



## Novel carbazole based sensitizers for efficient dye-sensitized solar cells: Role of the hexyl chain



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### ABSTRACT

Four novel D-D- $\pi$ -A type organic dyes (**DWH1–DWH4**) were designed and synthesized, in which 3,6-bis(thiophene or hexylthiophene)-disubstituted carbazole moieties were used as the electron donor, bithiophene units or their derivatives as the  $\pi$ -conjugated bridge, and a cyanoacrylic acid group as the electron acceptor. The photovoltaic performance data indicate that the tuning of the  $J_{sc}$  and  $V_{oc}$  values can be conveniently accomplished by incorporation of long alkyl chains into sensitizer, which not only improves the molar extinction coefficients of the absorption and enhances the solubility but also increases the electron lifetime by leading to an effective spatial separation of the charges.

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention because of their capability to convert solar light into electricity at low cost [1]. One of the key material issues in DSSCs is the photosensitizer, which plays a crucial role in getting a higher solar-to-electricity conversion efficiency. To date, overall conversion efficiencies of up to 12% [2], 11% [3], and 12% [4] were achieved from liquid DSSCs by employing zinc, ruthenium complex, and pure organic dyes, respectively. Organic dyes have many advantages, such as high molar extinction coefficient, simple structural modification, and lower cost than Ru complexes. Many organic dyes, including coumarin [5], indoline [6], triphenylamine [7], and carbazole derivatives [8], have been designed and developed. However, the use of organic dyes for DSSCs has a limitation because they tend to form aggregates on the semiconductor surface, resulting in self-quenching of the dye excited state [9]. Therefore, engineering of organic sensitizer with a reduced tendency toward

aggregation is paramount. A successful approach was introduced by incorporating some alkyl chains into the organic framework, which not only suppresses aggregate formation but also enhances the molar extinction coefficient of the organic sensitizer [10]. Another strategy is to incorporate more donor segments to the primary donor, thereby forming donor-donor- $\pi$  bridge-acceptor (D-D- $\pi$ -A) structures which benefit from lower tendency to aggregate [8b,11]. We have prepared a series of D-D- $\pi$ -A type organic sensitizers with duplex starburst triphenylamine and carbazole donors, achieving a strikingly high efficiency of 10% in liquid DSSCs [11i].

On the basis of the above strategies, we designed and synthesized four D-D- $\pi$ -A type organic dyes, that contain 3,6-bis(thiophene or hexylthiophene)-substituted carbazole as donor and cyanoacrylic acid as electron acceptor. These two moieties are bridged by bithiophene, thiophene and 3,4-ethylenedioxythiophene (EDOT), or 2-hexylthiophene and EDOT, to form four novel organic dyes, namely **DWH1**, **DWH2**, **DWH3**, and **DWH4**. The photophysical and electrochemical properties and device performance of the sensitizers were systematically investigated. By introducing the hexyl chain in thiophene donor and linker, the molar extinction coefficients of these dyes in visible absorption band were increased and the prevention of dye

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aggregates on the semiconductor was enhanced, which contributed to an increase in the short-circuit current. On the other hand, the long alkyl chains on the thiophene donor and bridge tend to form a packed layer preventing the  $I_3^-$  or cations from approaching the  $TiO_2$ , which can improve the open-circuit voltage.

## 2. Experimental section

### 2.1. Materials and reagents

Acetonitrile, chloroform, and 1,2-dichlorobenzene were dried over a molecular sieve without normal pressure distillation. Solvents used in the Suzuki coupling reaction were degassed by  $N_2$  bubbling for 20 min. Optically transparent fluorine doped  $SnO_2$  (FTO) conducting glass was purchased from Nippon Sheet Glass, Japan (15 U per square), and cleaned by a standard procedure. All other chemicals and reagents were used as received from commercial sources without further purification. **1**, **2b**, **3a**, **b**, **DWH1-4-CHO**, and **DWH1-4** were prepared according to the procedures listed in the [Supporting Information](#).

### 2.2. Characterization

$^1H$  and  $^{13}C$  nuclear magnetic resonance (NMR) spectroscopy was performed on a BRUKER 400 MHz with tetramethylsilane (TMS) as internal standard. Elemental analyses were carried out with an Elementar Vario EL Cube instrument. Mass spectral data were obtained on an ultrafleX-treme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). The absorption spectra of the dyes (in solution and adsorbed on  $TiO_2$  films) were observed with a Shimadzu UV-2450 spectrometer and fluorescence spectra were measured with a Hitachi F-4500 spectrometer. Cyclic voltammogram (CV) curves were obtained with a CHI 832 electrochemical analyzer using a normal three-electrode cell with dyesensitized photoanode as working electrode, a Pt wire counter electrode, and a regular Ag/AgCl reference electrode in saturated KCl solution which was calibrated with ferrocene/ferrocenium as external reference. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in  $CHCl_3$ .

