Preparation of protic ionic liquids containing cyclic oligosiloxane frameworks

T. Hirohara, T. Kai, J. Ohshita and Y. Kaneko

Protic ionic liquids (PILs) containing cyclic oligosiloxanes with ammonium side-chain groups (Am-CyS-IL and 2Am-CyS-IL) were successfully prepared by the hydrolytic condensation of 3-aminopropylmethoxymethylsilane and 3-(2-aminoethylamino)propylmethoxymethylsilane, respectively, in a water/methanol (1:19 v/v) mixed solution of bis(trifluoromethanesulfonylimide) (HNTf2). The differential scanning calorimetry (DSC) curves of Am-CyS-IL and 2Am-CyS-IL exhibited baseline shifts attributable to glass transition temperatures (T_g) of -2 °C and 9 °C, respectively, and endothermic peaks at their melting temperatures (T_m) were not detected for both compounds, indicating their amorphous structures. In addition, fluidity was visually observed for each compound at -35 °C and -45 °C, respectively. On the basis of these results, we concluded that Am-CyS-IL and 2Am-CyS-IL were PILs. To investigate the influence of the kind of siloxane framework on the nature of the ionic liquid, we prepared polyhedral oligomeric silsesquioxanes (POSSs) containing the same side-chain groups and counteranions (Am-POSS and 2Am-POSS) from 3-aminopropyltrimethoxysilane and 3-(2-aminoethylamino)propyltrimethoxysilane, respectively, using an HNTf2 catalyst. Am-POSS had a T_g of 15 °C and a T_m of 193 °C, and 2Am-POSS had a T_g of 32 °C and a T_m of 208 °C, which were estimated by DSC analyses. Furthermore, fluidity was not observed below 150 °C for both compounds, indicating that these POSS compounds were not PILs. These results suggest that the cyclic oligosiloxane frameworks are an important factor for the preparation of siloxane-based PILs exhibiting fluidity at low temperature. In addition, the present PILs containing cyclic oligosiloxane frameworks exhibited relatively high decomposition temperatures (T_d): Am-CyS-IL: T_d = 351 °C and T_d = 362 °C, 2Am-CyS-IL: T_d = 294 °C and T_d = 309 °C.

Introduction

Ionic liquids (ILs) are generally defined as molten salts below 100 °C or 150 °C. ILs are classified as aprotic ILs (AILs) or protic ILs (PILs) depending on the absence or presence of protons. PILs are prepared by a simple neutralization (proton transfer) reaction between a Bronsted acid and a Bronsted base. Therefore, they have the advantages of being easier to prepare and cheaper compared with AILs. So far, PILs have been widely studied due to their remarkable potential as electrolytes for fuel cells, lithium-ion batteries and capacitors, as biomass extraction solvents, and for carbon dioxide captures. In particular, because PILs have relatively good thermal stability, they are expected to be applied as thermostable proton conductors (solid electrolytes) for fuel cells. However, the decomposition temperatures (T_d) of PILs on pyrolysis are generally lower than those of AILs because of proton transfer from the cation back to the anion to reform the original acid and base neutral species.

