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A novel ruthenium-free TiO_2 sensitizer consisting of di-*p*-tolylaminophenyl ethylenedioxythiophene and cyanoacrylate groups

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A novel ruthenium-free organic dye, 3-(5-(4-(di-*p*-tolylamino)styryl)-2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-7-yl)-2-cyanoacrylic acid (coded as H01), is synthesized in a short sequence. The dye is composed of a di(*p*-tolyl)phenylamino moiety as an electron donor, a cyanoacrylate moiety as an electron acceptor, and an ethylenedioxythiophene unit as the spacer to bridge the donor and the acceptor. The as-prepared H01 dye is employed as a sensitizer in a dye-sensitized nanocrystalline TiO_2 solar cell, and the short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*ff*) of the device under AM 1.5 (100 mW cm^{-2}) irradiation, are 15.22 mA cm^{-2}, 0.67 V, and 0.72, respectively, corresponding to an overall conversion efficiency (*Eff*) of 7.33%.

Introduction

Dye-sensitized solar cells (DSCs) have received increasing attention over the past two decades because of strong industrial interest related to their potential low cost, easy preparation, and relatively high light-to-electric energy conversion efficiencies.[1] In DSCs, photo-sensitizing dye molecules are often assembled onto the surface of nano-structured semiconductor TiO_2 electrodes, making it possible to increase photocurrent and remarkably improve overall conversion efficiencies. Polypyridyl ruthenium complexes, such as N3/N719,[2,3] have been successfully employed in DSCs as sensitizers with high efficiencies of up to 11%. In contrast to such ruthenium complexes, Ru-free organic dyes have attracted much attention in the development of DSCs due to several advantages: (i) relatively high molar extinction coefficients (ε) due to intramolecular π–π^* transitions which enable efficient light harvesting, (ii) a variety of structure modification and easy purification, and (iii) no need for toxic and costly Ru metal. The high conversion efficiency of 9.03% was recently reported with an indoline dye (D149).[4] The value is comparable to those obtained for ruthenium dyes, and thus organic dyes have been recognized as more suitable alternatives to Ru complexes for practical applications. A number of efficient organic dyes, such as perylene,[5] cyanine,[6,7] xanthene,[8] merocyanine,[9] coumarine,[10] hemicyanine,[11] and triphenylamine dyes,[13] have been investigated. It is often accepted that the unidirectional electron flow in organic dyes leads to efficient electron injections to TiO_2. A molecular design strategy that fulfils this criterion was adopted on the dyes possessing donor-π space-acceptor structures, in which methine units,[12a] benzene,[7a] benzothiadiazole,[12b] thiophene,[12c,d] or bisthienothiophene[12e] are used as the spacer to bridge the donor and acceptor units.

3,4-Ethylenedioxythiophene (EDOT) is an attractive building block with an electron donating ability and physical/chemical stability as known for commercially available conductive polymers, PEDOT/PSS. There is a report on the synthesis of 'push–pull' π-conjugated chromophores using EDOT.[14] In our study, EDOT is introduced as a spacer to bridge triarylamine and cyanoacrylic acid moieties in a dye molecule. Here, a ditolylaminostyryl unit is employed as an electron donor because of the electron donating ability of its methyl groups and the non-planar structure of the unit. A cyanoacetic acid moiety functions as an electron acceptor as well as an anchoring group for the attachment onto the TiO_2 surface. The organic dye (coded as H01, as shown in Scheme 1), 3-(5-(4-(di-*p*-tolylamino)styryl)-2,3-dihydrothieno-[3,4-*b*][1,4]dioxin-7-yl)-2-cyanoacrylic acid, was synthesized in three steps in a high yield. The dye was employed as a sensitizer in DSCs, giving a high conversion efficiency of up to 7.33%, which is a little inferior to ruthenium dyes, N3 and N719, but found comparable to that of the commercial D149 organic dye.

Results and discussion

As shown in Scheme 2, the H01 dye was synthesized in a short sequence. 3,4-Ethylenedioxy thiophene-5-carbaldehyde was first coupled with *p*-(di-*p*-tolylamino)benzyl triphenylphosphonium bromide using the Wittig reaction, followed by a Vilsmeier–Haack reaction, and a condensation of the aldehyde with cyanoacetic acid was carried out in the presence of piperidine.

