Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material (SI)

Three-Dimensional Auxetic Properties in Group V-VI Binary Monolayer Crystals X_3M_2 (X=S, Se, M=N, P, As)

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Out-of-Plane NPR of 2-D X_3M_2

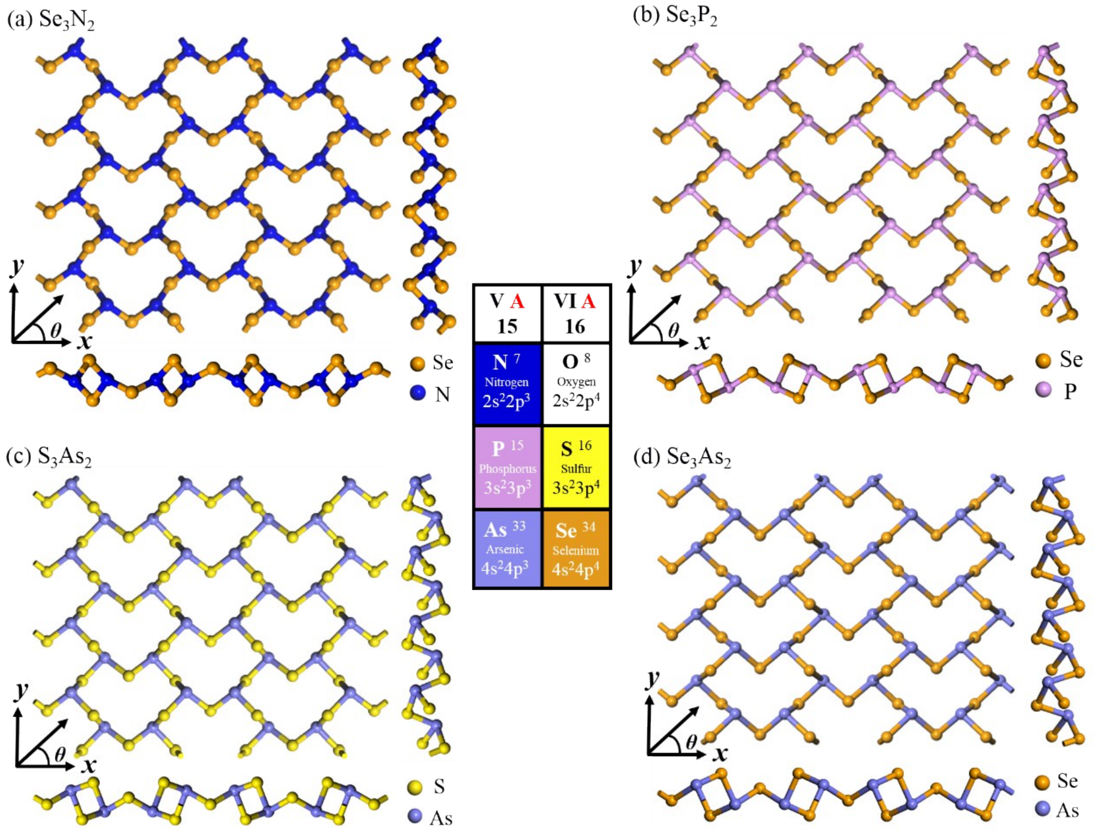

Figure S1 Atomic model of (a) Se_3N_2 (b) Se_3P_2 (c) S_3As_2 and (d) Se_3As_2. The inset shows group V and VI elements considered in this study (colored). θ defines the orientation relative to x axis.

