Air-Stable Thin Films with High and Anisotropic Electrical Conductivities Composed of a Carbon-Centered Neutral π-Radical

Hiroshi Ito,† Tsuyoshi Murata,† Takahiro Miyata,‡ Miwa Morita,‡ Ryotaro Tsuji,⋆† and Yasushi Morita†,‡,†,□

†Department of Applied Chemistry, Faculty of Engineering, Aichi Institute of Technology, Toyota, Aichi 470-0392, Japan
‡Material Solutions New Research Engine, KANEKA Corporation, Suita, Osaka 565-0871, Japan

Supporting Information

ABSTRACT: Air-stable thin films (50−720 nm thickness) composed of a carbon-centered neutral π-radical with high and anisotropic electrical conductivities were fabricated by vapor deposition of 4,8,12-trioxotriangulene (TOT). The thin films were air-stable over 15 months and were the aggregate of TOT microcrystals, in which a one-dimensional π-stacking column was formed through the strong singly occupied molecular orbital (SOMO)−SOMO interaction with two-electron-multicenter bond among the spin-delocalized π-planes. The orientations of the one-dimensional column of TOT were changed depending on the deposition rate and substrates, where face-on-oriented thin films were epitaxially grown on the graphite 0001 surface, and edge-on-oriented thin films were grown on glass, SiO₂, and indium tin oxide substrates under a high-deposition rate condition. The films showed high electrical conductivities of 2.5 × 10⁻² and 5.9 × 10⁻³ S cm⁻¹ along and perpendicular to the π-stacking column, respectively, for an edge-on oriented thin film.

INTRODUCTION

There have recently been intense challenges on the application of organic neutral radicals in various fields such as spin memories,1,2 electrical conductors,3,4 and thermal sensors5 because a molecule having an unpaired electron works under a field-effect interaction of singly occupied molecular orbital (SOMO)−SOMO interaction with two-electron-multicenter bond among the spin-delocalized π-planes. There are several successful reports on thin-film batteries, one of the most essential and general methods for the application to electronic devices, based on open-shell molecules such as nitroxide radicals,6−13 cyclopentadienyl radical,14 donor−acceptor type triphenylmethyl radicals,15 metal radical complexes,16 Blatter-type radicals,17,18 singlet biradicaloids,19−21 dithiadiazolyl radicals,20 and bis(dithiadiazolyl) diradicals.21,22 Neutral π-radicals, where the unpaired electron is included in a π-conjugated system, are a good candidate for thin-film fabrication because the delocalization of electronic spin increases thermodynamic stability.23 For example, vapor-deposited thin films of bis(dithiadiazolyl) diradical showed photoconductivity,24 and vapor-deposited thin films of phenalenyl-based singlet-biradicaloid exhibited ambipolar field-effect transistor (FET) properties.25 Both radicals achieved one-dimensional (1D) structures by strong intermolecular spin−spin interactions, and their thin films showed electron-transport abilities through the 1D structures. In general, organic semiconductors are anisotropic, and electron transport parallel to the substrate is advantageous for FET, while that vertical to the substrate is advantageous for photovoltaics and light-emitting diodes.26 The control of the molecular orientation within the thin film is, therefore, one of the most important subjects for the high-performance devices based on neutral π-radicals.

Although electrical conductivity is one of the representative transport properties, there are a few reports on thin-film electrical conductor based on neutral radicals. The bis-(dithiadiazolyl) diradical, of which single crystal conductivity was very low (10⁻⁸ S cm⁻¹) due to the strong π-dimerization within the π-stacking column,25 gave a thin film with a room-temperature conductivity of 10⁻⁹ S cm⁻¹.26 It should be noted that the charge doping of the bis(dithiadiazolyl) diradical using iodine increases their conductivity in 10 orders in the crystalline state.26 Recent reports on a nitroxide radical polymer thin film by the spin-coat and thermal annealing method exhibited a room-temperature conductivity of 0.28 S cm⁻¹.27 However as far as we know, the neutral radical thin film showing high and anisotropic electrical conductivity has not been reported.