The absorption and emission spectra of the H01 dye were measured in dimethylformamide (DMF) as shown in Fig. 1. The absorption maximum (λ_{max}) lies at 460 nm with a high molar extinction coefficient of 4.67×10^4 $M^{-1}cm^{-1}$, while the

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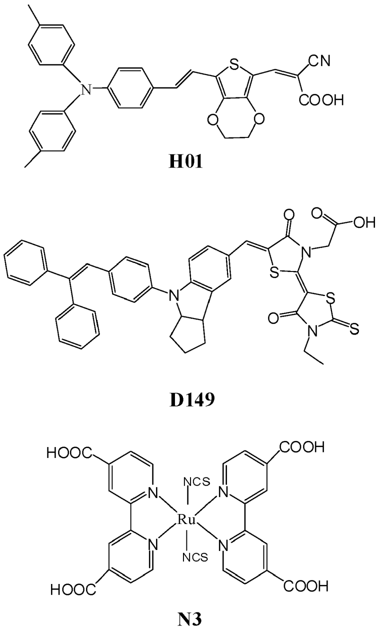
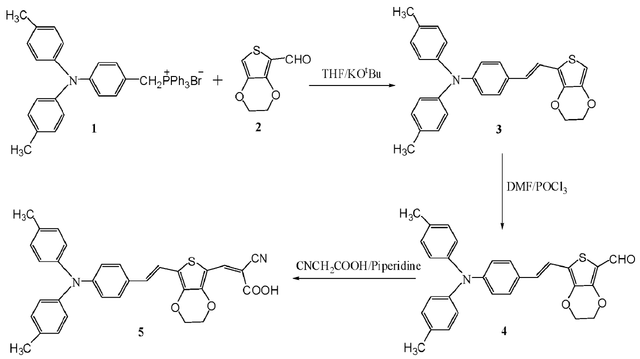


Scheme 1 Chemical structures of H01, D149 and N3 dyes.



Scheme 2 A synthetic route to the H01 dye.

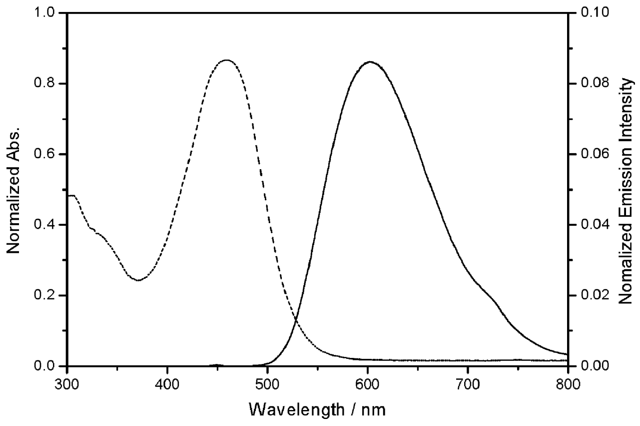


Fig. 1 Absorption (dashed line) and emission (solid line) spectra of H01 in DMF. The emission spectrum was obtained using the same solvent by excitation at 450 nm.

emission maximum is centered at 602 nm by excitation at 450 nm. The λ_{max} is red shifted around 23 nm when compared to that of the DS-1 previously reported,[12d] where a thiophene linker was used. The red shift favors light harvesting in the visible region for DSCs. In order to understand the possibility of electron transfer from the excited dye molecule to the conductive band of TiO_2 and the dye regeneration, the oxidation potential was measured in DMF solution with 0.1 M tetrabutylammonium hexafluorophosphate *via* square-wave voltammetry. The two oxidation potentials at 0.76 and 0.95 V (*versus* NHE) were achieved by averaging the corresponding anodic and cathodic peak potentials. The reduction potential was calculated from the first oxidation potential and the E_{0-0} determined from the intersection of absorption and emission spectra. The energy level of the dye excited state (−1.46 V *versus* NHE) is more negative than the band edge energy of the nanocrystalline TiO_2 electrode (−0.5 V *versus* NHE), and that of the dye cation (0.76 V *versus* NHE) is more positive than the I^-/I_3^- couple (0.5 V *versus* NHE), indicating that the electron injection process from the excited dye molecule to the TiO_2 conduction band and the subsequent dye regeneration are energetically favorable.

