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Supporting Information for

Alkaline-earth metal embedded expanded phthalocyanine nanosheets with direct band gap and high power conversion efficiency

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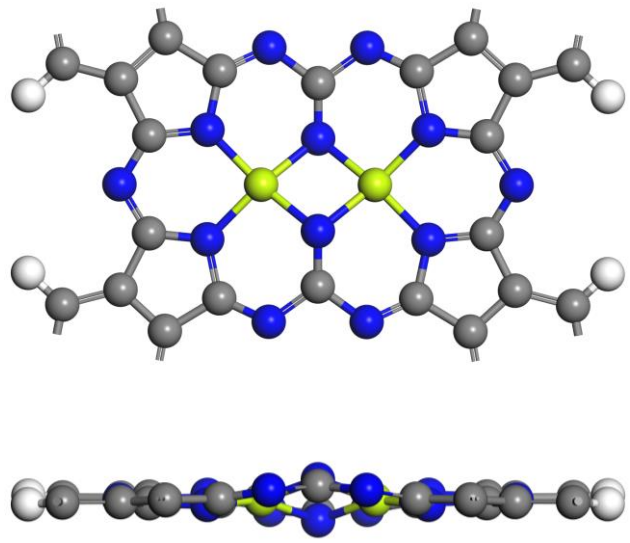
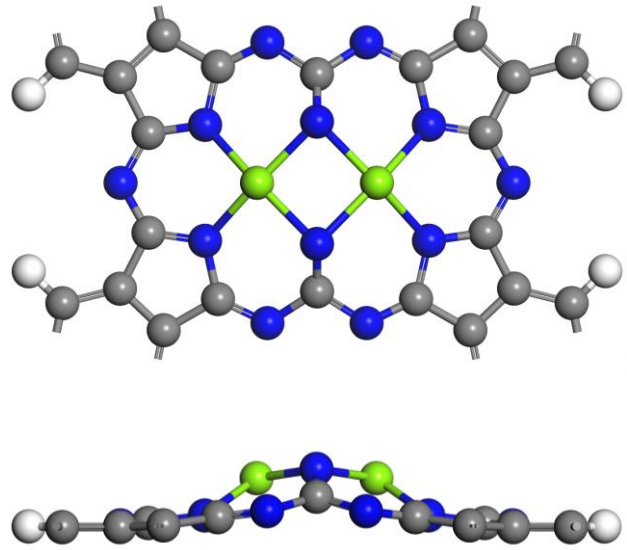
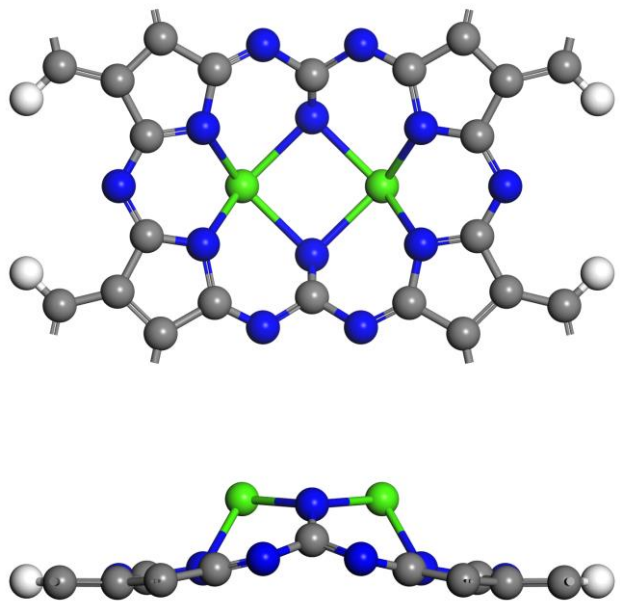
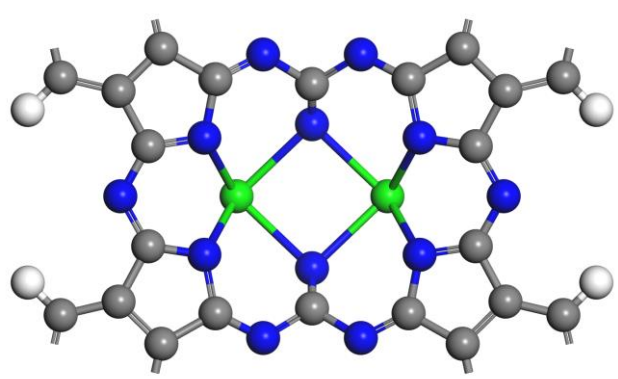
Table S1. The lattice parameters (Å), space groups and point groups of optimized crystal structures of M_2Pc monolayers.

M_2Pc	Optimized structure top (up) and side (down) views	Lattice constant	Space group	Point group
Be_2Pc		a = 12.34 Å b = 12.34 Å c = 15.09 Å	*C*2/*m* (#12)	C_{2h}
Mg_2Pc		a = 12.48 Å b = 12.48 Å c = 15.36 Å	*Cmm*2 (#35)	C_{2V}
Ca_2Pc		a = 12.40 Å b = 12.40 Å c = 15.53 Å	*Cmm*2 (#35)	C_{2V}
Sr_2Pc		a = 12.38 Å b = 12.38 Å c = 15.58 Å	*Cmm*2 (#35)	C_{2V}

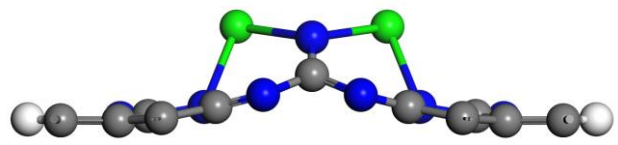
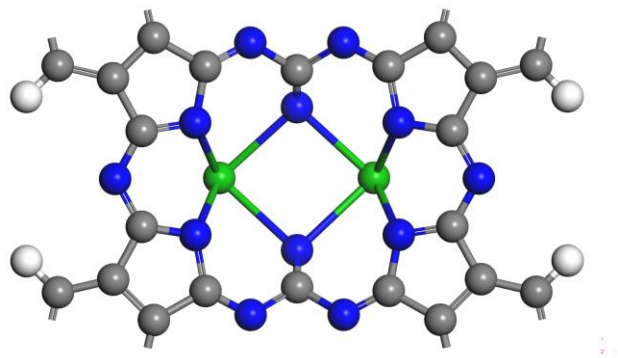
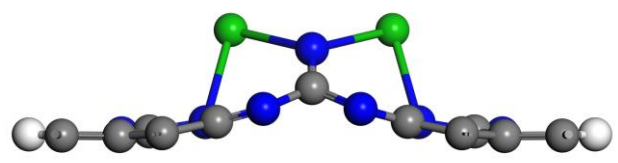
				
Ba_2Pc	 	a = 12.36 Å b = 12.36 Å c = 15.63 Å	*Cmm*2 (#35)	C_{2V}

Table S2. Calculated elastic constants (C_{ij}, N/m), Layer modulus (γ, N/m), Young's modulus (Y, N/m), Poisson's ratio (υ) of M_2Pc nanosheets.

Structure	C_{11}	C_{22}	C_{12}	C_{66}	γ	Young modulus		Poisson's ratio	
						Y_x	Y_y	υ_x	υ_y
Be_2Pc	71.7	70.2	24.0	18.4	47.5	63.5	62.1	0.34	0.33
Mg_2Pc	57.3	56.4	21.6	16.9	39.2	49.1	48.2	0.38	0.38
Ca_2Pc	44.2	44.4	22.2	15.3	33.2	33.1	33.3	0.50	0.50
Sr_2Pc	40.6	41.1	21.1	14.7	30.9	29.8	30.1	0.51	0.52
Ba_2Pc	38.1	38.7	20.4	14.3	29.4	27.3	27.8	0.53	0.54

Table S3. Calculated lattice parameters (Å), crystal structures for Mg_2Pc monolayer under biaxial strain from −5% to 10%.

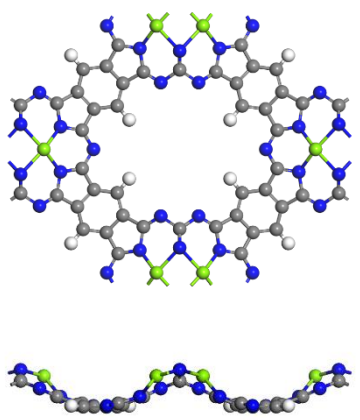
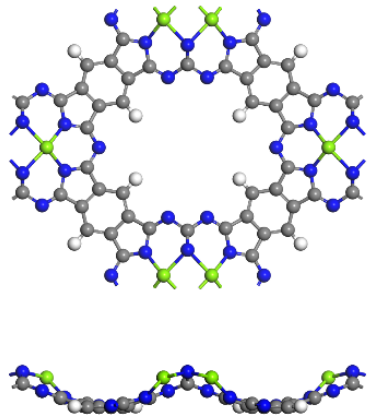
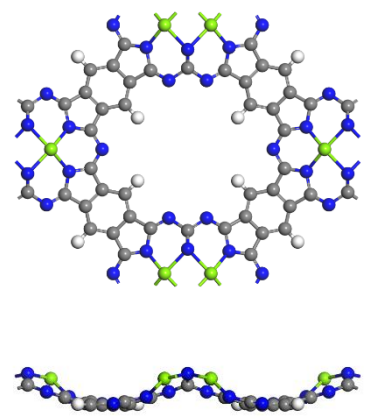
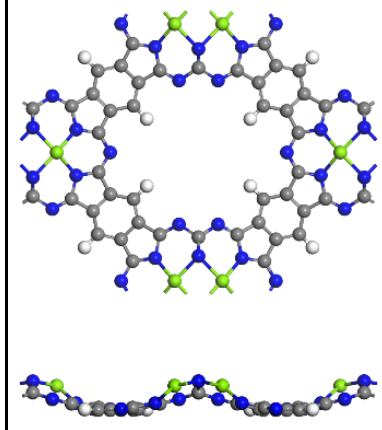
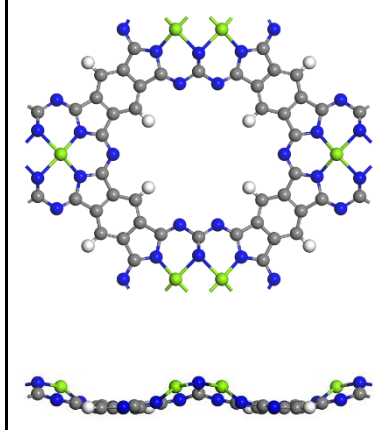
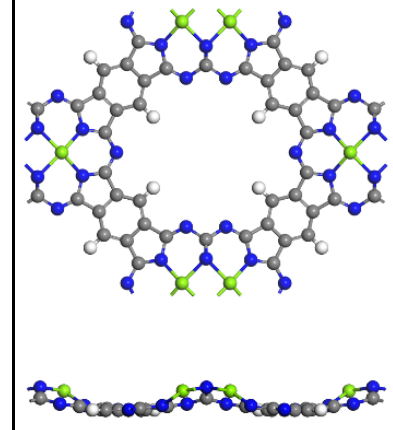
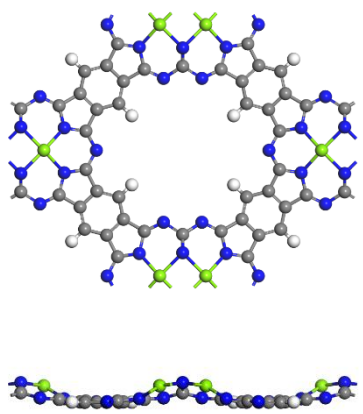
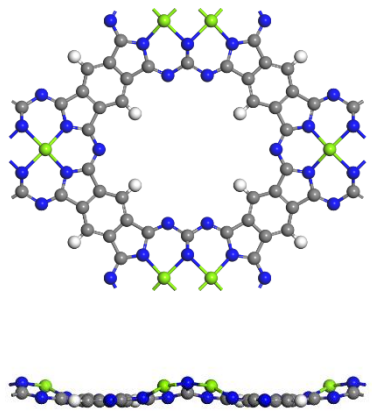
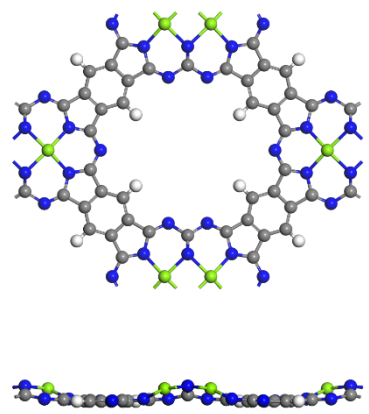
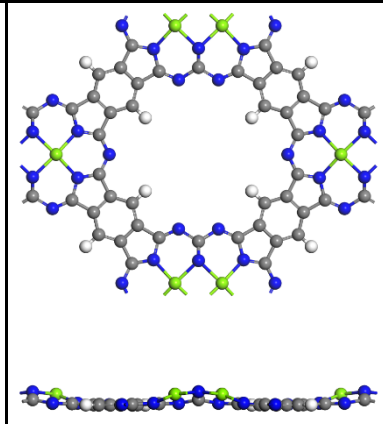
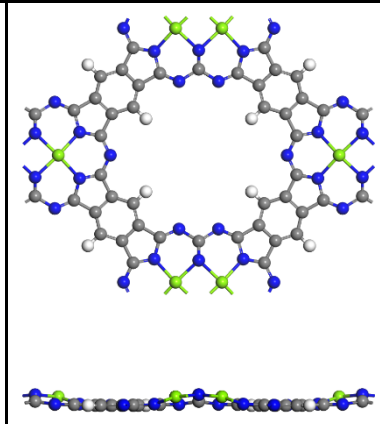
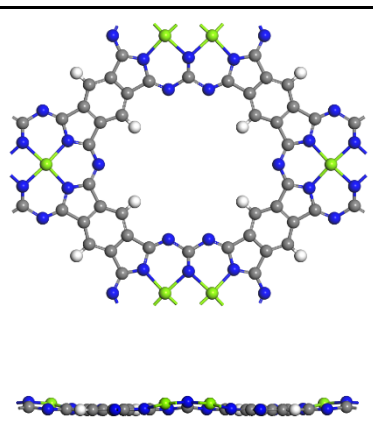
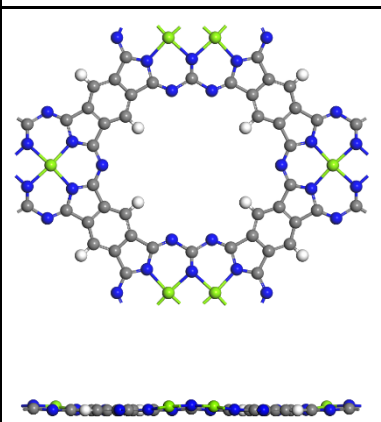
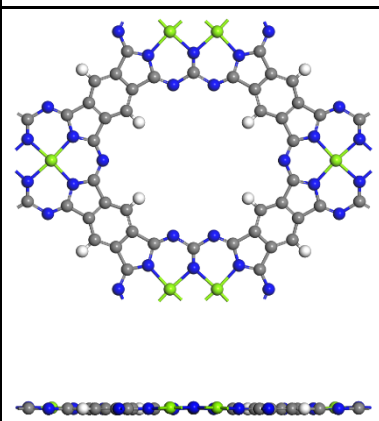
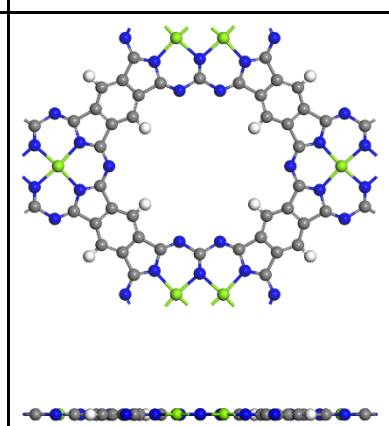
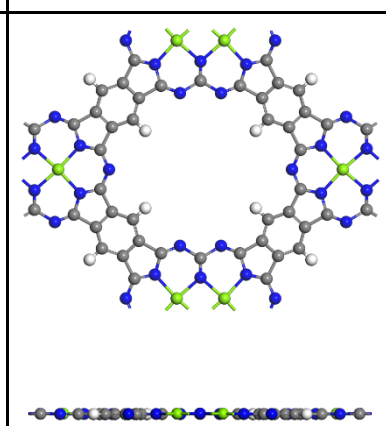
Strain	−5%	−4%	−3%	−2%	−1%	0%
Lattice constant	a = 14.54 Å b = 18.74 Å c = 15.36 Å	a = 14.69 Å b = 18.93 Å c = 15.36 Å	a = 14.85 Å b = 19.13 Å c = 15.36 Å	a = 15.00 Å b = 19.33 Å c = 15.36 Å	a = 15.15 Å b = 19.52 Å c = 15.36 Å	a = 15.31 Å b = 19.72 Å c = 15.36 Å
Mg_2Pc						
Strain	1%	2%	3%	4%	5%	
Lattice constant	a = 15.46 Å b = 19.92 Å c = 15.36 Å	a = 15.61 Å b = 20.12 Å c = 15.36 Å	a = 15.76 Å b = 20.31 Å c = 15.36 Å	a = 15.92 Å b = 20.51 Å c = 15.36 Å	a = 16.07 Å b = 20.70 Å c = 15.36 Å	
Mg_2Pc						
Strain	6%	7%	8%	9%	10%	
Lattice constant	a = 16.22 Å b = 20.90 Å c = 15.36 Å	a = 16.38 Å b = 21.10 Å c = 15.36 Å	a = 16.53 Å b = 21.30 Å c = 15.36 Å	a = 16.68 Å b = 21.50 Å c = 15.36 Å	a = 13.77 Å b = 17.75 Å c = 15.36 Å	
Mg_2Pc						

Table S4. Calculated lattice parameters (Å), crystal structures for Ca_2Pc monolayer under biaxial strain from −5% to 10%.

