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Organic dyes with imidazole derivatives as auxiliary donors for dye-sensitized solar cells: Experimental and theoretical investigation



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1. Introduction

Since the seminal work of dye-sensitized solar cells (DSSCs) was reported in 1991 by Grätzel and O'Regan, it has attracted the considerable attention of many research groups owing to their high efficiencies and low costs [1–3]. DSSCs typically contain four components: a mesoporous semiconductor metal oxide film, a dye, an electrolyte/hole transporter, and a counter electrode [4]. As a critical component in DSSCs, the dye sensitizers play a vital role in providing electron injection into conduction band (CB) of TiO₂ upon light irradiation. Nowadays, DSSCs based on ruthenium dyes and porphyrin dyes have shown very impressive solar to electric power conversion efficiencies. The DSSC based on black dye with donoracceptor type coadsorbent has reached an overall solar energy conversion efficiency (η) of 11.4% [5], and a new record efficiency of 12.3% has been obtained by co-sensitization of the porphyrin dye YD2-o-C8 and the organic dye Y123 [6]. Although ruthenium and porphyrin dyes have high efficiencies, the large-scale application of them is limited due to many practical issues. For example, the synthesis and purification of ruthenium and porphyrin dyes are very complicated and the yields of them are very low, especially the

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ABSTRACT

In order to study the influence of different imidazole derivatives in triphenylamine-based organic dyes, two different imidazole derivatives are introduced into the phenyl ring of the triphenylamine core, coded as **CD-4** and **CD-6**, respectively. Their photophysical, electrochemical properties and the performances of the corresponding dye-sensitized solar cells (DSSCs) are further investigated. Due to the better molar extinction coefficient, quantum efficiency (QE) and longer lifetime of excited electron, the DSSC based on **CD-4** has the higher overall conversion efficiencies as 4.11% than that of **CD-6** as 1.51% under full sunlight (AM 1.5G, 100 mW cm⁻²) irradiation. Density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations were carried out to study the ground state structures, the electronic structures and the optical properties of the two dyes. The simulated UV–vis absorption spectra for the two dyes are in excellent agreement with the experimental results.

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ruthenium dyes need noble metal Ru which is scarce and disadvantage to environmental protection.

For the above reasons, lots of efforts have been dedicated to the development of metal-free organic dyes due to their high molecular extinction coefficients, simple preparations, low costs, and environment friendly [7,8]. Up to now, many different types of organic dyes have been developed as the sensitizer for DSSCs. The DSSCs based on merocyanine [9,10], coumarin [11–13], indoline [14–16], squaraine [17,18], hemicyanine [19,20], phenothiazine [21–24], triphenylamine [25–27], fluorene [16,28,29], carbazole [30–32], tetrahydroquinoline [33–35] and benzo[1,2-b:4,5-b']difuran (BDF) [36] have been developed and shown good performances. In particular, it encourages to note that a promising η up to 10.3% has been demonstrated by Wang et al. [37].

Most organic dyes are consisted of electron donor, π spacer and acceptor. However, the rod-like molecules are elongated, which may facilitate the recombination of electrons with the triiodide and the formation of aggregates between the neighbor dye molecules [38]. Therefore, organic dyes with a starburst conformation were designed and synthesized by introducing additional electron donor groups into the D- π -A molecule to form the starburst 2D- π -A structure [39–41], which avoids the charge recombination process of injected electrons with the triiodide in the electrolyte and the formation of aggregates between the neighbor dye molecules. Among the organic dyes, triphenylamine and its derivatives are a



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starburst conformation, which is very helpful to avoid the formation of aggregates between neighbor dye molecules. Besides, imidazole derivatives could be used for the good auxiliary electron donor in the organic dyes based on the following reasons: 1) it has the conjugated chain which is advantage to the charge-transfer transition from the auxiliary electron donor to first electron donor: 2) charge recombination after electron injection maybe retarded because of decreasing positive charge density at the donor by electronic delocalization of the two substituents at positions 4 and 5 of the imidazolyl ring [42]. Based on these reasons, we introduce the different imidazole derivatives to the structure of triphenylamine, and the 2-cyanoacetic acid acts as acceptor group to constitute two new 2D $-\pi$ -A dyes coded as **CD-4** and **CD-6**. Their photophysical, electrochemical properties and the performances of the corresponding DSSCs are further investigated. At the same time, N719 acts as the purpose of comparison dye, which was successfully applied in DSSCs. The corresponding molecular structures of the two dyes and N719 are shown in Scheme 1.

