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Pi Interactions

# Synthesis and Solid-State Structures of a Tetrathiafulvalene-Conjugated Bistetracene

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**Abstract:** A tetrathiafulvalene (TTF)-conjugated bistetracene was synthesized and characterized in the molecular electronic structures based on the spectroscopic measurements and the single-crystal X-ray diffraction analysis. UV/Vis absorption and electrochemical measurements of **5** revealed the considerable electronic communication between two tetracenedithiole units by through-bond and/or through-space interactions. The difference in the crystal-packing structures of **5**, showing polymorphism, results in a variety of intermolecular electronic-coupling pattern. Of these, the π-stacking structure of **5 A** gave a large transfer integral of HOMOs (97 meV), which value is beyond hexacene and rubrene, thus, quite beneficial to achieve the high hole mobility.

## Introduction

Acenes are typical aromatic hydrocarbons composed of linearly fused benzene rings and of contemporary interest from a practical standpoint as functional organic materials.[1] It is known that the electronic properties of the bulk acenes depend heavily on their molecular-packing patterns. In this context, it is intrinsically important to predict or control the molecular arrangement of acenes in the solid state to provide the best performance of the organic-molecular devices. In general, an intermolecular interaction between the large acenes is governed exclusively by π–π stacking and C—H···π interactions.[2,3] The herringbone packing motif is believed to be responsible for the high carrier mobility of oligoacenes in the crystalline state, which is induced by the strong C—H···π interactions,[4] although a rubrene (5,6,11,12-tetraphenyltetracene) exhibits remarkable carrier mobility mainly due to the appropriate π–π stacking.[5] Recently, we have synthesized 13,13′-(3,5-bis(trifluoromethyl)-phenyl)-6,6′-bipentacene from a soluble bispentacenequinone precursor.[6] Bispentacene takes orthogonal conformation in the solid state and a pair of slipped π–π stacking of both pentacene planes results in the formation of two-dimensional grid-like network structure in the crystal.

Tetrathiafulvalene (TTF) is a representative of the electron donor and an important and potential functional organic molecule that has been used in various applications.[7] Although dibenzoTTF and dinaphthoTTF (**DN-TTF**) derivatives have been widely investigated, the π-extended TTF derivatives more than anthracene fusion, however, remain virtually unexplored, mainly because of their chemical instability and low solubility (Figure 1).[8,9] Hitherto practically only one example of dianthracenoTTF (**DA-TTF**) was reported.[8]

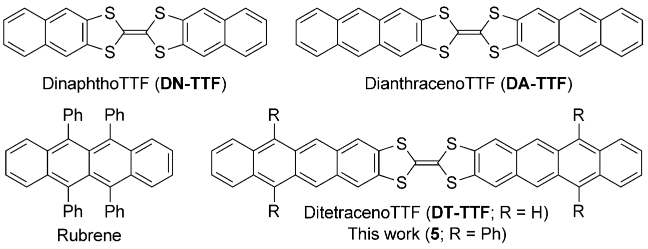

**Figure 1.** π-Extended TTF and rubrene.

Herein, we prepared, for the first time, a TTF-conjugated bistetracene **5** (Figure 1). The advantage of using such additional benzene rings is increase of intermolecular π–π interactions, which leads to a large transfer integral between molecules in the solid state.[10] To enhance the solubility of the compounds in this study, four phenyl groups were introduced at 5,5′,12,12′ positions. During its crystallization process, we have serendipitously discovered its polymorphism (**5-A** and **5-B**). These two crystal structures were predicted to have different electronic properties as a crystalline material. Based on the crystal data, the transfer integrals of **5-A** and **5-B** were estimated.

