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Optically and Electrically Driven Organic Thin Film Transistors with Diarylethene Photochromic Channel Layers

Ryoma Hayakawa,[†] Kenji Higashiguchi,[‡,§] Kenji Matsuda,*[,‡] Toyohiro Chikyow,[†] and Yutaka Wakayama*[,†,⊥]

[†]International Center for Materials Nanoarchitechtonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

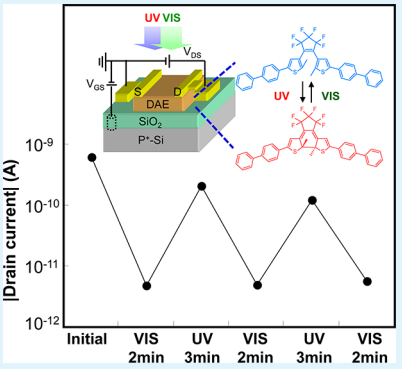
[‡]Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

[§]PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan

[⊥]Department of Chemistry and Biochemistry Faculty of Engineering, Kyushu University, 1-1 Namiki, Tsukuba 305-0044, Japan

Supporting Information

ABSTRACT: We achieved drain-current switching of diarylethene-channel field-effect transistors with light- and electric-field effects. The drain current was reversibly changed by alternating ultraviolet and visible light irradiation. Stress is placed on the fact that the on/off ratio realized by light irradiation was 1×10^2 (1×10^4%) and this value is much larger than those in other photochromism-based transistors. These results indicate that the drain current was effectively controlled by light irradiation. Furthermore, the on and off states modulated by light were maintained without light irradiation even after 1 week, exhibiting that our transistor works as an optical memory. We clarified that the light-driven modulation can be attributed to the transformation in the π-conjugation system accompanied by photoisomerization. These findings have the potential to attain high-performance optoelectrical organic devices including optical sensors, optical memory, and photoswitching transistors.



KEYWORDS: *photochromic channel layer, optical and electrical gates, thin film transistor*

1. INTRODUCTION

Organic electronic devices have attracted considerable attention for realizing printable and flexible logic circuits.[1−3] In the past decade, great progress has been made as regards the performance of organic field-effect transistors (OFETs). This has gone hand in hand with the synthesis of air-stable organic semiconductors and the exploration of new transistor structures and processing techniques.[4−8] For example, an extremely high carrier mobility of up to 5−16 $cm^2 V^{-1} s^{-1}$ has been reported in solution-processed OFETs.[6−8] Moreover, the use of gate insulator materials with a high dielectric constant, including polymer electrolyte materials, has made it possible to realize a high channel conductance of more than 1×10^3 S cm^{-1} and a low operating voltage of less than 1 V.[9−11] These efforts have become increasingly important in terms of the commercialization of OFETs.

On the other hand, the development of novel OFETs with specific functionality is attracting attention with a view to providing a new direction for organic electronics. Light-emitting OFETs, phototransistors and OFET-based sensors are representative examples of such attempts.[12−18] Against this background, we propose an external trigger as an alternative to bias gate voltage, namely a photofield effect transistor with photochromic channel layers. This approach offers attractive new prospects for realizing unique organic devices such as synapse-like organic circuits and human-eye-like sensors.

Photomemory and photoswitching effects have been demonstrated in two-terminal structures including crossbar structures and configurations based on scanning probe techniques, where photochromic molecules and their self-assembled monolayers (SAMs) are sandwiched between two electrodes.[19−21] In these studies, the conductivity was reversibly changed by light irradiation in the device structures. At the same time, there have been many reports on OFETs with photochromic molecules, where photochromic molecules, e.g. diarylethene, azobenzene and spiropyran molecules, are employed as photosensitive components at the interface between organic semiconductors and gate insulator layers and at the inside of polymeric semiconductors or polymeric gate insulators involving poly(3-hexylthiophene) and poly(methyl methacrylate).[22−30] Although the drain current through organic semiconductors has been modulated by light irradiation, the obtained variations did not exceed 400%. This light-induced current modulation is small because the channel and photo-

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chromic layers are separated, and thus the photoisomerization does not effectively manipulate the drain current through the channel layer.

