

Supplementary Information for

Crystal-structure simulation of molecular semiconductors: brickwork-related crystal structures of methylthiolated *peri*-condensed polyaromatic hydrocarbons

Kirill Bulgarevich,^a Kazuo Takimiya,^{a,b,c*}

^aRIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

^bDepartment of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8578 Japan

^cTohoku University Advanced Institute for Materials Research (AIMR), 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577 Japan

1. Methods

1.1 *Single-crystal growth*

Single-crystals of MT-pyrene, MS-pyrene, MT-perylene, and MT-peropyrene were obtained by using physical vapor transport (PVT) method under a flow of nitrogen gas. The pressure was reduced to < 20 Pa for MT-peropyrene while for other materials PVT was performed under atmospheric pressure. The temperatures of the source (target) zones were 230 (130), 230 (160), 270 (210) and 360 (220) °C, for MT-pyrene, MS-pyrene, MT-perylene, and MT-peropyrene respectively. The obtained crystals shaped as thin plates or needles were carefully transferred onto mesh-type apertures for single-crystal XRD analysis.

1.1 *Theoretical calculations*

For the calculation of intermolecular energies, a series of Gaussian input files were generated with varying intermolecular displacements in the *x*, *y*, and *z* directions in the Cartesian coordinate system. The basis set was set to b3lyp/6-31g(d) with dispersion correction employed,^{1, 2} and the basis set superposition error (BSSE) was corrected using the counterpoise method.³ The example of an input file for MT-perylene molecular pair where one molecule is rotated by roll, pitch, and yaw angles of -1.79, -0.49, -30.59 degrees and displaced by 1.80, -11.88, and 1.29 Å in *x*, *y*, and *z* directions, respectively, is provided in Table S1. Starting from Cartesian coordinates of a single molecule of interest, the input files for bimolecular intermolecular interactions calculation are generated and processed according to pseudo code of *in silico* crystallization described in Section 1.3 below.

Table S1. Gaussian input file content for intermolecular energy calculation of molecular pair of MT-perylene.

