

Communication

A Rapid One-Pot Synthesis of Novel High-Purity Methacrylic Phosphonic Acid (PA)-Based Polyhedral Oligomeric Silsesquioxane (POSS) Frameworks via Thiol-Ene Click Reaction

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Academic Editor: Ying-Ling Liu

Received: 9 May 2017; Accepted: 24 May 2017; Published: 27 May 2017

Abstract: Herein, we demonstrate a facile methodology to synthesis a novel methacrylic phosphonic acid (PA)-functionalized polyhedral oligomeric silsesquioxanes (POSSs) via thiol-ene click reaction using octamercapto thiol-POSS and ethylene glycol methacrylate phosphate (EGMP) monomer. The presence of phosphonic acid moieties and POSS-cage structure in POSS-S-PA was confirmed by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (¹H, ²⁹Si and ³¹P-NMR) analyses. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of POSS-S-PA acquired in a dithranol matrix, which has specifically designed for intractable polymeric materials. The observed characterization results signposted that novel organo-inorganic hybrid POSS-S-PA would be an efficacious material for fuel cells as a proton exchange membrane and high-temperature applications due to its thermal stability of 380 °C.

Keywords: thiol-ene; POSS; MALDI-TOF; nanomaterials; phosphonic acid

1. Introduction

In recent years, polyhedral oligomeric silsesquioxanes (POSSs), a family of nanostructured inorganic components with size tunability and functionality, have fascinated global research communities due to their wide range of potential applications in viscosity modifiers, catalysis, coating, drug-delivery vehicles, electronics, and renewable energy sources [1–3]. Additionally, it has strong attention due its unique physico-chemical properties and reactive organic terminal functional substituents [4–8]. The three-dimensional structure of the silicon–oxygen (Si–O) core is inevitably responsible for high thermal stability and stiffness, whereas the terminal organic reactive functional groups can be enabled to make the covalent bond between POSSs and polymers, which results in the solid progress of organic–inorganic hybrid materials [9,10]. POSS properties have been tuned [11–15] by incorporating various end-group moieties (functionalities), such as acrylates,

methacrylate, alcohols, amines, carboxylic acids, epoxides, fluoroalkyls, halides, and imides, through self-polymerization reactions, which include self-condensing vinyl polymerization, poly-condensation reactions, ring-opening polymerization, and “ene-click” reactions [16–18]. Methacrylate-functionalized POSSs provide improved thermal stability and flame retardancy. Further, the incorporation of phosphorus-, silicon-, and boron-containing compounds as POSS moieties is an effective way of improving its physicochemical properties and stiffness [9,19–21].

In this communication, we report on the development of a novel type of methacrylic phosphonic acid-functionalized POSSs for fuel cells. To the best of our knowledge, there is no report available based on the synthesis and characterization of methacrylate phosphate-functionalized POSSs (POSS-S-PA). Via thiol-ene click reaction chemistry, octamercapto thiol POSSs were functionalized with 7~8 phosphonic acid (PA) groups, paving the way for use as a potential candidate for proton exchange membrane fuel cells due to its anhydrous proton conduction group, high thermal, hydrolytic, and oxidative stabilities [21,22].

2. Material Synthesis

2.1. Materials

2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from Fischer, Seoul, Korea and used after purification. 3-Mercaptopropyl trimethoxysilane (MTS, 98%), anhydrous dichloromethane (DCM), triethyl amine (TEA), and methanol (MeOH, 99.9%) were donated by Sigma Aldrich, Yongin, Korea. Ethylene glycol methacrylate phosphate (EGMP, 98%) was purchased from Shanghai Angewchem Co., Ltd. (Shanghai, China).