For the preparation of DSCs, two layers of TiO_2 films, a main layer and a scattering layer, were prepared by doctor blading two different TiO_2 pastes on FTO (F-doped SnO_2) glass substrates. The first nano-porous layer is transparent with a thickness of 9 μm (TiO_2 particle size: 20 nm, PST-18NR, Catalysts & Chemicals Industries Co., Ltd, Japan). The second scattering layer is used with a thickness of 7 μm (TiO_2 particle size of 400 nm, PST-400C, Catalysts & Chemicals Industries Co., Ltd, Japan) for increasing the device light harvesting in the red region. For comparison, a commercial organic dye D149, standard N3 and N719 ruthenium dyes, and our previously reported HRS-1 ruthenium dye, were employed in DSCs. A dye solution (0.5 mM) was prepared with 1 mM chenodeoxycholic acid in *tert*-butyl alcohol–acetonitrile (1 : 1, v/v). The dye adsorbed TiO_2 film was clipped with a Pt-sputtered FTO glass used as a counter electrode, and filled with electrolytes containing 0.6 M 1-propyl-3-methylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (1 : 1, v/v). The photovoltaic performance of the devices was recorded under 100 mW cm^{-2} simulated air mass (AM 1.5) solar light illumination.

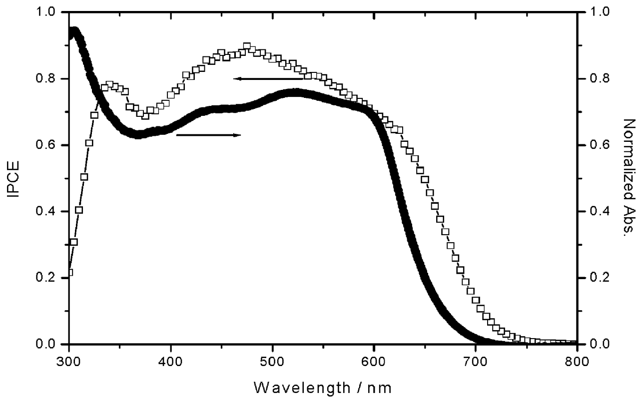


Fig. 2 The photocurrent action spectrum (dotted line) of H01 based DSC (cell active area: 0.167 cm^2), and absorption spectrum (solid line) of H01 adsorbed TiO_2 film.

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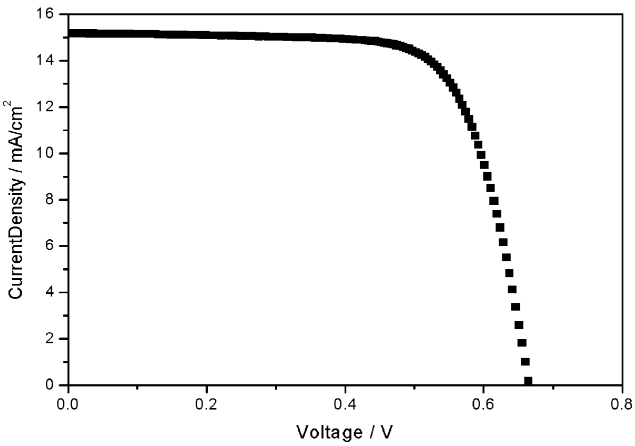


Fig. 3 Photocurrent density–voltage curve of the DSC with H01 under AM 1.5 simulated sunlight (100 mW cm^{-2}) illumination (thickness of TiO_2: 9 + 7 μm, active area: 0.167 cm^2).

Fig. 2 shows the incident photo-to-current conversion efficiency (IPCE) of the H01-based device as a function of the wavelength. The IPCE is more than 70% in a spectral range from 390 nm to 590 nm, and reaches its maximum of 86% at 472 nm. When reflection and absorption losses of the FTO glass substrate are considered, the net photo-to-electron conversion efficiency is almost unity in this spectral range. Fig. 3 also shows the UV-vis diffuse reflectance spectrum of the H01-adsorbed TiO_2 film, is consistent with the IPCE spectrum which means that efficient electron transfer occurs from the photo-excited dye to TiO_2.

