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

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<ABS-Head><ABS-HEAD>Graphical abstract <ABS-P> <ABS-P><xps:span class="xps\_Image">fx1</xps:span>

<ABS-HEAD>Highlights ► Two simple co-sensitizers were synthesized for N719-based DSSCs. ► The co-sensitizers could avoid dye aggregation and reduce charge recombination. ► Both  $J_{sc}$  and  $V_{oc}$  of the co-sensitized DSSCs were enhanced relative to single N719. ► Co-sensitization of a DSSC with N719 and LD04 exhibited the highest PCE of 8.955%.

### <ABS-HEAD>Abstract

<ABS-P>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<sub>3</sub><sup>-</sup> 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>).

<KWD>Keywords: Dye-sensitized solar cells; Co-sensitization; Absorption valley; Dye aggregation; Charge recombination

#### <H1>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 photoactive

materials and photo-anodes, utilization of new electrolytes 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 sensitizers [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 ( $\varepsilon$ ) 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<sub>2</sub> surface; (iii) it should be able to reduce the recombination of electrons in the TiO<sub>2</sub> film with  $I_3^$ by the formation of a compacted molecule monolayer covering the bare TiO<sub>2</sub> 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.

Fig. 1. is here

<H1>2. Experimental section

#### <H2>2.1. Materials and reagents

The starting materials 4-hexyloxyphenylboronic acid,

5-bromo-thiophene-2-carbaldehyde and 5-bromo-furan-2-carbaldehyde were purchased from Aladdin. The TiO<sub>2</sub> 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.

#### <H2>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<sub>2</sub> 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 × 10<sup>-4</sup> M) at a scan rate of 10 mV s<sup>-1</sup> 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.

<H2>2.3. Fabrication of DSSCs

The commercial TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> electrodes and Pt counter electrodes with a 25 µm 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.

### <H2>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 cm<sup>-2</sup>) (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:

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

The spectra of monochromatic IPCE for solar cells were performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA). The electrochemical impedance spectroscopy (EIS) of the DSSCs was recorded under dark conditions using an electrochemical workstation (CHI 660C, Shanghai Chenhua) over a frequency range from  $10^{-1}$  Hz to  $10^{5}$  Hz with a bias potential of 0.75 V. <H2>2.5. Synthesis

All reactions were carried out under nitrogen atmosphere. Suzuki coupling reaction of compound **1** with compounds **2** and **3** afforded corresponding Knoevenagel precursor compounds **4** and **5**, respectively. This reaction was carried out in methanol/tetrahydrofuran = 1:4 (v/v) medium by using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst under reflux condition for 12 h. These aldehyde intermediates (compounds **4** and **5**) were converted into corresponding target dyes through Knoevenagel condensation reaction by treating with cyanoacrylic acid using piperdine as catalytic for **LD03** and **LD04**, respectively. The synthetic routes of the dyes **LD03** and **LD04** are shown in Scheme 1.

### Scheme 1 is here

<H3>2.5.1. 5-(4-Hexyloxy-phenyl)-thiophene-2-carbaldehyde (4)

A mixture of 4-hexyloxyphenylboronic acid (1) (210 mg, 0.95 mmol), 5-bromo-thiophene-2-carbaldehyde (2) (120 mg, 0.63 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (37 mg, 0.03 mmol), 1 M aqueous solution of K<sub>2</sub>CO<sub>3</sub> (2 mL) and 20 mL methanol/tetrahydrofuran = 1:4 (v/v) were added in a 100 mL three-necked flask and degassed with nitrogen. Then, the reaction mixture was stirred at 67 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction was quenched by water and the organic layer

extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried with anhydrous MgSO<sub>4</sub> and the solvent was removed by rotary evaporation. The crude product was purified by silicon gel column chromatography (eluent petroleum ether: dichloromethane = 1: 1) to give a cream colored solid 150 mg. Yield: 55%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.89 (s, 1H), 7.73 (d, *J* = 3.2 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.29 (s, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 4.03 (t, *J* = 5.2 Hz, 2H), 1.86-1.80 (m, 2H), 1.52-1.47 (m, 2H), 1.38 (d, *J* = 2.4 Hz, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 182.65, 160.37, 154.72, 141.47, 137.68, 127.81, 125.57, 122.91, 115.13, 68.26, 31.57, 29.15, 25.69, 22.60, 14.03 ppm.

<H3>2.5.2. 5-(4-Hexyloxy-phenyl)-furan-2-carbaldehyde (5)

4-Hexyloxyphenylboronic acid (1) (190 mg, 0.86 mmol),

5-bromo-furan-2-carbaldehyde (**3**) (100 mg, 0.57 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (33 mg, 0.03 mmol) in 20 mL methanol/ tetrahydrofuran = 1:4 (v/v) and a 1 M K<sub>2</sub>CO<sub>3</sub> aqueous solution (2 mL) was degassed with nitrogen. Then, the reaction mixture was stirred at 67 °C for 12 h under nitrogen atmosphere. After the reaction, water was added and the mixture extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried with anhydrous MgSO<sub>4</sub> and then filtered. The solvent was removed by rotary evaporation. The crude product was purified by silicon gel column chromatography (eluent petroleum ether: dichloromethane = 1: 1) to give a white solid 136 mg. Yield: 58%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.62 (s, 1H), 7.77 (d, *J* = 6.8 Hz, 2H), 7.32 (d, *J* = 2.8 Hz, 1H), 6.97 (d, *J* = 6.8 Hz, 2H), 1.38 (d, *J* = 2.8 Hz, 4H), 0.94 (t, *J* = 2.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>) *δ*: 176.82, 160.53, 159.97, 151.62, 128.21, 126.97, 121.57, 114.96, 106.20, 68.22, 31.57, 29.52, 25.69, 22.59, 14.02 ppm; HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for (C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>): 273.1412; found, 273.1370.