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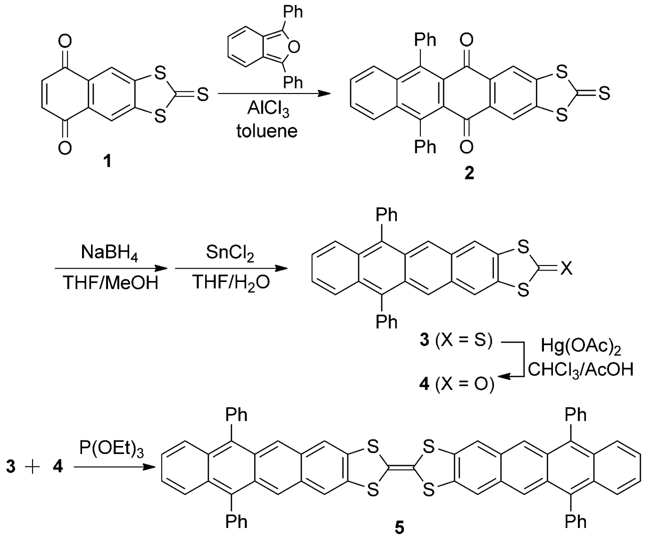
## Results and Discussion

### Synthesis and solid-state structures

The route for the synthesis of the tetraphenyl TTF-conjugated bistetracene **5** starts from a Diels–Alder reaction of the quinone **1**[11] with 1,3-diphenylisobenzofurane to form an adduct, then subsequent dehydration provided the tetracenequinone (**2**; Scheme 1). The quinone **2** was reduced with $NaBH_4$ and $SnCl_2$ to give tetracene thioketone (**3**), which was interconverted to ketone with $Hg(OAc)_2$ in 78 % yield.



**Scheme 1.** Synthesis of a TTF-conjugated bistetracene **5**.

The structures of **3** and **4** were confirmed by their $^1H$ NMR and high-resolution FAB mass spectroscopy data. Slow vapor diffusion of methanol into a chloroform solution of **3** and **4** gave good crystals suitable for X-ray diffraction analysis (Figure 2).[12] Both structures revealed a slightly curved but perfectly planar skeleton unambiguously, in which the phenyl groups take perpendicular orientation. In the solid state, **3** forms a face-to-face antiparallel dimeric structure with a stacking distance of 3.54 Å (Figure S10 in the Supporting Information). A short intermolecular S···S contact of 3.44 Å was also observed. Compound **4** also forms the face-to-face antiparallel dimeric structure (Figure S11 in the Supporting Information). The interplanar distances of 3.50 and 3.59 Å were observed.

Then, we tried to prepare a target compound **5** from **3** and **4** based on the phosphonate-induced cross-coupling reaction. After several experiments, we obtained **5** in 70 % yield as a red solid. The solubility of **5** in $CH_2Cl_2$ is 0.051 mg mL$^{-1}$. High-resolution atmospheric-pressure chemical ionization (APCI) mass spectroscopy detected the parent ion peak at $m/z = 908.2018$ (calcd for $C_{60}H_{36}S_4 = 908.1700$ $[M]^+$). The $^1H$ NMR spectrum of **5** in $CD_2Cl_2$ exhibited only aromatic protons at $\delta = 8.04$, 7.60–7.54, 7.45, and 7.18 ppm.

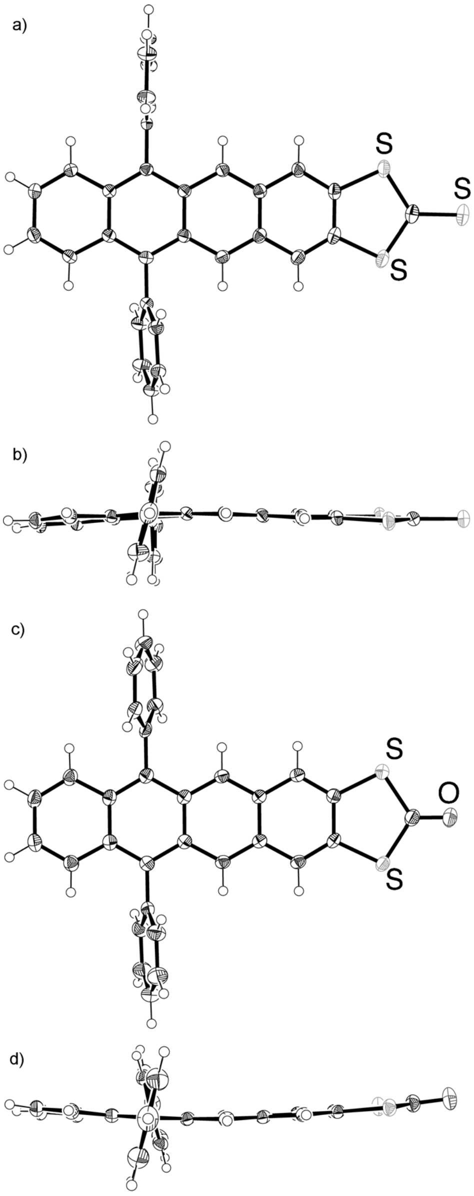


**Figure 2.** Crystal structures of **3** and **4**: a) top view of **3**; b) side view of **3**; c) top view of **4**; d) side view of **4**. Solvent molecules are omitted for clarity. Thermal ellipsoids represent 50 % probability.

