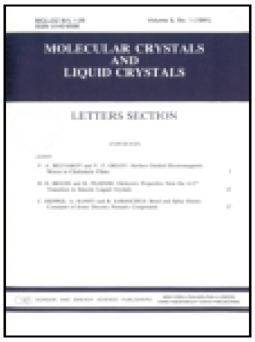

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Electronic Properties of 6,13-Bis(triisopropylsilylethynyl)pentacene Probed by Inner-Shell Spectroscopy

Hiromi Ikeura-Sekiguchi & Tetsuhiro Sekiguchi

To cite this article: Hiromi Ikeura-Sekiguchi & Tetsuhiro Sekiguchi (2015) Electronic Properties of 6,13-Bis(triisopropylsilylethynyl)pentacene Probed by Inner-Shell Spectroscopy, Molecular Crystals and Liquid Crystals, 622:1, 50-54, DOI: 10.1080/15421406.2015.1096990

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1096990

Mol. Cryst. Liq. Cryst., Vol. 622: pp. 50–54, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1096990

Electronic Properties of 6,13-Bis(triisopropylsilylethynyl)pentacene Probed by Inner-Shell Spectroscopy

HIROMI IKEURA-SEKIGUCHI[1],*
AND TETSUHIRO SEKIGUCHI[2]

[1]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
[2]Japan Atomic Energy Agency (JAEA), Tokai, Naka, Japan

The electronic properties of polycrystalline 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) was probed by inner-shell spectroscopies such as near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and electron emission spectroscopy at the Si K*-edge. Although the lowest unoccupied molecular orbital (LUMO) near the Fermi level is mainly on the acene unit, a small LUMO peak was observed in Si 1s NEXAFS spectra. Angle-dependent NEXAFS spectra indicate that a well-ordered structure is produced in the polycrystalline TIPS-pentacene. It was demonstrated that randomly oriented small single-crystal grains can be aligned by rubbing the powder sample.*

Keywords organic semiconductors; molecular orientation; TIPS-pentacene; X-ray absorption spectroscopy; electronic structure

Introduction

Organic electrically conducting π-stacked small molecules are widely regarded as promising materials for future application of low-cost and flexible nanoelectronics. Pentacene is one of the most promising organic semiconductors because of its excellent device performance. Pentacene shows an edge-to-face herringbone arrangement in crystal, while a soluble pentacene derivative, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) shows a face-to-face π–π stacking arrangement [1-2]. TIPS-pentacene has a pentacene backbone with two bulky silyl side groups that render the molecules soluble in organic solvents. The structure and orientation of organic semiconductors strongly influences charge carrier transport in organic field-effect transistors (OFETs) and luminescence properties of organic light-emitting devices (OLEDs).

Near-edge X-ray absorption fine structure (NEXAFS) analysis [3] is one of the most commonly used techniques to probe electronic structures of unoccupied molecular orbitals

---

*Address correspondence to H. Ikeura-Sekiguchi, National Institute of Advanced Industrial Science and Technology (AIST) 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan. E-mail: ikeura-sekiguchi@aist.go.jp

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

of organic semiconductors. The molecular orientation can be determined by NEXAFS with changing incidence angle of linearly polarized X-ray beam. NEXAFS spectra are typically described as electronic transitions from a core level to unoccupied valence orbitals with π^* or σ^* symmetry. Each feature can be attributed to the transition dipole moment vector of a specific orbital. For conjugated systems, π^* orbital lobes are perpendicular to the plane of conjugation. The transition dipole moment for π^* peaks has been used to determine the tilt angle of the π-conjugated plane with respect to the substrate plane.

For TIPS-pentacene, distinct two π^* and two σ^* peaks have been clearly observed in the C *K*-edge NEXAFS spectra [4], similar to pentacene [5]. Polarization dependence of the π^* peaks of TIPS-pentacene was measured to determine the average tilted angle of the acene plane to the surface plane [6]. Recently, owing to difficulties in controlling anisotropic carrier mobility in solution processing thin films [7], TIPS-pentacene films blended with conjugated polymers have been used to assist their ordering by reducing localized crystal anisotropy [8,9]. The angle-dependent NEXAFS spectroscopy is very powerful to analyze the molecular orientation even in non-crystalline systems. But, generally this technique cannot be used for blending systems containing the same atoms. Organic molecules contain carbon atoms; therefore, mixed organic samples need to be probed at the other absorption edges except for the C *K*-edge.

