



Synthesis of cyanovinyl thiophene with different acceptor containing organic dyes towards high efficient dye sensitized solar cells



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ABSTRACT

A series of donor- π -acceptor (D- π -A) metal-free organic dyes employing a diethylamine moiety as donor, phenyl with and without cyanovinyl thiophene unit as a π -spacer and acrylic acid, rhodanine-3-acetic acid, and benzimidazole-5-carboxylic acid as acceptor/anchor, have been designed and synthesized through simple synthetic procedures and investigated as photosensitizers for the dye-sensitized solar cell (DSSC) application. The effects of both the π -spacer and an acceptor modification upon the optoelectronic properties, theoretical and photovoltaic properties of the dyes were studied. In general, DSSCs fabricated with the dyes containing cyanovinyl thiophene unit as a π -spacer shows more than two times higher efficiency than the DSSCs fabricated without cyanovinyl thiophene unit. The maximum power conversion efficiency of 3.01% was achieved for the cyanovinyl thiophene unit in the π -spacer and acrylic acid acceptor dye based DSSC.

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1. Introduction

From the beginning of the last century, our energy demand has grown tremendously as a result of the rapid population growth along with their higher living standards. The most viable way for producing clean energy is through solar cell technology due to its sustainability and abundant supply of solar energy. After seminal report by O'Regan and Gratzel in 1991 [1], Dye-sensitized solar cells (DSSCs) have attracted lots of attention for their use in next-generation solar cell technologies owing to their multiple advantages, such as mechanical flexibility, light weight, high efficiency, and cost-effective fabrication method [2,3]. As a critical component in DSSCs for improving the efficiency, the metal-free organic chromophores have a great deal of interest in the last decades for many researchers due to their simple synthesis procedures and easy purification, high molar extinction coefficients, environmental concerns, and tunable structural modification. The extensively

studied metal free organic dyes usually contain donor (D) and acceptor (A) groups bridged by the π -conjugated unit (D- π -A). This is because of their intramolecular charge transfer processes and easy to design new dye structures for adjusting the energy levels and extend the absorption spectra [4,5]. In the past decades, a large variety of aromatic compounds containing nitrogen atom were studied as a donors, such as coumarin, triarylamine, indoline, carbazole, N,N-dialkylaniline, phenothiazine, etc. Compared to the donors, π -conjugated units and acceptors were studied very limited in the metal free organic dyes. The π -conjugated unit not only extends the absorption wavelength in the visible region, but also affects the rate of internal charge recombination and the electron injection from excited dyes to the semiconductor surface [6,7]. Hence, the π -conjugated unit modification plays a crucial role in the designing of metal free organic dyes for obtaining better DSSC performance. Widely used π -conjugated units are thiophene derivatives because of their intrinsic charge transport behavior, environmental and chemical stability as well as structural versatility [8,9]. However, the introduction of thiophene derivative is very complicated because their synthetic procedure consumes very expensive metal catalysts and the reaction conditions are very rigorously anhydrous and inert [10,11]. To avoid such problems, thiophene-2-acetonitrile was chosen as a starting material and by Knoevenagel Condensation reaction, where the thiophene

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derivative is easily introduced. Further in such processes, it does not need of expensive catalysts and also it follows simple reaction conditions. This synthetic route has another merit, i.e. the cyanovinyl group introduced along with thiophene moiety leads to extended π -conjugation and also reduces the gap between HOMO and LUMO energy levels. In addition, the need of the acceptor modification in this cyanovinyl thiophene based dyes were carried out for getting high solar cell performance. In this regard, acrylic acid, rhodanine-3-acetic acid, and benzimidazole-5-carboxylic acid were chosen.

On the basis of the foregoing points, a series of six metal free organic dyes, based on *N,N*-diethylamine as a donor, phenyl with and without cyanovinyl thiophene as a π -conjugation unit and acrylic acid, rhodanine-3-acetic acid, and benzimidazole-5-carboxylic acid as an acceptor were synthesized (as shown in Scheme 1) which are namely 3-(4-(diethylamino)phenyl)acrylic acid (EC), 3-(5-(1-cyano-2-(4-(diethylamino)phenyl)vinyl)thiophen-2-yl)acrylic acid (ETC), 2-(5-(4-(diethylamino)benzylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (ER), 2-(5-((5-(1-cyano-2-(4-(diethylamino)phenyl)vinyl)thiophen-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (ETR), 2-(4-(diethylamino)phenyl)-benzimidazole-5-carboxylic acid (EB), and 2-(5-(1-cyano-2-(4-(diethylamino)phenyl)vinyl)thiophen-2-yl)-1H-benzimidazole-5-carboxylic acid (ETB). Therefore in this article, the effects of π -conjugated unit and acceptor towards metal free organic dyes on the photophysical, electrochemical, theoretical properties, and DSSC performance of the dyes have been investigated orderly. This result strongly implies that along with π -conjugated unit acceptor modification also plays an important role for constructing the high efficient organic dyes for DSSCs.

