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The effects of the number of anchoring groups and *N*-substitution on the performance of phenoxazine dyes in dye-sensitized solar cells

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ABSTRACT

Four novel phenoxazine-based organic sensitizers were synthesized and applied to dye-sensitized solar cells. Cyanoacrylic acid as an additional anchoring group was introduced to the phenoxazine for efficient electron extraction from the donor part, and an *N*-substituent was added to suppress dye aggregation. The photophysical, electrochemical and photovoltaic properties of the solar cells based on these dyes were investigated to study the effects of these substituents on the performance of the dye-sensitized solar cells. The additional cyanoacrylic acid acceptor improved the short-circuit current because it widened the absorption ranges of the dyes, although it also increased the recombination rate. The *N*-methoxyphenyl unit decrease charge recombinations, resulting in higher open-circuit voltage. However, the bulky substituent decreased the amount of dye absorbed on the TiO_2. As a result, the fabricated cells with the four dyes exhibited similar overall conversion efficiencies and, of these cells, the solar cell based on the *N*-4-methoxyphenyl mono-cyanoacrylate substituted dye showed the highest conversion efficiency of 5.09% (short-circuit current = 10.11 mA/cm^2, open-circuit voltage = 690 mV, fill factor = 72.23%, an overall conversion efficiency = 5.09% under AM 1.5G conditions).

1. Introduction

The demand for environmentally friendly energy sources continues to increase due to depletion of traditional energy sources and due to environmental consideration. One of the attractive candidates of these new energy sources is solar energy, which is clean, renewable and limitless. Dye-sensitized solar cells (DSSCs) have been considered as one of the promising energy harvesting devices since the report of Ru-based photosensitizers in 1991 by Grätzel et al. [1]. The Ru complex sensitizers (N3, N719 and black dye) have shown high photoelectric conversion efficiencies of over 11% under AM 1.5 conditions [2]. Compared with them, metal-free organic dyes and organometallic dyes have advantages including lower cost, easier modification and purification, environmental friendliness and high molar extinction coefficient. The highest conversion efficiencies of organic dyes (10% [3]) and organometallic dyes (12.3% [4]) demonstrated that non-Ru dyes could be promising sensitizers for realizing highly efficient DSSCs. For these reasons, sensitizers containing coumarin [5], carbazole [6], fluorene [7], hemicyanine [8], indoline [9], merocyanine [10], perylene [11], polyene [12], porphyrin [4,13], phthalocyanine [14], triphenylamine [3,15] have been extensively studied.

Phenoxazine (POZ)-based sensitizers have exhibited higher conversion efficiencies than triphenylamine (TPA) and phenothiazine (PTZ)-based sensitizers, which are structurally similar [16–18]. This is because POZ-based sensitizers, with electron-rich nitrogen and oxygen heteroatoms, have stronger electron-donating ability than TPA and PTZ-based sensitizers. POZ-based sensitizers also show sufficient electrochemical properties for use in DSSCs [19]. However, despite their potential for application to DSSCs, POZ-based sensitizers have not been studied extensively.

We report the introduction of an additional cyanoacrylic acid moiety in the 7-position of the POZ chromophore as the second anchoring group. Compared to mono-anchoring sensitizers, this di-anchoring sensitizer has increased electron pathways and extended conjugations of the POZ moiety. Therefore, the short-circuit current (J_{sc}) can be improved by the bathochromic shift of the absorption spectrum. However, the di-anchoring dyes have exhibited lower open-circuit voltages (V_{oc}) compared to the mono-anchoring dyes. Therefore, to improve V_{oc} of cells based on di-anchoring dyes, a

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bulky methoxyphenyl ring was introduced to the POZ nitrogen atom. The steric hindrance by these bulky groups was expected to reduce dye aggregation and suppress the electron recombination between the electrons injected on the TiO_2 and the holes in the electrolyte to result in high $V_{oc.}$

Four POZ derivatives were designed and synthesized, *i.e.*, **POX**, **WB**, **WH1** and **WH2** as shown in Fig. 1. To examine the effects of the additional anchoring group and the *N*-substituents on the performance of DSSCs, photophysical and electrochemical properties of the dyes and photovoltaic performance of the cells based on these dyes were analyzed. In addition, electrochemical impedance spectroscopy (EIS) was used to investigate interfacial charge transport process. Density functional theory (DFT) calculations were also performed for further analysis of the results.

