



D- π -A- π -A featured dyes containing different electron-withdrawing auxiliary acceptors: The impact on photovoltaic performances



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ABSTRACT

Four novel D- π -A- π -A metal-free organic dyes **Q1-Q4** were synthesized and the impacts of the auxiliary acceptors on the photovoltaic performances were studied. **Q2** with quinoxaline as the auxiliary acceptor exhibited the best photovoltaic performance due to its highest short-circuit photocurrent density (17.22 mA cm⁻²), leading to a power conversion efficiency of 7.42% under simulated AM 1.5 G illumination. **Q1** with the strongest electron withdrawing group (pyrazino[2,3-g]quinoxaline) as the auxiliary acceptor showed the weakest performance, which can be attributed to electron trap and mismatch of energy-level. The results showed that the different electron-withdrawing property of auxiliary units significantly influenced the absorption, energy levels and photovoltaic performance. Incorporating auxiliary acceptor with moderate electron-deficient ability can extend the absorption range and adjust the molecular orbital energy levels, resulting in better photovoltaic performance.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention since the first report by Grätzel et al. in 1991 [1]. An impressively high efficiency of 13% has been achieved with a DSSC based on a porphyrin dye and cobalt redox mediator under AM 1.5 solar irradiation [2,3]. Metal-free organic dyes exhibit low-costs, flexibility and easy fabrication [4–9]. So far, the highest power conversion efficiency of metal-free organic dye is 13.0% [10]. These works highlight the potential of metal-free organic dyes for future applications [11,12].

In the past two decades, plenty of research on novel dyes made great contributions to improve the power conversion efficiency (PCE) of DSSCs based on metal-free organic dyes [13–15]. Donor- π -bridge-acceptor (D- π -A) configuration has been well-recognized as a fine candidate for high-performance organic dyes due to their easy synthesis and good performance [16–18]. Recent endeavors have incorporated additional acceptor. In 2011, Zhu and Tian proposed a concept of a D-A- π -A motif for designing a new

generation of efficient and stable organic dyes [19]. In the previous researches, some electron-withdrawing blocks, such as benzo-thiadiazole [19–21], diketopyrrolopyrrole [22], benzotriazole [23] and benzophenazine [24] have been employed to build D-A- π -A framework. It is reported that auxiliary acceptor is beneficial for modulating the energy levels, extending absorption wavelength, thus greatly improving photovoltaic performances. However, additional acceptor with strong electron withdrawing can be treated as an “electron trap” which suppresses the process of transporting electron from donor to acceptor as well as leads to mismatch in energy level [25]. Discovering a balance between the two aspects is a matter of cardinal significance. But it lacks systematical investigation on the effects of different electron-withdrawing auxiliary units on photovoltaic performances [26].

In order to study the relationship between different electron-withdrawing auxiliary acceptor and photophysical, electrochemical as well as photovoltaic performance in DSSCs systematically, we present the design and synthesis of three novel metal-free organic dyes **Q1-Q3** (Fig. 1) to explore the impacts of the auxiliary acceptors on the photovoltaic performances. As we've seen, quinoxaline unit (QA) has been embedded into the organic dyes as an auxiliary electron acceptor for efficient DSSCs by several groups [5,24,27]. In this paper, we applied QA to construct two organic

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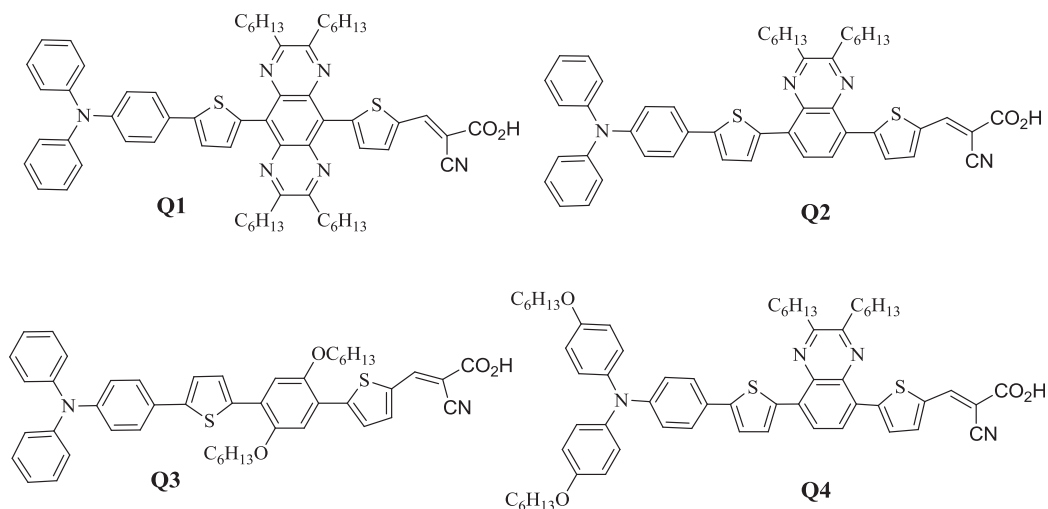


Fig. 1. Chemical structures of the dyes **Q1–Q4**.

dyes **Q2** and **Q4**, and imported pyrazino[2,3-*g*]quinoxaline (PZQA) into **Q1**. We prepared **Q3** with a benzene unit (BZ) in the π -bridge as a reference dye. The capability of electron withdrawing attenuates from PZQA, QA to BZ. In addition, two thiophene rings were introduced to the dyes while π -conjugation extension is an effective way to improve the short-circuit photocurrent density [28,29]. The photophysical, electrochemical and photovoltaic properties of the four dyes were systematically investigated.

