Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Band engineering realized by chemical combination in 2D group VA-VA materials

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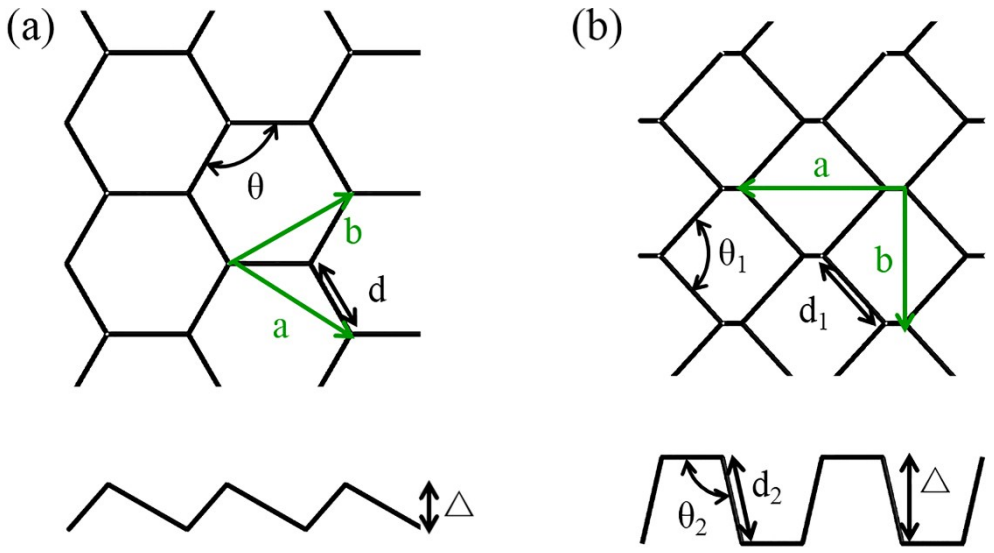

Figure S1. Top and side views of 2D buckled (a) and puckered (b) honeycomb structures.

Table S1. Calculated results for group IVA, group VA elements with honeycomb structures. A (Å), the lattice constants of 2D crystals; θ (deg), the values of angle between neighboring bonds; Δ (Å), the distances between two different parallel planes; d (Å), the nearest distances between neighboring atoms; Eg (eV), the calculated energy band gap. θ, Δ, d can be found in Figure S1.

	a = b		θ		Δ	d	Eg
C[1]	2.46		120		/	1.42	semimetal
Si[1]	3.83		116.4		0.44	2.25	semimetal
Ge[1]	3.97		113.0		0.64	2.38	semimetal
Sn[2]	4.66		110.39		0.90	2.83	semimetal
β-N[3]	2.27		99		0.70	1.49	3.96(PBE)
β-P	3.33[4]		93[5]		1.26[6]	2.27[4]	2.62(HSE)[7]
β-As[8]	3.61		92.22		1.39	2.50	1.64(PBE)
β-Sb[9]	3.94		91.31		1.55	2.76	2.28(HSE)
β-Bi	4.38[10]				1.74[10]	3.07[10]	0.99(HSE)[7]
	a (Å)	b (Å)	θ_1 (deg)	θ_2 (deg)	d_1 (Å)	d_2 (Å)	Eg (eV)
α-P[11]	4.58	3.32	96.00	103.51	2.24	2.28	1.51(HSE)
α-As[8]	4.77	3.68	94.64	100.80	2.50	2.49	0.83(PBE)
α-Sb[12]	5.27	4.10	91	99	2.88	2.85	0.84(HSE)
α-Bi[10]	5.15	4.51	/	/	3.10	3.10	0.14(HSE)

Table S2. The calculated results of molecule units, $(IV/V)_6H_6$. d (Å), the nearest distances between neighboring atoms; θ (deg), the values of angle between neighboring bonds; Δ, the distances between two different parallel planes; Ec (eV/atom), the cohesive energy of molecule units. The subscript A-A of d represents two IV/V atoms; the subscript A-H represents one IV/V atom and H atom.

