

Stepwise neutral-ionic phase transitions in a covalently-bonded donor/acceptor chain compound

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$\text{Ru}_2\text{F}_4\text{Ph-DMDCNQi}$ is the first example of a covalently-bonded donor (DMDCNQi) and acceptor ($\text{Ru}_2\text{F}_4\text{Ph}$) chain complex exhibiting neutral(N)-ionic(I) phase transitions. The $[-\{\text{Ru}_2\}-\{\text{DMDCNQi}\}-]$ chains run along the a axis and make π -stack arrangements along the b and c axes. N-I transitions successively occur at two critical temperatures $T_1 \sim 270\text{K}$ and $T_2 \sim 210\text{K}$. From crystal structure analysis at the laboratory level, averages of the charge transfer degree, δ , in high-temperature phase ($T > T_1$), intermediated phase ($T_1 > T > T_2$), and low-temperature phase ($T < T_2$) are estimated at 0, 0.5, and 1, respectively. Since the covalent bonding prevents dimerization, ferrimagnetically-coupled magnetic moments are ordered in the low-temperature phase. The presence of large magnetic moments as well as the staging feature of the N-I transitions may provide a good arena for dynamical functionalities originating from the correlations among charge, spin, and lattice.

In order to ascertain the valence state in the intermediate phase, an x-ray diffraction measurement on a single crystal was performed at BL8B, Photon Factory. Figure 1 shows oscillation photographs at the 200 K and 220 K. Superlattice reflections with the modulation vector $(0 \ 1/2 \ 1/2)$ are clearly observed at 220 K. Result of the crystal structure analysis at 240K suggests that two neutral chains (II and IV) with $\delta \sim 0$ and two ionic chains (I and III) with $\delta \sim 1$ are aligned to form an alternating stacking of N and I layers in the intermediate phase as shown in figure 2. This is the first observation of the self-organization of the N and I moieties.

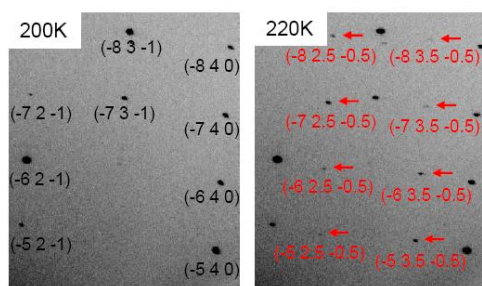


Figure 1 X-ray oscillation photographs.

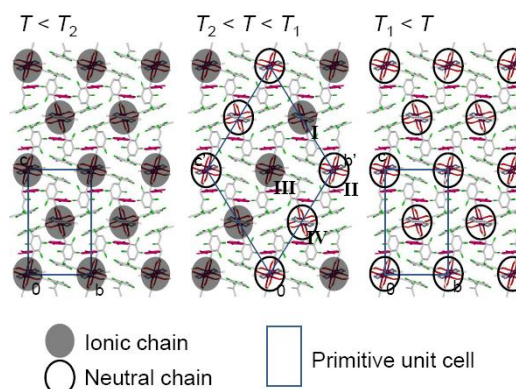


Figure 2 Arrangements of N and I chains.