



Synthesis and Investigation of Photovoltaic Properties of New Organic Dye in Solar Cells Device

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ABSTRACT

In this paper, we designed and synthesized free-metal dyes based on indoline. The proposed dyes were synthesized from phenothiazine as the starting material by standard reactions. The chemical structure of the synthesized dye was confirmed using FT-IR, ¹HNMR and DSC techniques. Spectrophotometric measurements of the organic dyes in acetonitrile and on a TiO₂ substrate were carried out in order to assess the changes in the dye. Maximum absorption wavelength for organic dye in solution is 453 nm and on TiO₂ film is 467 nm. Finally, the proposed dyes were used as sensitizer in a dye solar cell structure and their photovoltaic properties were investigated. The Conversion efficiency for the synthesized dye is 0.92%. Prog. Color Colorants Coat. 12 (2019), 33-38 © Institute for Color Science and Technology.

1. Introduction

Third generation of solar cell devices have attracted attention due to low cost, ease of assembling and flexibility of renewable energy preparation [1]. In order to increase the power conversion efficiency, many efforts such as synthesis of new materials and structure optimization have been devoted for hampering the further commercialization [2, 3]. The record power conversion efficiency of dye-sensitized solar cells (DSSCs) has been ascribed to the zinc-porphyrin complexes with cobalt electrolyte, for which the photon conversion efficiencies over 13% have been achieved [4]. However, concerning the cost and the purification difficulty for the organometallic dyes, metal-free organic dyes have gained more and more attention due to their advantages of high molar extinction coefficients, relatively low cost, ease of structure tuning and environmental friendliness [5, 6].

Liu et al. reported preparation of four artificial chlorine-type sensitizers. Chlorine has high absorption

properties in the Q band regions which help to improve the overall photovoltaic performance of DSSCs. The photon energy conversion capability of the DSSC is closely related to the geometry of the sensitizers used. The orientation of a satirically demanding 2,6-dichlorophenyl group towards either the 5- or 15-position (the anchor group is at the 20-position) gives better photon energy to electricity conversion efficiency [7]. Wang et al. synthesized two new D-A- π -A indoline dyes with different additional donors to investigate the influence of donor and bridge structure in indoline dyes on the photovoltaic properties of dye-sensitized solar cells employing iodine/cobalt electrolyte [8]. Wu et al. proposed development of two novel organic dyes containing julolidine as the electron donor and cyanoacetic acid or rhodanine-3-acetic acid as the electron acceptor bridged by bithiophene unit. The results demonstrated that sensitizers were quickly regenerated and the dye cations are efficiently captured by the redox mediator. The recombination rate ceased

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notably due to replacing of cyanoacetic acid to rhodanine-3-acetic acid [9]. Zhu et al. reported two new sensitizers based on triphenylamine-dicyanovinylene and used them for p-type dye-sensitized solar cells. This study suggested that amendment of the bridging moiety among triphenylamine and the carboxylic group by cumulative thiophene units is a promising way for averting charge recombination and hence boosting the power conversion efficiency [10]. Four new organic dyes were synthesized by Reddy et al. The dyes had electron rich thiophene spin off sasantennas and cyanoacrylic acid as acceptor, bridged by phenothiazine or phenoxazine. The light harvesting ability of the dyes could be improved by the alkyl-substituted thiophene units [11].

This paper describes the use of novel organic dyes based on indoline in individual and the spectrophotometric properties of the organic dyes in solution and on a nanoanatase TiO₂ substrate as well as electrochemical measurements were examined. The cyclic voltammetry (CV) data were used to determine the highest occupied molecular orbital, lowest unoccupied molecular orbital and the band gaps of the organic dyes. Finally, DSSCs were fabricated with organic dyes as photosensitizer in order to determine the photovoltaic behavior and conversion efficiencies of each condition in co-sensitization DSSCs. The structure of the dye molecule is given in Figure 1.

2. Experimental

2.1. Materials and instrumentation

All compounds used in this study were of analytical grade unless otherwise stated. The synthesis route and detailed characterization of intermediates and organic dyes have been described previously [12]. UV-visible spectrophotometry was carried out on a Cecil 9200

double beam transmission spectrophotometer to obtain molar extinction coefficients and absorption maxima.

