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Thiophene-fused coplanar sensitizer for dye-sensitized solar cells

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ABSTRACT

We have designed and synthesized a novel ladder-type heteroacene dye consisting uniquely of thiophene segments as a photosensitizer for the dye-sensitized solar cells (DSSCs). The onset of the IPCE spectrum for the dye not only reaches up to 700 nm with a high IPCE (>60%) but also a solar energy-to-electricity conversion efficiency of 2.31% is achieved. Even though the efficiency is slightly lower than those of other dyes reported previously, this work opens up a new strategy to design heteroaromatic fused photosensitizers for DSSCs.

Dye-sensitized solar cells (DSSCs) have grown one of the most blossoming alternatives for the photovoltaic conversion of solar energy as compared to the typical solid p–n junction photovoltaic devices.[1,2] Up to this time, the conventional ruthenium (Ru)-based sensitizers such as N3/N719[3,4] and black dye[5] have reached the promising solar-energy-to-electricity conversion efficiencies of 11% under AM 1.5 irradiation. In addition to Ru complexes, metal-free organic dyes have also been utilized as photosensitizers in DSSCs because of their wide variety of the structures, facile modification, high molar absorption coefficient, low cost, and environment-friendliness.[6–8] Generally, organic dyes should contain a structure of donor (D)-to-acceptor (A) bridged by a π-conjugation system and possess a broad and intense spectral absorption. Among the various types of π-conjugated compounds, the ladder π-electron systems, which have fully ring-fused cyclic skeletons, are a particularly growing class of materials.[9–12] Their rigid π-conjugated frameworks without any conformational disorder can not only strengthen the parallel p-orbital interactions to elongate effective conjugation length and facilitate π-electron delocalization, providing an effective way to extend the visible absorption region[13,14] but also suppress the rotational disorder around interannular single bonds and lower the reorganization energy, which in turn enhances the intrinsic charge mobility.[15–17]

Taking these positive points into account, the first successful examples of the ladder-type donor (D)-π-spacer-acceptor (A) sensitizers with pentaphenylene were reported by Müllen and co-workers.[6] Although such dyes exhibited high absorption coefficients up to 75,600 M^{-1} cm^{-1}, the efficiencies of these dye-based solar cells were below 2.3% in DSSCs with the low current a result of the short wavelength absorption of the dyes (λ_{max} = 442–457 nm) and the low driving forces for the dye regeneration.

One can also observe in DSSCs that thiophene is an important building unit for improved efficient devices. Thereby, in the one-dimensionally ladder-type framework, the introduction of a thiophene moiety seems to provide advantages in order to achieve high performance photovoltaic materials.[18] On the basis of the results reported above, we have tried to design a fused oligoacene dye with the combination of thiophene and phenylene units in one molecular skeleton. Herein, we report a new ladder-type π-conjugated heteroacene dye containing thiophene segments as coplanar π-conjugation system with the acceptor/anchor group (2-cyanoacrylic acid) and donor functionality (*N*,*N*-dimethylaniline) for use in DSSCs. (see Fig. 1) In addition, the bulky aryl side groups can suppress the aggregation for the dye on the TiO_2 surface, probably resulting in further efficient photocurrent generation.

The novel ladder-type π-conjugated heteroacene dye containing thiophenes is constructed by the stepwise synthetic protocol illustrated in Scheme 1. The diethyl 2,5-di(thiophen-2-yl)terephthalate (**2**) was synthesized by Stille coupling reaction of diethyl 2,5-dibromoterephthalate (**1**) with 2-stannylthiophene. Addition of 4-methylphenyllithium gave the corresponding diol and the desired thiophene-implanted coplanar chromophore (4,9-dihydro-4,4,9,9-tetrakis(4-methylphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (**3**)), which subsequently underwent bromination

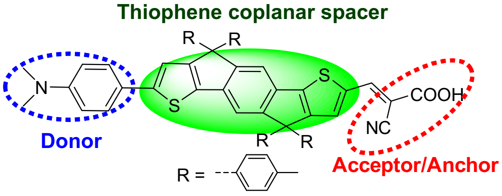

Figure 1. Chemical structure of the thiophene-fused coplanar sensitizer.