<H3>2.5.3. 2-Cyano-3-[5-(4-hexyloxy-phenyl)-thiophen-2-yl]-acrylic acid (LD03)

In a 100 mL three-necked flask, 5-(4-hexyloxy-phenyl)-thiophene-2-carbaldehyde (**4**) (80 mg, 0.28 mmol), cyanoacrylic acid (35 mg, 0.42 mmol), CHCl<sub>3</sub> (15 mL), a few drops of piperidine were added and heated to refluxed under a nitrogen atmosphere for 12 h. Then, water (10 mL) was added to the reaction mixture. The mixture was acidified with 2 M HCl (30 mL) and extracted with CHCl<sub>3</sub>. Organic phase was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and the crude product was purified by silicon gel column chromatography (eluent ethanol: dichloromethane = 1: 8) to give yellow solid 68 mg. Yield: 68%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.33 (s, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 5.6 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 4.03 (t, *J* = 4.8 Hz, 2H), 2.00-1.97 (m, 2H), 1.52-1.50 (m, 2H), 1.33 (d, *J* = 5.2 Hz, 4H), 0.94 (t, *J* = 4.8 Hz, 3H); HRMS (ESI, m/z): [M + H]<sup>+</sup> calcd for (C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>S): 356.1242; found, 356.1248.

<H3>2.5.4. 2-Cyano-3-[5-(4-hexyloxy-phenyl)-furan-2-yl]-acrylic acid (LD04)

5-(4-Hexyloxy-phenyl)-furan-2-carbaldehyde (**5**) (100 mg, 0.37 mmol), cyanoacrylic acid (47 mg, 0.56 mmol) and a few drops of piperidine in CHCl<sub>3</sub> (20 mL) was heated to refluxed under a nitrogen atmosphere for 12 h. After that water (10 mL) was added to the reaction mixture. The solution was acidified with 2 M HCl (30 mL) and extracted with CHCl<sub>3</sub>. Organic phase was dried over anhydrous MgSO<sub>4</sub> and then filtered. The

solvent was removed by rotary evaporation. The crude product was purified by silicon gel column chromatography (eluent ethanol: dichloromethane = 1: 8) to give a yellow solid 82 mg. Yield: 65%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.99 (s, 1H), 7.85 (d, *J* = 6.8 Hz, 2H), 7.38 (s, 1H), 7.01 (d, *J* = 6.4 Hz, 2H), 6.85 (s, 1H), 4.04 (t, *J* = 4.8 Hz, 2H), 1.83 (t, *J* = 5.6 Hz, 2H), 1.50 (t, *J* = 3.6 Hz, 2H), 1.38 (d, *J* = 2.0 Hz, 4H), 0.94 (t, *J* = 6.8 Hz, 3H).

<H1>3. Results and discussion

The co-sensitization of LD03 or LD04 with N719 on a TiO2 films was achieved via a stepwise approach, which accomplished adsorption of two dyes on the TiO<sub>2</sub> photoanodes in a consecutive manner. The J-V characteristics of the DSSCs based on individual sensitizer and co-sensitizers have been investigated under illumination (AM 1.5G. 100 mW cm<sup>-2</sup>). The J-V curves are shown Fig. 2 and corresponding photovoltaic parameters are summarized in Table 1 for devices made of LD03 dye alone, LD04 dye alone, N719 dye alone and the N719 + LD03, N719 + LD04 co-sensitized systems. Devices sensitized with only LD03 and LD04 yielded a PCE of 1.813% ( $J_{sc}$ = 3.905 mA cm<sup>-2</sup>,  $V_{oc}$  = 0.652 V and FF = 0.712) and 2.570% ( $J_{sc}$  = 5.027 mA cm<sup>-2</sup>,  $V_{\rm oc} = 0.710$  V and FF = 0.720), respectively. At the same time, the **N719** sensitized DSSC gave a  $J_{sc}$  of 16.883 mA cm<sup>-2</sup>, a  $V_{oc}$  of 0.714 V and a FF of 0.655, resulted in a PCE of 7.896%, while the co-sensitized DSSCs N719 + LD03 and N719 + LD04 showed PCEs of 8.598% ( $J_{sc} = 17.673 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.736 \text{ V}$  and FF = 0.661) and 8.955% ( $J_{sc} = 17.628 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.758 \text{ V}$  and FF = 0.670), respectively. Impressively, the co-sensitized DSSCs (N719 + LD03 and N719 + LD04) yielded

significant enhancement in PCEs of devices over the individually sensitized devices with improvements in both  $J_{sc}$  and  $V_{oc}$ . In order to present the enhanced performances compared with other co-sensitized molecules, the table containing photovoltaic parameters of previously reported single sensitizers and the co-sensitized systems has been listed in part of supporting information (see Table S1). Meanwhile, the corresponding chemical structures have also been listed in Fig. S1 to clearly understand the correlation between molecular structures and the photovoltaic performances.

