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Soluble 2,6-Bis(4-pentylphenylethynyl)anthracene as a High Hole Mobility Semiconductor for Organic Field-effect Transistors

Yuta Takaki,[1] Yutaka Wakayama,*[2,3] Yasushi Ishiguro,[2,3] Ryoma Hayakawa,[2] Masakazu Yamagishi,[4]
Toshihiro Okamoto,[4] Jun Takeya,[4] Kenji Yoza,[5] and Kenji Kobayashi*[1]
[1]*Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529*
[2]*International Center of Materials Nanoarchitectonics, National Institute for Materials Science,*
1-1 Namiki, Tsukuba, Ibaraki 305-0044
[3]*Department of Chemistry and Biochemistry, Faculty of Engineering, Kyushu University, 1-1 Namiki, Tuskuba, Ibaraki 305-0044*
[4]*Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo,*
5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561
[5]*Bruker axs, 3-9-B Moriya, Kanagawa-ku, Yokohama, Kanagawa 221-0022*

(E-mail: kobayashi.kenji.a@shizuoka.ac.jp, WAKAYAMA.Yutaka@nims.go.jp)

The balance between good solubility and high crystallinity is an advantageous characteristic of 2,6-bis(4-pentylphenylethynyl)anthracene (**1**). Organic field-effect transistors featuring either a vacuum-deposited film or a simple drop-cast film of **1** both showed high hole mobilities of 0.94 and 0.63 $cm^2 V^{-1} s^{-1}$, respectively.

Keywords: Organic field-effect transistor (OFET) | Anthracene | Good solubility

p-Type organic semiconductors have been studied intensively for their applications in high-performance organic field-effect transistors (OFETs).[1] To apply OFETs to flexible and printed electronics such as electronic paper, it is a prerequisite that the hole mobility of the OFETs is greater than $0.5\,cm^2 V^{-1} s^{-1}$ to exceed the mobility of amorphous silicon semiconductors.[1] Recent developments achieved on the basis of excellent molecular designs have led to very high hole mobilities of more than $1\,cm^2 V^{-1} s^{-1}$.[1,2] Air-stable organic semiconductors are important for OFETs, and it is desirable for such semiconductors to possess a large band gap and a HOMO level deeper than −5.0 eV. In this regard, the use of anthracene as a π-electronic core is more desirable than the use of pentacene.[3] The high solubility of organic semiconductors in common organic solvents is also important for solution-processable OFETs. In addition to spin-coating methods, several elaborate methods for solution-processed single crystal OFETs have been developed.[1b,4] However, reports on the construction of high-performance semiconductors by using only a simple drop-casting method are rare.[2a,5]

A large transfer integral is an essential factor for high hole mobility in organic semiconductors. This property is highly dependent on the crystal packing arrangement,[6] wherein a dense herringbone packing with π–π overlap between adjacent molecules (slipped π-stacking) or a brick-wall type of two-dimensional lamellar π-stacked packing is desirable.[1a,7] Meng and co-workers reported the use of 2,6-bis[2-(4-pentylphenyl)vinyl]-anthracene (**2**) (Chart 1) as an organic semiconductor for OFETs.[8] Although this was an anthracene-based derivative, the vacuum-deposited film of **2** with a top-contact/bottom-gate device configuration showed hole mobilities of up to 1.28 $cm^2 V^{-1} s^{-1}$.[8a] The high performance of the OFET containing **2** can be ascribed to the densely packed herringbone crystal structure arising from the high planarity of π-conjugated **2**.

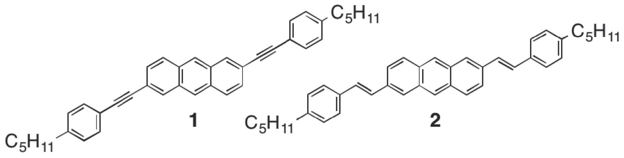

Chart 1.

