

# Novel organic dyes based on diarylmethylene-bridged triphenylamine for dye-sensitized solar cells



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## ABSTRACT

Three D- $\pi$ -A type organic dyes, including **TB-1**, **TTB-1** and **TTB-2**, which contained bridged triphenylamine (TPA) donor moieties, were synthesized and characterized for applications in dye-sensitized solar cells (DSSCs). Compared to **TB-1**, the 5-hexyl and 3-hexyl substituted thiophene rings were introduced onto the TPA core in **TTB-1** and **TTB-2**. Their photophysical, electrochemical and photovoltaic properties were investigated. The reference compound **L1** (the triphenylamine counterpart of **TB-1**) was also evaluated for comparison. Compared to **L1**, the bridged triphenylamine based dyes studied showed enhanced performances, suggesting reasonable design of the new dyes. Meanwhile, the investigation of the three bridged TPA dyes demonstrated that by grafting 5-hexyl substituted thiophene onto the bridged TPA, **TTB-1** had a significantly broader absorption spectrum in the UV–vis region, and thereby, its light harvesting ability was remarkably enhanced. Accordingly, the higher incident photon to current conversion efficiency (IPCE) of **TTB-1** indicated a higher short-circuit current. In contrast, the 3-hexyl substituted thiophene in **TTB-2** lead to larger steric hindrance, resulting in lower  $J_{sc}$  value. Similar structure of **TTB-1** and **TTB-2** afforded almost the same  $V_{oc}$ . Therefore, dye **TTB-1** showed the best performance, exhibiting power conversion efficiency of 4.35%, with  $J_{sc}$  of  $8.61 \text{ mA cm}^{-2}$  and  $V_{oc}$  of 704 mV under simulated AM 1.5 irradiation ( $100 \text{ mW cm}^{-2}$ ).

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## 1. Introduction

Dye-sensitized solar cells (DSSCs), which have been considered as one of the most promising and low-cost alternatives to conventional inorganic silicon-based solar cells, have attracted considerable attention since reported by O'Regan and Grätzel in the 1990's [1]. In general, the dye molecules absorb photons, and are activated to their excited states. The excited sensitizer molecules are capable of donating their electrons from the LUMO to the conducting band of  $\text{TiO}_2$ , initiating the subsequent electron transfer processes [2]. The implication is that, the sensitizer plays a crucial role in DSSCs, by directly affecting the light harvesting and

electricity conversion, and ultimately determining the power conversion efficiencies ( $\eta$ ) [3,4]. Up to date, a variety of sensitizers including transition metal-organic complexes [5–7], porphyrins [8,9], phthalocyanines [10], and metal-free organic molecules [11–14] have been studied. In recent years, the metal-free organic dyes have attracted much attention on account of their merits of high molar extinction coefficients, low cost, environment-friendly character and high flexibility of molecular design.

Molecules containing donor- $\pi$ -acceptor (D- $\pi$ -A) moieties are a type of commonly-used organic sensitizers. These D- $\pi$ -A moieties could result in electron push-pull, by allowing efficient intramolecular charge transfer (ICT), as a consequence of which, charge separation and photoelectron injection [15,16] could occur in DSSCs. Specifically, triphenylamine (TPA) represents one of the most studied electron donors, due to (i) its good electron donating property, and (ii) the fact that its oxidized form, namely,  $\text{TPA}^{+\bullet}$ , is a highly stabilized radical cation, so that the charge recombination process could be efficiently prevented [17]. The physical and optical properties of the sensitizers containing TPA could undergo

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further modification, by tuning the covalent structure of TPA moiety. For example, upon introduction of alkoxy and aromatic groups onto TPA, the energy levels of HOMO of the sensitizers could be elevated, leading to a remarkable red-shift of the absorption spectra and thus increasing the light harvesting ability [18–20]. Furthermore, the introduced alkoxy chains and aromatic groups could prevent dye aggregation, significantly improving device performance [21].