2. Experimental section

2.1. Materials and characterization

All solvents and other chemicals were reagent grade and used without further purification. 4,4'-dimethoxybenzil, 2,2'-thenil, 2-cyanoacetic acid and triphenylamine were purchased from Astatech. HRMS data were obtained with a micrOTOF-Q II instrument. ¹H NMR spectra were measured on Varian Mercury Plus 400 MHz and Bruke 500 MHz NMR instruments. Mp data were obtained on X4 melting point detector (FUKA, Beijing, China). INSPECT F Scanning electron microscopy (SEM) (FEI, Netherlands) is used to measure the thickness of the TiO₂ film. Absorption spectra were measured with SHIMADZU (model UV2550) UV–vis spectrophotometer. Cyclic voltammetry experiments were performed on a CH Instruments 660C electrochemical workstation with a scanning rate of 50 mV/s in dimethylformamide (DMF) (5.0×10^{-4} M) containing 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte, platinum as counter and work electrodes and Ag/AgCl as reference electrode.

2.2. Fabrication of DSSCs

 TiO_2 colloid was prepared according to the literature [43]. The washed FTO glass substrates were immersed in 40 mM $TiCl_4$ aq. at 70 °C for 30 min to form a compact layer of TiO_2 , which plays an important role in suppressing the charge recombination of DSSCs at the interface between FTO and electrolyte, then washed with water



Scheme 1. Molecular structures of CD-4, CD-6 and N719.

and ethanol. A thin film of TiO₂ was prepared on the FTO substrate with the compact TiO₂ layer through blade coating with glass rod. After drying the nanocrystalline TiO₂ layer at 80 °C, the TiO₂ thin film with more layers was achieved by repeating the blade coating above process two times. The resulting working electrode was composed of a 14 μ m thick transparent TiO₂ nanoparticle layer. Finally TiO₂ electrodes were treated at 450 °C for 30 min. After cooling to room temperature, the electrodes were immersed in 40 mM TiCl₄ aq. at 70 °C for 30 min, and washed with water and ethanol again, then recalcined at 450 °C for 30 min. After the sintering, when the TiO₂ electrodes cooled to 80 °C, the electrodes were immersed in a dye bath containing 0.2 mM CD-4, CD-6 or N719 in ethanol and left overnight. The films were then rinsed with ethanol to remove excess dye. In our experiment, open cells were fabricated in air by clamping the different dye electrode with platinized counter electrode. The electrolyte used here is composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.0653 M LiI, 0.03 M I₂, 0.28 M 4-tertbutylpyridine (TBP) and 0.05 M guanidium thiocyanate (GuSCN) in acetonitrile.

2.3. Fabrication of the samples for measuring the dye adsorbed amount and absorption spectra on TiO_2

The measurement of the dye adsorbed amount was according to the literature [44] and the adopted TiO₂ films were same as the fabrication of DSSCs. The measurement procedure as follows: the 14 μ m thickness (area: 7 \times 12 mm) TiO₂ films were sensitized for 12 h in a dye bath and further employed for the measurement of the dye adsorbed amount. The 5 μ m thickness TiO₂ films were sensitized for 12 h in a dye bath, which were adopted for absorption spectra measurement of the dyes on TiO₂ surface.

2.4. Photovoltaic characterization

The irradiation source for the photocurrent action spectrum measurement is a simulated AM 1.5G solar irradiation (100 mV cm^{-2}) (SAN-EI ELECTRIC, XES-301S). The current–voltage characteristics of photovoltaic devices were measured by using a KEITHLEY 2400 semiconductor parameter analyzer. The tested solar cells were masked to a working area of 0.16 cm². The action spectra of quantum efficiency (QE) for solar cell were performed by using QEX10 quantum efficiency measurement system. Electrochemical impedance spectroscopy (EIS) data were obtained in the dark under forward bias 0.7 V, scanning from 10^{-2} to 10^{5} Hz with ac amplitude of 10 mV by using CH Instruments 660C electrochemical workstation.

