



Alkyl chain length dependence of the charge-transfer, recombination and electron diffusion length on the photovoltaic performance in double donor-acceptor-based organic dyes for dye sensitized solar cells



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ABSTRACT

A series of double donor-acceptor organic dyes (C4–C12) have been synthesized to investigate the influence of the alkyl chain length between the two chromophores on the performance of dye sensitized solar cells (DSSCs). The chain length dependent performance was investigated further using the electrochemical impedance and stepped light induced transient measurement methods. Dye with longer alkyl chain (C6–C12) shows a broader and higher IPCE as well as photo-current density (J_{sc}) with an enhanced photovoltage (V_{oc}) relative to the reference PTZ-S. In contrast, C4 with shorter alkyl chain presents a relatively low IPCE within the whole spectral region, along with low J_{sc} and V_{oc} , which predominately arising from the short electron diffusion length with significant electron loss during charge transport. The higher J_{sc} and V_{oc} obtained with the devices incorporating C10 and C12 dyes with long alkyl chain resulted in a higher conversion efficiencies of 4.02% and 4.03%, respectively, (3.14% for single donor-acceptor dye PTZ-S). Density functional theory simulations were also performed to examine the effect of the alkyl chain length on electrochemical and optical properties of the dyes. Adsorption studies of the dyes on TiO_2 clusters were carried out to explain the variation in J_{sc} with the alkyl chain length.

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1. Introduction

In recent years, organic dyes have attracted considerable attention for use as sensitizers in dye sensitized solar cells (DSSCs) owing to their strong absorption in the visible region, as well as their optical, photo-physical and electrochemical properties, which can be tuned readily by peripheral substitutions [1–3]. The light-harvesting unit is a potent part of the dye sensitizer. Generally, the π -conjugated bridge structure with electron donor-acceptor (D- π -A) moieties is effective for intramolecular charge transfer.

DSSCs with these dyes show better performance [1–17]. If the light-harvesting units of the D- π -A sensitizer increase, the photovoltaic performance of DSSCs should increase. Therefore, there has been considerable interest in the design and synthesis of novel double donor-acceptor dyes bridged with an alkyl spacer system, which show dark current suppression, and improved absorption properties in the visible light range. The phenothiazine unit is a fairly strong donor, and organic dyes based on this unit have been applied successfully in the DSSCs research field and shown quite promising efficiencies [18–30]. Derong Cao et al. reported novel phenothiazine-based double branched (DB) dyes that contained double symmetric and asymmetric D- π -A systems bridged with a fixed alkyl chain, and obtained increased conversion efficiencies of DSSCs compared to the corresponding single D- π -A dyes [18–20]. The same group reported the impact of the position isomer of the

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linkage in DB organic dyes on the photovoltaic performance of DSSCs [21]. In 2015, they also examine the effects of the linkage location in DB organic dyes on the photovoltaic performance of DSSCs [23]. Recently, our group reported a novel DB dye with unsymmetrical anchoring groups and obtained higher efficiency as compared to those of cells sensitized with DB dyes with symmetrical anchoring groups [31].

Increasing the alkyl chain length is believed to reduce the charge recombination dynamics and increase the electron lifetime because the better surface protection would facilitate electron injection, leading to high overall conversion efficiency [32–42]. Qipeng Chai et al. reported that the alkyl chain length is crucial to the photovoltaic performance of cyclopentadithiophene-bridged sensitizers [43]. Why structural modification of the organic dyes can greatly influence the performance of the sensitizer based DSSCs is easy to understand [44–46]. Taking these points into consideration, a series of organic sensitizers with different alkyl chain spacers C4–C12 were designed to obtain greater insight into the impact on the photovoltaic performance of the solar cells under the conditions of introducing different alkyl chain spacers to the sensitizers that bear symmetric double donor-acceptor systems (Fig. 1). The bridged alkyl chain length of double branched dyes was expected to influence the surface coverage of the dyes on the TiO₂ films, affecting the performance of the device. The corresponding single branched dye PTZ-S was also synthesized for comparison (Fig. 1).

To determine the correlations between the device performance and the alkyl chain length, this study investigated the optical and electrochemical properties and the photovoltaic performance of the DSSCs based on these double donor-acceptor dyes bridged with different alkyl chain spacers. Density functional theory (DFT) and time dependent DFT (TDDFT) calculations were performed on five organic dyes. The experimental photophysical data were confirmed by the computational simulations. The variation of the excitation energies with respect to the alkyl chain length of the dyes was examined through TDDFT simulations. Moreover, the effects of the alkyl chain length on the solar cell performance was studied by electrochemical impedance (EIS) and the stepped light induced transient measurement (SLIM) technique. As the alkyl chain length was increased, the current density, open-circuit voltage and overall performance of DSSC increased due to the decreased recombination resistance and increased charge transport, diffusion length, and electron lifetime.

