Electronic Supplementary Material (ESI) for Nanoscale.

Two-Dimensional Silicon Crystals with Sizable Band Gap and Ultrahigh Carrier Mobility

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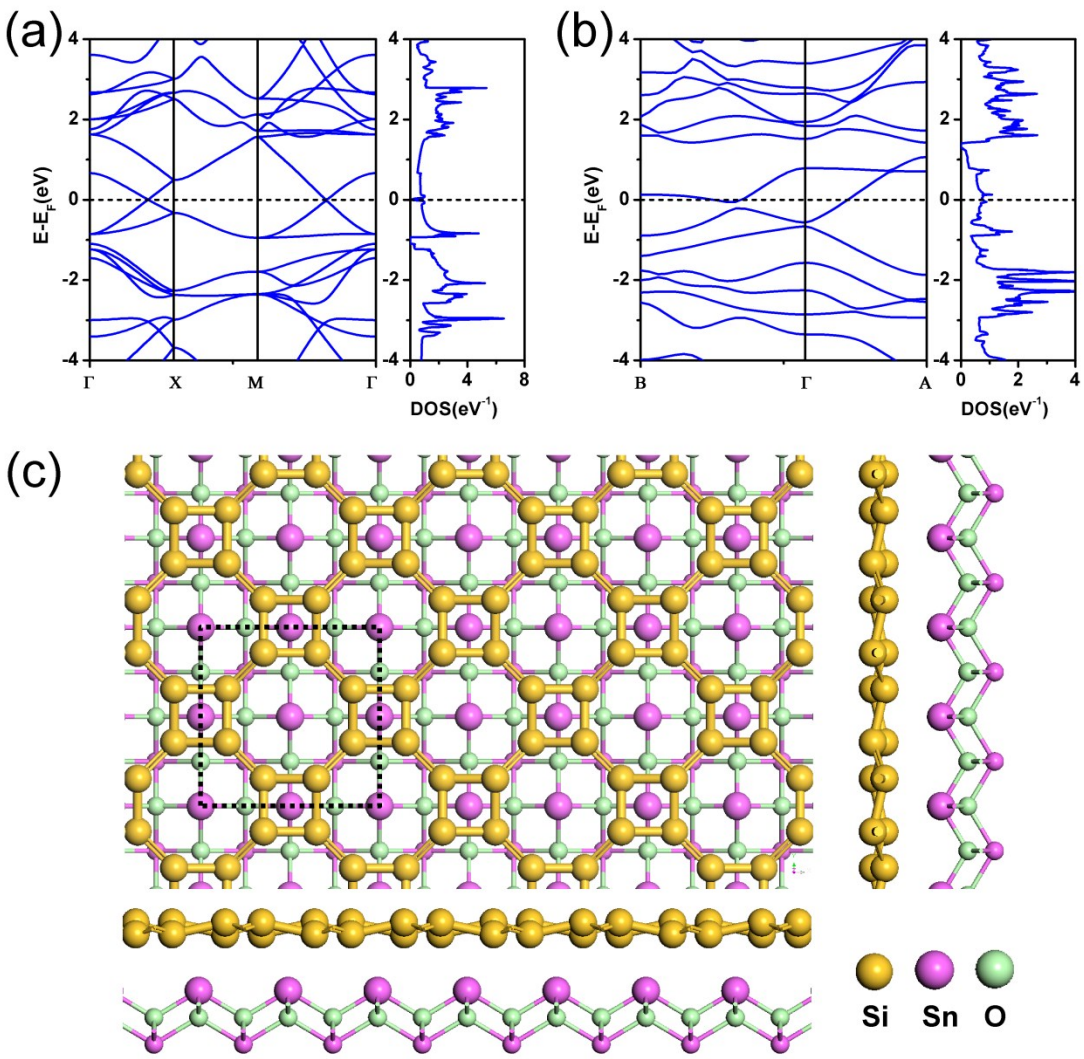

Figure S1 Band structure of (a) OT-silicene and (b) OP-silicene with PBE method and (c) the image of growth of OT-silicene on α-SnO (001) surface within a match of 1×1 OT-silicene on 2×2 α-SnO (001)

Table S1 Symmetry (as well as space group number), lattice parameters (a and b, Å; γ, °), particle thickness (d*z*, Å), bond length range (Å) and work function (eV, PBE/HSE06) of silicene, OT-silicene, OP-silicene, LHD-Si (or A-P6/mmm-Si_{10}) and new structures.

