X-ray decomposition of tin (IV) phthalocyanine dichloride

Yudai IZUMI, Maki OHARA, and Akinari YOKOYA
Institute for Quantum Life Science, Quantum Life and Medical Science Directorate, National Institutes for Quantum Science and Technology (QST), 4-9-1 Anagawa, Inage-ku, Chiba 263-8555, Japan

1 Introduction
Phthalocyanine derivatives of which axial ligands are bioactive molecules, such as drugs, are candidates for prodrugs. If the ligand releases can be induced by X-ray irradiations, phthalocyanine based prodrugs allow us to the selective release of medical ingredients at the target locations via localized X-irradiations.

In this study, we irradiated a pellet of tin (IV) phthalocyanine dichloride (SnCl$_2$Pc; Fig. 1), as a simple model of the phthalocyanine based prodrugs, with 3 keV X-rays and confirm whether the bond breakages between Sn and Cl can be induced using photoemission spectroscopy.

![Molecular structure of SnCl$_2$Pc](image)

Fig. 1. Molecular structure of SnCl$_2$Pc

2 Experiment
The reagents of SnCl$_2$Pc and tin (II) phthalocyanine (SnPc), which is a molecule with the chlorine atoms removed from SnCl$_2$Pc, were purchased from Tokyo Chemical Industries (Japan) and used without further purification. Powder of the reagent (~0.1 g) was pelletized at a pressure of ~0.3 GPa for 10 min.

Photoemission spectra of SnPc and SnCl$_2$Pc were measured at the BL-27A of the PF. The excitation photon energy was set at 3 keV. The pass energy was set at 44 eV. The binding energies of SnPc and SnCl$_2$Pc were compared with the literature data [1] in the N 1s region and calibrated. The SnCl$_2$Pc pellet was irradiated with 3 keV photons for 5 hours. After that, the photoemission spectra were measured again to confirm dissociation of SnCl$_2$Pc. The intensities of the photoelectrons were normalized for the N 1s peak intensity of each measurement without any subtraction of baselines.

3 Results and Discussion
Figure 2(a) shows the N 1s photoemission spectra of pristine SnCl$_2$Pc and SnPc. The spectra were similar to those found in the literature [1]. Peak shifts toward the lower binding energy side were induced by the irradiations (Fig. 2(b)). The peak of irradiated SnCl$_2$Pc was fitted well with three Voigt functions after subtracting the background. Comparing with the peak energies, the components were assigned to the SnCl$_2$Pc, SnPc, and triazines (C$_3$N$_2$H$_3$) [2] from the higher energy side. These results show that the bond breakages between the Cl atoms and SnPc framework were induced.

In Fig. 2(c), the photoemission spectra of pristine SnCl$_2$Pc and SnPc in the Sn 3d$_{5/2}$ region are shown. The spectrum of SnCl$_2$Pc after irradiation also shifted toward the lower binding energy side (Fig. 2(d)). The peak energies of fitted Voigt functions were similar to those of pristine SnCl$_2$Pc and SnPc, indicating that the SnCl$_2$Pc and SnPc coexisted at the sample surface after the 5 h of irradiation. It is consistent with the spectral changes observed in the N 1s region.

Figure 2(e) shows the Cl 1s photoemission spectra of pristine SnCl$_2$Pc and SnPc. No peak was observed for SnPc because it contains no chlorine atom. The pristine SnCl$_2$Pc showed a peak originating from Cl-Sn at around 2821.5 eV. After the 5 h of irradiation, the peak shifted toward the lower binding energy side, suggesting a new component originating from the decomposition product arose (Fig. 2(f)). The peak was fitted with two Voigt functions after subtracting the background. The main component originated from the SnCl$_2$Pc. The other component of which peak energy was ~2820.9 eV was assigned to chloride ions, comparing with the literature data [3]. It clearly shows that the bond breakages of Cl-Sn were induced by irradiation.

Thus, the N 1s, Sn 3d$_{5/2}$, and Cl 1s photoemission spectra showed the production of chloride ions and SnPc from the SnCl$_2$Pc after the X-ray irradiations, indicating that the bond breakages between ligands (Cl) and SnPc frameworks were induced by the photoionizations.

4 Conclusions
Ligand cleavages of SnCl$_2$Pc were induced by the 3 keV X-ray irradiations. It suggests that the SnPc framework can be used as X-ray dissociative prodrugs. Appropriate molecular design and its application are future prospects.

Acknowledgement
This work was supported by JST, CREST Grant Number JPMJCR1902, Japan.

References
Research Achievement
Y. Izumi et al., Chem. Phys. Lett. 822, 140508 (2023). * izumi.yudai@qst.go.jp

Fig. 2. (a, c, e) The N 1s, Sn 3d\(_{5/2}\), and Cl 1s photoemission spectra of pristine SnCl\(_2\)Pc (black) and SnPc (red), respectively. (b, d, f) The N 1s, Sn 3d\(_{5/2}\), and Cl 1s photoemission spectra of SnCl\(_2\)Pc after 5 h irradiations (blue), respectively. Open circles: the measurement data; Thick solid lines: the fitting curves; Thin solid lines: the divided components assigned to SnCl\(_2\)Pc (black), SnPc (red), triazines (green), and Cl\(^-\) (light blue).