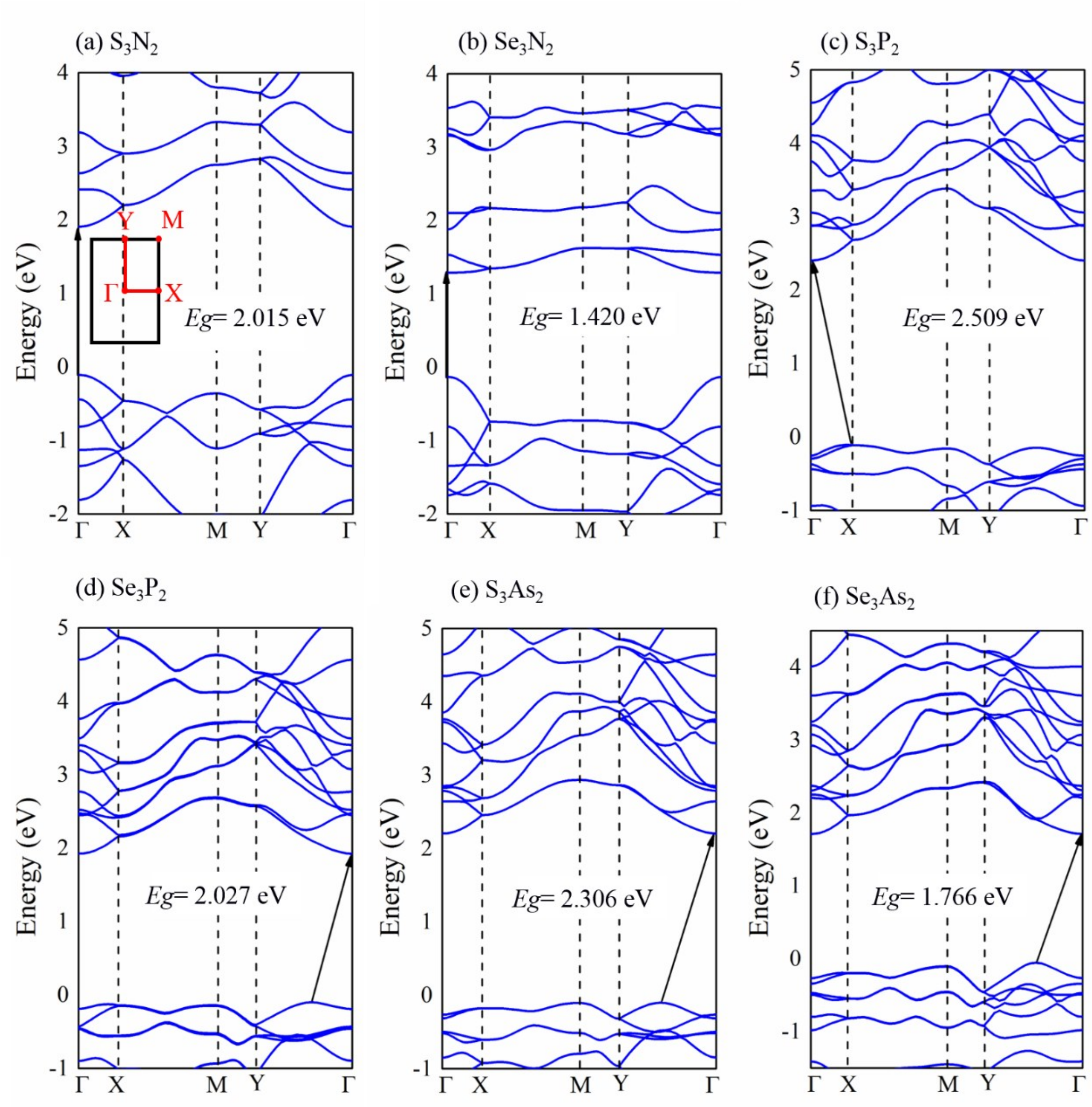

Figure S2 Energy band structures of X_3M_2 (X=S, Se; M=N, P, As). The inset in (a) shows the Brillouin zone and relevant high-symmetry k-points for all of the 2-D crystals X_3M_2.

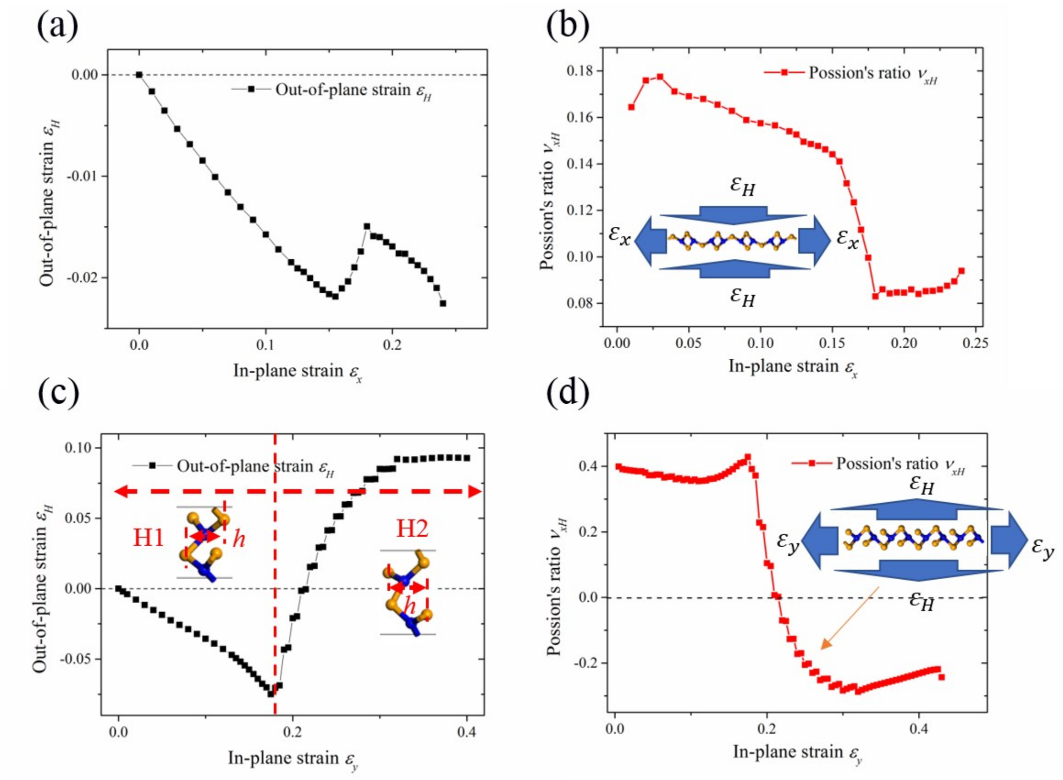

Figure S3 Out-of-plane strain and its corresponding Poisson's ratio of Se_3N_2 under tension in *x* direction (a), (b) and *y* direction (c), (d).