Structure	Space group	a	b	γ	d*z*	BL	WF
Silicene (P-3m1)	**(164)**	**3.868**	**3.868**	**120**	**0.449**	**2.278**	**4.60/4.66**
OT-silicene (P4/nbm)	**(125)**	**7.607**	**7.607**	**90**	**0.496**	**2.252, 2.304**	**4.76/4.87**
OP-silicene (P-1)	**(2)**	**5.709**	**7.711**	**68.27**	**0.824**	**2.244 - 2.293**	**4.76/4.86**
AA-3-Si (P6/mmm)	**(191)**	**4.133**	**4.133**	**120**	**2.410**	**2.386, 2.410**	**4.10/4.17**
Cmme-Si (Cmma)	**(67)**	**4.481**	**6.369**	**90**	**2.272**	**2.356 – 2.418**	**4.16/4.21**
A-P6/mmm-Si_{10}	**(191)**	**7.428**	**7.428**	**90**	**2.711**	**2.349, 2.366**	**4..90/5.26**
A-Pmma-Si_{10}	**(51)**	**6.401**	**7.428**	**90**	**2.714**	**2.332 – 2.366**	**5.16/5.54**
D-C2/m-Si_{16}	**(12)**	**6.497**	**10.923**	**90**	**3.449**	**2.311 – 2.424** [a]	**4.89/5.26**
D-Pmna-Si_{16}	**(53)**	**6.467**	**10.904**	**90**	**3.576**	**2.329 – 2.408** [a]	**4.97/5.33**
C_z-Pc-Si_{12}	**(7)**	**3.825**	**12.378**	**90**	**3.593**	**2.315 – 2.393** [a]	**5.10/5.44**
C_z-P2/c-Si_{12}	**(13)**	**3.823**	**12.224**	**90**	**3.789**	**2.311 – 2.398** [a]	**5.10/5.45**
C_a-P2/c-Si_{12}	**(13)**	**6.488**	**7.236**	**90**	**3.637**	**2.336 – 2.388** [a]	**4.85/5.24**
C_a-Pcca-Si_{24}	**(54)**	**6.484**	**14.498**	**90**	**3.632**	**2.327 – 2.385** [a]	**4.94/5.31**
OT-A-Pmm2-Si_5	**(25)**	**4.995**	**5.312**	**90**	**2.719**	**2.329 – 2.378**	**5.21/5.62**
OT-A-Pmma-Si_{10}	**(51)**	**5.000**	**10.595**	**90**	**2.717**	**2.323 – 2.374**	**5.28/5.70**
OP-D-C2/m-Si_{16}	**(12)**	**5.512**	**13.205**	**90**	**3.612**	**2.327 – 2.404** [a]	**4.96/5.34**
OP-D-Pmna-Si_{16}	**(53)**	**5.511**	**13.054**	**90**	**3.979**	**2.325 – 2.403** [a]	**5.01/5.39**

[a] Technically, we only considered the strong Si-Si bond (bond length range: form 2.25 to 2.45 Å) with typical sp^3 hybridization for all structures. However, there are also weak Si-Si bond in structures with mark "[a]", which can be regarded as the bonding of between neighbor sp^2 silicon atoms with larger bond length (about 2.6 – 2.7 **Å**). More concretely, the bond lengths of them are 2.707 (D-A-Si_{16}), 2.607 (D-Pmna-Si_{16}), 2.627 (C_z-Pc-Si_{12}), 2.635 (C_z-P2/c-Si_{12}), 2.631 (C_a-P2/c-Si_{12}), 2.637 (C_a-Pcca-Si_{24}), 2.591 (OP-D-C2/m-Si_{16}), 2.590 (OP-D-Pmna-Si_{16}) **Å**, respectively.