2. Experimental section

2.1. Materials and instruments

All solvents were purified according to the standard methods. All reagents were commercially obtained from Aladdin Chemical Co., Darui and J&K Chemical Co. and used without further purification unless otherwise specified use. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. All chromatographic separations were carried out on silica gel (300–400 mesh).

^1H and ^{13}C NMR spectra were measured on Bruker 400 MHz instruments in CDCl_3 and $\text{THF-}d_6$. HRMS spectra were recorded on an Agilent Technologies 1290 Infinity mass spectrophotometer. UV–vis absorption spectra of dye solutions and dye-adsorbed TiO_2 films were measured on Shimadzu UV-2450 spectrophotometer and UV-3010 spectrophotometer, respectively. The melting point was conducted on a SGW-X-4B microscopic melting point apparatus. Cyclic voltammetry (CV) measurements were recorded on a CHI660E electrochemical workstation using a typical three electrode electrochemical cell in a solution of tetrabutylammoniumhexafluorophosphate (TBAPF_6) in dry MeCN with a scan rate of 50 mV s^{-1} . Dye loaded TiO_2 film was used as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. The ferrocene/ferrocenium (Fc/Fc^+) redox couple (4.80 eV vs. vacuum) acted as an internal potential reference. The current density–voltage (J – V) characteristics of the DSSCs were measured by recording J – V curves using a Keithley 2400 source meter under simulated AM 1.5 G (100 mW cm^{-2}) illumination with a solar light simulator (Oriol, Model: 91192) without a mask. The incident monochromatic photo-to-current conversion efficiency (IPCE) was performed on a Spectral Products DK240 monochromator from 300 to 800 nm region.

2.2. Syntheses of dyes

2.2.1. 2,3,7,8-Tetrahexyl-5,10-di(thiophen-2-yl)pyrazino[2,3-*g*]quinoxaline (**2**)

A suspension mixture of zinc dust (2.05 g, 31.4 mmol) and compound **1** (0.90 g, 2.73 mmol) in acetic acid (15 mL) was kept at 70°C or 6 h. The reaction mixture turned pale green slowly. Then, 7,8-tetradecanedione (1.27 g, 5.60 mmol) was added. The mixture was stirred vigorously for 24 h at the same temperature. The excess zinc dust was removed off by vacuum filtration. The liquid after filtration containing acetic acid and excess 7,8-tetradecanedione was washed by deionized water and extracted by CH_2Cl_2 . The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate ($v/v = 40:1$) to give **2** as a red solid in 50.5% yield (914 mg), mp 87 – 89°C . ^1H NMR (400 MHz, CDCl_3) δ 8.32 (m, 2H), 7.55 (m, 2H), 7.18 (m, 2H), 3.00 (t, $J = 7.2 \text{ Hz}$, 8H), 1.92 (m, 8H), 1.41 (m, 8H), 1.30 (m, 16H), 0.84 (t, $J = 6.4 \text{ Hz}$, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.1, 135.3, 133.7, 132.4, 128.0, 126.9, 124.6, 34.1, 30.8, 28.3, 26.4, 21.6, 13.1. HRMS (ESI, m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{42}\text{H}_{59}\text{N}_4\text{S}_2$: 683.4176, found: 683.4183.

2.2.2. 5-(2,3,7,8-Tetrahexyl-10-(thiophen-2-yl)pyrazino[2,3-*g*]quinoxalin-5-yl)thio-phene-2-carbaldehyde (**3**)

To a solution of **2** (250 mg, 0.366 mmol) and dry DMF (0.142 mL, 1.83 mmol) in 1,2-dichloroethane (15 mL), POCl_3 (0.133 mL, 1.46 mmol) was added slowly over 20 min at 0°C under argon. Then the bath was heated to 70°C and maintained for 3 h. After cooling to room temperature, 0.1 M sodium hydroxide aqueous solution (10 mL) was added, and the mixture was extracted three times with CH_2Cl_2 . The combined organic fractions were washed with brine and dried over MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, $v/v = 30:1$) to give **3** as a dark red solid in 39.9% yield (104 mg), mp 88 – 91°C . ^1H NMR (400 MHz, CDCl_3) δ 10.05 (s, 1H), 8.44 (m, 2H), 7.89 (m, 1H), 7.68 (m, 1H), 7.28 (m, 1H), 3.11 (t, $J = 7.2 \text{ Hz}$, 8H), 1.99 (m, 8H), 1.49 (m, 8H), 1.38 (m, 16H), 0.92 (t, $J = 6.0 \text{ Hz}$, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 183.5, 156.9, 156.5, 145.2, 144.8, 143.5, 136.7, 136.0, 134.4, 134.3, 134.2, 134.0, 130.1, 129.9, 129.8, 125.8, 125.7, 125.7, 35.2, 35.2, 31.8, 31.8, 29.3, 29.2, 27.4, 27.4, 22.6, 22.6, 14.1, 14.1. HRMS (ESI, m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{59}\text{N}_4\text{O}_2\text{S}_2$: 711.4152, found: 711.4128.

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