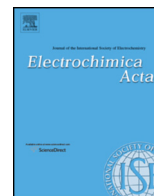




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## A new siloxane containing imidazolium iodide as electrolyte for dye-sensitized solar cell

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### ABSTRACT

New ionic liquids based on siloxane diimidazolium iodides (**SiDI1**, **SiDI2**, **SiDI3**) were synthesized and used as electrolytes in dye-sensitized solar cells. Modification with siloxane materials has been considered as the most effective method to improve the excellent optical transparency and thermal stability after a great many efforts. The synthesized siloxane diimidazolium iodides are viscous liquid with different color. These electrolytes have different chain length with siloxane moieties. Thermogravimetric analysis showed good thermal stability. Among the three **SiDI** based electrolytes, **SiDI1** showed a maximum photo-conversion efficiency of 6.2%. In addition, the performance of the DSSCs showed relatively reasonable compared with other conventional liquid type electrolytes.

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### 1. Introduction

Dye-sensitized solar cells have attracted a great attention due to their low production cost and high photo-conversion efficiencies since a new type of dye-sensitized solar cell has been reported by Grätzel [1,2]. The electrolytes are one of the key components and their properties have much effect on the conversion efficiencies. The supporting electrolyte used in DSSC is divided into three types: liquid electrolyte, gel-state electrolyte, and solid electrolyte. An electrolyte containing a suitable redox couple plays a very important role in determining the photovoltaic characteristics and durability of DSSC. Although there is the inherent drawback of the cell due to the volatility and possible leakage problem of liquid electrolytes during the long-term out-door operation.

Numerous efforts have been made to overcome this problem by replacing the liquid electrolytes with solid or quasi-solid state electrolytes composed of various polymers [3–6] and room temperature ionic liquids [7–9]. Among the onium cations with positive nitrogens, (such as quaternary ammonium, pyridinium, imidazolium) those derived from the imidazolium ring demonstrate to be the best choice in terms of melting point and electrochemical stability. Kubo et al. investigated the physical and physicochemical properties of a series of 1-alkyl-3-methylimidazolium iodide (alkyl

chain C3–C9) [10,11]. They found that the conductivity decreases as alkyl chain increases, which also affects viscosity by van der Waals forces. To improve the mobility of redox couple in the electrolyte and the photovoltaic performance, Grätzel et al. studied the solar cell based on low-viscosity ionic liquids [12]. These alkyl imidazolium cations were usually used as the counter ions of  $I_3^-/I^-$  couple in DSSC. Alkyl imidazolium cation may be adsorbed on the surface of semiconductor film to form the Helmholtz layer, which restricts the contact of tri-iodide and semiconductor film due to the recombination between tri-iodide and electrode in the conduction band of semiconductor. Kim et al. studied the solar cell based on ionic gel siloxane-substituted benzimidazolium iodide [13]. Unlike other usual ionic liquids, we designed imidazolium-based containing siloxane group with iodide as an anionic counterpart, which provided low viscosity and possibility to affect the formation of the stable Helmholtz layer on the surface of  $TiO_2$ , to prepare electrolytes for DSSC. Siloxane is thermally stable up to 350 °C, in addition to allowing relatively low permittivity, flexibility and hydrophobicity. The chain flexibility arises from the large angle of Si–O–Si linkage and the low bending force constant for this linkage, which provides low viscosity and good separation between hydrophobic siloxane and hydrophilic salts [14,15].

This paper reports on novel electrolyte consisting of imidazolium-based ionic liquids with short and long chain siloxane group. As the siloxane chains are the central part of the diimidazole molecule, the enrichment in mobility and solubility of the siloxane chains will be increased. We studied the effect of

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length of siloxane on the photovoltaic performance of DSSCs, and additionally the chemical structure and thermal properties were discussed. The photovoltaic performance and stability of the cell are investigated and discussed.

## 2. Experimental

### 2.1. Materials

Allyl alcohol, 1,1,3,3,5,5-hexamethyltrisiloxane, thionyl chloride, poly(dimethylsiloxane) hydride terminated (number average molecular weight,  $M_n \sim 580$ ), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, methyl iodide, sodium iodide, pyridine, and 1-methylimidazole were purchased from Sigma-Aldrich and 1,3-bis(chloromethyl)tetramethyldisiloxane were from TCI. Commercially available solvents, such as dichloromethane, chloroform, acetone, methanol, and ethyl ether were also used with or without further purification.

