

# Structural Requirements for Surface-Induced Aromatic Stabilization

Takuya Hosokai<sup>1</sup>, Keiichirou Yonezawa<sup>2</sup>, Kengo Kato<sup>2</sup>, Rintaro Makino<sup>2</sup>, Jinpeng Yang<sup>2</sup>, Kaveenga Rasika Koswattage<sup>2</sup>, Alexander Gerlach<sup>3</sup>, Frank Schreiber<sup>3</sup>, Nobuo Ueno<sup>2</sup>, Satoshi Kera<sup>2</sup>

<sup>1</sup>Department of Materials Science and Technology, Iwate University, 4-3-5 Ueda, Morioka, 0208551 Iwate, JAPAN

<sup>2</sup>Department of Nanomaterial Science, Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, 2638522 Chiba, JAPAN

<sup>3</sup>Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, Tübingen 72076, GERMANY

## ABSTRACT

Surface-induced aromatic stabilization (SIAS), a recently proposed mechanism leading to a formation of charge-transfer (CT) states at organic/metal (O/M) interfaces [G. Heimel, *et al.*, *Nat. Chem.* **5**, 187 (2013)], was investigated for an aromatic hydrocarbon, diindenoperylene (DIP), by means of synchrotron radiation-based ultraviolet photoelectron spectroscopy (UPS). By employing DIP and noble metal substrates (Ag and Cu), we confirmed the formation of CT states, indicating that an inclusion of a specific functional group with a hetero-atom within adsorbate molecules as suggested before is not necessarily required for the formation of CT states mediated by the SIAS. With a comparison of the mother and analogue molecules, perylene and PTCDA, we discuss the structural requirement for the realization of the SIAS.

## INTRODUCTION

The electronic structure of O/M interfaces is crucial for *Organic Electronics*, in which charge carrier injection at the interface strongly influences the device performance [1-4]. One remaining issue in this research field is a formation of CT states at the O/M interfaces. While it is known that the CT state is caused by an electron-transfer from the metal substrate to the former lowest unoccupied molecular orbital (LUMO) of the adsorbate, it was not well understood until recently why the CT state forms unexpectedly in specific O/M systems [5-8]. Heimel *et al.* succeeded to explain the mechanism leading to the formation of CT states in terms of SIAS [9]; the stabilization of the  $\pi$ -conjugation of the adsorbed molecules due to an electron donation from the substrate atoms to specific functional group (e.g. keto group or azo group) within the molecules lowers the LUMO level through the formation of a resonance state of the molecules, and subsequently induces the CT. In the literature [9] such a *specific functional group with hetero-atoms* is introduced as a key for the SIAS. However, it is not yet clear if the inclusion of hetero-atoms is prerequisite for realization of the SIAS.

In this paper, we will show that even functional groups without hetero-atoms yield a SIAS. We studied the interface electronic structure of DIP (C<sub>32</sub>H<sub>16</sub>, Fig. 1) monolayers on Ag and Cu polycrystalline surfaces by means of synchrotron radiation (SR)-based UPS (hereafter referred to as just UPS). We found the formation of CT states for DIP on both the noble metal surfaces, and such an interface structure is very similar to the case of PTCDA (C<sub>24</sub>H<sub>8</sub>O<sub>6</sub>), an analogous of DIP [6,7]. With a comparison of PTCDA and its mother molecule, perylene (C<sub>20</sub>H<sub>12</sub>), we will discuss the structural requirements for organic molecules forming CT states.

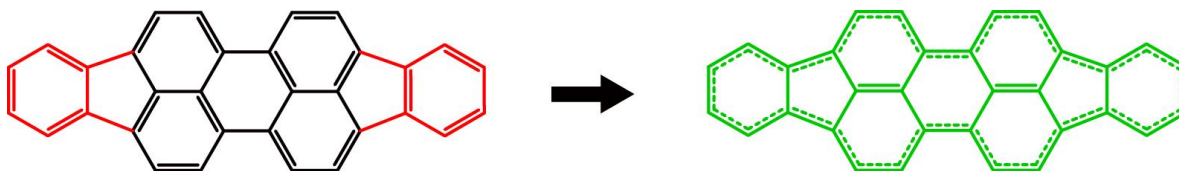


Fig. 1 Chemical structure (left) of DIP and its resonance structure (right) upon the SIAS. The red and black portions in the left figure represent indeno group and perylene core, respectively.

