

New pyran-based dyes as efficient sensitizers of *p*-type dye-sensitized solar cells

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ABSTRACT

The application of four pyran based dyes as sensitizers for *p*-type dye-sensitized solar cells (*p*-DSCs) is here proposed. The dyes differ for the nature of the electron acceptor group which functionalizes the pyran core. Such a structural variation significantly influences the optical properties of the dyes so that the new pyrans overall cover most of the visible spectrum. In some cases, the *p*-DSCs employing these pyran-based dyes display power conversion efficiency significantly higher than the device sensitized with sensitizer benchmark **P1**. The relevant photo-electrochemical activity of one of the reported dyes combined with its ability to absorb the visible radiation in the lower energy portion ($\lambda > 500$ nm) makes it a promising candidate to be used in a tandem DSC (*t*-DSC) with the photoanode sensitized by a dye typically absorbing the higher energy zone of the visible spectrum ($\lambda < 500$ nm).

1. Introduction

Dye-sensitized solar cells (DSCs) appear as one of the most promising technologies alternative to Si-based devices in photovoltaics (Gong et al., 2017; Hagfeldt et al., 2010). DSCs present several appealing features: their production process is extremely easier and cheaper as compared with traditional photovoltaics and compatible with roll-to-roll mass production concepts already existing from other industries (Hashmi et al., 2011). DSCs are generally transparent and by virtue of that they can be integrated in architectural elements with the consequent realization of building integrated photovoltaics (Yoon et al., 2011). Their compatibility with flexible substrates and lightness make them suitable also for powering portable electronic devices. Moreover, the high efficiency under artificial light renders them useful for radiation conversion in indoor conditions (Freitag et al., 2017). The heart of a DSC device is a wide bandgap semiconductor oxide, sensitized with a photoactive dye able to inject, upon photoexcitation, electrons (*n*-type) or holes (*p*-type) in the semiconductor substrate (Cavallo et al., 2017; Gerischer et al., 1968; Memming, 1972). A great amount of work has been done for the progress of *n*-type DSC, based on TiO₂ photoanode: starting from the seminal work of O’Regan and Gratzel (1991) continuous improvements have been reported so that power conversion efficiency (PCE, η) of this kind of device has now exceeding 14% in laboratory scale (Kakiage et al., 2015). Apparently, a plateau in

efficiency has been reached for *n*-DSC. A strategy to overcome this plateau is to realize a *t*-DSC device based on the connection of a *p*-type photocathode with a *n*-type photoanode (Nattestad et al., 2010; Xiong and Chen, 2012). This configuration could afford several advantages: first, by sensitizing the two photoelectrode with dyes having complementary absorption properties (Ameline et al., 2015; Naponiello et al., 2015) it will result possible to harvest a higher fraction of solar photons. Moreover, both photoelectrodes would contribute to the total photovoltage generated by the cell irrespective of the nature of the redox shuttle (He et al., 2000). It has been predicted that a *t*-DSC could, in principle, afford an efficiency up to 40% (Xu et al., 2015). The reported efficiency of *p*-DSCs are anyway significantly lower than the *n*-type counterparts and reach a maximum PCE of 2.5% (Perera et al., 2015). This is in part related to the fact that this field have been much less investigated (Dini, 2016) than the more developed DSC technology based on TiO₂ photoanode: it follows that the different part constituting this multicomponent solar cell device are far from being optimized. Different issues need to be solved regarding some intrinsic defects of NiO, the *p*-type semiconductor oxide typically used as photocathode in DSC devices (Bonomo and Dini, 2016), and these have been investigated in several reports (Bonomo et al., 2016b; Bonomo and Dini, 2016; D’Amario et al., 2015; Marrani et al., 2014; Odobel and Pellegrin, 2013). The redox shuttle used in the device configuration play a very important role as well with the redox potential of the typically used

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iodide/triiodide couple suffering of a not ideal energy alignment with NiO energy bands (Gibson et al., 2009; Odobel et al., 2010). Focusing on the properties required to the sensitizers it is clear that the primary role of the dyes in the DSC consists in harvesting the energy of the solar radiation and, successively, in generating a process of charge transfer after optical excitation. In doing so, the dye must absorb efficiently (i.e. with high molar extinction coefficients, $> 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$) the solar radiation in a spectral interval as wide as possible. The other requirement of the dye-sensitizer is its capability of transferring a charge to the semiconductor electrode upon decoupling of the photogenerated exciton (Hagfeldt et al., 2012). For the realization of the latter function, the sensitizer should adhere firmly to the semiconductor surface and has to be electrically connected with the electronic structure of the semiconducting electrode. Anchoring is typically achieved by functionalizing the dye with acidic groups (Galoppini, 2004). In the case of *p*-DSCs it is essential to reduce the extent of charge recombination process by pushing the photo-generated electron excess of the dye away from the site of anchoring on NiO surface (Dini, 2016). The design of novel dyes that contemporaneously satisfy all these conditions is then highly sought after in the search of *p*-DSCs with higher efficiency (Bonomo et al., 2017c, 2016a). An interesting class of dyes is represented by the family of pyran based derivatives: they have found different applications in different field of electronics and photonics, e.g. as red emitters in OLED (Yang et al., 2007), as photovoltaic materials (Awuah et al., 2011; Bonomo et al., 2017a; Maglione et al., 2016a; Xue et al., 2009), and as nonlinear optical materials (Ambrosio et al., 2011; Carella et al., 2007; Dini et al., 2016; Liu et al., 2001). The chemical structure of this class of dyes for DSC purposes is typically based on a pyran core functionalized with an electron acceptor group. The electron withdrawing group is symmetrically linked to the conjugated branches with donor character. Due to the versatility of the synthesis of this peculiar molecular skeleton, it is feasible to design and realize interesting photosensitizers for *p*-DSC through the positioning of the anchoring groups on the periphery of the dye. This approach leads to the generation of dyes in which the anchoring group is purposely located far away from the electron acceptor core (Nattestad et al., 2010). Based on this indication, we report here the photovoltaic performance of *p*-DSCs employing mesoporous NiO (Awais et al., 2014, 2011; Dini et al., 2015; Wood et al., 2016) photosensitized with the newly synthesized dyes reported in Fig. 1. The dyes were synthesized and investigated as photosensitizers for *n*-DSCs in a previous work of some of us. (Maglione et al., 2016b) They are based on a pyran core, functionalized with electron acceptor groups of different strength, symmetrically coupled to

