



## Dual-channel anchorable organic dye with triphenylamine-based core bridge unit for dye-sensitized solar cells



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### ABSTRACT

Dual-channel (DC) anchorable organic dye based on an acceptor– $\pi$ –donor–core bridge donor–donor– $\pi$ –acceptor structural motif, was synthesized and used as sensitizer for dye sensitized solar cells (DSSCs). DC dye linked the two donors using a core bridge donor such as triphenylamine unit, which makes two channels maintaining a particular distance ( $>4 \text{ \AA}$ ). The inter-planar DC5 exhibited dye aggregation and charge recombination due to strongly intermolecular  $\pi$ – $\pi$  stacking between the channels of DC dyes adsorbed on the  $\text{TiO}_2$  surface. As a result, a solar cell based on DC5 with a hole conductor coadsorbent of HC-A1 showed better photovoltaic performance with a  $J_{sc}$  of  $8.90 \text{ mA cm}^{-2}$ , a  $V_{oc}$  of 0.70 V, and an FF of 0.77, corresponding to an overall conversion efficiency ( $\eta$ ) of 4.80%.

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) are promising hybrid/organic photovoltaic devices for high efficiency, low cost solar energy conversion [1–4]. In these cells, the sensitizer is one of the key components for high power-conversion efficiency. Recently, interest in metal-free organic dyes as an alternative to noble metal complexes has increased due to their many advantages, such as the diversity of molecular structures, high molar extinction coefficients, simple synthesis, as well as low cost and negligible environmental issues [5–8]. By employing a combination of a zinc porphyrin dye (YD2-o-C8) and an organic dye (Y123) in conjunction with a tris(2,2'-bipyridine) cobalt(II/III) redox couple, Grätzel et al. reported a 12.3% efficiency DSSCs [9]. Many organic dyes based on the donor–( $\pi$ -spacer)–acceptor (D– $\pi$ –A) system, exhibiting relatively high DSSCs performance, have so far been designed and developed. A single D– $\pi$ –A sensitizer having a rod-like configuration may cause undesirable dye aggregation and charge recombination [10–13]. The intermolecular  $\pi$ – $\pi$  stacking of dye molecules can lead to

self-quenching of excited states and hence inefficient electron injection [14]. A common structural strategy for suppression of dye aggregation is the introduction of a bulky group to the donor part [15,16]. Another unique approach is bridging of two chromophores into a spiro configuration similar to Ru-sensitizers [17]. To enhance optical density and binding strength of the dye onto  $\text{TiO}_2$ , of particular interest is the synthesis of a dianchoring dye, which has been found to enhance the photocurrent due to the extended  $\pi$ -conjugated framework and higher molar extinction coefficient. Several dianchoring organic dyes have been synthesized for use in DSSCs, and have demonstrated better cell performance than single D– $\pi$ –A sensitizers with an improved photoresponse, photocurrent and stability [18–22].

In this study, we present an extension of dianchoring organic sensitizer, with the aim of further expanding the possibility of improving the optical and energetic properties of the sensitizers. The new approach, based on the acceptor– $\pi$ –donor–core bridge donor–donor– $\pi$ –acceptor structural motif, includes the use of two donors, two acceptors and a core bridge donor as a spacer. We have adapted diphenylamine as a donor group by using a core bridge donor such as triphenylamine units. The dual-channel anchorable organic dye which contained two separate light-harvesting units and two anchoring group in one molecule has higher molar extinction coefficient

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and increases the binding strength of dye on TiO<sub>2</sub> film. Also, the hexyloxy group was introduced into the triphenylamine moiety for increase the electron-donating ability and decrease the dye aggregation, charge recombination. For comparison, the photophysical properties and photovoltaic performances of a single D-π-A structured D21L6 were also studied (see Scheme 1, Fig. 1, Tables 1 and 2).

