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Supporting Information for

Contrasted behaviors of methylthiolated perylene and pyrene as organic semiconductors: implications of molecular electronic structure and crystal structure

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1. Optimized molecular structures of MT-perylene isomers

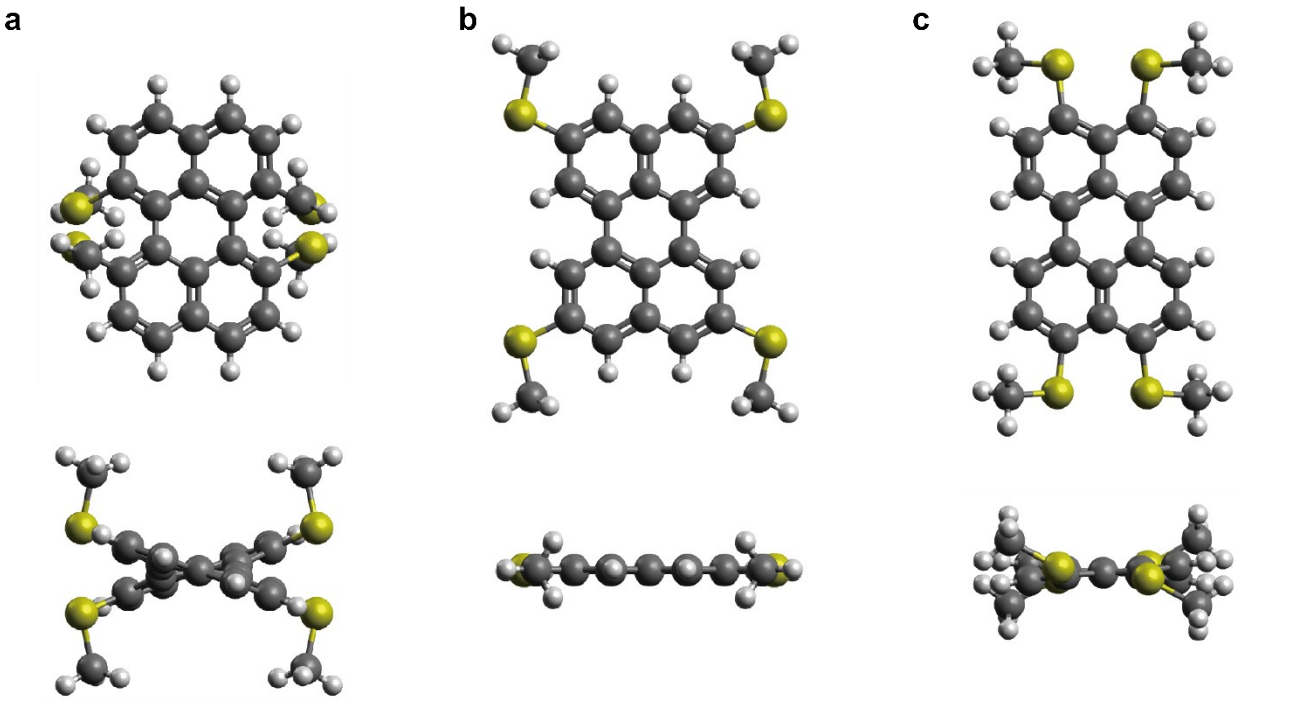

Fig. S1. Optimized molecular structures of (a) 1,6,7,12-, (b) 2,5,8,11-, and (c) 3,4,9,10-tetrakis(methylthio)perylenes. Note that only 2,5,8,11 isomer has a planar molecular structure.

