



# Impact of anchoring groups for improving the binding nature of organic dyes toward high efficient dye sensitized solar cells

Subbaiah Manoharan<sup>a</sup>, Abdullah M. Asiri<sup>b</sup>, Sambandam Anandan<sup>a,\*</sup>

<sup>a</sup> *Nanomaterials and Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India*

<sup>b</sup> *The Center of Excellence for Advanced Materials Research, King Abdulaziz University, P.O. Box 80203, Jeddah 21413, Saudi Arabia*

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## Abstract

A series of mono and bi-anchoring metal-free organic dyes containing diphenylamine or diethylamine as a donor which linked to the acrylic acid or nitro vinyl as acceptor through a phenyl  $\pi$ -spacer were synthesized through simple procedure and tested as photosensitizers for dye-sensitized solar cell applications. The synthesized dyes were well characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, mass spectrometry and elemental analysis. The optical, electrochemical, theoretical and photovoltaic properties of the synthesized dyes were investigated. Introduction of the additional electron acceptor unit leads to the significant improvement in the optoelectronic properties and DSSC performance. In general, bi anchoring dye based DSSCs show more than two times higher efficiency than the mono anchoring dye based DSSCs. Among the fabricated DSSCs, the carboxylic acid substituted bi anchoring dye (P2C) based DSSC show maximum power conversion efficiency of 3.86% under AM1.5 illumination (85 mW/cm<sup>2</sup>). In order to confirm the need of more number of anchoring groups for improving the efficiency of solar cells, dye molecules with nitro derivatives were synthesized and the results were compared.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted immense scientific and technological research interest since their first discovery in 1991 by O'Regan and Gratzel, and are now emerging as commercial products (O'Regan and Gratzel, 1991; Hardin et al., 2012). In order to improve the performances of DSSCs and to increase their commercial attractiveness, several different classes of materials are employed to fabricate DSSCs. Among them, Sensitizer is most critical component which is responsible for light

harvesting and the creation of electric charges. Moreover, the sensitizer structure also plays a role in controlling the electron transfer processes at the  $\text{TiO}_2$ /dye/electrolyte interface (Odobel et al., 2013). Up to now, Ruthenium sensitizer based DSSCs have shown 12.1% power conversion efficiency (PEC) (Yu et al., 2010), whereas fabricated DSSCs achieved 13% efficiency by employing a zinc porphyrin dye (Mathew et al., 2014). Even though various metal complexes show high efficiencies, the metal-free organic dyes have recently attracted considerable scientific attention due to advantages such as low cost, high molar extinction coefficient, easy structural modification, and simple synthesis procedure, which enhance efficiencies exceeding 10% (Liang and Chen, 2013).

\* Corresponding author. Tel.: +91 431 2503639; fax: +91 431 2500133.  
E-mail addresses: [sanand@nitt.edu](mailto:sanand@nitt.edu), [sanand99@yahoo.com](mailto:sanand99@yahoo.com) (S. Anandan).

A benchmark in the development of metal-free organic dyes came with the design of donor– $\pi$ -spacer–acceptor (D– $\pi$ –A) configuration, owing to an effective photoinduced intramolecular charge transfer processes (Ahmad et al., 2013). Binding strength of such organic dye molecules on the TiO<sub>2</sub> surface is one of the crucial factors to improve the solar energy conversion efficiency and device stability. Among the various types of metal-free organic dye molecules, most of the dyes containing mono anchoring group which may be the reason for inferior performance upon compared with metal complex sensitizers. However introduction up to four anchoring groups may tune the interfacial electron transfer processes at the maximum (De Angelis et al., 2007) due to enhanced binding strength of the dye molecules which act as an efficient photosensitizer for DSSCs. In the last five years, a significant number of multi-anchoring dye have been synthesized as sensitizers for DSSCs, which show better performance compared to monoanchoring dyes with an improved photoresponse, photocurrent and stability (Abbotto et al., 2011; Liu et al., 2011; Manfredi et al., 2014). Yang et al. reported the comparative study of triphenylamine based dyes with mono, bi and tri anchoring unit and found that the dye with bi anchoring unit shows best solar cell performance (4.77%) compared to mono and tri anchoring dyes (4.28% and 2.97%) which is because of broadening and red shift of the absorption spectrum (Yang et al., 2009). In addition, Sirohi et al. also reported that triphenylamine based dyes with bi-anchoring unit caused strong binding to TiO<sub>2</sub> and forced the dye molecule to non-planar conformation, thereby minimizing dye aggregation. These factors led to about 1.5 times higher efficiency of bi anchoring dyes (6.1%) compared to corresponding monoanchoring dye (4.2%) (Sirohi et al., 2012).

