

Supporting Information for:

## **POSS with Eight Imidazolium Iodide Arms for Efficient Solid-State Dye-Sensitized Solar Cells**

Wei Zhang, Juan Li, Shenghui Jiang, Zhong-Sheng Wang\*

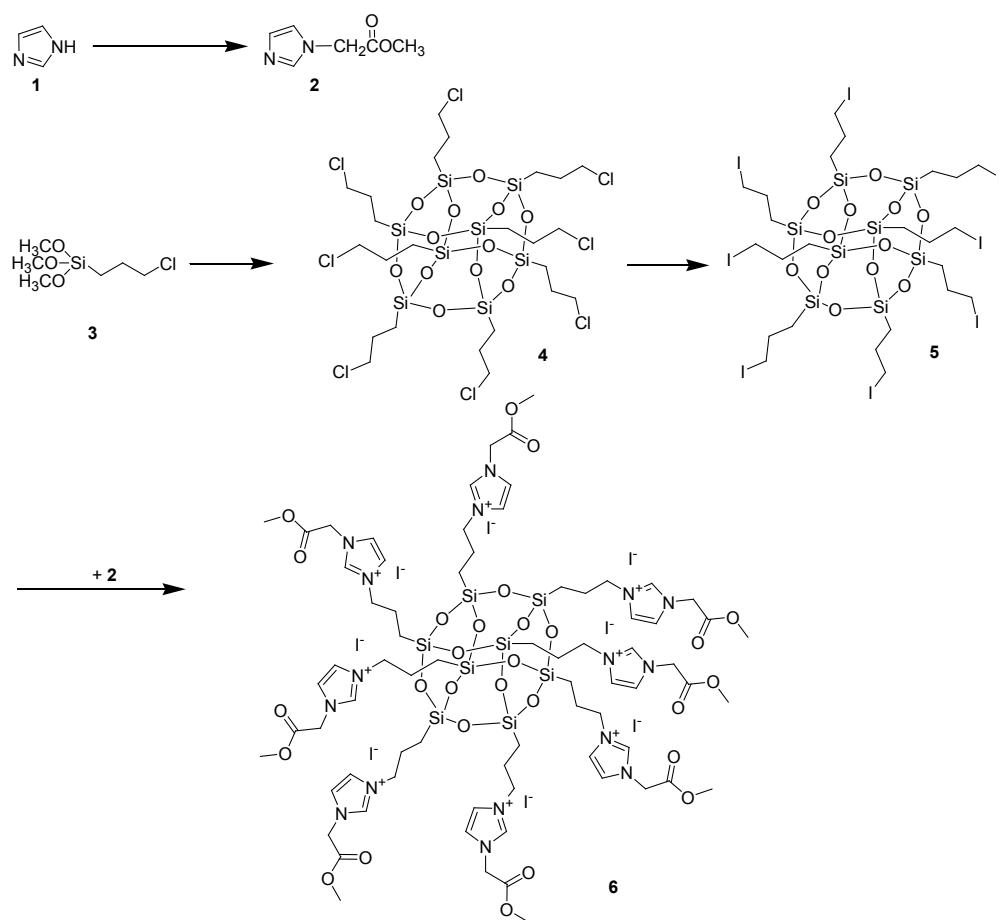
Department of Chemistry, Laboratory of Advanced Materials, Fudan University, 2205 Songhu Road, Shanghai 200438, P. R. China  
E-mail: zs.wang@fudan.edu.cn

### **Experimental Section**

#### **Materials and reagents**

LiI, NMBI, and I<sub>2</sub> were obtained from Acros. Organic solvents used in this work were purified using standard process. Other chemicals and reagents were used as received from commercial sources without further purification. Transparent conductive glass (F-doped SnO<sub>2</sub>, FTO, 14 Ω, transmittance of 80%, Nippon Sheet Glass Co., Japan) was used as the substrate for the fabrication of TiO<sub>2</sub> thin film electrodes.