2. Experimental

2.1. Materials and reagents

Phenoxazine, 1-bromobutane, 4-iodoanisole, copper-tin alloy, 18-crown-6, phosphorus oxychloride, cyanoacetic acid and piperidine were purchased from Sigma–Aldrich and used as received without further purification. All solvents (dimethylformamide, 1,2-dichlorobenznene, 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

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 500 and 600 MHz (Seoul National University National Center for inter-University Research Facilities) with the chemical shift against TMS. Mass data were measured with a JEOL JMS 600W mass spectrometer (Seoul National University National Center for inter-University Research Facilities). ATR-FTIR spectra were recorded on a Nicolet 6700 spectrometer by using the window ZnSe/diamond ATR accessory. UV–vis spectra and photoluminescence spectra were recorded on a Hewlett–Packard 8425A spectrophotometer and a Shimadzu RF-5301PC spectrofluorometer, respectively. Cyclic voltammetry spectra were obtained using a three-electrode cell with a 273A potentiostat (Princeton applied research, Inc.). Measurements were taken using an Ag wire (Ag/Ag^+), a glassy carbon and a platinum wire as the reference, working and counter electrodes, respectively, in the DMF solution containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte. A standard ferrocene/ferrocenium (Fc/Fc^+) redox couple was used to calibrate the oxidation peak. Photocurrent–voltage measurements were performed using a Keithley model 2400 source measure unit. Incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 300 nm to 1000 nm using a specially designed IPCE system for dye-sensitized solar cells (PV measurements, Inc.). Electrical impedance spectra (EIS) of DSSCs under dark with 0.55 V forward bias and under illumination at an open-circuit voltage 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. Impedance parameters were determined by fitting the impedance spectra using the Z-view software.

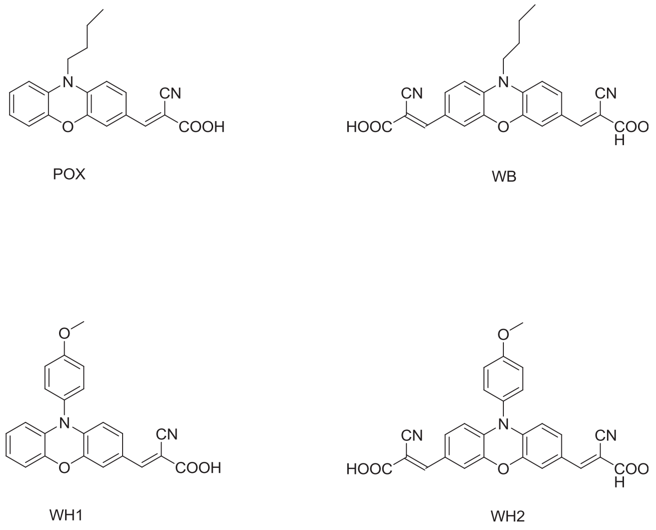

Fig. 1. Structure of **POX**, **WB**, **WH1** and **WH2**.

2.3. Fabrication of dye-sensitized solar cells and measurements

The nanocrystalline TiO_2 working electrode was comprised of a TiO_2 transparent layer (20 nm, synthesized) and a TiO_2 scattering layer (250 nm, G1). The Pt-coated counter electrode was prepared by a reported procedure [20]. TiO_2 electrodes were immersed in THF solution containing the dyes at 0.5 mM for 40 h at ambient temperature. They were then washed with ethanol and dried under a stream of nitrogen. The working and counter electrodes were sealed with Surlyn (60 μm, Dupont) and electrolyte was injected through a hole in the counter electrode. The electrolyte was comprised of 0.7 M 1-propryl-3-methyl-imidazolium iodide (PMII, synthesized), 0.2 M LiI (Aldrich), 0.05 M I_2 (Aldrich), and 0.5 M 4-*tert*-butylpyridine (Aldrich) in a mixed solvent of acetonitrile and valeronitrile (v/v, 85/18). The active area of the dye-coated TiO_2 film was *ca.* 0.24 cm^2, measured by analyzing the images from a CCD camera (moticam 1000). TiO_2 film thickness was measured by a 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. Light intensity was adjusted with an NREL-calibrated Si solar cell with KG-5 filter for approximating 1 sunlight intensity. Photocurrent–voltage measurements of the dye-sensitized solar cells were performed with an aperture mask 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. IPCE values were measured under halogen bias light at a low chopping speed of 10 Hz. All calculations were carried out using the 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**)

To a phenoxazine (1.5 g, 0.0082 mol) solution in dry DMSO (22.5 mL), sodium hydroxide (2.76 g, 0.069 mol) and 1-bromobutane (1.89 g, 0.0137 mol) were slowly added 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