes on (TiO<sub>2</sub>)<sub>38</sub> clusters have absolute deviations of 1–26 nm from their experimental values. The

Table 5				
Experimental and computational electronic absorptions	of W-series dves	adsorbed on	(TiO <sub>2</sub> )38	cluster

Dyes	Experimental (on TiO <sub>2</sub> )		Calculated [adsorbed on (TiO <sub>2</sub> ) <sub>38</sub> ]				
	$\lambda_{\max}$ (nm)	Deviation from that in THF	$\lambda_{\max}$ (nm)	Deviation from EXP.	Oscillator strength	Transition <sup>a</sup>	
W-1	450	-40	459	+9	2.157	HOMO $\rightarrow$ LUMO + 5 (66%), HOMO $\rightarrow$ LUMO + 6 (19%), HOMO $\rightarrow$ LUMO + 4 (5%)	
W-2	466	-35	486	+20	2.591	HOMO $\rightarrow$ LUMO + 2 (89%)	
W-3	455	-30	456	+1	2.081	HOMO $\rightarrow$ LUMO + 5 (77%), HOMO $\rightarrow$ LUMO + 4 (8%), HOMO $\rightarrow$ LUMO + 6 (7%)	
W-4	458	-47	484	+26	2.528	HOMO $\rightarrow$ LUMO + 4 (50%), HOMO $\rightarrow$ LUMO + 6 (29%), HOMO $\rightarrow$ LUMO + 5 (7%)	

<sup>a</sup> Transitions with contributions greater than 5% are listed.

electronic transitions are mainly arisen from HOMO located at dye molecules to higher unoccupied orbitals located at  $(TiO_2)_{38}$  clusters and/or dye molecules.

## 3.6. Calculated electronic transition upon photo excitation for the dye adsorbed on $TiO_2$

Table 6 lists the characteristics of the electron densities of the W-series dyes adsorbed on  $(TiO_2)_{38}$  clusters before and after photo excitation. Before photo excitation, the electron density of each dye molecule mainly resided on CPDT unit (50–65%) and had no population on  $(TiO_2)_{38}$  cluster. After excitation, for W-1, W-3, and W-4,  $(TiO_2)_{38}$  cluster received significant amount (31–58%) of electron density from the dye molecule. In contrast, after excitation,  $(TiO_2)_{38}$  cluster received a only very minor amount (4%) of electron from the W-2 dye molecule. These results indicate that the electron injection of W-2 dye to  $(TiO_2)_{38}$  is less efficient than other dyes studied in this article.

Data listed in Tables 1–3 reveal that W-1 and W-2 dyes possess some interesting relationships: (a). W-1 and W-2 dyes have similar amounts of dye loading on TiO<sub>2</sub> anode; (b). W-2 dye owns an approximately 40% larger optical-absorbance at its  $\lambda_{max}$  and has higher absorbance at all wavelengths compared to W-1 dye; and (c). W-1 and W-2 have similar open-circuit voltages ( $V_{oc}$ ). These three relationships provide us a system suitable to study whether the distinct electronic transitions affects the short-circuit current densities ( $J_{sc}$ ) and thereafter the conversion efficiencies ( $\eta$ ) of the corresponding devices or not. From the absorption profiles, we may expect W-2 sensitized DSSC should have larger  $J_{sc}$  than W-1 based device. However, experimental data show that  $J_{sc}$  of W-2 based device (9.74 mA/cm<sup>2</sup>) is *ca*. 8% lower than that ( $J_{sc} = 10.52$ ) of W-1 sensitized device. However, the calculation results show that 44% of

#### Table 6

Characteristics of electron densities of deprotonated organic W-series dyes adsorbed on  $(TiO_2)_{38}$  cluster before and after transition.

Dye	Transition	Percent contribution (%)					
		Donor	Thiophene <sup>a</sup>	Thiophene	CPDT	Anchor	(TiO <sub>2</sub> ) <sub>38</sub>
W-1	Before After	6 0	17 8	-	61 32	16 16	0 44
W-2	Before After	2 0	9 9	20 18	56 47	13 22	0 4
W-3	Before After	1 0	16 10	-	65 39	18 20	0 31
W-4	Before After	17 2	21 6	-	50 22	12 12	0 58

<sup>a</sup> This thiophene is connected with the donor.