%nprocshared=16				H(Fragment=1)	-5.7290	-3.1081	-0.8957
%mem=32GB				H(Fragment=1)	-5.9442	-4.6291	0.0011
# b3lyp/6-31g(d) counterpoise=2 empiricaldispersion=gd3				H(Fragment=1)	-5.7287	-3.1078	0.8971
				C(Fragment=2)	-0.6653	-10.4226	1.3144
2D-Energy analysis				C(Fragment=2)	0.5657	-11.1503	1.3022
				C(Fragment=2)	-0.6500	-9.0045	1.3590
0 1 0 1 0 1				C(Fragment=2)	1.8004	-10.4273	1.3355
C(Fragment=1)	2.8639	0.0000	0.0001	C(Fragment=2)	0.5476	-8.3200	1.3909
C(Fragment=1)	1.4340	0.0000	0.0000	C(Fragment=2)	1.7646	-9.0416	1.3787
C(Fragment=1)	3.5728	-1.2291	-0.0001	C(Fragment=2)	-1.9010	-11.1193	1.2819
C(Fragment=1)	0.7393	-1.2514	-0.0001	C(Fragment=2)	-1.9239	-12.4982	1.2385
C(Fragment=1)	2.8905	-2.4285	-0.0003	C(Fragment=2)	0.5268	-12.5803	1.2572
C(Fragment=1)	1.4756	-2.4266	-0.0003	C(Fragment=2)	-0.7050	-13.2166	1.2266
C(Fragment=1)	3.5728	1.2291	0.0002	C(Fragment=2)	3.0732	-11.1797	1.3227
C(Fragment=1)	2.8905	2.4285	0.0004	C(Fragment=2)	1.7996	-13.3328	1.2447
C(Fragment=1)	0.7393	1.2514	0.0001	C(Fragment=2)	3.0343	-12.6097	1.2778
C(Fragment=1)	1.4756	2.4266	0.0003	C(Fragment=2)	1.8354	-14.7184	1.2019
C(Fragment=1)	-0.7393	-1.2514	0.0001	C(Fragment=2)	3.0524	-15.4401	1.1898
C(Fragment=1)	-0.7393	1.2514	-0.0001	C(Fragment=2)	4.2653	-13.3374	1.2656
C(Fragment=1)	-1.4340	0.0000	-0.0001	C(Fragment=2)	4.2500	-14.7555	1.2213
C(Fragment=1)	-1.4756	2.4266	-0.0003	C(Fragment=2)	4.3050	-10.5434	1.3529
C(Fragment=1)	-2.8905	2.4285	-0.0004	C(Fragment=2)	5.5239	-11.2617	1.3408
C(Fragment=1)	-2.8639	0.0000	-0.0001	C(Fragment=2)	5.5010	-12.6407	1.2978
C(Fragment=1)	-3.5728	1.2291	-0.0003	S(Fragment=2)	0.7099	-6.5460	1.4480
C(Fragment=1)	-1.4756	-2.4266	0.0003	S(Fragment=2)	-3.4007	-13.4952	1.1945
C(Fragment=1)	-2.8905	-2.4285	0.0003	S(Fragment=2)	2.8901	-17.2141	1.1333
C(Fragment=1)	-3.5728	-1.2291	0.0001	S(Fragment=2)	7.0007	-10.2648	1.3843
S(Fragment=1)	3.6540	-4.0389	-0.0006	C(Fragment=2)	-1.0160	-5.9638	1.4517
S(Fragment=1)	3.6540	4.0389	0.0006	C(Fragment=2)	-4.7426	-12.2637	1.2214
S(Fragment=1)	-3.6540	4.0389	-0.0007	C(Fragment=2)	4.6160	-17.7963	1.1296
S(Fragment=1)	-3.6540	-4.0389	0.0006	C(Fragment=2)	8.3426	-11.4962	1.3571
C(Fragment=1)	5.4360	-3.6616	-0.0008	H(Fragment=2)	-1.6013	-8.4833	1.3672
C(Fragment=1)	5.4360	3.6616	0.0007	H(Fragment=2)	2.6864	-8.4715	1.4046
C(Fragment=1)	-5.4360	3.6616	-0.0005	H(Fragment=2)	-2.8162	-10.5371	1.2923
C(Fragment=1)	-5.4360	-3.6616	0.0008	H(Fragment=2)	-0.7606	-14.2988	1.1922
H(Fragment=1)	4.6570	-1.1937	0.0000	H(Fragment=2)	0.9136	-15.2886	1.1763
H(Fragment=1)	0.9725	-3.3870	-0.0005	H(Fragment=2)	5.2013	-15.2767	1.2132
H(Fragment=1)	4.6570	1.1937	0.0003	H(Fragment=2)	4.3606	-9.4611	1.3869
H(Fragment=1)	0.9725	3.3870	0.0003	H(Fragment=2)	6.4162	-13.2229	1.2874
H(Fragment=1)	-0.9725	3.3870	-0.0004	H(Fragment=2)	-1.5574	-6.3193	2.3328
H(Fragment=1)	-4.6570	1.1937	-0.0003	H(Fragment=2)	-1.5422	-6.2629	0.5409
H(Fragment=1)	-0.9725	-3.3870	0.0005	H(Fragment=2)	-0.9612	-4.8729	1.4865
H(Fragment=1)	-4.6570	-1.1937	0.0000	H(Fragment=2)	-4.7207	-11.6665	2.1372
H(Fragment=1)	5.7286	-3.1078	-0.8972	H(Fragment=2)	-5.6724	-12.8374	1.1953
H(Fragment=1)	5.7290	-3.1081	0.8956	H(Fragment=2)	-4.7051	-11.6104	0.3453
H(Fragment=1)	5.9442	-4.6291	-0.0011	H(Fragment=2)	5.1423	-17.4969	2.0402
H(Fragment=1)	5.7289	3.1081	-0.8957	H(Fragment=2)	5.1573	-17.4410	0.2484
H(Fragment=1)	5.9442	4.6291	0.0009	H(Fragment=2)	4.5611	-18.8872	1.0952
H(Fragment=1)	5.7287	3.1078	0.8971	H(Fragment=2)	8.3055	-12.1494	2.2333
H(Fragment=1)	-5.7289	3.1078	-0.8968	H(Fragment=2)	9.2724	-10.9225	1.3827
H(Fragment=1)	-5.7287	3.1081	0.8960	H(Fragment=2)	8.3204	-12.0936	0.4414
H(Fragment=1)	-5.9442	4.6291	-0.0006				

