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Photovoltaic performance of solid-state DSSCs sensitized with organic isophorone dyes: Effect of dye-loaded amount and dipole moment

Bo Liu [a,b], Xiaoyan Li [b], Miaoyin Liu [c], Zhijun Ning [a], Qiong Zhang [a], Chen Li [c], Klaus Müllen [c], Weihong Zhu [a,*]

[a] *Shanghai Key Laboratory of Functional Materials Chemistry, Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, PR China*
[b] *College of Chemistry and Material Science, Hebei Normal University, Hebei, Shijiazhuang 050016, PR China*
[c] *Max-Planck-Institute for Polymer Research, Mainz 55128, Ackermannweg 10, Germany*

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ABSTRACT

Two isophorone sensitizers (**S4** and **D-3**) were utilized in solid-state dye-sensitized solar cells (DSSCs) using *spiro*-OMeTAD as hole-transporting material. The dye-loaded amount of **D-3** was almost 1.5 times as that of **S4** which lead to higher light harvesting efficiency than **S4**. Moreover, the larger dipole moment along the direction for **D-3** could cause more negative charges located close to the TiO_2 surface than that of **S4**, resulting in a larger conduction band (CB) upshift of TiO_2 for **D-3** which was beneficial to an increase of V_{oc}. Promising results sensitized by **D-3** in solid-state DSSCs were achieved with a short-circuit photocurrent density ($J_{sc)}$) of 3.4 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 760 mV, a fill factor (*FF*) of 0.71, and an overall efficiency (η) of 1.92% while ruthenium dye **N3** produced a η of 2.55% under the same conditions (AM 1.5, 100 mW cm^{-2}).

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted intense interest due to their achievements of high performance in converting solar energy to electricity at low cost [1–4]. As the critical component of DSSCs, both ruthenium complexes [5,6] and metal-free organic dyes [7–13] have been investigated as sensitizers in the past decades. The ruthenium sensitizers exhibit a high solar-to-electrical energy conversion efficiency up to 11% under AM 1.5 irradiation by using I/I_3^- liquid electrolyte. However, the application of I/I_3^- liquid electrolyte brings several problems such as iodine sublimation, degradation of organic sensitizers, and solvent evaporation and leakage that result in critical challenge in hermetic sealing. Moreover, the use of rare metals with the heavy purification brings the major problem in cost and environmental issues. Therefore, it is highly expected to replace the liquid electrolyte DSSCs with a long-life stable solid-state device sensitized by organic dyes [14–18].

As well known, solid-state DSSCs usually produce higher open-circuit photovoltage than that of liquid-electrolyte-based DSSCs due to a smaller energy loss during the dye regeneration process [1]. However, the overall conversion efficiency of solid-state device remains significantly lower than that of liquid-electrolyte-based DSSCs due to the lower short-circuit photocurrent. Accordingly in solid-state DSSCs, it is preferable to explore thin TiO_2 electrode, around 1.5–3.0 μm, to ascertain quantitative collection of the photogenerated charge carriers and complete pore filling by the hole conductor [16]. A sensitizer with high molar extinction coefficient is helpful in pursuing high light capturing capability to compensate the limitation arisen from thin nanocrystalline TiO_2 electrode in solid-state devices.

With this in mind, two isophorone sensitizers (**S4** and **D-3**) were utilized in solid-state DSSCs using *spiro*-OMeTAD (Fig. 1) as hole-transporting material (HTM) which has been demonstrated as the most successful *p*-type organic HTM due to its twisted structure with good amorphism and solubility [19]. Detailed studies based on experimental results and theoretical calculations indicate that in addition with absorption spectra and energy levels, the dye-loaded amount and dipole moment are also very predominated with photovoltaic performance in solid-state DSSCs.

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* Corresponding author.
E-mail address: whzhu@ecust.edu.cn (W. Zhu).

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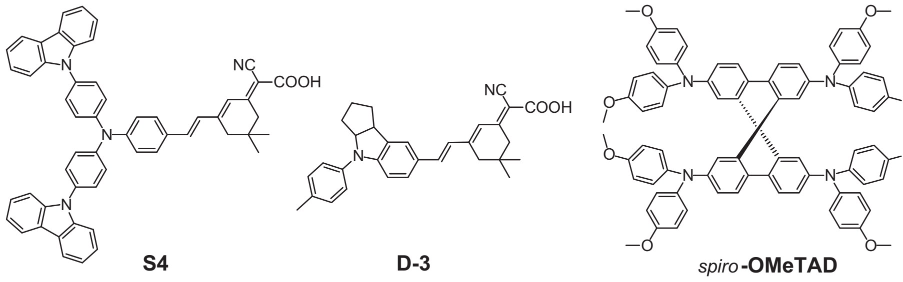

Fig. 1. Chemical structures of **S4**, **D-3**, and *spiro*-OMeTAD.