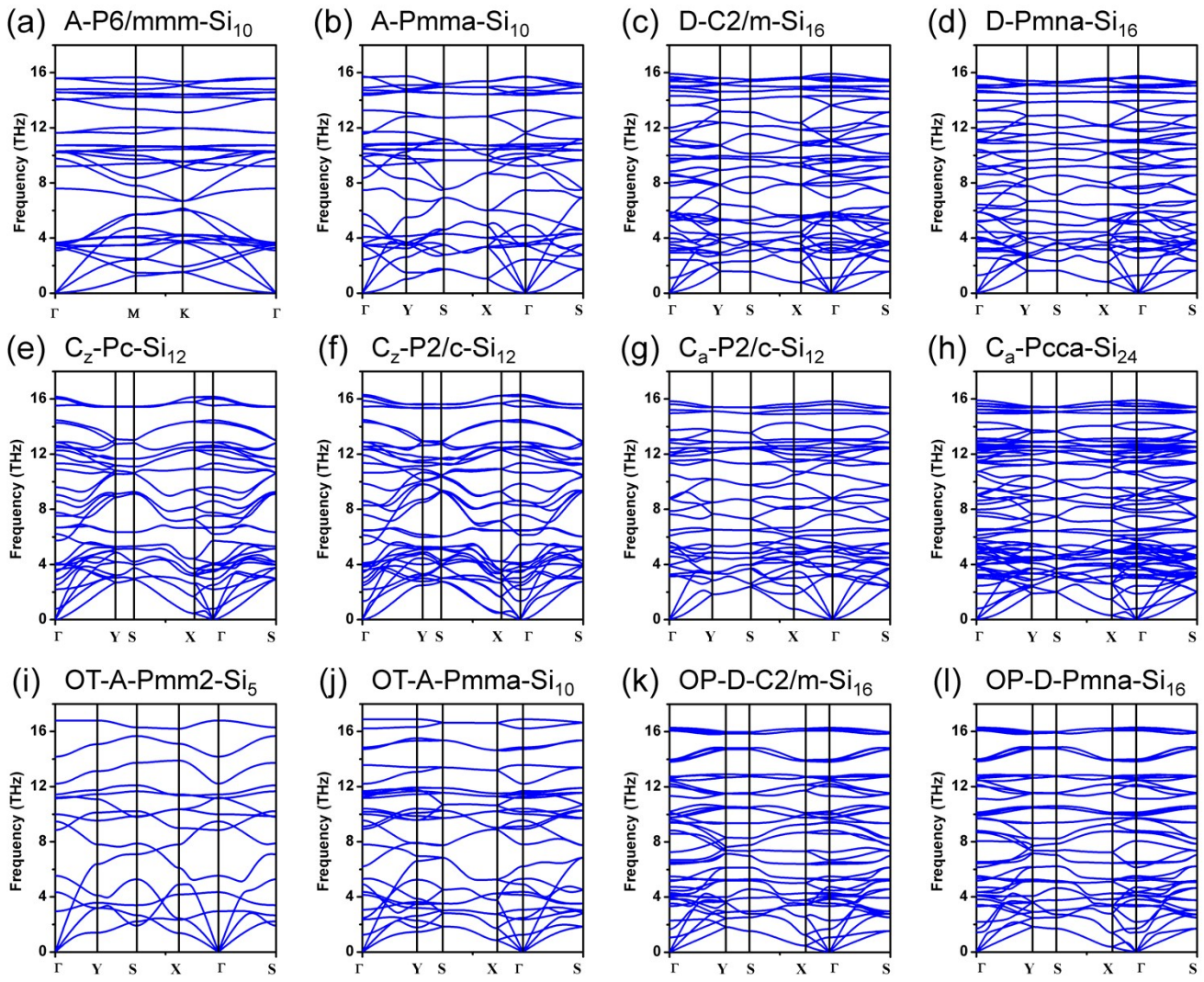

Figure S2 Phonon spectrum of constructed 2D silicene structures

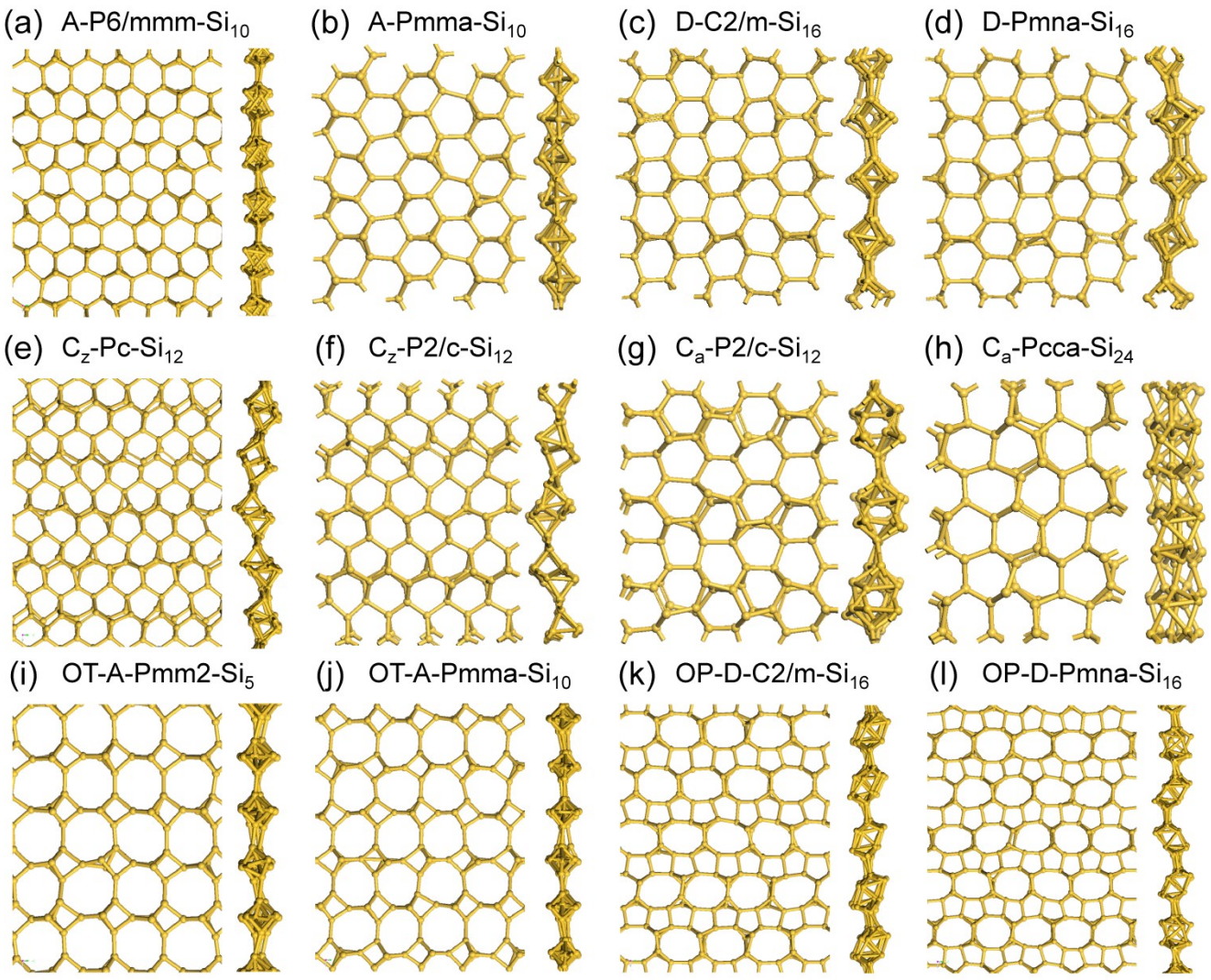

Figure S3 Snapshots (top view and side view) of constructed 2D silicene structures after 5ps BOMD simulation at 700 K with PBE method