So far, in the field of AILs, ILs containing siloxane frameworks have been reported. Siloxane compounds exhibit excellent thermal stability due to the high binding energy of their Si–O–Si linkages. An AIL containing polyhedral oligomeric silsesquioxane (POSS), a siloxane framework, was first prepared by Chujo, Tanaka, and co-worker. This POSS-AIL contained carboxylate anion side chains and imidazolium cations as counterions. Zhang et al. have also reported the preparation of an AIL containing POSS with imidazolium cations side chains and dodecyl sulfate anions as counterions. Meanwhile, we prepared a highly thermostable POSS-AIL containing imidazolium cationic side-chains and bis(trifluoromethanesulfonylimide) imide (NTf2) anions as counterions by a simple hydrolytic condensation method. In addition, AILs containing randomly structured oligomeric silsesquioxanes with imidazolium and quaternary ammonium side-chain groups were also prepared. More recently, a room-temperature POSS-AIL containing two types of cationic side-chain groups, i.e. imidazolium and quaternary ammonium groups, and NTf2 anions as counterions was prepared by a similar hydrolytic condensation method. Furthermore, as an example of AILs containing other types of...
siloxane frameworks, we prepared imidazolium salt type AILs containing cyclic siloxanes. In these siloxane-based AILs prepared by us, the use of a superacid catalyst is essential for structural control and indicating IL nature. The T_m values of the aforementioned AILs containing siloxane frameworks were higher than those of AILs with side-chain structures of the corresponding siloxane-based AILs. Therefore, PILs containing siloxane frameworks are expected to exhibit higher thermal stability. However, to the best of our knowledge, the preparation of PILs containing siloxane frameworks has not yet been reported.

To successfully prepare such siloxane-based PILs, we referred to our previous study of the facile preparation of a single-structured cyclic tetrasiloxane containing ammonium groups by the hydrolytic condensation of 3-aminopropyltriethoxymethylsilane using aqueous superacid trifluoromethanesulfonic acid (HOTf) as a catalyst. However, this cyclic tetrasiloxane was not an IL, i.e. its melting temperature (T_m) is ca. 310 °C. In general, it has been reported that T_m and/or flow temperatures of ILs containing NTf_2 anions are lower than those containing OTf anions with the same cationic species.

In this study, when the hydrolytic condensation of dialkoxysilanes containing primary and/or secondary amino groups, such as 3-aminopropyltrimethoxymethylsilane (APDMMMS) and 3-(2-aminooethylamino)propyltrimethoxysilane (AEAPDMMMS), were investigated using superacid HNTf_2 as a catalyst, we found that PILs containing cyclic oligosiloxane frameworks were successfully prepared. Here we report the preparation, characterizations and thermal properties of these PILs, and a comparison of the properties with POSSs containing the same side-chain groups and counterions.

### Experimental

**Materials**

APDMMMS, AEAPDMMMS, 3-aminopropyltrimethoxysilane (APTMS) and 3-(2-aminooethylamino)propyltrimethoxysilane (AEAPTMS) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. (Japan). All reagents and solvents were used without further purification.

**Preparation of PILs containing cyclic oligosiloxane with one ammonium group per repeating unit (Am-Cys-IL)**

A water/methanol (1 : 19 v/v) mixed solution of HNTf_2 (0.5 mol L^{-1}, 30 mL, 15 mmol) was added to APDMMMS (purity: 97%, 0.638 g, 3.0 mmol) with stirring at room temperature. The subsequent procedures were the same as those described above for the preparation of Am-Cys-IL, and 1.896 g of a viscous product (Am-Cys-IL) was obtained (yield, ~87%; the ideal chemical formula of one repeating unit of the product [CH_3SiO(CH_2)_3NH_3(CF_3SO_2)_2N, FW = 398.4] was used for this determination). 1H NMR (400 MHz, DMSO-d_6): δ 7.80-7.43 (3H, br, –NH_3), δ 2.83-2.64 (2H, br, –NH(CH_2)_3NH_3), δ 1.61-1.41 (2H, br, –SiCH_2CH_2NH(CH_2)_3NH_3), δ 0.63-0.37 (2H, br, –SiCH_2CH_2NH(CH_2)_3NH_3), δ 0.19 to −0.03 (3H, br, –SiCH_2CH_2NH(CH_2)_3NH_3) was used for this determination). 1H NMR (400 MHz, DMSO-d_6): δ −19.3 to −19.8 (D_2, cyclic tetramer), δ −21.6 to −21.9 (D_2, cyclic pentamer), δ −22.2 to −22.5 (D_2, cyclic hexamer).