two donor carbazole branches. The carbazole units are end-substituted with acrylic groups that allow a good adhesion of dyes on the semiconductor oxide surface during device assembly. A computational analysis performed on the dyes at DFT level also revealed that upon photoexcitation, the excess of electron density moves from the peripheral part of the molecules towards the pyran acceptor core. While the last feature negatively affects electron injection from the dyes to TiO₂ in the classical *n*-DSC, it could become beneficial if the same dyes are used instead as photosensitizers of *p*-DSCs. In fact, if the LUMO of the dye is localized far from NiO surface, the possibility of charge recombination between the injected hole and LUMO of the dye is reduced (Bonomo et al., 2016a). Theoretically the farther from NiO surface the localization of the LUMO energy level, the slower the rate of recombination phenomena. Consequently, the efficiency of the device increases accordingly. These considerations prompted us to investigate the series of pyran derivatives of Fig. 1 as photosensitizers in NiO-based *p*-DSCs.

2. Experimental

The details regarding the synthesis of the dyes as well as the their optical, electrochemical and the computed electronic properties, have been previously reported elsewhere (Maglione et al., 2016b). The dyes were used as photosensitizers in NiO based standard devices and their activity was compared with a reference cell sensitized with the dye benchmark P1, (Qin et al., 2008) which is largely employed as sensitizer in *p*-DSCs due to the relative easy and cheap synthesis and the high photo-conversion performance (Bonomo et al., 2017; Wild et al., 2016). Screen printed NiO photocathodes were made as previously reported (Bonomo et al., 2017b, 2016c): preformed NiO nanospheres (with a diameter smaller than 50 nm) have been grinded in a mortar and hydrochloric acid (1 mL), H₂O (5 mL), ethanol (30 mL), terpeneol (20 mL) and ethylcellulose (10% w/w in ethanol solution) were added. All chemicals employed were purchased from Sigma-Aldrich or Fluka at the highest degree of purity available and they were used without any further purification. Both addition and grinding of the various mixtures have been performed at room temperature. After the addition of terpeneol and ethylcellulose the solution has been homogenized by stirring and ultrasonic treatment. Then the mixture has been heated at 50 °C under continuous stirring till the paste had the appearance of a viscous slurry. Anhydrous terpeneol was used as a mixture of enantiomers. The ultrasonic homogenization was performed with a Ti-horn-equipped sonicator (Vibracell 72408 from Bioblock scientific). The resulting

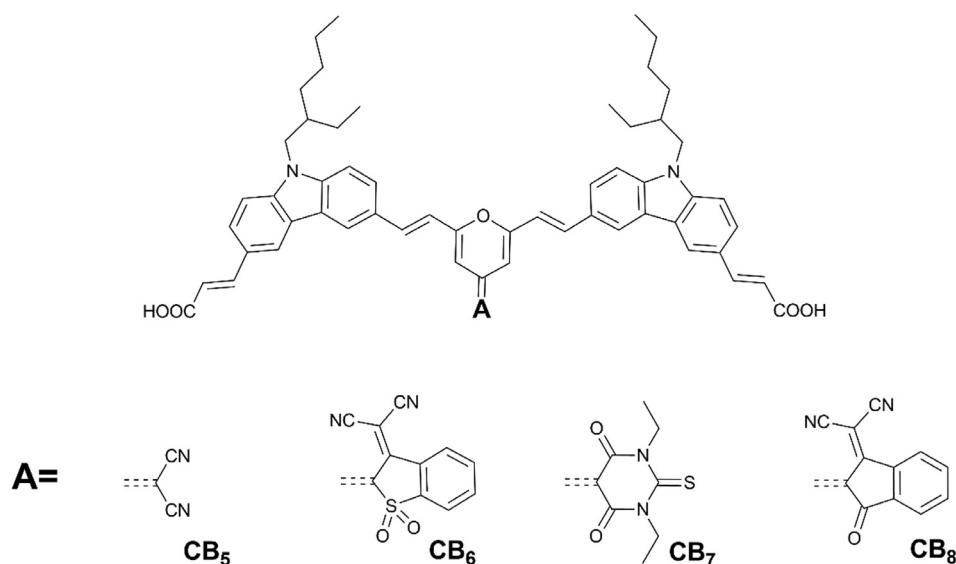


Fig. 1. Chemical structure of the investigated dyes.

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