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Stable organic dyes based on the benzo[1,2-b:4,5-b']dithiophene donor for efficient dye-sensitized solar cells

Yi-Fan Chen, Jun-Min Liu, Jian-Feng Huang, Li-Lin Tan, Yong Shen, Li-Min Xiao, Dai-Bin Kuang and Cheng-Yong Su

Two novel nonarylamine type organic compounds (CYF1 and CYF2) incorporating a substituted benzo[1,2-b:4,5-b']dithiophene unit as the electron donor have been synthesized and used as the sensitizers of dye-sensitized solar cells (DSSCs). The relationship between the chemical structure and photovoltaic performance has been investigated. It is found that a higher molar absorption coefficient, longer electron lifetime, and larger adsorption amount are observed for sensitizer CYF1, which contains a single π bridge and anchoring unit, relative to CYF2 with twin π bridges and anchoring units. As a result, under standard global AM 1.5 solar conditions, the device based on CYF1 sensitizer gives a higher conversion efficiency of 8.02% than that based on CYF2, which is the highest value for amine-free organic sensitizers without any strong donor units. Moreover, the CYF1- and CYF2-sensitized DSSCs exhibit excellent stability under 1000 Wm⁻² light soaking at 60 °C for 600 h. This is the first example of organic sensitizers based on benzo[1,2-b:4,5-b']dithiophene donors for efficient dye-sensitized solar cells.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention after Grätzel's report in 1991 due to their low-cost fabrication and design versatility combined with high performance. The sensitizer is one of the key components in DSSCs since it plays a significant role in the power conversion efficiency as well as the device stability. With great efforts, DSSCs based on zine, ruthenium complex and pure organic dyes have reached an overall conversion efficiency of over 13%, 11%, and 12%, respectively. Organic dyes have their unique advantages, such as tunable absorption and electrochemical properties, versatile structural modification, and lower cost than Ru complexes.

Traditionally, the most frequently used organic dyes in DSSCs are based on the arylamines or alkylamines donors. We have also prepared a series of organic sensitizers with triphenylamine and carbazole donors, achieving a highest efficiency of 10% in liquid DSSCs among these dyes. However, organic sensitizers using nonamine donors are still rare. Very recently, we have developed a new class of nonamine dyes based on cone-calix[4]arene donor containing four donor-π-acceptor (D-π-A) units, the conversion efficiencies of which are effectively enhanced compared to the corresponding dyes with a single D-π-A unit. To promote growth of DSSC research, novel organic dyes containing nonamine donors should be tested, which can significantly increase the choice of materials available, facilitate the understanding of DSSCs, and provide new opportunities for the development of good sensitizers. On the other hand, despite the fact amines are strong donors, they are nucleophiles and the lone pair on nitrogen increases their reactivity, resulting in the decrease of their intrinsic stability. Compared with amine-based organic sensitizers, amine-free organic sensitizers using thiophene derivatives as donors are more stable, because the delocalization of holes on the oligothiophene moiety of sensitizer may increase their photo- and chemical-stability.

In recent years there has been increasing interest in sensitizers with multiple-anchoring capability for DSSCs to increase electron extraction channels and enhance binding stability. Some research groups have reported the synthesis of dyes possessing double anchors for DSSCs. The D-(π-A)₂ dyes have higher photocurrent but lower photovoltage than single D-π-A type dyes due to their better light harvesting but inefficient dark current suppression and/or downward shift of the titania conduction band. Therefore, we became interested in organic dyes using an electron-excessive moiety, which can be incorporated into multi-acceptors, as a substitute for arylamines.

The benzo[1,2-b:4,5-b']dithiophene (BDT) unit, consisting of two thiophene rings with a benzene core, has been emerging recently as an attractive donor building block for conjugated polymers or acceptor-donor-acceptor (A-D-A) type molecules used in high performance organic solar cells (OSC) because of their outstanding properties, which include wide absorptions with high coefficients, excellent chemical and thermal stability, and facile structural modification. However, despite the extensive research into the development of OSCs based on
BDT donors, amine-free organic sensitizers using BDT as the electron donor for DSSCs, to the best of our knowledge, have not been reported, though BDT motifs were used in the spacer of arylamine-based dyes.\textsuperscript{11} We therefore set out to design and synthesize two novel sensitizers CYF1 and CYF2, containing a 4,8-bis-(5-(2-ethoxythiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene donor, a 2-cyanacrylic acid acceptor, and a 3,4'-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (CYF-1 CHO). Under a nitrogen atmosphere n-butyl lithium (1.6 M, 0.43 mL, 0.68 mmol) was dropwise added to THF (20 mL) solution of 1 (364 mg, 0.62 mmol) at 0 °C over 10 min. After stirring for 0.5 h, the mixture was warmed to room temperature and stirred for 1 h. Then SnBu₄Cl (241 mg, 0.74 mmol) was injected into the reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and then warmed to room temperature for 20 h. Subsequently, the reaction mixture was poured into ice water and extracted with dichloromethane. The organic phase was dried over anhydrous MgSO₄ and concentrated to afford the yellow crude product tributyl(8-(5-(2-ethoxythiophen-2-yl)-4-(5-(2-ethylpentyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)stannane (2) (512 mg) as a dark yellow oil.