2.5. Synthesis

Compound **2** [45] was prepared according to the reported literature (as shown in Scheme 2).

2.5.1. Synthesis of compound 3

A acetic acid (70 mL) solution of 4,4'-dimethoxybenzil (189.00 mg, 0.70 mmol), compound **2** (315.00 mg, 1.05 mmol) and ammonium acetate (1080.00 mg, 14.00 mmol) were charged sequentially in a three-necked flask and heated under reflux for 12 h. The reaction mixture was poured into ice-cold water. The resulting precipitate was filtered, washed with water, and dried. Then the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v:v) as eluent to afford compound **3** as a yellow solid (126.00 mg, yield 32.67%). Mp: 210 °C. ¹H NMR (500 MHz, CDCl₃) δ : 9.84 (s, 1H), 7.85–7.83 (d, *J* = 8.5 Hz, 2H), 7.72–7.71 (d, *J* = 8.5 Hz, 2H), 7.60–7.58 (d, *J* = 8.5 Hz, 2H), 7.40–7.35 (m, 5H), 7.23–7.18 (m, 4H), 7.10–7.09 (d, *J* = 9.0 Hz,



Scheme 2. Synthetic routes of the dyes CD-4 and CD-6. (a) POCl₃, DMF, reflux, 72 h (b) 4,4'-dimethoxybenzil, ammonium acetate, acetic acid, reflux, yield 32.67% (c) 2,2'-thenil, ammonium acetate, acetic acid, reflux, yield 18.46% (d) 2-cyanoacetic acid, piperidine, acetonitrile, reflux (CD-4, yield 72.36%; CD-6, yield 77.49%).

2H), 6.94–6.93 (d, J = 8.5 Hz, 2H), 6.87–6.85 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H). HRMS (ESI, m/z): calcd for C₃₆H₂₉N₃O₃: 551.2209, found 552.2426 [M + H]⁺.

2.5.2. Synthesis of compound 4

A acetic acid (50 mL) solution of 2,2'-thenil (154.00 mg, 0.70 mmol), compound **2** (210.00 mg, 0.70 mmol) and ammonium acetate (1080.00 mg, 14.00 mmol) were charged sequentially in a three-necked flask and heated under reflux for 15 h. The reaction mixture was poured into ice-cold water. The resulting precipitate was filtered, washed with water, and dried. Then the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v:v) as eluent to afford compound **4** as a yellow solid (65.00 mg, yield 18.46%). Mp: 198 °C. ¹H NMR (500 MHz, CDCl₃) δ : 9.84 (s, 1H), 7.84–7.82 (d, *J* = 8.5 Hz, 2H), 7.73–7.71 (d, *J* = 8.5 Hz, 2H), 7.43–7.42 (d, *J* = 5 Hz, 1H), 7.38–7.35 (t, *J* = 7.8 Hz, 2H), 7.33–7.30 (m, 2H), 7.25–7.18 (m, 6H), 7.14–7.13 (t, *J* = 4.25 Hz, 1H), 7.10–7.09 (d, *J* = 9.0 Hz, 2H), 7.00–6.99 (t, *J* = 4.25 Hz, 1H). HRMS (ESI, *m/z*): calcd for C₃₀H₂₁N₃OS₂: 503.1126, found 504.1264 [M + H]⁺.

2.5.3. Synthesis of CD-4

A CH₃CN (20 mL) solution of compound **3** (68.00 mg, 0.12 mmol), 2-cyanoacetic acid (35.00 mg, 0.41 mmol) and a few drops of piperidine were charged sequentially in a three-necked flask and heated to reflux under a nitrogen atmosphere for 10 h. After cooling to room temperature, the solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with dichloromethane/ethanol (6:1, v:v) as eluent to afford the dye **CD-4** as a deep yellow solid (55.00 mg, yield 72.36%). Mp: 225 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ : 8.16 (s, 1H), 8.09–8.07 (d, *J* = 8.4 Hz, 2H), 7.97–7.94 (d, *J* = 8.8 Hz, 2H), 7.47–7.43 (m, 6H), 7.29–7.24 (m, 5H), 6.98–6.93 (t, *J* = 9.2 Hz, 6H), 3.77 (s, 6H). HRMS (ESI, *m/z*): calcd for C₃₉H₃₀N₄O₄: 618.2267, found 619.2344 [M + H]⁺.

