

Electronic structure of axial ligand chain in chloroaluminum phthalocyanine

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1 Introduction

Chloroaluminum phthalocyanine (Cl-AlPc) is a metal Pc complex with an axial ligand Cl normal to the Pc ring plane. Cl-AlPc can form various structural configurations, such as a cofacial stack (head-to-tail) [1] and interleaved slipped stacks (head-to-head or tail-to-tail) [2]. Two major types of intermolecular interactions in Cl-AlPc are π -conjugated ring-ring interactions and metal-axial ligand dipole interactions based on the crystal structure [2]. Therefore, charge transfer can occur either via π - π stacking or through oligomer-like ($-\text{Al}-\text{Cl}-\text{Al}-$) metal chain sites. In order to understand electron transfer processes, site-selective X-ray absorption spectroscopy (XAS) spectra were measured using the normal (NA) and the spectator (SA) $KL_{2,3}L_{2,3}$ Auger electron yields (AEY) of Cl as a function of photon energy near the Cl K -edge to separate contributions from the delocalized ground state-like unoccupied partial density of state (DOS) and the localized core-excitonic DOS.

2 Experiment

Experiments were performed at beamline BL-27A with an InSb(111) double-crystal monochromator with an energy resolution of ca. 0.9 eV around Cl K -edge. Auger spectra were measured using a hemispherical analyzer (CLASS-100; Vacuum Science Workshop), with a pass energy of 44 eV. The X-ray energy was calibrated by reference to the lowest sharp peak of NaClO_3 (2830.5 eV).

3 Results and Discussion

Figure 1 shows Cl K -edge XAS recorded in AEY modes. Peak 1 and peak 2 could be assigned to the Cl $1s \rightarrow \sigma^*(\text{Cl}-\text{Al})$ transition consisting of the Cl $3pz$ molecular orbital and the Cl $1s \rightarrow \text{Cl } 3px,y/\text{Al } 3p$ transition, respectively. Peak 3 could also be assigned to the Cl $1s \rightarrow \text{Cl } 4p$ core-to-Rydberg transition. Peak 1 is split into two peaks labelled 1a and 1b. Peak 1b is clearly resolved by the NA-AEY below the continuum edge jump, while peak 1a is resolved by the SA-AEY. The origin of both peaks is considered to be the same transition state of $\sigma^*(\text{Cl}-\text{Al})$, whereas the exciton peak 1a is pulled down below the conduction band by the coulomb interaction between the core hole and the excited electron. Such doublet peaks indicate that these are the result of both resonant (peak 1a in SA-AEY) and DOS-like (peak 1b in NA-AEY) contributions based on previous observations of XAS features in the band insulator [3]. In Cl-AlPc, the core-exciton binding energy was measured to be ~ 0.9 eV, which depends on the degree of core-hole screening. The peak

area ratio of 1a–1b was approximately 1:1. This ratio is expected to result from a competition between the core-hole lifetime and the lifetime of an electron bound to a particular atom in the conduction band. Such an ultrashort lifetime of an initially bound electron at the $\sigma^*(\text{Cl}-\text{Al})$ state indicates that the Cl axial ligand participates in forming the conduction band of polycrystalline Cl-AlPc. These results also suggest that one-dimensional electron transfer or delocalization along the periodic Cl–Al chain is probable.

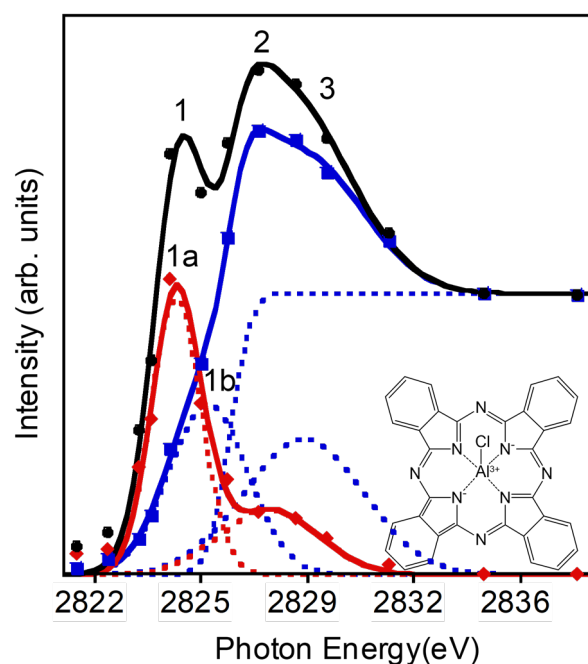


Fig. 1: Cl K -edge XAS of polycrystalline Cl-AlPc measured in AEY modes. Integrated intensities of SA (red closed diamond) and NA (blue closed square) components are shown with results of curve fitting (red and blue dotted lines).

References

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