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The effect of five-membered heterocyclic bridges and ethoxyphenyl substitution on the performance of phenoxazine-based dye-sensitized solar cells

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Phenoxazine derivatives with heterocyclic bridge units and an additional donor were synthesized and applied to dye-sensitized solar cells. To study the effects of these substituents on the DSSC performance, the photophysical, electrochemical, and photovoltaic properties of the dyes were investigated. The introduced heterocyclic bridge units furan and thiophene improved the short-circuit current due to the red-shifted absorption spectra of the dyes. The ethoxyphenyl ring introduced to the phenoxazine moiety as an additional donor broadened the spectrum of the dye, while the reduced adsorption of the dye caused by its non-planar structure limited the enhancement of the short-circuit current. Among the synthesized dyes, the one with furan as a bridge unit showed the best overall conversion efficiency of 5.26%.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention as promising solar devices since Grätzel et al. reported Ru-based photosensitizers in 1991 [1]. The Ru complex dyes typical used as sensitizers in DSSCs have shown high electronic conversion efficiencies of over 11% with good stability [2]. However, high production cost and difficulties in purification have limited their development for large-scale applications. Recently, more attention has been paid to sensitizers without Ru (metal-free organic dyes and organometallic dyes) due to their lower cost, easier modification and purification, high molar extinction coefficient, and environmental friendliness. As such, sensitizers without Ru such as triphenylamine [3], indoline [4], cyanine [5], coumarin [6], perylene [7], porphyrin [8], phthalocyanine [9], and phenothiazine [10] have been extensively studied. Among these, porphyrin derivatives have shown high electronic conversion efficiency (12.3%) [7].

For efficient DSSCs, organic dyes should have broad and red-shifted absorptions in the visible region. Accordingly, most organic dyes have the structure of donor–conjugated bridges–acceptor (D–π–A) to obtain a broad and red-shifted absorption spectrum. Among the various conjugated bridges, furan and thiophene have displayed the most remarkable results, showing wide and red-shifted absorption spectra, as well as high molar extinction coefficients [11]. In addition, to achieve enhanced photovoltaic performance, organic dyes with an additional donor (D–D–A or D–D–π–A) have been suggested [12]. The introduction of an additional donor group could increase the electron-donating capability, which would improve electron injection and charge separation. Phenoxazine (POZ) includes electron-rich oxygen and nitrogen atoms in a heterocyclic ring, which displays high electron-donating ability [13]. It also shows sufficient electrochemical properties, which implies that POZ could be a promising sensitizer in DSSCs [14]. However, despite these advantages, POZ-based sensitizers have not been reported extensively.

In this research, to study effects of conjugated bridges with a POZ moiety on photovoltaic performance, five-membered heterocyclic rings were introduced as a conjugated bridge unit to POZ

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molecules. The addition of these bridge units could extend the conjugation of the dye molecule, which red-shifted the absorption spectrum and increased the molar absorptivity of the dyes. Furthermore, to improve the donating power and molar extinction coefficient, an ethoxy phenyl ring was substituted in the 7 position of the POZ-furan dye as an additional donor.

Based on these strategies, three organic dyes (**WS1**, **WS2** and **WS3**) were designed and synthesized. The photophysical and electrochemical properties of the synthesized dyes were investigated in detail and density functional theory (DFT) calculations were also performed. Photovoltaic cells were assembled with the synthesized dyes and their photovoltaic properties were analyzed. In addition, electrochemical impedance spectroscopy (EIS) was used to study the interfacial charge transport process in the photovoltaic cells.

2. Experimental

2.1. Materials and reagents

Phenoxazine, N-bromosuccinimide and 4-ethoxyphenylboronic acid were purchased from TCI and used as received without further purification. 1-bromobutane, 5-formyl-2-furan-boronic acid, 5-formyl-2-thiophene-boronicacid, tetrakis(triphenylphosphine) palladium(0), phosphorus oxychloride, 4-ethoxyphenylboronic acid, cyanoacetic acid and piperidine were purchased from Sigma–Aldrich and used as received without further purification. All solvents (chloroform, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, dichloromethane, 1, 2-dichloroethane and acetonitrile) were obtained from Sigma–Aldrich and used as received. Other chemicals were reagent grade and used without further purification.