	d_{A-A}	d_{A-H}	θ	Δ	Ec
C_6H_6	1.40	1.09	120	/	-6.06
Si_6H_6	2.24	1.50	116.13	0.44	-3.68
β-P_6H_6	2.27	1.44	94.44	1.20	-4.02
β-As_6H_6	2.52	1.55	92.29	1.39	-3.90
β-Sb_6H_6	2.92	1.75	91.09	1.65	-3.51
β-Bi_6H_6	3.11	1.85	90.47	1.78	-3.32
α-P_6H_6	2.23/2.25	1.43	98.70/100.34	2.07	-4.03
α-As_6H_6	2.51/2.50	1.55	94.80/97.38	2.35	-3.89

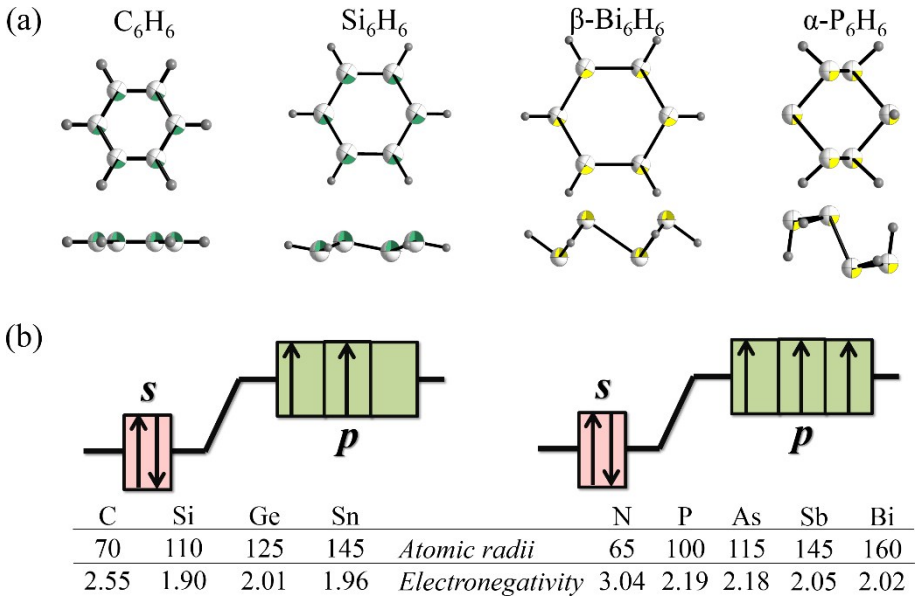

Figure S2. (a) Top and side views of C_6H_6, Si_6H_6, Bi_6H_6, P_6H_6 molecule units. Prefix α and β represent that the molecule unit is corresponding to α and β phase of 2D group VA materials, puckered and buckled structure, respectively. (b) Schematic diagram of different atomic orbitals. The data in the second line are the corresponding atomic radii (pm) and the data the third line are the corresponding electronegativity. The electronegativity is referred to as the Pauling scale, on a relative scale from around 0.7 to 3.98 (hydrogen = 2.20).[13, 14]

