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Investigation of Photovoltaic Properties of 1,8-Naphthalimide Dyes in Dye-sensitized Solar Cells

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ABSTRACT

In this paper we selected two metal-free dyes (Dye 1 and Dye 2) based on 1,8-naphthalimide. The proposed dyes were sensitized from acenaphthene as the starting material by standard reactions. Spectrophotometric measurements of the organic dyes in DMF and on TiO_2 substrate were carried out in order to assess changes in the status of the dyes. Maximum absorption wavelengths for Dye 1 and Dye 2 in solution are 427 nm and 434 nm and on TiO_2 films are 451 nm and 455 nm, respectively. Finally, the proposed dyes were used as sensitizer in a home-made dye solar cell structure and their photovoltaic properties were investigated. The conversion efficiency for Dye 1 and Dye 2 are 1.19 % and 1.34 %, respectively. Prog. Color Colorants Coat. 11 (2018), 253-258© Institute for Color Science and Technology.

1. Introduction

Demand for sustainable energy is constantly increasing. This is due to an imbalance between supply and demand, the increased population and the enhanced prices of fossil fuels. This has resulted in looking for alternative renewable energy, the focus of which is on dye sensitized solar cells (DSSCs or Gratzel cells) [1]. Inorganic dye molecules are commonly utilized in DSSCs but metal free organic dyes that are environment-friendly and easily synthesized have been utilized in DSSCs in 1993 [2, 3]. Several types of dyes such as coumarin dyes, polyene dyes, hemicyanine dyes, thiophene based dyes and indoline dyes have been prepared for a DSSCs application [4, 5]. In search for high efficiency organic dyes for solar cells, development of new materials offering optimized thermal and photochemical stabilities, as well as appropriate optical and electrical properties is of utmost importance [6].

Wang et al. synthesized two new D-A-π-A indoline dyes (XS45 and XS46) 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 [7]. Mao et al. derived three organic dyes from C219 with different electron donors to further improve the V_{OC} of the cell. The introduction of double D-A branches and the addition of thiophene as p-conjugated bridge increased the conversion efficiency of the DSSC. The J_{sc} increased due to the proposed modifications [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

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bridged by bithiophene unit, and named them as J5 and J6. The results demonstrated that the sensitizers were quickly regenerated and the dye cations are efficiently captured by the redox mediator. The recombination rate increased notably due to replacing of cyanoacetic acid to rhodanine-3-aceticacid [9]. Gharanjig et al. synthesized a series of novel metal-free organic dyes utilizing N-substituents carbazole as the fundamental electron donor group and cyanoacrylic acid or acrylic acid as electron acceptor anchoring groups. The results show that the dyes form j-type aggregates on the nano-TiO_2. The oxidation potential of the synthesized carbazole dyes is -0.2 V vs Fc/Fc^+; hence, their high performance in dye-sensitized solar cells [10]. Zhu et al. reported two new sensitizers based on triphenylamine dicyanovinylene for p-type dye-sensitized solar cells. This study suggested that modification of the bridging moiety among triphenylamine and the carboxylic group by cumulative thiophene units is a promising way to prevent charge recombination, enhancing the power conversion efficiency [11]. Hosseinnezhad et al. prepared a series of new organic dyes using double rhodanine as the fundamental electron-acceptor group and aldehydes with varying substituents as the electron-donor groups. These dyes were first purified and then characterized by analytical techniques. DSSCs were fabricated to determine the photovoltaic behavior and conversion efficiency of each individual dye [12].

In this study, organic dyes based on 1,8-naphthalimide synthesized previously were used [13]. This paper describes the use of novel organic dyes based on 1,8-naphthalimide in individual DSSCs for the first time. Co-sensitization is a novel approach to improve the performance of DSSCs. The spectrophotometric and electrochemical measurements of the organic dyes in solution and on anatase nano-TiO_2 substrate were carried out. The cyclic voltammetry (CV) data were used to determine the highest occupied molecular orbital, lowest unoccupied molecular orbital levels and band gaps of these organic dyes. Finally, DSSCs were fabricated with two different organic dyes as photosensitizer in order to determine the photovoltaic behavior and conversion efficiencies of each condition in co-sensitization DSSCs. The structure of dye molecules and the anti-aggregation agents are 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 characterization of intermediates and organic dyes are described elsewhere [13]. UV-visible spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer to obtain molar extinction coefficients and absorption maxima.