2.2. Analytical instruments and measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300, 500 and 600 MHz using DMSO with the chemical shift against TMS (Seoul National University National Center for Inter-University Research Facilities). Mass data were measured using a JEOL JMS 600 W mass spectrometer (Seoul National University National Center for Inter-University Research Facilities). UV–vis spectra were measured with a Hewlett–Packard 8425A spectrophotometer. Cyclic voltammetry spectra were obtained using a three-electrode cell with a 273 A potentiostat (Princeton applied research, Inc.). Measurements were performed using Ag wire (Ag/Ag$^+$), glassy carbon and platinum wire as the reference, working and counter electrodes, respectively, in CH_2Cl_2 solution containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte. A standard ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was employed to calibrate the oxidation peak. Photocurrent–voltage measurements were performed using a Keithley model 2400 source measure unit. A 1000 W Xe lamp (Spectra-physics) served as a light source, and it was adjusted using an NREL-calibrated silicon solar cell equipped with a KG-5 filter to approximate AM 1.5G sunlight intensity. The incident photon-to-current conversion efficiency (IPCE) was measured as a function of the wavelength from 300 nm to 800 nm using a specially designed IPCE system for dye-sensitized solar cells (PV measurements, Inc.). A 75 W Xe lamp was employed as a light source to generate a monochromatic beam. The electrical impedance spectra (EIS) of the DSSCs under dark with 0.60 V forward bias were measured with an impedance analyzer (Compactstat, IVIUM Tech) at frequencies of 10^{-1}–10^6 Hz. The magnitude of the alternative signal was 10 mV. The impedance parameters were determined by fitting the impedance spectra using Z-view software.

2.3. Fabrication of dye-sensitized solar cells and measurements

A Photoanode paste was prepared for a screen-printing process. The final composition of the paste comprised TiO_2 nanopowder (1 g), ethyl cellulose (0.5 g), terpineol (3.3 mL), and acetic acid (0.16 mL). After that, pre-washed FTO glass was coated by a doctor blade process and then heated at 70 °C for 30 min for drying. After the printing, the TiO_2 films were heated in four steps of 325 °C, 375 °C, 450 °C, and 500 °C for 5, 5, 15, and 15 min, respectively, using a high-temperature furnace (Lab house Co.). For the post-treatment, the coated and sintered TiO_2 films were immersed in $TiCl_4$ solution (40 mM in water) for 30 min at 70 °C. After washing, the films were annealed at 500 °C for 30 min. Counter electrodes were prepared by spin coating method using 5 mM H_2PtCl_6 solution (in ethanol) on one-holed FTO glass and heated at 400 °C for 20 min. After cooling at 60 °C, the TiO_2 electrodes were immersed in $EtOH/CH_2Cl_2$ solution containing the dyes at 0.5 mM for 48 h at ambient temperature. After dye absorption, the photoanodes were washed using anhydrous ethanol and dried under nitrogen flow. The dye-covered photoelectrode and Pt-electrode were assembled using ionomer surlyn with a hot-press at 80 °C. After assembling, the electrolyte solution (composed of 0.6 M BMII, 0.05 M I_2, 0.1 M LiI, and 0.5 M TBP in acetonitrile solvent) was injected into the one-holed FTO glass using a capillarity vacuum technique, and the hole was sealed with a cover-glass using the same surlyn. A black mask aperture was placed on the front electrode for better analysis of the photovoltaic characteristics. The active area of the dye-coated TiO_2 film was *ca.* 0.24 cm^2, which was measured by analyzing the images from a CCD camera (moticam 1000). The TiO_2 film thickness was measured by an α-step surface profiler (KLA Tencor).

Photocurrent–voltage (*I*–*V*) measurements were performed using a Keithley model 2400 source measure unit. A class-A solar simulator (Newport) equipped with a 150 W Xe lamp was used as the light source. The light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter for approximating the light intensity of 1 sun. Photocurrent–voltage measurements of the dye-sensitized solar cells were performed with an aperture mask by following a reported method. Incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 300 to 1000 nm using a specially designed IPCE system for dye-sensitized solar cells (PV measurements, Inc.). A 75 W xenon lamp was used as the light source for generating monochromatic beams. Calibration was performed using a silicon photodiode, which was calibrated based on the NIST-calibrated photodiode G425 standard. The IPCE values were measured under halogen bias light at a low chopping speed of 10 Hz. All calculations were carried out using Gaussian 09 software. Optimized geometries, energy levels, and frontier molecular orbitals of the dyes' HOMOs and LUMOs were calculated at the B3LYP/6-31G (d,p) level.

2.4. Synthesis of dyes

2.4.1. 10-Butyl-10H-phenoxazine (1)

Sodium hydroxide (7.36 g, 0.184 mol) and 1-bromobutane (6.62 g, 0.048 mol) were slowly added to a phenoxazine (4.0 g, 0.022 mol) solution in dry DMSO (50 mL) at room temperature and stirred for 24 h. Then, the reaction mixture was poured into water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography using ethyl acetate–hexane (1:10; v/v) as the eluent to give **1**, colorless viscous liquid (4.78 g, 91%).

^{1}H NMR (500 MHz, d$_6$-DMSO): $\delta = 6.81$ (d, $J = 8.7$ Hz, 2H), 6.63–6.67 (m, 4H), 3.53 (t, $J = 7.7$ Hz, 2H), 1.50-1.54 (m, 2H), 1.38-1.43 (m, 2H), 0.94 ppm (t, $J = 7.3$ Hz, 3H).