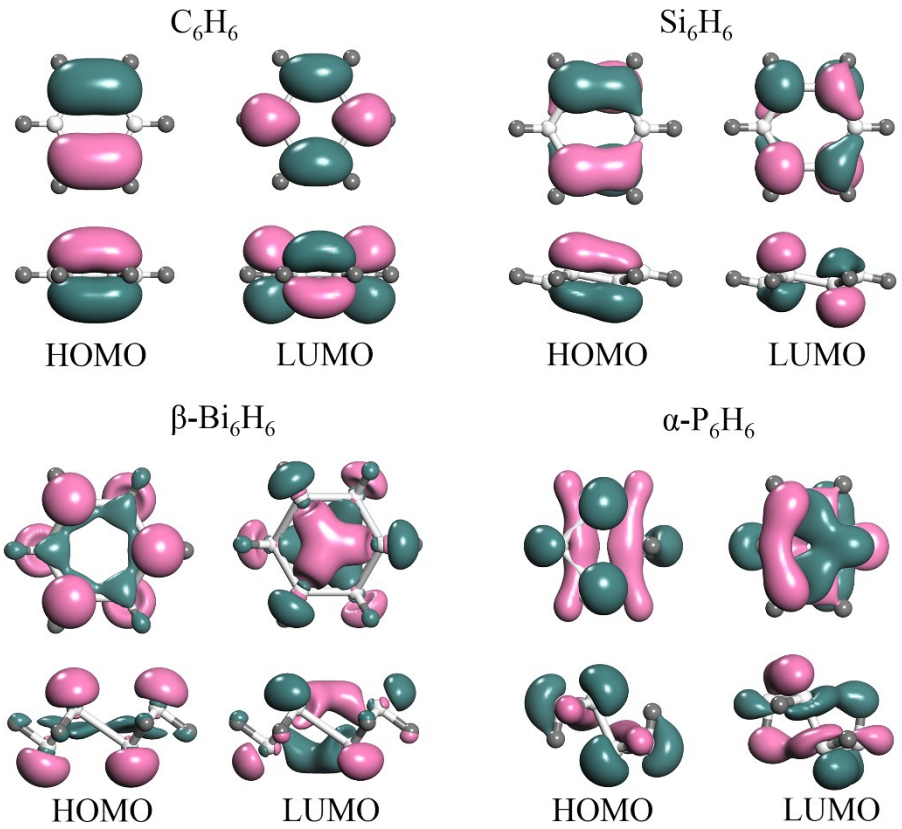

Figure S3. Top and side views of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in C_6H_6, Si_6H_6, β-Bi_6H_6, α-P_6H_6 molecule units. The isosurface value is set to 0.03 electron/Å^3.

