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EXAFS study on the spin crossover complex film, $[Fe(II)(R\text{-}trz)_3]$-Nafion

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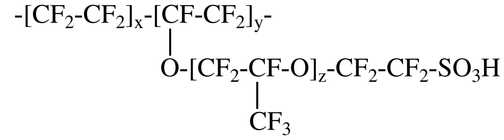
Introduction

Spin crossover complexes $[Fe(II)(R\text{-}trz)_3]X_2\ nH_2O$ (trz = triazole, R = H, NH_2, etc.; X = ClO_4, $C_nH_{2n+1}SO_3$, etc.) are attracting much attention from the viewpoint of molecular devices due to the large thermal hysteresis of spin transition around room temperature [1,2]. In order to realize molecular devices, the transparent film or single crystal is indispensable. However, the single crystal has not yet been obtained. We have synthesized the spin crossover complex film of $[Fe(II)(H\text{-}trz)_3]$ using ion exchange resin (Nafion) as counter anion, and measured the magnetic susceptibility and Fe *K*-edge EXAFS spectra for $[Fe(II)(H\text{-}trz)_3]$-Nafion.

Experimental

Nafion is composed of a polytetrafluoroethylene backbone with perfluorinated ether side chains terminated by sulfonic acid group as shown below,



$$-[CF_2\text{-}CF_2]_x\text{-}[\underset{\substack{|\\ O\text{-}[CF_2\text{-}\underset{\substack{|\\ CF_3}}{CF}\text{-}O]_z\text{-}CF_2\text{-}CF_2\text{-}SO_3H}}{CF}\text{-}CF_2]_y\text{-}$$

$[Fe(II)(R\text{-}trz)_3]$-Nafion was prepared in the following way. The acid form of Nafion was immersed in an aqueous solution of $FeSO_4$. After being immersed in the solution for 2 hours, the membrane was rinsed in methanol, and then it was immersed in methanol solution of Htrz at 330 K for 1 hour.

The temperature dependent magnetic susceptibility was measured by a Quantum Design MPMSXL SQUID susceptometer. Fe *K*-edge EXAFS spectra were taken in the conventional transmission mode at BL-10B in Photon Factory (operation energy of 2.5 GeV and stored current of 400-200mA) in Institute of Materials Structure Science. A water-cooled Si(311) channel-cut crystal was employed as a monochromator.

Results and discussion

Fe *K*-edge EXAFS spectra of $[Fe(R\text{-}trz)_3]$-Nafion (R = H, NH_2) are shown in Fig. 1. The peak around 7 Å corresponds to the Fe-Fe-Fe multiple scattering. Therefore, it is proved from this fact that the linear chain of $[Fe(R\text{-}trz)_3]$ exists in Nafion. The magnetic susceptibility as a function temperature implies the gradual low spin (LS) – high spin (HS) transition around 260 K, where the thermal hysteresis vanishes.

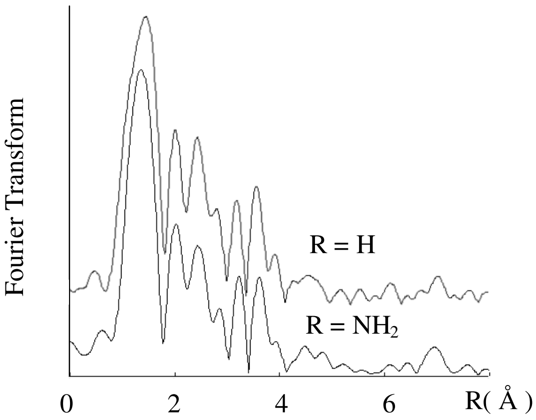


Fig. 1. Fourier Transform of EXAFS spectra of $[Fe(R\text{-}trz)_3]$-Nafion at 85 K

From the temperature dependence of χT for $[Fe(H\text{-}trz)_3]$-Nafion, it was found that even at 10 K, the HS still remains by ~40 %. The residual HS fraction would be attributed to the terminal Fe(II) site in the oligomer of $[Fe(II)(H\text{-}trz)_3]_n$ on Nafion film. In connection with this, the following should be mentioned. Fe(II) trimer complex, $[Fe_3(Et\text{-}trz)_6(H_2O)_6](CF_3SO_3)_6$ (Et-trz = 4-ethyl-1,2,4-triazole), the central Fe(II) site undergoes the LS-HS transition at about 200K, while the spin state of the terminal Fe(II) sites is the HS state between 2K and 300K [3]. It is considered that the mean size of $[Fe(H\text{-}trz)_3]_n$ oligomer is about n = 5 ~ 6. The disappearance of hysteresis suggested that interchain interaction play an important role in the hysteresis effect.

References

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