We recently succeeded in the synthesis and isolation of 4,8,12-trioxotriangulene (TOT, 1) and its derivatives28−34 as a new class of polycyclic carbon-centered organic neutral π-radicals with high air stability (Figure 1a).29 TOT neutral radicals are treatable under an ambient condition in both solid and solution states even without steric protection groups, and no decomposition was found until 350 °C.29 The origin of this high stability is spin delocalization over the 25π electronic system and electronic spin modulation by three oxygen atoms. TOT derivatives generally form face-to-face 1D π-stacking columns, namely, “π-stacked radical polymer”, in the solid state due to the strong intermolecular interaction of singly occupied

Received: August 21, 2019
Accepted: September 26, 2019
Published: October 9, 2019
molecular orbital (SOMO).\textsuperscript{35} The orientation control of the 1D column in thin films is highly attractive because the 1D column plays an essential role for their electronic properties such as strong magnetic interaction,\textsuperscript{23} high electrical conductivity (e.g., 2,6,10-tribromo-TOT: $1.8 \times 10^{-3}$ S cm$^{-1}$ in the crystalline state at room temperature)\textsuperscript{30} and near-infrared photoabsorption.\textsuperscript{29} Although neutral radical crystals with further higher electrical conductivities such as some zwitterionic bis(phenalenyl) boron complexes (0.3 S cm$^{-1}$, at most)\textsuperscript{36,37} and bis(dithiazolyl) radicals ($4 \times 10^{-2}$ S cm$^{-1}$, at most)\textsuperscript{38,39} have been reported, the electrical conductivities of TOT crystals are extremely high as a single component purely organic neutral radical. The pristine TOT forms a $\pi$-dimer with a staggered overlapping through strong SOMO–SOMO interaction via the two-electron-multicenter bonds (pancake bonding),\textsuperscript{40} and the $\pi$-dimers further stacks to construct a 1D column along the $c$-axis (Figure 1b).\textsuperscript{23} In this report, we show the air-stable thin-film fabrication (50–720 nm thickness) of 1 by the conventional vacuum vapor deposition method as the first example of thin films of a condensed polycyclic carbon-centered neutral $\pi$-radical with high and anisotropic electrical conductivities ($10^{-2}$ to $10^{-5}$ S cm$^{-1}$). The molecular orientations (edge-on/face-on, Figure 1c) and morphologies of the thin films are changed by the deposition conditions, and we discuss the relationship between molecular orientations and electronic properties of the thin films.

\section*{RESULTS AND DISCUSSION}

Morphologies and Orientations in Thin Films on SiO$_2$. Thin films of 1 were fabricated by the conventional vacuum vapor deposition method, and the conditions and properties of the films are summarized in Table S1 (50–720 nm thickness). The sublimation occurred over 150 $^\circ$C at 0.2–6 mPa, and no residual and ash were left in the crucible. This result implies that 1 was stable in this sublimation condition and shows a good agreement with our previous experiments, where the bulk 1 neutral radical did not show any obvious decomposition even at 350 $^\circ$C under air or N$_2$ conditions.\textsuperscript{23} The obtained thin films were highly air-stable, and no obvious decomposition was observed under air over 15 months and also annealing at 150 $^\circ$C for 5 h in air (Figure S1). Morphologies of the thin films on SiO$_2$ were observed by scanning electron microscopy (SEM) (Figure 2a–c). At a slow deposition rate ($v = 0.2$ Å s$^{-1}$), two kinds of microcrystals, block- and wire-like shapes, were found (Figure 2a). When the deposition rate increased, the wire-like microcrystals gradually decreased, and the block-like microcrystal grains obviously became small (Figure 2b, $v = 1.2$ Å s$^{-1}$). At $v = 5.8$ Å s$^{-1}$, a uniform dense film consisting only of the block-like microcrystals was obtained (Figures 2c and S2). The drastic change

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Chemical structure of 1, (b) crystal structure and 1D columnar structure of 1 determined by X-ray crystallography, (c) schematic images of molecular orientations in the thin films of 1. In (c), red-spaced plates indicate 1 molecules, and there is a small alternation in the plate-to-plate separation along the $\pi$-stacks.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{SEM images (a–d) and XRD spectra (e–h) of vapor-deposited thin films of 1. Thin films on SiO$_2$ at the low deposition rate ($v = 0.2$ Å s$^{-1}$) (a), at the middle deposition rate ($v = 1.2$ Å s$^{-1}$) (b), at the high deposition rate ($v = 5.8$ Å s$^{-1}$) (c), thin film on ITO at the high deposition rate ($v = 6.3$ Å s$^{-1}$) (d,g), and (h) 1 powder. (i) Absorption spectra of thin films of 1 on the glass substrate. The thin films were set perpendicular to the optical axis.}
\end{figure}
of morphologies was also investigated by X-ray diffraction (XRD) analyses.

