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Article

Enhancement of the Curie Temperature by Isomerization of Diarylethene (DAE) for an Organic–Inorganic Hybrid System: $Co_4(OH)_7(DAE)_{0.5}\cdot 3H_2O$

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Intercalation of an organic photochromic molecule into layered magnetic systems may provide multifunctional properties such as photomagnetism. 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), $Co_4(OH)_7(DAE)_{0.5}\cdot 3H_2O$, was synthesized by the anion exchange reaction between $Co_2(OH)_3(CH_3COO)\cdot H_2O$ and DAE. In the dark and under UV-irradiated (313 nm) conditions, $Co_4(OH)_7(DAE)_{0.5}\cdot 3H_2O$ with open and closed forms of DAE were obtained, respectively. The magnetic susceptibility measurements elucidated ferromagnetic intra- and interlayer interactions and Curie temperatures of $T_C = 9$ and 20 K for cobalt LDHs with the open and closed forms of DAE, respectively. The enhancement of the Curie temperature from 9 to 20 K by substitution of the open form of DAE with the closed form of DAE as an intercalated molecule is attributed to the delocalization of the π-electrons in the closed form of DAE, which enhances the interlayer magnetic interaction. The enhancement of the interlayer magnetic interaction induced by the delocalization of π-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 π-electron system is enormously higher than that (7.0 K) of the cobalt LDHs with hexanedioate. By UV irradiation at 313 nm, $Co_4(OH)_7(DAE)_{0.5}\cdot 3H_2O$ shows the photoisomerization of DAE from the open form to the closed one in the solid state, which leads to the enhancement of Curie temperature.

1. Introduction

Current research in the field of molecular solids involves the investigation of the possibilities of an organic–inorganic hybrid system having multifunctionality coupled with transport, optical, or magnetic properties. Multifunctional materials are expected to provide a unique interplay between these physical properties, such as phototunable conductivity[1] and field-induced superconductivity.[2] Among these multifunctional materials based on molecular solids, both from the fundamental and applied points of view, extensive studies have been performed for various photoinduced phenomena such as the light-induced excited spin-state trapping (LIESST) in spin-crossover complexes,[3,4] the photoinduced magnetism in transition metal cyanides,[5] the photoinduced valence transition for halogen-bridged gold mixed-valence complexes[6] and iodine-bridged binuclear Pt complexes,[7] the

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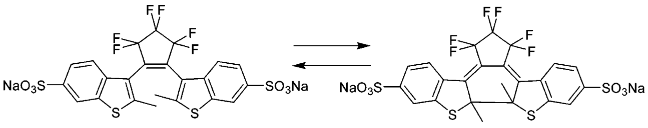
photoinduced transition between the metallic and insulating phases for organic salts,[8] and so forth.

Among various multifunctional materials, a molecular-based magnet is a leading candidate as a photocontrollable multifunctional material. Intercalated magnetic compounds, such as layered double hydroxides (LDHs),[9−11] oxalato-bridged bimetal compounds A[M(II)M′(III)(ox)$_3$] (A = cation, M, M′ = metal, ox = C_2O_4),[12−16] dithiooxalato-bridged bimetal compounds A[M(II)M′(III)(dto)$_3$] (A = cation, M, M′ = metal, dto = $C_2S_2O_2$),[17−24] or perovskite-type metal halides $A_2M(II)X_4$ (A = cation, M = metal, X = halogen),[25−27] provide an excellent opportunity to control their magnetic properties by the intercalation of various molecules. In particular, metal LDHs, $M_2(OH)_3A\cdot zH_2O$ (M = Cu, Co, A = organic anion), have tunable interlayer distances between 5 and 30 Å, which results in various types of magnetisms, such as ferromagnetism, ferrimagnetism, or antiferromagnetism.[28,29] Furthermore, the number of double bonds in the bridging intercalated anion is an essential feature in controlling the type of magnetic interaction, that is, the ferromagnetic or antiferromagnetic interaction between layers.[30]

In organic−inorganic hybrid systems, it is effective to use an organic photochromic molecule for producing photoswitchable materials. On the basis of this strategy, we have used a photochromic diarylethene anion, 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophene-6-sulfonate) (**1a**), as an intercalated molecule.



1a **1b**

Diarylethenes undergo a thermally irreversible and fatigue-resistant photochromic reaction.[31,32] According to the recent molecular orbital calculation, the π-electron system is divided at a contact between benzothiophene and cyclopentene part in the open-form of DAE, while that of the closed form is connected from end to end of molecule by connection between two benzothiophene units.[33] Using this photoswitchable π-electron system in a diarylethene, the ends of which are modified by nitronyl nitroxide radicals, as a photochromic spin coupler, Matsuda et al. have succeeded in controlling the magnetic exchange interaction between two nitronyl nitroxide radicals by photoirradiation, and they have shown that the antiferromagnetic interaction between both sides of nitronyl nitroxide radicals is enhanced from $J/k_B = -2.2$ K in the open form to $J/k_B = -11.6$ K in the closed form.[33,34]

By using a diarylethene anion as a magnetic coupler to change the magnetic properties of LDHs from a 2D to a 3D magnet, we have intercalated a diarylethene anion into Co-LDHs to control the magnetism by photoisomerization of diarylethene. By UV irradiation at 313 nm, $Co_4(OH)_7(DAE)_{0.5}\cdot 3H_2O$ (DAE = diarylethene anion) shows the photoisomerization of the diarylethene anion from the open form to the closed one in the solid state, which leads to the decreases in coercive field and remnant magnetization. Furthermore, the closed form is returned to the initial state (open form) almost reversibly by visible irradiation at 550 nm.[35]

