Electronic Supplementary Information (ESI)

A new 2D high-pressure phase of PdSe₂ with high-mobility transport anisotropy for photovoltaic applications

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1. The choice of the semiempirical correction methods

Considering that PdS_2 -type (SG *Pbca*) and monoclinic (SG *12/a*) $PdSe_2$ show layered structures (**Fig. 1** in the main text) and there exists vdW forces between the layers along the *c*-axis, we use semiempirical dispersion interaction correction methods (DFT-D) beyond traditional DFT calculations with GGA. The experimental structure parameters are used as the starting parameters to perform the structural optimization. In **Table S1** and **Table S2**, our theoretical calculated lattice parameters are compared with previous experimental data and calculation results. The calculated results by DFT-D are more close to the experimental data, especially in the *c*-axis direction in the orthorhombic PdS₂-type PdSe₂, where the value of the lattice constant *c* before correction is much larger than the experimental value, which indicates that the vdW force in these layered structure of PdSe₂ is significant. The structural parameters and the electronic properties of bulk PdSe₂ (SG *Pbca*) are very sensitive to the choice of the exchange-correlation functionals.^{[1],[2]} The significance of the vdW interactions in bulk PdSe₂ (SG *Pbca*) between the PdSe₂ layers have been pointed out by Akinola *et al.* They show that the structural parameters calculated by optB88 are closer to experimental values than those by optPBE, whereas optPBE is better for describing the

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electronic properties of bulk PdSe₂ (SG *Pbca*).^[1] Moreover, the PBE-TS series functionals have been proved to significantly improve the prediction of the structural parameters in bulk PdSe₂ (SG *Pbca*).^[2] Therefore, we choose the Tkatchenko-Scheffler method (denoted as DFT-D (TS)) of the semiempirical dispersion interaction correction. Our optimized lattice parameters are in satisfactory agreement with experiment data (**Table S2**), implying the validity of our choice with the DFT-D method.

	a(Å)	<i>b</i> (Å)	<i>c</i> (Å)	V(Å ³)	Х	у	Z	ref.
Exp.	5.741	5.866	7.691	259.01	0.112	0.117	0.407	[3]
Exp.	5.746	5.868	7.695	259.43	0.111	0.118	0.406	[4]
Cal.	5.875	5.982	7.772	273.14				[4]
Cal.	5.866	6.0	7.357	258.94	0.112	0.118	0.404	[5]
Cal.	5.85	5.99	7.95	287.58				[1]
Cal.	5.851	5.947	7.694	267.72				[2]
PBE	5.786	5.936	8.608	295.66	0.112	0.129	0.414	this work
DFT-D (TS)	5.848	5.947	7.758	269.88	0.114	0.119	0.408	this work

 Table S1 Calculated equilibrium lattice constants, cell volume and positional parameters for the

 PdS₂-type PdSe₂ (SG *Pbca*) compared with experimental data.

Table S2 Comparison of calculated (this work) equilibrium lattice parameters with experimentaldata for the monoclinic structure (SG I2/a).

Ref./method	<i>a</i> (Å)	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	V(Å ³)
Exp. ^[6] (single crystal)	6.710(2)	4.154(2)	8.914(2)	92.42(3)	248.24(4)
Exp. ^[6] (powder)	6.674(8)	4.142(3)	9.014(2)	91.98(1)	249.08(6)
Exp. ^[7]	6.659(7)	4.124(5)	4.438(6)	92.76(3)	121.7(4)
DFT-D (TS)	6.727(8)	4.015(6)	9.108(1)	92.23(1)	245.88
DFT-D3 method with Becke-Jonson damping	6.631(6)	3.901(5)	9.109(1)	92.20(5)	235.51
zero damping DFT-D3 method of Grimme	6.686(3)	3.952(8)	9.061(4)	92.03(1)	239.34
DFT-D2 method of Grimme	6.628(1)	3.893(5)	9.159(1)	92.10(7)	236.21

optB86b-vdW	6.664(1)	3.938(8)	9.211(3)	92.37(6)	241.57
optPBE-vdW	6.780(7)	4.159(8)	9.184(6)	92.80(9)	258.27
optB88-vdW	6.821(3)	4.203(1)	9.231(1)	92.73(5)	264.36
PBEsol	6.500(6)	3.751(3)	9.454(5)	90.05(1)	230.55
PBE	6.755(0)	4.153(3)	9.090(9)	92.82(8)	254.74

2. Birch-Murnaghan isothermal equation of state (BM-EOS)

The equilibrium volume and bulk modulus are analyzed by using Birch-Murnaghan isothermal equation of state (BM-EOS),^[8] which is given by equation (1):

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} \left(B_0' - 4 \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\} \right]$$
(1)

where *P* is the pressure, V_0 is the reference volume, *V* is the deformed volume, B_0 is the bulk modulus, and B_0' is the derivative of the bulk modulus with respect to pressure. The bulk modulus and its derivative are defined as

$$B_0 = -V \left(\frac{\partial P}{\partial V}\right)_{P=0} \tag{2}$$

$$B_{0}' = \left(\frac{\partial B}{\partial P}\right)_{P=0} \tag{3}$$

The expression for the equation of state is obtained by expanding the free energy f in the form of a series:

$$f = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{\frac{-2}{3}} - 1 \right]$$
(4)

