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# A high-efficiency cyanine dye for dye-sensitized solar cells

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## Abstract

A novel organic cyanine dye containing triphenylamine−benzothiadiazole dyad has been synthesized and applied successfully to sensitization of nanocrystalline $TiO_2$-based solar cell. Their absorption spectra, electrochemical, and photovoltaic properties were studied. Upon adsorption on a $TiO_2$ electrode, the absorption spectra of the cyanine dye are all broadened at both the red and blue spectral ends relative to its respective spectra in acetonitrile and ethanol mixture solution. An overall conversion efficiency of 7.62% ($J_{sc}$=22.10 mA cm$^{-2}$, $V_{oc}$=0.54 V, ff=0.48) is achieved under irradiation with 75 mW cm$^{-2}$ white light from a Xe lamp.

## 1. Introduction

During the past decade, dye-sensitized solar cells (DSSCs) have attracted a great deal of interest because of their relatively higher efficiency and low cost compared with conventional inorganic photovoltaic devices.[1] Up to now, DSSCs based on the Ru-complex dyes can produce photoelectric conversion yield of 11% under AM 1.5 irradiation.[1c] However, pure organic dyes not only have higher molar extinction coefficients, but can be obtained by simple preparation and purification procedures at lower cost. Recently, great progress has been made in this field and the highest overall photoelectric conversion efficiency of organic dye-sensitized solar cells has already reached the considerable level of 9%, indicating that organic dyes would be a promising type of sensitizer for dye-sensitized solar cells.[2,3]

It is well known that cyanine dyes have very high absorption extinction coefficients ($\sim 10^5$ M$^{-1}$ cm$^{-1}$), intense and broad absorption band in visible and near-infrared region, and excellent sensitizing properties in photography.[3c,e,4a] Especially, cyanine dyes adsorbed on the nanocrystalline $TiO_2$ film can form J-or H-aggregates, which contributed to hypsochromism and bathochromism, respectively. Relative high incident photo-to-electron conversion efficiency (IPCE) values are expected over a wider region of wavelength, which then will in turn enhance the conversion efficiency of light to electricity.[4a] Recently, we have succeeded in the synthesis of a series of hemicyanine and cyanine dyes and found that these dyes could perform excellent spectral sensitization by reasonable design.[4] In order to improve photoelectrical conversion efficiency and stability of cyanine dyes for DSSCs, introduction of new π-conjugation fragment into dye molecules is necessary.

In this work, a novel cyanine dye **I** that contained triphenylamine donor and carboxylic acid acceptor bridged by a low-band-gap benzothiadiazole conjugation fragment was synthesized, and we also synthesized the corresponding cyanine dye without benzothiadiazole (**II**, in Scheme 1) for the purpose of comparison. The introduction of triphenylamine moiety was expected to greatly locate the cationic charge from the $TiO_2$ surface and efficiently restrict recombination between conduction band electron and oxidized sensitizer.[2b] In benzothiadiazole-based fluorophores, the low-energy absorption is predominantly charge transfer in nature, and the same is true with the low-lying excited state also,[5] which will ensure and enhance the possibility of charge separation and migration in such system. Though benzothiadiazole-based polymers have been widely employed in photovoltaic

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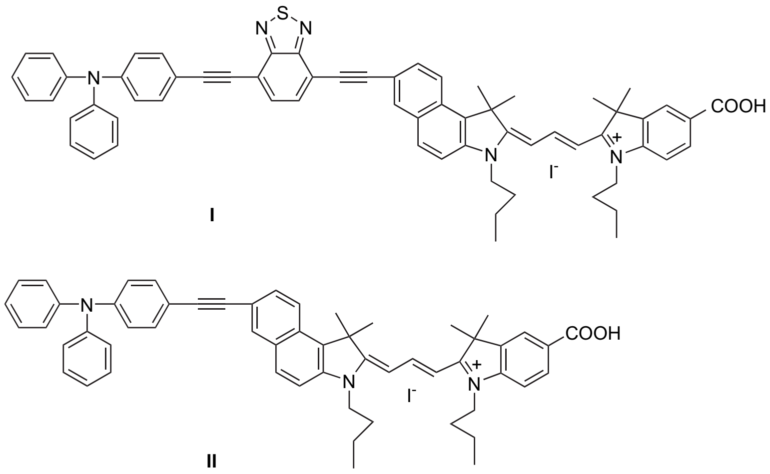