In this paper, we report the dimensional conversion in the magnetic network of Co-LDHs from 2D to 3D by the

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substitution of an intercalating molecule from the open form **1a** to the closed form **1b**, where the Curie temperature is enhanced from 9 to 20 K. This enhancement of the Curie temperature can be observed in the UV-irradiated condition of $Co_4(OH)_7[\mathbf{1a}]_{0.5}\cdot 3H_2O$. Moreover, to confirm the influence of the delocalized π-electron system in the intercalated molecule on the Curie temperature, we have also investigated the series of cobalt LDHs with hexanedioic acid, (*E*)-3-hexenedioic acid and (*E*,*E*)-2,4-hexadienedioic acid. In the former two compounds, the Curie temperatures are in the range between 7 and 8 K, while the last one shows the Curie temperature of 26 K. These facts show that the enhancement of the Curie temperature is caused by the delocalization of the π-electron in an intercalated anion.

2. Experimental Section

Reagents were of commercial grade. Perfluorocyclopentene was provided by NIHON ZEON. The sodium salt of **1a** was synthesized according to the literature;[33−39] $Co_2(OH)_3(CH_3COO)\cdot H_2O$ was prepared as a blue powder according to ref 26. The sodium salt of **1b** was synthesized by application of UV light to the aqueous solution of the salt of **1a** with an Asahi Spectra LAX-101 xenon lamp for 2 h.

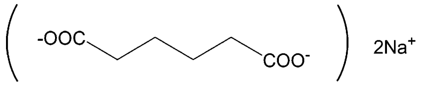
The intercalation compound, $Co_4(OH)_7(\mathbf{1a}$ or $\mathbf{1b})_{0.5}\cdot 3H_2O$ (**3a** or **3b**, respectively), was prepared by an anion-exchange reaction in the same manner as described in ref 35. A powder sample of $Co_2(OH)_3(CH_3COO)\cdot H_2O$ (0.5 mmol) was dispersed into an aqueous solution (0.02 M, 50 mL) of **1a** or **1b** and stirred for 12 h at 60 °C. The precipitate, a green powder, was washed with water and then dried at room temperature.

The sodium salts of hexanedioic acid (**4**), (*E*)-3-hexenedioic acid (**5**), and (*E*,*E*)-2,4-hexadienedioic acid (**6**) were prepared by the neutralization of these acids. The intercalation compounds, $Co_2(OH)_{3.6}(\text{hexanedioate})_{0.2}\cdot 1.1H_2O$ (**7**) or $Co_2(OH)_{3.6}((E)\text{-3-hexenedioate})_{0.2}\cdot 1.1H_2O$ (**8**), were prepared in the same manner as **3a** or **3b**. A powder sample of $Co_2(OH)_3(CH_3COO)\cdot H_2O$ (0.5 mmol) was dispersed in an aqueous solution (0.02 M, 50 mL) of the corresponding sodium dicarboxylate (**4** or **5**) and stirred for 12 h at 60 °C. $Co_2(OH)_{3.5}((E,E)\text{-2,4-hexadienedioate})_{0.25}\cdot H_2O$ (**9**) was prepared according to the following procedure. $Co_2(OH)_3(CH_3COO)\cdot H_2O$ was dispersed in an aqueous solution (0.02 M, 50 mL) of the corresponding sodium dicarboxylate (**6**) and stirred for 9 h at room temperature. The compositions of crystal waters were determined by thermogravimetric analysis. The stoichiometries of these Co-LDHs were determined by chemical analysis for C, H, S and thermogravimetric analysis for H_2O as follows. Anal. Calcd for $Co_8C_{23}H_{20}F_6S_4O_{20}$ $6H_2O$ ($Co_4(OH)_7(\mathbf{1a})_{0.5}\cdot 3H_2O$ (**3a**)): C, 16.90; H, 2.64; S, 7.84. Found: C, 17.17; H, 2.51; S, 8.49. Anal. Calcd for $Co_8C_{23}H_{20}F_6S_4O_{20}\cdot 6H_2O$ ($Co_4(OH)_7(\mathbf{1b})_{0.5}\cdot 3H_2O$ (**3b**)): C, 16.90; H, 2.64; S, 7.84. Found: C, 16.86; H, 2.45; S, 7.66. Anal. Calcd for $Co_{10}C_6H_{26}O_{22}\cdot 5.5H_2O$ ($Co_2(OH)_3(\mathbf{4})\cdot 1.1H_2O$ (**7**)): C, 6.35; H, 3.27. Found: C, 6.30; H, 3.25. Anal. Calcd for $Co_{10}C_6H_{24}O_{22}\cdot 5.5H_2O$ ($Co_2(OH)_3(\mathbf{5})\cdot 1.1H_2O$ (**8**)): C, 6.34; H, 3.10. Found: C, 6.49; H, 3.10. Anal. Calcd for $Co_8C_6H_{18}O_{18}\cdot 4H_2O$ ($Co_2(OH)_3(\mathbf{6})\cdot H_2O$ (**9**)): C, 8.48; H, 2.14. Found: C, 8.67; H, 2.34.