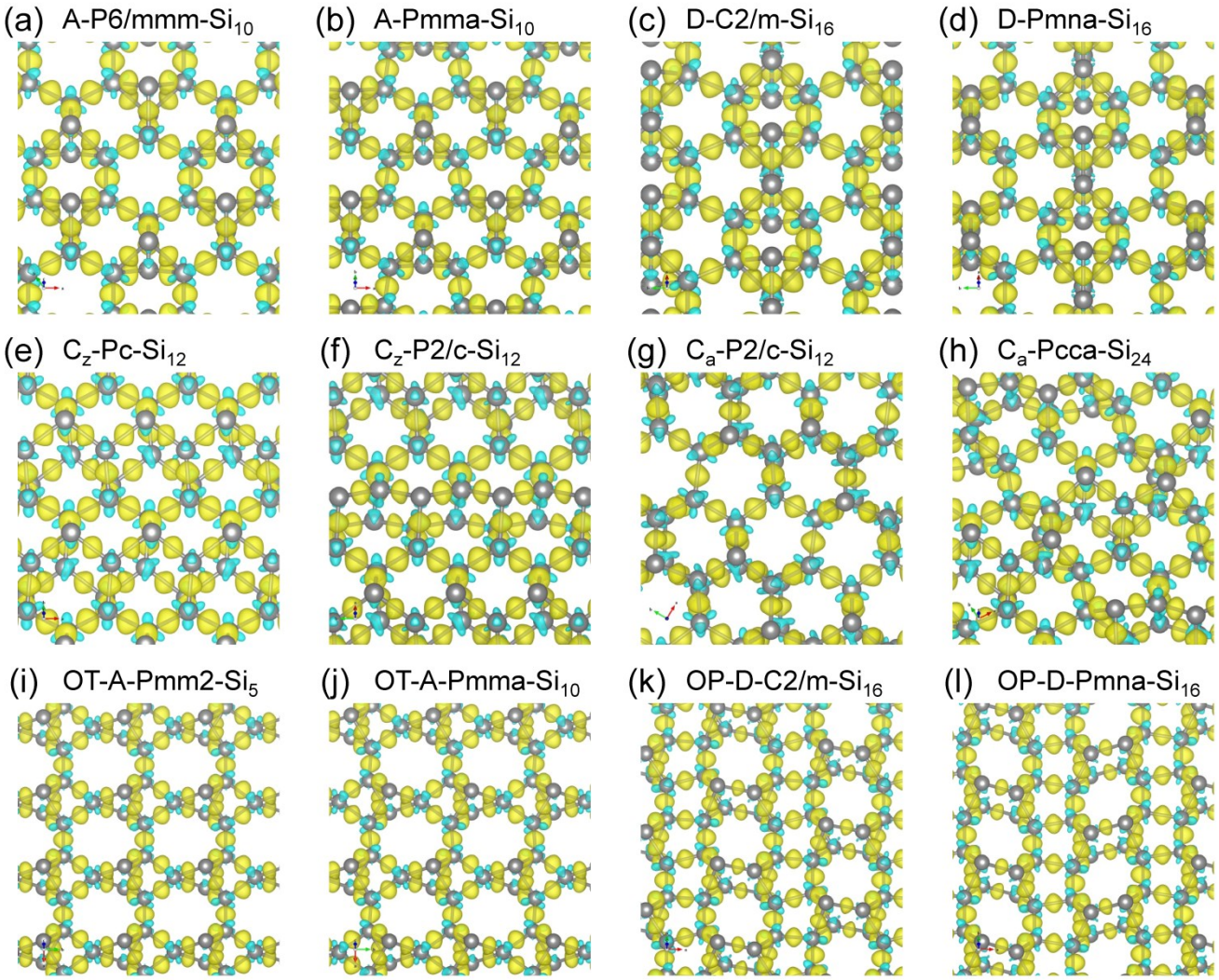

Figure S4 Deformation charge density of constructed 2D silicene structures. Yellow and blue color clouds represent zones with electron density increase and decrease, respectively, compared to isolated silicon atom. Isosurface is 0.01 e/Bohr^3

