# Crystal structures of $\beta$ -methylchalcogenated tetrathienoacenes: from one-dimensional $\pi$ -stacking to sandwich pitched $\pi$ -stacking structure

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### Contents

1.	Physicochemical properties of 1-3	S2-S3
2.	Transfer integrals of HOMO calculated for parent 4TA and 1–3	S4-S5
3.	Hirshfeld surface analysis of 1 and 2	<b>S</b> 6
4.	Summary of intermolecular interactions calculated by the SAPT method	S6-S9
5.	Band calculations of 1–3 and 4TA	<b>S10</b>
6.	Preparation and crystal structure of $\alpha$ -methylthiolated 4TA	S11-12
7.	NMR spectra	S13-S19
8.	References	S20

#### 1. Physicochemical properties of 1-3

Differential scanning calorimetry (DSC) curves recorded on a Shimadzu DSC-60 Plus at a heating and cooling rate of 10 °C min<sup>-1</sup>. Cyclic voltammograms were recorded on an ALS Electrochemical Analyzer Model 612D with the three-electrode system consisting of a platinum disc working electrode ( $\varphi = 3$  mm), a platinum wire counter electrode, and an Ag/AgCl reference electrode in a DCM solution containing a substrate (0.1 mM) and tetrabutylammonium hexafluorophosphate (0.1 M) at a scan rate of 100 mV s<sup>-1</sup>. The DFT calculations were carried out at the B3LYP / 6-31G\* level by using the Gaussian 16 (rev. C) program package.<sup>S1</sup>



Figure S1. Differential scanning calorimetry (DSC) curves of 1 (a), 2 (b), and 3 (c).



Figure S2. Cyclic voltammograms of 1 (a), 2 (b), and 3 (c) in the DCM solution.



Figure S3. The HOMOs (bottom) and LUMOs (top) of 1 (a), 2 (b), 3 (c), and parent 4TA (d). Note that the optimized structure of 3 is not planar.

**Table S1**. Calculated HOMO ( $E_{HOMO}$ ) and LUMO energy levels ( $E_{LUMO}$ ) and reorganization energies of hole transport ( $\lambda_h$ ) of **1–3** and parent 4TA. For comparison, electrochemically estimated  $E_{HOMOS}$  of **1–3** 

	$E_{\rm HOMO}$ / eV <sup>a)</sup>	$E_{ m LUMO}$ / eV <sup>a)</sup>	$\lambda_h$ / eV <sup>b)</sup>	$E_{\rm HOMO}^{\rm elec}$ / eV <sup>c)</sup>
1	-5.26	-1.18	0.341	-5.36
<b>2</b> <sup>d)</sup>	-5.35	-1.33	0.254	-5.47
<b>3</b> <sup>e)</sup>	-5.53	-1.47	0.378	-5.47
4TA	-5.42	-1.34	0.325	_

a) Calculated at the B3LYP / 6-31G\* level. b) Calculated at the B3LYP / 6-31G\*\* level. c) Estimated from the following equation:  $E_{\text{HOMO}}^{\text{elec}} = -4.80 - E_{\text{ox}}$ , where  $E_{\text{ox}}$  is the oxidation onset against the Fc/Fc<sup>+</sup> redox couple in the cyclic voltammogram. d) The molecular structure was optimized as a planar structure including the methylthio groups. e) The optimized molecular structure was not planar with the methylseleno groups standing from the 4TA core (see Figure S3c).

2. Transfer integrals of HOMO calculated for parent 4TA and 1-3<sup>S2</sup>



**Figure S4**. (a) Crystal structure of parent 4TA projected along the crystallographic *b*-axis with three possible two-dimensional slabs. (b-d) Transfer integrals of HOMOs calculated by Amsterdam Differential Functional program for the three two-dimensional slabs. Note that the  $\pi$ -stack along the crystallographic *b*-axis has the largest orbital overlap (149 meV), and the second largest orbital overlap is observed along the crystallographic *a*-axis direction (b). Thus, the layered structure on the crystallographic *ab* plane is selected as the primal one for discussion in the main text.



