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Exploring the role of the spacers and acceptors on the triphenylamine-based dyes for dye-sensitized solar cells

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ABSTRACT

Six triphenylamine-based dyes were explored for their application in dye-sensitized solar cells (DSSCs). Dyes 1–3 and dyes 4–6 possess cyanoacrylic acid (C-acceptor) and rhodanine-3-acetic acid (R-acceptor), respectively. Stilbene (in dyes 2 and 5) and bis(styryl)benzene (in dyes 3 and 6) were used as π -spacers. There is no π -spacer in the dye 1 and 4. To elucidate the role of π -spacers, optical, electrochemical, and photovoltaic properties of the dyes were studied. Among C-acceptor dyes, dye 2 exhibits the highest light-to-electricity conversion efficiency of 4.45%, followed by dye 3 (4.16%). Similarly, among R-acceptor dyes, dye 5 is the best. These results indicate that stilbene is a better π -spacer over bis(styryl)benzene. Although bis(styryl)benzene could extend the light absorption range (in dye-adsorbed TiO₂ film), its tendency to promote intermolecular π - π stacking is possibly the reason for its poor performance in DSSCs. Furthermore, the conjugation break in the R-acceptor moiety attached to the TiO₂ surface limits the electron injection of R-acceptor dyes poorer than C-acceptor dyes. Density functional theory calculations were performed for the dye-(TiO₂)₈ cluster, assuming a bidentate chelation of a carboxylic acid group with Ti⁴⁺ of TiO₂ anatase. The natural bond orbital (NBO) analysis indicated relatively more electron-accepting ability of cyanoacrylic acid over rhodanine-3-acetic acid.

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Introduction

For the past two decades, new generation solar cells such as dye-sensitized solar cells (DSSCs), organic solar cells, and perovskite solar cells have attracted much attention because of

their low cost and better photovoltaic properties [1–10]. Among these systems, the DSSC is a promising candidate for conversion of solar energy to electricity. With sustained efforts in this field, commercial DSSC module with 9% efficiency has been realized [11]. The efficiency of DSSCs is influenced by their

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components such as sensitizers, semiconductor photoanode, counter electrode, and electrolyte. Sensitizers are classified into two categories: metal-based and metal-free organic dyes. So far, ruthenium-based complexes and zinc porphyrins have achieved maximum power conversion efficiency (PCE) of 11% and 13%, respectively [12,13]. Owing to the high cost and low availability of Ru-based sensitizers, the current research mostly focuses on metal-free organic materials because of their large molar extinction coefficient, convenient synthetic routes and easy tuning of its structural arrangements [14–18]. Kakiage et al. [19] have shown the combination of ADEKA-1 (carbazole/alkyl-functionalized oligothiophene/alkoxysilyl-anchor moiety) and LEG4 (phenyldibutyl-oxy-substituted triphenylamine (TPA)/alkyl-functionalized cyclopentadithiophene/carboxyl-anchor moiety) dyes to result in a PCE of ~14% through their synergistic sensitization in DSSCs. Hitherto, dyes constituted of TPA- [20–23] and phenothiazine-based donors [24–28], and cyanoacetic acid-based [7,22,29,30] acceptors are commonly used as sensitizers because of their better PCE. In case of TPA-based dyes, the improved PCE is associated with TPA's coplanarity, chemical stability, and rich electron-donating nature [6,31,32]. Electron-rich sulfur and nitrogen heteroatom of phenothiazine suppresses the molecular aggregation [24,33]. Acceptor carboxyl group's ester linkage with Ti in TiO₂ is crucial for the electron injection from the dye's lowest unoccupied molecular orbital (LUMO) to the conduction band (CB) of TiO₂. In addition to the molecular engineering of the donors and acceptors, recent focus is on the development of new types of π -spacers as it is crucial for the electron transfer from the donor to acceptor fragments. π -Spacers are needed to fine-tune the highest occupied molecular orbital (HOMO) and LUMO energy levels of the dye such that the resultant bathochromic shift in its absorption spectrum enhances the DSSC's PCE. A large number of studies are reported on the π -spacers as they control the optoelectronic properties of the sensitizers [34–36]. Tian et al. [37] have explored TPA-based dyes with and without substituted stilbene spacer and found upward revision of PCE from 0.44% to 5% with the spacer. Teng et al. [38] compared the double- and triple-bond π -spacers containing TPA dyes and found that the double bond exhibits better performance in DSSCs due to its less electronegativity than the triple bond.