## 2. Experimental

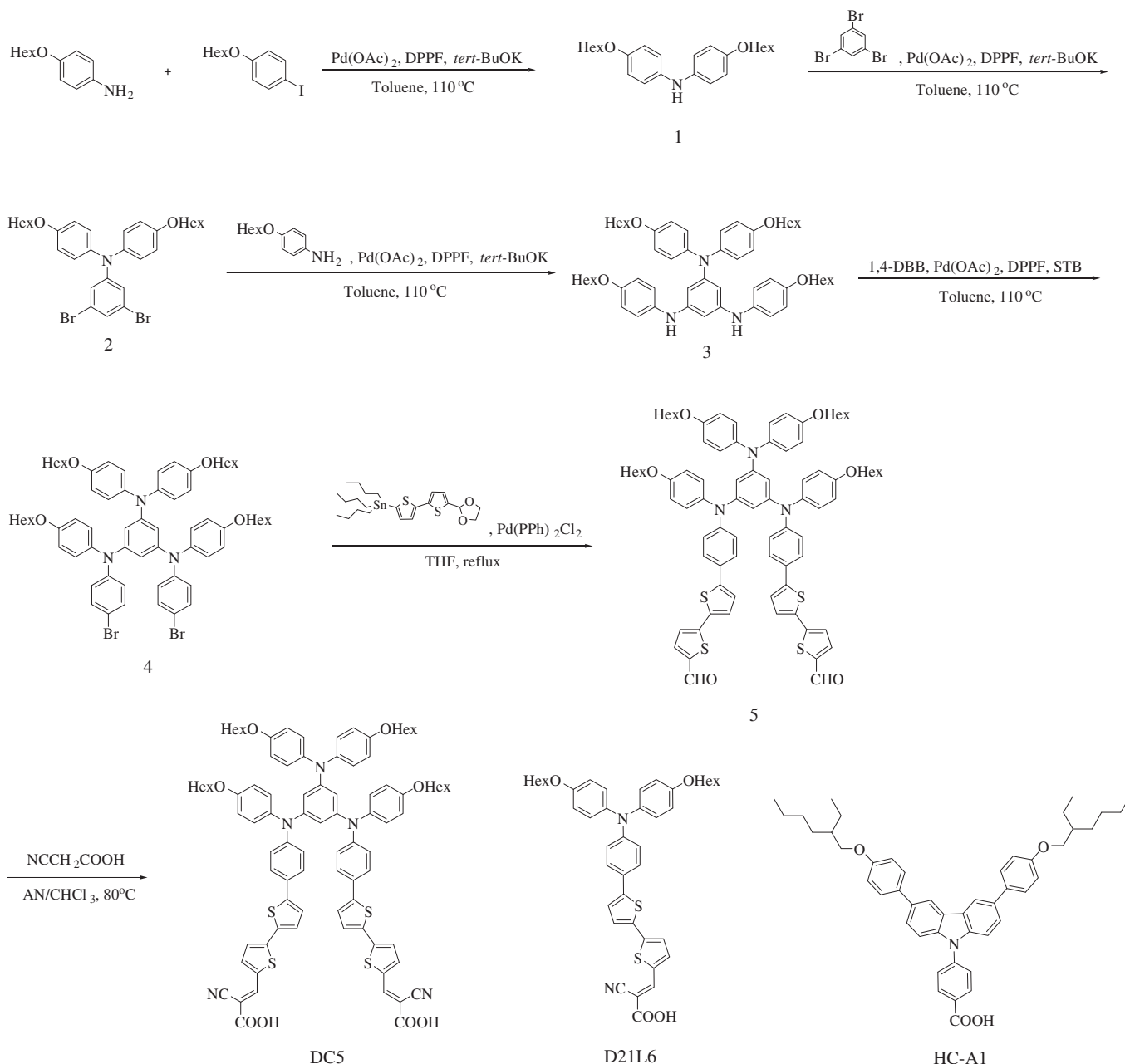
### 2.1. Materials

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Aldrich. (5'-(1,3-Dioxolan-2-yl)-2,2'-bithiophen-5-

yl)tributyl stannane [23] and D21L6 [24] were synthesized by following the same procedures as described previously.

### 2.2. Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature with Varian Oxford 300 spectrometers and chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. FTIR spectra were taken on a JASCO, 4200 + ATR Pro-450-S spectrophotometer. UV–visible absorption spectra were obtained in THF on a Shimadzu UV-2401PC spectrophotometer. Cyclic voltammetry was carried out with a Versa STAT3 (AMETEK). A three-electrode system was used and consisted of a reference electrode (Ag/AgCl), a working electrode, and a platinum wire electrode. The



**Scheme 1.** Chemical structures and synthesis of DC5 dye.

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