

## Supporting Information

# None-iodine solvent-free ionic liquid electrolytes for dye-sensitized solar cells

Jing Liu,<sup>†</sup> Jiayan Cong,<sup>†</sup> Lars Kloo,<sup>‡</sup> Xichuan Yang,<sup>†,\*</sup> and Licheng Sun<sup>†,‡,\*</sup>

<sup>†</sup>State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Linggong Rd. 2, 116024 Dalian, China

<sup>‡</sup>School of Chemical Science and Engineering, Center of Molecular Devices, Department of Chemistry, KTH Royal Institute of Technology, Teknikringen 30, 10044 Stockholm, Sweden

### Experiment.

The elemental analyses were carried out by elemental analyzer (Elementar Co. Ltd, Germany).  $J$ - $V$  characteristics were measured using an electrochemical workstation (LK9805, TIANJINLANLIKE, Co. Ltd, China) under simulate sun light from a solar simulator (16S-002, SolarLight, LTD. America) with a 500 W xenon light source giving an illumination of  $100 \text{ mW cm}^{-2}$ . Photovoltaic performance was test by using a metal mask with an aperture area of  $0.159 \text{ cm}^2$ . Incident photon-to-current conversion efficiency (IPCE) were recorded using monochromatic light from a system consisting of a xenon lamp, a monochromator and appropriate filters. The Mott-Schottky plots and EIS measurements were tested with electrochemical workstation (Zennium, Zahner, Germany).

### Device Fabrication.

FTO conducting glass was cleaned sequentially with abluent solution, deionized

water, acetone and ethanol in an ultrasonic bath. The screen-printing procedure was repeated with TiO<sub>2</sub> paste ( $\approx 20 \mu\text{m}$  colloidal particles, Heptachroma Co. Ltd, China) to get a transparent layers (thickness  $\approx 6 \mu\text{m}$ ). A scattering layer (thickness  $\approx 4 \mu\text{m}$ , Heptachroma Co. Ltd, China) was printed. The TiO<sub>2</sub> electrodes were heated at 520 °C for 30 min and then immersed in the 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C for 30 min, washed with water and ethanol, and annealed at 520 °C for 30 min again. The TiO<sub>2</sub> electrodes were immersed into the different dye solutions: N719 ethanol solution (0.2 mM) for 13 hours and TH305 CH<sub>2</sub>Cl<sub>2</sub> solution with chenodeoxycholic acid (saturated) as a coadsorbent for 2 hours, in the dark, at room temperature. After adsorption of the dyes, the electrodes were washed by ethanol. The counter electrode is Pt/FTO.

## Syntheses

All reagents were obtained from commercial sources and used up to the mustard. The 1-propyl-2,3-dimethylimidazolium bromide (DMPIBr) and 3-propyl-1,2-dimethylimidazolium iodide (DMPII) were obtained from Heptachroma Co. Ltd (China). 1-propyl-3-methylimidazolium iodide (PMII), 1,3-dimethylimidazolium iodide (DMII), 1-ethyl-3-methylimidazolium iodide (EMII) and 1-ethyl-3-methylimidazolium thiocyanate (EMISCN) was gained according to the literature.<sup>1</sup> *N*-butylbenzimidazole (NBB) was synthesized according to the literature.<sup>2</sup>

**Synthesis of tetramethylammonium sulfide (TMAS):** The synthesis methods were got from the report that we have reported.<sup>3</sup> A aqueous solution containing 25 wt.% tetramethylammonium hydroxide (8.00 g, 22 mmol; Sinopharm Chemical Reagent

Co., Ltd.) was mixed with a ammonium sulfide aqueous solution whose concentration is 17 % (4.67 g, 12 mmol; Yizhong Chemical plant in Tianjin Dagang), stirred and heated at 120 °C. With the water distilled, a white solid was leaved and then the solid was dried under vacuum at 40 °C.

**Synthesis of the polysulfide ( $S^{2-}/S_x^{2-}$ ) redox couple with tetramethylammonium cation:** A certain molar mass of sulfur and tetramethylammonium sulfide (TMAS) were dissolved in the acetonitrile, heated at 70 °C for 4 h, and then cooled in the air overnight. The solution was evaporated. A light brown solid was obtained. The elementary analysis was carried with the result content /% N: 6.973; C: 23.71; S: 37.45; H: 5.877, which led to the compound  $[N(CH_3)_4]^+ ]_2S_5^{2-}$ .

