Electronic Supplementary Information

for

Tailoring electronic properties of multilayer phosphorene by siliconization

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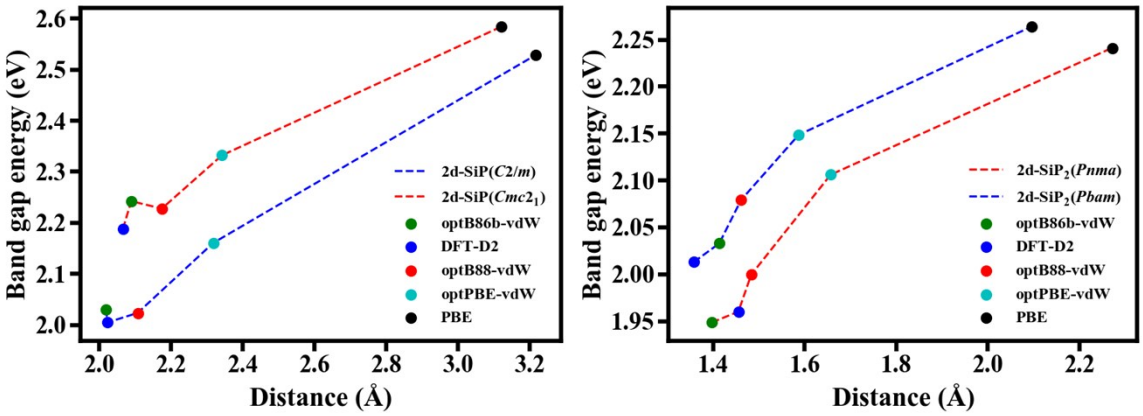

Figure S1 HSE energy gaps of bilayer 2d-SiP (left) and 2d-SiP_2 (right). The results are given for structures from different functionals.

