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RESEARCH ARTICLE

Intrinsically asymmetric atomic character regulates piezoelectricity in two-dimensional materials

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Supporting Information

Table S1 Calculated parameters for the fully relaxed $M_4X_3Y_3$ monolayers. Lattice constants *a* (Å); layer thickness *d* (Å) and atomic bond lengths $d_{M\text{-}X1}$, d_{MX2}, $d_{M\text{-}Y1}$, $d_{M\text{-}Y2}$, $d_{X\text{-}X}$ and $d_{Y\text{-}Y}$ (Å).

Monolayer	*a*	*b*	*h*	$d_{M\text{-}X1}$	$d_{M\text{-}X2}$	$d_{M\text{-}Y1}$	$d_{M\text{-}Y2}$	$d_{X\text{-}X}$	$d_{Y\text{-}Y}$
$Pd_4S_3Se_3$	5.87	6.03	3.73	2.35	2.44	2.54	2.46	2.09	2.39
$Pd_4S_3Te_3$	5.92	6.27	3.94	2.37	2.46	2.68	2.62	2.10	2.76
$Pd_4Se_3Te_3$	6.05	6.39	4.05	2.48	2.57	2.69	2.63	2.42	2.78
$Ni_4S_3Se_3$	5.32	5.76	3.58	2.19	2.36	2.39	2.32	2.12	2.40
$Ni_4S_3Te_3$	5.35	6.20	3.79	2.20	2.27	2.58	2.52	2.15	2.77
$Ni_4Se_3Te_3$	5.46	6.38	3.91	2.31	2.40	2.57	2.50	2.47	2.80

Table S2 Calculated parameters for the fully relaxed $M_4X_3Y_3$ monolayers. Lattice constants *a* (Å); layer thickness *d* (Å) and the relaxed-ion elastic coefficients C_{kl} (N/m) .

Monolayer	C_{11}	C_{22}	C_{12}	C_{66}
$Pd_4S_3Se_3$	48.78	22.87	43.09	21.21
$Pd_4S_3Te_3$	42.15	22.53	45.09	15.72
$Pd_4Se_3Te_3$	32.70	17.98	31.54	18.38
$Ni_4S_3Se_3$	39.17	29.98	13.60	26.72
$Ni_4S_3Te_3$	32.41	-35.00	-12.98	12.87
$Ni_4Se_3Te_3$	16.44	1.55	-2.00	20.13