2.5.4. Synthesis of CD-6

A CH₃CN (20 mL) solution of compound **4** (61.40 mg, 0.12 mmol), 2-cyanoacetic acid (31.00 mg, 0.36 mmol) and a few drops of piperidine were charged sequentially in a three-necked flask and heated to reflux under a nitrogen atmosphere for 10 h. After cooling to room temperature, the solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with dichloromethane/ethanol (6:1, v:v) as eluent to afford the dye **CD-6** as a deep yellow solid (53 mg, yield 77.49%). Mp: 208 °C. ¹H NMR (400 MHz, DMSO- d_6) δ : 8.19 (s, 1H), 8.15–8.09 (m, 2H), 8.00–7.97 (d, J = 8.8 Hz, 2H), 7.70–7.66 (d, J = 16.8 Hz, 2H), 7.49–7.45 (t, J = 8.0 Hz, 4H), 7.37–7.28 (m, 3H), 7.25–7.24 (d, J = 7.6 Hz, 2H), 7.18–7.13 (m, 2H), 7.05–7.02 (d, J = 8.8 Hz, 2H). HRMS (ESI, m/z): calcd for C₃₃H₂₂N₄O₂S₂: 570.1184, found 571.1266 [M + H]⁺.

2.6. Theoretical calculation methods

The dyes **CD-4** and **CD-6** before and after binding to (TiO₂)₉ [46] in vacuum are calculated at density functional B3LYP [47] level using the 6-31G* for C, H, O, N, S atoms and effective core potential (ECP) LANL2DZ and its accompanying basis set for Ti atom for both geometry optimizations and frequency calculations. None of the frequency calculations generated imaginary frequencies, indicating that the optimized geometries are true energy minima. Electronic populations of the HOMO and LUMO are calculated to show the position of the localization of electron populations along with the calculated molecular orbital energy diagram. As for the absorption, coulomb-attenuating method CAM-B3LYP [48] functional was chosen to calculate the vertical excitation energies and the oscillator strengths [49] within the framework of TD-DFT. The solvent effect of ethanol (the solvent used to record the experimental spectra) on the absorption spectra, was considered using nonequilibrium implementation of the conductor-like polarizable continuum model (CPCM), which returns valid solvent effects when there are no specific interactions between the solute and the solvent molecules [50]. All calculations have been performed with the Gaussian 09 packages [51].

3. Results and discussion

3.1. Synthesis and characterization of the new dyes

The synthesis of the two new triphenylamine-based organic dyes **CD-4** and **CD-6** is outlined in Scheme 2. The two dyes **CD-4** and **CD-6** were synthesized by the similar stepwise synthetic protocol. First, compound **2** was prepared according to the reported literature (as shown in Scheme 2). Then 4,4'-dimethoxybenzil and 2,2'-thenil were reacted with compound **2** and ammonium acetate in the acetic acid, respectively, which got compounds **3**, **4**. Finally, compounds **3**, **4** with about three fold excess of 2-cyanoacetic acid afforded the target dyes **CD-4** and **CD-6** in acetonitrile using piperidine as catalyst. The structures of all dye molecules were characterized unambiguously with proton nuclear magnetic resonance (¹H NMR) spectroscopy and mass analysis.



Fig. 1. Absorption spectra of CD-4 and CD-6 in ethanol.

3.2. Optical properties

The UV—vis absorption spectra of the dyes **CD-4** and **CD-6** are shown in Fig. 1, and the corresponding data are summarized in Table 1.

In ethanol solution, **CD-4** and **CD-6** exhibit two major bands appearing at 339–405 nm and 338–411 nm, respectively. The former is ascribed to a localized aromatic π – π * transition and the later is of charge-transfer character between the triphenylamine donating unit and the anchoring moiety. Noticeably, the dye **CD-4** has stronger absorption than that of **CD-6** over the entire absorption range. This result indicates that the imidazole derivative in **CD-4** has stronger electron donating ability than that of the imidazole derivative in **CD-6**. The molar extinction coefficients of the maximum absorption wavelengths (λ_{max}) for the two dyes are clearly high, which indicates good light harvesting abilities (see Fig. 1).