The structure of **5** was unambiguously revealed by single-crystal X-ray diffraction analysis (Figure 3).[12] Interestingly, recrystallization of **5** from toluene and ethanol exhibited polymorphism, giving rod-like crystals (**5-A**) and sheet-like ones (**5-B**), both of which included two toluene molecules in their unit cells (Figure S15 in the Supporting Information). The structure analyzed from the rod-like crystal is shown in Figure 3 a–c. Compound **5-A** is perfectly planar and forms face-to-face stacking columnar structure with the interplanar distance of 3.74 Å along the *a* axis. The phenyl units are slightly tilting from an orthogonal arrangement (64 and 70°). The neighboring TTF parts are deviated by about 4.8 Å.

To our surprise, the diffraction analysis of **5-B** exhibited smoothly curved S-shaped planar structure as shown in Fig-

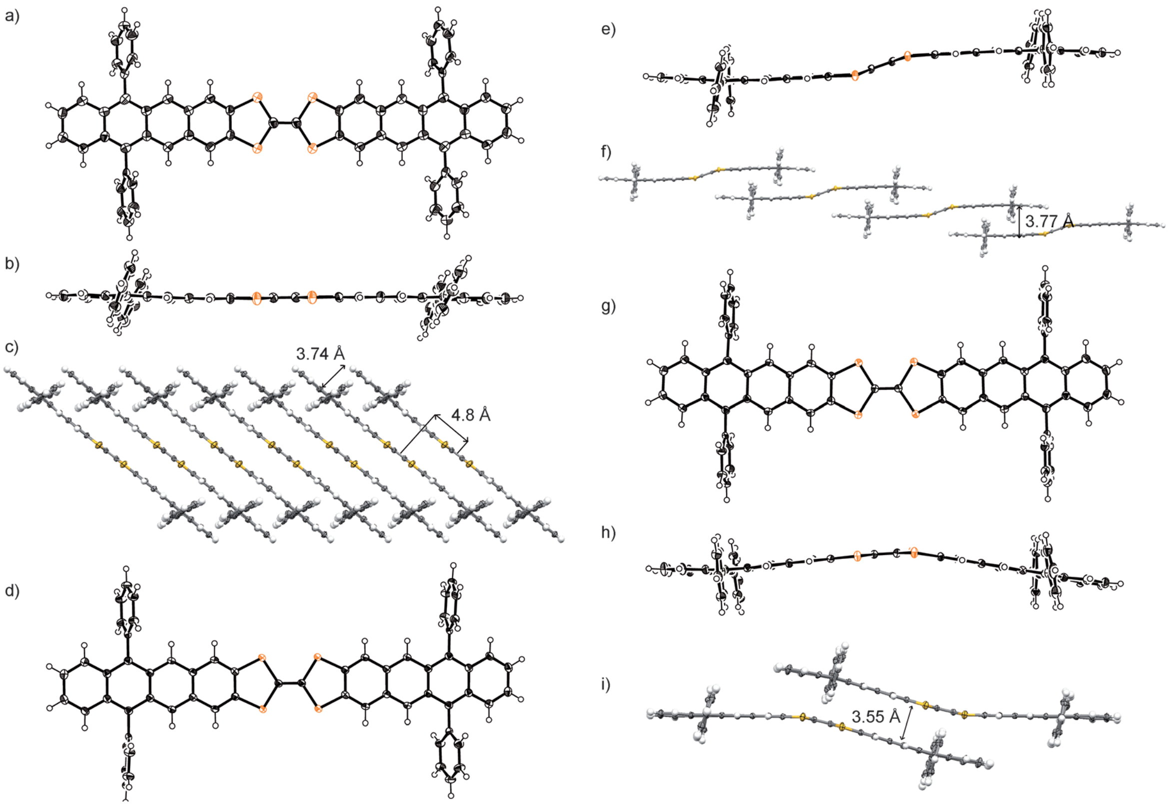


**Figure 3.** Crystal structures of a) top view; b) side view; and c) packing diagram of **5-A**; d) top view; e) side view; and f) packing diagram of **5-B**; g) top view; h) side view; and i) packing diagram of **5-C**. Solvent molecules are omitted for clarity. Thermal ellipsoids represent 50% probability.

