

## IV-D Progress of Conjugated Phenomena Coupled with Spin, Charge and Photon for Assembled Hetero-Molecular System

Intercalation of photochromic molecule into magnetic system provides fascinating multi-functionalities such as photo-magnetism, which gains much attention for their application to devices. The main subjects in this project are the development of photo-induced spin-crossover phenomena at room temperature by using the photo-isomerization of intercalated molecule, and the development of the transformation of magnetism for two-dimensional ferromagnetic system coupled with photochromic molecule.

### IV-D-1 Enhancement of the Curie Temperature by Photoisomerization of Diaryl-Ethene (DAE) for an Organic-Inorganic Hybrid System: $\text{Co}_4(\text{OH})_7(\text{DAE})_{0.5}\cdot 3\text{H}_2\text{O}$

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[*Inorg. Chem.* **45**, 10240–10247 (2006)]

Photomagnetism is one of the most attractive topics in recent research on molecular solids. Intercalation of an organic photochromic molecule into layered magnetic systems has a possibility to provide multifunctional properties such as photomagnetism. In order to build up a photosensitive multifunctional magnet, an organic-inorganic hybrid system coupled with a photochromic diarylethene anion, 2,2'-dimethyl-3,3'-(perfluorocyclopentene-1,2-diyl)bis(benzo[b]thiophene-6-sulfonate) (DAE), and cobalt LDHs (layered double hydroxides),  $\text{Co}_4(\text{OH})_7(\text{DAE})_{0.5}\cdot 3\text{H}_2\text{O}$ , was synthesized by the anion exchange reaction between  $\text{Co}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  and DAE.<sup>1,2</sup> In the dark and under UV (313 nm) irradiated conditions,  $\text{Co}_4(\text{OH})_7(\text{DAE})_{0.5}\cdot 3\text{H}_2\text{O}$  with the open and close-forms of DAE were obtained, respectively. The magnetic susceptibility measurements elucidated ferromagnetic intra- and inter-layer interactions and Curie temperatures of  $T_C = 9$  K and  $T_C = 20$  K for cobalt LDHs with the open and close-forms of DAE, respectively. The enhancement of the Curie temperature from 9 K to 20 K by substituting the open-form of DAE with the close-form of DAE as intercalated molecule is attributed to the delocalization of  $\pi$  electrons in the close-form of DAE, which enhances the inter-layer magnetic interaction. The enhancement of the inter-layer magnetic interaction induced by the delocalization of  $\pi$  electrons in intercalated molecules is strongly supported by the fact that the Curie temperature (26.0 K) of cobalt LDHs with (*E,E*)-2,4-hexadienedioate having a conjugated  $\pi$  electron system is enormously higher than that (7.0 K) of cobalt LDHs with hexanedioate, which is shown in Figure 1.<sup>2</sup> By UV irradiation of 313 nm,  $\text{Co}_4(\text{OH})_7(\text{DAE})_{0.5}\cdot 3\text{H}_2\text{O}$  shows the photoisomerization of DAE from the open-form to the close-one in solid state, which leads to the enhancement of Curie temperature, which is schematically shown in Figure 2.<sup>2</sup>

#### References

- 1) M. Okubo, M. Enomoto and N. Kojima, *Solid State Commun.* **134**, 777 (2005).
- 2) H. Shimizu, M. Okubo, A. Nakamoto, M. Enomoto and N. Kojima, *Inorg. Chem.* **45**, 10240 (2006).

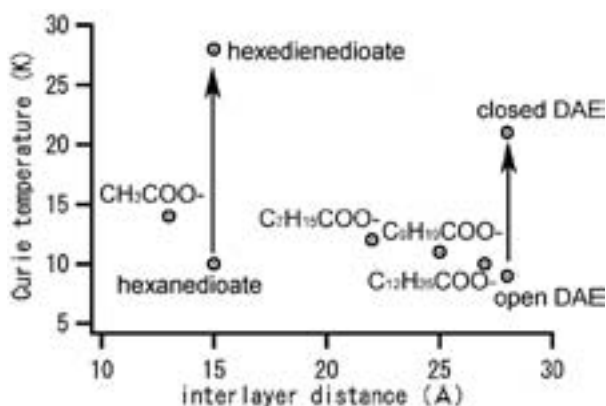


Figure 1. Relation between the interlayer distance and the Curie temperature of Co-LDHs.

