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Oxygen- and Sulfur-bridged Bianthracene V-shaped Organic Semiconductors

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Abstract

A series of oxygen- and sulfur-bridged bianthracene V-shaped π -electronic cores are facilely synthesized. We clarify their fundamental properties and aggregated structures in single crystals as well as measure their transistor performances in single crystal field-effect transistors. Both V-shaped molecules possess bent structures induced by the intermolecular interaction in a herringbone-packing manner. A theoretical calculation study reveals that the driving force of the bent structures originates from the strong dispersion energy. Additionally, the bent conformation plays a crucial role in the formation of a dense packing structure, resulting in an attractive intermolecular overlap. An examination of the charge transport indicates that the hole mobility is up to $2.0 \text{ cm}^2/\text{Vs}$. Finally, to understand the anisotropies of the mobility in single crystals, the transistors are evaluated when the channel direction is either parallel or orthogonal to the column direction in the herringbone packing along with their band structure calculations. Sulfur-bridged V-shaped π -electronic cores are more suitable for two-dimensional carrier-transport than oxygen-bridged analogs.

1. Introduction

Highly π -electron conjugated backbones are of great interest for applications to organic electronic devices; namely, organic field-effect transistors (OFETs)¹ and organic photovoltaics (OPVs).² In the case of OFETs, the π -electron system composed of benzene and heterole rings plays an important role in advancing research. Recently Takimiya *et al.* developed a series of tremendously promising and easy-to-handle organic semiconducting materials, namely, [1]benzothieno[3,2-*b*][1]benzothiophene (**BTBT**),³

dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT),⁴ and their alkyl-substituted derivatives.⁵ These materials exhibit excellent carrier mobilities, which are superior to that of currently used amorphous silicon. BTBT and DNTT have thieno[3,2-b]thiophene substructures corresponding to benzoand dibenzo[b,k]chrysene isostructures.⁶ These substructures are not acene-type but phenacene-type electronic structures. Notably, these thienoacenes exhibit a higher air stability than other linear acenes with the same number of the aromatic rings, such as tetracene and hexacene due to the lower-lying levels of the highest occupied molecular orbitals (HOMOs) as well as the elimination of the reactive position such as the central 6,13-positions of pentacene.⁷ Since the successful introduction of the thieno [3,2-b] thiophene substructure into a π -electronic backbone was achieved, many other research groups have started to develop extensively thieno[3,2-b]thiophene-containing derivatives and evaluate their charge-transport properties.^{4-5, 8}

Recently, we developed V-shaped π -electronic cores (π -cores), dinaphtho[2,3-*b*:2',3'-*d*]furan (**DNF**–**V**) and -thiophene (**DNT**–**V**) (See Fig. 1a), which are composed of oxygen- and sulfur-bridged binaphthalene.⁹ **DNF**–**V** and **DNT**–**V** have unique structural features with respect to their single-crystal structures. Unexpectedly, their molecular structures are not planar; instead, they exhibit a bent conformation in a herringbone packing manner with dihedral angles between the two naphthalene rings of 4.08° for **DNF**–**V** and 13.88° for **DNT**–**V** (Fig. 1a). Meanwhile their theoretical optimization on a single molecule results in a completely flat conformation.

We also evaluated their carrier transporting abilities with single crystal transistors. They exhibit high mobilities up to 1.1 cm^2/Vs for **DNF–V** and 1.5 cm^2/Vs for **DNT–V**, and their mobilities can be further improved by finely controlling the

aggregation form because these assuming π -cores. herringbone-packing structures, stack with а slight displacement in the molecular longitudinal axis. We introduced long alkyl side chains on the appropriate positions of their π -cores so that alkylated **DNF-V** and **DNT-V** form herringbone packing without displacement and exhibit hole mobilities as high as 1.3 and 9.5 cm²/Vs in solution-grown single-crystal transistors, respectively.⁹ Thus, V-shaped π -cores are promising candidates for solution processable organic semiconductors. Their FETs with binaphthalene species, however, exhibit non-negligible threshold voltages due to their deep HOMO levels. Such findings of DNF-V and DNT-V motivated us to elucidate the nature of a series of V-shaped π -cores and further investigate the extended V-shaped π -cores (Fig. 1a), namely dianthra[2,3-b:2',3'-d]furan (DAF-V) and dianthra[2,3-b:2'3'-d]thiophene (**DAT-V**).¹⁰