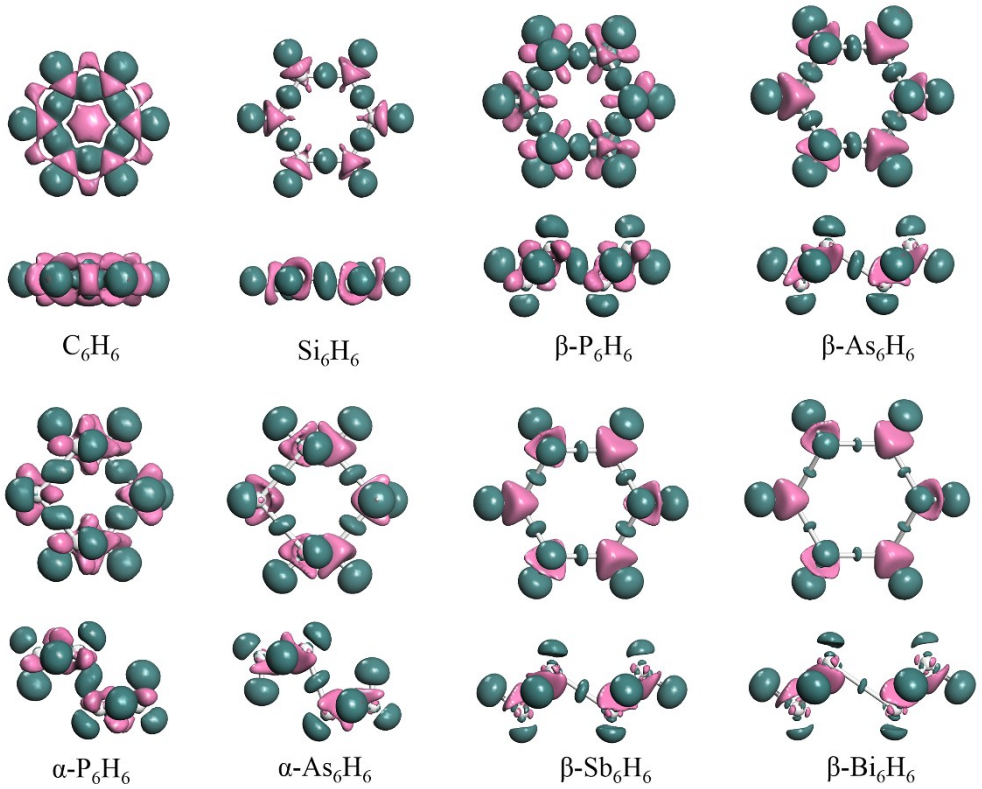

Figure S4. Top and side views of deformation charge densities of molecule units. The isosurface value is set to 0.05 electron/Å^3. Prefix α represents that the molecule unit is corresponding to phase α of 2D group VA materials, puckered structure. Prefix β represents that the molecule unit is corresponding to phase β of 2D group VA materials, buckled structure.

Table S3. The calculated results of group-VA monolayers in buckled structure. The parameters a (Å), θ (deg), Δ (Å), and d (Å) represents the lattice constant, bond angle, layer thickeness, bond length, respectively. Ec (eV/atom) represents the cohesive energy. Eg (eV) represnets the band gap at PBE/PBEsoc/HSE level respectively. D/I demonstrate that the band gap is direct or indirect.

β	a	θ	Δ	d	Ec	Eg PBE	Eg PBEsoc	Eg HSE
N	2.29	94.93	0.82	1.56	-3.28	3.86/I	3.86/I	5.81/I
P	3.28	93.09	1.23	2.26	-2.32	1.91/I	1.91/I	2.76/I
As	3.60	91.89	1.40	2.51	-2.29	1.59/I	1.47/I	2.17/I
Sb	4.05	89.57	1.67	2.87	-1.96	1.08/I	0.80/I	1.51/I
Bi	4.17	87.84	1.80	3.01	-1.44	0.56/D	0.51/I	0.94/D

Table S4. The calculated results of group-VA monolayers in puckered structure. The parameters a (Å), θ (deg), Δ (Å), and d (Å) represents the lattice constant, bond angle, layer thickeness, bond length, respectively. Ec (eV/atom) is the cohesive energy and Eg (eV) is the band gap. D/I demonstrate that the band gap is direct or indirect. θ_1, θ_2, d_1, d_2, θ, Δcan be found in Figure S5.

α	a	b	θ_1	θ_2	d_1	d_2	Δ	Ec	Eg PBE	Eg PBEsoc	Eg HSE
P	4.57	3.31	96.23	103.77	2.22	2.26	2.11	-2.57	0.87/D	0.87/D	1.55/D
As	4.70	3.68	94.65	100.32	2.50	2.48	2.39	-1.90	0.71/I	0.69/I	1.26/I
Sb	5.01	4.23	93.84	97.27	2.90	2.84	2.79	-1.77	0.36/I	0.35/I	0.51/I
Bi	5.14	4.42	92.68	96.11	3.06	2.98	2.95	-1.38	0.16/D	0.16/I	0.05/D

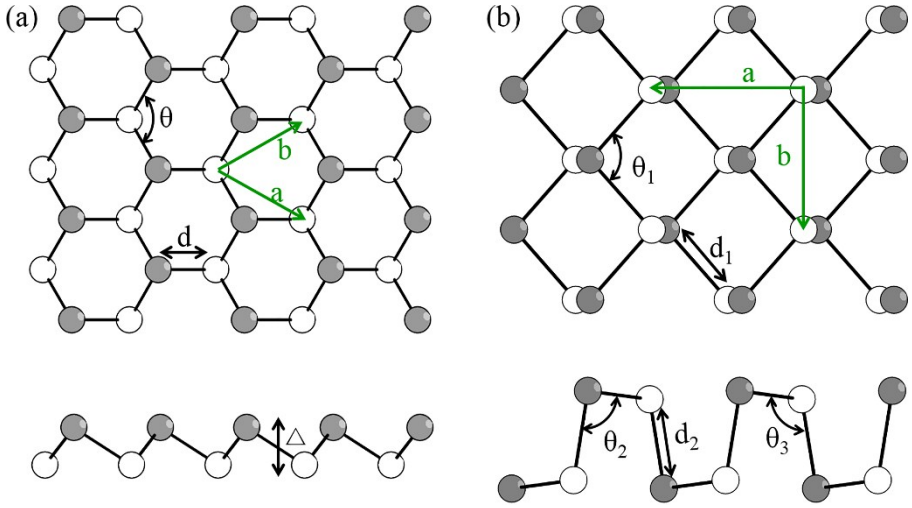

Figure S5. Top and side views of 2D buckled (a) and puckered (b) group VA-VA composites.

