Development of the New Organic Donor Ligand Metal Complex with Metallic Behavior, [$CuCl_{0.2}Br_{1.3}$(pyra-TTF)]

Shun Ichikawa[1], Hiroki Akutsu[1], Jun-ichi Yamada[1], Shin-ichi Nakatsuji[1], Hatsumi Mori[2]
[1]*Department of Science, University of Hyogo, Japan*
[2] *Institute for Solid State Physics, University of Tokyo, Japan.*
Email: ichikawa@sci.u-hyogo.ac.jp

Functional metal complexes to exhibit conductivity, magnetism, permitivity, optical response, and so on have attracted a great deal of interest. The authors have synthesized and studied new supramolecular copper complexes containing pyrazino-fused TTF derivatives as the ligands in order to obtain novel functional metal complexes. First, we synthesized [$CuCl_2$(BP-TTF)] [1] and [$CuCl_2$(pyra-TTF)] [2] (BP-TTF = bis(pyrazino) tetrathiafulvalene, pyra-TTF = pyrazinotetrathiafulvalene). These complexes reveal the antiferromagnetic interaction between Cu^{II} through the coordinated donor ligands. In addition, we succeeded in synthesizing the semiconducting supramolecular copper complex [$CuCl_{1.5}$(pyra-STF)] [3] (pyra-STF = pyrazinoselenathiafulvalene) with a novel crystal structure and comparatively high conductivity (σ_{RT} = 25 S cm^{-1}) by tuning the oxidation potential of organic donors. This time, we firstly synthesized the complex with metallic behavior, [$CuCl_{0.2}Br_{1.3}$(pyra-TTF)] (**1**) by use of Cl^- and Br^- anions and investigated its crystal structure and physical properties.

The X-ray structure analysis for **1** shows the donors form dimerized stacking columns to form β-type donor arrangement. In addition, 1-D supramolecular copper chains coordinated by pyra-$TTF^{+0.5}$, Cl^- and Br^- extend along the *c* axis. **1** shows the metallic behavior down to 250 K, and the conductivity of the single crystal of this complex at room temperature is 200 S cm^{-1}. The dimerization of the assembled pyra-$TTF^{0.5+}$ donor ligands is expected to be eased by the disorder of the mixed halide anion ligands to create metallic conduction paths.

[1] Shun Ichikawa, Shinya Kimura, Hatsumi Mori, Gosuke Yoshida, and Hiroyuki, Tajima, *Inorg. Chem.*, 45 (2006) 7575.
[2] Shun Ichikawa, Shinya Kimura, Kazuyuki Takahashi, Hatsumi Mori, Gosuke Yoshida, Yuichi Manabe, Masaki Matsuda, Hiroyuki Tajima and Jun-ichi Yamaura, *Inorg. Chem.*, 47 (2008) 4140.
[3] Shun Ichikawa and Hatsumi Mori, *Inorg. Chem.*, in press.