The absorption spectra of **CD-4** and **CD-6** on the surface of 5 μ m thick TiO₂ are shown in Fig. 2. When the two dye molecules are adsorbed on the TiO₂ films, the absorption peaks broaden, and are more or less red-shifted compared to those in ethanol solution, indicating strong interactions between the dyes and the TiO₂ surface, which should favor the light harvesting of the solar cells and thus increase the photocurrent response region. The red-shifted spectra of **CD-4** and **CD-6** may result from J-type aggregation [52] of the dyes on TiO₂ surface. Additionally, the λ_{max} of **CD-6** on TiO₂ film is red-shifted 30 nm in comparison to that in ethanol solution while **CD-4** shows a red shift of 25 nm, indicating that **CD-6** has a more tendency to form J-type aggregation on TiO₂ surface. Thus, the introduction of imidazole derivative bearing thiophene group is

Table 1

UV-vis and electrochemical data.

| Dye | $\lambda_{max}^{a}/nm(\varepsilon^{b}/M^{-1} \text{ cm}^{-1})$ | λ _{max} ^c /nm | E _{ox} ^d /V (vs. NHE) | Eg ^e /eV | E _{red} ^f /V (vs. NHE) |
|------|--|-----------------------------------|--|---------------------|---|
| CD-4 | 405 (28,979) | 430 | 1.08 | 2.55 | -1.47 |
| CD-6 | 411 (24,873) | 441 | 1.15 | 2.46 | -1.31 |

 a Absorption is measured in ethanol solutions (1.0 \times 10 $^{-5}$ M) at room temperature.

^b The molar extinction coefficient at λ_{max} of the absorption spectra.

^c Absorption spectra of the dyes adsorbed on TiO₂ electrodes.

^d E_{ox} was measured in DMF with 0.1 M *n*-Bu₄NPF₆ as electrolyte (scanning rate: 50 mV/s, working electrode and counter electrode: Pt wires, and reference electrode: Ag/AgCl), potentials measured vs. Ag/AgCl were converted to normal hydrogen electrode (NHE) by addition of +0.2 V.

 $^{\rm e}$ $E_{\rm g}$ was estimated from the absorption spectra of TiO₂ electrodes sensitized by the dyes.

 $^{\rm f}$ $E_{\rm red}$ was calculated from $E_{\rm ox} - E_{\rm g}$.



Fig. 2. Absorption spectra of TiO₂ films sensitized by CD-4 and CD-6.



Fig. 3. Plot of $(ahv)^2$ vs. hv.

advantage to form the J-type aggregation for the corresponding triphenylamine dyes on TiO₂ surface.

Based on the Tauc relation, the energy gap (E_g) can be obtained by plotting $(ahv)^2$ vs. hv and extrapolating the linear portion of



Fig. 4. Cyclic voltammograms of CD-4 and CD-6 dissolved in DMF.



Fig. 5. Schematic energy levels of ${\bf CD-4}$ and ${\bf CD-6}$ based on absorption and electrochemical data.

 $(ahv)^2$ to zero as shown in Fig. 3 [45]. The E_g of **CD-4** and **CD-6** are estimated to be 2.55 eV and 2.46 eV, respectively. The bigger red shift of **CD-6** adsorbed on TiO₂ film can be evidenced by the lower energy band-gap as compared with that of **CD-4**.

3.3. Electrochemical properties

Cyclic voltammograms were performed to evaluate the possibility of electron transfer from the excited dye molecule to the CB of TiO_2 and the regeneration of oxidized sensitizers. Cyclic voltammetry measurements were performed in dimethylformamide



3.4. Theoretical calculations

The ground state geometries and molecular orbital spatial distributions from HOMO - 1 to LUMO for **CD-4** and **CD-6** before and

Side of view



Fig. 6. The optimized ground state geometries for CD-4 and CD-6 before and after binding to (TiO₂)₉ in vacuum.

