



Synthesis and performance of new quinoxaline-based dyes for dye sensitized solar cell



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ABSTRACT

New quinoxaline-based dyes were synthesized and applied as a sensitizer for dye-sensitized solar cell. A quinoxaline moiety was used as an electron withdrawing group and triphenylamine and phenothiazine derivatives were introduced as electron donating groups. The dyes synthesized with the phenothiazine moiety showed greater conversion efficiency than dyes with the triphenylamine moiety leading to the best overall power conversion efficiency of 4.36%.

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1. Introduction

With increasing interest in alternative energy, researchers have focused on solar energy due to its sustainability and ease of access. Dye-sensitized solar cells (DSSC) convert light to electric energy [1]. DSSCs have attracted research because of their low cost and high power-conversion efficiency [2]. Dye molecules play a key role as sensitizers and have been studied to improve the efficiency of the solar energy to electricity conversion in DSSC [3]. Grätzel reached an efficiency of over 11% using N719 dye, a Ru-metal complex [4]; however, this dye is inefficient for large scale applications because the ruthenium atom is rare and expensive. For those reasons, metal-free dyes have gained interest due to easily-tunable absorption regions, high molecular extinction coefficients and lower cost when compared to metal complexes. Carbazole [5], coumarin [6], indoline [7,8], porphyrin [9,10], perylene [11,12], phthalocyanine [13,14], phenothiazine [15–18], squaraine [19] have been introduced in the literature as sensitizers for improving efficiency. Recently, the Grätzel group achieved an efficiency of 13% using porphyrin dye [20].

Generally, metal-free dyes for DSSCs feature a push-pull structure, in which the electron transfer occurs efficiently. Once the electrons in the dye are excited due to the absorption of light, an electron donor pushes and an electron acceptor pulls the electrons from the donor. The electrons transported to the acceptor can be injected into the conduction band of a semiconductor through anchoring groups linked to the acceptor.

Over the last several decades, various functional groups and their derivatives have been introduced as electron donors or acceptors. Among these, triphenylamine derivatives are excellent electron donors due to their electron-donating property and non-planar molecular configuration, which prevents aggregation [21,22].

Phenothiazine derivatives have shown better light conversion efficiency than similarly-shaped triphenylamine groups because a phenothiazine moiety with electron-rich heteroatoms, nitrogen and sulfur, has a strong electron donating ability. In addition, a non-planar structure like butterfly suppresses aggregation via intermolecular interaction [23].

Quinoxaline moieties have recently been investigated as electron acceptors in DSSCs, utilizing their strong electron-withdrawing property that stems from a high electron affinity derived from two symmetric unsaturated nitrogen atoms in the heterocycle [24]. Dong Wook Chang et al. [25] modified horizontally- or vertically-structured quinoxaline derivatives, and Takahiro

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Kono et al. [26] and Jie Shi et al. [27] studied quinoxaline-based DSSCs using the triphenylamine group as the electron donor, though neither study has introduced more powerful electron donors such as triphenylamine derivatives with alkoxy moieties. To the best of our knowledge, there has not yet been any attempt to utilize the phenothiazine and quinoxaline groups as electron donors and acceptors, respectively, for DSSCs.

In this study, triphenylamine and phenothiazine derivatives with an alkoxy group were introduced to 2, 3-positions of quinoxaline as an electron donor for the Y-shape, and a carboxylic group was introduced to the 6-position as an anchoring group. Introduction of the alkoxy groups on the electron donor was expected to improve the electron donating ability. The synthesized structures, **NQX1-4**, exhibited photovoltaic properties.

2. Experimental

2.1. Materials

All reagents and solvents were purchased commercially and used without further purification. (isopentyloxy)benzene, 4-(bis(4-methoxyphenyl)amino)benzaldehyde (**3a**), 10-(4-methoxyphenyl)-10H-phenothiazine-3-carbaldehyde (**5a**) and 4-acetamidobenzoic acid (**6**) were prepared following methods reported in literature [23,28–30].

2.2. Characterization

^1H and ^{13}C NMR spectra were recorded on a VARIAN UnityInova 300 MHz FT-NMR spectrometer. MALDI-TOF MS analysis was conducted on a Waters Limited MALDI-TOF spectrometer using a dithranol matrix. The UV–vis absorption spectra were measured on a Jasco V-670 spectrophotometer. Cyclic voltammetry (CV) was performed on a Bio-Logic (SP-200) with a three-electrode cell in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mVs^{-1} . A carbon electrode, Ag/AgCl electrode, and a platinum wire were used as working, reference, and counter electrodes, respectively.