2. Experimental

The FTO conducting glass (fluorine doped SnO_2, sheet resistance <15 Ω/squire, transmission >90% in the visible) was obtained from Geao Science and Educational Co. Ltd., China. *Spiro*-OMeTAD, $Li(CF_3SO_2)_2N$ and *tert*-butylpyridine (TBP) were purchased from Aldrich. All the other solvents and chemicals with reagent grade were produced by Sinopharm Chemical Reagent Co., Ltd., China and used as received. UV–visible spectra were determined with a Varian Cary 500 spectrometer. Fluorescent spectra were recorded on Varian Cary Eclipse spectrometer. The cyclic voltammogram was determined with a Versastat II electrochemical workstation (Princeton Applied Research) using the dye-loaded TiO_2 electrode as working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution, 0.1 M tetrabutylammonium hexafluorophosphoric was used as supporting electrolyte. After the measurement, ferrocene was added as the internal reference for calibration. The dye-loaded amount was determined by desorbing the dye from surface of TiO_2 electrodes into NaOH solution and analyzed with UV–visible absorption spectrometer. The synthesis of **S4** and **D-3** were described previously [20,21].

2.1. Preparation of dye-sensitized nanocrystalline TiO_2 electrode

TiO_2 colloidal dispersion (100–150 g dm^{-3}) containing 40 wt% poly(ethylene glycol) (MW 20,000) was prepared by following the procedure reported in the literature [1] except that autoclaving was performed at 220 °C instead of 200 °C. Films of nanocrystalline TiO_2 colloidal on FTO were prepared by sliding a glass rod over the conductive side of the FTO. The thicknesses of TiO_2 film are controlled by adhesive tapes with different thickness and determined to be 1.5 μm. Sintering was carried out at 450 °C for 30 min. These films were soaked in the 0.2 M aqueous $TiCl_4$ solution overnight in a closed chamber. After washed with deionized water and fully rinsed with ethanol, the electrode was heated again at 450 °C followed by cooling to 80 °C and dipping into 0.3 mM solutions of **D-3**, **S4** and ruthenium dye **N3**, respectively, in ethanol for 12 h at room temperature. The dye-loaded nanocrystalline TiO_2 electrode was afforded after washed with ethanol and dried.

Spiro-OMeTAD was used as HTM. A solution of *spiro*-OMeTAD (0.2 M) containing *tert*-butylpyridine (TBP, 0.1 M) and $Li(CF_3SO_2)_2N$ (0.2 M) as additives is then applied on the porous dye-loaded electrode. After allowing the solution to permeate partially for 1 min, it was then spin-coated at 1500 rpm for 30 s to form the hybrid heterojunction. The counter electrode was formed by vacuum evaporation of a gold film.

2.2. Photovoltaic performance measurements and characterization of DSSCs

The photovoltaic performances of the solar cells were measured under AM 1.5 irradiation (Newport Co., Ltd., 100 mW cm^{-2}). The photocurrent action spectra were measured with a Model SR830 DSP Lock-In Amplifier and a Model SR540 Optical Chopper (Stanford Research Corporation, USA) and other optical system. The active area of solar cells were 6.0 mm^2 controlled by a metal mask. Each value was an average of three samples.

3. Results and discussion

3.1. Photophysical and electrochemical properties

The sensitizers in DSSCs always play a great important role in realizing high power conversion efficiency. Generally, the efficiency of metal-free organic DSSCs can be improved by two channels: (i) improving short-circuit photocurrent density (J_{sc}) via increasing spectral response and molar extinction coefficients; (ii) increasing open-circuit photovoltage (V_{oc}) via tuning orbital levels. Accordingly, it is very flexible in molecular designs for metal-free organic sensitizers to improve the photovoltaic properties of DSSCs. Absorption peaks (λ_{max}) in $CHCl_3$ are observed at 480 and 532 nm in visible region for **S4** and **D-3**, respectively, corresponding to the typical intramolecular charge transfer (ICT) band (Fig. 1). Their molar extinction coefficients are determined to be 2.50×10^4 M^{-1} cm^{-1} at 480 nm (S4) and 3.52×10^4 M^{-1} cm^{-1} at 532 nm (**D-3**). Obviously, the donor indoline unit can exhibit better absorption performance with respect to triphenylamine unit. As known, the nano-TiO_2 electrode used in solid-state DSSCs is very thin (1.5–3.0 μm). Thus, a higher molar extinction coefficient is preferred. When adsorbed on TiO_2, the absorption of both dyes was broadened (Fig. 2 inset) and hypsochromically shifted to different extents. In contrast, the absorption thresholds are bathochromically shifted to about 700 nm. Notably, after anchoring on 1.5 μm