Our approach to overcoming these problems is to utilize photochromic thin films as the channel layers in OFETs (Figure 1a). A derivative of diarylethene molecules, 1,2-bis(2-methyl-5-(4-biphenyl)-3-thienyl)hexafluorocyclopentene, was used to handle transistor properties by alternating ultraviolet (UV) and visible (VIS) light irradiation. The details of the synthesis process are described in the Supporting Information. The photoisomerization between the open- and closed-ring isomers of this molecule involves considerable changes in the energy levels (Figure 1b and Figure S1c in the Supporting Information). This feature affects the carrier-injection barrier from a source electrode into a diarylethene channel layer. Or, the photoisomerization induces a large change in the π-conjugation in the molecules. Here, the π-conjugation is extended over the entire molecule in the closed-ring isomer, whereas that in the open-ring isomer is restricted to half of each molecule. The distinct π-conjugation system in both isomers provides different types of carrier transport by following reasons. First, conductance of various kinds of diarylethene molecules has been evaluated in single molecular junctions with nanogap electrodes.[31,32] In fact, the values of closed-ring isomers have been reported to be 1−3 orders of magnitude larger than those of open-ring isomers. Second, the change in π-conjugation system of the molecules induces the variation in the overlap of π-orbitals between neighboring molecules. The feature also contributes to change in the carrier transport with light irradiation.

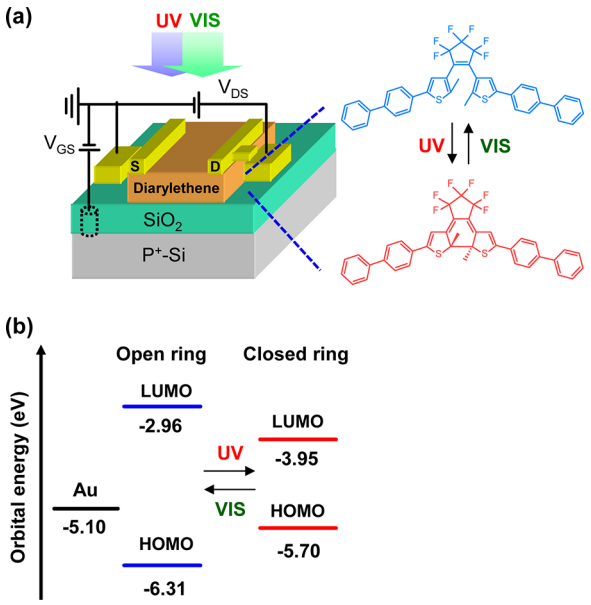

Figure 1. (a) Schematic illustration of an optically and electrically driven diarylethene transistor. (b) Energy levels of diarylethene molecules with open- and closed-ring configurations and the work function of Au. Here, the HOMO and LUMO levels of the respective isomers were estimated by cyclic voltammetry and absorption spectroscopy in solution.

In this paper, we demonstrate a reversible change in the drain current in the OFETs induced by light irradiation. The light-induced on/off ratio in the drain current reaches approximately 1×10^2 (10^4 %). These results clearly indicate that the carrier transport can be controlled by optical and electrical fields. We also discuss the mechanism of the observed photomodulation.