7-(5'-(4,8-bis-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)-3',4-dihexyl-[2,2'-bithiophen]-5-yl)2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (CYF-1 CHO). Under a nitrogen atmosphere n-butyl lithium (1.6 M, 0.43 mL, 0.68 mmol) was dropwise added to THF (20 mL) solution of 1 (364 mg, 0.62 mmol) at 0 °C over 10 min. After stirring for 0.5 h, the mixture was warmed to room temperature and stirred for 1 h. Then SnBu₄Cl (241 mg, 0.74 mmol) was injected into the reaction mixture at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and then warmed to room temperature for 20 h. Subsequently, the reaction mixture was poured into ice water and extracted with dichloromethane. The organic phase was dried over anhydrous MgSO₄ and concentrated to afford the yellow crude product tributyl(8-(5-(2-ethoxythiophen-2-yl)-4-(5-(2-ethylpentyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophen-2-yl)stannane (2) (512 mg) as a dark yellow oil.

Experimental Section

General

1H NMR spectra were recorded on a BRUKER 400 MHz spectrometer. Mass spectral data were obtained on an ultraHExtreme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). The absorption spectra of the dyes (in solution and adsorbed on TiO₂ films) were observed with a Shimadzu UV-2450 spectrometer and fluorescence spectra were measured with a Hitachi F-4500 spectrometer. Cyclic voltammograms (CV) curves were obtained with a CHI 832 electrochemical analyzer using a normal three-electrode cell with dye-sensitized TiO₂ films. Emission spectra, cyclic voltammograms (CVs), density functional theory (DFT) studies, and long-term cell stability were measured with a CHI 832 electrochemical analyzer.

Materials and reagents

Solvents were purified using MBRAUN MB SPS-800 system. Anhydrous solvents used in Suzuki coupling reaction were degassed by N₂ bubbling for 20 min. Optically transparent fluoride doped SnO₂ (FTO) conducting glass was purchased from Nippon Sheet Glass, Japan, (15 Ω/square), and cleaned by a standard procedure. All other chemicals and reagents were used as received from commercial sources without further purification. 4,8-bis-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (1)\textsuperscript{10} and 7-(5'-(4-bromo-3',4-dihexyl-[2,2'-bithiophen]-5-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (4)\textsuperscript{a} were synthesized according to the literatures.

Synthesis

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2 (512 mg), 4 (397 mg, 0.68 mmol), and Pt(PPh₃)₃ (35.8 mg, 0.031 mmol) were added into the toluene (30 mL) solution in sequence under nitrogen atmosphere. After being stirred at 100 °C for 1 h, the reaction mixture was poured into cold water and extracted with ethyl acetate. The organic layer was dried over anhydrous MgSO₄ and concentrated to afford a dark yellow solid. The crude product was purified by silica-gel column chromatography using a mixture of chloroform and petroleum ether (3:2, v/v) as eluent to afford the product CYF1-CHO (401 mg) as a red solid. Yield: 60%. 1H NMR (400 MHz, CDCl₃) δ (ppm): 9.93 (s, 1H), 7.66 (s, 1H), 7.61 (d, J = 8 Hz, 1H), 7.44 (d, J = 8 Hz, 1H), 7.31 (d, J = 8 Hz, 2H), 7.12 (s, 1H), 7.00 (s, 1H), 6.91 (t, J = 4 Hz, 2H), 4.41 (d, J = 4 Hz, 4H), 2.91-2.84 (m, 4H), 2.82-2.72 (m, 4H), 1.71-1.69 (m, 6H), 1.44-1.27 (m, 30H), 1.01-0.91 (m, 18H). 13C-NMR (400 MHz, CDCl₃) δ (ppm): 179.8, 168.1, 148.6, 146.2, 143.5, 141.2, 139.7, 138.5, 137.8, 137.6, 137.4, 137.3, 137.2, 137.0, 135.8, 132.8, 131.2, 131.0, 129.1, 128.7, 128.6, 128.2, 128.0, 127.8, 126.6, 125.7, 124.1, 123.8, 122.7, 119.3, 116.4, 65.6, 65.0, 41.8, 39.0, 34.6, 32.8, 32.0, 31.9, 30.7, 30.6, 30.4, 30.0, 29.6, 29.2, 26.1, 26.0, 24.0, 23.3, 22.9, 14.5, 14.3, 11.3. MALDI-TOF: m/z 1078.453 (M⁺).
1714.7323. ([M]+)

