Spontaneous buildup of giant surface potential by vacuum deposition of Alq_3 and its removal by visible light irradiation

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We observed high and persistent spontaneous buildup of the surface potential (SP) upon vacuum deposition of tris(8-hydroxyquinolinato) aluminum(III) (Alq₃) on an Au substrate under dark conditions. SP determined by the Kelvin probe method reached 28 V at a thickness of 560 nm and the surface of the Alq₃ film was positively charged. We propose a model in which preferential orientation of the dipole moments of Alq₃ molecules is the origin of this buildup of the SP. The intensity of second-harmonic generation was also dramatically increased by the deposition of Alq₃ under dark conditions, which supports the notion of a buildup of dipole layers. This giant surface potential was almost completely removed by irradiation of Alq₃ molecules with visible light, and irradiation during deposition also prevented the buildup of SP. © 2002 American Institute of Physics. [DOI: 10.1063/1.1518759]

I. INTRODUCTION

It is well known in surface science that an electric dipole layer is formed upon the deposition of small molecules on a metal surface.[1,2] The formation of this dipole layer can be detected as a change in the metal work function[3,4] $\Delta\Phi$. In this case, the dipole layer is formed by a metal-molecule interaction within a few molecular layers from the metal surface, and further deposition usually does not change $\Delta\Phi$.

Similar dipole layer formation confined to the interface also occurs with the molecular deposition of organic electronic materials (OEMs) used in organic electronic devices.[4,5] This latter phenomenon has attract considerable attention since the dipole layer affects the energy-level alignment between the OEM layer and the metal, which is crucial for injection of the charge carriers into OEM. There have even been attempts to insert another dipole layer between the metal and the OEM layer to control the energy-level alignment.[6–8] These were carried out by fixing self-assembled monolayers (SAMs) with polar groups on the metal surface, and the dipole layer is confined to the SAM layer. In all of these examples[4,6–10] of the formation of a

dipole layer right at the interface, the observed magnitude $\Delta\Phi$ was less than 2 eV.

For more general cases including thicker deposited layers, the change in the work function can be expressed in terms of surface potential (SP) ϕ_s, which is the change in the electrostatic potential just outside of the surface from the value for clean metal. For molecular adsorption, the relation

$$\Delta\Phi = -e\phi_s \tag{1}$$

holds, where $-e$ is the charge of an electron. As another contribution to ϕ_s for thick OEM films (e.g., $\sim$100 nm), band bending may occur, leading to Fermi-level alignment. This corresponds to the appearance of a space charge due to impurities (or dopants), which may add another 1 V or so to ϕ_s. Altogether, the value of ϕ_s in these cases does not exceed 3 V. The interfacial energy diagram in this case is illustrated in Fig. 1(a).

We report here our discovery of a spontaneous and persistent buildup of an enormous SP upon the simple vacuum deposition of tris(8-hydroxyquinolinato) aluminum(III) [Alq₃; Fig. 2(a)] on an Au substrate under dark conditions. Alq₃ is a representative light-emitting material used in organic electroluminescent (EL) devices.[11] The value of ϕ_s reached 28 V for 560-nm-thick Alq₃, with the vacuum side positively charged. We did not apply any electric field for poling during film formation. We propose that the preferential orientation of dipoles of Alq₃ molecules in the film possibly causes this large buildup of SP. The buildup of large dipole layers was

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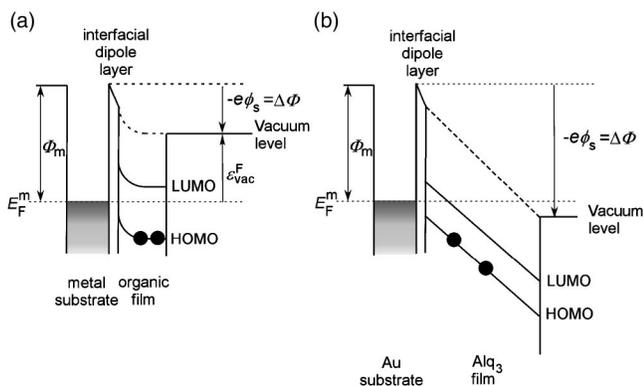
FIG. 1. (a) The energy diagram of an usual organic/metal interface with an interfacial dipole layer and band bending. E_F^m: Fermi level of the metal substrate Φ_m: work function of the metal substrate ϕ_s: surface potential of the Alq$_3$ film ε_{vac}^F: energy of the vacuum level relative to E_F^m. (b) Observed energy diagram of the Alq$_3$/Au system prepared under dark conditions.

confirmed by measurements of optical second-harmonic generation (SHG). The large SP of the Alq$_3$ film deposited under the dark condition was almost removed by irradiation with visible light.

