

Synthesis and Luminescence Properties of Silver(I) Halogenido Coordination Polymers Bridged by Pyrazine, Methylpyrazine, and Aminopyrazine

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

Keywords: Silver; Luminescence; Charge-transfer Transition; π - π^* Transition

Though luminescent Ag^{I} complexes have been prepared using various ligands, their number is still less than that of relating Cu^{I} complexes and characters of their emissive excited states (ESs) have not been well documented because of energetic competition between several possible emissive ESs. Here, aiming at the Ag^{I} complexes showing charge-transfer (CT) type emission, we utilized pyrazine (pyz), methylpyrazine (Mepyz) and aminopyrazine (ampyz) bearing a low-lying π^* orbital to obtain Ag^{I} complexes with the formula of $[\text{Ag}_2\text{X}_2(\text{PPh}_3)_2(\mu\text{-L})]_n$ (**AgX-L**: X = I, Br; L = pyz, Mepyz, ampyz).¹⁾

AgX-L were prepared as colorless single crystals by the reaction of AgX, PPh_3 , and excess amount of L in a mixed-solvent of CH_3CN and DMF. X-ray crystal structure analysis showed that the complexes are composed of $\{\text{Ag}_2\text{X}_2(\text{PPh}_3)_2\}$ units connected by L. All the complexes were strongly emissive at room temperature (Φ : 0.4 – 0.7) with the λ_{max} at around 500 nm (Table 1 and Figure 1). The blue-shift of the emission bands of **AgX-Mepyz** compared to those of **AgX-pyz** and their μs -order lifetimes imply that their emissive ESs are charge-transfer (CT) transitions from the $\{\text{Ag}_2\text{X}_2\}$ core to a π^* orbital of L. On the other hand, the ms-order lifetimes of **AgX-ampyz** indicated that their emissive ESs were not similar CT transitions although the blue-shift of their emission bands compared to those of **AgX-pyz** and **AgX-Mepyz** were expected one for CT type transitions. Because the emissive ESs of **AgX-bpy** (X = I, Br, Cl; bpy: 4,4'-bipyridine) have also been ascribed to the π - π^* transition in bpy,²⁾ those of **AgX-ampyz** were similarly ascribed to the π - π^* transition in ampyz. Due to the destabilization of the π^* orbital of the pyz ring by the amino group, the CT ES of **AgX-ampyz** was raised, which resulted in switching the lowest ES from CT to π - π^* one.

1) T. Kuwahara, *et al. Inorg. Chem. in print.* 2) M. Dosen, *et al. Inorg. Chem.* **2019**, 58, 8419.

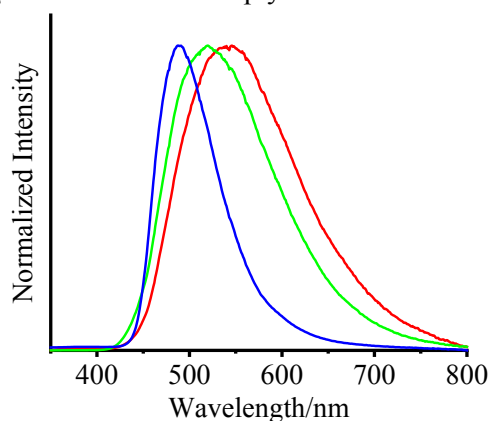


Figure 1. Emission spectra of **AgI-L** (L = pyz: red, L = Mepyz, green, L = ampyz; blue).

Table 1. Photophysical properties of **AgX-L**

L	X = I		X = Br	
	$\lambda_{\text{max}}/\text{nm}$	$\tau/\mu\text{s}$	$\lambda_{\text{max}}/\text{nm}$	$\tau/\mu\text{s}$
pyz	530	1.5	530	3.9
Mepyz	515	1.4	515	4.5
ampyz	490	1.0×10^3	490	5.4×10^3