^{57}Fe Mössbauer Study on Photoinduced Spin Transition of Ferrocene in Polymer Matrices

Yasuaki Einaga,* Masahiro Kotake, Yasuhiro Yamada,† and Osamu Sato††
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223-8522
†*Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162-8601*
††*Kanagawa Academy of Science and Technology, KSP, Sakado, Kawasaki 213-0012*

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A polymer matrix isolation technique was examined as a potentially novel strategy for realizing optically switchable materials. Not only was a ferricinium ion ($[Cp_2Fe^{III}]^+$) produced, but also was produced an isomer of ferrocene (Cp_2Fe) with high spin Fe^{II} in a poly(methyl methacrylate) (PMMA) matrix film containing CCl_4 by the photoillumination of ferrocene at low temperature. The high spin state could be maintained for an extended period when the sample was kept below ≈ 130 K. This is the first observation of a photoinduced spin transition for ferrocene. The strategy that we used to achieve the spin transition using optical stimuli may open up many possibilities for the development of new magneto-optical devices.

There has been a great interest in developing novel molecular compounds whose magnetic properties or spin states can be controlled by photoillumination.[1] So far, several optically switchable LIESST (light-induced excited spin state trapping) compounds have been designed.[2] However, the number of optically switchable molecular solids reported so far has not been great. In order to develop a variety of optically switchable materials, novel strategies to prevent rapid relaxation from the metastable state need to be developed.

Low temperature matrix isolation techniques have conventionally been used in order to detect unstable species, such as radicals, by spectroscopic methods and to understand their chemical reaction schemes.[3] The low temperature matrix isolation technique is not appropriate for practical applications in materials science because unstable compounds can only be obtained and detected in a cooled vacuum system. In this work we made use of a polymer matrix as a suitable reaction system in which a photoinduced spin transition could be realized by stabilizing the photoexcited metastable state. In addition, the polymer film materials prepared by this technique can be developed for a wide range of applications as photofunctional solid materials.

Ferrocene has a variety of derivatives that are very stable due to their unique electronic structure and which are used as starting materials in various reactions.[4] Ferrocene and its derivatives are also interesting in the field of molecule-based magnets.[5] Various photochemical reactions of ferrocene in solution have been reported previously, the mechanisms of which are mostly ascribable to MSCT (metal-to-solvent charge transfer) reactions. However, there have been very few research reports on the spin transitions of ferrocene or on its photochemical reactions in the solid state. Furthermore, although theoretical studies suggest that high-spin ferrocene can be obtained during the formation of ferrocene from C_5H_6 and Fe vapor,[6] we are the only group that has reported the direct observation of high-spin ferrocene in a low-temperature nitrogen matrix system.[7]

Here, we report on a photoinduced spin transition of ferrocene observed by using the polymer matrix isolation technique. Poly(methyl methacrylate) (PMMA) was used as a polymer matrix. ^{57}Fe-enriched ferrocene, synthesized according to the method in the literature,[8] was first dissolved in an acetone solution of PMMA containing CCl_4. A photofunctional PMMA film that exhibited a photoinduced spin transition was prepared by casting the above solution ($Cp_2Fe:CCl_4 = 1:400$) onto a clean glass plate at room temperature.

Figure 1 illustrates the ^{57}Fe Mössbauer spectra of the film at 7.5 K. Before illumination, the spectrum was almost identical to that of solid ferrocene, with doublet absorption peaks (I.S. $=$ 0.39 mm/s, Q.S. $=$ 2.36 mm/s)[9] that have been assigned to Fe^{II}(low spin) (Figure 1a). An Hg–Xe lamp with a glass filter (300–400 nm) was used to illuminate the samples with UV light (50 mW/cm^2). After illuminating the sample for 2 h, a new singlet peak (I.S. $=$ 0.29 mm/s) assigned to the ferricinium ion ($[Cp_2Fe^{III}]^+$) appeared in the spectrum (Figure 1b). This suggests that the Fe^{II} in ferrocene was oxidized to form Fe^{III} in the low-temperature polymer due to a photoinduced charge-transfer between the ferrocene and the CCl_4, similar to the MSCT reaction in solution:[10]

$$Cp_2Fe(II) + CCl_4 \xrightarrow{h\nu} [Cp_2Fe(III)]^+\ Cl^- + \bullet CCl_3$$

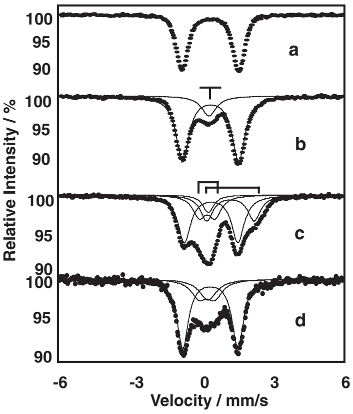


Figure 1. ^{57}Fe Mössbauer spectra of ferrrocene at 7.5 K in PMMA containing CCl_4. (a) Before illumination. (b) After illumination for 2 h. (c) After illumination for 10 h. (d) After annealing at room temperature.