Scheme 1. Molecular structures of cyanine dyes (**I** and **II**).

applications, to the best of our knowledge, there has only been one report on the application of small molecular dye containing a benzothiadiazole moiety in DSSCs.[5a]

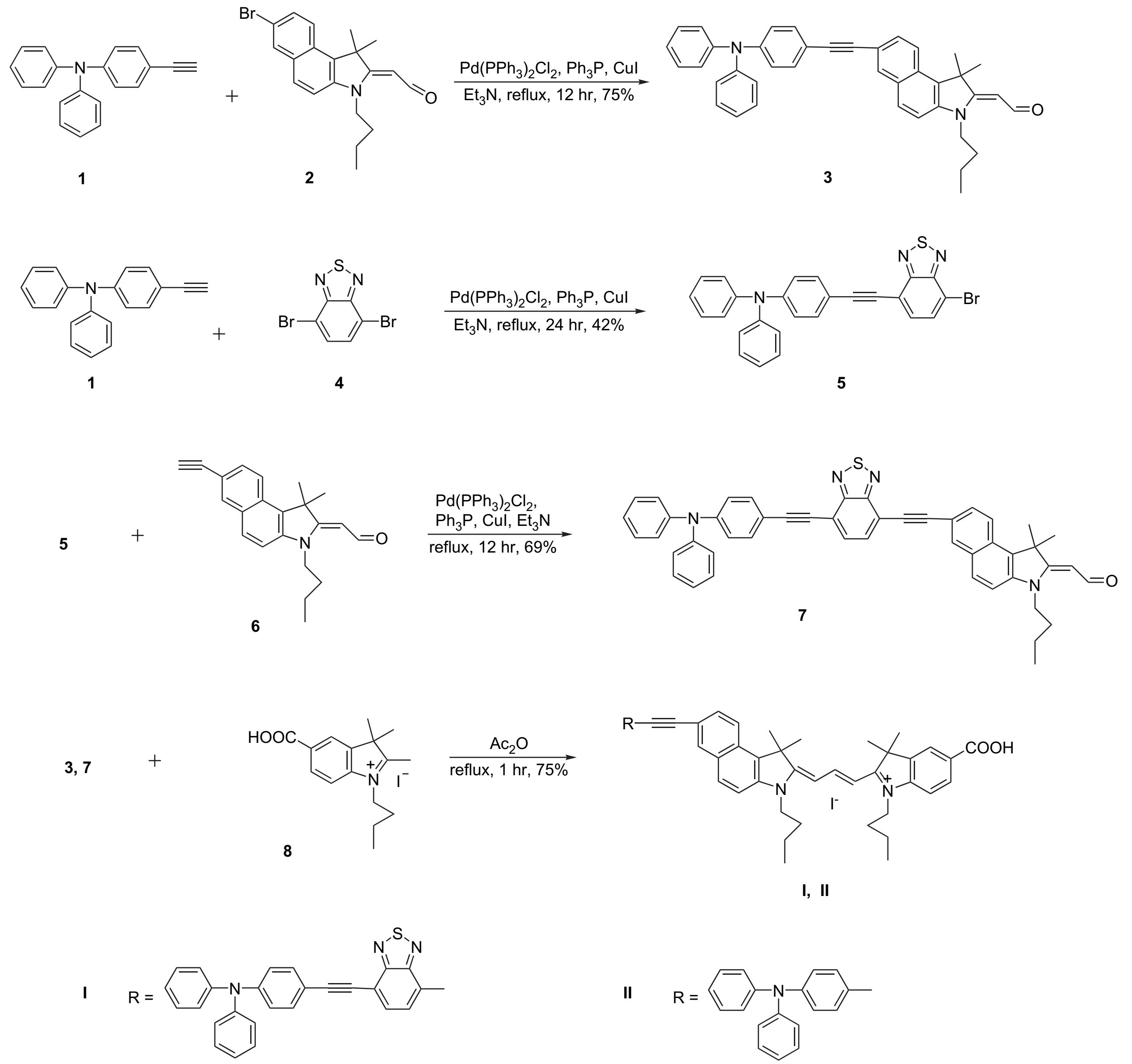
## 2. Results and discussion

The synthetic route of cyanine dyes **I** and **II** is depicted in Scheme 2. Two butyl chains on indole nucleus can improve the solubility and form a tightly packed insulating monolayer blocking the $I_3^-$ or cations approaching the $TiO_2$. 4-Ethynyltriphenylamine is attached to the core benzothiadiazole by Sonogashira coupling reaction. The reaction produced the di-substituted side products as well, fortunately monocapped compounds can be easily separated by column chromatography. In the next step, this bromo-exposed intermediate was reacted with 2-(7-ethynyl-3-butyl-2-methylene-1,1-dimethyl-1*H*-benzo[*e*]indolin-2-ylidene)acetaldehyde by Sonogashira coupling reaction. Finally, the target product was prepared via Knoevenagel condensation of the aldehyde with 5-carboxyl-1-butyl-2,3,3-trimethyl-3*H*-indolium iodide in the presence of acetic anhydride. All the intermediates and cyanine dyes (**I** and **II**) were characterized by standard spectroscopic methods.

Absorption spectra of cyanine dyes **I** and **II** in a dilute solution of acetonitrile/ethanol=1:1 are shown in Figure 1. Cyanine dyes **I** and **II** showed maximum absorption at 590 and 588 nm with vibrational shoulder peaks at 556 and 554 nm because of their similar conjugation systems. The triphenylamine unit is attributed to the feature absorption band of **II** at 348 nm. Triphenylamine–benzothiadiazole dyad resulted in the wide absorption band at 400–459 nm except for 326 nm. The extinction coefficient of **I** and **II** were $1.5\times10^5$ and $1.2\times10^5\ M^{-1}\,cm^{-1}$, respectively, which is very high in comparison to $1.39\times10^4\ M^{-1}\,cm^{-1}$ at 541 nm for *cis*-di(thiocyanato)-bis (2,2′-bipyridyl)-4,4′-dicarboxylate)ruthenium(II) ($N_3$).[6]The greater maximum absorption coefficients of the organic dyes allows for a correspondingly thinner nanocrystalline film to avoid a decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation.[3f] Figure 2 gives the absorption spectra of **I** and **II** on 4 μm thick $TiO_2$ films after 12 h adsorption. The absorption spectra of dyes attached to $TiO_2$ film were all broadened significantly on both sides compared with those in acetonitrile/ethanol solution, implying that the formation of dye aggregates is on the $TiO_2$ surface. It was found that the dyes used in this work formed Herring-bone aggregates on $TiO_2$ surface, and the broadened absorption spectra caused by dye aggregates on $TiO_2$ surface would benefit the photoelectrical conversion efficiency of the dye-sensitized solar cells.[3e] In addition, the fluorescence emission bands of the dyes in the visible region disappear when the dyes are adsorbed onto the nanocrystalline $TiO_2$ electrodes. The phenomena can be explained by the efficient electron injection from the excited singlet state of the dyes to the conduction band of $TiO_2$, suggesting that the two cyanine dyes are good sensitizers for nanocrystalline $TiO_2$ electrodes.

For the photo-induced electron injection into $TiO_2$, it is necessary that the energy level of the excited state of the dye is higher than that of conduction band of $TiO_2$. To judge the possibility of electron transfer from the excited dye to the conduction band of $TiO_2$, the highest occupied molecular orbital (HOMO) levels of −5.73 eV for **I**, −5.78 eV for **II** were measured by cyclic voltammetry (CV) in DMF using Ag/AgCl as a reference electrode. With reference to the absorption maxima of 649 nm (1.91 eV) and 642 nm (1.93 eV), corresponding to the gap between the HOMO and LUMO levels for **I** and **II**, respectively, the energy levels of the LUMO can be estimated to be −3.82 and −3.85 eV, respectively (Table 1), indicating that dye **I** has a more efficient electron injection ability. Obviously, the excited state energy levels for the two dyes are higher than the bottom of the conduction band of $TiO_2$ (−4.4 eV),[4b] clarifying that electron injection should be possible thermodynamically.

Photocurrent action spectra obtained with $TiO_2$ films coated with cyanine dyes **I** and **II** are shown in Figure 3. The dye-sensitized solar cells efficiently convert visible light to photocurrent efficiently in the range from 400 to 690 nm, which



Scheme 2. The synthetic procedures of the cyanine dyes (**I** and **II**).

corresponds well with the absorption of the electrode. As shown in Figure 3, **I**/$TiO_2$ electrode gives the high IPCE performance (>80%) in the range from 540 to 590 nm with the top value of 95% at 560 nm; however, the highest IPCE value of **II** (78%) was obtained at 560 nm. The broader action spectra of **I** indicated that **I** sensitized $TiO_2$ electrode would generate a higher conversion yield.