**Preparation of PILs containing cyclic oligosiloxane with two ammonium groups per repeating unit (2Am-Cys-IL)**

A water/methanol (1 : 19 v/v) mixed solution of HNTf_2 (0.5 mol L^{-1}, 30 mL, 15 mmol) was added to AEAPDMMMS (purity: 97%, 0.702 g, 3.0 mmol) with stirring at room temperature, and then this methanol solution was poured into chloroform (30 mL). The chloroform-insoluble part was isolated at 100 °C for 2 h, dissolved in methanol (1 mL) at room temperature, and then this methanol solution was poured into chloroform (30 mL). The chloroform-insoluble part was isolated by decantation, washed with chloroform (~30 mL x 3), and then dried by heating at 150 °C for ~10 h to yield 1.019 g of a viscous product (Am-Cys-IL); yield, ~85%; the ideal chemical formula of one repeating unit of the product [CH_3SiO(CH_2)_3NH_3(CF_3SO_2)_2N, FW = 398.4] was used for this determination). 1H NMR (400 MHz, DMSO-d_6): δ 8.48-8.23 (2H, br, –NH(CH_2)_3NH(CH_2)_3NH_3), δ 7.96-7.69 (3H, br, –NH(CH_2)_3NH(CH_2)_3NH_3), δ 2.91-2.68 (2H, br, –SiCH_2CH_2NH(CH_2)_3NH_3), δ 1.69-1.33 (2H, br, –SiCH_2CH_2NH(CH_2)_3NH_3), δ 0.78-0.40 (2H, br, –SiCH_2CH_2NH(CH_2)_3NH_3) was used for this determination). 1H NMR (400 MHz, DMSO-d_6): δ −67.3 (T_8), δ −69.4 (T_10).
Measurements

$^1$H and $^{29}$Si NMR spectra were recorded using a JEOL ECX-400 spectrometer (JEOL Ltd.). The atomic ratios of Si : S in the products were confirmed by energy-dispersive X-ray (EDX) analyses using an XL30 scanning electron microscope (FEI Co.). Matrix-assisted laser desorption ionization time-of-flight mass spectral (MALDI-TOF MS) analyses of the products were performed using a Shimadzu Voyager Biospectrometry Workstation Ver. 5.1 (SHIMADZU Co.) positive ion mode with 2,5-dihydroxybenzoic acid (DHB) as the matrix. Attenuated total reflectance infrared (ATR-IR) spectra were recorded using a JASCO FTIR-4200 spectrometer (JASCO Co.). Diﬀerential scanning calorimetry (DSC) analyses were performed using a DSC-60 Plus (SHIMADZU Co.). The sample was placed in an open container until the solvent evaporated. The resulting decomposition temperatures were determined from the 5% weight loss (T$_{5\%}$) and 10% (T$_{10\%}$) weight losses.

Results and discussion

Preparation and characterizations of Am-CyS-IL and 2Am-CyS-IL

A PIL containing a cyclic oligosiloxane with one ammonium group per repeating unit, Am-CyS-IL, was prepared according to the following procedure (Scheme 1a): APDMMMS was stirred in a water/methanol (1 : 19 v/v) mixed solution of HNTf$_2$ (0.5 mol L$^{-1}$) at room temperature for 2 h. Here, an excess amount of HNTf$_2$ was required (the feed molar ratio of HNTf$_2$/APDMMMS was 2.5). The resulting solution was heated at ca. 60 °C in an open container until the solvent evaporated. The resulting crude product was further heated at 100 °C for 2 h, washed with chloroform, and then dried at 150 °C for ~10 h to obtain Am-CyS-IL. Am-CyS-IL was soluble in high-polarity solvents, such as water, methanol and acetone, but insoluble in low-polarity solvents, such as chloroform, toluene and hexane.