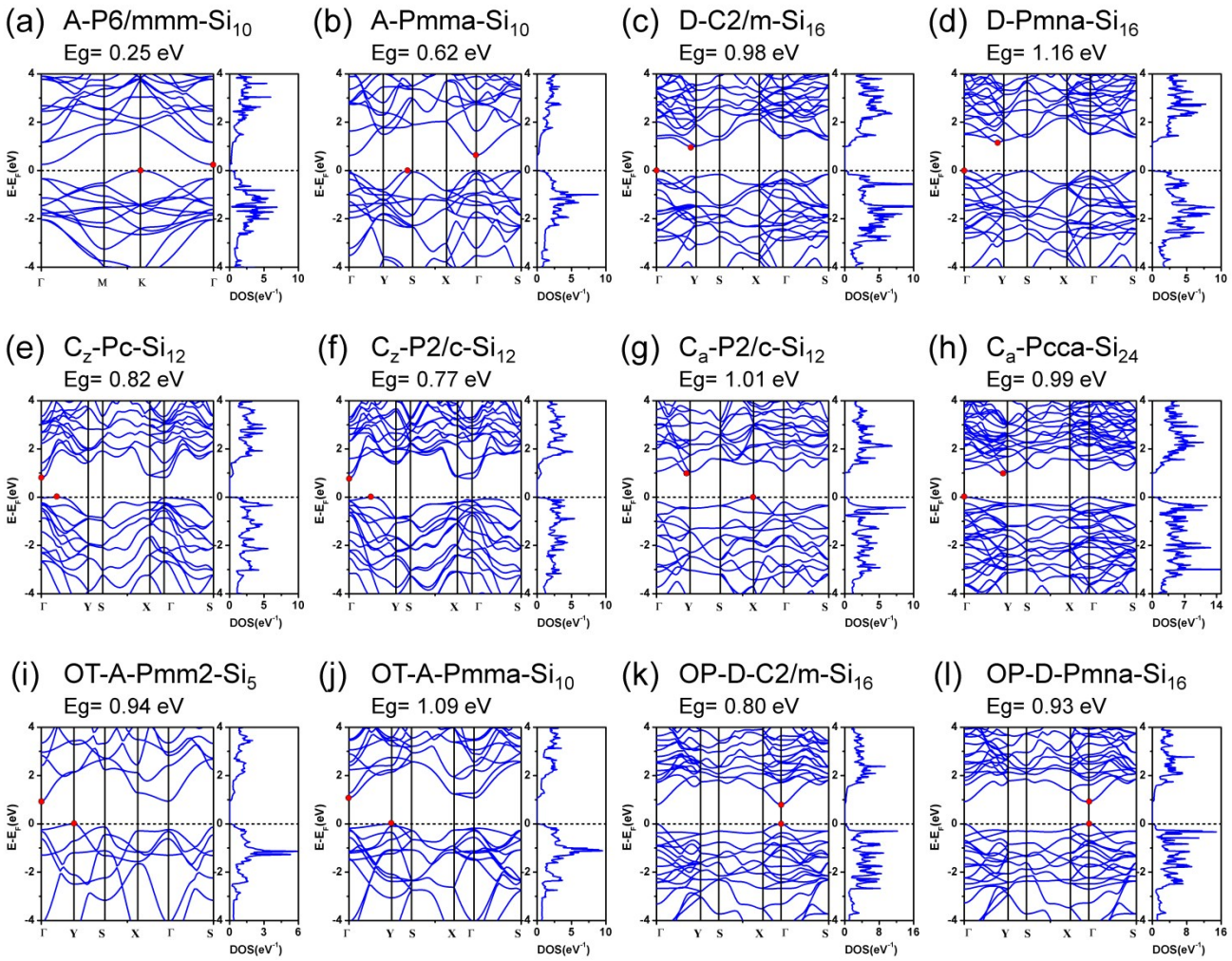

Figure S5 Band structure of constructed 2D silicene structures with PBE method. The CBM and VBM are marked by red spot.

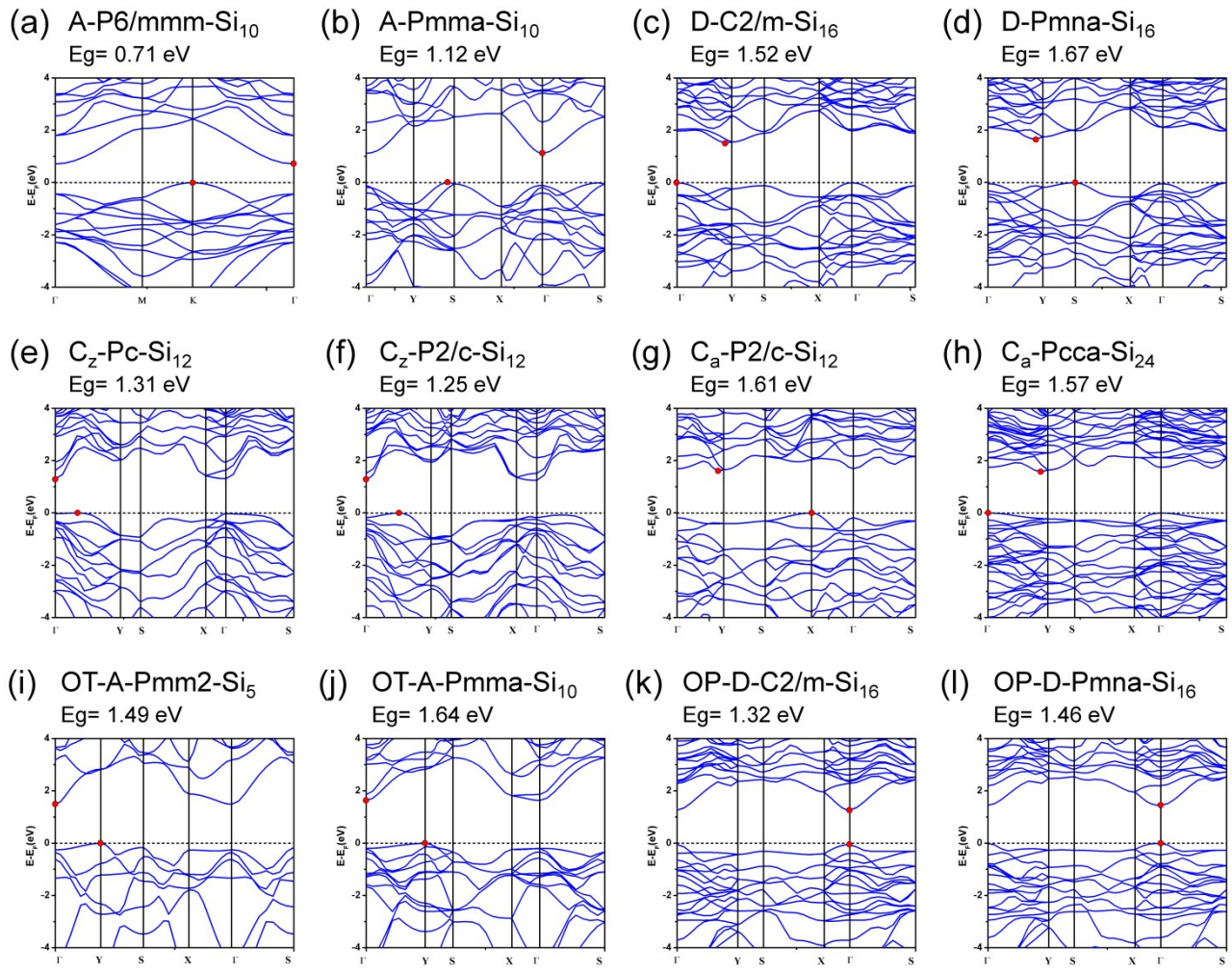

Figure S6 Band structure of constructed 2D silicene structures with HSE06 method. The CBM and VBM are marked by red spot.

