



Exploring the application of new carbazole based dyes as effective *p*-type photosensitizers in dye-sensitized solar cells



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ABSTRACT

Herein, we report the design and the synthesis of three new D-A type metal-free carbazole based dyes (C_{1-3}) as effective photosensitizers for *p*-type DSSCs. In this new design, the electron rich carboxy substituted carbazole unit has been attached to three different electron withdrawing species, viz. *N,N*-dimethyl barbituric acid, *N,N*-diethyl thiobarbituric acid and *N*-ethyl rhodanine. They were well-characterized by spectral, photophysical and electrochemical analyses. Further, their optical and electrochemical parameters along with molecular geometries, optimized from DFT have been employed to apprehend the effect of structures of C_{1-3} on their photovoltaic performances. Further, the photovoltaic performance of C_{1-3} was determined along with the standard dye **P1** and their PCE values were found to be in the order of **P1** (0.047%) > C_2 (0.040%) > C_1 (0.016%) > C_3 (0.001%). Interestingly, the NiO based *p*-type DSSC fabricated with C_2 carrying electron withdrawing *N,N*-diethyl thiobarbituric acid displayed V_{OC} as 59 ± 4 mV and *FF* as $29 \pm 1\%$, which are higher than that of benchmark reference **P1**. This is attributed to the highest light harvesting ability, the greatest regeneration driving force and the lowest interfacial charge recombination of C_2 among the tested dyes. Conclusively, the results showcase the potential of carbazole based D-A type sensitizers in the development of efficient *p*-type DSSCs.

1. Introduction

The field of dye-sensitized solar cells (DSSCs), which belongs to second generation thin film solar cell group has engrossed much attention towards the material science research due to very low manufacturing cost and sensible efficiency of DSSCs (Grätzel, 2005, 2009; Hagfeldt et al., 2010). Till now, the majority of the investigations in the area of DSSCs on their experimental as well theoretical studies are centered upon the sensitization of *n*-type organic semiconductors for DSSCs consisting of an active photoanode, *i.e.* TiO₂ and a passive cathode made of a platinum film. Besides, regular DSSCs are based on sensitized *n*-type semiconductor such as TiO₂. However, the parent *p*-type systems comprising a photoactive cathode, *i.e.* sensitized NiO film can also be envisioned for effective solar energy harvesting (Odobel et al., 2010, 2012; Odobel and Pellegrin, 2013). Indeed, the development of *p*-type DSSCs can provide an access to the design and development of new sandwiched ‘tandem’ dye-sensitized solar cells consisting of both photoactive anode and cathode (He et al., 1999, 2000;

Nakasa et al., 2005; Gibson et al., 2009; Nattestad et al., 2010; Farré et al., 2017). Obviously, such tandem cells make use of *n*-type as well as *p* type organic sensitizers in a single device. It is vital that, as per the Shockley-Queisser limit, the upper theoretical limit of *PCE* for the solar cell containing only one photoactive semiconductor under irradiation of AM 1.5G sunlight is 30%, while the limit for a solar cell carrying two photoactive semiconductors is 43%. Thus, efficient *p*-type photoactive cathode is a missing key element preventing the construction of tandem dye-sensitized solar cells. From a chemist point of view, the exploration of such systems is quite essential to investigate the parameters governing the photovoltaic performance, which is equally important for the rational design of highly efficient tandem type solar cells as a future demand. A thorough literature survey reveals that, there are very few reports on metal-free *p*-type sensitizers, but till date the reported efficiencies for *p*-type DSSCs are much lower than those of *n*-type DSSCs (Mishra et al., 2009; Yen et al., 2012). In principle, a suitable dye for *p*-DSSC need an excited state that induces electron shift from the donor moiety located close to the NiO surface to an acceptor unit at the

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extremity of the dye, consequently favoring the interfacial hole injection from the anchoring group of the dye to the valence band (VB) of photocathode, NiO. In recent years, most of the reported work has been focused on D- π -A configured design for developing *p*-type sensitizers owing to their effective photoinduced intramolecular charge transfer phenomenon (Morandeira et al., 2008; Borgström et al., 2005; Mori et al., 2008; Zhu et al., 2014). From the last two decades, several different dyes derived from coumarin, thiophene, perylene imides, porphyrins and erythrosine based chromophore have been reported as *p*-type sensitizers for generation of cathodic photocurrent in NiO based DSSCs (Odobel et al., 2010, 2012; Odobel and Pellegrin, 2013). However their photovoltaic performance was not promising. Recently, a series of triphenyl amine dyes with D- π -A configuration carrying different electron withdrawing groups has been synthesized as effective *p*-type sensitizers, in NiO coated solar cells, one among them, particularly 4-(bis-{4-[5-(2,2-dicyanovinyl)-thiophene-2-yl]-phenyl}amino)benzoic acid (P1) has been shown to possess the high photovoltaic performance (Qin et al., 2009, 2010). Encouraged by these reports, many organic dyes derived from triphenyl amine with push-pull design strategy have been synthesized as *p*-type sensitizers in order to study the effect of their structures on device performance (Li et al., 2010, 2014; Preat et al., 2011; Warnan et al., 2014; Liu et al., 2014a, 2014b; Click et al., 2014; Ameline et al., 2015; Zhang et al., 2015; Sun et al., 2015).