2. EXPERIMENTAL SECTION

A top-contact and bottom-gate-type diarylethene transistor was formed on a highly doped p^+-Si (001) wafer with a 200-nm-thick SiO_2 layer (Figure 1a). Here, the Si wafer and the oxide layer act as the gate electrode and the gate insulator, respectively. First, 45-nm-thick diarylethene thin films were grown on the substrate through a shadow mask with a vacuum deposition system at the optimized temperature of 40 °C. The base pressure was below 5×10^{-7} Pa. Here, we confirmed that the diarylethene molecules were stable for the thermal evaporation and the films underwent the photoisomerization from open-ring to closed-ring (see Supporting Information, Figure S2). Additionally, no cracking was observed in the films. We evaluated the crystal structure of diarylethene thin films by X-ray diffraction measurement (Bruker, D8 Discover) with a Cu Kα source (λ = 0.15418 nm). The films had an amorphous structure as shown in Figure S3a in the Supporting Information. Subsequently, 150-nm-thick Au layers were deposited on top of the diarylethene films as source and drain electrodes. The length and width of the channel were 50 and 400 μm, respectively.

The transistor properties were measured with a semiconductor device analyzer (Agilent B1500A) in a vacuum chamber at 1×10^{-5} Pa. For light irradiation, a xenon lamp (Asahi Spectra Co. Ltd., LAX 102) was used as a light source to perform the photoisomerization of the diarylethene films. Here, the UV and VIS lights include wavelengths in the 300 to 400 nm range and the 400 to 700 nm range, respectively. The powers of the irradiated lights were estimated to be 39 mW cm^{-2} for the UV region and 104 mW cm^{-2} for the VIS region with a laser power meter (Ophir Optics, PD300). The light was irradiated to the area of 1.5 × 1.5 cm^2, which covered the whole area of the transistor.

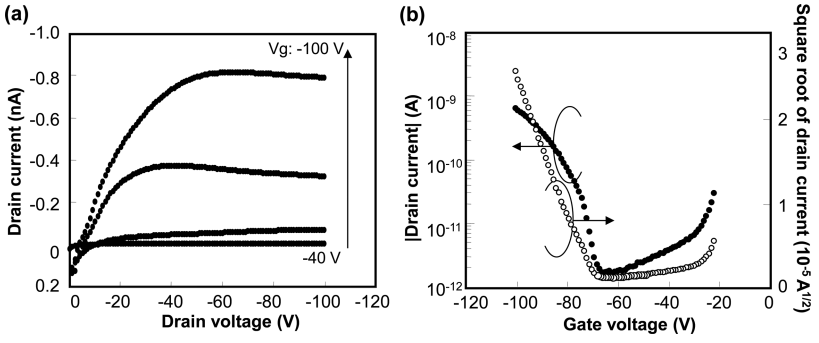

Figure 2. (a) Drain current−drain voltage and (b) drain current−gate voltage curves in diarylethene transistors. Here, the ratio of closed-ring isomer in the diarylethene layers was estimated to be 75%.

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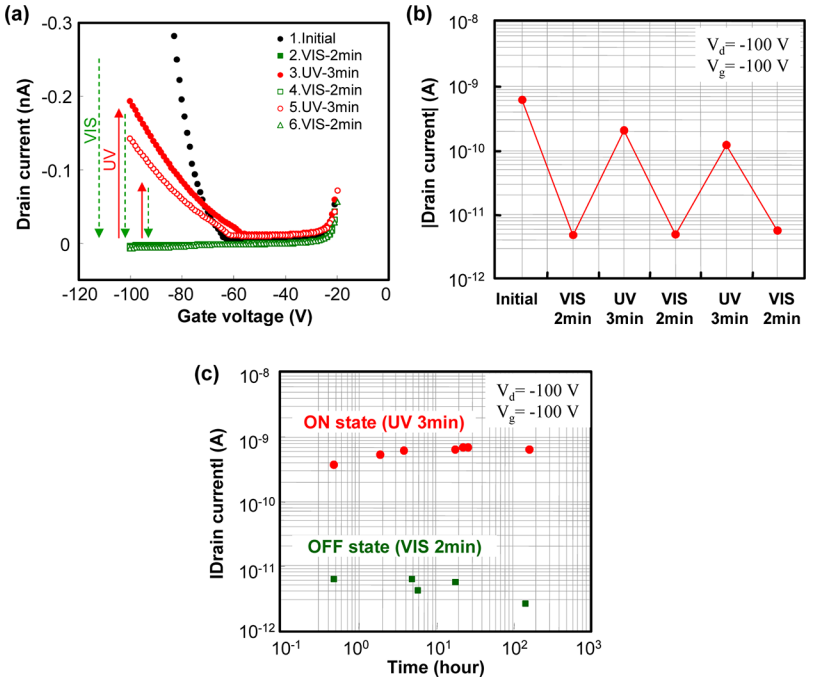

