Spin Crossover Complex Film, $[Fe^{II}(H\text{-}trz)_3]$-Nafion, with a Spin Transition around Room Temperature

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We have synthesized $[Fe^{II}(H\text{-}trz)_3]_n$ complex film by using ion-exchange resin(Nafion) as counter anion, and have found the spin crossover phenomenon about at 260 K. Moreover, we have proved the existence of straight one-dimensional Fe chain structure of $[Fe^{II}(H\text{-}trz)_3]_n$ on Nafion by means of EXAFS.

Recently, spin crossover phenomena converted between high spin (HS) state and low spin (LS) state have gained renewed importance since the discovery of the photo-induced spin transition called LIESST (Light Induced Excited Spin State Trapping) for $[Fe^{II}(ptz)_6](BF)_2$ (ptz = 1-propyltetrazole)[1] and the thermally induced spin transition with a large thermal hysteresis around room temperature for 1,2,4-triazole (= trz) bridged iron(II) complexes, $[Fe^{II}(H\text{-}trz)_{2.85}(NH_2\text{-}trz)_{0.15}]\,(ClO_4)_2\cdot H_2O$.[2] These properties have attracted much attention from the viewpoint of the photonic molecular device.

From the viewpoint of molecular devices, it is important to control the spin transition temperature T_c and the hysteresis width ΔT. In the case of triazole bridged polymeric Fe^{II} complex system, $[Fe^{II}(R\text{-}trz)_3]X_2$, the control of T_c and ΔT has extensively been carried out. In this system, T_c and ΔT remarkably depend on not only ligand molecule[3] (R-trz) but also counter anion[4] and crystal water.[5] In order to realize photonic devices, the synthesis of single crystal or transparent film is indispensable. However, single crystals of $[Fe^{II}(R\text{-}trz)_3]X_2$ have not yet been obtained. So that, we have tried to synthesize the spin crossover complex film based on $[Fe^{II}(R\text{-}trz)_3]$. The challenge to synthesize the spin-crossover complex film has been done for $[Fe(2\text{-}mephen)_3]^{2+}$ (2-mephen = 2-methyl-1,10-phenanthroline).[6] However, our work is the first time to synthesize $[Fe^{II}(R\text{-}trz)_3]$ complex film with a spin transition around room temperature. Here, we report the synthesis and the spin crossover phenomenon for $[Fe^{II}(R\text{-}trz)_3]$-Nafion (R = H, NH_2).

In the triazole-bridged iron(II) chain system, various kinds of molecules having $R\text{-}SO_3^-$ (R = C_nH_{2n+1}, C_6H_5, etc.) are acceptable as counter anion, from which the idea to synthesize the spin crossover complex film by using Nafion film (DuPont Co.) has been raised. Nafion is composed of a polytetrafluoroethylene backbone with perfluorinated ether side chains terminated by sulfonic acid group as shown in Figure 1. In the case of Nafion 117, the pendant $Y\text{-}SO_3H$ (Y = perfluorinated ether side chain) groups in the perfluorinated ionomer are known to form clusters of 40 Å diameter separated by a distance of 50 Å and interconnected through channels of 10 Å when they are swollen in water.[7]

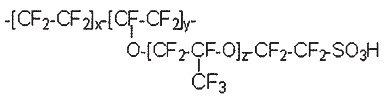

Figure 1. Molecular formula of Nafion 117: x = 6, y = 1, z = 1.

The spin crossover complex film, $[Fe^{II}(R\text{-}trz)_3]$-Nafion (R = H, NH_2), was prepared in the following way. The acid form of Nafion was immersed in an aqueous solution of $FeSO_4$. The mobile anions (SO_4^{2-}) are more or less completely excluded from the polymer matrix. Only Fe^{2+} ions are absorbed into Nafion membrane. After being immersed in the solution for 2 h, the membrane was rinsed in methanol, and then it was immersed in methanol solution of R-trz at 330 K for 1 h. All operations were carried out under nitrogen gas. The preparation process of $[Fe^{II}(R\text{-}trz)_3]$-Nafion is schematically shown in Figure 2.

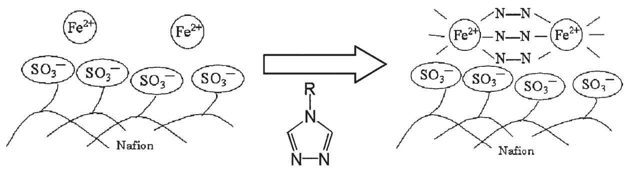

Figure 2. Schematic preparation process of $[Fe^{II}(R\text{-}trz)_3]$-Nafion. N-N represents 4-R-trz.

The colors of Nafion films after being immersed in methanol solution of NH_2-trz and H-trz are colorless and pale pink, respectively, at 290 K. However, their color became to be purple at liquid N_2 temperature, which implies the spin crossover phenomenon (Inset in Figure 3). Note that the colors of the HS state ($t_{2g}^4e_g^2$, $S = 2$) and the LS state (t_{2g}^6, $S = 0$) of $[Fe^{II}(R\text{-}trz)_3]X_2\cdot nH_2O$ (R = H, NH_2; X = ClO_4, etc.) are colorless and purple, respectively. In fact, the absorption spectrum of $[Fe^{II}(H\text{-}trz)_3]$-Nafion shows two broad bands at 18500 cm^{-1} and 24500 cm^{-1} corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively, in the LS state ($S = 0$), while it shows a broad band at 12500 cm^{-1} corresponding to the $^5T_{2g} \rightarrow {}^5E_g$ transition in the HS state ($S = 2$).

