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# **Supporting Information**

# Ferroelectricity in 2D metal phosphorous trichalcogenides and van der Waals heterostructures for photocatalytic water splitting

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## **Supplementary Methods**

**Phonon spectra of single-layer MPTs.** Finite-displacement method was adopted by combining VASP and Phonopy code. Single  $\Gamma$ -point and 5×5×1 supercell was used for the calculation. The convergence of energy is 10<sup>-8</sup> eV. There exist small imaginary acoustic phonon modes appear in the vicinity of the gamma point, which can be reduced by using larger supercells.

**Polarization reversal process of single-layer MPTs.** The minimum energy path for reversal of polarization was calculated by the nudged-elastic-band (NEB) method. The convergence criterion was set to 10<sup>-5</sup> eV for total energies and 0.05 eV/Å for forces during all the NEB calculations. Single-point energy and polarization value were given at each image. The two energy minima correspond to two ferroelectric (FE) phase structures with opposite polarizations, and the maximum corresponds to the paraelectric (PE) structure.

Ab initio molecular dynamics (AIMD) simulations of single-layer MPTs. AIMD simulations were carried out in the NVT thermostat with single  $\Gamma$ -point in a 4×4×1 supercell. The simulation temperature was varied from 50 K up to 800 K at an interval of 50 K. The duration of simulation was 10 ps in total and the timestep was 2 fs. The statistical average of  $Z_{M1}$ - $Z_{M2}$  as a function of the temperature is shown in Fig. S5 with a sigmoid fitting:

$$\Delta Z = \frac{A}{1 + \mathrm{e}^{(T - T_c)/d}} + B \tag{1}$$

AIMD result of monolayer AgBiP<sub>2</sub>Se<sub>6</sub> doesn't show first-order transition with an obvious transition temperature.

**Polarization reversal in the presence of domain walls.**  $4 \times 1 \times 1$  supercell was used in the domain wall calculations and three initial setups of polarization were constructed, which are up/up/up/up/up/up/up/down, and up/up/down/down respectively. NEB calculations were performed to obtain the energy barrier for polarization reversal.

**Polarization reversal modulated by electric field and strain.** Out-of-plane electric field was added in VASP under the dipole correction scheme, and the strength of electric field was varied from 0 V/Å to 0.3 V/Å at a stepsize of 0.05 V/Å. Uniaxial strain from -3% compressive strain to +3% tensile strain in the in-plane x direction was applied at a stepsize of 1%. NEB calculations were performed to obtain the energy barrier for the polarization reversal in the presence of electric field.

**pDOS and pCOHP analysis by LOBSTER.** The HSE06+D3 functional was used for PAW calculation. Local atomic orbital basis set pbeVaspFit2015 was used for projected crystal orbital Hamilton population (pCOHP) analysis. The atomic orbitals chosen for each element are given as follows: Cu 3d4s, Ag 4d5s, In 4d5s5p, Bi 5d6s6p, P 3s3p, S 3s3p, Se 4s4p.

 $CuInP_2S_6/Zn_2P_2Se_6$  and  $CuInP_2S_6/Mn_2P_2S_6$  heterostructures  $CuInP_2S_6$ ,  $Zn_2P_2Se_6$  and  $Mn_2P_2S_6$  belong to the metal phosphorous trichalcogenide family. The optimized lattice parameters of single-layer  $CuInP_2S_6$ ,  $Zn_2P_2Se_6$  and  $Mn_2P_2S_6$  are

6.126 Å, 6.296 Å and 6.101 Å respectively. To construct CuInP<sub>2</sub>S<sub>6</sub>-based bilayer heterostructures, a unit cell of CuInP<sub>2</sub>S<sub>6</sub> and a unit cell of Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub>/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> were used. The interlayer binding energy is given as

$$E_{binding} = E_{A/B} - E_A - E_B \tag{2}$$

in which  $E_{A/B}$ ,  $E_A$ ,  $E_B$  are total energies of the heterostructure and individual monolayers respectively. After optimization, the lattice parameter of the CuInP<sub>2</sub>S<sub>6</sub>/Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> heterostructure is 6.218 Å, which means a tensile strain of 1.5% is applied to monolayer CuInP<sub>2</sub>S<sub>6</sub> and a compressive strain of 1.2% is applied to monolayer Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub>. Meanwhile, the lattice parameter of CuInP<sub>2</sub>S<sub>6</sub>/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> heterostructure is 6.107 Å, which means a compressive strain of 0.3% is applied to monolayer CuInP<sub>2</sub>S<sub>6</sub> and a tensile strain of 0.1% is applied to monolayer MnP<sub>2</sub>S<sub>6</sub>. The interlayer binding energy of CuInP<sub>2</sub>S<sub>6</sub>/Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> and CuInP<sub>2</sub>S<sub>6</sub>/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> is -0.55 eV and -0.58 eV respectively, indicating the stability of the heterostructures.