2.2. Synthesis of POSS-S-PA

The synthesis of POSS-S-PA involves two steps. The first step includes the synthesis of POSS-SH from 3-mercaptopropyl trimethoxysilane by acid hydrolysis reaction [9], which is described as follows. The schematic representation of the synthetic route is sketched in Figure S1 (ESI). Firstly, 15 mL of stoichiometric MTS were mixed with 20 mL of concentrated HCl and 240 mL of an MeOH (anhydrous) solution in a three-neck flask, which was fitted with a condenser, as shown in Figure S1. In order to complete hydrosilylation reaction, the precursor solutions were subjected to acid hydrolysis followed by condensation reactions at 90 °C for 48 h. After the removal of solvent under reduced pressure, the obtained raw product was further dissolved in anhydrous dichloromethane and precipitated in distilled water (18.3 MΩ.cm at 25 °C), and this procedure was repeated three times to obtain the final product. The collected final product as a white-colored viscous liquid with a yield of 22% was dried under vacuum at 80 °C for 12 h. The thiol-ene click reaction between POSS-SH and EGMP was pictorially represented in Figure 1.

The second step for the synthesis of POSS-S-PA from POSS-SH is explained as follows: The methacrylic PA-terminated hybrid-network polymer POSS-S-PA was synthesized by the so-called “thiol-ene” reaction [19,23,24] using POSS-SH and EGMP. For synthesis, 10 mL of POSS-SH (10.1800 g, 1000 mL, and 10 mM) dissolved in 30 mL of anhydrous DCM and TEA (0.24 mM) were taken in a three-necked round bottom flask and subjected to constant stirring under an N₂ atmosphere for about 2 h at 40 °C. Then, freshly distilled EGMP (16.8080 g, 1000 mL, and 80 mM) was injected into the reaction mixture to carry out the polymerization reaction for 5 h at 40 °C. In order to retain the POSS-cage structure, EGMP was added slowly, dropwise, for up to 30 minutes. The obtained product was kept in a refrigerator overnight, and white precipitate was then separated from DCM using rotatory evaporation. The obtained white precipitate, designated as POSS-S-PA, was further purified by dissolving in methanol and re-precipitation in diethyl ether to remove unreacted POSS-SH, and then filtered and dried. The yield of light yellow POSS-S-PA was 64% and a schematic for the synthetic route is shown in Figure 1. Its corresponding instrumentation details are provided in the supplementary file.