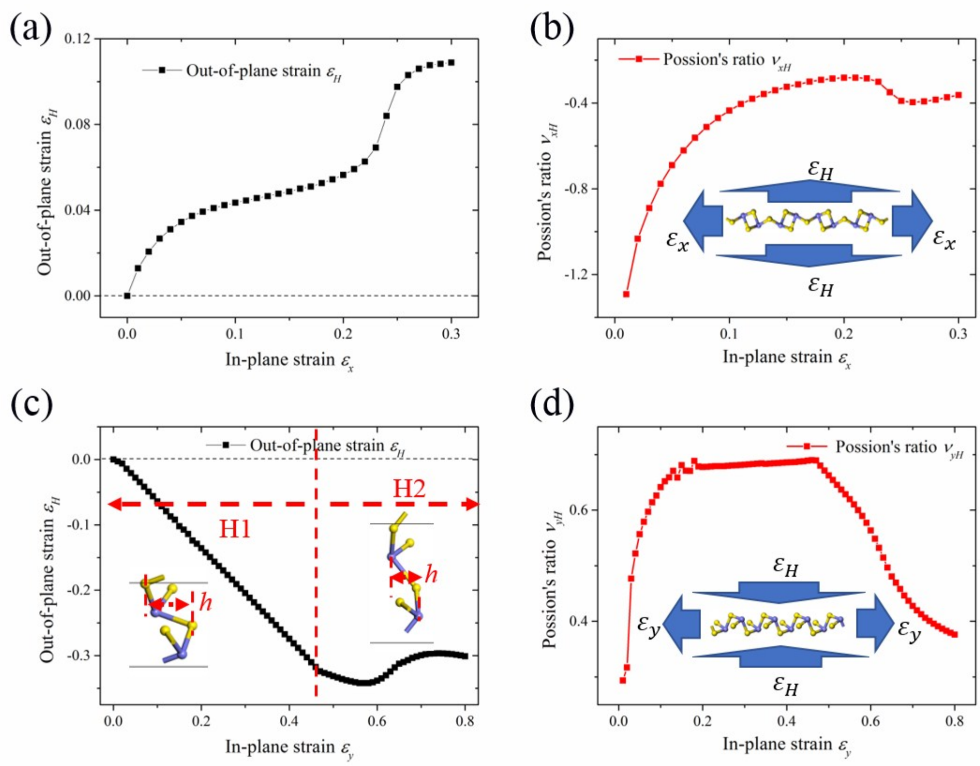

Figure S4 Out-of-plane strain and its corresponding Poisson's ratio of S_3As_2 under tension in *x* direction (a), (b) and *y* direction (c), (d).

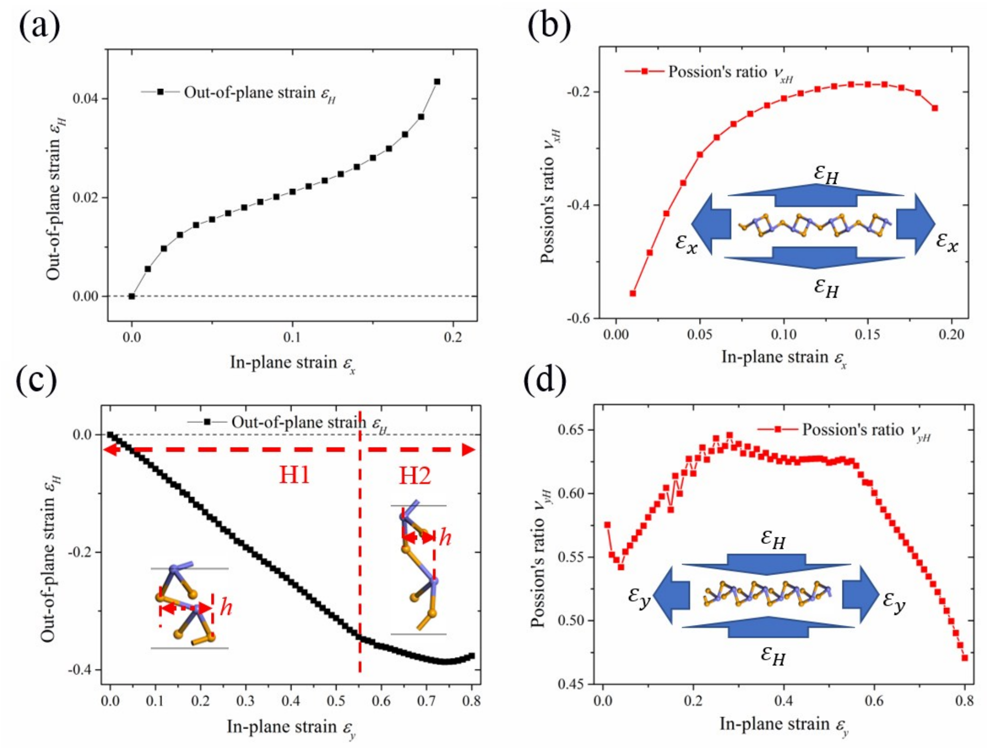

Figure S5 Out-of-plane strain and its corresponding Poisson's ratio of Se_3As_2 under tension in x direction (a), (b) and y direction (c), (d).