Figure 3. (a) Change in the drain current in the diarylethene transistors induced by UV and VIS light irradiation. (b) Optical modulation of the drain current (V_d= −100 V and V_g= −100 V) against a sequence of photoirradiation. (c) Retention properties of ON and OFF states induced by light irradiation (V_d= −100 V and V_g= −100 V).

To discuss the origin of photomodulation in transistor properties, we performed UV−vis spectroscopy measurements in diarylethene films with and without Au films, where diarylethene films were deposited on quartz substrates. The measurements were performed in a transmission-mode optical configuration for the samples without Au films. On the other hand, a reflection-mode configuration was used for the samples covered with Au films. Here, the incident angle of the light was fixed at 45°.

3. RESULTS AND DISCUSSION

Figure 2a shows the drain current (I_d) − drain voltage (V_d) characteristic of the diarylethene transistor. Before the measurement, the sample was irradiated with UV light for 5 min to elevate the closed-ring to open-ring isomer ratio. The ratio of closed-ring isomers was calculated to be 75% in the diarylethene layers. The conversion ratio was estimated by the ratio of absorption at isosbestic point and absorption at the λ_{max} of the closed-ring isomer (see Figure S4 in the Supporting Information for detail). The I_d−V_d curve confirmed that the diarylethene films worked as a p-type channel transistor. The drain current increased linearly at a low drain voltage, indicating a low contact resistance between the electrodes and diarylethene channel layers. The drain current was completely saturated at a high drain voltage. Figure 2b shows the dependence of the drain current and its square root on the gate voltage at a fixed drain voltage of −100 V. The on/off ratio multiplied by the gate voltage was calculated to be 1×10^3 (1×10^5%). The carrier mobility, μ_{sat}, and interface-trap density, D_{it}, were calculated by the following equations[33]

$$I_{D,sat} = \frac{W}{2L}\mu_{sat}C_i(V_G - V_T)^2 \quad (1)$$

$$S = (k_BT/e)\ln(10)(1 + D_{it}/eC_i) \quad (2)$$

where L and W are the channel length and width, respectively; C_i is the capacitance of the insulator per unit area (18.5 nF cm^{-2}); and $I_{D,sat}$, V_G, and V_T are the saturated drain current, the gate voltage, and the threshold voltage, respectively. S and D_{it} are the subthreshold swing and the interface-trap density, and k_B, e, and T are the Boltzmann constant, electric charge, and absolute temperature. The carrier mobility and the threshold voltage were $1.0 \pm 0.2 \times 10^{-5}$ cm^2 V^{-1} s^{-1} and −64 ± 10 V, respectively. The subthreshold swing was 12 ± 2 V dec^{-1}. From the values in subthreshold swing, interface-trap densities were estimated to be $2.3 \pm 0.8 \times 10^{13}$ cm^{-2} eV^{-1}.

We then examined the light-field effect on the drain current. Light irradiation was found to induce a marked modulation in the drain current as shown in Figure 3a. First, the drain current was completely suppressed after VIS light irradiation for 2 min. UV light irradiation for 3 min then induced a reversible change, and the diarylethene layer again worked as a transistor channel. In this way, a reversible change in the drain current was repeatedly observed by alternating the UV and VIS light irradiation. The change in the drain current at fixed drain and gate voltages of −100 V was plotted against the photoirradiation sequence (Figure 3b). An on/off ratio of about 1×10^2 (1×10^4%) was realized with the light irradiation. The value is remarkably greater than those of other transistors based on the photochromic reactions (10−400%).[22−30] Furthermore, the on and off states modulated by the light irradiation were maintained, even after one week under dark condition (Figure 3c). These results clearly indicate that our diarylethene transistor has the potential to behave as an optical memory.