#### Fig. 2 is here

#### Table 1 is here

To account for the enhanced  $J_{sc}$  upon co-sensitization, UV-vis absorption spectra have been carried out to study the combined light-harvesting effect of the two sensitizers. The absorption spectra of **LD03**, **LD04** and **N719** in butanol-acetonitrile (1/1, v/v) are shown in Fig. 3a and the photophysical data are collected in Table 2. As shown in Fig. 3a and Table 2, the dyes **LD03** and **LD04** showed strong absorptions near 392 nm ( $\varepsilon = 2.653 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) and 421 nm ( $\varepsilon = 3.028 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>), respectively, which were assigned to the localized  $\pi$ - $\pi$ \* transitions of the conjugated systems. Meanwhile, the **N719** appeared two broad visible bands at 530 nm ( $\varepsilon = 1.311 \times 10^4$ M<sup>-1</sup> cm<sup>-1</sup>) and 385 nm ( $\varepsilon = 1.271 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) as well as a UV absorption band at 310 nm ( $\varepsilon = 4.671 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>), the former two absorption bands were attributed to the metal-to-ligand charge transfer (MLCT) transitions while the latter at UV region was assigned to intraligand ( $\pi$ - $\pi$ \*) charge-transfer transitions [40]. It is obvious that

the  $\varepsilon$  values of LD03 and LD04 are much higher than those of N719 and I<sub>3</sub><sup>-</sup> (2.5 × 10<sup>4</sup>  $M^{-1}$  cm<sup>-1</sup>) in the low wavelength region of ~340-430 nm [33, 41]. Therefore, the co-sensitization of N719 with LD03 or LD04 can achieve enhanced  $J_{sc}$  in DSSCs through offsetting the loss of light absorption by I<sub>3</sub><sup>-</sup>. Also, the absorption spectra of individual dye N719 and co-sensitizers (N719 + LD03 and N719 + LD04) adsorbed onto the surface of TiO<sub>2</sub> films were depicted and shown in Fig. 3b. It is obvious that the maximal absorption peak for N719 locate at 535 nm. The absorption peak is slightly red-shifted by 5 nm for N719 when anchored at the  $TiO_2$  surface as compared to the solution spectrum. This result indicates that N719 formed J-aggregation on TiO<sub>2</sub> surface, which is not conducive to solar cells achieve better efficiency. Upon co-sensitization with LD03 or LD04 on TiO<sub>2</sub> film, the maximal absorption peak of N719 shifted back to 530 nm, which indicate that the co-sensitizers can prevent the aggregation of N719 and adjust the arrangement of N719 molecules toward a more nearly parallel configuration on the surface of TiO<sub>2</sub>, resulting in a better charge transfer [35]. Moreover, it is observed that the co-adsorbed TiO<sub>2</sub> films exhibit enhanced light absorption in the region of ~380-500 nm when compared with the individually sensitized N719 film, which ensure harvesting more sunlight, resulting in impressively improved  $J_{sc}$ .

#### Fig. 3 is here

Furthermore, for the co-sensitized systems, the enhancement of  $J_{sc}$  values is also understandable from the IPCE shown in Fig. 4. Amplification of IPCE spectra in the different wavelengths are shown in Fig. 4b and Fig. 4c. It is obvious that the DSSC

containing individual **N719** has a broad IPCE spectrum from 300-800 nm with a maximum value of 72.966% at 535 nm; but a dramatical decrease of the IPCE to 40% in the wavelength range of ~350-400 nm is due to the competitive light absorption between  $I_3^-$  and **N719**. It is found that **LD03** and **LD04** co-sensitized with **N719**, respectively, not only fill the valley, but also broaden the IPCE spectra (Fig. 4b and Fig. 4c) and consequently achieve better photocurrents. Meanwhile, addition of **LD03** restored the decrease and broadened the absorption of the IPCE spectrum more efficient than **LD04**, which are in good agreement with the  $J_{sc}$  values: **N719** + **LD03** (17.673 mA cm<sup>-2</sup>) > **N719** + **LD04** (17.628 mA cm<sup>-2</sup>) > **N719** (16.883 mA cm<sup>-2</sup>).

### Fig. 4 is here

The dip in IPCE spectrum of **N719** based DSSC near 400 nm was recovered to an extent by the cocktail DSSCs with **N719** and the dyes **LD03**, **LD04**, which required that the new two co-sensitizers could easily inject electron from the dyes into the TiO<sub>2</sub> film. In order to investigate the possibilities of electron transfer from the excited states of dyes to the CB edge of the TiO<sub>2</sub> electrode, and dyes regeneration from the redox couple in the electrolyte to the oxidized state dyes, the redox behaviors were performed by cyclic voltammetry (CV) in *N*, *N*-dimethylformamide. The CV curves are shown in Fig. 5a and the corresponding data are collected in Table 2. The first oxidation potentials (*E*<sub>ox</sub>) correspond to the highest occupied molecular orbitals (HOMO) levels. As shown in Fig. 5a and Table 2, the HOMO levels of the dyes are 1.327 V for **LD03** and 1.334 V for **LD04** *vs*. NHE; these values are more positive than the I<sup>7</sup>/I<sub>3</sub><sup>-</sup> redox potential value (0.4 V *vs*. NHE), which facilitate electron transfer from I<sup>-</sup> to the dyes.