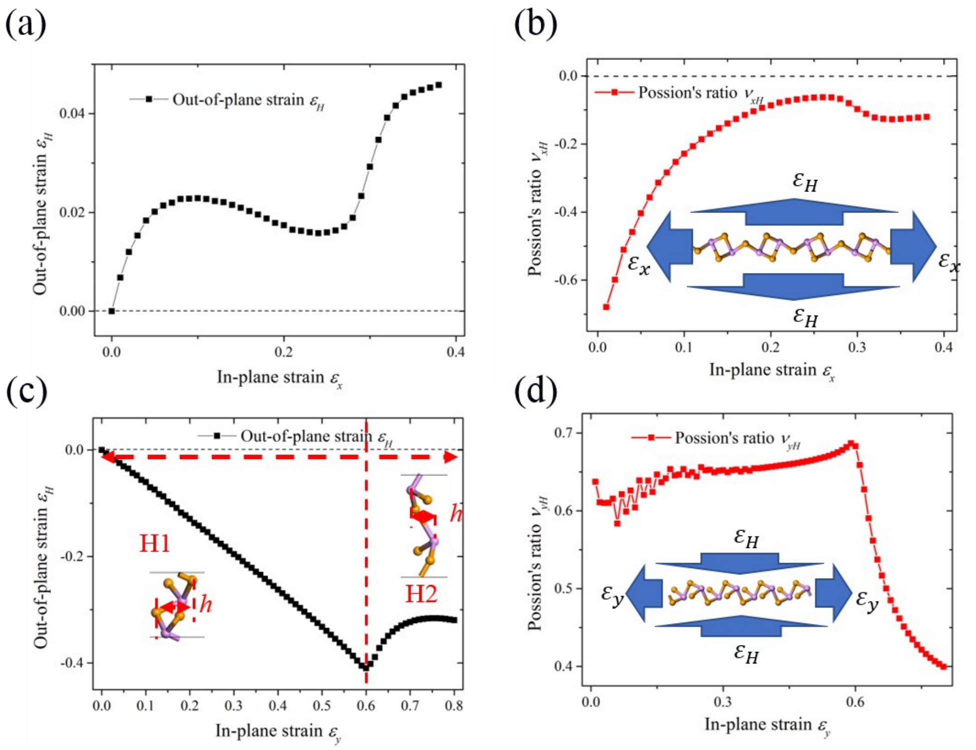

Figure S6 Out-of-plane strain and its corresponding Poisson's ratio of P_2Se_3 under tension in x direction (a), (b) and y direction (c), (d).

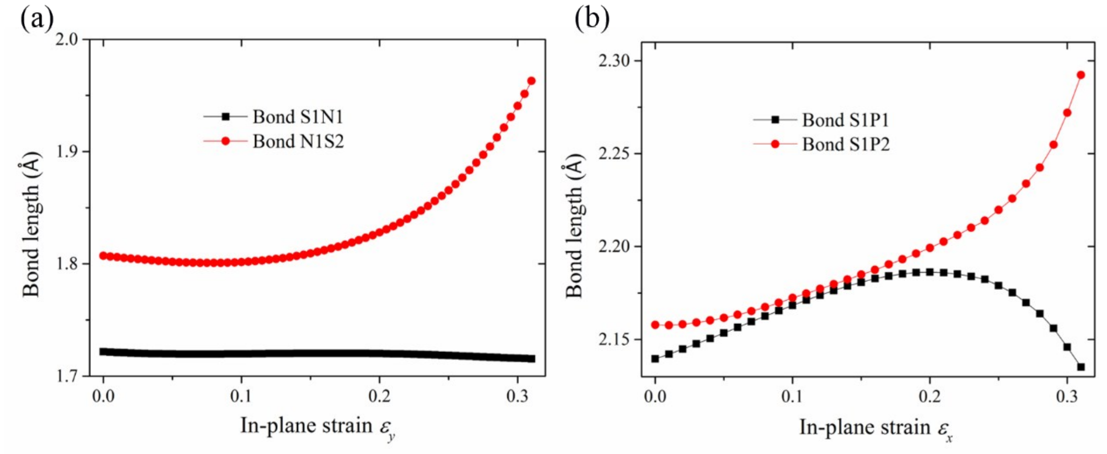

Figure S7 Bond length changes under tension (a) in y direction for S_3N_2 and (b) in x direction for S_3P_2.

Cross-Plane NPR of 3-D Bulk Form X_3M_2

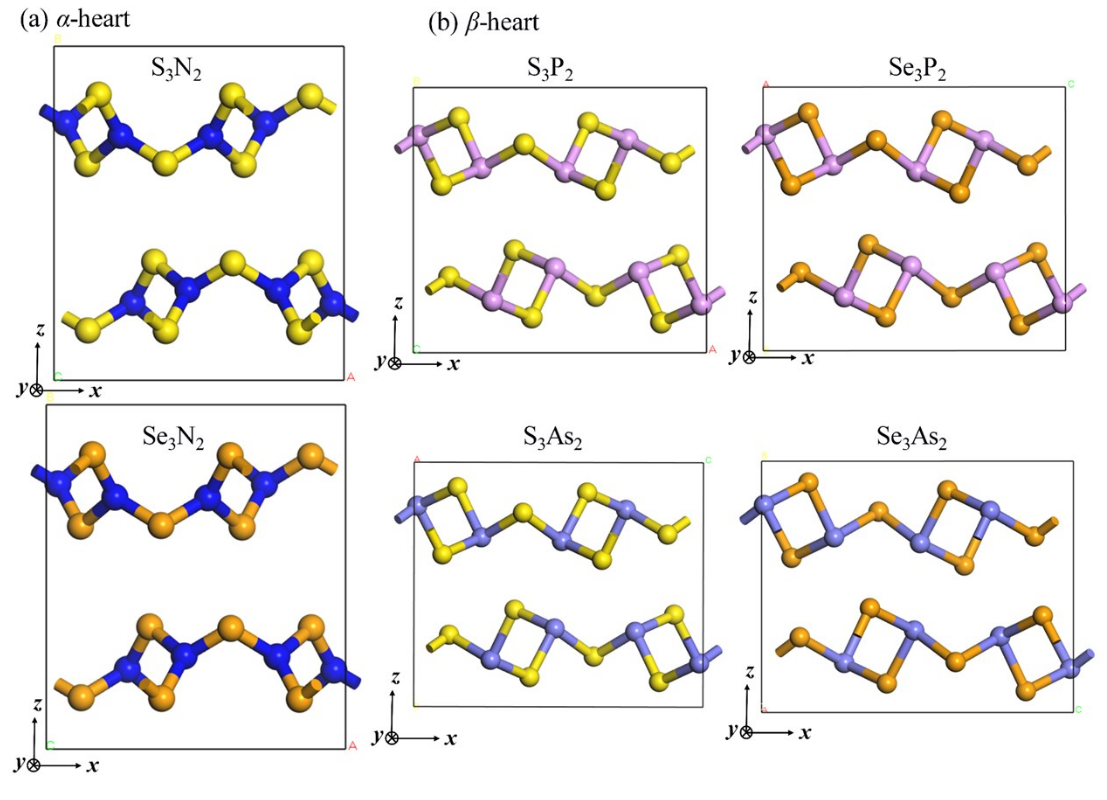

Figure S8 Atomic model of the most energetically favorable stacked (a) α-heart and (b) β-heart X_3M_2 bulk crystal.

