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Novel dyes based on naphthalimide moiety as electron acceptor for efficient dye-sensitized solar cells

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1. Introduction

Dye-sensitized solar cells (DSCs) have attracted great attention due to their relative high power conversion efficiency and low cost with respect to conventional inorganic photovoltaic devices [1–4]. DSCs based on Ru dyes have been intensively investigated and shown efficiencies up to 11% at simulated AM 1.5G irradiation [5–10]. However, the utilization of rare and expensive metals with substantial purification brings the major problem in cost. Therefore, an increasing attention has been directed to the application of metal-free organic dyes [11,12]. Several organic sensitizers based on coumarin [13–16], indoline [17,18], perylene [19–21], cyanine [22,23] and triphenylamine [24–26] derivatives have been developed as promising candidates with the high power conversion efficiency, and even realizing efficiencies higher than 9% [27–29].

1,8-Naphthalimide and its derivatives with a strong electronwithdrawing imide group have been extensively investigated due to their quite good chemical stability, a large Stokes shift, and high fluorescent quantum yield, known to act as solar energy collectors,

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ABSTRACT

Four novel naphthalimide-based dyes (D-1, D-2, D-3 and D-4) were synthesized and utilized as sensitizers in dye-sensitized solar cells (DSCs), in which the triphenylamine (TPA) or indoline groups, naphthalimide unit and carboxylic group were functionalized as electron donor, acceptor and anchoring group, respectively. The naphthalimide unit was employed as the π -conjugation ring and electron acceptor for effectively realizing intramolecular charge separation in the oxidized states. In the series of dyes, the LUMO orbital is delocalized mainly on naphthalimide moieties, especially on the carbonyl group. Consequently, the LUMO electrons are isolated from the carboxyl anchoring group (-CH₂CO₂H) due to the presence of the methylene group, which could suppress the electron injection efficiency from the excited dyes to the TiO₂ conduction band, thus leading to the inferior efficiencies of 1.10, 1.18, 2.27 and 2.70%, respectively, even though they exhibit broad spectral response and high extinction coefficients.

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supramolecular moieties for the study of photo-induced electron transfer, fluorescence switcher, liquid crystal displays, and electroluminescent (EL) materials [30–36]. Naphthalimide dyes as a kind of metal-free dves for DSCs have also been reported by our group. however, the unfavorable electron flow makes it a lower efficiency [37]. Meanwhile, the indoline unit has been demonstrated to possess a stronger electron-donating ability than triphenylamine (TPA) unit, giving remarkable power conversion efficiency as high as 9.52% under AM 1.5 [14]. Bearing these considerations in mind, we designed and synthesized a novel series of organic sensitizers (D-1, D-2, D-3 and D-4 shown in Fig. 1) with carboxylic acid as anchoring group. Essentially, these dyes were designed from the following considerations: i) substituting the TPA group with stronger electron-donating indoline unit to achieve higher *J*_{sc}; ii) improving the open-circuit voltages (V_{oc}) by the introduction of bis-substituted indoline units instead of the mono-substituted; and iii) employing the strong electron-withdrawing properties of imide group in naphthalimide unit as electron acceptor for effectively realizing intramolecular charge separation in the oxidized dye and decreasing the dark current. As demonstrated, we improved the open-circuit voltages (V_{oc}) by the introduction of bis-substituted indoline units instead of the mono-substituted. Moreover, the cell performance is greatly dependent upon the methylene group in the nature of the anchoring group (-CH₂CO₂H), resulting in the





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Fig. 1. Chemical structures of novel dyes (D-1, D-2, D-3 and D-4).

electronic uncoupling of naphthalimide core to the TiO₂ electrode with inferior performance. The naphthalimide dye D-4, which employed two indoline units as donor, exhibited a photoelectron performance with J_{sc} of 5.42 mA cm⁻², V_{oc} of 664 mV, *FF* of 0.75, and an overall conversion efficiency η of 2.70%.

