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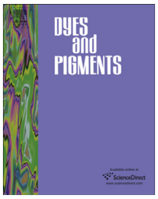

Synthesis and properties of new benzothiadiazole-based push-pull dyes for p-type dye sensitized solar cells

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ABSTRACT

We report the synthesis of three new push-pull dyes specially designed for the sensitization of mesoporous p type semi-conductor NiO for the construction of p type dye sensitized solar cells (pDSC). Their structure stems from the conjugation of the well-known tris(carboxy-arlyamine) anchoring moiety to a benzothiadiazole acceptor through a fluorene (**PP1**) or thiophene-fluorene linker (**PP2**). Appending a NDI secondary acceptor onto **PP2** yielded a dyad (**PP2-NDI**). The push-pull structure is here particularly adapted to the sensitization of p-type semi-conducting materials. All three dyes were investigated by spectroscopic and electrochemical techniques, and their electronic properties were modelled by TD-DFT. In all cases, the new sensitizers exhibit adequate absorption features (spanning from 400 nm to 600 nm, extinction coefficients between 20000 and 27000 M^{-1} cm^{-1}) and their thermodynamic parameters are all in favor of efficient interfacial charge transfers involving NiO. pDSC were constructed with all three dyes; high photoconversion efficiencies (PCE) were reached, especially in the case of dyad **PP2-NDI** (Jsc = 5.90 mA/cm^2, Voc = 143 mV, FF = 33.8%, PCE = 0.29%), due to a combination of outstanding electronic properties and increased charge separation state lifetime. Tandem DSC (tDSC) composed of a TiO_2 photoanode sensitized by the dye **D35** and a NiO photocathode sensitized by **PP2-NDI** were assembled with two different electrolytes (I_3^-/I^- or T_2/T^- based electrolytes). The latter gave PCE among the best ever reported for tDSC (Jsc = 5.90 mA/cm^2; Voc = 896 mV; FF = 63%, PCE = 2.80% in the case of the I_3^-/I^- electrolyte, Jsc = 4.52 mA/cm^2, Voc = 840 mV, FF = 60% and PCE = 2.27% for T_2/T^- based devices) unraveling the significance of the new dyes presented in this study.

1. Introduction

The conversion of solar light into a usable form of energy is one of the greatest challenges ever tackled by the scientific community [1]. Renewable, free and rather well distributed over the globe, sunlight, if mastered, would doubtlessly put an end to the hegemony of fossil fuels and the related energy crisis. Photovoltaic devices are certainly the most advanced artificial systems able to directly convert light into electricity [2]. Among them, dye sensitized solar cells (DSC) are particularly appealing devices owing to their stability, high efficiency, their aesthetic features and their short payback time, much shorter than the commercialized silicon based devices [3]. The latter are even inferior to DSC in many regards, such as flexibility, transparency and increased efficiency in low light conditions [4]. Classical DSC are based on the sensitization of a wide band gap n type semi-conductor, usually mesoporous TiO_2, by a dye exhibiting adequate electronic properties [3,5,6]. Upon light soaking, the dye injects electrons in the conduction band of TiO_2 while a redox mediator regenerates the photooxidized chromophore. Since they were brought to center stage by Grätzel and O'Regan in 1991 [7], an impressive progression of the photoconversion efficiencies (PCE) has been experienced, from

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7% to ca. 14% today [8]. Since year 2000, a new kind of DSC has emerged based on the sensitization of a mesoporous p-type semi-conductor (such as NiO) [9–12]. Those p-type dye sensitized solar cells (pDSC) are based on the injection of holes from a photo-excited dye into the valence band of the semi-conducting material. Importantly, pDSC and nDSC can be associated together to design a tandem dye sensitized solar cell (tDSC) featuring theoretical efficiencies above the Schockley-Queisser limit [13,14]. Previous works have shown in particular that tDSC exhibit larger photovoltages, independent of the redox mediator [12,15–19]. High photocurrents are attainable too if care is taken to use different dyes for each semi-conductor, exhibiting complementary absorption spectra in order to avoid screening of light by one dye or the other [13,18]. The mandatory step for constructing an efficient tDSC is that parent nDSC and pDSC are both efficient and very importantly that both short circuit currents are matched. While impressive photoconversion efficiencies (PCE) have been obtained for nDSC, pDSC still lag behind because of the built-in weaknesses of NiO (color, low conductivity) and counterproductive phenomena such as geminate and interfacial charge recombinations [20–23].

Significant work today is devoted to improving the PCE of pDSC, by fishing out a better semi-conducting material than NiO [24–31], determining new efficient redox mediators [17,25,32–36], or synthesizing new efficient dyes [36–50]. The latter obviously play a major part in the overall mechanism of a working pDSC. Within this realm, push pull dyes have early shown their qualities as sensitizers for pDSC [44,45,51–57]. They exhibit a strongly allowed donor to acceptor transition affording huge extinction coefficients; besides their color can be tuned by modifying the nature of the donor and acceptor groups. Additionally, if the anchor is tethered to the donor side, the hole injection is properly vectorialized, i.e. the very structure of a push pull sensitizer supports hole injection. The localization of the HOMO close to the semi-conductor's surface and of the LUMO as far as possible from the latter is a real advantage of push-pull sensitizers to favor hole injection and retard geminate charge recombination [14,44,50,52,56,58]. Push pull dyes are epitomized by the **P1** dye [44], the only dye for pDSC which is commercially available. Other push pull dyes have since been isolated, some displaying greater PCE than **P1** [18,46,47,59].