The thin film fabricated at a low rate of \( v = 0.2 \ \text{Å s}^{-1} \) showed a set of peaks (marked peaks, \( 2\theta = 27.5^\circ \) and \( 30.9^\circ \)) nearby the main peaks (Figure 2e) that were found for the powder sample (Figure 2h). The marked additional peaks would be afforded by the wire-like microcrystals because they were observed only in thin films of a low deposition rate (Figure 2a). The in-plane XRD pattern of the thin film on SiO\(_2\) at a high deposition rate (\( v = 5.8 \ \text{Å s}^{-1} \)) showed a strong peak at \( 2\theta = 27.0^\circ \) (Figure 2f), which corresponds to the interlayer distance along the \( c \)-axis \( d(102) = 3.26 \ \text{Å} \) (Figures S3 and S4). The out-of-plane XRD pattern, on the other hand, showed peaks at \( 2\theta = 9.8, 16.8, 19.6, \) and \( 25.8^\circ \), which correspond to the periodic structures \( [d(210) = 9.2, d(300) = 5.3, d(420) = 4.2, \) and \( d(510) = 3.5 \ \text{Å}, \) respectively] perpendicular to the \( \pi \)-stacking columns. These XRD spectra suggest that the microcrystals of \( 1 \) are aligned with the \( c \)-axis parallel to the SiO\(_2\) substrate and thus that the thin film has an edge-on orientation (Figure 1c). It has been reported that a \( \pi \)-molecule tends to stand perpendicular to a substrate giving an edge-on film, when the interaction between the \( \pi \)-molecule and the substrate is considerably weak in comparison with the interaction between \( \pi \)-molecules.\(^{27} \) The strong SOMO–SOMO interaction between \( 1 \) molecules forming the \( \pi \)-stacking column would prevent the interaction between the \( \pi \)-electronic system of \( 1 \) and SiO\(_2\), and thus the edge-on orientation was constructed on the SiO\(_2\) substrate. In addition, the acid/base interaction of carboxyl and/or C–H on the TOT skeleton with a highly polar surface of SiO\(_2\) substrates may promote the formation of edge-on thin films. The diffraction peaks observed in the thin film at a high deposition rate (\( v = 5.8 \ \text{Å s}^{-1} \)) were in good agreement with those of the single crystal (Figure S4). This indicates that the molecular arrangement in the thin film is identical to the crystalline state, and that the thin film is expected to exhibit a similar conductivity to that of the bulk sample.\(^{23} \)

A thin film of \( 1 \) deposited on a glass substrate was reddish brown which is similar to the color of the powder sample (Figure S5). Absorption spectra with a perpendicular incidence for the thin films showed a broad and strong near-infrared peak around 1050 nm (Figure 2i). This result also suggests the edge-on orientation because this absorption band is characteristic for the 1D column of \( 1 \) and is anisotropically observed only in the direction perpendicular to the optical axis.\(^{28} \) The absorption maxima showed a slight shift depending on the deposition rate. The spectrum of the high deposition rate (\( v = 5.8 \ \text{Å s}^{-1} \)) film is similar to that of the pristine powder (\( \lambda_{\text{max}} = 1038 \) and 1030 nm,\(^{25} \) respectively). On the other hand, the peak top was shifted to 1096 nm at a low deposition rate (\( v = 0.2 \ \text{Å s}^{-1} \)). The lower energy shift might be derived from minute differences in the \( \pi \)-stacking structure in the 1D column as shown in the wire-like microcrystals in the low-deposition rate film (Figure 2a).\(^{23,29} \) These observations indicate that \( 1 \) formed an edge-on-oriented film (Figure 1c) on the SiO\(_2\) substrate under the high deposition rate (\( v = 5.8 \ \text{Å s}^{-1} \)), where the molecules at the interface layer contact with the substrate at the molecular edge and the \( \pi \)-stacking columns were parallel to the SiO\(_2\) or glass substrates. It is expected that the electrical conductivity parallel to the substrate is much higher than that perpendicular to the substrate.