2. Experimental section

2.1. Materials and method

Thiophene-2-acetonitrile (Sigma-Aldrich), 4-diethylaminobenzaldehyde (Alfa Aesar), 3,4-diaminobenzoic acid (Alfa Aesar), Rhodanine-3-acetic acid (Sigma-Aldrich), Malonic acid (Alfa Aesar), Copper (II) acetate ($\text{Cu}(\text{OAc})_2$) (Sigma-Aldrich), and Tetrabutylammonium perchlorate (TBAP) (Sigma-Aldrich) were purchased and used without further purification. Phosphorus oxychloride (POCl_3), *N,N*-dimethylformamide (DMF), Ammonium acetate, glacial acetic acid, piperidine and nitrobenzene were

purchased from Merck. ^1H and ^{13}C NMR analysis were measured on Bruker 500 MHz NMR Spectrometer in deuterated chloroform or dimethylsulfoxide solution at 298 K. Chemical shifts (δ values) were recorded in units of ppm relative to tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra were obtained by ESI using Orbitrap mass spectrometer. The FT-IR spectra were obtained with a Thermo Scientific Nicolet iS5 FT-IR spectrometer. All reactions were monitored by using TLC plates. All chromatographic separations were carried out on silica gel (60–130 mesh).

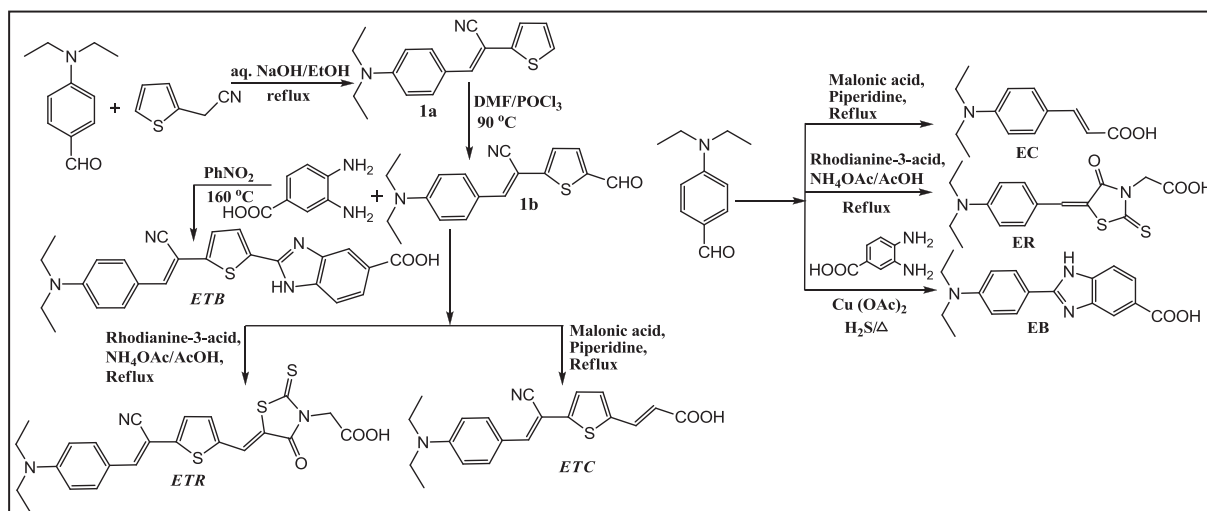
2.2. Photophysical and electrochemical measurements

Absorption and fluorescence spectra were measured in DMF solution on a T90+ UV-vis spectrometer 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 used as the quasi-reference electrode. The potentials were reported vs. ferrocene as standard using a scan rate of 0.1 V^{-1} . The CV experiments were performed with $3 \times 10^{-4} \text{ M}$ dye solution 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^2 light illumination with a frequency ranging between 10 kHz and 0.1 Hz at their open circuit potential (OCP) by using an Autolab PGSTAT potentiostat/galvanostat-84610.

2.3. Synthesis

2.3.1. 3-(4-(diethylamino)phenyl)-2-(thiophen-2-yl)acrylonitrile (1a)

4-diethylaminobenzaldehyde (2 g, 11.3 mmol) and thiophene-2-acetonitrile (1.44 mL, 13.6 mmol) were taken in a two neck round bottom flask containing 30 mL freshly distilled ethanol. 6 M NaOH (0.1 mL) was added to this reaction mixture at room temperature after that the resulting mixture was refluxed for 2 h. After cooling to room temperature, the mixture was poured into water and extracted with chloroform. The collected organic extracts were dried by Na_2SO_4 . The solvent was removed under vacuum and the residue was further purified by column chromatography on silica



Scheme 1. Molecular structures and synthetic procedure of the EC, ER, EB, ETC, ETR, and ETB Dyes.

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