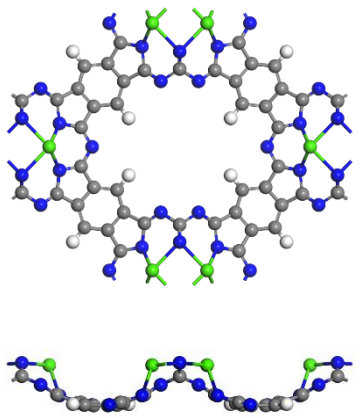
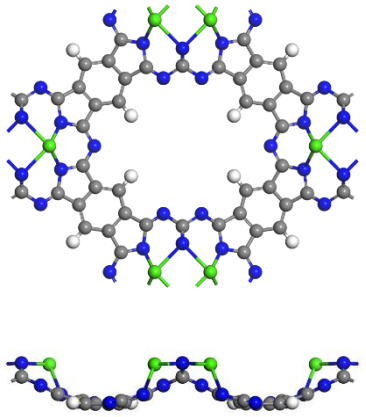
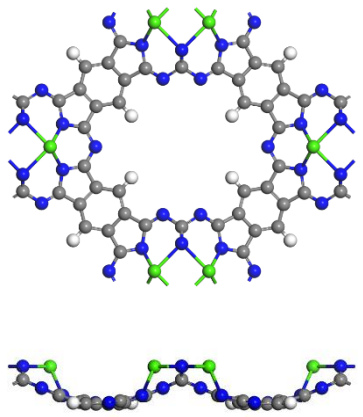
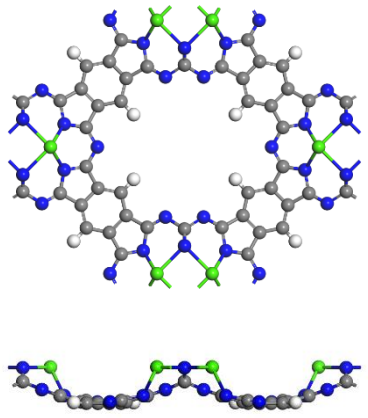
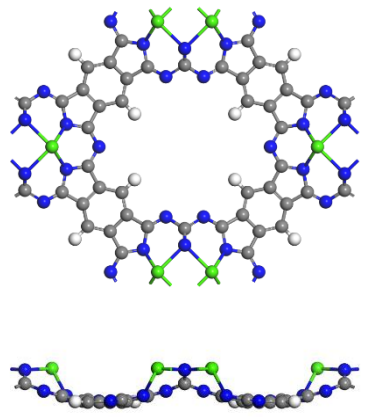
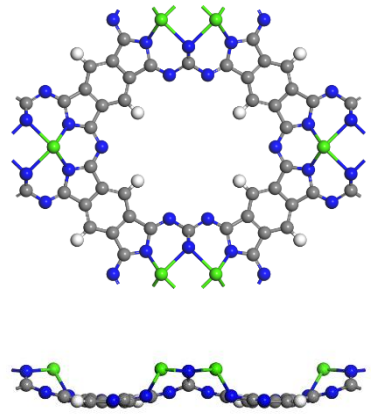
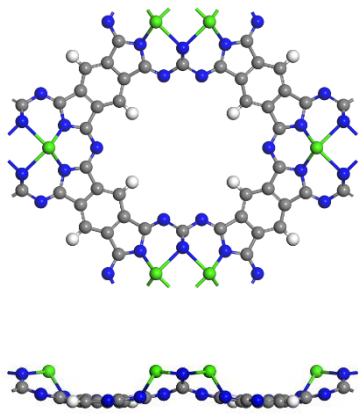
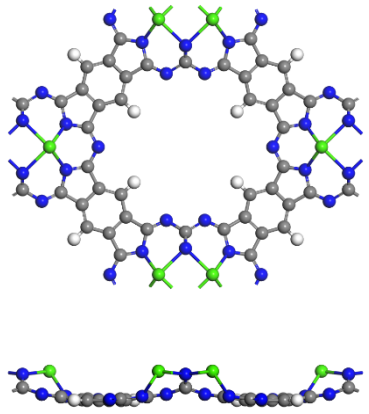
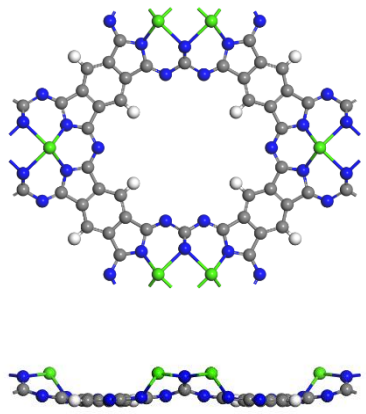
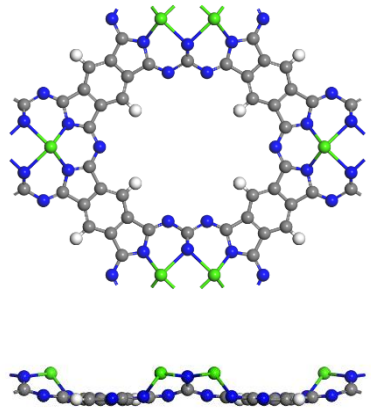
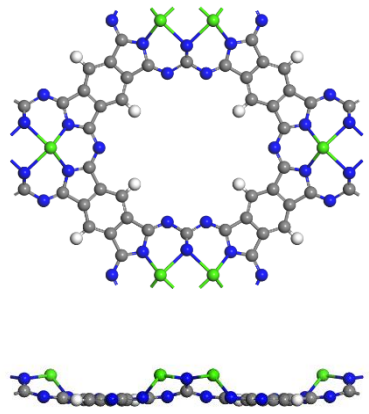
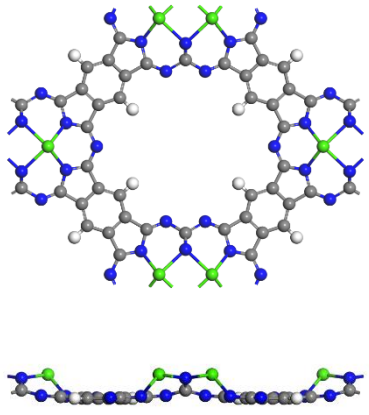
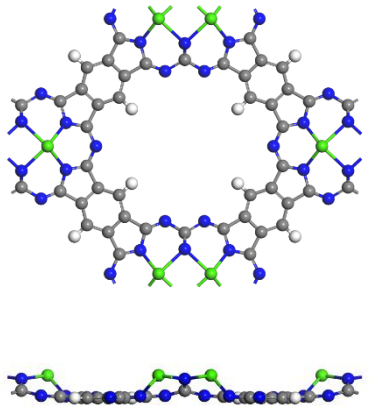
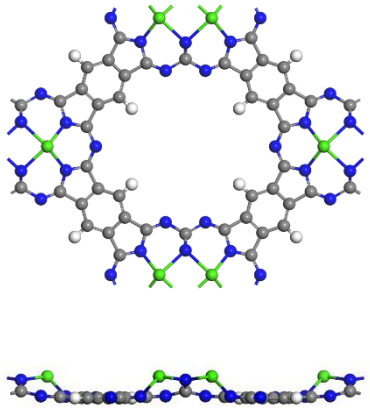
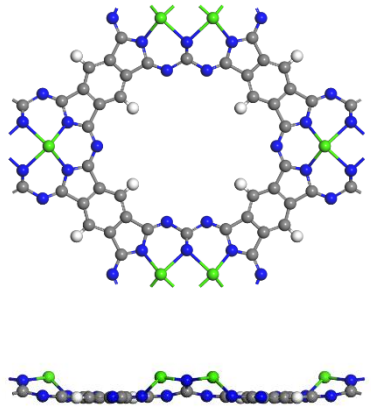
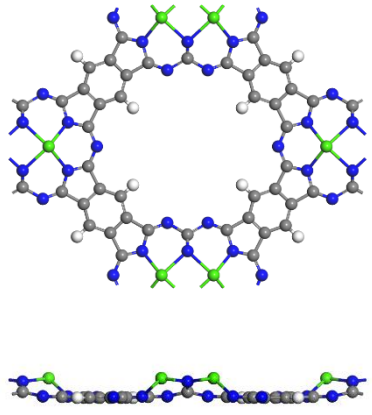
Strain	−5%	−4%	−3%	−2%	−1%	0%
Lattice constant	a = 14.50 Å b = 18.57 Å c = 15.54 Å	a = 14.65 Å b = 18.77 Å c = 15.54 Å	a = 14.81 Å b = 18.97 Å c = 15.54 Å	a = 14.96 Å b = 19.16 Å c = 15.54 Å	a = 15.11 Å b = 19.36 Å c = 15.54 Å	a = 15.26 Å b = 19.55 Å c = 15.54 Å
Ca_2Pc						
Strain	1%	2%	3%	4%	5%	
Lattice constant	a = 15.42 Å b = 19.75 Å c = 15.54 Å	a = 15.57 Å b = 19.95 Å c = 15.54 Å	a = 15.72 Å b = 20.14 Å c = 15.54 Å	a = 15.87 Å b = 20.33 Å c = 15.54 Å	a = 16.03 Å b = 20.53 Å c = 15.54 Å	
Ca_2Pc						
Strain	6%	7%	8%	9%	10%	
Lattice constant	a = 16.18 Å b = 20.72 Å c = 15.54 Å	a = 16.33 Å b = 20.92 Å c = 15.54 Å	a = 16.49 Å b = 21.12 Å c = 15.54 Å	a = 16.64 Å b = 21.31 Å c = 15.54 Å	a = 16.791 Å b = 21.51 Å c = 15.54 Å	
Ca_2Pc						

Table S5. Calculated lattice parameters (Å), crystal structures for Sr_2Pc monolayer under biaxial strain from −5% to 10%.

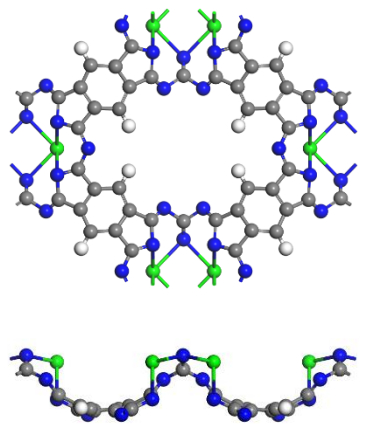
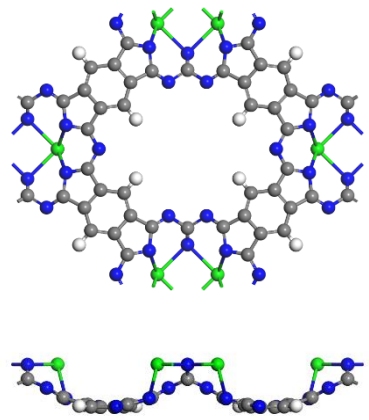
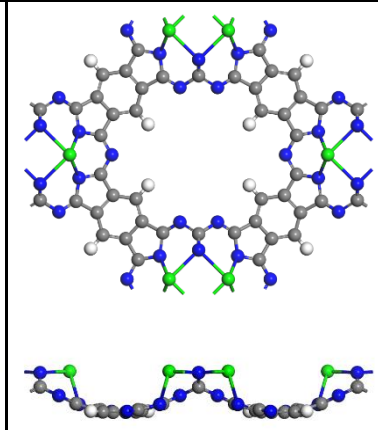
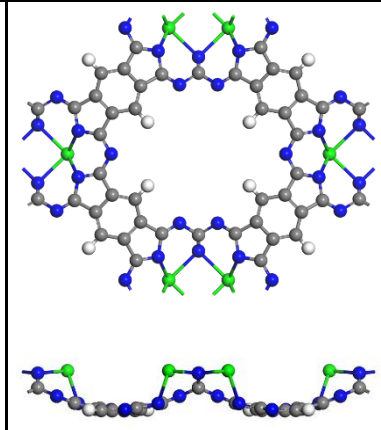
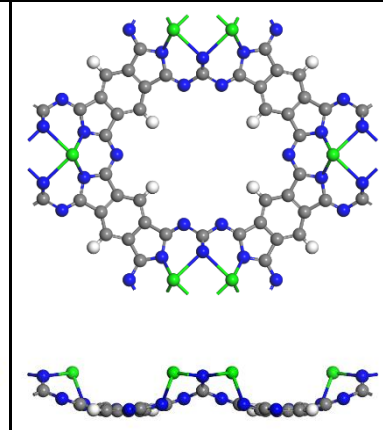
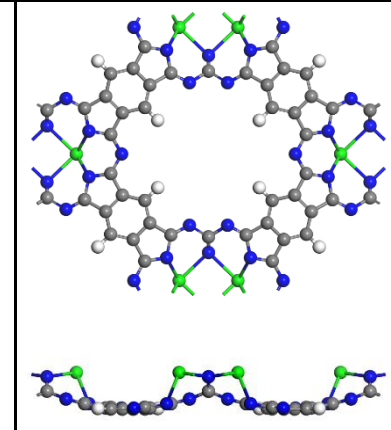
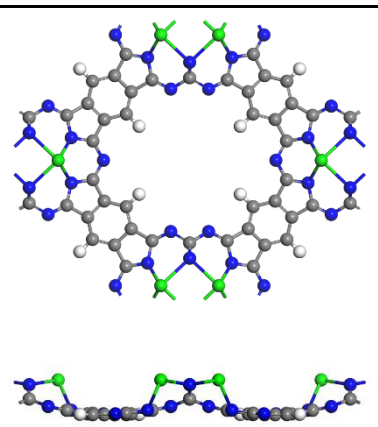
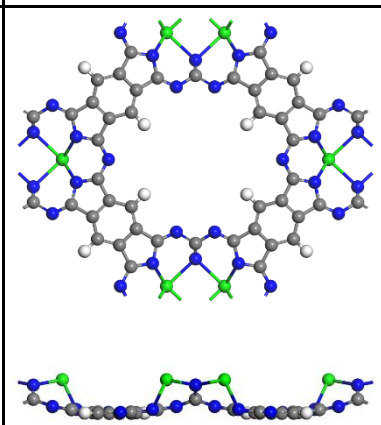
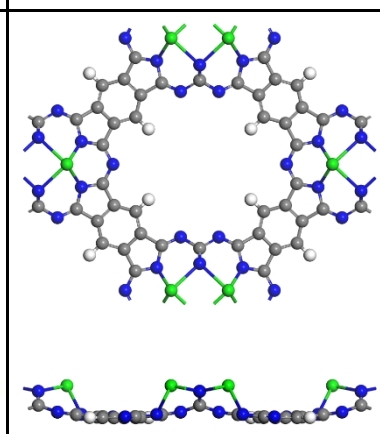
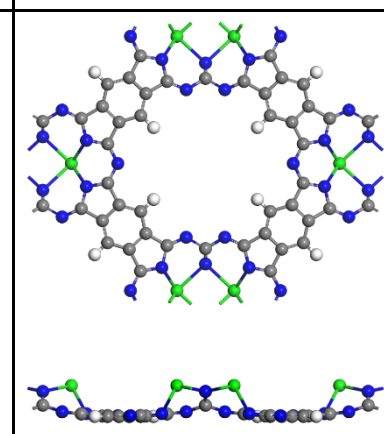
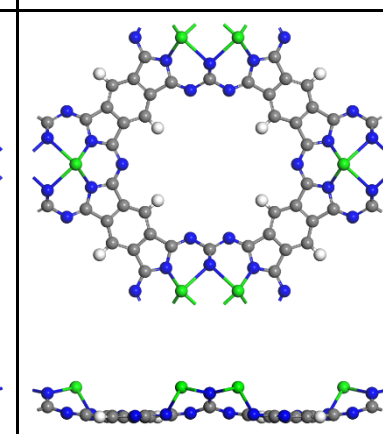
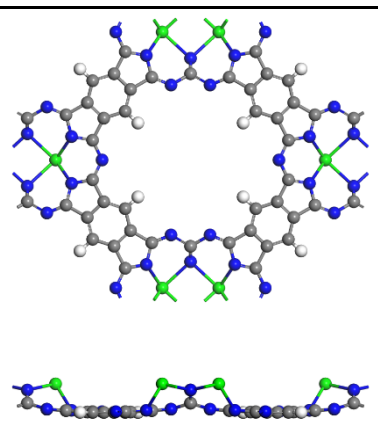
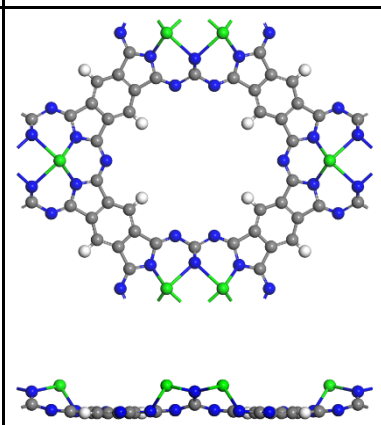
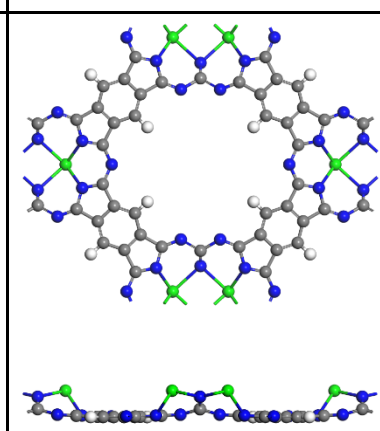
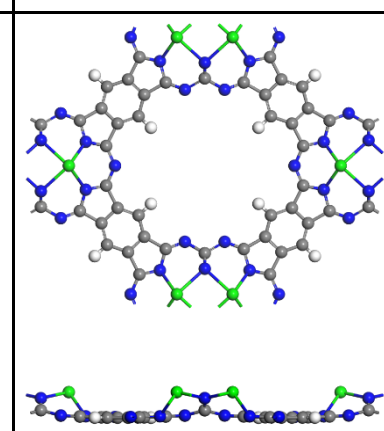
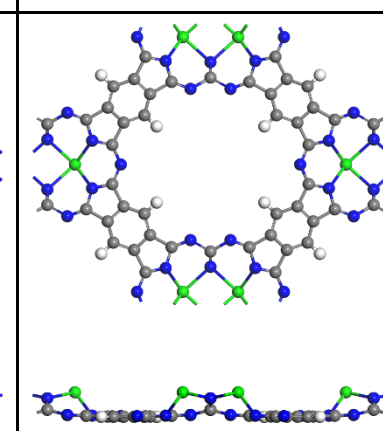
Strain	−5%	−4%	−3%	−2%	−1%	0%
Lattice constant	a = 14.49 Å b = 18.54 Å c = 15.58 Å	a = 14.64 Å b = 18.73 Å c = 15.58 Å	a = 14.79 Å b = 18.93 Å c = 15.63 Å	a = 14.945 Å b = 19.125 Å c = 15.58 Å	a = 15.10 Å b = 19.32 Å c = 15.63 Å	a = 15.25 Å b = 19.52 Å c = 15.58 Å
Sr_2Pc						
Strain	1%	2%	3%	4%	5%	
Lattice constant	a = 15.40Å b = 19.71 Å c = 15.58 Å	a = 15.55 Å b = 19.90 Å c = 15.58 Å	a = 15.71 Å b = 20.10 Å c = 15.58 Å	a = 15.86 Å b = 20.29 Å c = 15.58 Å	a = 16.01 Å b = 20.49 Å c = 15.58 Å	
Sr_2Pc						
Strain	6%	7%	8%	9%	10%	
Lattice constant	a = 16.17 Å b = 20.69 Å c = 15.58 Å	a = 16.32 Å b = 20.88 Å c = 15.58 Å	a = 16.47 Å b = 21.08 Å c = 15.58 Å	a = 16.62 Å b = 21.27 Å c = 15.58 Å	a = 16.77 Å b = 21.46 Å c = 15.58 Å	
Sr_2Pc						

Table S6. Calculated lattice parameters (Å), crystal structures for Ba_2Pc monolayer under biaxial strain from −5% to 10%.

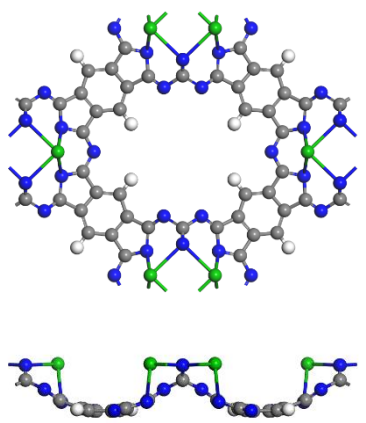
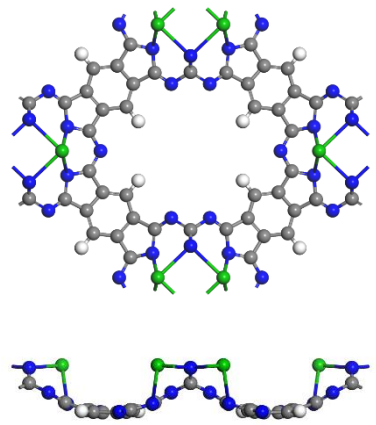
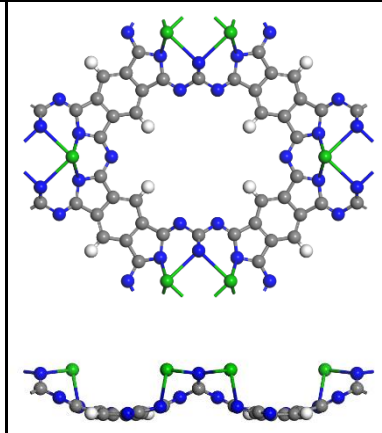
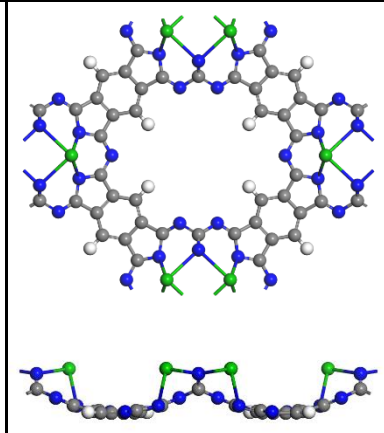
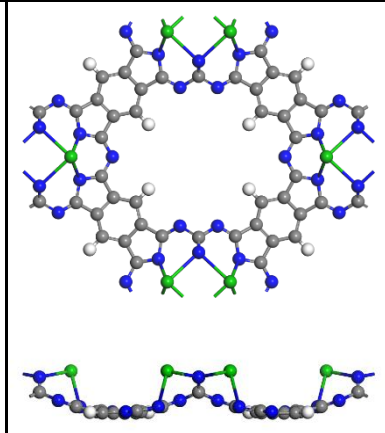
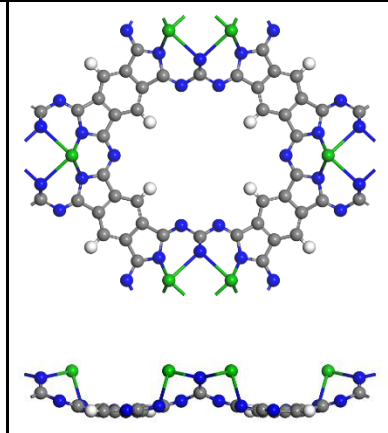
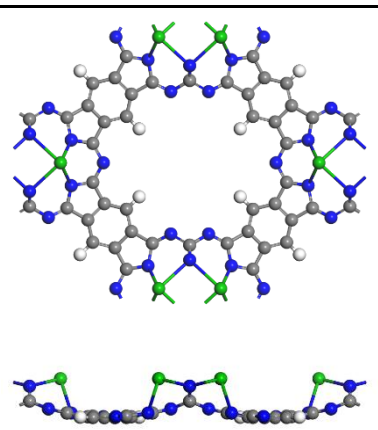
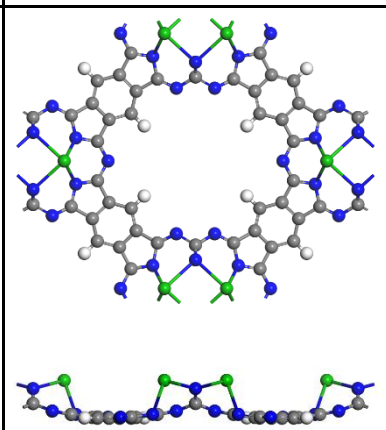
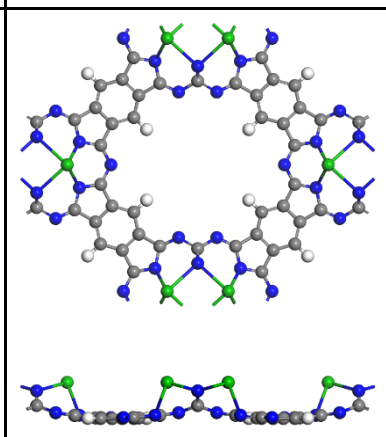
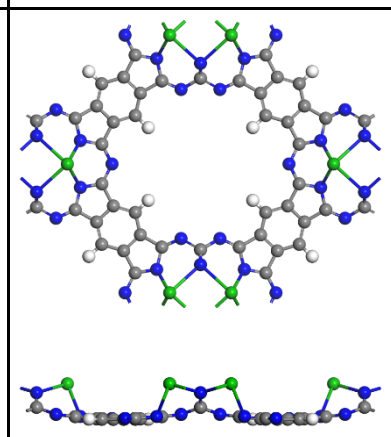
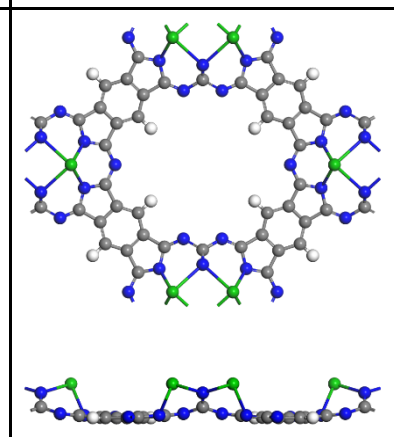
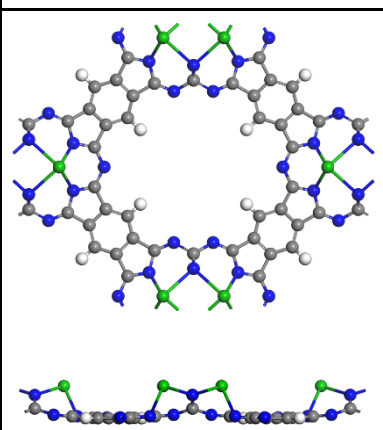
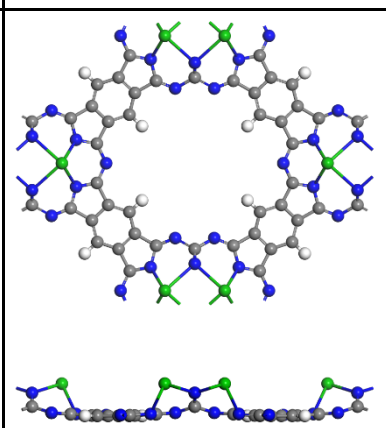
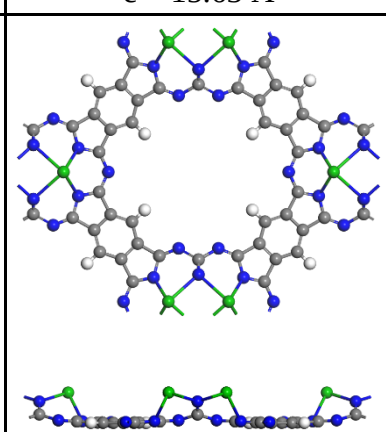
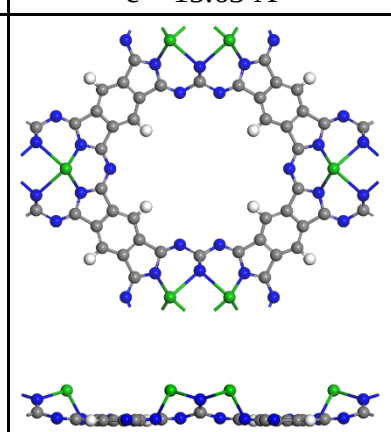
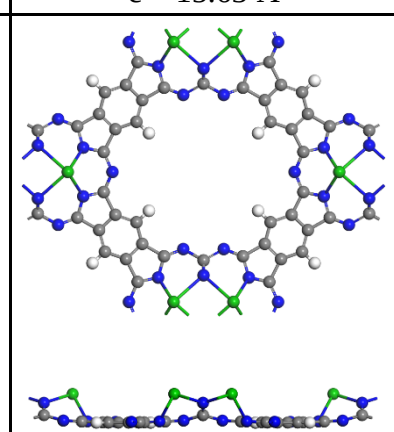
Strain	−5%	−4%	−3%	−2%	−1%	0%
Lattice constant	a = 14.48 Å b = 18.49 Å c = 15.63 Å	a = 14.63 Å b = 18.69 Å c = 15.63 Å	a = 14.78 Å b = 18.88 Å c = 15.63 Å	a = 14.93 Å b = 19.08 Å c = 15.63 Å	a = 15.09 Å b = 19.27 Å c = 15.63 Å	a = 15.24 Å b = 19.47 Å c = 15.63 Å
Ba_2Pc						
Strain	1%	2%	3%	4%	5%	
Lattice constant	a = 15.39 Å b = 19.66 Å c = 15.63 Å	a = 15.54 Å b = 19.85 Å c = 15.63 Å	a = 15.70 Å b = 20.05 Å c = 15.63 Å	a = 15.85 Å b = 20.24 Å c = 15.63 Å	a = 16.00 Å b = 20.44 Å c = 15.63 Å	
Ba_2Pc						
Strain	6%	7%	8%	9%	10%	
Lattice constant	a = 16.15 Å b = 20.63 Å c = 15.63 Å	a = 16.31 Å b = 20.83 Å c = 15.63 Å	a = 16.46 Å b = 21.02 Å c = 15.63 Å	a = 16.61 Å b = 21.22 Å c = 15.63 Å	a = 16.76 Å b = 21.41 Å c = 15.63 Å	
Ba_2Pc						

