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Field-modulation spectroscopy of pentacene thin films using field-effect devices: Reconsideration of the excitonic structure

Simon Haas,[1] Hiroyuki Matsui (松井弘之),[1,2] and Tatsuo Hasegawa (長谷川達生)[1,*]
[1]*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8562, Japan*
[2]*Department of Advanced Materials Science, The University of Tokyo, Kashiwa, Chiba 277-8561, Japan*

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We report pure electric-field effects on the excitonic absorbance of pentacene thin films as measured by unipolar field-effect devices that allowed us to separate the charge accumulation effects. The field-modulated spectra between 1.8 and 2.6 eV can be well fitted with the first derivative curve of Frenkel exciton absorption and its vibronic progression, and at higher energy a field-induced feature appears at around 2.95 eV. The results are in sharp contrast to the electroabsorption spectra reported by Sebastian *et al.* in previous studies [Chem. Phys. **61**, 125 (1981)], and leads us to reconsider the excitonic structure including the location of charge-transfer excitons. Nonlinear π-electronic response is discussed based on second-order electro-optic (Kerr) spectra.

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Electromodulation spectroscopy is a well-established technique for detecting slight changes in the optical-absorption spectrum of materials in an electric field.[1] The method is useful for unraveling the electronic states of semiconductors through the modulation of interband electronic excitation: as an example, oscillatory (Franz-Keldysh) features are observed in inorganic semiconductors such as Si or GaAs and are ascribed to band-edge optical absorption.[1,2] In the case of small-molecule organic semiconductors, several studies have been reported so far such as for acenes,[3] phthalocyanine,[4] and C_{60},[5] where the simple Stark shift of Frenkel exciton absorption demonstrates the strong excitonic effects in this class of materials.[6] Additionally, hidden or forbidden optical transitions can be retrieved through symmetry breaking of the system in an electric field.[7] Furthermore, it has been suggested that some spectral features appearing at higher energy should be ascribed to charge-transfer (CT) excitons in cases where the features do not simply follow the first derivative curve of the absorbance spectrum.[3,8] In these earlier studies, however, less attention was paid to some crucial issues, particularly carrier injection into the semiconductor from the electrodes as well as the quality of the semiconductor films. For example, the electroabsorption (EA) spectra of pentacene were measured on amorphouslike thin films with directly attached electrodes in surface cell geometry.[3,9] These issues are now more clearly understood due to the recent rapid progress in small-molecule organic thin-film transistors (OTFTs).[10]

Here, we report pure electric-field effects on the excitonic absorbance spectrum of undoped pentacene thin films by using field-effect device structures, in order to reinvestigate the excitonic structure of pentacene. We found that the use of unipolar device structures allowed us to separate and eliminate the effects of charge accumulation. The results show that the field-modulated spectra can be fitted fairly well to the first derivative curve of the Frenkel exciton absorption over the entire range between 1.8 and 2.6 eV, in sharp contrast to previous studies. Although pentacene can exhibit a rather high charge-carrier mobility and nearly bandlike conduction, we show that the optical-absorption spectrum is dominated by the lowest Frenkel, thus *localized*, excitonic absorption. We also discuss the fundamental electro-optic effects in terms of the Stark shift of the Frenkel exciton absorption and the nonlinear electric susceptibility.

In the experiment, we used semitransparent field-effect devices (*p*-type pentacene TFTs), schematically depicted in Fig. 1(a). The devices are composed of fused silica or CaF_2 as the substrate, Au (4.5 nm)/Ti (1 nm) as the gate electrode, parylene-C (100–200 nm) as the gate dielectric layer, a semiconducting pentacene layer (50–60 nm) and semitransparent Au (7–8 nm) as source/drain electrodes. The thickness of the parylene layer was kept below 200 nm in order to prevent the dominant occurrence of Fabry-Perot interference; the effect has been found to produce large modulation signals.[11] The pentacene layer was evaporated at a rate of 0.25–0.5 Å/s and a pressure of 1×10^{-6} mbar to obtain polycrystalline thin films composed of dendritic grains about 200–600 nm in size.[12] All device fabrication and measurement processes after parylene deposition were carried out without exposure to air by using a glove box and a continuous-flow cryostat (Oxford Microstat). For the optical measurements, we used a Cassegrain-type microscope system combined with a grating monochromator. The monochromatized light was focused onto one of the semitransparent top electrodes and the trans-