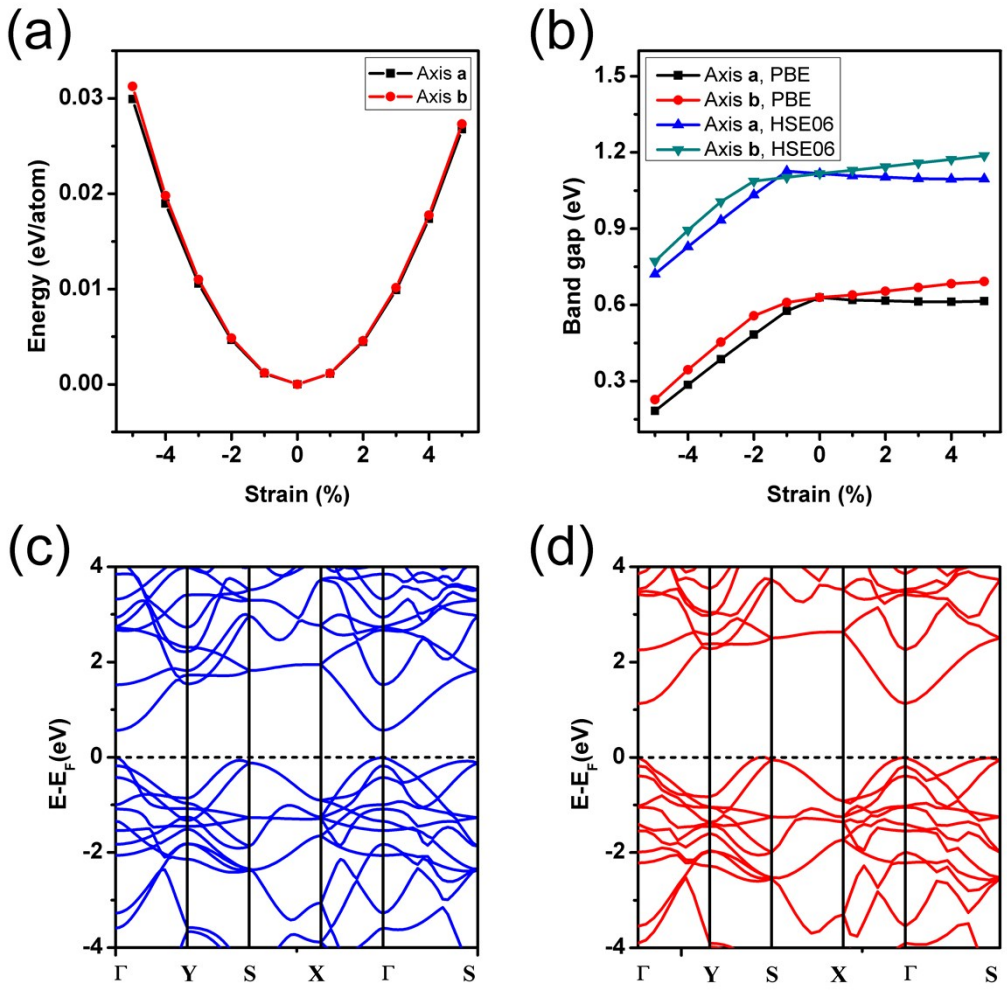

Figure S7 (a) Relative energy of per atom under different strain, (b) Band gap in PBE and HSE06 in different directions (**a** and **b**) under different strain, (c) Band structure with PBE method under strain of (-1% at axis **a** with fixed **b**) and (d) Band structure with HSE06 method of (-1% at axis **a** with fixed **b**) for structure A-Pmma-Si_{10}

Table S2. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for A-P6/mmm-Si_{10}. (C_a= C_b=C_{11}= 78 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-0.42	-0.42	0.35	0.35
m_d (m_e)*	0.42	0.42	0.35	0.35
E_l (eV)	-3.39	-3.39	-1.61	-1.61
μ ($cm^2V^{-1}s^{-1}$)	819	819	5232	5232

* m_e is the static mass of electron and it is the same to Table S2-S9.

Table S3. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for A-Pmma-Si_{10}. (C_a=C_{11}= 77 N/m, C_b=C_{22}= 79 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-1.25	-0.29	0.59	0.17
m_d (m_e)	0.60	0.60	0.32	0.32
E_l (eV)	-1.78	-3.80	-2.38	-2.27
μ ($cm^2V^{-1}s^{-1}$)	690	670	1533	6002

Table S4. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for D-C2/m-Si_{16}. (C_a=C_{11}= 79 N/m, C_b=C_{22}= 85 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-0.52	-0.29	0.23	0.33
m_d (m_e)	0.39	0.39	0.28	0.28
E_l (eV)	-1.37	-3.54	-2.65	-4.81
μ ($cm^2V^{-1}s^{-1}$)	4420	1277	3720	847

Table S5. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for D-Pmna-Si_{16}. (C_a=C_{11}= 77 N/m, C_b=C_{22}= 85 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-0.58	-0.30	0.23	0.36
m_d (m_e)	0.42	0.42	0.29	0.29
E_l (eV)	-1.06	-3.47	-2.44	-3.01
μ ($cm^2V^{-1}s^{-1}$)	5992	1193	4130	1914

Table S6. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for OT-A-Pmm2-Si_5. (C_a=C_{11}= 73 N/m, C_b=C_{22}= 72 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-2.23	-0.29	0.18	0.88
m_d (m_e)	0.80	0.80	0.40	0.40
E_l (eV)	0.26	-5.19	-4.65	-0.16
μ ($cm^2V^{-1}s^{-1}$)	12892	245	999	170173