Under irradiation of Xe lamp (75 mW $cm^{-2}$), the photoelectrochemical properties of **I** and **II** sensitized $TiO_2$ electrodes are listed in Table 2, and the corresponding photocurrent–voltage curves are shown in Figure 4. The dye-coated $TiO_2$ film, as working electrode, was placed on top of an FTO glass as a counter electrode, on which Pt was sputtered. The redox electrolyte was introduced into the inter-electrode space by capillary force. An overall conversion efficiency ($\eta$) values of 7.62% and 6.58% were achieved from the DSSCs based on cyanine dyes **I** and **II**, respectively, both of which are much higher than the efficiency obtained from the DSSCs on other cyanine dyes reported previously. We have done comparable studies with ruthenium dye **N719** with good efficiency in order to certain about the reliability of the measurements, and the performance parameters of **N719** are also presented in Table 2. It is found that the conversion efficiency of **N719** is 9.50% under the same conditions and little higher than that of **I**, indicating that the photovoltaic performance measurement is reliable. The solar cell performance is encouraging in which triphenylamine possess a twisted nonplanar geometry, which will decelerate the recombination of charges in the charge-separated state. On the other hand, there is an easily polarizable and electron-deficient benzothiadiazole conjugation bridge in cyanine dye **I**, which will ensure and enhance the possibility of charge separation and migration in such

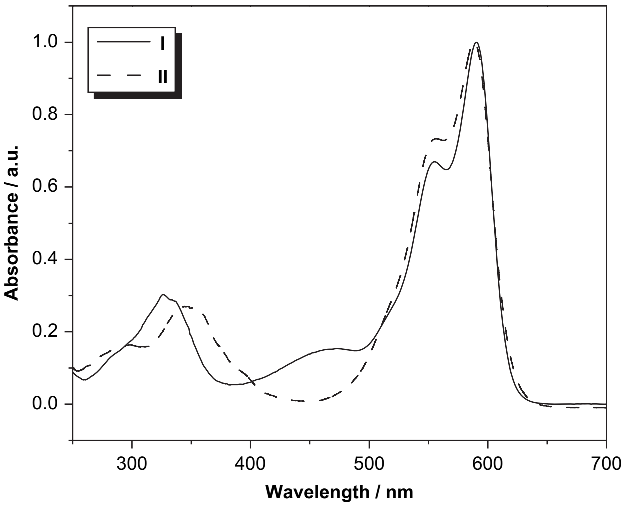


Figure 1. Absorption spectra of **I** and **II** in acetonitrile/ethanol (v/v 1:1).

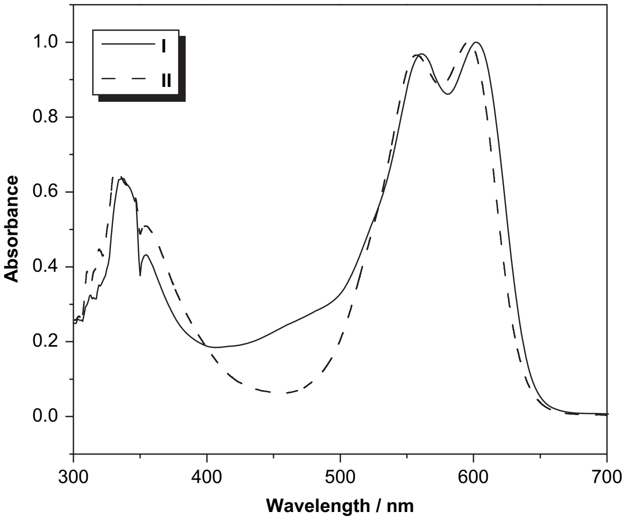


Figure 2. Absorption spectra of **I** and **II** on $TiO_2$ electrode after adsorption for 12 h.

system. Compared with **II**, dye **I** exhibits broader absorption and higher molar extinction coefficient in visible region, which is more efficient to capture solar radiation energy. Accordingly, power conversion efficiency of **I** was higher than that of **II** sensitized solar cell.

In conclusion, we have designed and synthesized a novel cyanine dye with triphenylamine–benzothiadiazole dyad for dye-sensitized solar cells with a conversion efficiency of 7.62%, a short-circuit photocurrent of 22.10 mA $cm^{-2}$, an open-circuit voltage of 0.54 V, and a fill factor (ff) of 0.48 under illumination with 75 mW $cm^{-2}$ white light from Xe lamp, which is a considerably high level for organic dyes. We believe that the development of highly efficient organic cyanine dyes over 8% of power conversion efficiency can be possible through the more rational structural modifications, and these optimal works are now in progress.