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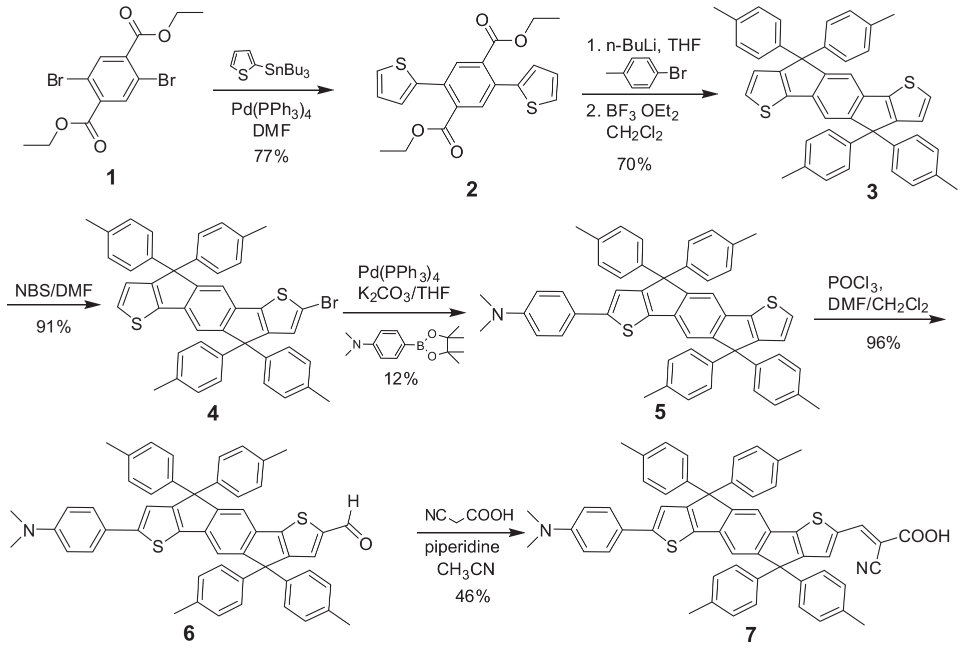

Scheme 1. Synthetic route of the thiophene-fused coplanar sensitizer **7**.

with NBS in DMF to generate the mono bromothiophenyl compound **4**. Suzuki coupling of **4** with *N*,*N*-dimethylaniline-4-boronate ester yielded the key intermediate **5**. The thiophene unit was converted to the corresponding carbaldehyde **6** via Vilsmeier–Haack reaction.[19] Upon condensation of **6** with cyanoacetic acid by Knoevenagel reaction in the presence of piperidine, the target thiophene-fused coplanar sensitizer **7** was isolated as a dark-red solid. Thanks to the bulky aryl substituents as the solubilizing groups, the coplanar sensitizer **7** shows excellent solubility in common organic solvents, overcoming the planarity–solubility tradeoff to facilitate its processability.

Optical properties: The UV–vis absorption of the coplanar sensitizer **7** was investigated in chloroform and on the TiO_2 film, respectively, as depicted in Figure 2. The absorption of **7** shows a broad peak centered at 500 nm with extinction coefficient (ε) of 84,000 M^{-1} cm^{-1}, arising from π–π^* charge transfer transition in the chromophore backbone. Notably, the absorption of the coplanar sensitizer **7** is substantially bathochromically shifted with significantly higher molar extinction coefficient as compared to the mother ladder-type pentaphenylene-based dyes (the absorption maxima of the dyes range from 442 to 457 nm and their molecular coefficients are at less than 76,000 M^{-1} cm^{-1}).[6] This is due to the introduction of thiophenes as heteroaromatic electron-rich building segments instead of phenylene groups in the dye.

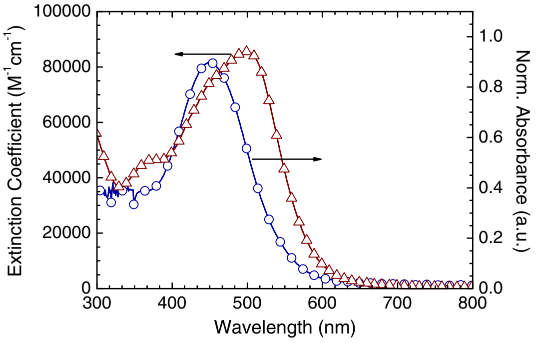

Figure 2. UV–vis absorption spectra of the thiophene-fused coplanar sensitizer **7** in $CHCl_3$. (-△-) and on the TiO_2 film (-○-).

The absorption peak of the coplanar sensitizer **7** is blue-shifted by adsorption on the TiO_2 surface (Fig. 2). The blue shift of the absorption spectrum by adsorption on the TiO_2 surface is also observed in other organic dyes,[20,21] which is presumably attributed to the deprotonation of the dye by adsorption on the TiO_2 surface (i.e., the carboxylate anion). In addition, we cannot count out that the interactions between TiO_2 surface and the adsorbed dye molecule may lead to the formation of H-type aggregate.[22]

Photovoltaic performance of DSSCs: Nano-crystalline TiO_2 colloids prepared by a sol-gel hydrolysis method[23] were used for making the TiO_2 paste. The TiO_2 paste was consisted of TiO_2 nano-crystalline, ethylcellulose as a binder, and α-terpineol as a solvent. The TiO_2 paste was printed on a F-doped SnO_2 conducting glass (TEC Glass-TEC 8, Pilkington) and subsequently sintered at 500 °C for 1 h. The thickness of the TiO_2 thin film was 15 μm and the active area of the TiO_2 electrode was 0.25 cm^2. The coplanar sensitizer **7** was dissolved at a concentration of 0.3 mM in an absolute ethanol. The TiO_2 film was immersed in the dye solution and kept at room temperature for 1 day to allow the dye to be adsorbed to the TiO_2 surface. A detailed fabrication process is described in Supplementary data.