2. Experimental section

2.1. General procedure

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400 and 100 MHz, respectively. HRMS spectra were obtained using a Waters LCT Premier XE spectrometer. UV–vis spectra were determined with a Varain Cary 500 spectrometer. The cyclic voltammograms of dyes were estimated with a Versastat II electrochemical workstation using a normal three-electrode cell with dye-coated TiO₂ electrode as working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution. Tetrabutylammonium hexaflourophosphate (TBAPF₆) 0.1 mol L⁻¹ was used as the supporting electrolyte in CH₂Cl₂.

2.2. Materials

Optically transparent FTO conducting glass (fluorine doped SnO₂, sheet resistance < 15 Ω /square, transmission > 90% in the visible) was obtained from the Geao Science and Educational Co. Ltd. of China and cleaned by a standard procedure. Titanium (IV) isopropoxide and 3-methyl-2-oxazolidinone were purchased from Aldrich. Lithium iodide was from Fluka. All other solvents and chemicals used were produced by Sinopharm Chemical Reagent Co., Ltd., China

(reagent grade) and used as received. The starting material of 4-bromo-1,8-naphthalic anhydride is commercially available.

2.3. Preparation of dye-sensitized nanocrystalline electrode TiO₂

The dye-sensitized TiO₂ electrode was prepared via a modified procedure reported in the literature [38]. A screen-printed double layer of TiO₂ particles was used as photoelectrode. A 3 μ m thick film of 13 nm sized TiO₂ particles (Ti-Nanoxide T/SP) was first printed on the FTO conducting glass and further coated by a 4 µm thick second layer of 400 nm light-scattering anatase particles (Ti-Nanoxide 300). Sintering was carried out at 275, 325 and 375 °C for 5 min, 450 and 500 °C for 15 min, respectively. Before immersed in the dye solution, these films were soaked in 0.2 mol L^{-1} aqueous TiCl₄ solution overnight. After washed with deionized water and fully rinsed with ethanol, the films were heated again at 450 °C for 30 min, followed by cooling to 80 °C and dipping into a 3×10^{-4} mol L⁻¹ solution of dyes in methanol-chloroform (4:1, v/v) for 12 h at room temperature. To prepare the counter electrode, the Pt catalyst was deposited on the cleaned FTO glass by coating with a drop of H₂PtCl₆ solution (0.02 mol L^{-1} in 2-propanol solution) with the heat treatment at 400 °C for 15 min. A hole (0.8 mm diameter) was drilled on the counter electrode by a Drill-press. The perforated sheet was cleaned by ultrasound in an ethanol bath for 10 min.

In the assemblage of DSCs, the dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt gasket of 25 mm thickness made of the ionomer Surlyn 1702 (Dupont). The redox electrolyte was injected through a pre-drilled hole in the counter electrode by capillary force and driven into the cell by means of vacuum backfilling, then the hole in the counter electrode was sealed by a film of Surlyn 1702 and a cover glass (0.1 mm thickness) using a hot iron bar. The electrolyte employed was a solution of 0.6 mol L⁻¹ BMII (1-butyl-3-methyl imidazolium iodide), 0.1 mol L⁻¹ LiI, 0.05 mol L⁻¹ I₂, 0.5 mol L⁻¹ TBP (4-tertbutylpyridine) in acetonitrile.

2.4. Photoelectrochemical measurements

The photocurrent action spectra were measured with a Model SR830 DSP Lock-In Amplifier and a Model SR540 Optical Chopper (Stanford Research Corporation, USA), a 7IL/PX150 xenon lamp with power supply, and a 7ISW301 Spectrometer. The irradiation source for the photocurrent density–voltage (J–V) measurement is an AM 1.5 solar simulator (91160, Newport Co., USA). The incident light intensity was 100 mW cm⁻² calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.159 cm². Volt–current characteristics were performed on Model 2400 Sourcemeter (Keithley Instruments, Inc., USA).