In order to prove that the one-dimensional Fe chain structure of $[Fe^{II}(H\text{-}trz)_3]_n$ is formed on Nafion film, we measured the Fe K-edge EXAFS spectra for $[Fe^{II}(R\text{-}trz)_3]$-Nafion (R = H, NH_2). The Fe K-edge EXAFS spectra were taken in the conventional transmission mode at Beam Line-10B in the Photon Factory in the Institute of Materials Structure Science, Tsukuba. The Fourier transforms of each spectrum at 65 K are shown in Figure 4. The main peak at about 1.7 Å of the Fourier transform corresponds to the Fe-N scattering. A noticeable feature is the existence of peak around 7 Å. In the normal EXAFS spectroscopy, any distinct peak does not appear in this range. However, in the case that the Fe atoms are arranged in a straight chain, the multiple scattering is

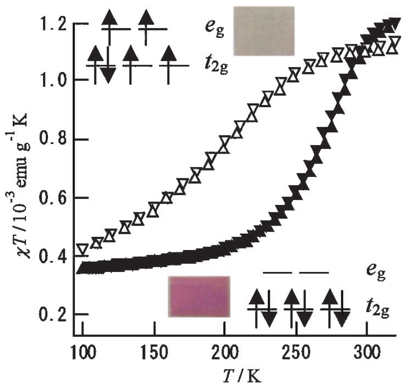

Figure 3. χT as a function of temperature for $[Fe^{II}(H\text{-}trz)_3]$-Nafion, $[Fe^{II}(NH_2\text{-}trz)_3]$-Nafion in cooling mode (▼, ▽) and heating mode (▲, △), respectively. The susceptibility of the vertical axis is the value per unit mass which includes the membrane mass. Inset shows the color (purple) in the low-spin state ($T = 77$ K) and that (colorless) in the high-spin state ($T = 300$ K).

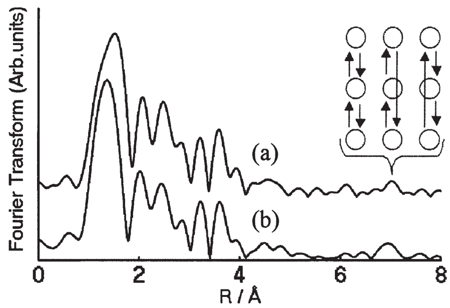

Figure 4. Fourier transforms of Fe K-edge EXAFS oscillation function $k^3\chi(k)$ for (a) $[Fe^{II}(H\text{-}trz)_3]$-Nafion and (b) $[Fe^{II}(NH_2\text{-}trz)_3]$-Nafion at 65 K. Inset shows the multiple scattering from the next nearest neighbor Fe-Fe-Fe shell which is responsible for the EXAFS spectrum at about 7 Å.

generally enhanced, so that the significant peak appears at long radius region.[8] The peak at about 7 Å corresponds to the Fe-Fe-Fe multiple scattering, which proves the existence of straight one-dimensional Fe chain structure.

In order to investigate the detailed spin crossover phenomenon, we measured the temperature dependence of magnetic susceptibility(χ) for $[Fe^{II}(H\text{-}trz)_3]$-Nafion film and $[Fe^{II}(NH_2\text{-}trz)_3]$-Nafion film. The static magnetic susceptibility was measured by using a Quantum Design MPMSXL SQUID susceptometer. The sample was sealed in an aluminum capsule to avoid a loss of crystal water in heating process. The applied magnetic field was 1 kG. The temperature was swept in quite slow rate of 0.1 K/min for heating and cooling process in order to investigate the thermal hysteresis at the spin transition. The χT as a function of temperature for $[Fe^{II}(H\text{-}trz)_3]$-Nafion film and $[Fe^{II}(NH_2\text{-}trz)_3]$-Nafion are shown in Figure 3. The spin transition for $[Fe^{II}(H\text{-}trz)_3]$-Nafion takes place at about $T_{1/2} = 260$ K ($T_{1/2}$ is defined as the temperature at which the fraction of HS induced by the spin transition is a half.). The thermal hysteresis width is confirmed to be 3 K. The spin transition for $[Fe^{II}(NH_2\text{-}trz)_3]$-Nafion takes place at about $T_{1/2} = 198$ K. In this case, the thermal hysteresis vanishes.

The magnetic susceptibility as a function of temperature shows residual paramagnetic fraction below 200 K, which is attributed to the HS state of Fe^{II}. The line profile of ESR below 10 K is typical one of the HS state of Fe^{II}. The residual HS fraction would be attributed to the terminal Fe^{II} site in the oligomer of $[Fe(H\text{-}trz)_3]_n$ on Nafion film. In connection with this, the following should be mentioned. In the case of the Fe^{II} trimer complex, $[Fe^{II}_3(Et\text{-}trz)_6(H_2O)_6](CF_3SO_3)_6$ (Et-trz = 4-ethyl-1,2,4-triazole), the central Fe^{II} site undergoes the LS-HS transition at about 200 K, while the spin state of the terminal Fe^{II} sites is the HS state between 2 K and 300 K.[9]

In conclusion, we have succeeded in synthesizing transparent $[Fe^{II}(R\text{-}trz)_3]$ complex film by using ion-exchange film (Nafion) as counter anion, which shows the spin crossover phenomenon at about 260 K. In our preparation process, it is possible to prepare the homogeneous $[Fe^{II}(R\text{-}trz)_3]$ complex film of 300 mm × 300 mm. The development of transparent $[Fe^{II}(R\text{-}trz)_3]$-Nafion film will open a large field of photonic molecular devices based on spin-crossover phenomenon.

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