Table 1
Optical properties and redox potential of **I** and **II**

| Dye | $\lambda_{max}$[a] (nm) | ε[b] ($M^{-1}$ $cm^{-1}$) | Adsorption[c] (mol $cm^{-2}$) | HOMO[d] (eV) | LUMO[d] (eV) |
|---|---|---|---|---|---|
| **I** | 590 | $1.5\times10^5$ | $2.76\times10^{-8}$ | −5.73 | −3.82 |
| **II** | 588 | $1.2\times10^5$ | $3.96\times10^{-8}$ | −5.78 | −3.85 |

[a] Adsorption maximum in $CH_3CN/C_2H_5OH=1:1(10^{-5}$ M).

[b] Molar extinction coefficient at $\lambda_{max}$.

[c] Adsorption amount per unit area of $TiO_2$ film.

[d] Redox potentials of dyes ($2\times10^{-4}$ M) were measured in $CH_3CN$ with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 25 mV $s^{-1}$.

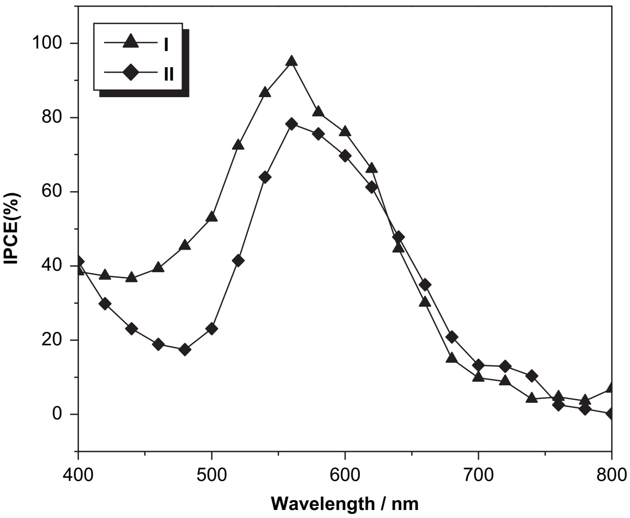


Figure 3. Photocurrent action spectra of the $TiO_2$ electrodes sensitized by **I** and **II**.

Table 2
Performances of dyes (**I** and **II**) and **N719** sensitized solar cell

| Dye | $J_{sc}$ (mA $cm^{-2}$) | $V_{oc}$ (V) | ff | η (%) |
|---|---|---|---|---|
| **I** | 22.10 | 0.54 | 0.48 | 7.62 |
| **II** | 15.79 | 0.57 | 0.55 | 6.58 |
| **N719** | 27.25 | 0.64 | 0.41 | 9.50 |

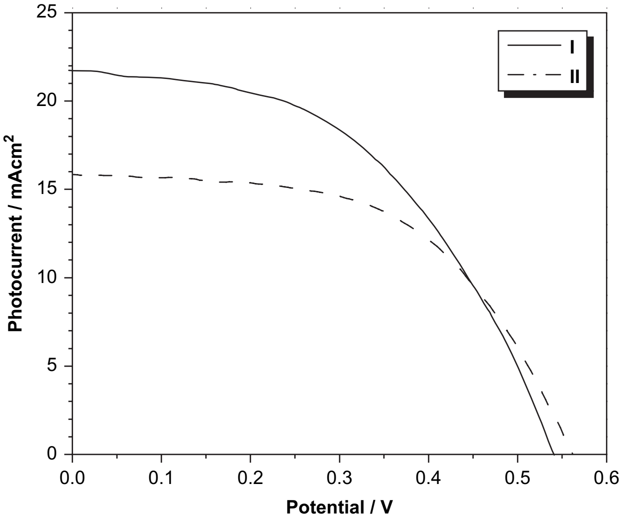


Figure 4. Photocurrent–voltage curve of **I** and **II** sensitized $TiO_2$ electrodes under 75 mW $cm^{-2}$ light intensities.