The $^1$H NMR spectrum of Am-CyS-IL in DMSO-$d_6$ exhibited signals attributable to 3-aminopropyl and methyl groups, but signals due to the methoxy groups of APDMMS were not observed (Fig. 1a), indicating that the APDMMMS reagent was not present in the product. The EDX pattern of Am-CyS-IL revealed that the Si : S atomic ratio was ca. 1.00 : 1.99, indicating that the molar ratio of the ammonium cation to the NTf$_2$ anion in Am-CyS-IL was ca. 1 : 1 (Fig. 2a). In the MALDI-TOF MS analysis of Am-CyS-IL, several peaks were observed that corresponded to the masses of cyclic siloxane tetramer, pentamer and hexamer (Fig. 3a). The $^{29}$Si NMR spectrum of Am-CyS-IL in DMSO-$d_6$ at 40 °C showed three multiple signals in the D$^2$ region (−19.3 to −19.8 ppm for cyclic tetrasiloxane, −21.6 to −21.9 ppm for cyclic pentasiloxane, and −22.2 to −22.5 ppm for cyclic hexasiloxane) and no signals in the D$^3$ region at ca. −15 ppm (Fig. 4a). Furthermore, the aforementioned $^1$H NMR spectrum of Am-CyS-IL exhibited multiple signals, a, attributable to methyl groups at 0.20 to −0.01 ppm (Fig. 1a). These results indicate that Am-CyS-IL was a mixture of cyclic tetra-, penta- and hexasiloxanes, with some stereoisomers.

A PIL containing a cyclic oligosiloxane with two ammonium groups per repeating unit, 2Am-CyS-IL, was prepared using almost the same procedure as that of Am-CyS-IL but using...
another organodialkoxy silane containing two amino groups, AEAPDMMS, as a starting material (Scheme 1b). 2Am-CyS-IL was soluble in high-polarity solvents, such as water, methanol and acetone, but insoluble in low-polarity solvents, such as chloroform, toluene and hexane.

The $^1$H NMR (Fig. 1b) and EDX (Fig. 2b) results of 2Am-CyS-IL indicated that the AEAPDMMS reagent was not present in the product, and that the molar ratio of ammonium cations to NTf$_2$ anions in 2Am-CyS-IL was ca. 1 : 1. The MALDI-TOF MS results indicated the existence of a mixture of cyclic siloxane tetramer and pentamer (Fig. 3b). Furthermore, the $^{29}$Si NMR spectrum of 2Am-CyS-IL showed three signals in the D$^2$ region (−19.1 to −20.1 ppm for cyclic tetrasiloxane, −21.3 to −21.8 ppm for cyclic pentasiloxane, and −22.1 to −22.4 ppm for cyclic hexasiloxane) and no signals in the D$^3$ region at ca. −15 ppm (Fig. 4b), supporting the formation of cyclic siloxanes. In addition, these compounds had some stereoisomers, as demonstrated by the $^1$H NMR spectrum with multiple signals, a, due to the methyl groups at 0.27 to 0.01 ppm (Fig. 1b) and the $^{29}$Si NMR spectrum with three multiple signals, as described above (Fig. 4b).

To confirm the formation of ionic pairs of the resulting products (Am-CyS-IL and 2Am-CyS-IL), we compared the ATR-IR spectra of these products and their starting materials (APDMMS and AEAPDMMS). The IR spectra of APDMMS and AEAPDMMS showed absorption peaks attributable to the bending vibration of amino groups at 1575 and 1595 cm$^{-1}$, respectively (Fig. 5a and b). Conversely, those of Am-CyS-IL and 2Am-CyS-IL exhibited two typical absorption peaks attributable to the bending vibration of ammonium cations at 1610 and 1497 cm$^{-1}$ for Am-CyS-IL (Fig. 5c) and at 1605 and 1511 cm$^{-1}$ for 2Am-CyS-IL (Fig. 5d). In addition, these spectra did not exhibit absorption peaks due to the bending vibration of amino groups. Therefore, we concluded that cationic species (ammonium cations) were included in Am-CyS-IL and 2Am-CyS-IL. Meanwhile, because the NTf$_2$ anion is extremely stable, NTf$_2$ must be present as the anionic species in these compounds.

