Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Substrate Dependent Molecular Orientation in Thin Films of Bisazomethine Dye Studied by Metastable Atom Electron Spectroscopy and Ultraviolet Photoelectron Spectroscopy

T. Hosokai [a], S. Kera [b], K. K. Okudaira [b], N. Ueno [b] & S. Matsumoto [c]

[a] Graduate School of Science and Technology, Chiba University, Chiba, Japan

[b] Faculty of Engineering, Chiba University, Chiba, Japan

[c] Department of Environmental Sciences, Faculty of Education and Human Sciences, Yokohama National University, Kanagawa, Japan

Version of record first published: 22 Sep 2010

To cite this article: T. Hosokai, S. Kera, K. K. Okudaira, N. Ueno & S. Matsumoto (2007): Substrate Dependent Molecular Orientation in Thin Films of Bisazomethine Dye Studied by Metastable Atom Electron Spectroscopy and Ultraviolet Photoelectron Spectroscopy, Molecular Crystals and Liquid Crystals, 472:1, 43/[433]-50/[440]

To link to this article: http://dx.doi.org/10.1080/15421400701544877

Mol. Cryst. Liq. Cryst., Vol. 472, pp. 43/[433]–50/[440], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701544877

Taylor & Francis
Taylor & Francis Group

Substrate Dependent Molecular Orientation in Thin Films of Bisazomethine Dye Studied by Metastable Atom Electron Spectroscopy and Ultraviolet Photoelectron Spectroscopy

T. Hosokai
Graduate School of Science and Technology, Chiba University, Chiba, Japan

S. Kera
K. K. Okudaira
N. Ueno
Graduate School of Science and Technology, Chiba University, Chiba, Japan; Faculty of Engineering, Chiba University, Chiba, Japan

S. Matsumoto
Department of Environmental Sciences, Faculty of Education and Human Sciences, Yokohama National University, Kanagawa, Japan

Metastable atom electron spectroscopy and ultraviolet photoelectron spectroscopy were used to characterize orientation of bisazomethine dye molecules (DE2) in thin films deposited on graphite and ITO. We found that the molecular orientation of DE2 in multilayers is largely different on these substrates. On graphite, the molecules lie flat in a monolayer and become standing up with increasing the film thickness, while on ITO they lie nearly flat independent of the film thickness.

Keywords: bisazomethine dye; metastable atom electron spectroscopy; molecular orientation; ultraviolet photoelectron spectroscopy; vacuum deposited thin film

The present work was partly supported by 21st Century COE Program (Frontiers of Super Functionality Organic Devices) and a Grant-in-Aid for Young Scientists (A) from MEXT.

Address correspondence to S. Kera, Graduate School of Science and Technology, Chiba University, Chiba 2638522, Japan. E-mail: kera@faculty.chiba-u.jp

INTRODUCTION

Controlling a molecular aggregation is one of the most important concepts for a fabrication of desired organic devices. For example, J-aggregates, which have been used as a photography sensitizer, are well known for its large non-linear optical properties, very intense and sharp fluorescence emission, and have attracted considerable attention as promising materials for opto-electronic devices [1].

Recently, for a vacuum deposited films of *N*,*N*′-bis[4-(*N*,*N*-diethylamino)benzylidene]diaminomaleonitlire (DE2, Fig. 1), one of bisazomethine dyes, Matsumoto *et al*. found that various aggregates including J-aggregates are formed depending on the deposition conditions [2]. Although it is well known that conventional ionic J-aggregates in thin films for opto-electronic devices are unstable, J-aggregates of DE2 can survive over several years in air, since it is composed of the non-ionic dye. Thus stable and large area J-aggregates thin films can be easily obtained by the vacuum deposition of DE2. However, the performance of the J-aggregates has not been used effectively, because various aggregates including the J-aggregates exist in the films [3]. In order to control more the molecular aggregations of DE2, the film morphology using an atomic force microscopy (AFM) and a crystal structure have been studied [4,5].

It is known, on the other hand, that different molecular aggregations can be formed on different substrates [6]. Therefore, to develop the desirable J-aggregates thin films of DE2, it is necessary to investigate the molecular aggregation and orientation in DE2 thin films deposited on different substrates and their thickness dependences.