**Figure S5**. (a) Crystal structure of  $\beta$ -MeO-4TA (1) projected along the crystallographic *b*-axis and two possible two-dimensional slabs designated with red and blue dotted squares. The slab with blue dotted square (crystallographic *ab*-plane) does not form a layered structure of  $\pi$ -clouds, and thus the layered structure on the crystallographic *bc* plane is selected as the primal one for discussion in the main text (b).



**Figure S6**. (a) Crystal structure of  $\beta$ -MT-4TA (2) projected along the crystallographic *b*-axis and two possible two-dimensional slabs designated with red and blue dotted squares. The slab with blue dotted square (crystallographic *ab*-plane) does not form a layered structure of  $\pi$ -clouds, and thus the layered structure on the crystallographic *bc* plane is selected as the primal one for discussion in the main text (b).



**Figure S7**. (a) Crystal structure of  $\beta$ -MS-4TA (3) projected along the crystallographic *a*-axis and two possible two-dimensional slabs designated with red and blue dotted squares (b, c). Transfer integrals of HOMOs calculated by Amsterdam Differential Functional program for the two two-dimensional slabs. Note that the  $\pi$ -stack along the crystallographic *a*-axis has the largest orbital overlap (80.8 meV), which is smaller than the orbital overlap in the  $\pi$ -stack aggregates in 4TA. The second largest orbital overlap is observed along the crystallographic *c*-axis direction (b). Thus, the layered structure on the crystallographic *ac* plane is selected as the primal one for discussion in the main text.

# 3. Hirshfeld surface analysis <sup>S3</sup> of 1 and 2



Figure S8. Hirshfeld surface mapped with  $d_e$  for 1 (a) and 2 (b). The red depression parts represent intermolecular CH- $\pi$  contacts.

## 4. Summary of intermolecular interactions calculated by the SAPT method <sup>S4</sup>

Table S2. Intermolecular interaction energies (kcal mol <sup>-</sup> )	<sup>1</sup> ) of dimers in the packing structure of 4TA <sup>a</sup>
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pair	$E_{ m es}$	$E_{\mathrm{ex}}$	$E_{ m ind}$	$E_{ m disp}$	$E_{\rm total}$
$\pi$ -stack (1)	-5.87	14.72	-1.26	-21.91	-14.33
CH-CH (2)	-0.52	1.72	-0.24	-2.03	-1.06
CH-CH (3)	0.17	0.29	-0.09	-0.97	-0.59
CH-π (4)	-1.26	2.41	-0.40	-3.83	-3.08
Side-by-side (5)	-4.76	9.26	-1.01	-8.13	-4.63

a) Obtained from zeroth-order symmetry-adapted perturbation theory (SAPT0) calculations with jun-cc-pvdz basis.  $E_{es}$ ,  $E_{ind}$ ,  $E_{disp}$ , and  $E_{total}$  are electrostatics, exchange, induction, dispersion, and total intermolecular interaction energy, respectively.  $E_{total} = E_{es} + E_{ex} + E_{ind} + E_{disp}$ .



pair	$E_{ m es}$	$E_{ m ex}$	$E_{ m ind}$	$E_{ m disp}$	$E_{ m total}$
$\pi$ -stack (1)	-5.63	18.92	-1.55	-26.7	-14.93
end-to-end (2)	-2.76	2.53	-0.53	-5.48	-6.24
face-to-end (3)	-3.46	6.02	-0.90	-7.18	-5.50
face-to-end (4)	-0.94	2.02	-0.43	-3.63	-2.98
(5)	-5.34	12.03	-1.35	-11.51	-6.16
(6)	-6.59	15.29	-1.78	-12.18	-5.27
(7)	-3.68	8.88	-1.07	-9.54	-5.42
(8)	-1.67	2.72	-0.39	-4.07	-3.41
(9)	-1.08	2.67	-0.35	-2.73	-1.49
(10)	-1.13	1.42	-0.25	-2.16	-2.12
(11)	-0.32	2.37	-0.30	-3.80	-2.05