Remarkably, carbazole based dyes have been studied extensively in several applications which include *n*-type DSSCs (Venkateswararao et al., 2014; Soni et al., 2015), bulk heterojunction (Li et al., 2005; Kang et al., 2015) and perovskite-sensitized solar cells (Wang et al., 2011). The striking features of carbazole core such as hole transporting character, possession of high molar extinction coefficient, facile functionalization at different positions and ease of synthesis have attracted great numbers of researchers to design and synthesize its several derivatives for the afore said uses. However, till now no references are available in the literature on synthesis of D-A type carbazole based dyes to explore their potential as *p*-type sensitizers in NiO based DSSCs.

Keeping aforesaid facts in view, in the present work, we have focused our attention to design and investigate three new carbazole based dyes with D-A configuration as *p*-type sensitizers for DSSC application. In the new design, carbazole core acts as a donor, carboxylic acid functions as an anchoring group, while electron withdrawing *N,N*-dimethyl barbituric acid, *N,N*-diethyl thiobarbituric acid and *N*-ethyl rhodanine work as electron acceptor units (Fig. 1). Further, certain prerequisites such as broad absorption in UV-Vis. range, significantly high molar extinction coefficient, thermodynamic feasibility for hole injection as well as dye regeneration, proper HOMO-LUMO levels, selection of anchoring groups, etc. which determine the photovoltaic performance largely, have been considered while designing new sensitizers for improved efficiency. Thus, it is anticipated that the new molecules employed as photosensitizers in the DSSCs would show

better photovoltaic performance.

Accordingly, the designed dyes were synthesized from simple 9*H*-carbazole following multistep synthesis pathway. The chemical structures of new dyes C₁₋₃ as well as benchmark reference dye P1 are depicted in Fig. 1. All the new intermediates and final molecules were characterized using ¹H NMR, ¹³CNMR, Mass spectroscopy and elemental analysis. Further, photophysical studies were carried out in order to investigate their optical properties. Also, the dyes were subjected to cyclic voltammetric studies in order to determine their frontier molecular orbital (FMO) energy levels. Furthermore, Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed in order to acquire information on their optimized geometry and frontier molecular orbitals.

2. Experimental section

2.1. Materials and methods

The chemicals and reagents such as carbazole, bromohexane, sodium hydride, silver oxide, lithium hydroxide monohydrate, *N,N*-dimethyl barbituric acid, *N,N*-diethyl thiobarbituric acid and *N*-ethyl rhodanine were procured from Sigma-Aldrich, Alfa Aesar and Spectrohem companies and used without purifying further. All the solvents used in the reactions are of synthetic grade and dried prior to use. The reaction progress was monitored by TLC technique. The intermediates and target molecules were purified using column chromatography. ¹H NMR and ¹³C NMR spectra were recorded in DMSO-*d*₆ solvent on a Bruker Avance 400 MHz spectrometer. The chemical shift (δ) was expressed in ppm with tetramethylsilane (TMS) as an internal standard and coupling constant (*J*) is expressed in Hz. Mass spectral and elemental analyses of the new molecules were carried out using LC-MS6410Q (Agilent Technologies) and Flash EA1112 CHNS elemental analyzer (Thermo Scientific), respectively. High-resolution mass spectra were recorded for key precursor 4 using waters HPLC-TOF mass analyzer. The UV-Visible absorption spectra of the dyes were recorded at room temperature using Analytik Jena SPECORD S 600 spectrophotometer. Further, the fluorescence emission spectra were obtained using Jasco FP 6200 spectrophotometer. The experimental GSOP and ESOP values were estimated using cyclic voltammetry (CV). The cyclic voltammograms of the dyes were recorded in acetonitrile with [0.1 M (*n*-Bu) NPF₆] as a supporting electrolyte at the scan rate of 100 mV s⁻¹ using Ivium vertex electrochemical workstation, using the conventional three-electrode system as reported in our previous publications. Finally, Turbomole V7.1 software package was utilized to perform the DFT and TD-DFT simulations. For device fabrication studies, conductive glass substrates (F-doped SnO₂) were purchased from Solaronix (TEC15, sheet resistance 15 Ω /square). A set-up comprising Oriol solar simulator (AM 1.5G, 100 mW/cm²) calibrated with a silicon cell covered

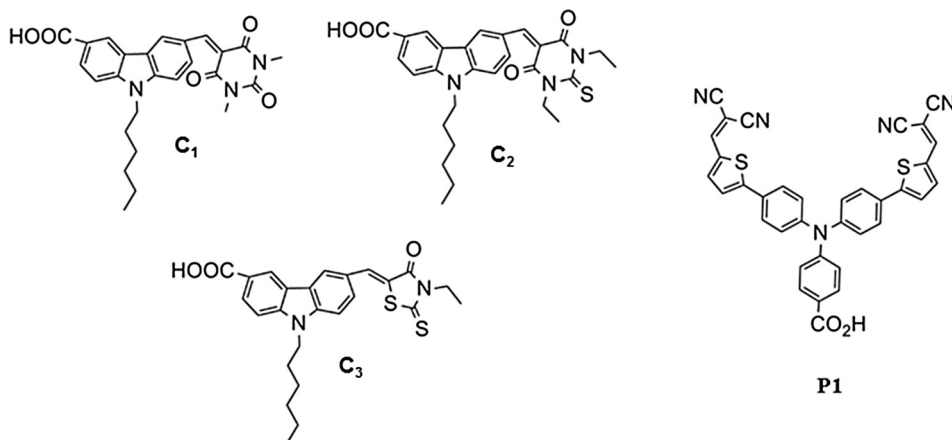


Fig. 1. Chemical structures of designed dyes C₁₋₃ and benchmark reference dye P1.

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