2. Characterization of MT-perylene

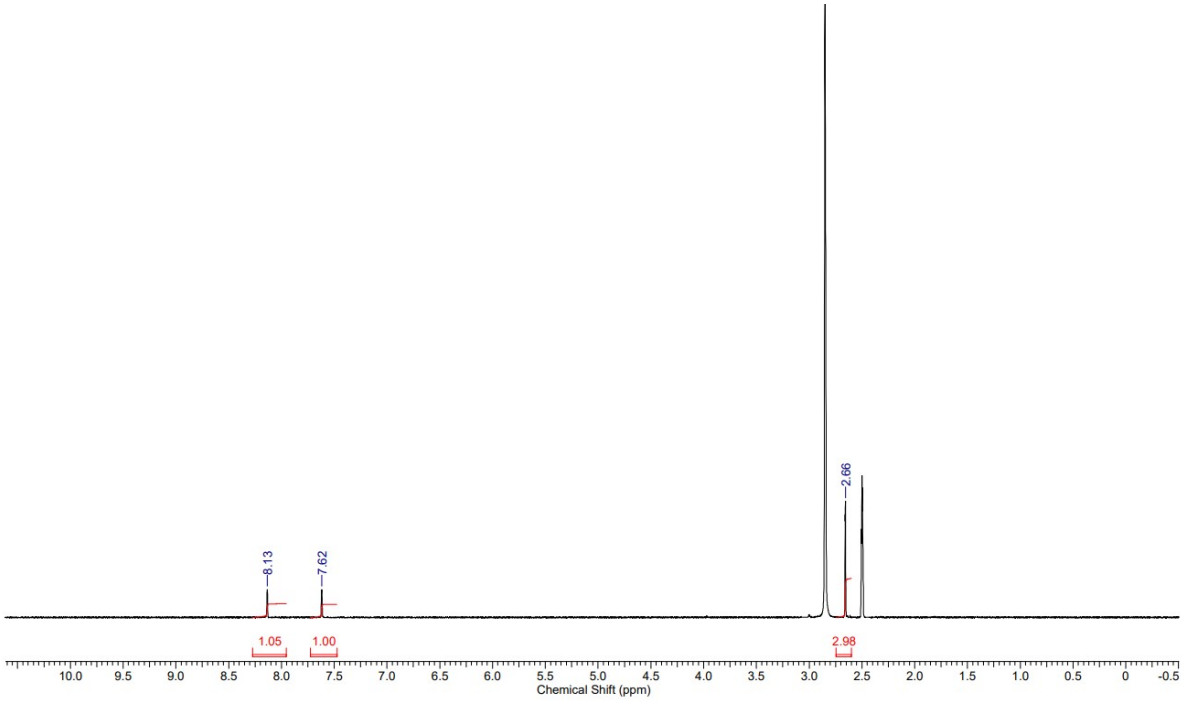

Fig. S2. ^{1}H NMR spectra of MT-perylene in DMSO-d_6 at 120℃.