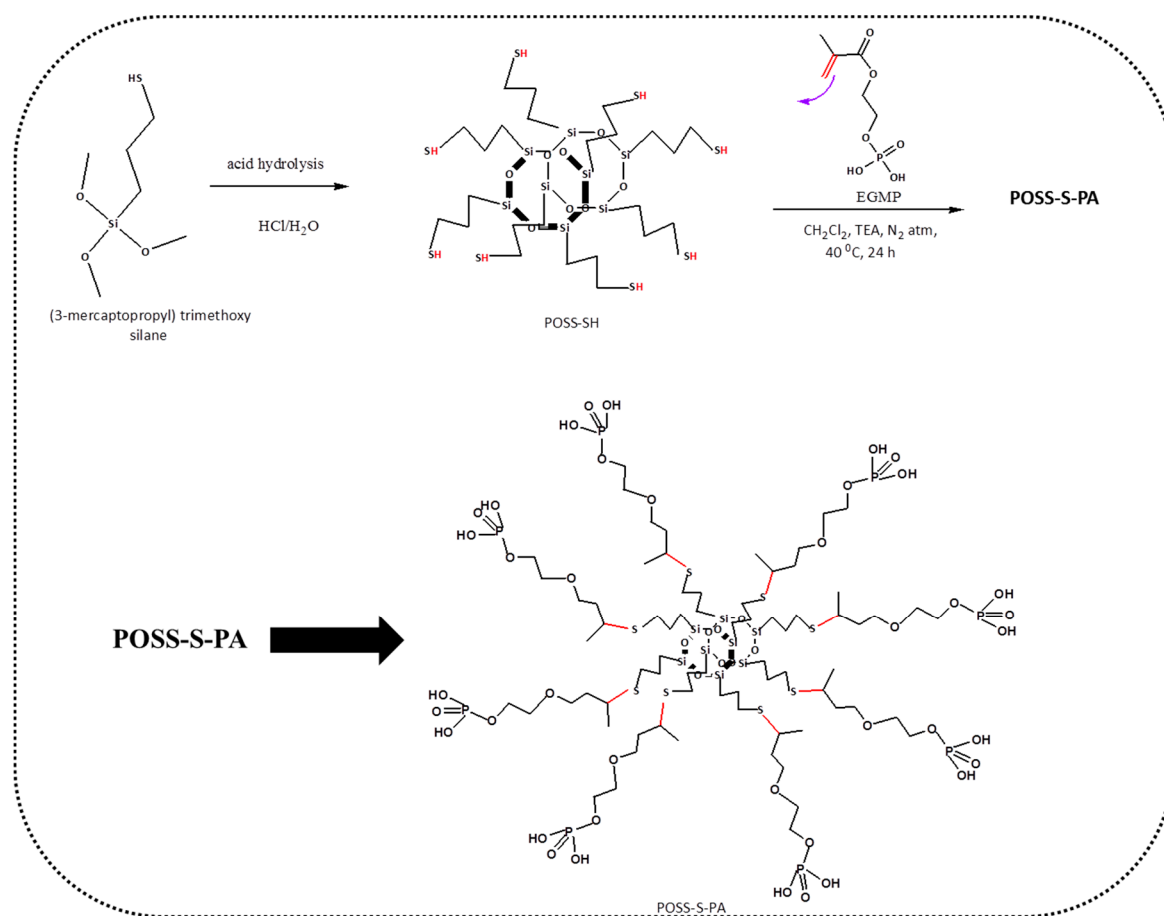


Figure 1. Pictorial representation of thiol-ene click reaction between POSS-SH and EGMP.

3. Results and Discussions

A novel methacrylic POSS-S-PA has been synthesized using octamercapto thiol-POSS and ethylene glycol methacrylate phosphate (EGMP) monomer via thiol-ene click reaction. Further, as-prepared POSS-S-PA was characterized by NMR, FTIR, MALDI-TOF, TG-DTG, and SEM analyses to confirm their hybrid structure.

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of precursor MPTS and product POSS-SH are given in Figure S2 (ESI) which confirms the formation of POSS-SH from MPTS. Figure 2a,b show the $^1\text{H-NMR}$ spectra of POSS-SH and POSS-S-PA. From the $^1\text{H NMR}$ spectrum of POSS-SH, three signals are observed at 0.72, 1.68, and 2.52 ppm due to methylene protons on the mercaptopropyl arm and another triplet signal is exhibited at 1.34 ppm, which is attributed to thiol proton. The peak analysis provides an integral of 2:2:2:1 for an eight-armed thiolated POSS peak of 1, 2, 3, and 4, respectively. In POSS-S-PA, the successful completion of reaction between POSS-SH and EGMP has been confirmed by the absence of thiol triplet peak at 1.34 ppm as well as the absence of resonance from the ethylene proton in the range 4.5–6.5 ppm as shown in Figure 2b. The important proton NMR peaks of POSS-S-PA and its assignments are as follows: 0.78 (t, Si-CH₂), 1.62 (s, Si-CH₂-CH₂), 2.31 (t, Si-CH₂-CH₂-CH₂), 0.93 (m, S-CH₂) 2.09 (m, S-CH₂-CH-CH₃) 1.83 (s, CH-CH₃) 4.14 (t, CO-CH₂), 4.25 (m, -CH₂-P), 2.60 (s, P-OH).

