Supporting Information

High performance solution crystallized thin-films transistors based on V-shaped thieno[3,2-f:4,5-f']bis[1]benzothiophene semiconductors

Chikahiko Mitsui¹, Hiroaki Tsuyama², Ryoji Shikata³, Yoshinori Murata³, Hiroyuki Kuniyasu¹, Masakazu Yamagishi⁴, Hiroyuki Ishii⁵, Akito Yamamoto¹, Yuri Hirose⁶, Masafumi Yano³, Tsunayoshi Takehara⁷, Takeyuki Suzuki⁷, Hiroyasu Sato⁸, Akihito Yamano⁸, Eiji Fukuzaki², Tetsuya Watanabe², Yoshihisa Usami², Jun Takeya^{1,6}, Toshihiro Okamoto^{1,9}*

¹ Department of Advanced Materials Science, Graduate School of Frontier Sciences, The Univ. of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.

² Fuji Film Corp., 577 Ushijima, Kaisei-machi, Ashigarakami-gun, Kanagawa 258-8577, Japan.

³ Graduate School of Science and Engineering, Kansai Univ., 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan.

⁴ National Institute of Technology, Toyama College, 13 Hongo-machi, Toyama, Toyama 939-8630, Japan.

⁵ Division of Applied Physics, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.

⁶ PI-Crystal Inc., 2-7-38 Nishimiyahara, Yodogawa, Osaka 532-0004, Japan.

⁷ Comprehensive Analysis Center (CAC), The Institute of Scientific and Industrial Research (ISIR), Osaka Univ., 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

⁸ Rigaku Corp., 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan.

⁹ PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan.

Contents

- 1. Theoretical Predictions of **TBBT-V** Derivatives for Molecular Design
- 2. Solubility Test
- 3. Ionization Potentials
- 4. Chemical Stability Test by means of Time-dependent UV-vis Absorption Spectra
- 5. Thermal Analyses
- 6. Single-crystal Analyses
- 7. Theoretical Calculations: Transfer Integral (TI) and Band Calculation
- 8. Optical Microscopy and Transmission X-ray Diffraction
- 9. Thin-film Morphology
- 10. Transistor Performance
- 11. References

1. Theoretical Predictions of TBBT-V Derivatives for Molecular Design

HOMO and LUMO Energy Levels (B3LYP/6-31G(d))

The Kohn–Sham energy levels of **TBBT–V** and its derivatives were calculated at the B3LYP/6-31G(d) level of theory with the SPARTAN 14 package, Wavefunction Inc. (Figure S1). The HOMO level of **TBBT–V** core ($E_{HOMO} = -5.46 \text{ eV}$) is almost similar to that of **DNT–V** core ($E_{HOMO} = -5.41 \text{ eV}$). The introduction of an electron-donating alkyl group into the **TBBT–V** core leads to an effective rise of the HOMO level because the HOMO coefficient of **TBBT–V** core at α –position of terminal thiophene unit exists. Furthermore, the introduction of a thienyl group as a linker also lead a rise of HOMO level. Depending on the position of the alkyl group onto the thienyl group, the HOMO of α –C1–Th–TBBT–V at the alpha positions is slightly higher than that of β –C1–Th–TBBT–V because the thienyl group bears large contributing HOMO coefficients at the alpha positions. These trends are identical to the result of the PYS plots shown in Figure S2.



Figure S1. DFT calculation of HOMO levels of TBBT–V, C₁–TBBT–V, α –C1–Th–TBBT–V, and β –C1–Th–TBBT–V in comparison (B3LYP/6-31G(d) level).

2. Solubility test

To a weighed sample of around 1 mg was added 50 μ L of commonly used solvents chloroform, toluene, and *o*-dichlorobenzene (*o*DCB), repeatedly. The resulting suspension was shaken and sonicated at room temperature (~23 °C) and 60 °C. The total amount of solvent (mL) was converted into solubility in wt%. The results are summarized in Table S1.

Table S1. Solubility test of **TBBT–V** and its derivatives in chloroform (CHCl₃), toluene, and *o*-dichlorobenzene (*o*DCB) at room temperature, together with reported **DNT–V** and C_{10} –**DNT–VW** for comparison.