## 3. Experimental section

### 3.1. Materials and instruments

The FTO conducting glass (fluorine doped $SnO_2$, sheet resistance <15Ω/square, transmission >90% in the visible) was obtained from Geao Science and Educational Co. Ltd., China, and cleaned by a standard procedure. Titanium(IV) isopropoxide and 3-methyl-2-oxazolidinone were purchased from Aldrich. Lithium iodide was purchased 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 4-ethynyltriphenylamine (**1**), 2-(7-bromo-3-butyl-2-methylene-1,1-dimethyl-1*H*-benzo[*e*]indolin-2-ylidene)acetaldehyde (**2**), 2-(7-ethynyl-3-butyl-2-methylene-1,1-dimethyl-1*H*-benzo[*e*]indolin-2-ylidene)acetaldehyde (**6**), and 5-carboxyl-1-butyl-2,3,3-trimethyl-3*H*-indolium iodide (**8**) were synthesized following the known procedure.[4a]

$^1$H NMR spectra were obtained with a Bruker AM-500 or AM-400 spectrometer. The mass spectra were conducted on a 4700 Proteomics analyzer spectrometer. UV–visible spectra were determined with a Varian Cary 500 spectrometer. Fluorescent spectra were recorded on Varian Cary Eclipse spectrometer. The cyclic voltammograms of dyes were estimated with a Versastat II electrochemical workstation (Princeton Applied Research) using a normal three-electrodes cell with a Pt working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution.

### 3.2. Preparation of dye-sensitized nanocrystalline $TiO_2$ electrodes

$TiO_2$ 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,[7] except that autoclaving was performed at 220 °C instead of 200 °C. Optically transparent conducting glass (FTO, transmission >90% in the visible, sheet resistance 15 Ω/square) was obtained from the Geao Science and Educational Co. Ltd. of China. Films of nanocrystalline $TiO_2$ colloidal on FTO were prepared by sliding a glass rod over the conductive side of the FTO. Sintering was carried out at 450 °C for 30 min. Before immersion in the dye solution, these films were soaked in the 0.2 M aqueous $TiCl_4$ solution overnight in a closed chamber, which has been proved to increase the short-circuit photocurrent significantly.[8] After being washed with deionized water and fully rinsed with ethanol, in the end heated again at 450 °C followed by cooling to 80 °C and dipping into a $3\times10^{-4}$ M solution of dye **I** or **II** in alcohol for 12 h at room temperature. The DSSCs were sealed with KC-904 hot melt adhesive tape (Kouuci, shanghai) and leaving two sides hole for injecting electrolyte.

### 3.3. Photo-electrochemical measurements and characterization of DSSC

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. Volt–current characteristic were performed on Model 2400 Source meter (Keithley Instruments, Inc., USA) and a 500 W xenon lamp served as a white light source in conjunction with a GRB3 filter. Here a GRB3 filter was used to cut off infrared light to protect the electrode from heating. The redox electrolyte solution was composed of 0.5 M LiI, 0.05 M $I_2$ in the mixture of acetonitrile and 3-methoxypropionitrile (volume ratio 7:3). The effective area of photocells is 0.15 cm$^2$. The intensity of the illumination source was measured using a power meter.

#### 3.3.1. [3-Butyl-7-(4-diphenylamino-phenylethynyl)-1,1-dimethyl-1,3-dihydrobenzo[e]indol-2-ylidene]-acetaldehyde (3)

2-(7-Bromo-3-butyl-2-methylene-1,1-dimethyl-1*H*-benzo[*e*]-indolin-2-ylidene)-acetaldehyde **2** (0.42 g, 1.13 mmol), 4-ethynyltriphenylamine **1**(0.3 g, 1.13 mmol), $PPh_3$ (2.9 mg, 0.01 mmol), $Pd(PPh_3)_2Cl_2$ (2.9 mg, 0.01 mmol), and CuI (5.2 mg, 0.02 mmol) were added in 20 mL triethylamine. The mixture was stirred in Ar atmosphere under reflux for 12 h. After the solvent was removed by rotate evaporator, the residue was extracted with chloroform and water. The organic layer was dried with anhydrous magnesium sulfate overnight. Followed by the solvent was evaporated, the remained solid was purified column chromatography (silica gel) with eluent tetrachloromethane/ethyl acetate=5:1 (v/v) to afford 0.47 g product, yield 75%. $^1$H NMR ($CDCl_3$, 500 MHz), δ: 10.08 (d, *J*=9.0 Hz, 1H), 8.04 (d, *J*=1.5 Hz, 1H), 8.00 (d, *J*=9.0 Hz, 1H), 7.81 (d, *J*=8.9 Hz, 1H), 7.62–7.58 (m, 1H), 7.42 (s, 1H), 7.40 (s, 1H), 7.32–7.29 (m, 5H), 7.18 (d, *J*=8.9 Hz, 1H), 7.13 (s, 2H), 7.12 (d, *J*=7.1 Hz, 2H), 7.07 (s, 1H), 7.04 (s, 1H), 7.01 (s, 1H), 5.50 (d, *J*=9.0 Hz, 1H), 3.79 (t, *J*=7.7 Hz, 2H), 1.95 (s, 6H), 1.79–1.72 (m, 2H), 1.47–1.42 (m, 2H), 1.01 (t, *J*=7.2 Hz, 3H).