## EXPERIMENT

All the experiments were done at beamline 8 (bending magnet) (BL8B) of the Ultraviolet Synchrotron Orbital Radiation Facility (UVSOR) storage ring at the Institute for Molecular Science, where monochromatized SR by a plane-grating monochromator was available [10].

Purified DIP, and Ag and Cu wires (purity: 99.99 and 99.999 %, respectively) were installed in a preparation chamber with a base pressure of  $1 \times 10^{-7}$  Pa and were thoroughly degassed overnight before use. Ultrasonically cleaned native silicon wafers were installed from a load-lock chamber and transferred into the preparation chamber. After annealing of the silicon wafers at 673 K for 1 h, (111) oriented polycrystalline Ag or Cu films (a nominal film thickness [ $\delta$ ]: 50 nm) were fabricated on the wafers by vacuum-deposition as the substrates. Without breaking the vacuum, the cleanliness of their surfaces was confirmed by UPS at a base pressure:  $3 \times 10^{-8}$  Pa. Thin films of DIP were then grown on top of the metal surfaces by vacuum-deposition. The deposition rate measured with a quartz crystal microbalance was set to be 0.5 ~ 0.6 nm/min for the Ag and Cu film, and 0.05 ~ 0.19 nm/min for DIP films. The deposition rate of DIP was gradually increased during the deposition run to save the experimental time. The substrate temperature was kept at room temperature (~296 K) during the depositions and measurements.

UPS spectra were measured using a high-angular-resolution analyzer with a multichannel detector system (VGARUPS10) and synchrotron light of  $h\nu = 28$  eV. The angle of incident photons and the detected photoelectrons were  $45^\circ$  and  $0^\circ$  relative to the surface normal, respectively. The angular and energy resolutions are  $\pm 0.2^\circ$  and about 150 meV, respectively. The secondary cut-off energy position was measured to estimate the work function (WF) by biasing the sample with -5 V during the measurements.

## DISCUSSION

1. Determination of monolayer thickness of DIP on polycrystalline Ag and Cu surfaces.

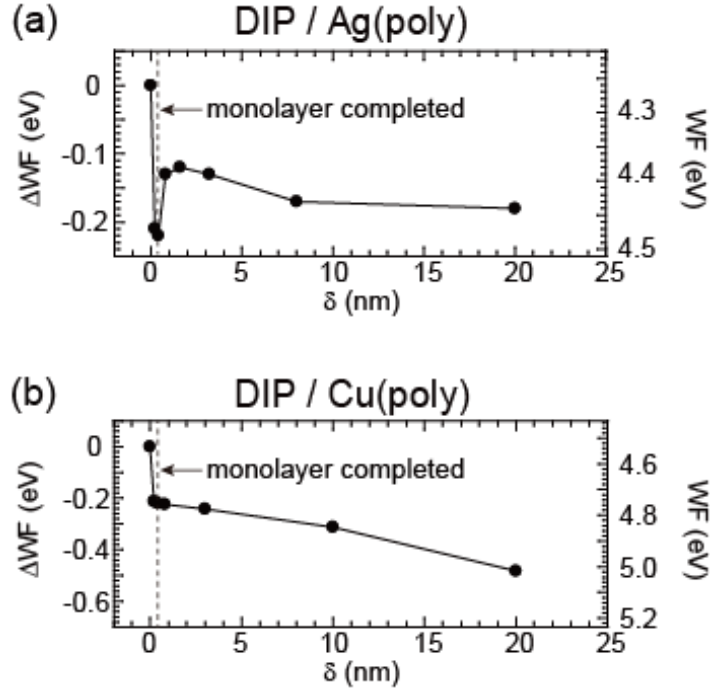


Fig. 2 A film thickness ( $\delta$ )-dependence of WF (right axis) and WF shift (left axis) of DIP/Ag (a) and Cu (b) systems.