\[\text{MALDI-TOF: } m/z \text{ 1714.7323. ([M]+)]}\]

Fabrication of Cells

The anatase TiO₂ nanoparticles were synthesized according to our previous literature. First, the Ti(OBu)₄ (10 mL) was added to the ethanol (20 mL) under stirring for 10 min. Then a mixture of deionized water (50 mL) and acetic acid (18 mL) was added to the solution with vigorous stirring for 1 h. The solution was moved to an autoclave and heated at 200 °C for 12 h. Finally, the precipitations were washed with deionized water and ethanol for several times, respectively. The white powder was obtained after drying in air. The as-prepared TiO₂ nanoparticles were anatase crystals with diameters of about 20 nm, as confirmed by SEM, TEM, and XRD. The prepared TiO₂ powder (1.0 g) was ground for 40 min in the mixture of acetic acid (0.2 mL), ethanol (8.0 mL), ethyl cellulose (0.5 g), and terpineol (3.0 g) to form a slurry, and then the slurry was sonicated for 5 min to obtain a viscous white TiO₂ paste. The TiO₂ paste was then screen-printed onto the surface of FTO coated glass forming photoanode film. The thickness of films can be easily controlled through repeating screen-printing times. Afterwards, a programmed heating process was carried out to remove the organic substances in the film. The as-prepared TiO₂ films (~15 µm) were soaked in a 0.04 M aqueous solution of TiCl₄ for 30 min at 70 °C and then sintered at 520 °C for 30 min. After cooling to 80 °C, the TiO₂ electrodes were immersed into 0.3 mM organic dye solution (CHCl₃/ACN/BuOH = 1/2/2, v:v:v) of the dyes and kept at room temperature for 6 h for cells with liquid electrolyte and for 12 h for cells with gel electrolyte, respectively. And then the prepared TiO₂ working electrodes were sandwiched together with Pt-counter electrode. The active area of the dye-coated TiO₂ film was 0.16 cm². The electrolyte was injected into the inter-electrode space. The electrolyte solution is composed of 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.03 M I₂, 0.05 M LiI, 0.1 M guanidinium thiocyanate (GuSCN), and 0.5 M 4-tetralonylpyridine (TBP) in acetonitrile and valeronitrile (85:15, v:v).

Characterization of Cells

The TiO₂ film thickness and active area of the dye-coated TiO₂ film was measured by using a profilometer (Ambios, XP-1). The current–density voltage (J-V) curves of the DSSCs were recorded by using a Keithley 2400 source meter under the illumination of AM 1.5 G simulated solar light. The incident photon-to-current conversion efficiencies (IPCEs) of DSSCs were measured on the basis of a Spectral Products DK240 monochromator. Electrochemical impedance spectroscopy (EIS) was measured using an electrochemical workstation (Zahnner, Zennium) with a frequency response analyzer at a bias potential of -800 mV in the dark with a frequency range from 10 MHz to 1 MHz. The dye-adsorbed amounts on the TiO₂ film were measured using a Shimadzu UV-2450 spectrometer. Intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) measurements were conducted using an electrochemical workstation (ZAHNER, Zennium) and were performed under a modulated LED light (457 nm) driven by a source supply (ZAHNER, PP210). The illumination intensity ranged from 30 to 150 mW cm⁻². The light intensity modulation was 20% of the base light intensity over the frequency range of 10⁻¹⁻¹⁰ Hz.

