



## Novel organic dyes incorporating a carbazole or dendritic 3,6-diiodocarbazole unit for efficient dye-sensitized solar cells



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### ABSTRACT

Four organic photosensitizers incorporating a carbazole or 3,6-diiodocarbazole unit as the electron donor, a benzene/thiophene or oligothiophene moiety as the conjugated spacer, and 2-cyanoacrylic acid as the electron acceptor have been synthesized. The photovoltaic performance data are quite sensitive to the structural modification of sensitizer. The introduction of the benzene/thiophene linker benefits from lower tendency to aggregate, but disfavors the electron transport between donor and acceptor. The addition of a thiophene unit in the bridge efficiently red-shifts the absorption response, however, organic dyes have some  $\pi$ – $\pi$  aggregation. Incorporation of 3,6-diiodocarbazole as a dendritic donor unit not only enhances the molar extinction coefficients of the absorption but also suppresses the charge recombination with electrolyte.

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO<sub>2</sub> have attracted significant attention as low-cost photovoltaic devices due to their high conversion efficiencies over 11% in standard air mass 1.5 and good stability [1]. In these cells as one of the key components ruthenium dyes are used as light absorbers. But the high cost of ruthenium, the necessity of purification treatments, and the low molar extinction coefficients make the research on alternative, metal-free organic dyes appealing for their application in large DSSC modules [2]. Organic photosensitizers have the advantage of high extinction coefficients in the visible region [3]. Also, the position and intensity of the charge transfer transition in organic dyes can be tuned by simple structural modifications such as variation of donor strength and nature of the conjugation pathway [3b]. Therefore, enormous progress has been made in this field, and several organic photosensitizers based on coumarin [4],

indoline [5], and triphenylamine [6] derivatives have been developed as promising candidates with the power conversion efficiency closing to ruthenium dyes [3b,7]. Although organic photosensitizers exhibit excellent spectral properties, they tend to form aggregates on the semiconductor surface, resulting in self-quenching of the dye excited state. Another disadvantages of organic photosensitizers are low long-term stability and easy interfacial recombination dynamics, thus leading to low open-circuit photovoltage. Many efforts have been made to design efficient organic photosensitizers through structural modifications in order to prevent the aggregation of dyes and to diminish the charge recombination between the electrons on TiO<sub>2</sub> film and acceptors [3b,8]. A successful approach was achieved by introducing more donor segments to the primary donor, thereby forming donor-donor- $\pi$  bridge-acceptor (D-D- $\pi$ -A) structures. Compared with the D- $\pi$ -A structure constructed by extending  $\pi$ -conjugated bonding bridges, D-D- $\pi$ -A dyes benefit from lower tendency to aggregate and better thermo-stability, and meanwhile their absorption regions can be extended and molar extinction coefficients can be enhanced. Tian et al. has reported a series of D-D- $\pi$ -A structural organic dyes incorporating several donor groups into the triphenylamine framework with starburst configuration, resulting in the red-shift

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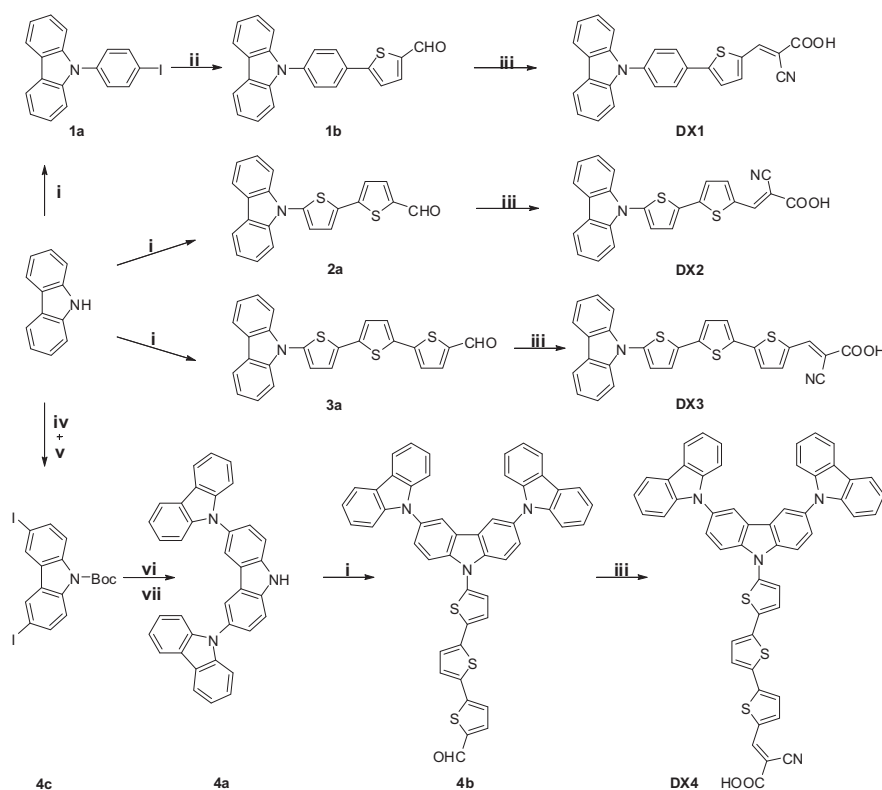
in absorption and the suppression of charge recombination with electrolyte [9].