Adsorption of water molecule on  $CuInP_2S_6/Mn_2P_2S_6$  with  $CuInP_2S_6$  in the -P state. One water molecule is placed on the surface of both  $CuInP_2S_6$  and  $Mn_2P_2S_6$ . The most stable structure is shown in Fig. S10a and Fig. S10e. The adsorption energy of H<sub>2</sub>O on the heterostructure is defined as

$$E_{\text{adsorption}} = E_{\text{hetero}-\text{H}_2\text{O}} - E_{\text{hetero}} - E_{\text{H}_2\text{O}}$$
(3)

where  $E_{\text{hetero-H}_2O}$ ,  $E_{\text{hetero}}$ ,  $E_{\text{H}_2O}$  are the energies of H<sub>2</sub>O-adsorbed system, pristine heterostructure, and H<sub>2</sub>O molecule. We found that in both cases the adsorption energy was negative, which is -0.17 eV for H<sub>2</sub>O-Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and -0.22 eV for H<sub>2</sub>O-CuInP<sub>2</sub>S<sub>6</sub>. The water molecule could be stabilized by the heterostructure, which is required for the water-splitting process.<sup>1, 2</sup>

**Free energy calculations.** Free energy changes ( $\Delta G$ ) along the water splitting reaction pathway are calculated according to the approach proposed by Nørskov et al.<sup>3, 4</sup> The free energy change is defined as

$$\Delta G = \Delta E + \Delta E_{\rm ZPE} - T \Delta S \tag{4}$$

where  $\Delta E$  is the energy change of the step,  $\Delta E_{ZPE}$  and  $\Delta S$  are the zero-point energy (ZPE) change and the entropy change, respectively, for the adsorbed species. The ZPE and entropy changes of the catalyst were not included in our calculations. The HER has two steps:

$$^{*} + \mathrm{H}^{+} + e^{-} \rightarrow \mathrm{H}^{*}$$
 (a)

$$\mathrm{H}^* + \mathrm{H}^+ + e^- \rightarrow * + \mathrm{H}_2 \tag{b}$$

While the OER follows four steps:

$$* + H_2O \rightarrow OH^* + H^+ + e^-$$
(c)

$$OH^* \rightarrow O^* + H^+ + e^-$$
 (d)

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^-$$
(e)

$$OOH^* \rightarrow *+O_2 + H^+ + e^-$$
(f)

The free energy change after taking into account the pH effect and the external potential can be written as

$$\Delta G_a = G_{H^*} - 1/2G_{H_2} - G_* + \Delta G_U + \Delta G_{pH}$$
(5-a)

$$\Delta G_b = G_* + 1/2G_{\rm H_2} - G_{\rm H^*} + \Delta G_U + \Delta G_{\rm pH}$$
(5-b)

$$\Delta G_c = G_{\rm OH^*} + 1/2G_{\rm H_2} - G_* - G_{\rm H_2O} + \Delta G_U - \Delta G_{\rm pH}$$
(5-c)

$$\Delta G_d = G_{O^*} + 1/2G_{H_2} - G_{OH^*} + \Delta G_U - \Delta G_{pH}$$

$$(5-d)$$

$$\Delta G_e = G_{\rm OOH^*} + 1/2G_{\rm H_2} - G_{\rm O^*} - G_{\rm H_2O} + \Delta G_U - \Delta G_{\rm pH}$$
(5-e)

$$\Delta G_f = G_* + 1/2G_{\rm H_2} - G_{\rm OOH^*} + G_{\rm O_2} + \Delta G_U - \Delta G_{\rm pH}$$
(5-f)

where  $\Delta G_{\rm pH} = 0.0592 \times \text{pH}$  represents the change of free energy contributed by the pH at 298.15 K.