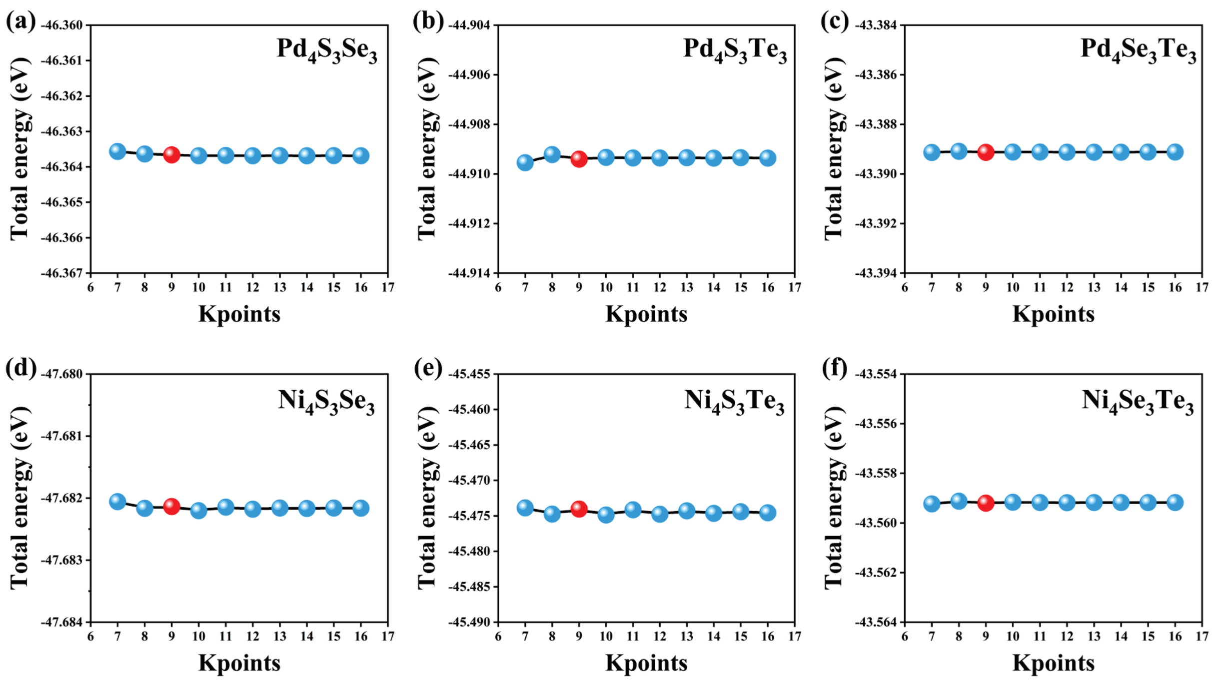

Fig. S1 The test of k-points for $M_4X_3Y_3$ monolayers. Kpoints equaling to 9 represents that the Brillouin zone is sampled by a 9 × 9 × 1 k-point mesh.

After a test of the k-points for $M_4X_3Y_3$ monolayers, we found that the maximum energy difference values between 9 × 9 × 1 k-points and other larger k-points (10 × 10 × 1 ~ 16 × 16 × 1) are only 0.00085 eV/unit, accounting for 0.002%. Therefore, 9 × 9 × 1 k-point mesh is full enough to sample the first Brillouin zone.