Fig. 3 shows the *I–V* curve of the H01-based DSC. The short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*ff*) of the device with the H01 sensitizer under AM 1.5 (100 mW cm^{-2}) irradiation, are 15.22 mA cm^{-2}, 0.67 V, and 0.72, respectively, corresponding to an overall conversion efficiency (*Eff*) of 7.33%. For comparison, DSCs were prepared with D149, DS-1, N3, N719 and HRS-1 as sensitizers, respectively. All the devices were prepared under the comparable condition, and their photovoltaic data are summarized in Table 1. All the devices gave comparable V_{oc} and *ff* values. The difference in *Eff* values mainly comes from the J_{sc} values for the devices with different dyes. N3, N719 and HRS-1 based devices gave J_{sc} values (mA cm^{-2}) of 18.15, 19.03 and 20.01, respectively, corresponding to *Eff* values (%) of 8.37, 8.92 and 9.51. In the case of D149, the device gives a J_{sc} of 16.10 mA cm^{-2}, a V_{oc} of 0.69 V, an *ff* of 0.68, and an *Eff* of 7.52%, comparable to that of the H01-based device. The DSCs sensitized by DS-1 give a J_{sc} of 14.3 mA cm^{-2}, a V_{oc} of 0.67 V, an *ff* of 0.73 and an *Eff* of 6.71%. As for the comparison of structural analogues H01 and DS-1, the overall efficiency increased by 10% when the thiophene linker in DS-1 was replaced by EDOT. The comparison of IPCE and absorption spectra of H01 with those of DS-1 that were reported previously[12d] show that the much higher efficiency of H01 is ascribed to the more effective light-to-electricity conversion in the near IR region. It is worth noting that the high efficiencies of H01 and DS-1 with respectable *ff* and V_{oc} values are explained as due to unidirectional electron flow at the dye-covered nc-TiO_2 with the help of the electron donating and oleophilic *p*-tolylaminophenyl groups coupled with cyanoacrylate anchoring groups.[1h]

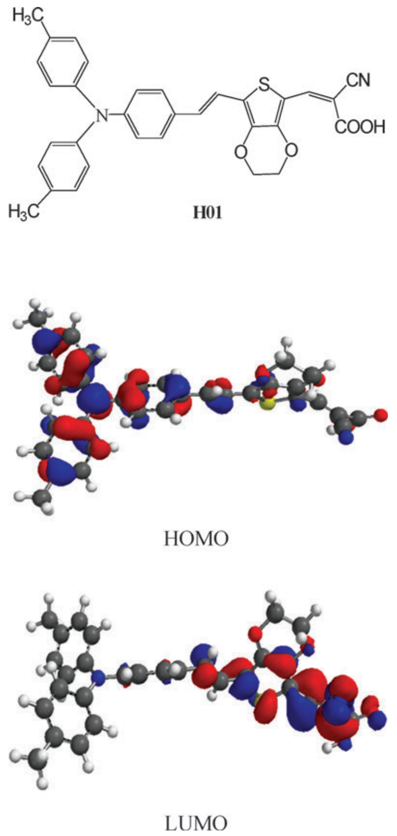
Table 1 Photovoltaic performance of DSCs[a]

Dye	J_{sc}/mA cm^{-2}	V_{oc}/V	*ff*	*Eff* (%)
H01	15.22	0.67	0.72	7.33
D149	16.10	0.69	0.68	7.52
DS-1	14.30	0.65	0.73	6.71
N3	18.15	0.68	0.68	8.37
N719	19.03	0.68	0.68	8.92
HRS-1	20.01	0.68	0.69	9.51

[a] All the data were averaged using four samples.

Although the performances of the N3, N719 and HRS-1 based devices in the present conditions are superior to that of the H01-based device, further improvement of the conversion efficiency may be expected if the chemical structure of the H01 dye is modified to extend π conjugation for increasing light harvesting in the near-IR region.

The relatively high conversion efficiency of H01 may also be due to the donor–acceptor structure consisting of a *p*-tolylaminophenyl moiety and a cyanoacrylate group (Scheme 3) which may dramatically improve the charge transfer from photo-excited dye molecules to TiO_2. In fact, the electron distribution of the H01 dye calculated by density functional theory (DFT) at a B3LYP/6–31 + G (D) level shows that the electron distribution of the HOMO is more localized than the thiophene homolog dye D5[12c] and DS-1, and the electron density locates at the ditolylamino nitrogen



Scheme 3 The chemical structure and frontier orbitals of H01 dye.

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atom, while the LUMO is more localized in the cyanoacrylate anchoring group than the thiophene homolog of DS-1 and D5. Thus, the HOMO–LUMO excitation induced by light irradiation could move the electron distribution from the donor sites to the anchoring cyanoacrylate moiety. Assuming that the molecular orbital geometry can be caused by the dye anchored to TiO_2, the position of the LUMO close to the anchoring group would favor the orbital overlap with the titanium 3d orbital and thus the push–pull structure of the H01 dye can enhance electron injection from the dye to TiO_2.