**Scheme S1.** Synthetic route for POSS-8EsPImI



**Synthesis of compound 2**

Absolute dry methanol (100 mL) and sodium (4.6 g, 0.2 mol) were charged into a 250 mL three-necked flask equipped with a condensing tube and stirred at room temperature for 2 h. Then imidazole (13.6 g, 0.2 mol) was added to the above mixture under nitrogen, which was heated to 50 °C. After stirring for 1 h, methyl chloroacetate (21.7 g, 0.2 mol) was added dropwise to the above system. The reaction was kept at 50 °C for an additional 16 h and then allowed to cool down to room temperature. After filtration, the solvent was removed *via* rotary evaporation until viscous oil remained. Silica gel chromatography with CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (20:1, V:V) as eluent afforded the pure product as a pale yellow solid in a yield of 67.0% (mp: 60~64 °C). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400

Hz,  $\delta$  ppm): 7.44 (s, 1H); 7.03 (s, 1H); 6.89 (s, 1H), 4.66 (s, 1H); 3.72 (s, 1H);  $^{13}\text{C}$  NMR (DMSO-d<sub>6</sub>, 100 MHz,  $\delta$  ppm): 168.2, 138.3, 129.8, 120.2, 53.1 and 48.0.

#### Synthesis of compound 4

Compound **4** was synthesized by the following method described by Dittmar *et al.*.<sup>1</sup> Methanol (90 mL), 3-chloropropyltrimethoxysilane (3.975 g, 0.02 mol) and concentrated hydrochloric acid (4.5 mL) were mixed. Hydrolysis and rearrangement reactions were allowed to carry out for 3 days at 60 °C, and then colorless crystals were obtained after dried in vacuum with a yield of 20%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 Hz,  $\delta$  ppm): 3.54 (t, 16H); 1.87 (m, 16H); 0.80 (t, 16H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$  ppm): 47.3, 26.5, 9.5.

#### Synthesis of compound 5

A mixture of **4** (2.0 g, 2 mmol), sodium iodide (9.0 g, 60 mmol), tetrabutylammonium iodide (22.0 g, 60 mmol) and iodopropane (10.0 mL, 8 mmol) in 2-butanone (160 mL) was heated to reflux for 72 h.<sup>2</sup> After the solvent was evaporated, 100 mL water was added to system followed by extraction with 100 mL CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed twice with water, once with brine (100 mL each), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was rinsed with CH<sub>3</sub>OH followed by filtration. The filter cake was washed several times with CH<sub>3</sub>OH and dried in vacuum to yield 2.96 g (86.5%) of **5** as a colorless solid.  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 Hz,  $\delta$  ppm): 3.22 (t, 16H); 1.92 (m, 16H); 0.78 (t, 16H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$  ppm): 27.6, 13.7, 10.4.

#### Synthesis of compound 6 (**POSS-8EsPImI**)

1-(2-methoxy-2-oxylethyl) imidazolium (1.82 g, 13.0 mmol) and **5** (1.77 g, 1.3 mmol) were dissolved in THF (20 mL) and the mixture was stirred at RT for 48 h. Pale yellow and viscous solid was obtained after pouring the upper solution. After washing with THF followed by drying for three

cycles, pale yellow solid of **6** was obtained (2.32 g, yield of 80%).  $^1\text{H}$  NMR (DMSO-d<sub>6</sub>, 400 Hz,  $\delta$  ppm): 9.22 (d, 8H); 7.89 (d, 8H); 7.77 (s, 8H); 5.29 (s, 24H); 4.26 (s, 16H); 3.74 (t, 16H); 1.80 (m, 16H); 0.58 (t, 16H).  $^{13}\text{C}$  NMR (DMSO-d<sub>6</sub>, 100 MHz,  $\delta$  ppm): 168.0, 137.9, 124.6, 122.7, 53.7, 51.6, 50.4, 24.0, 8.4.  $^{29}\text{Si}$  NMR (DMSO-d<sub>6</sub>, 100 MHz,  $\delta$  ppm): -66.84.