Table S7. Calculated electronic band structures for Be_2Pc monolayer under biaxial strain from −5% to 10%.

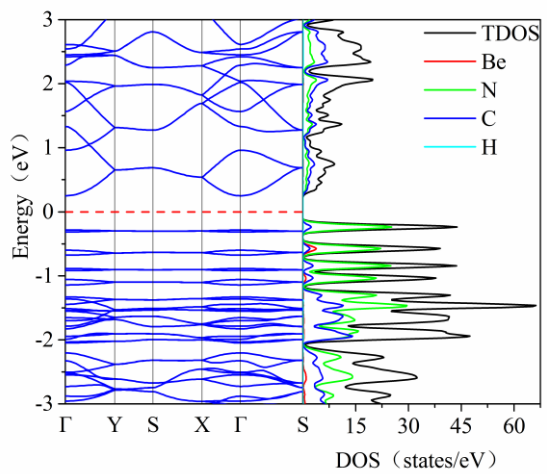
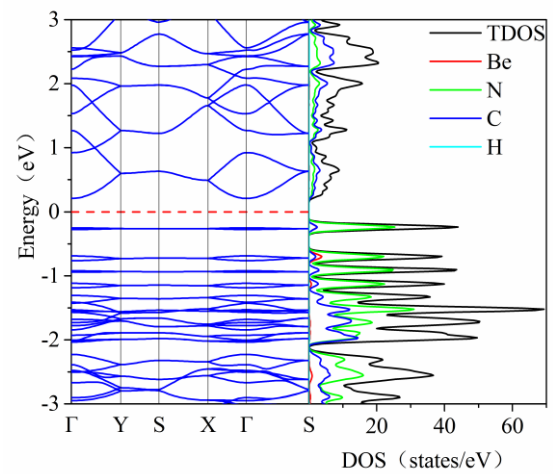
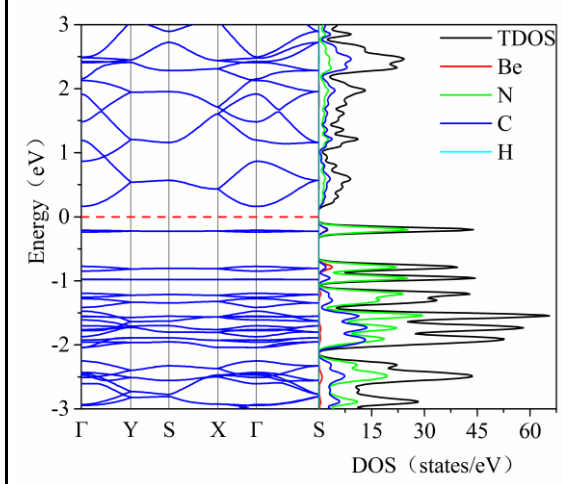
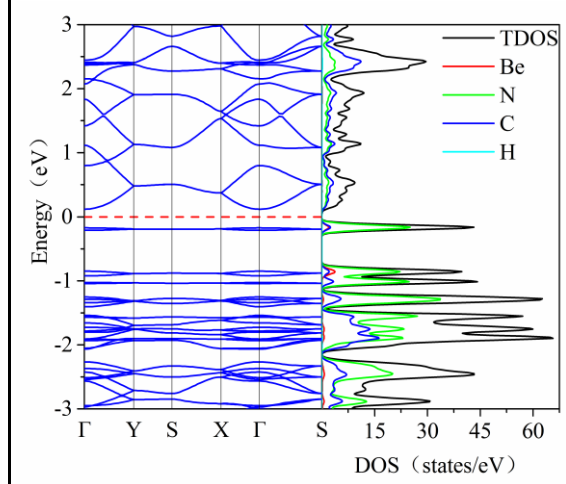
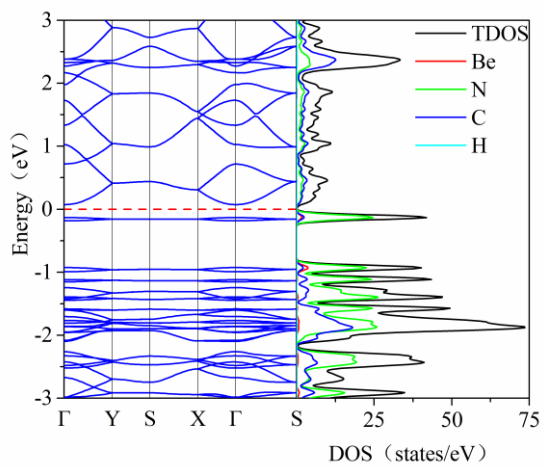
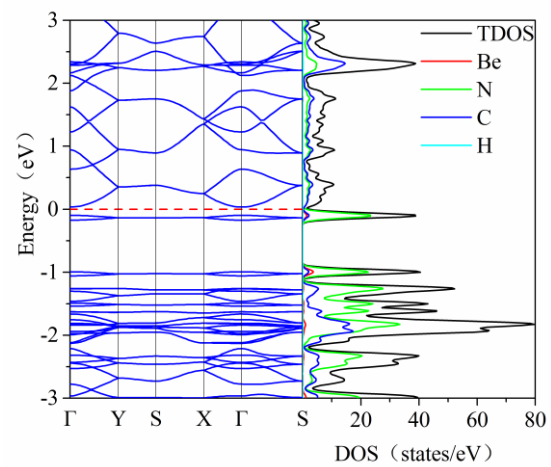
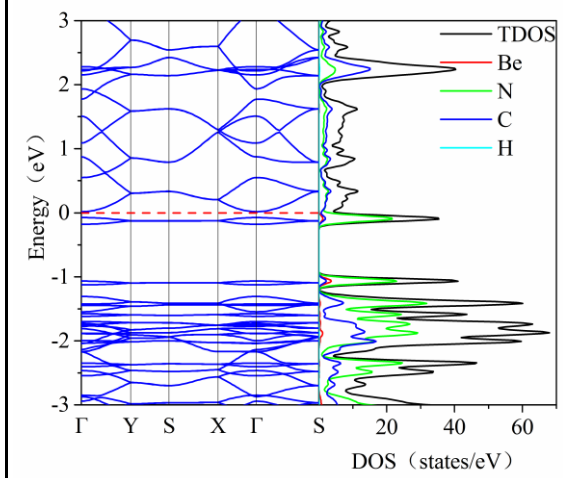
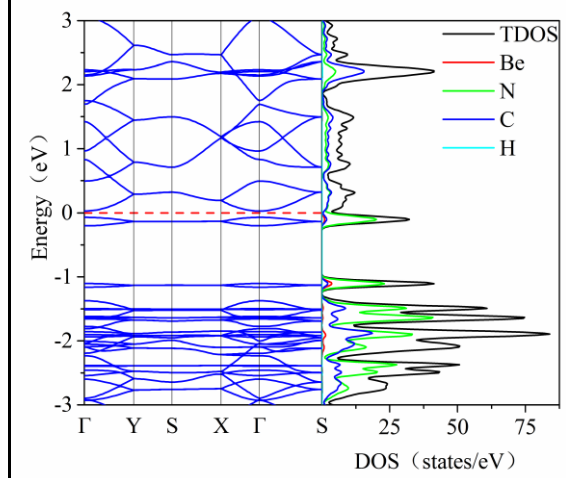
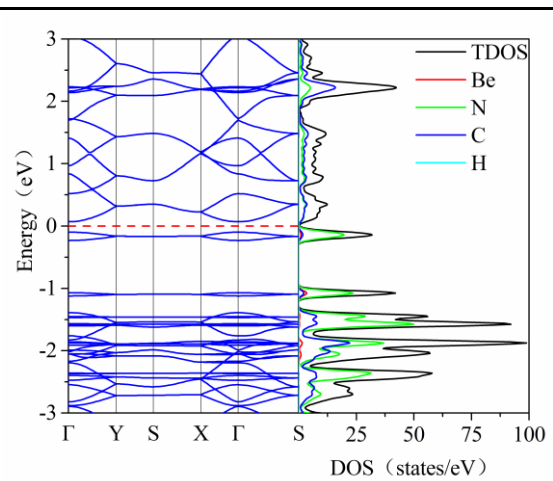
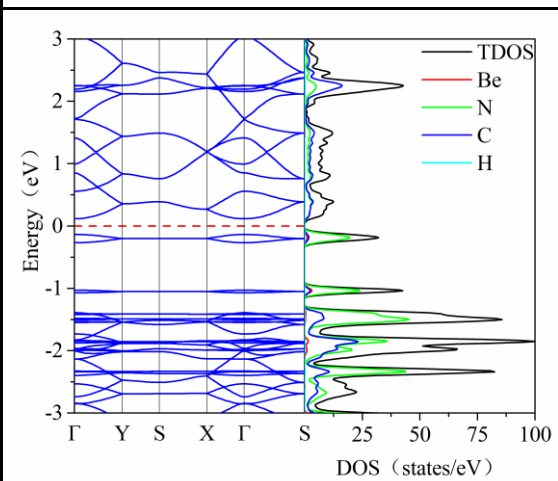
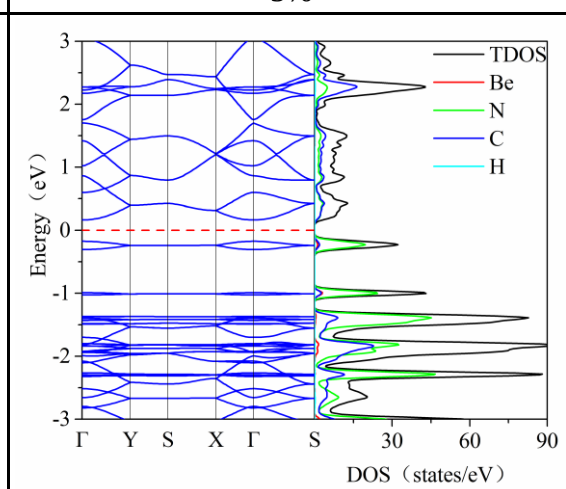
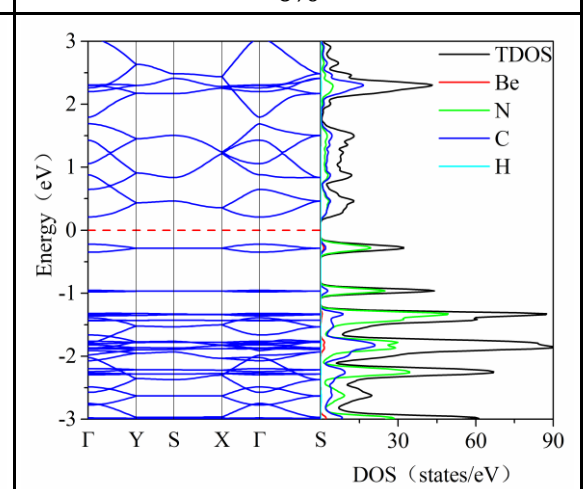
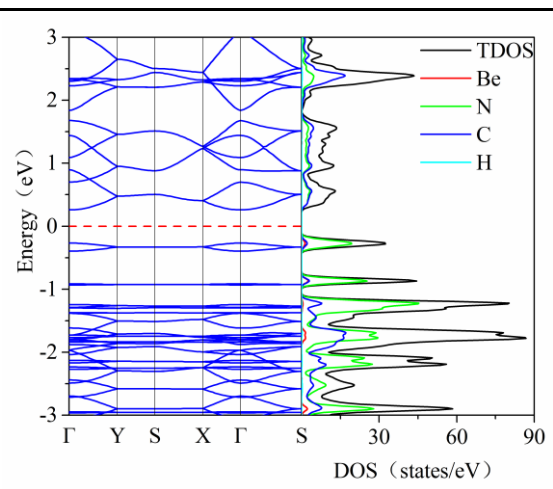
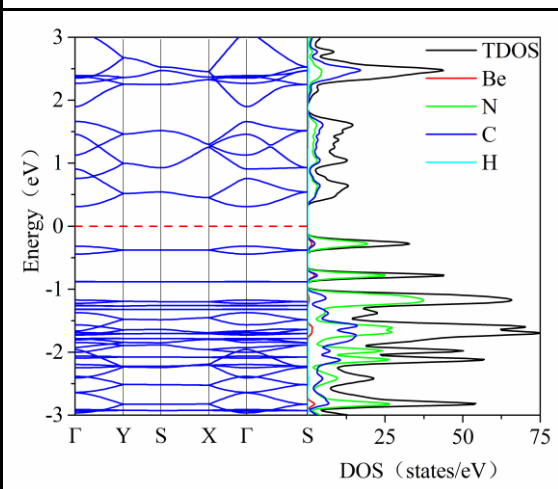
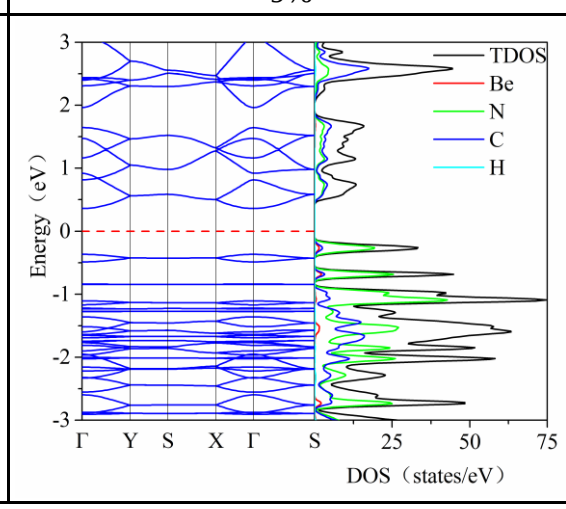
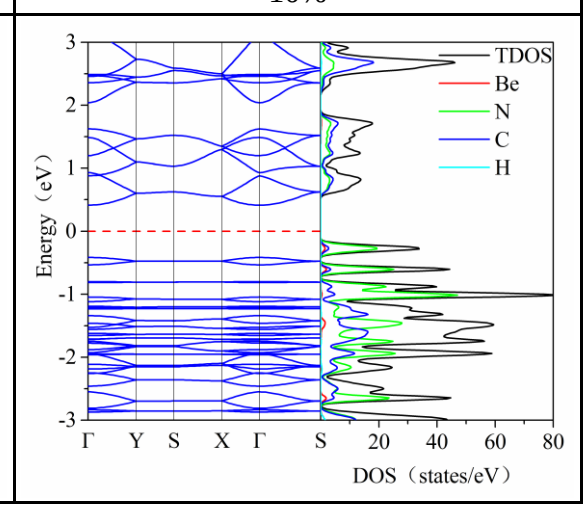
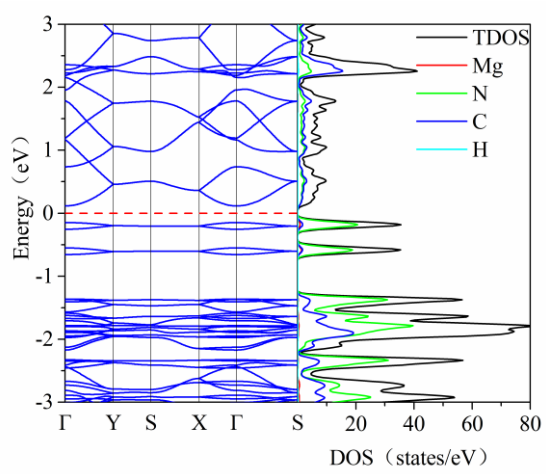
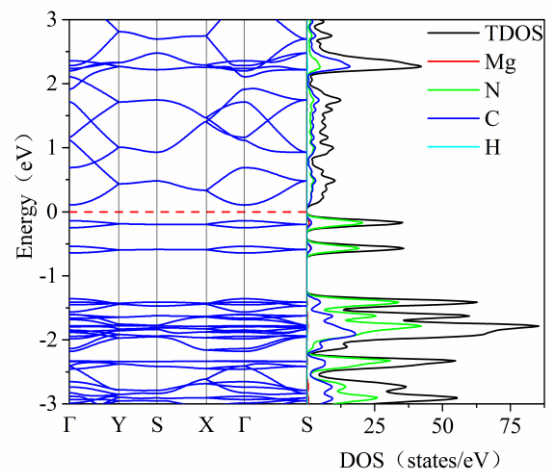
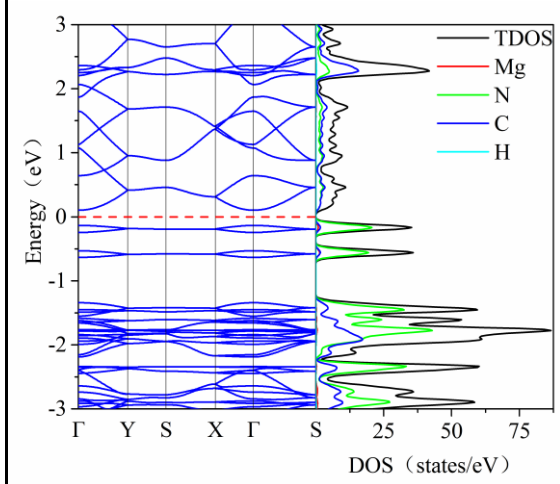
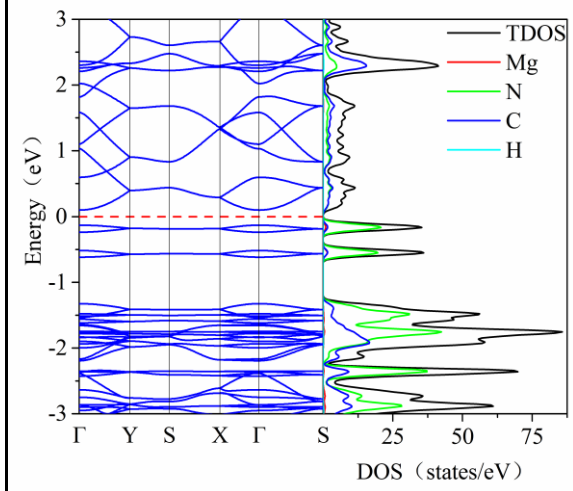
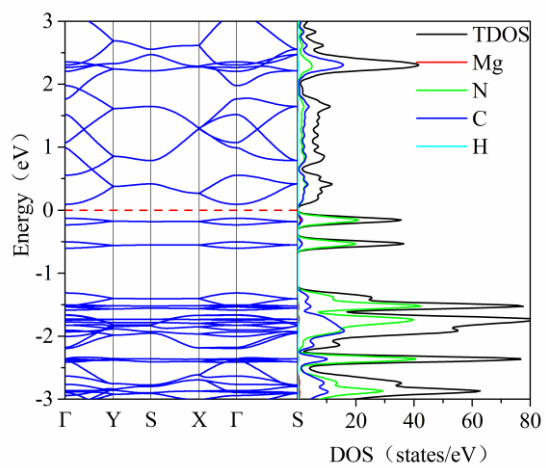
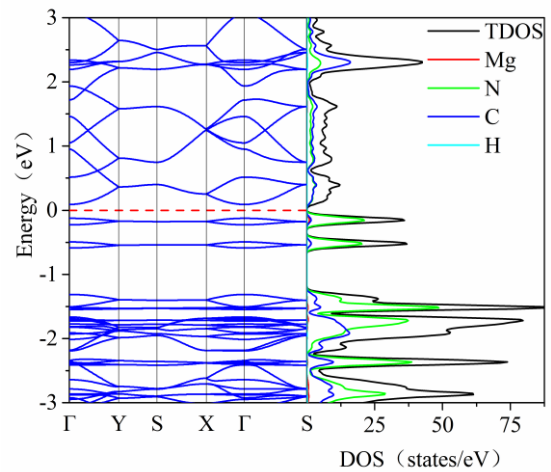
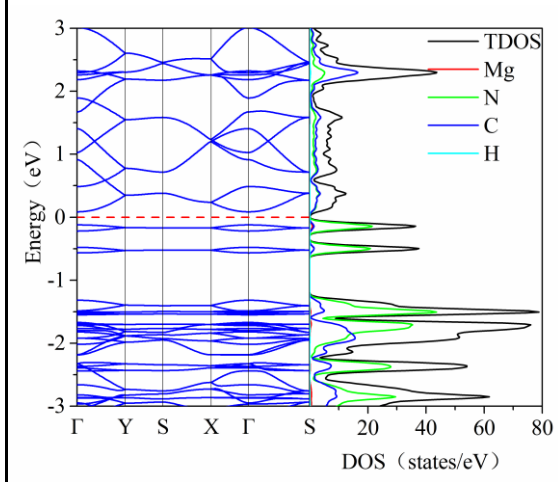
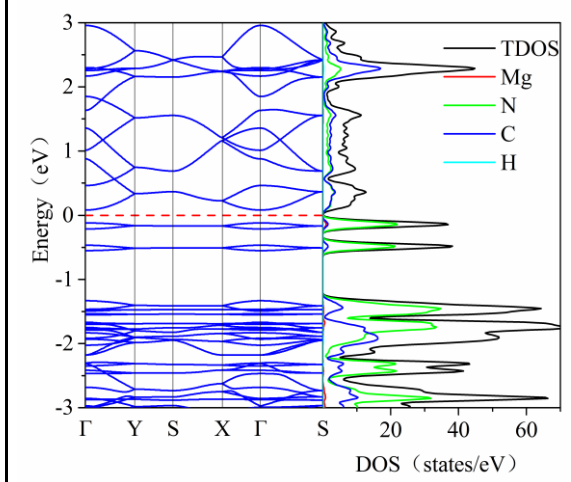
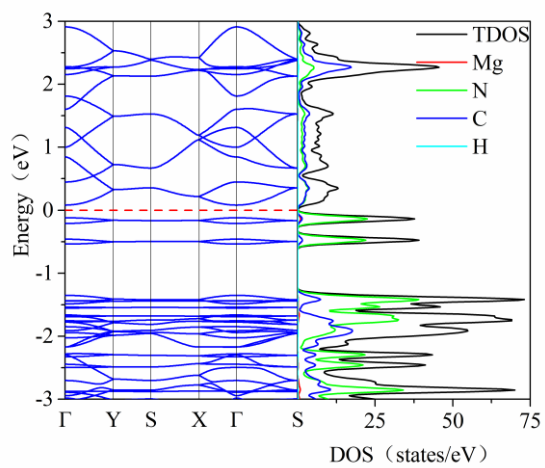
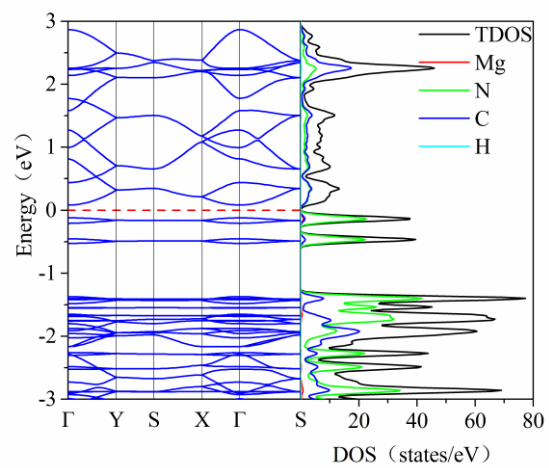
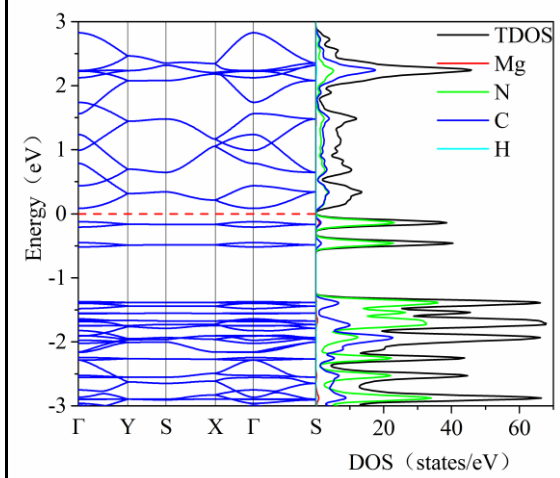
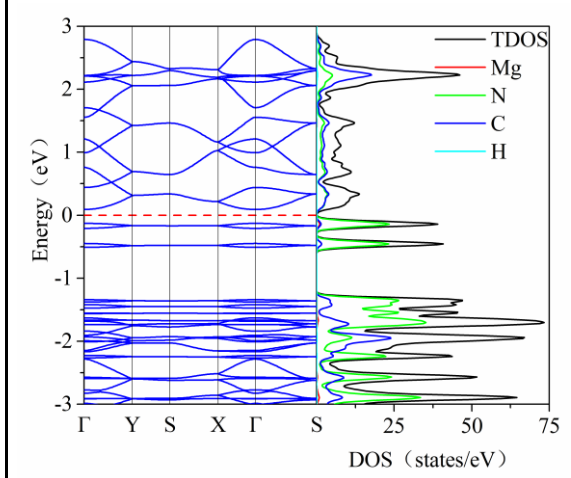
Strain	−5%	−4%	−3%	−2%
Be_2Pc				
Strain	−1%	0%	1%	2%
Be_2Pc				
Strain	3%	4%	5%	6%
Be_2Pc				
Strain	7%	8%	9%	10%
Be_2Pc				