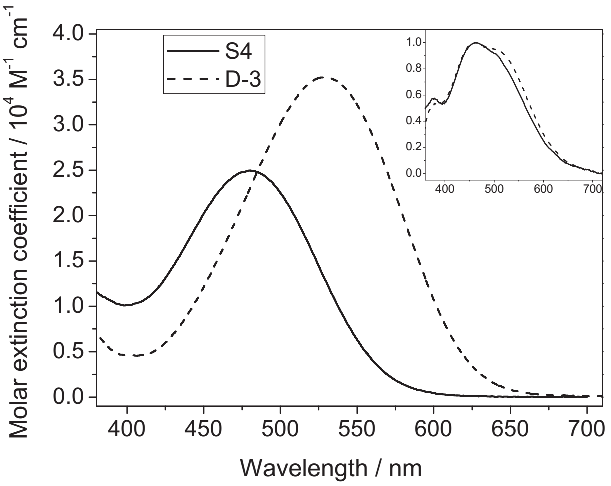

Fig. 2. Absorption spectra of **S4** and **D-3** in $CHCl_3$ and on 1.5 μm TiO_2 film (inset).

TiO_2, the spectral shape of **S4** and **D-3** almost becomes same in visible region (Fig. 2 inset), which means more serious H-aggregation was happened to **D-3** compared to **S4**.

Moreover, the tuning of HOMO energy levels in **S4** and **D-3** can be conveniently realized by alternating the donor moiety. Based on cyclic voltammograms, the HOMO level of **S4** and **D-3** are 1.31 and 0.92 V (*vs* NHE), respectively, suggesting that the oxidized dyes can accept electrons from *spiro*-OMeTAD (0.81 V *vs* NHE) [22] and regenerate efficiently. Also, the LUMO levels of **S4** and **D-3** are corresponding to −0.86 and −0.85 V (*vs* NHE), which are more negative than the E_{cb} of TiO_2 (−0.5 V *vs* NHE), thus ensuring that the injection of excited electrons to the conduction band (CB) of TiO_2 is thermodynamically favorable. Approximately, same LUMO levels of two dyes may lead to the same driving force of electron injection.

3.2. Studies on photovoltaic performances

The solid-state DSSCs were fabricated with a thin film (1.5 μm) of nanocrystaline-TiO_2 electrode using *spiro*-OMeTAD as HTM, and the preliminary results are shown in Fig. 3 and summarized in Table 1. It is interesting to find that solid-state DSSCs sensitized with **S4** and **D-3** showed quite different results. Compared with **D-3**, the sensitizer of **S4** produced much lower J_{sc} and V_{oc}, 2.19 mA cm^{-2} and 689 mV, respectively, and the overall power conversion efficiency (η) of **S4** is 0.97% (Table 1). In contrast, the η of **D-3** is 1.92%, which is 2 times as high as **S4**. As a reference, ruthenium dye **N3** produced a η of 2.55% under the same conditions (AM 1.5, 100 mW cm^{-2}).

Table 1
Photovoltaic performance of solid-state DSSCs sensitized with different sensitizers using *spiro*-OMeTAD as HTM (AM 1.5, 100 mW cm^{-2}).

Sensitizers	J_{sc}/mA cm^{-2}	V_{oc}/mV	*FF*	η %
S4	2.19	689	0.64	0.97
D-3	3.40	760	0.71	1.92
N3	6.81	760	0.48	2.55

As well known, besides absorption spectrum and molar extinction coefficient, the dye-loaded amount of sensitizer also has great effect on the light harvesting efficiency (LHE). Thus, we evaluated the dye-loaded amounts and LHE of both dyes. Due to the large influence of systematic deviation on such thin TiO_2 electrode (1.5 μm), we determined the dye-loaded amounts of both dyes on 6 μm TiO_2 electrode, which would not affect the comparison of two sensitizers. The dye-loaded amount was determined by desorbing the dye from surface of TiO_2 electrode into NaOH solution and analyzed with absorption spectrometer. As a result, there were 3.5×10^{-8} mol of **S4** adsorbed on 1 cm^2 TiO_2 electrode while 5.1×10^{-8} mol of **D-3** were adsorbed on the same area, suggesting that less amount of **S4** molecules have adsorbed on unit TiO_2 and acted in the process of light harvesting due to its relatively large molecular size with two star-burst triphenylamine units, which would also take place in the situation utilizing 1.5 μm TiO_2 as electrode.