Front of view

after binding to (TiO₂)₉ in vacuum are shown in Figs. 6 and 7, respectively. As shown in Fig 6, the imidazole ring and phenyl ring of the triphenylamine core is coplanar, expressing strong conjugation degree, which is advantage to electron transfer from auxiliary electron donor to triphenylamine core. The dihedral angel between two substituents at positions 4 and 5 of the imidazolyl ring in **CD-4** and **CD-6** are 69.0° and 42.6°, respectively. So, **CD-4** shows a better steric hindrance, indicating that it has the better ability of anti-aggregation on the TiO₂ surface, which is very important to improve the performances of DSSCs. When the two dyes are bonded to (TiO₂)₉ cluster, the Ti–O bonds of **CD-4**–(TiO₂)₉ and **CD-6**– $(TiO_2)_9$ are about 2.04 Å, suggesting that the two dyes could adsorb on the TiO₂ anatase (101) surface firmly. As shown in Fig 7, it is found that HOMOs of CD-4 and CD-6 are mainly localized on the auxiliary donor and triphenylamine area, whereas LUMOs are distributed at the 2-cyanoacetic acid units and neighbor benzene ring, which indicates that there are good electronseparated states between HOMOs and LUMOs. The LUMOs of the two dyes are mainly distributed at the anchoring group (-COOH), which could lead to a strong electronic coupling with TiO₂ surface and boost the electron injection efficiency. Thus, the HOMO \rightarrow LUMO excitation induced by light irradiation could move the excited electron from the auxiliary donor and triphenylamine unit to the 2-cyanoacetic acid, and injected into the CB of TiO₂ through the anchoring group. In order to prove the conclusion, the HOMO – 1, HOMO and LUMO of dyes–(TiO₂)₉ complex were also studied. As shown in Fig. 7, there is the electron distribution mostly delocalized on the dve molecule in the HOMO and HOMO -1. whereas the LUMO shows injected electron delocalized dominantly on the (TiO₂)₉ cluster. The result indicates that efficient electron



Fig. 8. The simulated UV-vis absorption spectra for free dyes in ethanol.

injection from LUMOs of dyes to the CB of TiO_2 can be performed through a carboxylic acid acceptor group and the intermolecular charge-transfer (CT) transition takes place in the dye– $(TiO_2)_9$ complex when the dye sensitizers were adsorbed on TiO_2 surface.

The simulated UV–vis absorption spectra by TD-DFT calculations are shown in Fig. 8, and the major electron excitations and corresponding electron transition are listed in Table 2. It can be found that the broad band in 270–500 nm region for **CD-4** is composed of three electron excitations calculated at 396.7, 314.8 and 283.0 nm while **CD-6** is at 393.3 and 304.5 nm. The results



Fig. 7. Electron distributions in HOMO-1, HOMO and LUMO orbitals of CD-4 and CD-6 before and after binding to (TiO₂)₉ in vacuum.

Table 2 Electronic transition configurations, computed excitation energies and oscillator strengths (*f*) for the main optical transitions of the absorption bands in visible and near-UV region for **CD-4** and **CD-6** in ethanol solution (H - 1 = HOMO - 1, H = HOMO, L = LUMO, etc.).

| Dye | Wavelength (nm) | E (eV) | f | Composition | |
|--------------|---|--------------------------------------|--|---|--|
| CD-4 CD-6 | 396.7 314.8 283.0 393.3 304 5 | 3.13 3.94 4.38 3.15 4.07 | 1.3802 0.6197 0.5874 1.3818 0.7778 | $\begin{array}{l} H - 0 \rightarrow L + 0(+49\%) \\ H - 0 \rightarrow L + 1(+66\%) \\ H - 0 \rightarrow L + 2(+67\%) \\ H - 0 \rightarrow L + 2(+67\%) \\ H - 0 \rightarrow L + 0(+57\%) \\ H - 0 \rightarrow L + 2(+68\%) \end{array}$ | $\begin{array}{l} H - 1 \rightarrow L + 0(+41\%) \\ H - 1 \rightarrow L + 0(17\%) \\ H - 1 \rightarrow L + 1(+11\%) \\ H - 1 \rightarrow L + 0(+33\%) \\ H - 1 \rightarrow L + 0(+10\%) \end{array}$ |

correspond well with the experimental results that **CD-4** is at 404, 340 and 291 nm and **CD-6** is at 408 and 340 nm. The simulated absorption spectra have the similar absorption bands to the experimental spectra, which also shows the accuracy of this theoretical calculation. From the view of Table 2, the λ_{max} of **CD-4** correspond to H-0 \rightarrow L + 0(+49%) and H – 1 \rightarrow L + 0(+41%), while **CD-6** is H – 0 \rightarrow L + 0(+57%) and H – 1 \rightarrow L + 0(+33%). By this token, not only λ_{max} of the two dyes come from the transition from the HOMO to LUMO, but also come from the HOMO – 1 to LUMO.