Figures 2(a) and 2(b) show the  $\delta$ -dependent WF shift ( $\Delta WF$ ) of the DIP/Ag and Cu systems, respectively. Till  $\delta = 0.4$  nm we find an abrupt decrease of the WF by 0.22 eV for both the systems. At larger  $\delta$ s the WF shows a zigzag shift for the DIP/Ag system (Fig. 2(a)) and a gradual decrease for the DIP/Cu system (Fig. 2(b)). The abrupt decrease of WF on metal substrates (as shown in Figs. 2(a) and 2(b)) is usually explained by a monolayer formation of organic molecules: the WF decreases due to a push-back effect [5, 11]. The  $\delta$ -value of 0.4-nm is a typical coverage of a monolayer of planar molecules with lying-flat orientation, and actually such an orientation is reported for DIP deposited on both polycrystalline and single crystalline surfaces of noble metals including Ag and Cu [12-16]. Hence, we suppose that the DIP monolayer is formed at  $\delta = 0.4$  nm with lying-flat orientation on both Ag and Cu surfaces. As will be shown later, this can be confirmed by results of valence band UPS spectra. For the multilayer regime ( $\delta > 0.4$  nm), the change in WF is purely attributed to organic thin films, and can be ascribed to a gradual change in film structure or an increase of spontaneous structural defects, so-called band-bending phenomena [17, 18]. Since the full understanding of the WF shift, in particular for the multilayer regime, is not the main subject in this paper, we leave this issue for future work of a  $\delta$ -dependent structure of DIP thin films on the respective metal surfaces.

## 2. Interface electronic structure of DIP/Ag and Cu systems.

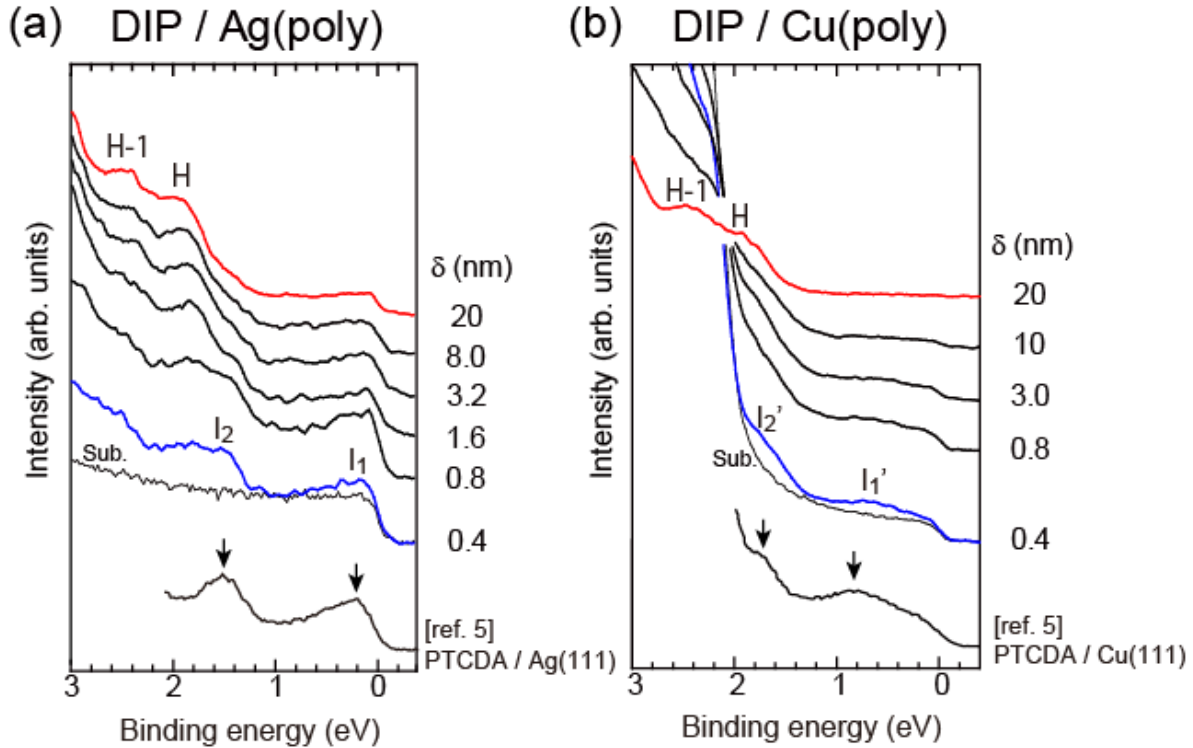


Figure 3  $\delta$  dependence of valence band UPS spectra of DIP/Ag (a) and Cu (b) systems. PTCDA monolayer spectrum on Ag(111) and Cu(111) (taken from Ref. [5]) is also depicted at the bottom in (a) and (b), respectively. Both the bare substrate spectra are superimposed to the DIP monolayer spectra ( $\delta = 0.4$  nm) to emphasize the interface states. The arrows indicate the former-LUMO and former-HOMO derived states of PCTDA [5].