We also noticed that the on/off ratio gradually decreased with repeated photoswitching. Several reasons can be considered for the deterioration in switching properties. First possibility is that the photoisomerization is suppressed in the films by conformation change from open-ring to closed-ring. However, no degradation in photoswitching appeared in the absorption measurements (see Figure S2b in the Supporting

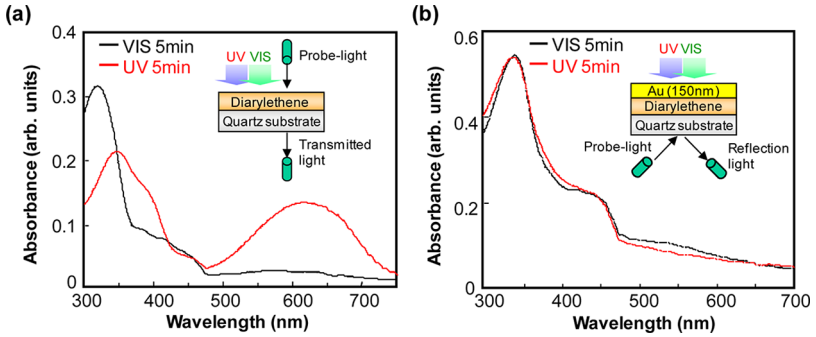

Figure 4. UV−vis spectra of diarylethene films on quartz substrates (a) uncovered and (b) covered with Au thin films with UV and VIS light irradiation. Here, measurement a was carried out in a transmission-mode optical configuration for the samples without Au films. On the other hand, a reflection-mode configuration was used for the samples covered with Au thin films in measurement b, where the incident angle of the light was fixed at 45°.

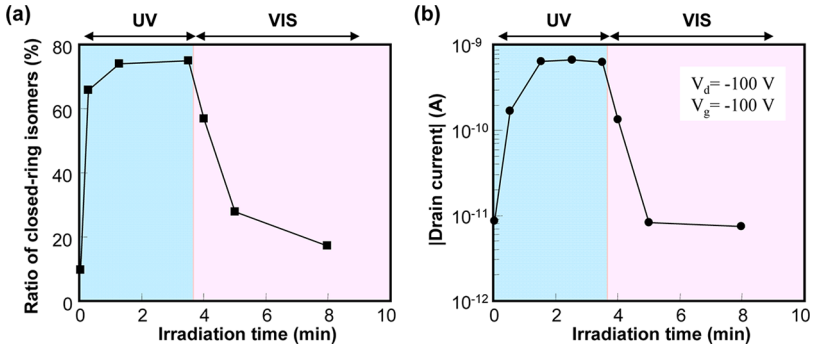

Figure 5. Irradiation time dependence of (a) the ratio of closed-ring isomers in the films and (b) the drain current (V_d = −100 V and V_g = −100 V) in diarylethene transistors.

Information, which proves the photoisomerization takes place even in the film.

Another possibility is caused by the carrier-trapping sites generated by light irradiation near the interfaces between films and gate insulators. The reason is that the photoswitching accompanies with the markedly change in the subthreshold swing from 12 V dec^{-1} to 25 V dec^{-1} (see Table S1 in the Supporting Information). The drastic increase in subthreshold swing well corresponds to the degradation in the on-current and carrier mobility (see Figure S5 in the Supporting Information). The interface-trap density estimated from the subthreshold swing was varied approximately twice from 2.3 × 10^{13} cm^{-2} eV^{-1} to 5.0 × 10^{13} cm^{-2} eV^{-1} with light irradiation. In contrast, the threshold voltage remained constant in the range of ±5 V. These results exhibit that the fatigue in the photoswitching is caused by the photogenerated defects near the SiO_2/diarylethene interface, and not by the intrinsic issues with the molecules.