The zero-zero band gaps ( $E_{0.0}$ ) were 2.956 V for **LD03** and 2.804 V for **LD04**, estimated from the intersection of the normalized absorption and emission spectra. The normalized absorption and emission spectra of **LD03** and **LD04** were recorded in butanol-acetonitrile (1/1, v/v) solution, as shown in Fig. 5b and Fig. 5c, resprctively. The lowest unoccupied molecular orbital (LUMO) were calculated from the  $E_{HOMO}$  - $E_{0.0}$ . As a result, the LUMO levels of co-sensitizers **LD03**, **LD04** are -1.629 and -1.470 V, respectively, which are more negative than the CB edge of TiO<sub>2</sub> (-0.5 V vs. NHE), which indicate that the electron injection from excited co-sensitizer into the CB of TiO<sub>2</sub> is thermodynamically favorable. The energy diagram of the two co-sensitizers is shown in Fig. 6.

#### Fig. 5 is here

#### Fig. 6 is here

#### Table 2 is here

The high photocurrents of DSSCs based on co-sensitization were manifested by UV-vis absorption spectrum and IPCE response. In addition, the co-sensitized systems have higher  $V_{oc}$  than single **N719** is worth being investigated. To elucidate the reasons for the differences between the  $V_{oc}$  values, the electrochemical impedance spectroscopy (EIS) was measured to investigate the effects on charge recombination, transport and collection under a bias of 0.75 V with a frequency range of  $10^{-1}$  Hz to  $10^{5}$  Hz in the dark [42, 43]. The equivalent circuit (Fig. 7a) has been used to fit the EIS of the DSSCs, and the corresponding fitting data are summarized in Table 3.  $R_s$  represents the series resistance.  $C_{\mu}$  and  $R_{ct}$  are the chemical capacitance and the charge recombination

resistance at the TiO<sub>2</sub>/dye/electrolyte interface, respectively.  $C_{Pt}$  and  $R_{Pt}$  are the interface capacitance and charge transport resistance at the counter electrode/electrolyte interface, respectively. Fig. 7b and 7c show the Nyquist and Bode phase plots for DSSCs based on LD03, LD04, N719, N719 + LD03 and N719 + LD04. As shown in Fig. 7b, two major semicircles for each DSSC were observed in the EIS Nyquist plot. The small semicircle at a higher frequency is attributed to charge transfer at Pt counter electrode/electrolyte interface  $(R_{Pt})$ . It is obvious that the DSSCs based on single sensitizer and co-sensitized system have similar values of  $R_{\rm Pt}$  $(3.99-10.74 \Omega)$  although existence of slightly small discrepancies, which are consistent with many literatures [44, 45]. On the other hand, the larger semicircle in the lower frequency range is related to the resistance of electron transport at the TiO<sub>2</sub>/dye/electrolyte interface, *i.e.*, the charge recombination resistance between electrons on the TiO<sub>2</sub> CB and  $I_3^-$  species in the electrolyte ( $R_{ct}$ ). A smaller  $R_{ct}$  value means a faster charge recombination rate and a larger dark current, ultimately achieving a smaller  $V_{oc}$ . It can be seen from Table 3 the fitted values of the  $R_{ct}$  were in the order of LD03 (26.34  $\Omega$ ) < LD04 (31.14  $\Omega$ ) < N719 (33.70  $\Omega$ ) < N719 + LD03  $(36.86 \Omega) < N719 + LD04 (67.57 \Omega)$ , which appears to be consistent with the aforementioned variation trend of  $V_{oc}$  values.

From the Nyquist plots, we can also achieve another important data  $R_s$ . The  $R_s$  is equal to the value of high-frequency intercept on the real axis. The fitted values of  $R_s$ for **LD03**, **LD04**, **N719**, **N719** + **LD03** and **N719** + **LD04** are 21.80, 22.10, 24.76, 31.49 and 25.33  $\Omega$ , respectively. It is evident that the  $R_s$  of DSSCs based on single

sensitizer and co-sensitized system showed considerable fluctuation, which are consistent with many literatures [44, 46] and can be explained by the FF obtained in *J-V* curves under standard global AM 1.5 illumination. As we know, the  $R_s$  has a significant effect on FF, and a higher  $R_s$  seems to a lower FF. As shown in Table 1, it is obvious that the DSSCs based on single co-sensitizers (**LD03** and **LD04**) have higher FF, which is in accordance with smaller similar  $R_s$  (21.80-22.10 $\Omega$ ). Meanwhile, the DSSCs based on **N719**, **N719** + **LD03** and **N719** + **LD04** show the lower FF, which are closely linked to the higher  $R_s$  (24.76-31.49  $\Omega$ ).

Furthermore, the changing tendencies of  $V_{oc}$  values can be manifested by electron lifetime ( $\tau_e$ ), which is estimated from peak frequency (f) in the lower frequency region of EIS Bode phase plots using  $\tau_e = 1/(2\pi f)$ . From Fig. 7c, it can be seen that for the devices, the peak frequency decreased in the order of LD03 > LD04 > N719 > N719 + LD03 > N719 + LD04, and the electron lifetimes were enhanced in reverse with the calculated values of LD03 (5.871 ms) < LD04 (10.978 ms) < N719 (13.467 ms) < N719 + LD03 (16.104 ms) < N719 + LD04 (20.528 ms). The longer electron lifetimes for co-sensitized DSSCs are indicative of effective suppression of the back reaction of the injected electron with the I<sub>3</sub><sup>-</sup> in the electrolyte, resulting in the higher  $V_{oc}$ . Meanwhile, we can also understand the relation between the electron lifetime and  $V_{oc}$ . The  $V_{oc}$  value of a DSSC depends on the difference between the quasi-Fermi level of TiO<sub>2</sub> and the redox potential of the electrolyte ( $E_{redox}$ ) as it is illustrated by the following equation:

$$V_{\rm oc} = \frac{E_{\rm CB}}{q} + \frac{kT}{q} \ln\left(\frac{n}{N_{\rm CB}}\right) - \frac{E_{\rm redox}}{q} \quad (2)$$

where  $E_{CB}$  is the CB edge of TiO<sub>2</sub>, q is the electron charge, k is the Boltzmann constant, T is absolute temperature, n is the number of electrons in TiO<sub>2</sub> and  $N_{CB}$  is the effective density of states.  $E_{redox}$  is constant for both DSSCs due to the same electrolyte was used  $(I^{-}/I_{3})$  in both cases. Therefore,  $V_{oc}$  depends only on the first two terms, *i.e.*, E<sub>CB</sub> and electron concentration in TiO<sub>2</sub>. Since N719, LD03 and LD04 are able to inject electrons from their excited states into TiO<sub>2</sub>, the electron density is obviously increased in case of the co-sensitized DSSCs. Moreover, small molecule LD03 and LD04 tend to fill up the spaces of large-molecule N719 layer, which would greatly increase the overall surface molecular coverage, leading to impede the I<sub>3</sub><sup>-</sup> percolating to the TiO<sub>2</sub> surface and suppression of the back reaction, while electron lifetime in CB of TiO<sub>2</sub> is increased. The longer electron lifetime in the co-sensitized DSSCs is beneficial for charge accumulation in CB of TiO<sub>2</sub> under open circuit voltage, thus increasing electron density and Fermi level of TiO<sub>2</sub>. Therefore, the  $V_{\rm oc}$ value of a DSSC increases in accordance with its electron lifetime. Overall, co-sensitization of **N719** with **LD03** or **LD04** effectively blocks the interfacial charge recombination loss and enhances the electron lifetime, which accounts well for the higher  $V_{\rm oc}$  value.

In order to further illuminate the enhancement of recombination resistances for the co-sensitized systems, we recorded the dark current-voltage characteristics. Dark current can give a measure of the recombination of injected electrons with  $I_3^-$  in the

electrolyte in a DSSC. Dark *J-V* characteristics of the solar cells sensitized by single **N719** and the co-sensitized systems (**LD03** + **N719** and **LD04** + **N719**) are presented the Fig. 7d and reveal that dark currents are lower for the co-sensitized DSSCs, indicating suppression of the charge recombination rate, ultimately achieved higher recombination resistances.

#### Fig. 7 is here

#### Table 3 is here

Generally speaking, the two new co-sensitizers possess the following key features: (i) hexyloxy-substituted phenyl as an electron-donating unit, thiophene or furan as  $\pi$ -spacer and cyanoacrylic acid group as an acceptor and anchor, these results being **LD03** and **LD04** with a strong absorption around 400 nm that could effectively overcome the competitive light absorption by I<sub>3</sub><sup>-</sup>; (ii) hexyloxy group was added in **LD03** and **LD04** to avoid dye aggregation; (iii) compared with Ru-complex dye **N719**, the two new dyes have simple molecular structures and small volumes. It is well-known that small molecules with alkyl chains tend to form densely packed monolayer due to the weak steric hindrance [47]. Furthermore, the post-adsorption of small molecules into the interstitial sites of large-molecule layer would greatly increase the overall surface molecular coverage, thus impeding the I<sub>3</sub><sup>-</sup> percolating to the TiO<sub>2</sub> surface (see Fig. 8) [48]. For these reasons, dyes **LD03** and **LD04** are suitable as co-sensitizers for the **N719** to enhance photovoltaic performances of DSSCs.

Fig. 8 is here

#### <H1>4. Conclusions

In conclusion, two organic donor-( $\pi$  conjugated spacer)-acceptor dyes were synthesized as co-sensitizers for N719 based DSSCs, in which employ thiophene (LD03) or furan (LD04) as the  $\pi$ -linkers in combination with the hexyloxy-substituted phenyl electron-donating unit and cyanoacrylic acid acceptor. The absorption and IPCE spectra reveal that the dyes can overcome the competitive light absorption by  $I_3^-$  and lead to the improvement of  $J_{sc}$ . Meanwhile, the co-sensitizers can prevent the aggregation of N719 and adjust the arrangement of N719 molecules toward a more nearly parallel configuration on the surface of TiO<sub>2</sub>. Furthermore, the EIS data indicate that the strategy of co-sensitization can reduce recombination of injected electron in TiO<sub>2</sub> with the  $I_3^-$  and enhance electron lifetime, resulting in higher  $V_{oc}$ . Consequently, with respect to the DSSC with N719 alone, PCEs were improved by 8.891% and 13.412% in N719 + LD03 and N719 + LD04 DSSCs, respectively, and the highest PCE was achieved by a DSSC fabricated with N719 + LD04 (PCE = 8.955%,  $J_{\rm sc} = 17.628$  mA cm<sup>-2</sup>,  $V_{\rm oc} = 0.758$  V and FF = 0.670). We hope that the present work can provide a reference for the synthesis of simple, low-cost co-sensitizers and achievement of more promising co-sensitized solar cells.

#### <ACK>Acknowledgements

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#### <REF>References

#### <BIBL>

[1] B. O'Regan, M. Grätzel,;1; A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films, Nature 353 (1991) 737.

[2] M. Grätzel,;1; Recent Advances in Sensitized Mesoscopic Solar Cells, Acc. Chem. Res. 42 (2009) 1788.