Results and discussion

Synthesis
The synthesis of sensitizers CYF1 and CYF2 is shown in Scheme 1. The starting material 1, i.e. 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene, coupled with 1 and 2 equivalents of SnBu₃Cl through stille coupling reaction to afford 2 and 3, respectively. Then, 2 reacted with 1 equivalent of 4 (or 3 reacted with 2 equivalents of 4) in the presence of Pd(PPh₃)₄ to generate CYF1-CHO (or CYF2-CHO). Finally, CYF1 and CYF2 were obtained from CYF1-CHO and CYF2-CHO, respectively, via a Knoevenagel condensation with cyanoacetic acid by refluxing in acetonitrile in the presence of piperidine. The chemical structures of these new compounds have been verified using ¹H NMR, ¹³C NMR spectroscopy, and mass spectroscopy.

**UV-vis absorption properties**

The UV-vis absorption spectra of sensitizers CYF1 and CYF2 in THF solution are depicted in Fig. 1a, and the corresponding data are summarized in Table 1. CYF1 and CYF2 exhibit two major absorption bands in the range of 300-600 nm. The band below 400 nm corresponds to the π-π* transition and the other band at 450-550 nm can be assigned to the intramolecular charge transfer (ICT) from the donor unit to the cyanoacrylic acid acceptor moiety to produce an efficient charge-separated state. The λ_max at ICT band of CYF2 red-shifts about 17 nm from the CYF1 because of the longer conjugated π-chromophore in CYF2. However, the molar extinction coefficients of CYF1 at π-π* band are much higher than those of CYF2, and its ICT absorption band is also more intense relative to CYF2, which indicates that stronger ICT interactions occur in CYF1, in agreement with the report in other ICT systems with increased number of electron-withdrawing group. This can be explained by the disperse of the electron push-pull effect resulting from two competing anchoring groups in sensitizer CYF2.

The absorption spectra of organic sensitizers CYF1 and CYF2 on the TiO₂ films are shown in Fig. 1b. Extension of CYF1 and CYF2 spectra beyond 600 nm implies the existence of J-aggregation of dye molecules on the TiO₂ surface. The ICT band of the CYF1-loaded TiO₂ film displays no obvious shift in comparison to that in THF, indicating the ICT from the BDT donor to the acceptor was not weaken despite the anchoring group being deprotonated. By contrast, the ICT band for CYF2 exhibits only unresolved shoulders at around 500 nm, probably due to the absorption band overlapping. A slight hypsochromic shift of the absorption maximum of CYF2 occurs when compared with that dissolved in THF, which could be ascribed to the deprotonation of the twin anchoring groups.

![Scheme 1 synthesis of CYF1 and CYF2](image)

**Fig. 1** Absorption spectra of CYF1 and CYF2 (a) in THF solution and (b) on TiO₂.

**Molecular orbital calculations**

The electronic structure calculations of CYF1 and CYF2 were carried out using the TD-DFT and B3LYP-3-21G* program. All dihedral angles between the thiophene planes in CYF1 and CYF2 dyes are listed in Table S1. The angles between BDT and 2-(2-ethylhexyl) thiophene plane in CYF1 (A1-A2) and CYF2 (B1-B2) are as large as 53.2° and 53.5°, respectively, which can prevent π-π aggregation of dye. On the other hand, the coplanarity between the DBT donor and the close bridging thiophene ring in CYF1 (A1-A3) and CYF2 (B1-B3) dyes is
distinct, as verified by the 9.2° and 9.7° of the dihedral angles, respectively, which may favor the electron transport process.

The calculated molecular orbitals of CYF1 and CYF2 with isodensity plots of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are illustrated in Fig. 2. The HOMOs of CYF1 and CYF2 are delocalized on the donor groups and extend to the π bridges, whereas the LUMOs of these molecules are concentrated on the cyanoacrylic moieties. It was expected that the LUMOs of CYF2 are stretched out to two-anchoring parts of carboxylic groups. As a result, the HOMO-LUMO excitation could transfer the electron distribution from the DBT donor to the cyanoacrylic moiety through the π-conjugation bridge.

Fig. 2 Frontier molecular orbitals (HOMO and LUMO) of CYF1 and CYF2 calculated with DFT on the B3LYP/6-31G* level.