Powder X-ray diffraction patterns were recorded at room temperature on a RIGAKU X-ray diffractometer using a Cu Kα radiation in the range of $2\theta = 3-15°$ for all complexes. In the case of **3a**, the reproducibility of powder pattern is in good agreement with the previous report.[35]

The DC and AC magnetic susceptibilities of powder sample **3b** were measured by a Quantum Design MPMS5 SQUID susceptometer in the temperature range between 2 and 300 K, which was corrected for Pascal's constant (-3.77×10^{-4} emu/mol), for the former and the temperature range between 2 and 40 K at a frequency of 375 Hz under alternating field of 0.4 G for the latter.

The DC and AC magnetic susceptibilities of powder sample **3a**, which have been previously reported in the ref 35, were also measured under the same conditions for **3b** to confirm the reproducibility of magnetic properties and to compare with **3b**. The Curie temperature of each compound was determined by the maximum point in the imaginary part of the AC magnetic susceptibility. From the viewpoint of photomagnetism, the AC magnetic susceptibility was measured after UV irradiation at 313 nm with a power of 40 mW/cm^2 for 1 day to powder sample of **3a**, which was spread on a glass slide. The values of these magnetic susceptibilities were normalized by the composition of $Co_2(OH)_{3.5}(\mathbf{1a}$ or $\mathbf{1b})_{0.25}\cdot 1.5H_2O$ for comparison with the series of Co-LDHs intercalating six-carbon dianions **7**−**9**. The AC magnetic susceptibilities of powder samples of **7**−**9** were measured under the same conditions for **3a** and **3b** to determine the Curie temperature.



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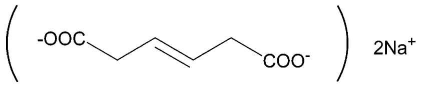

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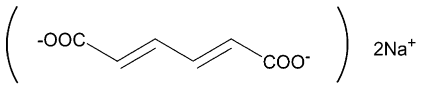

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3. Results and Discussion

3.1. Structure. (a) Interlayer Distance of Co-LDHs Intercalating DAE. There are very few structural reports on the series of LDHs, and they are limited to EXAFS[40] and powder X-ray diffraction.[41] The structural information in this research was obtained by powder X-ray diffraction. For layered materials, the peaks derived from the interlayer distance were observed strongly, although intralayer peaks were hardly observed because of the disorder of the pillared organic molecules,[28] as well as the preferred orientation. The X-ray diffraction patterns of **3a** and **3b** are shown in Figure 1. This figure shows that both the open and closed forms of DAE are intercalated between the adjacent Co layers. The peaks of the Co-LDHs intercalating the closed form of DAE are broader than those of the Co-LDHs intercalating the open form of DAE since the open-form of DAE coexists as a

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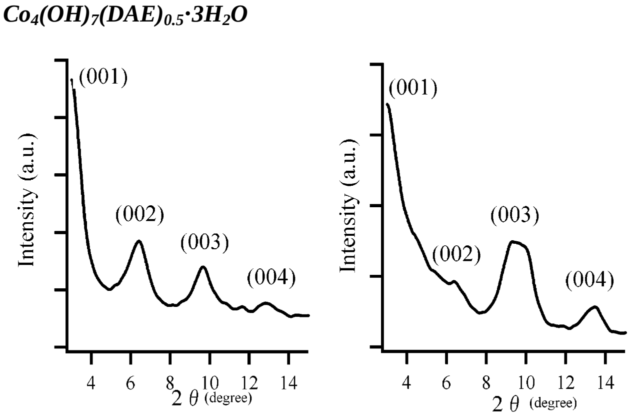


Figure 1. X-ray powder diffraction of **3a** (left) and **3b** (right).

