What makes brickwork crystal structures favorable? A case study on methylthiolated arenes and heteroarenes for high-mobility molecular semiconductors

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1. Packing parameters of reported brickwork crystal structures

Table S1. Packing parameters of reported brickwork-related crystal structures.

Compounds	*F*(*x*) / Å	*F*(*y*) / Å	*F*(*z*) / Å	*S*(*x*) / Å	*S*(*y*) / Å	*S*(*z*) / Å	*E*(*x*) / Å	*E*(*y*) / Å	*E*(*z*) / Å
TIPS-pentacene	-6.694	1.030	3.370	-1.632	18.721	2.359	16.196	0.800	-0.108
TES-pentacene	-6.276	0.972	3.400	-2.165	16.700	3.259	18.109	4.154	-1.159
4Cl-TAP[a]	-6.219	0.359	3.577	0.741	18.256	3.534	18.087	2.309	-0.036
	6.323	0.609	-3.270	-0.800	-18.267	-3.812	-17.983	-1.341	0.344
CH-NDI	-0.817	-4.192	3.339	1.634	8.383	0.000	18.421	0.466	0.000
MO-pyrene	-5.572	0.507	3.517	2.294	8.070	1.648	12.989	-0.794	-0.030
MT-pyrene	-5.549	0.109	3.417	3.453	8.464	1.692	14.230	0.166	0.387
MS-pyrene	-5.546	-0.334	3.519	-2.040	8.425	2.198	14.320	-1.719	0.067
MS-pyrene (iBW)[d]	-3.852	-1.748	3.470	-5.962	7.788	1.153	14.401	1.206	0.272
MT-perylene	-3.366	-1.068	3.342	-4.552	9.907	1.543	12.780	3.743	0.258
MT-perylene (iBW)[d]	-3.373	-0.870	3.351	1.718	11.919	1.525	12.765	3.609	0.218
MT-peropyrene	-5.742	0.010	3.400	-2.182	8.446	1.772	18.509	0.388	0.365
MT-peropyrene (iBW)[b]	-3.730	-1.618	3.439	-1.675	7.827	1.576	18.507	-0.140	-0.050
MT2-anthracene (iBW)[b]	-4.042	-0.538	3.479	-1.325	6.632	3.615	12.163	-1.261	0.128
MT2-anthracene (PP)[c]	-4.063	-1.003	3.494	-1.428	5.973	4.306	7.657	-2.291	3.992
MT-anthracene	-1.947	-4.163	3.422	3.895	8.331	0.000	13.898	-1.560	0.000
MS-BDT (BW)	-3.929	0.806	3.481	-0.492	7.168	1.282	12.342	-1.235	0.038
MS-BDT (PP)	-3.962	0.743	3.497	4.950	6.954	1.276	10.580	3.089	4.405
MT-BDT (PP)[e]	-3.906	0.781	3.468	4.437	6.979	1.245	8.343	6.198	-2.223
MT-NDT (PP)	-3.917	0.202	3.477	2.053	7.096	1.696	7.311	-3.132	4.466
MT-ADT (PP)[e]	-5.804	0.130	3.480	1.390	7.098	1.805	6.846	-2.534	4.930
Me_4-TES-pentacene (PP)[c]	-6.012	-1.042	3.378	1.872	16.361	5.585	6.737	0.210	5.227
Cl_2-anthracene	-1.664	0.491	3.454	0.794	7.175	1.526	9.245	-1.251	2.468
Br-anthracene	-5.368	-1.471	3.491	1.715	5.520	2.717	8.026	-0.469	4.838
Br-pyrene	-1.898	-0.018	3.432	-1.363	8.659	1.449	11.213	1.777	-0.371
Br-pyrene (PP)[e]	-1.900	-0.039	3.437	-0.467	8.687	1.888	9.378	1.743	2.958

[a] The crystal structure of 4Cl-TAP consists of two crystallographically independent molecules, and thus, there exist two different 2D π-stacking relationships, yet they are almost identical in terms of the molecular overlap structure. [b] iBW: inclined brickwork structure. [c] PP: pitched π-stacking structure.

