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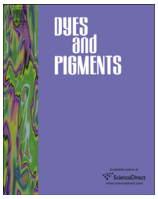

Molecular engineering of largely π-extended metal-free sensitizers containing benzothiadiazole units: Approaching 10% efficiency dye-sensitized solar cells using iodine-based electrolytes

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ABSTRACT

Based on the structural motif of a robust organic dye, new largely π-extended organic sensitizers for dye-sensitized solar cells (DSSCs) have been designed to optimize the interactions between the dye/TiO_2 layer and the redox electrolyte. The molecular tailoring was performed by *i)* positioning an alkyl chain onto the π-spacer and *ii)* increasing the bulkiness of the electron-donor. A deep theoretical investigation reveals that the main electronic transitions of the three dyes own only a weak charge-transfer character. Notwithstanding these unusual photo-excitation dynamics experimentally supported by solvatochromism, impressive photovoltaic performances are obtained for the three sensitizers, reaching power conversion efficiencies up to 9.8% under 1.0 sun illumination, that were remarkably higher than those shown by N719 standard. This result represents one of the highest performances exhibited by fully organic sensitizers employing the I^-/I_3^- redox shuttle.

1. Introduction

The prospected low manufacturing cost and potential building integration of dye-sensitized solar cells (DSSCs) continue to fuel a vivid research effort mainly devoted to the dye optimization [1]. The state-of-the-art of DSSC efficiencies has until recently been a prerogative of ruthenium-based complexes (~11%) [2] and zinc-porphyrin sensitizers (~13%) [3]. Although the vast majority of highly performing fully-organic sensitizers currently exhibits lower performances (~10%) [4], a conspicuous share of the DSSC scientific community remains intrigued by the molecular engineering potential of metal-free dyes, also considering that the use of a low-abundance metal such as ruthenium as well as the many low-yielding steps needed to obtain suitably functionalized porphyrins might jeopardize the perspective of full-scale DSSC mass production. The great efforts aimed at unravelling the potential of fully organic sensitizers has been recently realised in the obtainment of devices with outstanding efficiencies (up to 12.5%) [5], sustaining the research for more and better performing organic dyes.

For years, the molecular design of efficient sensitizers has been dominated by the rule of putting into conjugation an electron-donating and electron-accepting unit (the latter suitably designed to act as the anchoring group for the inorganic semiconductor) via an electron-rich π-segment (namely the D–π–A architecture) [6]. The consequent "push–pull" configuration governs the photo-induced shift of the electron density towards the anchoring region bound on the inorganic semiconductor, thereby promoting the electron transfer step [7]. The molecular engineering of the π-bridge has been mainly devoted to the amplification of the light-harvesting properties of the corresponding sensitizers; nonetheless, the mere conjugation extension of the chromophoric core was proven as detrimental for device performance [8]. Recently, the incorporation of a further electron-withdrawing unit within the π-

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bridge (leading to a D–A–π–A architecture) has opened new routes for improving the light-harvesting and stability of the corresponding organic sensitizers [9]. However, placing an electron-deficient aromatic unit within the π-bridge leads to structure–property relationships that cannot be trivially anticipated. By gathering electron density at the excited state of the corresponding D–A–π–A sensitizer, the introduction of a further electron-withdrawing system within the π-spacer could indeed prevent an efficient electron transfer onto the TiO_2 surface [10]. Consequently, the position of the electron-accepting aromatic unit with respect to the anchoring moiety as well as the introduction of functional groups causing distortion of the chromophore backbone have to be accurately pondered when drawing the “molecular blueprint” of a D–A–π–A sensitizer. Our role in perfectioning the D–A–π–A sensitizers has mainly been focused on the π-bridge extension as well as on the judicious selection of low-environmental impact structures and synthetic strategies [11] with in the awareness that even minor structural modification can exert a significant influence on the performance of a selected class of organic dyes.

In this contribution, the properties and the photovoltaic performances of new D–A–π–A fully organic sensitizers (**G4** and **G5**, Fig. 1) have been investigated. These dyes have been assembled on the basis of the structural motif characterizing a robust organic dye (**G3**), that achieved high power conversion efficiency (8.6%) and exhibited an excellent stability during device operation [11a]. The new sensitizers were conceived to gain a control at the interface between the dye/TiO_2 layer and the redox electrolyte, aiming at enhancing the corresponding device photocurrent and photovoltage. The molecular tailoring of the **G3** scaffold was consequently carried out by suitable positioning an alkyl chain onto the π-spacer (**G4** *vs* **G3**) and by increasing the bulkiness of the electron-donating unit (**G5** *vs* **G4**) extending its conjugation. Remarkable power conversion efficiencies (PCE) up to 9.8% were achieved by **G5** (the best of the series) using iodine-based electrolytes; the obtained PCE were found to be higher than those shown by traditional N719 standard dye formulations [12].