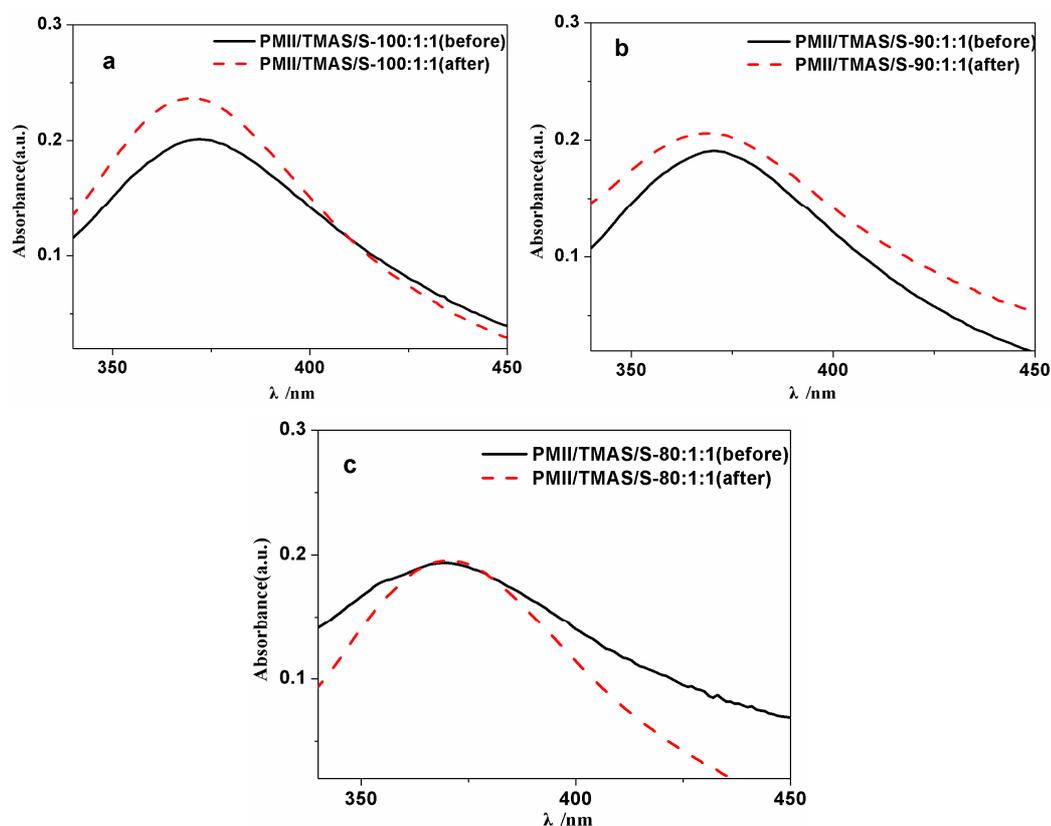
**Synthesis of the polysulfide ( $S^{2-}/S_x^{2-}$ ) redox couple with imidazolium cation:** A methanol of 1 equivalent 1-propyl-2.3-dimethylimidazolium bromide and 1 equivalent KOH was stirred at room temperature for 12 h to get the hydroxide ionic liquid solution. Then 1 equivalent ammonium sulfide aqueous solution was added in to the ionic liquid solution, heated at 120 °C to distill the solvent. At last a brown solid was got, that is the 1-propyl-2.3-dimethylimidazolium sulfide (DMPIS). The polysulfide ( $S^{2-}/S_x^{2-}$ ) redox couple was gained as the polysulfide ( $S^{2-}/S_x^{2-}$ ) redox couple with tetramethylammonium cation. The elementary analysis was carried with the result content /% N: N: 12.19; C: 34.57; S: 11.75; H: 6.168.

