Raising the metal–insulator transition temperature of VO$_2$ thin films by surface adsorption of organic polar molecules

To cite this article: Hiroki Shioya *et al* 2015 *Appl. Phys. Express* **8** 121101

View the article online for updates and enhancements.

You may also like

- The characteristics of polar molecule ER fluids and a new type of polar molecule ER fluid
  Kunquan Lu and Rong Shen

- Cold and ultracold molecules: science, technology and applications
  Lincoln D Carr, David DeMille, Roman V Krems et al.

- Resonant quenching of Rydberg atomic states by highly polar molecules
  A A Narits, E S Mironchuk and V S Lebedev

Raising the metal–insulator transition temperature of VO₂ thin films by surface adsorption of organic polar molecules

Hiroki Shioya[1*†], Yoshiaki Shoji[2], Noriya Seiki[2], Masaki Nakano[1], Takanori Fukushima[2], and Yoshihiro Iwasa[1,3*]

[1]*Quantum-Phase Electronics Center and Department of Applied Physics, University of Tokyo, Bunkyo, Tokyo 113-8656, Japan*
[2]*Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
[3]*RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan*
E-mail: shioya@sanken.osaka-u.ac.jp; iwasa@ap.t.u-tokyo.ac.jp

We report a molecular adsorption effect on the first-order metal–insulator transition of vanadium dioxide (VO₂) thin films. The phase transition temperature is shifted higher by the adsorption of particular polar and rigid tripodal molecules on the film surfaces. The shift becomes larger with increasing dipole moment magnitude, which ranges from 0 to 20 D. The orientation of polar molecules aligned on the surface is most likely responsible for the higher shift of the transition temperature. Coating the surfaces with polar molecules, as demonstrated in this work, might provide a unique way of controlling the phase transition of materials. © 2015 The Japan Society of Applied Physics

Vanadium dioxide (VO₂) is a well-known classical strongly correlated oxide, which shows metal–insulator phase transition (MIT) with a structural change from the high-temperature metallic tetragonal phase to the low-temperature insulating monoclinic phase.[1–4] In addition to scientific interests regarding the driving mechanism of MIT and a unique phase diagram associated with the first-order nature,[5,6] a phase transition temperature (T_{MI}) higher than room temperature in a bulk state is beneficial for practical use in electronic and optoelectronic device applications. Therefore, there have been many studies on developing ways of controlling T_{MI} and its related optical/electronic/structural properties using external stimuli, such as photon irradiation,[7–10] current excitation,[11] electric-field effect,[12–17] and strain application.[18–20]

So far, organic molecules with a large dipole moment have been employed to control the properties of semiconductor devices. The surface adsorption and alignment of such dipolar molecules induce a significant change in the work function of a semiconductor and lead to dramatic shifts of the Schottky barrier height[21] and the threshold voltage of field-effect transistors,[22] depending on the direction and magnitude of the dipole moment. Moreover, it has been reported that this surface adsorption by dipolar molecules provides a viable way of controlling the properties of materials as demonstrated by a significant increase in the electrical conductivity of organic single crystals,[23] suppression of the magnetism in ferromagnetic thin films,[24] and tuning of the superconducting transition temperature in cuprate superconductors.[25] Accordingly, we expect that the MIT of VO₂ thin films could be controlled by the surface adsorption of polar organic molecules.

In this Letter, we present an experimental study of T_{MI} control upon coating VO₂ films with polar molecules whose dipole moments are tuned by the chemical molecular design. We found that T_{MI} is raised by the adsorbed polar molecules and increases with the molecular dipole moment magnitude. Our observations suggest that the electronegative group of molecules faced on the films increases the potential energy at their surface, modifying the charge carrier distribution. This electrostatic field effect results in the polar magnitude dependence of the T_{MI} shift. The present polar molecule

coating method is simpler than other previous techniques, offering a route to engineering the phase transition in strongly correlated oxide films.

