Study of coupling between electron conduction and spin fluctuation in novel organic charge transfer complexes with TANC

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We have succeeded to synthesize organic conductors with a novel electron acceptor, 5,6,11,12-tetraazanaphthacene (TANC; see Figure 1). The TANC molecule forms highly conductive compounds in various combinations with metal ions. In particular, several Cu-TANC systems are highly attractive complexes in terms of formation of both π-electron conductive bands and coordinating structure between the acceptor molecule and copper spin sites. Employing these properties is an important approach to construct π-d interaction systems, such as the $(DCNQI)_2Cu$ system,[1] where DCNQI denotes *N*,*N*'-dicyanoquinodiimine.

In the case of $[Cu^{1.5+}(TANC)](NO_3)_{0.5}$, Cu ions and TANC radicals are alternately linked through coordinate interaction between Cu-N atoms along the *b*-axis, as shown in Fig. 2(a). These flat-ribbon structures stack with each other to form 2D layers in the *ab*-plane, while NO_3 anion layers are segregated from each Cu-TANC layers (see Figs. 1(b) and (c)). While the conductivity of this complex shows semiconducting behavior, the single crystal exhibits a high conductivity of 50 S cm^{-1} at 300 K along the *a*-axis, which is the stacking direction of the TANC molecules. Moreover, conductivity shows highly anisotropic behavior, that is, σ||a / σ||b ~ 8.3, which corresponds to the segregated stacked structure of Cu-TANC 2D layers. Interestingly, X-ray photoelectron spectroscopy results indicate the coexistence of Cu^+ and the Cu^{2+} at a 1 : 1 ratio in the Cu-TANC layers. Moreover, the infrared reflectivity measurement reveals that electrons fluctuate between these two valence states at copper ion sites in both the directions of stacking (*a*-axis) and flat-ribbon (*b*-axis) structures.

On the other hand, the TANC complex family, Ag(TANC), also forms a similar conductive layer without a counter anion layer, such as the NO_3 layer in $[Cu^{1.5+}(TANC)](NO_3)_{0.5}$. The anisotropic conductivity measurement for the Ag complex at room temperature shows that σ||a / σ||b ~ 13, which reflects the low-dimensional character of the Ag complex compared with the Cu one. Infrared reflectivity study supports this observation. The reflectivity component, which is normal to the stacking direction, is negligible, while the parallel component can be observed similar to that in the Cu complex.

To understand how electron conduction occurs in the TANC complexes, we carried out μSR measurements on $[Cu^{1.5+}(TANC)](NO_3)_{0.5}$. We found that the depolarization rate at 300 K is proportional to $H^{-1/2}$, which suggests the existence of the 1D diffusion behavior of spin-excited states

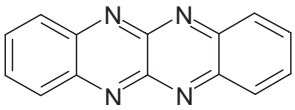

Figure 1

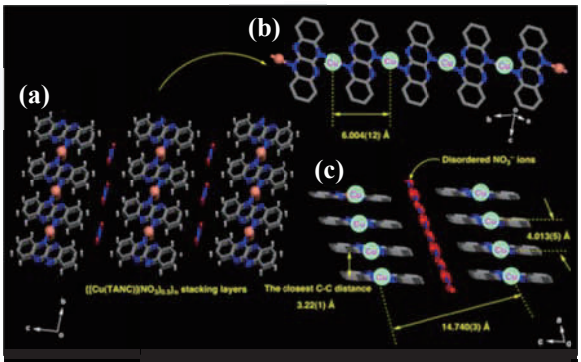

Fig. 2. Crystal structures of $\{[Cu(TANC)](NO_3)_{0.5}\}_n$

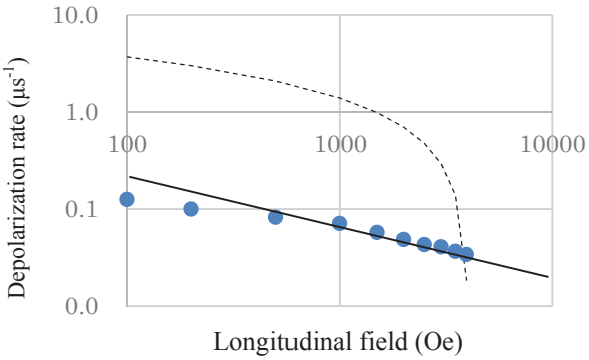

Fig. 3. The field dependence of the depolarization rate at 300 K.

(the solid line in Fig. 2) rather than 2D diffusion (the broken line in Fig. 2). This behavior was also observed at 200 and 100 K. Since we have predicted from our previous light experiments that electrons are conductive in these high-temperature regions, the present μSR results support our prediction. At this moment, we are not sure whether this 1D diffusion behavior occurs in the line of the Cu^+ and Cu^{2+} connection or in the direction of TANC stacking. Comparison between the μSR data of the Cu and Ag complexes will answer this question.

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