The molecular designs of **DAF–V** and **DAT–V** present several expected advantages (Fig. 1b). 1) Based on theoretical calculations, the relatively small reorganization energies under hole transport (λ_h) are estimated to be 89 meV for **DAF–V** and 99 meV for **DAT–V**, which are smaller than those of **DNF–V** (114 meV), **DNT–V** (138 meV),¹¹ and **DNTT** (130 meV). These relatively small reorganization energies suggest that bianthracene-fused congeners have a high potential as carrier transporting materials. 2) The HOMO energy levels are higher than those of naphthalene fused analogs due to the π -electron extension. 3) The variable orbital coefficient of the HOMO is on the bridging group 16 element. 4) Similar to the case of reported **DNT–V** and **DNF–V**, the molecular shape should influence the aggregated structure in the solid state, depending on the bridging elements and π -conjugated length.

Herein we report a study on the chemistry and material science of oxygen- and sulfur-bridged bianthracene V-shaped π -cores compared with binaphthalene analogs. To understand the potential utilities of V-shaped π -cores as active semiconducting materials, we describe the synthetic method and their fundamental properties, single-crystal structures, theoretical calculations, and charge transporting capabilities evaluated by single crystal transistors.





Figure 1. a) Chemical structures and molecular structures in single crystals of **DNT–V** and **DNF–V**, and the chemical structures of **DAF–V** and **DAT–V** in this work. b) Calculated reorganization energies of holes, λ_h (blue squares) and HOMO levels of V-shaped derivatives with HOMO configurations calculated at the B3LYP/6-31G(d) level.

2. Experimental

2.1. Materials: Reagents and Starting Materials

BBr₃ and *N*,*N*-dimethylcarbamoyl chloride were purchased from Tokyo Chemical Industry Co. Fe(acac)₃ was purchased from Sigma–Aldrich. 1,1,2,2-Tetrachloroethane and *o*-dichlorobenzene (*o*DCB) were purchased from Wako Pure Chemical Industries. *n*-BuLi, triethylamine, pyridine, and all anhydrous solvents were purchased from Kanto Chemical Co. DMF was distilled prior to use. Zeolite HSZ-360 was purchased from the Tosoh Corporation. 2-Methoxyanthracene was synthesized according to a modified procedure from the literature.¹²

2.2. Methods: Typical Synthesis and Characterization

All reactions were carried out under a nitrogen atmosphere. Air- or moisture-sensitive liquids and solutions were transferred via a syringe or a Teflon cannula. Analytical thin-layer chromatography (TLC) was performed on glass plates with a 0.25-mm 230-400 mesh silica gel containing a fluorescent indicator (Merck Silica gel 60 F254). TLC plates were checked under exposure to an ultraviolet lamp (254 nm and 365 nm) and visualized by dipping into 10% phosphomolybdic acid in ethanol and subsequent heating on a hot plate. Flash-column chromatography was performed on Kanto silica gel 60. Open-column chromatography was performed on Wakogel C-200 (75-150 µm). All NMR spectra were recorded on JEOL ECA600 or JEOL ECS400 spectrometer. The chemical shifts are reported in parts per million (ppm, δ scale) from the residual protons in deuterated solvent for ¹H NMR (δ 7.26 ppm for chloroform, δ 5.93 ppm for 1,1,2,2-tetrachloroethane, and δ 2.04 ppm for acetone) and from the solvent carbon for ¹³C NMR (*e.g.*, δ 77.16 ppm for chloroform, δ 74.00 ppm for 1,1,2,2-tetrachloroethane, and δ 29.80 ppm for acetone). The data are presented in the following format: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant in Hertz (Hz), signal area integration in natural numbers, and assignment (in italics). Mass spectra were measured on a JEOL JMS-T100LC

APCI/ESI mass spectrometer. Melting points and elemental analyses were collected on a Mettler Toledo MP70 Melting Point System and on a J-Science Lab JM10 MICRO CORDER, respectively.

