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Comparative studies of organic dyes with a quinazoline or quinoline chromophore as π-conjugated bridges for dye-sensitized solar cells

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ABSTRACT

A new series of organic D–π–A dyes bearing either quinazoline or quinoline as the conjugated bridges in the chromophore with a diphenylamine moiety as the electron donor and a cyanoacetic acid unit as the electron acceptor, have been designed and synthesized for photoconversion in dye sensitized solar cells (DSSCs). The absorption spectra, density functional theory calculations, electrochemical and photovoltaic properties of these dyes are systematically investigated. Among the four dyes the sensitized solar cell based upon the quinoline dye bearing butoxy groups gave a short circuit photocurrent density of 7.04 mA cm^{-2}, an open circuit voltage of 0.52 V, and a fill factor of 0.69, corresponding to an overall conversion efficiency of 2.51% using I^-/I_3^- redox couple-based liquid electrolyte without 4-*tert*-butylpyridine additives under standard global AM 1.5 irradiation (100 mW cm^{-2}). The photovoltaic performance of the dye with 4,4′-dibutoxy diphenylamine as the donor and quinoline unit as the π-bridge was higher than that of the other photosensitizers, which is mainly attributed to the higher molar extinction coefficient and broader absorption band. The experimental results demonstrate that rational molecular engineering is crucial for constructing highly efficient charge transfer sensitizers.

1. Introduction

In recent years, increasing energy demands and environmental issues such as fossil fuel shortage and global warming have lead to the search for clean renewable energy sources [1,2]. Due to the unlimited solar-energy supply, conversion devices that convert solar energy directly into electricity are very attractive [3]. As one of the most promising alternatives to conventional inorganic semiconductor solar cells, such as silicon solar cells, dye-sensitized solar cells (DSSCs) have attracted considerable interest from both the academic and industrial communities because of their high photo-to-current conversion efficiency (PCE) and easy, low cost manufacturing processes [4,5]. In DSSCs, the sensitizer adsorbed on a mesoporous oxide film is a critical component, which exerts significant influence on the PCE as well as the stability of the devices. To develop high-efficiency organic photosensitizers for DSSCs, a comprehensive understanding of the structure–property relationship of dyes is warranted. During the past two decades, numerous organic dyes have been developed with their advantages such as relatively low production cost, high molar absorption coefficient and flexibility in tailoring their molecular structures [5]. Recently, Grätzel et al. reported wrapped porphyrins incorporating a benzothiadiazole moiety, thus achieving the highest PCE of 13% by using a cobalt (II/III) redox based electrolyte [6].

Due to the effective photo-induced intramolecular charge transfer (ICT) characteristics, most of the efficient organic sensitizers are modeled on the donor–π spacer–acceptor (D–π–A) system. In fact, the π spacer is of critical role in tuning the energy gap as well as the electronic and steric properties of the dye molecule, which would strongly affect the device performances. Especially, in order to extend the absorption to a longer wavelength region for better light harvesting, electron-deficient units [7], such as thiazole [8], pyridine [9], pyrimidine [10], benzotriazole [11],

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squaraine [12], phthalimide [13], pyrazino[2,3-*g*]quinoxaline [14] and quinoxaline moieties [15–17] have been incorporated in the conjugated spacer.

It is well-known that quinoline and its aza-analog quinazoline are strong electron-accepting molecules due to their high electron affinity originating from the unsaturated nitrogen atoms. Although there are a few reports on the applications of quinoline units for DSSCs [18,19], the utilization of quinazoline unit in organic sensitizers has not yet been reported to our best knowledge. Here we designed a series of organic D–π–A dyes (**Q1**–**4**) with either quinazoline or quinoline as the conjugated bridges, as shown in Chart 1. The molecular structures of the dyes were designed according to the following merits: firstly, the quinazoline or quinoline-containing π-system which favors planar geometry is necessary for effective ICT from donor to acceptor. Secondly, the integration of two electron-deficient acceptors (i.e. quinazoline and cyanoacetic acid) appears to give appropriate energy levels and essential ICT character. Finally, the 4,4′-disubstituted diphenylamine (DPA) moiety is adopted as the donor unit not only for its strong electron-donating ability, but also its contribution to suppressing dye aggregation owing to its nonplanar structure and substituent [20]. Herein, these dyes show evident bathochromic shift in absorption, and thus effectively improve the light-harvesting range. The effects of the donor and the conjugating bridge on the photophysical properties and performance of DSSCs used these dyes are discussed.

