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Development of pH-Sensitive Spin-crossover Iron(II) Complex Films, [Fe^{II}(diAMsar)]–Nafion: Manipulation of the Spin State by Proton Concentration

Hajime Kamebuchi, Taketomo Jo, Hideharu Shimizu, Atsushi Okazawa, Masaya Enomoto,[†] and Norimichi Kojima[*]
Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo,
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902

(Received June 24, 2011; CL-110530; E-mail: cnori@mail.ecc.u-tokyo.ac.jp)

We newly synthesized transparent films composed of pH-sensitive spin-crossover complex [Fe^{II}(diAMsar)] (diAMsar: 1,8-diaminosarcophagine) and an ion-exchange polymer, Nafion, having different colors corresponding to proton concentration. The UV–vis spectroscopic measurements revealed that the films, which were provided under pH 4, 7, and 10 conditions, showed the spin state depending on pH.

There are a lot of reports about spin-crossover Fe^{II} complexes with octahedral FeN$_6$ geometry.[1] Almost all spin-crossover Fe^{II} complexes have a π-conjugated ligand with a low-lying π^* orbital (such as pyridine, bipyridine, phenanthroline, etc.) which induces the stabilization of t$_{2g}$ orbitals through π back donation. As a rare case, Martin et al. reported that the spin equilibrium between t_{2g}^6 ($^1A_{1g}$) and $t_{2g}^4e_g^2$ ($^5T_{2g}$) took place in the Fe^{II} complexes coordinated by a hexaamine cage ligand, sarcophagine (sar) and its derivatives.[2] They investigated the magnetic behavior of [Fe^{II}(sar)] complexes in detail and clarified that spin-crossover phenomena took place in solution, not in the solid state.[3,4] It shoud be noted that their complexes consist of the σ-donating ligand without π back donation. In particular, the spin-transition temperature of [Fe^{II}(diAMsar)] (diAMsar: 1,8-diaminosarcophagine) complex in the solution is dependent on pH due to the protonation/deprotonation of the terminal amino groups.[4] This property indicates that [Fe^{II}(diAMsar)] has potential as a molecular device responding to proton concentration as external stimuli, though nonliquid conditions are unacceptable for such devices.

Pioneering work for related research has been reported as studies on [Fe^{II}(2-mephen)$_3$] (2-mephen: 2-methyl-1,10-phenanthroline) and [Fe^{II}(R-trz)$_3$] (R = H, NH$_2$; trz: 1,2,4-triazole) in Nafion, which are transparent films that show spin-crossover.[5–9] Nafion, which was developed by DuPont Co. in 1960s, is an ion-exchange resin consisting of a linear polymer of fluorocarbon and sulfonic acid or carboxylic acid groups and applied to fuel cells,[10] sensors,[11] and catalysts[12] due to its durability, chemical and thermal stability, and permselectivity. In the case of Nafion 117, reverse micelles consisting of perfluoroalkylether groups with hydrophilic SO$_3$H groups form 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,[13,14] and the side chain terminated by SO$_3$H groups behaves as a counter anion as well as transparent substrate. By achievement of intermediate cooperation between liquid and solid, it is expected to realize spin-crossover complex films and manipulate the spin state by proton concentration.

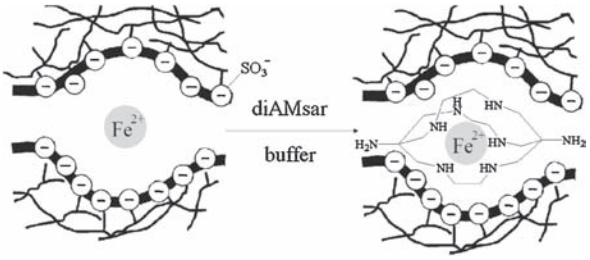

Figure 1. Schematic representation of preparing [Fe^{II}-(diAMsar)]–Nafion.

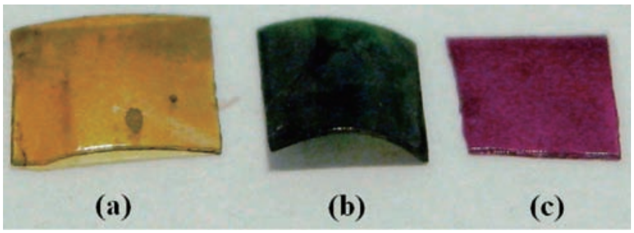

Figure 2. pH Dependence of the color of [Fe^{II}(diAMsar)]–Nafion film, (a) pH 4, (b) pH 7, and (c) pH 10.

The transparent films, [Fe^{II}(diAMsar)]–Nafion, were prepared as follows: Nafion 117 was pretreated by immersing in 10% aqueous solution of HNO$_3$ for 12 h. The acid form of Nafion was immersed in 5% aqueous solution of FeSO$_4$·7H$_2$O for 24 h, leading to absorption of Fe^{II} ions into Nafion. The membrane was rinsed with distilled water and subsequently immersed in buffer solution (pH 4, 7, and 10) dissolving diAMsar ligand for 24 h. The preparation is illustrated in Figure 1. All operations were carried out under inert atmosphere. The cage ligand, diAMsar, was synthesized according to the literature.[15]