## DSCs Properties

### 1. DSCs based on N719

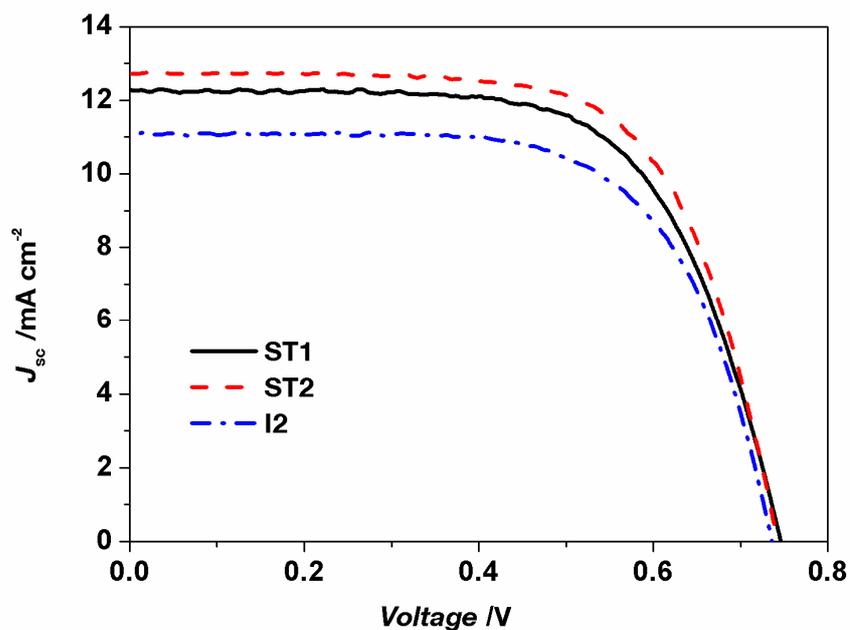
To test the amount of sulfide/polysulfide for suppressing the formation of  $I_3^-$ ,

UV-vis spectra measurements were taken. The sensitizer of DSCs was N719 and the components of electrolytes were PMII/TAMS/S.



**Figure S1.** The UV-*vis* spectra of electrolytes from related solar cells before and after the  $J-V$  measurements by changing the ratio of  $I^-$  and sulfur/polysulfur redox a) 100: 1: 1; b) 90: 1: 1; c) 80: 1: 1.

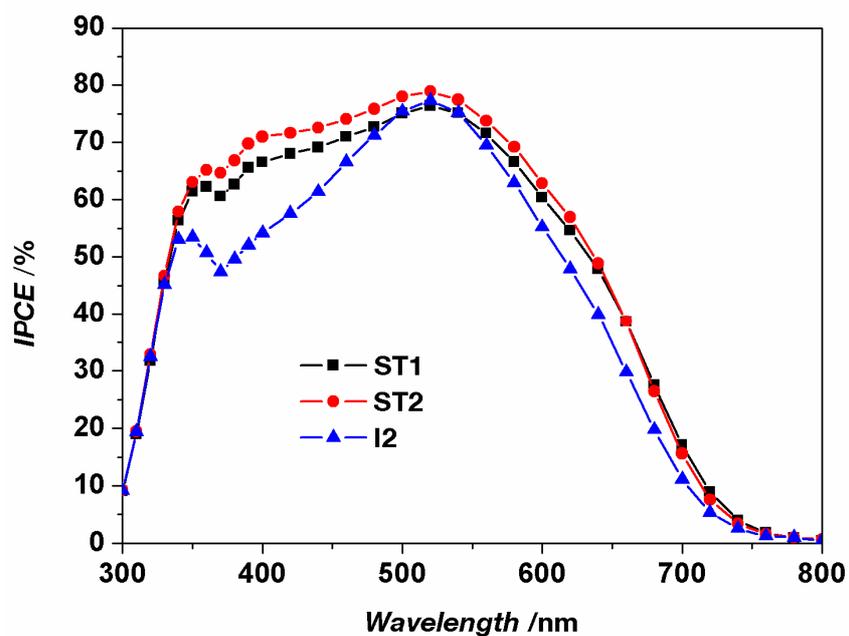
The N719-sensitized DSCs containing electrolytes **ST1** and **ST2** were compared with the reference electrolyte **I2** which has a lower iodine concentration than **I1**. The composition of **I2** is PMII/EMISCN/ $I_2$ /NBB/GuSCN (12/8/0.15/1/0.2).