2.2. Electrochemical measurements

Electrochemical measurements of the synthesized dyes were carried out in acetonitrile. 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 the working and the counter electrodes. All electrode potentials were calibrated with respect to ferrocene (Fc)/ ferrocenium (Fc^+) redox couplet. An acetonitrile solution of each dye containing tetrabutyl ammonium 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}[14].

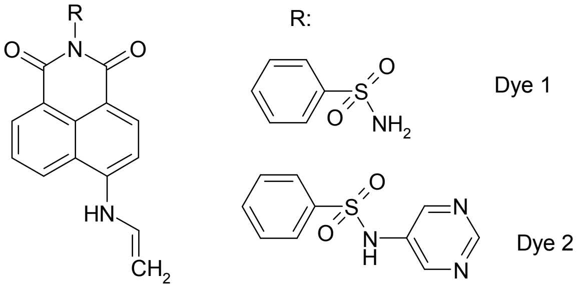

Figure 1: Chemical structure of organic dyes.

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

A nanocrystalline TiO_2 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 3α,7α-dihydroxy-5β-cholic acid (cheno) for 18 hr. The visible bands in the absorption spectrum of the dyes after adsorption on nano-TiO_2 film only appeared after dipping the TiO_2 electrodes 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. Acenonitrile-ethylene carbonate (v/v=1:4) containing tetrabutyl ammonium iodide (0.5 mol dm^{-3}) was used as the electrolyte. The dye-adsorbed TiO_2 electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [15-17].

An action spectrum was measured under monochromatic light with a constant photon number (5×10^{15} 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 mask (5.0 mm×4 mm) by using a Bunko-Keiki CEP-2000 system.

3. Results and Discussion

The starting material for the preparation of naphthalimide derivatives was 4-nitro-1,8-naphthalic anhydride. The synthesized dyes were prepared by imidation, reduction and allylation reactions from 4-nitro-1,8-naphthalic anhydride. The imidation of aromatic cyclic anhydrides involves nucleophilic substitution, in which the reaction of attacking amine is carried out in an acetic acid under a reflux condition. For preparing 4-nitro-N-substituted-1,8-naphthalimide, 4-nitro-1,8-naphthalic anhydride was reacted with the corresponding amine and the completion of reaction was tested by TLC. Preparation of 4-amino(allylamino)-N-substituted-1,8-naphthalimide as an intermediate plays a very significant role in the naphthalimide dyestuff and colored polymer series. Reduction of 4-nitro-N-substituted-1,8-naphthalimides with tin(II) chloride and hydrochloric acid in ethanol as the solvent gave 4-amino-N-substituted-1,8-naphthalimides. 4-Allylamino-N-substituted-1,8-naphthalimides were synthesized by the reaction of 4-nitro-N-substituted-1,8-naphthalimides with allylamine in DMF as the solvent [13, 18].

The wavelength of maximum absorption (λ_{max}) and the molar extinction coefficients (ε_{max}) for the synthesized dyes in DMF are listed in Table 1, together with the λ_{max} of the corresponding dyes adsorbed on the TiO_2 film. The absorption peaks at organic can be assigned to an intra-molecular charge transfer between the donor group and the acceptor group [19], providing an efficient charge-separation for the excited state. For the Dye 2, when an extra electron acceptor was linked to the vinyl bridge, the λ_{max} had a bathochromic shift from 427 nm for Dye 1 to 434 nm for Dye 2. This shift of the maximum absorption peak arises from the fact that the stronger electron acceptor of the 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 [20]. Upon dye adsorption on the photo-anode surface (TiO_2), the wavelength of maximum absorption is bathochromically shifted by 24 and 21 for Dye 1 and Dye 2, respectively, as compared to the corresponding spectra in solution, implying that dyes adsorbed on the TiO_2 surface contain partial J-type aggregates [21, 22]. 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.

Table 1: Absorption properties of the synthesized dyes.

Dye	λ_{max} (nm)^a	ε ($M^{-1}cm^{-1}$)	λ_{max} (nm)^b	λ_F (nm)^a
1	427	16857	451	527.5
2	434	10000	455	527

a) DMF b) on photoanode (TiO_2) substrate

The fluorescent characteristics of dyes measured in DMF are represented in Table 1. In DMF solution, dyes show intense green fluorescence due to the charge transfer from electron donating group to the accepting group. The fluorescence emission maxima of the synthesized Dye 1 and Dye 2 in DMF are 527.5 and 527, respectively.