[3] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson,;1; Dye-Sensitized Solar Cells, Chem. Rev. 110 (2010) 6595.

[4] A. Connell, P.J. Holliman, E.W. Jones, L. Furnell, C. Kershaw, M.L. Davies, C.D. Gwenin, M.B. Pitak, S.J. Coles, G. Cooke,;1; Multiple linker half-squarylium dyes for dye-sensitized solar cells; are two linkers better than one?, J. Mater. Chem. A 3 (2015) 2883.

[5] S. Franco, J. Garín, N.M.n.d. Baroja, R. Pérez-Tejada, J. Orduna, Y. Yu, M. Lira-Cantú,;1; New D-π-A-Conjugated Organic Sensitizers Based on 4H-Pyran-4-ylidene Donors for Highly Efficient Dye-Sensitized Solar Cells, Org. Lett. 14 (2012) 752.

[6] H. Tian, I. Bora, X. Jiang, E. Gabrielsson, K.M. Karlsson, A. Hagfeldt, L. Sun,;1; Modifying organic phenoxazine dyes for efficient dye-sensitized solar cells, J. Mater. Chem. 21 (2011) 12462.
[7] A. Connell, P.J. Holliman, M.L. Davies, C.D. Gwenin, S. Weiss, M.B. Pitak, P.N. Horton, S.J. Coles, G. Cooke,;1; A study of dye anchoring points in half-squarylium dyes for dye-sensitized solar cells, J. Mater. Chem. A 2 (2014) 4055.

[8] C.J. Martin, B. Bozic-Weber, E.C. Constable, T. Glatzel, C.E. Housecroft, I.A. Wright,;1; Development of scanning electrochemical microscopy (SECM) techniques for the optimization of dye sensitized solar cells, Electrochim. Acta 119 (2014) 86.

[9] J. Yang, P. Ganesan, J. Teuscher, T. Moehl, Y.J. Kim, C. Yi, P. Comte, K. Pei, T.W. Holcombe, M.K. Nazeeruddin, J. Hua, S.M. Zakeeruddin, H. Tian, M. Grätzel,;1; Influence of the donor size in D-pi-A organic dyes for dye-sensitized solar cells, J. Am. Chem. Soc. 136 (2014) 5722.

[10] J.M. Andrés-Castán, S. Franco, B. Villacampa, J. Orduna, R. Pérez-Tejada,;1; New efficient tert-butyldiphenyl-4H-pyranylidene sensitizers for DSSCs, RSC Adv. 5 (2015) 106706.

[11] R. Pérez-Tejada, N. Martínez de Baroja, S. Franco, L. Pellejà, J. Orduna, R. Andreu, J. Garín,;1; Organic sensitizers bearing a trialkylsilyl ether group for liquid dye sensitized solar cells, Dyes Pigments 123 (2015) 293.

[12] Z. Wan, C. Jia, Y. Duan, L. Zhou, Y. Lin, Y. Shi,;1; Phenothiazine–triphenylamine based organic dyes containing various conjugated linkers for efficient dye-sensitized solar cells, J. Mater. Chem. 22 (2012) 25140.

[13] M. Zhang, Y. Wang, M. Xu, W. Ma, R. Li, P. Wang,;1; Design of high-efficiency organic dyes for titania solar cells based on the chromophoric core of cyclopentadithiophene-benzothiadiazole, Energy Environ. Sci. 6 (2013) 2944.

[14] I. Stengel, N. Pootrakulchote, R.R. Dykeman, A. Mishra, S.M. Zakeeruddin, P.J. Dyson, M. Grätzel, P. Bäuerle,;1; Click-Functionalized Ru(II) Complexes for Dye-Sensitized Solar Cells, Adv. Energy Mater. 2 (2012) 1004.

[15] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B.F. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M.K. Nazeeruddin, M. Grätzel,;1; Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers, Nat. Chem. 6 (2014) 242.

[16] C.-Y. Chen, M. Wang, J.-Y. Li, N. Pootrakulchote, L. Alibabaei, C.-h. Ngoc-le, J.-D. Decoppet, J.-H. Tsai, C. Grätzel, C.-G. Wu, S.M. Zakeeruddin, M. Grätzel,;1; Highly Efficient Light-Harvesting Ruthenium Sensitizer for Thin-Film Dye-Sensitized Solar Cells, ACS Nano 3 (2009) 3103.

[17] Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li, P. Wang,;1; Donor/acceptor indenoperylene dye for highly efficient organic dye-sensitized solar cells, J. Am. Chem. Soc. 137 (2015) 3799.

[18] M. Cheng, X. Yang, F. Zhang, J. Zhao, L. Sun,;1; Tuning the HOMO and LUMO Energy Levels of Organic Dyes withN-Carboxomethylpyridinium as Acceptor To Optimize the Efficiency of Dye-Sensitized Solar Cells, J. Phys. Chem. C 117 (2013) 9076.

[19] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka,;1; Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells, J. Am. Chem. Soc. 131 (2009) 6050.

[20] H.S. Kim, C.R. Lee, J.H. Im, K.B. Lee, T. Moehl, A. Marchioro, S.J. Moon, R.

Humphry-Baker, J.H. Yum, J.E. Moser, M. Grätzel, N.G. Park,;1; Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%, Sci. Rep. 2 (2012) 591.

[21] H. Zhou, Q. Chen, G. Li, S. Luo, T.B. Song, H.S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang,;1; Interface engineering of highly efficient perovskite solar cells, Science 345 (2014) 542.