2.5. Synthesis of D-1, D-2, D-3 and D-4

Synthesis of D-1.1-benzhydryl-4-bromobenzene (1.0 g, 3.1 mmol) was dissolved in dry THF (20 mL) under nitrogen and cooled to $-78 \degree C n$ -Butyllithium (2.5 M in hexanes, 1.85 mL, 4.63 mmol) was added dropwise and the mixture was stirred at $-78 \degree C$ for 45 min, then B(OCH₃)₃ (2.1 mL, 9.30 mmol) was added dropwise and the mixture was allowed to warm up slowly to room temperature and used for the next Suzuki coupling reaction without purification. The unpurified mixture was reacted with compound 2 (0.22 g, 0.63 mmol) under Suzuki coupling reaction using Pd(PPh₃)₄ (0.18 g, 0.15 mmol) and K₂CO₃ aqueous solution (3 mL, 2 mol L⁻¹) as catalysts in THF (15 mL) for 12 h. After cooling, the solvent was removed in vacuo and the residual material was extracted with CH₂Cl₂. The organic phase was washed with water and brine, and dried over

Na₂SO₄. After evaporation of the solvent, the crude product was used for the next hydrolysis reaction without further purification.

To a THF solution (15 mL) of crude product 5 was added a 1 mol L⁻¹ aqueous lithium hydroxide solution (10 mL). The mixture was reacted at room temperature for 24 h. After the removal of most THF, the reaction mixture was neutralized with 1 mol L⁻¹ HCl, and then filtered to give yellow solid product. The crude product was purified by silica gel column chromatography (CH₂Cl₂/MeOH = 15:1 v/v) to give D-1 as a yellow solid (0.13 g, 48% for two steps). ¹H NMR δ (400 MHz, DMSO-d₆): 8.54 (d, *J* = 7.4 Hz, 2H), 8.41 (d, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.15 (m, 8H), 4.44 (s, 2H). ¹³C NMR δ (100 MHz, DMSO-d₆): 168.44, 168.21, 152.92, 151.99, 150.91, 137.51, 136.58, 136.22, 135.89, 135.61, 134.98, 134.43, 133.31, 133.00, 132.59, 129.99, 129.04, 127.74, 127.12, 126.09, 48.54. HRMS (ESI) calcd for C₃₂H₂₁N₂O₄ [M - H]⁺ 497.1501, found 497.1499.

The Synthesis of D-2, D-3 and D-4 were followed according to the procedure as described above for the synthesis of D-1.

D-2. (0.15 g, 45% for two steps), ¹H NMR δ (400 MHz, DMSO-d₆): 8.53 (m, 2H), 8.47 (d, J = 8.4 Hz, 1H), 7.87 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.37 (s, 1H), 7.25 (m, 5H), 6.99 (d, J = 8.4 Hz, 1H), 4.95 (m, 1H), 4.64 (s, 2H), 3.92 (m, 1H), 2.3 (s, 3H), 2.07 (m, 1H), 1.82 (m, 3H), 1.65 (m, 1H), 1.46 (m, 1H). ¹³C NMR δ (100 MHz, DMSO-d₆): 163.38, 163.14, 147.81, 146.79, 139.39, 135.44, 132.62, 131.13, 130.60, 130.50, 129.83, 129.66, 129.23, 128.92, 128.23, 127.71, 127.41, 127.08, 126.29, 122.42, 120.05, 119.87, 106.76, 68.36, 44.50, 43.44, 34.89, 33.07, 24.00, 20.35. HRMS (ESI) calcd for C₃₂H₂₅N₂O₄ [M – H]⁺ 501.1814, found 501.1833.