Compounds	Solubility (wt%)				
Compounds	CHCl ₃	Toluene	oDCB		
TBBT–V	0.17	0.15	0.25		
C ₁₀ -TBBT-V	1.1	0.54	0.99		
	< 0.01	< 0.01	< 0.01		
$\alpha - C_{10} - 1 n - 1 BB1 - V$	0.017^{1}	0.019^{1}	0.016^{1}		
β -C ₁₀ -Th-TBBT-V	< 0.01	< 0.01	< 0.01		
	0.093 ¹	0.065 ¹	0.055 ¹		
DNT-V	0.18	0.17	0.25		
C ₁₀ -DNT-VW	0.47	0.38	0.47		
1 at 60 °C.					

3. Ionization Potentials

Thin films (ca. 100 nm) of all of **TBBT–V** derivatives were thermally evaporated on ITO coated quartz substrates and measurements were performed in vacuum. The photoelectron yield spectra are depicted in Figure S2.



Figure S2. Photoelectron yield chart of **TBBT–V** derivatives in thin film after light illumination from a D_2 lamp *in vacuo*.

4. Chemical Stability Test by means of Time-dependent UV-vis Absorption Spectra

The absorptions of C_{10} -TBBT-V and β - C_{10} -Th-TBBT-V were measured in solution under ambient condition. To evaluate the chemical stability of TBBT-V derivatives, time-dependent UV-vis absorption spectra were carried out for a period of about 12 days. It was found that the spectra of all compounds do not change over time, indicating that they have high chemical stability.



Figure S3. Time-dependent UV-vis absorption spectra of C_{10} -TBBT-V in solution (5.03 x 10⁻⁶ M, CH₂Cl₂).



Figure S4. Time-dependent UV-vis absorption spectra of β -C₁₀-Th-TBBT-V (1.01 x 10⁻⁶ M, CH₂Cl₂).

5. Thermal Analyses

Their thermal properties were investigated by themorgravimetric-differencial thermal analysis (TG–DTA) in the range of room temperature to 500 °C. No thermal decomposition was observed in C_{10} –TBBT–V, implying that they can be purified by thermal sublimation. Very high $T^{95\%}$ of C_{10} –Th–TBBT–V derivatives possessing the decyl-thienlyl substituents is due to the increase in molecular weight.



Figure S5. TG–DTA plots of C_{10} –**TBBT–V** in the range of room temperature to 500 °C in a flow of nitrogen gas (scan rate: 5 °C/min, 100 cc/min).



Figure S6. TG–DTA plots of α –C₁₀–Th–TBBT–V in the range of room temperature to 500 °C in a flow of nitrogen gas (scan rate: 5 °C/min, 100 cc/min).



Figure S7. TG–DTA plots of β –C₁₀–Th–TBBT–V in the range of room temperature to 500 °C in a flow of nitrogen gas (scan rate: 5 °C/min, 100 cc/min).

6. **Single-Crystal Analyses**

Single crystals were obtained by means of recrystallization from certain organic solvents. Those of C₁₀–TBBT–V and β –C₁₀–Th–TBBT–V were grown with the two-layer diffusion method using toluene as a good solvent and isopropyl alcohol and t-butyl alcohol as poor solvents. Single-crystal diffraction data were collected on a Rigaku R-AXIS RAPID II imaging plate diffractometer with $CuK\alpha$ radiation for C₁₀–TBBT–V (Table S2).

The crystal structures of C_{10} -TBBT-V are shown in Figure S8–S12. In terms of the molecular structure, C_{10} -TBBT-V exhibited a bent structure, like the reported C_{10} -DNT-VW^[1] (see Figure S9). Such a bent structure can be explained in terms of the characteristic V-shaped molecule. That is, the herringbone packing of V-shaped TBBT-V affects the planarity of a neighboring TBBT-V, laying both in a head-to-head (H-to-H) and tail-to-tail (T-to-T) position. This is because the exchange-repulsion energy is decreased when the planar **TBBT-V** is distorted out-of-plane along both the H and the T molecules. Likewise, such distortion should also increase the attractive term with respect to C-H $\cdots\pi$ intermolecular interaction. Regarding the packing structures, they take a typical herringbone-type packing structure (see Figure S11 and S12), like high-performance semiconductors.