1.3 Pseudo code for “in silico crystallization” algorithm

1. Initialize molecule *O*:
 - Optimize molecule geometry using Gaussian.
 - Set molecule *O* at origin (0, 0, 0).
 - Align molecule *O*'s plane on the *xy*-plane.
 - Align molecule *O*'s long axis on the *x*-axis.
2. Place molecules *F*, *S*, *E*:
 - Position molecule *F* at van der Waals contact with *O* in the face-to-face (*F*) direction.
 - Position molecule *S* at van der Waals contact with *O* in the side-to-side (*S*) direction.
 - Position molecule *E* at van der Waals contact with *O* in the end-to-end (*E*) direction.
3. Define positions for combinations of *FSE* vectors:
 - For each linear combination of *FSE* (e.g., *FE* for *F* + *E*), define the position of the molecule.
4. Move cluster and calculate interactions for face-to-face direction:
 - Generate a grid of points around *O*.
 - Move molecule *F* with respect to *O* according to the grid of points.
 - Move molecules that contain vector *F* (e.g., *FE*) with molecule *F*.
 - Generate Gaussian input files for intermolecular interaction energy calculation for each point for molecular pairs (*O*, *F*) and (*O*, *FE*).
 - Calculate the intermolecular interactions between pairs (*O*, *F*) and (*O*, *FE*).
 - Add the calculated interaction values together.
5. Update vector *F*:
 - Update vector *F* as minimum energy position determined in step 4.
6. Move cluster and calculate interactions for side-to-side direction:
 - Perform step 4 for molecule *-S* instead of *F*, and *SF* and *SFE* instead of *FE*.
7. Update vector *S*:
 - Update vector *S* (*-S*) as minimum energy position determined in step 6.
8. Move cluster and calculate interactions for end-to-end direction:
 - Perform step 4 for molecule *E* instead of *F*, and *FE* and *-S-E*, and *SFE* instead of *FE*.
9. Update vector *E*:
 - Update vector *E* as minimum energy position determined in step 8.
10. Repetition:
 - Repeat steps 4-9 two more times.
11. Alternate step 4 (skipped unless specified otherwise):
 - Perform step 4, but without molecule *FE*.
12. Alternate step 7 (skipped unless specified otherwise):
 - Update vector *S* (*-S*) as the second local minimum energy position determined in step 6.
13. Alternate step 8 (skipped unless specified otherwise):
 - Perform step 8, but use molecule *-SE* instead of *-S-E*.
14. Brickwork structure polymorph candidate simulation:
 - Obtain 2M-CL-BW structure from results of above steps 1-10

- Obtain 2M-ZL-BW structure from results of above steps 1-10, with steps 7 and 8 replaced with 12 and 13, respectively.
 - Obtain 1M-CL-BW structure from results of above steps 1-10, with step 4 replaced with 11.
 - Obtain 1M-ZL-BW structure from results of above steps 1-10, with steps 4, 7, and 8 replaced with 11, 12, and 13, respectively.
15. Inclined brickwork simulation:
- For a structure obtained in step 14, generate rotation matrix using Equation 1 of the main text, and F and E vectors of the structure.
 - Position molecule S rotated by matrix A with respect to O at van der Waals contact with O in the side-to-side (S) direction.
16. Update vector S for inclined brickwork:
- Perform steps 6 and 7, but mirror the molecules $-S$, SF , and SFE by xz -plane and rotate by matrix A .
17. Repetition:
- Repeat step 16 one more time.
18. Inclined brickwork polymorph candidate simulation:
- Start from 2M-CL-BW structure in steps 15-17 to obtain 2M-CL-iBW structure.
 - Start from 2M-ZL-BW structure in steps 15-17 to obtain 2M-ZL-iBW structure.
 - Start from 1M-CL-BW structure in steps 15-17 to obtain 1M-CL-iBW structure.
 - Start from 1M-ZL-BW structure in steps 15-17 to obtain 1M-ZL-iBW structure.
19. CIF files generation:
- Assuming $P1$ cell, convert molecular coordinates of step 1 into internal coordinates using appropriate linear combination of FSE vectors for each structure obtained in step 14 as crystal lattice vectors.
 - Assuming $P1$ cell, convert molecular coordinates of step 1 and of molecule $-S$ mirrored by xz -plane and rotated by matrix A into internal coordinates using appropriate linear combination of FSE vectors for each structure obtained in step 18 as crystal lattice vectors.