In this study, the electronic properties of the polycrystalline TIPS-pentacene were probed by inner-shell spectroscopies such as NEXAFS spectroscopy and electron emission spectroscopy at the Si *K*-edge. To assign the NEXAFS spectra, molecular-orbital calculations were preliminary performed. The orientation of the acene unit was investigated using angle-dependent NEXAFS near the Si *K*-edge.

Experimental Methods

Experiments were performed using synchrotron radiation at the beamline BL–27A of the Photon Factory, High Energy Accelerator Research Organization (KEK–PF) in Tsukuba. BL–27A is equipped with an InSb(111) double-crystal monochromator with an energy resolution of ca. 0.8 eV around the Si *K*-edge. NEXAFS spectra were measured by monitoring the sample drain current near the Si *K*-edge (1835–1870 eV). Such energies were chosen to excite the Si 1*s* core electron to the unoccupied orbitals of TIPS-pentacene. Angle-dependent NEXAFS data were obtained by changing the angle between the incoming X-ray beam and the sample surface. We used TIPS-pentacene polycrystalline powder (Sigma-Aldrich Corporation) without further purification. The as-received powdered sample was pressed and roughly rubbed on a conductive carbon tape using dielectric paper. All spectra were recorded at room temperature.

Results and Discussion

Figure 1 shows a wide scan spectrum of X-ray photoelectron spectroscopy (XPS) for TIPS-pentacene. XPS peaks of C1*s* and Si 1*s* and a Si $KL_{2,3}L_{2,3}$ Auger electron peak were clearly observed. The Si 1*s* ionization threshold determined by XPS is around 1842 to 1843 eV. Figure 2 shows Si *K*-edge NEXAFS spectra of TIPS-pentacene at different X-ray incidence angles θ between the direction of incident synchrotron light X-ray propagation and the surface plane. The lowest-occupied molecular orbital (LOMO) is observed as a small shoulder peak 1 near the Fermi level, although the LUMO is mainly on the acene unit. To investigate the electron-transfer mechanism through the π-π stacking of the acene unit, Si $KL_{2,3}L_{2,3}$ resonant Auger spectroscopy (RAS) spectra were measured at the LUMO peak.

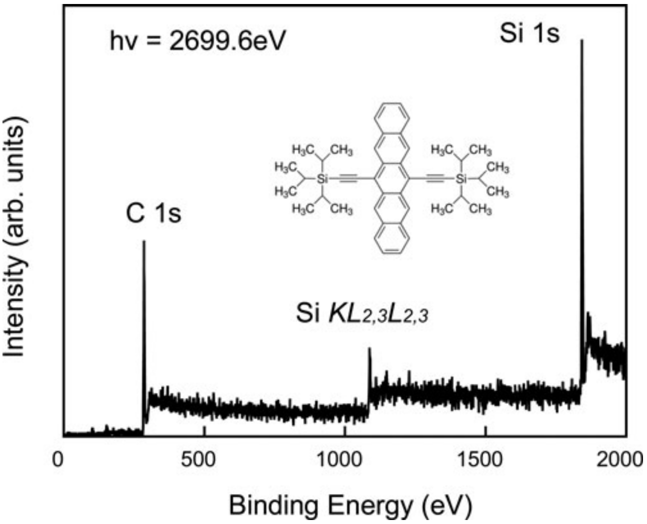

Figure 1. Wide-scan XPS of TIPS-pentacene.

RAS combined with the core-hole-clock method can be applied to probe electron transfer through the empty conduction band in the attosecond domain [10]. However, normal Auger peaks indicating ultra-fast electron transfer to neighboring molecules were not observed during core-hole decay, which is usually observed in inorganic semiconductors and metals. This suggests that TIPS-pentacene may have a different mechanism from inorganic semiconductors and may not be suitable for the fabrications of n-type semiconductors.