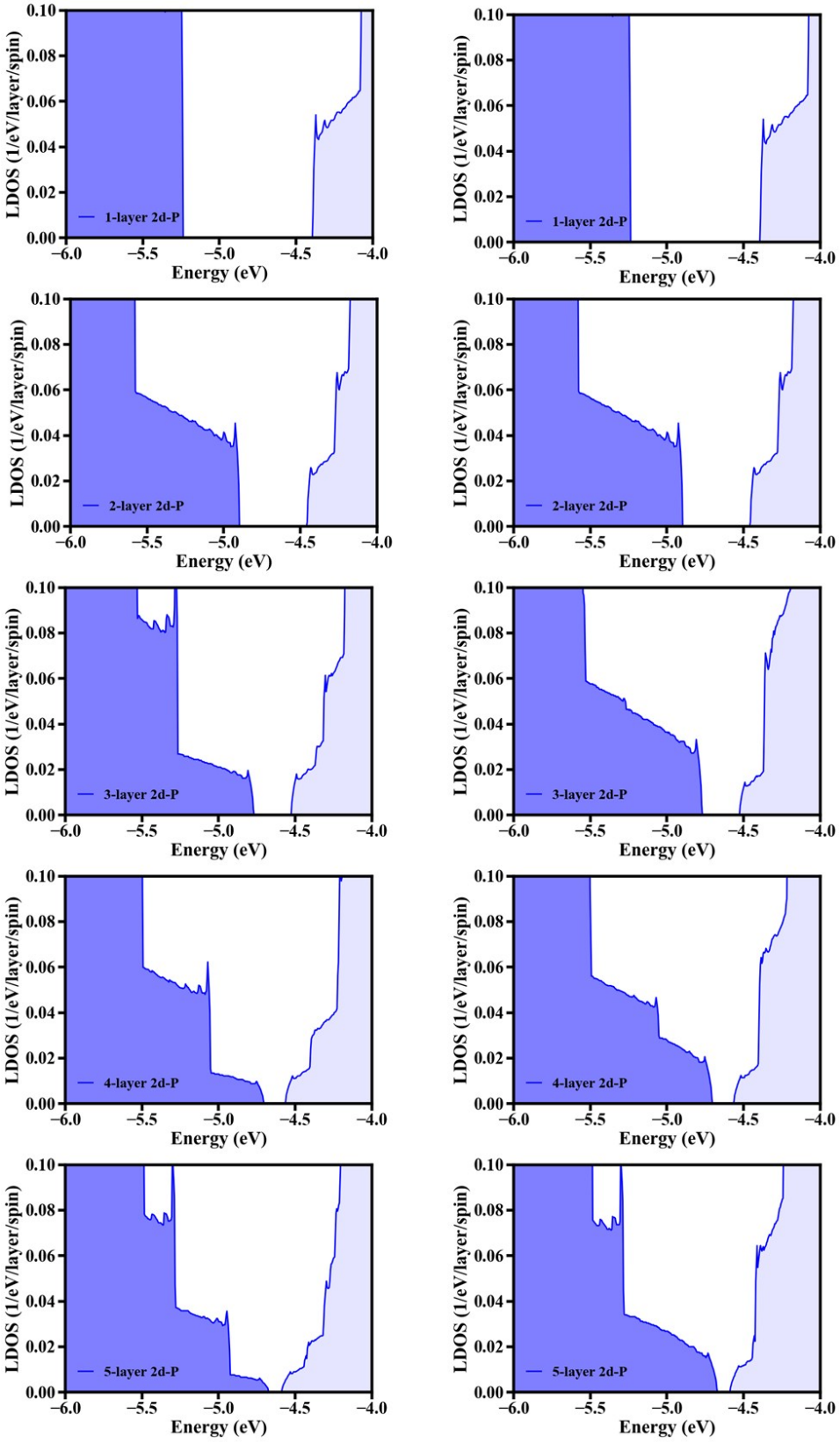

Figure S2 Local densities of states (LDOS) projected on the outermost (left column) and central (right column) layers of 2d-P with different thicknesses computed using optB88-vdW functional. All energies are given with respect to the vacuum level.

