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Giant Enhancement of Excitonic Electrooptic Response in Trap-Reduced Organic Transistors

Satoshi Matsuoka¹, Jun'ya Tsutsumi², and Tatsuo Hasegawa¹

¹*Department of Applied Physics, The University of Tokyo, Tokyo, 113-8656, Japan*

²*Research Institute for Advanced Electronics and Photonics (RIAEP), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan*

Abstract

Organic field-effect transistors (FETs) exhibit excellent switching characteristics when they involve trap-eliminated semiconductor interfaces with highly hydrophobic gate dielectric layers. In this study, we investigated the excitonic electrooptic response by delocalized carrier accumulation at the trap-eliminated interfaces of pentacene single-crystal FETs. We found that gate modulation (GM) imaging, which sensitively visualizes the variation in optical microscope images between the gate-on and gate-off states, exclusively reveals the unique enhancement of electrooptic response under the application of drain voltages (V_d). The V_d -unbiased GM image exhibits a uniform spatial distribution, which is consistent with the accumulated carrier density in the channel. In contrast, the V_d -biased GM image presents a peculiar spatial distribution with fairly sharp increases around the edges of the source/drain electrodes. Furthermore, the following intriguing features were observed: 1) The sharp increase in the GM signal distribution around the electrode edge is similar to the lateral electric field distribution as measured by Kelvin probe force microscopy, and 2) the GM spectra, extracted from the respective GM images measured at different wavelengths, present a second-derivative-like shape that implies the broadening of exciton absorption. Based on these observations, we investigated the origin of this unique effect in terms of the enhanced violation of exciton coherence by delocalized carrier accumulations under drain bias. The gate-induced holes that are weakly bound to shallow traps should be detrapped by lateral electric fields, which eventually generate valence band holes and thus enhance the electrooptic response. These findings should elucidate the spatial coherence of the molecular excitons that are responsible for the various unique photoelectric characteristics of organic electronic devices.

I. INTRODUCTION

The absorption band of small-molecule organic semiconductors (OSCs) in the visible range originates, in most cases, from molecular (or Frenkel) excitons associated with the lowest electronic excitation of intramolecular π -conjugated electronic systems [1, 2]. The unique nature of molecular excitons in crystalline OSCs is that the electron–hole relative motion is confined (or localized) to the respective molecules, whereas the exciton wavefunctions are coherently extended over the entire crystal through intermolecular Coulomb interactions and concomitant exciton band formation. When charge carriers are injected and accommodated in OSCs, the excitonic optical responses should undergo a unique variation. Charge-modulation spectroscopy (CMS) based on field-effect transistor (FET) device structures is known as a unique method for probing tiny changes in exciton absorption spectra caused by gate-induced charge carrier accumulations [3–9]. However, despite the high usability of CMS, the spectral features of several small-molecule OSCs are often complicated and not well understood; this is because of the bleaching [3–5, 9], energy shift [6–8], or splitting [5, 6, 9] of the original exciton absorption.

Recently, an innovative technique, referred to as gate-modulation (GM) imaging, was developed to obtain spatially resolved electrooptic responses of channel OSC layers via highly sensitive and collective sensing of difference optical microscope images between the gate-on and gate-off states [10–15]. Using this imaging technique, it was reported that the microscopic GM signals of pentacene polycrystalline thin films exhibit a markedly inhomogeneous spatial distribution, including drastic sign changes over the intragrain and grain boundaries [16, 17]. The observed spectral features could be ascribed to inhomogeneous trap distributions between the inside and boundary of the grains. The results indicate that the rather complicated spectral features of the usual CMS, as stated above, originate from such spatially inhomogeneous GM signals. However, it is not yet clear how the trap density affects the variation of the excitonic electrooptic response of molecular semiconductors by charge accumulation. The issue is of fundamental and critical importance, as it is closely associated with the effect of the spatial coherence of molecular excitons on the unique photoelectric characteristics of organic electronic devices.