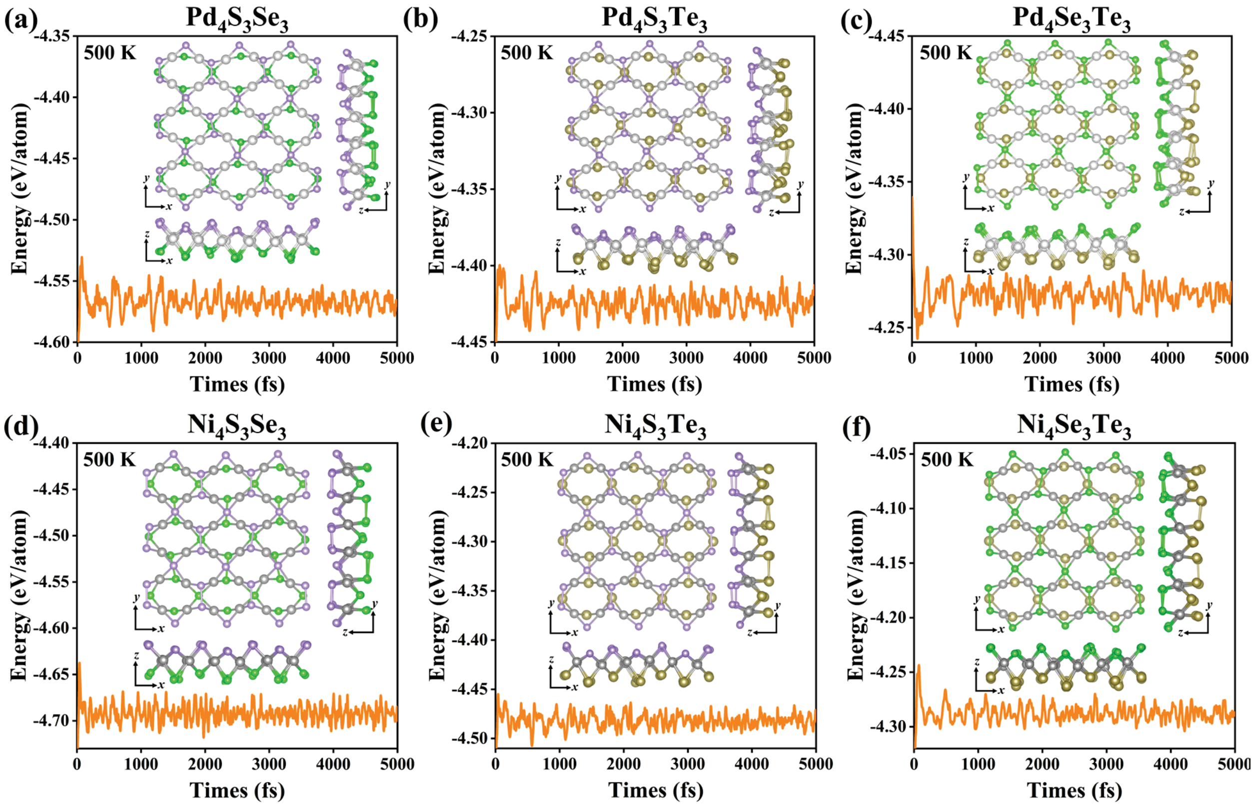

Fig. S2 The *ab initio* molecular dynamics (AIMD) simulations for $M_4X_3Y_3$ monolayers. Insets present the crystal structures at the end of the AIMD simulations.