II. EXPERIMENTS

Alq$_3$ was purchased from Aldrich (99.95% purity) and purified once by vacuum sublimation. ϕ_s was measured by the Kelvin probe (KP) method[12] in an ultrahigh vacuum (UHV) system with a base pressure of $<2\times10^{-10}$ Torr. A commercial Kelvin probe (McAllister Inc. KP-6000) was attached to this system. The Au substrate was prepared *in situ* by depositing Au on a Si wafer.

Alq$_3$ was deposited under UHV on the Au substrate in an incremental manner, with KP measurement at each step of
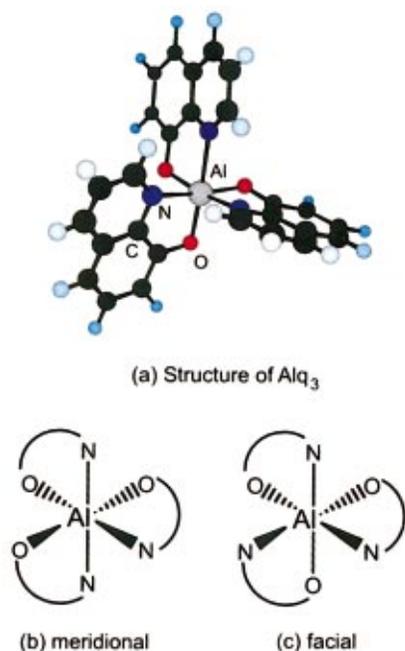
FIG. 2. (Color) (a) Molecular structure of Alq$_3$, (b) meridional isomer, and (c) facial isomer.
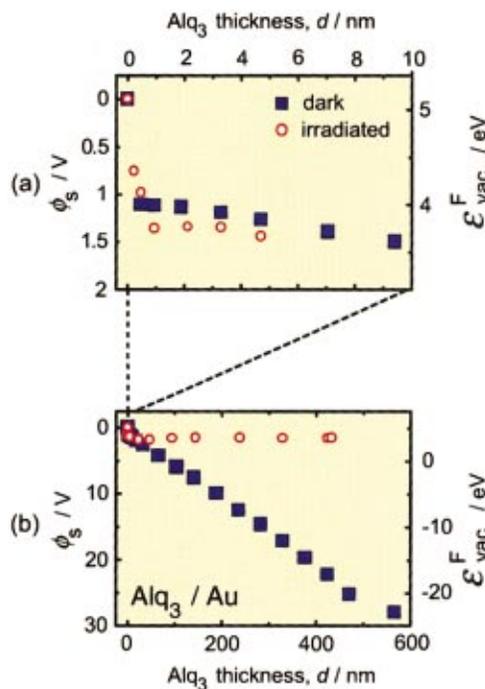
FIG. 3. (Color) The development of a surface potential upon the deposition of Alq$_3$. The abscissa is the Alq$_3$ thickness d. The ordinates at the left and the right are the surface potential ϕ_s and the energy of the vacuum level relative to the Fermi level of the Au substrate, ε_{vac}^F, respectively. (a) The results for small d. The rapid change at $d<1$ nm corresponds to interfacial dipole layer formation. (b) The results for the whole thickness region. Solid squares: under dark conditions and open circles: under irradiation with white light.

deposition. The thickness of the Alq$_3$ film was monitored by a quartz microbalance. Since we found that this phenomenon is affected by light, as described later, the ionization gauges were turned off and all viewing ports were covered with filters to reduce the light absorbed by Alq$_3$.[13] Hereafter, this experimental condition is referred to as the "dark condition."