D-3. (0.10 g, 35% for two steps), ¹H NMR δ (400 MHz, DMSO-d₆): 8.58 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 8H), 7.09 (t, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 8H), 6.98 (d, *J* = 8.4 Hz, 4H), 6.75 (d, *J* = 8.4 Hz, 4H), 4.63 (s, 2H). ¹³C NMR δ (100 MHz, DMSO-d₆): 169.82, 163.08, 146.74, 146.64, 146.19, 134.50, 130.74, 130.47, 130.26, 129.91, 129.53, 127.21, 124.68, 123.66, 120.70, 120.15, 42.62. HRMS (ESI) calcd for C₅₀H₃₄N₃O₄ [M - H]⁺ 740.2549, found 740.2554.

D-4. (0.11 g, 30% for two steps), ¹H NMR δ (400 MHz, CDCl₃): 8.63 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.25–6.54 (m, 14H), 4.95 (m, 2H), 4.52 (s, 2H), 3.63 (m, 2H), 2.31 (s, 6H), 2.07–1.45 (m, 12H). ¹³C NMR δ (100 MHz, CDCl₃): 164.95, 149.09, 147.06, 133.88, 132.24, 131.44, 131.02, 130.62, 130.30, 129.61, 129.11, 127.59, 126.86, 126.25, 125.35, 120.95, 120.04, 106.16, 68.61, 44.97, 43.83, 34.79, 33.11, 24.15, 20.60. HRMS (ESI) calcd for C₅₀H₄₂N₃O₄ [M – H]⁺ 748.3175, found 748.3179.

3. Results and discussion

3.1. Design and synthesis of sensitizers

The sensitizers in DSCs always play a great important role in realizing high power conversion efficiency. Generally, the efficiency of metal-free organic DSCs can be improved by two channels: i) improving J_{sc} via increasing spectral response and molar extinction coefficients; ii) increasing V_{oc} via tuning orbital levels and inhibiting dark current. Accordingly, it is very flexible in molecular designs for metal-free organic sensitizers to improve the photovoltaic properties of DSCs.

In traditional Donor- π -Acceptor (D- π -A) system, herein we introduce the naphthalimide and indoline or TPA unit to sensitizers as electron acceptor and donor, respectively. The incorporation of naphthalimide unit shows several favorable characteristics in the beneficial of light harvesting and efficiency. The imide group with strong electron-withdrawing nature has serious effect on the whole molecular polarity. Compared with traditional acceptors, the electron-withdrawing ability of imide group at the naphthalimide unit

is more powerful, which is even stronger than that of the cvanogroup [39]. Accordingly, the incorporated naphthalimide moiety can be further expected to reinforce the intramolecular charge transfer (ICT) process, which is effective for realizing intramolecular charge separation in the oxidized dye and distinctly decreasing the dark current. Moreover, extending π -conjugated bonding bridges would lower the stability of dve molecules [40]. The introduction of the naphthalimide π -conjugation ring instead of methine unit will simultaneously expand the π -conjugation system and improve the stability of dye molecules. By incorporating the naphthalimide unit directly to the anchoring carboxylic group, the excited electrons will flow directly from the donor moieties to the carboxylic groups which are anchored on nanoporous TiO₂ film, avoiding the unbeneficial transferring direction of photo-generated electrons [37]. What's more, the incorporation of indoline units can be expected to broaden the spectral region of absorption and improve the molar extinction coefficients.

The brief synthetic route of naphthalimide dyes (D-1, D-2, D-3 and D-4) is shown in Fig. 2. The important intermediate of 4,5dibromo-l,8-naphthalic anhydride (10) was prepared by the established literature procedure [41]. The corresponding 1,8-naphthalic anhydrides (1 and 10) were imidated with glycine methyl ester hydrochloride [42]. Mono- and bis-substituted 1,8-naphthalimide derivatives were synthesized through Suzuki cross-coupling with the corresponding boronic acids (3 and 4) utilizing Pd(PPh₃)₄ as catalyst in a biphasic mixture of aqueous K₂CO₃ and THF. Finally, the target dyes were obtained via hydrolysis under basic conditions using a standard protocol [18], which were fully characterized by ¹H NMR, ¹³C NMR and HRMS.