**Thermal properties of Am-CyS-IL and 2Am-CyS-IL**

The DSC analyses of Am-CyS-IL and 2Am-CyS-IL were performed at a heating rate of 20 °C min$^{-1}$ under a nitrogen flow (50 mL min$^{-1}$). The baseline shifts assigned to $T_g$ were observed at −2 °C for Am-CyS-IL (Fig. 6a) and at 9 °C for 2Am-CyS-IL (Fig. 6b). Conversely, endothermic peaks due to $T_m$ were not detected for both compounds (Fig. 6a and b), indicating that Am-CyS-IL and 2Am-CyS-IL were amorphous compounds. In addition, sharp diffraction peaks were not observed in the XRD
patterns of Am-CyS-IL and 2Am-CyS-IL (Fig. 7a and b), supporting their amorphous or poorly crystalline structures.

The flow temperatures of Am-CyS-IL and 2Am-CyS-IL were confirmed as follows. Samples in glass vessels were maintained in a horizontal position at 150 °C for 15 min, and then the vessels were cooled to room temperature, still in the horizontal position. Next, the vessels were maintained in a horizontal position at various temperatures (varied in 5 °C intervals) for 15 min, and then held for 15 min while tilting at each temperature. During this procedure, Am-CyS-IL and 2Am-CyS-IL showed obvious fluidity at ~35 °C (Fig. 8a) and ~45 °C (Fig. 8b), respectively. On the basis of these results, we concluded that Am-CyS-IL and 2Am-CyS-IL were PILs.

To investigate the amount of water in these PILs, the weight losses at 150 °C were evaluated by TGA (Fig. 9a and b). Consequently, these values were 1.1% for Am-CyS-IL and 0.3% for 2Am-CyS-IL, indicating that these PILs contain a little moisture. However, because these samples were dried at 150 °C for 10 h after synthesis, it is presumed that they slightly absorbed moisture in the environment.

The thermal stabilities of Am-CyS-IL and 2Am-CyS-IL against pyrolysis were investigated by TGA at a heating rate of 10 °C min⁻¹ up to 1000 °C under a nitrogen flow (250 mL min⁻¹). The T₅₀ and T₈₅ values were 351 and 362 °C, respectively, for Am-CyS-IL (Fig. 9a). These values were higher than those of the propylamine–NTf₂ salt (281 and 295 °C), having the side-chain structure of Am-CyS-IL, with a T₅₀ of ~65 °C and a Tₘ of 28 °C (Fig. 9c). These results indicate that the thermal stability of Am-CyS-IL was enhanced by the incorporation of the cyclic oligosiloxane frameworks. The cyclic oligosiloxane frameworks could suppress molecular tumbling, resulting in the prevention of degradation.⁹ On the other hand, the T₅₀ and T₈₅ values of 2Am-CyS-IL were 294 and 309 °C (Fig. 9b), which are almost the same as those of the N-propylethylenediamine–NTf₂ salt (299 and 309 °C), having the side-chain structure of 2Am-CyS-IL, with a T₅₀ of ~29 °C and a Tₘ of 85 °C (Fig. 9d). Because the side-chain groups of 2Am-CyS-IL are long, the suppression of molecular tumbling would not work. The weights of the residues of Am-CyS-IL (ca. 12%; Fig. 9a) and 2Am-CyS-IL (ca. 10%; Fig. 9b) at 900 °C were almost the same as the theoretical SiO₂ yields (15% and 8%, respectively).
Influence of structures of siloxane frameworks on IL nature

To investigate the influence of the structures of the siloxane frameworks on the nature of the ILs, we prepared POSS compounds containing the same side-chain groups and counterions (Am-POSS and 2Am-POSS). In our previous studies, POSS compounds containing ammonium side-chain groups were prepared by the hydrolytic condensation of APTMS,\textsuperscript{17} \textit{AEAPTMS}\textsuperscript{18} and an APTMS/\textit{AEAPTMS} mixture\textsuperscript{18} using aqueous superacid HOTf. Therefore, to obtain POSS compounds containing the same counterions as Am-Cys-II and 2Am-Cys-II, the hydrolytic condensation of APTMS and \textit{AEAPTMS} was performed using HNTf$_2$ as a catalyst, respectively (Scheme 2).