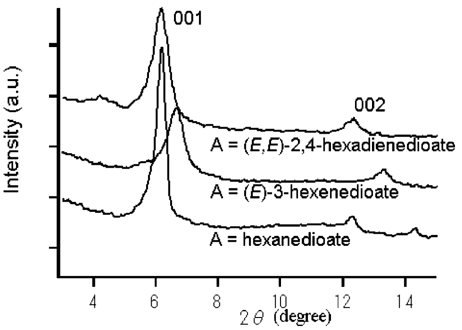


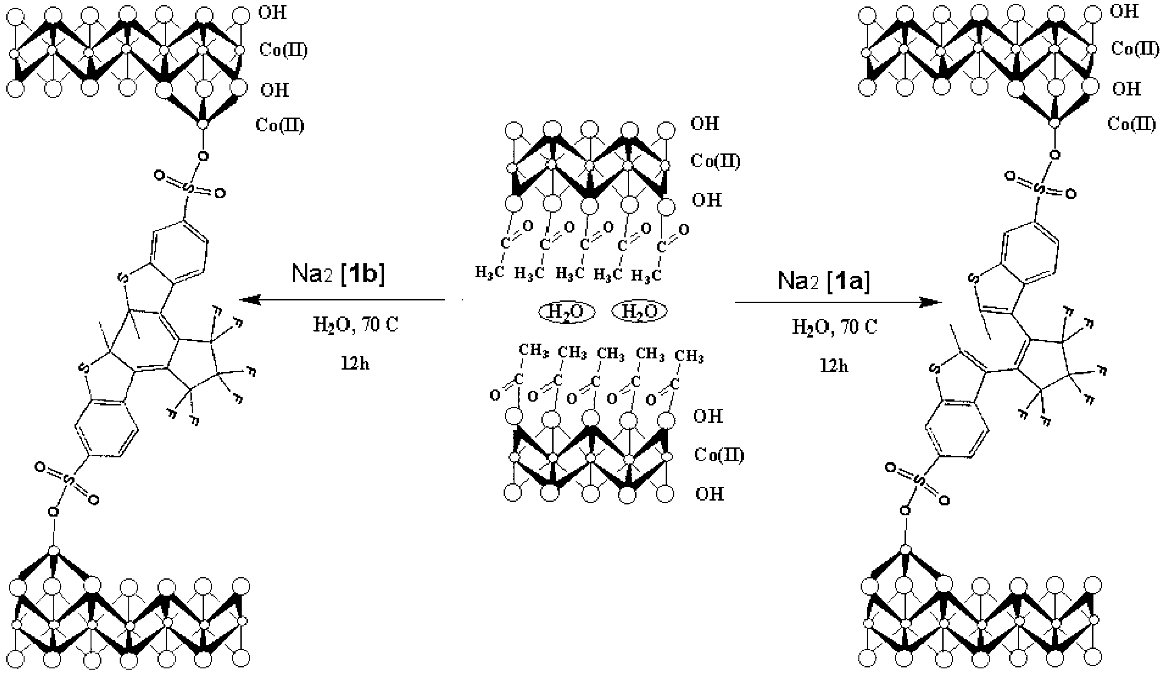
Figure 2. Powder X-ray diffraction of $Co_2(OH)_{4-x}(A)_{x/2}$, **7** (A = hexanedioate), **8** (A= (*E*)-3-hexenedioate), or **9** (A = (*E*,*E*)-2,4-hexadienedioate).

minor fraction with the closed form of DAE, which causes the disorder of **1b**. As estimated from Figure 1, the interlayer distance of **3a** is 27.5 Å, and that of **3b** is about 28 Å. As is generally known, a Co(II) tetrahedrally coordinated by four oxygen atoms displays a blue color and a Co(II) octahedrally coordinated by six oxygen atoms displays a pale pink color. Acoording to Kurmoo,[42] the crystal structure of Co-LDHs is characterized by two kinds of layer structures, single-deck layers of only octahedral cobalt ions and triple-deck layers consisting of both octahedral and tetrahedral cobalt ions. Co-LDHs with single-deck layers and triple-deck layers display pale pink and green colors, respectively, reflecting the colors of octahedral and tetrahedral cobalt ions. Because of the green color of the samples, the interlayer distances, and the compositions between the DAE and Co sites of **3a** and **3b**, the layers of Co-LDHs consist of octahedral and tetrahedral cobalt ions by the ratio of 7:1, which allows us to assume the schematic model shown in Scheme 1. The interlayer distance (28 Å) of **3b** is slightly longer than that (27.5 Å) of **3a**, reflecting the slight elongation of the molecular length of close form of diarylethene compared to that of open one.[33]

(b) Interlayer Distance of 7, 8, or 9. The intercalation of hexanedioate (**4**), (*E*)-3-hexenedioate (**5**), or (*E*,*E*)-2,4-hexadienedioate (**6**) into Co-LDHs was also confirmed by powder X-ray diffraction as shown in Figure 2. The interlayer distances of the Co-LDHs intercalating six-carbon dianions **7**, **8**, and **9** are estimated to be 14.7, 14.2, and 14.7 Å, respectively. There is no difference between the interlayer distances of **7** and **9**, while the interlayer distance of **8** is slightly shorter. To summarize, the interlayer distances of **7**, **8**, and **9** are almost equal. Therefore, the Co-LDHs intercalating six-carbon dianions **7**, **8**, and **9** are a favorable system for the investigation of the effect of the π-electrons of the intercalated molecules on the magnetic properties of Co-LDHs when the interlayer distance is maintained.

3.2. Magnetic Properties. (a) Magnetic Properties of Co-LDHs Intercalating DAE. We measured the AC and DC magnetic susceptibilities of **3a** and **3b** to clarify the effect of DAE's isomerization on the magnetic properties of Co-LDHs. The magnetizations of **3a** and **3b** measured at 2 K were saturated at 2.24−2.60 μ_B, a value is similar to the saturated magnetization (lower than 3 μ_B) of Co-LDHs with

Scheme 1. Representation of Synthesis and Crystal Structures of Co-LDHs Intercalating Open-Form DAE (left) and Closed-Form DAE (right)