Table S7. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for OT-A-Pmma-Si_{10}. (C_a=C_{11}= 73 N/m, C_b=C_{22}= 71 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-3.69	-0.36	0.23	0.89
m_d (m_e)	1.15	1.15	0.45	0.45
E_l (eV)	0.17	-4.50	-4.35	-0.66
μ ($cm^2V^{-1}s^{-1}$)	12678	180	794	8668

Table S8. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for OP-D-C2/m-Si_{16}. (C_a=C_{11}= 90 N/m, C_b=C_{22}= 66 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-0.15	-0.76	0.16	0.17
m_b (m_e)	0.34	0.34	0.16	0.16
E_l (eV)	-3.85	-0.71	-2.32	-5.90
μ ($cm^2V^{-1}s^{-1}$)	2536	10791	13911	1485

Table S9. Mobility calculation details parameters of hole (h) and electron (e) in direction **a** and **b** for OP-D-Pmna-Si_{16}. (C_a=C_{11}= 90 N/m, C_b=C_{22}= 37 N/m)

	h(**a**)	h(**b**)	e(**a**)	e(**b**)
Effect mass (m_e)	-0.22	-11.03	0.22	1.06
m_b (m_e)	1.56	1.56	0.48	0.48
E_l (eV)	-3.59	0.38	-2.21	-6.04
μ ($cm^2V^{-1}s^{-1}$)	433	317	3717	42

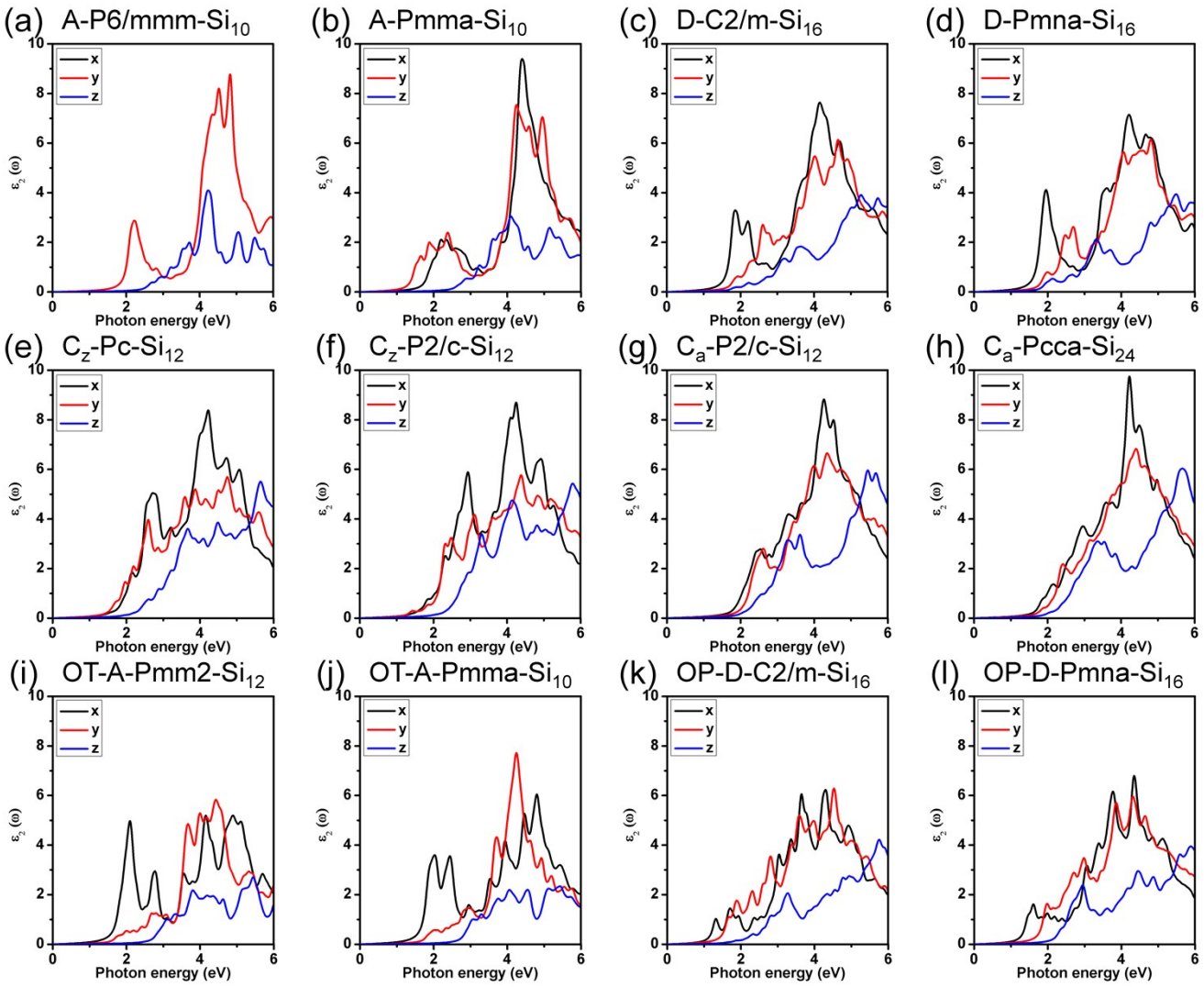

Figure S8 Photo absorption in different direction of constructed 2D silicene structures. Coincidentally, lattice parameters of **a**, **b** and **c** are in same direction of *x*, *y* and *z*, respectively.