Table S1 Cross-plane interlayer Poisson's ratio for X_3M_2 bulk crystals (X=S, Se; M=N, P, As) and other bulk crystals reported before.

	ν_{xH*}	ν_{yH}
Black phosphorus [1]	~ -0.5	~ 0.3
Bulk arsenene [2]	/	-0.125
Bulk S_3N_2	0.325	0.049
Bulk Se_3N_2	0.943	0.041
Bulk S_3P_2	0.411	**-0.457**
Bulk Se_3P_2	0.192	**-0.101**
Bulk S_3As_2	0.278	**-0.025**
Bulk Se_3As_2	0.152	**-0.065**

* For black phosphorene and arsenene, x and y represent armchair and zigzag directions, respectively.

α-heart X_3M_2 Bulk Crystals

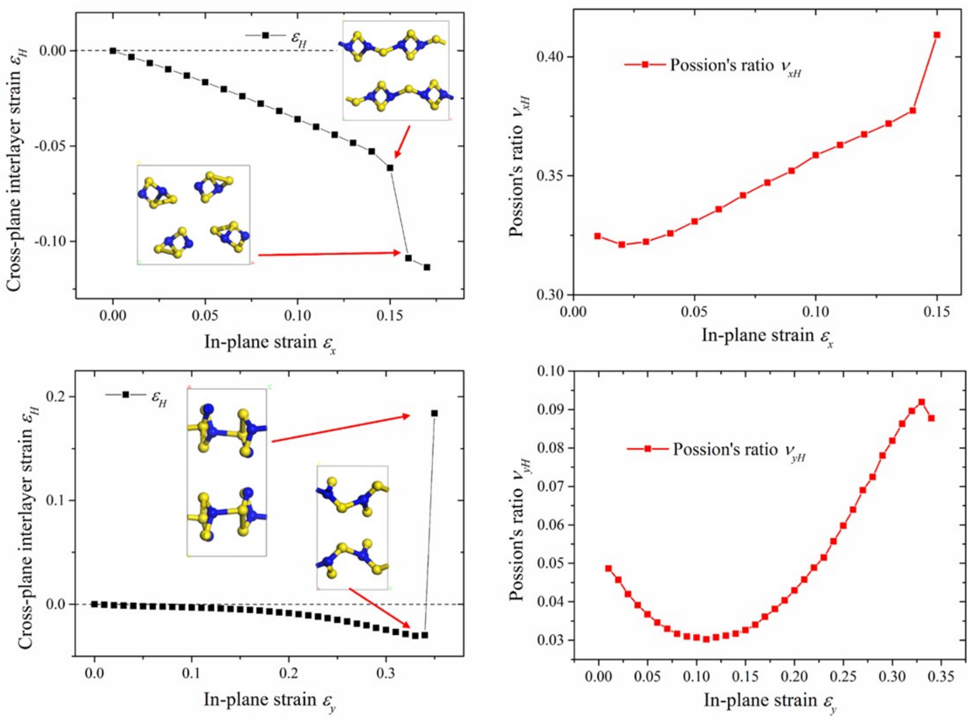

Figure S9 Cross-plane interlayer strain and its corresponding Poisson's ratio of S_3N_2 bulk crystal under tension in *x* and *y* direction.

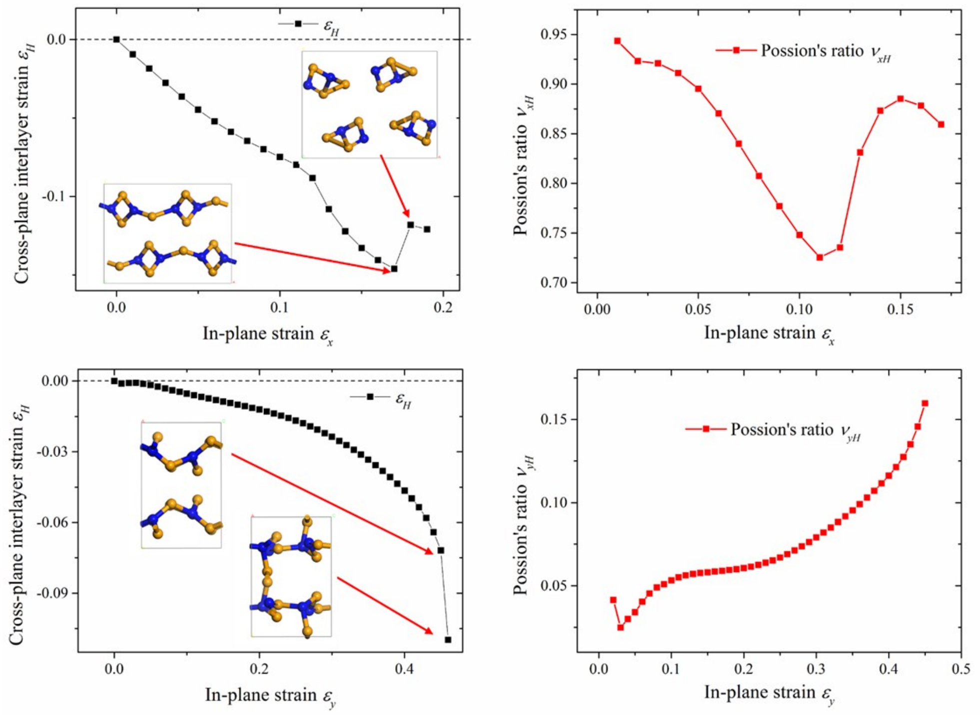

Figure S10 Cross-plane interlayer strain and its corresponding Poisson's ratio of Se_3N_2 bulk crystal under tension in *x* and *y* direction.