C ₁₀ -TBBT-V			
formula	$C_{36}H_{48}S_3$		
FW	576.96		
<i>T</i> /K	293		
wavelength/Å	1.54187(Cu <i>Kα</i>)		
color	colorless		
crystal size, mm	$0.551 \times 0.132 \times 0.005$		
crystal system	monoclinic		
space group	$P2_{1}/c$ (#14)		
a/Å	7.6675(11)		
b/Å	6.1022(8)		
$c/{ m \AA}$	69.473(10)		
α /deg	90.000		
β /deg	92.129(8)		
γ/deg	90.000		
V/Å	3248.3(8)		
Ζ	4		
$D_{\rm X}/{ m g~cm^{-3}}$	1.180		
μ/mm^{-1}	2.237		
reflections collected	21664		
unique reflections	3384		
refined parameters	352		
GOF on F^2	0.986		
$R1 \left[I > 2\sigma(I)\right]^{a}$	0.1019		
wR2 (all data) ^b	0.2571		
$\Delta ho_{ m min}$, $_{ m max}$ / e Å ⁻³	-0.48, 0.43		

Table S2. Crystal data for C₁₀–TBBT–V.

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ^b $wR2 = [\Sigma (w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2)^{1/2}]$







Side View*



A Plane Angle between A and B: 12.42°

*Decyl groups are omitted for clarify.

Figure S9. Plane angles of C₁₀–DNT–VW in comparison.

The result is most simply understood by the degree of displacement in the horizontal direction of the molecular long axis, as illustrated and summarized in Figure S10.



Figure S10. Displacement of C_{10} -TBBT-V (a), together with C_{10} -DNT-VW (b) in comparison.



Figure S11. Packing structures of C₁₀–TBBT–V.



Figure S12. Packing structures of C₁₀–TBBT–V.

7. Theoretical Calculations: Transfer Integral (TI)

Based on the packing structure, we estimated HOMO and NHOMO levels at the B3LYP/6-31G(d), and intermolecular electronic couplings by the transfer integral (*t*) for holes at the PBEPBE/6-31G(d) level. HOMO and NHOMO levels based on the molecular structure are shown in Figure S13. Transfer integrals in C_{10} -TBBT-V and C_{10} -DNT-VW are summarized in Figure S14 and Table S3.



Figure S13. HOMO and NHOMO levels of C₁₀–TBBT–V and C₁₀–DNT–VW.



Figure S14. a) Packing structures of C_{10} -TBBT-V with transfer integrals between HOMOs. b) Packing structures of C_{10} -DNT-VW with transfer integrals between HOMOs and NHOMOs.

Table S3. Estimation of intermolecular interaction based on the single-crystal dat	ta of
C_{10} -TBBT-V, together with C_{10} -DNT-VW in comparison.	

Compounda	TIs $(t, \text{meV})^a$			Displacements $(Å)^b$		
Compounds	$t_{ m HH}$	$t_{ m HT}$	t_{TT}	H to H	H to T	T to T
C ₁₀ -TBBT-V	-66.8	+51.8	-10.1	0.64	0.23	1.33
	-00.0	+51.0		0.35		1.01
C ₁₀ -DNT-VW	-13.7 ^c	$+17.6^{\circ}$	-32.4 ^c	0.00	0.00	0.00
	-60.6^{d}	$+45.2^{d}$	-36.7 ^d	0.00	0.00	

^aTIs (t_{HT} : Head-to-Tail, t_{HH} : Head-to-Head, t_{TT} : Tail-to-Tail), ^bDisplacements between the centers of mass. ^c TIs between HOMOs. ^d TIs between NHOMOs.

Electronic band structure calculations were conducted based on the packing structure with 2-dimensional periodic boundary condition at the PBEPBE/6-31G(d) level. The energies are plotted and labeled as $\Gamma = (0, 0, 0), X = (0.5, 0, 0), Y = (0, 0.5, 0)$ in the reciprocal lattice space. Effective hole masses around Gamma were calculated as $m^* = \hbar^2 \left(\frac{\partial^2 E(k)}{\partial k^2}\right)^{-1}$ along the directions parallel to the lattice vector a and b, respectively.



Figure S15. Band structures and effective masses of a) C_{10} -TBBT-V and b) C_{10} -DNT-VW.

8. Optical Microscopy and Transmission X-ray Diffraction

The solution-crystallization films of β -C₁₀-Th-TBBT-V were observed by polarization microscopy. The high-quality thin films with the best device performances of each derivative are illustrated in Figure S16a for β -C₁₀-Th-TBBT-V. The films have large single domain crystals with sizes of sub-millimeter, which allows easy fabrication of OFETs with single domain crystals. We made devices as the crystals growing direction fits the channel length direction. Cracks occasionally appeared on the surface of the films along the channel direction, which were not fatal for the device performance in most cases.