2.3. Methods: Typical Fundamental Properties and Structural Analyses

UV-vis absorption was measured on a JASCO V-570 spectrophotometer. Photoluminescence was measured using a Hitachi F-4500 fluorescence spectrophotometer. The TG–DTA measurement was carried out with a Rigaku Thermo Plus EVO II TG 8120 apparatus. Photoelectron yield spectroscopy (PYS)¹³ was performed on a Sumitomo Heavy Industries Advanced Machinery PYS-202 apparatus. The XRD data for the single crystal of **DAF–V** and **DAT–V** were collected on Rigaku R-AXIS RAPID II and R-AXIS 191-R imaging plate diffractometers with CuK α radiation, respectively. FET characteristics were measured using a Keithley 4200 semiconductor parameter analyzer.

2.4. Synthetic procedure

Synthesis of 2-Methoxyanthracene (1)

To a suspension of 2-methoxyanthracene-9,10-dione (2.38 g, 10.0 mmol) in 200 mL of *i*-PrOH was added NaBH₄ (2.27 g, 60.0 mmol, 6.0 mol amt.). The mixture was gradually heated to the reflux temperature and maintained for 24 h. (Caution: gas evolves during the reaction) After cooling to 0 °C in ice water, the mixture was carefully hydrolyzed with a 1 N hydrochloric acid aqueous solution, and the resulting vellow precipitate was collected by filtration. After dissolving the collected yellow solid by chloroform, the crude material was purified by a short pad of a silica gel column employing chloroform to afford the desired compound (1.32 g, 6.33 mmol, 63%) as a pale-yellow solid. ¹H NMR (600 MHz, CDCl₃): δ 3.97 (s, 3H, OCH₃), 7.16 (d, J = 8.4 Hz 1H, ArH), 7.21 (s, 1H, ArH), 7.40–7.46 (m, 2H, ArH), 7.90 (d, J = 8.4 Hz, 1H, ArH), 7.95, (d, J = 8.4 Hz, 1H, ArH), 7.97 (d, J = 8.4 Hz, ArH), 8.28 (s. 1H, ArH), 8.35 (s, 1H, ArH). The spectral data of this compound were identical to those reported previously.¹⁴ Synthesis of 3,3'-Dimethoxy-2,2'-bianthracene (2)

To a solution of 2-methoxyanthracene (3.00 g, 14.4 mmol) in THF (51 mL) was added 1.60 M n-BuLi in hexane (9.9 mL, 15.8 mmol, 1.1 mol amt.) at 0 °C. After stirring at 0 °C for 1 h, Fe(acac)₃ (5.58 g, 15.8 mmol, 1.1 mol amt.) was added at 0 °C. The resultant mixture was stirred at room temperature for 10 h. After the reaction was finished, the resulting red precipitate was collected by filtration. The crude material was purified by silica gel column chromatography (hexane:chloroform = 60:40) to afford a pale-yellow solid (1.54 g, 3.72 mmol, 52%). M.p.: 239-240 °C. ¹H NMR (600 MHz, CDCl₃): δ 3.94, (s, 6H, OCH₃), 7.32 (s, 2H, ArH), 7.41 (dd, J = 7.8 Hz, 7.8 Hz, 2H, ArH), 7.46 (dd, J = 7.8Hz, 7.8 Hz, 2H, ArH), 7.94-7.99 (m, 6H, ArH), 8.34 (s, 2H, ArH), 8.39 (s, 2H, ArH). ¹³C NMR (150 MHz, CDCl₃): δ 55.8, 103.6, 124.0, 124.5, 125.6, 126.4, 127.8, 128.3, 128.4, 130.5, 130.6, 131.4, 132.3, 132.8, 156.3. TOF HRMS (APCI): Calcd for C₃₀H₂₃O₂ [M+H] 415.1698, found, 415.1707.