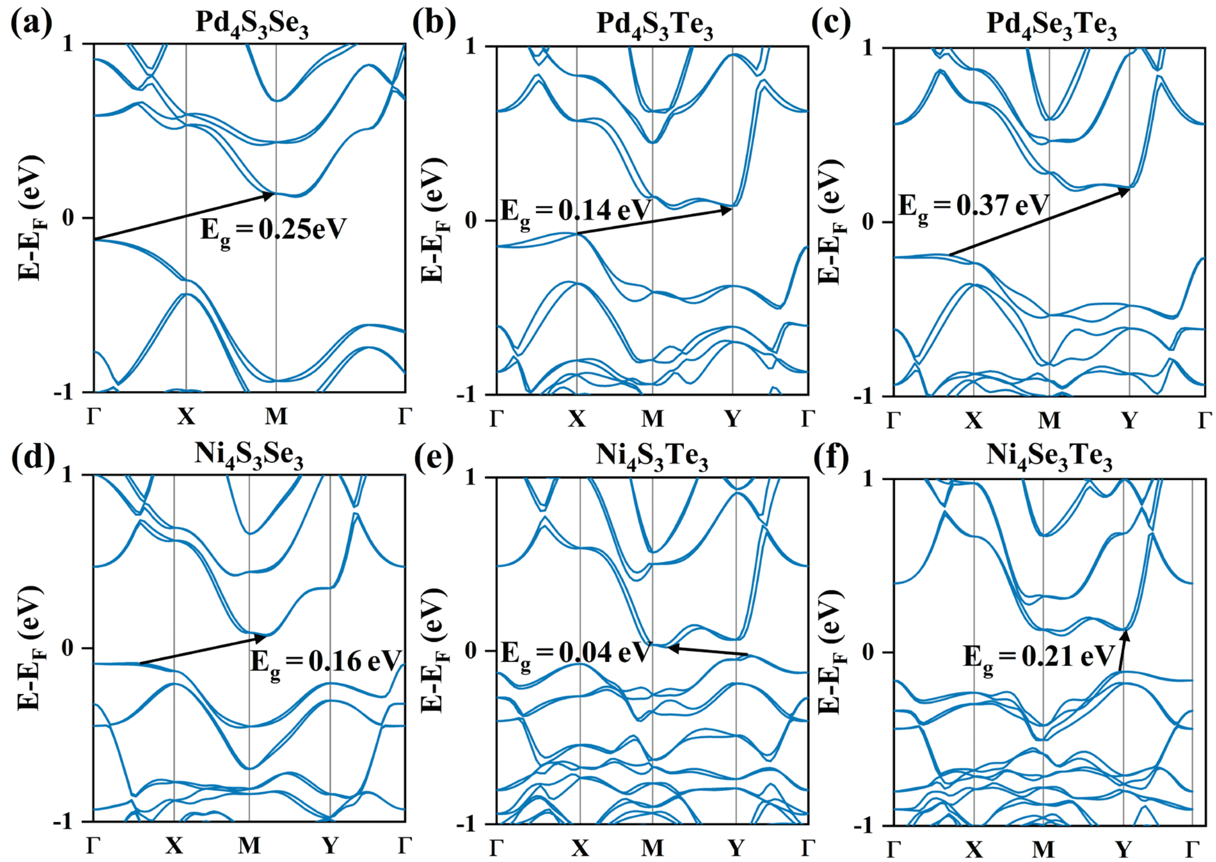

Fig. S3 Electronic band structures with spin-orbit coupling (SOC) based on the PBE functional for $M_4X_3Y_3$ monolayers. Fermi level is set at zero.