2.2. Synthesis of organic dye

Acetonitrile (20 mL) was separately added to 17.6 mmol starting material containing 42 mmol of cyanoacrylic acid and 8 drops of piperidine. The mixture was stirred for 2 h at 90°C. After the reaction was completed, the resultant precipitate was filtered and purified through silica gel column chromatography (ethyl acetate:hexane=1:2). Yield: 85%; mp 249.3 °C; FTIR (KBr) (Cm⁻¹): 1648 C=O str., 1452, 1600: C=C str., 1482: C-N str.; ¹H-NMR (CDCl₃), δ (ppm): 2.28 (6H, CH₃), 3.88 (3H, OCH₃), 6.82-6.79 (d, 4H), 7.21-7.25 (dd, 2H), 7.84-7.80 (d, 4H), 7.89 (s, 2H), 8.00-8.06 (d, 4H), 8.66-8.70 (d, 4H), 9.71 (s, 1H, COOH); ¹³CNMR (CDCl₃, δ/ppm): 50.78, 55.34, 59.41, 109.13, 115.77, 116.11, 117.22, 120.07, 120.91, 121.42, 122.45, 123.31, 124.16, 125.71, 126.74, 127.15, 128.61, 129.41, 129.85, 130.24, 131.12, 133.28, 135.31, 137.11, 139.12, 141.17, 142.37, 165.44;

2.3. Electrochemical measurements

Electrochemical measurements of the synthesized dyes were carried out in acetonitrile solution. The oxidation potential (E_{ox}) was measured using three small-sized electrodes. Ag quasi reference electrode (QRE) was used as the reference. Platinum wires were used as working and counter electrodes. All electrode potentials were calibrated with respect to ferrocene(Fc)/ferrocenium (Fc⁺) redox couplet. An acetonitrile solution of each dye containing tetrabutylammonium perchlorate (0.1 mol dm⁻³) and ferrocene (ca. 1 mmol dm⁻³) was prepared. The electrochemical measurements were performed at a scan rate of 100 mV s⁻¹ [13].

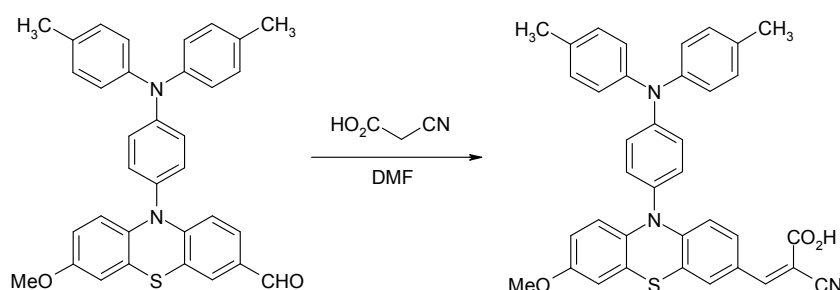


Figure 1: Chemical structure of the organic dye.

2.4. Dye-sensitized solar cells (DSSCs) assembly and photovoltaic characteristics

A nanocrystalline TiO₂ film was coated on a transparent glass support. The dye was adsorbed by dipping the coated glass in a 5×10⁻⁵ M ethanolic solution of the dye containing 7% 4-tert-butylpyridine and 50 mM 3 α ,7 α -dihydroxy-5 β -cholic acid (cheno) for 18 hr. The visible bands in the absorption spectrum of the dyes after adsorption on the nano-TiO₂ film only appeared after the TiO₂ electrodes were dipped in the dye solution for at least 18 hr. The presence of 4-tert-butylpyridine and cheno is necessary to avoid surface aggregation of the sensitizer. Finally, the film was washed with an acetonitrile-ethanol 1:1 mixed solution. Acetonitrile-ethylene carbonate (v/v=1:4) containing tetrabutyl ammonium iodide (0.5 mol dm⁻³) was used as the electrolyte. The dye-adsorbed TiO₂ electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [14-16].

An action spectrum was measured under monochromatic light with a constant photon number (5×10¹⁵ photon cm⁻² s⁻¹). J-V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm⁻²) through a shading mast (5.0 mm×4 mm) by using a Bunko-Keiki CEP-2000 system.

3. Results and Discussion

The organic dye was synthesized as schematically shown in Figure 1. Starting material 1 was prepared in a similar way as described in the literature [12]. This compound was allowed to react with dimethyl methyl cyanoacetate by the Knoevenagel reaction in the presence of piperidine to give organic dye. The chemical structures of all novel synthesized dyes were confirmed using DSC, FT-IR and ¹HNMR spectroscopy.

The wavelength of maximum absorption (λ_{max}) and the molar extinction coefficients (ϵ_{max}) for the synthesized dye in acetonitrile are listed in Table 1, together with the λ_{max} of the corresponding dyes adsorbed on the TiO₂ film. The absorption peaks at organic can be assigned to an intra-molecular charge transfer between the donor and acceptor groups [17],

providing an efficient charge-separation for the excited state. For the synthesized dye, when an extra electron acceptor was linked to the vinyl bridge, the λ_{max} had a bathochromic shift. The shift in maximum absorption peak arises from the fact that more stronger electron acceptor of two acceptor groups intensifies the overall electron withdrawing ability of the system and hence lowering the level of the lower unoccupied molecular orbital (LUMO), thus reducing the gap between the higher unoccupied molecular orbital (HOMO) and the LUMO states [18]. Upon dye adsorption on to a photo-anode surface (TiO₂), the wavelength of maximum absorption is bathochromically shifted as compared to the corresponding spectra in solution, implying that dyes adsorbed on to the TiO₂ surface contain partial J-type aggregates [19, 20]. The molar extinction coefficients of Dye 1 and Dye 2 in DMF at their respective λ_{max} are also shown in Table 1, indicating that these novel dyes have good light harvesting abilities.