### 2.3. Fabrication of cells

The anatase  $TiO_2$  nanoparticles were synthesized according to our previous literature [12]. First, the  $Ti(OBu)_4$  (10 mL) was added to the ethanol (20 mL) under stirring for 10 min. Then a mixture of deionized water (50 mL) and acetic acid (18 mL) was added to the solution with vigorous stirring for 1 h. The solution was moved to an autoclave and heated at 200 °C for 12 h. Finally, the precipitations were washed with deionized water and ethanol for several times, respectively. The white powder was obtained after drying in air. The as-prepared  $TiO_2$  nanoparticles were anatase crystals with diameters of about 20 nm, as confirmed by SEM, TEM, and XRD. The prepared  $TiO_2$  powder (1.0 g) was ground for 40 min in the mixture of acetic acid (0.2 mL), ethanol (8.0 mL), ethyl cellulose (0.5 g), and terpineol (3.0 g) to form a slurry, and then the slurry was sonicated for 5 min to obtain a viscous white  $TiO_2$  paste. The  $TiO_2$  paste was then screen-printed onto the surface of FTO coated glass forming photoanode film. The thickness of films can be easily controlled through repeating screen-printing times. Afterward, a programmed heating process was carried out to remove the organic substances in the film. The as-prepared  $TiO_2$  films (~15  $\mu m$ ) were soaked in a 0.04 M aqueous solution of  $TiCl_4$  for 30 min at 70 °C and then sintered at 520 °C for 30 min. After cooling to 80 °C, the  $TiO_2$  electrodes were immersed into 0.3 mM optimal organic solution ( $CHCl_3/ACN/tBuOH = 1/2/2$ ) of the dyes and kept at

room temperature for 6 h for cells with liquid electrolyte and for 12 h for cells with gel electrolyte, respectively. And then the prepared  $TiO_2$  working electrodes were sandwiched together with Pt-counter electrode. The active area of the dye-coated  $TiO_2$  film was 0.16  $cm^2$ . The electrolyte was injected into the inter-electrode space. The electrolyte solution is composed of 0.6 M 1-methyl-3-propyl imidazolium iodide (PMII), 0.03 M  $I_2$ , 0.05 M LiI, 0.1 M guanidinium thiocyanate (GuSCN), and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile and valeronitrile (85:15, v/v).

### 2.4. Characterization of cells

The  $TiO_2$  film thickness and active area of the dye-coated  $TiO_2$  film were measured by using a profilometer (Ambios, XP-1). The current-density voltage (J-V) curves of the DSSCs were recorded by using a Keithley 2400 source meter under the illumination of AM 1.5 G simulated solar light. IPCEs of DSSCs were measured on the basis of a Spectral Products DK240 monochromator. Electrochemical impedance spectroscopy (EIS) was measured using an electrochemical workstation (ZAHNER, Zennium) with a frequency response analyzer at a bias potential of -800 mV in the dark with a frequency ranging from 10 mHz to 1 MHz. The dye-adsorbed amounts on the  $TiO_2$  film were measured using a Shimadzu UV-2450 spectrometer. Intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) measurements were conducted using electrochemical workstation (ZAHNER, Zennium) and were performed under a modulated LED light (457 nm) driven by a source supply (ZAHNER, PP210). The illumination intensity ranged from 30 to 150  $mW cm^{-2}$ . The light intensity modulation was 20% of the base light intensity over the frequency range of  $10^{-1}$ – $10^3$  Hz.

## 3. Results and discussion

### 3.1. Synthesis

The synthetic approach of **DWH1-4** is outlined in [Scheme 1](#). The dyes were conveniently synthesized from **1** [8a] via a three-step process involving Suzuki coupling reaction, phase transfer catalyzed N-alkylation, followed by Knoevenagel condensation of aldehydes with cyanoacetic acid. **3a** (or **3b**) was prepared by Suzuki coupling reaction of **1** and **2a** (or **2b** [13]) in the presence of  $K_3PO_4$  as base and  $Pd(PPh_3)_4$  as catalyst followed by Boc deprotection of the amine group. Then, **3a** and **4a** [8a], **3b** and **4a**, **3b** and **4b** [14], or **3b** and **4c** [11i] were reacted by the N-arylation reaction to produce **DWH1-CHO**, **DWH2-CHO**, **DWH3-CHO**, or **DWH4-CHO**, and finally **DWH1-4** were obtained by Knoevenagel condensation, which can convert carbaldehydes to cyanoacrylic acids.

### 3.2. Photophysical properties

The UV–Vis absorption spectra of sensitizers **DWH1–DWH4** are shown in [Fig. 1](#), and their photophysical data are listed in [Table 1](#). **DWH2** has a higher molar extinction coefficient at 250–525 nm than **DWH1**, owing to the introduction of long hexyl chains on the thiophene donor. **DWH3** exhibits an improved red shift of its absorption spectrum and larger molar extinction coefficient in the range of 420–550 nm when compared with **DWH2**. The observation could be interpreted in terms of the stronger electron donating capability of EDOT than thiophene linker [11h]. The absorption bands at 350–550 nm of **DWH4** are more intense and broader than those of **DWH3**, which could be ascribed to the existence of a hexyl group in the conjugated system. The results imply that the electron-donating hexyl chains at thiophene donor and bridge in the dye contribute to its light-harvesting ability. Thus, **DWH4**

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