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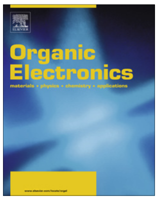

Characterization of two new $(A–\pi)_2–D–A$ type dyes with different central D unit and their application for dye sensitized solar cells

G.D. Sharma [a,*], K.R. Patel [b], M.S. Roy [c], R. Misra [d]

[a] *R&D Center for Science and Engineering, JEC Group of Colleges, Jaipur Engineering College Campus, Kukas, Jaipur 303101, Rajasthan, India*
[b] *Department of Physics, JNV University, Jodhpur, India*
[c] *Defence Laboratory, Jodhpur 342011, India*
[d] *Department of Chemistry, Indian Institute of Technology, Indore 452017, MP, India*

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ABSTRACT

We report the photophysical, electrochemical and theoretical properties of two dyes with same acceptor, π-linker and anchoring acceptor unit and different TPA (**D1**) and pyran (**D2**) donor central unit. The change in the central unit resulted in corresponding different photophysical and electrochemical properties. The dye sensitized solar cell fabricated using dye **D1** showed the higher incident photon to current efficiency of 54%, a short circuit current (J_{sc}) of 11.86 mA/cm^2, an open circuit voltage of 0.64 V, and fill factor (FF) of 0.68, corresponding an overall power conversion efficiency of 5.16% which is higher than that for **D2** based DSSCs (4.42%). The difference in the PCE of DSSCs based on **D1** and **D2** is partly, due to the smaller amount of dye loading, higher dark current and charge recombination rate of **D1** based DSSC. The electrochemical spectra of DSSCs demonstrated longer electron life time and charge recombination resistance and small charge transport resistance for **D1** sensitized DSSC, results the higher PCE.

1. Introduction

Lot of research efforts has been devoted to develop efficient dye sensitized solar cells (DSSCs), over past two decades due to their low cost potential for photovoltaic technology, since the first report by Gratzel et al. [1]. A DSSC is composed of a photoelectrode (meso-structured metal oxide semiconductor, typically TiO_2 or ZnO) impregnated with dye molecule, counter electrode and electrolyte containing redox species, iodide/tri-iodide between two electrodes. In a DSSCs, upon irradiation, light is absorbed the dye sensitizer, which results electron injection from the photoexcited dye into the conduction band of TiO_2. Subsequently, the oxidized dye is regenerated by the electron donation form the redox species. In this process, the electrons flow from the photoelectrode to counter electrode, whereas the redox mediator is in turn reduced. The dyes based on ruthenium (Ru) complex dyes and zinc porphyrins have been extensively used as sensitizers for DSSCs and demonstrated power conversion efficiencies (PCEs) more than 10–11% [2] and 12% [3], respectively. However, the large scale application of Ru complexes has been limited due to their high cost of purification. In comparison, dyes based on metal complexes, metal free dyes have high molar extinction coefficients and can be prepared at lower costs and are suitable substitutes for large scale application of DSSCs [4]. The highest overall PCE of DSSCs based on these dyes has been reached above 10% [5]. However, the PCE of the DSSCs sensitized with metal

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* Corresponding author. Tel.: +91 0291 2730045.
E-mail address: sharmagd_in@yahoo.com (G.D. Sharma).

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free sensitizers are lower than the metal based sensitizers due to in part, their relatively narrow absorption spectrum.

The PCE of the DSSC is determined by short circuit current (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) of the device. The J_{sc} value can be enhanced by extending the absorption range of organic sensitizer and harvest the sunlight over a broad spectral range.

Generally, metal free dyes are constituted by donor (D), π-bridge (π) and acceptor (A) moieties, i.e. D–π–A structure. Recently, an auxiliary acceptor group was integrated into a traditional D–π–A structure [6], and achieved bathochromically shift in absorption band of organic sensitizer due to enhanced donor–acceptor interactions, which results in an increased light harvesting efficiency and an increased J_{sc} value. However, the metal free dye based DSSCs are know to generate lower PCEs than those Ru based polypyridyl complexes; this is probably a result of the formation of dye aggregates on the semiconductor surface, leading to the self quenching of excited states and the reduction in the yield of electron injection from the dye into the conduction band of TiO_2 [7]. Since the V_{oc} of DSSC is related with the quasi Fermi position of TiO_2 and charge recombination rate in the device [8], the charge recombination at the TiO_2/dye/electrolyte interface may causes a reduction in V_{oc}. In the DSSCs based on organic dyes, there is a faster interfacial charge recombination between the injected electron and I_3^- ions in the electrolyte or dye cations formed in DSSCs, resulting in a reduced V_{oc}. Therefore, to achieve the improvement in value of V_{oc}, suppression of the electron recombination with either oxidized dye should be minimized. The design of multi-donor [9] or multi-acceptor [10] based dyes have been proven to be effective method for reducing the intermolecular interactions, retarding charge recombination rates, and therefore enhancing the V_{oc} of DSSC. Tian et al., have reported that the aggregation between the dye molecules can also be suppressed incorporating non-planar triarylamines in the donor unit [11].