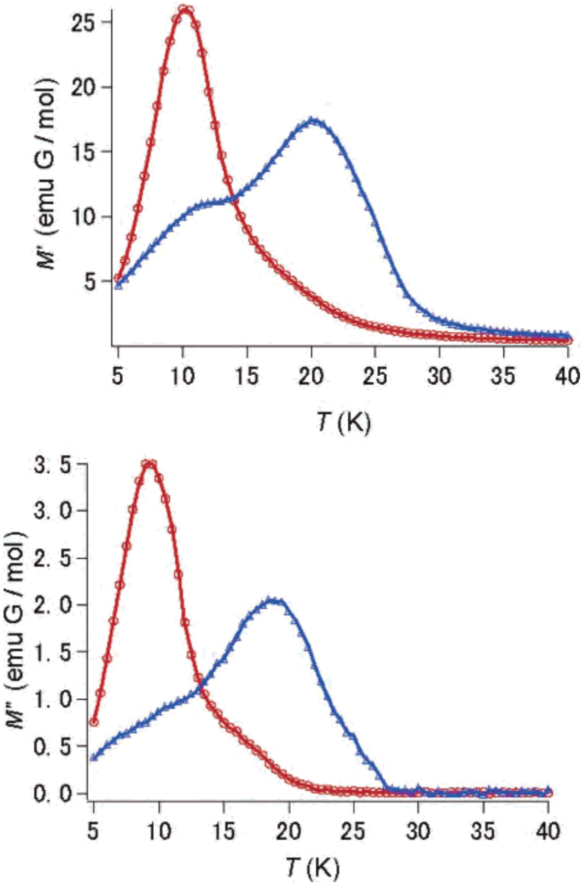


Figure 3. Real (***M′***) and imaginary (***M″***) parts of AC magnetic susceptibility for **3a** (○) and **3b** (△).

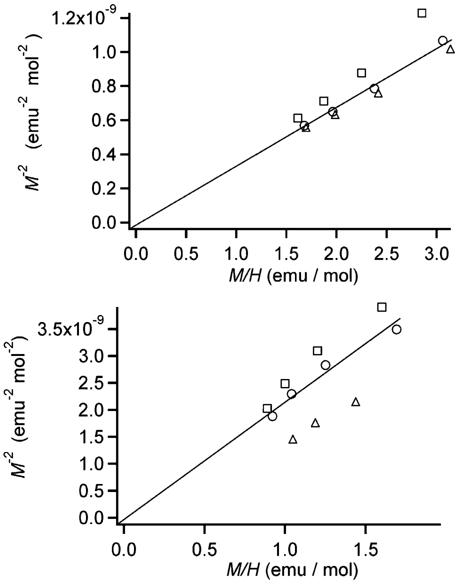


Figure 4. Arrott plot of Co-LDHs intercalating DAE. The upper plot is the Arrott plot of **3a** which was measured at 9.0 (□), 10.0 (○), and 12.0 K (△). The lower plot is the Arrott plot of **3b** which was measured at 20.0 (□), 22. (○), and 24.0 K (△).

triple-deck layers consisting of both octahedral and tetrahedral cobalt ions, $Co_5(OH)_8(O_2CC_6H_4CO_2)$?$2H_2O$,[42] in which both of the intralayer and interlayer magnetic interactions are essentially ferromagnetic except for the antiferromagnetic interaction between octahedral cobalt ions and tetrahedral cobalt ions. The antiferromagnetic interaction between octahedral cobalt ions and tetrahedral cobalt ions within the triple-deck layer causes partial compensation of the spin subnetworks.[42] As reported in previous paper,[35] we have confirmed that both of the intra- and interlayer magnetic interactions of **3a** are ferromagnetic from the analyses of the field dependence of magnetization at 2 K and the temperature dependence of magnetic susceptibility. Therefore, the small value (2.24−2.60 μ_B) of the saturated magnetization is attributed to the antiferromagnetic interaction between octahedral cobalt ions and tetrahedral cobalt ions within the triple-deck layer. The temperature-dependent AC magnetic susceptibilities of **3a** and **3b** are shown in Figure 3. The Curie temperatures are estimated, from the temperature at the peak of magnetic susceptibility, to be 9 and 20 K for **3a** and **3b**, respectively. The shoulder appearing in the AC magnetic susceptibility of **3b** at around 10 K is attributed to the fact that **3a** coexists as a minor fraction with **3b**. As shown in Figure 4, to obtain the Curie temperature more precisely, we carried out the Arrott plot for **3a** and **3b** from the data of DC magnetic susceptibility. The Arrott-plot gives the Curie temperature when the extrapolated line of the isothermal M^{-2} versus M/H plot runs through the origin of the coordinate axes. From this analysis, the Curie temperatures are estimated to be 10 and 22 K for **3a** and **3b**, respectively. From the results of AC and DC magnetic susceptibility measurements, the Curie temperatures are consistent with each other.

The Curie temperature of the Co-LDHs is sensitive to the interlayer distance that is controlled by the size of intercalated molecule.[10,35] According to refs 10 and 35, the Curie temperature of Co-LDHs decreases from 23 to 8 K with an increase in the interlayer distance from 10 to 25 Å. In the cases of **3a** and **3b**, however, the Curie temperature is remarkably enhanced from 9 to 20 K by substitution of the intercalated molecule **1a** with **1b**, despite the interlayer distance of **3b** being slightly longer than that of **3a**. which conflicts with the above-mentioned relationship between the size of intercalated molecule and the Curie temperature. In this way, the π-electron system in the intercalating anion is considered to be the origin of the anomalous enhancement of the Curie temperature of **3b**.

(b) Effect of the π-Electron on the Curie Temperature of Co-LDHs Intercalating the Carboxylate Anion. As mentioned in the previous section, the Co-LDHs intercalating six-carbon dianions **7**, **8**, and **9** are a favorable system for the investigation of the π-electron effects of intercalated molecules on the magnetic properties of Co-LDHs while the interlayer distance is maintained. The temperature-dependent AC magnetic susceptibilities of **7**, **8**, and **9** are shown in Figure 5. From the temperature at the peak of magnetic susceptibility, the Curie temperatures are estimated to be 7, 8, and 26 K for **7**, **8**, and **9**, respectively. The Curie temperature (26 K) of cobalt LDHs with (*E*,*E*)-2,4-hexa-

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(42) Kurmoo, M. *Metal-Organic and Organic Molecular Magnets*; Day, P., Underhill, E. A.; The Royal Society: London, 1999; pp 185−205.