In this study, we report that an unexpectedly large excitonic electrooptic response is observed using clean and trap-eliminated single-crystal semiconductor interfaces of pentacene. We utilized the most hydrophobic amorphous perfluoropolymer, Cytop, as the gate dielectric. Notably, Cytop has recently been reported to provide organic FETs with excellent switching characteristics at low operational voltages owing to the elimination of interfacial carrier trap states [18, 19]. In particular, we found that the variation in exciton absorption was considerably enhanced by the multiple application of gate and drain potentials in single-crystal devices. We discuss the origin of the enhanced excitonic response in terms of the effects of both delocalized carrier accumulation and lateral field application on molecular excitons that have extended the spatial coherence of wave

functions at the OSC interfaces.

II. EXPERIMENT

High-quality flake-like pentacene single crystals were grown by the physical vapor transport (PVT) technique, as schematically depicted in Fig. 1 [20–22]. The growth was achieved with a source temperature of 560 K and N_2 gas flow of $30 \text{ cm}^3\text{min}^{-1}$ for 10 hours. In the device fabrication, a Cytop layer with a thickness of either 250 or 400 nm was fabricated on semi-transparent substrates composed of quartz glass and an ultrathin gold gate electrode with a thickness of 6 nm. After gold source and drain electrodes were formed, the pentacene single crystals were laminated on top of the Cytop layer. The obtained device exhibits a sharp switching characteristic from approximately 0 V, with a small subthreshold swing (SS) value of 0.2 V dec^{-1} , mobility of $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and negligible hysteresis [23, 24]. The small SS value is ascribed to the low interfacial trap density associated with both the low surface free energy and the low bulk permittivity [18, 25].

The GM imaging measurements were conducted with a home-assembled apparatus of an optical microscope and a highly sensitive CMOS area image sensor. The FET devices were irradiated with monochromatic light from a halogen light source. The transmitted optical images were captured by the CMOS sensor in synchronization with the square-wave modulated gate bias alternating between 0 V (gate-off state) and -80 V (gate-on state) at 40 Hz. We obtained the GM images by the difference image between these states. The states were presented with respect to $\Delta T/T$, where T and ΔT are the optical transmittance of the device and variation of the transmittance owing to the modulated gate bias in each pixel, respectively. The obtained GM images were integrated 2^{14} (=16,384) times to reduce noise and visualize the GM signal clearly.

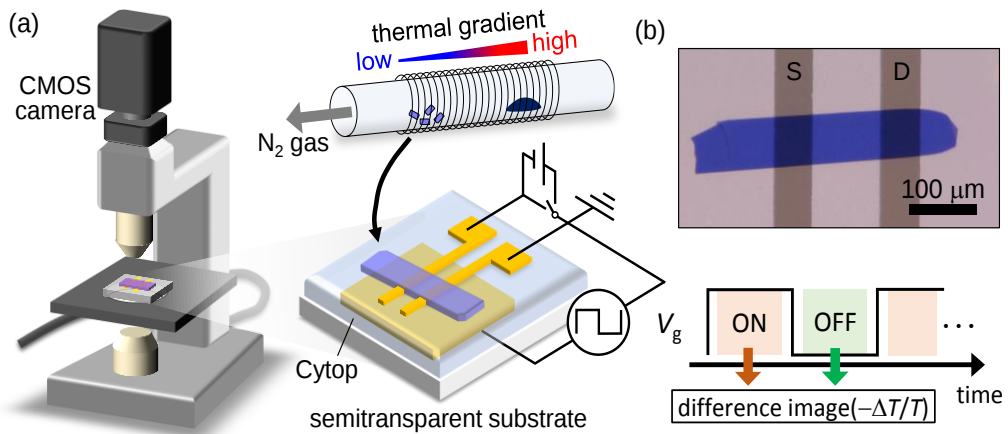


FIG. 1 (a) Schematics for a setup of GM imaging measurements, a furnace of the PVT, and a single crystal FET, which is composed of a Cytop gate dielectric, which were used for the GM imaging measurements. (b) An optical micrograph of a pentacene single crystal FET.

As a reference device, we manufactured polymer FETs based on the typical donor-acceptor-type copolymer, poly{3,6-dithiophen-2-yl-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-alt-hienylenevinylene-2,5-yl} (PDVT-10) [26]. We used the same semitransparent substrates composed of a Cytop gate dielectric layer, as mentioned above. The semiconductor channel layer was coated using the push coating technique [27]. The device exhibits excellent transfer characteristics with a mobility of $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and negligible hysteresis.

