Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

Preference for Propellane motif in Pure Silicon Nanosheets

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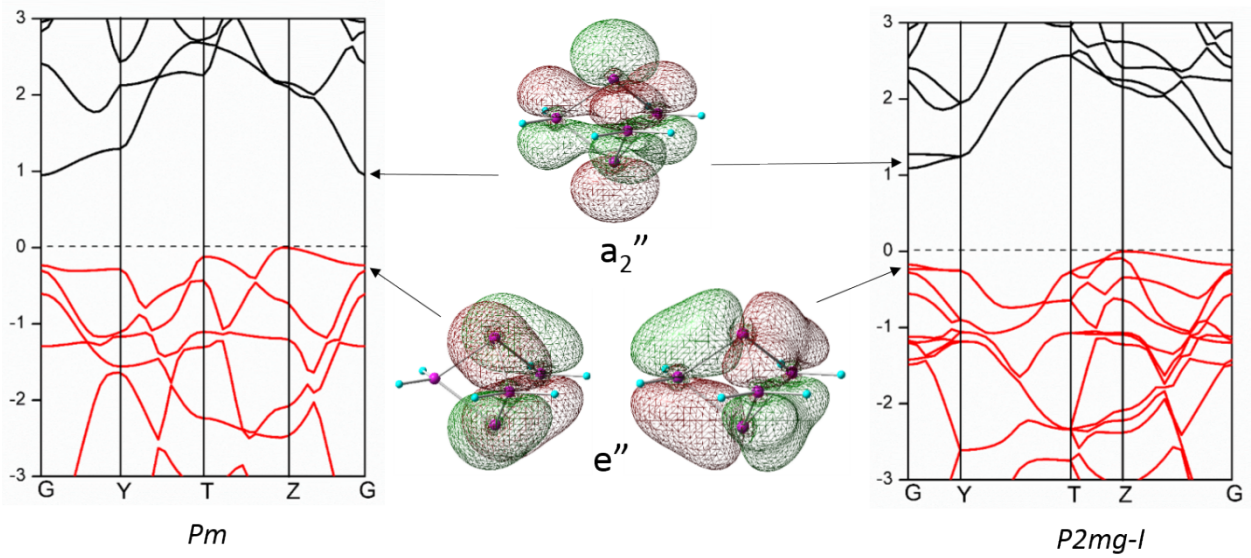
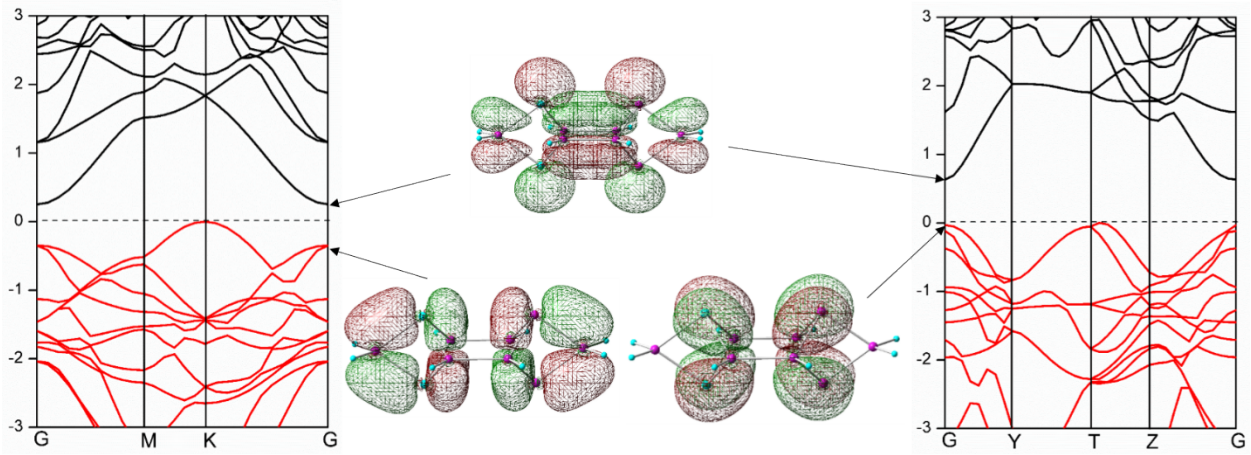
S1. Band Structure Analysis of Tail-to-Head Propellane Sheets