In this study, two new dyes have been designed with bis(styryl)benzene π -spacer. TPA was chosen as the donor fragment, while the acceptor part is either cyanoacrylic acid

or rhodanine acetic acid. Fig. 1 shows the molecular structures of TPA dyes (1–6) used in this study, wherein dyes 1, 2, 4, and 5 are reference dyes. Dyes 1, 2, 4, and 5 are already reported in the literature [37–41]. The photophysical, electrochemical, photovoltaic, and electrochemical impedance properties of DSSCs using these dyes were systematically investigated. To the best of our knowledge, this is the first report on using bis(styryl)benzene as the π -spacer in the DSSC. The synthetic pathway of these dyes utilizes the Weinreb amide-based building block.

Experimental methods

TPA, chenodeoxycholic acid (CDCA), cyanoacrylic acid, rhodanine-3-acetic acid, 1-butyl-3-methylimidazolium iodide, t-butyl pyridine (TBP), and valeronitrile were purchased from Sigma-Aldrich. Iodine, lithium iodide, and tetrabutyl ammonium perchlorate (TBAP) were purchased from Alfa Aesar. Lithium aluminium hydride (LiAlH₄) and phosphorus oxychloride were obtained from Spectrochem. Sodium hydride and ammonium acetate were purchased from SD Fine Chemicals. Titania (TiO₂) paste (18NR-T), platinum paste (PT1), and fluorine-doped SnO₂ (FTO)-conducting glass (MS001695-10) were purchased from Dyesol Ltd., Australia. All the solvents used were of spectrometric grade and used without further purification. Tetrahydrofuran (THF) was dried by distilling in the presence of Na-Ph₂CO. Thin-layer chromatography (TLC) to check the running reaction was done using precoated silica gel sheets obtained from Merck Germany. Column chromatography was carried out by using 100–200 mesh silica gel as a stationary phase. A combination of ethyl acetate, dichloromethane, and hexane was used as the mobile phase. The melting point of the dyes was measured by packing dye in open capillary on a melting point apparatus and was uncorrected. Dye-mixed KBr pellets were used for fourier-transform infrared (FTIR) measurement using FT/IR-4100 spectrometer. The proton nuclear magnetic resonance (¹H NMR, 400 or 500 MHz) and carbon nuclear magnetic resonance (¹³C NMR, 100 or 125 MHz) spectra were recorded on a Bruker spectrometer in CDCl₃ or deuterated dimethyl sulfoxide (DMSO-*d*₆) solvent with tetramethylsilane as the internal standard. High resolution mass spectrometry (HRMS) was recorded with a micromass-quad time of flight (MICRO-Q TOF) mass

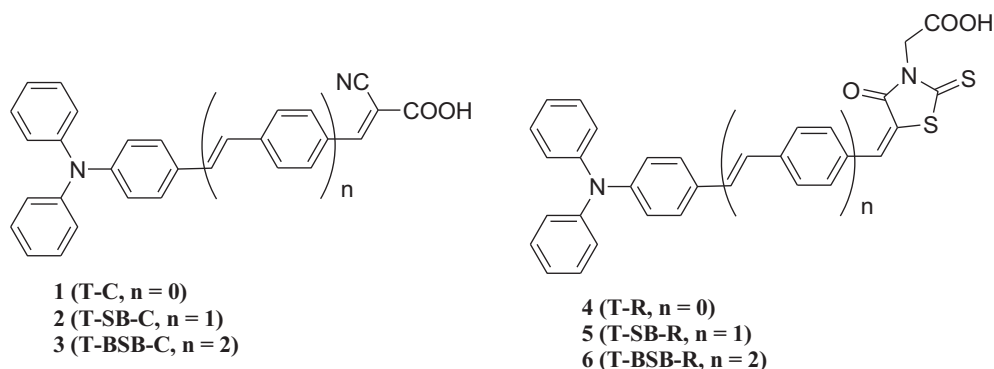


Fig. 1 – Structures of triphenylamine-based dyes 1–6.

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