Synthesis of 2,2'-Bianthracene-3,3'-diol (3)

To a yellow suspension of 3,3'-dimethoxy-2,2'-bianthracene (1.04 g, 2.51 mmol) in dichloromethane (10 mL) was added 1.0 M BBr₃ (7.5 mL, 7.5 mmol, 3.0 mol amt.) in dichloromethane at 0 °C. The resulting mixture was stirred at room temperature for 5 h. After the crude material was poured into iced water, the organic layer was extracted with THF and EtOAc, and then dried over MgSO₄. The solvent was subsequently removed to ~20 mL *in vacuo*, and acetone was added to afford a yellow solid (844 mg, 2.18 mmol, 87%), which was collected by vacuum filtration. After

removing the solvent in the mother liquor, the crude material was purified by silica gel column chromatography (hexane:THF = 70:30) to afford the desired compound (844 mg, 0.23 mmol, additional 9%). Yield: 96%. M.p.: 279–280 °C. ¹H NMR (600 MHz, acetone-d₆): δ 7.43–7.52 (m, 4H, Ar*H*), 7.54 (s, 2H, Ar*H*), 8.04 (d, *J* = 9.2 Hz, 2H, Ar*H*), 8.07 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.18 (s, 2H, Ar*H*), 8.38 (s, 2H, Ar*H*), 8.57 (s, 2H, Ar*H*), 8.81 (s, 2H, O*H*). ¹³C NMR (150 MHz, acetone-d₆): δ 108.9, 123.9, 125.1, 126.3, 127.2, 128.5, 129.1, 129.2, 131.4, 131.8, 132.0, 133.3, 134.0, 154.3. TOF HRMS (APCI): Calcd for C₂₈H₁₉O₂ [M+H] 387.1385, found, 387.1378. *Synthesis of Dianthra[2,3-b:2',3'-d]furan (DAF–V*)

To a yellow suspension of 2,2'-bianthracene-3,3'-diol (1.55 g, 4.00 mmol) in 80 mL of *o*DCB was added 465 mg of Zeolite HSZ-360 and the reaction mixture was stirred at 160 °C for 20 h. After the reaction mixture was cooled to room temperature, the resulting yellow precipitate was collected by filtration. The collected material was purified by vacuum sublimation to afford the desired compound (1.14 g, 3.09 mmol, 77%) as a yellow solid. M.p.: N.A. ¹H NMR (600 MHz, CDCl₂CDCl₂, 120 °C): δ 7.44–7.49 (m, 4H, Ar*H*), 7.92 (s, 2H, Ar*H*), 8.00 (d, *J* = 8.4 Hz, 2H, Ar*H*), 8.04 (d, *J* = 8.4 Hz, 2H, Ar*H*), 8.49 (s, 2H, Ar*H*), 8.62 (s, 2H, Ar*H*), 8.66 (s, 2H, Ar*H*). The ¹³C NMR spectrum could not be recorded due to the low solubility. TOF HRMS (APCI): Calcd for C₂₈H₁₆O: C, 91.28; H, 4.38. Found C, 91.34; H, 4.53.

Synthesis of O, O'-[2,2'-Bianthracene]-3,3'-diyl bis(dimethylcarbamothioate) (4)

To a yellow suspension of 2,2'-bianthracene-3,3'-diol (483 mg, 1.25 mmol) in THF (7.5 mL) were added triethylamine (0.39 mL), pyridine (10.0 mL), and N,N-dimethylcarbamothioic chloride (402 mg, 3.25 mmol, 2.6 mol amt.). The resulting vellow suspension was heated at 65 °C for 20 h. After removing the solvent in vacuo, the crude material was purified by silica gel column chromatography (hexane:ethylacetate = 80:20) to afford the desired compound (430 mg, 0.767 mmol, 61%) as a pale-yellow solid. Mp.: 233–234 °C. ¹H NMR (600 MHz, CDCl₃): δ 3.01 (s, 6H, NCH₃), 3.11 (s, 6H, NCH₃), 7.47-7.51 (m, 4H, ArH), 7.81 (s, 2H, ArH), 8.01-8.03 (m, 4H, ArH), 8.19 (s, 2H, ArH), 8.46 (s, 2H, ArH), 8.47 (s, 2H, ArH). ¹³C NMR (150 MHz, CDCl₃): δ 38.5, 43.2, 120.4, 125.6, 126.0, 126.1, 126.9, 128.1, 128.5, 129.8, 130.6, 131.2, 131.8, 131.9, 132.3, 149.8, 187.4. TOF HRMS (APCI): Calcd for C₃₄H₂₉N₂O₂S₂ [M+H] 561.1670, found, 561.1855. Synthesis of Dianthra[2,3-b:2',3'-d]thiophene (**D**AT-V)