The intensity of peak 1 depends on the incidence angle. Peaks 2 and 4 are enhanced at the normal incidence of the X-rays. Peaks 1 and 3 are slightly enhanced at the grazing incidence. The polarization dependence indicates that a well-ordered structure is produced by rubbing the bulk powder. In general, NEXAFS spectra of polycrystalline powder which has single crystals oriented in all directions show no polarization dependence [11], even

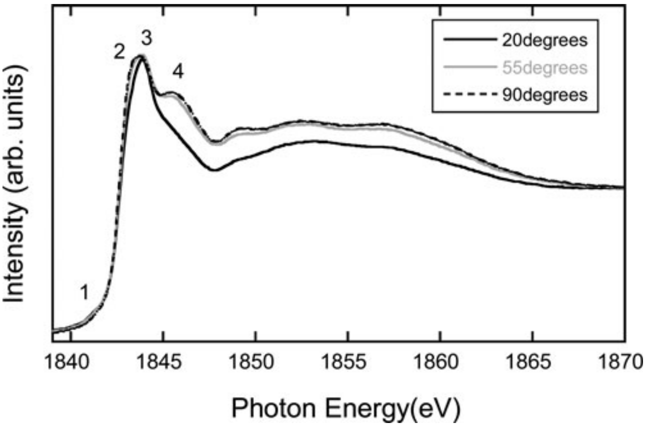

Figure 2. Angle-dependent NEXAFS spectra of TIPS-pentacene as a function of X-ray incidence angle near the Si K-edge.

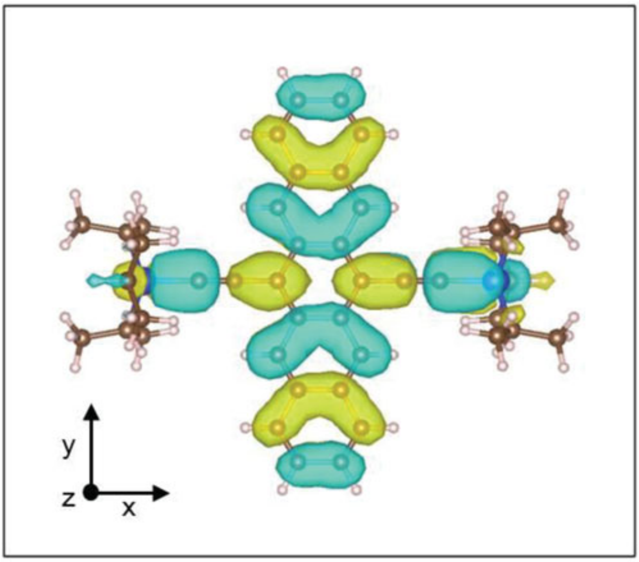

Figure 3. (Coler online) The Si 1s core-excited LUMO structure of TIPS-pentacene.

after pushing and rubbing treatment. In the pentacene case, powder consisting of small single-crystal grains could be aligned due to strong $\pi - \pi$ interactions. Ordering effect by rubbing of the bulk powder might be unique to pentacene [12] and possibly acene derivertives.

To assign electronic transition and also direction of dipole moments of these absorption peaks, molecular-orbital calculations using self-consistent local-density theory with the discrete variational (DV) - Xα method [13] were preliminary performed after the geometry was optimized by B3LYP functional with 6-31G* basis-set [14]. Obtained core-excited LUMO strucrure is shown in Fig. 3. The LUMO is delocalized over the acene and the acetyl unit and its electron distribution is similar to the calculation of ground state in substituted pentacene molecules [15]. Molecular orbitals at peaks 2 - 4 are mainly localized on the TIPS side group, differently from the LUMO. Peaks 2 and 4 are also slightly localized on the acene unit. Peak 1 can be assigned to Si 1s $\rightarrow \pi^*$ transition with a transition moment along the out-of-plane axis (z-axis), Peaks 2 and 4 can be assigned to Si 1s $\rightarrow \sigma^*$ transitions with a transition moment along the long axis of the acene unit (y-axis), while peak 3 can be assigned to Si 1s $\rightarrow \sigma^*$ transition with a transition moment along the short axis of the acene unit (x-axis). As a result of the angle-dependent NEXAFS spectra, TIPS-pentacene is found to be aligned with its long molecular axis relatively oriented parallel to the surface. It should be noted that NEXAFS peaks above the ionization threshold are not usually utilized for quantitative analysis of the angle dependence. For TIPS-pentacene, peaks 2 - 4 lie above the Si 1s ionization threshold. A more detailed analysis will be required to separate these peaks convoluted with the continuum for quantitative analysis of the polarization dependence.

