

# Understanding structure-property correlation of metal free organic dyes using interfacial electron transfer measurements



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## ABSTRACT

Triphenylamine-bithiazole based two metal-free organic dyes were designed and synthesized employing D- $\pi$ -A strategy for dye sensitized solar cells (DSSCs) which differed in the anchoring group attached to it. The photophysical, electrochemical and photovoltaic properties of the dyes were investigated in detail. The HOMO-LUMO analysis proved that the energetics of both the dyes were properly placed with respect to TiO<sub>2</sub> and iodide/triiodide electrolyte in order to have efficient electron injection and regeneration, respectively. Photovoltaic characteristics of the dyes were studied in the presence of a coadsorbent exhibiting a maximum efficiency of 4.7%. The electron lifetimes obtained from open circuit voltage decay (OCVD) measurements shows that addition of co-adsorbent **CDCA** helped in reducing aggregation of both TPA-bithiazole dyes thereby improving the photovoltage for devices with co-adsorbent and a better efficiency in comparison to the dye alone devices. Fundamental insights into the interfacial charge transfer processes occurring in devices were obtained using electrochemical impedance spectroscopy (EIS) measurements. EIS measurements indicated that the device sensitized by the compound having cyanoacrylic acid as anchoring group in presence of coadsorbent exhibited the largest resistance for recombination between the electrons injected to TiO<sub>2</sub> and electrolyte leading to a better lifetime and photovoltage.

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## 1. Introduction

Finding new alternative sources of energy has become a challenge for the scientific community due to the depleting fossil fuel reserves, environmental pollution and related issues. Harvesting and converting of solar energy through photovoltaic technology is the most promising way to address these issues. In this context, dye sensitized solar cells (DSSC) is of particular importance due to its high efficiency, low cost and simple fabrication using solution techniques (Hagfeldt and Grätzel, 2000; Wu and Zhu, 2013; Grätzel, 2001; Hagfeldt et al., 2010). Photoconversion efficiencies (PCE) up to 13% were reported using ruthenium and based metal complexes (Grätzel, 2009; Wang et al., 2014; Mathew et al., 2014; Yella et al., 2011). Metal-free dye sensitizers are on the other hand becoming more popular recently owing to their lower cost, easy purification, tailor made design properties and higher molar absorption coefficients (Eom et al., 2016; Zhu et al., 2011; Hung et al., 2015; Vinayak et al., 2016; Kakiage et al., 2015). Recently, efficiency up to 14.7% was reported using metal free sensitizers coupled with suitable redox shuttles (Kakiage et al., 2015). The

efficiency of DSSCs can be improved by the optimization of the design of sensitizers (Lee et al., 2015), use of different kinds of electrolytes (Wu et al., 2015), incorporation of co-adsorbents (Choi et al., 2014) and co-sensitizers. Use of various anchoring groups is of particular importance in the design approach of sensitizers as they influence the dye loading efficiency, electron-transport properties and charge recombination rates (Zhang and Cole, 2015). Conventionally, a donor- $\pi$ -acceptor (D- $\pi$ -A) design strategy is being used to get organic dyes with excellent PCEs. The D- $\pi$ -A model induces intramolecular electronic communication through the polarization of electron cloud towards the acceptor, which facilitates efficient electron injection to TiO<sub>2</sub>.

Anchoring dye molecules on the surface of semiconducting metal oxides like TiO<sub>2</sub> is imperative for the injection of electrons from the excited state of dyes to the conduction band of TiO<sub>2</sub>. Mainly covalent bonding between the dye and TiO<sub>2</sub> is responsible for the strong electronic coupling between them (Zhang and Cole, 2015). Cyanoacrylic acid is the commonly used acceptor and anchoring group in metal-free organic dyes for DSSC. In recent years, many new anchoring groups were being used for developing efficient organic dyes for solar cell applications (Zhang and Cole, 2015). Among the new anchoring groups, rhodanine derivatives emerged as a promising candidate for DSSC (Yang et al., 2010;

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Soni et al., 2015; Ahn et al., 2015; Lan et al., 2015; Qian et al., 2015). When a donor moiety is connected covalently to a rhodanine containing carboxylic acid moiety, efficient anchoring on to the mesoporous TiO<sub>2</sub> surface was observed (Yang et al., 2010; Soni et al., 2015; Ahn et al., 2015; Lan et al., 2015; Qian et al., 2015). The rhodanine derivatives not only act as an anchoring group but also enhance the absorption characteristics because of their ability to function as strong electron acceptors (Yang et al., 2010; Soni et al., 2015; Ahn et al., 2015; Lan et al., 2015; Qian et al., 2015).

In the present work, we have designed and synthesized two novel triphenylamine-bithiazole based dyes for applying as photosensitizers in dye sensitized solar cells (Chart 1). The dyes exhibited structural similarity with respect to donor and  $\pi$  bridge, but vary in terms of anchoring groups viz., cyanoacrylic acid (TP-CAA) and rhodanine 3-acetic acid (TP-RAA). In these molecules, a D- $\pi$ -A strategy was employed, in which triphenylamine act as donor (D), bithiazole as a  $\pi$ -bridging unit for conjugation and cyanoacrylic acid/rhodanine derivative as acceptors (A). Triphenylamine derivatives are one of the most promising candidates for DSSC because of their strong donor property, easiness to introduce functional groups, and their unique propeller structure that prevents aggregation on the surface of TiO<sub>2</sub> (Kanaparthi et al., 2012). Introduction of bithiazole spacers with hexyl groups to the triphenylamine was to widen the absorption spectra coupled with enhanced solubility and restricted aggregation on the semiconductor surface (He et al., 2011). The selected anchoring groups for this work not only play a significant role in surface adsorption but also act as excellent electron acceptors which are essential for the intramolecular electron transfer promoted from the excited donor of the dye to the TiO<sub>2</sub> upon light absorption.