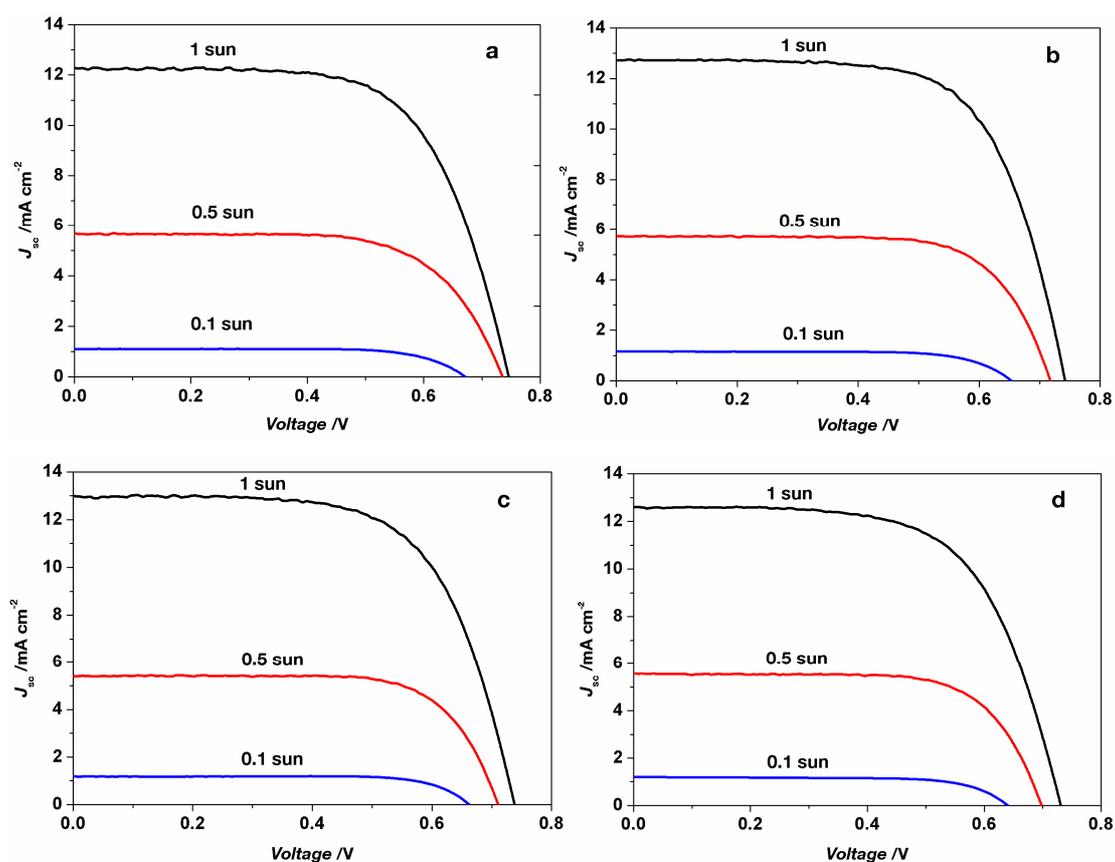
**Figure S2.** The  $J$ - $V$  curves of the DSCs sensitized by N719 with ST1, ST2 and I2 as electrolytes.

**Table S1.** Photovoltaic properties<sup>a</sup> of N719-sensitized DSCs based on electrolytes ST1, ST2 and I2 under AM 1.5G illumination,  $100 \text{ mW}\cdot\text{cm}^{-2}$ .

electrolyte	$V_{oc}$ [mV]	$J_{sc}$ [ $\text{mA}\cdot\text{cm}^{-2}$ ]	$ff$ [%]	$\eta$ [%]
ST1	747	12.28	0.65	6.0
ST2	743	12.72	0.68	6.4
I2	737	11.17	0.66	5.4