Metastable atom electron spectroscopy (MAES) is known as the most surface sensitive spectroscopy since metastable atoms as a

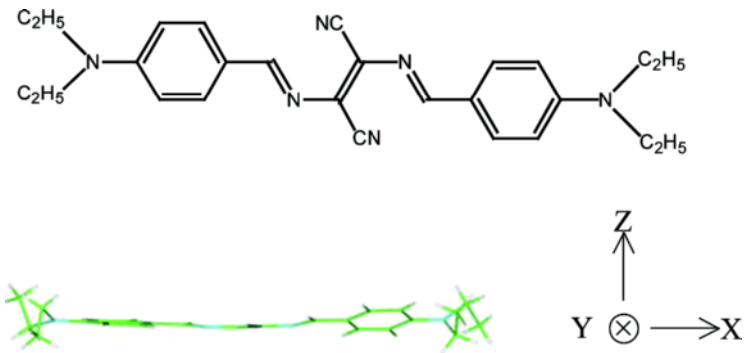

FIGURE 1 Chemical structure of *N*,*N*′-bis[4-(*N*,*N*-diethylamino)benzylidene]diaminom-aleonitlire (DE2) and a steric structure in the single crystal of DE2 used for the present MO calculation [5].

probe can not penetrate into the bulk of a solid [7,8]. Furthermore, the probe interacts with a molecular orbital (MO) extending outside the surface, selectively. The relative intensity of the MO bands in MAES spectra thus provides an information on the geometrical orientation of molecules in the outermost layer [7,8]. Contrary, ultraviolet photoelectron spectroscopy (UPS) measures the valence electrons existing in the $\sim$1-nm-thick surface region and gives integrated information of MO bands in this region. By comparing intensities of related spectral features in MAES and UPS spectra, we can obtain the molecular orientation at the outermost surface [7,8].

In this study, we investigated molecular orientation of DE2 in thin films deposited on different substrates, graphite and indium-tin-oxide coated glass (ITO), using MAES and UPS. As described in a reference [9], it is expected that the graphite has a crystallographical surface proper to prepare piled-up monolayers, while the ITO has a rough surface that prevents epitaxial growth but provides crystalline films or amorphous films. The results demonstrate that the orientation of DE2 in thin films is different on these substrates. On graphite, the molecules orient flat in a monolayer region and become standing-up gradually with increase in the film thickness, while on ITO the molecules lie nearly flat with the molecular short-axes slightly inclined independent of the thickness.

EXPERIMENT

A highly oriented pyrolytic graphite (HOPG) and ITO were used as the substrates. A root mean square surface roughness of the ITO was 1.24 nm measured by AFM. The HOPG substrate was cleaved in air just before loading into the preparation chamber (7×10^{-8} Pa) and cleaned by *in situ* heating at 400°C for 24 h. The ITO substrate was ultrasonically washed with acetone, 2-propanol, and de-ionized water for 10 min consecutively and blow dried in nitrogen just prior to loading into the preparation chamber. DE2 was synthesized by the reported procedure [10]. The DE2 was purified twice by a column chromatography. Thin films of DE2 were prepared by vacuum evaporation on the substrates after degassing sufficiently in the preparation chamber. The deposition amount and rate ($0.2 \sim 0.3$ Å/min) were measured with a quartz microbalance. Decomposition of DE2 upon the vacuum deposition was not observed by ultraviolet-visible absorption spectroscopy of the DE2 solutions that were prepared by resolving the vacuum-deposited DE2 thin films in chloroform.

MAES and UPS (He I) spectra were measured by an ultrahigh vacuum electron spectrometer [7] with newly equipped 180° hemispherical

analyzer (SPECS-PHOIBOS100). The metastable atoms of He^* (2^3S; 19.82 eV, 2^1S; 20.62 eV) were produced by cold discharge of pure helium gas, and the He^* (2^1S) component was quenched by a dc helium lamp (quench lamp) in order to measure the spectra excited only by He^* (2^3S). All measurements were performed at room temperature. The Fermi level (E_F) was determined from UPS of a thick Au film, and all spectra presented here are displayed using the binding energy (E_B) from E_F of substrates.

