



Synthesis and photovoltaic performance of a novel asymmetric dual-channel co-sensitizer for dye-sensitized solar cell beyond 10% efficiency



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ABSTRACT

In this paper, we report the design and synthesis of a new bi-anchoring indole based co-sensitizer **DBA-8** with A- π -D-A (acceptor- π bridge-donor-acceptor) architecture, carrying indole moiety as a donor and barbituric acid as acceptor/anchoring groups. Its photo-physical and electrochemical properties along with molecular geometries, calculated from Density Functional Theory (DFT) are employed to comprehend the effect of co-sensitizer structure on photovoltaic characteristics of DSSCs. The abovementioned organic dye (**DBA-8**) was employed as a co-sensitizer along with well-known ruthenium based sensitizer **NCSU-10** in order to broaden the spectral responses of the co-sensitized DSSC. In the present work, for the first time we are demonstrating the profound role of a dual-anchoring co-sensitizer that can play in ameliorating the overall performance of a solar cell. The photovoltaic studies indicated that, the co-sensitizer **DBA-8** succeeded in increasing the light harvesting ability in the device significantly. Notably, the device co-sensitized using 0.2 mM **DBA-8** along with ruthenium based chromophore **NCSU-10**, showed a maximum efficiency of **10.68%** ($J_{sc} = 25.14 \text{ mAcm}^{-2}$, $V_{oc} = 0.695 \text{ V}$, $ff = 61.2\%$). Further, the good agreement between the theoretically and experimentally obtained λ_{max} data vindicate that, the energy functional and basis set employed in this study can be successfully utilized for predicting the absorption spectra of new photosensitizers, with great precision before synthesis. Furthermore, all these findings showcase the vast potential of bi-anchoring molecules in improving the overall performance of the dye-sensitized solar cells.

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1. Introduction

Solar energy is the most abundant source of alternative and sustainable energy known to mankind. Ever since the successful exhibition of Dye-Sensitized Solar Cells (DSSCs) technology by Grätzel and co-workers, DSSCs have been extensively investigated owing to their low cost, relative ease of fabrication, flexibility and better cost-to-efficiency ratio [1]. In the recent years, many approaches have been explored to develop effective sensitizers having improved light-to-electricity conversion efficiency and

enhanced photo-stability [2]. Although, the best-performing devices are sensitized with ruthenium based chromophores such **N3**, **N719**, and **black dye**, they are afflicted by many problems, such as high cost, scarcity of metal and lengthy purification steps [3–5]. On the other hand, the metal-free organic sensitizers are gaining much interest due their low cost, facile synthesis, eco-friendliness, high molecular extinction coefficients and exceptional light-harvesting prowess [6–9]. With regard to design of such sensitizers, as per the literature, the donor-(π -spacer)-acceptor (D- π -A) approach is the most extensively explored molecular architecture for efficient metal-free organic dye sensitizers [10,11]. The aforementioned design facilitates effective photo-induced intramolecular charge transfer (ICT) from the donor moiety to the acceptor group via the π -conjugation bridge. Typically, in most of the aforesaid dyes,

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various organic core scaffolds such as triarylamine, carbazole, indole and phenothiazine, are employed as electron-donating moieties [12]. Further, π -conjugating moieties are known to play a vital role in enhancing electrochemical and spectroscopic properties as well as increasing the overall stability of the resulting molecules. Thus, in our new design, we have adopted indole as a principal donor moiety because of its excellent light harvesting capability, electron donating ability and stability; thiophene has been employed as π -conjugating moiety due to its excellent charge transporting capability, polarizability, as well as tunable electrochemical and spectroscopic properties including enhanced molar extinction coefficients at longer absorption wavelengths. Further, in addition to the core as well as π -spacer moieties, fine tuning of the structure and number of anchoring groups are also equally important for the development of efficient organic sensitizers [13].

Lately, quite a lot of organic sensitizers containing two anchoring groups have been reported in the literature [14a–c]. These di-anchoring organic sensitizers possess several advantages over their mono-anchoring counter-parts, which include: (i) panchromatic response due to extended π -conjugation (ii) multi binding abilities to TiO_2 nanoparticles (iii) increased number of electron extraction channels (iv) improved efficiency and (v) enhanced stability. Further, the presence of only one anchoring group per molecule in the organic sensitizers may lead to serious impairments with respect to their ruthenium based counter-parts, wherein 1 to 4 anchoring groups are prevailing for the efficient injection of photo-excited electrons into the conduction band of TiO_2 through the anchoring carboxylate functional groups by metal-to-ligand charge transfer (MLCT) process [15]. On the other hand, di-anchoring sensitizers are known to exhibit lower open-circuit photovoltage (V_{oc}) compared to their mono-anchoring counterparts. The aforesaid trait can be attributed to enhanced charge recombination process in di-anchoring sensitizers [16]. Therefore, there is a great yearning to optimize the structure of dual anchoring dyes for more efficient DSSCs. Keeping this in view, Abbotto and co-workers reported several symmetric di-branched and di-anchoring organic dyes carrying A- π -D- π -A architecture. These dyes exhibited enhanced light-harvesting properties as well as higher stability than its mono-anchoring analogs [17]. However, most of the available literature on di-anchoring sensitizers have focused on the symmetric architecture, while reports on the asymmetric di-anchoring dyes are quite rare. Further, the performance of the DSSCs based on metal-free organic dyes has not been found to be up to the mark due to their narrow absorption spectrum. Taking all the aforesaid points into consideration, researchers have employed co-sensitization approach, wherein an effective ruthenium based dye is co-sensitized using an organic chromophore with complementary absorption profile, in order to enable the DSSC to harvest maximum number of photons [18].