[22] W.S. Yang, J.H. Noh, N.J. Jeon, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok1, High-performance photovoltaic perovskite layers fabricated through intramolecular exchange, Science 348 (2015) 1234.

[23] G. Niu, X. Guo, L. Wang,;1; Review of recent progress in chemical stability of perovskite solar cells, J. Mater. Chem. A 3 (2015) 8970.

[24] S. Zhang, X. Yang, Y. Numata, L. Han,;1; Highly efficient dye-sensitized solar cells: progress and future challenges, Energy Environ. Sci. 6 (2013) 1443.

[25] A. Mishra, M.K. Fischer, P. Bauerle,;1; Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules, Angew. Chem. Int. Ed. 48 (2009) 2474.
[26] A. Hagfeldtt, M. Grätzel,;1; Light-Induced Redox Reactions in Nanocrystalline Systems, Chem. Rev. 95 (1995) 49.

[27] M. Konstantakou, P. Falaras, T. Stergiopoulos,;1; Blocking recombination in Ru(II) complex-sensitized solar cells by incorporating co-adsorbents as additives in the Co(II)/(III)-based redox electrolytes, Polyhedron 82 (2014) 109.

[28] A. Kaltzoglou, M. Antoniadou, D. Perganti, E. Siranidi, V. Raptis, K. Trohidou, V. Psycharis, A.G. Kontos, P. Falaras,;1; Mixed-halide Cs<sub>2</sub>SnI<sub>3</sub>Br<sub>3</sub> perovskite as low resistance hole-transporting material in dye-sensitized solar cells, Electrochim. Acta 184 (2015) 466.

[29] M. Bidikoudi, D. Perganti, C.-S. Karagianni, P. Falaras,;1; Solidification of ionic liquid redox electrolytes using agarose biopolymer for highly performing dye-sensitized solar cells, Electrochim. Acta 179 (2015) 228.

[30] V.-M. Guérin, T. Pauporté,;1; From nanowires to hierarchical structures of template-free electrodeposited ZnO for efficient dye-sensitized solar cells, Energy Environ. Sci. 4 (2011) 2971.
[31] C. Magne, T. Moehl, M. Urien, M. Grätzel, T. Pauporté,;1; Effects of ZnO film growth route and nanostructure on electron transport and recombination in dye-sensitized solar cells, J. Mater. Chem. A 1 (2013) 2079.

[32] J. Zhang, Y. Kusumawati, T. Pauporté,;1; Dye-Sensitized Solar Cells Based on TiO<sub>2</sub> Nanotube and Shelled Arrayed Structures, Electrochim. Acta 201 (2016) 125.

[33] L. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. Zhang, X. Yang, M. Yanagida,;1;High-efficiency dye-sensitized solar cell with a novel co-adsorbent, Energy Environ.Sci. 5 (2012)6057.

[34] C. Qin, Y. Numata, S. Zhang, A. Islam, X. Yang, K. Sodeyama, Y. Tateyama, L. Han,;1; A Near-Infraredcis-Configured Squaraine Co-Sensitizer for High-Efficiency Dye-Sensitized Solar Cells, Adv. Funct. Mater. 23 (2013) 3782.

[35] C.-M. Lan, H.-P. Wu, T.-Y. Pan, C.-W. Chang, W.-S. Chao, C.-T. Chen, C.-L. Wang, C.-Y. Lin, E.W.-G. Diau,;1; Enhanced photovoltaic performance with co-sensitization of porphyrin and an organic dye in dye-sensitized solar cells, Energy Environ. Sci. 5 (2012) 6460.

[36] S. Zhang, A. Islam, X. Yang, C. Qin, K. Zhang, Y. Numata, H. Chen, L. Han,;1; Improvement of spectral response by co-sensitizers for high efficiency dye-sensitized solar cells, J. Mater. Chem. A 1 (2013) 4812.

[37] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel,;1; Porphyrin-Sensitized Solar Cells with Cobalt

(II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency, Science 334 (2011) 629.

[38] L.H. Nguyen, H.K. Mulmudi, D. Sabba, S.A. Kulkarni, S.K. Batabyal, K. Nonomura, M. Grätzel, S.G. Mhaisalkar,;1; A selective co-sensitization approach to increase photon conversion efficiency and electron lifetime in dye-sensitized solar cells, Phys. Chem. Chem. Phys. 14 (2012) 16182.

[39] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa, M. Hanaya,;1; Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes, Chem. Commun. 51 (2015) 15894.

[40] Z. Wu, Y. Wei, Z. An, X. Chen, P. Chen,;1; Co-sensitization of N719 with an Organic Dye for Dye-sensitized Solar Cells Application, Bull. Korean Chem. Soc. 35 (2014) 1449.

[41] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Grätzel, 1; Conversion of light to electricity by

cis-X2bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, and SCN<sup>-</sup>) on nanocrystalline titanium dioxide electrodes, J. Am. Chem. Soc. 115 (1993) 6382.

[42] J. Bisquert,;1; Chemical capacitance of nanostructured semiconductors: its origin and significance for nanocomposite solar cells, Phys. Chem. Chem. Phys. 5 (2003) 5360.

[43] F. Fabregat-Santiago, J. Bisquert, L. Cevey, P. Chen, M. Wang, S.M. Zakeeruddin, M.

Grätzel,;1; Electron Transport and Recombination in Solid-State Dye Solar Cell with

Spiro-OMeTAD as Hole Conductor, J. Am. Chem. Soc. 131 (2009) 558.