**Table S3**. Intermolecular interaction energies (kcal mol<sup>-1</sup>) of dimers in the packing structure of  $1^{a}$ )

a) Obtained from zeroth-order symmetry-adapted perturbation theory (SAPT0) calculations with jun-cc-pvdz basis.  $E_{es}$ ,  $E_{ex}$ ,  $E_{ind}$ ,  $E_{disp}$ , and  $E_{total}$  are electrostatics, exchange, induction, dispersion, and total intermolecular interaction energy, respectively.  $E_{total} = E_{es} + E_{ex} + E_{ind} + E_{disp}$ .



pair	Ees	$E_{ m ex}$	$E_{\mathrm{ind}}$	$E_{ m disp}$	Etotal
$\pi$ -stack (1)	-10.83	29.07	-2.58	-37.65	-21.99
end-to-end (2)	-3.37	3.71	-0.63	-5.45	-5.74
face-to-end (3)	-3.09	5.93	-0.97	-9.83	-7.96
face-to-end (4)	-2.89	6.67	-0.99	-9.25	-6.46
(5)	-4.60	9.26	-1.12	-8.90	-5.36
(6)	-1.60	5.62	-0.61	-5.62	-2.21
(7)	-0.09	0.01	-0.03	-0.49	-0.61
(8)	-1.10	1.13	-0.19	-1.64	-1.81

**Table S4**. Intermolecular interaction energies (kcal mol<sup>-1</sup>) of dimers in the packing structure of  $2^{a}$ )

a) Obtained from zeroth-order symmetry-adapted perturbation theory (SAPT0) calculations with jun-cc-pvdz basis.  $E_{es}$ ,  $E_{ex}$ ,  $E_{ind}$ ,  $E_{disp}$ , and  $E_{total}$  are electrostatics, exchange, induction, dispersion, and total intermolecular interaction energy, respectively.  $E_{total} = E_{es} + E_{ex} + E_{ind} + E_{disp}$ .



pair	Ees	$E_{\rm ex}$	$E_{ m ind}$	$E_{ m disp}$	E <sub>total</sub>
$\pi$ -stack (1)	-7.52	17.55	-1.55	-26.88	-18.4
edge-to-edge (2)	-6.64	11.5	-1.24	-11.97	-8.36
slipped edge (3)	-0.80	1.76	-0.30	-3.64	-2.98
end-to-end (4)	-1.16	3.97	-0.48	-6.02	-3.69
face-to-end (5)	-4.28	7.57	-1.14	-9.35	-7.19

**Table S5**. Intermolecular interaction energies (kcal mol<sup>-1</sup>) of dimers in the packing structure of  $3^{a}$ )

a) Obtained from zeroth-order symmetry-adapted perturbation theory (SAPT0) calculations with aug-cc-pvdz basis.  $E_{es}$ ,  $E_{ex}$ ,  $E_{ind}$ ,  $E_{disp}$ , and  $E_{total}$  are electrostatics, exchange, induction, dispersion, and total intermolecular interaction energy, respectively.  $E_{total} = E_{es} + E_{ex} + E_{ind} + E_{disp}$ .



## 5. Band calculations of 1–3 and 4TA

Band structure calculations were carried out with Quantum Espresso program<sup>S5</sup> employing a plane-wave basis set, the Perdew-Burke-Ernzerhof (PBE) functional,<sup>S6</sup> and PAW pseudopotentials,<sup>S7</sup> and using  $1 \times 12 \times 12$  (for 4TA, **1**, and **2**) or  $12 \times 12 \times 1$  (for **3**) k-point Pack-Monkhorst net with the geometry determined by the single crystal X-ray analysis.



**Figure S9**. Band structures of 1–3 (a–c) and parent 4TA (d). The reciprocal coordinates of the high-symmetry points are defined as shown in Figures. The insets are expanded diagrams close the HOMO band.

