

トリフェニルアルシンを用いた強発光性銅(I)配位高分子の発光特性

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Luminescent Properties of Strongly Emissive Copper(I) Coordination Polymers with Triphenylarsine (*Graduate School of Science and Technology, Kyoto Institute of Technology*)
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Luminescent copper(I) complexes have a variety of supramolecular architectures and luminescent properties¹⁾. In this work, 1D-coordination polymers with dinuclear rhombic $\{\text{Cu}_2\text{X}_2\}$ cores ($\text{X} = \text{Br}, \text{I}$) were easily synthesized by spontaneous evaporation method, using triphenylarsine (AsPh_3) and a series of bidentate *N*-heteroaromatic co-ligands (**Figure 1. (a), (b)**). Some of the coordination polymers in this work exhibited strong phosphorescence even at room temperature (Φ_{PL} : up to **0.95**), and the emission color was dependent on the *N*-heteroaromatic co-ligand. The emission efficiencies of the coordination polymers were stronger than those of the discrete ones that were reported in our previous work²⁾. In addition, the luminescence of the coordination polymers was more resistant to mechanical stimuli unlikely to the discrete ones. Interestingly, coordination polymer $[\text{Cu}_2\text{X}_2(\text{AsPh}_3)_2(2\text{-methylpyrazine})]_n$ was converted to discrete complex $\text{Cu}_2\text{X}_2(\text{AsPh}_3)_2(2\text{-methylpyrazine})_2$, and the emission color was drastically changed when the ligand vapor exposed (**Figure 1. (c)**).

Keywords : coordination polymer, arsine, copper, luminescent property, chromic property

発光性銅(I)錯体は多様な超分子構造や発光特性をもつことで知られている¹⁾。本研究ではトリフェニルアルシン(AsPh_3)と種々の架橋性 *N*-ヘテロ芳香族配位子を用いて、自然蒸発法により、二核菱形の $\{\text{Cu}_2\text{X}_2\}$ ユニット($\text{X} = \text{Br}, \text{I}$)をもつ1次元鎖の配位高分子を合成した(**Figure 1. (a), (b)**)。合成した錯体のいくつかは室温でも強い燐光発光を示し(Φ_{PL} : up to **0.95**)、その発光色は用いた共配位子の種類によって変化した。また類似の孤立した低分子錯体²⁾の結果と比較して、構造の剛直性に伴い発光強度が向上した。さらに興味深いことに、2-メチルピラジン(meprz)を共配位子として用いた配位高分子($[\text{Cu}_2\text{X}_2(\text{AsPh}_3)_2(\text{meprz})]_n$)について、過剰量の配位子蒸気に曝すことで低分子錯体($\text{Cu}_2\text{X}_2(\text{AsPh}_3)_2(\text{meprz})_2$)へと錯体構造が変化し、かつその発光色が大きく変化する事が分かった(**Figure 1. (c)**)。

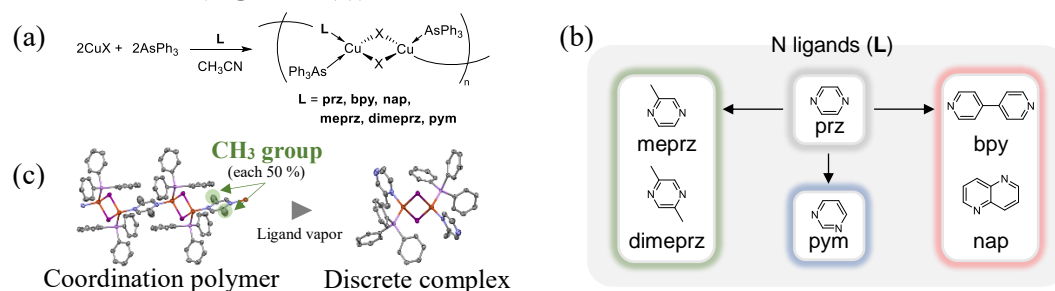


Figure 1. (a) Synthetic route, (b) bidentate co-ligands, and (c) specific change in this study.

1) J. Troyano, F. Zamora, S. Delgado, *Chem. Soc. Rev.* **2021**, 50, 4606-4628.

2) R. Kobayashi, H. Imoto, K. Naka, *Eur. J. Inorg. Chem.* **2020**, 37, 3548-3553.