$$\mathrm{LHE} = 1 - 10^{(-A)} \tag{1}$$

where A is the absorption intensity of dye-loaded TiO_2. According to the definition of LHE (Eq. (1)), the corrected LHE curves are roughly 80% of values, arisen from 20% loss in absorption light and reflection from the FTO-coated substrate [14]. Obviously, due to the higher molar extinction coefficient and larger dye-loaded amount, the LHE values of **D-3** were higher than those of **S4** in all visible region. As shown in Fig. 4, for **D-3**, there was a broad absorption flat with high LHE values (>60%) from 425 to 540 nm, where were around only 40% in the same area for **S4**. As a result, the higher LHE values could guarantee better light harvesting capability for the thin nanocrystalline TiO_2 electrode (1.5 μm), which was critically required for high efficient solid-state DSSCs. In short, being comparable in other conditions, **D-3** with higher LHE could capture much more photons on unit area TiO_2 electrode, resulting in a reasonably higher J_{sc}.

3.3. Analysis with theoretical calculations

There was also much difference between two dyes regarding to V_{oc}. Comparing with **S4** (689 mV), the V_{oc} of **D-3** was increased to 760 mV (Table 1). Generally, the V_{oc} is greatly dependent upon the difference between the conduction band (CB) energy level of TiO_2 and the redox potential of HTM, while the dark-current generated from the recombination of electrons also has a great effect on it. Thus, the upshift in CB energy level and the prevention of charge recombination can efficiently enhance the photovoltage [17]. It is believable that larger dipole moment along the direction from sensitizer to TiO_2 (vertical) could suppress the dark-current more effectively, thus resulting in an

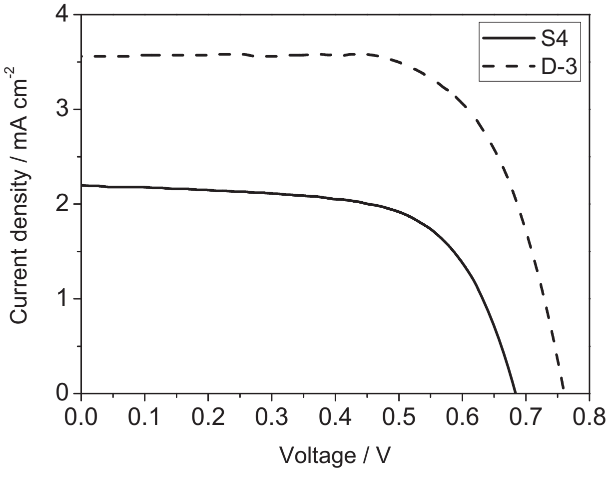

Fig. 3. Photovoltaic performance of solid-state DSSCs sensitized by **S4** and **D-3** using *spiro*-OMeTAD as HTM.

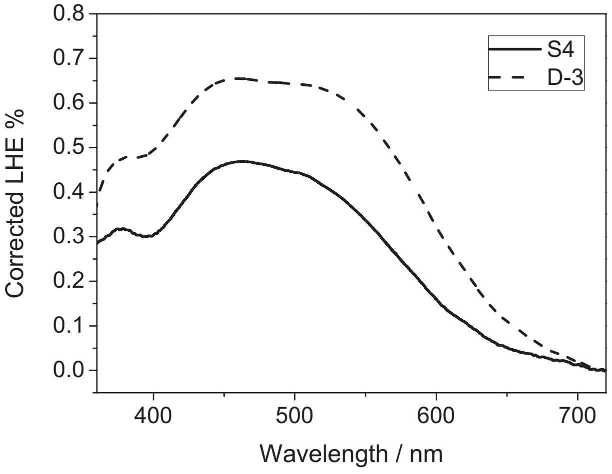

Fig. 4. Corrected LHE of **S4** and **D-3** on 1.5 μm TiO_2.