Conclusions

The LUMO mainly on the acene unit of TIPS-pentacene was observed in the Si 1*s* NEXAFS spectra. This indicates that molecular orientations in blending systems for organic molecules and polymers can be analyzed using the LUMO peak at the different absorption edge from the C *K*-edge. The polarization dependence of Si 1*s* absorption peaks shows that a well-ordered structure of the polycrystalline TIPS-pentacene is produced by rubbing the bulk powder, which is aligned with its long molecular axis relatively oriented parallel to the surface.

Acknowledgments

We thank the staff of the Photon Factory and BL-27A (JAEA) for supporting our experiments. This work was supported by a Japan Society for the Promotion of Science (JSPS) KAKENHI (23550037) Grant-in Aid for Scientific Research (C). This work was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2010G653 and 2013G714).

References

[1] Anthony, J. E. (2006). *Chem. Rev.*, *106*, 5028.
[2] Hegmann, F. A., Tykwinski, R. R., Lui, K. P. H., Bullock, J. E., & Anthony, J. E. (2002). *Phys. Rev. Lett.*, *89*, 227403.
[3] Stöhr, J. (1992). *NEXAFS spectroscopy*, Springer Series in Surface Science, Vol. 25, Springer, Berlin.
[4] Hu, W. S., Tao, Y. T., Hsu, Y. J., Wei, D. H., & Wu, Y. S. (2005) *Langmuir*, *21*, 2260.
[5] Yoshikawa, G., Miyadera, T., Onoki, R., Ueno, K., Nakai, I., Entani, S., Ikeda, S., Guo, D., Kiguchi, M., Kondoh, H., Ohta, T., & Saiki, K. (2006). *Surf. Sci.*, *600*, 2518.
[6] Gnoli, A., Ustunel, H., Toffoli D., Yu L., Catone, D., Turchini, S., Lizzit, S., Stingelin, N., & Larciprete, R. (2014). *J. Phys. Chem. C*, *118*, 22522.
[7] Headrick, R. L., Wo, S., Sansoz F., & Anthony, J. E. (2006). *Appl. Phys. Lett.*, *92*, 063302.
[8] Madec, M.-B., Crouch, D., Llorente, G. R., Whittle, T. J., Geoghegan, M., & Yeates, S. G. (2008). *J. Mater. Chem.*, *18*, 3230.
[9] Kang, J., Shin, N., Jang, D. Y., Prabhu, V. M., & Yoon, D. Y. (2008). *J. Am. Chem. Soc.*, *130*, 12273.
[10] Ikeura-Sekiguchi, H., & Sekiguchi, T. (2007). *Phys. Rev. Lett.*, *99*, 228102.
[11] Ikeura-Sekiguchi, H., & Sekiguchi, T. (2014). *Jpn J. Appl. Phys.*, *53*, 02BB07.
[12] Drummy, L.F., Miska, P. K., Martin, D.C. (2004). *J. Mater. Sci.*, *39*, 4465.
[13] Adachi, H., Tsukada, M., & Satoko, C. (1978). *J. Phys. Soc. Jpn.*, *45*, 875.
[14] Frisch, M. J., Trucks, G.W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A., Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C., Farkas, O., Tomasi, J., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Andres, J. L., Gonzalez, C., Head-Gordon, M., Replogle, E. S., & Pople, J. A. (1998). Gaussian 98 W, Revision A.9, Gaussian Inc.: Pittsburgh, PA.
[15] Appleton, A. L., Brombosz, S. M., Barlow, S., Sears, J. S., Breads, J.-L., Marder, S. R., & Bunz, U. H. F. (2010). *Nat. Commun. 1*, 91.