On the basis of the above considerations, bi-anchored dyes containing carboxylic acid and nitro groups were synthesized here to establish higher binding nature, extension of the absorption to longer wavelengths, higher molar extinction coefficient and decrease the HOMO–LUMO gap and, hence, prove beneficial for its photo-stability and higher efficiency compared to monoanchored dyes. Hence in this manuscript, a series of six organic dyes namely 3-(4-(diethylamino)phenyl)acrylic acid (EC), *N,N*-diethyl-4-(2-nitrovinyl)aniline (EN), 3-(4-(diphenylamino)phenyl)acrylic acid (PC), 4-(2-nitrovinyl)-*N,N*-diphenylaniline (PN), 3,3'-(4,4'-(phenylazanediy)bis(4,1-phenylene))diacrylic acid (P2C), and 4-(2-nitrovinyl)-*N*-(4-(2-nitrovinyl)phenyl)-*N*-phenylaniline (P2N) based on diphenylamine or diethylamine as a donor which linked to the acrylic acid or nitro vinyl as acceptor through a phenyl  $\pi$ -spacer were synthesized (as shown in Scheme 1) and characterized through optoelectronic, theoretical and photovoltaic properties. In order to confirm the necessary of anchoring groups for improving the binding nature, dye molecules with nitro derivatives were compared.

## 2. Experimental section

### 2.1. Materials and methods

Nitromethane (Alfa Aesar), triphenylamine (Sigma–Aldrich), 4-diethylaminobenzaldehyde (Alfa Aesar), malonic acid (Alfa Aesar) were purchased and used without further purification. Ammonium acetate, glacial acetic acid, piperidine, pyridine, *N,N*-dimethylformamide (DMF) and Phosphorus oxychloride (POCl<sub>3</sub>) were purchased from Merck. <sup>1</sup>H and <sup>13</sup>C NMR studies were measured on Bruker 500 MHz NMR Spectrometer in deuterated chloroform or dimethylsulfoxide solution at 298 K. Chemical shifts ( $\delta$  values) were recorded in units of ppm relative to tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were obtained by ESI (Orbitrap mass spectrometer). The FT-IR spectra were obtained with a Thermo Scientific Nicolet iS5 FT IR Spectrometer. All reactions were monitored using TLC plates. All chromatographic separations were carried out on silica gel (60–130 mesh).

### 2.2. Photophysical and electrochemical measurements

Absorption and fluorescence spectra were measured in DMF solution on a T90+ UV–Vis absorption spectrophotometer and Shimadzu RF-5301 PC spectrofluorophotometer respectively. Electrochemical measurements were performed on a Metrohm Autolab PGSTAT potentiostat/galvanostat-84610. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a glassy carbon (GC) working electrode, a platinum wire auxiliary electrode, and a silver wire was used as the quasi-reference electrode. The potentials were reported vs ferrocene as standard using a scan rate of 0.1 V s<sup>-1</sup> and the sample solutions contained 3 × 10<sup>-4</sup> M sample and 0.1 M tetrabutylammonium perchlorate (TBAP) in anhydrous DMF as a supporting electrolyte under Argon atmosphere. Electrochemical impedance spectroscopy (EIS) measurements were done under 85 mW/cm<sup>2</sup> light illumination by using an Autolab PGSTAT potentiostat/galvanostat-84610. The impedance spectra were recorded with a frequency ranging between 10 kHz and 0.1 Hz at their open circuit potential (OCP).

### 2.3. Synthesis of sensitizers

Scheme-1 shows synthesis of sensitizers starting from triphenylamine. 4-formyltriphenylamine (1a) (Lai et al., 1997) and 4,4'-diformyltriphenylamine (1b) (Mallegol et al., 2005) were synthesized from triphenylamine by following the reported procedures available in the literature which are then used as the starting material for the synthesis of desired end products. 3-(4-(diethylamino)phenyl)acrylic acid (EC) and 3-(4-(diphenylamino)phenyl)acrylic acid (PC) dyes were synthesized as mentioned in literature (Subbaiah et al., 2013).

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