To investigate the effects of polar molecule adsorption, we designed triptycene-based dipolar molecules (**1**, **2**, and **3**) featuring a rigid three-bladed propeller-shaped structure [Figs. 1(a)–1(c), respectively]. One side of the triptycene skeletons of **2** and **3** is functionalized with three-aligned electron-withdrawing cyano (CN) and dicyanoethynyl [CH=C(CN)₂] groups, respectively, while the other sides possess electron-donating groups. This tripodal substitution pattern is beneficial for not only providing a large dipole moment with the molecules but also strong anchoring toward Lewis acidic vanadium sites on the VO₂ surface [Fig. 1(g)]. In contrast, owing to its high structural symmetry, molecule **1** has no net dipole moment. Compounds **1**–**3** were synthesized using a common precursor, 1,8,13-tribromo-4,5,16-trihydroxytriptycene (see the online supplementary data at http://stacks.iop.org/APEX/8/121101/mmedia). In order to estimate the magnitude of the molecular dipole moment, density functional theory (DFT) calculations were carried out on **1** and **2** as well as **3′** (a model of compound **3**) at the B3LYP/6-31G(d) level of theory (see the online supplementary data at http://stacks.iop.org/APEX/8/121101/mmedia). In the optimized geometry, **1** has no overall dipole (0 D), because the two sets of three CN groups on each side of the triptycene skeleton are directed precisely opposite to one another [Fig. 1(d)]. On the other hand, **2**, having three electron-donating hydroxyl (OH) groups on the opposite side of the CN groups, displays a large dipole moment of 13 D [Fig. 1(e)]. The calculated dipole moment of **3′** (20 D) is even larger than that of **2**, since the CH=C(CN)₂ groups are more electron-withdrawing than the CN groups [Fig. 1(f)]. Importantly, dipoles of **1**–**3** are likely to align vertically to the VO₂ surface upon adsorption via "threefold" anchoring of the CN or CH=C(CN)₂ groups [Fig. 1(g)], which is beneficial for us to take full advantage of the molecular dipole. Because **2** and **3** polarize in OH/OR ($\delta+$) and CN/CH=C(CN)₂ ($\delta-$) fashions, respectively, the adsorbed triptycene layers are expected to increase the potential energy at the surface of VO₂ films [Fig. 1(g)].

10-nm-thick VO₂(001) epitaxial thin films were grown on titanium dioxide (TiO₂) (001) single-crystal substrates (Shinkosha) by pulsed laser deposition at around 400 °C at an