Table S5. The calculated results of 2D buckled group VA-VA composites. The parameters a, θ (deg), Δ (Å), and d (Å) represents the lattice constant, bond angle, layer thickness, bond length, respectively. Ec (eV/atom) represents the cohesive energy and Eg (eV) represents the band gap at different functional (PBE, PBEsoc, and HSE). D/I demonstrate that the band gap is direct or indirect. θ, Δ, d can be found in Figure S5.

β	a	θ	Δ	d	Ec	Eg PBE	Eg PBEsoc	Eg HSE
NP	2.72	98.76	0.86	1.80	-3.45	1.81/I	1.81/I	2.82/I
NAs	2.97	98.26	0.96	1.97	-3.38	1.71/I	1.71/I	2.74/I
NSb	3.27	99.45	1.01	2.14	-2.76	1.67/I	1.65/I	2.53/I
NBi	3.47	100.33	1.04	2.26	-2.38	0.71/I	0.62/I	1.71/I
PAs	3.44	91.95	1.33	2.39	-2.34	1.76/I	1.67/I	2.42/I
PSb	3.72	91.61	1.45	2.59	-2.13	1.66/I	1.51/I	2.29/I
PBi	3.87	92.21	1.49	2.69	-1.91	1.46/D	1.14/I	2.09/D
AsSb	3.86	91.44	1.52	2.70	-2.07	1.47/I	1.27/I	2.01/I
AsBi	4.00	91.72	1.56	2.79	-1.90	1.07/D	0.72/D	1.61/D
SbBi	4.23	90.85	1.69	2.97	-1.77	0.96/D	0.38/I	1.42/D

Table S6. The calculated results of 2D puckered group VA-VA composites. The parameters a/b (Å), θ (deg), and d (Å) represents the lattice constant, bond angle, bond length, respectively. Ec (eV/atom) is the cohesive energy and Eg (eV) is the band gap (HSE06 functional). D/I demonstrate that the band gap is direct or indirect. θ_1, θ_2, θ_3, d_1, d_2 can be found in Figure S4.

α	a	b	θ_1	θ_2	θ_3	d_1	d_2	Ec	Eg PBE	Eg PBEsoc	Eg HSE
NP	4.17	2.70	103.16	97.65	123.71	1.72	1.82	-3.78	1.66/I	1.65/I	2.71/I
NAs	4.20	2.96	102.28	95.52	119.69	1.90	1.96	-3.21	1.89/I	1.85/I	2.83/I
NSb	4.17	3.30	103.45	91.17	117.28	2.11	2.11	-3.04	1.77/I	1.69/I	2.57/I
NBi	3.76	3.52	100.48	86.83	108.71	2.29	2.21	-2.71	1.46/I	1.27/I	2.19/I
PAs	4.62	3.51	95.37	99.64	103.81	2.37	2.38	-2.32	0.87/D	0.86/D	1.50/D
PSb	4.28	3.91	96.94	88.30	105.01	2.61	2.55	-2.14	0.52/I	0.44/I	0.95/I
PBi	4.45	4.10	96.69	90.93	101.09	2.74	2.64	-1.98	0.56/I	0.53/I	0.98/I
AsSb	4.55	4.02	95.64	90.03	103.85	2.71	2.65	-2.05	0.25/D	0.23/D	0.62/D
AsBi	4.60	4.23	96.10	91.57	99.72	2.85	2.77	-1.93	0.53/D	0.38/D	0.64/D
SbBi	4.78	4.48	94.72	87.03	102.55	3.04	2.96	-1.78	0.48/D	0.30/I	0.49/D

