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

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Polyhedral oligomeric silsesquioxane functionalized with eight imidazolium iodide arms has been designed and synthesized for use as solid-state electrolytes in solid-state dye-sensitized solar cell, which exhibits power conversion efficiency of 7.11% under one sun illumination and good long-term stability under one sun soaking.

Dye-sensitized solar cells (DSSCs) are becoming more and more attractive because of their potential low cost, high power conversion efficiency, easy fabrication, and environmental friendliness.¹ A typical DSSC consists of a dye-sensitized nanocrystalline semiconductor electrode, a redox electrolyte, and a counter electrode. The most commonly used electrolyte in high-performance DSSCs is iodide/triiodide (I^-/I_3^-) dissolved in a volatile organic solvent.² However, the leakage or volatilization of the liquid solvent in the electrolyte significantly deteriorates the long-term stability of the DSSCs. Thus, it is necessary to develop all-solid-state electrolytes to replace the liquid electrolytes.³ Recently, we reported solid imidazolium-based ionic conductors for use in solid state DSSCs (ssDSSCs), which exhibited good photovoltaic performance.⁴ However, the wettability of solid electrolytes on the TiO₂ surface is a big problem limiting solar cell performance. For example, crystal growth inhibitor should be added into the electrolyte to improve the interfacial contact between solid electrolytes and TiO2 towards better photovoltaic performance.⁴ Therefore, synthesis of new solid electrolytes with good wettability on TiO₂ is of significance to achieve good performance.

Polyhedral oligomeric silsesquioxane (POSS) was discovered in 1946 by Scott.⁵ In consideration of its unique three-dimensional cage structure composed of Si-O bonds (Figure 1), different functional groups could be easily attached to POSS to expand its properties. In this communication, eight ester-propyl-substituted imidazolium iodide⁴ (EsPImI, Figure S1) arms were linked to POSS, forming POSS-8EsPImI. POSS has good wettability on the TiO₂ surface due to the presence of Si-O bonds, which is favourable for good pore filling of TiO₂ with this POSS based solid electrolyte. The linked imidazolium iodides act as iodide source for efficient dye regeneration. When **POSS-8EsPImI** mixed with appropriate amount of I₂, LiI and 1-methylbenziimidazole (NMBI, solid) as the solid electrolyte, the ssDSSC produced a power conversion efficiency of 7.11% in combination with an organic dye (Figure S2).⁶



Figure 1. The structure of POSS (white ball = H) and **POSS-8EsPImI** (white ball = EsPImI): purple ball = Si, red ball = O

The synthesis of **POSS-8EsPImI** (Figure 1, Scheme S1) is detailed in the Supporting Information (SI). The structure of **POSS-8EsPImI** was confirmed by ¹H, ¹³C, ²⁹Si NMR and

HRMS (Figure S3) and infrared (IR) spectrum (Figure S4). The IR band of the trisilanol silsesquioxane cage appears at 1118 cm^{-1} which is accompanied by CH₃ stretching (2951 cm⁻¹) and the corresponding deformational mode (1234 cm⁻¹).⁷ IR band at 1752 cm^{-f} is attributed to C=O in the ester group. The band at 1561 cm⁻¹ is assigned to the C=C stretching in the imidazolium ring, while the bands at 3143 and 3082 cm^{-1} are attributed to C-H stretching in the imidazolium ring.⁸ The decomposition temperature of POSS-8EsPImI is determined to be 120 °C by thermogravimetric analysis (TGA, Figure S5a). POSS-8EsPImI is amorphous as revealed by the differential scanning calorimetry (DSC) curve (Figure S5b), where glass transition takes place in the range of 52 °C. This feature avoids crystallization of the ionic conductor during electrolyte injection followed by drying and facilitates pore filling of TiO₂ with the solid electrolyte. The pore filling and interfacial contact between solid electrolyte and TiO₂ are expected to improve owing to the amorphous feature and the presence of Si-O bonds.

The conductivity of the solid electrolyte, which is crucial to the performance of ssDSSCs, was measured by electrochemical impedance spectroscopy (Figure S6). The conductivity of POSS-8EsPImI was 0.061 mS cm⁻¹, which was enhanced significantly to 0.17 mS cm⁻¹ when doping iodine to **POSS**-**8EsPImI** (molar ratio, **POSS-8EsPImI**/ $I_2 = 1.5/1$). This remarkable increase in ionic conductivity originates from the formation of polyiodides such as I_3^- ions by means of reaction between iodide and iodine. The formation of polyiodides facilitates the charge transfer along the polyiodide chain by the Grotthus-type exchange mechanism, which is the major reason for the remarkable enhancement of conductivity.⁹ Introduction of LiI to the above mixture (molar ratio, POSS-8EsPImI/I2/LiI = 1.5/1/3) further increased the conductivity to 0.78 mS cm⁻¹. This is attributed to the increased concentration of iodide and Li⁺ ions. The conductivity of 8EsPImI/I₂/LiI was 0.77 mS cm⁻¹, comparable to that of **POSS-8EsPImI**/I₂/LiI. This suggests that linking EsPImI to POSS hardly influenced the conductivity of the ionic liquid. When NMBI, which like 4-tertbutylpyridine is a useful additive in electrolyte for voltage enhancement,¹⁰ was added to the above mixture electrolyte (molar ratio, POSS-**8EsPImI**/ I_2 /LiI/NMBI = 1.5/1/3/10), the conductivity changed negligibly as shown in Figure S6. It is noted that the abovementioned molar ratios in the solid electrolyte were determined by optimizing the solar cell performance.