β-heart X_3M_2 Bulk Crystals

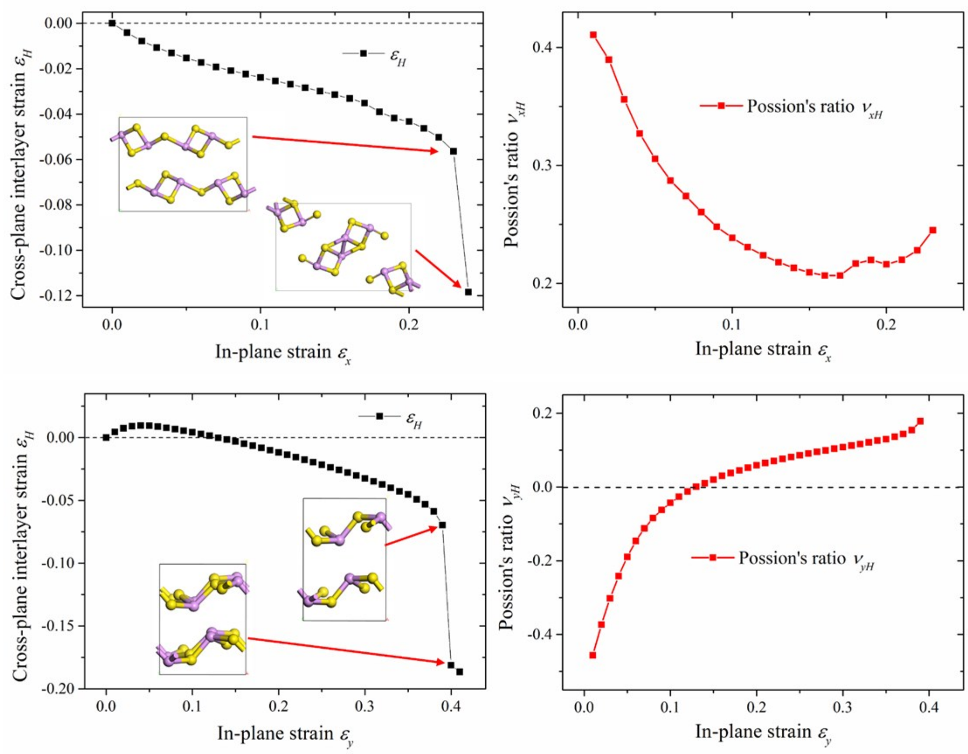

Figure S11 Cross-plane interlayer strain and its corresponding Poisson's ratio of S_3P_2 bulk crystal under tension in *x* and *y* direction.

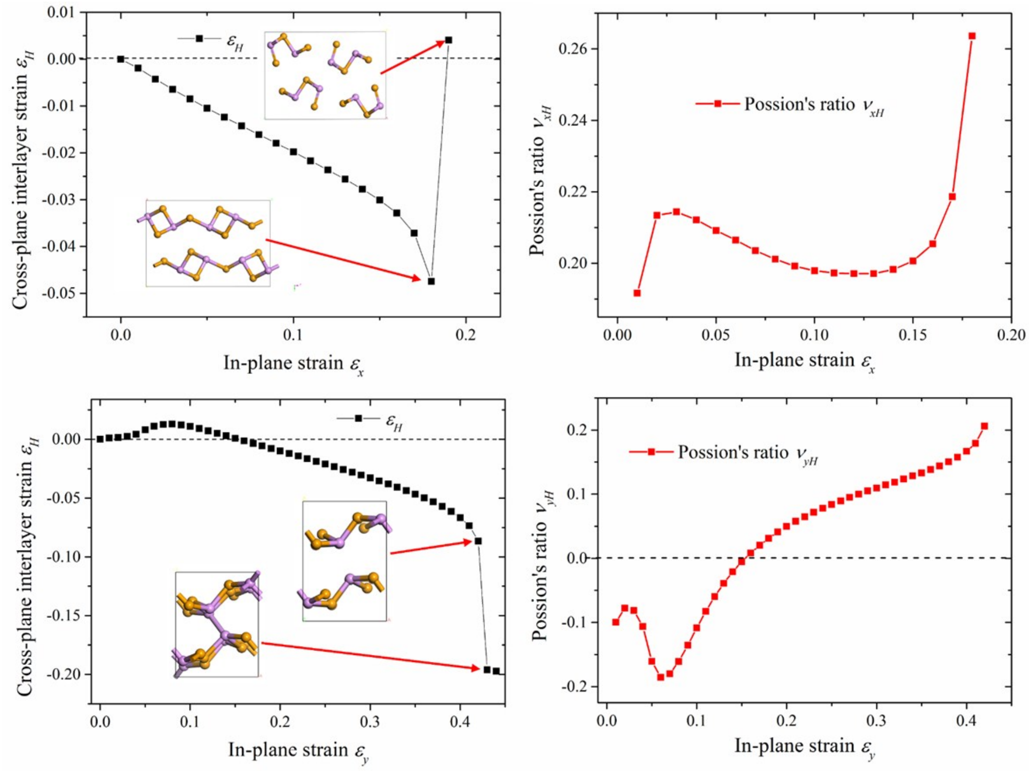

Figure S12 Cross-plane interlayer strain and its corresponding Poisson's ratio of Se_3P_2 bulk crystal under tension in *x* and *y* direction.