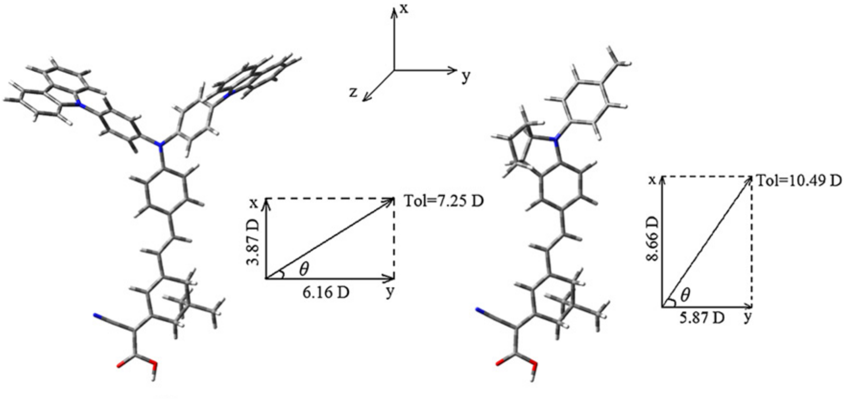

Fig. 5. Optimized geometrical structures and calculated total dipole moments of **S4** and **D-3**.

increase in open-circuit voltage [23]. Here the V_{oc} difference (71 mV) between **S4** and **D-3** can be arisen from the dipole moment analysis. Thus we further calculated dipole moments and adsorption angles with their optimized geometry by hybrid density functional theory (B3LYP) with 6-31G* basis set as implemented in the Gaussian 03 program [24].

As shown in Fig. 5 and Table 2, the *z*-axis extends out of the plane of the page and the TiO_2 surface plane is parallel to the *y*- and *z*-axis. Considering their bidentate binding mode, the dye molecules are positioned in such way that the C_2 axis of carboxylate group is parallel to the *x*-axis. The anchored orientations of **S4** and **D-3** on TiO_2 were simulated, and the components of dipoles parallel to the *z*-axis were fixed at zero [25]. The vertical component of dipoles (*x* components) of **S4** and **D-3** possessed the same direction but with different magnitude of 3.87 and 8.66 D, respectively (Table 2). Once adsorbed on TiO_2, the larger dipole moment along the direction for **D-3** could lead to more negative charges located close to the TiO_2 surface than that of **S4**, resulting in a larger CB energy level upshift [17].

Meanwhile, the adsorption angle θ was increased from 32.14° (**S4**) to 55.87° (**D-3**) when the donor segment was changed from two star-burst triphenylamine to indoline group (Table 2). As reported, the adsorption form can affect the interfacial charge recombination to a considerable extent in liquid electrolyte DSSCs [25–27]. In the solid-state DSSCs sensitized with **S4** and **D-3**, the blocking moiety would be inclined to the surface of TiO_2 when the adsorption angle θ is too small, that is, the π-conjugated system would be exposed to the HTM (*spiro*-OMeTAD), resulting in charge recombination between *spiro*-OMeTAD and excited electrons of sensitizers. Moreover, while the adsorption angle θ became smaller, the HTM molecules were brought very close to TiO_2 by the low-lying binding site, resulting in an increase in the interfacial charge recombination. Consequently, a large adsorption angel θ is preferred to suppress the dynamic charge recombination, that is, the more favorable dipole moment and adsorption form of **D-3** can lead to a larger CB upshift in energy level and more effective suppression of charge recombination, which in turn results in a higher V_{oc} than that of **S4**.

Table 2
Calculated dipole components for **S4** and **D-3**.

	Dipole moments/*D*			θ
	x	*y*	total	
S4	3.87	6.16	7.25	32.14°
D-3	8.66	5.87	10.49	55.87°

4. Conclusions

In summary, two isophorone dyes (**S4** and **D-3**) were successfully applied as sensitizers in solid-state DSSCs. Detailed studies based on experimental results and theoretical calculations indicated that besides absorption spectra and energy levels, the dye-loaded amount, dipole moment and adsorption form were also very important factors of photovoltaic performance. **D-3** could capture more photons on unit area TiO_2 electrode due to higher LHE, resulting in a reasonably higher J_{sc}. The more favorable dipole moment and adsorption form of **D-3** leaded to a larger CB upshift in energy level and more effective suppression of charge recombination, which in turn results in a higher open-circuit photovoltage than that of **S4**. The encouraging performances sensitized with **D-3** in solid-state DSSCs were achieved with a J_{sc} of 3.4 mA cm^{-2}, a V_{oc} of 760 mV, a *FF* of 0.71, and an overall efficiency η of 1.92% while **N3** produced a η of 2.55% under the same conditions (AM 1.5, 100 mW cm^{-2}).

Acknowledgments

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