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Triarylene linked spacer effect for dye-sensitized solar cells

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ABSTRACT

The effect of switching the phenylene and thiophenylene units in the triarylene bridge of organic donor-bridge-acceptor dyads on the performance of dye-sensitized solar cells is investigated. A thiophenylene group displays several distinctive advantages over those of a phenylene group. The electron-donating nature of thiophenlene elevates the electron energy level of the dyads and narrows down the energy gap of the electronic transition, therefore elongates the absorption wavelength. The presence of thiophenylene unit along the bridge also increases the planarity of the molecular geometry, therefore enhances the degree of π-delocalization; however, it also speeds up the rate of charge recombination. The multiple effects of thiophene group along the bridge are examined systematically on two types of dye derivatives, i.e., the **T**-series and the **M**-series dyes. Among all the dyes, the ones containing a phenylene–thiophenylene–thiophenylene bridge (T-PSS) showed the highest performance. A typical device made with **T-PSS** displayed the maximal monochromatic incident photon-to-current conversion efficiency of 65% in the wavelength region between 350 nm and 515 nm, a short-circuit photocurrent density 15.88 mA cm^{-2}, an open-circuit photovoltage 0.64 V, and a fill factor 0.60, that corresponds to an overall conversion efficiency of 6.13%. The packing order of **T-PSS** can be further improved by adding deoxycholic acid to an overall conversion efficiency of 6.71%.

1. Introduction

Under the global shortage of fossil fuels and the threat of increased greenhouse effect, it is in an urgent demand to develop renewable energy resources. Solar energy had been recognized as the most promising solution in the future. In the past two decades, dye-sensitized solar cells (DSSCs) have received considerable attention due to their improved efficiency and reduced fabrication cost. Since the first report by O'Regan and Grätzel in 1991 on high performance dye-sensitized solar cells using Ru-complexes, researches in this area have progressed very fast [1]. To date the three landmark ruthenium (II) complexes, i.e., N3, N719, and the black dye, have achieved maximal power conversion efficiencies exceeding 11% [2–5]. Compared with metallic materials, organic dyes have the advantages of environmental friendliness, higher structural flexibility, lower cost, easier preparation, purification, etc. A wide variety of organic dyes have been reported in the literatures including the derivatives of coumarin [6–8], indoline [9], cyanine [10,11], merocyanine [12], hemicyanine [13,14], perylene [15–20], dithiensilole [21–23], spirobifluorene [24–26], porphyrin [27–30], etc., whilst most of them exhibited an energy-to-electricity conversion efficiency in the range of 5–9%. In our previous studies we have investigated a series of organic donor–bridge–acceptor (D–B–A) dyads, in which an amine donor group (D) and a cyanoacrylic acid acceptor group (A) are connected by a triaryl linkage bridge (B) [31–36]. These D–B–A dyads exhibited remarkable quantum efficiency while fabricated into DSSCs. It was found that the device performance was closely related to the nature of the triaryl bridge. The electronic properties of phenylene (P) and thiophene (S) moieties on the bridges influence the rate of charge migration, therefore affects the quantum efficiency. In this report we prepared two series of dyes with different combinations of P and S groups, and analyse their efficiency on light harvesting in a systematic manner.

2. Experimental section

2.1. General information

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were distilled freshly according to standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on Brucker (AV 400/AV 500 MHz) spectrometer in $CDCl_3$, and DMSO-d_6 as a solvent. Chemical shifts are reported in scale downfield from the peak for tetramethylsilane. Absorption spectra were recorded on a Jasco-550 spectrophotometer. Emission spectra and photoluminescence quantum yield were obtained from a Hitachi F-4500 spectrofluorimeter. The

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emission spectra in solutions were measured in spectral grade solvent by a 90° angle detection. The redox potentials were measured by using cyclic voltammetry on CHI 620 analyser. All measurements were carried out in THF solutions containing 0.1 M tetrabutylammonium hexaflouro-phosphate ($TBAPF_6$) as the supporting electrolyte at an ambient condition after purging 10 min with N_2. The conventional three electrode configuration was employed, which consists of a glassy carbon working electrode, a platinum counter electrode, and a Ag/Ag^+ reference electrode calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an internal reference. Mass spectra were recorded on a VG70-250S mass spectrometer.

The chemicals, i.e., magnesium, 1,2-bis(diphenyl-phosphino) ethane nickel(II) chloride ($NiCl_2$(dppe)), 2-bromothiophene, 2,5-dibromothiophene, di-*p*-tolylamine, bis(4-methoxyphenyl)amine, 4,4′-dibromobiphenyl, 1,4-dibromobenzene, palladium(II) acetate ($Pd(OAc)_2$), 1,1′-bis(diphenylphosphanyl) ferrocene (dppf), *n*-butyllithium (1.6 M in hexane), trans-dichlorobis(triphenylphosphine) palladium (II) ($PdCl_2(PPh_3)_2$), N,N-dimethylformamide, 2-(tributylstannyl)thiophene, 5-bromothiophene-2-carbaldehyde, 4-bromobenzaldehyde, triisopropyl borate, N-bromosuccinimide (NBS), tri-*n*-butyltin chloride, cyanoacetic acid, ammonium acetate, and acetic acid glacial, were purchased from ACROS, Alfa, Merck, Lancaster, TCI, Sigma-Aldrich, Showa, separately. Chromatographic separations were carried out by using silica gel from Merk, Kieselgel si 60 (40–63 μm).