RESULTS AND DISCUSSION

Before showing the observed spectra, we describe typical molecular orbital (MO) patterns of DE2 in Figure 2(a–e). The MOs were obtained

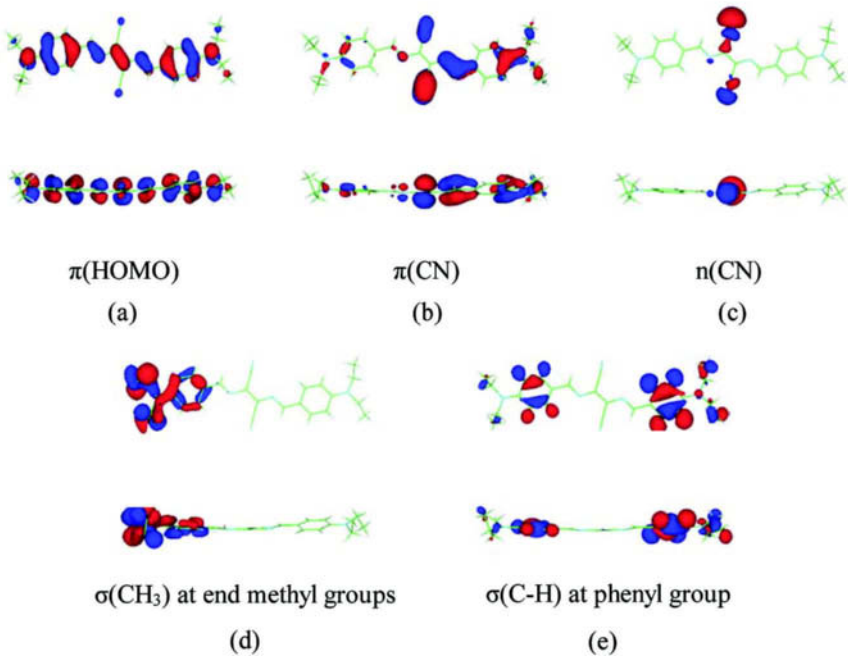

FIGURE 2 Spacial distributions of typical MOs of DE2 for MAES features. (a) highest occupied molecular orbital (π orbital) distributed perpendicular to the molecular plane, (b) π orbital localized at the cyano groups, (c) non-bonding orbital localized at the cyano groups, (d) σ orbital distributed at end methyl groups, (e) σ orbital distributed to phenyl groups. The red and blue parts indicate the positive and negative phases of the MOs, respectively.

by calculation using the density functional theory (DFT) (B3LYP/6-31G(d)). The special distribution of the MOs is employed to discuss a molecular orientation of DE2 in the films both on the HOPG and ITO substrates in the following discussions.

Figure 3(a) shows the film thickness (Θ) dependence of UPS spectra of DE2 thin films deposited on the ITO, where the spectrum of the ITO is also shown. In the spectrum of the 3-Å-thick film, many spectral bands, which are grouped into A, B and C, are observed. From a MO calculation with DFT, the spectral bands can be assigned as follows. Bands in group A are ascribed to π orbitals which are distributed perpendicular to the molecular plane, bands in group B arise mainly