Table 1. Absorption and electrochemical data of the dyes

<table>
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<th>dye</th>
<th>ε/10⁴M⁻¹cm⁻¹ (λmax/nm)</th>
<th>1/εV (vs. Fe/Fe⁺)</th>
<th>1E₀.0/eV (vs. vacuum)</th>
<th>1E_HOMO/eV (vs. vacuum)</th>
<th>1E_LUMO/eV (vs. vacuum)</th>
<th>amounts/10⁶ mol cm⁻²</th>
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</thead>
<tbody>
<tr>
<td>CYF1</td>
<td>3.82 (501)</td>
<td>0.35</td>
<td>2.23</td>
<td>-5.15</td>
<td>-2.92</td>
<td>4.15</td>
</tr>
<tr>
<td>CYF2</td>
<td>4.77 (484)</td>
<td>0.45</td>
<td>2.16</td>
<td>-5.25</td>
<td>-3.09</td>
<td>2.09</td>
</tr>
</tbody>
</table>

*a* The Ag/AgCl reference electrode was calibrated using Fe/Fe⁺. 
* b* E₀.0 was determined from the intersection of absorption and emission spectra in THF. 
* c* E_HOMO [eV] = -(E_{ox}(vs. Fe/Fe⁺) + 4.8). 
* d* E_LUMO [eV] = E_HOMO + E₀.0.

**Photovoltaic properties**

The photovoltaic performance of CYF1- and CYF2-sensitized solar cells with liquid electrolyte is shown in Fig. 3a. The J_sc, Voc, and FF values for the CYF1 based DSSC are 17.87 mA cm⁻², 683 mV, and 0.66, respectively, which corresponds to a η of 8.01%. To the best of our knowledge, this is the first time such a high efficiency has been obtained for liquid-based DSSCs with amine-free organic sensitizers. Under the same conditions, the DSSC based on CYF2, which has two anchoring units, features J_sc, Voc, FF, and η values of 14.64 mA cm⁻², 592 mV, 0.68, and 5.85%, respectively. The superior performance of sensitizer CYF1 relative to CYF2 is particularly noteworthy.

To elucidate the difference between the J_sc values, the incident photon-to-current conversion efficiencies (IPCEs) for the DSSCs based on sensitizers CYF1 and CYF2 are shown in Fig. 3b. All cells tested can convert the light to photocurrents in the wide wavelength region up to about 750 nm. The IPCE spectrum of the cell based on CYF1 exhibits a plateau between 420 and 590 nm with an IPCE value of over 80%, while CYF2 based cell displays an IPCE spectrum with a similar spectral pattern, but with decreased intensity and maximum. The result agrees well with the trends in their absorption spectra both in solution and on the TiO₂ film. Consequently, the increase of J_sc values for sensitizer CYF1 compared with CYF2 could be attributed to its wider IPCE spectra and better dye adsorption (Table 1).

**Electrochemical properties**

The electrochemical properties of the sensitzers were measured using cyclic voltammetry (CV) in CH₂Cl₂ and their electrochemical data were listed in Table 1.¹⁴ The first oxidation potentials, corresponding to the HOMO energy levels of sensitizers CYF1 and CYF2, were determined to be -5.15 and -5.25 eV, respectively, which are more positive than the 1/I₃⁻ redox couple (-4.9 eV), providing a thermodynamic driving force for efficient dye regeneration. Accordingly, the LUMO energy levels of dyes CYF1 and CYF2, estimated from the oxidation potentials and absorption/emission data, were calculated to be -2.92 and -3.09 eV, which are more negative than the conduction edge of the TiO₂ (-3.9 eV), indicating that the electron injection process is energetically permitted. Although the electron donating group, π-conjugated bridge, and electron acceptor of the two sensitizers are identical, the difference of the energy levels can be traced to the diverse number of π-conjugated and anchoring groups.
Fig. 3 (a) Photocurrent density vs. voltage and (b) incident photon-to-current conversion efficiency spectra for DSSCs based on CYF1 and CYF2 under AM 1.5 G simulated solar light (100 mW cm⁻²).

Electrochemical impedance spectroscopy (EIS) analysis was performed to explain the different $V_{oc}$ values obtained for the DSSCs based on CYF1 and CYF2. The second semicircle ($R_{rec}$) in the Nyquist plot is attributed to charge transfer at the TiO₂/dye/electrolyte interface. Obviously, a larger $R_{rec}$ indicates a slower charge recombination, smaller dark current, and higher $V_{oc}$. Fig. 4a shows the radius of the second semicircle of CYF1 is larger than that of CYF2, implying its electron recombination resistance is higher than CYF2. Electron lifetimes ($\tau$) obtained from curve fitting is 184.1 and 81.8 ms for CYF1 and CYF2, respectively, which corresponds well with the $V_{oc}$ values obtained in $J-V$ curves. Though CYF1 and CYF2 have similar chemical structures, the $V_{oc}$ values are greatly affected by the number of the π-conjugated bridges and anchoring groups. The observation indicates that introduction of two π-conjugated bridges and anchoring units does not improve the $V_{oc}$. We deduce the cell based on CYF2 gives the lower $V_{oc}$ value due to the two factors: (1) the extra protons released from the D-(x)-A₂ molecules will lower the Fermi level of TiO₂, leading to the $V_{oc}$ decrease; (2) the lower dye loading leaves more void space for electrolyte penetration, resulting in a lower dark current. The Bode phase plots (Fig. 4b) show the middle-frequency peak of the cell based on CYF1 shifts to a lower frequency relative to CYF2, displaying a longer lifetime for CYF1, supporting the difference in the electron lifetime for TiO₂ film derivatized with the two sensitizers.