#### 3.3.2. [4-(7-Bromo-benzo[1,2,5]thiadiazol-4-ylethynyl)-phenyl]-diphenylamine (5)

4-Ethynyltriphenylamine **1** (0.27 g, 1 mmol), 4, 7-dibromo-2,1,3-benzothiadiazole **4** (0.29 g, 1 mmol), $PPh_3$ (2.9 mg, 0.01 mmol), $Pd(PPh_3)_2Cl_2$ (2.9 mg, 0.01 mmol), and CuI (5.2 mg, 0.02 mmol) were added into 30 mL solution (triethylamine/THF=2:1). The mixture was stirred in Ar atmosphere under reflux for 24 h. After the solvent was removed by rotate evaporator, the residue was extracted with dichloromethane and water. The organic layer was dried with anhydrous magnesium sulfate overnight. Followed by the solvent was evaporated, the remained solid was purified column chromatography with eluent of dichloromethane/petroleum ether=1:3 (v/v) to afford 0.2 g product, yield 42%. $^1$H NMR ($CDCl_3$, 400 MHz), δ: 7.83 (d, *J*=7.6 Hz, 1H), 7.63 (d, *J*=7.6 Hz, 1H), 7.50 (d, *J*=8.8 Hz, 2H), 7.31 (t, *J*=8.0 Hz, 4H), 7.14 (d, *J*=7.6 Hz, 4H), 7.10 (t, *J*=7.6 Hz, 2H), 7.04 (d, *J*=8.4 Hz, 2H).

#### 3.3.3. {3-Butyl-7-[7-(4-diphenylamino-phenylethynyl)-benzo[1,2,5]thiadiazol-4-yl ethynyl]-1,1-dimethyl-1,3-dihydro-benzo[e]indol-2-ylidene}-acetaldehyde (7)

The intermediate was synthesized according to the procedure as described above for the synthesis of **3**, giving product

**7** in 69% yield. $^{1}$H NMR ($CDCl_3$, 500 MHz), $\delta$: 10.16 (d, $J$=8.9 Hz, 1H), 8.23 (d, $J$=1.2 Hz, 1H), 8.07 (d, $J$=8.8 Hz, 1H), 7.85 (d, $J$=8.8 Hz, 1H), 7.82 (d, $J$=7.2 Hz, 1H), 7.77 (d, $J$=7.6 Hz, 1H), 7.73 (d×d, $J$=8.8 Hz, 1H), 7.52 (d, $J$=8.8 Hz, 2H), 7.33–7.31 (m, 4H), 7.21 (d, $J$=8.8 Hz, 1H), 7.15 (d, $J$=8.4 Hz, 4H), 7.10 (t, $J$=7.2 Hz, 2H), 7.05 (d, $J$=8.8 Hz, 2H), 5.50 (d, $J$=8.8 Hz, 1H), 3.79 (t, $J$=7.8 Hz, 2H), 2.00 (s, 6H), 1.76–1.70 (m, 2H), 1.47–1.43 (m, 2H), 1.01 (t, $J$=7.2 Hz, 3H). HRMS ($m/z$) calcd for $C_{48}H_{38}N_4OS^+$([M]$^+$): 718.9065, found: 718.9061.