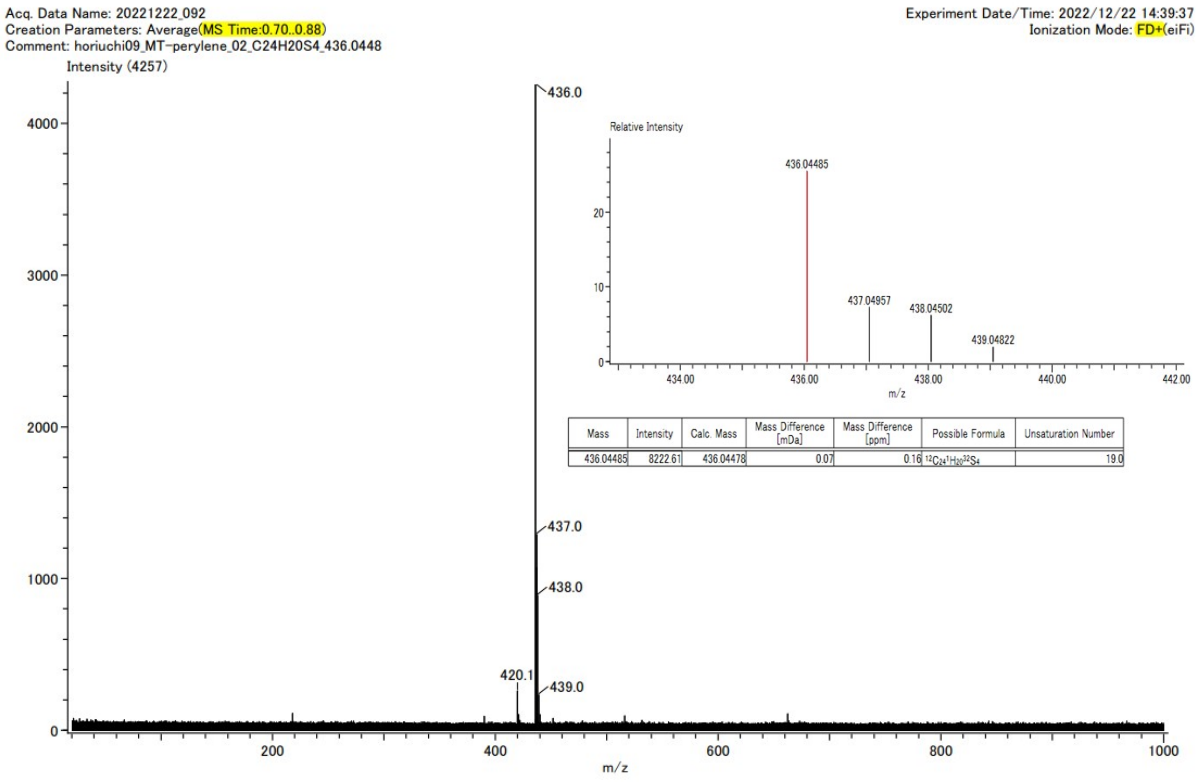

Fig. S3. HRMS spectra of MT-perylene.