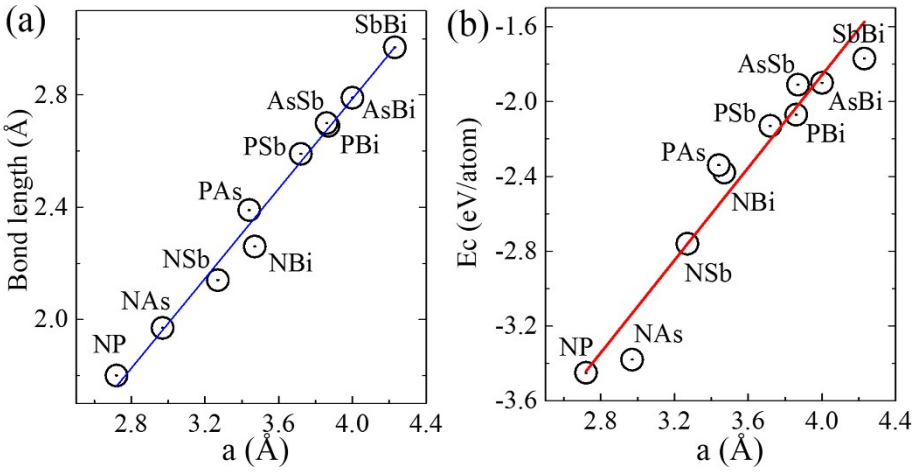

Figure S6. Plots of bond length and cohesive energy Ec against lattice constant of 2D buckled group VA-VA composites, showing a nearly linear relationship.

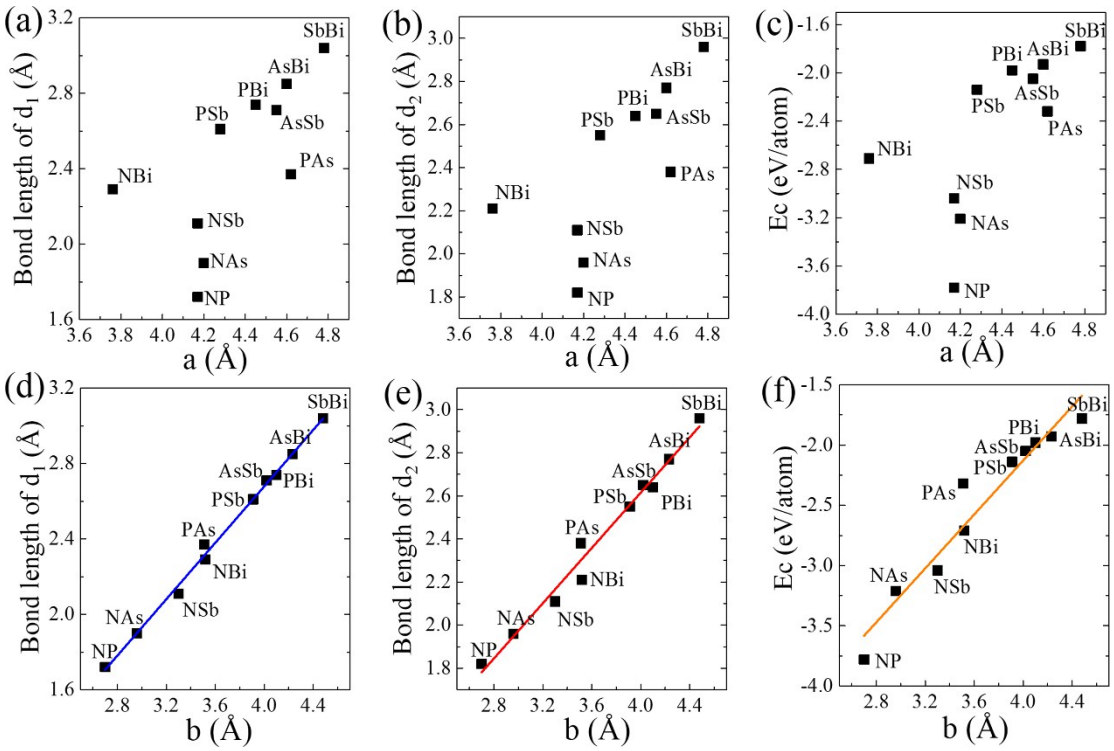

Figure S7. Plots of bond length and cohesive energy Ec against lattice constant a and b of 2D puckered group VA-VA monolayers, respectively.