3.2. Optical properties of sensitizers

The absorption spectra of dyes (D-1, D-2, D-3 and D-4) in methanol-chloroform (4:1, v/v) solutions are shown in Fig. 3, and the data are listed in Table 1. All dyes show broad absorption spectra in the visible region. Generally, the absorption bands at around 300 nm can be ascribed to the $\pi - \pi^*$ electron transition, and bands at around 450 nm to the ICT band between TPA or indoline based donor and the naphthalimide-carboxylic acid, resulting in an efficient charge separation excited state [43]. Mono-TPA based D-1 shows the absorption band (λ_{max}) at 419 nm with a relatively low molar extinction coefficient (8200 M⁻¹ cm⁻¹). In contrast, monoindoline based D-2 shows red shift absorption at 458 nm, the bis-TPA based D-3 red shifts to 438 nm with higher molar extinction coefficient (14700 M⁻¹ cm⁻¹). Moreover, the bis-indoline based dye D-4 shows the largest absorption band red shifted to 473 nm. Apparently, the indonline unit has stronger electron-donating capability than that of TPA, and the incorporation of bis-donor unit instead of the mono-donor is further beneficial to the red shift in the absorption band.

In order to monitor the light response, a monolayer of theses dyes was loaded on a thin TiO_2 film (3 µm in thickness). As shown in Fig. 4, the absorption spectra of D-2 and D-4 became broadened significantly with respect to those in methanol-chloroform solution. Notably, the spectral onsets of D-2 and D-4 were extended by 100 and 50 nm, respectively. Consequently, the indoline unit can efficiently decrease the band-gap and optimize energy levels, thus resulting in a longer responsive wavelength to NIR region with several favorable characteristics of the beneficial light harvesting and photocurrent generation in DSCs. Compared to that in solutions, the absorption spectra of mono-donor based D-1 and D-2 on thin TiO₂ film have slightly blue-shifted by 2 and 21 nm, respectively. In contrast, the absorption peaks of bis-donor based dyes D-3 and D-4 on TiO₂ film exhibit a red shift by 4 and 33 nm, respectively.



Fig. 2. Synthetic route of dyes D-1, D-2, D-3 and D-4.

3.3. Electrochemical properties

For highly efficient DSCs, suitable LUMO and HOMO levels of sensitizer are generally required to match the conduction band (E_{cb}) of TiO₂ electrode and the HOMO level of I_3^-/I^- , respectively. That is, the LUMO level must be more negative than the E_{cb} of TiO₂ electrode for the injection of electrons, and the HOMO level must be more positive than the HOMO level of I_3^-/I^- to accept electrons,



Fig. 3. Absorption spectra of dyes D-1, D-2, D-3 and D-4 in methanol-chloroform (4:1, $\nu/\nu).$

and regenerate from the oxidized state [44]. Thus, the electrochemical properties of dyes were studied to clarify their HOMO and LUMO levels, using SCE as a reference electrode, 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte (Table 1). The HOMO levels corresponding to the first oxidation potentials (E_{ox} vs NHE) are 1.08, 0.79, 0.93 and 0.61 V, respectively, which are sufficiently more positive than the I_3/I^- redox potential value. And the LUMO levels are -1.42, -1.45, -1.43 and -1.46 V,

able 1
Optical and electrochemical properties of dyes D-1, D-2, D-3 and D-4.

Dyes	λ_{max}^{a}	$\lambda_{max}{}^{b}$	ϵ at λ_{max}^{a}	HOMO ^c	E_{0-0}^{d}	LUMO
	nm	nm	$M^{-1} cm^{-1}$	V vs NHE	V vs NHE	V vs NHE
D-1	419	417	8200	1.08	2.50	-1.42
D-2	458	437	5100	0.79	2.24	-1.45
D-3	438	442	14700	0.93	2.36	-1.43
D-4	473	506	19000	0.61	2.07	-1.46

^a Maximum absorption in methanol-chloroform (4:1, v/v) solutions.