ure 3 d–f. This clearly indicates the flexibility of the TTF-conjugated tetracene framework. The phenyl groups displayed a perpendicular conformation (78 and 88°). Importantly, in the crystal, a slipped π–π stacking of tetracene planes resulted in the formation of one-dimensional chain-like structure (Figure 3 f). The interplanar distance is averagely 3.77 Å. This is a new potential structural motif for extended TTF or bridged acene semiconducting materials.

Interestingly, the subtle change of the crystallizing solvent from toluene/ethanol to *o*-xylene/ethanol (just one methyl group addition for crystalline solvent) results in the drastic alternation of molecular arrangement in the crystal. From *o*-xylene and ethanol, the plate-shaped orange single crystals of **5** (**5-C**) were formed. The structure of **5-C** is shown in Figure 3 g–i, which is totally different from those of **5-A** and **5-B**, including ten *o*-xylene molecules in the unit cell. The main skeleton of the bistetracene is bent at the central TTF unit, and the half plane of bistetracene stacked each other to form dimeric structure with a distance of 3.55 Å surrounded by many *o*-xylene molecules (Figure 3 i and S14 in the Supporting Information).

### Spectroscopic analysis

UV/Vis absorption and fluorescence spectra of **4** and **5** in $CH_2Cl_2$ are shown in Figure 4. Compared to tetracene ($\lambda_{max}$ = 475 nm in $CHCl_3$), **4** exhibits distinctly redshifted absorption at $\lambda$ = 514 nm with the clear vibrational bands and a small Stokes shift (408 $cm^{-1}$), indicating essentially the same but slightly enhanced electronic structure of **4** compared with tetracene. The absorption spectrum of **5** ($\lambda_{max}$ = 510 nm) becomes very broad with less vibronic structure and exhibits redshifted absorption-edge compared to **4**, suggesting the considerable electronic communication between two tetracenedithiole units by through-bond and/or through-space interactions. Moreover, the fluorescence spectrum of **5** is remarkably redshifted, reflecting the red-shifted absorption spectrum. The fluorescence quantum yields of **4** and **5** are 66 and 23%, respectively, thus the larger molecular size and the ethene-linkage of **5** would lead to enhance nonradiative process.

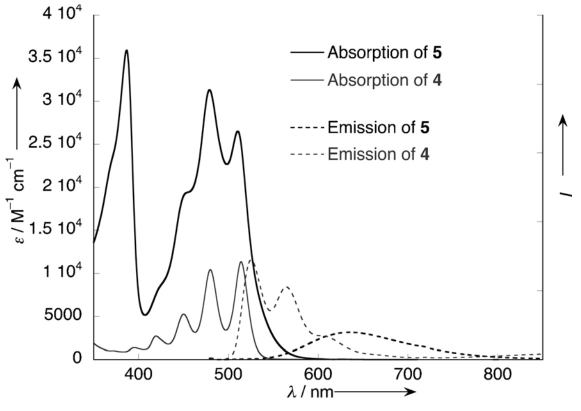


**Figure 4.** UV/Vis absorption and fluorescence spectra of **4** and **5** in $CH_2Cl_2$.

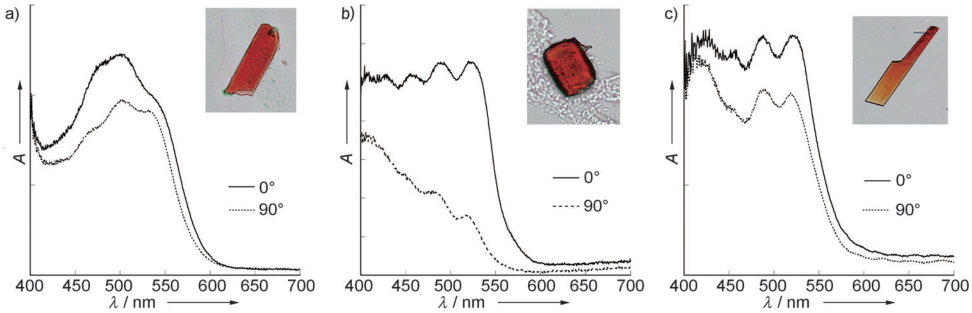


**Figure 5.** Polarized absorption spectra of the single crystals of a) **5-A**; b) **5-B**; and c) **5-C** with photographs of each crystal at 0 °C.