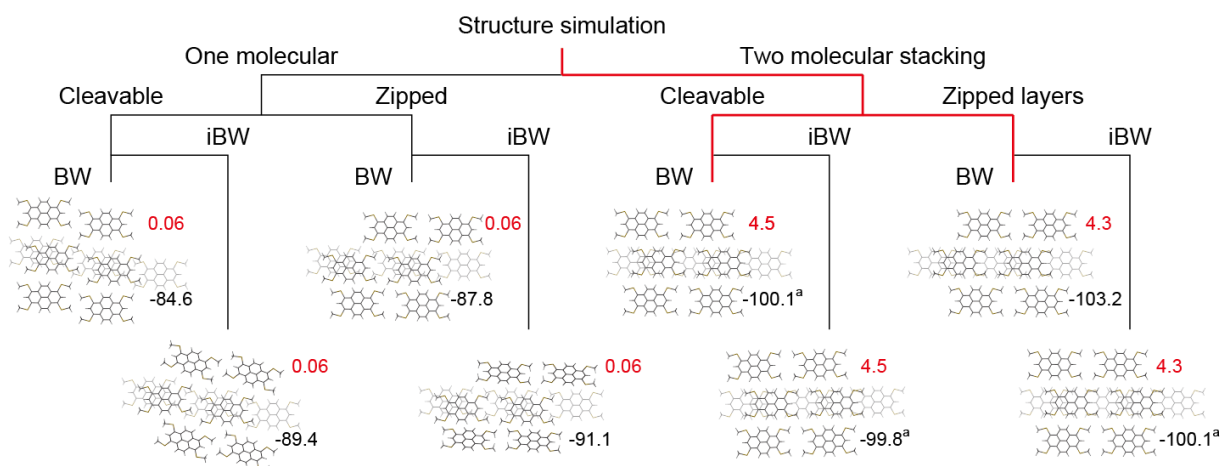
The grids used in step 4 and its variants (steps 6, 8, and 16) are the subject of optimization for good balance between accuracy of simulation and calculation time. The grids used for simulation in this paper are summarized in Table S2.

Table S2. Grid sizes used in in silico crystallization. The grid is generated around the point corresponding to vectors F , S , or E . The sizes are x_s , y_s , and z_s in x , y , and z directions, respectively, and number of steps are n_x , n_y , and n_z in x , y , and z directions, respectively. Grid is generated in both positive and negative directions except for equivalent orientations.

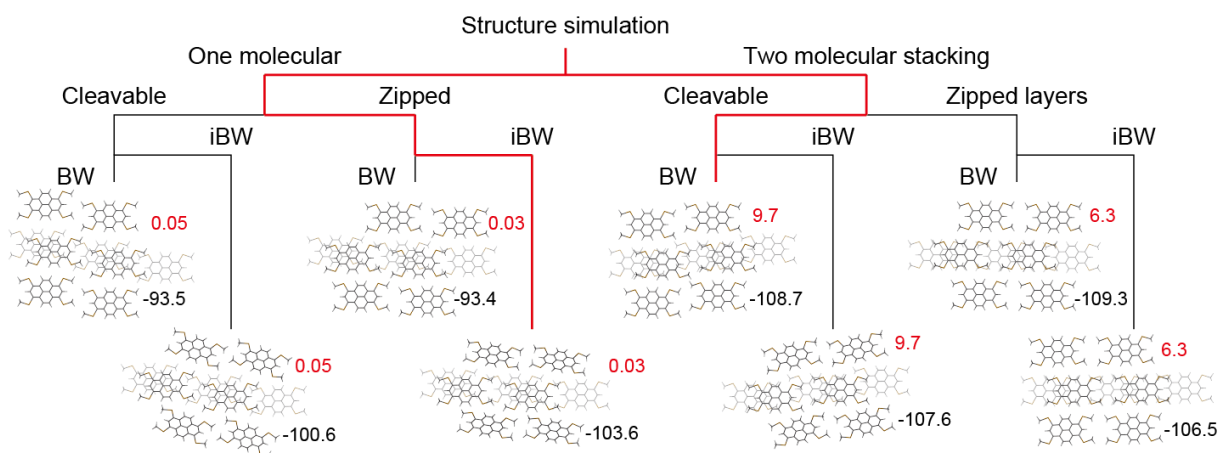
Structure	Cycle	Step	x_s	y_s	z_s	n_x	n_y	n_z
BW	1	4	0.50	0.50	0.00	21	4	0
		6	0.50	0.50	0.00	22	2	0
		8	0.50	0.50	0.00	4	8	0
	2	4	0.50	0.50	0.04	3	3	2
		6	0.30	0.30	0.50	2	2	2
		8	0.30	0.30	0.30	2	2	2
	3	4	0.20	0.20	0.02	3	3	2
		6	0.20	0.20	0.20	2	2	2
		8	0.20	0.20	0.20	2	2	2
iBW	1	16	0.50	0.50	0.50	22	2	1
	2	16	0.20	0.20	0.20	2	2	2