However, the high planarity of the conformationally rigid π-conjugated structure of **2** greatly reduces the solubility of the compound in common organic solvents, which makes the use of **2** as a solution-processable organic semiconductor difficult. Based on these considerations, we have designed 2,6-bis(4-pentylphenylethynyl)anthracene (**1**).[3e,3g] The replacement of the double bonds in **2** by triple bonds in **1** allows for free rotation of the *p*-pentylphenyl groups connected to the anthracene ring in solution, which we anticipated would lead to significant improvement of the solubility of **1** compared with that of **2**. It was also expected that the coplanar conformation between the *p*-pentylphenyl group and anthracene ring in **1** would be maintained so as to maximize the extended π-conjugation in the solid state, with the assistance of crystal packing forces.[9] Herein, we report the crystal packing structure and OFET properties of soluble **1**. Notably, devices constructed with either a vacuum-deposited film or a simple drop-cast film of **1** showed high hole mobilities of 0.94 and 0.63 $cm^2 V^{-1} s^{-1}$, respectively.[10]

Compound **1** was synthesized in 66% yield by the Sonogashira cross-coupling reaction of 2,6-dibromoanthracene[3a] with *p*-pentylphenylacetylene (Scheme S1). In marked contrast to **2**, compound **1** is soluble at room temperature in a range of organic solvents such as chloroform, toluene, and *o*-dichlorobenzene.[11] TG-DTA analysis indicates that **1** is thermally stable at around 200 °C and has an endothermic peak at 165 °C arising from phase transition (Figure S2).

DFT calculations at the B3LYP/6-31G(d,p) level showed that the HOMO energy levels (and HOMO–LUMO gaps) of **1**, **2**, and pentacene are −5.07 eV (gap = 3.04 eV), −4.91 eV (2.99 eV), and −4.61 eV (2.21 eV), respectively (Figure S3). This result suggests that **2** possesses slightly more extended π-conjugation than **1**, whereas **1** seems to be more air-stable than **2** because the HOMO energy level of **1** is 0.16 eV deeper than that of **2**. The HOMO level of **1** in *o*-dichlorobenzene was −5.63 eV, determined by the peak of differential pulse voltammogram (Figure S4). In the UV–vis absorption spectra (Figure S5a), λ_{max}

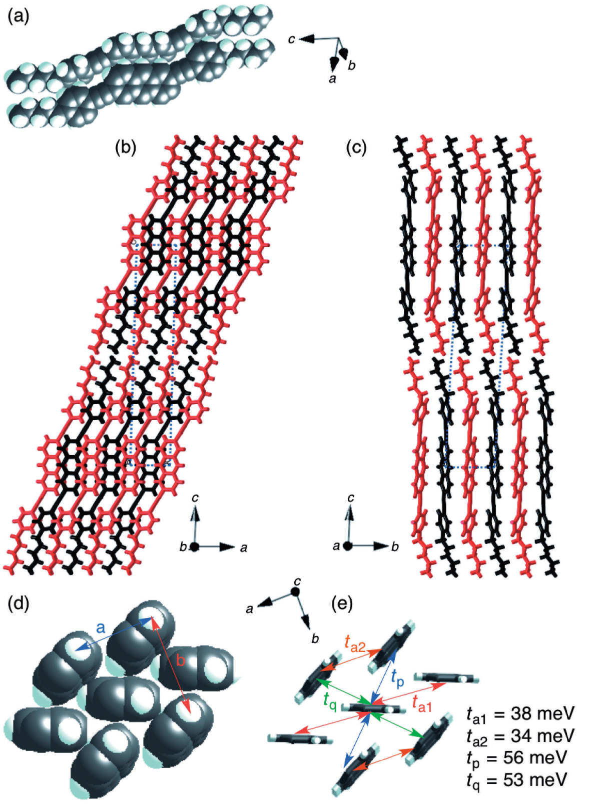

Figure 1. X-ray crystal structure of **1**.[14] (a) Molecular structures of **1** (two conformers). 3-D packing structure of **1**: (b) front view and (c) side view, wherein two conformers are shown in red and black. (d) Herringbone packing of **1**, wherein the *p*-pentylphenylethynyl groups are omitted for clarity. (e) Herringbone packing of **1** with transfer integral values (*t*) in the ADF program.[15]

of **1** in the drop-cast film prepared from the *o*-dichlorobenzene solution appeared at 441 nm, which was red-shifted by 24 nm relative to that of **1** in *o*-dichlorobenzene. This result suggests that, in the drop-cast film, **1** forms a herringbone packing structure including J-aggregate and/or a coplanar conformation between the *p*-pentylphenyl group and the anthracene ring, leading to extended π-conjugation.[9,12]

