Photo-Induced Long-Lived Intramolecular Electron Transfer in a Co Valence Tautomeric Complex

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A photo-induced valence tautomerism was observed in a Co complex, [$\mathrm{Co^{III\text{-}LS}}$(phen)(3,5-DBSQ)(3,5-DBCat)]. In this system, visible light illumination induces an electron transfer from 3,5-DBCat to $\mathrm{Co^{III\text{-}LS}}$, producing [$\mathrm{Co^{II\text{-}HS}}$(phen)(3,5-DBSQ)$_2$]. The resultant photo-induced metastable state could be trapped more than 1 h at 5 K.

There has been a great interest in the study of the optical properties of spin-crossover complexes and valence tautomeric compounds.[1,2] Recently, we have reported that a CoFe Prussian blue analogue exhibits a photo-induced electron transfer with extremely long lifetime at low temperature.[3] However, the number of the optically switchable molecular solids reported has been quite small,[3,4] meaning that the design of such tunable compounds is still a challenge. Here, we describe a photo-induced long-lived intramolecular electron transfer observed in a Co valence tautomeric complex,[2,5–9] [$\mathrm{Co^{III\text{-}LS}}$(phen)(3,5-DBSQ)(3,5-DBCat)], where LS, phen, 3,5-DBSQ and 3,5-DBCat are low-spin, 1,10-phenanthroline, 3,5-di-*tert*-butyl-1,2-semiquinonate and 3,5-di-*tert*-butyl-1,2-catecholate, respectively.[10] In this system, visible light illumination induces an electron transfer from 3,5-DBCat to $\mathrm{Co^{III\text{-}LS}}$, producing [$\mathrm{Co^{II\text{-}HS}}$(phen)(3,5-DBSQ)$_2$], where HS represents high-spin. The resultant photo-induced metastable state can be trapped more than 1 h at 5 K. This is a unique system that provides insight into the factors that affect electron transfer in molecular compounds. Furthermore, it is important to note that the large change in the optical, structural, and magnetic properties that accompany the valence tautomeric interconversion have potential applications in molecular optical switching materials.

The Co complex, [$\mathrm{Co^{II\text{-}HS}}$(phen)(3,5-DBSQ)$_2$]·$\mathrm{C_6H_5CH_3}$, was prepared as previously described.[8] Adams et al. reported that it shows abrupt phase transition at around 240 K,[8] which can be expressed as follows.

$$[\mathrm{Co^{II\text{-}HS}(phen)(3,5\text{-}DBSQ)_2}] \leftrightarrows [\mathrm{Co^{III\text{-}LS}(phen)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)}]$$

The transition involves the color change from dark green-brown to blue-black. The blue-black complex, [$\mathrm{Co^{III\text{-}LS}}$(phen)(3,5-DBSQ)(3,5-DBCat)], has an absorption band at around 600 nm, which contains some charge transfer from 3,5-DBCat to $\mathrm{Co^{III\text{-}LS}}$.[9] It has been reported that the excitation of the spin-allowed ligand(3,5-DBCat)-to-metal($\mathrm{Co^{III\text{-}LS}}$) charge-transfer (LMCT) band of [$\mathrm{Co^{III\text{-}LS}}$(phen)(3,5-DBSQ)(3,5-DBCat)] in toluene solution results in a transient generation of [$\mathrm{Co^{II\text{-}HS}}$ (phen)(3,5-DBSQ)$_2$] via an S = 1/2 LMCT excited state.[2] This suggests that the photo-illumination effects of the solid-state [$\mathrm{Co^{III\text{-}LS}}$(phen)(3,5-DBSQ)(3,5-DBCat)] complex at 5 K should be investigated by exciting the LMCT band. In order to excite the LMCT band, a laser-diode pumped Nd:YAG laser with the wavelength of 532 nm was used as a light source. The light was guided via an optical fiber into the SQUID magnetometer. When the sample was illuminated at 5 K, the increase in the magnetization value was observed. That is, the magnetization value increased from ca. 1.6 to ca. 3 μ_B after illumination (Figure 1). This suggests that the valence tautomeric conversion was induced by illumination (Figure 2). The change in the magnetization persisted for periods of at least 1 h, after the illumination was stopped. The temperature dependence of μ_{eff} after illumination shows that the relaxation occurs at around 50 K. The change in the magnetization by light could be repeatedly observed at least several times.

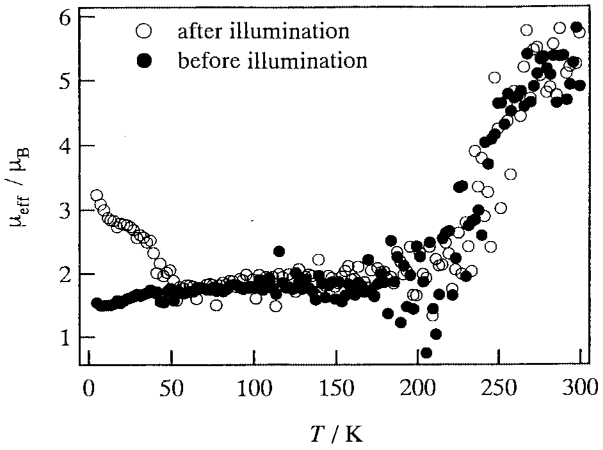

Figure 1. μ_{eff} versus T plots before (●) and after (○) illumination. The sweep rate is 2 K min^{-1}.