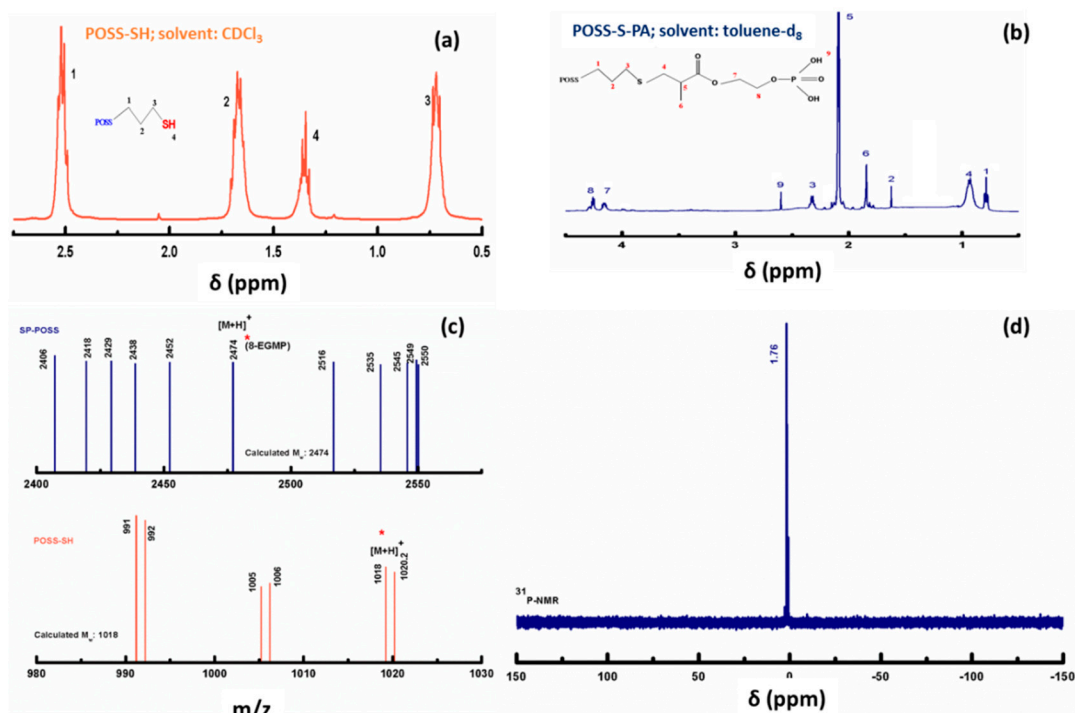


Figure 2. (a) ^1H -NMR spectrum of POSS-SH; (b) ^1H -NMR spectrum of POSS-S-PA; (c) MALDI-TOF-MS spectrum of POSS-SH and POSS-S-PA; (d) ^{31}P -NMR spectrum of POSS-S-PA.

Besides, the MALDI-TOF MS spectrum shows two strong signals at 1018 and 2474 m/z for POSS-SH and POSS-S-PA, respectively, as displayed in Figure 2c. These peaks represent the mass of silsesquioxanes (SQ) cage with octamers like eight propyl and EGMP groups, respectively. For the same, the calculated values are 1017 and 2474 m/z . In addition, some other unassigned signals are observed along with main peaks, but the ultimate product for a building block of the octamer SQ cage is confirmed by elemental and NMR analyses. The unassigned peaks observed may be due to the hexamer and heptamer of the SQ cage, which could not be isolated selectively during the synthesis. The elemental analysis data of both POSS-SH and POSS-S-PA are as follows: POSS-SH: Calculated—C 47.9, H 9.39 and S 42.67; found—C 47.82, H 10.20 and S 42.60%; POSS-S-PA: Calculated—C 45.35, H 6.82, O 33.80 and S 14.03; found—C 45.12, H 6.82, O 33.98 and S 14.08%. These observations are strongly consistent with earlier results [25,26].