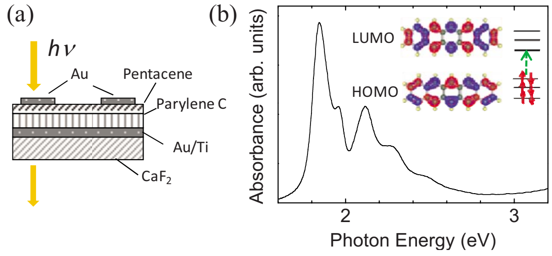

FIG. 1. (Color online) (a) Schematic of the semitransparent pentacene TFT device for optical measurements in transmittance. (b) Absorbance of a pentacene film on fused silica, with a schematic of the HOMO-LUMO optical excitation.

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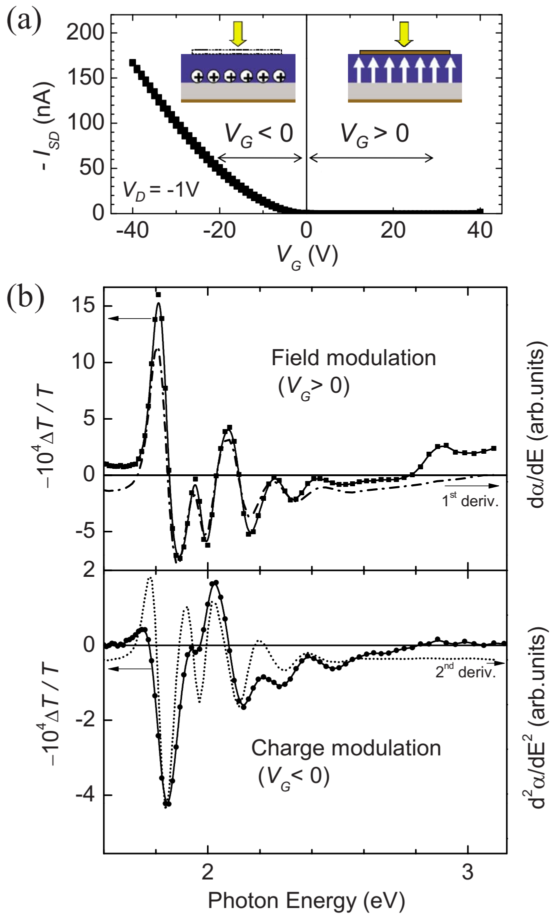

FIG. 2. (Color online) (a) Electrical transfer characteristic of the unipolar pentacene TFT. The insets show schematics for $V_G<0$ and $V_G>0$, corresponding to charge and field modulation, respectively. (b) Field-modulated and charge-modulated absorption spectra.

mitted light was detected by a Si photodiode (UV/VIS) or an InAs detector (NIR). Square-wave gate bias pulses between 0 and V_G were applied at frequencies of 0.1–1.0 kHz,[13] and the modulated transmittance signal (ΔT) was detected by lock-in technique to obtain the modulated absorption spectra $\Delta\alpha d=-\Delta T/T$ (α is the absorption coefficient, d the film thickness, and T the transmittance signal).

Figure 2(b) presents the modulated spectra under negative and positive gate biases. It is clear that the spectra are much different from each other, due to the unipolar nature of the pentacene OTFTs. From a comparison with the transfer curve [Fig. 2(a)], it is evident that the charge density is modulated by applying a negative gate bias whereas field modulation is achieved by applying a positive gate bias. It is also found that the field-modulated features of the whole spectrum are very similar for various electric-field strengths, as presented in Fig. 3. The amplitude of the field-induced change in the absorption $\Delta\alpha$ is proportional to the square of the positive gate bias, as shown in the inset of Fig. 3 while that for the charge modulation is proportional to the negative gate bias. It is concluded that the use of TFT devices allowed us to obtain pure electric-field modulation, by eliminating the hole injection. We note here that such discrimination of charge and field effects has been discussed for metal-insulator-semiconductor (MIS) devices based on unintentionally doped poly- and oligothiophenes,[14,15] where the full depletion mode should correspond to the field modulation of nominally intrinsic semiconductors in the present study.