### 2.2. Synthesis of bis(1-methyl-3-methylene imidazolium iodide) tetramethyldisiloxane, (SiDI1)

A solution of 1,3-bis(chloromethyl)tetramethyldisiloxane (3.0 g, 12.97 mmol), sodium iodide (7.78 g, 51.89 mmol) in 50 mL acetone was refluxed at 60 °C for 24 h. The reaction mixture was allowed to cool to room temperature and filtered. The filtrate was concentrated on a rotary vacuum evaporator to get gummy mass which was washed with dichloromethane and water three times to give 1,3-bis(iodomethyl)tetramethyldisiloxane; yield: 5.21 g (97%). Then, a solution of 1,3-bis((1-methylimidazolium iodide)-3-methyl)tetramethyl-disiloxane (3.0 g, 7.24 mmol) and 1-methylimidazole (1.43 g, 13.22 mmol) in acetonitrile (30 mL) was refluxed at 85 °C for 24 h. The reaction mixture was evaporated and washed with ethyl ether. After removal of residual ethyl ether by vacuum evaporation at 60 °C for 6 h, bis(1-methyl-3-methylene imidazolium iodide)tetramethyldisiloxane, SiDI1 was obtained as a yellow oil to yield 3.98 g (95%).  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ ,  $\delta$  = ppm): 8.84 (s, N-CH=N, 2H), 7.59 (d, N-CH=CH-N, 2H), 7.42 (d, N-CH=CH-N, 2H), 3.77 (s, N-CH<sub>2</sub>-Si, 4H), 3.71 (s, N-CH<sub>3</sub>, 6H), 0.0 (s, Si-CH<sub>3</sub>, 12H).

### 2.3. Synthesis of 1,5-bis(3-iodo propyl)-1,1,3,3,5,5-hexamethyltrisiloxane

A mixture 1,1,3,3,5,5-hexamethyltrisiloxane (3.0 g, 14.39 mmol), allyl alcohol (2.01 g, 34.54 mmol) and a catalytic amount of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (1 drop) in toluene (30 mL) was refluxed for 24 h with continuous stirring. The reaction mixture was evaporated and then dissolved in methyl alcohol. It was passed through a plug of celite. The residual methanol was removed by vacuum evaporation to obtain 1,5-bis-(3-hydroxypropyl)-(1,1,3,3,5,5-hexamethyltrisiloxane) (4.44 g, 95% yield). Thionyl chloride (10.99 g, 92.4 mmol) was carefully added to a mixture of 1,5-bis-(3-hydroxypropyl)-(1,1,3,3,5,5-hexamethyltrisiloxane) (3 g, 9.24 mmol) and pyridine (0.07 g, 0.92 mmol) at 0 °C in an ice-water bath with constant stirring. After addition, the mixture was allowed to warm to room temperature and then refluxed at 70 °C for 12 h. The reaction mixture was then cooled to room temperature and the excess thionyl chloride was evaporated. The residue was washed with 40 mL distilled and the mixture was extracted with ethyl acetate (3 × 50 mL). The combined ethyl acetate extracts were successively washed with 100 mL saturated NaHCO<sub>3</sub> solution and H<sub>2</sub>O (2 × 100 mL), then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The ethyl acetate was removed on a rotary evaporator to give 1,5-bis-(3-chloropropyl)-(1,1,3,3,5,5-hexamethyltrisiloxane)

as a brown oil; yield: 3.01 g (90%). A solution of (1,1,3,3,5,5-hexamethyltrisiloxane)-1,5-dipropylchloride (3.0 g, 8.30 mmol), sodium iodide (4.98 g, 33.19 mmol) in acetone (50 mL) was refluxed at 60 °C for 24 h. The reaction mixture was allowed to cool to room temperature and filtered. The filtrate was evaporated under reduced pressure and then dissolved in dichloromethane. The reaction mixture was filtered and evaporated to remove dichloromethane on a rotary evaporator to give 1,5-bis-(3-iodopropyl)-1,1,3,3,5,5-hexamethyltrisiloxane as a brown oil; yield: 4.38 g (97%).