However, after further illumination of the sample for 10 h at 7.5 K, not only the singlet peak ($[Cp_2Fe_{III}]^+$), but also new two species were observed (Figure 1c). The new small asymmetric doublet (I.S. $=$ 0.24 mm/s, Q.S. $=$ 0.70 mm/s) was assigned to $[Cp_2Fe^{III}][Fe^{III}Cl_4]$ precipitates. These precipitates are formed by prolonged UV illumination of the ferrocene solution in the presence of halocarbons etc.[11] The Mössbauer spectrum of the precipitate obtained after UV illumination of a solution containing ferrocene and CCl_4 showed a doublet peak (I.S. $=$ 0.24 mm/s, Q.S. $=$ 0.70 mm/s) at room temperature (not shown), which indicates the presence of only Fe^{III}. However, to our surprise, another new doublet species (I.S.= 0.99 mm/s, Q.S.= 2.20 mm/s) was assigned to the Fe^{II} high spin state. In a similar experiment at room temperature, only Fe^{III} species were observed as a photoproduct, even after prolonged illumination. Moreover, a similar experiment without the CCl_4 at low temperature did not show any photoproducts at all (not shown).

The sample that had been illuminated was then annealed at room temperature and the Mössbauer spectrum was measured at 7.5 K. As shown in Figure 1d, the Fe^{II} high-spin species disappeared to be replaced by an Fe^{II} low-spin species, while the Fe^{III} species remained after annealing because both of the Fe^{III} species (the $[Cp_2Fe^{III}]^+Cl^-$ salt and the $[Cp_2Fe^{III}][Fe^{III}Cl_4]$ precipitates) were very stable, even at room temperature.

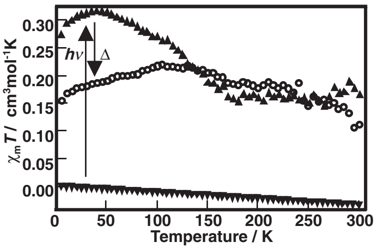
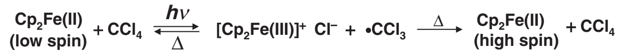


Figure 2. $\chi_m T$ versus T plots for ferrocene in PMMA containing CCl_4. The film was cooled from 300 to 5 K (▼) and illuminated with UV light for 8 h via an optical fiber at 5 K. Then, it was warmed from 5 to 300 K (▲) and cooled again from 300 to 5 K (○).

By analogy with our previous low-temperature nitrogen matrix isolation system,[7] it was considered that the new high spin species could be assigned to an isomer of ferrocene containing high spin Fe^{II}. We propose a reaction scheme as follows:



$$\underset{\text{(low spin)}}{Cp_2Fe(II)} + CCl_4 \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} [Cp_2Fe(III)]^+ Cl^- + \bullet CCl_3 \xrightarrow{\Delta} \underset{\text{(high spin)}}{Cp_2Fe(II)} + CCl_4$$

While the MSCT (metal-to-solvent charge transfer) reaction of ferrocene to the ferricinium ion is induced directly by photoabsorption, the inverse reactions of the ferricinium ion to form low spin ferrocene and high spin ferrocene may be considered to be thermal reactions that may occur without photoabsorption. This kind of thermal recombination reaction is normally prevented in a low-temperature matrix, but on photoillumination the matrix substances around the ferricinium ions and CCl_3 radicals are heated and annealed due to the photo absorption followed by non-illuminative de-excitation of the ferricinium ions and CCl_3 radicals.

UV–vis absorption spectra at 10 K support the results. Interestingly, a new absorption band at around 750 nm was only observed after prolonged illumination at 10 K, while it was not observed at room temperature. The new absorption band was consistent with the spin-allowed d–d absorption frequencies of Fe^{II} ions in high spin complexes. Moreover, IR spectra also support these assignments. A new peak at around 530 cm^{-1} was observed after illumination only by measurement at 10 K, while it was not observed at room temperature. We believe that the new peak might be assigned to the Cp tilt of Fe^{II} high spin ferrocene.

It is known that the Cp–Fe inter-atomic distance for the ferricinium ion is longer than that for ferrocene (low spin).[4] Theoretical studies suggest that the energy-minimized structure of high spin ferrocene has a longer Cp–Fe inter-atomic distance than that of low spin ferrocene.[6,12] It is suggested that the recombination reaction leading to high spin ferrocene was realized in the present system because of the reaction environment in the low temperature polymer matrix.