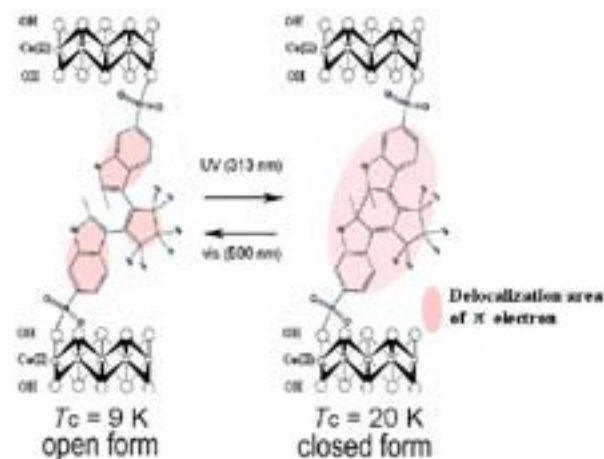


Figure 2. Schematic representation of the photoinduced conversion between Co-LDHs with open-form of DAE having  $T_C = 9$  K and Co-LDHs with closed-form of DAE having  $T_C = 20$  K.

### IV-D-2 Charge Transfer Phase Transition and Ferromagnetism in Organic-Inorganic Hybrid System, $\text{A}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3](\text{A} = (\text{C}_n\text{H}_{2n+1})_4\text{N}, \text{Spiropyran}, \text{etc.}; \text{dto} = \text{C}_2\text{O}_2\text{S}_2)$

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[*Synth. Met.* **153**, 473–476 (2005), *Eur. J. Inorg. Chem.* 1198–1207 (2006)]

In the case of mixed-valence complexes whose spin states are situated in the spin-crossover region, it is expected that new types of conjugated phenomena coupled with spin and charge take place. Recently, we have discovered a new type of first order phase transition around 120 K for  $(n\text{-C}_3\text{H}_7)_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3](\text{dto} = \text{C}_2\text{O}_2\text{S}_2)$ , where the thermally induced charge transfer between  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  occurs reversibly.<sup>1)</sup>  $(n\text{-C}_4\text{H}_9)_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$  also undergoes the charge transfer phase transition around 140 K, while the charge transfer phase transition does not take place for  $(n\text{-C}_n\text{H}_{2n+1})_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3](n = 5 \text{ and } 6)$ , where the spin configuration of  $\text{Fe}^{\text{II}}$  ( $S = 2$ ) and  $\text{Fe}^{\text{III}}$  ( $S = 1/2$ ) exists between 2 K and 300 K. Moreover,  $(n\text{-C}_n\text{H}_{2n+1})_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$  ( $n = 3\text{--}6$ ) undergo the ferromagnetic phase transition. The Curie temperatures for  $n = 3$  and 4 are 6.5 K and 6 K & 13 K, respectively, while those for  $n = 5$  and 6 are 19 K and 25 K, respectively.<sup>2)</sup>

As mentioned above, these phase transitions remarkably depend on the size of intercalated cation, which implies a possibility to control the magnetic properties of two-dimensional honeycomb network structure of  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]_\infty$  by means of the isomerization of intercalated cation. From this viewpoint, we have synthesized a photo-sensitive organic-inorganic hybrid system,  $(\text{SP})[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3](\text{SP} = \text{spiropyran})$ , and investigated the photo-induced effect on the magnetic properties through the medium of photo-isomerization of spiropyran.<sup>3)</sup> When the UV light is irradiated for  $(\text{SP})[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$  in KBr pellet between 300 K and 77 K, a new absorption spectrum with wide half-width appears around 550 nm, which corresponds to the  $\pi\text{-}\pi^*$  transition in the open form of  $\text{SP}^+$ , which implies that the photo-isomerization of  $\text{SP}^+$  takes place even at 77 K in the solid state of  $(\text{SP})[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ . The zero-field cooled magnetization (ZFCM) has two peaks at 5 K and 15 K, which implies the coexistence of two ferromagnetic phases. The peak of ZFCM at 5 K disappears after UV irradiation. These UV irradiation effects on the magnetic properties imply that the photo-isomerization of SP from the closed form to the open one stabilizes the high-temperature phase with  $\text{Fe}^{\text{III}}(S = 1/2)\text{--}\text{Fe}^{\text{II}}(S = 2)$  and destabilizes the low-temperature phase with  $\text{Fe}^{\text{III}}(S = 5/2)\text{--}\text{Fe}^{\text{II}}(S = 0)$ . Consequently, it is concluded that the charge transfer transition between  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  in  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$  is induced by the photo-isomerization of SP in  $(\text{SP})[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ .

## References

- 1) N. Kojima, W. Aoki, M. Itoi, Y. Ono, M. Seto, Y. Kobayashi and Yu. Maeda, *Solid State Commun.* **120**, 165 (2001).
- 2) M. Itoi, Y. Ono, N. Kojima, K. Kato, K. Osaka and M. Takata, *Eur. J. Inorg. Chem.* 1198 (2006).
- 3) I. Kashima, M. Okubo, Y. Ono, M. Itoi, N. Kida, M. Hikita, M. Enomoto and N. Kojima, *Synth. Met.* **153**, 473 (2005).