### *3.3.4. 2-[(3-Butyl-1,1-dimethyl-5-carboxyl-indoline-2-ylidene)propenyl]-[3-butyl-7-(4-diphenylamino-phenylethynyl)-1,1-dimethyl]-1H-benz[e]indolium iodide (**I**)*

The mixture of intermediate **7** (718.91 mg, 0.1 mmol), intermediate **8** (388.26 mg, 0.1 mmol), and 3 mL acetic anhydride was stirred under reflux for 1 h. The reaction mixture was poured into 50 mL water and the solution was stirred at room temperature until a precipitate was formed. The solid was filtered and washed twice with water (10 mL). The crude product was purified through silica gel column with $N,N'$-dimethylformylamine/ethanol=50:1 (v/v) as eluent to afford 81.7 mg, yield 75%. $^{1}$H NMR (DMSO-$d_6$, 500 MHz), $\delta$: 8.51 (t, $J$=13.5 Hz, 1H), 8.46 (s, 1H), 8.43 (d, $J$=8.9 Hz, 1H), 8.23 (d, $J$=9.0 Hz, 1H), 8.17 (s, 1H), 8.01 (t, $J$=8.4 Hz, 2H), 7.92 (t, $J$=8.1 Hz, 2H), 7.83 (d, $J$=9.0 Hz, 1H), 7.51 (d, $J$=8.6 Hz, 3H), 7.38 (t, $J$=7.8 Hz, 4H), 7.22–7.07 (m, 6H), 6.93 (d, $J$=8.6 Hz, 2H), 6.69 (d, $J$=13.5 Hz, 1H), 6.57 (d, $J$=13.0 Hz, 1H), 4.31 (s, 2H), 4.14 (s, 2H), 2.00 (s, 6H), 1.79–1.72 (m, 10H), 1.47–1.42 (m, 4H), 0.97–0.85 (m, 6H); $^{13}$C NMR ($CDCl_3$, 400 MHz), $\delta$: 176.1, 173.6, 170.2, 154.4, 154.3, 148.8, 146.9, 140.3, 140.2, 134.1, 133.1, 132.9, 132.8, 131.9, 131.6, 130.5, 129.9, 129.6, 129.3, 127.5, 125.4, 125.2, 124.1, 123.8, 121.8, 121.6, 119.5, 118.0, 116.1, 114.7, 112.1, 109.5, 105.1, 98.8, 96.9, 87.1, 84.9, 50.9, 48.6, 30.2, 29.7, 29.3, 28.2, 27.8, 27.5, 20.4, 14.2, 14.0; HRMS ($m/z$) calcd for $C_{64}H_{58}N_5O_2S^+$ ([M−I$^-$]$^+$): 960.4306, found: 960.4304.

### *3.3.5. 2-[(3-Butyl-1,1-dimethyl-5-carboxyl-indoline-2-ylidene)propenyl]-{3-butyl-7-[7-(4-diphenylamino-phenylethynyl)-benzo[1,2,5]thiadiazol-4-ylethynyl]-1,1-dimethyl}-1H-benz[e]indolium iodide (**II**)*

The product was synthesized according to the procedure as described above for the synthesis of **I**, giving product **II** in 71% yield. $^{1}$H NMR (DMSO-$d_6$, 500 MHz), $\delta$: 8.50 (t, $J$=13.6 Hz, 1H), 8.35 (d, $J$=8.9 Hz, 1H), 8.28 (s, 1H), 8.15 (d, $J$=8.8 Hz, 1H), 8.12 (s, 1H), 8.03 (d, $J$=8.5 Hz, 1H), 7.85 (d, $J$=9.2 Hz, 1H), 7.72 (d, $J$=9.0 Hz, 1H), 7.48 (d, $J$=8.5 Hz, 2H), 7.40–7.36 (m, 5H), 7.18–7.11 (m, 6H), 6.92 (d, $J$=8.5 Hz, 2H), 6.58 (d, $J$=13.5 Hz, 1H), 6.55 (d, $J$=13.2 Hz, 1H), 4.30 (s, 2H), 4.15 (s, 2H), 1.98 (s, 6H), 1.79–1.71 (m, 10H), 1.47–1.42 (m, 4H), 0.97–0.93 (m, 6H); $^{13}$C NMR (DMSO-$d_6$, 400 MHz), $\delta$: 175.5, 174.0, 148.1, 147.2, 147.1, 145.0, 144.4, 143.9, 139.9, 134.0, 132.8, 132.6, 131.6, 130.6, 129.7, 129.4, 127.0, 125.0, 124.1, 123.7, 123.6, 122.1, 122.0, 120.6, 115.6, 104.1, 91.4, 88.5, 50.9, 48.9, 45.2, 30.0, 29.7, 28.3, 27.9, 20.4, 19.2 14.2, 14.0; HRMS ($m/z$) calcd for $C_{56}H_{56}N_3O_2^+$ ([M−I$^-$]$^+$): 802.4373, found: 802.4369.

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## References and notes

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