In principle, it is proved that the performance of DSCs can be improved and maintained with high reliability when intrusion of water and oxygen molecules is prevented during fabrication of DSCs. This is because the presence of water induces hydrolysis of dye molecules anchored by carboxyl groups on nc-TiO_2, and the presence of oxygen leads to oxidative dye degradation by highly oxidative singlet-state oxygen produced by energy transfer from triplet-state photo-excited dye molecules to the ground-state triplet-state oxygen. In fact, several cyanoacrylate dye-based DSCs are known to possess high stabilities when they are fabricated using moisture-proof sealant and oxygen-barrier materials.[17] This means that the cell efficiency and stability of the H01-based DSCs can be maintained if all the fabrication procedures could be carried out in glove boxes, *e.g.*, a nitrogen-filled glove box kept with an atmosphere of ppm-order water and oxygen content (*i.e.*, oxygen-free atmosphere with very low dew-point). In addition, the H01 dye with an oleophilic *p*-tolylphenylamino group could avoid the dissociation from TiO_2 surface even in the presence of water contaminants.

Experimental

General

All reactions were carried out under a nitrogen atmosphere. THF was distilled from sodium and benzophenone under a nitrogen atmosphere. DMF, dichloromethane and $POCl_3$ were distilled from CaH_2 under an N_2 atmosphere. 3-Dihydrothieno-[3,4-*b*]dioxine and cyanoacetic acid were purchased from Aldrich. Phosphonium salt **1**[15] and 2,3-dihydrothieno[3,4-*b*]-dioxine-5-carbaldehyde **2**[16] were prepared according to literature procedures. All other chemicals and solvents used in this work were analytical grade from the Beijing Chemical Factory. All chromatographic separations were carried out on silica gel (200–300 mesh). ^1H and ^{13}C NMR spectra were recorded on a BRUKER DMX-400 (400 MHz for ^1H) and a BRUKER DMX-300 (400 MHz for ^{13}C) with tetramethylsilane as internal standard. MALDI-TOF mass spectrometric measurement was performed on BRUKER BIFLEX III, and high-resolution mass spectra (HRMS) were recorded on a JEOL JMS-HX110A spectrometer.

Methods

Synthesis of 4-(2,3-dihydrothieno[3,4-*b*]dioxin-5-yl)vinyl)-*N*,*N*-tolylamine (3). *t*-BuOK (1.000 g, 8.93 mmol) was added to a suspension of phosphonium salt **1** (4.202 g, 6.69 mmol) in 60 ml of THF at room temperature under an N_2 atmosphere. After cooling to 0 °C, compound **2** (0.941 g, 5.53 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 h and at room temperature for 5 h, then 20 ml of water was added to the solution. Dichloromethane was added to the reaction mixture, and the organic phase was washed with water, and dried with $MgSO_4$. The crude product was collected and used in the next step without further purification.

Synthesis of 7-(di-*p*-tolylamino)styryl)-2,3-dihydrothioeno-[3,4-*b*]dioxine-5-carbaldehyde (4). A mixture of DMF (3 ml) and CH_2Cl_2 (60 ml) was cooled to 0 °C, then $POCl_3$ (1.20 ml) was added dropwise under an N_2 atmosphere. After stirring for 10 min, a solution of compound **3** (2.42 g, 5.46 mmol) in CH_2Cl_2 (20 ml) was added slowly. The solution was allowed to warm to room temperature, and refluxed for 4 h. After cooling to 0 °C, the solution was added to 50 ml of iced water, and stirred for 10 min, followed by neutralization with aqueous NaOH (10%, w/w). The mixture was extracted with CH_2Cl_2, and the organic phase was washed with water and dried with $MgSO_4$. The crude product was subjected to silica gel column chromatography with a CH_2Cl_2–hexane mixture (2 : 1, v/v) to give an orange powder (2.06 g, 81%). ^1H NMR (400 MHz, d_6-DMSO): δ = 9.81 (s, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.1 Hz, 4H), 7.09 (d, J = 5.0 Hz, 2H), 6.96 (d, J = 8.1 Hz, 4H), 6.81 (d, J = 8.6 Hz, 2H), 4.43 (d, J = 18.72 Hz, 4H), 2.28 (s, 6H). MALDI-TOF: m/z: 467.6.