Furthermore, the on- and off-currents were found to be restored by keeping the samples in dark condition (Figure 3c). The on-current gradually increased, whereas the off-current reduced according to the reduction in interface defects (see Figure S6 in the Supporting Information). The result also supports that the deterioration in the photoswitching is ascribed to the defects generated by light irradiation. Hence, the formation of high-quality film and modification of the interfaces between gate insulators and the films would further improve the fatigue properties in the transistors.

Finally, we discuss the origin of the light-induced change in the drain current in our transistors. Here, we consider two possible reasons for the optical manipulation. As illustrated in Figure 1b, one is a change in the carrier-injection barrier, which is defined by the energy difference between the work function of Au and the HOMO level of the molecule. The larger barrier of the open isomer can prevent carrier injection from the Au electrode into the diarylethene film, resulting in the absence of drain current after VIS-light irradiation. The other reason is the transformation in a π-conjugation system of the diarylethene molecules accompanied by photoisomerization. Here, the π-conjugation is extended over the entire molecule in the closed-ring isomer, whereas that in the open-ring isomer is divided to half of each molecule. The transformation in the π-conjugation of the molecule induces the variation in the overlap of π-orbitals between neighboring molecules. Therefore, the diarylethene films would exhibit distinct types of carrier transport by the ratio of respective isomers. From the geometry of the π-conjugation of each isomer, the films with closed-ring isomers are expected to be more conductive than those with open-ring isomers.

To reveal the origin of optical manipulation, we obtained the absorption spectra of the diarylethene films with and without Au films. For these experiments, quartz plates were used as substrates. The thicknesses of the diarylethene and Au films were the same as those used in the transistors. Figure 4a shows UV−vis spectra of diarylethene thin films without Au layers after UV and VIS light irradiation. A characteristic absorption peak was observed at a wavelength of 320 nm for the open-ring isomer upon VIS light irradiation, while a peak was observed at 612 nm for the closed-ring isomer under UV light irradiation. Contrastingly, in the sample covered completely with Au film, no transition from open-ring to closed-ring was observed with either UV or VIS light irradiation (Figure 4b). This result

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makes it clear that the irradiated light did not penetrate through the Au electrode to the diarylethene film beneath. That is, the diarylethene molecules in the vicinity of the electrode did not undergo photoisomerization.

To support above-mentioned conclusion, we also compared the change in the threshold voltages of the samples with different ratios of open-ring and closed-ring isomers (see Figure S7 in the Supporting Information). Here, diarylethene films were irradiated with either UV or VIS light before deposition of Au electrodes to change the initial ratio between open-rings and closed-rings. The threshold voltages, where open-ring isomers are dominant in the initial stage, was higher (−58 V) than that of the closed-ring isomer (−34 V). This is because HOMO level in the open-ring isomer is lower than that of the closed one. Note that, the threshold voltages in respective devices were constant regardless of the photoswitching. The result also indicates that no photoisomerization of molecules occurred underneath electrodes. Based on these results, we conclude that the possibility of a change in the carrier-injection barrier can be ruled out.