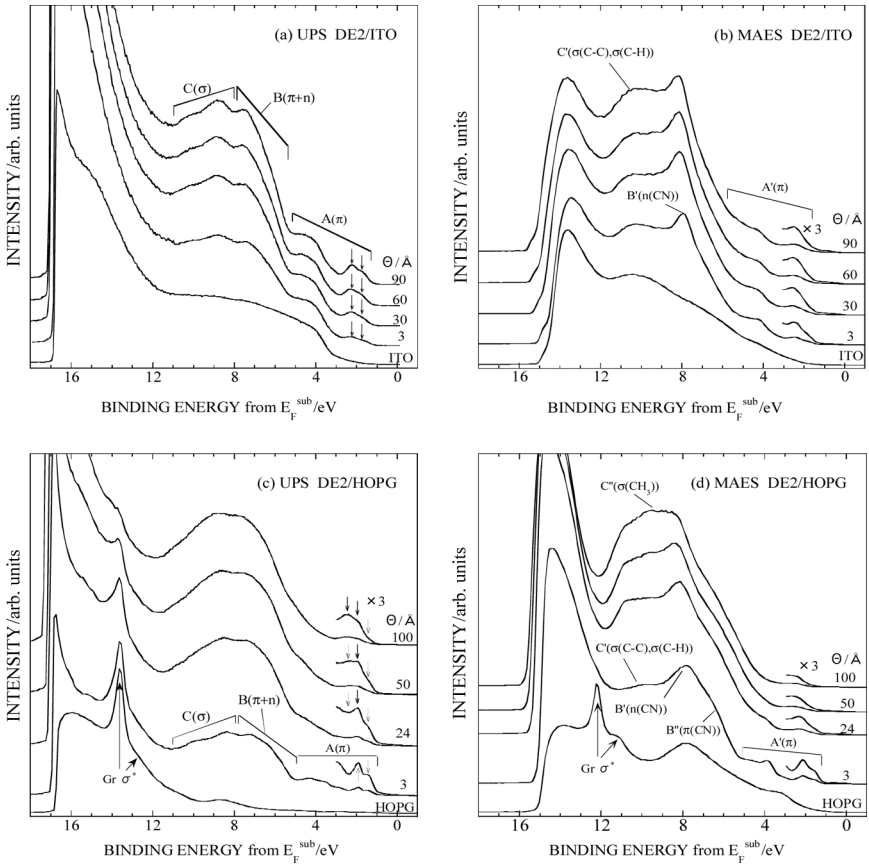

FIGURE 3 Thickness dependences of UPS and MAES spectra of DE2 thin films on ITO and HOPG. (a) UPS spectra of DE2/ITO, (b) MAES spectra of DE2/ITO, (c) UPS spectra of DE2/HOPG, (d) MAES spectra of DE2/HOPG.

from π and non-bonding orbitals mainly localized at the cyano groups [π(CN) + n(CN)], and bands in group C are attributed toσorbitals which are distributed at phenyl [σ(C-C) + σ(C-H)] and diethyl [$\sigma(CH_3)$, σ(C-C) + $\sigma(CH_2)$] groups. Above $\Theta = 3$ Å, similar spectra are observed independent of the film thickness.

Figure 3 (b) shows the Θ dependence of MAES spectra of DE2 thin films on the ITO and the substrate spectrum. In the MAES spectrum at $\Theta = 3$ Å, bands in group A′, band B′ and band C′ are observed. Bands in group A′ are ascribed to π orbitals, which correspond well with group A in the UPS, band B′ arises mainly from n(CN) orbitals distributed parallel to the molecular plane [11], and band C′ comes from σ(C-C) and σ(C-H) orbitals localized at phenyl groups. With increase in Θ, bands in group A′, band B′ and band C′ are also seen and the spectral shape stays unchanged. The clear appearance of these specific electronic states in MAES spectra implies that these orbitals are existing at the outermost surface, and thus gives an information of the molecular orientation. It has to be noted here that on the ITO that molecular orientation of DE2 in thin films is independent of Θ, since the MAES spectra show little thickness dependence.

When we compare the UPS [Fig. 3(a)] and MAES [Fig. 3(b)], intensities of some corresponding spectral bands are different. For example, bands B′ [n(CN)] and C′ [σ(C-C) + σ(C-H) at phenyl groups] spectra are strong in the MAES and π orbitals [A and A′] are observed similarly in both UPS and MAES spectra. These results indicate that molecules are not standing and oriented nearly flat with their short-axes slightly tilted. If molecules are standing, MAES cannot observe electrons in π, n(CN) and σ orbitals at phenyl groups.

Figure 3(c) show the Θ dependence of UPS spectra of DE2 thin films deposited on the HOPG with the substrate spectrum. In all spectra, the sharp substrate peak at $E_F{}^{Sub} = 13.6$ eV and small shoulder around 12.6 eV are seen. They originate from the σ^* conduction bands of HOPG [Gr(σ^*)] [12]. These substrate features become smaller with increase in Θ, demonstrating actual increase in the film thickness. In the UPS spectrum at $\Theta = 3$Å, many spectral bands, which are also grouped into A, B and C, can be seen as for DE2 on the ITO. With increase in Θ, however, the UPS bands in groups A$\sim$C become broad and their E_B positions are shifted to the high E_B side, and similar shift is also observed in the vacuum level. The valence-band shift is 0.5 eV and the corresponding vacuum-level shift is 0.6 eV at 100Å. The shifts in thick films are usually considered to originate from the charging of the film upon ionization. However, we could not observe time dependence of the shifts, which is an indication of the charging effect, in all measurements for the thicker films. Therefore, the band shift is not

due to the charging of the films, and may be explained by appearance of small electric dipoles which are induced by the continuous change in the molecular orientation along the film-thickness direction [12]. The continuous change in the molecular orientation is discussed latter using MAES spectra. It is of note that the substrate peak Gr(σ^*) remains even at 100 Å, suggesting that thick domains and very thin domains are coexisting in the 100-Å films. It is convinced that the broadening of the spectral bands for thicker films originates from the multidomain structure of the films, where the molecular packing is different in each domain, since the polarization energy is different depending on molecular packing structure [13].