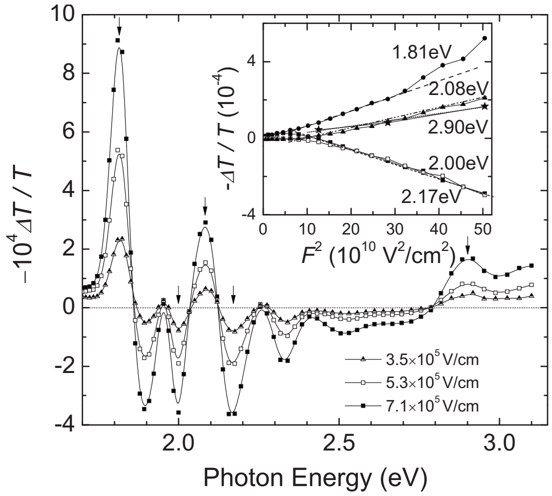

FIG. 3. Field-modulation spectra for various electric-field strengths. Inset: electric-field dependence.

The obtained $\Delta\alpha$ spectrum by field modulation closely resembles the first derivative of the absorbance, as presented in Fig. 2(b). This indicates that the excitonic absorption experiences a homogeneous quadratic Stark effect with an energy shift of ΔE and change in absorption $\Delta\alpha=d\alpha/dE\ \Delta E$, over the entire range between 1.8 and 2.6 eV. The ΔE shift for all spectral features is quite uniform and reaches about 0.12 meV at the maximum applied electric field of $\sim 6\times 10^5$ V/cm within the pentacene film. The features strongly suggest that only a single electronic transition including its vibronic progression appears in the spectrum within the UV/VIS range. Note that the transition dipole for the lowest electronic excitation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is polarized parallel to the molecular short axis,[16] and therefore lies within the plane of the pentacene polycrystalline thin film with the (001) direction perpendicular to the substrate.[17] The peak at 1.85 eV and the shoulder at 1.97 eV are due to the 0–0 intramolecular HOMO-LUMO excitation, where the former corresponds to a Davydov component with polarization along a in the pentacene unit cell, and the latter to another Davydov component along b.[18,19] The latter shows strong vibronic progression with major components of 150–190 meV (1200–1600 cm^{-1}), which most likely originate from aromatic C=C stretching and C—H bending modes,[20] although the assignment of the lower-energy component is still unclear.

Next, we present the quantitative evaluation results for the excitonic Stark shift in terms of the second-order electro-optic Kerr effects. For this purpose, we converted the $\Delta\alpha$ spectrum into the nonlinear electric susceptibility $\chi^{(3)}(-\omega;\omega,0,0)$.[21] We evaluated the difference extinction coefficient Δk spectrum from the field-modulated $\Delta\alpha$ spectra. After Kramers-Kronig transformation of the $\Delta\alpha$ spectrum into the Δn spectrum, the third-order nonlinear electric

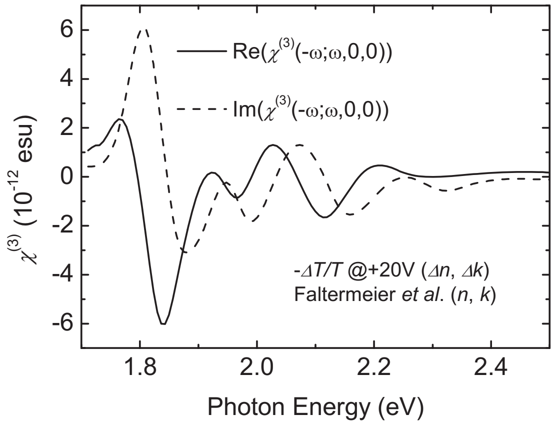

FIG. 4. Real and imaginary parts of the third-order nonlinear optical susceptibility, as derived from field modulation according to Videlot *et al.* (Ref. 21)

susceptibility $\chi^{(3)}(-\omega;\omega,0,0)$ can be expressed by the following relationships:[21]

$$\mathrm{Re}[\chi^{(3)}(-\omega;\omega,0,0)] = \frac{n\Delta n - k\Delta k}{2\pi F^2},$$

$$\mathrm{Im}[\chi^{(3)}(-\omega;\omega,0,0)] = \frac{k\Delta n + n\Delta k}{2\pi F^2}. \qquad (1)$$

Here, we used n and k as reported in literature,[22] and F is the electrical field strength. The real and imaginary parts of the $\chi^{(3)}(-\omega;\omega,0,0)$ spectrum are plotted in Fig. 4. Note that the electro-optic responses are ascribed to the intrinsic nature of insulating pentacene. Comparable to the values for thin films of oligothiophenes,[21] we find a nonlinear susceptibility of 6×10^{-12} esu. Such a comparatively large electro-optic effect is characteristic of organic π-electronic materials, owing to the high polarizability of the extended electron system.[23] The particularly large dipole moment between the ground state and Frenkel exciton as well as the dipole moment between the Frenkel exciton and higher forbidden excited states should be responsible for the nonlinearity. Such nonlinear electric response has recently been used for detecting the dynamic nature of insulating regions by using time-resolved microscopic optical second-harmonic generation;[24] the method provides a unique approach for studying the transient electric-field distribution in the channels of pentacene OTFTs.