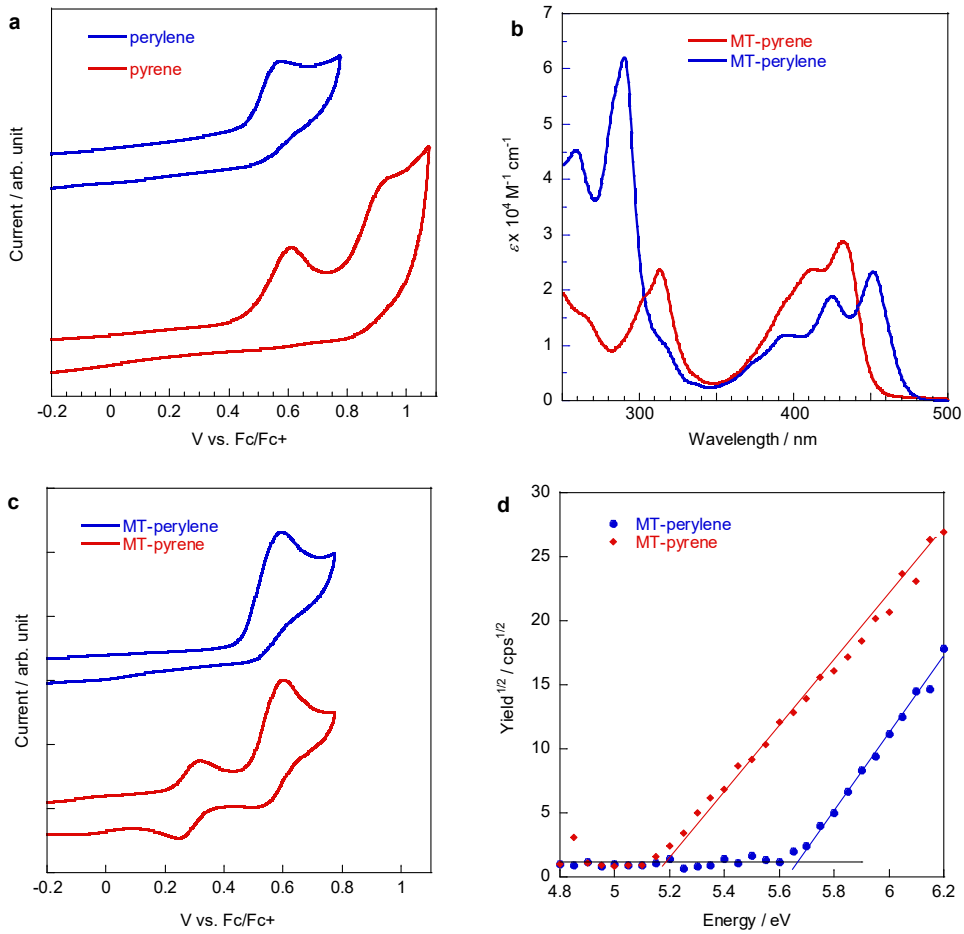

Fig. S4. Cyclic voltammograms of parent perylene and pyrene (a) and physicochemical properties of MT-perylene in comparison with those of MT-pyrene (b-d); (b) UV-vis absorption spectra in chloroform solution, (c) cyclic voltammetry measured in benzonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate with the platinum working and counter electrodes, and Ag/AgCl electrode as the reference electrode (the potentials were calibrated against the standard Fc/Fc^+ couple measured under the identical conditions), and (d) ionization potential evaluated by photoelectron spectroscopy in air. From the onset of the oxidation peaks, the E_{HOMO} of parent perylene and pyrene were estimated to be –5.24 and –5.26 eV, respectively.

Table S1. Summary of physicochemical properties of MT-perylene and MT-pyrene.

	E_{ox} (onset) / V[a]	E_{HOMO} / eV [b]	λ_{onset} / nm	E_g / eV [c]	IP / eV
MT-perylene	0.45	–5.25 [d]	475	2.61	5.68
MT-pyrene	0.22	–5.02 [d]	452	2.73	5.20

[a] V vs. Fc/Fc^+. b Estimated from the following equation: $E_{HOMO} = -4.80 - E_{ox}$. [c] Estimated from the absorption onset. [d] E_{HOMO}s of parent perylene and pyrene were estimated to be –5.24 and –5.26 eV, respectively.

3. Crystal structure and transfer integrals of MT-perylene

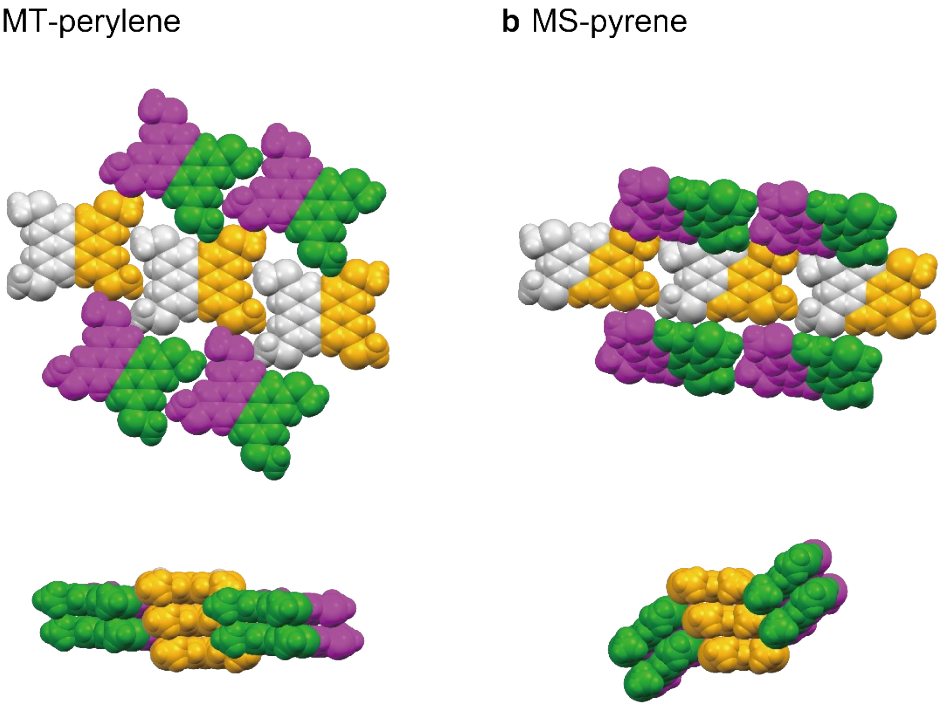

Fig. S5. MS-pyrene's inclined brickwork structure (b) compared to that of MT-perylene (a).

