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Study on the spin crossover transition and glass transition for Fe(II) complex film, [Fe(II)(H-triazole)$_3$]@Nafion, by means of Mössbauer spectroscopy

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Abstract [Fe(II)(H-trz)$_3$]@Nafion (trz = triazole) is a transparent spin crossover complex film, where the spin crossover transition between the low-spin (S = 0) and the high-spin (S = 2) states takes place between 225 K and 300 K. In this film, two doublets corresponding to the low-spin and high-spin states were observed in the ^{57}Fe Mössbauer spectra, reflecting the spin crossover transition. From the analysis of ^{57}Fe Mössbauer spectra, the Debye temperatures of the low-spin and high-spin sites were estimated at 185 K and 176 K, respectively, in the temperature range between 10 K and 150 K. In this film, the total intensity of the Mössbauer spectra corresponding to the low-spin and high-spin sites drastically decreases above 200 K, reflecting the glass transition of Nafion, where the lattice vibration of $[Fe(H\text{-}trz)_3]_n^{2n+}$ is softened just as in solution due to micro-Brown motion of the segment of Nafion polymer membrane.

Keywords Spin crossover · Nafion · Glass transition · Mössbauer spectroscopy

1 Introduction

Transition metal complexes with d^4-d^7 configuration in an octahedral field have a possibility of spin transition between the low-spin (LS) and the high-spin (HS)

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states. The spin crossover phenomenon has attracted much attention since the discovery of the photo-induced spin transition (light induced excited spin state trapping (LIESST)) for $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole) [1], and the thermally-induced spin transition with large thermal hysteresis around room temperature for 1,2,4-triazole (= H-trz) bridged Fe(II) complexes, $[Fe(H\text{-}trz)_{2.85}(NH_2\text{-}trz)_{0.15})](ClO_4)_2 \cdot H_2O$ [2]. In particular, the triazole bridged polymeric Fe(II) chain system has a possibility of molecular device such as display or memory at room temperature. However, these triazole-bridged complexes have been obtained as only powdered sample due to their rapid precipitation.

We have synthesized a transparent film, $[Fe(II)(H\text{-}trz)_3]$@Nafion, in which Nafion (an ion-exchange resin having side chain terminated by sulfonic acid group) behaves as a counter anion as well as a transparent substrate (see Fig. S1 in Electronic Supplementary Materials) and investigated the detailed LIESST effect [3]. Nafion, which was developed by DuPont Company in 1960s, is composed of a linear polymer of fluorocarbon and sulfonic acid groups and has been applied as fuel cell, sensor and catalyst due to its durability, chemical and thermal stability, and permselectivity. In the case of Nafion 117, reverse micelle consisted of perfluoroalkylether groups with hydrophilic SO_3H groups forms clusters of ca. 4 nm diameter separated by a distance of ca. 5 nm and interconnected through channels of ca. 1 nm when they are swollen with water [4]. In this paper, we report the spin transition and glass transition for the transparent spin crossover complex film, $[Fe(II)(H\text{-}trz)_3]$@Nafion, by means of ^{57}Fe Mössbauer spectroscopy.

2 Experimental

$[Fe(II)(H\text{-}trz)_3]$@Nafion was obtained according to the previous literature [3]. For ^{57}Fe Mössbauer spectroscopic measurement, ^{57}Co in Rh was used as a Mössbauer source. The Mössbauer spectra were calibrated by using the six lines of a body-centered cubic iron foil (α-Fe), the center of which was taken as zero isomer shift.

3 Results and discussions

3.1 Spin crossover transition

Figure 1a shows the temperature dependence of ^{57}Fe Mössbauer spectra for $[Fe(II)(H\text{-}trz)_3]$@Nafion, whose Mössbauer parameters are summarized in Table S1. In the spectra, two doublets corresponding to the LS and HS states coexist between 10 K and 258 K, which is consistent with the temperature dependence of magnetic susceptibility. As shown in Fig. 1b, the absorption intensity ratio of HS to LS states abruptly increases at about 200 K, reflecting the spin crossover transition.

In connection with the isomer shift for $[Fe(II)(H\text{-}trz)_3]$@Nafion, Lavrenova et al. reported the correlation between the isomer shift in the LS state (δ_{LS}) at 77 K and the spin transition temperature T_c for triazole-bridged Fe(II) compounds [5]. In general, a ligand having high π acceptability would withdraw electrons from d orbital to low-lying π^* orbital, so called π back donation, causing a reduction in the screening of the *s*-electrons of the iron and the decrease in the isomer shift. Through the hybridization

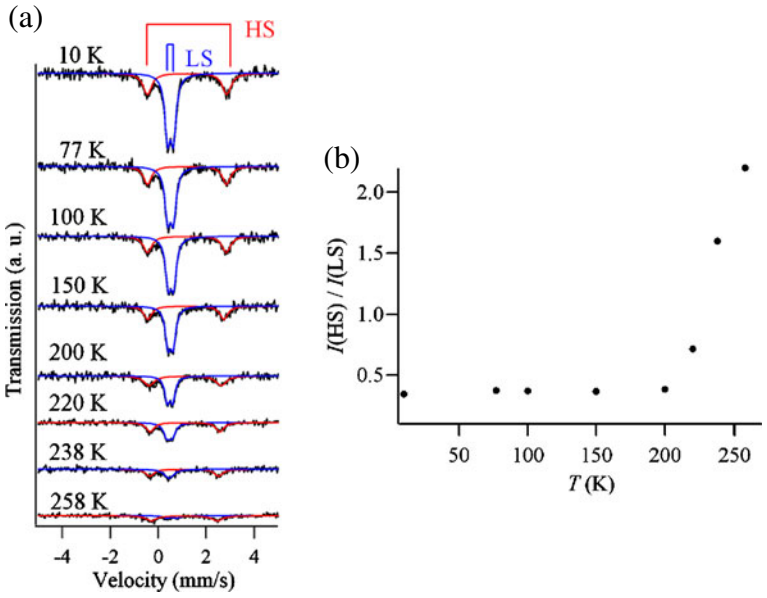

Fig. 1 **a** ^{57}Fe Mössbauer spectra for [Fe(II)(H-trz)$_3$]@Nafion at various temperatures. **b** Temperature dependence of the absorption intensity ratio of HS to LS states