Returning to the field-modulated $\Delta\alpha$ spectrum, the observed spectrum is clearly very different from that in previous studies.[3] The reported spectrum was composed of two separate ranges where the features in the low-energy range (1.8–2.0 eV) follow the first derivative of the absorption spectrum while the high-energy range (2.0–2.4 eV) could be fitted by the second derivative. It was proposed that these two ranges should be ascribed to the Frenkel and CT excitons, respectively. Nonetheless, it was also pointed out that the latter assignment and such range splitting by itself could be problematic due to the overlap with vibronic satellites of the Frenkel exciton.[25] In striking contrast, our experimental results clearly indicate that no CT exciton formation could be identified around 2.0–2.4 eV in pentacene polycrystalline films, although the crystallinity and thereby the intermolecular CT should be even more enhanced compared to that reported in previous studies on amorphous films. Our conjecture is that the previous studies might have detected spectral broadening around 2.0–2.4 eV due to the amorphous nature of the films as well as to charge injection; in general, a second derivativelike curve is obtained by spectral broadening.

In the spectra, another field-induced feature is clearly detected at 2.95 eV, around which the pentacene absorption spectrum exhibits no particular feature. In accordance with EA measurements in other molecular materials, we could ascribe the induced absorption to the activation of an optically forbidden transition,[7] most probably associated with the interaction with higher CT exciton states or free-electron-hole pair generation. The results indicate that the electron-hole binding energy in the Frenkel exciton is as large as 1 eV. This value is consistent with the binding energy for polymers.[26,27] Although pentacene can exhibit a high charge-carrier mobility and nearly bandlike conduction, we showed that the optical-absorption spectrum is dominated by the lowest localized (Frenkel) excitonic absorption due to the strong electron-hole Coulomb interactions. This shows that either the localized or delocalized nature of charges can be highlighted, depending on the experimental method.[28] Actually, a very recent study illustrated that single-grain 6,13-bis(triisopropylsilylethynyl) (TIPS)-pentacene TFTs show clearly bandlike transport properties whereas (charge modulation) spectroscopy revealed the strongly localized character of the mostly trapped accumulated charge carriers.[29] According to photoconductivity measurements in pentacene, in contrast, charge-carrier generation should occur above around 2.2 eV.[30] There has been much debate as to whether or not the intrinsic charge-carrier generation in molecular crystals after the excitation of a Frenkel exciton located energetically near the conduction-band transition is buried under the exciton transition. The issue has become critically important for the design of efficient organic photovoltaic cells. Our results may imply that free-electron-hole states should be generated by autoionization of a localized excited molecular state followed by thermalization,[30] possibly due to the branching between ionizing and nonionizing transitions.[3]

In summary, pure electric-field effects on the excitonic absorbance of pentacene thin films are presented as measured by unipolar field-effect devices. We found that the use of TFT/MIS structures allowed us to clearly separate these effects from charge accumulation effects. The results show that the field-modulation spectrum is dominated by the Stark shift of the absorbance from the lowest Frenkel exciton over the entire range between 1.8 and 2.6 eV whereas no sign of a CT exciton was observed in this energy range. Based on the measurements, we also evaluated the fundamental electro-optic response, which reaches as high as 6×10^{-12} esu for $\chi^{(3)}$. Finally, we observed a field-induced feature at higher energy around 2.95 eV, and the present results suggest that the electron-hole binding energy should be as large as 1 eV. This indicates that the excitonic effects are much greater than those previously discussed, although the material has recently shown nearly bandlike conduction.

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*t-hasegawa@aist.go.jp

[1] H. T. Grahn, *Introduction to Semiconductor Physics* (World Scientific, Singapore, 1999).

[2] G. T. Reed and A. P. Knights, *Silicon Photonics: An Introduction* (Wiley, West Sussex, UK, 2004).