To further confirm the different photovoltaic behaviors of two sensitizers, intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) were performed. As shown in Fig. 5a, the recombination time ($\tau_{rec}$) of DSSCs based on CYF1 sensitizers under various incident light intensities is longer than that based on CYF2, consistent with the EIS results described above. On the other hand, Fig. 5b shows the electron transport time ($\tau_{d}$) of DSSCs based on CYF1 sensitizers is shorter than that of CYF2. It is known that the adsorption of Li⁺ in the TiO₂ electrodes increases the local cation density and assists the electron diffusion along the TiO₂ network. Therefore, we speculate that the more protons released from the CYF2 sensitizers with twin carboxyl groups might limit the access of Li⁺ to the TiO₂ surface due to electrostatic repulsion, and thus prolong the electron transport time.

**Fig. 4** (a) EIS Nyquist plots (i.e. minus imaginary part of the impedance $-Z''$ vs. the real part of the impedance $Z'$ when sweeping the frequency) and (b) EIS Bode plots (i.e. the impedance $-Z''$ vs. the frequency) for DSSCs based on CYF1 and CYF2 sensitizers.

**Fig. 5** (a) Incident light intensity dependent recombination time constants, and (b) incident light intensity dependent transport time constants for DSSCs based on CYF1 and CYF2 sensitizers.

**Long-term stability**

The long-term stability of DSSCs based on CYF1 and CYF2 was measured under AM 1.5 light for at least 600 h, as shown in Fig. 6. After 1000 h light soaking, the $V_{oc}$ of CYF1 based cells decreases by 67 mV and the $FF$ declines from 0.68 to 0.66, but the $J_{sc}$ increases by 1.05 mA cm⁻². As a consequence, the efficiency decreases from 7.48% to 7.04% and remains at 94% of the initial value. The cells based on CYF2 were also subjected to testing under the same conditions. The $V_{oc}$ value decreases by 66 mV and the $FF$ remains constant, but the $J_{sc}$ increases by 1.39 mA cm⁻². And thus the overall efficiency remains at 95% (4.75%) of the initial value (5.00%). The results demonstrate that the CYF1 and CYF2 sensitizers sustain without noticeable decline in performance.
Fig. 6 Variations of photovoltaic parameters ($\eta$, $J_{sc}$, $V_{oc}$, and $FF$) with aging time for DSSC devices based on CYF1 and CYF2 under AM 1.5 light soaking at 60 °C.

Conclusions

In summary, two novel amine-free organic sensitizers based on BDP donor, CYF1 and CYF2, with a single and twin π bridges and anchoring groups, respectively, have successfully synthesized and applied in DSSCs. The cell based on CYF1 gives an improved conversion efficiency of 8.08%, compared to CYF2, which can be due to higher molar absorption coefficients, longer electron lifetimes, and larger adsorption amounts. To the best of our knowledge, this is the first time such a high efficiency has been obtained for liquid DSSCs with amine-free organic sensitizers without any strong donor units. Moreover, the CYF1 and CYF2 sensitizers containing BDP donors show excellent stability, which remain at 94% and 95% of the initial value under 100 mW cm$^{-2}$ light soaking at 60 °C for 500 h, respectively. We believe that the use of BDP as a donor in organic sensitizers presents new opportunities for the development of efficient amine-free organic sensitizers.

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Notes and references

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Electronic Supplementary Information (ESI) available: Cyclic voltammograms of the two sensitizers. The dihedral angles between the phenyl planes and thiophene units in the two sensitizers. See DOI: 10.1039/b000000x/


A stable sensitizer incorporating the benzo[1,2-b:4,5-b']dithiophene donor was applied in DSSCs, showing the highest efficiency for amine-free organic dyes.