†Present address: Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan.
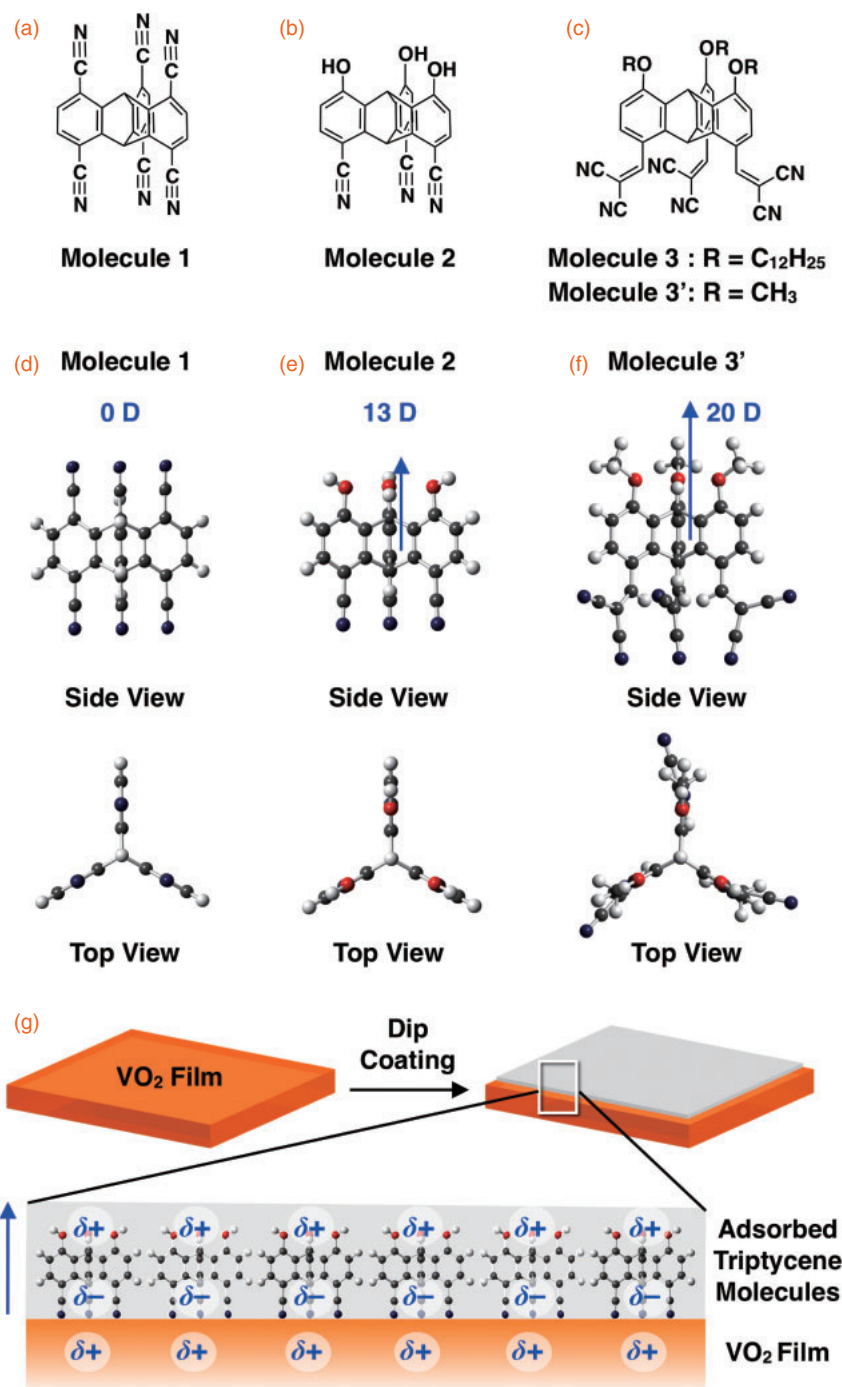
Fig. 1. Structures of polar tripodal triptycenes (a) **1**, (b) **2**, (c) **3**, and calculation model **3′**, possessing cyano (–CN) or dicyanoethynyl [–CH=C(CN)₂] groups for anchoring to VO₂ film surfaces. Optimized structures at the B3LYP/6-31G(d) level (top: side views, bottom: top views) are shown in (d) **1**, (e) **2**, and (f) **3′**. The blue arrows and digits stand for the direction and magnitude (in D) of the electric dipolar moment, respectively. (g) Schematic illustrations of surface coating of VO₂ film and electron depletion effect caused by aligned dipoles of adsorbed triptycenes.

oxygen pressure of 10 mTorr.[26] Subsequently, we fabricated electrodes of Ti/Au (5 nm/30 nm) as the terminals for electrical transport measurements by photolithography, electron-beam evaporation, and lift-off process. The face of VO₂ films with electrodes was flipped and dipped in acetone solutions of **1**, **2**, and **3** (1×10^{-4} mol/L), and the entire sample was heated at 41 °C until the solvent was completely evaporated. Then, we evaluated the influence of the molecular adsorption on the T_{MI} of VO₂ films by comparing the T_{MI} shifts before and after the molecular adsorption and their relationships with the magnitude of dipole moments. The adsorption layer is characterized by X-ray photoelectron spectroscopy (XPS) and time-
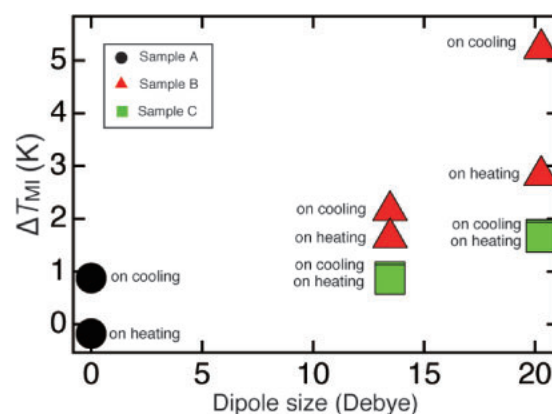
of-flight low-energy atom scattering (TOFLAS) spectroscopy (see the online supplementary data at http://stacks.iop.org/APEX/8/121101/mmedia). Figure S3 in the online supplementary data (http://stacks.iop.org/APEX/8/121101/mmedia) shows the TOFLAS spectrum of the VO₂ film whose surface is coated with **2**. The absence of N peaks in the spectrum strongly implies that **2** is adsorbed on the film surface via three CN groups. Taking the similar molecular structure of **3** into account, it is reasonable to assume that **3** is also adsorbed on the film surface via three CH=C(CN)₂ groups.