O, *O'*-[2,2'-Bianthracene]-3,3'-diyl bis(dimethylcarbamothioate) (561 mg, 1.0 mmol) was heated in a sealed Pyrex tube at 300 °C for 8 h. The reaction mixture was cooled to ambient temperature. The crude material was purified by vacuum sublimation to afford the desired compound (261 mg, 0.68 mmol, 68%) as an orange solid. M.p.: N.A. ¹H NMR (600 MHz, CDCl₂CDCl₂, 120 °C): δ 7.44–7.48 (m, 4H, Ar*H*), 7.99–8.06 (m, 4H, Ar*H*), 8.27 (s, 2H, Ar*H*), 8.42 (s, 2H, Ar*H*), 8.63 (s, 2H, Ar*H*), 8.84 (s, 2H, Ar*H*). The ¹³C NMR spectrum could not be recorded due to low solubility. TOF HRMS (APCI): Calcd for C₂₈H₁₇S [M+H] 385.1051, found, 385.1044. Anal. Calcd for C₂₈H₁₆S: C, 87.47; H, 4.19. Found C, 87.33; H, 4.38.

2.5. Fabrication of single-crystal transistors and FET measurements

Single crystals of semiconducting materials were grown by a physical vapor transport (PVT) technique.¹⁵ As the active layers, the crystals were laminated on SiO_2 (500 nm)/doped Si substrates, and the surfaces, which were preliminarily treated with heptadecafluorodecyltrimethoxysilane, self-assembled a monolayer (FDTS-SAM). On the semiconducting crystals, a 7,7,8,8-tetracyano-2,3,5,6-tetrafluoroquinodimethane

(F_4 -TCNQ) layer (1–2 nm) and a gold layer (30 nm) as the source and drain electrodes, respectively, were thermally deposited using a shadow mask to construct devices with a top-contact-bottom-gate configuration. All fabrication processes and measurements were performed under ambient air.

3. Results and Discussion

3.1. Synthesis

First, oxygen- and sulfur-bridged bianthracenes were successfully synthesized using the reported synthetic protocols that include two kinds of key reactions, dehydration using Zeolite¹⁶ and a Newman-Kwart rearrangement¹⁷ by heat, to construct the DAF-V and DAT-V core structures, respectively. Starting from 2-methoxyanthracene, the homo-coupling reaction proceeded via deprotonation using n-butyl lithium followed by oxidation using an iron (III) reagent (Fig. 2). Subsequently, demethylation afforded 2,2'-bianthracene binols as the key precursors. Finally, dehydration proceeded to afford **DAF-V** by treatment with a Zeolite catalyst, while the thermal conversion after the introduction of thiocarbamovl moieties afforded DAT-V by way of the Newman-Kwart rearrangement.¹⁷ Finally the desired products were further purified by multiple sublimations. The thermal stabilities of these molecules were evaluated by TG-DTA measurements (Fig. S1).



Figure 2. Synthetic route for DAF-V and DAT-V.

3.2. Ionization Potentials

The ionization potentials of these materials were determined by photoelectron yield spectroscopy (PYS);¹³ those of DAF-V and DAT-V in vacuum deposited thin films on ITO-coated quartz substrates are 5.46 and 5.31 eV, respectively (Fig. S2). These values are smaller than those of the corresponding naphthalene-fused analogs (5.93 eV for DNF-V and 5.72 eV for DNT-V), resulting from the elongation of the π -electron conjugation system. The smaller ionization potentials of DAF-V and DAT-V should help reduce the threshold voltage of the p-type FET compared with the naphthalene-fused systems because the threshold voltage ideally results from the injection barrier of the gold electrodes (4.9-5.1 eV). Furthermore, the threshold voltage also depends on the film quality and the resultant interface carrier traps in an actual device.

