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New D-π-A type indole based chromogens for DSSC: Design, synthesis and performance studies

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ABSTRACT

Three new Donor-π-Acceptor type dyes **D$_{1-3}$** carrying 3-(1-hexyl-1*H*-indol-3-yl)-2-(thiophen-2-yl) acrylonitrile as backbone with three different acceptor units were designed and synthesized as promising sensitizers for solar cell application. The new dyes were characterized using various spectral and elemental analyses. Their optical and electrochemical properties were investigated using spectrophotometry and cyclic voltammetry respectively, while their photovoltaic performance was evaluated by a device fabrication study. The devices were subjected to electrochemical impedance spectroscopy to gain an insight into the interfacial charge transfer and recombination process while in use. Further, density functional theory study was carried out to investigate their Frontier Molecular Orbital energy states. The study reveals that the dye carrying 4-aminobenzoic acid as an acceptor showed the highest photovoltaic efficiency among the three dyes. This can be attributed to the longer electron lifetime and lower recombination rates. Additionally, a Single crystal X-ray diffraction study confirmed the structure of a key intermediate.

1. Introduction

During the past two decades dye sensitized solar cells (DSSCs) have attracted tremendous attention of many researchers owing to their low-costs, light weight, moderate efficiency, flexibility and easy fabrication. Since O'Regan and Grätzel reported the fabrication of DSSC in 1991 [1], this fascinating field has emerged as a viable alternative to the conventional silicon based solar cells, for harvesting the abundant solar energy to provide electricity. In fact, ever increasing energy demand, continuous depletion of non-renewable resources and drastic climate changes across the globe have forced the scientists to take up intensive research on various types of solar cells for harvesting light energy directly from the sun.

Typically, DSSC's contain five components, viz. a mesoporous semiconductor, metal oxide film, a dye, an electrolyte/hole transporter and a counter electrode; out of them the dye is a crucial element, exerting significant influence on the conversion efficiency as well as the stability of the cells. The dyes are usually classified into two broad categories, viz. ruthenium based complexes [2] and metal-free organic dyes [3]. Even though the former class of compounds offer higher efficiency than the latter, they are plagued by numerous problems such as high costs, tedious purification steps and environmental issues. The latter type is an attractive alternative because of their facile synthesis, high molecular extinction coefficient, relative environmental friendliness, and tunable electrochemical and absorption properties [4]. For these reasons a lot of effort has been dedicated to the design and development of new metal free organic dyes as potential sensitizers, among which D-π-A (electron donor-π conjugation bridge-electron acceptor) type organic chromogens are gaining much importance nowadays. Interestingly, in a D-π-A configuration, an efficient electron transfer can happen from the donor to the acceptor through the π-conjugation bridge upon photo-excitation of the dye molecule. Then, the negative charge accumulated on the acceptor can be injected into the conduction band of the metal oxide used in a DSSC.

Among various D-π-A sensitizers reported in the literature, dyes based on carbazole [5–8], coumarin [9,10], fluorine [11–13], triphenylamine [14–16], phenothiazine [17–20] and indoline [21–24] have been shown to be the most promising candidates with respectable conversion efficiencies, mainly because of their favorable electronic structures to act as good electron donor moieties.