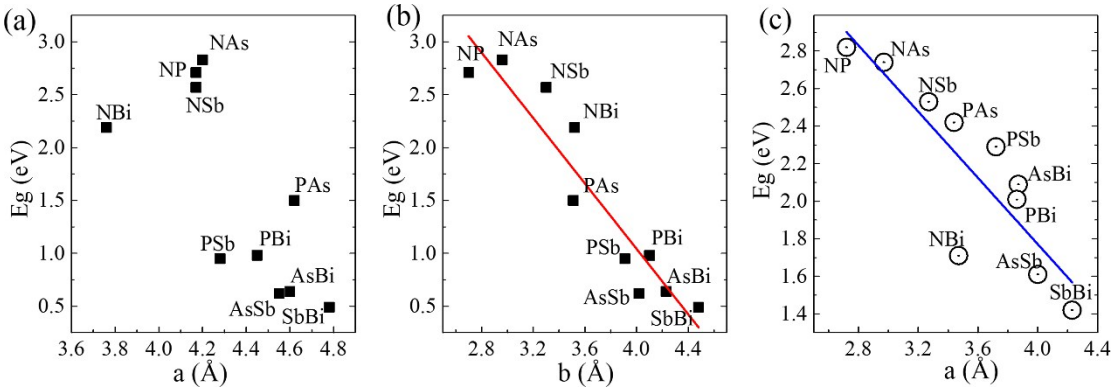

Figure S8. (a-b) Plots of band gap Eg against lattice constant a and b in 2D puckered VA-VA monolayers, respectively. (c) Plots of band gap Eg against lattice constant in 2D buckled VA-VA monolayers.