2. Experimental

2.1. Materials and reagents

All reagents and solvents for synthesis were obtained from commercial sources and used without further purification. Solvents for measurements of spectroscopy are high performance liquid chromatography (HPLC) grade. 2-Methyl-6-nitroquinazoline (**1a**) [21], 2-methylquinazolin-6-amine (**2a**) [21], 2-methyl-6-nitroquinoline (**1b**) [22] and 2-methylquinolin-6-amine (**2b**) [22] were prepared according to reported procedures.

2.2. Analytical instruments and measurements

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker (AV 300/AV 400 MHz) spectrometer. The chemical shifts were recorded in parts per million (ppm) with tetramethylsilane (TMS) as internal reference. Mass spectra were determined using a Micromass GCT TOF or Thermo LTQ Orbitrap or MALDI-TOF mass spectrometer. FTIR spectra were acquired on a Bruker VECTOR22 infrared spectrophotometer. UV–vis absorption spectra of the dyes in solution and the absorption of dye-sensitized TiO_2 films (thickness 4 μm) based on the dyes were obtained using a Shimadzu UV–vis 2450 spectrophotometer. The redox potentials were measured by using cyclic voltammetry on a CHI620D multipurpose electrochemical analyzer. All measurements were performed in CH_2Cl_2 solutions containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte at ambient temperature after purging 20 min with N_2. The conventional three electrode configuration was employed, which consists of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode. Ferrocene was added as an external standard at the end of each measurement (0.63 V *vs.* NHE). For better understanding of the molecular structure and electron distribution, the geometries of the **Q1**–**4** are optimized by density functional theory (DFT) calculations using the Gaussian 09 program (Revision C.01) at the B3LYP/6-31G (d) level. The excitation transitions of dyes **Q2** and **Q4** were calculated using time-dependent DFT (TDDFT) calculations with B3LYP/6-31G (d). The incident photo-to-current conversion efficiency (IPCE) of the DSSCs was measured using a 300 W Xe lamp light source with monochromatic light in the range of 300–800 nm. The photocurrent–voltage (*J*–*V*) characteristics of the solar cells were carried out using a Keithley 2420 3A source meter controlled by test-point software under solar simulator.

2.3. Fabrication of dye-sensitized solar cells

The dye-sensitized TiO_2 electrodes were prepared by following the procedure reported in the literature [23,24]. The mesoporous

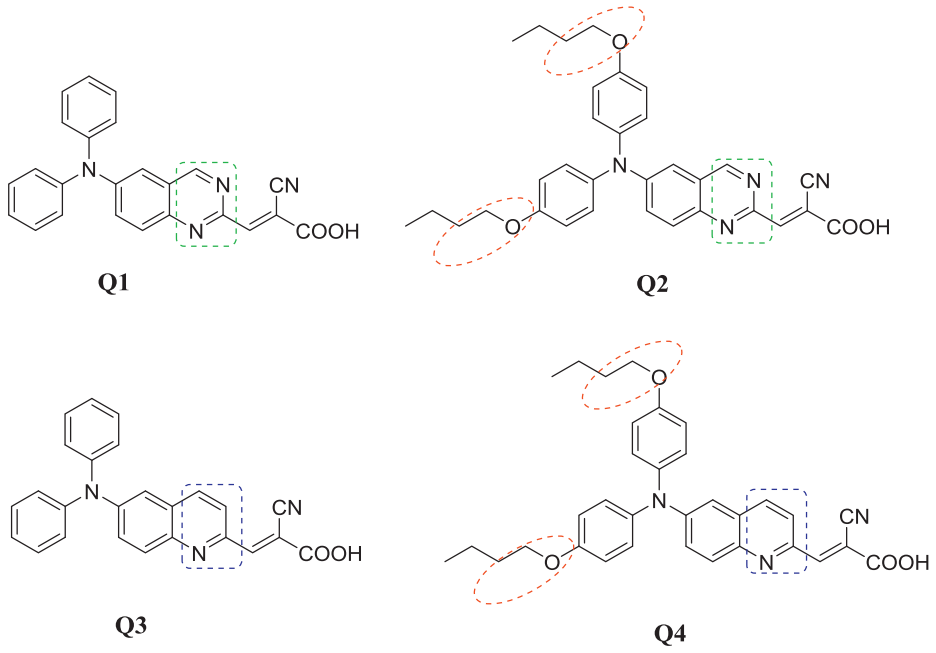

Chart 1. Molecular structures of dyes **Q1**–**4**.