Next, we compared the change in the ratio of closed-ring isomers in the films and the variation in the drain current against a sequence of light irradiation (Figure 5) to clarify that the optical switching in the drain current was induced by photoisomerization in the transistor channel. Here, the conversion ratio of closed-ring isomer was calculated from absorption measurements. The films used for the estimation are different from those employed in the transistor evaluation under light irradiation. However, we can compare both results because the details of film growth conditions and light irradiation processes are same in both experiments. Prior to the measurement, the samples were irradiated with VIS light for 5 min to initiate the state of the diarylethene molecules into an open-ring isomer. We found that the drain current under light irradiation closely depends on the ratio of closed-ring isomers in the films. The ratio of the closed-ring isomers began to increase immediately after UV light irradiation and then saturated at 2 min (Figure 5a). Eventual conversion ratio from open-ring to closed-ring was 75%. Meanwhile, the ratio of closed-ring isomers was decreased with VIS light irradiation. In the same way, the drain current increased with UV light irradiation and reached a constant value at 2 min (Figure 5b). After that, the drain current was completely suppressed by irradiating VIS light for 1.5 min. The result clearly demonstrates that the transition in π-conjugation system accompanied by the photoisomerization is responsible for the photoswitching in our transistors.

4. CONCLUSIONS

We demonstrated optical control of the drain current in OFETs with diarylethene channel layers. The drain current was reversibly changed by alternating UV and VIS light irradiation. Importantly, the on/off ratio realized by light irradiation was 10^2 (10^4 %) and this value is greater than those of other transistors based on the photochromic reactions. The result indicated that the drain current was effectively manipulated by light irradiation. We showed that the drain current modulation can be attributed to the transformation in the π-conjugation system accompanied by photoisomerization. Our finding demonstrates the potential to achieve high-performance optoelectrical organic devices including optical sensors, optical memory, and photoswitching transistors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional results, including synthesis scheme of diarylethene molecules, film structural analysis by X-ray diffraction measurements and estimation of conversion ratio in photoisomerization, are described. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: WAKAYAMA.Yutaka@nims.go.jp; kmatsuda@sbchem.kyoto-u.ac.jp.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99−117.
(2) Gelinck, G.; Heremans, P.; Nomoto, K.; Anthopoulos, T. D. *Adv. Mater.* **2010**, *22*, 3778−3798.
(3) Noh, Y. Y.; Zhao, N.; Caironi, M.; Sirringhaus, H. *Nat. Nanotechnol.* **2007**, *2*, 784−789.
(4) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dotz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679−686.
(5) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. *J. Am. Chem. Soc.* **2007**, *129*, 15732−15733.
(6) Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. *Nature* **2011**, *475*, 364−367.
(7) Nakayama, K.; Hirose, Y.; Soeda, J.; Yoshizumi, M.; Uemura, T.; Uno, M.; Li, W.; Kang, M. J.; Yamagishi, M.; Okada, Y.; Miyazaki, E.; Nakazawa, Y.; Nakao, A.; Takimiya, K.; Takeya, J. *Adv. Mater.* **2011**, *23*, 1626−1629.
(8) Soeda, J.; Hirose, Y.; Yamagishi, M.; Nakao, A.; Uemura, T.; Nakayama, K.; Uno, M.; Nakazawa, Y.; Takimiya, K.; Takeya, J. *Adv. Mater.* **2011**, *23*, 3309−3314.
(9) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. *Nature* **2007**, *445*, 745−748.
(10) Panzer, M. J.; Frisbie, C. D. *J. Am. Chem. Soc.* **2007**, *129*, 6599−6607.
(11) Kaihovirta, N. J.; Wikman, C. J.; Makela, T.; Wilen, C. E.; Osterbacka, R. *Adv. Mater.* **2009**, *21*, 2520−2523.
(12) Sekitani, T.; Yokota, T.; Zschieschang, U.; Klauk, H.; Bauer, S.; Takeuchi, K.; Takamiya, M.; Sakurai, T.; Someya, T. *Science* **2009**, *326*, 1516−1519.
(13) Takahashi, T.; Takenobu, T.; Takeya, J.; Iwasa, Y. *Adv. Funct. Mater.* **2007**, 1623−1628.
(14) Caboni, A.; Orgiu, E.; Scavetta, E.; Barbaro, M.; Bonfiglio, A. *Appl. Phys. Lett.* **2009**, *95*, 123304−1−123304−3.
(15) Noh, Y. Y.; Kim, D. Y.; Yoshida, Y.; Yase, K.; Jung, B. J.; Lim, E.; Shim, H. K. *Appl. Phys. Lett.* **2005**, *86*, 043501.
(16) Zaumseil, J.; Friend, R. H.; Sirringhaus, H. *Nat. Mater.* **2006**, *5*, 69−74.
(17) Muccini, M. *Nat. Mater.* **2006**, *5*, 605−613.
(18) Dong, H.; Zhu, H.; Meng, Q.; Gong, X.; Hu, W. *Chem. Soc. Rev.* **2012**, *41*, 1754−1808.