**Electrical Conductivities of Thin Films.** It is well known that the morphology and arrangement of an organic molecule in vapor-deposited thin films are highly sensitive to the substrates.\(^{27,41} \) The vapor deposition of \( 1 \) on indium tin oxide (ITO) at a high deposition rate (\( v = 6.3 \ \text{Å s}^{-1} \)) formed a thin film with a different morphology from that on the SiO\(_2\) substrate, where the film consisted of a larger size of microcrystals (Figure 2d). The in-plane XRD pattern showed a strong peak at \( 2\theta = 27.0^\circ \) similar to the films on the SiO\(_2\) substrate, and there was no peak in the out-of-plane measurement (Figure 2g), indicating that \( 1 \) formed another edge-on thin film on the ITO substrate. In an edge-on-oriented film, the 1D columns of \( 1 \) are parallel to the substrate (Figure 1c), the electron mobility parallel to the substrates would be advantageous than that perpendicular to the substrate.\(^{39} \) The electrical conductivity of the thin film of \( 1 \) on the glass substrate at the high deposition rate (\( v = 6.3 \ \text{Å s}^{-1} \)) was measured by the two-probe method (Figure 3a,b). The electrical conductivity parallel to the substrate was found to be \( 2.5 \times 10^{-2} \ \text{S cm}^{-1} \) at the room temperature (Figure 3c). This very high electrical conductivity is similar to that of the single crystal of 0.32 S cm\(^{-1} \) at room temperature measured by the four-probe method as expected (Figure 3c). The slight decrease in the electrical conductivity in the thin film is caused by the randomness of the orientation of the 1D columns within the parallel direction to the substrate, and a higher conductivity is expected if the orientation of the 1D columns is aligned in this direction. The electrical conductivity of the thin-film became smaller with decreasing temperature because of the small semiconducting activation energy (82 meV), which is also comparable to that of the single crystal (90 meV). The similarity of the conducting properties of the thin film and single crystal implies that the effect of impurity during vapor deposition is negligible. It should be also noted that the thin-film electrical conductivity of \( 1 \) (\( 2 \times 10^{-3} \ \text{S cm}^{-1} \)) is much higher than the thin films prepared from of single-component organic molecules such as bis(dithiadiazolyl) diradical (10\(^{-9} \) S cm\(^{-1} \))\(^{22} \) and 2,5-bis-methylthio-7,7′,8,8′-tetracyanoquinodimethane (2 \( \times 10^{-5} \) S cm\(^{-1} \))\(^{42} \) and also comparable to the single-
crystal conductivities of zwitterionic bis(phenalenyl) boron complexes (0.3 S cm$^{-1}$)\textsuperscript{36,37} and bis(dithiazoyl) radicals (4 \times 10^{-2} S cm$^{-1}$)\textsuperscript{38,39} The high electrical conductivity of the thin film of 1 originates not only from the highly oriented $\pi$-stacking columns as the conducting pathway but also from the suppression of grain boundary resistance in the uniform dense thin film. On the other hand, the electrical conductivity vertical to the thin film, which is perpendicular to the $\pi$-stacked column (Figure 3b), was measured as 5.9 \times 10^{-5} S cm$^{-1}$. Although the anisotropy of electrical conductivities of these two films cannot be directly compared because the substrates were not the same, the electron mobility along the $\pi$-stacking column is significantly higher than that perpendicular to the column.

**Thin Film on Graphite.** Heteroepitaxy is often used to obtain highly ordered thin films.\textsuperscript{35} Graphite has rich $\pi$-electrons on the 0001 surface of a hexagonal crystal system ($a = b = 2.46 \text{ Å}, \gamma = 120^\circ$) and is often used as the substrate for epitaxially face-on oriented ultrathin and/or monolayer films of polycyclic aromatic carbons.\textsuperscript{41,44,45} The crystal system of 1 is trigonal ($a = b = 18.2 \text{ Å}, \gamma = 120^\circ$),\textsuperscript{23} and the c-axis epitaxial growth with a face-on orientation is expected because of the acceptable misfit ($\{d(100)_{\text{sub}} - d(800)_{\text{TOT}}/d(100)\}_{\text{sub}} = 7.5\%$) in organic heteroepitaxial systems.\textsuperscript{45} Furthermore, it has been reported that weak intermolecular interactions such as hydrogen bonds parallel to the $\pi$-molecular plane promote the face-on orientation in thin films.\textsuperscript{46,47} In the crystal structure of 1, a 2D network is constructed by C–H--O hydrogen bonds parallel to the molecular plane (ab-plane)\textsuperscript{23} and is expected to stabilize the face-on orientation. The vapor-deposited thin film of 1 on the graphite 0001 surface of highly oriented pyrolytic graphite (HOPG) (Figure 4a) and graphite sheets (Figures 4b–d) showed drastically different morphologies compared with those on the SiO$_2$ and glass substrates. The cross-section SEM images of the thin film clearly showed that columnar microcrystals of 1 densely stood on the substrates to form sheer cliff-like morphologies (Figure 4c,d). The out-of-plane XRD pattern of the thin film on a well-peeled graphite sheet showed only a peak at $2\theta = 27.0^\circ$ that corresponds to the interlayer distance ($d(102) = 3.26 \text{ Å}$) in the c-axis together with the peaks of graphite substrates (Figure 4e, top). On the other hand, the in-plane XRD pattern showed peaks that correspond to the periodic structures perpendicular to the 1D columns in the ab-plane, and the (102) peak at $2\theta = 27.0^\circ$ was not found (Figure 4e, bottom). These observations clearly indicate that the thin films on graphite substrates have an almost completely face-on orientation on the graphite 0001 surfaces. The drastic molecular orientation change between the films on SiO$_2$ and graphite was also seen in the change of the color of each film. A vapor-deposited thin film on the single-layer graphene-SiO$_2$ substrate showed high coloration, while that on the SiO$_2$ substrate was greenish brown (Figure 4f). This is because the 1D column perpendicular to the optical axis selectively absorbs red to near-infrared light (edge-on film, 700–1300 nm, Figure 4g). The anisotropy of the electrical conductivity of the face-on film is expected to be exactly opposite to that of the edge-on film, and it is expected that the conductivity is higher in the vertical direction. However, because of the contact resistance between the thin film and the electrode as well as the difficulty in the deposition of a metal electrode on the thin film, we could not perform the accurate measurement of the electrical conductivity. The face-on orientation was kept up to the film thickness of 700 nm at least in the SEM observation regardless of the deposition rate ($v = 0.1–3 \text{ Å s}^{-1}$, Table S1), showing that the SOMO–SOMO interaction in the 1D $\pi$-stacking column was strong enough to set more than 1500 molecules.