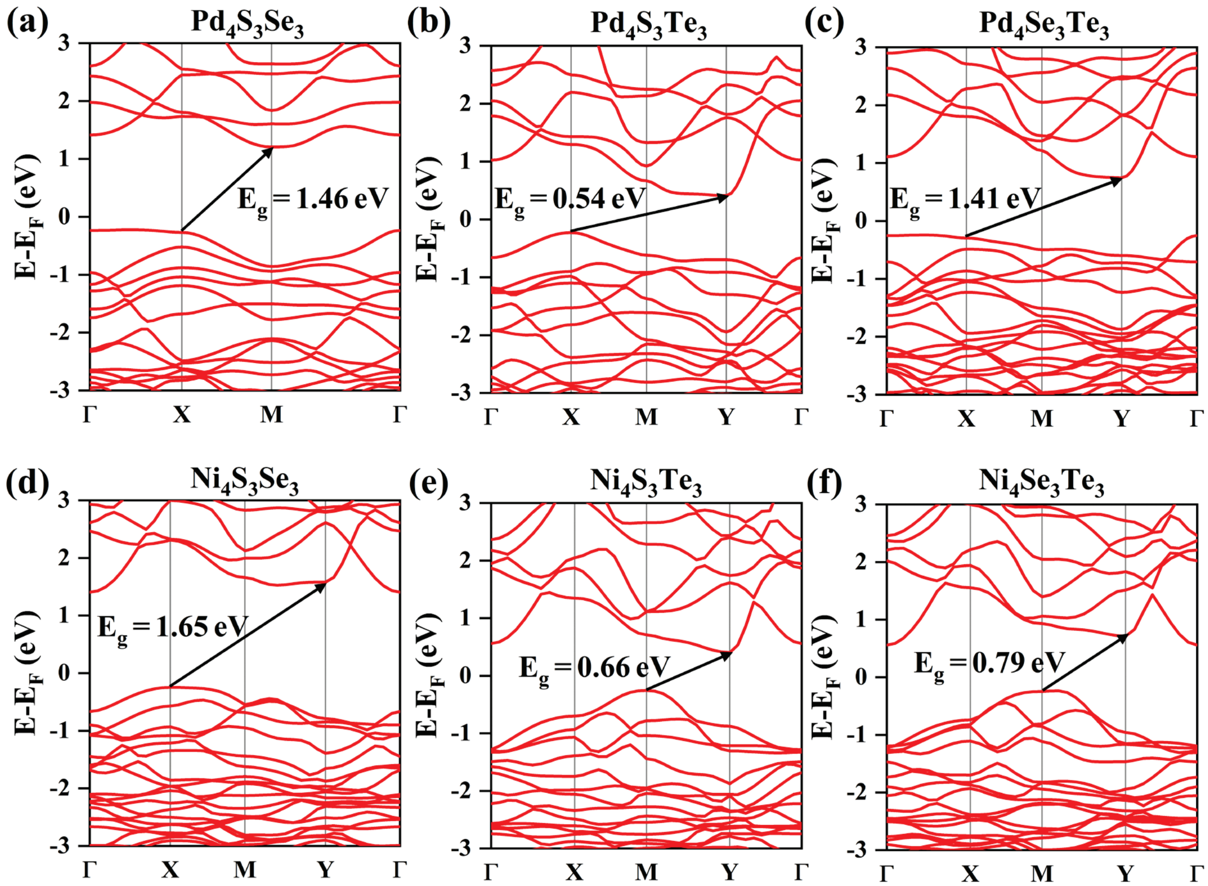

Fig. S4 Electronic band structures based on the Heyd-Scuseria-Ernzerhof (HSE06) functional for $M_4X_3Y_3$ monolayers. Fermi level is set at zero.

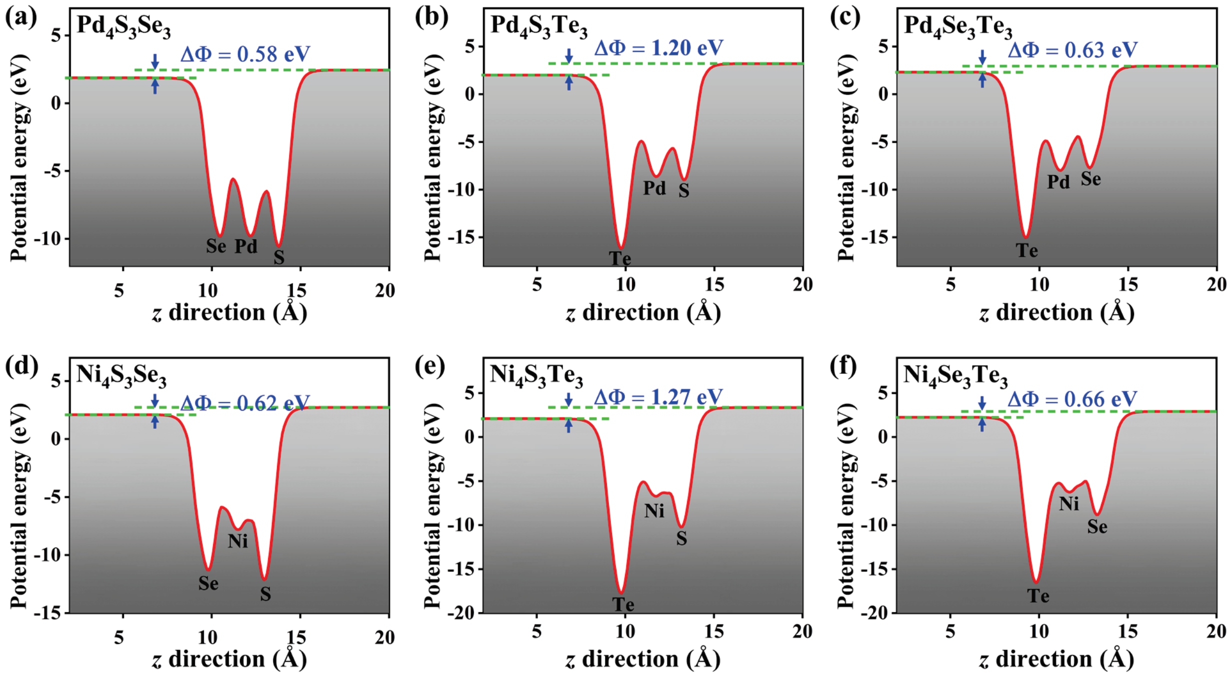

Fig. S5 Plane averaged electrostatic potentials for $M_4X_3Y_3$ monolayers.