## 2. Experimental section

### 2.1. Materials and characterization techniques

The reagents and materials for synthesis were purchased from Sigma-Aldrich, Merck, TCI and Spectrochem chemical suppliers, and are used as received. Air and water sensitive synthetic steps were performed in an argon atmosphere using standard Schlenk techniques. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker-500 MHz spectrometer. The compounds were thoroughly purified using the recycling preparative HPLC system of Japan Analytical Industry Co., Ltd LC-9220 II NEXT SERIES (eluent CHCl<sub>3</sub>). Absorption spectra were recorded using Shimadzu

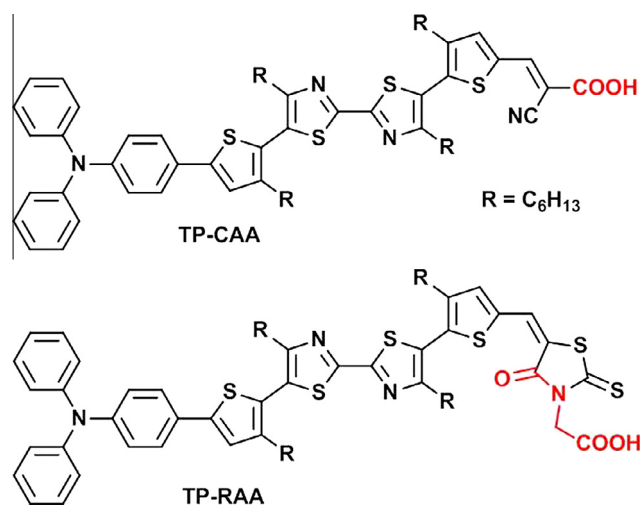


Chart 1. Structure of compounds used in the study.

UV-Visible-2401PC spectrophotometer. Steady-state fluorescence experiments were performed using a SPEX Fluorolog F112X spectrofluorimeter. Cyclic voltammetry experiments were performed using a BAS 50W voltammetric analyser. Density functional theory (DFT) calculations were performed at the B3LYP/6-31G\* (d,p) level using Gaussian 09 program.

### 2.2. Fabrication and characterization of DSSC

The FTO plates used for TiO<sub>2</sub> deposition were systematically cleaned using detergent, distilled water, acetone, isopropanol and kept for UV-ozone treatment for 30 min. Deposition of TiCl<sub>4</sub> was done by immersing electrodes into a 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C for 30 min and then washed with distilled water and ethanol. The photoanodes were then annealed at 500 °C for 30 min. After cooling, transparent TiO<sub>2</sub> paste of particle size 8–10 nm was deposited followed by annealing at 125 °C for 10 min. This was followed by the deposition of TiO<sub>2</sub> paste consisting of 400 nm particle size and annealed at 125 °C for 10 min. This was followed again by TiCl<sub>4</sub> treatment and annealing at 500 °C for 30 min followed by washing with water and ethanol. The electrodes were then put into programmed heating at 325 °C for 15 min, 375 °C for 15 min, 450 °C for 15 min, and 500 °C for 30 min and slowly cooled down to room temperature. Electrodes were then immersed into dye solutions in THF (0.3 mM) with and without coadsorbent, chenodeoxycholic acid (CDCA) (10 mM) and kept at room temperature for 15 h. Counter electrodes were prepared by coating with a drop of H<sub>2</sub>PtCl<sub>6</sub> solution (2 mg of Pt in 1 mL ethanol) on FTO plates having pre-drilled holes. The electrodes were then assembled with hot press using 25  $\mu$ m surlyn spacer. The space in between both the electrodes were filled with liquid iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) electrolyte which was composed of various compositions of 1-butyl-3-methylimidazolium iodide (BMII), lithium iodide (LiI), iodine (I<sub>2</sub>) and 4-*tert*-butyl pyridine (TBP) in acetonitrile. The drilled holes were sealed with microscopic cover slide and surlyn to avoid electrolyte leakage. Three cells were fabricated for each condition and the cells were measured after keeping it for 12 h in dark.

The photovoltaic performance of the fabricated DSSCs were measured using an AM 1.5 solar simulator (Newport Instruments, USA) equipped with a source meter (Keithley 2400) at 25 °C. The IPCE measurement of the devices was performed under DC mode using a 250 W xenon lamp coupled with Newport monochromator. The J-V properties of cells were measured using square shade mask with an active area of 0.25 cm<sup>2</sup> (without mask active area is 0.36 cm<sup>2</sup>). The power of the simulated sunlight was calibrated by using a reference cell supplied by Newport instruments. Open circuit voltage (V<sub>oc</sub>) decay measurements are done at open circuit. The cell was in the dark at the beginning of the measurement, and then the lights were turned on until the voltage got stabilized, followed by switching the light off and recording the decay of photovoltage. Lifetime data was transformed from the voltage decay part of the measurement through previously reported methods (Soman et al., 2014). The electrochemical impedance spectroscopy measurements of the devices were carried out using a micro Autolab ( $\mu$ 3AUT70904) equipped with frequency response analysis (FRA) mode under forward bias in dark. The measurements were performed in a frequency range of 0.1–10<sup>5</sup> Hz with an ac amplitude of 10 mV.

## 3. Results and discussion

### 3.1. Synthesis

The dyes were synthesized starting from 2-octanone as shown in Scheme 1. Compounds 1–6 were already reported in our previ-

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