^b Maximum absorption on TiO₂ film (3 μ m thick)

 $^{\rm c}$ Cyclic voltammetry of the oxidation behavior of the dyes adsorbed on TiO_2 film was measured in dry acetonitrile containing 0.1 M tetrabutylammonium hexa-fluorophosphate (TBAPF₆) as supporting electrolyte (working electrode, dye-coated TiO_2 electrode; reference electrode, a saturated calomel electrode in saturated KCI solution calibrated with ferrocene/ferrocenium (Fc⁺/Fc) as reference; counter electrode, Pt).

^d The zeroth–zeroth transition E_{0-0} values were estimated from the energy at the absorption threshold wavelength of dyes adsorbed on TiO₂.



Fig. 4. Normalized absorption spectra of Dyes D-1, D-2, D-3 and D-4 adsorbed on $\rm TiO_2$ film (3 μm in thickness).

respectively, which are also more negative than E_{cb} of TiO₂ electrode (-0.5 V vs. NHE), indicating that the electron injection process from the excited dye molecule to TiO₂ conduction band is thermodynamically favorable. Notably, the introduction of stronger electron-donating indoline unit can make the HOMO levels in the series of dyes more negative (D-2 < D-1 and D-4 < D-3). Among them, the bis-indoline based D-4 exhibits the highest LUMO level, indicative of high injection driving force to photo-induced electrons.

3.4. Performances of DSCs

Fig. 5 shows the action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for these naphthalimide dyes, obtained from a sandwich-type cell using platinized ITO glass as counter electrodes and 0.5 mol L^{-1} LiI, 0.05 mol L^{-1} I₂, 0.6 mol L^{-1} methylbutylimidazoliumiodide, 0.5 mol L^{-1} *tert*-butylpyridine in acetonitrile solution as electrolyte. D-4 gives broader IPCE spectra than the other three dyes in the spectral range of 400–700 nm, which is in accordance with their absorption spectra on TiO₂ films (Fig. 4). With respect to the mono-donor based dyes D-1 and D-2, both bis-donor based dyes D-3 and D-4 have higher IPCE values which may benefit from their higher LHE.

The photovoltaic performances of solar cells constructed from these organic dye-sensitized TiO_2 electrodes were measured under standard global AM 1.5 illumination (100 mW cm⁻²). Their photovoltaic data as well as N719 are summarized in Table 2, and

Table 2

Performance parameters of dye-sensitized solar cells.^a

Dye	J_{sc} (mA cm ⁻²)	$V_{oc} (\mathrm{mV})$	FF	η (%)
D-1	2.51	597	0.73	1.10
D-2	2.90	594	0.68	1.18
D-3	4.62	662	0.74	2.27
D-4	5.42	664	0.75	2.70
N719	11.95	727	0.68	5.91

^a The listed data are results from the measurement which has the closest values to the average of 6 times.

the corresponding photocurrent-voltage curves are shown in Fig. 6. We obtained a solar energy to electricity conversion efficiency of 1.10% ($J_{sc} = 2.51 \text{ mA cm}^{-2}$, $V_{oc} = 597 \text{ mV}$, FF = 0.73), 1.18% ($J_{sc} = 2.90 \text{ mA cm}^{-2}$, $V_{oc} = 594 \text{ mV}$, FF = 0.68), 2.27% ($J_{sc} = 4.62 \text{ mA cm}^{-2}$, $V_{oc} = 662 \text{ mV}$, FF = 0.74) and 2.70% ($J_{sc} = 5.42 \text{ mA cm}^{-2}$, $V_{oc} = 664 \text{ mV}$, FF = 0.74) with DSCs based on D-1, D-2, D-3 and D-4, respectively. In contrast with D-1 and D-2, the improved cell performance of D-3 and D-4 can be mainly attributed to the bathochromic shift in the absorption band, resulting in a J_{sc} increase in the high IPCE values.