Herein we present our own contribution in this field, presenting two new push pull dyes **PP1** and **PP2** (Chart 1) based on the association of the well-known trisarylamine anchor (TPA) [60,61] and the benzothiadiazole acceptor (BTD) [53,62,63]. TPA has been widely used as anchoring group in many dyes for pDSC because it favors hole injection thanks to its electron-rich character. Besides, the presence of two COOH anchors provides additional stability to the dye monolayer [55,58]. Regarding the acceptor fragment, BTD shows excellent properties that materialized into a collection of successful opto-electronic devices [62–65], including sensitizers for pDSC [53]. In particular BTD exhibits a reversible reduction potential of ca. −1.2 V vs. SCE, providing sufficient driving force for regeneration of the photo-reduced dye by a great many redox mediators. In the case of **PP1**, the TPA donor is linked to the BTD acceptor by a fluorene spacer which is known to favor the electronic communication between the two ends [66,67]. Moreover, the presence of 2-ethylhexyl chains on the fluorene moiety provides solubility to the dyes and could passivate the surface of the semi-conductor by preventing the redox mediator from approaching too close and curbing therefore the interfacial charge recombination. In the case of **PP2**, a thiophene moiety is inserted between the BTD and fluorene fragments; increasing the distance and conjugation between donor and acceptor sides entails a rise of the dipole and thus an increase of the extinction coefficient while shifting the transition to the red, both appreciable features for a performant sensitizer. Moreover, the probability of geminate charge recombination decreases as the acceptor (where the electron density is localized after hole injection) is farther away from the semi-conductor's surface [40,50].

In order to further curb down the extent of geminate charge recombination, a secondary electron acceptor (naphthalene diimide, NDI) was affixed to **PP2** to yield **PP2-NDI**. Within such a dyad, a secondary "dark" electron transfer from the photo-reduced chromophore onto the secondary acceptor shifts the electron farther away from the semi-conducting material resulting in longer lived charge separation states by several orders of magnitude [37,38,68,69].

The syntheses, electronic properties of those three new dyes are disclosed in this contribution, as well as the photovoltaic performances of associated p-type photovoltaic devices. We found that the push-pull nature of the dyes entailed the presence of an intense charge transfer transition in the visible domain, assisting besides the hole injection in the valence band of NiO; appending a secondary acceptor to the best performing push-pull dye afforded the highest PCE in the series because of an improved photo-induced

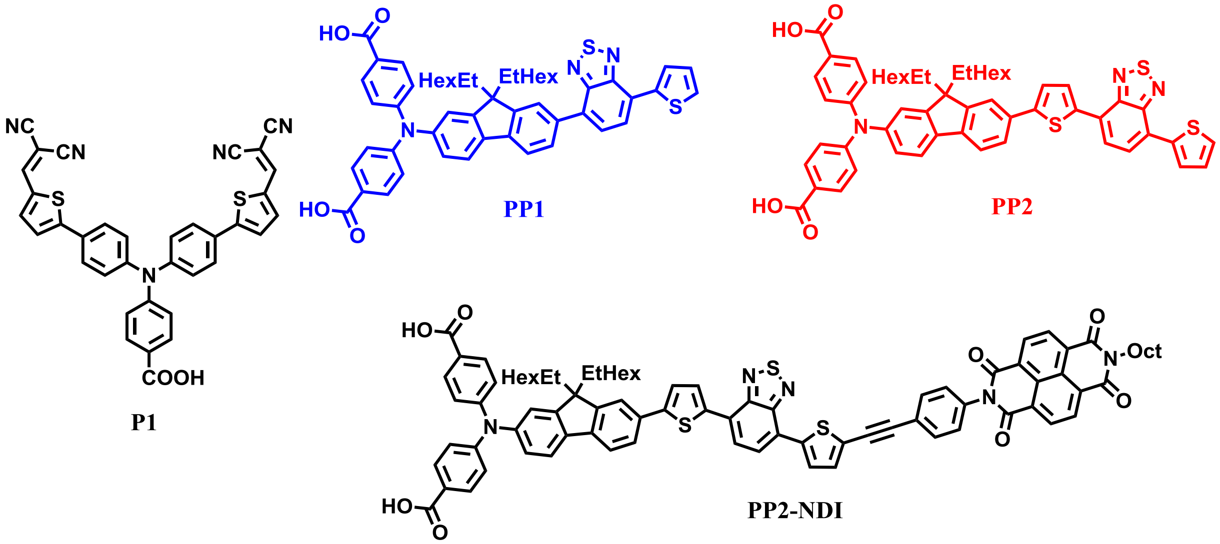

Chart 1. Structures of **P1** and of the dyes investigated in this work.