Figure 2 shows the resistance versus temperature curves of the VO₂ thin films of samples A and B, with and without

(a) Effects of molecule 1 (D=0)

(b) Effects of molecule 2 (D=13)

(c) Effects of molecule 3 (D=20)
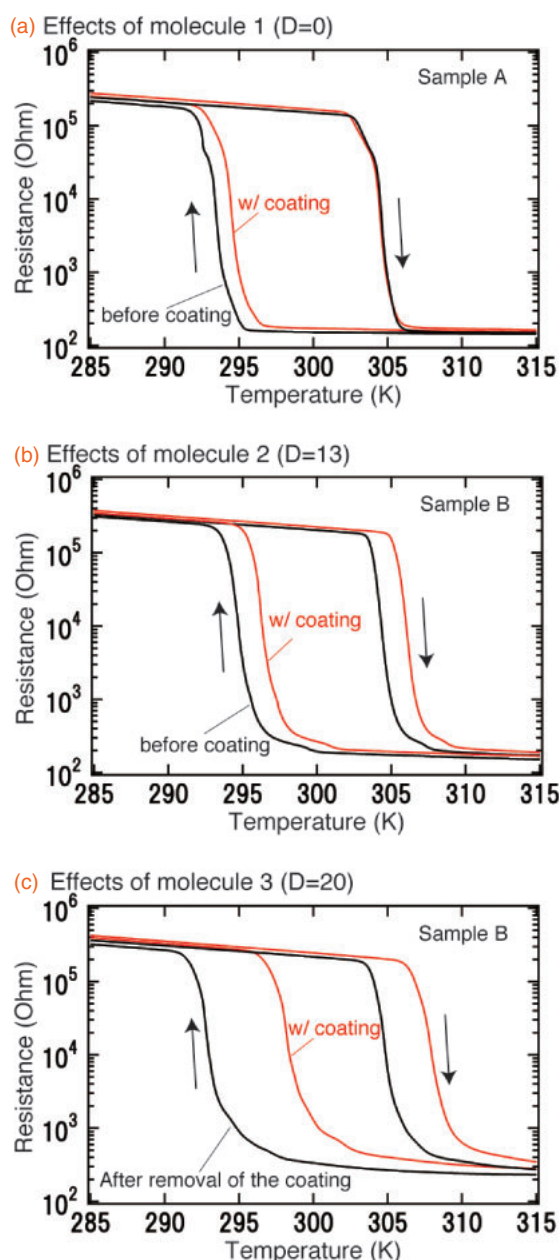
Fig. 2. Resistance vs temperature curves of the VO_2 films with and without surface coating with (a) **1**, (b) **2**, and (c) **3**. Black and red curves correspond to resistance as a function of temperature, without and with surface coating, respectively. Generally, UV ozonization slightly modifies the surface states because of the corrosive high-energy UV irradiation; therefore, the surface-cleaned film does not always show exactly the same T_{MI} as that observed before molecular adsorption.

Fig. 3. Relationship between the transition temperature (T_{MI}) shifts and the calculated dipole moment of the dipolar molecules. Sample A was employed to test **1**. Samples B and C were employed to test **2** and **3**.

for both cooling and heating cycles is confirmed, implying the same mechanism underlying the cause of the T_{MI} shifts. Note that the observed phenomena are reversible. T_{MI} shifted to the higher temperature by the molecular adsorption returns to the lower temperature if the adsorbed molecules are removed from the VO_2 surface by ultrasonication in acetone and subsequent UV ozonization. The increased resistance after coating may be associated with the depletion near the surface of the film. Furthermore, stable behaviors of the resistance curves after coating imply the stability of the coated layers on the VO_2 films.

There are multiple possibilities that are known to shift the T_{MI} of VO_2 films. Cracks in the film with thermal cycling[27] are known to cause relaxation of the strained thin VO_2 film resulting in T_{MI} up-shift; however, this scenario is unlikely since the cracks are known to form only in films thicker than 13 nm. Also, the strain effect can be ruled out, because the strain effect on the VO_2 film is a volume effect, meaning that the major strain effect on the VO_2 film is caused by the bulk TiO_2 substrate, rather than the thin adsorption molecular layers. Oxygen vacancies in the films are also known to change T_{MI}. However, oxygen vacancy formation can also be excluded. After the cleaning by sonication and UV ozonization, T_{MI} decreased as shown in Figs. 2(b) and 2(c). On the other hand, the role of UV ozonization is to promote the oxidation of the film surface, which reduces the number of oxygen vacancies. Since the oxygen vacancies are known to lower the transition temperature, the observed reduction in transition temperature cannot be explained by the ozonization.