Figures 3(a) and 3(b) show the  $\delta$  dependence of valence band UPS spectra of DIP/Ag and Cu systems, respectively, where a spectrum of each substrate and PTCDA monolayer (taken from Ref. [5]) are also depicted. As discussed before,  $\delta = 0.4$  nm corresponds to the formation of a complete monolayer and thus multilayer films grow above this value. Multilayer spectra of DIP are reported for other substrates, i.e. polycrystalline Au, graphite and SiO<sub>2</sub> [19, 20]. On the Au the highest occupied molecular orbital (HOMO) and the HOMO-1 are located at the binding energy of  $\sim 1.9$  and  $\sim 2.5$  eV, respectively [19]. These features are also found in Figs. 3(a) and 3(b) (see the top spectra). Therefore, we attribute two features (as denoted to H and H-1) to the HOMO and the HOMO-1, respectively. On the other hand, the monolayer spectra ( $\delta = 0.4$  nm) on both substrates exhibit new features at the lower binding energy side: 0.09 eV ( $I_1$ ) and 1.5 eV ( $I_2$ ) for the DIP/Ag system and 0.6 eV ( $I_1'$ ) and 1.7 eV ( $I_2'$ ) for the DIP/Cu system. Since these features are suppressed for thicker films, they are ascribed to the states of the DIP monolayer on these metals (interface states). We note that very similar features are also seen for PTCDA monolayer/Ag(111) or Cu(111) systems (see the bottom spectra in Fig. 3(a) and 3(b)). For  $\delta = 20$  nm of the DIP/Ag system, the interface features as well as the substrate features are still visible, which indicates the strong island growth of DIP films on the Ag surface.

A formation of interface states is a sign of a strong substrate-molecule interaction. Actually, a large chemical shift was observed for the Ag(111) and Cu(111) systems, as a result of electron transfer from the Ag and Cu substrates to the adsorbed DIP molecules, but not for Au(111) (a case of physisorption [19]) by using X-ray photoelectron spectroscopy (XPS) [21].

The strong interaction can be qualitatively related with the bonding distance of DIP to those substrate surfaces; the distance is in the order of Cu(111) < Ag(111) < Au(111), and thus the interaction strength is thought to be Cu(111) > Ag(111) > Au(111) [21]. Such a hierarchy of the interaction strength and the formation of interface states for DIP in Figs. 3(a) and 3(b) is very similar to PTCDA [5,22]. Therefore, it can be concluded that the interface states of the DIP systems in Fig. 3(a) and 3(b) are the former-LUMO and former-HOMO derived states of DIP molecules formed by CT/electron transfer from the substrates to the DIP, respectively.

So far, the former-LUMO at O/M interfaces is observed for  $\pi$ -conjugated organic molecules consisting of aromatic hydrocarbon with functional groups having hetero-atoms, in particular oxygen. For this kind of molecules a site-specific interaction between the hetero-atoms and metal substrates triggers the SIAS, and so CT states are produced by electron-transfer from the metal to the LUMO of the adsorbates [9]. Hence, the inclusion of the hetero-atoms seems to be a key for the SIAS. In this study, however, it is clear that the hetero-atoms are not necessarily required for the formation of CT states. On the other hand, it is reported that no CT states are formed for the mother molecule, perylene, deposited on Ag(111) and Cu(111), suggesting only the perylene core itself does not play a role for the CT state formation [23]. Irrespective to having the hetero-atoms or not, therefore, we suggest that a combination of a specific chemical structure and functional groups is a key for inducing the SIAS on metal substrates, as indeno-group for perylene molecules (DIP) (see Fig. 1).

## CONCLUSIONS

The  $\delta$ -dependent electronic structure of DIP/Ag and Cu was studied by means of UPS. We found interface states for both systems, which are derived from CT from metal substrates to the LUMO of the DIP monolayer through SIAS. Therefore, our results indicate that SIAS can occur for the aromatic hydrocarbon without any hetero-atoms. This result gives further insight into the SIAS, and may open new possibilities to manipulate the O/M interface properties by modifying or designing new organic molecules or seeking existing molecules which have not been employed for interface studies.

## ACKNOWLEDGMENTS

The authors are very grateful to the staff of the UVSOR facility for their support in various ways. This work was supported by Joint Study of Program of the Institute for Molecular Science [24-549 and 25-556], global COE program (G-03) and JSPS KAKENHI (Nos. 23360005, 24245034, 25870034).