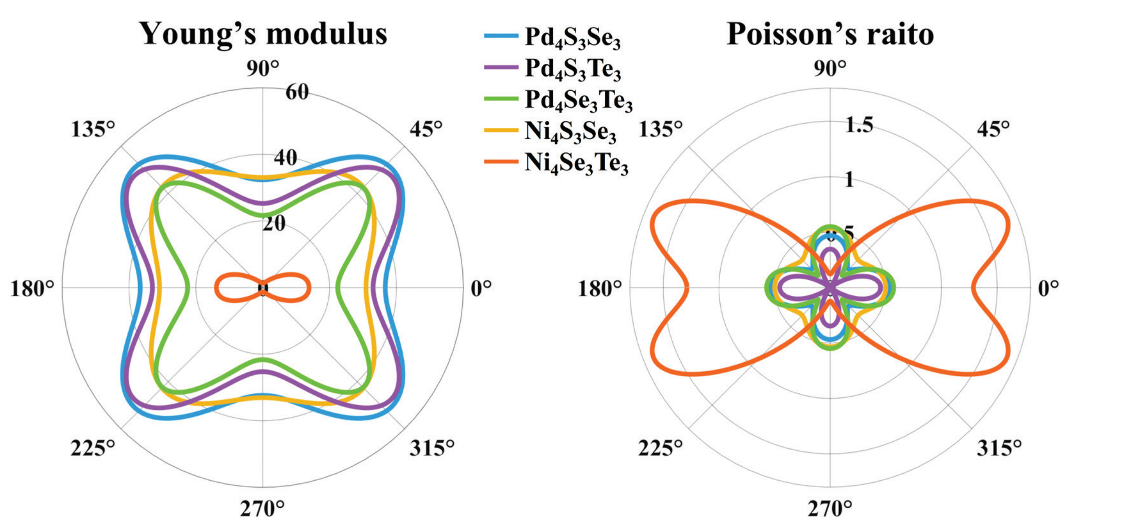

Fig. S6 Angle-dependent Young's modulus $Y(\theta)$ and Poisson's ratio $v(\theta)$ of $M_4X_3Y_3$ monolayers.

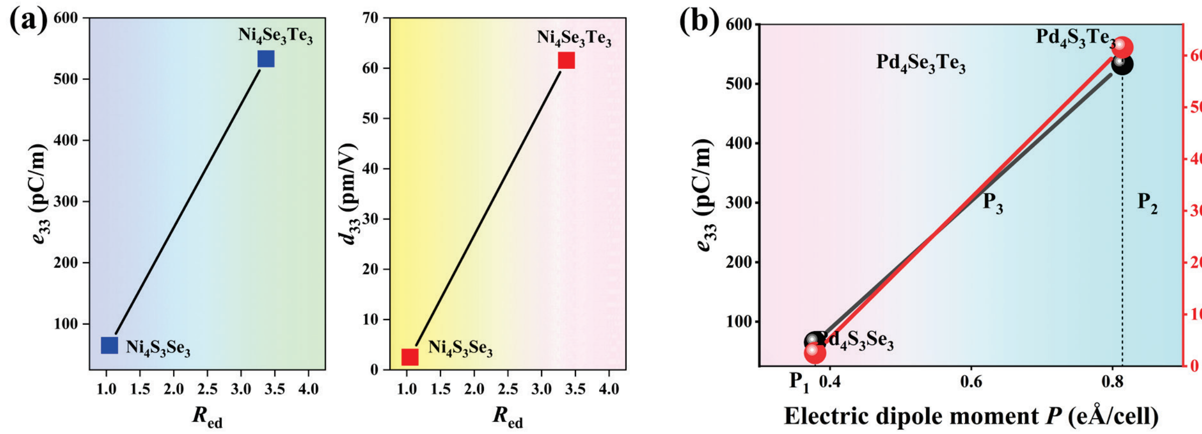

Fig. S7 (a) The out-of-plane piezoelectric stress (e_{33}) and strain coefficients (d_{33}) as a function of the electronegativity difference ratio R_{ed}, (b) the e_{33} and d_{33} as a function of the electric dipole moment P for $Ni_4X_3Y_3$ monolayers.