The oxidation potential (E_{ox}) of Dye 1 and Dye 2 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 Dyes. The oxidation peak potential (E_{pa}) vs Fc/Fc^+ in acetonitrile for Dye 1 and Dye 2 can therefore be calculated to be +1.17 V and +1.11 V, respectively. 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 equals it if the electrochemical oxidation is a reversible step [23, 24]. The E_{ox}-$E_{0\text{-}0}$ level of Dye 1and Dye 2 is calculated to be –0.73 V and –0.76 V vs Fc/Fc^+ in acetonitrile.

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behavior of Dye 1 and Dye 2 molecules and their structures as sensitizers for nanocrystalline anatase TiO_2. A typical photocurrent–photovoltage (J–V) curve for cells based on Dye 1 and Dye 2 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}) [25].

According to the results shown in Table 2, under the standard global AM 1.5 solar condition, the conversion efficiencies of cells containing Dye 1and Dye 2 are 1.19 % and 1.34%, respectively. Higher conversion efficiency of Dye 2 sensitizer is probably due to the stronger electron withdrawal ability from the combination of the two acceptor groups. The conversion efficiency of solar energy to electricity of the present organic dyes could be improved by extending the conjugated length of the organic dyes or by incorporation of a thiophene π-bridge [26, 27].

Table 2: Photovoltaic performance of DSSCs based on Dye 1 and Dye 2.

Dye	V_{OC} (V)	J_{SC} ($mA.cm^{-2}$)	FF	η (%)
1	0.58	3.59	0.57	1.19
2	0.56	4.19	0.57	1.34

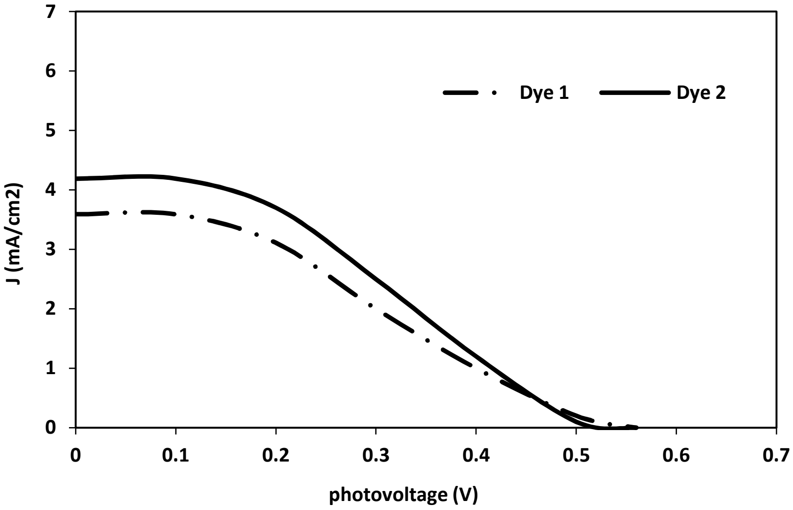

Figure 2: Current density-voltage characteristics for Dye 1 and Dye 2.

4. Conclusions

Two metal-free organic dyes (D-π-A) as sensitizers in DSSCs were designed and synthesized based on 1,8-naphthalimide by employing two different acceptor units. The spectrophotometric properties of the prepared organic dyes in solvent and on TiO_2 films were examined. According to the results, Dye 2 containing two acceptor groups showed bathochromic shifts compared to Dye 1. In all cases, the absorption maxima of Dye 1 and Dye 2 applied on TiO_2 film gave a bathochromic effect compared to the corresponding dye spectra in solution. Finally, the prepared dyes were utilized in home-made DSSCs and their photovoltaic behaviors were assessed. A solar energy to electricity conversion efficiency of 1.19 and 1.34 percent were achieved for Dye 1and Dye 2, respectively. Dye 2 containing stronger acceptor group gave higher conversion efficiency than Dye 1. Detailed experiments and investigations on interfacial charge transfer processes in these dyes are currently in progress aiming to further increase the overall performances of DSSCs fabricated with this new group of dyes.

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