



Highly efficient carbazole based co-sensitizers carrying electron deficient barbituric acid for NCSU-10 sensitized DSSCs



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ABSTRACT

Herein, we report a comparative study of four interesting metal-free carbazole based organic dyes with different structural configurations, carrying electron deficient barbituric acid (C₁₋₄), as effective co-sensitizers in DSSCs sensitized with NCSU-10 dye. The new entities comprise different structural architectures, viz. D-A (C₁), D-π-A (C₂), D-D-π-A (C₃) and D-A-π-A (C₄) configurations with same accepting/anchoring moiety. They consist of carbazole as donor scaffold linked to barbituric acid as an acceptor/anchoring unit *via* different π-spacers. This paper describes the study of all the four co-sensitizers with regard to their structural, photophysical, electrochemical, theoretical and photovoltaic investigations. Also, it includes their structure-performance correlation study in detail. The devices co-sensitized with C₁₋₄ displayed the superior photovoltaic performance when compared to NCSU-10 alone. The results ameliorate the role of efficient co-sensitizers to yield DSSC with improved performance.

1. Introduction

One of the major forms of energy usable by the mankind is electricity. The generation of electricity from the clean and environmental friendly source has accelerated much added research on organic photovoltaics. Over the past two decades, dye-sensitized solar cells (DSSCs), which belong to a thin film photovoltaic technology has received much attention after the pioneering work reported by Grätzel group (O'Regan and Grätzel, 1991; Wu et al., 2015). Among the components of DSSCs, photosensitizer (dye) plays a vital role on the overall performance of the photovoltaic cell, which includes photons harvesting and initiating the electrochemical processes in the cell for power generation (Panicker et al., 2016). Till date, the majority of investigations on sensitizers in *n*-type metal-based DSSCs, are centred on Ruthenium (II) complexes due to their attractive photophysical, electrochemical properties and better photovoltaic performance compared to Cu, Fe, Os, Ir-based sensitizers (Grätzel, 2005; Pashaei et al., 2016). Although, the best performing cells exploit Ru (II) complex based chromophores such as N3, N719, black dye and NCSU-10, as active sensitizers, there are certain limitations such as use of rare noble metals, their availability, high cost, environmental hazard and problems associated with purification, have restricted their further development (Nazeeruddin et al., 1993; Chen et al., 1996; Wang et al., 2011; El-

Shafei et al., 2012; Cheema et al., 2014; Tang et al., 2015). In contrast, metal-free organic dyes possess several advantages over the former class, such as design versatility, high molar extinction coefficients, tunable photophysical spectral behavior and cost effectiveness in their synthesis (Mishra et al., 2009; Ning et al., 2010; Giribabu et al., 2017). However, compared to Ru (II) complexes, the metal-free sensitizers displayed limitations on photovoltaic performance due to their narrow absorption profiles and the absence of metal-ligand charge transfer (MLCT) bands as observed in the former class (Hagfeldt et al., 2010). In addition, it is well-established that, the light harvesting ability of the sensitizers is one of the considerable factors influencing the photovoltaic performance (Tseng et al., 2014; Wang et al., 2015). Essentially a dye to act as an ideal sensitizer, it should possess a broad and intense absorption characteristic in the UV–Visible and near IR region. Moreover, it should have favorable anchoring functionalities to adsorb on the surface of the semiconductor (Abbotto et al., 2009; Hart et al., 2012). In order to achieve these characteristics in sensitizers, several approaches are being attempted for the development of DSSCs with improved performance.

Among them, co-sensitization is an efficient approach to achieve panchromatic absorption of DSSCs which involves merits of both Ru (II) complex dyes and metal-free organic sensitizers in the same fabricated device and thereby facilitating the cell to harvest a maximum number

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of incident photons (Sharma et al., 2014). The metal-free organic dyes, to be used as ideal co-sensitizers in DSSCs, should possess some key requirements such as (i) they should not adsorb completely with the main sensitizer while efficiently suppressing the dye aggregation on the surface of mesoporous TiO₂, (ii) they should possess large molar extinction coefficient near IR region or below 450 nm. (iii) they should be able to form a compact monolayer on the surface of TiO₂, reducing the electron recombination at the TiO₂/dye/electrolyte interface (Singh et al., 2013; Luo et al., 2016b). Many heterocyclic dyes based on indole, carbazole, phenothiazine, thiophene etc. have been reported to be effective co-sensitizers (Mishra et al., 2009). One of the exciting examples is co-sensitization of a porphyrin dye YD2-o-C8 with a metal-free dye Y123, which displayed an optimum efficiency of 12.3% (Yella et al., 2011). Further, co-sensitization of the black dye with a thiophene-based organic dye Y1, which brings about an improvement in PCE of 11.28% (Han et al., 2012). Later, Luo and his coworkers reported two new thiophene and furan based D- π -A configured dyes carrying cyanoacetic acid as effective co-sensitizers for N719-based DSSCs (Luo et al., 2016a). Recently, Saritha et al. studied two new D-D- π -A configured carbazole-based dyes containing cyanoacetic acid as effective co-sensitizers for N719-based DSSCs, displaying enhanced PCE of 8.01% with higher J_{SC} value (19.33 mA·cm⁻²) than that of N-719 alone (Saritha et al., 2017). After tedious optimization, a record efficiency of 14.3% was achieved for a co-sensitized DSSC, employing metal-free carbazole based dye ADEKA-1 and triphenylamine based organic dye LEG4 as active co-sensitizers in same fabricated device using a cobalt phenanthroline-based electrolyte (Kakiage et al., 2014; Urnikaite et al., 2017; Wang et al., 2017). Among the various reported acceptor/anchoring moieties, electron deficient barbituric acid has been considered to be one of the active scaffolds, since it contains active NH/OH functionality which would facilitate effective binding of the sensitizer/co-sensitizer on the surface of TiO₂ (Hosseinzadeh et al., 2015; Salimi Beni et al., 2015). However, in the literature, very limited references are available on the co-sensitization using carbazole-based dyes carrying barbituric acid as an anchoring moiety. Against this background, in the present paper, we describe a comparative study of four dyes with different configurations, viz. D-A (C₁), D- π -A (C₂), D-D- π -A (C₃) and D-A- π -A (C₄) as effective co-sensitizers in the construction of NCSU-10 sensitized DSSCs (Naik et al., 2018a, 2018b, 2018c, 2017a, 2017b, 2017c). The chemical structures of organic co-sensitizers C₁₋₄ along with that of NCSU-10 are depicted in Fig. 1. It appears there exists a good matching in structures of C₁₋₄ and Ru (II) based complex, NCSU-10. In this paper, a comparative account of detailed photophysical, electrochemical, theoretical and photovoltaic studies of C₁₋₄ has been discussed, including their structure-property relationship.