For considering a possible mechanism for the positive ΔT_{MI}, an important indication is that the surface adsorption of nonpolar triptycene **1** does not cause notable T_{MI} shifts as compared with the cases of **2** and **3**. This observation rules out an electron transfer mechanism from the VO_2 film to **1**, because **1** possesses the highest electron-accepting capability among the molecules employed (see the online supplementary data at http://stacks.iop.org/APEX/8/121101/mmedia). Combined with the observed strong correlation between the magnitude of molecular dipoles and the degree of ΔT_{MI} (Fig. 3), one possible scenario is that the molecular dipoles are aligned in the same direction on the surface of VO_2 films and induce the rearrangement of the charge distribution on top of the VO_2 films [Fig. 1(g)], resulting in the change in T_{MI}. If the molecules are aligned in the same direction as

surface coating with **1**, **2**, and **3** (see the online supplementary data at http://stacks.iop.org/APEX/8/121101/mmedia for data of sample C). It is clearly seen that the thermal hysteresis originating from the temperature-driven MIT is shifted to the higher temperature in all cases of polar triptycenes (**2** and **3**). We defined the metal–insulator transition temperature T_{MI} as the midpoint of the resistance jump. The shift of T_{MI} upon molecular coating increases with increasing dipole moment of the adsorbed molecules. Strictly speaking, ΔT_{MI} is defined as the difference in T_{MI} of a molecular-coated VO_2 film from that immediately before the coating. ΔT_{MI} is summarized against the calculated electric dipole moment of the adsorbed molecules in Fig. 3. A clear correlation between the ΔT_{MI} values and the magnitudes of the molecular dipole moments

© 2015 The Japan Society of Applied Physics

the molecular alignment model presented in Fig. 1(g) with comparable density and uniformity, the produced electrostatic field should deplete electrons on the surface of VO_2 films depending on the magnitude of the polar molecules, which might stabilize an insulating state and increase T_{MI}.

Finally, we point out a notable aspect of the surface adsorption effect on the MIT behavior, especially by polar molecules **2** and **3**, which change T_{MI} relevantly. The temperature vs resistance curves display parallel shifts to the high-temperature region upon molecular adsorption (Fig. 2), indicating that polar molecules adsorbed on the film surface affect the electronic properties of the entire VO_2 film of 10 nm thickness. This thickness is beyond the electrostatic screening length, which should be less than 1 nm in the present case by considering the Thomas–Fermi screening model. This implies that the molecule adsorption on the VO_2 surface works as stimuli to trigger a structural phase transition. The observed single-step transitions after coating shown in Fig. 2 indicate that the transition temperature shift occurs uniformly in the entire film, although the polar molecular adsorption is the surface phenomenon. A similar smooth shift of the phase transition temperature was also observed in cuprate superconductors[25] coated with polar organic molecules.

In conclusion, we investigated the effects of polar molecule adsorption on the first-order metal–insulator transition of VO_2 thin films. We found that the transition temperature of VO_2 is shifted higher upon surface adsorption with particular types of dipolar triptycene molecules in the aligned state, and that a larger molecular dipole results in a larger shift of the positive ΔT_{MI}. The surface coating with polar tripodal molecules, as demonstrated in the present work, might be an effective means of controlling the electronic state of functional materials.