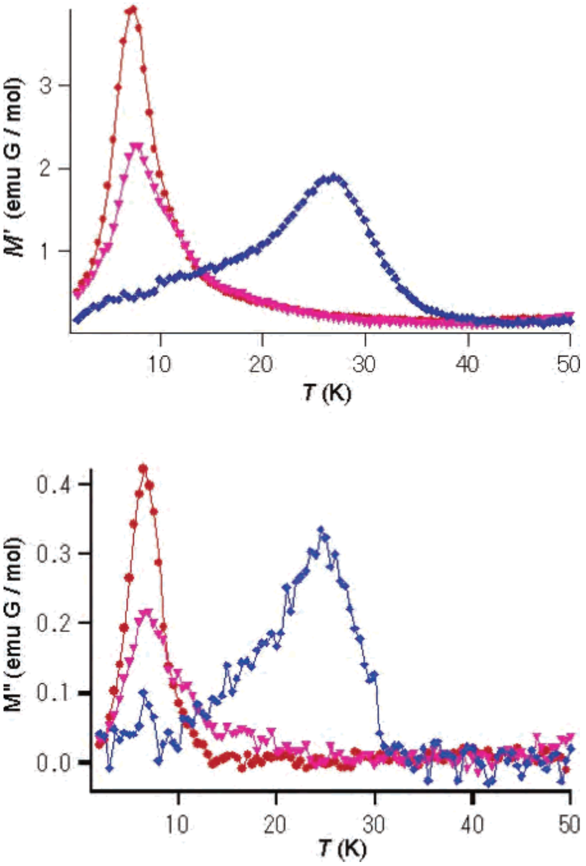

Figure 5. AC magnetic susceptibility of 7 (●), 8 (▼), and 9 (◆). The Curie temperatures of them are determined from the maximum point of AC magnetic susceptibility.

dienedioate (**6**), having a conjugated π-electron system, **9**, is enormously higher than that (7 K) of cobalt LDHs with hexanedioate **4** (**7**), despite the same interlayer distance of 14.7 Å. Therefore, it is obvious that the conjugated π-electron system of the intercalated anion acts as an enhancer of interlayer magnetic interaction, which causes a strong superexchange interaction or spin polarization through the medium of delocalized π-electrons in the intercalated anion. In Co-LDHs lacking the π-conjugated system in the intercalated anion, meanwhile, the dominant interlayer interaction is dipole−dipole interaction which is weak because of long interlayer distance.

3.3. Origin of the Enhancement of Curie Temperature for 3a and 3b. According to Drillon et al.,[30] the Cu-LDHs with **4** have ferromagnetic intralayer and antiferromagnetic interlayer interactions. As a result, this complex shows a ferrimagnetic transition at 15.7 K. Cu-LDHs with **6** also show a ferrimagnetic transition at 16.0 K, while Cu-LDHs with **5** behave as three-dimensional ferromagnets.[29] In our case, the Curie temperature for Co-LDHs with **6** is 26 K, which is enormously higher than those (7 K, 8 K) of Co-LDHs with **4** and **5**, as mentioned above. These results suggest that the conjugated π-electron system of intercalated anions, rather than the interlayer distance, plays an important role in the increase of the Curie temperature for the case of Co-LDHs.

The ground spin state of cobalt(II) in Co-LDHs is characterized as $S = 3/2$ (high spin) according to the DC magnetic susceptibility measurement.[35] In general, the ground high spin state of Co^{2+}, ${}^4T_{1g}$ ($t_{2g}^5e_g^2$), behaves as Ising spin because of the strong spin−orbit interaction. The characteristic property of Ising spin is reflected in large anisotropy of the g value in EPR, for example, Co^{2+} in TiO_2 has $g_x = 2.079$, $g_y = 5.885$, and $g_z = 3.735$.[43]

The Hamiltonian for a quasi-two-dimensional Ising-type magnet with interaction between adjacent layers is described as

$$H = -2J\sum_{\text{intralayer}}(S_i^z S_j^z) - 2J\xi\sum_{\text{interlayer}}(S_i^z S_j^z)$$