The experiments of SHG were carried out using another high-vacuum chamber with a base pressure of less than 10^{-8} Torr using a substrate prepared by vacuum-depositing Au on a Si wafer in a separate vacuum chamber. To sensitively monitor the change in the dipole moment normal to the substrate, SHG measurements were carried out under $p_{in}\rightarrow p_{out}$ polarization. The sample was irradiated with a p-polarized fundamental beam 4 mm in diameter from a Ti-Sapphire laser (Tsunami: Spectra Physics, 0.8 W, 120 fs) with an incidence angle of about 45° through a quartz window. We chose a fundamental beam of 758 nm to avoid the light absorption by Alq$_3$ molecules. The p-polarized SHG signal (379 nm) at about 45° from the surface was detected by photon counting with a photomultiplier outside the vacuum chamber. We averaged the results of three measurements for 10 sec at each thickness. KP measurements confirmed that laser irradiation did not greatly affect the surface potential.

III. RESULTS AND DISCUSSION

The solid squares in Fig. 3 show the dependence of ϕ_s on the thickness (d) measured under the dark condition. By definition, ϕ_s for a clean Au surface is zero. On the right

ordinate, we also show the absolute value of the energy of the vacuum level relative to the Fermi level of the metal substrate ε_{vac}^{F} [Fig. 1(a)], which corresponds to $\Phi_m - e\phi_s$, where Φ_m is the work function of the clean Au film. A value of $\Phi_m = 5.1 \pm 0.1$ eV was obtained by calibrating the work function of the reference electrode by measuring six metals with known work functions.[14] Note that a positive shift of ϕ_s corresponds to a decrease in ε_{vac}^{F} and the formation of an electric dipole layer with the vacuum side positively charged. In the initial stage of deposition up to $d = 1$ nm [Fig. 3(a)], ϕ_s increased rapidly, corresponding to the formation of the interfacial dipole layer mentioned above. After this shift, ϕ_s increased linearly over a wide range of thickness ($d = 5–550$ nm) with a mean slope of about 0.05 V/nm. Even at $d \geq 500$ nm, no saturation of ϕ_s was seen [Fig. 3(b)]. The large value of ϕ_s was maintained after several hours in UHV, and was not affected by exposure to air.

We also examined the present system by ultraviolet photoemission spectroscopy in the thin-film region ($d \leq 20$ nm). The whole spectrum was rigidly shifted by an amount corresponding to ϕ_s, consistent with the KP results. The invariance of the spectral line shape indicates that the electronic structure of Alq$_3$ is not greatly affected by contact with the Au substrate, and also excludes the possibility of significant charge transfer. The results of KP under the dark condition mentioned above give the energy diagram in Fig. 1(b). The surface potential is large enough for the vacuum level to be below the Fermi level of the Au substrate. Band bending leading to Fermi-level alignment, which is usually on the order of 1 eV as described above, is not likely the main source of the large ϕ_s. Actually, the assumption of Fermi-level alignment leads to a curious situation of a "negative work function," since $|\Delta\Phi| \gg \Phi_m (= 5.1$ eV).

There are two possible origins of this buildup of large ϕ_s. First, the charges may be trapped or accumulated near the interface and/or surface, and the second is the alignment of the molecular dipoles in the film. The former case is unlikely, since the charge carriers will not be easily generated. Since the desorption temperature of organic compounds at the vacuum evaporation is not high, electrons or ions cannot be emitted from the heating sources. Also, amounts of Alq$_3$ molecules excited thermally across the (HOMO-LUMO) gap are negligibly small (HOMO and LUMO are the highest occupied and the lowest unoccupied molecular orbitals, respectively), making such excitation not plausible as the origin of the charge carriers. Even if such charge carriers are generated and trapped, the electric field in the film, which is comparable in strength with the driving condition of the EL devices (5×10^7 V/m), will not be in direction to drive the carriers to the surface and interface, but will derive them into the film and lead to neutralization. This suggests that the trapped/accumulated charge is not the main origin of the buildup of large ϕ_s.

On the other hand, the latter model of dipole alignment is supported by the preliminary experimental results using coronene. This nonpolar molecule did not show a buildup of large ϕ_s. This result suggests that the dipole moments of the molecules play an essential role for the formation of the giant surface potential. Thus, we ascribe this phenomenon to

the molecular dipole orientation, although further examination of the dependence on substrate, substrate temperature, and annealing are desirable.

When we adopt the molecular mechanism, the linear relation between ϕ_s and the thickness in Fig. 3(b) indicates uniform growth of the Alq$_3$ layer with a constant dipole per unit volume p. In this case, the net charge appears only on both sides of the Alq$_3$ layer. The density of this charge is equal to p and can be estimated from the observed surface potential ϕ_s and the film thickness d by the following equation, which is similar to that for an electric capacitor:

$$E = \phi_s / d = p/\varepsilon_0, \qquad (2)$$

where E and ε_0 are the macroscopic electric field in the Alq$_3$ layer and the permittivity of the vacuum, respectively. This equation corresponds to the observed linearity of ϕ_s with respect to the Alq$_3$ thickness. Using Eq. (2), the observed value of $\phi_s = 28$ V at $d = 560$ nm gives $p = 0.44$ mC/m^2.