### DSSC Fabrication and Photovoltaic Measurements

TiO<sub>2</sub> films (12  $\mu\text{m}$ ) composed of 6  $\mu\text{m}$  nanoparticle (20 nm) layer in direct contact with the FTO substrate and 6  $\mu\text{m}$  light scattering particle (80% 20 nm TiO<sub>2</sub> + 20% 100 nm TiO<sub>2</sub>) layer were fabricated with a screen printing method<sup>3</sup> and used in this study. The films were sintered at 500 °C for 2 h to achieve good necking of neighboring TiO<sub>2</sub> particles. The film thickness was measured with a surface profiler (Veeco Dektak 150, USA). The sintered films were then treated with 0.05 M TiCl<sub>4</sub> aqueous solution at 70 °C for 30 min followed by calcinations at 450 °C for 30 min. When TiO<sub>2</sub> electrodes were cooled down to 120 °C, the electrodes were dipped in dye solutions (0.3 mM in toluene) for 24 h at RT. The Pt-coated FTO as a counter electrode and the dye-loaded film were separated by a hot-melt Surlyn film (30  $\mu\text{m}$ ) and sealed together by pressing them under heat. The methanol solution of the solid electrolyte was injected repeatedly into the interspace between the working and the counter electrodes from the two holes predrilled on the back of the counter electrode and dried on a hot plate with the temperature of 50 °C until the TiO<sub>2</sub> porous film was filled with solid-state electrolyte. The cell was further dried at 50 °C under vacuum for 1 h to remove methanol. Finally, the two holes were sealed with a Surlyn film covered with a thin glass slide under heat. The working performance of the DSSC was tested by recording the current density-voltage ( $J-V$ ) curves with a Keithley 2400 source meter (Oriel) under illumination of simulated AM1.5G solar light coming from a solar simulator (Oriel-94043A equipped with a Xe lamp and an AM1.5G filter). The light intensity was calibrated using a standard Si solar cell

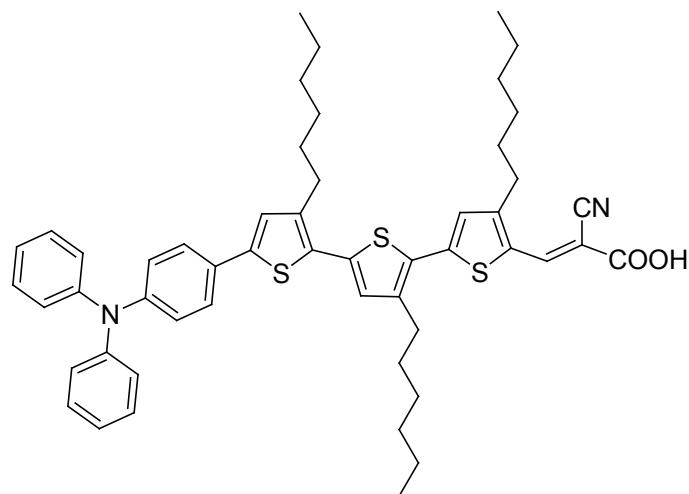
(Newport 91150). Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with an Oriel-74125 system (Oriel Instruments). The intensity of monochromatic light was measured with a Si detector (Oriel-71640).