2. Interlayer configuration in inclined brickwork structures

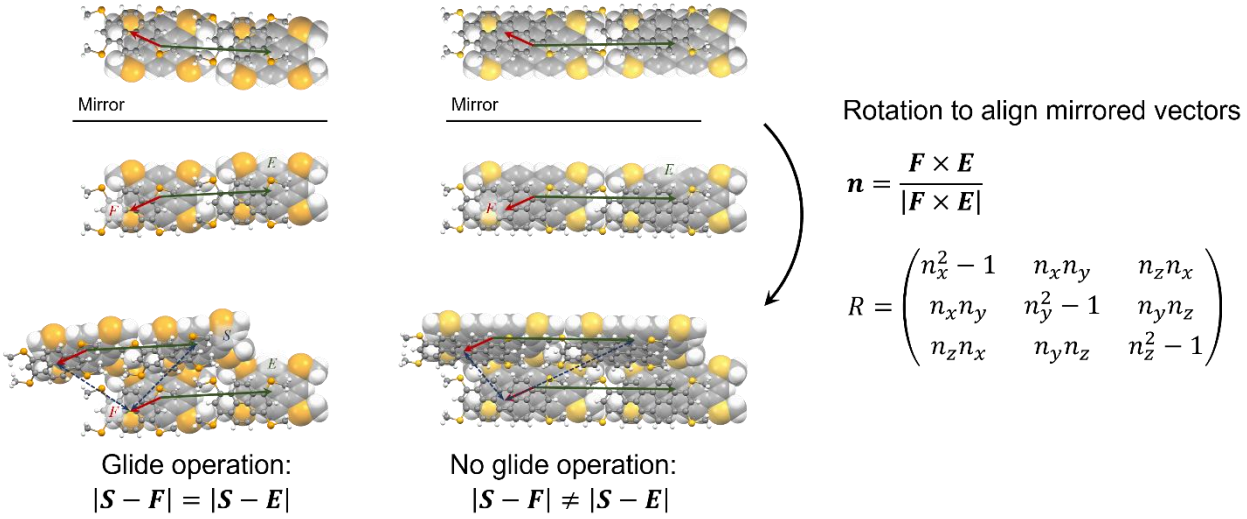

Fig. S1. Construction of experimental inclined brickwork structures of MS-pyrene (left) and MT-peropyrene (center) based on virtual brickwork layers (top). Inclination between the brickwork layers is understood based on the alignment of two vectors that define the brickwork layers (right), regardless of the existence of the glide symmetry in the crystal structure. For the inclined brickwork structures, the glide symmetry in the $P2_1/n$ space group (left) introduces the symmetry between the vectors in the *S* (molecular side-to-side) direction.

3. Definition of *F* and *E* vectors in pitched π-stack structures

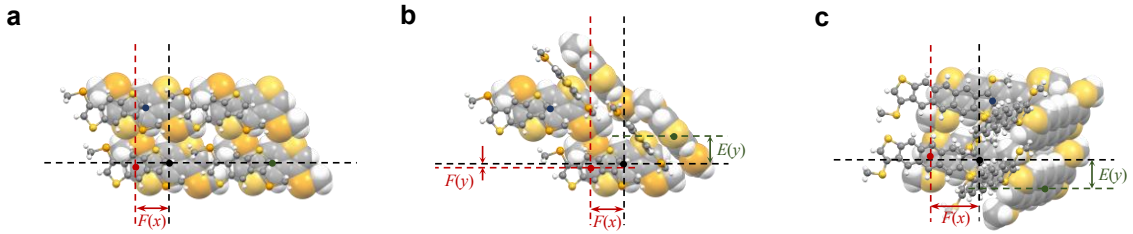

Fig. S2. Definition of *F* and *E* vectors in the brickwork structure of MS-BDT (a), pitched π-stack structure of MS-BDT (b), and pitched π-stack structure of MT-ADT (c). Note that *F* vectors are almost identical (a) and (b), but *F*(*x*) is much larger in (c) than in (a) and (b) (see also Table S1).

4. Theoretical Calculations

The transfer integrals were computed using Gaussian 16 program at B3LYP/6-31G(d) level in accordance with the ChArge TraNsfer Integral Package (CATNIP).[1,2]

1. J. Kirkpatrick, "An approximate method for calculating transfer integrals based on the ZINDO Hamiltonian," *Int. J. Quantum Chem.* 2008, **108**, 1, pp. 51–56

2. E. F. Valeev, V. Coropceanu, D. A. da Silva Filho, S. Salman, and J.-L. Brédas, "Effect of electronic polarization on charge-transport parameters in molecular organic semiconductors," *J. Am. Chem. Soc.* 2006, **128**, 30, pp. 9882–6.