III. RESULTS AND DISCUSSION

A. Enhancement of GM signal under drain fields

Figure 2 presents the GM images of a pentacene single crystal FET obtained at a wavelength of 670 nm (photon energy 1.85 eV), which roughly corresponds to the peak energy of exciton

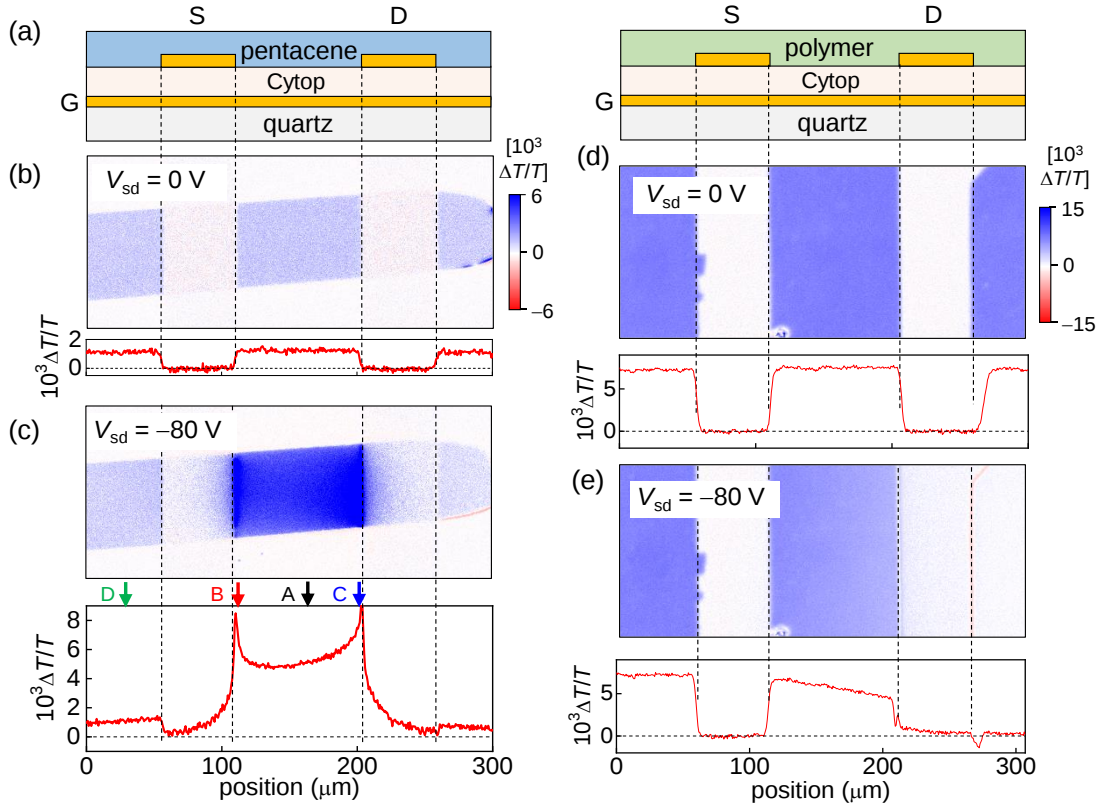


FIG. 2 (a) Cross-sectional schematics of pentacene (left) and polymer (right) FETs used for GM imaging measurements. (b–e) Microscope GM images of the pentacene single crystal FET (b, c) and the PDVT-10 FET (d, e), obtained with a modulated gate bias at $V_{g_mod} = -80 \text{ V}$ without drain bias (b, d) and with dc drain biases at $V_{d_dc} = -80 \text{ V}$ (c, e). Profiles of GM signal distribution along the semiconducting channel layer are extracted from the respective GM images, and are presented in the lower panel of each microscope GM image.

absorption [28, 29]. The device exhibits a rather uniform spatial distribution of the GM signal ($\Delta T/T \sim 1 \times 10^{-3}$, blue-colored) over the entire channel, with a clear step rise at the electrode edge, when the drain field is not applied (*i.e.*, the drain potential is the same as the source potential). The sign of the observed GM signal is positive, indicating an increase in transmittance, and the signal intensity is proportional to the modulated gate bias (or the accumulated carrier density), as seen in Fig. 4(d). The results indicate that a decrease in exciton absorption is ascribed to charge accumulation within the channels.