POSSs with one ammonium group (Am-POSS) and two ammonium groups (2Am-POSS) per repeating unit were prepared according to the following procedure (Scheme 2): APTMS and \textit{AEAPTMS} were stirred in 0.5 mol L\textsuperscript{−1} aqueous HNTf$_2$ solutions at room temperature for 2 h, respectively. Here, excess amounts of HNTf$_2$ were required (feed molar ratio of HNTf$_2$/amino group was 2.5). The subsequent procedures were the same as those described above for the preparation of Am-Cys-II and 2Am-Cys-II.

Characterization of Am-POSS and 2Am-POSS was performed using $^1$H NMR (Fig. 10), EDX (Fig. 11) and $^{29}$Si NMR (Fig. 12) measurements. Especially, the $^{29}$Si NMR results indicated that these compounds were mixtures of cage-like octasilsesquioxane (T$_8$-POSS) and cage-like decasilsesquioxane (T$_{10}$-POSS) (Fig. 12). However, the molar ratio of ammonium cations to NTf$_2$ anions in 2Am-POSS was ca. 1 : 0.79, i.e. a non-equimolar ratio (Fig. 11b). This is probably because it is difficult for HNTf$_2$ to approach the amino side-chain groups in 2Am-POSS due to their bulky nature.
The DSC curve of Am-POSS showed a baseline shift due to \( T_g \) at 15 °C and an endothermic peak due to \( T_m \) at 193 °C (Fig. 13a). In addition, the XRD pattern of Am-POSS showed several sharp diffraction peaks (Fig. 14a), indicating that Am-POSS was a crystalline compound. Furthermore, this POSS compound did not exhibit fluidity at 150 °C (Fig. 15a), indicating that it was not an IL. On the other hand, the DSC curve of 2Am-POSS exhibited a baseline shift due to \( T_g \) at 32 °C and an endothermic peak due to \( T_m \) at 208 °C (Fig. 13b). Additionally, the XRD pattern of 2Am-POSS also supported the formation of a crystalline structure, i.e. several sharp diffraction peaks were detected (Fig. 14b). Furthermore, this compound did not show fluidity at 150 °C (Fig. 15b). Based on these results, we concluded that the cyclic oligosiloxane frameworks with flexible structures compared with POSS are important for the preparation of siloxane-based PILs exhibiting fluidity at low temperature.

Incidentally, Am-POSS and 2Am-POSS exhibited high thermal stabilities in the TGA analyses. The \( T_{d5} \) and \( T_{d10} \) values were 372 and 384 °C for Am-POSS (Fig. 9e) and 304 and 327 °C for 2Am-POSS (Fig. 9f).

