Luminescence Properties of Silver(I) and Copper(I) Coordination Polymers Bridged by Dimethylpyrazine

(*Graduate School of Science and Engineering, University of Toyama*) Taiki Kuwahara, Hideki Ohtsu, ○Kiyoshi Tsuge

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We have been studying about luminescent copper(I) and silver(I) complexes with the $\{M_2X_2\}$ unit coordinated by PPh_3 and N-heteroaromatic ligands. Though the copper complexes with this unit have been widely studied,[1] examples of silver congeners are still limited. Recently, we have prepared the silver coordination polymers having the $\{M_2X_2\}$ unit, $[Ag_2X_2(PPh_3)_2(\mu\text{-}L)]_n$ (X: I, Br; L: pyrazine (pyz), aminopyrazine (ampyz), methylpyrazine (Mepyz)) by using excess amount of bridging ligands, revealing their efficient luminescence from charge-transfer (CT) exited state (ES).[2] Here, we report the synthesis and luminescence properties of 2,4-dimethylpyrazine (Me_2pyz) complexes $[Ag_2X_2(PPh_3)_2(\mu\text{-}Me_2pyz)]_n$ (X: I, Br, Cl; **AgX-Me$_2$pyz**) together with the corresponding copper complexes $[Cu_2X_2(PPh_3)_2(\mu\text{-}Me_2pyz)]_n$ (X: I, Br; **CuX-Me$_2$pyz**).

The silver and copper complexes **MX-Me$_2$pyz** were prepared by the reaction of MX, PPh_3, and Me_2pyz in appropriate reaction ratios in organic solvents. Single crystal X-ray structure analysis showed that they are one dimensional coordination polymers composed of $\{M_2X_2(PPh_3)_2\}$ unit and bridging Me_2pyz and that they form isomorphous crystals. Both the silver and the copper complexes are strongly emissive at room temperature in the solid state as shown in Fig. 1. Their emission maxima and quantum yields are listed in Table 1, together with their averaged emission lifetime. By comparison with the pyz, ampyz, and Mepyz complexes,[2] their emissive ES were ascribed to the CT transition from $\{M_2X_2\}$ core to the π^* orbital of Me_2pyz. Because 4d orbitals of the silver ion are more stable than the 3d orbitals of the copper ion, the silver complexes showed the emission bands at higher energy than the copper complexes. Comparison of the excitation and emission spectra implied that the silver complexes undergo larger relaxation at ES than the copper complexes reflecting more flexible nature of the coordination geometry of a silver ion .

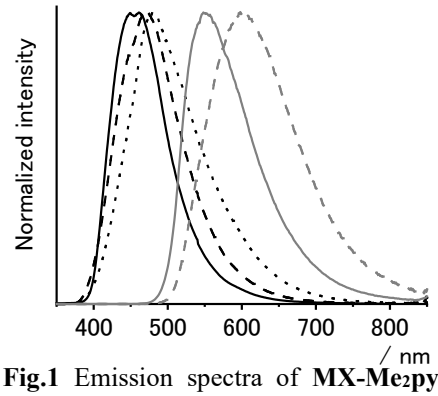

Fig.1 Emission spectra of **MX-Me$_2$pyz** (λ_{ex}: 330 nm). M: Ag (black), Cu (grey); X: I (solid), Br (broken), Cl (dotted).

Table 1. Photophysical properties of **MX-Me$_2$pyz**.

X	M = Ag			M = Cu		
	λ_{max}/nm	Φ	τ_{av}/μs	λ_{max}/nm	Φ	τ_{av}/μs
I	455	0.80	1.3	548	0.90	4.1
Br	470	0.65	5.9	600	0.65	8.0
Cl	480	0.90	11.7	--	--	--

1) K. Tsuge, *et al*., *Coord. Chem. Rev*. **2016**, *306*, 636. 2) T. Kuwahara, *et al.*, *Inorg. Chem*. **2021**, 60, 1299.