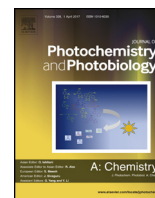




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Invited paper

## Additional donor bridge as a design approach for multi-anchoring dyes for highly efficient dye-sensitized solar cells



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## ABSTRACT

This work presents an approach for designing efficient multi-anchoring dyes for dye-sensitized solar cells by using additional donor as a bridging group between donor-acceptor (D-A) side arms. With triarylamine as the additional donor and phenothiazine-cyanoacrylic acid as the D-A side arm, the multi-anchoring dyes exhibited higher molar extinction coefficients in the intramolecular charge transfer bands, less dye aggregation on the TiO<sub>2</sub> surface, and better DSSC performance than that of the mono-anchoring reference dye. The best cell efficiency of 7.06% was obtained from the di-anchoring dye with two additional donor units **T2P2** showing the largest charge recombination resistance of 99.7 Ω, open circuit voltage of 0.83 V, and short-circuit photocurrent density of 12.72 mA cm<sup>-2</sup>. The improvement in performance of the designed dyes suggests that additional donor is a potential bridging group for efficient multi-anchoring sensitizers.

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### 1. Introduction

Molecular engineering of sensitizers for dye-sensitized solar cells (DSSCs) offers an indispensable tool in an effort of developing better molecular sensitizers for low-cost, environmentally friendly, and highly efficient photovoltaic devices [1,2]. The organic donor- $\pi$  bridge-acceptor (D- $\pi$ -A) structure has recently become a promising design approach for dye molecules because of no use of toxic or expensive metal, simple synthesis, and large structural variation compared with organometallic ruthenium(II)-based dyes [3–5]. Although record efficiencies were achieved by using D- $\pi$ -A dyes [6,7], the long-term stability of DSSCs remains a central issue for the practical use of these devices [8,9]. The D- $\pi$ -A sensitizers with a single binding contact at the TiO<sub>2</sub> surface generally contribute to weak surface adsorption of the dyes that potentially leads to the dye leaching and subsequently the poor long-term stability [10–13]. Using multi-anchoring dyes not only results in stronger bonding to the TiO<sub>2</sub> surface [11,14], but it also provides additional advantages over their mono-anchoring

analogs in terms of light harvesting [15] and electron transfer [11,16–18].

Owing to the long-wavelength absorption and the high absorptivity, most of the reported multi-anchoring dyes gave large photocurrent [10,19]. However, the low photovoltage caused by the shift of TiO<sub>2</sub> band-edge [20], charge recombination [21], and strong molecular interaction of highly  $\pi$ -conjugated molecules [22,23] limits the overall DSSC performance. Thus, various molecular design strategies have been explored to solve the issue [11,17,18,24–27]. Among a number of contributing factors that influence the DSSC performance, the choice of a donor is especially critical for the design of the multi-anchoring sensitizers [28,29]. For example, di-anchoring D(- $\pi$ -A)<sub>2</sub> and tri-anchoring D(- $\pi$ -A)<sub>3</sub> dyes with triarylamine donor frequently showed lower open-circuit voltage ( $V_{oc}$ ) [20,21,30–32], while the phenothiazine-based D(- $\pi$ -A)<sub>2</sub> dyes containing an alkoxyphenyl group as a bulky substituent at the nitrogen atom of the phenothiazine ring showed better performance by suppressing dye aggregation and dark current when compared to their mono-anchoring counterparts and the benchmark N719 [24,25]. The attachment of  $\pi$ -A branches at the  $\pi$  position in the D- $\pi$ (- $\pi$ -A)<sub>2</sub> architecture has been demonstrated to enhance electron injection and also suppress dark current [18]. Nevertheless, such an extension of the  $\pi$ -conjugation further required additional co-adsorbent or a large bulky donor to

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prevent dye aggregation [26]. Moreover, employing the di-anchoring double D- $\pi$ -A sensitizers ((D- $\pi$ -A)<sub>2</sub>) gave the PCE enhancement of 45–94% compared to the corresponding mono-anchoring sensitizer [11,17] which was the result of a cross-shaped geometry of the (D- $\pi$ -A)<sub>2</sub> dye leading to the weak intermolecular interaction. In contrast, the performances of most tri-anchoring dyes were lower than the mono-anchoring analog [30–33].