The presence of PA terminal groups in the synthesized sample is further confirmed by ^{31}P -NMR analysis, and it is displayed in Figure 2d. It shows a sharp signal at 1.6 ppm, which arises due to the diacid form of the phosphonate units in POSS-S-PA. From the ^{29}Si NMR spectrum of Figure 3a, two signals are exhibited in the T^3 region, which confirms the presence of the POSS cage structure. The main signals are observed from -66.10 to -66.38 ppm and from -66.40 to -66.70 ppm and assigned to the cage-like octamer (T^8) and the cage-like decamer (T^{10}), respectively. Moreover, the absence of a silanol group signal in the ^{29}Si NMR spectrum of POSS-S-PA confirms the stable SQ cage structure without any degradation during the course of reaction.

FTIR spectroscopy analysis is performed to confirm the various structural organization in POSS-S-PA functional groups as well as to distinguish thiol and double bonds conversion individually [27,28]. Figure 3b represents the attenuated total reflection (ATR)-FT-IR spectra of POSS-SH and POSS-S-PA hybrids. The observed peaks are at 1100–1080 and 2626 cm^{-1} attributed to characteristic Si–O–Si stretching and S–H stretching vibrations of POSS-SH, respectively [29,30]. The thiol-ene click reaction formed POSS-S-PA is confirmed by the presence of C=O, C–H stretching and P–OH peaks are at 1732, 2850–3050, and 3600 cm^{-1} , respectively, as well as the absence of an

S–H peak in the region of 2620 cm^{-1} . The observed FTIR peaks and its corresponding assignments of POSS-SH and POSS-S-PA are tabulated in Table 1. The observed results are highly consistent with earlier literature based on the thiol-methacrylate system [31,32].