The intramolecular interaction in **5** was also confirmed by cyclic voltammetry (CV). The CV of **4** in PhCN displayed reversible oxidation potential at 0.52 V (vs. ferrocene/ferrocenium$^+$ ion couple) and irreversible one at 0.96 V (Figure S9 in the Supporting Information). On the other hand, the CV of **5** exhibits three oxidation potentials at 0.38, 0.61, and 0.65 V as fully reversible waves. From the first oxidation potential, we could estimate HOMO level to be −5.18 eV.[13] Reduction potentials were not detected at these conditions.

To investigate the solid-state properties of each crystal, UV/Vis absorption spectra of the single crystals of **5-A**, **5-B**, and **5-C** have been measured (Figure 5). The peak absorption wavelengths of the crystalline state were all at approximately 530 nm, which are distinctly longer than that observed in solution, thus indicating intermolecular interactions and deformation effects of **5** within the crystalline packing structure. The changes in optical density seen on rotating the crystal samples under the polarized microscope indicate that the bistetracenes are anisotropically oriented in the crystal. Especially, the molecular orientation in **5-B** stands perpendicular to the substrate based on the crystal analysis, resulting in the large difference of its absorption spectra depending on the angle of the polarized light. Those in **5-A** and **5-C** are obliquely oriented to the substrate.

## Theoretical calculations

To understand their electronic features, MO calculations of the model compounds **DN-TTF**, **DA-TTF**, and **DT-TTF** were performed at B3LYP/6-31G(d) level by using Gaussian 09 package (Figure 6).[14] At a glance, the HOMOs of **DN-TTF** and **DA-TTF** are localized on the TTF unit, whereas that of **DT-TTF** is localized on the tetracene units. Although the energy level of the orbital, which has a large MO coefficient on the TTF part, slightly lowers when the acene becomes larger, the degenerated occupied MOs localized on the acene parts (HOMO−1 and HOMO−2 for **DN-TTF** and **DA-TTF**) rise steeply with the increase of the fused benzene rings, becoming HOMO and HOMO−1 at the tetracene stage in reverse.

Next question to be answered was why does **5** take various conformations in the solid state. To understand the nature of the TTF-conjugated bistetracene **5**, we have calculated the potential energy of each conformer based on the crystal structures (Figure 7). Curiously, DFT calculations revealed that the lowest-energy structure of **5** is a V-shaped conformer, and the energy of the planar molecule (**5-A**) is 9.9 kcal mol$^{-1}$ higher, which difference corresponds to an inversion barrier. Notably, this is similar to the bowl-to-bowl inversion barrier of corannulene (11.5 kcal mol$^{-1}$).[15] Even the energy of the S-shaped conformer is 6.5 kcal mol$^{-1}$ higher than that of the optimized one, indicating that the lattice energy based on van der Waals interactions is large enough to transform the TTF part. Thus, the difference in the packing structures of **5-A**, **5-B**, and **5-C** could be originated from the soft π linkage of TTF unit. The herringbone structure is not favorable for **5** with the peripheral phenyl rings.

