



# A co-sensitized approach to efficiently fill the absorption valley, avoid dye aggregation and reduce the charge recombination



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## ABSTRACT

Compared with the development of novel organic dyes, co-sensitization is a much more convenient way to achieve highly efficient dye-sensitized solar cells (DSSCs). Here, two simple donor-( $\pi$  conjugated spacer)-acceptor dyes, in which hexyloxy-substituted phenyl as an electron donor, cyanoacrylic acid as the electron acceptor and different spacers thiophene (**LD03**) or furan (**LD04**) as the  $\pi$ -linkers, were designed and synthesized as co-sensitizers for **N719**-based DSSCs. The photophysical, electrochemical, photovoltaic performances and electrochemical impedance spectroscopy of these DSSCs were investigated in detail. When compared to the DSSCs fabricated from individual **N719**, the co-sensitized DSSCs (**N719+LD03** and **N719+LD04**) showed significantly enhanced power conversion efficiencies (PCEs), short-circuit photocurrent density ( $J_{sc}$ ) and open circuit voltage ( $V_{oc}$ ) simultaneously, which owing to the co-sensitizers could effectively overcome the competitive light absorption by  $I_3^-$  in the electrolyte, avoid dye aggregation and reduce the charge recombination. Consequently, the co-sensitized DSSC (**N719+LD04**) gave the highest PCE of 8.955% ( $J_{sc}$  = 17.628 mA cm<sup>-2</sup>,  $V_{oc}$  = 0.758 V and fill factor = 0.670), exhibiting an improvement of 13.412% compared to the device sensitized with **N719** alone (PCE = 7.896%) under illumination (AM 1.5G, 100 mW cm<sup>-2</sup>).

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## 1. Introduction

As a kind of prospective photovoltaic devices, dye-sensitized solar cells (DSSCs) have been intensively investigated since DSSCs were reported for the first time by Grätzel and co-workers in 1991 [1]. Generally, a conventional DSSC contains three components: a dye-sensitized TiO<sub>2</sub> photoanode, a redox electrolyte/hole transporter and a counter electrode [2]. Upon irradiation, light is absorbed by sensitizer, which creates a high-energy state and results in electron injection from the photoexcited sensitizer into the conduction band (CB) of TiO<sub>2</sub>; the oxidized sensitizer is subsequently backed to the ground state by electron transfer from redox couple. As a key component of DSSCs, the sensitizer plays an important role in light harvesting, electron injection as well as the device stability [3]. To date, many efforts have been devoted to develop new and highly efficient sensitizers, which can be divided into two general classes: metal-complex sensitizers and metal-free organic sensitizers [4–18]. For DSSCs using single sensitizer, the

record high power conversion efficiencies (PCEs) over 13% [15], 11.5% [16] and 12.5% [17], have been achieved for zinc-porphyrin, ruthenium complex and metal-free organic sensitizers, respectively, which were lower than that of perovskite solar cells. Perovskite solar cells, as a new class of thin film solid state solar cells, have received widespread attention in recent years [19–21]. The highest certified efficiency over 20% was recently reported for a solar cell based on formamidinium lead iodide, which was fabricated by an intramolecular exchange process [22]. However, there are two key issues for the application of perovskite solar cell in industry, toxicity and device stability. Meanwhile, the perovskite materials (typically CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>) are susceptible to the following factors: oxygen and moisture, UV light, solution process (solvents, solutes, additives) and temperature [23]. Therefore, significant degradation of organic-inorganic halide perovskite materials is typically observed under ambient conditions. Compared with perovskite solar cells, the DSSCs have unique advantages, such as low production cost, excellent stability, environmental friendly and easy of fabrication [24–26]. However, it is necessary to further improve the PCEs to enable successful commercialization. Many attempts, such as innovation of photo-active materials and photo-anodes, utilization of new electrolytes

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and counter electrodes, co-sensitization of two or multiple dyes, have been conducted to improve the photovoltaic efficiencies of DSSCs [27–32].

Among various approaches, co-sensitization is an effective strategy to enhance photovoltaic properties of DSSCs through combination of two or more dyes on semiconductor film together. This strategy usually can improve the light harvesting ability both in the absorption intensity and absorption breadth so as to increase photocurrents of the devices. To date, series of co-sensitization systems have been proposed and demonstrated improved photovoltaic performances with respect to DSSCs based on individual sensitizer [33–38]. It is worth noting that the three record-breaking DSSCs are related to the strategy of co-sensitization. In 2012, a record efficiency (11.4%) was achieved for DSSCs based on a co-sensitized system of metal-free dye and black dye by the work of Han and coworkers [33]. Subsequently, a new record high PCE of 12.3% was reported with co-sensitization of a porphyrin dye **YD2-o-C8** and a metal-free dye **Y123** [37]. In 2015, an impressive photovoltaic performance was achieved 14.7% with collaborative sensitization by silyl-anchor and carboxy-anchor dyes [39]. To the best of our knowledge, the PCE of 14.7% represented the highest PCE value reported to date for DSSCs. Overall, these results indicate that there is still room for improving photovoltaic performance by co-sensitization. According to the previous report, the ideal candidate for a co-sensitizer should have following characteristics: (i) it should have a large molar extinction coefficient ( $\epsilon$ ) in the infrared region or around 400 nm to recover the dip in the incident photon-to-current conversion efficiency (IPCE) spectra induced by  $I_3^-$ ; (ii) the structure of the co-sensitizer should be suitable for avoiding competitive adsorption with main sensitizer while effectively suppressing the aggregation of dyes on the  $TiO_2$  surface; (iii) it should be able to reduce the recombination of electrons in the  $TiO_2$  film with  $I_3^-$  by the formation of a compacted molecule monolayer covering the bare  $TiO_2$  surface [33].