where ξ denotes a parameter of interlayer magnetic interaction with a value from 0 to 1. The ξ dependence of the Curie temperature is calculated on the basis of this Hamiltonian with the Monte Carlo method.[44] From the results of this calculation, the normalized value of the Curie temperature for the three-dimensional limit to the two-dimensional limit, $T_C(\xi = 1)/T_C(\xi = 0)$, is 2.0. As already mentioned, the Curie temperatures of Co-LDHs with the open-form of DAE anion (**1a**) and the closed form of DAE anion (**1b**) are 9 and 20 K, respectively. The ratio of these Curie temperatures is 2.2, which is close to the calculated value of $T_C(\xi = 1)/T_C(\xi = 0)$. Considering the extremely weak dipole−dipole interaction between the cobalt layers of **3a** with interlayer distance of 27.5 Å, we think that the magnetism of **3a** is quasi-2D magnet, which solely depends on the intralayer exchange interaction estimated as $J_{\text{intra}}/k = 6.7$ K, according to the theory of the 2D Ising model.[45] The magnetism of **3b** depends on not only the intralayer exchange interaction but also the interlayer interaction caused by a π-electron-mediated exchange interaction or a spin polarization. Therefore, the remarkable difference between the Curie temperatures of **3a** and **3b** suggests that the quasi-two-dimensional sheet with a Co^{2+} magnetic layer becomes a three-dimensional magnetic structure with the substitution of the closed form of the DAE anion (**1b**) for the open form of DAE anion (**1a**) in Co-LDHs. When the small change of interlayer distance between **3a** and **3b** is considered, the remarkable difference between the Curie temperatures of **3a** and **3b** should be attributed to a change of the π-electron system in DAE rather than a change of distance between the adjacent magnetic layers. As mentioned in the Introduction, the π-electron system of DAE can be controlled by photoirradiation selectively. In fact, the DAE derivative, whose ends are modified by a nitronyl nitroxide functional group, shows that the antiferromagnetic interaction between both sides of nitronyl nitroxide radicals is enhanced from $J/k_B = -2.2$ K in the open form to $J/k_B = -11.6$ K in the closed form.[33,34] This result suggests the possibility of transforming the organic−inorganic hybrid system, $Co_4(OH)_7(DAE)_{0.5}\cdot 3H_2O$, from a 2D to a 3D ferromagnet with the use of the photoisomerization of DAE from open to closed form.

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(44) Todo, S.; Miyashita, S. Private communication.

(45) Drillon, M.; Hornick, C.; Laget, V.; Rabu, P.; Romero, F. M.; Rouba, S.; Ulrich, G.; Ziessel, R. *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 125.

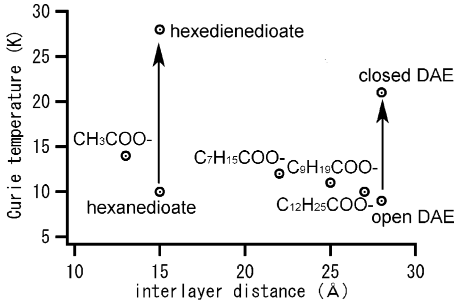


Figure 6. Relationship between the interlayer distance and the Curie temperature of Co-LDHs. The Curie temperatures of Co-LDHs with CH_3COO^-, $C_7H_{15}COO^-$, $C_9H_{19}COO^-$, and $C_{12}H_{25}COO^-$ are quoted from ref 10. Arrows show the enhancement of Curie temperature induced by the π-electron system of the intercalated anions.

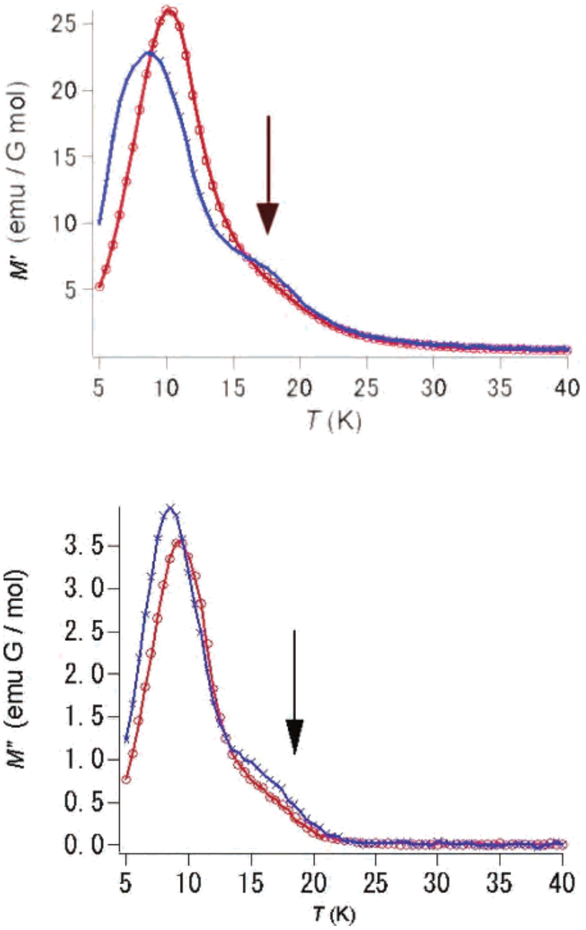


Figure 7. AC magnetic susceptibility of **3a** before UV irradiation (○) and after UV irradiation (×). The arrow points out the appearance of the shoulder of AC magnetic susceptibility after irradiation UV of 313 nm.

The relation between the Curie temperature of Co-LDHs and interlayer distance and the enhancement of the Curie temperature induced by the π-electron system of intercalated anions is shown in Figure 6. Generally, the Curie temperatures of Co-LDHs become lower with the expansion of the spatial extension.[10] However, the existence of conjugated π-electron system in the intercalated anions remarkably enhances the Curie temperature of LDHs.