Thin plate-like single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of **1** in benzene. The molecular and crystal packing structures of **1** are shown in Figure 1.[13] Two kinds of molecules of **1**, with slightly different conformations, are present in the unit cell (Figure 1a).[14] The anthracene ring and the phenyl ring are almost coplanar, leading to efficiently extended π-conjugation, although the triple bonds are bent at ca. 12° with respect to the anthracene mean plane. The crystal packing structure of **1** is similar to that of **2**.[8a] Molecules of **1** assume a typical lamella-like layer-by-layer structure consisting of alternate alkyl and 2,6-bis(phenylethynyl)anthracene layers along the *c*-axis (Figures 1b and 1c), wherein the interlayer distance of **1** was 33.22 Å. In the 2,6-bis(phenylethynyl)anthracene layer, the molecules adopt a herringbone packing arrangement in the *ab* plane (Figure 1d). The intermolecular distances between the anthracene core parts of **1** were $a = 5.92$ Å and $b = 7.43$ Å, whereas those for **2** were $a = 5.85$ Å and $b = 7.23$ Å, and $a = 6.27$ Å and $b = 7.79$ Å for pentacene.[8a] These results indicate that **1** is densely packed in a manner similar to **2**. By using the Amsterdam Density Functional (ADF) program package,[15] intermolecular electronic couplings of HOMO (transfer integral, *t*) based on the packing structure of **1** were estimated as $t_{a1} = 38$ meV, $t_{a2} = 34$ meV, $t_p = 56$ meV, and $t_q = 53$ meV (Figure 1e), which suggests that two-dimensional carrier transport in the *ab* plane is facilitated. These values of **1** were comparable to those of **2** ($t_a = 33$ meV and $t_p = 59$ meV) (Figure S7), which suggests that **1** and **2** should exhibit similar carrier transport ability.

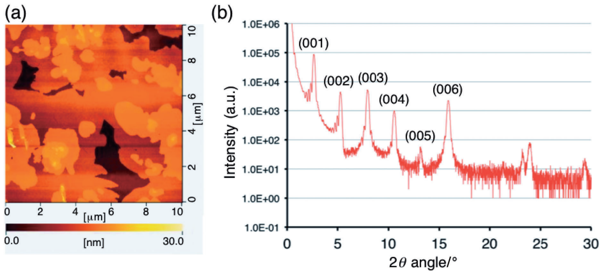

Figure 2. (a) AFM image (10 µm × 10 µm) and (b) XRD pattern of the vacuum-deposited film of **1**.

AFM images of the vacuum-deposited film of **1** (Figures 2a and S8) revealed that the thin film is composed of wide terrace structures with each step of ca. 3.32 nm, which is consistent with the interlayer distance of 3.32 nm elucidated by the X-ray crystallographic analysis, as noted above. The XRD pattern of the vacuum-deposited film of **1** on the bear Si/SiO$_2$ substrate (Figures 2b and S9a) showed that a series of peaks assignable to (00*l*) reflections were clearly observed, which corresponds well with the (00*l*) reflections from single-crystal data; the interlayer distance (*d*-spacing) calculated from these reflections was 3.33–3.36 nm. These results clearly indicate that the molecules of **1** in the vacuum-deposited film are aligned nearly perpendicular to the substrate and form layer-by-layer structures; that is, the crystallographic *c*-axis of **1** is oriented nearly perpendicular to the substrate, and the *ab* plane (the conduction plane) is parallel to the substrate. The XRD pattern of a simple drop-cast film of **1** was the same as that of the vacuum-deposited film (Figure S9c), indicating that the packing structure of **1** in the drop-cast film is the same as that of **1** in the vacuum-deposited film.

OFETs of **1** with a top-contact/bottom-gate configuration were fabricated by vacuum deposition on bare Si/SiO$_2$ substrates at substrate deposition temperatures (T_{sub}) in the range of 50 to 80 °C. The performance of the device was evaluated under ambient conditions in air. All of the OFETs based on **1** showed typical p-channel transistor responses (Table S2 and Figure S11). The highest FET performance was observed for the device at $T_{\mathrm{sub}} = 70$ °C, which showed hole mobility $\mu = 0.94\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, threshold voltage $V_{\mathrm{th}} = -12.1$ V, and on/off current ratio $I_{\mathrm{on}}/I_{\mathrm{off}} = 1.6 \times 10^7$ (Figure 3a). These values were comparable to those of OFETs based on **2**.[8a] On HMDS-treated substrates, the highest FET performance of **1** was observed for the device at $T_{\mathrm{sub}} = 60$ °C, which showed $\mu = 0.63\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, $V_{\mathrm{th}} = -20.7$ V, and $I_{\mathrm{on}}/I_{\mathrm{off}} = 6.8 \times 10^6$ (Figure S11f). Thus, surface treatment of the Si/SiO$_2$ substrates did not improve the performance of the device based on **1**. The balance between good