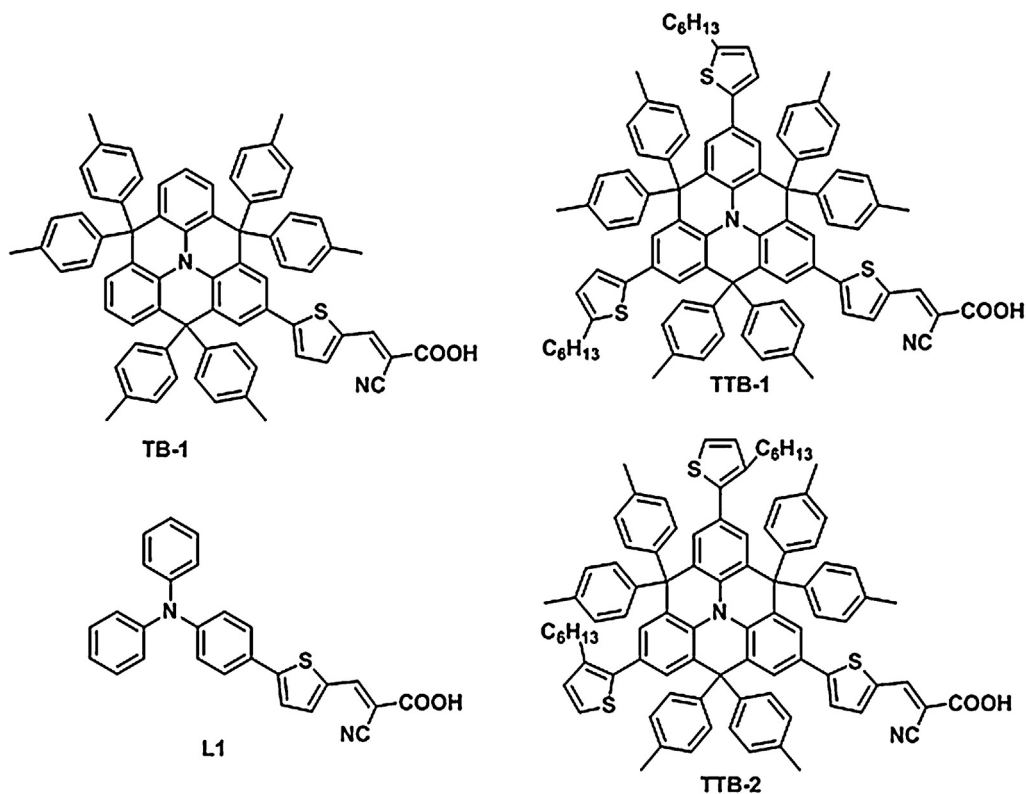
Another approach to modify TPA structures is to introduce bridged triphenylamine. This method is of significance, owing to its distinguished merits that it creates almost planar core structures. When functionalized with bulky substituents, not only could it increase the charge-separation lifetime by the delocalization of the generated radical cation over a planar amine unit, but also inhibit dye aggregation [22,23]. In this regard, bridged triphenylamine has been applied as a donor unit for metal-free organic sensitizers and considerable performances were achieved [24,25]. Whereas, the investigation of bridged TPA applied in DSSCs is still very rare to date. To further explore the possibility of the bridged-TPA as sensitizers, in this paper we report the design, synthesis and application of three new organic dyes **TB-1**, **TTB-1** and **TTB-2**. They are composed of diarylmethylene-bridged triphenylamine, thiophene and cyanoarlic acid, which function as electron donor,  $\pi$ -spacer and electron acceptor, respectively. In contrast to **TB-1**, both **TTB-1** and **TTB-2** contain thiophene rings with hexyl chains at the 5- or 3-position on the bridged TPA core, respectively. At the same time, dye **L1** with triphenylamine as the donor and thiophene as the  $\pi$ -spacer was also evaluated as the reference compound. Their photophysical properties and photovoltaic performances were investigated. Under AM 1.5G irradiation with 100 mW/cm<sup>2</sup> simulated sunlight, the bridged TPA based dye **TB-1** showed better power conversion efficiency compared to **L1**. And the 5-hexyl substituted **TTB-1** shows the highest efficiency of 4.35% (Scheme 1).

## 2. Experimental details

All starting materials were purchased from commercial suppliers (Sigma–Aldrich, J&K Scientific, and Energy Chemical) and used without further purification. Tetrahydrofuran (THF) for synthesis was freshly distilled over Na-K alloy under argon atmosphere prior to use. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a BRUKER AVANCE III 600 MHz NMR Instrument in CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub>, using tetramethylsilane as an internal reference. MALDI-TOF was performed on a Bruker Autoflex instrument, using 1,8,9-trihydroxyanthracene as a matrix. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. The HRMS was measured on Thermo Scientific Q Exactive instrument. UV–vis absorption spectra were recorded on a spectrophotometer (UV-2450, Shimadzu). Electrochemical experiments were performed using a CH Instruments electrochemical workstation (model 660A). The experiments were carried out in CH<sub>2</sub>Cl<sub>2</sub> under Ar atmosphere containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as a supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup>. The potentials are quoted against the ferrocene internal standard.

### 2.1. Synthesis

The general synthetic routes for the intermediates and the final compounds are outlined in Scheme 2. 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**), 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) and bridged triphenylamine were synthesized as described in the literature [26–28]. The intermediate **4** was synthesized by palladium-catalyzed Suzuki coupling reaction of compound **3** and 5-formyl-2-thiophene-boronic acid. **6** and **7** were synthesized by palladium-catalyzed Suzuki coupling reaction of compound **5** and the corresponding substrates. The final compounds were



**Scheme 1.** Chemical structures of the reference compound **L1** and the diarylmethylene-bridged triphenylamine based dyes **TB-1**, **TTB-1** and **TTB-2**.

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