The most intriguing observation is that the device exhibits an enhanced GM signal owing to the application of the drain bias, as presented in Fig. 2(c). The GM signal intensity under the drain bias is approximately five times larger than that without the drain bias. Notably, these observations are contradictory to the naive presumption that the GM signal should be proportional to the accumulated carrier density: according to the general understanding of FET operation, the total number of charge carriers under the drain bias should be smaller than that without the drain bias. The carrier density under the saturation regime should decrease almost linearly with the distance from the source electrode edge (as expressed by the gradual channel approximation) and should be completely depleted at the pinch-off point near the drain electrode edge. Thus, the enhanced GM signal is not consistent with the pure concept of carrier accumulation within the channels.

The observed GM image also presents a peculiar spatial distribution of the GM signal within the channel: the signal exhibits fairly sharp increases at both electrode edges; further, it increases gradually from the source to the drain. When the source and drain electrodes are interchanged, the above profile is clearly reversed with regard to the center of the channel. We also noticed that on the source and drain electrodes, the GM signal distribution exhibits a tail-like decay with increasing distance from the channel in both directions, although no GM signal is observed on the electrodes without a drain bias. This observation is in contrast to the general assumption that the GM signal should be proportional to the accumulated carrier density because the carrier density should be substantially small on top of the source and drain electrodes, even with drain biases.

Here, we note that the GM signal is not detectable when the gate voltage is not biased, even if the drain voltage is modulated. This indicates that the pure field modulation (or electro-absorption) signal is much lower than the observed GM signal. Therefore, the observed substantial enhancement of the GM signal under the drain bias is attributable to the effect of biased drain fields on the accumulated charge carriers. Such an enhancement in the electrooptic response, realized by a combined application of drain and gate potentials, has not been reported, to date, for any material or device. It is important to note that no such enhancement was observed in pentacene polycrystalline FETs with hydrophilic silicon dioxide gate dielectrics [16, 17], or in pentacene-single-crystal FETs composed of typical polymer gate dielectrics, such as PMMA or *c*-PVP.

We conducted similar GM imaging measurements for the FET composed of a PDVT-10 channel

layer and a Cytop gate dielectric layer. Figures 2(d) and 2(e) present the observed GM images without and with drain bias, respectively. The results are shown for the measurements at a wavelength of 830 nm (photon energy 1.49 eV), which corresponds to the absorption peak due to HOMO-LUMO excitation. The GM signal distribution without the drain bias is homogeneous over the entire channel, similar to the case of the pentacene single-crystal FET. Meanwhile, no enhancement is observed in the GM response in the case with the drain bias: the GM signal gradually decreases almost linearly with the distance from the source electrode edge to the drain electrode edge, the distribution of which seems to obey the gradual channel approximation of the carrier density within the channel. This result implies that the device with the Cytop gate dielectric layer does not necessarily enhance the GM signal. We consider that the enhancement effect should manifest itself only in the case of highly delocalized carriers accumulated at the trap-eliminated semiconductor–dielectric interfaces.