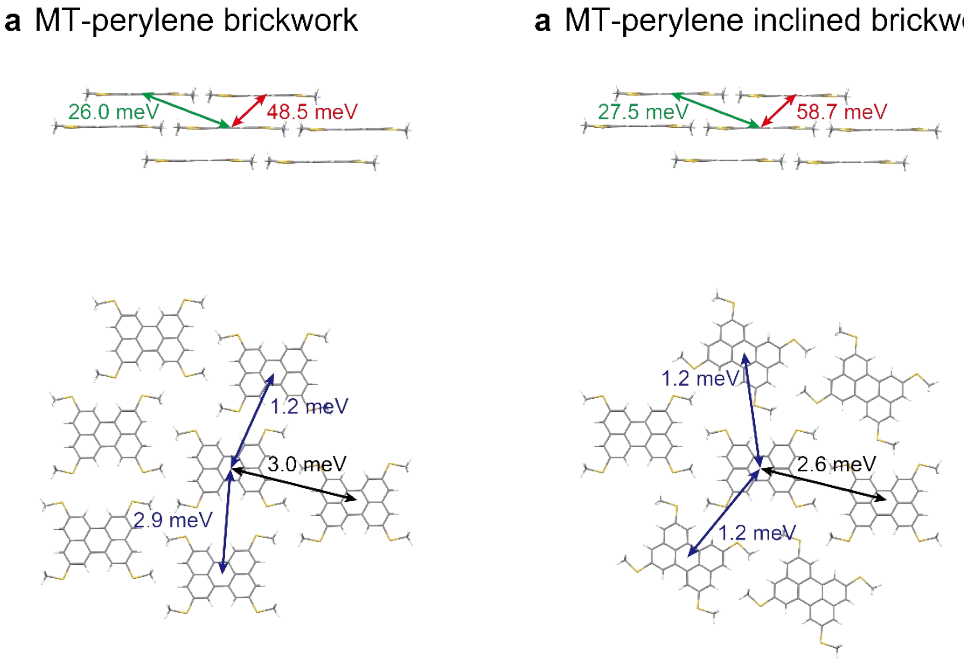

Fig. S6. Calculated transfer integrals of brickwork and inclined brickwork structure of MT-perylene.

Table S2. Crystallographic data of MT-perylene brickwork structure.

Temperature / K	300	200	100
Formula	$C_{24}H_{20}S_4$	$C_{24}H_{20}S_4$	$C_{24}H_{20}S_4$
Molecular Weight	436.64	436.64	436.64
Crystal Habit	plate	plate	plate
Crystal System	*triclinic*	*triclinic*	*triclinic*
Space Group	*P*−1	*P*−1	*P*−1
a /Å	4.8974(3)	4.8846(3)	4.8621(3)
b /Å	9.4432(5)	9.3854(5)	9.3471(5)
c /Å	11.1155(7)	11.0554(4)	11.0114(8)
α /°	89.740(5)	90.232(4)	90.500(5)
β /°	79.373(5)	100.626(4)	100.650(5)
γ /°	87.973(5)	91.646(4)	91.424(4)
V /Å^3	504.93(5)	497.90(4)	491.61(5)
Z	1	1	1
R	0.0472	0.0540	0.0620
R_w	0.1541	0.1565	0.1709
GOF	1.095	1.069	1.064

Table S3. Crystallographic data of MT-perylene inclined brickwork structure.

Temperature / K	300	200	100
Formula	$C_{24}H_{20}S_4$	$C_{24}H_{20}S_4$	$C_{24}H_{20}S_4$
Molecular Weight	436.64	436.64	436.64
Crystal Habit	plate	plate	plate
Crystal System	*monoclinic*	*monoclinic*	*monoclinic*
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a /Å	4.8598(2)	4.8514(2)	4.8336(2)
b /Å	22.1181(10)	22.0402(9)	21.9293(8)
c /Å	9.4583(4)	9.4012(3)	9.3596(3)
α /°	90	90	90
β /°	92.098(4)	91.773(3)	91.596(3)
γ /°	90	90	90
V /Å^3	1015.99(8)	1004.75(7)	991.71(6)
Z	2	2	2
R	0.0525	0.0792	0.0754
R_w	0.1615	0.2088	0.2270
GOF	1.107	1.143	1.090