Semiconductive Nature of Lead(II) Coordination Polymers with Benzenethiol Derivatives

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Conductive metal-organic frameworks (MOFs) and coordination polymers (CPs) have attracted increasing attention in recent years for diverse applications in electrocatalysis and chemiresistive sensing.[1] Among them, sulfur-coordinated CPs (S-CPs) containing $(–M–S–)_n$ network have been extensively investigated because they often exhibit small band gap as well as excellent band-like transport.[2] However, to the best of our knowledge, there is a general lack of reports concerned with the crystal structures of S-CPs due to their low crystallinity.

Herein, we reported the synthesis of Pb(II) S-CPs, $[Pb(X\text{-}SPhOMe)_2]_n$ (X = *ortho* (**KGF-32**), *meta* (**KGF-33**), and *para* (**KGF-34**)) and discussed their crystal structures and semiconductive properties. Single crystals of **KGF-32**, **KGF-33**, and **KGF-34** were obtained as pale-yellow needle crystals, light-yellow needle crystals, and dark-brown plate crystals, respectively. Single crystal X-ray structural analyses revealed that **KGF-32** and **KGF-33** incorporating methoxy group on *ortho* or *meta* positions formed an 1D structure composed of one-dimensionally extended $(–Pb–S–)_n$ chain, whereas **KGF-34** which had methoxy substituent on *para* position shows the formation of 2D structure with $(–Pb–S–)_n$ layer (**Figure 1**). Time-resolved microwave conductivity (TRMC) experiments demonstrated that **KGF-34** exhibits highest TRMC signal intensity ($\varphi\Sigma\mu_{max} = 1.4 \times 10^{-3}$ cm^2 V^{-1} s^{-1}) among all MOFs and CPs to date. First-principles calculations showed that a 2D layer comprising a $(–Pb–S–)_n$ network plays a crucial role in the high photoconductivity. In this presentation, we will discuss the detail of crystal structure and semiconductive nature for **KGF-32**, **KGF-33**, and **KGF-34**.

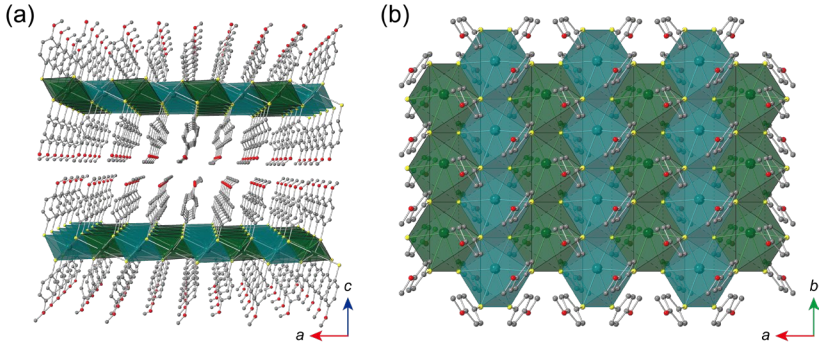

Figure 1. Crystal structure of **KGF-34**.

1) L. S. Xie, G. Skorupskii, M. Dinca, *Chem. Rev.* **2020**, *50*, 8536. 2) Y. Kamakura, D. Tanaka, *Chem. Lett.* **2021**, *50*, 523.