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Molecular engineering of carbazole-fluorene sensitizers for high open-circuit voltage DSSCs: Synthesis and performance comparison with iodine and cobalt electrolytes

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ABSTRACT

A rational molecular engineering strategy was set up to prepare an original series of efficient carbazole-based sensitizers for dye-sensitized solar cells. The new D–π–A dyes, including a fluorene core in the π-bridge, auxiliary thienyl groups on the donor and multiple anti-stacking chains, showed particularly favorable optoelectronic properties for DSSC application. Accordingly, the new dyes achieved up to 6.5% power conversion efficiency in standard devices (7.5 μm-thick transparent TiO_2 and iodine-based electrolyte). The dyes were afterwards employed in thin-film devices (2 μm-thick transparent TiO_2) and tested in the presence of three different electrolytes including I_3^-/I^-, $[Co^{II}(bpy)_3(PF_6)_2]/[Co^{III}(bpy)_3(PF_6)_3]$ or $[Co^{II}(bpy\text{-}pz)_2(PF_6)_2]/[Co^{III}(bpy\text{-}pz)_2(PF_6)_3]$ as redox mediators. Overall performance under these conditions was around 4% PCE, whatever the electrolyte. However, remarkable open-circuit voltages were observed with cobalt-based electrolytes. In particular, with $[Co(bpy\text{-}pz)_2]$ the three dyes afforded V_{OC} above 800 mV, even reaching as high as 919 mV, thus compensating the slight decrease in photocurrent arising from the low-mobility of the Co-complexes.

1. Introduction

Since the pioneering work of B. O'Regan and M. Grätzel in 1991 [1], dye-sensitized solar cells (DSSCs) have attracted great interest due to their versatility, ease of manufacture and aesthetic features. They are now acknowledged as economically viable photovoltaic systems [2] and therefore represent a real low-cost alternative to traditional silicon-based p–n junction solar cells. In such photovoltaic devices the sensitizer is often considered a cornerstone as it solely carries out the sunlight harvesting capacity and it is therefore crucial for converting solar power into electricity. Two main classes of dyes for DSSCs exist: polypyridyl ruthenium coordination complexes and fully organic dyes. The metal-free dyes are highly advantageous because of their higher molecular extinction coefficient, lower cost and more favorable environmental impact compared to the metal-based dyes. But above all, they present a prodigious degree of modularity that inspires large numbers of research groups [3–5]. Organic photosensitizers for DSSCs are typically designed following the D–π–A structural pattern that encompasses three main parts: an electron-rich head or donor (D), a π-conjugated bridge (π) and an electron-withdrawing group or acceptor (A) which also holds an anchoring function to chemically bind the dye onto the semiconducting metal oxide. This so-called "push–pull" structure favors efficient intramolecular charge transfer processes and thus strong light-harvesting properties. Additionally, the photosensitizer can influence key electron transfer processes occurring at the semiconductor/dye/electrolyte interface which also determine overall efficiency of the device. For example, the dye structure can affect electron injection into the conduction band of TiO_2, or conversely it can reduce loss in electron transfer processes such as recombination of injected electrons in the conduction band of TiO_2 with the electrolyte or with oxidized dye molecules. In order to control of the aforementioned electron

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transfer processes it is therefore imperative to customize the dyes through smart molecular engineering so that their energy levels match well with those of the other components of the DSSC device. Overall, both the tuning of photosensitizer visible-light absorption properties and the rational design of multifunctional molecular systems are important prospects through which optimization of DSSC efficiency can be achieved.

Bearing in mind that carbazole-based dyes are good candidates to reach high open-circuit photovoltage values [6–10], and therefore good power conversion efficiencies (PCE) in DSSCs, we intended to synthesize a new family of push–pull photosensitizers bearing carbazole as the electron donating unit. Accordingly, we herein describe a new design strategy to prepare novel organic D–π–A sensitizers with high light-harvesting capacity. Our molecular engineering approach consists in two main points, the first one being the introduction of a fluorene core in the π-conjugated bridge of carbazole-based dyes, the second is the presence of auxiliary electron-rich antennae on the donating part of the molecules. The structure of the new dyes is schematized in Fig. 1 and their molecular structure is given in Fig. 2.