**Figure S3.** The IPCE spectra of the DSCs sensitized by N719 with ST1, ST2 and I2 as electrolytes.

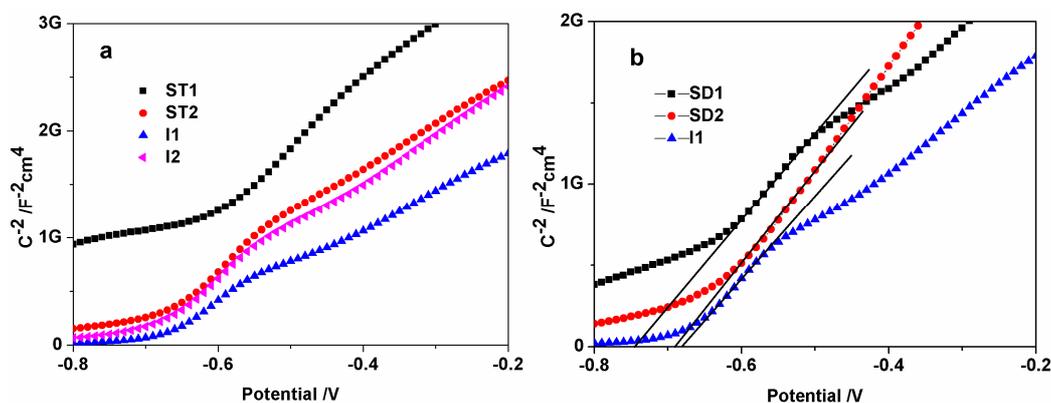


**Figure S4.** The  $J$ - $V$  curves of N719-sensitized DSCs containing the electrolytes ST1 (a), ST2 (b), SD1 (c) and SD2 (d) under illumination at different light intensities (1,

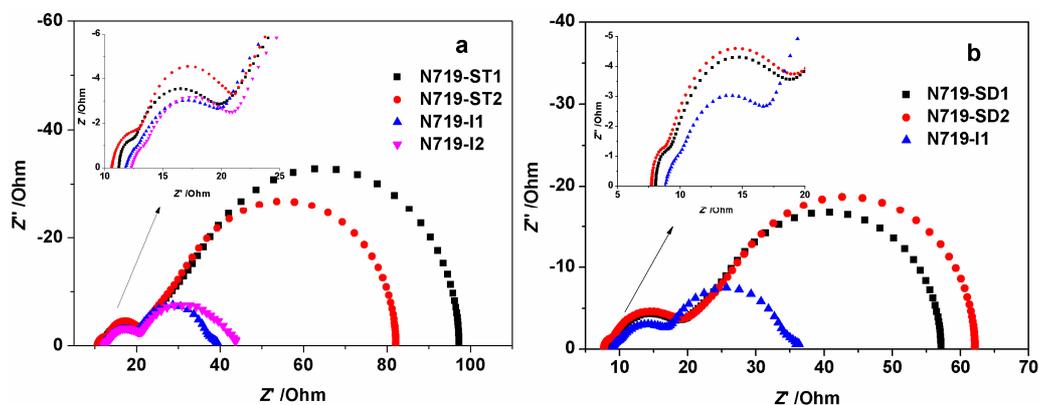
0.5 and 0.1 sun, respectively).

**Table S2.** The photovoltaic properties of N719-based DSCs containing electrolytes ST1, ST2, SD1 and SD2 under 0.5 sun illumination.

electrolyte	$V_{oc}$ [mV]	$J_{sc}$ [ $\text{mA}\cdot\text{cm}^{-2}$ ]	$ff$ [%]	$\eta$ [%]
ST1	736	5.66	0.67	5.7
ST2	718	5.72	0.71	6.0
SD1	711	5.41	0.72	5.7
SD2	699	5.57	0.70	5.6