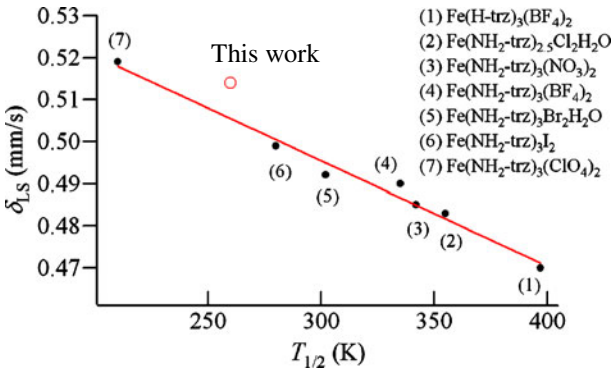

Fig. 2 Correlation between the isomer shift in the LS state at 77 K (δ_{LS}) and the spin transition temperature $T_{1/2}$ quoted from ref. [5]. The *red line* is the linear approximation by the least square method, and the *red open circle* corresponds to [Fe(II)(H-trz)$_3$]@Nafion

of the t_{2g} orbital and the π^* orbital, the ligand field splitting increases, leading to the increment of spin transition temperature. Figure 2 shows δ_{LS} versus T_c plots at 77 K and the linear approximation by the least square method. Since the δ_{LS} for [Fe(II)(H-trz)$_3$]@Nafion at 77 K is 0.514 (mm/s), its spin transition temperature is estimated at ca. 226 K by the extrapolation from the linear correlation between δ_{LS} and $T_{1/2}$. This value is lower than $T_{1/2} = 260$ K obtained from the magnetic susceptibility measurement.

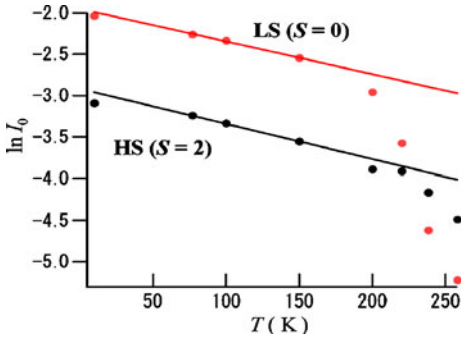

Fig. 3 Intensity of the Mössbauer spectra of the LS and HS states as a function of temperature for [Fe(II)(H-trz)$_3$]@Nafion

3.2 Glass transition of Nafion

The intensities of the ^{57}Fe Mössbauer spectra corresponding to the LS and HS states gradually become weak with increasing temperature above 150 K, and the signals almost vanish at 258 K. To investigate the hardness of lattice in the oligomer of $[Fe(H\text{-}trz)_3]_n^{2n+}$, Debye temperatures Θ_D of LS and HS states were estimated between 10 K and 150 K, where the ratio of HS to LS states is constant as shown in Fig. 1b. From the temperature dependence of the intensity of Mössbauer spectra, Θ_D of the HS and LS states can be determined using the following equation:

$$\ln\ I_0 = \ln\left(\frac{f_s n_A \sigma_0}{2}\right) - \frac{6E_R}{k\Theta_D^2}T$$

where I_0 is the absorption intensity, f_s the recoilless fraction of the Mössbauer source, n_A the area concentration of the Mössbauer nuclear, σ_0 the Mössbauer absorption cross section, E_R the recoil energy and k is the Boltzmann constant. Figure 3 shows $\ln I_0$ versus T plots, from which we can determine Θ_D to be 185 K (LS state) and 176 K (HS state), respectively, between 10 K and 150 K. Above 150 K, the plots exhibits the deviation from the linear approximation, and the values of Θ_D become small. These results show that the lattice vibration of $[Fe(H\text{-}trz)_3]_n^{2n+}$ in Nafion is softened above 150 K, and this behavior is derived from the micro-Brown motion of polymer chain segment. Nafion is known to exhibit the glass transition at 180 K, as a result, the motion in the oligomer of $[Fe(H\text{-}trz)_3]_n^{2n+}$ is softened just as in solution (see Fig. S2). Above 180 K, the recoilless fraction decreases with increasing temperature, and Mössbauer spectra of [Fe(II)(H-trz)$_3$]@Nafion cannot be observed around room temperature. Bauminger et al. reported the similar result with respect to $[Fe(II)(H_2O)_6]$ in Nafion [6]. Unfortunately, individual Θ_D of LS and HS states cannot be determined due to the spin transition above 200 K, but nonetheless we determined the average Θ_D to be 51 K from the analysis of $\{\ln I_0(LS) + \ln I_0(HS)\}$ versus T plots above 200 K (see Fig. S3).

4 Conclusion

We observed the spin crossover transition for [Fe(II)(H-trz)$_3$]@Nafion and estimated its spin transition temperature by means of ^{57}Fe Mössbauer spectroscopy. In addition, we also estimated the Debye temperature for the LS and HS sites between 10 K

and 150 K. Above 150 K, the Debye temperature remarkably decreased, suggesting that the lattice vibration of $[Fe(H\text{-}trz)_3]_n^{2n+}$ is softened due to the glass transition of Nafion.

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