The short circuit current J_{sc} is always corresponding to the molar extinction coefficient of dye molecules. Compared with D-1, D-2 has a lower molar extinction coefficient, but a higher J_{sc} , which might be probably due to the broader absorption of D-2 (up to 550 nm). However, compared with N719, all the dyes have lower J_{sc} , which might be resulted from the fact that the methylene group in the naphthalimide framework disrupts the π -conjugation between naphthalimide and the carboxylic acid, hence decreasing the electron injection efficiency in a dynamic manner [45].

A larger V_{oc} is also a prerequisite for higher power conversion efficiencies in DSCs. As listed in Table 2, the open-circuit voltages (V_{oc}) of bis-donor based dyes D-3 and D-4 are higher than that of mono-donor based D-1 and D-2, which can be resulted from the retardation of charge recombination at the nanocrystallite/dye/ redox electrolyte interface [46,47]. What's more, the power conversion efficiencies of bis-donor dyes are almost twice higher than those of the corresponding mono-donor dyes due to a better light harvesting ability from the bis-donor dyes. Interestingly, the fill factors (FF) of four dyes are even better than that of N719. Among them, D-4 with bis-indoline units has the highest power conversion efficiency up to 2.70%, further confirming that the indoline substituted dyes are superior to the corresponding TPA substituted ones. And the introduction of multi-donor units is beneficial to the improvement of power conversion efficiencies.



Fig. 5. IPCE action spectra of solar cells sensitized with dyes D-1, D-2, D-3 and D-4 (subtract the affection of TiO_2).



Fig. 6. Photocurrent–voltage curves of solar cells sensitized with dyes D-1, D-2, D-3 and D-4.



Fig. 7. Calculated frontier molecular orbitals of HOMO and LUMO and experimental energy level diagrams of D-1, D-2, D-3 and D-4.

To get a deep insight into the geometrical and electronic properties of DSCs based on these naphthalimide dyes, density functional theory (DFT) calculations [48] were performed by hybrid density functional theory (B3LYP) with 6-31G* basis set as implemented in the Gaussian 03 program for the geometry optimization. The isodensity plots of the frontier molecular orbitals of dyes are shown in Fig. 7. Obviously, the HOMO orbital is almost delocalized over TPA and indoline moieties. But the LUMO is delocalized mainly on the naphthalimide moieties, especially on the carbonyl, and as a result, the position of the LUMO is isolated from the carboxyl anchoring group (-CH₂CO₂H) due to the presence of the methylene group, which could suppress the electron injection efficiency from the excited dyes to the TiO₂ conduction band via the carboxyl group, and thus, leading to the inferior efficiencies of 1.10, 1.18, 2.27 and 2.70%, respectively, even though they exhibit broad spectral response and high extinction coefficients. [49]

4. Conclusions

Four novel dyes (D-1, D-2, D-3 and D-4) with naphthalimide unit as electron acceptor have been designed and synthesized. The design concept reveals the working principle of organic dyes in DSCs. The indonline unit has stronger electron-donating capability than that of triphenylamine, and the incorporation of bis-donor unit instead of the mono-donor is further beneficial to the red shift in the absorption band. The incorporation of the naphthalimide π conjugation ring instead of methine unit could simultaneously expand the π -conjugation system and improve the dye stability. Due to the appropriate energy levels and bathochromic shift in the UV-vis absorption band on TiO₂, bis-indoline dye D-4 showed the solar energy to electricity conversion efficiency of 2.27% (J_{sc} = 4.62 mA cm⁻², $V_{oc} = 662$ mV, FF = 0.74) under AM 1.5 solar simulator (100 mW cm⁻²). In addition, the result also reveals that the uncoupled or nonconjugated anchoring group (-CH₂CO₂H) results in the electronic uncoupling of naphthalimide core to the TiO₂ electrode with inferior performance. Further improvement in the power conversion efficiency sensitized with naphthalimide dyes are undergoing with the modification of anchoring groups.

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