

Unexpected photoinduced dynamics in charge-transfer metal-organic frameworks, (NPr₄)₂[Fe₂(Cl₂An)₃]

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The compound (NPr₄)₂[Fe₂(Cl₂An)₃], classified as a D₂A₃-type honeycomb-layered system, exhibits charge-transfer (CT) phase transition ($T_c = 317$ and 354 K). At around T_c , CT occurs between Fe and Cl₂An ions which has been confirmed by magnetic, structural, and spectroscopic measurements [1]. This compound possesses three different charge-ordered states; a low-temperature (LT) phase [(Fe³⁺)₂(Cl₂An²⁻)(Cl₂An³⁻)₂]²⁻ (fully electron transferred state), an intermediate (IM) phase [(Fe^{2.5+})₂(Cl₂An²⁻)(Cl₂An^{2.5-})₂]²⁻ (charge-disproportionated state), and a high-temperature (HT) phase [(Fe²⁺)₂(Cl₂An²⁻)₃]²⁻. The mechanism of phase transitions in this system has been discussed as multi-stability due to the balance between the valence and the Coulomb interaction like the neutral-ionic (NI) phase transition. It should be noted that there is no clear structural change at each T_c probably due to the rigid bond nature between Fe and Cl₂An molecules, contrary to the existence of dimerization of the lattice in the typical NI system, TTF-CA [2]. Therefore, the phase transition of this system can be viewed as the pure electron system, then an efficient photo-induced CT phase transition can be expected.

To observe photoinduced response of this material, we excite the CT transition (~ 0.8 eV) and probe the reflectivity change in the energy range from mid-IR to UV at room temperature, LT phase. As a result, the ultrafast and highly efficient CT phase transition has been observed judging from the spectral change around intra-molecular transition (2.6 eV) and CT transition. In addition, the photoinduced transient reflectivity spectra just after CT excitation in the mid-IR energy range clearly show an interesting spectral shape which is different from the expected one from the spectral change due to the thermal phase transition. Therefore, the photoinduced state of this material should be classified as a photoinduced hidden state. Especially, the appearance of a broad structure at around 0.2 eV is characteristic. The assignment of this broad structure is not clear at present, but it is suggestive that Raman spectra at the temperature above T_c show the appearance of A_g symmetry mode at the frequency close to the photoinduced structure. Judging from the similarity of the frequency as well as the anisotropy of the spectrum, the electron-molecular vibration coupled mode (e-mv mode) [3] can be a candidate for this structure. This result suggests the disappearance of the inversion center from the Cl₂An ions, then unexpected temporal lattice deformation may occur in this system. The precise dynamics will be discussed in the presentation.

References

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