1) F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
2) A. S. Barker, H. W. Verleur, and H. J. Guggenheim, Phys. Rev. Lett. **17**, 1286 (1966).
3) C. N. Berglund and H. J. Guggenheim, Phys. Rev. **185**, 1022 (1969).
4) J. B. Goodenough, J. Solid State Chem. **3**, 490 (1971).
5) M. M. Qazilbash, M. Brehm, B.-G. Chae, P.-C. Ho, G. O. Andreev, B.-J. Kim, S. J. Yun, A. V. Balatsky, M. B. Maple, F. Keilmann, H.-T. Kim, and D. N. Basov, Science **318**, 1750 (2007).
6) J. H. Park, J. M. Coy, T. S. Kasirga, C. Huang, Z. Fei, S. Hunter, and D. H. Cobden, Nature **500**, 431 (2013).
7) A. Cavalleri, Cs. Tóth, C. W. Siders, J. A. Squier, F. Ráksi, P. Forget, and J. C. Kieffer, Phys. Rev. Lett. **87**, 237401 (2001).
8) K. Shibuya, D. Okuyama, R. Kumai, Y. Yamasaki, H. Nakao, Y. Murakami, Y. Taguchi, T. Arima, M. Kawasaki, and Y. Tokura, Phys. Rev. B **84**, 165108 (2011).
9) M. Liu, H. Y. Hwang, H. Tao, A. C. Strikwerda, K. Fan, G. R. Keiser, A. J. Sternbach, K. G. West, S. Kittiwatanakul, J. Lu, S. A. Wolf, F. G. Omenetto, X. Zhang, K. A. Nelson, and R. D. Averitt, Nature **487**, 345 (2012).
10) M. Suda, R. Kato, and H. M. Yamamoto, Science **347**, 743 (2015).
11) H.-T. Kim, B.-G. Chae, D.-H. Youn, S.-L. Maeng, G. Kim, K.-Y. Kang, and Y.-S. Lim, New J. Phys. **6**, 52 (2004).
12) M. Nakano, K. Shibuya, D. Okuyama, T. Hatano, S. Ono, M. Kawasaki, Y. Iwasa, and Y. Tokura, Nature **487**, 459 (2012).
13) H. Ji, J. Wei, and D. Natelson, Nano Lett. **12**, 2988 (2012).
14) K. Liu, D. Fu, J. Cao, J. Suh, K. X. Wang, C. Cheng, D. F. Ogletree, H. Guo, S. Sengupta, A. Khan, C. W. Yeung, S. Salahuddin, M. M. Deshmukh, and J. Wu, Nano Lett. **12**, 6272 (2012).
15) J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, and S. S. P. Parkin, Science **339**, 1402 (2013).
16) M. Nakano, K. Shibuya, N. Ogawa, T. Hatano, M. Kawasaki, Y. Iwasa, and Y. Tokura, Appl. Phys. Lett. **103**, 153503 (2013).
17) D. Okuyama, M. Nakano, S. Takeshita, H. Ohsumi, S. Tardif, K. Shibuya, T. Hatano, H. Yumoto, T. Koyama, H. Ohashi, M. Takata, M. Kawasaki, T. Arima, Y. Tokura, and Y. Iwasa, Appl. Phys. Lett. **104**, 023507 (2014).
18) Y. Muraoka and Z. Hiroi, Appl. Phys. Lett. **80**, 583 (2002).
19) B. Hu, Y. Ding, W. Chen, D. Kulkarni, Y. Shen, V. V. Tsukruk, and Z. L. Wang, Adv. Mater. **22**, 5134 (2010).
20) N. B. Aetukuri, A. X. Gray, M. Drouard, M. Cossale, L. Gao, A. H. Reid, R. Kukreja, H. Ohldag, C. A. Jenkins, E. Arenholz, K. P. Roche, H. A. Dürr, M. G. Samant, and S. S. P. Parkin, Nat. Phys. **9**, 661 (2013).
21) A. Vilan, A. Shanzer, and D. Cahen, Nature **404**, 166 (2000).
22) S. Kobayashi, T. Nishikawa, T. Takenobu, S. Mori, T. Shimoda, T. Mitani, H. Shimotani, N. Yoshimoto, S. Ogawa, and Y. Iwasa, Nat. Mater. **3**, 317 (2004).
23) M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson, and V. Podzorov, Nat. Mater. **7**, 84 (2008).
24) T. C. Kreutz, E. G. Gwinna, R. Artzi, R. Naaman, H. Pizem, and C. N. Sukenik, Appl. Phys. Lett. **83**, 4211 (2003).
25) I. Carmeli, A. Lewin, E. Flekser, I. Diamant, Q. Zhang, J. Shen, M. Gozin, S. Richter, and Y. Dagan, Angew. Chem., Int. Ed. **51**, 7162 (2012).
26) K. Shibuya, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. **96**, 022102 (2010).
27) K. Kawatani, T. Kanki, and H. Tanaka, Phys. Rev. B **90**, 054203 (2014).