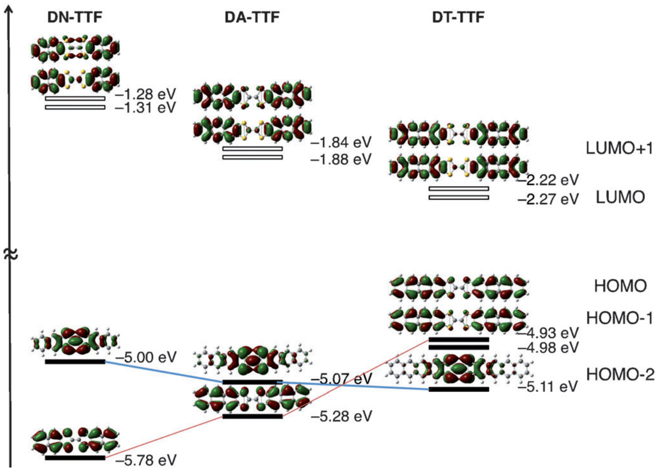


**Figure 6.** Molecular-orbital diagrams of **DN-TTF**, **DA-TTF**, and **DT-TTF**.

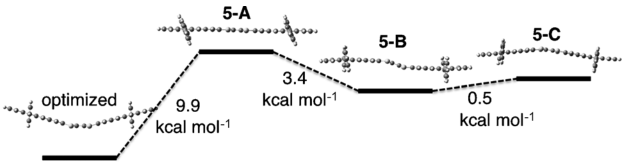


**Figure 7.** Relative potential-energy diagrams of the various conformers of **5** based on the B3LYP/6-31G* level of theory.

The π stacking structure can maximize the intermolecular orbital overlap and thus, the structures of **5-A** and **5-B** are expected to have large intermolecular orbital couplings of the HOMOs in the molecular π stacks. Intermolecular transfer integral *V* (meV) values between the HOMOs of neighboring molecules were calculated with the Amsterdam density functional (ADF) program package,[16] and the calculated *V* values are shown in Figure 8. As was expected, *V* values in the stacking

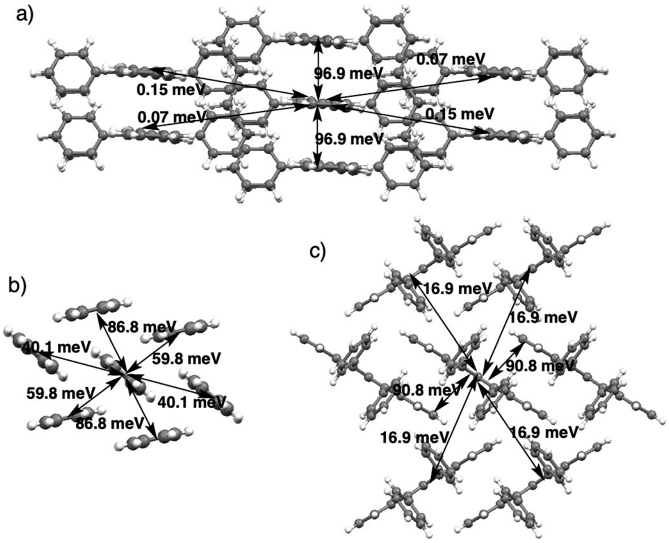


**Figure 8.** The calculated transfer integrals of a) **5-A**; b) hexacene; and c) rubrene.

direction are very large for **5-A** (ca. 97 meV) and moderate for **5-B** (ca. 16 meV), whereas *V* values in the transverse directions are almost negligible ($\leq 1$ meV), indicating that the electronic structures of **5** are most likely one dimensional. It is noteworthy that the transfer integral for **5 A** is larger than that for pentacene (79 meV),[4a] even those for hexacene (87 meV) and rubrene (91 meV), so that a significantly higher hole mobility of **5-A** should be expected.

## Conclusion

The TTF-conjugated bistetracene **5** could be synthesized and characterized in the molecular electronic structures based on the crystal data. Due to the flexible TTF unit and the peripheral phenyl groups, **5** exhibits a variety of molecular structures with face-to-face interactive manner in crystals. The $\pi$–$\pi$ interaction affords large intermolecular orbital coupling of HOMOs in **5-A**, resulting in the anisotropic 1D electronic structure as a whole. **DT-TTF** without the peripheral phenyl groups is a next attractive target, because previous studies of acene-TTF hybrid have demonstrated that the high carrier mobility was achieved by the elongation of acene units.[17]

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**Keywords:** density functional calculations · pi interactions · polymorphism · tetracenes · X-ray diffraction

