

Search and realization of novel electronic properties of surfaces and interfaces and of nanostructures

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Using the van-der-Waals density functional theory, we have been investigating the electronic structure of *x*-form phthalocyanine (Pc) crystals and the iodine (I) doping effect on this structure. We employ the program package 'Vienna Ab initio Simulation Package' (VASP) [1-4] on system B (ohtaka) in the present study.

The Pc is a planar π -conjugated macrocyclic molecule which can include an atom of various species at its center position. The *x* crystal is constituted of a square-lattice arrangement of molecular chains with double period and with molecular planes normal to the stacking direction. Doped iodine I atoms can enter one-dimensional open channels between these molecular chains.

(A) *x*-SiPc and *x*-SiPcI crystals

Although the synthesis of *x*-SiPc crystals is still in its infancy, we chose Si for center atoms, because we found that SiPc molecules (monomers) have Si p_z derived orbitals right above the LUMO, which may overlap each other in the *x*-form stacking.

Last academic year, we elucidated the following points:

- (1) Because Si atomic chains dimerize, Si p_z orbitals cannot form metallic bands.
- (2) The staggering angle becomes 40° , because H_2 -like bonding orbitals are created between laterally neighboring molecular planes.
- (3) I doping decreases the band occupancy from half-filling, as is observed experimentally as the Mott insulator-metal transition.
- (4) If we assume equally spaced I atomic chains, they form metallic bands with an effective-mass ratio of 0.15.

This academic year, we examined the stability of equally spaced I atomic chains.

We calculated the force working on an I atom when it is displaced in the chain-axis direction and the electronic structure is optimized with atom positions fixed. We found that the restoring force operates on each I atom displaced. The arrangement of *x*-SiPc chains act to create equally spaced I atomic chains.

According to X-ray analysis, the I atoms, whose average positions are equally spaced, have elongated temperature factors along the chain axis. This is interpreted as indicating that I atomic chains are trimerized without interchain correlations. Therefore, we analyzed the stability of trimerized I atomic chains in *x*-SiPcI crystals. We considered crystals with six-fold period in the stacking direction, and performed structure optimization assuming formation of trimers. The result is exhibited in Fig. 1. This trimerization turned out to lower the total energy by 58.6 meV per unit cell. The I-I bond length in each trimer is 3.00\AA , and the distance between neighboring trimers is 3.58\AA . The

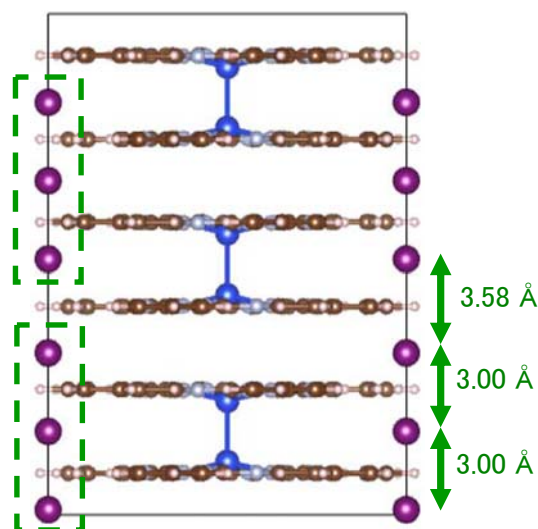


Fig. 1 Side view of the *x*-SiPcI crystal structure with trimerized I atomic chains.

trimerization induces a band gap at E_F , which prevent I atomic chains from making metallic bands. The SiPc chains operate to create equally space I atomic chains, while the I atoms try to form trimerized chains. These effects compete with each other, but the trimerization effect is larger.

(B) LiPc chain

In preparation for next year's study of x -LiPc and x -LiPcI crystals, we analyzed the electronic structure of a single x -LiPc chain. This molecular chain has a double period in the stacking direction, and two molecules in a primitive unit cell are stacked face-to-face with a staggering angle of 45° . Figure 2 exhibits the band dispersions on the Γ -Z line. A pair of the bands b185 and b186 are formed by band folding at E_F at the Z point. The bands b185~b190 with significant dispersions originate from π electrons. Figure 3 show the electron-density distributions (isosurfaces) of those two states at E_F which are formed by π electrons. The orbital of each state is localized to one of the two molecules in the unit cell, and each state is occupied by one electron, namely, an unpaired electron. Although our band theory cannot treat Mott

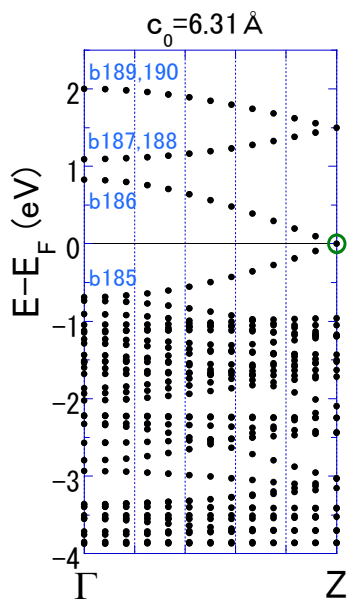


Fig. 2 Band dispersions on the Γ -Z line of a single x -LiPc chain. The green circle represents the two degenerate states at E_F .

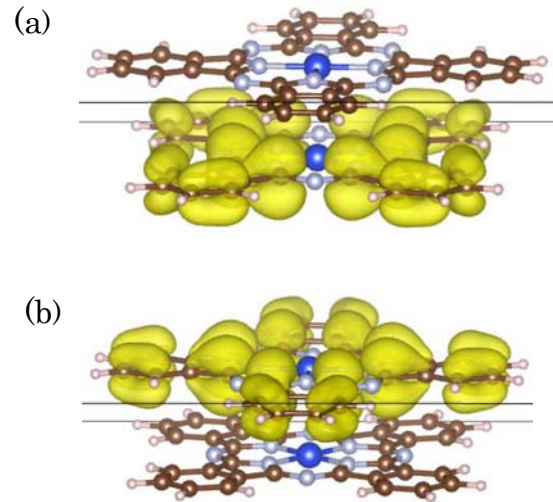


Fig. 3 Electron-density distributions (isosurfaces) of the two degenerated states at E_F at the Z point, as marked by the green circle in Fig. 2.

insulators directly, presence of these unpaired electrons strongly suggests appearance of Mott insulators, as is observed experimentally [5]. By chemical I doping and dedoping, Teruya et al. successfully converted insulators of x -LiPc to metals of x -LiPcI and vice versa reversibly [5].

Next academic year, we examine the electronic structure of x -LiPc and x -LiPcI crystals and the I doping effect. We will be able to elucidate how I doping affects the band structure, and induce the insulator-metal transition, and what the electron states of I atomic chains are like.

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