The photovoltaic performance of the DSSCs was obtained using a liquid electrolyte comprising 0.6 M 1-hexyl-2,3-dimethyl-imidazolium iodide, 0.1 M lithium iodide, 0.05 M iodine, and 0.5 M 4-*tert*-butylpyridine in acetonitrile.[24] The photovoltaic performance was recorded under the simulated AM 1.5 irradiation (100 mW cm^{-2}).

The action spectrum of monochromatic incident photon-to-current conversion efficiency (IPCE) for the DSSC based on the coplanar sensitizer **7** is presented in Figure 3. As expected, the IPCE spectrum of the DSSC based on the coplanar sensitizer **7** is bathochromic-shifted, when compared to that based on the ladder-type pentaphenylene-based dyes,[6] which is in good agreement with absorption behavior of **7** described above. The onset of the IPCE spectrum of the DSSC based on **7** is 700 nm and a high IPCE (>60%) is observed in the range from 440 to 520 nm with a maximum value of 65.5% at 475 nm.

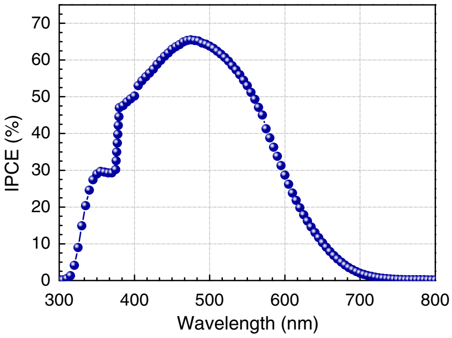

Figure 3. IPCE spectrum for dye-sensitized solar cell based on thiophene-fused coplanar sensitizer **7**.

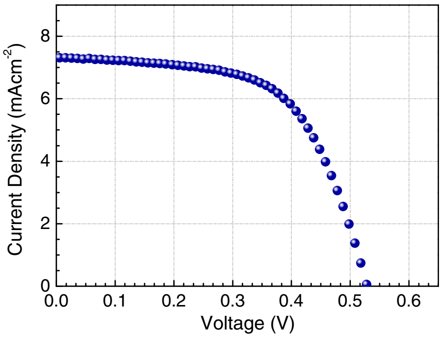

Figure 4. J–V curve obtained with dye-sensitized solar cell based on thiophene-fused coplanar sensitizer **7** under AM 1.5 irradiation (100 mW cm^{-2}).

The solar energy-to-electricity conversion efficiency, η (%) under white-light irradiation (e.g., AM 1.5G) can be obtained from the following equation:

$$\eta = (J_{sc} \times V_{oc} \times \mathrm{FF}) \times 100/I_0 \qquad (1)$$

where I_0 (mW cm^{-2}) is the photon flux (100 mW cm^{-2} for AM 1.5G), J_{sc} (mA cm^{-2}) is the short-circuit current density under irradiation, V_{oc} (V) is the open-circuit voltage, and FF represents the fill factor. As depicted in Figure 4, a η value of 2.31% (J_{sc} = 7.3 mA cm^{-2}, V_{oc} = 0.53 V, and FF = 60.3%) is obtained with the DSSC based on **7** under AM 1.5 solar condition.

By considering the high molar extinction coefficient and the broad absorption of the dye **7** in our experiments, the further enhanced device performance could be expected. The low performance of DSSCs based on the dye **7** is mainly due to the low current value, which can be the result of the relatively decreased IPCE. Although the efficiency of the dye **7** still needs to be further improved with respect to high-end applications, the preliminary result can be comparable with or better than those of the optimized performance of DSSCs constructed with the parent ladder-type pentaphenylene-based dyes (η = 1.1–2.3%). We are currently studying the molecular structures of the further extended thiophene-fused coplanar sensitizers to help us better understand the DSSCs based on heteroaromatic fused molecular structures.

In summary, a novel ladder-type donor (D)-π-spacer-acceptor (A) heteroaromatic dye is synthesized as a photosensitizer for DSSC applications in which the thiophene-fused coplanar building block serves as a π-conjugated electron spacer. The electron-donating moiety is substituted to *N*,*N*-dimethylaniline, and the electron-withdrawing part/anchor is 2-cyanoacrylic acid. In comparison with the parent ladder-type pentaphenylene-based dyes, the bathochromic shift of the absorption spectrum is achieved by introduction of thiophenes as electron-rich groups. A maximum η value of 2.31% is reached under AM 1.5 irradiation (100 mW cm^{-2}) with a DSSC based on the thiophene-fused coplanar sensitizer 7 (J_{sc} = 7.3 mA cm^{-2}, V_{oc} = 0.53 V, and FF = 60.3%). Although the efficiency of the resulting rigid coplanar dye molecule has somewhat lower relative to other dyes such as Ru-complex and other metal-free organic dyes, this work has launched the heteroaromatic-fused molecular structure into the possibility of sensitizers based on π-spacer bridged donors and acceptors. We believe that the development of highly efficient organic sensitizers is possible through sophisticated structural modification based on the ladder-type heteroaromatic dyes, and work on these is now in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.03.091.

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