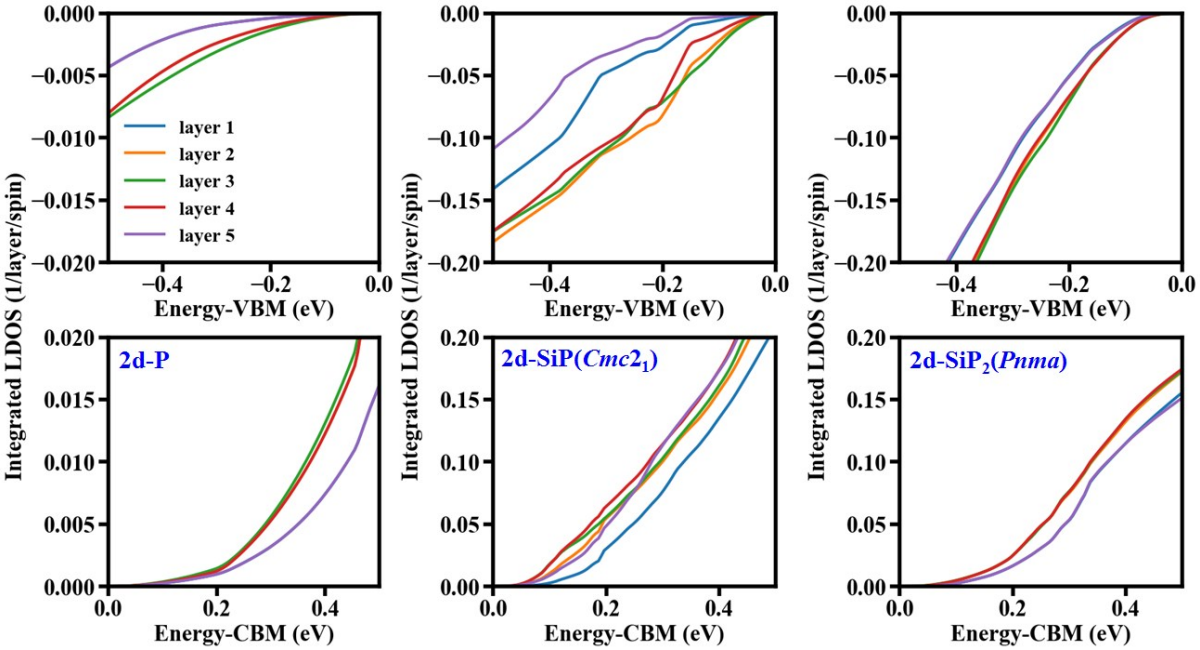

Figure S3 Integrated layer-resolved local densities of states (LDOS) for 5-layer 2d-P, 2d-SiP($Cmc2_1$), and 2d-SiP_2($Pnma$) computed using HSE. The k-point grids adopted in HSE calculations are scarcer compared to those in optB88-vdW (see Table S1). The integrated LDOS are calculated by integrating the LDOS over energy and given with respect to that for VBM (or CBM).

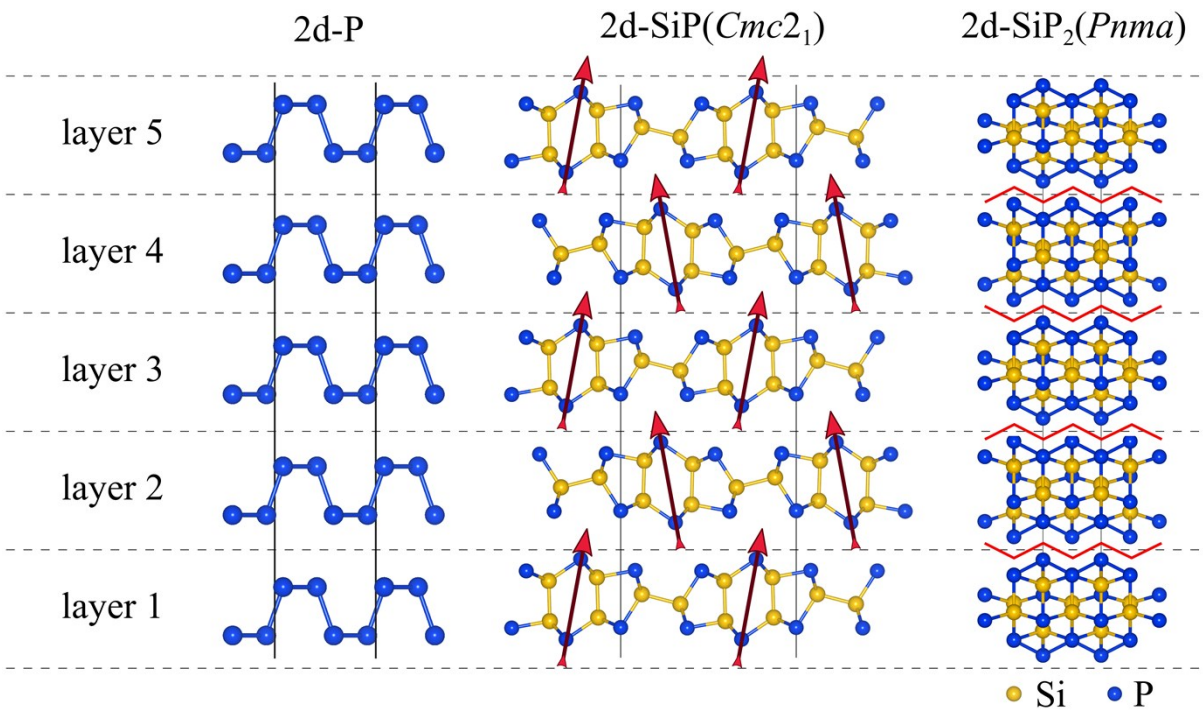

Figure S4 Illustration of the layer indexing for 5-layer 2d-P, 2d-SiP(*Cmc*2$_1$), and 2d-SiP$_2$(*Pnma*).

Table S1 The k-point grids used in different calculations. The 6×2×1 supercells (144 atoms) are used for BOMD simulations and the conventional standard cells are analyzed otherwise.