Si sheet with *Pm* symmetry has only one propellane per unit cell and is easy to correlate the bands with the MOs of propellane molecule. The frontier MOs are shown next to the bands. As in the case of molecular propellane (D_{3h}), the topmost valence band is doubly degenerate and lowest conduction band is non-degenerate corresponding to e” and a_2” respectively. The e” is split at G since the symmetry is reduced from D_{3h} to C_{2v} in the extended lattice. The LUMO a_2” is antibonding across radial p orbitals of the Si_{bh} atoms stabilized by the mixing of perpendicular p-orbitals from Si_b atoms. The band originating from this MO is most bonding at G and runs up. The HOMO e” is the degenerate π with a nodal plane in the Si_b triangle which is stabilized by the tangential p-orbitals at the Si_{bh} atoms. The degeneracy will be split along the Brillioun zone with the band having a nodal point at one of the Si_b atoms running up along G to Z and the other from the degenerate pair going down. The slope will be small in the former as the connecting points are nodal regions and forms the highest point of the valence band. *P2mg-I* has a similar connection between propellane units, but the unit cell has two propellane fragments resulting in doubling of bands. Across the propellane units, the antibonding combination of e” forms the topmost valence band and the bonding combination of a_2” forms the lowest conduction band. However, since the nature of interactions between two lattices are similar to *Pm*, the bands run the same fashion as that of *Pm* and the band gaps also remain very close (0.95 eV and 1.08 eV respectively for *Pm* and *P2mg-I*).

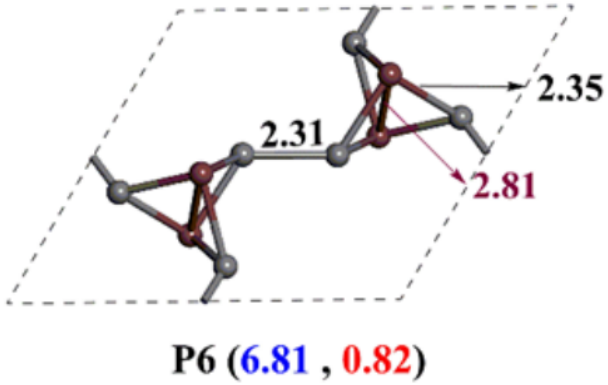
S2. Band Structure Analysis of Tail-to-Tail Propellane Sheets



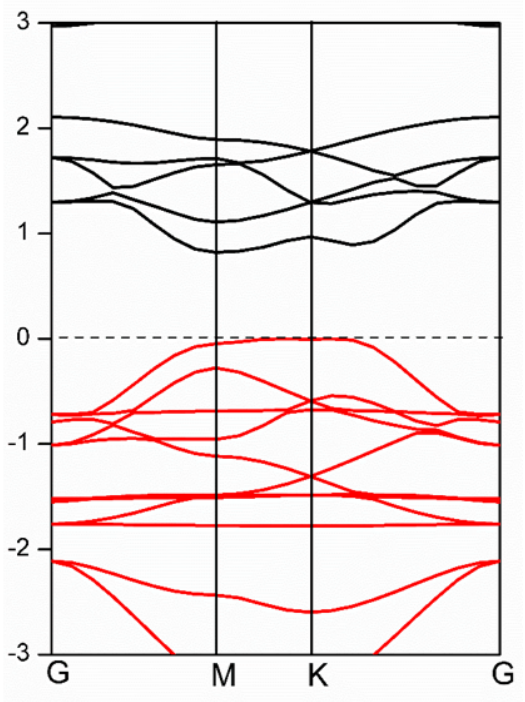
P6mm *P2mg-II*

The band structures of *P6mm* and *P2mg-II* where the propellane units are connected in a tail-to-tail fashion are remarkably similar. The frontier MOs of a propellane dimer formed from a tail-to-tail connection is shown beside the band structure diagram. As in the case of *P2mg-I*, the upper valence bands corresponds to the antibonding combination of e" across *tbp* units. In P6mm, the local D_{3h} symmetry of propellane is preserved so they remain degenerate at G. However in P2mg-II due to the breakdown of D_{3h} symmetry there is finite mixing between these frontier MOs at G. This leads to increased band gap in P2mg-II.

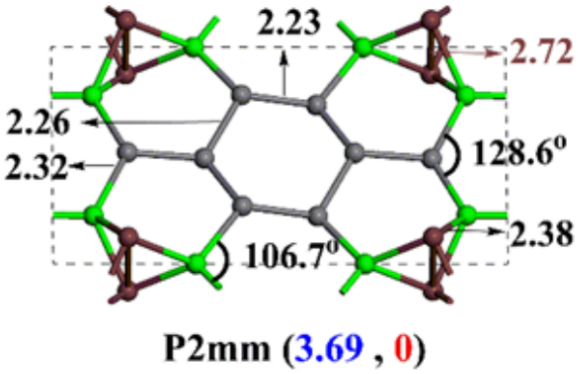
S3. Optimized geometry and Band Structure of *tbp* head-to-head isomer with *P6* symmetry