**CONCLUSIONS**

In conclusion, by utilizing the high stability of the TOT neutral radical, we successfully fabricated air-stable thin films of 1 by the conventional vapor-deposition method as the first thin film of the neutral $\pi$-radical having a fused polycyclic structure with high and anisotropic electrical conductivities (10$^{-2}$ to 10$^{-5}$ S cm$^{-1}$). A large number of stable neutral radicals have been reported, however, those stable even in the vaporized state under high temperature and vacuum (0.2–6 mPa) conditions to give a vapor-deposited thin film are limited.\textsuperscript{9–12,15,17–22} In the TOT thin films, 1D $\pi$-stacking columns were formed by the strong SOMO–SOMO interaction. The anisotropic orientation of the 1D columns depended on the substrates: edge-on-oriented thin films were obtained on glass, SiO$_2$, and ITO under a high deposition rate, and face-on oriented thin films were achieved on the graphite 0001 surface. The electrical conductivity of the edge-on oriented thin films showed high anisotropy: the electrical conductivity parallel to the substrate was considerably higher than that vertical to the substrate (10$^{-5}$ vs 10$^{-5}$ S cm$^{-1}$). It is worth noting that the neutral radical thin films showing anisotropic and high electrical conductivity have not been known before the TOT thin film of the present study. The present result suggests the potential for the TOT neutral radical as a molecular building block of organic electronic materials and may provide a new milestone in the material exploration in the development of organic electronic devices. Moreover, the 1D structure of $\pi$-radical aggregation and the resultant anisotropic electrical conductivities compared with those on the SiO$_2$ and glass substrates. The cross-section SEM images of the thin film clearly showed that columnar microcrystals of 1 densely stood on the substrates to form sheer cliff-like morphologies (Figure 4c,d).

![Figure 4. SEM images of the surface (a,b) and cross-section (c,d) of thin films of 1 fabricated on the graphite 0001 surface. Substrates: (a) HOPG, (b,c) graphite sheet, and (d) graphite sheet peeled 24 times with scotch tape. (e) Out-of-plane and in-plane XRD spectra of the thin film of (d). (f,g) Photograph and absorption spectra of thin films fabricated on graphene/SiO$_2$ and SiO$_2$.](image-url)
conductive thin films would be obtained by using mixed-valence compounds prepared by carrier doping of the neutral π-radical.26,30

**EXPERIMENTAL SECTION**

**Materials.** Neutral radical 1 was prepared as we had reported.23 All of the substrates were commercially available materials. The nonalkali glass and ITO/glass substrates were cleaned in an ultrasonic bath for 10 min in Shibata clean A (Shibata Scientific Tech. Ltd.), pure water, and 2-propanol. The substrates dried in an oven were then exposed to a UV-ozone atmosphere for 30 min. HOPG was freshly cleaved with the Scotch tape. Graphite sheet (GRAPHINITY, KANEKA Corp.) was used without pretreatment (SEM measurement) or peeled 24 times with the Scotch tape (SEM and XRD measurement). Single-layer graphene—SiO₂ (Graphene Platform Corp.) was used as purchased.