In this work, we report a novel class of organic photosensitizers, containing carbazole or carbazole dendrimer donors and cyanoacrylic acid acceptors (**DX1–DX4**). They are linked via a  $\pi$ -bridge constituted by benzene/thiophene or oligothiophene. Carbazole is a common heterocyclic compound with interesting photo- and electro-chemistries [10], and it is known as an OPC [11] (organic photo conductor) or a hole-transporting material [12]. The incorporation of hole-conductors of carbazole moieties into organic dyes as electron donors have been proved to exhibit supersensitized effects by retarding interfacial charge-recombination dynamics and thus achieving long-lived photoinduced charge separation [13]. Moreover, the dendritic carbazole, which has a rigid and highly twisted starburst structure, shows unique functions in several devices or systems that involve electron transfer [14]. Use of the dendritic carbazole donor could be not only beneficial to high molar extinction coefficients of the absorption but also helps to suppress dark current upon appropriate incorporation of D-D- $\pi$ -A structure. We therefore set out to synthesize a novel dye (**DX4**) consisting of a 3,6-Diiodocarbazole donor, a 2-cyanoacrylic acid acceptor, and an oligothiophene spacer at the first time. With these dyes as the photosensitizers, we fabricated corresponding DSSCs, and found that the electro-optical properties of **DX4** relative with **DX1–3** show significant improvements which manifests in the overall efficiency for the DSSCs.

## 2. Experimental section

### 2.1. General methods

All reagents were obtained from commercial sources and used as received. Tetrahydrofuran (THF), methylbenzene (MB) and chloroform ( $\text{CHCl}_3$ ) was purified using MBRAUN MB SPS-800 system. Other solvents were dried over sodium or calcium hydrides and distilled before used.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Mercury-Plus 300FT-NMR spectrometer in  $\text{DMSO}-d_6$  or  $\text{CDCl}_3$ , respectively. IR spectra were obtained on a Thermo Scientific Nicolet 330 infrared spectrophotometer. MS data were obtained using an LCQ DECA XP liquid chromatographymass spectrometry. UV–vis absorption spectra were measured using a Shimadzu UV-2450 spectrometer. Emission spectra were measured using Shimadzu RF-5301PC spectrometer. Cyclic voltammograms (CV) were recorded using a CHI 832 electrochemical analyzer with FTO/ $\text{TiO}_2$ /Dye as working electrode, Ag/AgCl as reference electrode, Pt wire as counter electrode. CVs were measured with 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) as a supporting electrolyte in  $\text{CH}_2\text{Cl}_2$ . Scan rate was kept as  $50 \text{ mV s}^{-1}$  for all compounds. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of triarylamine organic dyes obtained from the theoretical calculations were coupled with the redox potential obtained from the CV measurements as shown in main text. **4a** [14] and **4c** [15] were synthesized according to



(i)  $\text{Cu}$ ,  $\text{K}_2\text{CO}_3$ , 18-Crown-6, 1,2-dichlorobenzene; (ii)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{NaCO}_3$ ,  $\text{THF}+\text{H}_2\text{O}$ ;  
 (iii) piperidine,  $\text{CHCl}_3+\text{CH}_3\text{CN}$ ; (iv)  $\text{KI}$ ,  $\text{KIO}_3$ ,  $\text{HAc}$ ; (v) DMAP, acetone (vi)  $\text{CuI}$ ,  
 $\text{K}_3\text{PO}_4$ , dioxane; (vii) TFA, water, anisole and toluene.

**Scheme 1.** Synthesis of carbazole -based dyes **DX1**, **DX2**, **DX3**, and **DX4**.

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