	HSE	Relaxation	Correction	LDOS (optB88-vdW)	LDOS (HSE)	BOMD
2d-P	7×7×1	14×14×1	-	48×48×1	7×7×1	-
2d-SiP	7×7×1	18×8×1	18×8×1	48×16×1	7×7×1	1×1×1
2d-SiP_2	9×4×1	18×8×1	18×8×1	48×16×1	9×4×1	1×1×1

Table S2 Summary of electronic properties of bulk P, SiP, and SiP_2. The results are given for optB88-vdW relaxed structures

System	HSE band gap (eV)
P	0.38
SiP(*Cmc*2_1)	1.88
SiP(*C*2/*m*)	1.59
SiP_2(*Pnma*)	2.00
SiP_2(*Pbam*)	1.83

Table S3 Summary on the computed properties of 2d-P systems

Functional	Number of layers	Lattice constant a (Å)	Lattice constant b (Å)	HSE band gap (eV)	Interaction energy (meV/atom)
DFT-D2	1	4.57	3.31	1.56	0
DFT-D2	2	4.51	3.31	1.03	-39
DFT-D2	3	4.48	3.32	0.77	-53
DFT-D2	4	4.47	3.32	0.64	-59
DFT-D2	5	4.46	3.32	0.54	-64
optB86b-vdW	1	4.51	3.30	1.46	0
optB86b-vdW	2	4.43	3.32	0.88	-59
optB86b-vdW	3	4.41	3.32	0.60	-79
optB86b-vdW	4	4.40	3.32	0.47	-90
optB86b-vdW	5	4.37	3.32	0.33	-96
optB88-vdW	1	4.58	3.32	1.52	0
optB88-vdW	2	4.53	3.33	1.04	-55
optB88-vdW	3	4.51	3.33	0.80	-73
optB88-vdW	4	4.49	3.34	0.68	-83
optB88-vdW	5	4.49	3.34	0.61	-89
optPBE-vdW	1	4.63	3.32	1.56	0
optPBE-vdW	2	4.58	3.33	1.13	-47
optPBE-vdW	3	4.57	3.33	0.94	-63
optPBE-vdW	4	4.56	3.33	0.83	-71
optPBE-vdW	5	4.56	3.34	0.77	-76
PBE	1	4.63	3.30	1.59	0
PBE	2	4.59	3.30	1.22	-5
PBE	3	4.58	3.30	1.04	-7
PBE	4	4.57	3.30	0.94	-7
PBE	5	4.56	3.30	0.87	-8

Table S4 Summary on the computed properties of 2d-SiP($Cmc2_1$) systems

Functional	Number of layers	Lattice constant a (Å)	Lattice constant b (Å)	HSE band gap (eV)	Band gap correction (eV)	Corrected HSE band gap (eV)	Interaction energy (meV/atom)
DFT-D2	1	3.52	10.37	2.68	0.01	2.66	0
DFT-D2	2	3.52	10.39	2.22	0.03	2.19	-20
DFT-D2	3	3.52	10.40	2.02	0.03	1.99	-28
DFT-D2	4	3.52	10.40	1.94	0.03	1.91	-31
DFT-D2	5	3.52	10.41	1.89	0.03	1.86	-34
optB86b-vdW	1	3.52	10.37	2.68	0.03	2.65	0
optB86b-vdW	2	3.52	10.40	2.29	0.05	2.24	-32
optB86b-vdW	3	3.52	10.42	2.10	0.06	2.04	-44
optB86b-vdW	4	3.52	10.42	2.02	0.07	1.95	-49
optB86b-vdW	5	3.52	10.42	1.98	0.07	1.90	-53
optB88-vdW	1	3.54	10.47	2.68	0.01	2.67	0
optB88-vdW	2	3.55	10.50	2.29	0.06	2.23	-32
optB88-vdW	3	3.55	10.51	2.12	0.07	2.04	-43
optB88-vdW	4	3.55	10.51	2.04	0.08	1.96	-49
optB88-vdW	5	3.55	10.52	2.00	0.08	1.92	-52
optPBE-vdW	1	3.54	10.47	2.67	0.01	2.66	0
optPBE-vdW	2	3.55	10.49	2.37	0.04	2.33	-28
optPBE-vdW	3	3.55	10.50	2.22	0.06	2.16	-38
optPBE-vdW	4	3.55	10.50	2.15	0.07	2.09	-43
optPBE-vdW	5	3.55	10.51	2.12	0.07	2.05	-46
PBE	1	3.53	10.43	2.67	0.01	2.66	0
PBE	2	3.53	10.43	2.60	0.02	2.58	-1
PBE	3	3.53	10.43	2.57	0.02	2.54	-1
PBE	4	3.53	10.43	2.55	0.03	2.53	-1
PBE	5	3.53	10.43	2.54	0.03	2.52	-2