#### 6. Preparation and crystal structure of $\alpha$ -methylthiolated 4TA ( $\alpha$ -MT-4TA)

Preparation of 2,6-bis(methylthio)thieno[2",3":4',5']thieno[2',3'-d]thieno[3,2-b]thiophene ( $\alpha$ -MT-4TA) To a solution of 5 (302 mg, 0.60 mmol) in dioxane (5 mL) and acetic acid (1 mL) was added zinc powder (205 mg, 3.1 mmol), and the mixture was refluxed for 5 h. The progress of the reaction was monitored by a gas chromatography mass spectroscopy analysis (GC-MS), and additional portions of acetic acid (2 mL in total)/zinc powder (205 mg, 3.1 mmol in total) were necessary to complete the conversion to 4TA. After cooling, the mixture was filtered, and the filtrate was extracted with chloroform (10 mL  $\times$  2). The combined extracts were washed with an aqueous solution of sodium thiosulfate (5%, 10 mL  $\times$  3) and brine (10 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo. Purification by flash column chromatography on silica gel (hexane:chloroform = 9:1) gave 4TA as a pale vellow solid (132 mg, 0.52 mmol, 87%). To a solution of 4TA (30 mg, 0.12 mmol) in tetrahydrofuran (2.5 mL) was added dropwise *n*-butyllithium (1.58 M in hexane, 170 µL, 0.27 mmol) at -70 °C, and the mixture was allowed to warm to 0 °C over 5 h. Then the mixture was again cooled to -20 °C, and dimethyldisulfide (30 µL, 0.34 mmol) was added to the mixture, and the resulting mixture was allowed to warm to room temperature over 1 h. The reaction mixture was quenched by the addition of water (5 mL) and extracted with ether (5 mL  $\times$  2). The combined extracts were washed with an aqueous solution of saturated ammonium chloride (10 mL  $\times$  2) and brine (10 mL), dried (MgSO<sub>4</sub>) and concentrated in vacuo. Purification by flash column chromatography on silica gel (eluent: hexane) gave the title compound as a pale yellow solid (23 mg, 0.067 mmol, 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  (ppm) 7.33 (s, 2H), 2.56 (s, 6H). The single crystals of  $\alpha$ -MT-4TA for a single crystal X-ray analysis were obtained by the slow vapor-diffusion of methanol into the chloroform solution of  $\alpha$ -MT-4TA.



**Figure S10.** (a) Crystal structure of  $\alpha$ -MT-4TA projected along the crystallographic *b*-axis and two possible two-dimensional slabs designated with blue and red dotted squares (b, c). Transfer integrals (meV) of HOMOs calculated by Amsterdam Differential Functional program for the each two-dimensional slab.<sup>S2</sup> Note that the  $\pi$ -stack along the crystallographic *b*-axis has the largest orbital overlap (102 meV).

Compound	<i>α</i> -MT-4TA
Formula	$C_{12}H_8S_6$
Molecular Weight	344.54
Temperature / K	100(2)
Crystal Habit	plate
Crystal System	monoclinic
Space Group	$P2_{1}/c$
a /Å	15.4846(12)
b /Å	3.9838(3)
c /Å	10.9197(8)
eta /°	103.673(8)
$V/\text{\AA}^3$	654.52(9)
Ζ	4
$R, R_{ m w}$	0.0561, 0.1501
GOF	1.060

**Table S6.** Crystallographic data of  $\alpha$ -MT-4TA (CCDC-2081896).

# 7. NMR spectra



**Figure S11.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3,6-dibromo-2,5-bis[2-(trimethylsilyl)ethynyl]thieno[3,2-*b*]thiophene.



**Figure S12.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3,6-Bis(ethylsulfanyl)-2,5-bis[2-(trimethylsilyl)ethynyl]thieno[3,2-b]thiophene (4).



Figure S13. <sup>1</sup>HNMR spectrum of 3,7-diiodothieno[2'',3'':4',5']thieno[2',3'-d]thieno[3,2-b]thiophene (5).



**Figure S14.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3,7-dimethoxythieno[2'',3'':4',5']thieno[2',3'-d]thieno[3,2-b]thiophene (**1**).



**Figure S15.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3,7-bis(methylthio)thieno[2'',3'':4',5']thieno[2',3'-d]thieno[3,2-b]thiophene (**2**).



**Figure S16.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3,7-bis(methylseleno)thieno[2",3":4',5']thieno[2',3'-d]thieno[3,2-b]thiophene (3).



**Figure S17** <sup>1</sup>H NMR spectrum of 2,6-bis(methylthio)thieno[2",3":4',5']thieno[2',3'-d]thieno[3,2b]thiophene ( $\alpha$ -MT-4TA).

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