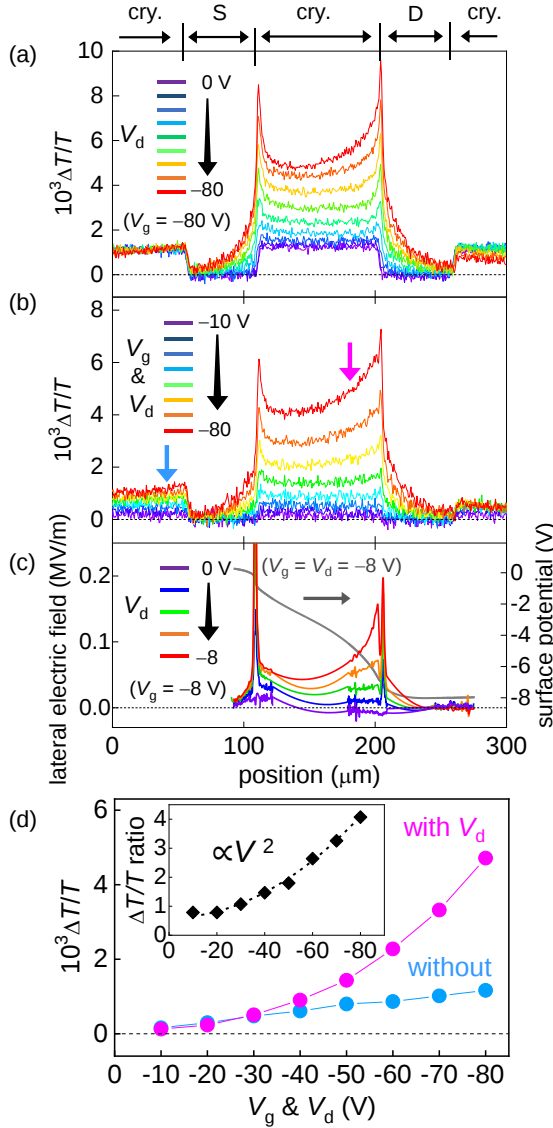


FIG. 3 (a) Bias-dependent GM signal profiles along the channel layer of pentacene single-crystal FET with Cytop gate dielectric layer, measured at different dc drain biases ($V_{d_dc} = 0 \sim -80$ V) under the same modulated gate bias ($V_{g_mod} = -80$ V) and (b) under modulated drain and gate biases ($V_{d_mod} = V_{g_mod} = -10 \sim -80$ V). (c) Lateral electric field distributions derived from the spatial differentiation of surface potential (which is shown by a gray curve), measured at different dc drain biases ($V_{d_dc} = 0 \sim -8$ V) and at constant dc gate bias ($V_{g_dc} = -8$ V) by Kelvin probe force microscopy. (d) Variations of GM signal intensity are plotted as a function of modulated gate bias: with modulated drain bias (pink) and without drain bias (light blue) and the ratio between the cases with and without the drain bias (inset).

B. Drain-bias dependent GM signal and lateral field distribution

Figure 3 presents the profiles of GM signal distributions measured at 1.85 eV with different combinations of dc and modulated-ac biases. Note that the GM signal observed outside the source electrode, as shown in Figs. 3(a) and 3(b), can be utilized as a reference GM signal without the drain bias, which is only proportional to the applied modulated gate bias. From the comparisons, the ratio of the GM signals with and without the drain bias was estimated, the result of which is shown in the inset of Fig. 3(d). The ratio shows a clear square dependence on the applied drain bias. Eventually, the GM signal presents a cubic dependence on the modulated bias when the drain and gate are equipotential, and both are used as the modulated bias.

We also conducted Kelvin probe force microscopy measurements [30, 31] to investigate the lateral electric field distribution within the channel, the results of which are shown in Fig. 3(c). The strong lateral fields around the electrode edges are because of the large potential drops, either associated with the contact resistance or the pinch-off state around the drain electrode. In particular, the field distribution profile exhibits a fairly sharp rise around the electrode edge, and such features are quite similar to those of the GM signal profile.

C. Spectral analyses of GM signal under drain fields

GM (or CMS) spectra of pentacene single crystals both with and without drain biases were extracted from the respective GM images measured at different wavelengths, the results of which are shown as $-\Delta T/T$ ($=\Delta\alpha d$; variation of absorbance multiplied by layer thickness d) spectra in Fig. 4. The GM signal is clearly enhanced under the drain bias over the entire photon energy region of the exciton absorption. The spectral features observed around the main exciton absorption peak at 1.7–1.9 eV are quite similar to each other for all the spectra measured at different positions with the drain biases (at areas A, B, and C) and without the drain bias (at area D), despite the considerable difference in signal intensity. This feature is roughly consistent with the second derivative of the original exciton absorption spectrum, and can be attributed to the spectral broadening of the exciton absorption owing to carrier injection [9]. By contrast, a distinct difference between the GM (or CMS) spectra obtained with and without the drain bias is observed at the higher energy side, at approximately 1.9–2.1 eV, while the spectral features are roughly common to all the channel positions under the drain bias (at areas A, B, and C). We consider that the spectral feature newly observed under the drain bias could be ascribed to the generation of free electron–hole pairs, as referred later [32].