**Vapor Deposition.** The thin films of 1 were fabricated on the substrates by vacuum evaporation under a pressure of 0.2–6 mPa, using vapor evaporation chambers, ULVAC VPC-260 or Kenix KXX-250. The substrates were horizontally fixed above the evaporation source in a crucible (d = 30 or 90 mm), and the crucible was gradually heated from room temperature to 220–270 °C, and the sublimation occurred over 150 °C. Almost all substrate 1 mounted in the crucible evaporated under the deposition conditions. The deposition was monitored by the measurement of the thickness by a quartz crystal resonator in the chamber. The thickness of the resulting film was measured using the cross-section SEM image or stylus profilometry (Veeco Dektak 150) because of the poor sensitivity of the quartz crystal resonator especially in the case of d = 30 mm. The averaged deposition rate was obtained by dividing the film thickness by the deposition time. The deposition conditions and thickness are summarized in Table S1. The Au/1/ITO and Au/1/glass cells were fabricated by the following method: Au electrodes were evaporated through shadow masks in a vacuum with a pressure of ca. 2 mPa onto the thin films of 1 deposited on an ITO electrode or a glass substrate. The cells were annealed at 150 °C for 5 h before electrical measurement.

**Measurements.** Electronic spectra of KBr pellets or thin films on glass substrates were measured on a UV/visible/NIR scanning spectrophotometer (HITACHI U-4000). Morphology of the thin films was observed on a high-resolution SEM (Hitachi High-Technologies FE-SEM SU6600). The XRD measurements were performed by a diffractometer (Rigaku SmartLab). The temperature-dependent electrical conductivities of the edge-on film parallel and perpendicular to the substrate were measured using the direct current (dc) two-probe method. As for the measurement parallel to the substrate, the two-probe method using comb-shaped electrodes was performed because of very high resistance. The gold comb-shaped electrodes were formed by vacuum evaporation of gold on the film of 1 with a gap of 0.25 mm (top contact, Figure 3a). In the case of the measurement perpendicular to the substrate, the thinness of the film prevented a measurement with the four-probe method, and we measured in the two-probe method, where the films of 1 were formed on the ITO electrode, and then, gold was evaporated on the film of 1.

The cells were attached onto the thermal stage (As-One HI-1000), and electrical measurement data parallel and perpendicular to the substrate were obtained using a picoammeter/voltage source (Keithley 6487) and dc voltage current source (ADCMT 6243), respectively. dc electrical conductivity of the single crystal of 1 along the π-stacking direction was measured by using a Keithley 2001 multimeter combined with the standard four-probe technique. Four gold wires of 10 μm diameter were attached to a single crystal of 1 with carbon paint (Jeol Dotite Paint XC-12) using gold wires of 10 μm diameter using carbon paste.

**ASSOCIATED CONTENT**

Supporting Information

Summary of vapor deposition conditions, absorption spectra of thin films, schematic images of morphologies, crystal structure with characterization of XRD peaks, simulated XRD spectra, photograph of the thin film deposited on SiO₂, high-resolution SEM images of thin films, and schematic images of the cells used in the two-probe electrical conductivity measurements of 1 (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: Ryotaro.Tsuji@kaneka.co.jp (R.T.).
*E-mail: moritay@aitech.ac.jp (Y.M.).

**ORCID**

Tsuyoshi Murata: 0000-0001-6861-5456
Yasushi Morita: 0000-0002-2124-0201

**Author Contributions**

Y.M. and R.T. planned this project. H.I. and Takahiro Miyata demonstrated the thin-film fabrications and the absorption spectral analysis. H.I. measured the electrical conductivities of the thin films. Tsuyoshi Murata measured the electrical conductivities of the single crystal. M.M. performed the XRD and SEM analyses. All authors wrote and reviewed the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by Core Research for Evolutional Science and Technology (CREST) Basic Research Program “Creation of Innovative Functions of Intelligent Materials on the Basis of Element Strategy” of Japan Science and Technology Agency (JST).

**REFERENCES**

1. Simõo, C.; Mas-Torrent, M.; Crivillers, N.; Lloveras, V.; Artés, J. M.; Gorostiza, P.; Veciana, J.; Rovira, C. A robust molecular platform for non-volatile memory devices with optical and magnetic responses. Nat. Chem. 2011, 3, 359–364.
2. Raman, K. V.; Kamerbeek, A. M.; Mukherjee, A.; Atodiresei, N.; Sun, T. K.; Lazić, P.; Caciuc, V.; Michel, R.; Stalke, D.; Mandal, S. K.; Blügel, S.; Münzenberg, M.; Moodera, J. S. Interface-engineered templates for molecular spin memory devices. Nature 2013, 493, 509–513.
3. Haddon, R. C. Design of organic metals and superconductors. Nature 1975, 256, 394–396.