3.3. Photophysical Properties

To obtain insight into the photophysical properties of these compounds, absorption and emission spectrum measurements were performed in solution (Figs. 3, S4, S5, and Table 1). The anthracene-fused DAF-V and DAT-V exhibit bathochromically shifted absorption bands compared to the naphthalene-fused analogs of DNF-V and DNT-V due to the extension of π -electron conjugation. The longest absorption maximum of DAT-V is observed at 495 nm, whereas that of anthra[2,3-*b*]thiophene is at 435 nm, suggesting that π -electron conjugation occurs over the whole molecule in DAT-V.¹⁸ Additionally, sulfur-bridged compounds exhibit a red-shifted absorption maximum wavelength compared with the corresponding oxygen-bridged ones, where an oxygen atom with a strong electronegativity suppresses π -electron conjugation. Notably, the anthracene-fused derivatives are air stable in thin film regardless of the smaller ionization potential, as revealed by the time-dependent absorption spectrum measurements. After exposure to ambient conditions, the spectrum remains the same for DAF-V and DAT-V. Together with the photoluminescence spectrum measurements (Fig. 3), the Stokes shifts of the oxygen-bridged derivatives are determined to be 470 cm^{-1} for DNF-V and 390 cm^{-1} for DAF-V, which are smaller than those of sulfur-bridged analogs (760 cm^{-1} for **DNT-V** and 520 cm^{-1} for **DAT-V**). With this knowledge, we infer that the sulfur-bridged π -core has an inherently larger structural relaxation than the corresponding oxygen-bridged one in the exited state.



Figure 3. UV-vis absorption (solid line) and fluorescence (dotted line) spectra of **DAF–V** and **DAT–V** in *o*DCB.

Table 1. Photophysical properties of **DAF–V** and **DAT–V** in *o*DCB and those of **DNF–V** and **DNT–V** for comparison.

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Compd	$\lambda_{\mathrm{abs}}{}^{a)}$	$\lambda_{\rm em}^{\ \ b)}$	Stokes shift	
	(nm)	(nm)	(cm^{-1})	
DAF-V	477	486	390	
DAT-V	495	508	520	
DNF-V	384	391	470	
DNT-V	406	419	760	
)				

^{*a*)} Longest absorption maximum wavelength.

^{b)} Shortest emission maximum wavelength.

3.4. Aggregated Structures

To clarify the molecular and packing structures via X-ray single-crystal analysis, we successfully obtained platelet single crystals using the PVT technique.¹⁵ Intriguingly, X-ray analysis reveals that **DAF–V** and **DAT–V** have more bent structures with dihedral angles between two anthracene planes of 9.54°

and 17.17° compared with the naphthalene analogs of DNF-V (4.06°) and **DNT-V** (13.88°), respectively (**DAT-V** in Fig. 4a. **DAF-V** in Fig. S6), although these single molecular structures optimized by DFT calculations have completely planar geometries. These molecules stack in a herringbone manner, which is a favorable two-dimensional carrier transport similar to those of high-performance semiconductors (such as pentacene and DNTT) (Fig. 4b). As observed in DNF-V and DNT-V, DAF-V and DAT-V also form assembled structures with molecular displacements of 0.73 Å and 1.20 Å in the molecular longitudinal direction (Fig. 4c), which are larger than those of the corresponding naphthalene-fused analogs (0.15 Å for DNF-V and 0.99 Å for DNT-V, Fig. S7). These results indicate that there is room to elevate the carrier transporting abilities of DAF-V and DAT-V by finely tuning the molecular packing structures and the resultant transfer integrals by functionalization of various substituents such as alkyl side chains. Regarding the Head-to-Head (H-to-H) and Tail-to-Tail (T-to-T) molecules (Fig. 4b), the V-shaped molecules effectively interact with each other via intermolecular interactions (e.g. van der Waals force) such that the molecular geometries are transformed into a unique non-planar structure (Fig. 4c). Thus, the dihedral angles in the crystal may rely on the structural features due to the incorporated group 16 elements and the intermolecular interaction energy. The difference in the van der Waals radius between sulfur and oxygen atoms causes smaller obtuse angles in DNT-V and DAT-V (ca. 135°) compared to those of DNF-V and DAF-V (ca. 148°), resulting in larger bent angles for diaryl[2,3-b:2',3'-d]thiophenes (DArT-Vs) (Figs. 4a and S6). Moreover, the stronger intermolecular interaction affords the longer π -electron conjugation system, which likely induces a larger bent angle than the corresponding naphthalene-fused analogs.