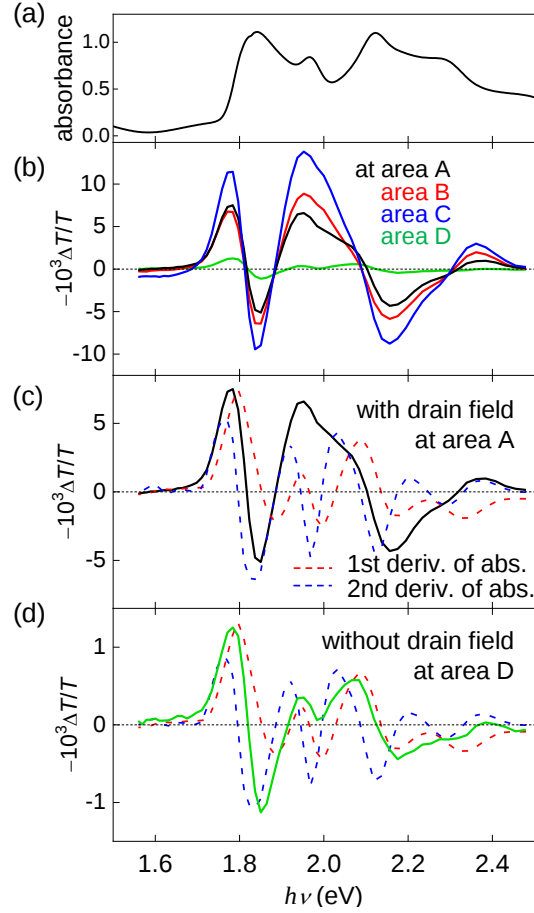


FIG. 4 (a) Optical absorption spectrum and (b) GM spectra measured at different positions with the drain biases (at areas A, B, and C, as depicted in Fig. 2(c)) and without the drain bias (at area D), for pentacene single-crystal FETs with Cytop gate dielectric layer. Comparisons of the GM spectra measured (c) with and (d) without drain biases, with the first and second derivatives of the absorption spectrum (red and blue dashed curves, respectively).

D. Origin of enhanced GM signal under drain fields

The square electric field dependence of the electrooptic response, as shown in Fig. 3(d), is frequently observed in electro-absorption measurements, such as the Franz–Keldysh effect [33,34], the Stark effect [6-8] and/or the quantum-confined Stark effect [35-37]. However, the lateral electric field applied in the present device (0.8 MVm^{-1}) is much smaller than the applied electric fields used in the conventional electro-absorption measurements (5.6 MVm^{-1}). Furthermore, the first-derivative-like component due to the Stark shift of the exciton absorption is not observed in the enhanced GM spectra, as evidenced in this study. Thus, it is clear that the enhanced GM signal does not originate from the electro-absorption; rather, it originates from the multiplicative effect, which is only observed by the field application on highly delocalized carriers at semiconductor-dielectric interfaces.

Second-derivative-like CMS spectra, observed around the main exciton absorption, were reported for highly ordered polymeric semiconductors, including PDVT-10 [9]. It was indicated that the second-derivative-like spectra should originate from the broadening of the original exciton absorption, and should be ascribed to the effect of carrier accumulations for violating the exciton coherence. Thus, the observation of enhanced second-derivative-like CMS spectra under the drain bias indicates that the application of drain potential should be effective in enhancing the effect of accumulated carriers on the exciton coherence over a wider area of channels. As the carriers injected into the channel layers are accommodated at carrier traps located within the channels or channel interfaces in organic FETs, the change in exciton absorption should be ascribed to the change in exciton coherence around the trapped carriers. These carriers should be delocalized or very weakly localized in trap-eliminated single-crystal FETs composed of Cytos. Therefore, it is reasonable to consider that the lateral electric fields should help to detrap the holes, which are weakly bound to shallow traps, into valence band states that have larger spatial extensions in the crystals, as shown in Fig. 5. In fact, the appearance of spectral features at 1.9–2.1 eV should be closely associated with the enhancement of free electron–hole pair generation within the channels [32]. The generation of holes in the valence bands should increase the effective number of molecules that are affected by the holes, which eventually leads to the enhancement of the GM signal. In this context, we suggest that the observed considerable enhancement effects should be correlated with the giant oscillator strength effect, which was introduced to describe enhanced exciton absorption owing to isotopic impurities