2. Results of *in silico* crystallization

MT-pyrene



MS-pyrene



MT-peropyrene

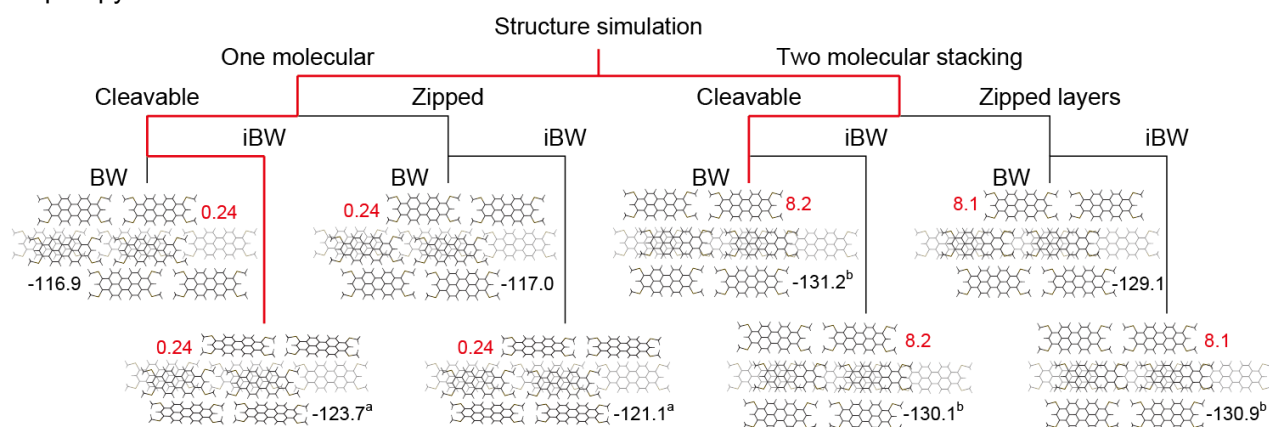


Figure S1. Eight polymorph candidates of MT-pyrene, MS-pyrene, and MT-peropyrene. The hopping mobilities (in cm² V⁻¹ s⁻¹) and $E_{\text{int}}(15)$ energies (in kcal mol⁻¹) of the structures are indicated as red and black values, respectively. Semitransparent molecules represent those situated behind (beneath) the fully opaque ones. The simulation results that were almost identical are grouped and denoted by superscripted letters 'a', 'b', and 'c', signifying high structural similarity within each group but not across different groups. The conditional branching to the experimentally confirmed polymorphs is indicated by the red lines.

Table S3. Cartesian coordinates of molecules (centers of mass) and the distances [$\text{\AA}$] between the origin (O) and centers of mass of various neighboring molecules in the predicted inclined brickwork structure of MT-perylene.

MT-perylene simulated inclined brickwork					MT-perylene inclined brickwork (experimental, 100K)				
Mol.	x	y	z	distance	Mol.	x	y	z	distance
<i>F</i>	3.50	−0.90	3.43	4.98	<i>F</i>	3.382	−0.834	3.354	4.835
<i>S</i>	7.49	9.28	−2.19	12.12	<i>S</i>	7.644	9.185	−2.132	12.138
<i>E</i>	−12.79	3.50	0.05	13.26	<i>E</i>	−12.775	3.574	0.213	13.267
<i>FE</i>	−9.29	2.60	3.48	10.26	<i>FE</i>	−9.393	2.741	3.567	10.415
<i>SF</i>	10.99	8.38	1.24	13.88	<i>SF</i>	11.026	8.351	1.223	13.885
<i>SFE</i>	−1.80	11.88	1.29	12.08	<i>SFE</i>	−1.749	11.926	1.436	12.138
<i>SE</i>	−5.30	12.78	−2.14	14.00	<i>SE</i>	−5.131	12.759	−1.918	13.885

References

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