Figure 4. a) Chemical structure with the definition of Tail (T) and Head (H) and the molecular structure of **DAT-V** in a single crystal. b) Packing structure of **DAT-V**. c) Attractive intermolecular interaction between neighboring molecules with a molecular displacement of 1.20 Å in the molecular longitudinal direction. d) Effective intermolecular orbital overlap in HOMO.

3.5. Theoretical Calculation of the Bent-shaped Structure in the Crystal

By a computational study based on the crystal structures of **DNT–V**, we further clarified the driving force of the bent

molecular structure. All calculations in this section were carried out with the GAMESS suite of program codes.¹⁹ In a single DNT-V molecule, the bent structure is less stable (by 1.3 kcal/mol) than the planar one with a C_{2x} symmetry, according to DFT calculations (B3LYP/6-31G(d) level). In the DNT-V packing structure, the intermolecular interaction energies, including electrostatic, dispersion, and exchange-repulsion energies, were also compared between the bent and planar conformation using the distances between the center masses of adjacent molecules (Table S1 and Fig. S8). Regarding the electrostatic and exchange-repulsion energies, forming a more densely packed structure is slightly unfavorable for the bent structure. Conversely, due to the increment in the dispersion energy by 2.4 kcal/mol, the molecules in the bent conformation may get closer to the neighboring molecule by ~ 0.4 Å in Tail-to-Tail molecules. In total, the stabilization energy afforded by the intermolecular interaction for all segments (T-to-T, H-to-T, and H-to-H) is 2.9 kcal/mol, offsetting the destabilization energy (1.3 kcal/mol) from the planar to the bent conformation. Thus, the energetically favorable bent structures of these compounds are endowed with a densely packed structure in the single crystal. Such an effective molecular orbital overlap, as illustrated in Fig. 4d, yields the high carrier-transporting property in electronic devices.

3.6. Single Crystal FET Device Performance

To evaluate the intrinsic carrier-transporting properties of DAF-V and DAT-V, FETs were fabricated using single crystals. Platelet single crystals obtained by PVT were manually laminated on the FDTS-SAM-treated Si/SiO₂ substrates.²⁰ On top of the laminated single crystals, F₄-TCNQ and Au electrodes were successively deposited through a shadow mask to achieve a top-contact-bottom-gate configuration (Fig. S9). In the devices, the molecular dipole of FDTS-SAM injects holes to positively shift threshold voltage. F₄-TCNQ in these devices has almost no affect on threshold voltage but reduce effectively contact resistance. To understand the anisotropy of the mobility in a single crystal, we fabricated devices where the channel directions are either parallel or orthogonal to the column direction in the herringbone packing, respectively. To distinguish between the column and transverse directions, in-plane X-ray diffraction analysis confirmed the crystal orientations.

Figures 5 and S10-16 show representative transfer and output characteristics of **DAT–V** and other compounds. These materials exhibit *p*-type characteristics with a negligible or small hysteresis. Noticeably, FETs based on anthracene-fused **DAF–V** and **DAT–V** exhibit linear contact in the output characteristics, indicating a small injection barrier compared with those of **DNF–V** and **DNT–V**, which is consistent with a smaller ionization potential (See Figs. S10-13).

From the slope of the transfer curve in the saturation region for the best performance device, we evaluated the hole mobility for both column and transverse directions. The estimated mobilities for **DAF–V** are up to 0.3 cm²/Vs for the column direction and 1.2 cm²/Vs for the transverse direction, whereas those of **DAT–V** are 1.1 cm²/Vs for the column direction and 2.0 cm²/Vs for the transverse direction (Table 2). Hence, the mobility values obtained for **DAT–V** are slightly higher and more isotropic than those obtained for **DAF–V**.



Figure 5. a) Microscopic image with the crystal direction in the device and the packing structure of **DAT–V**. Channel length and width are 100 μ m and 53 μ m, respectively. b) Transfer and c) output characteristics of **DAT–V** based FET in the channel direction orthogonal to the column direction.

 Table 2. Single-crystal FET performances of V-shaped materials.

Commd -	$\mu (\text{cm}^2/\text{Vs})^{a}$		
Compa	Column	Transverse	
DAF-V	0.6	1.2	
DAT-V	1.1	2.0	
DNF-V	0.2	0.8	
DNT-V	1.5	1.5	

^{*a*)} Maximum hole mobility estimated in the saturation regime in the column and transverse directions among four devices.