(19) Kronemeijer, A. J.; Akkerman, H. B.; Kudernac, T.; van Wees, B. J.; Feringa, B. L.; Blom, P. W. M.; de Boer, B. *Adv. Mater.* **2008**, *20*, 1467−1473.
(20) Uchida, K.; Yamanoi, Y.; Yonezawa, T.; Nishihara, H. *J. Am. Chem. Soc.* **2011**, *133*, 9239−9241.
(21) Mativetsy, J. M.; Pace, G.; Elbing, M.; Rampi, M. A.; Mayor, M.; Samori, P. *J. Am. Chem. Soc.* **2008**, *130*, 9192−9193.
(22) Zhang, H.; Guo, X.; Hui, J.; Hu, S.; Xu, W.; Zhu, D. *Nano Lett.* **2011**, *11*, 4939−4946.
(23) Crivillers, N.; Orgiu, E.; Reinders, F.; Mayer, M.; Samori, P. *Adv. Mater.* **2011**, *23*, 1447−1452.
(24) Yoshida, M.; Suemori, K.; Uemura, S.; Hoshino, S.; Takada, N.; Kodzasa, T.; Kamata, T. *Jpn. J. Appl. Phys.* **2010**, *49*, 04DK09−1−04DK09−4.
(25) Shen, Q.; Cao, Y.; Liu, S.; Steigerwald, M. L.; Guo, X. *J. Phys. Chem. C* **2009**, *113*, 10807−10812.
(26) Lutsyk, P.; Janus, K.; Sworakowski, J.; Generali, G.; Capelli, R.; Muccini, M. *J. Phys. Chem. C* **2011**, *115*, 3106−3114.
(27) Shen, Q.; Wang, L.; Liu, S.; Cao, Y.; Gan, L.; Guo, X.; Steigerwald, M. L.; Shuai, Z.; Liu, Z.; Nuckolls, C. *Adv. Mater.* **2010**, *22*, 3282−3287.
(28) Zhang, Y.; Li, H.; Qi, C.; Guo, X. *J. Mater. Chem.* **2012**, *22*, 4261−4265.
(29) Orgiu, E.; Crivillers, N.; Herder, M.; Grubert, L.; Patzel, M.; Frisch, J.; Pavlica, E.; Duong, D. T.; Bratina, G.; Salleo, A.; Koch, N.; Hecht, S.; Samori, P. *Nat. Chem.* **2012**, *4*, 675−679.
(30) Raimondo, C.; Crivillers, N.; Reinders, F.; Sander, F.; Mayor, M.; Samorì, P. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 12375−12380.
(31) Dulic, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; ade Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. *J. Phys. Rev. Lett.* **2003**, *91*, 207102−1−4.
(32) Kim, Y.; Hellmuth, T. J.; Sysoiev, D.; Pauly, F.; Pietsch, T.; Wolf, J.; Erbe, A.; Huhn, T.; Groth, U.; Steiner, U. E.; Scheer, E. *Nano Lett.* **2012**, *12*, 3736−3742.
(33) Pope, M.; Swenberg, C. *Electronic Processes in Organic Crystals and Polymers*, 2nd ed.; Oxford University Press, Oxford, U.K., 1999.

NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on April 17, 2013, with graphics and text errors that were due to production. The corrected version was reposted on April 19, 2013.