Table S8. Calculated electronic band structures for Mg_2Pc monolayer under biaxial strain from −5% to 10%.

Strain	−5%	−4%	−3%	−2%
Mg_2Pc				

Strain	−1%	0%	1%	2%
Mg_2Pc				

Strain	3%	4%	5%	6%
Mg_2Pc				

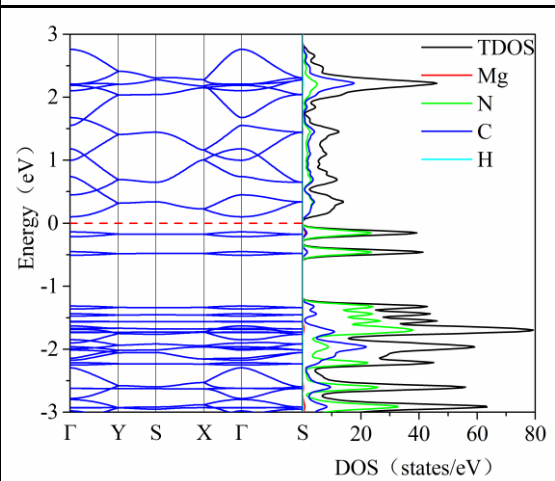
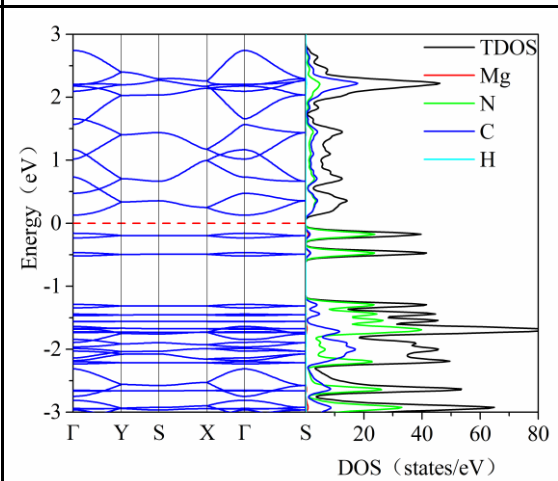
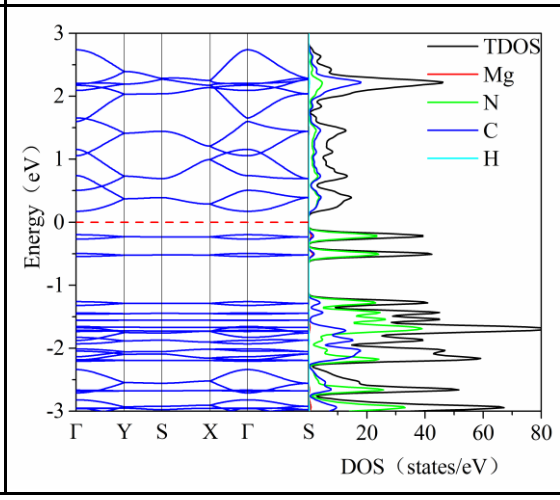
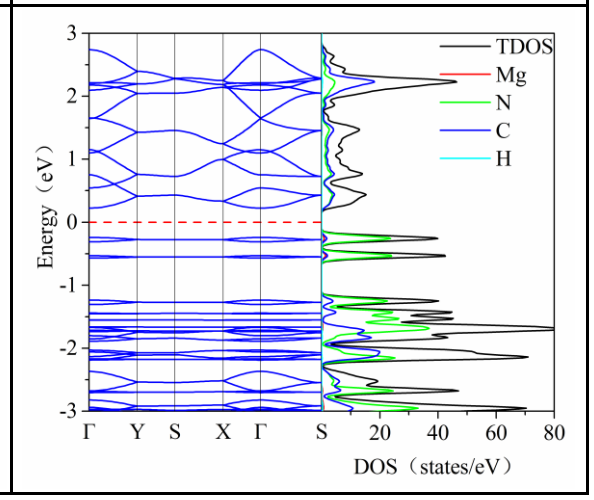
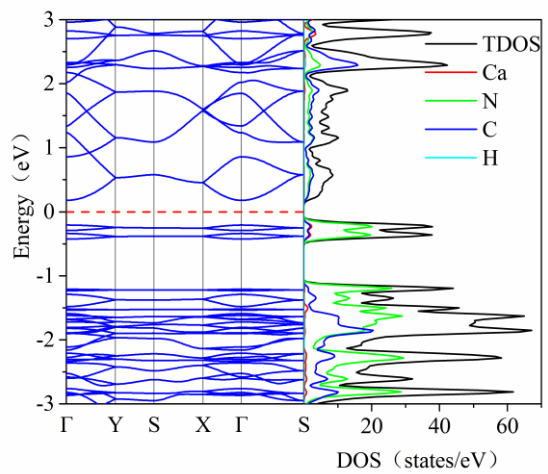
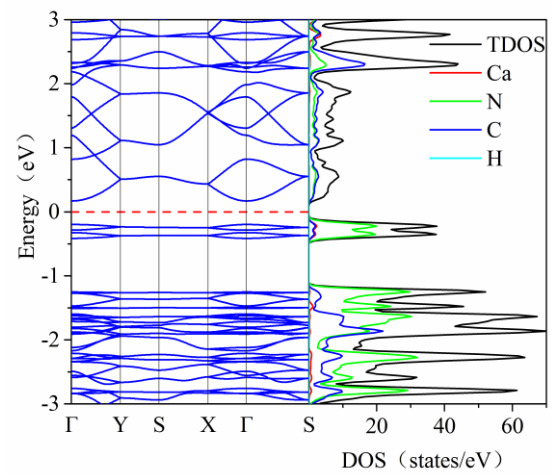
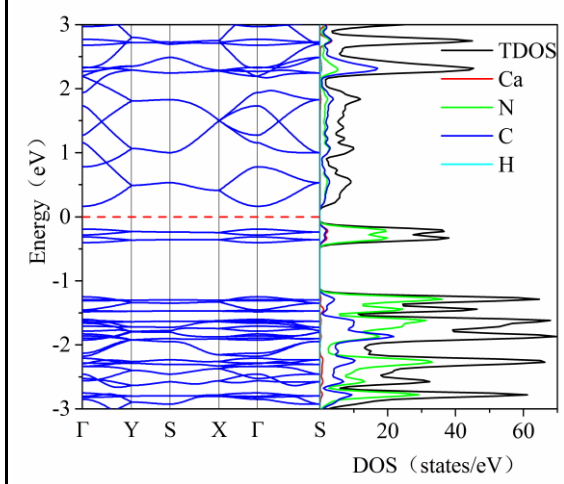
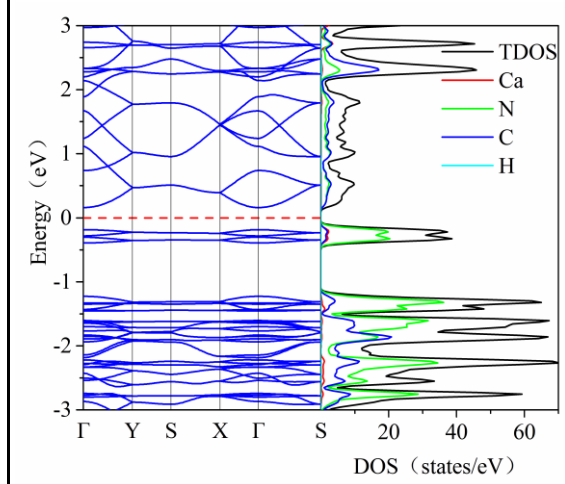
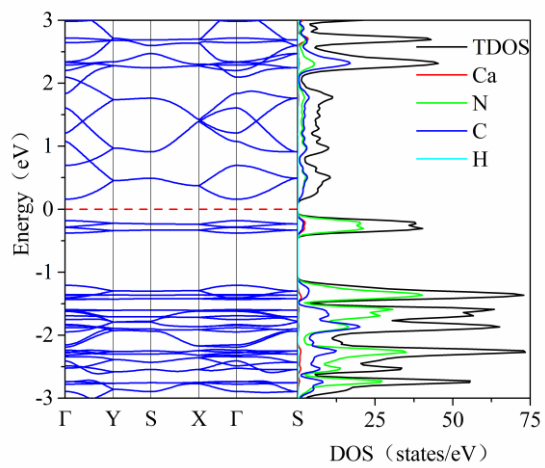
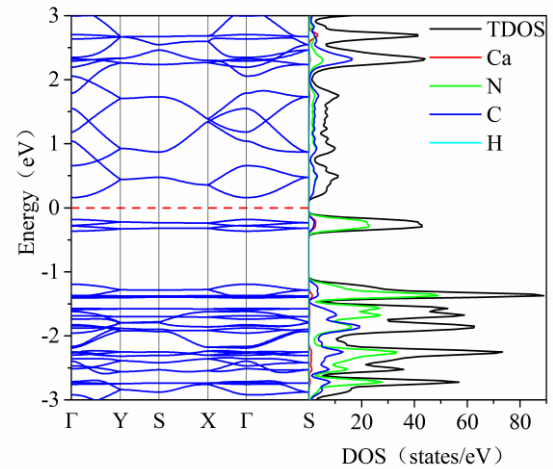
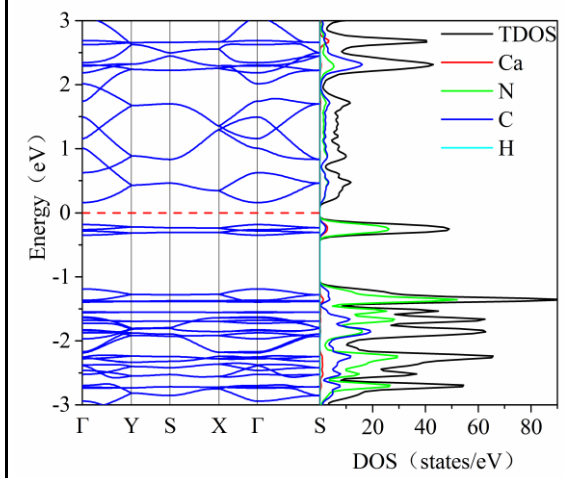
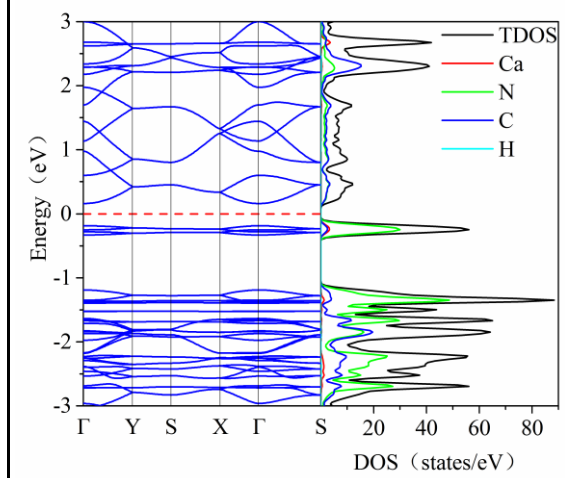
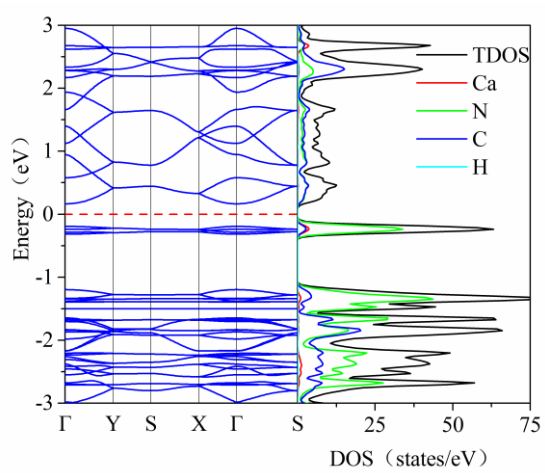
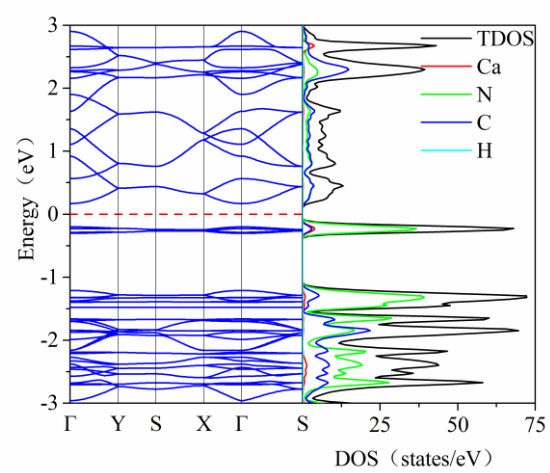
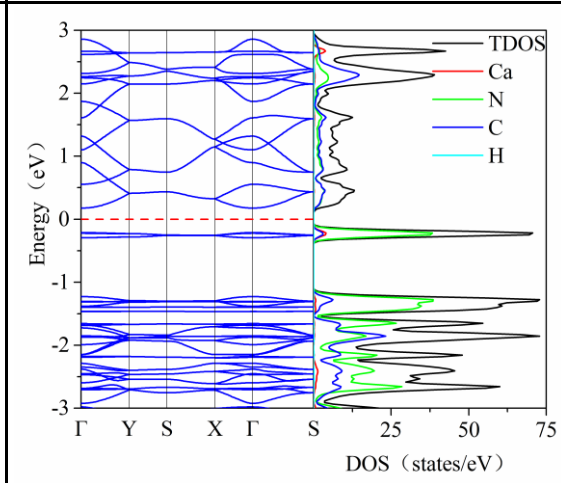
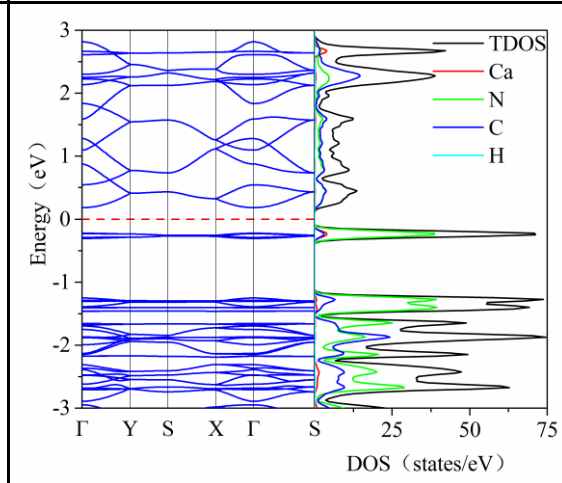
Strain	7%	8%	9%	10%
Mg_2Pc				

Table S9. Calculated electronic band structures for Ca_2Pc monolayer under biaxial strain from −5% to 10%.

