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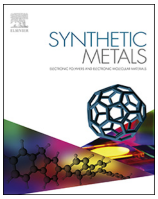

D-π-A conjugated polymer dyes-covered TiO_2 compact layers for enhancing photovoltaic performance of dye-sensitized solar cells

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ABSTRACT

Three donor-conjugated units (triphenylamine (TPA)) and phenothiazine (PTZ))-side chain acceptor (cyanoacrylic acid (CAA)) donor-π-acceptor (D-π-A) conjugated polymers with different conjugated units (thiophen and/or 3, 4-ethylenedioxythiophene) were rationally designed and synthesized. The electronic properties and energy levels could be effectively tuned via methodically altering the conjugated units of the resulted polymers (PTPAPTZ, PTPAPTZ-1 and PTPAPTZ-2). Regulating the molecular orbital energy levels can be considered as a direct and effective method to get bathchromic and broad spectra shifts in polymer dyes. Photoelectrochemical cells based on the dye sensitized solar cells (DSSCs) format were fabricated putting the polymers as sensitizers. Device based on PTPAPTZ-2 exhibits a power conversion efficiency of 4.71% with short circuit photocurrent density of 10.8 $mA{\cdot}cm^{-2}$, overrating all polymer DSSCs previously disclosed.

1. Introduction

DSSCs have attracted consecutive increasing attention in the field of photovoltaic devices because of the simple construction, ease of fabrication and inexpensive production cost [1,2]. As a key component of DSSCs, sensitizers are regarded to be critical factor for solar cell properties owing to its efficient light-harvesting [3]. Until now, photosensitizes including metal complexes [4] and metal-free organic dyes [5,6] were designed to improve the performance of the solar cells. Nevertheless, the extensive application of DSSCs based on metal-complex photosensitizes may be hindered by its high manufacturing cost, poor long-term stability, inferior processibility and unfriendly to the environment [7]. Thus, metal-free sensitizers such as polymer-based sensitizers have been developed in the drive to exploit the application in DSSCs [8].

In recent years, conjugated polymers, as prospective polymer-sensitizers owing to the superiorities of ample large absorption coefficient, adjustable energy levels, excellent structural stability and easy to film have gradually attracted the researchers' great attention [9]. To reach the high power conversation efficiencies (PCE), few sensitizers of DSSCs were constructed via incorporation of D-π-A conjugated polymers using its versatile semiconductor and optical properties [10,11]. Among the limited reports about polymer dyes applied in DSSCs, the D-π-A structure have gained most research attention targeting for high performance organic dyes, since it enable efficient electron injection and effectively avoid recombination [12–14]. Intramolecular charge transfer (ICT) from the subunit donor to acceptor can be induced by π-bridge push-pull system in the context of dyes light-harvesting [15]. Owing to the specific structure, the absorption spectra and the highest and lowest occupied molecular orbital (correspondingly HOMO and LOMO) energy levels of polymers can be adjusted via altering D-π-A segments. Conjugated thiophene segments-linked P2 synthesized by Knoevenagel method of electron donor (TPA) and electron acceptor (CAA) constructing units certified a relatively good PCE (3.39%) [16]. Bake et al. reported a multifunctional conjugated polymer which was fabricated by carbazole (as electron donor) and CAA (as electron acceptor) linked through vinylene and terthiophene. For the first time, polymer dye sensitizer was obtained over 4% of PCE in DSSCs [10]. These results revealed that the adjustment of π units is the efficiently short cut to obtain supernal short circuit photocurrent density (J_{sc}), but also achieve desired open circuit voltage (V_{oc}).

To the best of our knowledge, thiophene, benzene and 3, 4-

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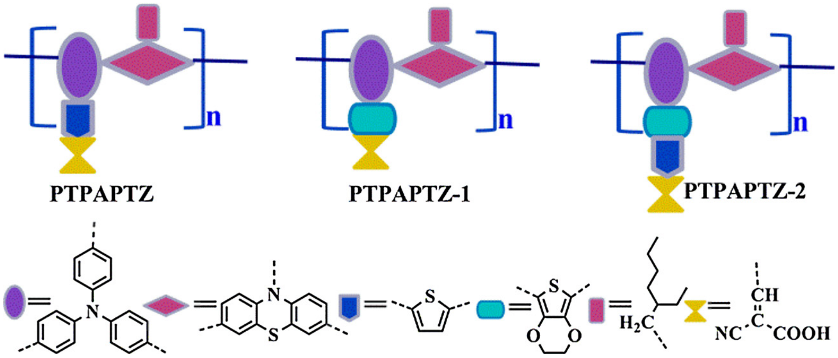

Fig. 1. Constructions of three polymer dyes.

ethylenedioxythiophene (EDOT) as electron-donating aromatic moieties pay the significant role in enlarging π conjugated units [17]. Bathochromic shift, an intensification of the absorptivity and an increased lifetime of the excited-state can be induced by the attachment of thienyl units and/or its derivatives [18]. To achieve the purpose of tuneable HOMO- and LOMO-energy levels, a series of small organic molecular dyes were synthesized by lengthening π-conjugate units between TPA donor and CAA acceptor [19]. Besides, the introduction of the EDOT group increases the spectral response and perhaps renders a better degree of charge separation, resulting in a leap in the photovoltaic performance in comparison to the thiophen conjugated parent compound [20–22].