3.7. Band Calculation Based on Single Crystal Structures

To understand the carrier transporting properties in detail, we further carried out band calculations of the obtained crystal structures using a plane wave basis with the vdW-DF2 functional²¹ as implemented in the Quantum ESPRESSO.²² The cutoff energies for wave functions and electronic densities are

80 Ry and 800 Ry, respectively and the k-point sampling **Table 3.** Effective masses of V-shaped materials.

Commit	Effective mass (m^*/m_0)		
Compa	Column	Transverse	
DAF-V	11.9	2.7	
DAT-V	8.2	3.0	
DNF-V	7.9	1.5	
DNT-V	3.3	3.3	

is 4 x 4 x 4 (Fig. S17).

Theoretically, the carrier mobility is inversely proportional to the effective mass, as described in the following equation; $\mu = q\tau/m^*$ (μ : mobility, q: carrier charge, τ . relaxation time, m^* : effective mass).²⁰ From the band dispersion at the top of the valence band on the electronic band structures, the estimated effective masses of the V-shaped materials are summarized in Table 3. Their effective masses in the direction with a small value are similar and range from 1.5 to 3.3. However, there is a significant difference in the values between the column and transverse directions for **DAF**–V. Apparently, the 2D valence band surfaces corresponding to the conducting layer of **DNF–V** and **DAF–V** exhibit an elliptic contour, while those of **DNT–V** and **DAT–V** are circular (Figs. 6 and S18), suggesting that the mobilities of **DAT–V** are more isotropic than those of **DAF–V**.



Figure 6. Packing structures and 2D valence band surfaces of a) **DAF–V** and b) **DAT–V**. Contour lines are plotted in 20-meV increments.

4. Conclusion

In this work, oxygen- and sulfur-bridged π -extended V-shaped materials, DAF-V and DAT-V, are synthesized, and their unique structural features and carrier-transporting capabilities are systematically clarified. These molecules assemble to form herringbone-packing structures. Their molecular geometries in a crystal assume a bent conformation with bent angles larger than those of naphthalene analogs. A theoretical calculation study revealed that such a bent conformation originates from the strong dispersion energy between neighboring molecules. Furthermore, the bent structures of these compounds apparently play a crucial role in forming densely packed structures and the resultant increment of intermolecular orbital overlap compared to planar geometries. In fact, in single-crystal transistors, they exhibit an excellent FET performance with hole mobilities of up to 1.1 cm²/Vs for **DAF-V** and 2.0 cm²/Vs for **DAT-V**. Finally, we examined the anisotropy of their mobilities in single crystals by means of transistors with channel directions parallel or orthogonal to the column direction in the herringbone packing, and their band calculation based on the crystal structures. Consequently, the sulfur-bridged V-shaped π -electronic cores are more suitable for two-dimensional carrier-transport than the corresponding oxygen-bridged analogs. As previously reported, although DNT-V has a somewhat large displacement in the aggregated structure. alkyl-substituted DNT-V (Cn-DNT-VW) with both-side alkyl chains at terminal benzene rings achieves an aggregated structure without displacement, resulting in larger and well-balanced transfer integrals, realizing a much higher carrier mobility. Since DAF-V and DAT-V also form assembled structures with slight molecular displacements, the carrier transporting abilities of bianthracene-fused analogs may be further elevated via functionalization on these π -core structures.

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Graphical Abstract

<Title> Oxygen- and Sulfur-bridged Bianthracene V-shaped Organic Semiconductors

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<Summary> A series of oxygen- and sulfur-bridged V-shaped π -cores are synthesized and their physicochemical properties, aggregated structures, and charge transporting properties are investigated. Notably, they exhibit anomalous bent conformations in single crystals, resulting in an attractive intermolecular overlap. Their charge transporting examinations indicate a hole mobility up to 2.0 cm²/Vs. An investigation of the anisotropy in the mobility evaluated by single-crystal FETs and band calculations reveal that sulfur-bridged V-shaped π -cores are more suitable for two-dimensional carrier-transport than oxygen-bridged analogs.

<Diagram>