Strain	−5%	−4%	−3%	−2%
Ca_2Pc				

Strain	−1%	0%	1%	2%
Ca_2Pc				

Strain	3%	4%	5%	6%
Ca_2Pc				

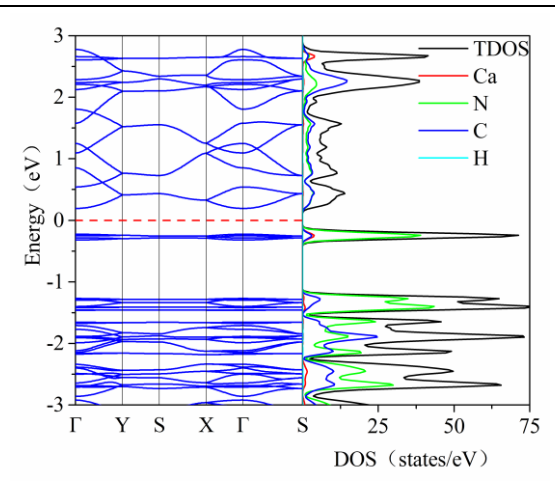
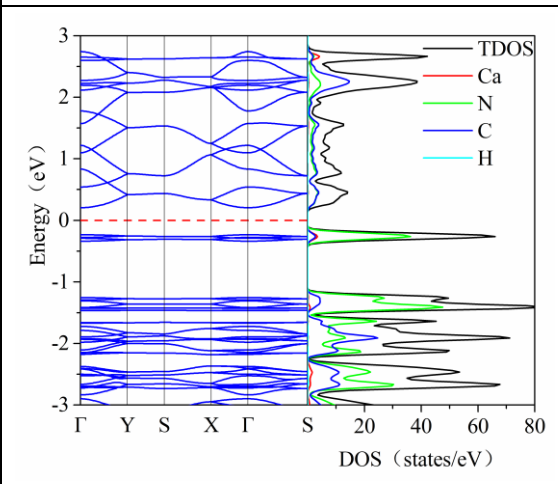
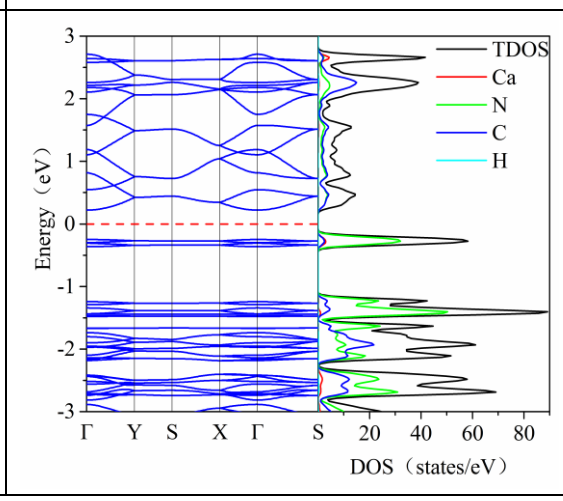
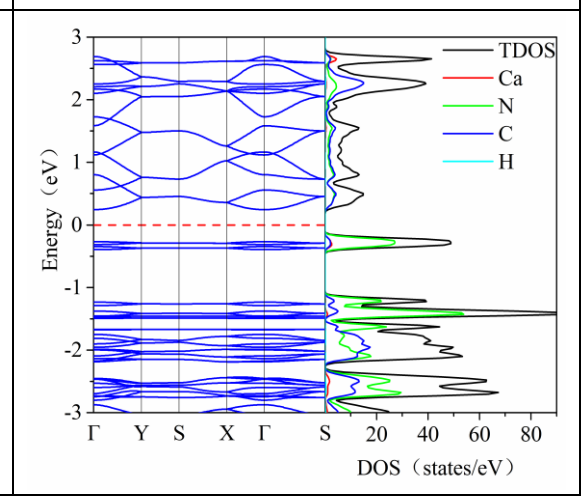
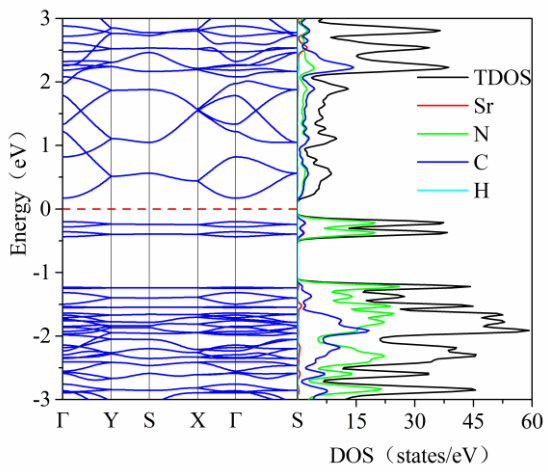
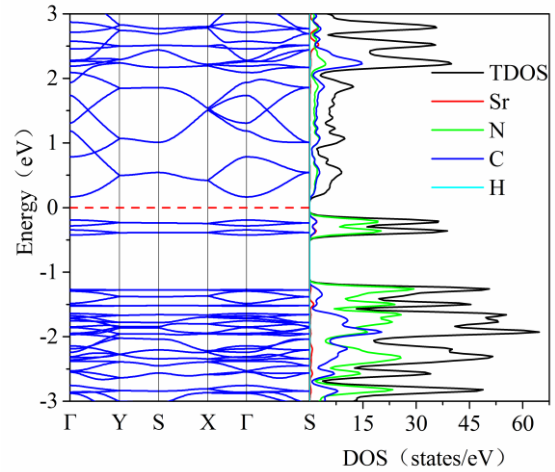
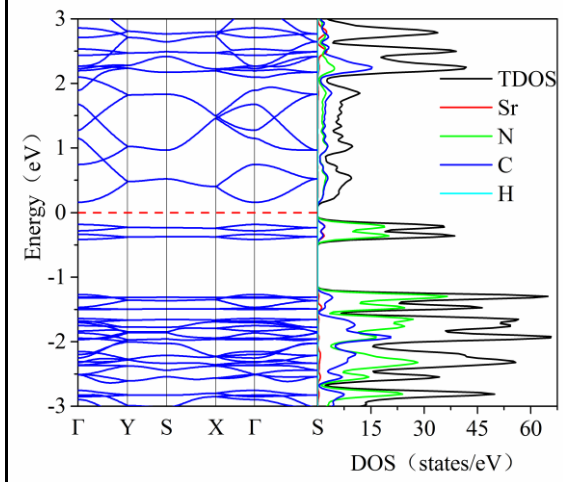
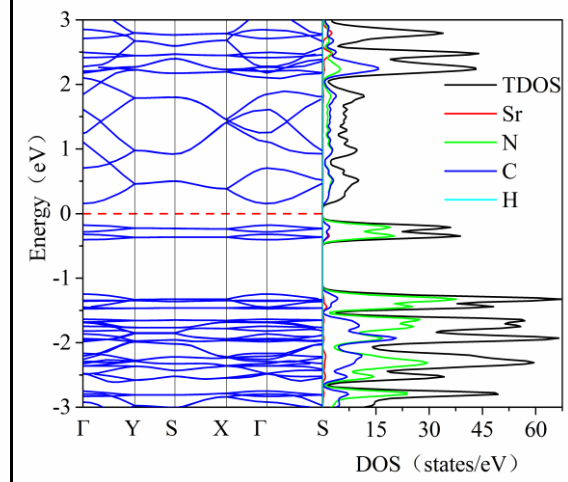
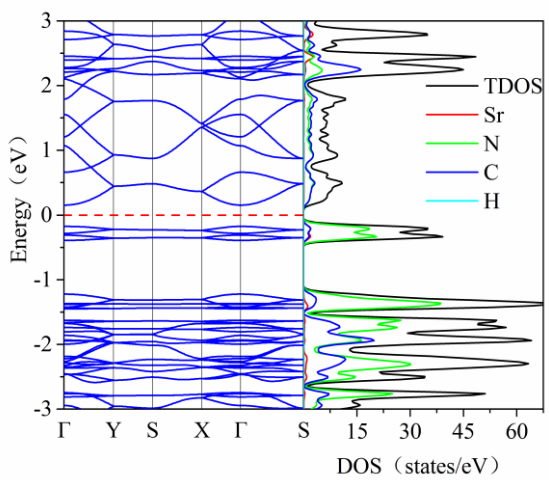
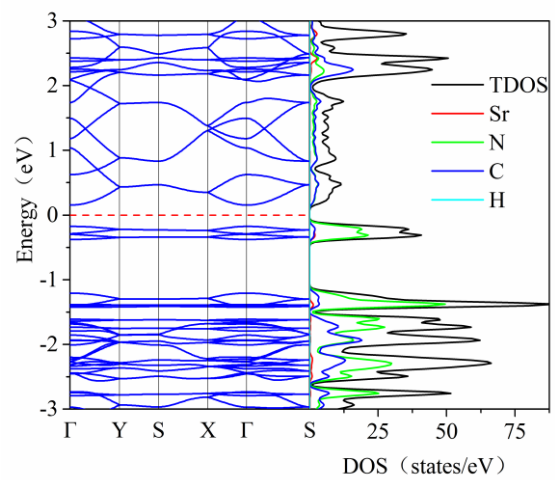
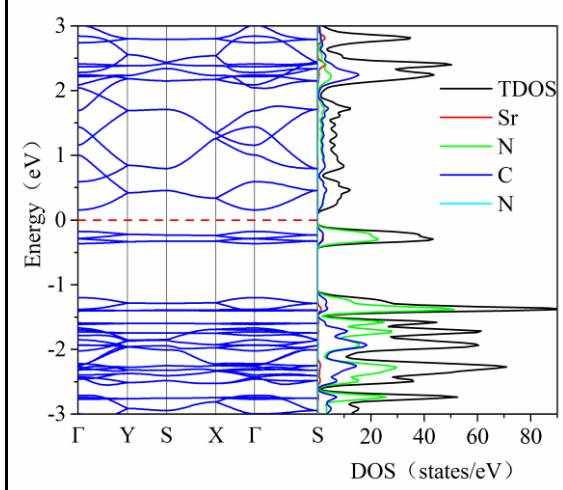
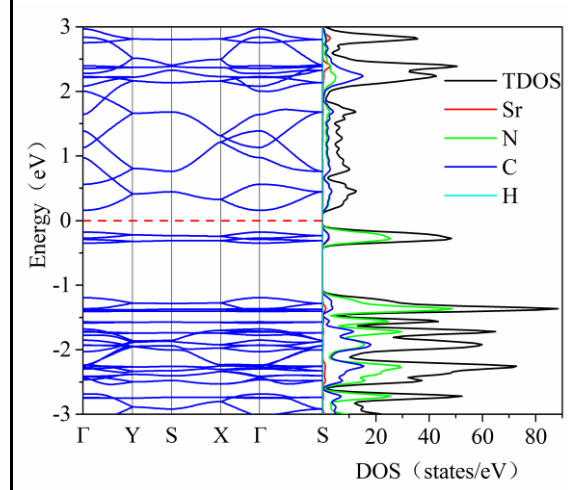
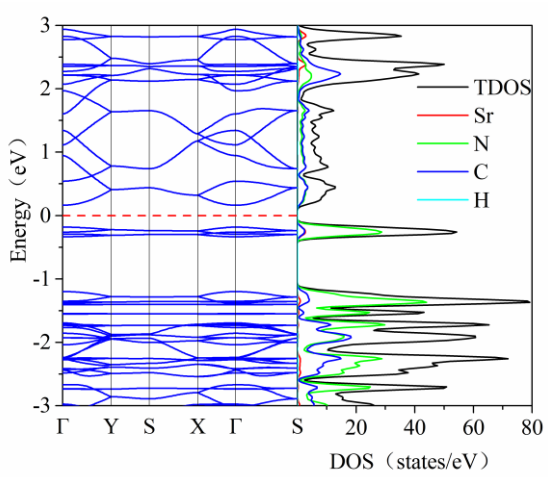
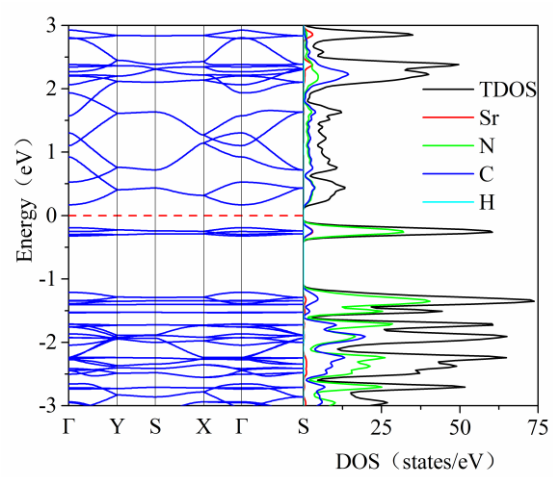
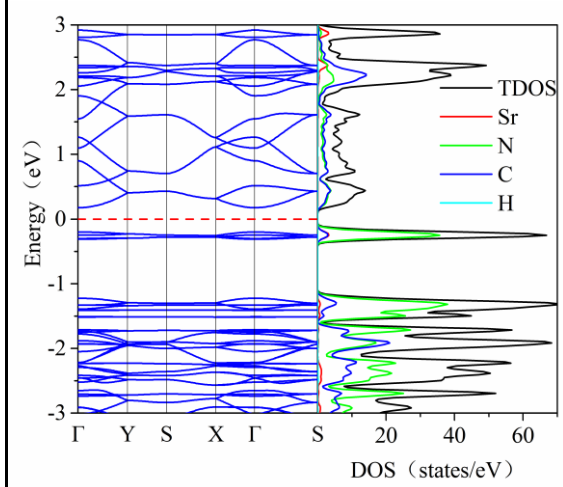
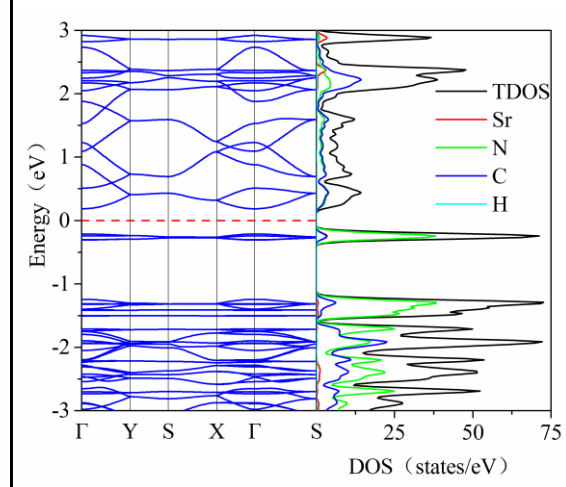
Strain	7%	8%	9%	10%
Ca_2Pc				

Table S10. Calculated electronic band structures for Sr_2Pc monolayer under biaxial strain from −5% to 10%.

Strain	−5%	−4%	−3%	−2%
Sr_2Pc				

Strain	−1%	0%	1%	2%
Sr_2Pc				

Strain	3%	4%	5%	6%
Sr_2Pc				

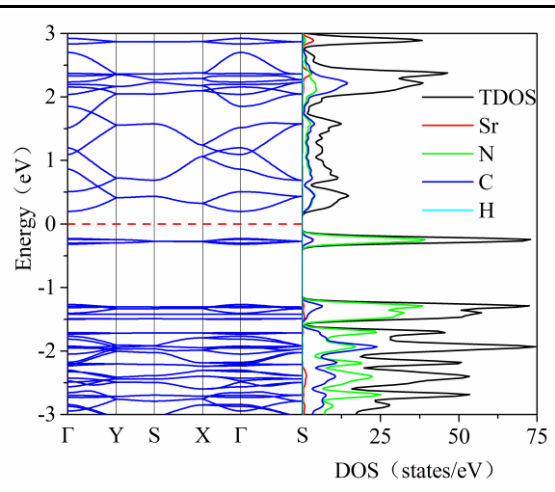
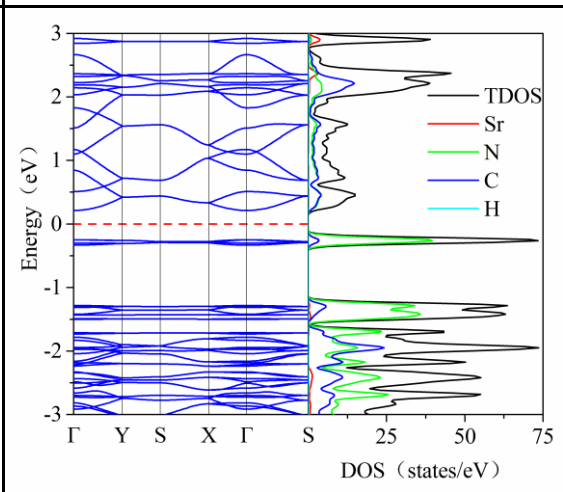
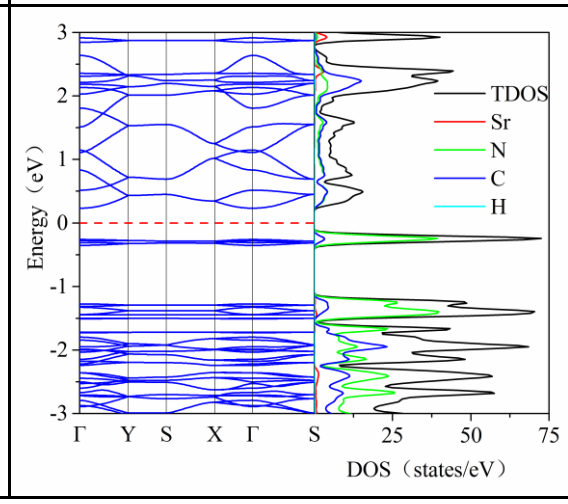
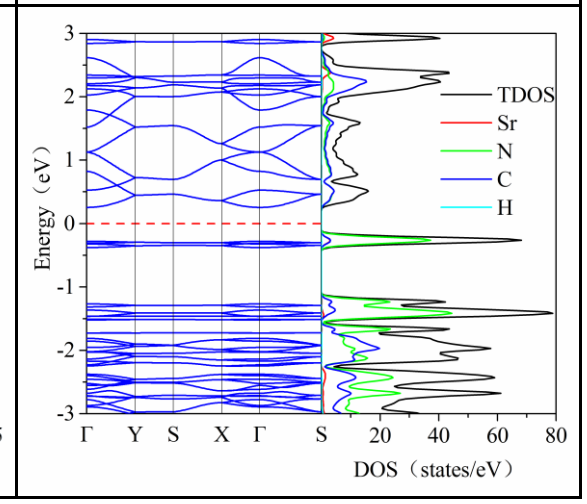
Strain	7%	8%	9%	10%
Sr_2Pc				

Table S11. Calculated electronic band structures for Ba_2Pc monolayer under biaxial strain from −5% to 10%.

