3P028

ニッケル錯体をカチオンとする
磁性サーモクロミックイオン液体の開発

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Preparation of Magnetic Thermochromic Ionic Liquids from Cationic Nickel Complexes

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[Introduction]

Recently, metal-containing ionic liquids (ILs) with interesting physical properties have been reported. We previously reported the preparation and properties of vapochromic ILs based on solvatochromic metal complexes with diamine and diketone ligands.[1)] These ILs contain either copper or nickel ions, and exhibit property changes upon coordination of solvent molecules, associated with the transformation from square planar to octahedral coordination (Fig. 1). To investigate the effects of intramolecular coordination on their physical properties, alkoxy side chains were linked to the diamine ligands of the complexes. Solvatochromic copper complexes with these ligands have been reported[2)]. In this study, we synthesized the nickel complexes as shown in Fig. 2. The thermochromism behaviors and magnetic properties of these ILs were investigated.

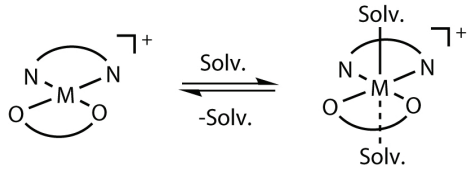

Fig. 1. Coordination changes in vapochromic ionic liquids.

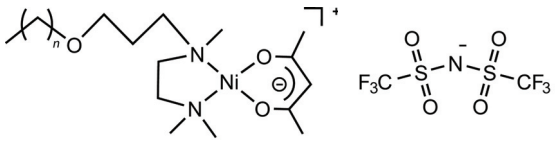

Fig. 2. Structural formulas of ionic liquids prepared in this study.

[Results and Discussion]

1. Synthesis and thermal properties

The ionic liquids were synthesized by the reaction of nickel nitrate and the ligands, followed by anion exchange using Li[Tf_2N]. [Ni-**C3**][Tf_2N] (T_m = 79.5 °C, T_g = −47 °C) and [Ni-**C32**][Tf_2N] (T_g = −44 °C) are blue solid and red liquid, respectively.

2. Thermochromic behavior

These two ILs show thermochromic behavior. [Ni-**C3**][Tf_2N] is a light blue solid at room temperature and turns to a red liquid above melting point. This liquid changes to a blue color when cooled. [Ni-**C32**][Tf_2N] is a red liquid at room temperature, and it turns to orange as the temperature decreases. The temperature-dependent UV/Vis spectra of [Ni-**C3**][Tf_2N] and [Ni-**C32**][Tf_2N] are shown in Figs. 3 and 4, respectively. With decreasing temperature, there is a decrease in the peak intensity for the four-coordinated species (λ_{max} = 490 nm), and an increase in the peak intensity for the five- or six-coordinated species (λ_{max} = 1000 nm), for both salts. Thermochromism occurs when the metal center is coordinated by the oxygen atom of the ether side chain and/or by the anion as the temperature decreases. Furthermore, [Ni-**C32**][Tf_2N] shows a lower six-coordinated species ratio than [Ni-**C3**][Tf_2N] at the same temperature. This indicates that the elongated side chain is more difficult to bend, even at low temperatures.

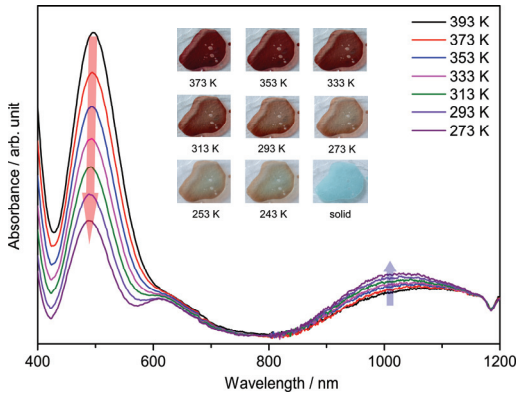

Fig. 3. Temperature dependence of the UV/Vis spectra of [Ni-**C3**][Tf_2N].

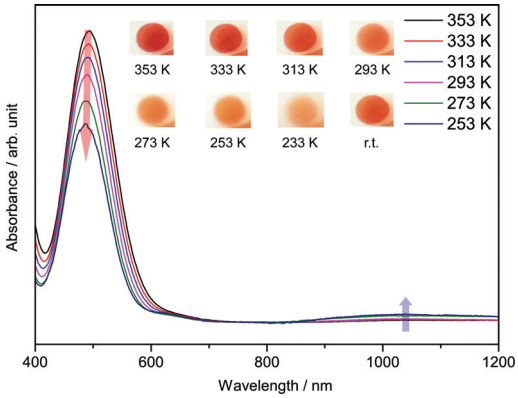

Fig. 4. Temperature dependence of the UV/Vis spectra of [Ni-**C32**][Tf_2N].

3. Magnetic properties

The magnetic susceptibilities of [Ni-**C3**][Tf_2N] were constant in the solid state, and showed a decrease upon melting (Fig. 5). This is because the complex adopts the high spin state (S = 1) in the solid state due to octahedral six-coordination, whereas the ratio of the diamagnetic four-coordinated species increases in the liquid state. The ratios of each species were determined from the $\chi_M T$ values at each temperature, which were in accordance with the thermochromic behavior.

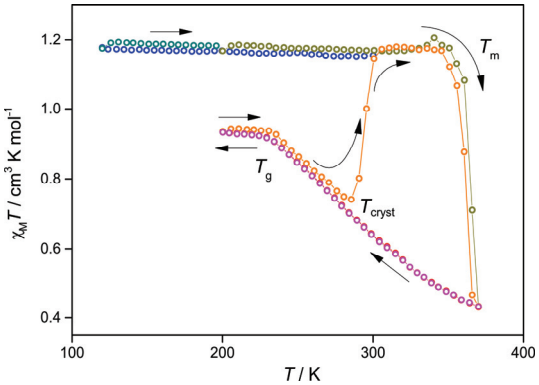

Fig. 5. Temperature dependence of the magnetic susceptibilities of [Ni-**C3**][Tf_2N].

[References]

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2) X. Lan, H. Hosokawa, Y. Funasako, T. Mochida, *Eur. J. Inorg. Chem.* **17**, 2804 (2016).