Table S5 Summary on the computed properties of 2d-SiP(*C*2/*m*) systems

Functional	Number of layers	Lattice constant a (Å)	Lattice constant b (Å)	HSE band gap (eV)	Band gap correction (eV)	Corrected HSE band gap (eV)	Interaction energy (meV/atom)
DFT-D2	1	3.52	10.37	2.68	0.02	2.66	0
DFT-D2	2	3.52	10.39	2.03	0.03	2.01	-20
DFT-D2	3	3.53	10.40	1.80	0.04	1.76	-27
DFT-D2	4	3.53	10.41	1.70	0.05	1.65	-31
DFT-D2	5	3.53	10.41	1.65	0.06	1.60	-33
optB86b-vdW	1	3.52	10.37	2.68	0.03	2.65	0
optB86b-vdW	2	3.53	10.41	2.09	0.06	2.03	-32
optB86b-vdW	3	3.53	10.42	1.86	0.09	1.77	-44
optB86b-vdW	4	3.53	10.43	1.76	0.10	1.67	-49
optB86b-vdW	5	3.53	10.43	1.71	0.10	1.62	-53
optB88-vdW	1	3.54	10.46	2.68	0.01	2.67	0
optB88-vdW	2	3.55	10.50	2.11	0.09	2.02	-32
optB88-vdW	3	3.55	10.51	1.90	0.10	1.80	-43
optB88-vdW	4	3.56	10.52	1.81	0.09	1.71	-49
optB88-vdW	5	3.56	10.52	1.76	0.09	1.67	-52
optPBE-vdW	1	3.54	10.47	2.67	0.01	2.66	0
optPBE-vdW	2	3.55	10.49	2.23	0.07	2.16	-28
optPBE-vdW	3	3.55	10.50	2.05	0.09	1.96	-38
optPBE-vdW	4	3.55	10.51	1.98	0.10	1.87	-43
optPBE-vdW	5	3.55	10.51	1.94	0.11	1.83	-46
PBE	1	3.53	10.43	2.67	0.01	2.66	0
PBE	2	3.53	10.43	2.55	0.02	2.53	-1
PBE	3	3.53	10.43	2.49	0.02	2.47	-1
PBE	4	3.53	10.43	2.46	0.02	2.44	-1
PBE	5	3.53	10.43	2.44	0.02	2.42	-1

Table S6 Summary on the computed properties of 2d-SiP_2(*Pnma*) systems

Functional	Number of layers	Lattice constant a (Å)	Lattice constant b (Å)	HSE band gap (eV)	Band gap correction (eV)	Corrected HSE band gap (eV)	Interaction energy (meV/atom)
DFT-D2	1	3.45	10.02	2.22	0.01	2.21	0
DFT-D2	2	3.45	10.04	2.01	0.00	2.01	-23
DFT-D2	3	3.45	10.04	1.97	0.00	1.97	-31
DFT-D2	4	3.44	10.04	1.93	0.00	1.93	-36
DFT-D2	5	3.44	10.04	1.92	0.00	1.92	-38
optB86b-vdW	1	3.45	9.95	2.22	0.01	2.20	0
optB86b-vdW	2	3.45	10.02	2.03	0.00	2.03	-36
optB86b-vdW	3	3.45	10.03	1.97	0.00	1.97	-49
optB86b-vdW	4	3.45	10.04	1.94	0.00	1.94	-55
optB86b-vdW	5	3.45	10.05	1.93	0.00	1.93	-59
optB88-vdW	1	3.47	10.10	2.26	0.01	2.24	0
optB88-vdW	2	3.47	10.16	2.09	0.01	2.08	-35
optB88-vdW	3	3.47	10.17	2.07	0.01	2.06	-48
optB88-vdW	4	3.47	10.18	2.04	0.00	2.04	-54
optB88-vdW	5	3.47	10.18	2.03	0.00	2.03	-58
optPBE-vdW	1	3.47	10.20	2.31	0.02	2.29	0
optPBE-vdW	2	3.47	10.25	2.16	0.01	2.15	-31
optPBE-vdW	3	3.47	10.27	2.15	0.02	2.13	-42
optPBE-vdW	4	3.47	10.27	2.13	0.01	2.12	-48
optPBE-vdW	5	3.47	10.27	2.13	0.01	2.12	-51
PBE	1	3.45	10.28	2.36	0.03	2.33	0
PBE	2	3.45	10.31	2.29	0.02	2.26	-1
PBE	3	3.45	10.31	2.28	0.04	2.24	-2
PBE	4	3.45	10.31	2.26	0.03	2.23	-2
PBE	5	3.45	10.31	2.26	0.04	2.22	-2