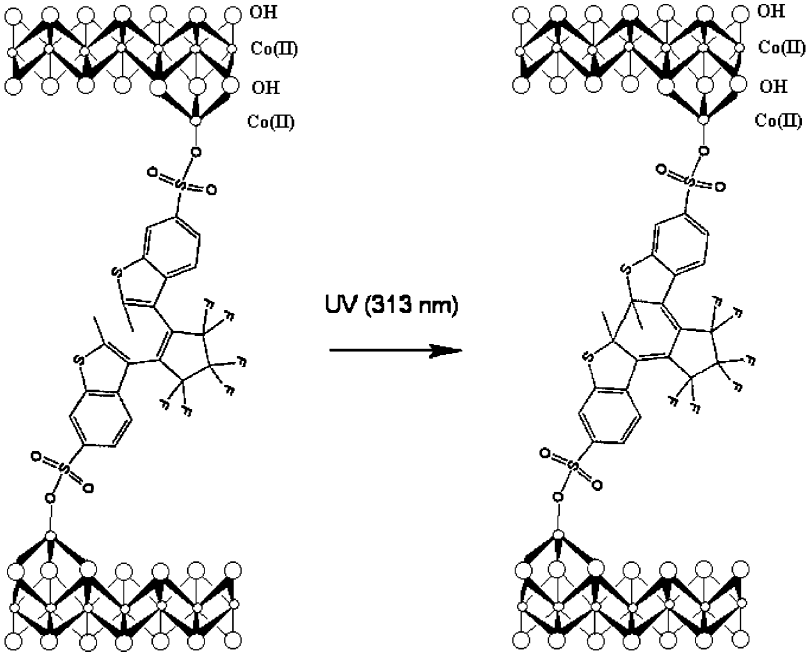
3.4. Enhancement of T_C by Photoisomerization of DAE. Figure 7 shows the AC magnetic susceptibilities as a function of temperature for **3a** before and after UV irradiation of 313 nm at room temperature. As shown in Figure 7, after UV irradiation of 313 nm, the shoulder of AC magnetic susceptibility emerged at 18 K. From the similarity between the temperature of this shoulder and the temperature at the peak top of AC magnetic susceptibility for **3b**, this shoulder implies the appearance of the ferromagnetic phase with the closed form of DAE (**1b**) in **3a**. This result suggests that the photoisomerization of **1a** occurs in the solid state of **3a** by UV irradiation. Since the photoisomerization partially occurs on the surface of the compound, the magnitude of the shoulder is small compared with the peak of the AC magnetic susceptibility for **3b**. In connection with this, it should be mentioned that our previous report has proposed no photoinduced change of the Curie temperature in the AC magnetization for the solid state of **3a**,[35] while we have found the shoulder around 18 K in the AC magnetization by photoirradiation to the same compound. From the reproducible result of the latter, the appearance of the shoulder by photoirradiation is an essential phenomenon for **3a**. We suppose that the change of the magnetic susceptibility is obscure, since photoirradiation is insufficient for grains of powder sample in the previous experiment. In the case of **3a**, UV irradiation of 313 nm does not completely penetrate into the sample because of the strong optical absorption corresponding to the $\pi-\pi^*$ transition of DAE. Therefore, the photoisomerization of DAE from the open form to the closed one for **3a** is not complete, which is responsible for the fact that the photoinduced shoulder around 18 K in AC magnetic susceptibility for **3a** is small compared with the peak of the AC magnetic susceptibility at 20 K for **3b**. The photoisomerization of DAE from the open form to the closed one in **3a** is less than 5% judging from the AC magnetic susceptibility. To produce a prominent photoinduced effect on the AC magnetic susceptibility around 20 K for **3a**, the photoisomerization of DAE induced by two-photon excitation of 630 nm is indispensable and in progress.

As described in Scheme 2, this character gives us a photoswitchable paramagnetic−faramagnetic transformation between 9 and 20 K because UV irradiation makes it the ferromagnetic phase of **3b**, while visible light provides the paramagnetic phase of **3a** in this temperature range. When the photoisomerization occurs in this temperature region, we can select the magnetism as the paramagnetic phase with **3a** or the ferromagnetic phase with **3b** by selecting the wavelength of irradiated light.

4. Conclusion

The cobalt-based organic−inorganic compounds were prepared by anion exchange reaction, using the photochromic diarylethene anion. From the magnetic susceptibility measurements, the ferromagnetic transition temperature changes from 9 to 20 K with substitution of the intercalated anion from the open form of DAE (**1a**) to the closed form of DAE (**1b**). To confirm the influence of the π-electron system in the intercalated anion to the magnetic properties, we also carried out magnetic susceptibility measurement by using Co-LDHs with a series of saturated or unsaturated six-carbon

Scheme 2. Representation of the Photoinduced Conversion between Co-LDHs with the Open Form of DAE (left) and Co-LDHs with the Closed Form of DAE (right)



dianions. From the result of magnetic susceptibility measurement, the Curie temperature shifts from 7−8 to 26 K by the extension of π-electron system of the intercalated anion from hexanedioate or (*E*)-3-hexenedioate to (*E*,*E*)-2,4-hexadienedioate. Therefore, the change of the Curie temperatures between **3a** and **3b** can be attributed to the change of the π-electron system in the DAE molecule. Moreover, the appearance of a shoulder at ∼18 K in the AC magnetic susceptibility for **3a** with UV irradiation of 313 nm suggests that the magnetism of this compound can be controlled by photoirradiation. In the temperature region between 9 and 20 K, **3a** and **3b** are a paramagnet and a ferromagnet, respectively. Therefore, it is possible to demonstrate a photoinduced paramagnetic−ferrromagnetic transformation for **3a** in the temperature region between 9 and 20 K, and this work is in progress.

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