### Characterizations.

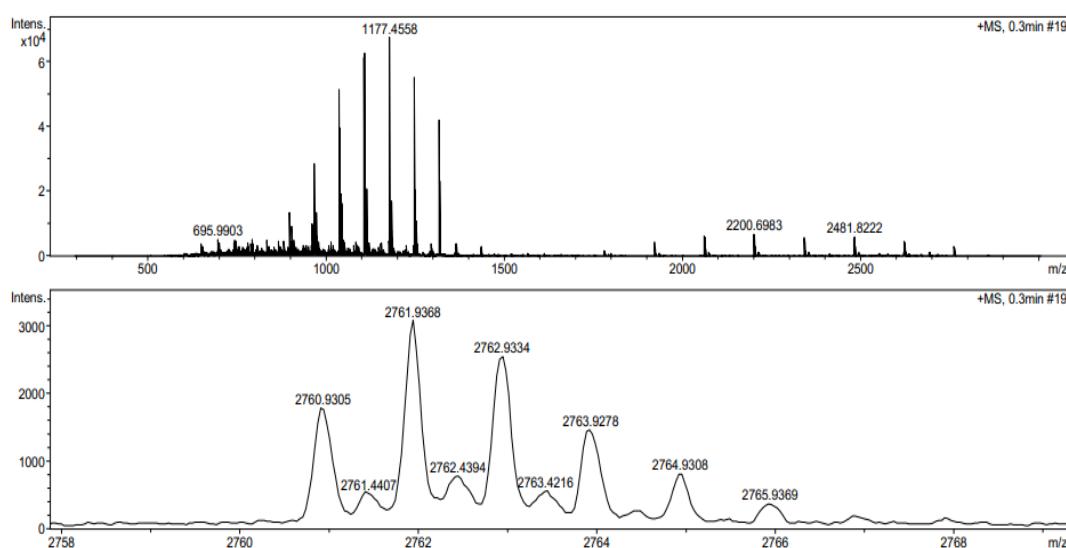
The structure of **POSS-8EsPImI** was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR (Varian 400 MHz NMR spectrometer). Fourier transition infrared (FT-IR) measurements were performed on Shimadzu IRAffinity-1 FT-IR spectrometer. The ionic conductivity of the solid electrolytes, which were sandwiched between two identical Pt electrodes, was determined by an ac impedance technique (frequency range: 1 Hz to 1 MHz) using an electrochemical workstation (Zahner CIMPS-1, Germany). The applied bias and ac amplitude were set at open-circuit condition and 10 mV, respectively.



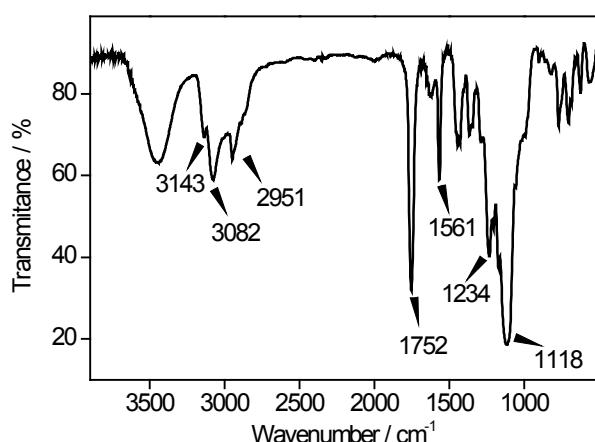
**Figure S1.** Chemical structure of EsPImI



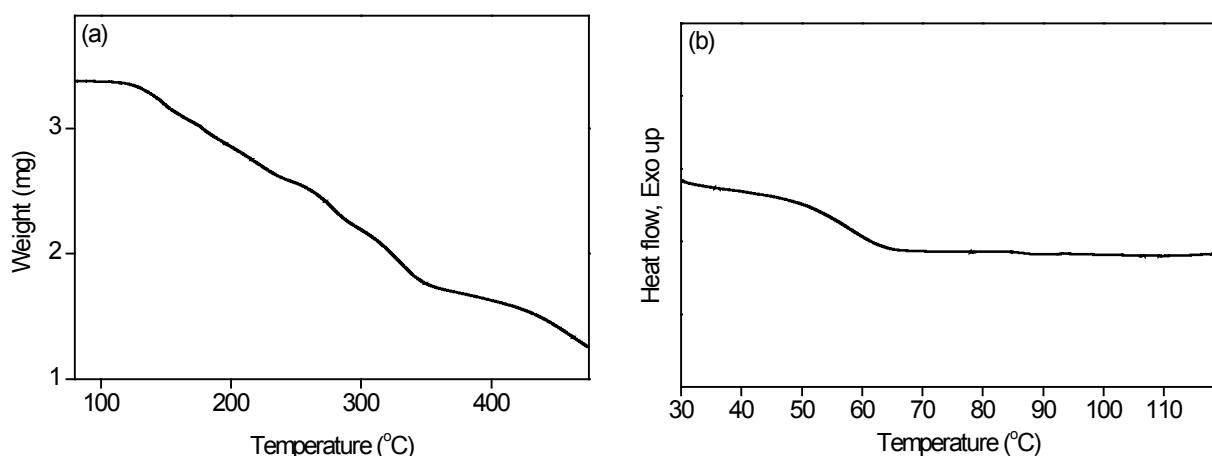
**Figure S2.** Chemical structure of the metal- free organic dye used in this work.