The ssDSSCs based on the solid electrolytes with various compositions were tested under illumination of AM1.5G simulated solar light (100 mW cm⁻²). For **POSS-8EsPImI**/I₂ electrolyte (molar ratio, 1.5/1), the DSSC produced short-circuit photocurrent density (J_{sc}) of 11.08 mA cm⁻², open-circuit photovoltage (V_{oc}) of 0.60 V, and fill factor (FF) of 0.62, corresponding to power conversion efficiency (η) of 4.12% (Figure 2a). The η was improved to 5.81% ($J_{sc} = 15.63$ mA cm^{-2} , $V_{\text{oc}} = 0.63 \text{ V}$, FF = 0.59) using the **POSS-8EsPImI**/I₂/LiI solid electrolyte (molar ratio, 1.5/1/3), as shown in Figure 2a. The increase in η is mainly attributed to the enhancement of J_{sc} because of the positive shift of conduction band edge of TiO₂ caused by the adsorption of Li^+ ions on TiO_2 surface¹¹ and the increased conductivity as well. When NMBI was added to the above electrolyte (molar ratio of POSS-8EsPImI/I2/LiI/NMBI was 1.5/1/3/10), V_{oc} increased to 0.74 V but J_{sc} decreased to 14.12 mA cm⁻². The observed increase in V_{oc} and decrease in $J_{\rm sc}$ is likely attributed to the negative shift of conduction band edge of TiO₂ caused by the basic NMBI.¹⁰ As a result, the η was improved to 7.11%. Figure 2b displays the incident

monochromatic photon-to-electron conversion efficiency (IPCE) as a function of wavelength. The IPCE values in he visible spectral range were the lowest for the **POSS-8EsPImI**/ I_2 among the three electrolytes. The IPCE increased significantly upon addition of LiI to **POSS-8EsPImI**/ I_2 , which decreased to some extent upon further addition of NMBI. The IPCE order is the same as that of J_{sc} .



Figure 2. J-V curves (a) and IPCE spectra (b) for the ssDSSCs

The filling of pores in TiO₂ film with solid electrolytes is crucial to achieve good performance. Figure 3 shows the scanning electronic microscopy (SEM) images for TiO₂ films before and after solid electrolyte filling. The surface of bare TiO₂ film is porous, which becomes non-porous and smooth when the solid electrolyte is filled in the film. This indicates that the pores in TiO_2 are filled with the solid electrolyte very well, which accounts for the good photocurrent and efficiency. However, for the solid ionic liquid (EsPImI, Figure S1) that is not linked to the POSS, pore filling is not good due to the serious ionic crystallization (Figure S7). For this reason, EsPImI only produces n of 2.07% without adding the crystal growth inhibitor and produces 3.81% efficiency with small amount of crystal growth inhibitor. Despite the comparable conductivity, the solid electrolyte based on POSS-8EsPImI yields much higher efficiency than the corresponding solid electrolyte based on EsPImI without or with crystal growth inhibitor. It is evident the combination of POSS and ionic liuid can improve photovoltaic performance remarkably.

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Figure 3. SEM images of TiO_2 before (a, top view; b, side view) and after (c, top view; d, side view) addition of the solid electrolyte (POSS-8EsPImI/I_2/LiI/NMBI) followed by drying

The performance of the ssDSSC was recorded over a period of 1000 h under one-sun soaking using an unoptimizable cell (Figure 4). J_{sc} , V_{oc} , FF and η remained almost constant during light soaking, suggesting that this ssDSSC is long-term stable.



Figure 4. Performance evolution of the ssDSSC under one-sun light soaking

In summary, novel ionic liquid functionalized POSS has been designed and synthesized for use in ssDSSCs, which have achieved power conversion efficiency of 7.11% and good longterm stability under one-sun soaking. The combination of POSS with imidazolium iodides improves the pore filling of TiO₂ and facilitates interfacial contact between solid electrolytes and TiO₂, resulting in good photovoltaic performance. Improvement of efficiency can be expected by further structural modification of POSS and choice of better dye.

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Electronic Supplementary Information (ESI) available: details of syntheses and characterizations of **POSS-8EsPImI** and the experimental details. See DOI: 10.1039/c000000x/

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