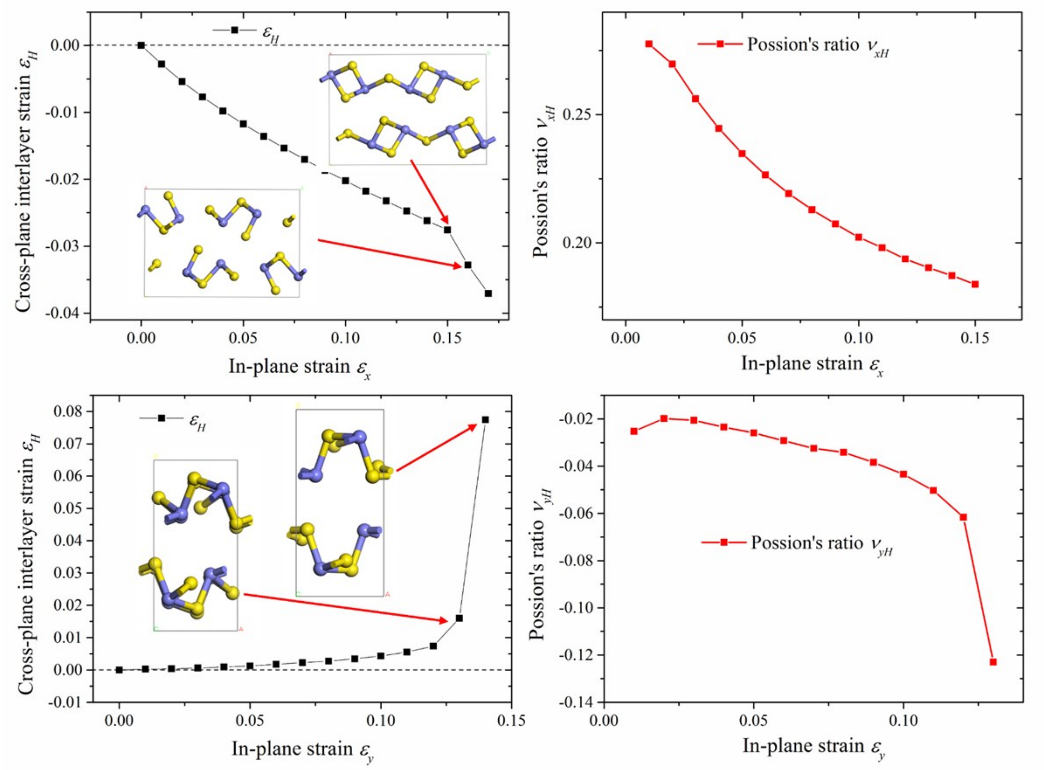

Figure S13 Cross-plane interlayer strain and its corresponding Poisson's ratio of S_3As_2 bulk crystal under tension in *x* and *y* direction.

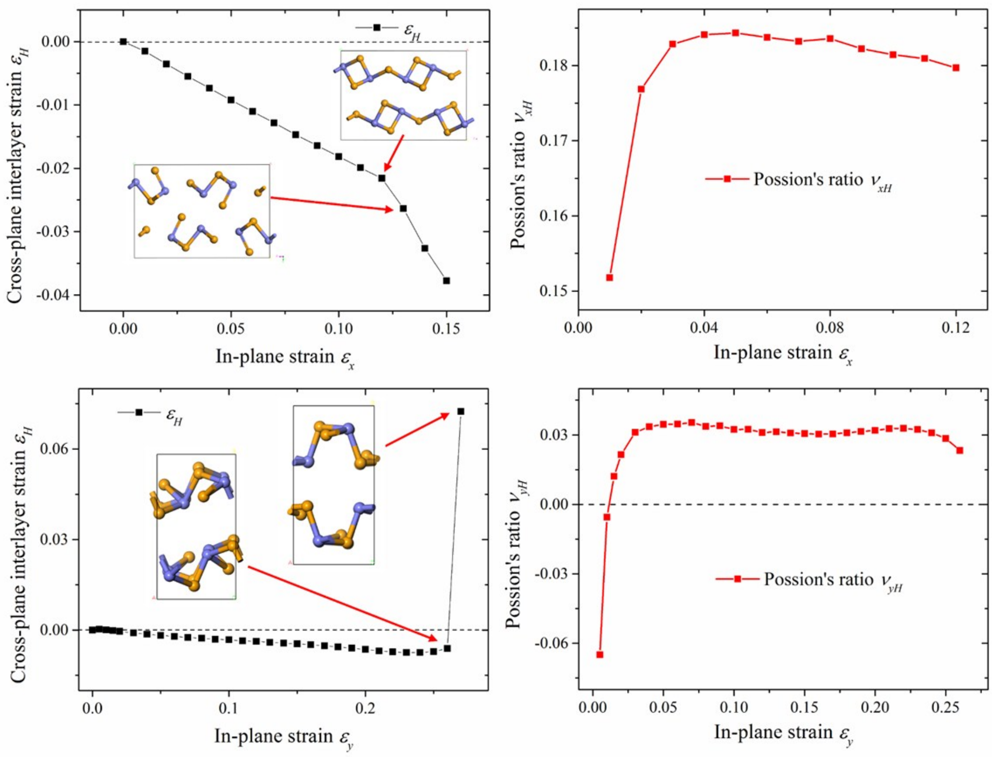

Figure S14 Cross-plane interlayer strain and its corresponding Poisson's ratio of Se_3As_2 bulk crystal under tension in *x* and *y* direction.