**Author Contributions**

Y.M. and R.T. planned this project. H.I. and Takahiro Miyata demonstrated the thin-film fabrications and the absorption spectral analysis. H.I. measured the electrical conductivities of the thin films. Tsuyoshi Murata measured the electrical conductivities of the single crystal. M.M. performed the XRD and SEM analyses. All authors wrote and reviewed the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by Core Research for Evolutional Science and Technology (CREST) Basic Research Program “Creation of Innovative Functions of Intelligent Materials on the Basis of Element Strategy” of Japan Science and Technology Agency (JST).

**REFERENCES**

1. Simõo, C.; Mas-Torrent, M.; Crivillers, N.; Lloveras, V.; Artés, J. M.; Gorostiza, P.; Veciana, J.; Rovira, C. A robust molecular platform for non-volatile memory devices with optical and magnetic responses. Nat. Chem. 2011, 3, 359–364.
2. Raman, K. V.; Kamerbeek, A. M.; Mukherjee, A.; Atodiresei, N.; Sun, T. K.; Lazić, P.; Caciuc, V.; Michel, R.; Stalke, D.; Mandal, S. K.; Blügel, S.; Münzenberg, M.; Moodera, J. S. Interface-engineered templates for molecular spin memory devices. Nature 2013, 493, 509–513.
3. Haddon, R. C. Design of organic metals and superconductors. Nature 1975, 256, 394–396.
(4) Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S. H.; Haddon, R. C.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S.; Schneemeyer, L. F.; Waszczak, J. V. Conducting charge-transfer salts based on neutral π-radicals. *Nature* 1993, 365, 821–823.

(5) Morita, Y.; Suzuki, S.; Fukui, K.; Nakazawa, S.; Kitagawa, H.; Kishiha, H.; Okamoto, H.; Naito, A.; Sekeina, A.; Ohashi, Y.; Shiro, M.; Sasaki, K.; Shiomi, D.; Sato, K.; Takui, T.; Nakasuji, K. Thermochromism in an organic crystal based on the coexistence of σ- and π-dimers. *Nat. Mater.* 2008, 7, 48–51.

(6) Ratera, I.; Veciana, J. Playing with organic radicals as building blocks for functional molecular materials. *Chem. Soc. Rev.* 2012, 41, 303–349.

(7) Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds; Hicks, R. G., Ed.; Wiley-VCH: Chichester, 2010.

(8) Thomas, S.; Li, H.; Bredas, J. L. Emergence of an antiferromagnetic Mott insulating phase in hexagonal π-conjugated covalent organic frameworks. *Adv. Mater.* 2019, 31, 1900355.

(9) Caro, J.; Fraxedas, J.; Jürgens, C.; Santiso, J.; Rovira, C.; Veciana, J.; Figueras, A. The first oriented thin films based on a nitronyl nitroxide radical. *Adv. Mater.* 1998, 10, 608–610.

(10) Fraxedas, J.; Caro, J.; Santiso, J.; Figueras, A.; Gorostiza, P.; Sanz, F. Molecular organic thin films of p-nitrophenyl nitronyl nitroxide: surface morphology and polymorphism. *Phys. Status Solidi B* 1999, 215, 859–863.

(11) Wang, Y.; Wang, H.; Liu, Y.; Di, C.-a.; Sun, Y.; Wu, W.; Yu, G.; Zhang, D.; Zhu, D. Imino nitroxide pyrene for high performance organic field-effect transistors with low operating voltage. *J. Am. Chem. Soc.* 2006, 128, 13058–13059.

(12) Casu, M. B. Nanoscale studies of organic radicals: surface, interface, and spintrance. *Acc. Chem. Res.* 2018, 51, 753–760.

(13) Gallagher, N.; Zhang, H.; Jungeboer, T.; Giangrisostomi, E.; Ovsyannikov, R.; Pink, M.; Rajca, S.; Casu, M. B.; Rajca, A. Thermally and magnetically robust triplet ground state diradical. *J. Am. Chem. Soc.* 2019, 141, 4764–4774.

(14) Lamansky, S.; Thompson, M. E. Vacuum deposition of thin films of pentaphenylcyclopentadienyl radical and their electronic properties. *Chem. Mater.* 2002, 14, 109–115.