In order to determine the direction of the crystals, we also performed transmission X-ray diffraction measurement. The diffractions were measured with using a Rigaku R-AXIS RAPID II imaging plate diffractometer with CuK α radiation. The obtained diffraction patterns are also shown in Figure S16b-c. The Laue spots for β -C₁₀-Th-TBBT-V, observed from the in-plane diffraction measurement were attributed under assuming that β -C₁₀-Th-TBBT-V have the crystal structure similar to that of C₁₀-TBBT-V. In similar manner, the β -C₁₀-Th-TBBT-V film can also have favorable transport channel.



Figure S16. (a) Polarization microscopic image, (b) in-plane diffraction pattern, and (c) out-of-plane diffraction pattern of the β -C₁₀-Th-TBBT-V solution-crystallized film.

9. Thin-film Morphology

We observed the crystalline thin films with higher mobility, C_{10} -TBBT-V and β - C_{10} -Th-TBBT-V films, by atomic force microscopy (AFM) together with transimission X-ray diffraction to investigate the morphology. AFM images are shown in Figure S17 for C_{10} -TBBT-V and Figure S18 for β - C_{10} -Th-TBBT-V. At a glance, both images show molecularly-flat surfaces. C_{10} -TBBT-V film has the step height of ca. 3.7 nm, which is comparable with the size of the bent molecule in the crystal phase. The fact is consistent with the transmission XRD result that *c**-axis, corresponding to molecular long axis, is perpendicular to the substrate surface. In the β - C_{10} -Th-TBBT-V film, we detected the step height of ca. 8.2 nm. The height is slightly smaller than twice size of molecular long axis in the planar molecule optimized by DFT calculation. The slight mismatch is considerable because a β - C_{10} -Th-TBBT-V molecule possibly make bent structure as well as other TBBT-V derivatives and the bent molecule should have the length shorter than optimized geometry molecule. The result supports that β - C_{10} -Th-TBBT-V crystal shows structure favorable to transport.



Figure S17. a) AFM image of the C_{10} -TBBT-V solution-crystallized film, b) its height profile along the white dash line in the image, and c) molecular structure in crystal phase.



Figure S18. a) AFM image of the β -C₁₀-Th-TBBT-V solution-crystallized film, b) its height profile along the white dash line in the image, and c) molecular structure optimized by DFT calculation.

10. Transistor performance

Typical transfer characteristics and output characteristics of transistors based on α -C₁₀-Th-TBBT-V, β -C₁₀-Th-TBBT-V, and C₁₀-DNT-VW as a reference were shown in Figure S19, Figure S20, and Figure S21, respectively. The devices operate as p-type transistors with negligible hysteresis as well as transistors based on C₁₀-TBBT-V in main text. Transistor parameters, maximum and average values of mobility, μ_{max} and μ_{ave} , and threshold voltage, V_{th} are summarized in Table S4. As expected, devices with TBBT-V derivatives run at voltage lower than C₁₀-DNT-VW transistors; C₁₀-DNT-VW devices with 200 nm-thick SiO₂ have $V_{th} = -30$ to -25 V. C₁₀-Th-TBBT-Vs show threshold voltage values lower than C₁₀-TBBT-V, which is consistent that thienyl substituents delocalize HOMO orbitals effectively more than decyl group.



Figure S19. a) Transfer characteristics in saturation regime and b) output characteristics of a typical transistor with a α -C₁₀-Th-TBBT-V solution-crystallized film.



Figure S20. a) Transfer characteristics in saturation regime and b) output characteristics of a typical transistor with a β -C₁₀-Th-TBBT-V solution-crystallized film.



Figure S21. a) Transfer characteristics in saturation regime and b) output characteristics of a typical transistor with a C_{10} -DNT-VW solution-crystallized film.

Compound	$(\text{cm}^2 \text{ V}^{-1} \text{s}^{-1})^a$	$(\text{cm}^2 \text{ V}^{-1} \text{s}^{-1})^a$	$V_{\mathrm{th}}\left(\mathrm{V} ight)^{b}$	$I_{ m on}$ / $I_{ m off}$
C ₁₀ -TBBT-V	6.2	4.6	-1520	10^{6}
α-C ₁₀ -Th-TBBT-V	0.55	0.53	010	10^{5}
β–C ₁₀ –Th–TBBT–V	2.3	1.6	-510	10^{6}
(D) (10) 11			• • • •	

Table S4. OFET characteristics of TBBT-V derivatives

^{*a*} Data from 6-10 good-looking devices. Estimated from saturation regime. ^{*b*} SiO₂ 200 nm.