**Conclusions**

In this study, we found that PILs containing cyclic oligosiloxane frameworks, Am-Cys-II and 2Am-Cys-II, could be successfully prepared by the hydrolytic condensation of APDMMS and AEAPDMMS using a water/methanol (1 : 19 v/v) mixed solution of HNTf₂. The DSC curves of Am-Cys-II and 2Am-Cys-II exhibited baseline shifts attributable to \( T_g \) at ~2 °C and 9 °C, respectively, and endothermic peaks at \( T_m \) were not detected for both compounds, indicating their amorphous structures. In addition, fluidity was visually observed for each compound at ~35 °C and ~45 °C, respectively, indicating that Am-Cys-II and 2Am-Cys-II were PILs. For comparison, POSSs containing the same side-chain groups and counteranions, Am-POSS and 2Am-POSS, were prepared from APTMS and AEAPTMMS, respectively, using an HNTf₂ catalyst. Am-POSS had \( T_g \) of 15 °C and \( T_m \) of 193 °C, and 2Am-POSS had \( T_g \) of 32 °C and \( T_m \) of 208 °C. Furthermore, fluidity was not observed below 150 °C for either compound, indicating that these POSS compounds were not PILs. These results suggest that the cyclic oligosiloxane frameworks are an important factor for the preparation of siloxane-based PILs exhibiting fluidity at low temperature. The present PILs containing cyclic oligosiloxane frameworks exhibited relatively high thermal stabilities (Am-Cys-II: \( T_{d5} = 351 \) °C and \( T_{d10} = 362 \) °C, 2Am-Cys-II: \( T_{d5} = 294 \) °C and \( T_{d10} = 309 \) °C).

**Acknowledgements**

We acknowledge the support of Prof. Y. Suda, Dr M. Wakao and Dr H. Shinchi of the Graduate School of Science and Engineering, Kagoshima University (Japan) in MALDI-TOF MS measurements. This work was supported by JSPS KAKENHI (Grant-in-Aid for Challenging Exploratory Research) Number 15K13711.

**References and Notes**

1. T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2008, **108**, 206.
2. T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2015, **115**, 11379.
3. S. Y. Lee, A. Ogawa, M. Kanno, H. Nakamoto, T. Yasuda and M. Watanabe, *J. Am. Chem. Soc.*, 2010, **132**, 9764.
4. S. Menne, J. Pires, M. Anouti and A. Balducci, *Electrochem. Commun.*, 2013, **31**, 39.
5. L. Mayrand-Provencher, S. Lin, D. Lazzerini and D. Rochefort, *J. Power Sources*, 2010, **195**, 5114.
6. E. C. Achnivu, R. M. Howard, G. Li, H. Gracz and W. A. Henderson, *Green Chem.*, 2014, **16**, 1114.
7. R. Vijayaraghavan, S. J. Pas, E. I. IZgorodina and D. R. MacFarlane, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19994.
8. T. J. Simons, T. Verheyen, E. I. IZgorodina, R. Vijayaraghavan, S. Young, A. K. Pearson, S. J. Pas and D. R. MacFarlane, *Phys. Chem. Chem. Phys.*, 2016, **18**, 1140.
9. K. Tanaka, F. Ishiguro and Y. Chujo, *J. Am. Chem. Soc.*, 2010, 132, 17649.
10. J. Tan, D. Ma, X. Sun, S. Feng and C. Zhang, *Dalton Trans.*, 2013, 42, 4337.
11. T. Ishii, T. Enoki, T. Mizumo, J. Ohshita and Y. Kaneko, *RSC Adv.*, 2015, 5, 15226.
12. T. Ishii, T. Mizumo and Y. Kaneko, *Bull. Chem. Soc. Jpn.*, 2014, 87, 155.
13. A. Harada, S. Koge, J. Ohshita and Y. Kaneko, *Bull. Chem. Soc. Jpn.*, 2016, 89, 1129.
14. T. Kubo, S. Koge, J. Ohshita and Y. Kaneko, *Chem. Lett.*, 2015, 44, 1362.
15. S. Kinoshita, S. Watase, K. Matsukawa and Y. Kaneko, *J. Am. Chem. Soc.*, 2015, 137, 5061.
16. Y. R. Mirzaei, B. Twamley and J. M. Shreeve, *J. Org. Chem.*, 2002, 67, 9340.
17. Y. Kaneko, M. Shoiriki and T. Mizumo, *J. Mater. Chem.*, 2012, 22, 14475.
18. T. Tokunaga, M. Shoiriki, T. Mizumo and Y. Kaneko, *J. Mater. Chem. C*, 2014, 2, 2496.