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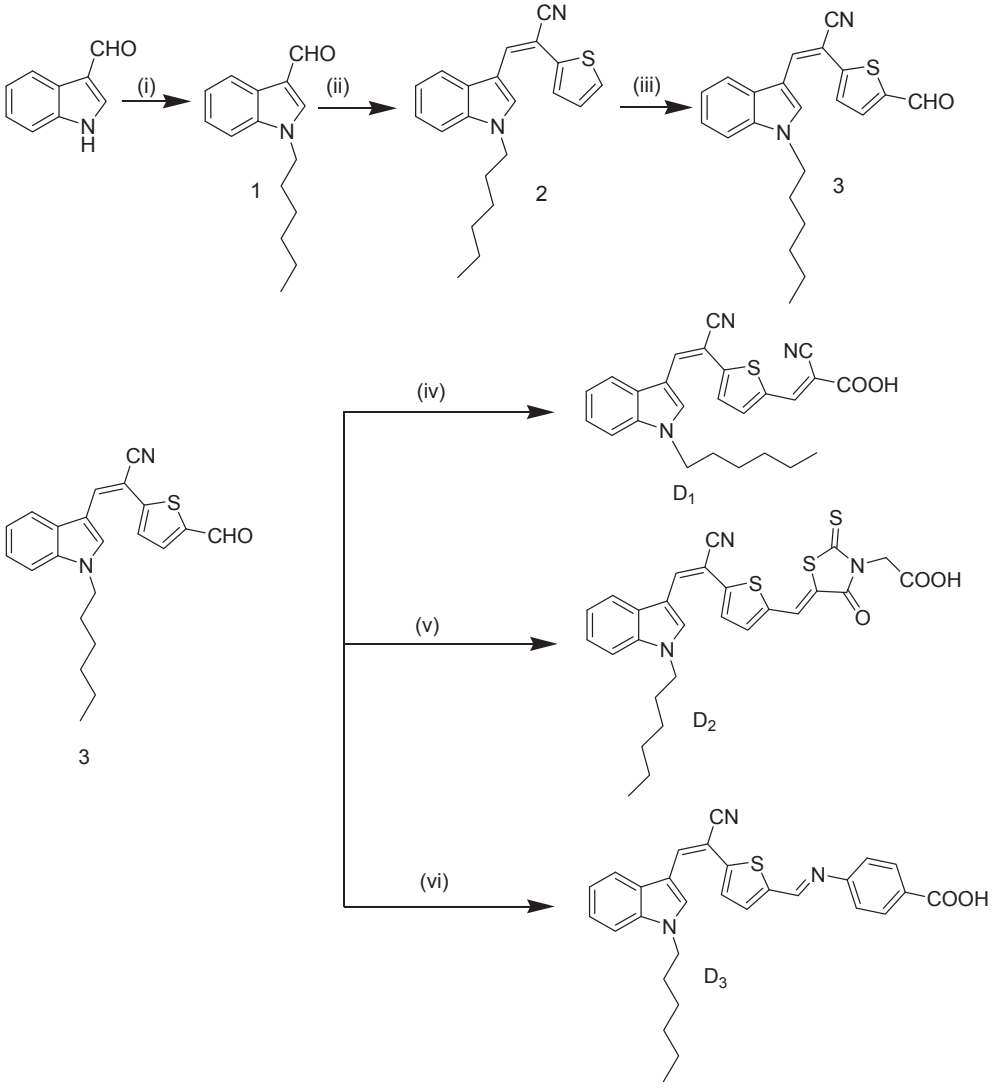
Besides, indole based dyes have displayed efficiency as high as 9.5% [25], primarily due to the excellent electron donating ability of indole ring and its exceptional light capturing capability. Apart from the electron donor moiety, the acceptor segment is also recognized for its significance in performance control of DSSC. In this context, certain functionalized acids such as cyanoacetic acid, rhodanine-3-acetic acid and 4-aminobenzoic acid have been adopted as efficient electron acceptors in most cases, mainly due to their strong electron-withdrawing properties and anchoring capabilities on the TiO_2 surface through an ester linkage. On the other hand, thiophene is found to exhibit excellent charge transporting capability [4]. In addition, thiophene derivatives have been widely used as building blocks for sensitizers because of their well-known polarizabilty, as well as tunable spectroscopic and electrochemical properties. Their presence in between the donor and acceptor groups not only enhances the π-conjugation but also increases the overall stability of the resulting molecules. Whereas, introduction of cyanovinylene unit into chromophores is a good approach to expand π-conjugation (reduce band gap) and thereby shift the absorption maxima to higher wavelengths with enhanced molar extinction coefficients [26]. Keeping these facts in view, we have focused our attention to synthesize and study three new dyes (**$D_{1–3}$**) with a general D-π-A configuration, wherein the indole ring acts as an electron donor, thiophene and cyanovinylene linkers function as the π-conjugation bridge, while cyanoacetic acid, rhodanine-3-acetic acid and 4-aminobenzoic acid behave as different electron acceptors. All the important prerequisites have been taken into account while designing the new sensitizers. Hence, it is expected that the new chromophores would show better performance as they possess required critical features.

Accordingly, we have synthesized three new sensitizers by following the simple synthetic protocols as shown in Scheme 1. The newly synthesized compounds were well-characterized by FTIR, ^{1}H NMR, ^{13}C NMR, mass spectral and elemental analyses. The electronic and structural properties of the new dyes were investigated by UV–Vis and fluorescence spectroscopy while the HOMO and LUMO energy levels and hence band-gap were calculated by cyclic voltammetry and DFT studies. Further, these dyes were used to fabricate DSSC and their photovoltaic performance was investigated. Also, EIS studies were performed to investigate the interfacial charge transfer and recombination process within DSSC. The effect of their structure on the optical, electrochemical,



Scheme 1. Synthetic route of the sensitizers. (i) 1-Bromohexane, K_2CO_3, DMF, RT (ii) 2-(thiophen-2-yl)-acetonitrile, NaOMe, CH_3OH, RT. (iii) $POCl_3$, DMF, RT. (iv) Cyanoacetic acid, ammonium acetate, glacial CH_3COOH, 110 °C. (v) Rhodanine-3-acetic acid, ammonium acetate, glacial CH_3COOH, 110 °C. (vi) 4-Amino benzoic acid, CH_3OH, 80 °C.