[44] C. Zhong, J. Gao, Y. Cui, T. Li, L. Han,;1; Coumarin-bearing triarylamine sensitizers with high molar extinction coefficient for dye-sensitized solar cells, J. Power Sources 273 (2015) 831.
[45] X.-F. Zang, Z.-S. Huang, H.-L. Wu, Z. Iqbal, L. Wang, H. Meier, D. Cao,;1; Molecular design of the diketopyrrolopyrrole-based dyes with varied donor units for efficient dye-sensitized solar cells, J. Power Sources 271 (2014) 455.

[46] Z. Wan, L. Zhou, C. Jia, X. Chen, Z. Li, X. Yao,;1; Comparative study on photovoltaic properties of imidazole-based dyes containing varying electron acceptors in dye-sensitized solar cells, Synth. Met. 196 (2014) 193.

[47] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides,;1; Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology, Chem. Rev. 105 (2005) 1103.
[48] S. Chang, H. Wang, Y. Hua, Q. Li, X. Xiao, W.-K. Wong, W.Y. Wong, X. Zhu, T. Chen,;1; Conformational engineering of co-sensitizers to retard back charge transfer for high-efficiency dye-sensitized solar cells, J. Mater. Chem. A 1 (2013) 11553.

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### <Figure>Figure captions:

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

<Figure>Fig. 2. (a) *J-V* curves for DSSCs sensitized with LD03 and LD04; (b) *J-V* curves of DSSCs based on N719 and co-sensitized systems (N719 + LD03 and N719 + LD04).

<Figure>Fig. 3. (a) UV-vis absorption spectra of LD03, LD04 and N719 in butanol-acetonitrile (1/1, v/v) solution; (b) UV-vis spectra of the N719 and co-sensitized systems anchored onto nanoporous TiO<sub>2</sub> films.

<Figure>Fig. 4. (a) IPCE spectra for DSSCs sensitized with N719, co-sensitized with

**N719** and **LD03** or with **N719** and **LD04**; (b) and (c) amplification of IPCE spectra in different wavelengths.

<Figure>Fig. 5. (a) Cyclic voltammograms of the dyes in *N*, *N*-dimethylformamide solution; (b) and (c) the normalized absorption and emission spectra of the LD03 and LD04 in butanol-acetonitrile (1/1, v/v) solution, respectively.

<Figure>Fig. 6. Schematic energy levels of the two co-sensitizers based on absorption and electrochemical data.

<Figure>Fig. 7. (a) Equivalent circuit for the DSSCs. (b) Nyquist plots and (c) Bode phase plots for DSSCs based on the single sensitizer and co-sensitization measured in the dark under 0.75 V bias. (d) *J-V* curves under dark condition for DSSCs sensitized by N719 and co-sensitized systems.

<Figure>Fig. 8. The spatial arrangement of the two types of dyes adsorbed on  $TiO_2$  surface.

<Table>Table 1 Photovoltaic properties of LD03, LD04, N719 and the co-sensitized systems.

Dye	$J_{ m sc}$ / mA cm <sup>-2</sup>	$V_{ m oc}/{ m V}$	FF	PCE/%
LD03	LD03 3.905		0.712	1.813
LD04	5.027	0.710	0.720	2.570
N719	16.883	0.714	0.655	7.896
N719+LD03	17.673	0.736	0.661	8.598
N719+LD04	17.628	0.758	0.670	8.955

<Table>Table 2 Absorption and electrochemical data of dyes LD03 and LD04.

		$\varepsilon$ at $\lambda_{max}$		E <sub>HOMO</sub> <sup>b</sup> /		E <sub>LUMO</sub> <sup>d</sup> /
Dye	$\lambda_{max}^{a}/nm$	$/10^4  M^{-1}$	$\lambda_{\rm ex}^{\rm a}/{\rm nm}$	V vs.	$E_{0-0}^{\mathrm{c}}/\mathrm{V}$	V vs.
		cm <sup>-1</sup>		NHE		NHE
LD03	392	2.653	460	1.327	2.956	-1.629
LD04	421	3.028	463	1.334	2.804	-1.470

<sup>a</sup> Absorption maximum ( $\lambda_{max}$ ) and emission spectra ( $\lambda_{ex}$ ) in 2 × 10<sup>-5</sup> M butanol-acetonitrile (1/1, v/v) solution.

<sup>b</sup>  $E_{\text{HOMO}}$  values were measured in *N*, *N*-dimethylformamide with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte (scanning rate: 10 mV s<sup>-1</sup>, working electrode: Pt disk, counter electrode: Pt wire and reference electrode: Ag/AgCl), potentials measured *vs*. Ag/AgCl were converted to NHE by addition of +0.2 V, namely  $E_{\text{HOMO}} = E_{\text{ox}} + 0.2$ .

<sup>c</sup>  $E_{0-0}$  values were calculated from the intersection of the normalized absorption and emission spectra.

 $^{d} E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}.$ 

<Table>Table 3 EIS parameters of the DSSCs.

Dye	$R_{ m S}\left(\Omega ight)$	$R_{\rm ct}$ ( $\Omega$ )	$R_{\mathrm{Pt}}$ ( $\Omega$ )	$ au_e/\mathrm{ms}$
LD03	21.80	26.34	6.84	5.871
LD04	22.10	31.14	6.56	10.978
N719	24.76	33.70	3.99	13.467
N719+LD03	31.49	36.86	5.90	16.104
N719+LD04	25.33	67.57	10.74	20.528

### TDENDOFDOCTD