Based on the above requirements, we reported the synthesis and characterization of two simple donor-( $\pi$  conjugated spacer)-acceptor type dyes containing hexyloxy-substituted phenyl as electron-donating unit, thiophene or furan as  $\pi$ -spacer, cyanoacrylic acid group as acceptor and anchor, coded as **LD03** and **LD04**, respectively, which were applied in DSSCs by co-sensitization with **N719**. The chemical structure of two co-sensitizers is shown in Fig. 1. It was found that the short-circuit photocurrent density ( $J_{sc}$ ) and open circuit voltage ( $V_{oc}$ ) of the co-sensitized DSSCs (**N719**+**LD03** and **N719**+**LD04**) were significantly enhanced relative to the DSSC sensitized with individual **N719**, resulting in impressively improved photovoltaic performances. Consequently, the co-sensitized DSSC based on **LD04** with **N719** gave the highest PCE of 8.955%, exhibiting an improvement of 13.412% compared to

the device sensitized with **N719** alone (PCE = 7.896%) under the same conditions.

## 2. Experimental section

### 2.1. Materials and reagents

The starting materials 4-hexyloxyphenylboronic acid, 5-bromothiophene-2-carbaldehyde and 5-bromo-furan-2-carbaldehyde were purchased from Aladdin. The  $TiO_2$  electrodes and electrolyte solution (DHS-Et23) were achieved from Dalian Heptachroma Solar Tech, Co., Ltd., China. The solvents (methanol and tetrahydrofuran) were dried by standard procedures. All other solvents and chemicals obtained from commercial sources, and used as received without further purification.

### 2.2. Characterization

NMR spectra were obtained with a Brücker AM 400 spectrometer (relative to TMS). High resolution mass spectra (HRMS) were determined with a Waters ESI mass spectrometer. The UV–vis absorption spectra of the dyes either in butanol-acetonitrile (1/1, v/v) solution or on the adsorbed  $TiO_2$  films (individual sensitizer and co-sensitizers) were measured by HITACHI (model U-2910) UV–vis spectrophotometer. Emission spectra were performed using a HITACHI (model F-4600) spectrophotometer. Cyclic voltammetry (CV) experiments were performed in *N,N*-dimethylformamide ( $5 \times 10^{-4}$  M) at a scan rate of  $10 \text{ mV s}^{-1}$  with a three electrode configuration consisting of a Pt wire counter electrode, a Ag/AgCl (saturated KCl) reference electrode and a Pt disk working electrode, using 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte.

### 2.3. Fabrication of DSSCs

The commercial  $TiO_2$  electrodes were sintered at 500 °C for 30 min in an air atmosphere prior to use. After cooling down to around 80 °C, the  $TiO_2$  electrodes were immersed in a dye bath containing 0.2 mM **LD03**, **LD04** and **N719** in solution butanol-acetonitrile (1/1, v/v), then kept at room temperature for 15 h in the dark. Afterward, the dye-adsorbed  $TiO_2$  electrodes were rinsed with ethanol to get rid of the excess dyes and dried in air flow. Typically, co-sensitized electrode was immersed in a solution (0.2 mM **N719** in butanol-acetonitrile (1/1, v/v)) for 15 h and then washed with ethanol. It was further immersed in a solution (0.2 mM **LD03** or 0.2 mM **LD04** in butanol-acetonitrile (1/1, v/v)) for 3 h and then washed with ethanol. The final process for the fabrication of the DSSCs was performed by assembling the dye-adsorbed  $TiO_2$  electrodes and Pt counter electrodes with a 25  $\mu\text{m}$  thick thermoplastic Surlyn frame. An electrolyte solution was injected into interlayer between two electrodes through a hole which was then sealed with thermoplastic Surlyn covers and a glass coverslip.

### 2.4. Photovoltaic characterization

The current-density voltage (*J*-*V*) curves of the DSSCs were measured using an electrochemical workstation (CHI 660C, Shanghai Chenhua) under AM 1.5G simulated solar light (100 mW  $\text{cm}^{-2}$ ) (CHF-XM-500W, Trusttech Co. Ltd., Beijing, China). The incident light intensity ( $P_{in}$ ) was calibrated with a standard Si solar cell. The PCE of the DSSC is calculated from  $J_{sc}$ ,  $V_{oc}$ , fill factor (FF) and  $P_{in}$  according to the following equation:

$$\text{PCE}(\%) = \frac{V_{oc} J_{sc} \text{FF}}{P_{in}} \times 100 \quad (1)$$

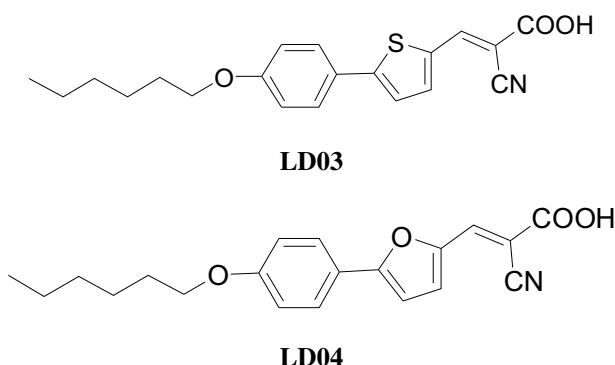


Fig. 1. Chemical structure of the two new co-sensitizers.

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