Role of F4-TCNQ

Roles of F₄–TCNQ were investigated for both C_{10} –TBBT–V and β – C_{10} –Th–TBBT–V and transistor performances were depicted in Figure S22–S23 and summarized in Table S5. Clearly, F₄–TCNQ for C_{10} –TBBT–V film exhibited the reduced threshold voltage, which consists with reduction of hole-injection barrier, because this material assumes relatively large ionization potential of 5.26 eV. On the contrary, organic semiconducting materials with small IP around 5.0 eV near to the WF of gold electrode does not require the use of acceptor material. Thus, we also investigated the effect of F₄-TCNQ for C₁₀–Th–TBBT–V with IP of 5.01 eV. Indeed, the C₁₀–Th–TBBT–V based FET exhibited the same threshold voltage –10V to 0 V on both condition with or without F₄-TCNQ, indicating the strong acceptor is unnecessary for this material.



Figure S22. left) Transfer characteristics in saturation regime and right) output characteristics of a typical transistor with a C_{10} -TBBT-V solution-crystallized film without F₄-TCNQ.



Figure S23. left) Transfer characteristics in saturation regime and right) output characteristics of a typical transistor with a β -C₁₀-Th-TBBT-V solution-crystallized film without F₄-TCNQ.

Compound	F ₄ -TCNQ	$\mu_{\rm max} \ ({\rm cm}^2 { m V}^{-1} { m s}^{-1})^a$	$(\text{cm}^2 \text{ V}^{-1} \text{s}^{-1})^a$	$V_{\mathrm{th}}(\mathbf{V})^{b}$	$I_{ m on}$ / $I_{ m off}$
C ₁₀ -TBBT-V	Use	6.2	4.6	-1520	10^{6}
C ₁₀ –TBBT–V	None	6.9	4.4	-3040	10^{6}
β–C ₁₀ –Th–TBBT–V	Use	2.3	1.6	-510	10^{6}
β -C ₁₀ -Th-TBBT-V	None	2.2	2.0	-510	10^{6}

Table S5. Effect of F₄-TCNQ on OFET characteristics of TBBT-V derivatives

^{*a*} Data from 6-10 good-looking devices. Estimated from saturation regime. ^{*b*} SiO₂ 200 nm.

Transistor Performances Dependent on Film Morphology Prepared by Edge-casting, Drop-casting, and Vacuum Deposition Method

Besides edge-casting method, drop-casting and vacuum deposition methods were also examined for C_{10} -TBBT-V. The transistor performances are depicted in Figure S24 and S25, and summarized in Table S6. Drop-casted film exhibited moderately high mobility up to 4.0 cm²/Vs, which is slightly lower than that of single crystalline film prepared by

edge-casting method. In addition, due to the lack of orientation in crystal growth by drop-casting, mobilities among 10 devices are mostly deviated, thus the average mobility is about half of the maximum value. On the other hand, vacuum deposition afforded the uniform films in the form of polycrystalline, so that maximum mobility is about one-third lower than that of single crystalline film. In polycrystalline film, deviation of mobilities is quite small. That is the maximum and average mobility values are comparable to be 1.8 and $1.5 \text{ cm}^2/\text{Vs}$, respectively.



Figure S24. left) Transfer characteristics in saturation regime and right) output characteristics of a typical transistor with a C_{10} -TBBT-V drop-casted film.



Figure S25. left) Transfer characteristics in saturation regime and right) output characteristics of a typical transistor with a C_{10} -TBBT-V vacuum deposition film prepared at the substrate temperature of 60 °C.

Table S6. Effect of film preparation method on OFET characteristics of C10–TBBT–V derivatives

Method	Substrate temperature (°C)	$(\mathrm{cm}^{2}\mathrm{V}^{-1}\mathrm{s}^{-1})^{a}$	$(\text{cm}^2 \text{ V}^{-1} \text{s}^{-1})^a$	$V_{\mathrm{th}}(\mathrm{V})^{b}$	$I_{ m on}$ / $I_{ m off}$
Edge-cast	40	6.2	4.6	-1520	10^{6}
Drop-cast	40	4.0	2.0	-2137	10^{6}
Vacuum deposition	60	1.8	1.5	-1520	10^{6}
Vacuum deposition	100	1.1	1.0	-1520	10^{6}

^{*a*} Data from 6-10 good-looking devices. Estimated from saturation regime. ^{*b*} SiO₂ 200 nm.

11. References

[1] T. Okamoto, C. Mitsui, M. Yamagishi, K. Nakahara, J. Soeda, Y. Hirose, K. Miwa, H. Sato, A. Yamano, T. Matsushita, T. Uemura, J. Takeya, *Adv. Mater.* **2013**, *25*, 6392.