2. Results and discussion

2.1. Synthesis and characterization

Differently from the previously reported synthesis of **G3**, which could be accomplished by C–H activation reactions [11a], the syntheses of **G4** and **G5** posed additional complications due to the unsymmetrical placement of the *n*-hexyl functionality with respect to the benzothiadiazole core (Scheme 1). Concerning the electron-donating building block, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*- bis((2-ethylhexyloxy)phen-4-yl)aniline it was obtained following a literature procedure [11a]. Conversely, the preparation of the electron-donating unit of **G5** started with the reaction of bromo-triphenylamine with two equivalents of *N*-iodosuccinimide (NIS) to afford the diiodo-derivative **1**. A Suzuki cross-coupling reaction between **1** and two equivalents of 2-((2-ethylhexyloxy)phen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave the bromo-derivative **2** prone to be functionalized with bis(pinacolato)diboron affording the relevant boronic ester **3**. Concerning the synthesis of the chromophoric π-bridge, the benzothiadiazole-containing derivative **4** was reacted in a Suzuki coupling with an equimolar amount of thienyl-boronic acid yielding the unsymmetrically substituted compound **5**. A selective bromination on the activated thiophene ring with *N*-bromo-succinimide (NBS) afforded the corresponding bromo-derivative **6**. A Suzuki reaction between **6** and 4-formylphenyl boronic acid placed the aldehyde functional group for the subsequent conversion into the anchoring moiety. A further NBS bromination of the so obtained intermediate **7** yielded the bromo-derivative **8**. The synthetic procedures were completed by carrying out a Suzuki cross-coupling between **8** and the relevant boronic-esters of the electron donating groups, concluded by a Knovenagel condensation of the obtained aldehydes **9** and **10** with cyanoacetic acid affording **G4** and **G5**, respectively.

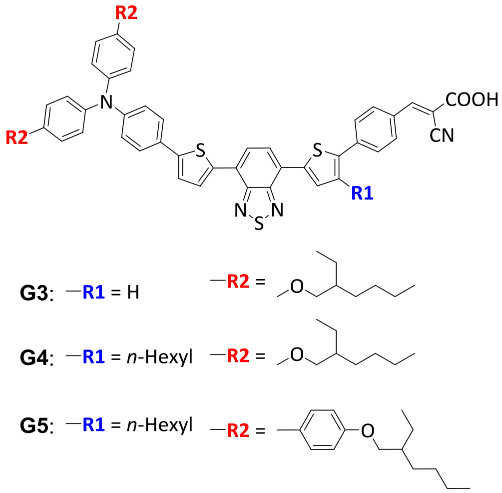

Fig. 1. Chemical structures of **G3**, **G4** and **G5**.

The UV–Vis absorption of **G3-5** in THF are depicted in Fig. 2A highlighting that all sensitizers exhibit two major absorption bands at 350–400 nm and 500–550 nm, often simplistically ascribed to localized aromatic $\pi-\pi^*$ transitions or to intramolecular charge-transfer (ICT) transitions. However, a deeper insight into the nature of these two absorption bands has been provided by theoretical calculations (*vide infra*). Concerning the absorption wavelengths, the dye structural tailoring seems to have a non-negligible effect on the absorption profiles of the triad. The absorption peaks falling in the UV region are located at 378 (**G3**), 370 (**G4**) and 354 (**G5**) nm, with molar extinction coefficients of 41,600, 33,600 and 48,600 M^{-1} cm^{-1} respectively, whereas the lower energy bands peaked at 535 (**G3**), 527 (**G4**) and 524 (**G5**) nm, with corresponding molar extinction coefficients of 38,300, 27,900 and 30,100 M^{-1} cm^{-1}. Their absorption onsets in THF solution followed the trend observed for the maxima (641, 635 and 624 nm for **G3**, **G4** and **G5**, respectively), confirming potentially significant light-harvesting properties for all dyes. Nevertheless, it is apparent how the introduction of the alkyl chain onto the π-bridge induces a blue-shift of the absorption maxima in **G4** and **G5** with respect to **G3** with a corresponding lowering of the relevant molar extinction coefficients.

Suitable investigation of the solvatochromic behavior of an organic dye can be useful to predict the influence on the absorption profile consequent to the sensitizer immobilization on TiO_2 surface. The formation of titanium carboxylate upon dye adsorption process might indeed cause a detrimental blue-shift [13]. The absorption properties of the dyes in their deprotonated form can be evaluated in solution using a large excess of triethylamine (TEA) thus bypassing the complications due to scattering and aggregation that can occur carrying out the investigation on titania [14]. As shown in Fig. 2A, the **G3-5** absorption profiles recorded in the presence of excess of TEA are very similar to the corresponding ones recorded in THF (the blue-shift of the absorption bands being contained within 5 nm) substantiating the assumption that the original light-harvesting properties of these molecules are preserved from the deprotonation-induced blue-shift. It can also be anticipated that the peculiar structural motifs of these D–A–π–A dyes lead to