Figure 3(d) shows the Θ dependence of the MAES spectra of DE2 thin films on the HOPG with the substrate spectrum. In the substrate spectrum, the sharp peak of the σ^* conduction bands of HOPG [Gr(σ^*)] is also seen as in the UPS spectra [Fig. 3(c)]. We note here that the intensity of the σ^* peak suddenly disappears when Θ is 3 Å, while the σ^* peak in UPS decrease gradually with increase in Θ. The result demonstrates that the HOPG surface is fully covered by the molecules at 3 Å and a monolayer is formed. At $\Theta = 3$ Å, several bands in group A′, band B′ and shoulder B″ are observed, while band C′ and band C″, which are clearly seen above 3 Å, are weak. Band B″ is ascribed toπorbitals localized at the cyano group [π(CN)], and band C″ is mainly attributed to $\sigma(CH_3)$ in diethyl groups. With increase in Θ, band C′ becomes intense, band C″ appears more clearly above 24Å, and bands in group A′ become obscure. These results demonstrate that on the HOPG the molecular orientation at the film surface changes depending on Θ, which is markedly different from on the ITO. The thickness dependence of the intensity of each band implies that the molecules in the 3-Å film, which corresponds to the monolayer, lie flat on the HOPG, because C′[σ(C-C) and σ(C-H) at the phenyl group] and C″ [$\sigma(CH_3)$] are very weak, π and n(CN) bands are clearly seen. With increase in Θ, the molecules are oriented with the long-axes tilted, since π bands in group A′ become weak and peak C″ due to $\sigma(CH_3)$ in the diethyl groups appears clearly in MAES spectra.

CONCLUSION

We found that the molecular orientation and packing of DE2 in thin films is different on these substrates. On graphite, the molecules lie flat in the monolayer and orient with the long-axes tilted with increasing the film thickness, while the molecules on the ITO lie nearly flat both in the ultrathin and thicker films. The results indicate that

molecular aggregation/packing of DE2 in thin films can be controlled by selecting substrate.

REFERENCES

[1] Kobayashi, T. ed., (1996). *J-aggregates*, World Scientific: Singapore.
[2] Matsumoto, S., Kobayashi, T., Aoyama, T., & Wada, T. (2003). *Chem. Comm.*, 1910.
[3] Kobayashi, T., Matsumoto, S., Tanaka, T., Kunugita, H., Ema, K., Aoyama, T., & Wada, T. (2005). *Phys. Chem. Chem. Phys.*, *7*, 1726.
[4] Matsumoto, S., Satoh, M., Tsuchida, D., Kobayashi, T., Aoyama, T., & Wada, T. (2005). *Transaction of MRS-J*, *30*, 345.
[5] Matsumoto, S., Shirai, K., Kobayashi, T., Wada, T., & Shiro, M. (2004). *Zeitschrift fur Kristallographie*, *219*, 239.
[6] Forrest, S. R. (1997). *Chem. Rev.*, *97*, 1943.
[7] Kera, S., Setoyama, H., Onoue, M., Okudaira, K. K., Harada, Y., & Ueno, N. (2001). *Phys. Rev. B*, *63*, 115204–115208.
[8] Harada, Y., Masuda, S., & Ozaki, H. (1997). *Chem. Rev.*, *97*, 1793.
[9] Ozaki, H. (2000). *J. Chem. Phys.*, *113*, 6361.
[10] Shirai, K., Matsuoka, M., & Fukunishi, K. (2000). *Dyes. Pigm.*, *47*, 107.
[11] Masuda, S., Hayashi, H., Harada, Y., & Kato, S. (1991). *Chem. Phys. Lett.*, *180*, 279.
[12] Yamane, H., Yabuuchi, Y., Fukagawa, H., Kera, S., Okudaira, K. K., & Ueno, N. (2006). *J. Appl. Phys.*, *99*, 093705.
[13] Fukagawa, H., Yamane, H., Kataoka, T., Kera, S., Nakamura, M., Kudo, K., & Ueno, N. (2006). *Phys. Rev. B*, *73*, 245310–245315.