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[12] Crystallographic data for **3**: $C_{31}H_{18}S_3{\cdot}CHCl_3$, $M_w = 606.00$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.49920(10)$, $b = 16.9929(3)$, $c = 19.5302(4)$ Å, $\beta = 104.6960(10)^\circ$, $V = 2728.39(8)$ Å$^3$, $\rho_{calcd} = 1.475$ g cm$^{-3}$, $Z = 4$, $R_1 = 0.0333$ $[I > 2.0\sigma(I)]$, $R_w = 0.0980$ (all data), GOF = 1.032. Crystallographic data for **4**: $C_{31}H_{18}OS_2$, $M_w = 470.57$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.3693(2)$, $b = 27.5630(5)$, $c = 13.7529(3)$ Å, $\beta = 103.4210(10)^\circ$, $V = 4560.80(15)$ Å$^3$, $\rho_{calcd} = 1.371$ g cm$^{-3}$, $Z = 8$, $R_1 = 0.0398$ $[I > 2.0\sigma\ I]]$, $R_w = 0.1065$ (all data), GOF = 1.023. Crystallographic data for **5 A**: $C_{62}H_{36}S_4{\cdot}2(C_7H_8)$, $M_w = 1093.42$, triclinic, space group $P\bar{1}$ (No. 2), $a = 5.9266(8)$, $b = 13.6535(18)$, $c = 17.760(2)$ Å, $\alpha = 110.147(3)$, $\beta = 94.314(3)$, $\gamma = 90.948(3)^\circ$, $V = 1344.0(3)$ Å$^3$, $\rho_{calcd} = 1.351$ g cm$^{-3}$, $Z = 1$, $R_1 = 0.0808$ $[I > 2.0\sigma(I)]$, $R_w = 0.2055$ (all data), GOF = 1.018. Crystallographic data for **5-B**: $C_{62}H_{36}S_4{\cdot}2(C_7H_8)$, $M_w = 1093.42$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.9635(3)$, $b = 10.9709(3)$, $c = 12.5854(3)$ Å, $\alpha = 112.5040(10)$, $\beta = 99.3790(10)$, $\gamma = 94.2860(10)^\circ$, $V = 1364.10(6)$ Å$^3$, $\rho_{calcd} = 1.331$ g cm$^{-3}$, $Z = 1$, $R_1 = 0.0358$ $[I > 2.0\sigma(I)]$, $R_w = 0.0954$ (all data), GOF = 1.057. Crystallographic data for **5-C**: $C_{62}H_{36}S_4{\cdot}5(C_8H_{10})$, $M_w = 1439.95$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.0068(3)$, $b = 13.7967(3)$, $c = 22.8243(6)$ Å, $\alpha = 101.1170(10)$, $\beta = 90.1660(10)$, $\gamma = 106.6900(10)^\circ$, $V = 3842.27(16)$ Å$^3$, $\rho_{calcd} = 1.245$ g cm$^{-3}$, $Z = 2$, $R_1 = 0.0488$ $[I > 2.0\sigma(I)]$, $R_w = 0.1212$ (all data), GOF = 1.038. CCDC 936781 (**3**), CCDC 936782 (**4**), CCDC 936783 (**5-A**), CCDC 936784 (**5-B**), and CCDC 948526 (**5-C**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] Although the mobility test on the crystals of **5-A** was tried by means of a single-crystal FET method, the crystals were not suitably stable for the measurement probably due to the presence of solvent molecules in the crystal.

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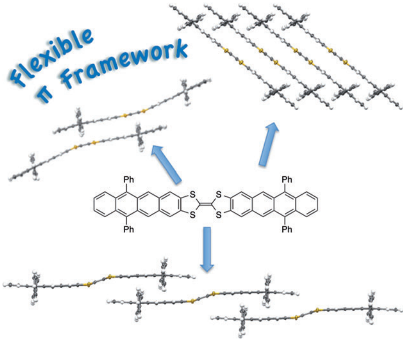
# FULL PAPER

**High hole mobility**: A tetrathiafulvalene (TTF)-conjugated bistetracene was synthesized and characterized in the molecular electronic structures, as well as the packing structures. A variety of crystal packing of compound could be originated from the soft $\pi$ linkage of TTF unit. The $\pi$-stacking structure affords large intermolecular orbital coupling of HOMOs, which is quite beneficial to enhance the charge-carrier mobility (see figure).



**Pi Interactions**

*M. Yamashita, D. Kuzuhara, N. Aratani,*
H. Yamada**

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**Synthesis and Solid-State Structures of a Tetrathiafulvalene-Conjugated Bistetracene**