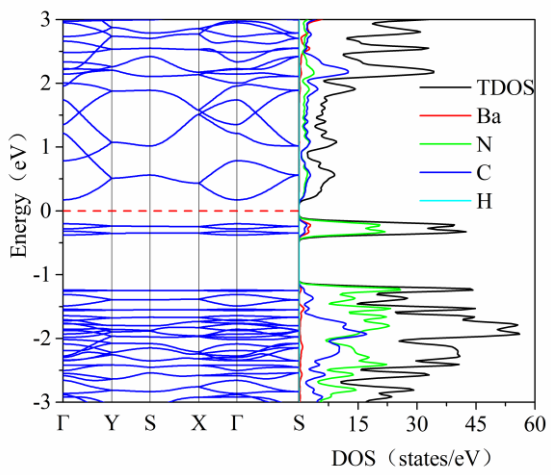
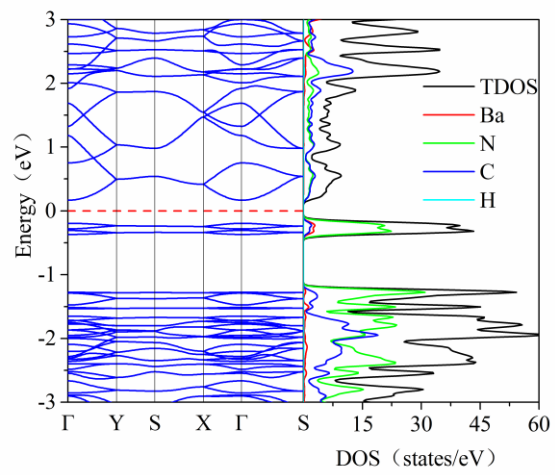
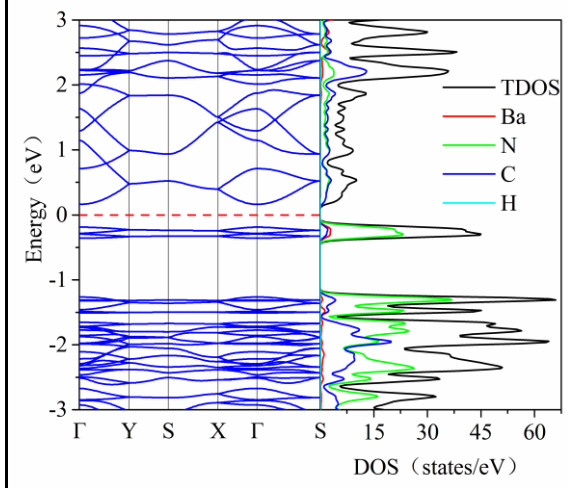
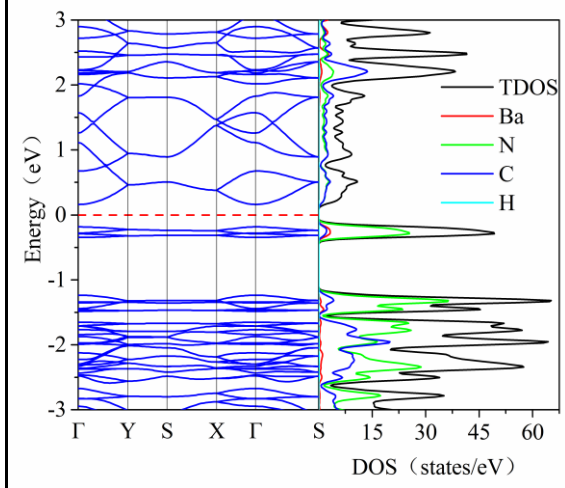
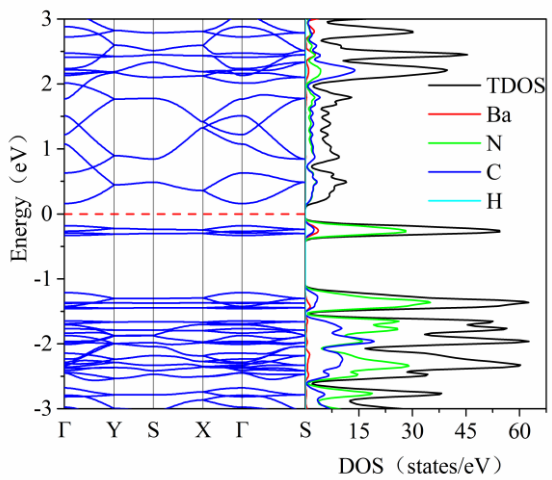
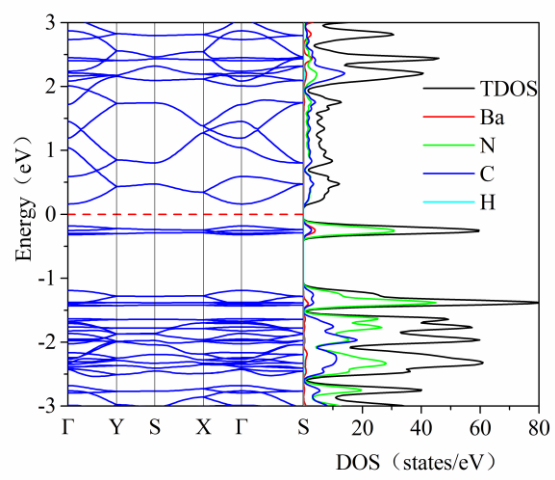
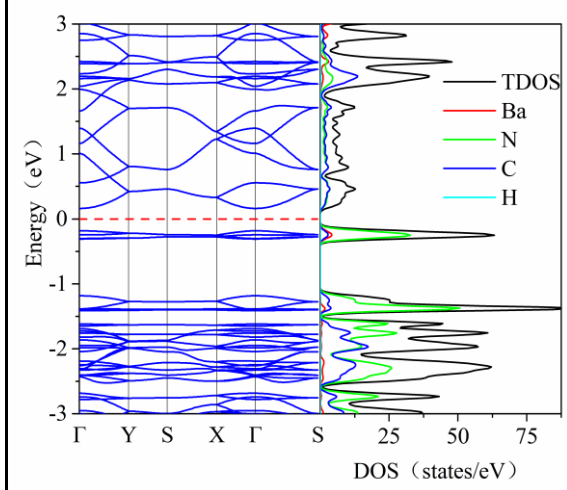
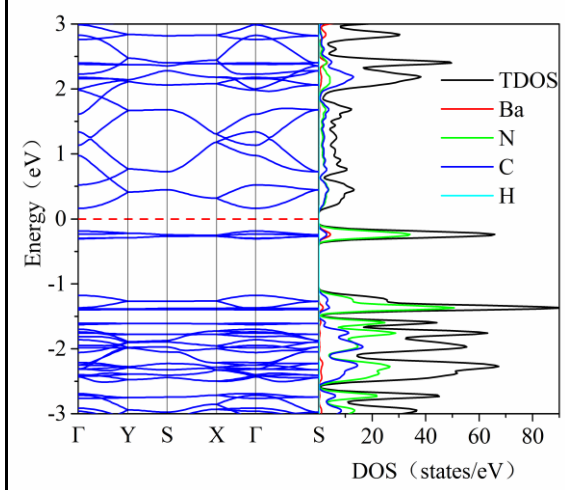
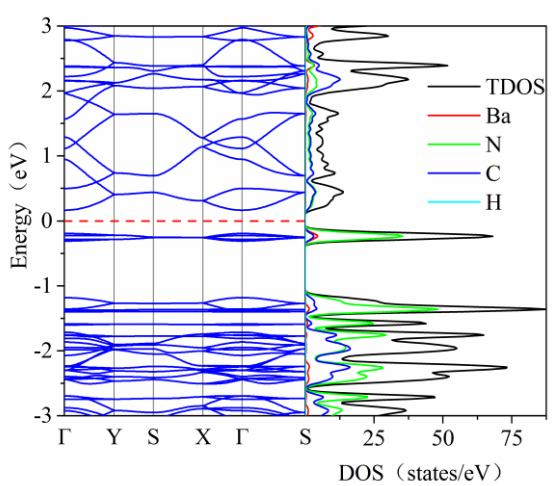
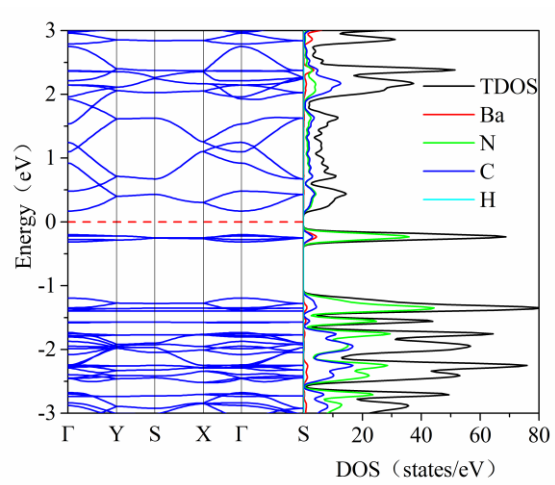
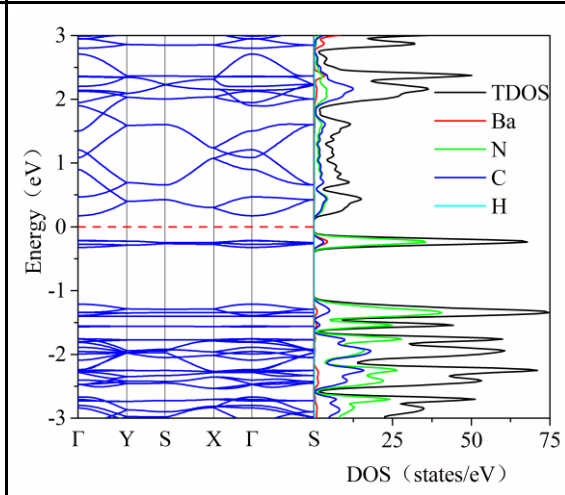
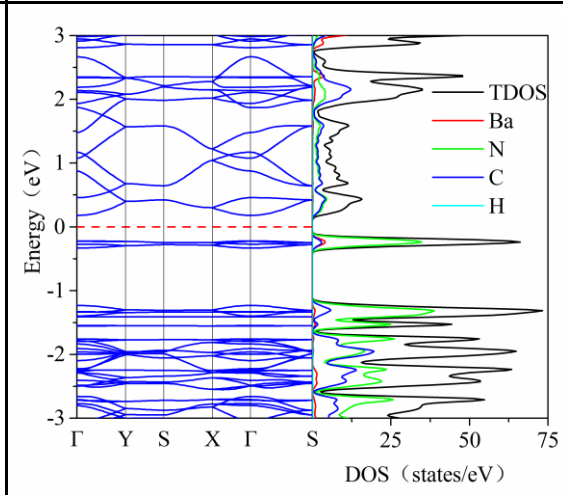
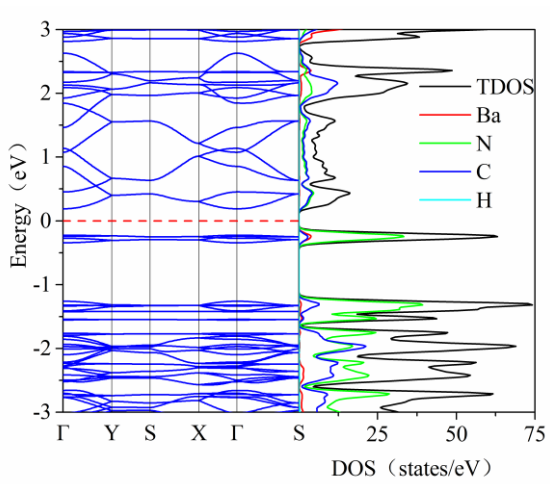
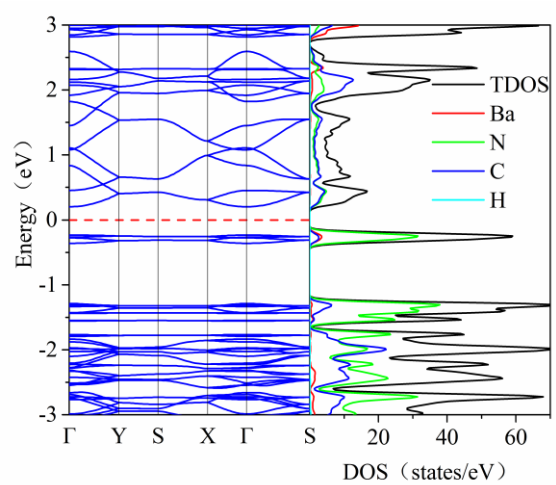
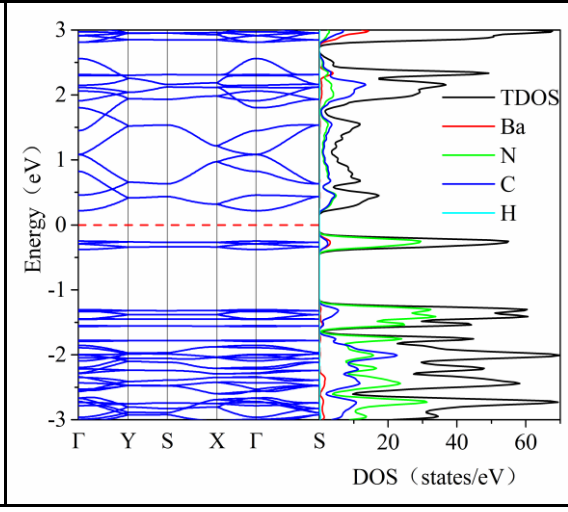
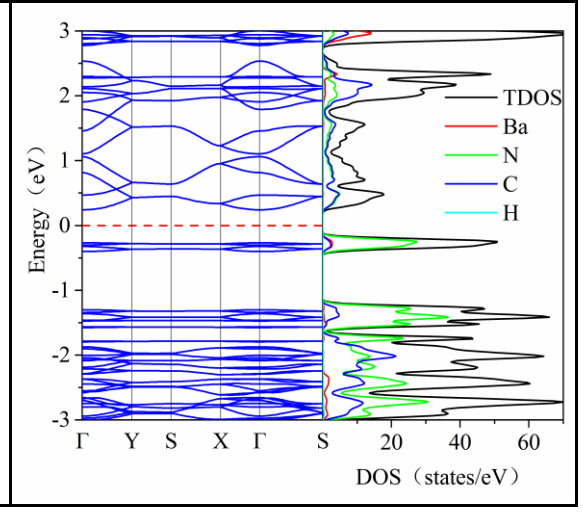
Strain	−5%	−4%	−3%	−2%
Ba_2Pc				
Strain	−1%	0%	1%	2%
Ba_2Pc				
Strain	3%	4%	5%	6%
Ba_2Pc				
Strain	7%	8%	9%	10%
Ba_2Pc				

Table S12. Computed effective mass (m^*, m_0), deformation potential constant (E_1, eV), 2D elastic modulus (C_{2D}, N/m), and carrier mobility (μ, $cm^2\ V^{-1}\ s^{-1}$) of electrons and holes along x and y directions for the M_2Pc sheets at 300 K.

Structure	carrier type	m^*_x	m^*_y	E_{1x}	E_{1y}	$C_{2D\text{-}x}$	$C_{2D\text{-}y}$	μ_x	μ_y
Be_2Pc	electron	0.49	0.45	0.52	0.58	64.92	61.24	19782.18	20597.23
	hole	4.02	2.59	4.59	1.20	64.92	61.24	8.95	23.61
Mg_2Pc	electron	0.57	0.57	1.98	1.63	54.59	56.55	1174.43	1079.76
	hole	3.17	1.65	1.41	1.59	54.59	56.55	70.27	144.36
Ca_2Pc	electron	0.55	0.44	3.54	1.61	49.45	47.65	682.49	579.20
	hole	3.69	1.37	1.70	1.97	49.45	47.65	35.95	103.12
Sr_2Pc	electron	0.56	0.45	1.91	1.55	47.19	44.94	1227.48	1369.72
	hole	3.17	1.21	1.64	1.89	47.19	44.94	49.51	137.94
Ba_2Pc	electron	0.57	0.48	1.91	1.56	45.58	43.04	1110.55	1193.05
	hole	3.46	1.20	1.55	2.07	45.58	43.04	38.15	125.31

Table S13. Calculated band gap of the donor (E_g), conduction band offset (ΔE_c), open circuit voltage (V_{oc}), the ratio of short circuit current density to AM1.5 solar energy flux (J_{sc}/P_{solar}), and PCE of heterostructures.

Heterostructure (donor/acceptor)	E_g (eV)	ΔE_c (eV)	V_{oc} (eV)	J_{sc}/P_{solar}	η
Be_2Pc/2H−$MoSe_2$	1.21	0.05	0.86	0.422	23.61%
Mg_2Pc/2H−$MoTe_2$	1.35	0.24	0.81	0.388	20.44%
Ca_2Pc/2H−WTe_2	1.39	0.36	0.73	0.378	17.91%
Sr_2Pc/GaN	1.35	0.14	0.91	0.389	22.88%
Ba_2Pc/GaN	1.34	0.31	0.73	0.390	18.42%

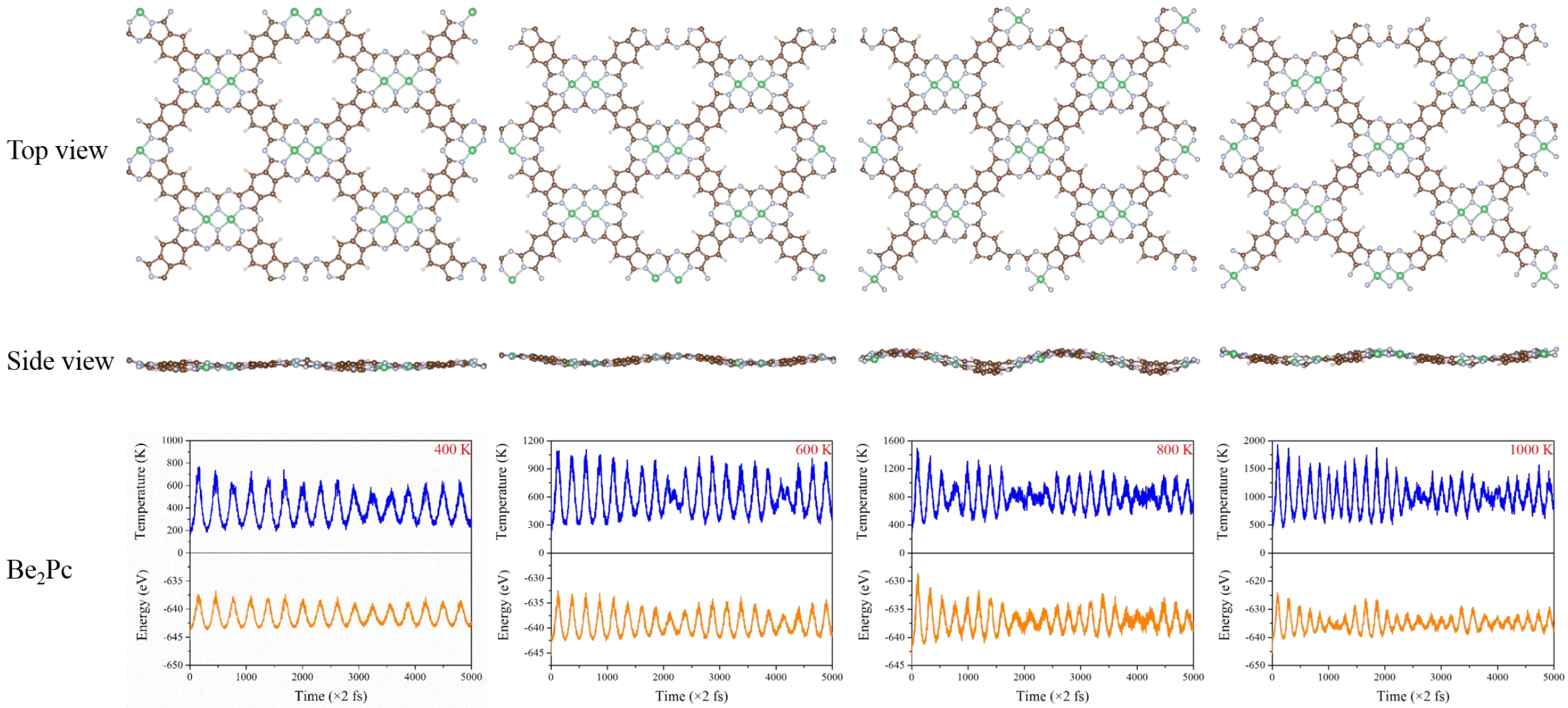


Figure S1. AIMD simulations results (include the final snapshot, the evolution of total energy and temperature versus the simulation time) for the Be_2Pc monolayers at 400, 600, 800 and 1000 K, respectively.

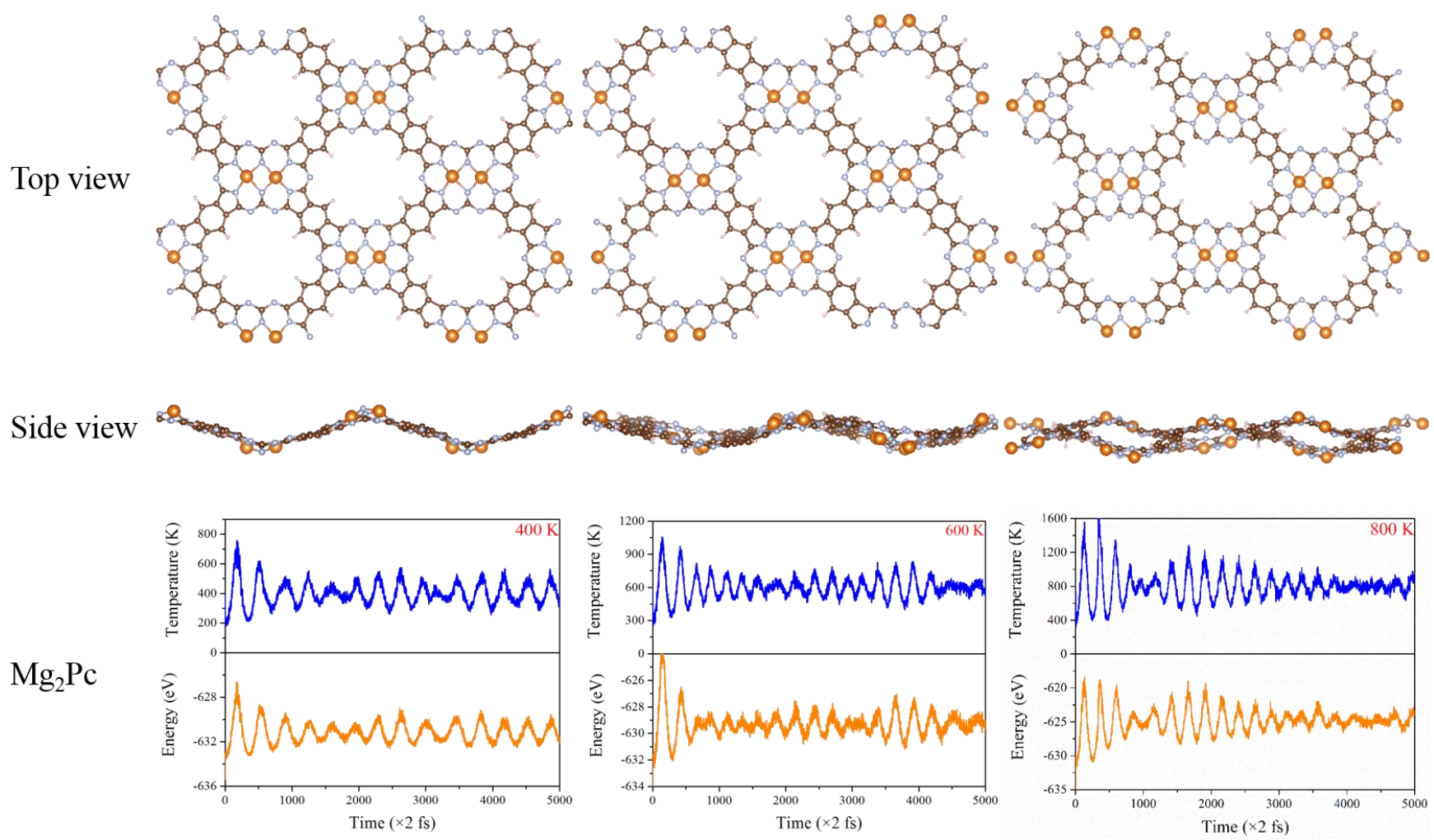


Figure S2. AIMD simulations results (include the final snapshot, the evolution of total energy and temperature versus the simulation time) for the Mg_2Pc monolayers at 400, 600 and 800 K, respectively.