The internal energy, E(V), is found by integration of the pressure:

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}} \right] \right\}$$
(5)

3. Pressure-induced electronic structure changes of monoclinic bulk PdSe₂ (SG *I*2/a)

As shown in Fig. S1(a), the calculated band structure with PBE functional indicates the monoclinic I2/a phase is a semimetal at ambient-pressure, where the conduction band minimum (CBM) and the valence band maximum (VBM) are cross over the Fermi level, forming a pair of electron and hole pockets located between C₂(-0.298, 0.701, 0) and Y₂(-0.5, 0.5, 0). The CBM mainly originates from the Pd 4d states, whereas the VBM mainly originates from a symmetric distribution of Pd 4d and Se 4p states. The PBE functional often underestimates the band gap value, and the HSE screened Coulomb hybrid density functional open a tiny gap of ~ 0.1 eV for the monoclinic I2/a phase. We note that in the case of *Pbca* phase, previous experimental measurements show a band gap of 0.4 eV.^[9] However, traditional PBE-GGA functional finds metallic behavior,^[5] whereas the modified Becke-Johnson (mBJ) potential predicts semiconductor behavior with an indirect gap of 0.03 eV.^[9] In addition, Akinola et al. claim that the energy level of VBM is higher than that of CBM, where optB88 predicting a negative band gap (-0.24 eV) and optPBE yields a much smaller negative band gap (-0.02 eV).^[1] In fact, this negative band gap behavior is a semimetal electronic structure, similar to the predicted results in the present work for the monoclinic I2/a phase within GGA-PBE. Therefore, it requires caution to choose proper functional for theoretical investigation on the monoclinic I2/a phase. It deserves to carry out further electric conductivity experiments and optical measurements to clarify the ground state electronic structure of monoclinic I2/a phase.

The band widths further broaden along with the compression. At pressure of 4 GPa, within PBE functional, the conduction bands overlap with the valence bands, giving rise to metallic behaviors for the monoclinic I2/a phase (**Fig. S1(b**)). On the contrary, HSE functional predicts a semimetal band structure at 4 GPa, where the CBM locates lower than the VBM, forming a pair of

electron and hole pockets between C₂ and Y₂ point. Further increasing the pressure, the monoclinic I2/a phase transforms to C2/m phase at 4.5 GPa and $P\bar{3}m1$ phase at 17.5 GPa, accompanied by electronic structure changing from semimetal (Fig. S1(b)) to metal (Fig. S1(c) and (d)). The strong hybridizations of the Se 4*p* and Pd 4*d* states contribute to the electronic structure around Fermi level. Even within HSE functional, the high pressure C2/m and $P\bar{3}m1$ phases still display metallic band structures. As shown in Fig. 1 in the main text, although the monoclinic I2/a, C2/m and hexagonal $P\bar{3}m1$ phases all exhibit layered structures, the Se-Se distances inside the (Se₂)²⁻ dimer are obviously elongated along with the structure transformation from the I2/a phase to C2/m and $P\bar{3}m1$ phases, resulting in a breakdown of the Se-Se dimer and a noticeably expansion of the interlayer distances. The structural phase transition leads to the coordination geometry changing from the PdSe₄ square-planar to PdSe₆ octahedron and a decrease of the interlayer coupling as well as an increase of the electronic hybridization, further giving rise to a semimetal (I2/a phase) to metal (C2/m and $P\bar{3}m1$ phase) transition.



Fig. S1 Fat band structure along the high symmetric points in the Brillouin zone at different pressure for: (a) I2/a phase at 0 GPa, (b) I2/a phase at 4 GPa, (c) C2/m phase at 4.5 GPa and (d) $P\bar{3}m1$ phase at 17.5 GPa. The bands are projected onto Se 4p and Pd 4d states, denoted by blue and red color balls. The size of the color balls is proportional to the contribution from the corresponding state. The band structures calculated with HSE are plotted with solid lines for the I2/a phase in (a) and (b). The Fermi level is set to zero energy.



Fig. S2 Electronic band structures of the 2D monoclinic monolayer PdSe₂ calculated with GGA (PBE) by DFT-D corrections. The SOC interactions have tiny influences on the dispersion of the band.



Fig. S3 Variations of the band gaps (a) and band edge positions (b) under applied biaxial strains on the 2D monoclinic monolayer PdSe₂.



Fig. S4 Total energy differences between strained and unstrained monoclinic monolayer $PdSe_2$ along *x* and *y* directions.



Fig. S5 Band structure of monoclinic monolayer PdSe₂ for the conventional cell with GGA (PBE) and HSE, the corresponding Brilioun zone as implied inside.



Fig. S6 Band edges of the CBM and VBM (corrected by the vacuum energy) as a function of strain along x and y directions for the 2D monoclinic monolayer PdSe₂. Solid lines are the fitting curves. The fitted slopes correspond to the deformation potential.

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