An Alq$_3$ molecule is known to have a permanent dipole moment μ, which is estimated by density functional theory[15] to be 4.1 and 7.1 D for the two possible isomeric forms [meridional and facial, Figs. 2(b) and 2(c)], respectively; only the meridional form has been observed in the crystalline state,[16] while the possible existence of the facial isomer is theoretically pointed out for metal complexes of Alq$_3$.[17] Assuming a perfect orientation of dipoles perpendicular to the surface, p becomes μ/v, where v is the volume per molecule, which is ca. 0.5 nm^3 according to x-ray crystallographic analysis.[16] Thus, we obtain $p = 27$ and 47 mC/m^2 for the meridional and facial isomers, respectively. These values are several tens times larger than the observed value. This suggests that the molecular orientation of Alq$_3$ is mostly random, but dipoles have some preference for a perpendicular orientation, leading to a large ϕ_s. Several possible structures could lead to such partial dipolar order, e.g., a homogeneous molecular film with some dipolar order and a film with some dipole-ordered domains. For the case of highly polar molecules mixed into less polar molecules prepared by the codeposition of two components (including the limit of pure neat solid of highly polar molecules), domain formation by the polar molecules was deduced based on an analysis of the spectral shift of fluorescence.[18] This suggests that similar domain formation may also occur in the neat film studied here, with the preferred orientation of the dipoles perpendicular to the substrate surface.

The uniform slope of ϕ_s with respect to d in the thick region suggests unchanged growing conditions, and the initial stage of deposition seems to determine the entire process. As described above, the rapid change in ε_{vac}^{F} at the early stage of deposition ($d \leq 1$ nm) indicates the formation of an interfacial dipole layer with the vacuum side positively charged. This interfacial effect may induce some orientation of the Alq$_3$ molecules in the subsequent thin layer with the vacuum side also positively charged, and this mechanism may also influence further growth of the film.

The observed large macroscopic dipole is similar to those observed in electrets and ferroelectrics. The observed polarization of Alq$_3$ is two orders of magnitude smaller than that of a copolymer of vinylidene fluoride and trifluoroeth-
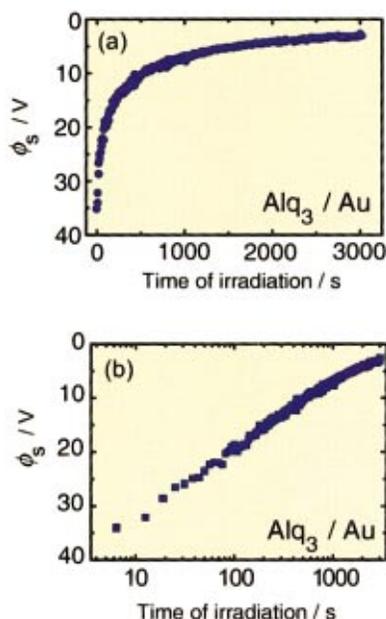
FIG. 4. (Color) Change in surface potential vs irradiation time t [(a) linear scale for t and (b) logarithmic scale] with white light using a 30-W incandescent lamp at a distance of ca. 18 cm through a vacuum window. The film thickness was about 600 nm.

ylene (approximately 80 mC/m^2 after 10^8 V/m poling), which is a well-known ferroelectric polymer.[19] On the other hand, it is comparable to those for typical ferroelectric liquid crystals.[20] As another example of the spontaneous formation of a large macroscopic dipole without poling, dipoles in a ferroelectric polymer film sandwiched between two materials with different surface energies can be aligned by annealing ("surface energy poling").[21]

Buildup of the dipole layer was also confirmed by SHG measurements, where incident laser light of frequency ν is converted to light with doubled frequency 2ν. The SHG intensity is expected to be proportional to the square of the second-order susceptibility, which roughly follows the magnitude of the dipole moment.[22] The SHG intensity showed a dramatic increase from 11.3 counts per second (cps) for the bare Au substrate to 651.7 cps upon deposition of 450-nm Alq$_3$, confirming the formation of a large dipole. The SHG intensity with a thin layer ($d \leq 150$ nm) followed the expected quadratic dependence on film thickness, although the behavior with thicker deposition was slightly complicated, probably due to an interference effect.[23] A detailed analysis is underway, and the results will be published elsewhere.[24]