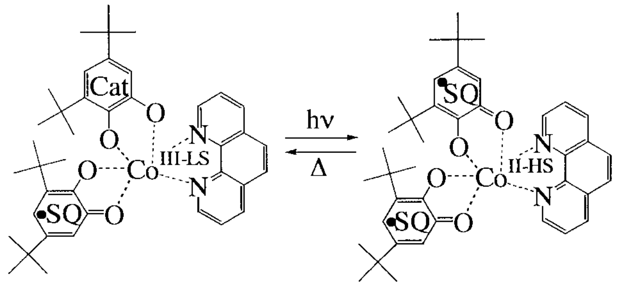

Figure 2. Photo-induced valence tautomerism observed at 5 K. The notations, hν, Δ, SQ and Cat represent illumination, thermal treatment, 3,5-DBSQ (3,5-di-*tert*-butyl-1,2-semiquinonate) and 3,5-DBCat (3,5-di-*tert*-butyl-1,2-catecholate), respectively.

In order to elucidate the electronic state of the metastable one, IR spectra of the Co complex were measured (Figure 3). The spectral region between 1600 and 1200 cm^{-1} contains strong bands associated with the C–O stretching modes that are sensitive to the charge of the ligand moieties. IR spectrum at room temperature shows an absorption peak at around 1480 cm^{-1}, characteristic for the C–O stretch vibrations of 3,5-DBSQ.[11] On cooling, the peak significantly decreased at around 240 K, although it is still observed at 18 K. This is consistent with the fact that one of the two 3,5-DBSQ ligands in the complex is reduced to be 3,5-DBCat due to the thermally induced valence tautomerism. Furthermore, a new peak appears at around 1290 cm^{-1}, which is ascribable to the C–O stretch vibrations of 3,5-DBCat.[11] When the complex, [Co$^{III\text{-}LS}$(phen)(3,5-DBSQ)(3,5-DBCat)], is illuminated at 18 K (ca. 30 mW/cm^2), the peak at around 1480 cm^{-1} is increased and the peak at around 1290 cm^{-1} is significantly decreased. This shows that the electron transfer from 3,5-DBCat to Co$^{III\text{-}LS}$ is induced by the visible light. The IR spectra at around 1290 cm^{-1} show that about 70 % moieties change from [Co$^{III\text{-}LS}$(phen)(3,5-DBSQ)(3,5-DBCat)] to [Co$^{II\text{-}HS}$(phen)(3,5-DBSQ)$_2$] by illumination. The metastable state, [Co$^{II\text{-}HS}$(phen)(3,5-DBSQ)$_2$], is recovered to the original one by heating the sample to ca. 100 K, supporting that the observed photo-effect is reversible.

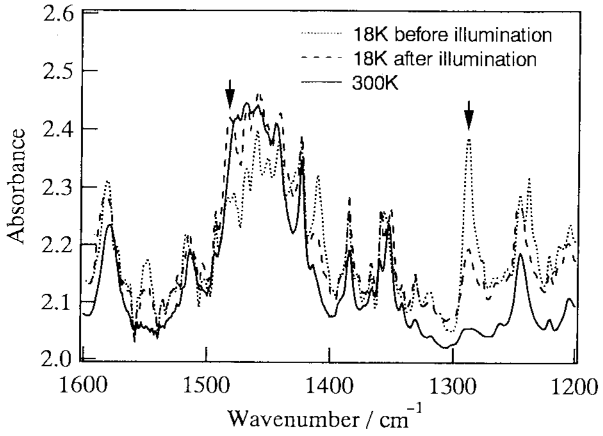

Figure 3. IR spectra at 300 K, before illumination at 18 K and after illumination at 18 K.

It is important to note that photomechanical effects have been reported in several valence tautomeric compounds.[12–15] However, the lifetime is much faster than our observation presented here. It has been reported, for example, that the photo-induced excited state of a semiquinone complex of a platinum group metal returns to its initial state in less than 0.1 s.[12]

We have succeeded in observing the long-lived intramolecular electron transfer in a Co valence tautomeric compound. It should be noted that similar photo-effects could be observed for [Co$^{III\text{-}LS}$(tmen)(3,5-DBSQ)(3,5-DBCat)]·1/2$C_6H_5CH_3$, where tmen is *N*,*N*,*N*',*N*'-tetramethylethylenediamine. The photo-induced valence tautomerism is of interest in connection with the development of optically tunable molecule-based magnets.

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