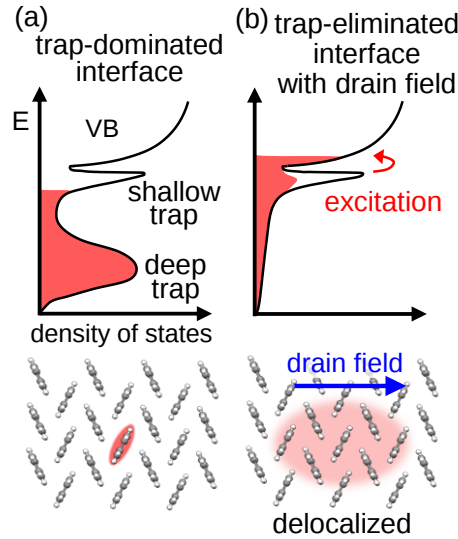


Fig. 5 (a) Schematics for charge carrier distributions near valence band states (a) in conventional trap-dominated organic FETs, and (b) in trap-eliminated organic FETs under drain bias. Top: Excitation of holes from the shallow trap states to the valence band states owing to the drain field. Bottom: Spatial extensions of carriers within organic crystals in the respective cases.

with shallow discrete levels near the exciton band [2, 38], in which the exciton coherence with spatial extension plays a critical role. Although the detailed enhancement mechanism remains uncertain, the enhancement effect of the GM signal observed in this study is quite intriguing and promising for elucidating the unexplained physical phenomena of the excitonic responses in molecular crystals.

IV. Summary

We observed the unique excitonic electrooptic response of organic semiconductors due to electric field applications on highly delocalized carriers. We utilized trap-eliminated organic FETs composed of fairly clean semiconductor–dielectric interfaces between the most hydrophobic amorphous perfluoropolymer, Cytop, and high-quality flake-like single crystals of pentacene. We found that the GM image, which sensitively visualizes the variation of the optical microscope image between the gate-on and gate-off states, exhibits a significant signal enhancement and peculiar distribution under the application of the drain voltage (V_{sd}). The V_{sd} -unbiased GM image exhibits a rather uniform spatial distribution over the entire channel, whereas the V_{sd} -biased GM image presents a peculiar spatial distribution whose feature is fundamentally different from the distribution of the accumulated carrier density within the channel. The V_{sd} -biased GM signal distribution exhibits fairly sharp increases at the edges of the source/drain electrodes, the feature of which is rather similar to the distribution profiles of the lateral electric field, as observed by Kelvin probe force microscopy. No such feature is obtained in the case of semiconducting polymer FETs composed of a Cytop gate dielectric layer.

We assessed the origin of the observed unique electrooptic effect in terms of the enhanced violation of exciton coherence by delocalized carrier accumulations. We consider that the enhanced effect under drain bias is associated with the detrapping of holes that are weakly bound to shallow traps, which eventually generate valence band holes. The band holes have larger spatial extensions than the trapped holes; therefore, the detrapping effect should more considerably affect the molecular exciton absorption. In particular, the exciton coherence should be reduced by the delocalized carrier accumulations, which results in the broadening of the exciton absorption. This is consistent with the observed second-derivative-like GM spectra of the main exciton absorption. Such an intriguing enhancement effect in the electrooptic response has not been reported to date for any material or device. We believe that our findings should significantly advance progress in understanding the spatial coherence of the molecular excitons that are responsible for the various unique photoelectric characteristics of organic electronic devices.

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