[3] L. Sebastian, G. Weiser, and H. Bässler, Chem. Phys. **61**, 125 (1981).

[4] Y. Tokura, T. Koda, Y. lyechika, and H. Kuroda, Chem. Phys. Lett. **102**, 174 (1983).

[5] B. C. Hess, D. V. Bowersox, S. H. Mardirosian, and L. D. Unterberger, Chem. Phys. Lett. **248**, 141 (1996).

[6] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, Oxford, 1999).

[7] T. Koda, A. Ishiguro, N. Kaneta, H. Kishida, Y. Tokura, and K. Ishikawa, Synth. Met. **71**, 1723 (1995).

[8] L. M. Blinov, S. P. Palto, G. Ruani, C. Taliani, A. A. Tevosov, S. G. Yudin, and R. Zamboni, Chem. Phys. Lett. **232**, 401 (1995).

[9] Both surface cell and sandwich-type samples have been frequently used in electroabsorption measurements. In a comparative study, it has been pointed out that the surface cell geometry more likely suffers from inhomogeneous electric-field distributions [C. Videlot-Ackermann *et al.*, Appl. Surf. Sci. **253**, 1517 (2006)]. Therefore, the sandwich-type geometry (in which the field direction corresponds to the direction in our study) might exhibit higher resolution.

[10] For a recent review, see D. Braga and G. Horowitz, Adv. Mater. **21**, 1473 (2009), and references therein.

[11] H. Matsui and T. Hasegawa, Appl. Phys. Lett. **95**, 223301 (2009).

[12] H. Matsui and T. Hasegawa, Jpn. J. Appl. Phys. **48**, 04C175 (2009).

[13] In this frequency range, no phase shift between the applied modulation voltage and measured signal could be observed; therefore, the out-of-phase component was basically zero and only the in-phase signal was evaluated.

[14] P. J. Brown, H. Sirringhaus, and R. H. Friend, Synth. Met. **101**, 557 (1999).

[15] M. G. Harrison, R. H. Friend, F. Garnier, and A. Yassar, Synth. Met. **67**, 215 (1994).

[16] M. L. Tiago, J. E. Northrup, and S. G. Louie, Phys. Rev. B **67**, 115212 (2003).

[17] C. D. Dimitrakopoulos, A. R. Brown, and A. Pomp, J. Appl. Phys. **80**, 2501 (1996).

[18] V. Zanker and J. Preuss, Z. Angew. Phys. **27**, 363 (1969).

[19] M. Brinkmann, S. Graff, Ch. Straupe, J. C. Wittmann, Ch. Chaumont, F. Nuesch, A. Aziz, M. Schaer, and L. Zuppiroli, J. Phys. Chem. B **107**, 10531 (2003).

[20] T. M. Halasinski, D. M. Hudgins, F. Salama, L. J. Allamandola, and T. Bally, J. Phys. Chem. A **104**, 7484 (2000).

[21] C. Videlot-Ackermann, T. Isoshima, A. Yassar, T. Wada, H. Sasabe, and D. Fichou, Synth. Met. **156**, 154 (2006).

[22] D. Faltermeier, B. Gompf, M. Dressel, A. K. Tripathi, and J. Pflaum, Phys. Rev. B **74**, 125416 (2006).

[23] *Nonlinear Optics of Organic Molecules and Polymers*, edited by H. S. Nalwa and S. Miyata (CRC Press, USA, 1997).

[24] T. Manaka, E. Lim, R. Tamura, and M. Iwamoto, Appl. Phys. Lett. **87**, 222107 (2005).

[25] B. Petelenz, P. Petelenz, H. F. Shurvell, and V. H. Smith, Jr., Chem. Phys. **119**, 25 (1988).

[26] S. Polymers, in *Chemistry, Physics and Engineering*, 2nd ed., edited by G. Hadziioannou and G. Malliaras (VCH-Wiley, Weinheim, 2006), Vol. 1.

[27] T. Hasegawa, Y. Iwasa, H. Sunamura, T. Koda, Y. Tokura, H. Tachibana, M. Matsumoto, and S. Abe, Phys. Rev. Lett. **69**, 668 (1992).

[28] S. Fratini and S. Ciuchi, Phys. Rev. Lett. **103**, 266601 (2009).

[29] T. Sakanoue and H. Sirringhaus, Nature Mater. **9**, 736 (2010).

[30] E. A. Silinsh and V. Čápek, *Organic Molecular Crystals* (AIP Press, New York, 1994).