(15) Reig, M.; Gozálvez, C.; Jankauskas, V.; Guidelis, V.; Grauzulevicius, J. V.; Fajard, L.; Julià, L.; Velasco, D. Stable all-organic radicals with ambipolar charge transport. *Chem.—Eur. J.* 2016, 22, 18551–18558.

(16) Prigodin, V. N.; Raju, N. P.; Pokhodnya, K. I.; Miller, J. S.; Desgreniers, S.; Secco, R. A.; Oakley, R. T.; Robertson, C. M.; Assoud, A.; Yong, W.; Steven, E.; Dube, P. A.; Tse, J. S.; Desgreniers, S.; Secco, R. A.; Oakley, R. T. Fine tuning the performance of multiorbital radical conductors by substituent effects. *Science* 2019, 365, 281–284.

(17) Mailman, A.; Wong, W. L.; Winter, S. M.; Claridge, R. C. M.; Robertson, C. M.; Assoud, A.; Yong, W.; Steven, E.; Dube, P. A.; Tse, J. S.; Desgreniers, S.; Secco, R. A.; Oakley, R. T. Fine tuning the performance of multiorbital radical conductors by substituent effects. *J. Am. Chem. Soc.* 2017, 139, 1625–1635.

(18) Kertesz, M. Pancake bonding: an unusual π-stacking interaction. *Chem.—Eur. J.* 2019, 25, 400–416.

(19) Bryan, C. D.; Cordes, A. W.; Goddard, J. D.; Haddon, R. C.; Hicks, R. G.; MacKinnon, C. D.; Mawhinney, R. C.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. J. Preparation and solid state characterization of 4,4′-bis(1,2,3,5-dithiadiazolyl) J. Chem. Soc. Commun. 1994, 1447–1448.

(20) Bryan, C. D.; Cordes, A. W.; Haddon, R. C.; Hicks, R. G.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. J. Preparation and characterization of the disjoint diradical 4,4′-bis(1,2,3,5-dithiadiazolyl) J. Chem. Soc. Commun. 1994, 1447–1448.

(21) Morita, Y.; Murata, T.; Ueda, A.; Yamada, C.; Kanzaki, Y.; Shiomi, D.; Sato, K.; Takui, T. Trioxotriangulene: air- and thermally stable organic carbon-centered neutral π-radical without steric protection. *Bull. Chem. Soc. Jpn.* 2018, 91, 922–931.

(22) Wang, T.; Kafle, T. R.; Kettel, B.; Liu, Q.; Wu, J.; Chan, W.-L. Growing ultra-flat organic films on graphene with a face-on stacking via moderate molecule-substrate interaction. *Sci. Rep.* 2016, 6, 28895.
(41) Noh, Y.-Y.; Kim, J.-J.; Yoshida, Y.; Yase, K. Effect of molecular orientation of epitaxially grown platinum(II) octaethyl porphyrin films on the performance of field-effect transistors. Adv. Mater. 2003, 15, 699−702.
(42) Zambounis, J. S.; Mizuguchi, J.; Rihs, G.; Chauvet, O.; Zuppiroli, L. Optical and electrical properties of evaporated 2,5-bismethylthio-7,7',8,8'-tetracyanoquinodimethane. J. Appl. Phys. 1994, 76, 1824−1829.
(43) Liu, S.; Wang, W. M.; Briseno, A. L.; Mannsfeld, S. C. B.; Bao, Z. Controlled deposition of crystalline organic semiconductors for field-effect-transistor applications. Adv. Mater. 2009, 21, 1217−1232.
(44) Toda, Y.; Yanagi, H. Electroluminescence of epitaxial perylene films. Appl. Phys. Lett. 1996, 69, 2315−2317.
(45) Yase, K.; Han, E.-M.; Yamamoto, K.; Yoshida, Y.; Takada, N.; Tanigaki, N. One-dimensional growth of phenylene oligomer single crystals on friction-transferred poly(p-phenylene) film. Jpn. J. Appl. Phys. 1997, 36, 2843.
(46) Watanabe, Y.; Sasabe, H.; Kido, J. Review of molecular engineering for horizontal molecular orientation in organic light-emitting devices. Bull. Chem. Soc. Jpn. 2019, 92, 716−728.
(47) Nakamura, T.; Shioya, N.; Shimoaka, T.; Nishikubo, R.; Hasegawa, T.; Saeki, A.; Murata, Y.; Murdey, R.; Wakamiya, A. Molecular orientation change in naphthalene diimide thin films induced by removal of thermally cleavable substituents. Chem. Mater. 2019, 31, 1729−1737.