## REFERENCES

1. H. Ishii, K. Sugiyama, E. Ito, K. Seki, *Adv. Mater.* 11, 605 (1999).
2. N. Koch, *Chem. Phys. Chem.* 8, 1438 (2007).
3. S. Braun, W. R. Salaneck, M. Fahlmann, *Adv. Mater.* 21, 1450 (2009).
4. J. Hwang, A. Wan, A. Kahn, *Mater. Sci. Eng. Rep.* 64, 1 (2009).

5. S. Duhm, H. Glowatzki, V. Cimpeanu, J. Klankermayer, J. P. Rabe, R. L. Johnson, N. Koch, *J. Phys. Chem. B* 110, 21069 (2006).
6. S. Duhm, A. Gerlach, I. Salzmann, B. Bröcker, R. L. Johnson, F. Schreiber, N. Koch, *Org. Electronics* 9, 111 (2008).
7. J. Ziroff, F. Forster, A. Schöll, P. Puschnig, F. Reinert, *Phys. Rev. Lett.* 104, 23304 (2010).
8. M. Wießner, J. Kübert, V. Feyer, P. Puschnig, A. Schöll, F. Reinert, *Phys. Rev. B* 88, 075437 (2013).
9. G. Heimel, S. Duhm, I. Salzmann, A. Gerlach, A. Strozecka, J. Niederhausen, C. Bürker, T. Hosokai, I. Fernandez-Torrente, G. Schulze, S. Winkler, A. Wilke, R. Schlesinger, J. Frisch, B. Bröker, A. Vollmer, B. Detlefs, J. Pflaum, S. Kera, K. J. Franke, N. Ueno, J. I. Pascual, F. Schreiber, N. Koch, *Nat. Chem.* 5, 187 (2013).
10. K. Seki, H. Nakagawa, K. Fukui, E. Ishiguro, R. Kato, T. Mori, K. Sakai, M. Watanabe, *Nucl. Instrum. Meth. A* 246, 264 (1986).
11. G. Witte, S. Lukas, P. S. Bagus, C. Wöll, *Appl. Phys. Lett.* 87, 263502 (2005).
12. M. B. Casu, I. Biswas, B.-E. Schuster, M. Nagel, S. Schuppler, T. Chassé, *Appl. Phys. Lett.* 93, 024103 (2008).
13. M. B. Casu, S.-A. Savu, B.-E. Schuster, I. Biswas, C. Raisch, H. Marchetto, Th. Schmidt, T. Chassé, *Chem. Comm.* 48, 6957 (2012).
14. X.-N. Zhang, D. G. de Oteyza, Y. Wakayama, H. Dosch, *Surf. Sci.* 603, 3179 (2009).
15. D. G. de Oteyza, E. Barrena, H. Dosch, Y. Wakayama, *Phys. Chem. Chem. Phys.* 11, 8741 (2009).
16. H. Huang, J.-T. Sun, Y.P. Feng, W. Chen, A.T.S. Wee, *Phys. Chem. Chem. Phys.* 13, 20933 (2011).
17. H. Yamane, Y. Yabuuchi, H. Fukagawa, S. Kera, K. K. Okudaira, N. Ueno, *J. Appl. Phys.* 99, 093705 (2006).
18. T. Hosokai, H. Machida, A. Gerlach, S. Kera, F. Schreiber, N. Ueno, *Phys. Rev. B* 83, 195310 (2011).
19. A. C. Dürr, N. Koch, M. Kelsch, A. Rühm, J. Ghijsen, R. L. Johnson, J.-J. Pireaux, J. Schwartz, F. Schreiber, H. Dosch, A. Kahn, *Phys. Rev. B* 68, 115428 (2003).
20. Y. L. Huang, W. Chen, H. Huang, D. C. Qi, S. Chen, X. Y. Gao, J. Pflaum, A. T. S. Wee, *J. Phys. Chem. C*, 113, 9251 (2009).
21. C. Bürker, N. Ferri, A. Tkatchenko, A. Gerlach, J. Niederhausen, T. Hosokai, S. Duhm, J. Zegenhagen, N. Koch, F. Schreiber, *Phys. Rev. B* 87, 165443 (2013).
22. L. Kilian, A. Hauschild, R. Temirov, S. Soubatch, A. Schöll, A. Bendounan, F. Reinert, T.-L. Lee, F. S. Tautz, M. Sokolowski, E. Umbach, *Phys. Rev. Lett.* 100, 136103 (2008).
23. K. Manandhar and B. A. Parkinson, *J. Phys. Chem. C* 114, 15394 (2010).