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Photo-induced magnetized state of Co(DTBSQ)(DTBCat)(phen)·$C_6H_5CH_3$ studied by X-ray absorption spectroscopy

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Introduction

Recently Sato *et al*. found a photoinduced phase transition in Co(DTBSQ)(DTBCat)(phen)·$C_6H_5CH_3$ (DTBSQ=3,5-di-*tert*-butyl-semiquinone, DTBCat=3,5-di-*tert*-butyl-catechol and phen=1,10-phenanthroline) at low temperature. From the IR spectra it is suggested that the $DTBCat^{2-}$ anion is converted back to $DTBSQ^{-}$ after visible-light (532 nm) irradiation, indicating the charge transfer from $DTBCat^{2-}$ to Co(III). There seems to be two possibilities that account for the Co valency; one is Co(II)HS, the same as the HT phase, and the other is a new state of Co(II)LS.

In this work, we have measured and analyzed Co *K*-edge XANES and EXAFS to identify the photoinduced phase [1].

Experimental

The Co *K*-edge XAFS spectra of the low-temperature (LT) and high-temperature (HT) phases were recorded with the transmission mode at BL10B, while those of the photoinduced (PI) phase were taken with the fluorescence yield mode using a Lytle detector at BL9A. For the latter, a liquid He cryostat was employed to yield 11 K with high stability, and the sample, whose thickness is as thin as possible for the visible light (532 nm from a Nd:YAG laser) to penetrate, was kept irradiated during the XAFS measurements.

Results and discussion

Figure 1 shows the Co *K*-edge XANES. The spectral features and the edge energy positions clearly indicate that the HT [Fig. 1(a)] and LT [Fig. 1(b)] phases consist of hight-spin Co(II) and low-spin Co(II), respectively. This is consistent with the previous findings [2]. Upon irradiation at 11 K, the spectrum changes drastically [Fig. 1(c)] and becomes similar to the HT one. When the spectrum was simulated by summing 35% of the LT spectrum and 65% of the HT one, the experimentally obtained spectrum is actually well reproduced, as shown with the dashed line in Fig. 1(c). It is thus concluded that the PI phase is essentially identical to the HT phase of Co(II)HS. Since the spectrum of the Co(II)LS state should noticeably be dissimilar to that of Co(II)HS as is found in some Co(II) spin-crossover complexes, the possibility of Co(II)LS for the PI state is clearly excluded. After whole the XAFS measurements, the sample was once heated to 100 K and was subsequently cooled down again, the spectrum is converted completely to the LT phase [see Fig. 2(d)], this indicating no detectable radiation damages due to visible lights or X-rays.

The EXAFS spectra were analysed according to the conventional procedure. The obtained coordination numbers *N* and the interatomic distances *R* are as follows:
N=6.1±1.6 and *R*=2.081±0.021 Å for the HT phase,
N=6.1±1.1 and *R*=1.899±0.011 Å for the LT phase, and
N=4.6±2.2 and *R*=1.95±0.04 Å for the PI phases.
The PI phase provides an intermediate distance between the HT and LT phases.

In summary, it is revealed that the PI phase is essentially equivalent to the HT Co(II)HS phase. Upon irradiation, one electron in $DTBCat^{2-}$ is transferred to Co(III)LS, yielding Co(II)HS and $DTBSQ^{-}$ as

$$\text{LS-Co}^{(\text{III})}(\text{DTBSQ}^{-})(\text{DTBCat}^{2-})(\text{phen}) \xrightarrow{h\nu\ (532\,\text{nm})} \text{HS-Co}^{(\text{II})}(\text{DTBSQ}^{-})_2(\text{phen})\ .$$

References

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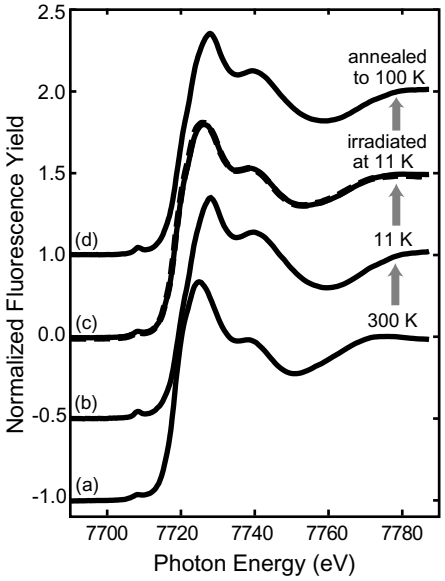

Fig. 1 Co *K*-edge XANES of (a) the HT phase, (b) the LT phase, (c) the PI phase and (d) the annealed phase after irradiation.