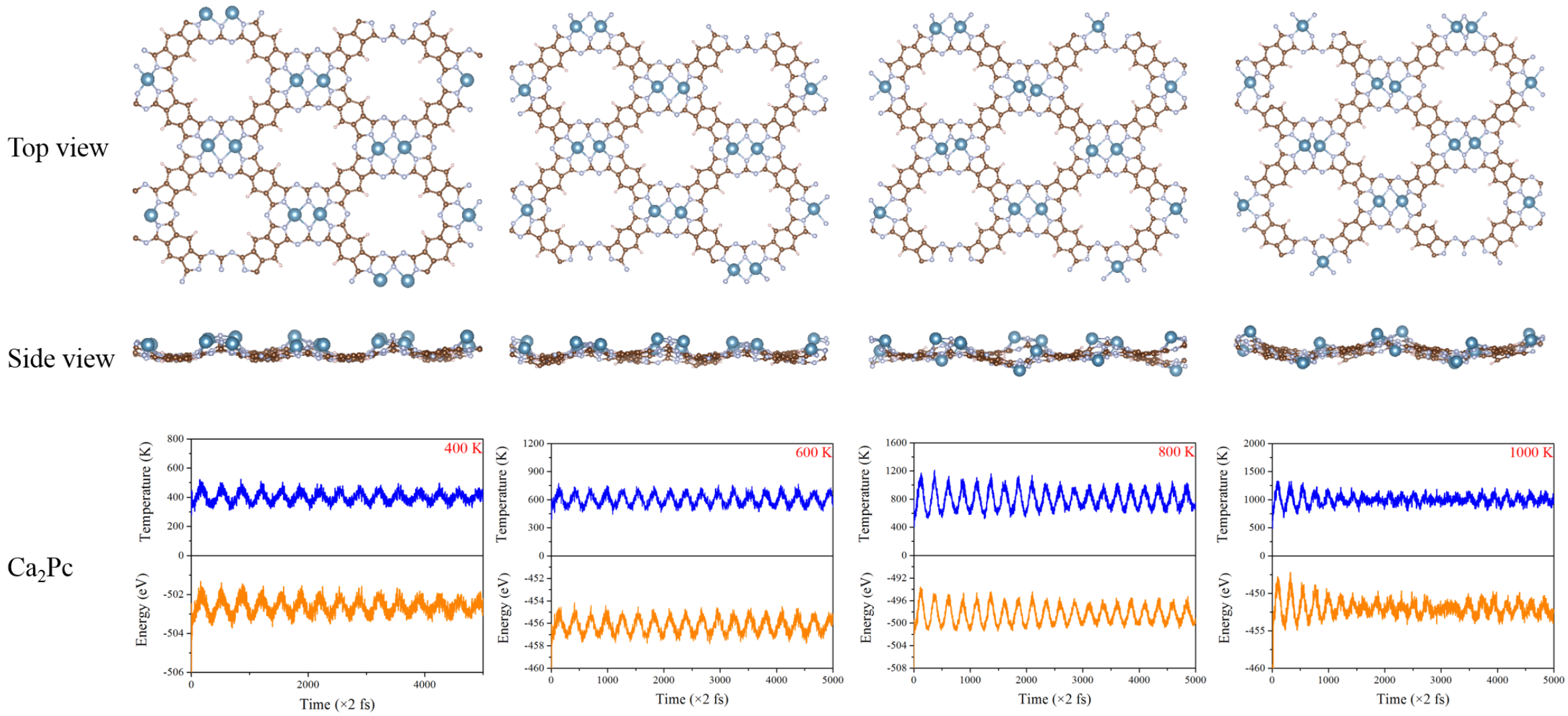


Figure S3. AIMD simulations results (include the final snapshot, the evolution of total energy and temperature versus the simulation time) for the Ca_2Pc monolayers at 400, 600 800 and 1000 K, respectively.

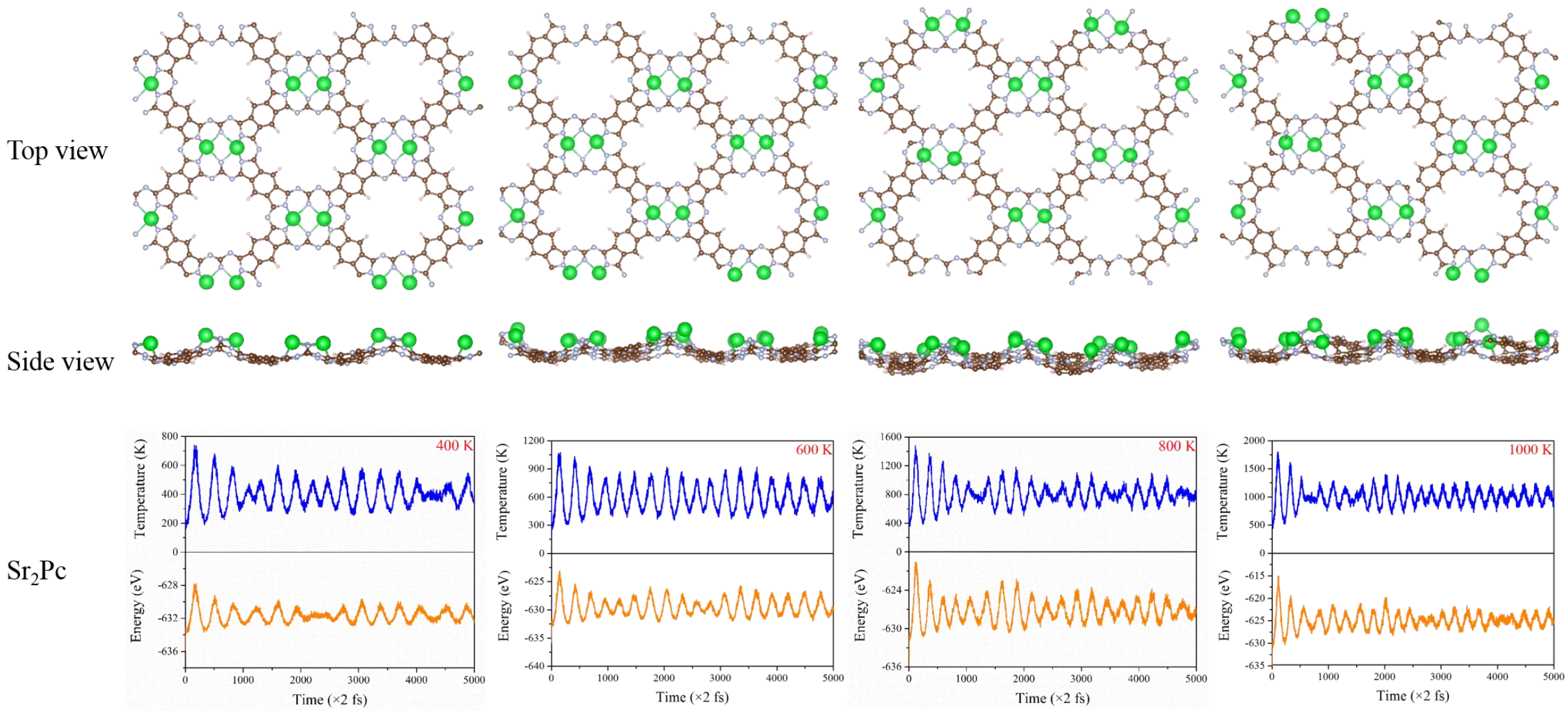


Figure S4. AIMD simulations results (include the final snapshot, the evolution of total energy and temperature versus the simulation time) for the Sr_2Pc monolayers at 400, 600 800 and 1000 K, respectively.

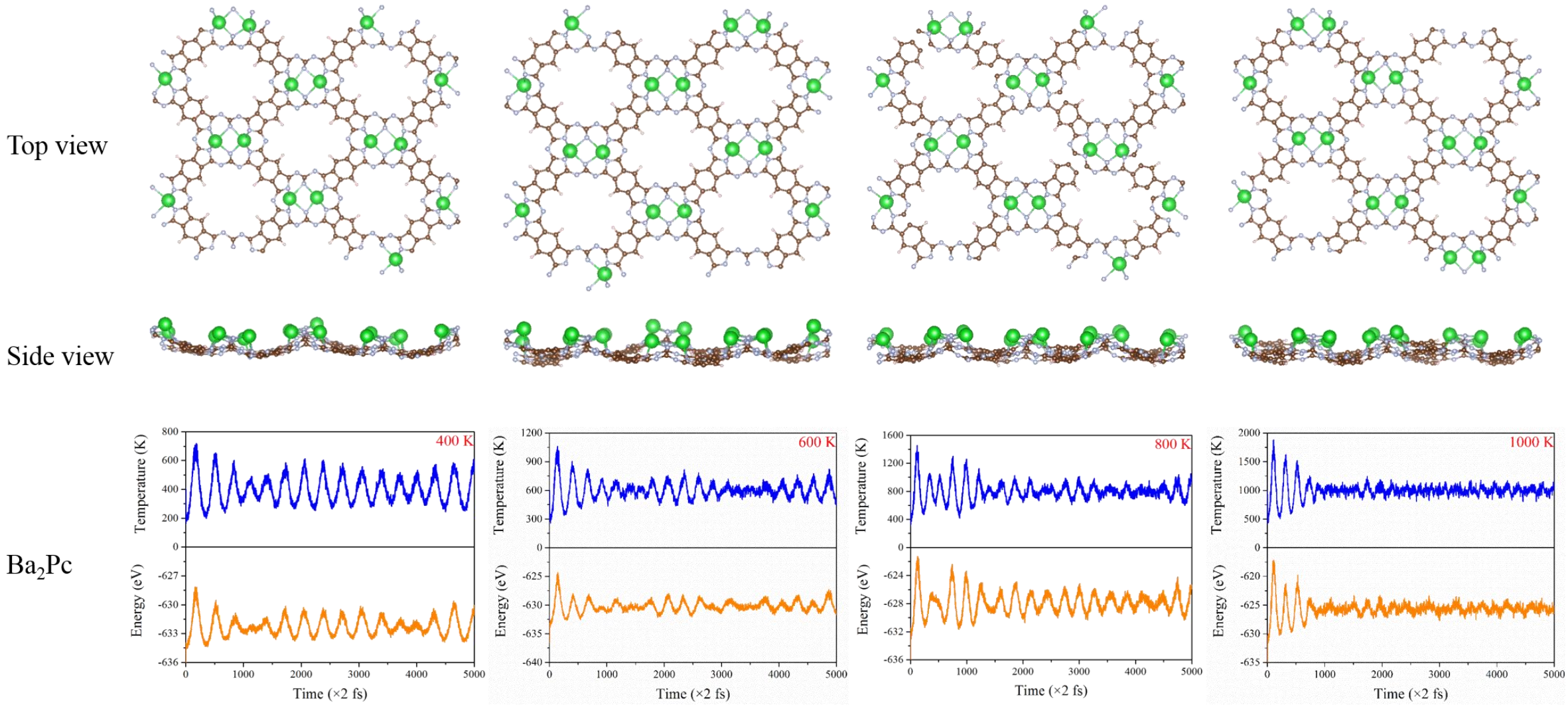


Figure S5. AIMD simulations results (include the final snapshot, the evolution of total energy and temperature versus the simulation time) for the Ba_2Pc monolayers at 400, 600 800 and 1000 K, respectively.

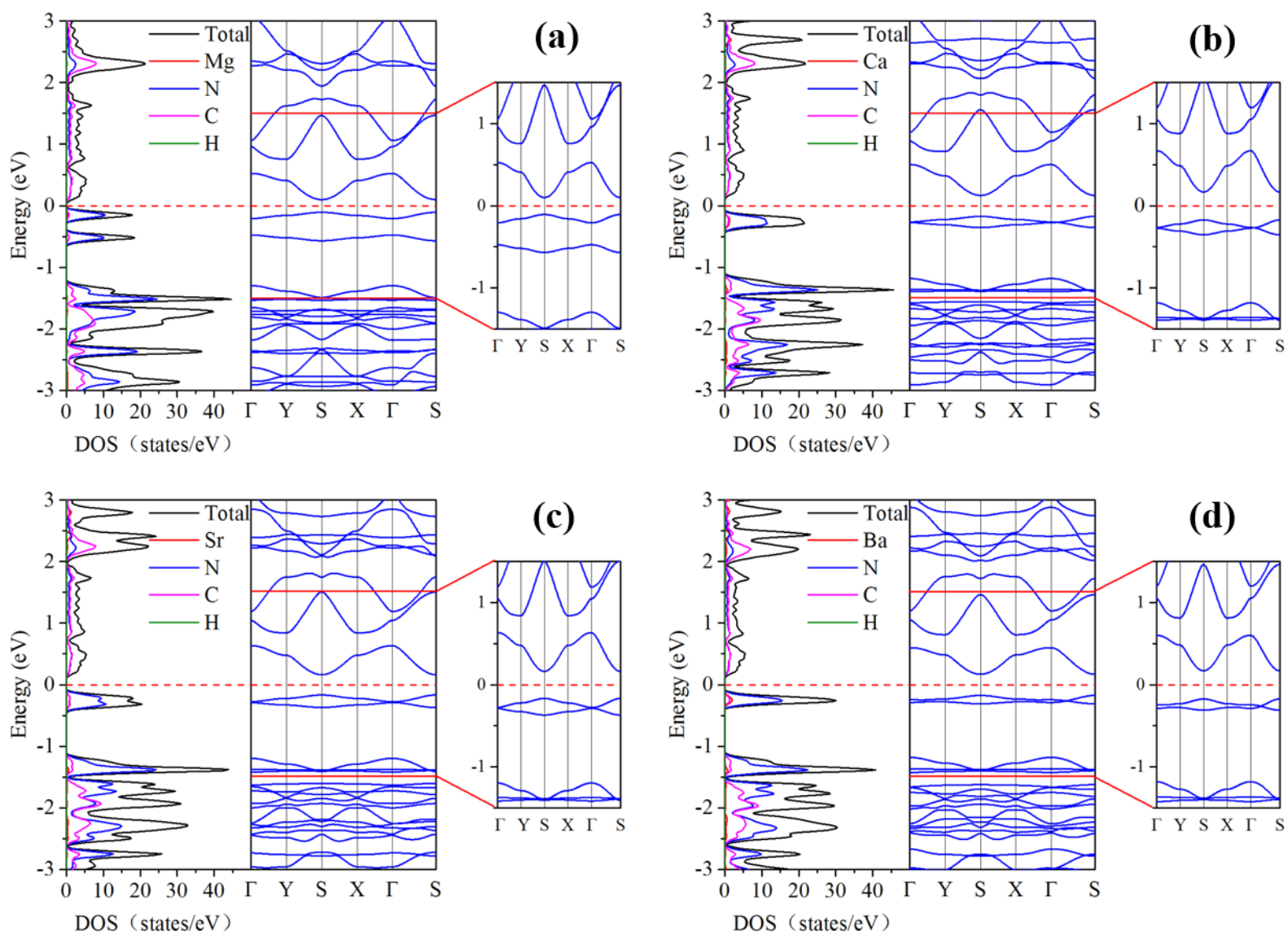


Figure S6. Calculated electronic band structures and corresponding total density of states (DOS) based for (a) Mg_2Pc, (b) Ca_2Pc, (c) Sr_2Pc and (d) Ba_2Pc monolayers at the PBE level. The Fermi level (E_F) is set to zero and marked with the dotted line.

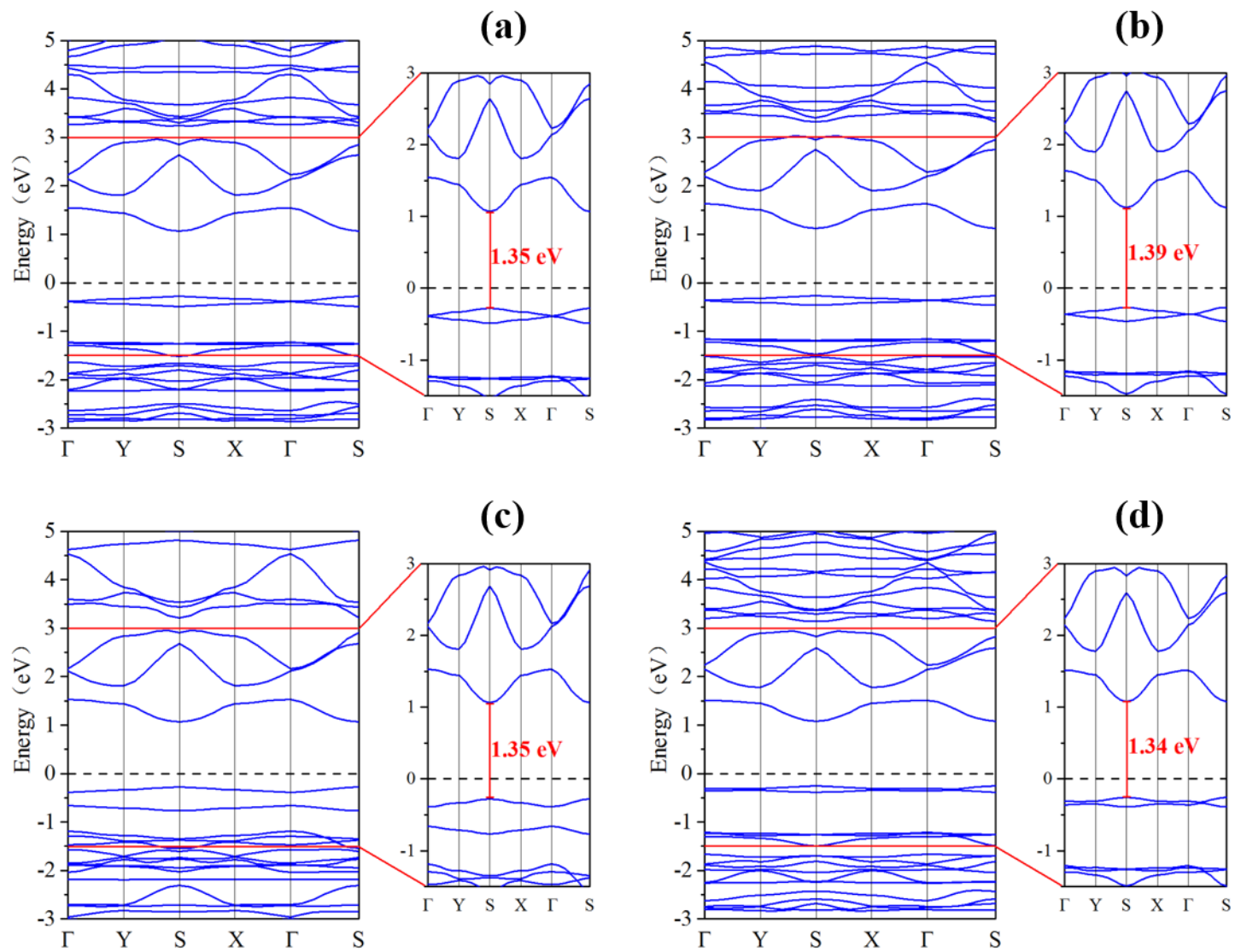


Figure S7. Calculated band structures of (a) Mg_2Pc, (b) Ca_2Pc, (c) Sr_2Pc and (d) Ba_2Pc monolayers at the HSE06 level. The Fermi level is set at 0 eV.

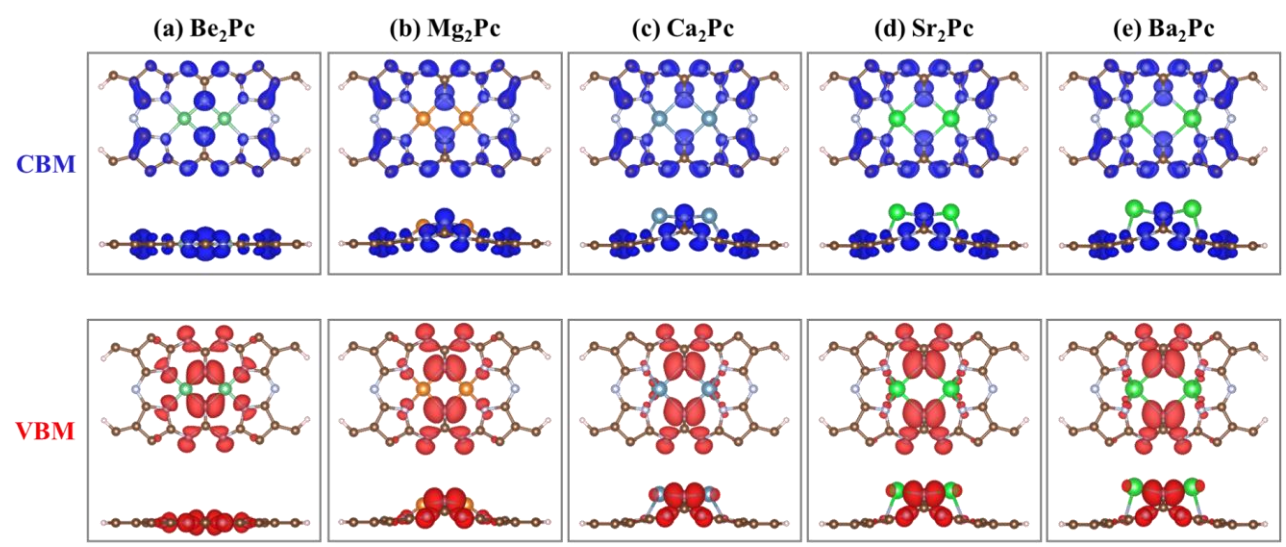


Figure S8. The partial charge density distribution of the CBM (blue) and VBM (red) for the M_2Pc monolayers. The isosurface value is 0.003 e/Bohr^3.