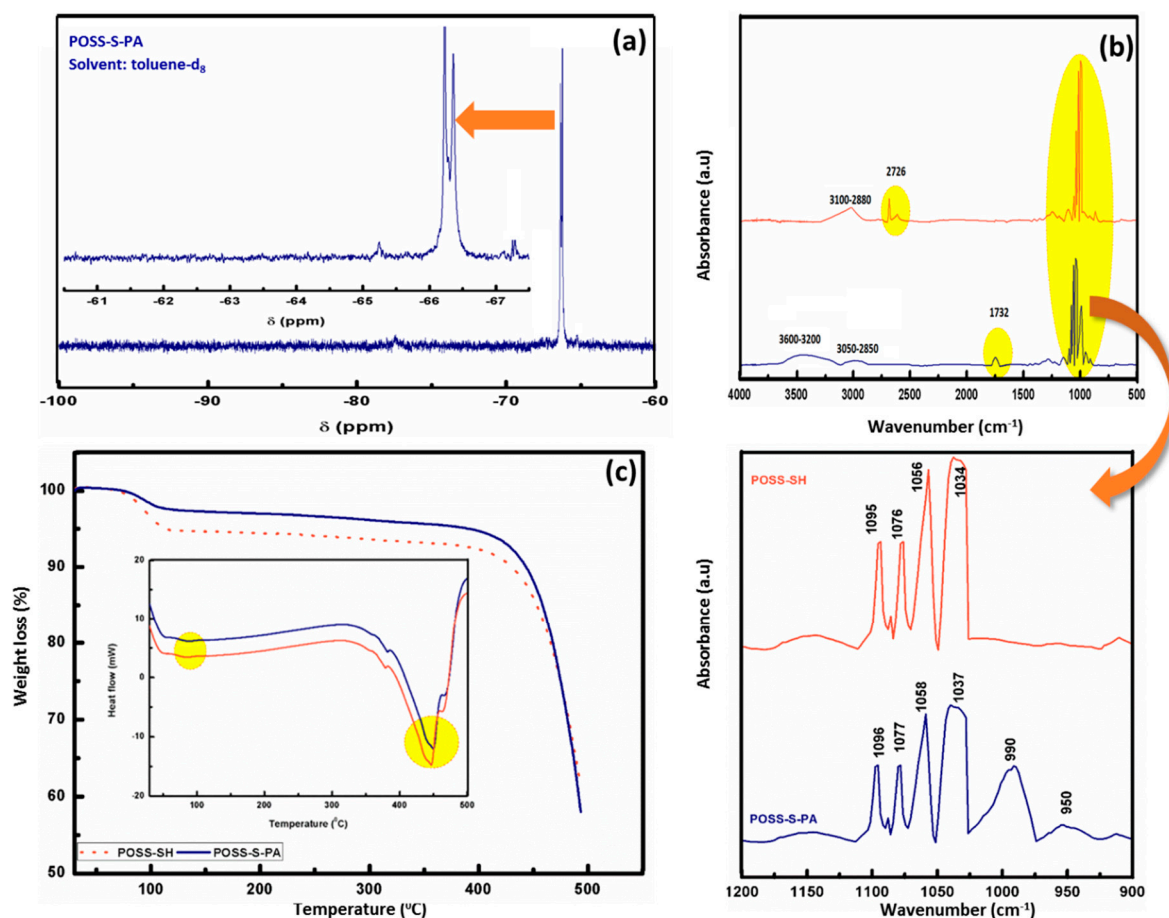


Figure 3. (a) ^{29}Si -NMR spectrum of POSS-S-PA; (b) FT-IR spectra of POSS-SH and POSS-S-PA; (c) TG-DTA thermogram of POSS-SH and POSS-S-PA.

Table 1. Peak positions and its corresponding assignments of POSS-SH and POSS-S-PA.

| FTIR Frequency Wavenumber (cm^{-1}) | | Assignments |
|--|-----------|---------------------------------|
| POSS-SH | POSS-S-PA | |
| 1095–1056 | 1096–1058 | Si–O–Si |
| - | 990, 950 | P–O stretching & P–C stretching |
| - | 1736 | C=O |
| 2690 | - | S–H |
| 3100–2880 | 3050–2850 | C–H stretching |
| - | 3200–3600 | P–OH stretching |

TG-DTA curves of POSS-SH and POSS-S-PA hybrids are provided in Figure 3c. From the curves, the weight loss is observed for less than 5% up to $120\text{ }^{\circ}\text{C}$, which may be due to the volatilization of free and hydrogen bonded water; thereafter, the continuous weight loss is observed until $434\text{ }^{\circ}\text{C}$, attributed to the decomposition of terminal groups in the POSS core and the complete decomposition of POSS backbones. The related DTA curve with respect to heat flow also shows a similar type of thermal variation during the entire weight loss curve, which is given in inset of Figure 3c. The morphological properties of POSS-SH and POSS-S-PA hybrids were investigated by FE-SEM analysis (Figure 4a,b). It

can be seen from the SEM micrograph that POSS-SH consists of a 3D-skeletal like morphology, with a combination of spherical and hexagonal shaped grains. For POSS-S-PA (Figure 4b), the SEM image consists of larger-sized grains due to the agglomeration.