2.3. DSSC fabrication

A 0.1M titanium (IV) bis(ethyl acetoacetate)diisopropoxide solution in butanol was coated on the FTO glass plate (Pilkington-TEC8) by a spin coater (at 1000 rpm for 10s and then, at 2000 rpm for 40s) and the substrate was heated to 450 °C for 30 min in a furnace to form a 20-nm thickness. A 20-nm TiO_2 paste (PST-18 NR, CCIC) was coated by a doctor blading method and annealed at 450 °C for 30 min (~11 μm). The scattering layer was developed by a doctor blading method using a 400-nm TiO_2 particle (PST-400C, CCIC) and treated under 450 °C for 30 min (~4 μm) to improve light absorption. The treated substrate was further exposed to an aqueous 50 mM TiCl_4 solution at 70 °C for 20 min and sintered at 450 °C for 30 min. After sintering, the substrate was immersed in a 5×10^{-4} M dye solution of chloroform for 2 h at room temperature for dye adsorption (in the case of N719 dye, the substrate was immersed for 24 h), rinsed with chloroform and dried. To prepare the counter electrode, a 0.01M H_2PtCl_6 solution in isopropyl alcohol was coated on the cleaned FTO plate using a spin coater (at 1000 rpm for 10s and at 2000 rpm for 40s, subsequently) and heated at 450 °C for 30 min. The Pt-coated electrode was then drilled to make two holes, washed with ionized water and dried. The prepared electrodes were assembled into a sandwich-type structure using surllyn film (25 μm) with a hot press at 90 °C. After assembly, an electrolyte solution (0.6 M DMPII, 0.1M LiI, 0.1M I_2 , 0.5M TBP in acetonitrile) was injected into the cell through the

holes and the holes were sealed with a cover glass using the additional surllyn film. The active area of the dye-coated TiO_2 film was 0.25 cm^2 .

2.4. Measurements

The photocurrent density-voltage (J-V) curves were collected using a Keithley Model 2400 source meter and a solar simulator with a 300W Xenon arc-lamp Newport under AM 1.5 illumination (100 mWcm^{-2}). A photomask on the residual area of the dye fabricated cell was used to reduce scattered light (the active area of the DSSC was 0.25 cm^2). The incident photon-current conversion efficiency (IPCE) was recorded in the wavelength range of 300–800 nm using a model QEX7 solar cell spectral response measurement system (PV Measurements, Inc).

2.5. Synthesis

2.5.1. 1-iodo-4-(isopentyloxy)benzene (**1b**)

Sulfuric acid (24.2 ml) was carefully added to methanol (400 ml) in a 3-neck flask under stirring and then cooled to 0 °C. Potassium iodide (50.7 g, 1.82 mol) and (isopentyloxy)benzene (49.2 g, 0.3 mol) was slowly added sequentially to the solution. After warming to room temperature, 30% hydrogen peroxide (63.6 ml) was slowly added drop wise and then stirred at 60 °C for 14 h. The resulting mixture was cooled to room temperature, poured into water and extracted with chloroform. The organic phase was washed with a sodium metabisulfate aqueous solution, dried over anhydrous sodium sulfate, and concentrated to produce a yellow oil (87 g, 0.3 mol). ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): δ (ppm) = 7.58–7.55 (d, J = 9.0 Hz, 2H, ArH), 6.79–6.76 (d, J = 9.0 Hz, 2H, ArH), 3.97–3.93 (t, J = 6.6 Hz, 2H, $-\text{CH}_2-$), 1.80–1.70 (m, J = 6.6 Hz, 1H, $-\text{CH}-$), 1.61–1.55 (q, J = 6.6 Hz, 2H, $-\text{CH}_2-$), 0.92–0.89 (d, 6H, $-\text{CH}_3$). ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$): δ (ppm) = 158.5, 137.9, 117.2, 82.8, 66.0, 37.3, 24.5, 22.4.

2.5.2. 4-(isopentyloxy)-N-(4-(isopentyloxy)phenyl)-N-phenylaniline (**2b**)

Copper powder (26.8 g, 0.42 mol) and copper iodide (0.187 g, 0.98 mmol) were added to a solution of **1b** (87 g, 0.3 mol) and aniline (13.1 g, 0.14 mol) in *o*-dichlorobenzene (100 ml), and potassium carbonate (77.6 g, 0.56 mol) under a N_2 condition. The resulting mixture was vigorously refluxed for 24 h, cooled to room temperature and filtered with benzene. The filtrate was concentrated and purified by column chromatography on silica gel using dichloromethane/hexane (1:2) as an eluent. The yield of the yellow viscous liquid was 35 g (60%). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 7.22–7.17 (t, 2H, ArH), 7.09–7.06 (d, J = 9.0 Hz, 4H, ArH), 6.99–6.97 (d, J = 7.5 Hz, 4H, ArH), 6.94–6.89 (t, J = 7.5 Hz, 1H, ArH), 6.87–6.84 (d, J = 9.0 Hz, 2H, ArH), 4.01–3.97 (t, J = 6.6 Hz, 4H, $-\text{CH}_2-$), 1.93–1.84 (m, J = 6.6 Hz, 2H, $-\text{CH}-$), 1.75–1.68 (q, J = 6.6 Hz, 4H, $-\text{CH}_2-$), 1.02–1.00 (d, 12H, $-\text{CH}_3$). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm) = 155.2, 148.8, 140.9, 128.8, 126.3, 120.7, 115.3, 115.1, 66.5, 38.1, 25.0, 22.6.

2.5.3. 4-(bis(4-(isopentyloxy)phenyl)amino)benzaldehyde (**3b**)

The solution of **2b** (30 g, 0.072 mol) in DMF (320 ml) was stirred at 0 °C. Phosphorus oxychloride (17.7 g, 0.115 mol) was added drop wise, and stirred at room temperature for an additional 30 min. The resulting mixture was heated to 80 °C, stirred for 12 h, cooled to room temperature, and poured into water. After stirring for 30 min, the emulsion was extracted with ether. The organic solvent was washed with brine, dried over anhydrous sodium sulfate and concentrated. The residue was purified by column chromatography on silica gel using chloroform as an eluent to produce a yellow

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