2.2. Fabrication of DSSCs

The FTO conducting glass (FTO glass, fluorine doped tin oxide overlayer, transmission >90% in the visible, sheet resistance 8 Ω square^{-1}), titania-oxide pastes of Ti-nanoxide T/SP and Ti-nanoxide R/SP were purchased from Solaronix. A thin film of TiO_2 (16–18 μm thick) was coated on a 0.25 cm^2 FTO glass substrate, while the thickness was measured by Veeco Dektak 150. It was immersed in a THF solution containing 3×10^{-4} M dye sensitizers for at least 12 h, then rinsed with anhydrous acetonitrile and dried. Another piece of FTO with sputtering 100 nm thick Pt was used as a counter electrode. The active area was controlled at a dimension of 0.25 cm^2 by adhering 60 μm thick polyester tape on the Pt electrode. The photocathode was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between two electrodes. An acetonitrile solution containing LiI (0.5 M), I_2 (0.05 M) and 4-*tert*-butylpyridine (0.5 M) was used as the electrolyte. Devices made of a commercial dye N719 under the same condition (3×10^{-4} M, Solaronix S.A., Switzerland) was used as a reference.

2.3. Property measurements of DSSCs

The cell parameters were obtained under an incident light with intensity 100 mW cm^{-2} measured by a thermopile probe (Oriel 71964), which was generated by a 300 W Xe lamp (Oriel 6258) passing through an AM 1.5 filter (Oriel 81088). The current–voltage (*J*–*V*) parameters of DSSCs were recorded by a potentiostat/galvanostat model CHI650B (CH Instruments, USA). The light intensity was further calibrated by an Oriel reference solar cell (Oriel 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100) at a short circuit condition. Electrochemical impedance spectra of DSSCs were recorded by an Impedance/Gain-Phase analyser (SI 1260, Solartron). The frequencies explored ranged from 10 mHz to 65 kHz. The ac amplitude was set at 20 mV. The photovoltage transients of assembled devices were recorded using a digital oscilloscope (Tektronix, TDS 3012b). Pulsed laser excitation was applied by a Q-Switched Nd:YAG laser (Quanrel, brilliant B) with 10 Hz repetition rate at 532 nm and a 7 ns pulse width at half-height. The laser energy of 3 mJ cm^{-2} to cover the area of the device size was slightly larger than 0.25 cm^2. The recombination lifetime of injected electrons with oxidized dyes was measured by transient photovoltages at open circuit with the presence of LiI electrolyte (0.5 M) in acetonitrile. The average electron lifetime can be estimated approximately by fitting a decay of the open circuit voltage transient with $\exp(-t/\tau)$, in which t is time and τ is an average time constant before recombination.

2.4. Theoretical calculation

The structures of dye were optimized by using B3LYP/6-31G* hybrid functional. For the excited states, a time-dependent density functional theory (TDDFT) with the B3LYP functional was employed. All analyses were performed under Q-Chem software. The frontier orbital plots of HOMO and LUMO were drawn by using GaussView 03.

3. Results and discussion

3.1. Synthesis

The structure of organic dyes involved in this report is shown in Fig. 1, and their synthesis is outlined in Scheme 1. Four types of triarylene bridging structures are designed, i.e., thiophenylene–thiophenylene–thiophenylene (**SSS**), phenylene–thiophenylene–thiophenylene (**PSS**), phenylene–phenylene–thiophenylene (**PPS**), and phenylene–phenylene–phenylene (**PPP**). Two kinds of substituents, i.e., methyl (**T**) and methoxy (**M**) groups, are attached to the *para*-position of the diphenylamine moiety. The synthesis of **PPS** series compounds has been reported previously [32]. The synthesis of **SSS** series compounds started with a terthiophenylene unit, that was made by a coupling reaction between 2-bromothiophene and 2,5-dibromothiophene through a Kumada procedure [37–39]. The terthiophenylene was doubly brominated by a treatment with N-bromosuccinimide (NBS), followed by amination reactions on one side of the compound to yield **3 T** and **3 M**. The amine donor moieties were attached onto thiophene and elongating spacer with benzaldehyde by a Stille coupling reaction or Suzuki–Miyaura coupling reaction [40,41]. The final step was a Knoevenagel condensation between compounds 4 and 6 and cyanoacetic acid in the presence of ammonium acetate [42]. All of products were confirmed by their spectroscopic characteristics.

To build the C – N bonds by the Buchwald–Hartwig coupling reaction to yield **2, 3** in 52–78% yields [43]. Extension of the aryl chain was accomplished by carbon – carbon bond coupling reactions for adding a thiophenyl and a phenyl moiety subsequently. The yields of **4** and **5** were quite satisfactory, i.e, in a range of 67–73%. Finally the cyanoacrylic acid moiety was generated *via* Knoevenagel condensation by fusing up with a cyanoacetic acid. All final products can be crystallized into yellow to deep red colour solids.

3.2. Photophysical properties

Absorption spectra of organic dyes in THF solution (3×10^{-5} M) were shown in Fig. 2a. All compounds exhibit a major absorption band in the visible region, which is derived from a intramolecular charge-transfer transition (ICT). Other higher energy bands, mostly located in the UV region, can be assigned to π–π* transitions of the aromatic chromophores. An apparent red shift can be observed in the ICT bands along with the increase of the numbers of thiophene units. The trend of wavelengths appears to be **T-SSS** > **T-PSS** > **T-PPS** > **T-PPP**. A similar trend also exists in the **M**-series of compounds. This phenomenon can be ascribed mainly to the electron donating effect of the sulphur atom, so that the potential energy level of the highest occupied molecular orbitals (HOMOs) of a thiophenyl group is elevated with respect to that of a phenyl group. The HOMO–LUMO (lowest unoccupied molecular orbital) gap is narrowed down, thus results to a lower energy of transition. This effect can be justified by the oxidation potential of respective