Synthesis of 3-(5-(4-(di-*p*-tolylamino)styryl)-2,3-dihydrothieno-[3,4-*b*][1,4]dioxin-7-yl)-2- cyanoacrylic acid (5). To 40 ml of CH_3CN, compound **4** (0.5 g, 1.07 mmol), cyanoacetic acid (0.21 g, 2.35 mmol) and piperidine (0.11 g, 1.18 mmol) were added. The mixture was refluxed for 4 h under an N_2 atmosphere. After cooling, solvent removal by rotary evaporator was carried out, followed by purification by column chromatography over silica gel with CH_2Cl_2–CH_3OH (4 : 1, v/v) yielded the product as purple powder (0.43 g, 75%). ^1H NMR (400 MHz, d_6-DMSO): δ = 8.12 (s, 1H), 7.55 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.1 Hz, 4H), 7.18 (d, J = 16.2 Hz, 1H), 7.08 (m, 5H), 6.90 (d, J = 8.6 Hz, 2H), 4.45 (d, J = 18.72 Hz, 4H), 2.31 (s, 6H). ^{13}C NMR (300 MHz, d_6-DMSO): δ = 164.1, 148.8, 148.3, 144.0, 139.4, 138.4, 133.2, 131.7, 130.2, 128.4, 128.2, 127.4, 125.1, 120.3, 117.3, 114.5, 108.6, 93.6, 65.8, 64.6, 20.4. HRMS (FAB, positive mode) found 534.1609, $C_{32}H_{26}N_2O_4S$ requires 534.1613.

Fabrication of the DSCs. Two layers of TiO_2 films, main layer and scattering layer, were prepared by doctor blading TiO_2 pastes on an FTO glass substrate (Ω/ε, Nippon Sheet Glass). The main layer (thickness: 9 μm, TiO_2 particle size: 13 nm, from Solaronix Ti-Nanoxide T) and scattering layer (thickness: 7 μm, TiO_2 particle size, 400 nm, from CCI in Japan) were prepared from these two different TiO_2 colloids, respectively. The first layer of TiO_2 was heated at 450 °C for 30 min., and the second layer was heated at 520 °C for 20 min. The resulting film was further treated with a 0.04 M $TiCl_4$ aqueous solution. The H01 and N3 dye solutions were prepared in ethanol at a concentration of 0.5 mM. In the case of H01, 1 mM chenodeoxycholic acid was added to prevent unfavorable dye aggregation on TiO_2 phases. For D149, a 0.5 mM dye solution was prepared with 1 mM chenodeoxycholic acid in *tert*-butyl alcohol–acetonitrile (1 : 1, v/v) as reported.[16]

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The TiO_2 films were left in the solution at room temperature for 12 h. A Pt-sputtered FTO glass was used as a counter electrode. The electrolyte was composed of 0.6 M 1-propyl-3-methylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (1 : 1, v/v). The photovoltaic performance of the devices was recorded under 100 mW cm^{-2} simulated air mass (AM) 1.5 solar light illumination. The H01 and N3 dye solutions were prepared in ethanol at a concentration of 0.5 mM. In the case of H01, 1 mM chenodeoxycholic acid was added to prevent unfavorable dye aggregation on TiO_2 phases. For D149, a 0.5 mM dye solution was prepared with 1 mM chenodeoxycholic acid in *tert*-butyl alcohol–acetonitrile (1 : 1, v/v) as reported. The dyed TiO_2 film was clipped with a Pt-sputtered FTO glass used as counter electrode, and then filled with electrolyte consisting of 0.6 M 1-propyl-3-methylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (1 : 1, v/v). The photovoltaic performance of the devices was recorded under 100 mW cm^{-2} simulated air mass 1.5 solar light illumination.

Conclusions

We have successfully synthesized a novel ruthenium-free organic dye (H01) in a short sequence with ethylenedioxythiophene (EDOT) unit as a spacer to bridge the di-*p*-tolylaminophenyl donor and cyanoacrylate acceptor. We have also demonstrated that the photovoltaic performance of H01 is almost comparable to that of the well-known D149 organic dye. More efficient near-IR absorbing dyes based on the simple modification of H01 structure are being researched by our group.

Acknowledgements

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