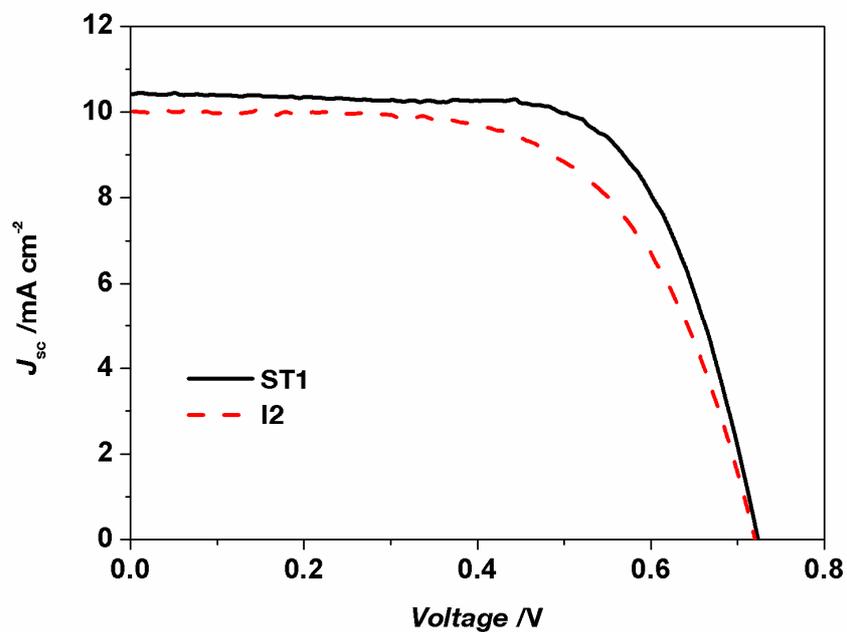
**Figure S5.** Mott-Schottky plots of  $\text{TiO}_2$  with the electrolytes a) ST1, ST2, I1 and I2, b) SD1, SD2 and I1.



**Figure S6.** EIS of DSCs based on N719 with a) ST1, ST2, I1 and I2, b) SD1, SD2 and I1.

## 2. DSCs based on TH305

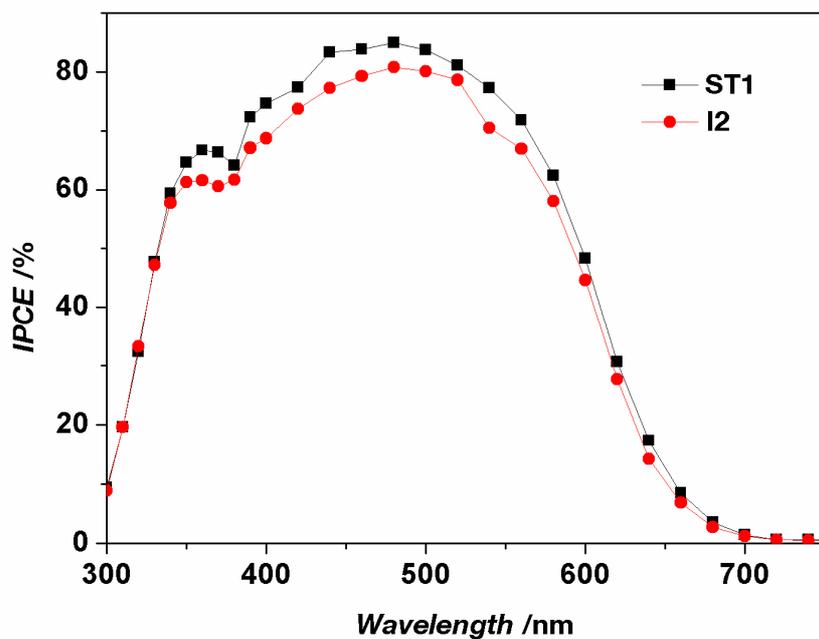
The **TH305**-sensitized DSCs containing electrolytes **ST1** were compared with the reference electrolyte **I2**.