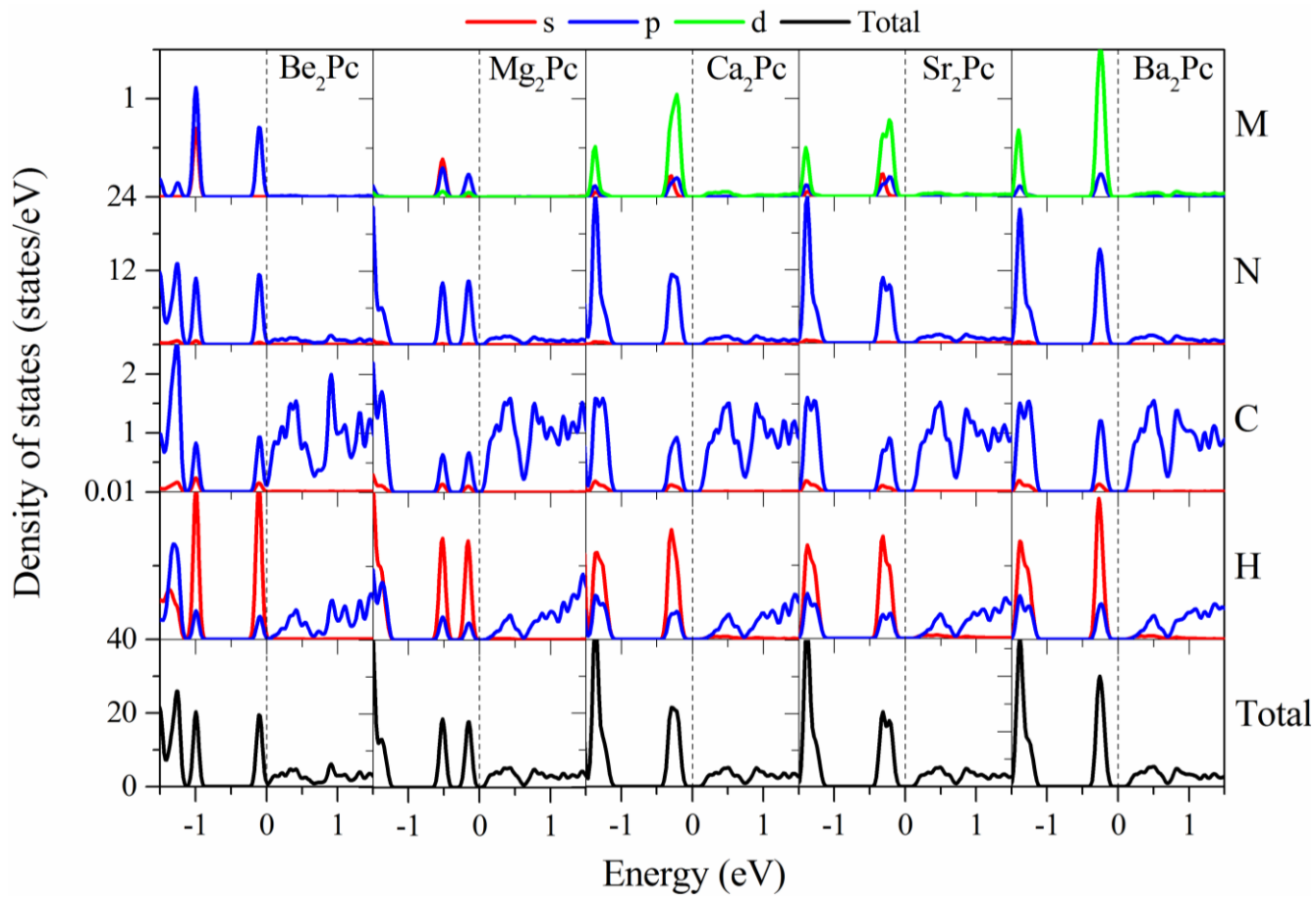


Figure S9. Calculated PDOS of the 2D M_2Pc monolayers in the range of −1.5 to 1.5 eV. Rows represent the PDOS contributions from different types of atoms. The last row shows TDOS for each material.

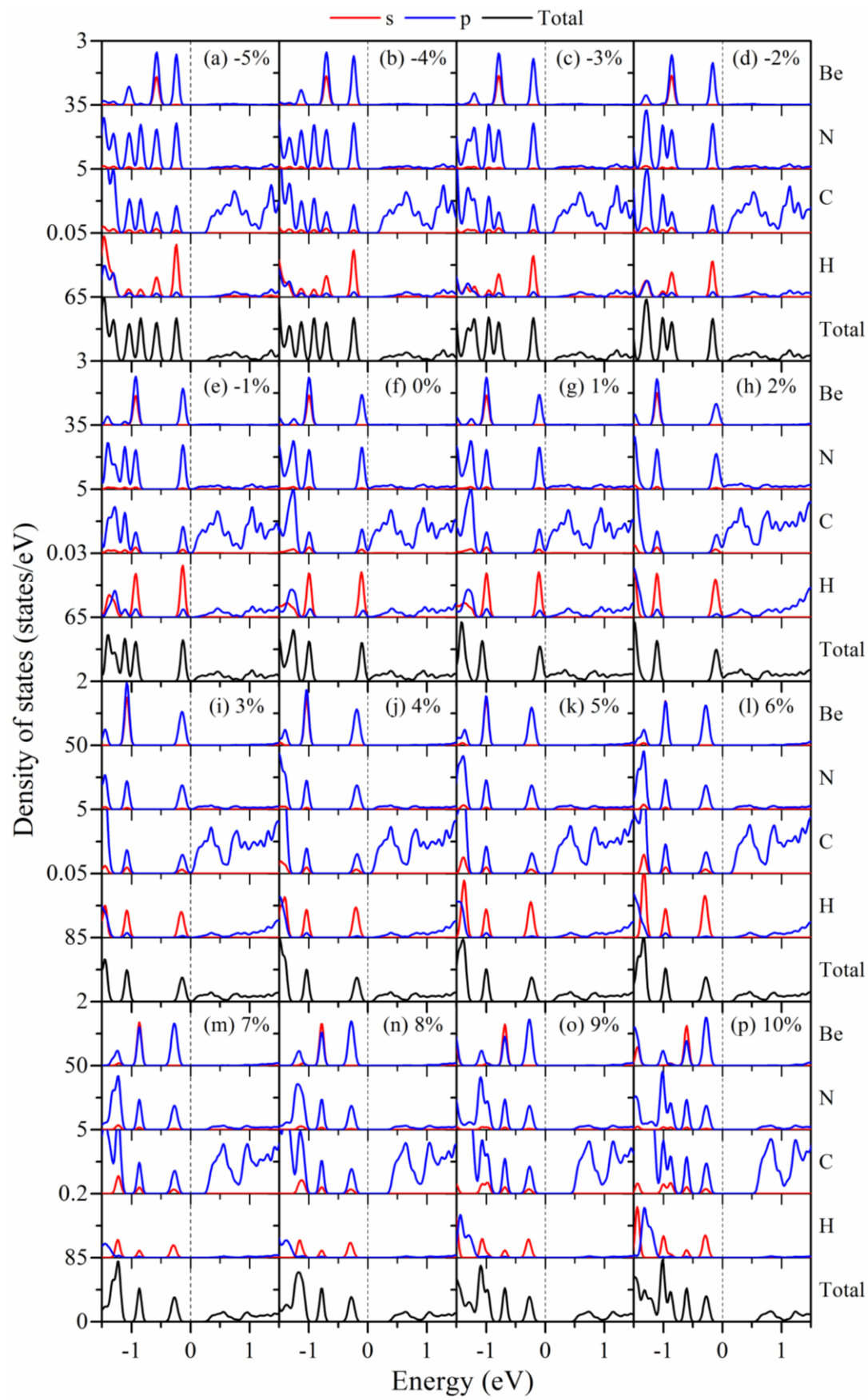


Figure S10. The evolution of PDOS on different atoms near the Fermi level versus biaxial strain from −5% to 10% for Be_2Pc monolayer. The Fermi level has been set to 0 eV.

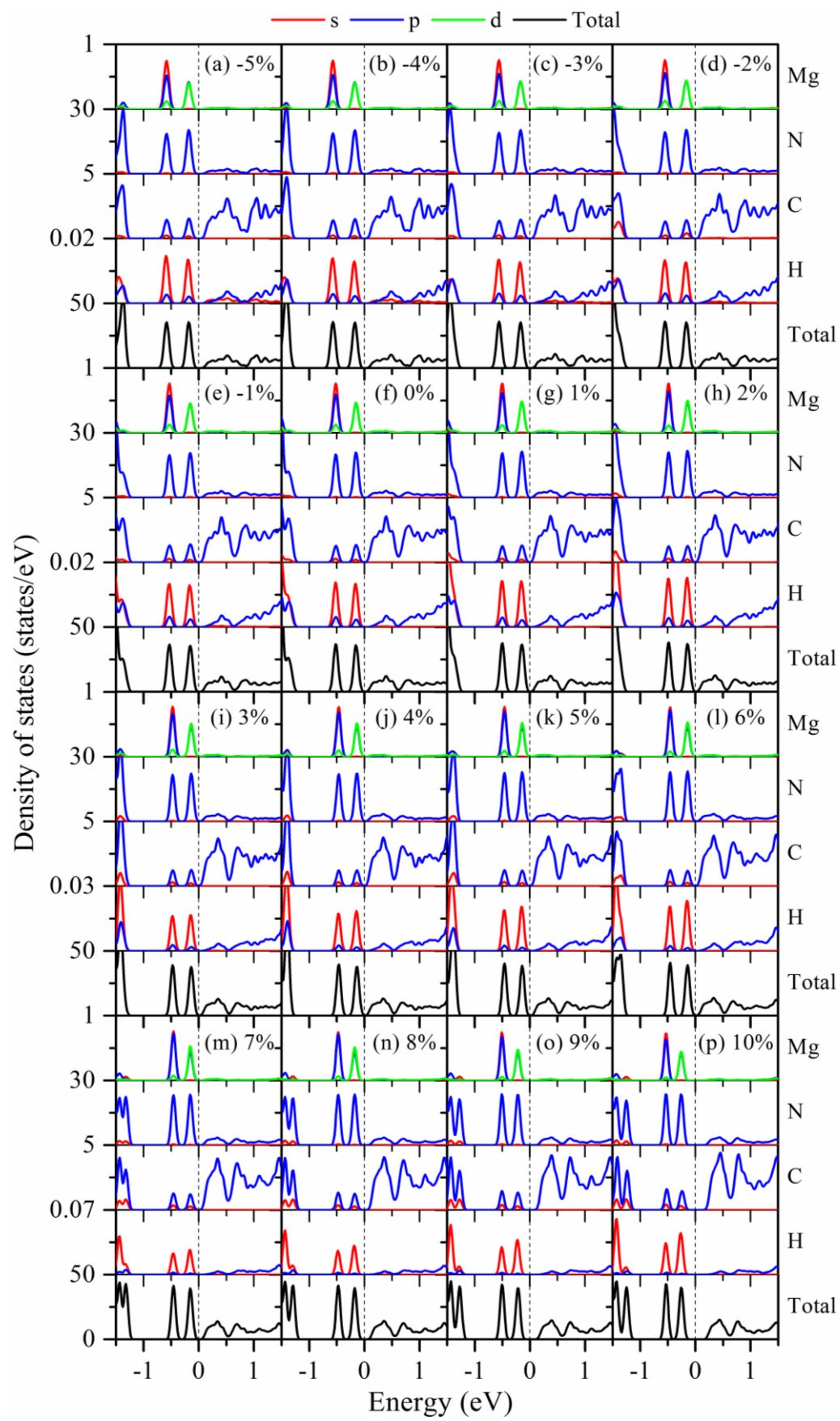


Figure S11. The evolution of PDOS on different atoms near the Fermi level versus biaxial strain from −5% to 10% for Mg_2Pc monolayer. The Fermi level has been set to 0 eV.

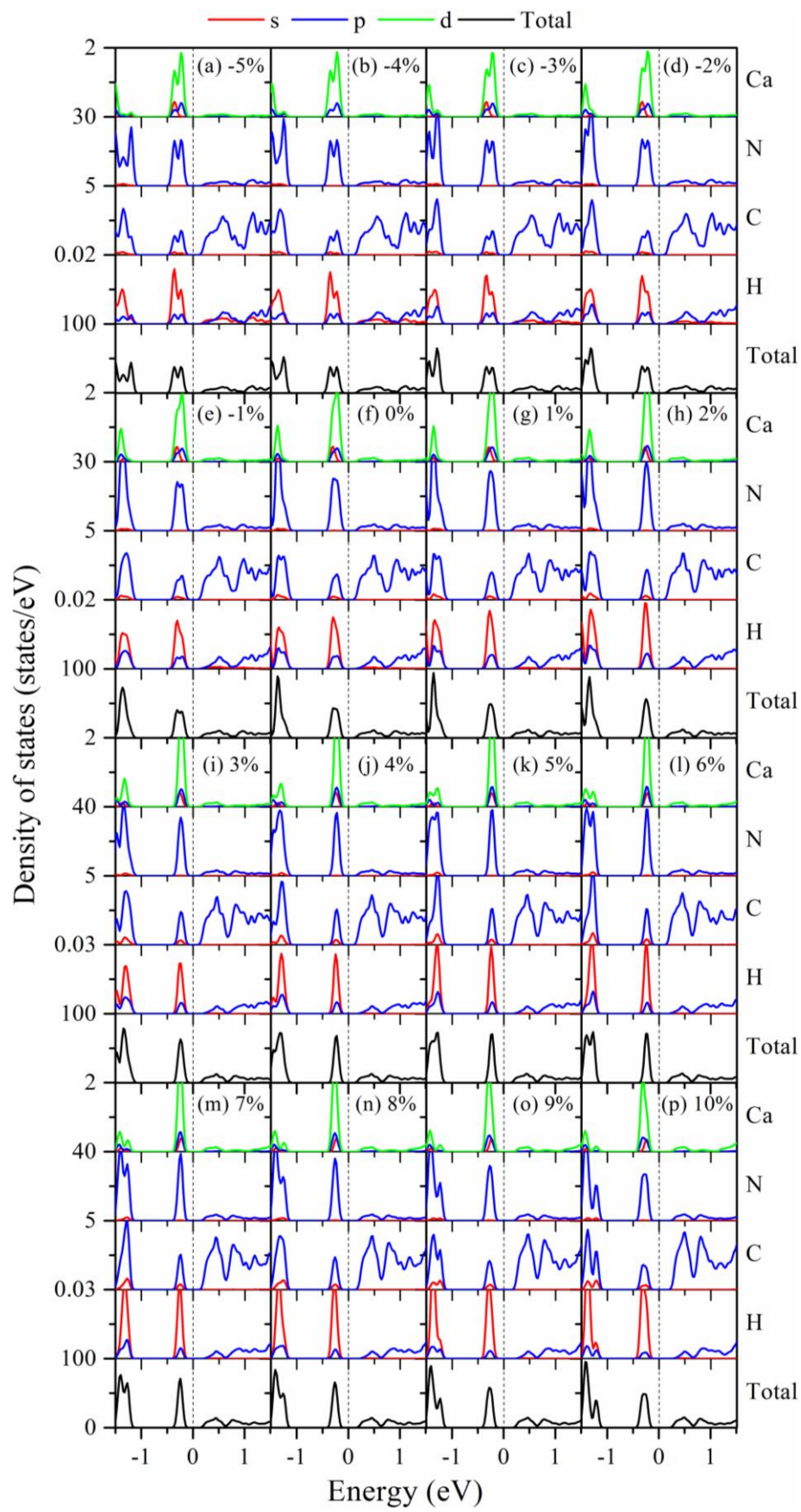


Figure S12. The evolution of PDOS on different atoms near the Fermi level versus biaxial strain from −5% to 10% for Ca_2Pc monolayer. The Fermi level has been set to 0 eV.

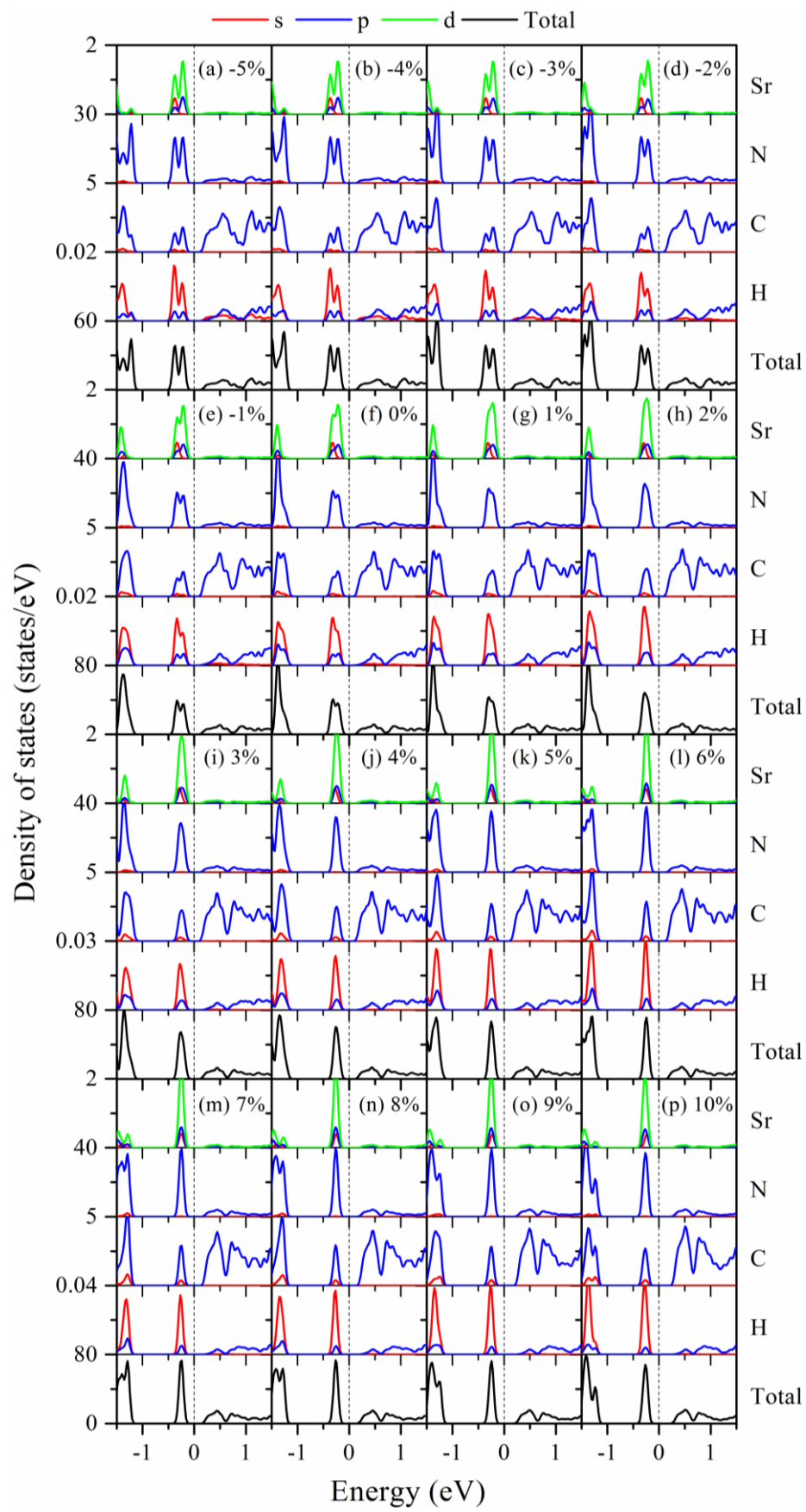


Figure S13. The evolution of PDOS on different atoms near the Fermi level versus biaxial strain from −5% to 10% for Sr_2Pc monolayer. The Fermi level has been set to 0 eV.

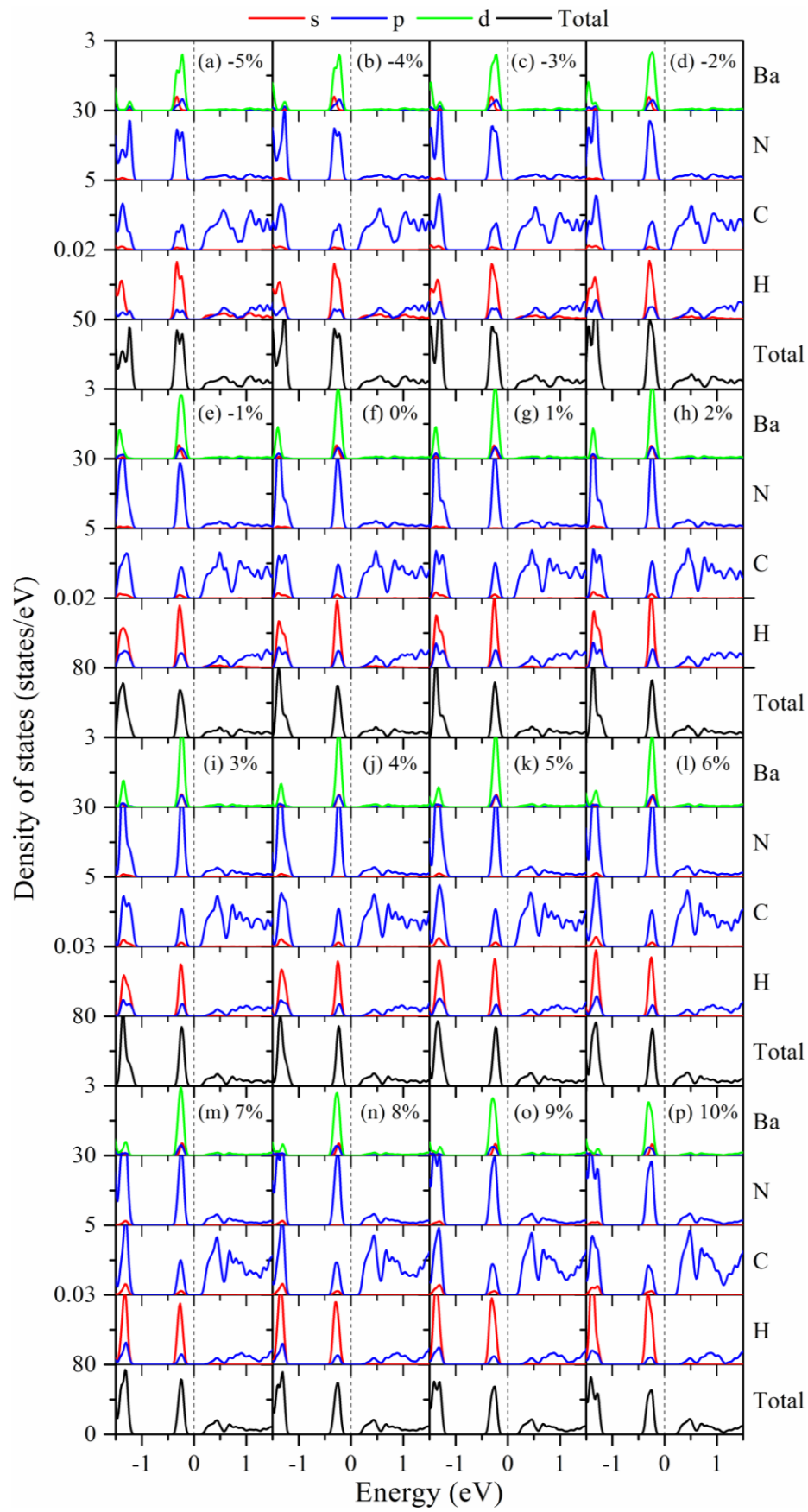


Figure S14. The evolution of PDOS on different atoms near the Fermi level versus biaxial strain from −5% to 10% for Ba_2Pc monolayer. The Fermi level has been set to 0 eV.