The presence of the photoinduced spin transition and thermally-induced relaxation were also confirmed by the magnetic properties (Figure 2). All of the values for the temperature dependence of $\chi_m T$ for the film before illumination were negative, which corresponds to it having diamagnetic properties with no spin ($^1A_{1g}$: $(^1e_{2g})^4(2a_{1g})^2$). The UV light from the Hg–Xe lamp was guided via an optical fiber into a SQUID magnetometer. When the sample was illuminated for 8 h at 5 K, an increase in the magnetization value from negative to 0.28 $cm^3mol^{-1}K$ was observed. The change in the magnetization persisted for periods of at least 10 h after the illumination was stopped. More so, when the temperature was raised to room temperature and then lowered again to 5 K, the increased value was found to have relaxed back to a value of 0.15 $cm^3mol^{-1}K$. Note that the $\chi_m T$ values obtained after illumination did not reflect the number of generated spins precisely because the photoreaction was not saturated due to the much lower power of the UV light guided via an optical fiber into a SQUID magnetometer (1 mW/cm^2). However, the tendency for a photoinduced increase and thermally-induced decrease in the $\chi_m T$ values was consistent with the Mössbauer data in Figure 1 and showed the relaxation temperature to be ca. 130 K. That is, the high spin ferrocene that was produced could relax back to low spin ferrocene by annealing.

In summary, high spin ferrocene was observed directly for the first time by the photoillumination of a low-temperature polymer matrix system. The low-temperature matrix isolation technique that is used for detecting an unstable species can also be used as a novel strategy for the preparation of optically switchable molecular solids.

References and Notes

1 a) P. Gütlich, Y. Garcia, and T. Woike, *Coord. Chem. Rev.*, **839**, 219 (2001). b) O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *Science*, **272**, 704 (1996). c) V. Escax, A. Bleuzen, C. C. D. Moulin, F. Villain, A. Goujon, F. Varret, and M. Verdaguer, *J. Am. Chem. Soc.*, **123**, 12536 (2001). d) A. Goujon, F. Varret, V. Escax, A. Bleuzen, and M. Verdaguer, *Polyhedron*, **20**, 1339 (2001). e) Y. Einaga, O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *J. Am. Chem. Soc.*, **121**, 3745 (1999). f) Y. Einaga, T. Yamamoto, T. Sugai, and O. Sato, *Chem. Mater.*, **14**, 4846 (2002). g) Y. Einaga, M. Taguchi, G.-M. Li, T. Akitsu, Z.-Z. Gu, T. Sugai, and O. Sato, *Chem. Mater.*, **15**, 8 (2003).

2 a) S. Schenker and A. Hauser, *J. Am. Chem. Soc.*, **116**, 5497 (1994). b) S. Schenker, A. Hauser, and A. Dyson, *Inorg. Chem.*, **35**, 4676 (1996). c) M. A. Berkgamp, P. Gütlich, T. L. Netzel, and N. J. Sutin, *J. Phys. Chem.*, **87**, 3877 (1983). d) P. Gütlich, A. Hauser, and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, **33**, 2024 (1994) and references therein. e) S. Hayami, Z.-Z. Gu, M. Shiro, Y. Einaga, A. Fujishima, and O. Sato, *J. Am. Chem. Soc.*, **122**, 7126 (2000).

3 a) H. J. Himmel, L. Manceron, A. J. Downs, and P. Pullumbi, *J. Am. Chem. Soc.*, **124**, 4448 (2002). b) V. Venkatesan, K. Sundararajan, and K. S. Viswanathan, *J. Phys. Chem. A*, **106**, 7707 (2002). c) I. Norman and G. Porter, *Nature*, **174**, 508 (1954).

4 a) M. Rosenblum, in "Chemistry of the Iron Group Metallocenes," Interscience, New York (1965). b) T. Bernstein and F. H. Herbstein, *Acta Crystallogr.*, **B24**, 1640 (1968).

5 a) J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein, *J. Am. Chem. Soc.*, **109**, 769 (1987). b) J. S. Miller, A. J. Epstein, and W. M. Reiff, *Science*, **240**, 40 (1988). c) J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.*, **88**, 201 (1988).

6 M. L. McKee, *J. Phys. Chem.*, **96**, 1683 (1992).

7 Y. Einaga, Y. Yamada, and T. Tominaga, *J. Radioanal. Nucl. Chem.*, **218**, 97 (1997).

8 G. Wilkinson, *Org. Synth.*, **4**, 473 (1963).

9 Mössbauer spectra were calibrated using the known hyperfine splitting of α-iron.

10 Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).

11 a) L. P. Motz and R. P. Pinnell, *J. Organomet. Chem.*, **54**, 255 (1973). b) O. Traverso and F. Scandola, *Inorg. Chim. Acta*, **4**, 493 (1970).

12 T. E. Taylor and M. B. Hall, *Chem. Phys. Lett.*, **114**, 338 (1985).

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