Extended Abstract of PSA-19

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Interface charge transfer between metal phthalocyanine and fluorinated hexaazatrinaphthylene molecules

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(Received: May 30, 2019; Accepted: August 6, 2019)

Photoelectron spectroscopy is an important tool to characterize charge transfer mechanism at organic/organic interfaces. A typical donor/accepter interface made of fluorinated hexaazatrinaphthylene (HATANA-F6) and metal phthalocyanine (MPc) molecules shows a distinct characteristics of interface charge transfer. Even though the electron affinity of HATANA-F6 is lower than the ionization energy of CuPc or boron subphthalocyanine chloride (SubPc), the charge transfer occurs at the interface where the central atoms in the phthalocyanine molecules play a major role. This result seems to exhibit one of the non-conventional charge transfer model of hybrid state formation.

1. Introduction

Charge transfer (CT) between organic/organic (OO) interfaces is a prime important issue in soft electronic devices. The CT behavior influences electrical conductivity by electrical doping, charge injection and separation, and even optical characteristics. One of promising small molecules for future optical and electronic devices, metal phthalocyanine (MPc) derivatives have attracted long attention because of their strong orbital conjugation, optical absorption, and crystalline order in solid phase. However, the molecular orientation as well as electron affinity and ionization potential control the CT mechanism in various ways. For example, planer or bent shape of MPc molecules make different energy level alignment at donor/acceptor interface and corresponding open circuit voltages in solar cell devices [1].

Here we compare two model OO interface between 2,3,8,9,14,15-hexafluoro-5,6,11,12,17,18-hexaazatrinaphthylene (HATNA-F6) and CuPc (SubPc). The HATNA-F6 and MPc form a simple donor-accepter heterojunction. In Fig. 1, the CuPc is planar while the SubPc is non-planar. Since the SubPc makes different OO interfaces depending on its molecular orientation, the CT behavior shows different characteristics from planar CuPc. Photoelectron spectroscopy in core level as well as valence band region has been used to determine the electronic properties of two different interfaces between MPc and HATNA-F6. Even though the electron affinity of HATANA-F6 is lower than the ionization energy of CuPc or SubPc [2], the CT occurs at the interface. In particular, central atom in MPcs plays an important role. This is another example of hybrid CT mechanism, which is different from ion complex formation.

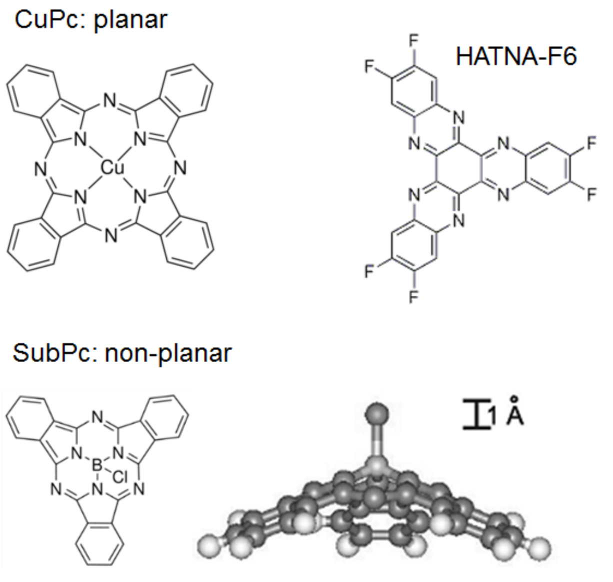

Fig. 1 Molecular structures of metal phthalocyanine molecules (CuPc and SubPc) and electron transport molecule (HATNA-F6).

2. Experimental

Molecular layers were produced on an Au substrate by thermal evaporation in a UHV chamber and transferred to an analysis without exposure to air. The evaporation rate was in the order of 0.1 Å/s. Either HATNA-F6/MPc or MPc/HATNA-F6 stacks are compared with various overlayer thicknesses upto 10 nm. Photoelectron spectrometer is equipped with a hemispherical electron analyzer (Resolve 120, PSP), a He I discharge lamp (ħω = 21.2 eV) for UPS, and a monochromatized Al Kα X-ray (Focus 600, Specs) for XPS. In the UPS measurement, the samples were biased to -10 V to observe the secondary cutoff region for the work function measurement. Photoelectrons were detected at surface normal geometry. The energy scales of the UPS spectra are aligned by matching the Fermi energy (E_F) calibrated using a clean Au(111) single crystal. The total instrumental energy resolution was less than 0.15 eV for UPS and 0.8 eV for XPS measurements.

3. Results

Fig. 2 shows a series of B 1s core levels measured by XPS for HATNA-F6 films on SubPc underlayer. The initial binding energy (BE) of SubPc B 1s at 192 eV is shifted to the higher BE by 0.5 eV upon 0.5 nm HATNA-F6 deposition, and the new BE keeps constant afterwards. This amount of core level shift is not consistent with the work function change upon the HATNA-F6 deposition. Thus, this shift right after HATNA-F6 deposition is not due to band bending or interface dipole but to a partial interface CT from SubPc to HATANA-F6 through the B atom. This CT behavior is observed when the B atom faces HATNA-F6. A similar behavior is not observed in the Cu 2p core level for HATNA-F6 films on CuPc underlayer, in which the Cu atom is not involved in the CT formation.

The B 1s core level shift SubPc is consistent with the F 1s core level shift of HATNA-F6. However, as the electron affinity of HATANA-F6 is lower than the ionization energy of CuPc or SubPc, the core level shift is rather marginal and full CT is not expected. Thus, hybrid CT through B and F atoms is a probable CT pathway.

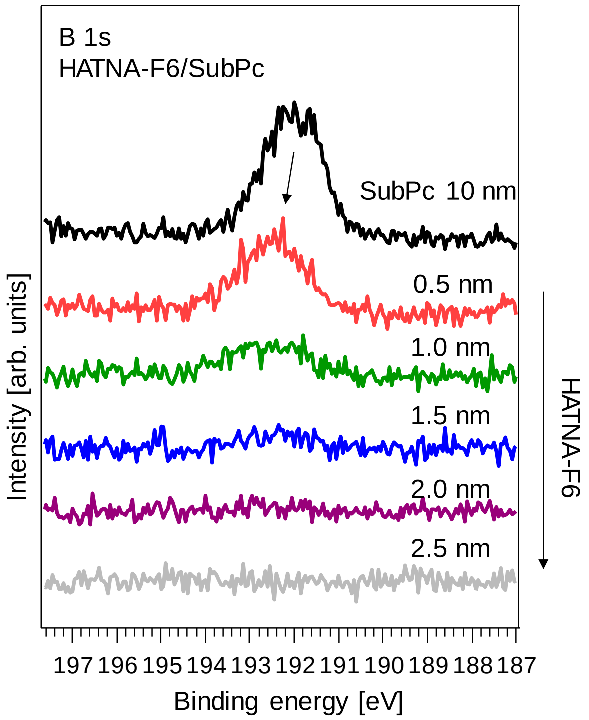

Fig. 2 A series of B 1s core levels for HATNA-F6 films as a function of thickness on 10 nm SubPc underlayer..

4. Conclusion

We investigated interface CT behavior between fluorinated hexaazatrinaphthylene (HATANA-F6) and metal phthalocyanine molecules by photoelectron spectroscopy. Even though full CT does not occur at the interface, the central B atom in the SubPc molecule plays an important role in the partial CT through hybrid state formation. However, the planar CuPc molecule shows marginal CT behavior at the interface.

5. References

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