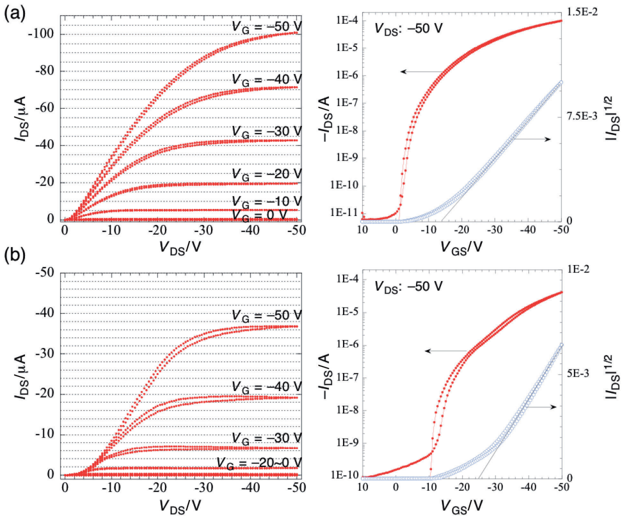

Figure 3. Output characteristics (left) and transfer characteristics at $V_{DS} = -50\,V$ (right) of the **1**-based FET devices on the bear Si/SiO_2 substrates: (a) vacuum-deposited film ($T_{sub} = 70\,°C$) and (b) drop-cast film prepared from *o*-dichlorobenzene solution.

solubility and high crystallinity is an important characteristic of **1**. The solution-processed OFET devices of **1** with a top-contact/bottom-gate configuration were fabricated by using a simple drop-casting method, whereby a solution of **1** in *o*-dichlorobenzene (3.9 mM, several μL) was dropped on the bare Si/SiO_2 substrate and slowly dried in air at room temperature overnight (Figure S10). The device without thermal annealing showed $\mu = 0.63\,cm^2\,V^{-1}\,s^{-1}$, $V_{th} = -22.1\,V$, and $I_{on}/I_{off} = 4.9 \times 10^5$ (Figure 3b). Notably, the mobility of the drop-cast film is comparable to that of the vacuum-deposited film on OFETs based on **1**.

In summary, we have demonstrated that (1) the replacement of the double bonds in **2** by triple bonds in **1** leads to significant improvement of the solubility of **1**, compared with that of **2**, while maintaining high crystallinity, (2) the crystal packing structure including the dense herringbone packing arrangement of **1** was similar to that of **2**, and (3) the FET performance of the vacuum-deposited film of **1** was comparable to that of **2**. For the OFET devices based on **1**, it should be emphasized that the mobility of the drop-cast film is comparable to that of the vacuum-deposited film. These results suggest that the use of triple bonds in place of double bonds in extended π-conjugated aromatics is a promising approach that can be incorporated into the molecular design of solution-processable organic semiconductors.

Supporting Information is available on http://dx.doi.org/10.1246/cl.160731.

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10 S.-G. Lee et al. reported FET properties of 2,6-bis(4-hexylphenylethynyl)anthracene, wherein OFETs of this compound fabricated by a spin-coating method on the OTS-treated Si/SiO_2 substrates showed $\mu = 0.004\,cm^2\,V^{-1}\,s^{-1}$. S.-H. Jang, H.-J. Kim, M.-J. Hwang, E.-B. Jeong, H.-J. Yun, D.-H. Lee, Y.-H. Kim, C.-E. Park, Y.-J. Yoon, S.-K. Kwon, S.-G. Lee, *Bull. Korean Chem. Soc.* **2012**, *33*, 541.

11 Solubility of **1** in organic solvents at room temperature: $1.8\,mg\,mL^{-1}$ (3.5 mM) in $CHCl_3$, $1.6\,mg\,mL^{-1}$ (3.1 mM) in toluene, and $2.6\,mg\,mL^{-1}$ (5.0 mM) in *o*-dichlorobenzene.

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13 An ORTEP view and crystal data are shown in Figure S6 and Table S1, respectively. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-1479834. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

14 Carbon atoms C2–C5 of the pentyl chains of the two conformers of **1** were disordered. The occupancy factors were 0.725 and 0.275 for one conformer and 0.657 and 0.343 for the other conformer. In Figure 1, the pentyl chains with minor occupancy factors are omitted for clarity.

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