the electron density of W-1 is directly transferred to (TiO<sub>2</sub>)<sub>38</sub> cluster after photo excitation (EDDM shown Fig. 6a) indicating that the electron injection of W-1 follows both the direct and indirect photosensitization processes. The direct photosensitization processes arise from the optical electron transfer, which the excited state of the sensitizer can be considered as an oxidized state and TiO<sub>2</sub> can be described as a reduced state [56]. The indirect photosensitization (based on photo induced electron transfer) is a multistep process involving consecutive electron transfer to the appropriate band of a semiconductor (e.g. TiO<sub>2</sub>). Therefore, the direct photosensitization should give rise to a more efficient electron injection although the back electron transfer process might also be attainable [57]. On the other hand, only 4% of the electron density of W-2 was directly transferred to the (TiO<sub>2</sub>)<sub>38</sub> cluster after photo excitation (EDDM shown Fig. 6b) indicating that the electron injection of W-2 mainly followed the indirect photosensitization. The indirect photosensitization is generally considered less efficient for the electron transfer to the conduction band of  $(TiO_2)_{38}$ cluster but the back electron transfer is retarded by an energy barrier. It is known that the  $J_{sc}$  is proportional to the efficiency of the electron injection from the excited sensitizers to TiO<sub>2</sub> anode [58]. Therefore, our calculations suggest that W-1 based device should have a larger  $J_{sc}$  compared to W-2 sensitized device, consistent with the experimental data. Moreover, W-2 dye which has higher LUMO energy level should have a high electron injection driving force compared to W-1 dye. We calculate a model molecule (W-5 dye, structure displayed in Figure S12 of ESI) with a molecular framework similar to W-1 but without the thiophene spacer. The result shows that 75% of electron density on W-5 is transferred to (TiO<sub>2</sub>)<sub>38</sub> cluster directly (detailed data not shown). Therefore the lower efficiency of the electron transfers (from dye to  $(TiO_2)_{38}$ ) for W-2 dye compared to W-1 dye may be due to W-2 dye has a longer electron transfer path (an additional thiophene ring).

Among all dyes studied, W-4 sensitized device has the highest  $\eta$  and largest  $J_{sc}$ . These results may be ascribed to the highest dye



**Fig. 6.** Electron density difference maps (EDDMs) of the transitions for (a) W-1 dye and (b) W-2 dye on TiO<sub>2</sub>. Cyan indicates an increase in electron density; light blue indicates a decrease. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

loading and largest optical absorbance of W-4 dye. On the other hand, our calculations show that W-4 has more than 50% of its electron density transferred to  $(TiO_2)_{38}$  cluster after photo excitation, which mainly followed the direct photosensitization. As discussed above, the direct photosensitization should result in a higher  $J_{sc}$  and therefore  $\eta$ , consistent with the experimental data. Furthermore, the molecular framework of W-4 is analogous to that of W-1, but with a TPA (instead of carbazole) unit as a donor. The higher charge transfer efficiency for W-4 dye compared to W-1 dye (58% vs 44%) suggests TPA is a better electron donor moiety compared to carbazole.

#### 4. Conclusion

A series of metal free donor-conjugated spacer-acceptor (D- $\pi$ –A) organic dyes containing cyclopentadithiophene unit in the spacer are synthesized and their photovoltaic performance is tested. These designed photosensitizers provide a suitable system to investigate the effects of the conjugated spacer and donor on the short-circuit current  $(J_{sc})$  of the corresponding DSSCs. The measured J<sub>sc</sub> values are well rational with the quantity of the direct electron injection derived from the theoretical calculations. Our study shows that extending the length of the conjugated spacer may red-shift the  $\lambda_{max}$  and increase the absorption coefficient of the dye molecule, however, theoretical calculations are also efficiently rationalized with the charge transfer from dye to (TiO<sub>2</sub>)<sub>38</sub> cluster decreases upon increasing the length of the conjugated spacer. The electron injection of W-1 and W-4 dyes to TiO<sub>2</sub> follows both the direct and indirect mechanisms; on the other hand, W-2 mainly follows an indirect electron injection mechanism and thus has a smaller *I*<sub>sc</sub> value. The distribution of the frontier orbitals of the W-series dyes is also very sensitive to the donor moiety; the calculation data show that TPA group is a better donor than carbazole to drive the electron density of the sensitizers to TiO<sub>2</sub> directly. Therefore W-4 dye (with TPA as a donor) sensitized DSSC has the highest efficiency (5.0%) among the dyes studied in this article. The efficiency is  $\sim$  75% of the N719 based device ( $\eta = 6.7\%$ ) fabricated in the similar conditions. The calculated electron density difference maps (EDDMs) before and after photo excitation provide a better understanding of the photovoltaic performance of cyclopentadithiophene-containing sensitizers at the electronic and structural levels.

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#### Appendix A. Supplementary material

Details of the experiment, including the synthesis and characterization of all intermediates, IR, NMR spectra of the W-series dyes, as well as the fabrication and photovoltaic performance measurement of DSSCs can be found, in the online version, at http://dx.doi.org/10.1016/j.dyepig.2013.08.016

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