In-Plane NPR of 2-D Crystals X_3M_2

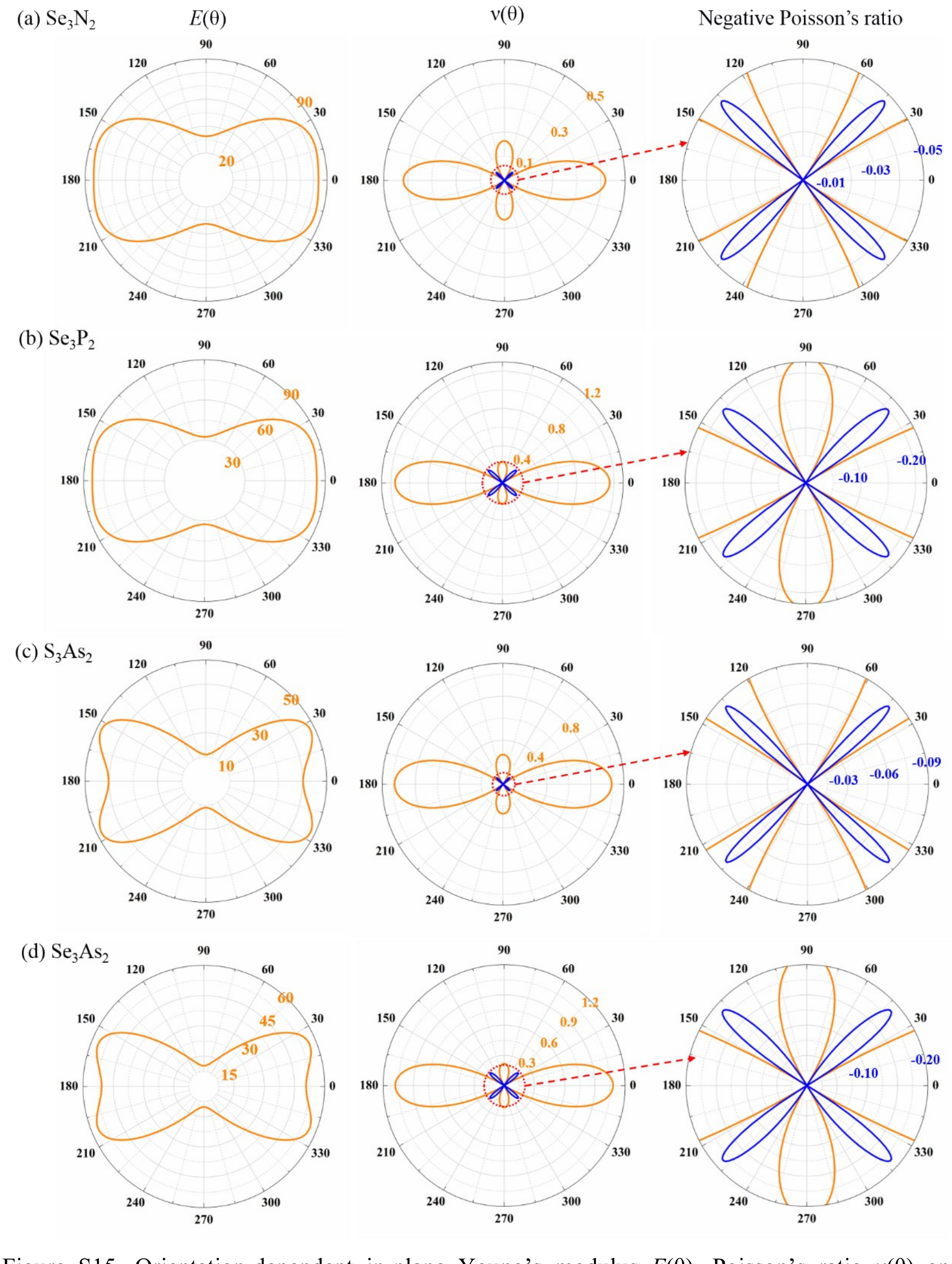

Figure S15. Orientation-dependent in-plane Young's modulus $E(\theta)$, Poisson's ratio $\nu(\theta)$ and negative Poisson's ratio of (a) N_2Se_3 (b) P_2Se_3 (c) As_2S_3 (d) Se_3As_2.

Table S2 Extremes of the in-plane Young's modulus and Poisson's ratio for X_3M_2 (X=S, Se; M=N, P, As)

Formula	**Young's Modulus**				**Possion's Ratio**			
	Maximum		Minimum		Maximum		Minimum	
	E (GPa)	θ (°)	E (GPa)	θ (°)	υ	θ (°)	υ	θ (°)
S_3N_2	82.26	45	26.38	90	0.7405	0	**-0.0259**	45
Se_3N_2	84.92	18	32.59	90	0.4182	0	**-0.0468**	44
S_3P_2	63.60	17	17.07	90	0.8229	0	0.0157	45
Se_3P_2	56.67	23	9.74	90	1.1553	0	**-0.1999**	42
S_3As_2	48.14	26	10.97	90	0.8229	0	**-0.0836**	44
Se_3As_2	56.46	22	10.24	90	1.0799	0	**-0.1857**	42

Equation S1

Variables defined with elastic constants C_{ij} for calculating orientation-dependent in-plane Young's modulus $E(\theta)$ and Poisson's ratio $v(\theta)$.

$$\upsilon_{ZZ} = \frac{C_{12}}{C_{22}}$$

$$d_1 = \frac{C_{11}}{C_{22}} + 1 - \frac{C_{11}C_{22} - C_{12}^2}{C_{22}C_{66}}$$

$$d_2 = -(2\frac{C_{12}}{C_{22}} - \frac{C_{11}C_{22} - C_{12}^2}{C_{22}C_{66}})$$

$$d_3 = \frac{C_{11}}{C_{22}}$$

$$Y_{ZZ} = \frac{C_{11}C_{22} - C_{12}^2}{C_{22}}$$

Reference

1. Y. Du, J. Maassen, W. Wu, Z. Luo, X. Xu and P. D. Ye, *Nano Letters*, 2016, **16**, 6701-6708.
2. J. Han, J. Xie, Z. Zhang, D. Yang, M. Si and D. Xue, *Applied Physics Express*, 2015, **8**, 041801.