Inspired by these research results mentioned above, three definitely designed dyes (named PTPAPTZ, PTPAPTZ-1 and PTPAPTZ-2) fabricated through inexpensive TPA, PTZ as main chain electron donor and CAA as anchoring electron acceptor parts, can be closely linked to thiophene and its derivatives EDOT (Fig. 1). Investigating this structure-property relationship is significant to provide useful guidance for designing predominant light-harvesting and high-efficiency polymer sensitizers. In this work, high efficient, red-shifted, large absorbance and long lifetime of excited-state dyes may be constructed by the introduced excellently chromophore [23]. Importantly, structure-function relationships of dyes were discussed by altering π-bridge. Besides, the experience in designing small molecule dyes was used for references and alkyl chains was embed into the polymer dyes in order to increase solubility. Moreover, chain-conjugated frameworks interactions may be prevented and the likelihood of trapping or quenching of excitons also may be eliminated by the side chains [24,25]. Based on these aspects, surprisingly, superior DSSCs (PTPAPTZ-2) fabricated with the low cost and versatile chemical modification, showed a relatively high-photovoltaic properties (ŋ = 4.71%).

2. Experimental section

2.1. Materials

All chemical regents and solvents were of analytical-grade and used as gained without further purification unless otherwise specified. Toluene and tetrahydrofuran (THF) were freshly distilled over sodium/diphenyl ketone prior to use. 2-Ethylhexyl bromide, Lithium bis(trifluoromethylsulfonyl)amide (LiTFSI), CAA, *N*-Bromosuccinimide (NBS), piperidine, Guandine thiocyanate (GNCS), 4-*tert*-butylpyridine (TBP), tetrakis (triphenylphosphine) ($Pd(PPh_3)_4$), 1,3-dimethyl imidazole iodine (DMII), 1-Ethyl-3-methylimidazolium Bis(trifluoro methanesulfonyl) imide (EMITFSI), 5-Formyl-2-thiopheneboronic acid were provided by Energy Chemical Inc.

2.2. Measurements

2.2.1. Molecular weight measurements

The molecular weights determinations experiments of polymer dyes were operated on Gel permeation chromatography (GPC) machine (waters 2414) affiliated 3 columns. This instrument' accuracies range from 10^3 to 10^6 and use polystyrene as an internal standard.

UV–vis, photo-luminescence and voltammetric measurements

The UV–vis absorption and emission spectra of dyes were correspondingly recorded on a Hitachi U-3010 spectrophotometer and LS55 luminescence spectrometer (Perkin Elmer). The emitted light was detected with a red-sensitive photomultiplier tube (Hamamatsu R928). Cyclic voltammetry measurements were performed using electrochemical workstation equipped with three electrode electrochemical cell. Three electrodes were composed of Ag/AgCl (sat. KCl) as the reference electrode calibrated with Ferrocene/Ferrocenium (Fc/Fc+) as an internal reference, glass carbon as working electrode and platinum as counter electrode. Cyclic voltammetry of the oxidation behaviour of the polymer dyes, were performed in anhydrous *N, N*-dimethyl formamide (DMF) with tetrabutylammonium hexaflourophosphate (0.1 M, $TBAPF_6$) as supporting electrolyte.

2.2.2. Theoretical computation

All the calculations were performed using Gaussian 09 package [26,27]. The ground-state geometry optimizations were employed with hybrid Lee − Yang − Parr density correlation functionals (B3LYP) with basis set (6-31G**), while the computed vertical excitations energies were based on TD-DFT/MPW1K/6-31G**.28 The C-PCM method has been used to simulate the solvents effects on absorption spectra and geometries.

2.2.3. Solar cell fabrication

An inter-connected double-layer TiO_2 film with screen-printed was used as negative electrode. A 7 μm thick transparent film with the average diameter of 20 nm was deposited on fluorine-doped tin-oxide conducting substrate, and then the scattering TiO_2 film with the average size of 400 nm was coated on the top substrate. The nanostructure TiO_2 film thickness was measured by a bench-top stylus profilometer (Ambios XP-1). A cycloidal TiO_2 electrode (area: about 0.28 cm^2) was stained by immersing it into a dye solution of 150 μM PTPAPTZ or PTPAPTZ-1 or PTPAPTZ-2 in common solvents of tetrahydrofuran (THF)/acetonitrile (AN) (v/v = 1/1) for 10 h and dried by air flow, the sensitizer-coated TiO_2 electrode was assemble using thermally platinized fluorine-doped tin-oxide electrode. The electrodes were sealed with a 35 μm-thick hot-melt gasket made of Bynel (DuPont). The internal space of cell was perfused using liquid electrolytes via vacuum back-filling system. The electrolyte-injecting hole made with a sand-blasting drill on the counter electrode glass substrate, was sealed with a Bynel sheet and a thin glass covered by heating the assessments of devices was made by the two electrolytes. Infiltrated