Table S7 Summary on the computed properties of SiP_2(*Pbam*) systems

Functional	Number of layers	Lattice constant a (Å)	Lattice constant b (Å)	HSE band gap (eV)	Band gap correction (eV)	Corrected HSE band gap (eV)	Interaction energy (meV/atom)
DFT-D2	1	3.45	10.01	2.22	0.01	2.21	0
DFT-D2	2	3.45	9.94	1.96	0.00	1.96	-21
DFT-D2	3	3.45	9.92	1.94	0.02	1.93	-29
DFT-D2	4	3.45	9.86	1.85	0.00	1.85	-33
DFT-D2	5	3.45	9.84	1.81	0.00	1.81	-35
optB86b-vdW	1	3.45	9.94	2.21	0.01	2.20	0
optB86b-vdW	2	3.45	9.85	1.96	0.01	1.95	-35
optB86b-vdW	3	3.45	9.81	1.87	0.01	1.86	-47
optB86b-vdW	4	3.45	9.79	1.80	0.00	1.80	-54
optB86b-vdW	5	3.45	9.78	1.77	0.00	1.77	-57
optB88-vdW	1	3.47	10.10	2.25	0.01	2.24	0
optB88-vdW	2	3.47	10.01	2.00	0.00	2.00	-34
optB88-vdW	3	3.48	9.99	1.98	0.01	1.97	-46
optB88-vdW	4	3.48	9.97	1.93	0.01	1.92	-52
optB88-vdW	5	3.48	9.96	1.90	0.01	1.90	-55
optPBE-vdW	1	3.47	10.20	2.31	0.02	2.29	0
optPBE-vdW	2	3.47	10.16	2.11	0.01	2.11	-30
optPBE-vdW	3	3.47	10.15	2.10	0.04	2.06	-40
optPBE-vdW	4	3.48	10.14	2.06	0.03	2.03	-46
optPBE-vdW	5	3.48	10.14	2.06	0.03	2.03	-49
PBE	1	3.45	10.29	2.37	0.03	2.34	0
PBE	2	3.45	10.28	2.27	0.03	2.24	-1
PBE	3	3.45	10.29	2.26	0.05	2.22	-2
PBE	4	3.45	10.27	2.23	0.05	2.19	-2
PBE	5	3.45	10.27	2.22	0.05	2.18	-2

Table S8 Layer groups of the considered 2d materials

System	1 layer	2 layers	3 layers	4 layers	5 layers
2d-P	*Pman*	*Pbma*	*Pman*	*Pbma*	*Pman*
2d-SiP(*Cmc*2_1)	*C*2/*m*11	*Cm*11	*Cm*11	*Cm*11	*Cm*11
2d-SiP(*C*2/*m*)	*C*2/*m*11	*C*2/*m*11	*C*2/*m*11	*C*2/*m*11	*C*2/*m*11
2d-SiP_2(*Pnma*)	*Pm*2_1*b*	*P*2_1/*m*11	*Pm*2_1*b*	*P*2_1/*m*11	*Pm*2_1*b*
2d-SiP_2(*Pbam*)	*Pm*2_1*b*	*P*2/*m*11	*Pm*2_1*b*	*P*2/*m*11	*Pm*2_1*b*