According to the previous reports on mono-anchoring dyes in DSSCs, the addition of an extra donor (D'), e.g., D'-D- $\pi$ -A, could improve the DSSC performance relative to the D- $\pi$ -A analogs in terms of dye aggregation, charge recombination [31,34], and long-term stability [35,36]. Apart from the donor strength enhancement, a theoretical study also revealed that the presence of an additional secondary donor can be beneficial to further increasing the photocurrent because of the long-range charge shift from the terminal donor D' to the acceptor via a cascade effect [37]. Consistent with these findings, this work presents a new approach for designing multi-anchoring dyes by adding D' at the bridging position among two and three donor side arms. As shown in Fig. 1, the core structure of the designed dyes consists of triarylamine as additional donor (D'), phenothiazine as primary donor (D), and cyanoacrylic acid as acceptor (A). Both donors were selected since their non-planar geometries are known to reduce the molecular aggregation [38–40]. The combination of phenothiazine and arylamine as the double donor unit has been shown to increase light harvesting ability [41–43]. All phenyl groups on triarylamine were capped with electronically neutral methyl groups at the para-position to reduce the reactivity in bromination reaction. The series of the new organic dyes comprises two di-anchoring dyes (TP2 and T2P2) and a tri-anchoring dye (TP3). Their DSSC performances were compared with the mono-anchoring analog, TP. TP2 and T2P2 consisting of three and four donor units, respectively, were designed to investigate the effect of the number of additional donors. Furthermore, the concept of using the double donor in tri-anchoring, as in TP3, was investigated. All synthesized dyes were characterized experimentally and computationally, and their photoelectrochemical and photovoltaic characteristics in the DSSC devices were also studied.

## 2. Results and discussion

### 2.1. Synthesis

All dyes were synthesized according to the reactions shown in Scheme 1. Brominated intermediates (1 and 3a–d) were prepared as described in the Supporting information. Phenothiazine and triarylamine units were used to construct aldehydes 5a–d by Suzuki–Miyaura cross coupling reaction as the key synthetic step.

Phenothiazine unit was synthesized from the reaction of 1 and *n*-BuLi at -78 °C and subsequently with *N*-formylmorpholine to obtain 2 in 67% yield. Bromoarenes 3a–d were converted to the corresponding boronate esters 4a–d by its reaction with bis (pinacolato)diboron in the presence of palladium-Xphos catalytic system. Without a chromatographic purification, the crude products of boronate esters were coupled with 2 to obtain the corresponding aldehydes 5a–d. The aldehydes were reacted with cyanoacetic acid in the presence of NH<sub>4</sub>OAc in acetic acid to give the final dye products TP, TP2, T2P2, and TP3 in high yields. The dye structures were confirmed by NMR and HRMS, and their NMR spectra are shown in Figs. S1–S4 of the Supporting information.

### 2.2. Optical properties

The photophysical properties of all dyes were investigated by UV–vis absorption spectroscopy in chloroform solution and on TiO<sub>2</sub> film. The spectra of dyes are shown in Fig. 2, and the corresponding data are summarized in Table 1. Di- and tri-anchoring dyes showed two separate absorption bands in nearly identical regions as the reference mono-anchoring dye. The bands in high-energy region (<400 nm) correspond to the  $\pi$ - $\pi^*$  transitions of the conjugated backbone, and the low-energy bands (>400 nm) can be assigned to the intramolecular charge transfer (ICT) transitions. The absorption maxima ( $\lambda_{\text{max}}$ ) of the ICT bands varied only in a small range ( $\lambda_{\text{max}}$  467–471 nm) for the multi-anchoring dyes. In addition, the molar extinction coefficients ( $\epsilon$ ) of these ICT bands substantially increased in the order of TP ( $1.37 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), TP2 ( $3.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), and TP3 ( $4.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), which are linearly dependent on the

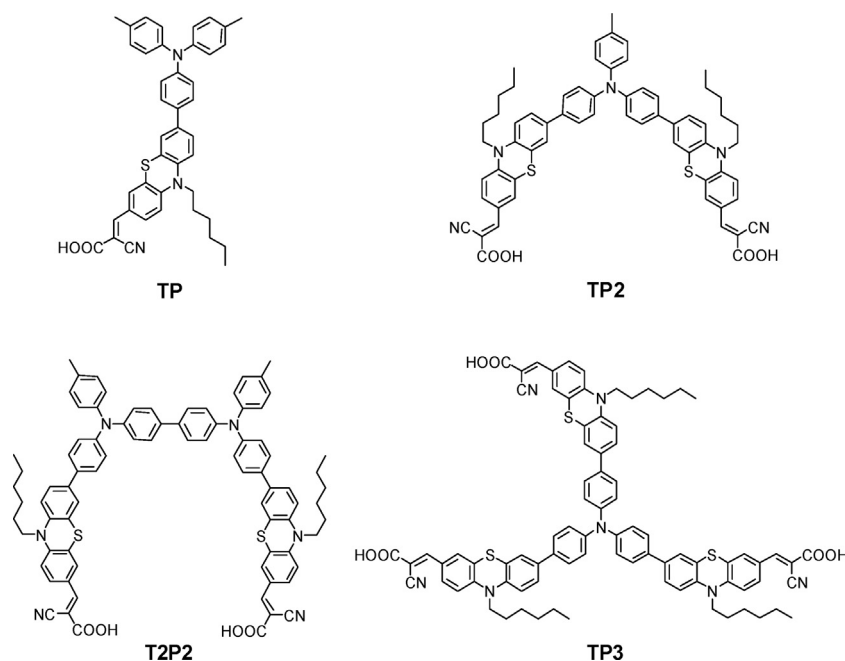


Fig. 1. Molecular structures of di-anchoring (TP2, T2P2), tri-anchoring (TP3) and mono-anchoring (TP) dyes.

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