3.5. Photovoltaic properties

The quantum efficiency (QE) and the photocurrent density—photovoltage (J-V) curves of the corresponding DSSCs are shown in Figs. 9 and 10. The detailed photovoltaic parameters are summarized in Table 3.

As shown in Fig. 9, the DSSC based on CD-4 shows a higher QE value in the spectra range of 300-600 nm than that of CD-6, producing a maximum QE of 46.57% at 476 nm. The QE spectra changing tendencies of the dyes are in excellent agreement with their UV-vis absorption spectra. The J-V curves of the DSSCs based on CD-4, CD-6 and N719 performed under simulated AM 1.5 solar irradiation (100 mW cm^{-2}) are shown in Fig. 10, where N719 is included for comparison. According to the data in Table 3, the η values of 4.11% and 1.51% were obtained by the DSSCs based on CD-4 and CD-6, respectively. Under the same measurement conditions, the DSSC based on N719 generated an efficiency of 5.71% $(J_{sc} = 15.24 \text{ mA cm}^{-2}, V_{oc} = 0.65 \text{ V}, \text{ and } ff = 0.57)$. It's clear that the J_{sc} values are in order of **CD-4** (J_{sc} = 8.60 mA cm⁻²) > **CD-6** $(J_{sc} = 5.33 \text{ mA cm}^{-2})$, which are in good agreement with the QE results (Fig. 9) of the two dyes. According to Fig. 10 and Table 3, it is clear that introducing different imidazole derivatives into the formwork of triphenylamine core will give a big difference to the



Fig. 9. The QE spectra of the DSSCs sensitized with CD-4 and CD-6.



Fig. 10. Current density-voltage curves of DSSCs based on CD-4, CD-6 and N719.

photovoltaic performances of DSSCs. In comparison with **CD-6**, both the J_{sc} and V_{oc} values of **CD-4** are improved by introducing the p-methoxyphenyl group rather than thiophene group to imidazole part. The higher J_{sc} of **CD-4** can be deduced from the higher molar extinction coefficient and QE than that of **CD-6**.

To further investigate why dyes CD-4 and CD-6-sensitized solar cells have such a different performance, the adsorbed amount of dyes CD-4 and CD-6 on TiO₂ surface were measured and are shown in Table 3. By desorbing the dye in a basic solution, the dye adsorbed amount was estimated by measuring the absorption spectra of the resultant solution. The concentrations of CD-4 and **CD-6** on TiO₂ surface were determined as 9.73 \times 10⁻⁸ and 2.24×10^{-7} M cm⁻², respectively, which indicates that the J_{sc} value of CD-6-sensitized DSSC should be higher than that of CD-4. However, the measurement result is completely different as the I_{sc} value of CD-6-sensitized DSSC is lower than that of CD-4. This result maybe due to CD-6 having a better planarity on the imidazole unit than that of **CD-4**, which leads to the formation of π -stacked aggregation and further causes CD-6 residing in the adsorbed system rather than attach to the TiO₂ surface. When chenodeoxycholic acid (CDCA) is used as coadsorbent to dissociate the π stacked sensitizer aggregation, the DSSC based on CD-6 afford a higher J_{sc} value (6.26 mA cm⁻²) while that of **CD-4** shows a lower J_{sc} value (7.99 mA cm⁻²). The result indicates that **CD-4** has a better ability of anti-aggregation than **CD-6**, which is in accordance with above analysis for the adsorbed amount of the dyes. The best performance in this work was observed for the device made with CD-4, which exhibited a J_{sc} of 8.60 mA cm⁻², V_{oc} of 0.63 V, ff of 0.75 and η of 4.11%.