We also found that ϕ_s is affected by light absorption by Alq$_3$ during and after film deposition. When we deposited Alq$_3$ under light irradiation with a 30-W incandescent lamp through a viewing port at a distance of approximately 18 cm from the sample, only the buildup of ϕ_s at small d due to interfacial dipole layer formation was observed, as shown in Fig. 3 (open circles). The large ϕ_s built up by depositing Alq$_3$ in the dark was also reduced by light irradiation under similar conditions. This is shown in Fig. 4(a), where the abscissa is the irradiation time t. As shown in Fig. 4(b), the value of ϕ_s decreased linearly with $\log_{10}(t)$. The originally

large ϕ_s was reduced to about 3 V within 1 h. This effect was negligibly small when we inserted a filter to remove light with a wavelength shorter than 600 nm. Therefore, we conclude that this change is due to the electronic excitation of Alq$_3$.

The SHG intensity was also reduced to 214.0 cps after similar irradiation with white light for 1 h, indicating randomization of the dipole orientation. The remaining SHG intensity may be due to (i) the surface or interface of the Alq$_3$ film, where inversion symmetry is absent and (ii) a contribution from the magnetic dipole and electric quadrupole.[23,25,26] These results of KP and SHG experiments indicate that the electronic excitation of Alq$_3$ molecules prevents or disrupts the orientation of molecular dipoles.

Although the detailed origin of this effect by light irradiation is not yet clear, we note that Alq$_3$ has a nearly spherical shape and may rotate with only a slight potential barrier. Alq$_3$ tends to form an amorphous film by the usual vapor deposition to prepare EL devices,[17] with possibly a somewhat loose molecular packing to allow for molecular rotation. If the dipole moment of Alq$_3$ in the excited state is not parallel to that in the ground state, molecules in the excited state may be rotated by the local electric field, leading to a loss of dipole order even after the molecule returns to the ground state. Recent theoretical calculations[27] actually indicate that the dipole moment in the lowest-excited state is almost perpendicular to that in the ground state, and the excited state has a rather long lifetime component of 10 ns.[28]

Ichikawa and coworkers[29] recently found by electron diffraction that the orientation of crystalline Alq$_3$ film grown epitaxially on KCl can be controlled by polarized light. In their case, however, molecules in films of $d \geq 12$ nm did not reorient. The difference between their results and ours may be due to closer and more ordered packing of the molecules in the crystalline state.

IV. CONCLUSION

Using the Kelvin probe method, we observed the spontaneous buildup of a large and persistent surface potential ϕ_s upon the vacuum deposition of Alq$_3$ under dark conditions, with the surface of the film positively charged. This indicates the buildup of a large dipole layer, which was also confirmed by the observation of a large second harmonic generation. Based on these results, we conclude that the dipole moments of Alq$_3$ molecules show a moderate degree of alignment. This orientation was hindered or almost completely disrupted by irradiation of Alq$_3$ with visible light, indicating that the direction of the dipole moments is randomized through electronic excitation.

This is an observation of the spontaneous formation of a large macroscopic dipole with the simple vacuum deposition of organic molecules. Furthermore, the quenching observed upon irradiation is so effective that it can be seen under usual laboratory illumination (which may explain why an SP buildup was not observed in previous studies on Alq$_3$). Thus, we should be aware of such effects when preparing films of polar molecules by vacuum deposition. This caution applies not only to structural studies but also to studies on

interfacial electronic structures in relation to electronic devices. Most studies of Alq$_3$ interfaces to date have been carried out without much control of illumination, and the results have not been very reproducible. This situation may be improved by the application of the present results.

These unique findings may lead to various possible applications such as control of the surface potential by light irradiation. If the decay of the built-up surface potential by irradiation can be suppressed by a proper choice of material, an electret may be conveniently prepared by simple vacuum deposition, or a solar cell with a large open circuit voltage may be prepared. Details of these phenomena and their mechanisms are under investigation, along with similar phenomena using other materials.

ACKNOWLEDGMENTS

[1] A. Zangwill, *Physics at Surface* (Cambridge University, Cambridge, 1988), p. 185.