2. Experimental segment

2.1. Materials, methods and instruments

The molecular design and synthetic methods for the dyes C₁₋₄ have been reported in our previous papers (Naik et al., 2018a, 2018b, 2017a, 2017c). In the present work, their UV-Vis. absorption spectra were recorded using SPECORD S600 spectrophotometer, whereas PL emission spectra were obtained using Jasco FP-6200 spectrophotometer. The cyclic voltammetric (CV) measurements were performed on an Ivium Vertex electrochemical workstation by using the three electrode system, consisting of dye casted on glassy carbon electrode as the working electrode, Pt electrode as a counter and Ag/AgCl as a reference electrode. All three electrodes were immersed in the acetonitrile solution consisting an electrolyte [0.1 M (n-Bu) N (BF₄) in acetonitrile] and data were recorded at a scan rate of 100 mV/s. Further, DFT calculations were performed with the help of Turbomole, 7.1 V software package. Furthermore, *J-V* (Current-Voltage) characteristics of co-sensitized DSSC devices were measured under AM 1.5G illumination from a solar simulator (SOL3A, Oriol). Finally, *IPCE* (Incident photon

conversion efficiency) experiments were conducted using QEX10 PV measurement system.

3. Results and discussion

3.1. Photophysical and electrochemical studies

The UV-vis absorption and fluorescence emission of co-sensitizers C₁₋₄ were recorded in 10⁻⁵ chloroform solutions and their corresponding results are summarized in Table 1. Fig. 2 depicts the UV-vis absorption spectra of the co-sensitizers C₁₋₄. A strong absorption maxima corresponding to intermolecular charge transfer (ICT) from carbazole donor to the barbituric acid moiety was observed in the region of 446–524 nm. Interestingly, highly conjugated dye C₄ with D-A- π -A configuration displayed red shift when compared to other dyes. Further fluorescence emission spectra of co-sensitizers C₁₋₄, recorded at their absorption maxima (λ_{abs}) are portrayed in Fig. 3. From the emission spectra, it is clear that, the dyes show strong luminescence maxima in the region of 516–624 nm. The optical band-gap was also calculated from the intersection between normalized absorption and emission spectra (Table 1).

The CV studies were performed for co-sensitizers (C₁₋₄) in order to evaluate their excited state oxidation potential/lowest unoccupied molecular orbital (ESOP/LUMO) and ground state oxidation potential/highest occupied molecular orbital (GSOP/HOMO) energy levels. The ESOP and GSOP of the sensitizers were measured to gauge the prospects of effective charge injection as well as regeneration of dyes. The estimated GSOP/HOMO and ESOP/LUMO energy levels are tabulated in Table 1. It is apparent that, the calculated GSOP/HOMO levels of co-sensitizers C₁₋₄ were found to possess more negative values than the Nernst potential of I₃⁻/I⁻ electrolyte system (Qu and Meyer, 2001), showing that the oxidized dye can be effectively reduced and regenerated by the electrolyte species. Further, the estimated ESOP/LUMO levels of C₁₋₄ were found to be higher than the potential of CB of TiO₂ (Oskam et al., 2001). Conclusively, all the dyes fulfilled the prerequisites for an effective electron injection and dye regeneration process in the fabricated devices (Koops et al., 2009). However, because of the presence of different conjugated electron-bridge structures, all the dyes demonstrated distinct HOMO and LUMO energy levels. Fig. 4 depicts the energy level diagram, showing the GSOP and ESOP values of dyes C₁₋₄. The experimental results indicated the presence of ample driving force for effective dye regeneration and an efficient electron injection in the fabricated cell.

3.2. Theoretical investigations

DFT method is considered to be one of the most reliable approaches used in the computational and materials simulations after the pioneering work by Hohenberg and Kohn in 1964 (Cao et al., 2016). It offers an attractive balance between low computational cost and high accuracy for predicting ground state properties of the materials. In the present study, DFT calculations were performed using Turbomole V7.1 software package. We have carried out the DFT simulations for all the dyes at B3LYP Ex-change correlation functional using def-TZVPP basis set, to gain insight into their electronic structures (Becke, 1993; Peach et al., 2008; Naik et al., 2018b). Fig. 5 depicts the optimized molecular geometries of co-sensitizers C₁₋₄ and their corresponding electron density delocalized in their respective FMO energy levels as obtained from T-mole visualizer. As evidenced from their HOMO-LUMO energy levels, the electron density predominantly localized on carbazole has been shifted towards electron accepting barbituric acid, but to a different extent due to their varied π -spacer configuration.

3.3. Photovoltaic performance

In order to evaluate the co-sensitization behavior of the dyes C₁₋₄

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