Firstly, the fluorene core is known to display valuable chemical and electronic characteristics, in particular it was already reported that superior spectroscopic properties can be observed by substituting a naphthalene by a fluorene unit in the π-conjugated spacer of the push–pull dye Prodan [11]. This resulted in red-shifted absorption and emission wavelengths, increased molar extinction coefficient and a better photostability. These remarkable properties make fluorene-based dyes very attractive for applications in organic and hybrid photovoltaics, and this prompted us to explore such approach in association with a carbazole donor group in D–π–A dyes for DSSCs. Secondly, auxiliary electron-donor groups were added to the dye structure, in addition to the electron-rich carbazole motif, in order to reinforce the electron richness of the dyes donating head and therefore the push–pull effect occurring within such π-conjugated molecules. Hence, thiophene and thienothiophene units were chosen as auxiliary donors as it was demonstrated that they can enhance the absorption coefficient of Ru-coordination complexes by increasing the conjugation length of the ancillary ligands [12,13]. Similarly, in the case of organic dyes, the presence of additional donor groups is expected to increase the strength of the photoinduced intramolecular charge transfer (ICT) process guaranteeing intense visible-light absorption. Additionally, long alkyl chains were placed on the fluorene and on the donating groups to prevent aggregation between the neighboring dye molecules once grafted onto TiO_2 surface. The presence and number of alkyl chains along the molecular backbone of the dyes is of significant importance to suppress electronic recombination phenomena [14]. A bi-thiophene unit was chosen to play the role of π-conjugated bridge since this motif allows a long delocalization pathway to be created between the electron-donating moiety and the remote electron-withdrawing part of the molecule [15]. This feature is highly required to observe strong absorption in the visible region of the solar spectrum. Finally, the electron-withdrawing part of the dyes was composed of a cyanoacrylic acid function acting as charge acceptor and anchoring group.

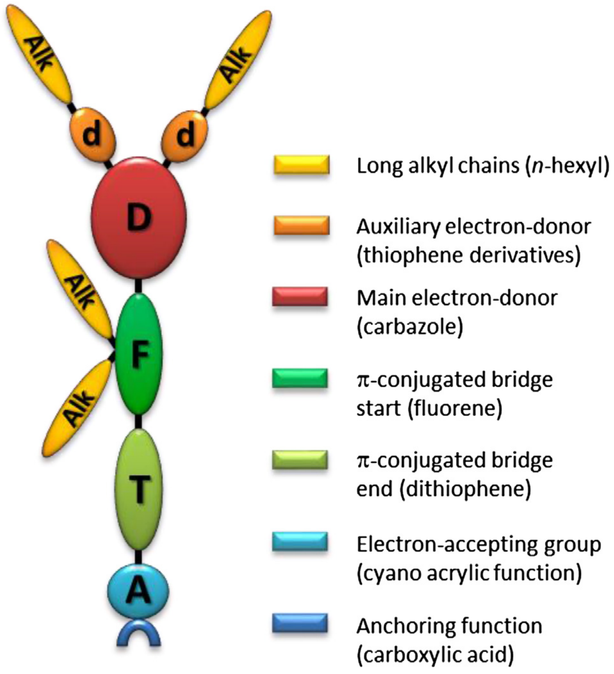

Fig. 1. Schematic representation of the new dyes structure.

The dyes were subsequently tested in DSSCs in the presence of three different types of electrolyte including either I_3^-/I^-, $[Co^{II}(bpy)_3(PF_6)_2]/[Co^{III}(bpy)_3(PF_6)_3]$ or $[Co^{II}(bpy\text{-}pz)_2(PF_6)_2]/[Co^{III}(bpy\text{-}pz)_2(PF_6)_3]$ as redox mediator, with $E^0 = +0.40$ V, +0.56 V and +0.86 V *vs.* NHE, respectively. The latter was expected to yield high photovoltage values. However, because of the relatively low mobility of the cobalt complexes the use of such redox shuttles was restricted to TiO_2 thin-films, i.e. using a transparent active layer of 2 microns thickness.

2. Experimental part

2.1. Materials and methods

All reagents were obtained from commercially available sources and used without further purification, otherwise stated. 5-bromo-2-thiopheneacetonitrile and 2-(2′-hexyl-5′-thieno[3,2-b]thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were prepared according to literature procedures [16]. Solvents were dried from appropriate drying agents (sodium for pentane, diethyl ether and THF; calcium hydride for dichloromethane, chloroform and methanol) and freshly distilled under nitrogen before use. ^1H NMR and ^{13}C NMR analyses were performed on Bruker Avance III 200, Avance III 300, Avance II 400 and Avance III 600 spectrometers. Chemical shift values are given in ppm with reference to solvent residual signals. HR-MS analyses were performed on Qstar (ESI ionization mode) and AccuTOF Jeol (FD ionization mode) spectrometers. UV–visible absorption and emission fluorescence spectra were recorded on a UV-1650PC SHIMADZU spectrophotometer and on a FluoroMax-4 HORIBA spectrofluorometer, respectively. Attenuated total reflectance (ATR-FTIR) spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer. The ATR spectrum of TiO_2 particles was subtracted from the one of the TiO_2-grafted dye and the reported spectra were normalized with respect to the C≡N stretching mode. Cyclic voltammetry analyses were carried out on an Autolab PGSTAT100 potentiostat/galvanostat. Measurements were performed in CH_2Cl_2 solution including 0.1 M of Bu_4NPF_6 as salt support, at scan rate of 100 mV s^{-1}, using a three-electrode system: the working electrode was a Pt disc, the reference electrode was Ag/AgCl (calibrated with ferrocene ($FeCp_2$) as internal reference) and the counter electrode was a Pt mesh. Potentials were afterwards referred to the Normal Hydrogen Electrode (NHE) by addition of 630 mV [17]. DFT and TD-DFT calculations were performed with Gaussian09 [18]. Molecular geometry was optimized using the B3LYP functional and the MPW1K/6-31g(d) basis set in vacuo conditions.