Further, numerous donor and π -conjugation segments have been extensively explored for organic sensitizers, but not enough attention has been paid to the nature of acceptor/anchoring groups. The aforesaid observation stems from the fact that, till date only a few selected molecules are employed as anchoring units, such as cyanoacrylic acid, rhodanine-3-acetic acid etc. Therefore, in this paper, we have explored the effectiveness of barbituric acid moiety as acceptor/anchoring unit in TiO_2 based solar cells.

Keeping all the aforesaid points in view, we have designed an unsymmetrical di-anchoring organic co-sensitizer (**DBA-8**) having one donor and two acceptor/anchoring groups. The newly designed co-sensitizer incorporates an indole core, and a thiophene π -bridge attached to barbituric acid acceptor unit on one arm, whereas on the other arm barbituric acid is directly attached to indole donor; hence it leads to the formation of unsymmetrical di-anchoring organic co-sensitizers **DBA-8**. Further, a hexyl alkyl chain is

attached on the indole unit to assist in suppressing dye aggregation and unwanted electron recombination reactions in DSSC while also improving the solubility of the dye in common organic solvents. The newly designed co-sensitizer is expected to show a broad spectral response, while sustaining decent charge injection characteristics. It has been synthesized using simple synthetic strategy. Further, the compound (**DBA-8**) is used as co-sensitizer along with ruthenium-based sensitizer **NCSU-10** [19] to increase its photo-voltaic efficiency by counteracting the competitive light absorption owing to triiodide species in 400–500 nm region of the electromagnetic spectrum. Moreover, it is hoped that, due the significant molecular size difference between the organic co-sensitizer and the ruthenium-based **NCSU-10** dye, the metal-oxide surface can be impregnated more efficiently, as the small sized organic dye molecules can get adsorbed conveniently onto the gaps between the large ruthenium based sensitizer (**NCSU-10**) molecules. Also, the **DBA-8** has been subjected to molecular modeling studies in order to understand its profound electronic and optical properties using the Turbomole software package. Fig. 1 shows the chemical structures of the organic co-sensitizer **DBA-8** and ruthenium-based sensitizer **NCSU-10**.

2. Results and discussions

2.1. Synthesis and structure characterization

The synthetic pathway for the new co-sensitizer (**DBA-8**) is depicted in Scheme 1. In the synthesis, N-alkylation of 5-bromo-1H-indole was carried out using 1-bromohexane to give compound **1**. It was then subjected to Vilsmeier-Haack formylation to yield indole-3-carboxaldehyde derivative **2**. The product was then coupled with 5-formylthiophen-2-ylboronic acid via Suzuki coupling to obtain a bi-heterocyclic aldehyde **3**. Finally, Knoevenagel condensation of this aldehyde **3** with barbituric acid in presence of methanol produced the co-sensitizer **DBA-8**.

2.2. Photophysical properties

The absorption as well as emission spectra of the new co-sensitizer were obtained in DMSO and are depicted in Fig. 2(a) and (b), respectively; while the pertaining spectral characteristics are summarized in Table 1. From the absorption spectrum, it is clear that, the dye exhibits two separate bands. The absorption band, in the range of 400 nm, can be attributed to the π - π^* electronic excitations confined within the indole donor and thiophene π -conjugated fragment, whereas, the band in 460 nm can be ascribed to the charge transfer (CT) from donor system to the two acceptor moieties [11]. Additionally, the fluorescence emission spectrum of **DBA-8** was recorded at its excitation wavelengths and the pertaining results are presented in Table 1, while the corresponding emission spectrum is presented in Fig. 2(b). Here, the large values of Stokes shift found in this sensitizer can be attributed to the effective charge transfer from the indole donor segment to the two barbituric acid acceptor moieties. In addition, Fig. 2(a) also shows the UV-visible spectrum of ruthenium sensitizer **NCSU-10**.

Further, the origin of the charge transfer transition is also confirmed by comparing the absorption spectrum of the sensitizer **DBA-8** with its precursor. From Fig. 3, it is evident that, the peak corresponding to π - π^* transition is retained in all the precursors, whereas the peak at longer wavelength appears only after the introduction of aldehyde or barbituric acid units on the indole core. The aforesaid red shift in the absorption profile reflects the electron withdrawing property of aldehydic groups as well as barbituric acid segments.

Further, the absorption peak due to charge transfer observed at

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