The fluorescent characteristics of the dye measured in acetonitrile are presented in Table 1. In acetonitrile solution, dyes show intense fluorescence due to the charge transfer from the electron donating group to the accepting group. The maximum fluorescence emission of the synthesized dye in acetonitrile is 532.5.

The oxidation potential (E_{ox}) of organic dye was measured in acetonitrile by cyclic voltammetry. There are two distinct redox waves observed in the voltammogram. The first oxidative wave (I) was due to the oxidation of the internal standard of ferrocene, whereas the second wave (II) near was due to the electrochemical oxidation of the dye. The oxidation peak potential (E_{pa}) for the synthesized dye can therefore be calculated to be +1.19 V vs Fc/Fc⁺ in acetonitrile. Although the standard E_{ox} value is usually not easily obtained experimentally, it can be approximately estimated from the cyclic voltammetric peak potential method, which are the same if the electrochemical oxidation is a reversible step [21-23]. The $E_{\text{ox}}-E_{0-0}$ level of organic dye is calculated to be -0.75 V vs Fc/Fc⁺ in acetonitrile.

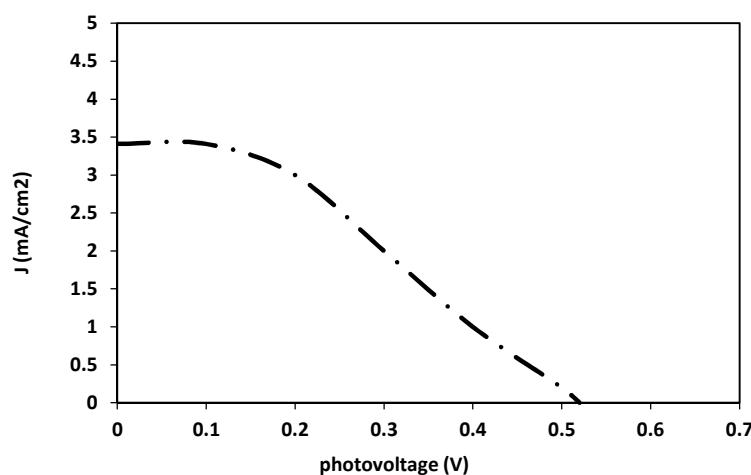
Table 1: Absorption properties of the synthesized dye.

λ_{max} (nm) ^a	ϵ (M ⁻¹ cm ⁻¹)	λ_{max} (nm) ^b	λ_{F} (nm) ^a
453	15892	467	532.5

a) Acetonitrile b) on photo-anode (TiO₂) substrate

Table 2: Photovoltaic performance of DSSCs based on the synthesized dye.

V_{oc} (V)	J_{sc} (mA.cm ⁻²)	FF	η (%)
0.52	3.41	0.52	0.92

**Figure 2:** Current density-voltage characteristics for the synthesized dye.

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of organic dye molecules and its structure. The DSSCs utilized this dye as sensitizer for nanocrystalline anatase TiO₂. A typical photocurrent–photovoltage (J – V) curve for cell based on the organic dye is depicted in Figure 2. The detailed photovoltaic parameters are also summarized in Table 2. The solar energy to electricity conversion efficiency (η) of the DSSCs is calculated from short circuit current (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{in}) [24, 25].

According to the results shown in Table 2, the conversion efficiencies of solar cells containing organic under standard global AM 1.5 solar conditions is 0.92%. The conversion efficiency of synthesizer is probably due to the stronger electron withdrawal ability of the combination of cyanine acceptor groups. The conversion efficiency of solar energy to electricity of the present organic dyes can be improved either by extending the conjugated length of the organic dyes or

incorporation of a thiophene π -bridge [26–28].

4. Conclusions

A new metal-free organic dye (D- π -A) to be used as sensitizers in DSSCs were designed and synthesized based on indoline by employing cyanoacrylic acid as acceptor units. The spectrophotometric properties of the prepared organic dyes in solvent and on TiO₂ films were examined. The absorption maxima of the synthesized dyes applied on the surface of a TiO₂ film gave a bathochromic effect compared to the corresponding dye spectra in solution. Finally, the prepared dye was utilized in constructed DSSCs and their photovoltaic behaviors were assessed. A solar energy to electricity conversion efficiency of 0.92% was achieved for the synthesized dye. Detailed experiments and investigation of the interfacial charge transfer processes of these dyes are currently in progress aiming to further increase the overall performance of DSSCs fabricated with this new dyes.

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