3.6. Electrochemical impedance spectroscopy (EIS) analysis

Electrochemical impedance spectroscopy (EIS) analysis [55,56] was performed to study the interfacial charge-transfer processes

| e 3 | | | | | |
|-----------------------|----------|-------|------------------|---------|-----------------|
| ovoltaic performances | of DSSCs | based | on CD-4 , | CD-6 an | d N719 . |

Tabl

Phot

| Dye | $J_{sc}/mA \ cm^{-2}$ | V _{oc} /V | ff | Adsorbed amount [10 ⁻⁴ mM cm ⁻²] | τ_e/ms | η% |
|----------------------------|-----------------------|--------------------|------|---|----------------------|------|
| CD-4 | 8.60 | 0.63 | 0.75 | 0.973 | 13.5 | 4.11 |
| CD-6 | 5.33 | 0.51 | 0.55 | 2.24 | 2.0 | 1.51 |
| CD-4 + 5 mM CDCA | 7.99 | 0.64 | 0.66 | / | 1 | 3.36 |
| CD-6 + 5 mM CDCA | 6.26 | 0.53 | 0.61 | 1 | / | 2.02 |
| N719 | 15.24 | 0.65 | 0.57 | 1 | / | 5.71 |

in DSSCs based on the different dyes. The Nyquist and Bode plots for **CD-4** and **CD-6**-sensitized cells are shown in Fig. 11a and b, respectively. With the bias voltage applied, the first small semicircle (higher than 10^3 Hz) is attributed to charge-transfer at the Pt/electrolyte interface, the second larger semicircle at lower frequencies (in the 10–100 Hz region) to the charge recombination processes at the TiO₂/dye/electrolyte interface. As shown in Fig. 11a, the radius of second larger semicircle at lower frequencies is in the order **CD-4** > **CD-6**, indicating that the recombination rate is in the order **CD-6** > **CD-4**. This is the main reason why the V_{oc} value of **CD-4** (0.63 V) is higher than that of **CD-6** (0.51 V).

As shown in the Bode phase plots (Fig. 11b), the low-frequency peak is indicative of the charge-transfer process of injected electrons in TiO₂. The higher V_{oc} of **CD-4** can be further explained by electron lifetime. The obtained electron lifetimes of DSSCs based on the **CD-4** and **CD-6** are 13.5 ms and 2.0 ms by the equation $\tau_e = 1/2\pi f$ (*f* is the frequency of the low-frequency peak). The longer electron lifetimes of **CD-4** could explain the significant enhancement in V_{oc} for **CD-4** sensitized cell in comparison with that of **CD-6** (as shown in Table 3). Here, the corresponding imidazole derivative in **CD-4** can increase electron lifetime by 6.75-fold with respect to **CD-6**, indicating that imidazole derivative in **CD-4** is better auxiliary electron donor than that in **CD-6**.



Fig. 11. EIS spectra of DSSCs based on the dyes measured at 0.70 V forward bias in the dark: (a) Nyquist and (b) Bode phase plots.

4. Conclusions

In summary, we have designed and synthesized two new triphenvlamine-based organic dyes, which constituted the 2D $-\pi$ -A structure and were applied in DSSCs. The effects of introducing different imidazole derivatives into the formwork of triphenylamine core on the optical, electrochemical and photovoltaic properties were studied. The DSSC based on **CD-4** has obtained the η value of 4.11% ($J_{sc} = 8.60 \text{ mA cm}^{-2}$, $V_{oc} = 0.63 \text{ V}$, ff = 0.75) while that of **CD-6** has obtained only 1.51%, ($J_{sc} = 5.33 \text{ mA cm}^{-2}$, $V_{oc} = 0.51 \text{ V}$, ff = 0.55). The *I*_{sc} of **CD-4** is higher than that of **CD-6**, which can be deduced from the better molar extinction coefficient and QE. At the same time, the EIS results are in good agreement with the different V_{oc} values of DSSCs based on the two dyes. The higher V_{0c} of **CD-4** can be further explained by the longer electron lifetime. The DFT and TD-DFT calculations are very good to explain the experimental results, especially the simulated UV-vis absorption spectra for the two dyes are in excellent agreement with the experimental UV-vis absorption spectra, which indicates that the theoretical calculation is very important for exploring high efficiency organic dyes. Our findings demonstrate that the corresponding imidazole derivative in CD-4 is very promising electron donor, introducing it into the triphenylamine dye can strongly improve photovoltaic performance. Although the overall conversion efficiencies of the two dyes are not very high, the results will still afford significant value for future development of efficient 2D $-\pi$ -A sensitizers. Further structural optimization, such as broadening the absorption spectra and tuning the energy levels, is very likely to generate more efficient sensitizers and this work is currently underway in our laboratory.

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