[2] P. Jakob and D. Menzel, Surf. Sci. **201**, 503 (1988).

[3] H. Lüth, *Surfaces and Interfaces in Solid Materials*, 3rd ed. (Springer-Verlag, Berlin, 1998) Chap. 9.

[4] H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Adv. Mater. **11**, 605 (1999) and references cited therein.

[5] S. Narioka, H. Ishii, D. Yoshimura, M. Sei, Y. Ouchi, K. Seki, S. Hasegawa, T. Miyazaki, Y. Harima, and K. Yamashita, Appl. Phys. Lett. **67**, 1899 (1995).

[6] I. H. Campbell, S. Rubin, T. A. Zawodzinski, J. D. Kress, R. L. Martin, D. L. Smith, N. N. Barashkov, and J. P. Ferraris, Phys. Rev. B **54**, 14 321 (1996).

[7] I. H. Campbell, J. D. Kress, R. L. Martin, N. N. Barashkov, and J. P. Ferraris, Appl. Phys. Lett. **71**, 3528 (1997).

[8] S. F. J. Appleyard, S. R. Day, R. D. Pickford, and M. R. Willis, J. Mater. Chem. **10**, 169 (2000).

[9] I. G. Hill, A. Rajagopal, A. Kahn, and Y. Hu, Appl. Phys. Lett. **73**, 662 (1998).

[10] R. Schlaf, C. D. Merritt, L. A. Crisafulli, and Z. H. Kafafi, J. Appl. Phys. **86**, 5678 (1999).

[11] C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).

[12] D. P. Woodruff and T. A. Delchar, *Modern Techniques of Surface Science* (Cambridge University, Cambridge, 1986).

[13] A. Aziz and K. L. Narasimhan, Synth. Met. **114**, 133 (2000).

[14] N. Hayashi, H. Ishii, Y. Ouchi, and K. Seki, J. Appl. Phys. (in press). Evaporated films of Au, Ag, Cu, Mg, Pb, and Ca were measured. Based on a comparison of the values for the contact potential difference obtained with the reported values of their work functions, the work function of the reference electrode was estimated to be 4.3 eV.

[15] A. Curioni, M. Boero, and W. Andreoni, Chem. Phys. Lett. **294**, 263 (1998).

[16] M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, and A. Sironi, J. Am. Chem. Soc. **122**, 5147 (2000).

[17] A. Curioni and W. Andreoni, J. Am. Chem. Soc. **121**, 8216 (1999).

[18] M. A. Baldo, Z. G. Soos, and S. R. Forrest, Chem. Phys. Lett. **347**, 297 (2001).

[19] M. Jimbo, T. Fukuda, H. Takeda, F. Suzuki, K. Horino, K. Koyama, S. Ikeda, and Y. Wada, J. Polym. Sci., Polym. Phys. Ed. **24**, 909 (1986).

[20] E. Demus, Ed., *Handbook of Liquid Crystals* (Wiley-VCH, Weinhelm, 1998).

[21] J. Ide, S. Tasaka, and N. Inagaki, Jpn. J. Appl. Phys., Part 1 **38**, 2049 (1999).

[22] A. Yariv, *Quantum Electronics*, 3rd ed. (Wiley, New York, 1989) Chap. 16.

[23] H. Hoshi, T. Yamada, K. Ishikawa, H. Takezoe, and A. Fukuda, Phys. Rev. B **52**, 12 355 (1995).

[24] K. Tsuboi *et al.* (unpublished).

[25] B. Koopmans, A. Janner, H. T. Jonkman, G. A. Sawatzky, and F. van der Woude, Phys. Rev. Lett. **71**, 3569 (1993).

[26] H. Hoshi, T. Yamada, K. Ishikawa, H. Takezoe, and A. Fukuda, Phys. Rev. B **53**, 12 663 (1996).

[27] W. Sampor, J. Kalinowski, G. Marconi, P. Di Marco, V. Fattori, and G. Giro, Chem. Phys. Lett. **283**, 373 (1998).

[28] W. Humbs, H. Zhang, and M. Grasbeek, Chem. Phys. **254**, 319 (2000).

[29] H. Ichikawa, T. Shimada, and A. Koma, presented at the workshop, "Advanced Spectroscopy of Organic Materials for Electronic Applications," Glumsloev, Sweden, 4–7 July 2001.