

# X-ray decomposition of tin (IV) phthalocyanine dichloride

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## 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 ( $\text{SnCl}_2\text{Pc}$ ; 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.

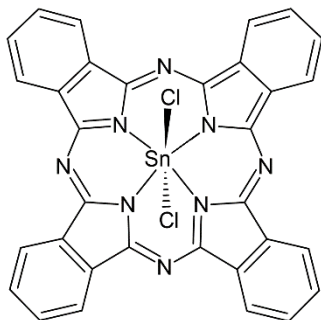


Fig. 1. Molecular structure of  $\text{SnCl}_2\text{Pc}$

## 2 Experiment

The reagents of  $\text{SnCl}_2\text{Pc}$  and tin (II) phthalocyanine ( $\text{SnPc}$ ), which is a molecule with the chlorine atoms removed from  $\text{SnCl}_2\text{Pc}$ , 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  $\text{SnPc}$  and  $\text{SnCl}_2\text{Pc}$  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  $\text{SnPc}$  and  $\text{SnCl}_2\text{Pc}$  were compared with the literature data [1] in the N 1s region and calibrated. The  $\text{SnCl}_2\text{Pc}$  pellet was irradiated with 3 keV photons for 5 hours. After that, the photoemission spectra were measured again to confirm dissociation of  $\text{SnCl}_2\text{Pc}$ . 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  $\text{SnCl}_2\text{Pc}$  and  $\text{SnPc}$ . 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  $\text{SnCl}_2\text{Pc}$  was fitted well

with three Voigt functions after subtracting the background. Comparing with the peak energies, the components were assigned to the  $\text{SnCl}_2\text{Pc}$ ,  $\text{SnPc}$ , and triazines ( $\text{C}_3\text{N}_3\text{H}_3$ ) [2] from the higher energy side. These results show that the bond breakages between the Cl atoms and  $\text{SnPc}$  framework were induced.

In Fig. 2(c), the photoemission spectra of pristine  $\text{SnCl}_2\text{Pc}$  and  $\text{SnPc}$  in the Sn  $3d_{5/2}$  region are shown. The spectrum of  $\text{SnCl}_2\text{Pc}$  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  $\text{SnCl}_2\text{Pc}$  and  $\text{SnPc}$ , indicating that the  $\text{SnCl}_2\text{Pc}$  and  $\text{SnPc}$  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  $\text{SnCl}_2\text{Pc}$  and  $\text{SnPc}$ . No peak was observed for  $\text{SnPc}$  because it contains no chlorine atom. The pristine  $\text{SnCl}_2\text{Pc}$  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  $\text{SnCl}_2\text{Pc}$ . 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  $\text{SnPc}$  from the  $\text{SnCl}_2\text{Pc}$  after the X-ray irradiations, indicating that the bond breakages between ligands (Cl) and  $\text{SnPc}$  frameworks were induced by the photoionizations.

## 4 Conclusions

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

## Acknowledgement

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## References

- [1] C. Song *et al.*, *Mater. Lett.* **270**, 127666 (2020).
- [2] J. -K. Sun *et al.*, *J. Materials Chem. C* **6**, 9065 (2018).
- [3] J. S. Gibson *et al.*, *Phys. Rev. B* **98**, 165402 (2018).

## Research Achievement

Y. Izumi *et al.*, *Chem. Phys. Lett.* **822**, 140508 (2023).

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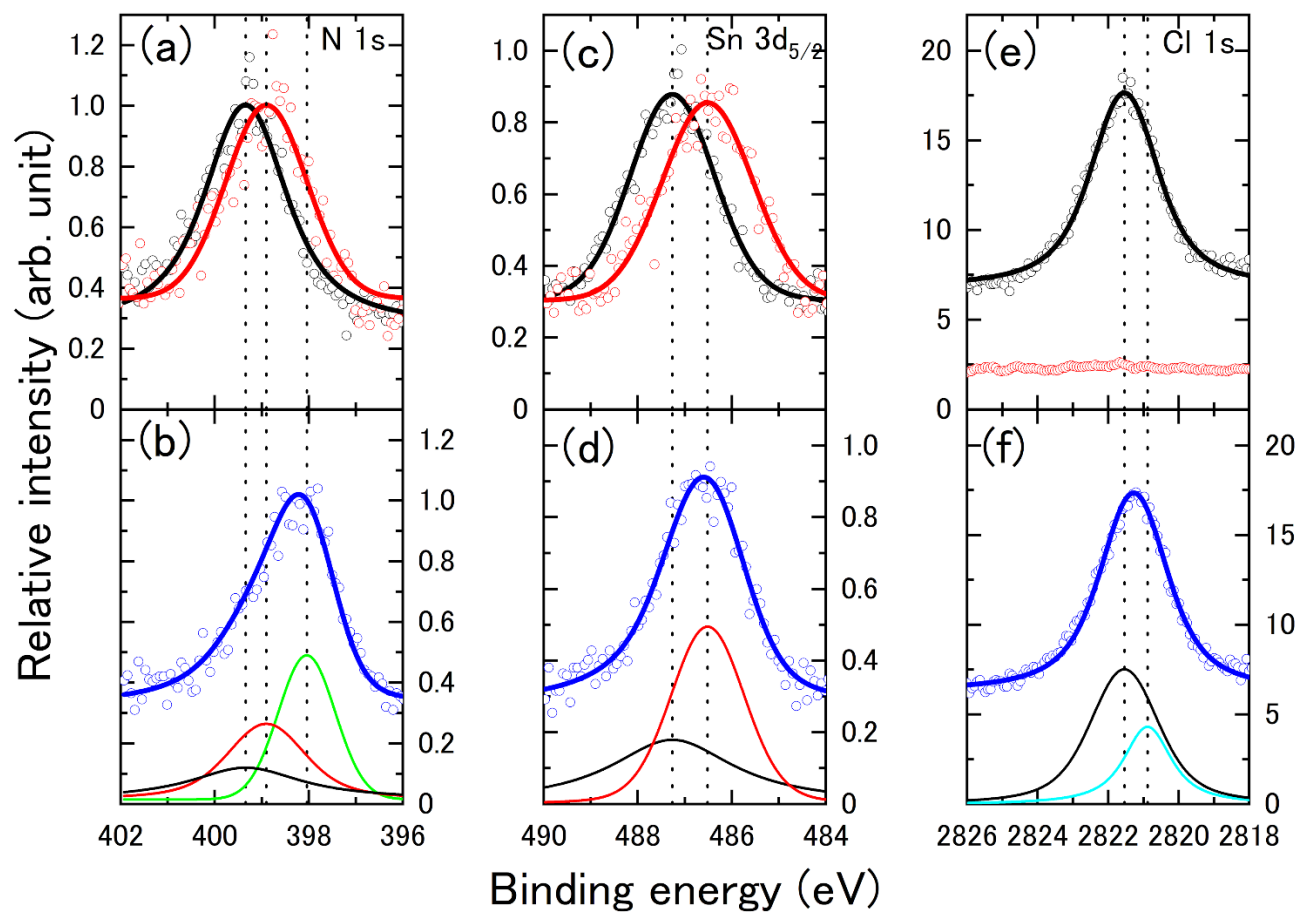


Fig. 2. (a, c, e) The N 1s, Sn 3d<sub>5/2</sub>, and Cl 1s photoemission spectra of pristine SnCl<sub>2</sub>Pc (black) and SnPc (red), respectively. (b, d, f) The N 1s, Sn 3d<sub>5/2</sub>, and Cl 1s photoemission spectra of SnCl<sub>2</sub>Pc after 5 h irradiations (blue), respectively. Open circles: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