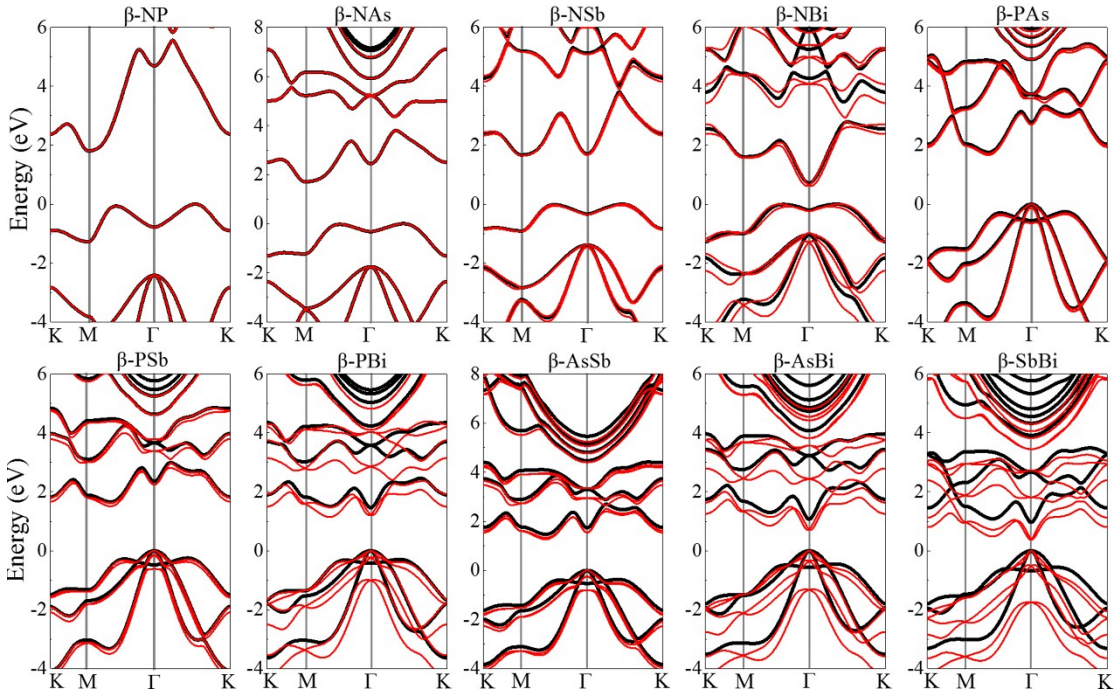

Figure S9. Band structures of 2D buckled group VA-VA monolayers calculated by PBE method without (black lines) and with SOC (red lines).

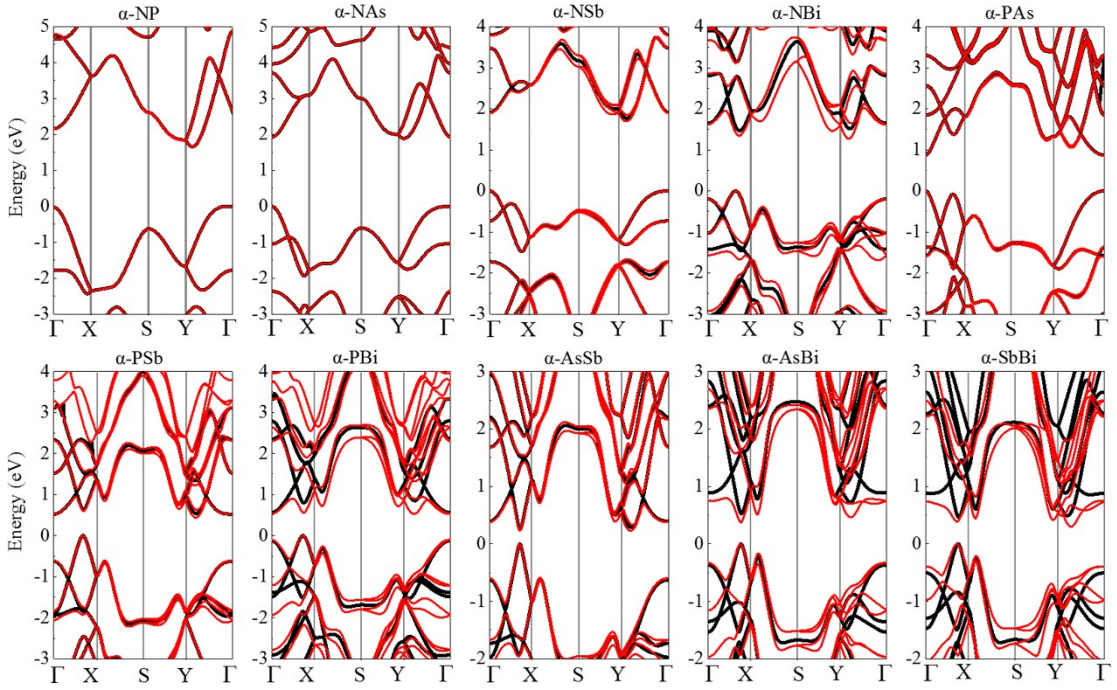

Figure S10. Band structures of 2D puckered group VA-VA monolayers calculated by PBE method without (black lines) and with SOC (red lines).

Table S7. The Rashba parameters of monolayer β-Bi and β-XBi, including location, Rashba momentum k_0 (Å^{-1}), and the corresponding Rashba energy E_R (meV), Rashba parameter α_R (eVÅ).

β	location	k_0	E_R	α_R
Bi	VB	0.14	80	1.1
NBi	CB	0.06	24	0.8
PBi	CB	0.02	17	1.7
AsBi	CB	0.04	18	0.9
SbBi	CB	0.02	11	1.1

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