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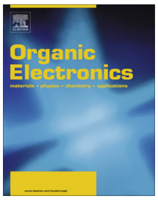

2,6-Conjugated Bodipy sensitizers for high-performance dye-sensitized solar cells

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ABSTRACT

A series of novel 2,6-conjugated Bodipy metal-free organic dyes (**UY5–8**) with phenothiazine (PTZ) moiety as electron donor for the dye-sensitized solar cells (DSSCs) have been designed and synthesized. The optical, electrochemical properties and photovoltaic performances are extensively investigated. The structure–property relationship shows that the introduction of various auxiliary conjugated spacers and anchoring groups are favorable to changing the efficiency of DSSCs. Among these dyes, **UY7** comprised of furan with lower resonance energy as linker and cyanoacetic acid unit as electron acceptor possesses a flatter structure and longer electron recombination lifetime. Hence, a DSSCs using **UY7** showing best photovoltaic performance with a short-circuit photocurrent density (J_{sc}) of 13.64 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 590 mV and a fill factor (*ff*) of 0.66, corresponding to an overall conversion efficiency (η) of 5.31% under 100 mW cm^{-2} simulated AM 1.5 G solar irradiation. This is the best reported result in the solar cell with a Bodipy dye as photosensitizer.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted significant attention since the first report in 1991 by Grätzel and O'Regan group [1]. Among all components of the DSSCs, sensitizers play the key role in achieving high power conversion efficiencies. Up to now, DSSCs incorporating Ru(II)-polypyridine based sensitizers have already achieved efficiencies above 11% using an AM 1.5 solar simulator [2–4]. However, the Ru based dyes are expensive and environmentally hazardous. Compared to the Ru dyes, metal-free organic dyes have several advantages, such as higher molar extinction coefficients, more flexible in molecular design and lower cost. Various organic dyes have been used as the sensitizers, and impressive power conversion efficiencies in the range of 8–10% have been achieved [5–9].

Bodipy (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) dye is a well-known fluorophore and has been vigorously investigated in bimolecular labeling and fluorescence imaging due to their high absorption coefficient in the visible and near-IR ranges, large fluorescence quantum yield, long excited-state lifetime and high hole carrier mobility [10]. However, DSSCs using Bodipy-based sensitizer are few [11–24]. In most cases, the Bodipys were functionalized with strong donor groups at the 3- and 5-positions and a phenyl modified cyanoacetic acid moiety at the

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8-position. Energy transfer through the Bodipy spacer tends to be less efficient in this type because the acceptor at 8-position shows poor conjugation with Bodipy, and typically exhibits poor electron flow from the donor to the anchor group [18]. DSSCs based on the above modification gave only moderate cell parameters and a maximal efficiency of 2.46% by Akkaya's group [18]. Recently, the notion of developing Bodipy dyes modified with 2, 6-donor/acceptor motif to form the D–π–A systems has been proposed by our group [19,20], relatively high efficiency of nearly 2.26% has already been reported. Such promising results drive the quest to find new and appropriate groups for such 2,6-motif dye structure to achieve higher power conversion efficiencies.

Phenothiazine (PTZ) and its derivatives have shown promising applications in the development of photovoltaic devices, owing to its electron-rich nitrogen and sulfur atoms in a heterocyclic structure with high electron-donating ability. In addition, its nonplanar butterfly conformation can sufficiently inhibit molecular aggregation and the formation of intermolecular excimers [25]. Meanwhile, the substituent on nitrogen of PTZ can further enhance charge separation at the oxide-solution interface. By introducing the PTZ moiety into the Bodipy-based organic dyes, we expect that the absorption region can be extended and the aggregation will be reduced.

The charge transfer property of PTZ-Bodipy sensitizers can be well tuned by simple incorporation of an auxiliary electron-donating group, such as thiophene or thiophene-base heterocycles as the π spacer. Furan, thiophene's oxygen analogue, which has a smaller resonance energy (16 kcal mol^{-1}) in the spacer than the thiophene (29 kcal mol^{-1}), would be more efficient for the hole location and reinforce the stability of the dye sensitizers [26]. Some reports also have shown that incorporation of a furan linker could somewhat improve the solubility of the sensitizers [27,28]. Furthermore, the electrons from the photoexcitation of the dye molecules are injected to conduction band of the semiconductor through the electron acceptor parts, changes in the electron acceptor of the dye sensitizers can result in a significant variation of electronic and photovoltaic properties.

Based on the above consideration, we designed and synthesized four novel dyes with a 2,6-conjugated Bodipy segment as the π spacer which incorporated PTZ with high electron-donating ability as the donor, five-membered heteroaromatic rings with low resonance energy (thiophene or furan) as an auxiliary π linker, and cyanoacetic acid or rhodanine-3-acetic acid as the electron acceptor. The molecular structures of sensitizers **UY5–8** are shown in Chart 1. The optical, electrochemical and photovoltaic properties of the DSSCs based on the four dyes were systematically investigated and correlated with their chemical structures.

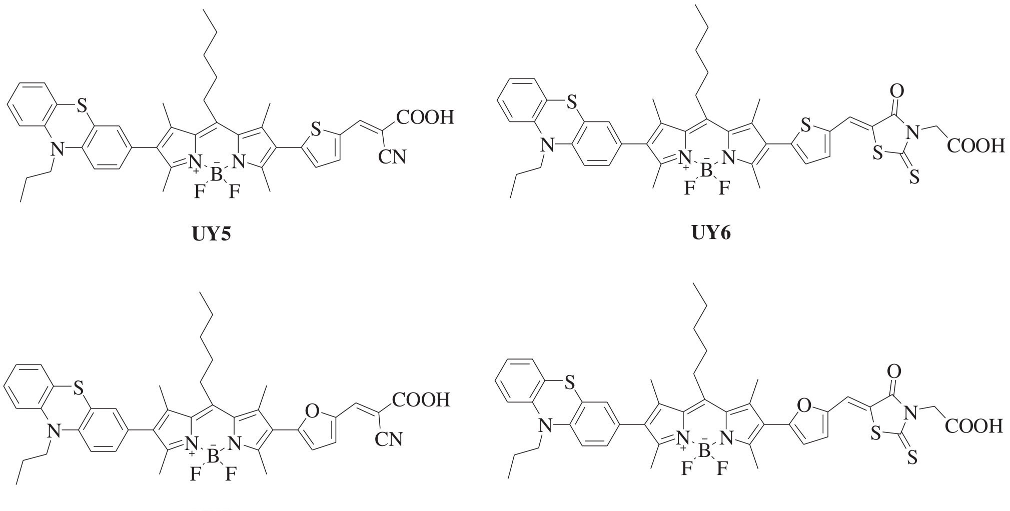
2. Experimental

2.1. Materials and reagents

Solvents for organic synthesis were reagent grade, and were dried prior to use, and solvents for measurements of spectroscopy are HPLC grade and used without further purification. All chemicals were purchased from commercial sources and used as received. Compound **1** [19], **2** [29] and **5** [30] were synthesized according to literature procedures. All chromatographic separations were carried out on silica gel column (200–300 mesh).

2.2. Analytical measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV400 spectrometer with the chemical shifts against tetramethylsilane (TMS). Mass spectra were measured on an autoflex™ speed MALDI-TOF and Thermo LTQ Orbitrap mass spectrometer. FTIR spectra were acquired on a Bruker VECTOR22 infrared spectrophotometer. UV/Vis absorption spectra of the dyes in solution and the absorption of dye-sensitized TiO_2 films (thickness 2.5 μm) based on the



UY5

UY6

UY7

UY8

Chart 1. Molecular structures of Bodipy dyes.