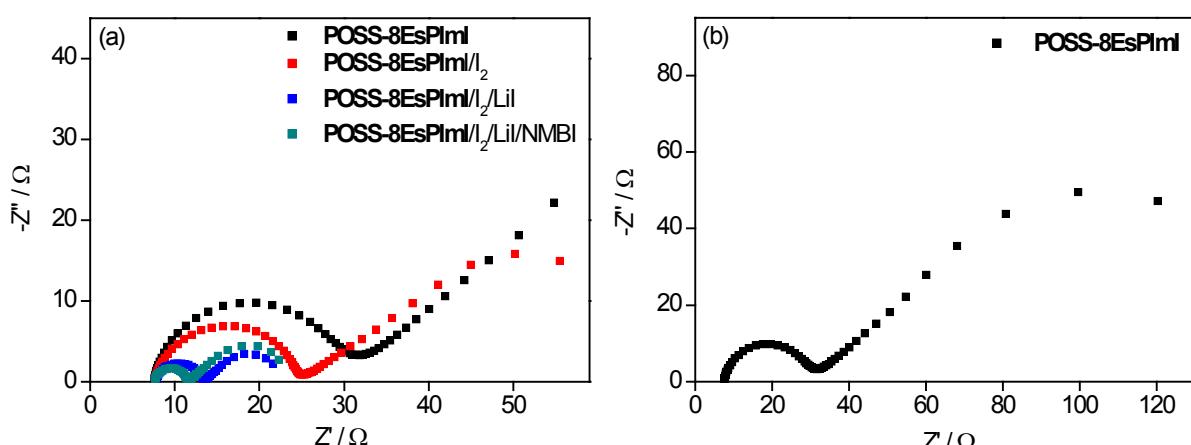
**Figure S3.** Mass spectrum of POSS-8EsPImI.



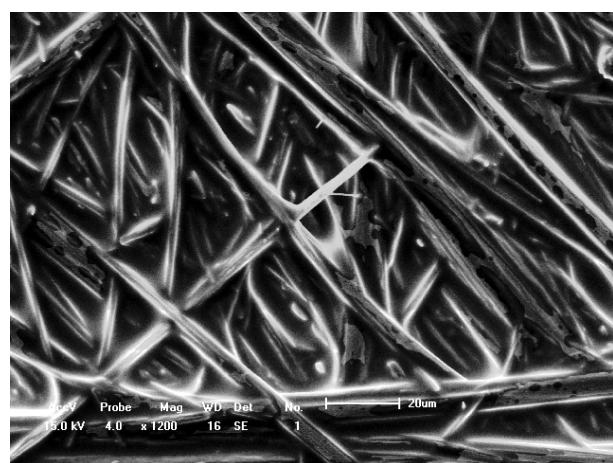
**Figure S4.** FT-IR spectrum of POSS-8EsPImI.



**Figure S5.** (a) TG and (b) DSC curve of POSS-8EsPImI.



**Figure S6.** EIS spectra of dummy cells with **POSS-8EsPImI**, **POSS-8EsPImI/I<sub>2</sub>** (1.5/1), **POSS-8EsPImI/I<sub>2</sub>/LiI** (1.5/1/3), **POSS-8EsPImI/I<sub>2</sub>/LiI/NMBI** (1.5/1/3/10).



**Figure S7.** SEM image of  $\text{TiO}_2$  film filled with EsPImI

## References

1. U. Dittmar, J.B. Hendan, U. Floerke, H.C. Marsmann. *J Organomet Chem*, 1995, **489**, 185.
2. D. Heyl, E. Rikowski, R.C. Hoffmann, J.J. Schneider and W.D. Fessner. *Chem. Eur. J.*, 2010, **16**, 5544.
3. Z-S. Wang, H. Kawauchi, T. Kashima, and H. Arakawa, *Coord. Chem. Rev.* 2004, **248**, 1381.