Table S10 Elastic constants and Young's stiffness in direction x (direction **a**) and y (direction **b**) for silicene, OT-silicene, OP-silicene, LHD (or A-P6/mmm-Si_{10}) and new silicene structures. (In unit of N/m)

Structure	C_{11}	C_{12}=C_{21}	C_{22}	C_{66}	Y_x	Y_y
silicene	**69**	**21**	**69**	**24**	**62**	**62**
OT-silicene	**44**	**30**	**44**	**22**	**24**	**24**
OP-silicene	**58**	**15**	**46**	**15**	**53**	**42**
A-P6/mmm-Si_{10}	**78**	**25**	**78**	**27**	**70**	**70**
A-Pmma-Si_{10}	**77**	**25**	**79**	**30**	**70**	**72**
D-C2/m-Si_{16}	**79**	**18**	**85**	**25**	**75**	**81**
D-Pmna-Si_{16}	**77**	**17**	**85**	**25**	**73**	**81**
C_z-Pc-Si_{12}	**90**	**22**	**79**	**31**	**84**	**73**
C_z-P2/c-Si_{12}	**87**	**10**	**32**	**30**	**84**	**31**
C_a-P2/c-Si_{12}	**92**	**20**	**82**	**28**	**87**	**77**
C_a-Pcca-Si_{24}	**92**	**21**	**82**	**28**	**87**	**77**
OT-A-Pmm2-Si_5	**73**	**14**	**72**	**7**	**70**	**70**
OT-A-Pmma-Si_{10}	**73**	**14**	**71**	**8**	**70**	**68**
OP-D-C2/m-Si_{16}	**90**	**14**	**66**	**22**	**87**	**63**
OP-D-Pmna-Si_{16}	**90**	**8**	**37**	**21**	**88**	**37**

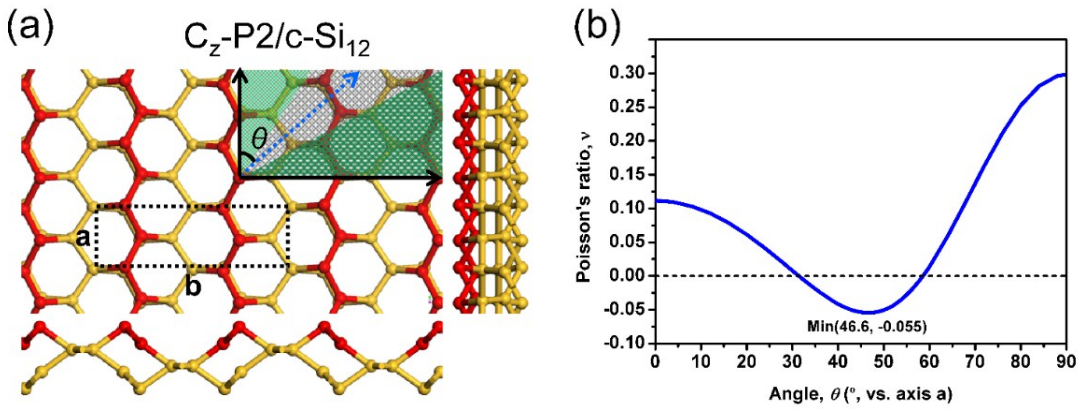

Figure S9 (a) The illustration of Poisson's ratio distribution in different directions in x-y plane of C_z-P2/c-Si_{12}. (The gray angle region represents negative value while the green angle regions represent positive value. And the blue arrow is the specified direction $\boldsymbol{\theta}$.) (b) The variation of Poisson's ratio (ν) value in different directions (represented by angle θ, vs. axis **a**) in *x*-*y* plane of C_z-P2/c-Si_{12}. Duo to the limitation of symmetry, only concise angle region with an angle ranging from 0 to 90 degree is shown.

The value of ν(θ) can be calculated via equations given by Ref.62 as listed as below:

$$\nu(\theta) = \frac{(\nu_{yx}cos^4\theta - d_1cos^2\theta sin^2\theta + \nu_{yx}sin^4\theta)}{(cos^4\theta + d_2cos^2\theta sin^2\theta + d_3sin^4\theta)}, \quad \text{(ES1)}$$

where，θ is the included angle between axis *y* (here, axis *y* is corresponding to axis **a** while axis *x* is axis **b** in C_z-P2/c-Si_{12}) and specified direction $\boldsymbol{\theta}$, and ν_{yx}, d_1, d_2 and d_3 are defined as:

$$\nu_{yx} = C_{bb}/C_{aa}, \quad \text{(ES2)}$$

$$d_1 = \frac{C_{bb}}{C_{aa}} + 1 - \frac{C_{bb}C_{aa} - C_{12}C_{12}}{C_{aa}C_{66}} \quad \text{(ES3)}$$

$$d_2 = -\left(2\frac{C_{12}}{C_{aa}} - \frac{C_{bb}C_{aa} - C_{12}C_{12}}{C_{aa}C_{66}}\right) \quad \text{(ES4)}$$

$$d_3 = \frac{C_{bb}}{C_{aa}} \quad \text{(ES5)}$$

Here, the C_{bb} (as C_{22} in Table S10), C_{aa} (as C_{11} in Table S10), C_{12} and C_{66} are 32.5, 87.0, 9.7 and 30.4 N/m, of which the data are more precise than Table S10, respectively. The calculated value of ν(θ) is ν(θ = 0°) = 0.111, ν(θ = 32°) = 0, ν(θ = 46.6°) = -0.055, ν(θ = 58°) = 0 and ν(θ = 90°) = 0.298. The angle region with negative value is from 32 to 58 degree for concise angle region (0 to 90 degree) (as 28.9% for full directions in *x*-*y* plane).