The pH dependence of the film color is shown in Figure 2. The colors of [Fe^{II}(diAMsar)]–Nafion films in pH 4, 7, and 10 are yellow, green, and purple, respectively, reflecting the spin states of [Fe^{II}(diAMsar)] complex. In the case of pH 7, the optical absorption spectrum measured on a JASCO MSV-370 spectrometer under inert atmosphere shows a broad band at around 13000 cm^{-1} corresponding to the $^5T_{2g} \rightarrow {}^5E_g$ transition in the high-spin (HS; $S = 2$) state, while it shows a broad band at around 18000 cm^{-1} corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in the low-spin (LS; $S = 0$) state at pH 10 as shown in Figure 3. As for the case of pH 4, the band corresponding to the $^5T_{2g} \rightarrow {}^5E_g$ transition is hardly observed due to the desorption of Fe^{II} ions by ion exchange with H$^+$ in the acid buffer. The optical results indicate that the amino group become protonated with increasing proton concentration, leading to weaker ligand field by the volume expansion of the cage ligand due to the electrostatic repulsion between the Fe^{II} ion and NH$_3^+$ group (Scheme S1[16]). As a result, the fraction of the HS state in spin

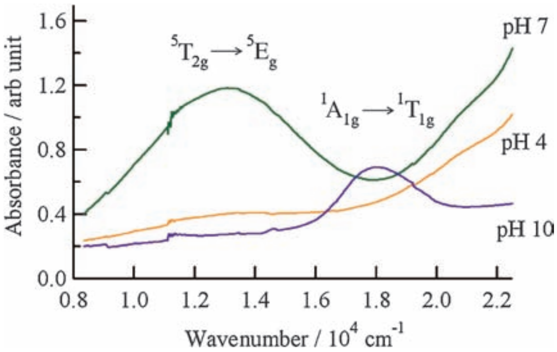

Figure 3. UV–vis absorption spectra of [Fe$^{\mathrm{II}}$(diAMsar)]–Nafion films at room temperature.

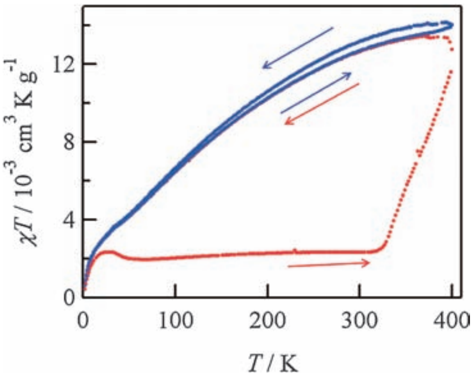

Figure 4. Temperature dependence of χT for [Fe$^{\mathrm{II}}$(diAMsar)]–Nafion film (pH 10). The applied magnetic field is 5000 Oe. The red and blue circles represent the first and second heating–cooling cycles, respectively.

equilibrium increases. In contrast, the LS state is dominant in lower proton concentration due to the absence of expansion as mentioned above.

Figure 4 shows the magnetic behavior of [Fe$^{\mathrm{II}}$(diAMsar)]–Nafion prepared under pH 10. The magnetic susceptibility was measured on a Quantum Design MPMS-5S SQUID magnetometer under 5000 Oe. The film was cut into small pieces, and they were sealed in an alminium capsule to avoid the oxidation of the sample. Heating and cooling processes were repeated twice between 2 and 400 K. In the first heating mode, the magnetic susceptibility multiplied by temperature, χT, abruptly increases at 325 K reflecting the LS–HS transition, and it increased linearly up to 400 K. Subsequently, in the first cooling process, χT gradually decreases showing a convex curve, which is believed to be due to spin equilibrium. The χT values for the second heating and cooling modes are similar to that of the first cooling process in the whole temperature range. In the case of pH 7, the incremention was also observed and the maximum of χT was lower than that of pH 10, which reflects the total amount of Fe$^{\mathrm{II}}$ ion (Figure S1[16]). The hump observed at 34 K probably corresponds to the antiferromagnetic transition of oxygen included in the membrane. Residual paramagnetic fraction below 325 K in the first heating process is derived from the HS component and/or [Fe$^{\mathrm{II}}$(H$_2$O)$_6$] having HS state.

In the case of [Fe$^{\mathrm{II}}$(diAMsar)]–Nafion film (pH 10), despite that the [Fe$^{\mathrm{II}}$(diAMsar)] complex is isolated in the cavity of Nafion, the LS–HS transition at 325 K is anomalously abrupt, which would be attributed to the dehydration. In fact, almost all the water escape from Nafion around 320 K (Figure S2[16]), which presumably influences the ligand field in the [Fe$^{\mathrm{II}}$(diAMsar)] complex. In order to confirm the effect of dehydration on the spin state in [Fe$^{\mathrm{II}}$(diAMsar)]–Nafion, we measured χT for a sample encapsulated with epoxy resin (STYCAST 1266), where the χT value remained unchanged between 50 and 365 K (Figure S3[16]).

In connection with the anomalous convex curve of χT in the cooling process, the possibilities that the dehydration induced decomposition of [Fe$^{\mathrm{II}}$(diAMsar)] complex and that the gentle curve of χT–T plots reflects the antiferromagnetic interaction between the fragments cannot be denied. In order to make clear these problems, ^{57}Fe Mössbauer spectroscopic measurement is indispensable and in progress.

In conclusion, we successfully developed transparent [Fe$^{\mathrm{II}}$(diAMsar)]–Nafion films and manipulated the spin state of [Fe$^{\mathrm{II}}$(diAMsar)] complex by proton concentration. To our knowledge, this work is the first report showing the pH-sensitive spin-crossover complex film, which will open the possibility of visual indicators for proton flow.

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References and Notes

† Present address: Department of Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

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