2. Experimental

2.1. Synthesis

The synthetic routes of C4–C12 are displayed in Scheme 1. The structures of the compounds were identified by ¹H NMR. The ¹H NMR spectra of the final product are shown in Supporting Information (ESI).

2.1.1. 10-Hexyl-10H-phenothiazine (1)

An oven dried, 250 mL round bottom flask (RBF) was charged with *N,N*-dimethylformamide (DMF) (100 mL), 1-bromohexane (10.7 g, 0.065 mol), and sodium hydride (1.8 g, 0.075 mol). Subsequently, a DMF solution of phenothiazine (10 g, 0.05 mol) was added to the mother solution, and the reaction mixture was maintained at room temperature for 10 h. After the reaction was complete, the solution was neutralized with a dilute HCl aqueous solution. The mixture was extracted with chloroform/water. The organic solution was then concentrated. The resulting crude oily product was purified by column chromatography on silica gel with hexane. The product was obtained as a colorless liquid. Yield: 11.2 g (79%). ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 7.20 (d, 2H), 7.14 (d, 2H), 6.99 (d, 2H), 6.91 (t, 2H), 3.84 (t, 2H), 1.67–1.60 (m, 2H), 1.41–1.27 (m, 2H), 1.23–1.19 (m, 4H), 0.86–0.80 (m, 3H).

2.1.2. 10-Hexyl-10H-phenothiazine-3-carbaldehyde (2)

An oven dried, 250 mL round bottom flask was charged with a solution of DMF (13.2 g, 0.18 mol) and 1,2-dichloroethane (20 mL). Subsequently, 10-hexyl-10H-phenothiazine, 1 (5.0 g, 0.017 mol) in 1,2-dichloroethane (20 mL) was added slowly to the mixture for 30 min POCl₃ (10.7 g, 0.07 mol) was then added drop wise over a 30 min period. The mixture was stirred for 10 h at 90 °C, and then poured into ice water (300 mL), neutralized with an aqueous solution of NaOH, and extracted three times with chloroform. The solvent was removed under reduced pressure. The resulting product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:5 v/v). The product was obtained as a yellow solid. Yield: 2.7 g (51%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.79 (s, 1H), 7.63 (d, 1H), 7.58 (s, 1H), 7.17 (d, 1H), 7.11 (d, 1H), 6.97 (d, 1H), 6.92 (d, 1H), 6.88 (d, 1H), 3.88 (t, 2H), 1.85–1.76 (m, 2H), 1.43–1.30 (m, 6H), 0.87 (m, 3H).

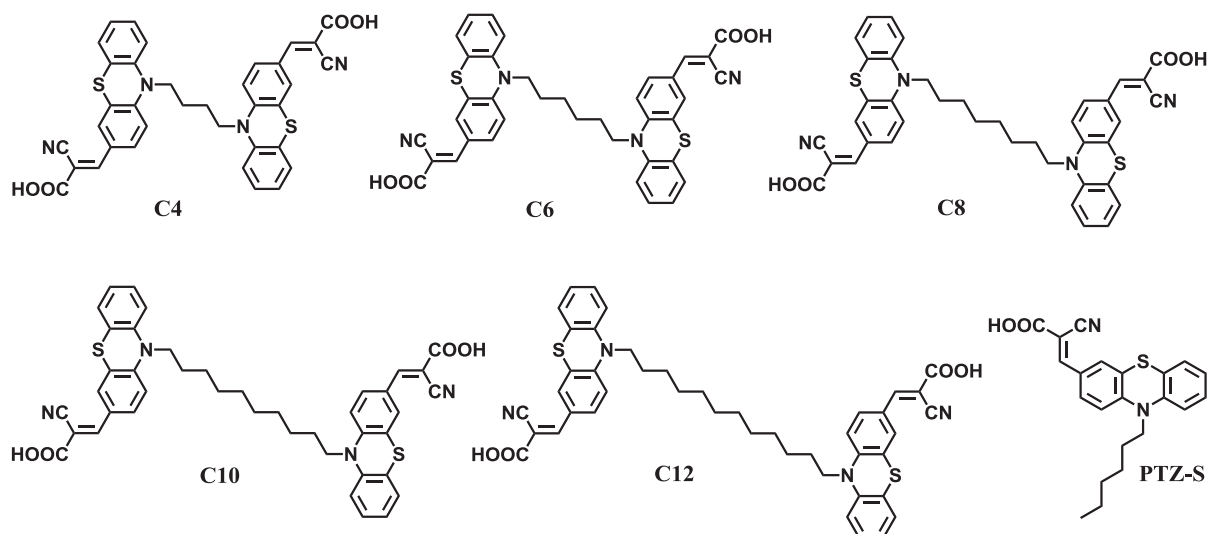


Fig. 1. Chemical structures of the new sensitizers C4–C12 and reference sensitizer PTZ-S.

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