### 2.4. Synthesis of bis(1,5-dipropyl-3-methylimidazolium iodide)-1,1,3,3,5,5-hexamethyltrisiloxane (SiDI2)

A solution of 1,5-bis(3-iodopropyl)-1,1,3,3,5,5-hexamethyltrisiloxane (3.0 g, 5.51 mmol), 1-methylimidazole (1.09 g, 13.22 mmol) in acetonitrile (30 mL) was refluxed at 85 °C for 24 h. The reaction mixture was evaporated and washed with ethyl ether. The remaining ethyl ether was taken out by vacuum evaporation at 60 °C for 6 h to yield 3.71 g (95%).  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ ,  $\delta$  = ppm): 9.10 (s, N-CH=N, 2H), 7.74 (d, N-CH=CH-N, 2H), 7.68 (d, N-CH=CH-N, 2H), 4.09 (t, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 3.81 (s, N-CH<sub>3</sub>, 6H), 1.64–1.72 (m, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 0.40 (t, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 0.0 (s, Si-CH<sub>3</sub>, 18H).

### 2.5. Synthesis of bis(1-methyl-3-propyl imidazolium iodide) terminated poly(dimethylsiloxane) (SiDI3)

Bis(3-iodopropyl)-poly(dimethylsiloxane) was prepared as follows the previous procedure of SiDI2. A solution of bis(3-iodopropyl)-poly(dimethylsiloxane) (3.0 g, 5.51 mmol), 1-methylimidazole (1.09 g, 13.22 mmol) in acetonitrile (30 mL) was refluxed at 85 °C for 24 h. The reaction mixture was evaporated and washed with THF. The residual THF was removed by vacuum evaporation at 60 °C for 6 h to yield 3.36 g (95%).  $^1\text{H NMR}$  (400 MHz, DMSO- $d_6$ ,  $\delta$  = ppm): 9.12 (s, N-CH=N, 2H), 7.76 (d, N-CH=CH-N, 2H), 7.70 (d, N-CH=CH-N, 2H), 4.11 (t, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 3.83 (s, N-CH<sub>3</sub>, 6H), 1.70–1.78 (m, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 0.42 (t, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>, 4H), 0.0 (s, Si-CH<sub>3</sub>, 36H).

### 2.6. Preparation of electrolytes and DSSC fabrication

Organic solvent based three different liquid type electrolytes were prepared by dissolving siloxane diimidazolium iodides (SiDI1, SiDI2, SiDI3) with 0.1 M guanidinium thiocyanate (GNCS), 0.05 M I<sub>2</sub> and 0.5 M tert-butylpyridine (TBP) in 3-methoxypropionitrile. In every electrolyte, the concentration of siloxane diimidazolium iodides (SiDI1, SiDI2, SiDI3) were fixed as 0.5 M. Commercial titanium dioxide paste (Ti-Nanoxide HT, Solaronix SA) was used as the TiO<sub>2</sub> source. A thin layer of TiO<sub>2</sub> paste with an area of 0.2 cm<sup>2</sup> was deposited on fluorine doped tin oxide (TCO30-8, ~8 Ω/cm<sup>2</sup>, Solaronix, SA) glass substrate by doctor blade technique and successive sintering at 450 °C for 30 min in air. The resulting TiO<sub>2</sub> photoelectrodes were immersed into the dye solution (N719, Ru535 bis-TBA, Solaronix, SA) for 24 h in dark. The sandwich-type solar cell was assembled by sealing a Pt coated conducting glass on the photoelectrode.

### 2.7. Measurements

The  $^1\text{H NMR}$  spectra were recorded on a Bruker DRX (400 MHz) spectrometer using deuterated dimethylsulfoxide (DMSO- $d_6$ ) solvent and tetramethylsilane as an internal standard. And thermogravimetric analyses (TGA) were performed with Perkin-Elmer TGA7 at a heating rate of 20 °C/min under an ambient air flow

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