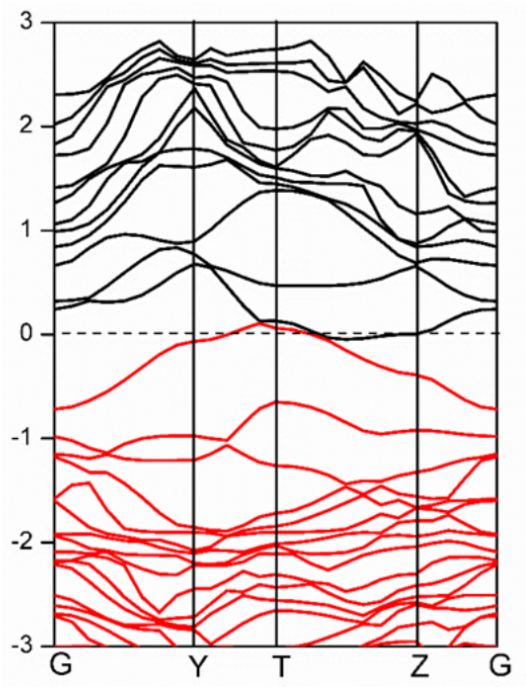


P6 (6.81 , 0.82)



S4. Optimized geometry and Band Structure of tbp isomer with Si=Si spacer





S5. Cartesian coordinates of optimized structure of $Si_{10}H_8$ isomers at B3LYP/6-311+g**

(a) D_{2h}

Total Energy = 2899.98201 a.u.

Si	-1.176063	1.629397	0.000000
Si	-4.108702	0.000000	0.000000
Si	-1.176063	-1.629397	0.000000
Si	1.176063	-1.629397	0.000000
Si	4.108702	0.000000	0.000000
Si	1.176063	1.629397	0.000000
Si	-2.197397	0.000000	1.380204
Si	2.197397	0.000000	1.380204
Si	2.197397	0.000000	-1.380204
Si	-2.197397	0.000000	-1.380204
H	-1.776868	2.990572	0.000000
H	1.776868	2.990572	0.000000
H	4.952042	1.222223	0.000000
H	1.776868	-2.990572	0.000000

H	-1.776868	-2.990572	0.000000
H	-4.952042	1.222223	0.000000
H	-4.952042	-1.222223	0.000000
H	4.952042	-1.222223	0.000000

(b) C_{2v}

Total Energy = 2899.95992 a.u.

Si	0.000000	1.469632	1.324816
Si	0.000000	1.648029	-3.385762
Si	0.000000	-1.469632	1.324816
Si	0.000000	-1.648029	-3.385762
Si	0.000000	0.000000	4.492457
Si	0.000000	0.000000	-0.515218
Si	-1.371846	0.000000	2.567453
Si	-1.392969	0.000000	-2.432717
Si	1.371846	0.000000	2.567453
Si	1.392969	0.000000	-2.432717
H	0.000000	2.951878	1.388759
H	0.000000	2.988745	-2.748627
H	0.000000	1.212614	5.352163
H	0.000000	-1.212614	5.352163
H	0.000000	-2.988745	-2.748627
H	0.000000	-2.951878	1.388759
H	0.000000	1.769964	-4.866035
H	0.000000	-1.769964	-4.866035

(c) C_{2v}

Total Energy = 2899.92144 a.u.

Si	0.325625	1.066012	0.000000
Si	-0.325625	-1.066012	0.000000
Si	-0.537126	2.776110	1.396628
Si	-0.537126	2.776110	-1.396628

Si 0.537126 4.348701 0.000000
H -0.013086 5.727784 0.000000
H 2.020954 4.370685 0.000000
Si -2.433054 2.924429 0.000000
H -3.179445 4.212156 0.000000
H -3.358258 1.766082 0.000000
Si 0.537126 -2.776110 -1.396628
Si 0.537126 -2.776110 1.396628
Si -0.537126 -4.348701 0.000000
H 0.013086 -5.727784 0.000000
H -2.020954 -4.370685 0.000000
Si 2.433054 -2.924429 0.000000
H 3.358258 -1.766082 0.000000
H 3.179445 -4.212156 0.000000

S6. Optimized geometrical parameters of various 2D-Silicon nanosheets

1. P6mm-I

Total Energy = 1068.9735 eV
Lattice Parameters; a = b= 7.4219
Si 0.63482 0.81741 0.00000
Si 0.33333 0.66667 0.04345

2. P2mg-II

Total Energy = 1069.1323 eV
Lattice Parameters; b= 7.4087 c = 6.3944
Si -0.48085 0.00000 0.68086
Si -0.25000 -0.04297 0.82225
Si -0.25000 0.00000 0.12514

3. Pm

Total Energy = 534.0703 eV
Lattice Parameters; b = 5.3085 c= 4.9901
Si 0.00000 0.28052 0.39523
Si 0.00000 0.00000 0.03140

Si -0.08167 0.00000 0.64073

4. P2mg-I

Total Energy = 1068.1969 eV
Lattice Parameters; a = 10.5788 c = 4.9957
Si 0.10958 0.00000 0.48699
Si 0.25000 0.00000 0.12263
Si 0.25000 -0.08994 0.73371

5. P6

Total Energy = 1063.9530 eV
Lattice Parameters; a = b = 9.6043
Si 0.49744 0.37826 0.00000
Si 0.33333 0.66667 0.09371