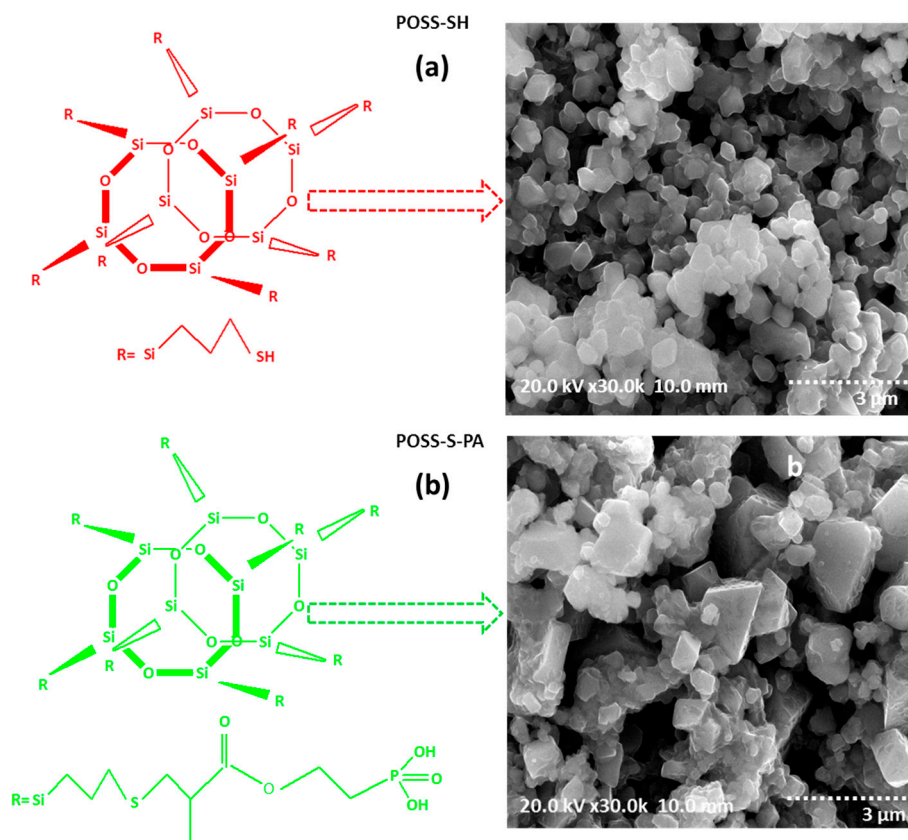


Figure 4. Structure and SEM image of (a) POSS-SH and (b) POSS-S-PA hybrids.

4. Conclusions

In summary, a novel strategy of a PA-functionalized SQ cage was successfully prepared with high yields by a rapid one-pot synthesis via thiol-ene click reaction. The excellent purity of the as-prepared POSS-S-PA framework was confirmed by NMR, FTIR, and MALDI spectral analyses. Our hybrid structure of POSS-S-PA possessed good thermal stability, which was exposed by TG-DTA. From the observed results, POSS-S-PA would be an excellent inorganic–organic hybrid material for high-temperature applications and as a proton exchange membrane in fuel cells to help to increase the protonic transport, which in turn improves its protonic conductivity and cell performance.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4360/9/6/192/s1, Figure S1: Schematic diagram for acid hydrolysis of 3-mercaptopropyl trimethoxysilane; Figure S2: ^1H and ^{13}C -NMR spectra of 3-mercaptopropyl trimethoxysilane and POSS-SH.

Acknowledgments: Hee Woo Rhee thankfully acknowledges Global Frontier R&D Program on Center for Multiscale Energy System funded by the National Research Foundation under the Ministry of Science, ICT & Future Planning, Korea (2011-0031570) and the Korea Center for Artificial Photosynthesis (KCAP) located in Sogang University funded by the Minister of Science, ICT and Future Planning (MSIP) through the National Research Foundation of Korea (No. 2009-0093883). Hee Woo Rhee was also supported by the Human Resources Development program (No. 20114010203090) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea Government Ministry of Trade, Industry and Energy for their financial support. Hyun-Seok Kim is grateful to Ministry of Trade, Industry and Energy (MOTIE, Korea) under Sensor Industrial Technology Innovation Program (No. 10063682) and the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2014R1A1A2058814) for their financial support.

Author Contributions: K. Karuppasamy, Hee Woo Rhee and Hyun-Seok Kim planned the project and the experiments. K. Karuppasamy and K. Prasanna performed the experiments. All authors Hyun-Seok Kim, Dhanasekaran Vikraman, A. Kathalingam and Liviu Mitu contributed to the data analysis and the discussions leading up to the writing of the manuscript. K. Karuppasamy, Dhanasekaran Vikraman, A. Kathalingam and Hyun-Seok Kim took part in the main discussions that led to the final manuscript; all authors read and finalized the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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