Pyran (Py) containing dyes have been used for organic light emitting diodes [12] and bulk heterojunction solar cells [13,14]. You et al. have explored the use of these type of dyes as sensitizer for DSSCs [15]. More recently, D–π–A conjugated sensitizers based on 4H-pyran-4-ylinene donor have been used as sensitizer for DSSCs and achieved PCE of 5.4% [16]. Triphenylamine (TPA) and its derivatives are very good electron donors and have shown promising applications in the development of bulk heterojunction solar cells. In this study, we report the use of two dyes **D1** and **D2** which contain TPA and pyran as central unit, respectively. The acceptor and anchoring group cyanoacrylic acid was attached with the central TPA and Py in **D1** and **D2** respectively. Besides, both dye contained terminal cyanovinylene 4-nitrophenyls units, which broaden absorption spectra towards longer wavelength region.

2. Experimental details

Optical absorption spectra of the dyes were recorded at room temperature in quartz cuvettes using Shimaru UV–visible spectrophotometer in THF solution. The cyclic voltammetric (CV) measurements were performed on an CHI 620 electrochemical workstation in THF by using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The CV experiments were performed at room temperature with a three-electrode cell consisting of a platinum wire as auxiliary electrode, a non-aqueous Ag/AgCl reference electrode and a glassy carbon working electrode. The redox potentials were calibrated using ferrocene as internal standard.

For the the optical absorption spectra in dye thin film, the dye molecules were coated on the TiO_2 film (4 μm), and corresponding spectra were recorded with Shimatzu spectrophotometer equipped with an integrating sphere. The baseline was corrected with a bare TiO_2 coated FTO substrate.

The fluorine doped tin oxide (FTO) glass plates were cleaned with a detergent solution using ultrasonic bath for 20 min and then rinsed with de-ionized water and ethanol. The FTO plates were immersed in $TiCl_4$ (30 mM) at 50 °C for 30 min and then washed with distilled water and ethanol. A transparent nano-crystalline layer of the TiO_2 on the FTO glass plates were prepared by doctor blade technique using TiO_2 paste (Dyesol, 18NR-T) and dried at 100 C and subsequently heated at 450 °C for 20 min under ambient condition after that these plates cooled up to room temperature. The TiO_2 electrodes were again treated with $TiCl_4$ at 50 °C for 30 min and sintered at 450 °C for 20 min. After cooling down to room temperature, it was immersed in the dye solution (0.3 mM in THF) and kept at room temperature for overnight (12 h). The electrode was then rinsed with ethanol and dried. The counter electrodes were prepared by coating with a drop of the H_2PtCl_4 solution on pre-cleaned FTO glass plate and then heating at 350 °C for 15 min. The dye adsorbed TiO_2 electrode and Pt-counter electrode were assembled in sandwiched type cell using a spacer (25 μm thick surlyn) and heating at 80 °C. The electrolyte was composed of 0.1 M LiI, 0.6 M 1-propyl-2,3-dimethylimidazolium iodide (DMPII), 0.05 M I_2 and 0.5 M tert-butylpyridine (TBP) in a solvent mixture of acetonitrile(ACN)/3-methoxypropionitrile (MPN) with a volume ratio of 1:1. The electrolyte solution was injected into the gap of electrodes, through a drilled hole in counter electrode of the cell and the hole was sealed with hot melt glue after the injection of electrolyte.

The surface of the DSSC was covered by a mask with light illuminated area of 0.25 cm^2 and then illuminated the device using a solar simulator. The current–voltage characteristics of the DSSCs were obtained with computer controlled Keithley source meter. The incident photon to current efficiency (IPCE) values are obtained, illuminating the device through monochromatic light using a monochromator and stimulated light source and the resultant photocurrent was measured with source meter under short circuit condition. The monochromator was incremented from 350 to 800 nm and the IPCE (λ) was estimated by $\mathrm{IPCE}(\lambda) = 1240(J_{sc}/\lambda P_{in})$, where λ (nm) and P_{in} is the wavelength and illumination intensity of incident monochromatic light and J_{sc} is the short circuit photocurrent.