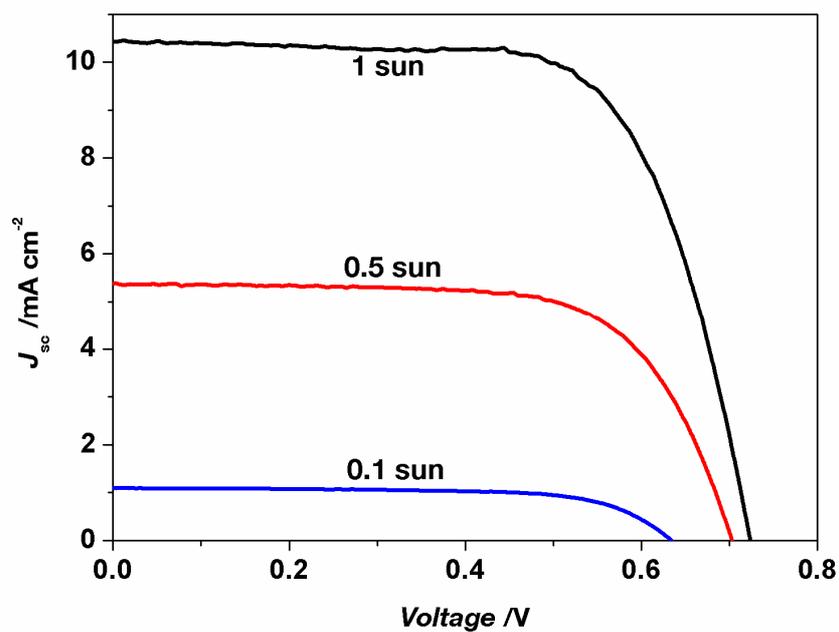
**Figure S7** The  $J$ - $V$  curves of the DSCs sensitized by **TH305** with **ST1** and **I2** as electrolytes.

**Table S3.** The photovoltaic properties of the DSCs containing **ST1** and **I2**.

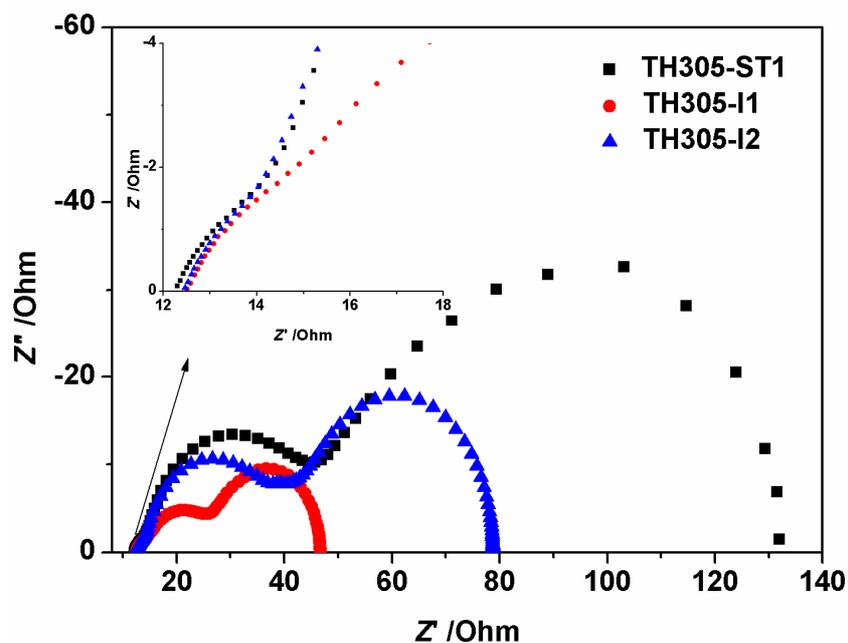
electrolyte	$V_{oc}$ [mV]	$J_{sc}$ [ $\text{mA}\cdot\text{cm}^{-2}$ ]	$ff$ [%]	$\eta$ [%]
<b>ST1</b>	724	10.42	0.69	5.2
<b>I2</b>	721	10.02	0.62	4.5



**Figure S8.** The IPCE spectra of the DSCs sensitized by **TH305** with **ST1** and **I2** as electrolytes.



**Figure S9.** The  $J$ - $V$  curves of DSCs based on **TH305** containing **ST1** under different light intensity illumination.



**Figure S10.** EIS of DSCs based on TH305 with ST1, I1 and I2.

### Reference

- (1) Cao, Y.; Zhang, J.; Bai, Y.; Li, R.; Zakeeruddin, S.; Grätzel, M.; Wang, P. *J. Phys. Chem. C*. 2008, 112, 13775-13781.
- (2) Qingxiang, L.; Lina, Y.; Jincheng, F. *Journal of Organometallic Chemistry*. 2007, 692, 3655-3663.
- (3) Cong, J.; Yang, X.; Hao, Y.; Kloo, L.; Sun, L. *RSC Adv.* 2012, 2, 3625-3629.