 $\Delta G_U = -e \times U$  with U the potential exerted on an electron by the electrode. In photocatalysis, U is taken as the difference between the absolute potential (4.44 V) of standard hydrogen electrode (SHE) and the CBM position of photocatalyst (with respect to the vacuum level, measured in V) for HER, and it is taken as the difference between the VBM position and absolute potential of SHE for OER.



### **Supplementary Figures and Tables**

**Fig. S1** Bulk structures and cleavage energy. (a) Bulk structure of metal phosphorous trichalcogenides from top and side views. (b) Cleavage energy calculated with a six-layer model.

Table S1 ICSD structural data and ferroelectric properties of bulk MPTs

System	ICSD	Space Group	Polarization Ordering	Transition Temperature (K)
CuInP <sub>2</sub> S <sub>6</sub>	79219	Cc	Ferroelectric	315
CuBiP <sub>2</sub> S <sub>6</sub> <sup>a</sup>	N. A.			
CuInP <sub>2</sub> Se <sub>6</sub>	88074	P31c	Ferroelectric	236
CuBiP <sub>2</sub> Se <sub>6</sub>	170643	P31c	Anti-ferroelectric	173
AgInP <sub>2</sub> S <sub>6</sub>	202185	P31c	Paraelectric	N. A.
AgBiP <sub>2</sub> S <sub>6</sub> <sup>a</sup>	170639	P1		
AgInP <sub>2</sub> Se <sub>6</sub>	71968	P31c	Paraelectric	N. A.
AgBiP <sub>2</sub> Se <sub>6</sub>	170640	R3h	Anti-ferroelectric	< 300

 $^aBulk\ ferroelectric\ phase\ structures\ of\ CuBiP_2S_6\ and\ AgBiP_2S_6\ were\ constructed\ by\ elemental\ substitutions\ based\ on\ AgInP_2S_6.$ 

Table S2 Summary of optimized structures of single-layer MPTs. M1 = Cu/Ag, M2 = In/Bi, X = S/Se; a, b: lattice constant;  $Z_{M1}$ ,  $Z_{M2}$ : displacement of metal atoms M1 and M2; M1-X, M2-X, and P-X: the corresponding bond length

System	a=b	Thickness	$Z_{\rm M1}$	$Z_{ m M2}$	M1-X	M2-X	P-X
	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)
CuInP <sub>2</sub> S <sub>6</sub>	6.126	3.39	1.37	-0.26	2.23/3.67	2.77/2.60	2.06/2.03
CuBiP <sub>2</sub> S <sub>6</sub>	6.290	3.48	1.35	-0.27	2.25/3.68	2.93/2.78	2.06/2.03
CuInP <sub>2</sub> Se <sub>6</sub>	6.455	3.54	1.29	-0.28	2.36/3.68	2.88/2.74	2.24/2.20
CuBiP <sub>2</sub> Se <sub>6</sub>	6.594	3.60	1.26	-0.30	2.38/3.66	3.02/2.92	2.24/2.20
AgInP <sub>2</sub> S <sub>6</sub>	6.251	3.41	1.17	-0.28	2.48/3.56	2.76/2.62	2.05/2.04
AgBiP <sub>2</sub> S <sub>6</sub>	6.417	3.46	1.21	-0.33	2.51/3.59	2.91/2.81	2.05/2.03
AgInP <sub>2</sub> Se <sub>6</sub> <sup>a</sup>	6.542	3.57	< 0.01	< 0.01	2.89	2.80	2.21
AgBiP <sub>2</sub> Se <sub>6</sub>	6.704	3.60	1.04	-0.34	2.64/3.50	3.00/2.95	2.23/2.20

<sup>a</sup>Monolayer AgInP<sub>2</sub>Se<sub>6</sub> adopts the centrosymmetric structure, with six equivalent bonds and no shift of metal atoms.



**Fig. S2** Phonon spectra of monolayer MPTs. (a)  $CuInP_2S_6$ . (b)  $CuBiP_2S_6$ . (c)  $CuInP_2Se_6$ . (d)  $CuBiP_2Se_6$ . (e)  $AgInP_2S_6$ . (f)  $AgBiP_2S_6$ . (g)  $AgInP_2Se_6$ . (h)  $AgBiP_2Se_6$ . We found tiny small imaginary frequencies for the out-of-plane acoustic phonon mode (ZA) around the G-point. These imaginary frequencies are due to numerical errors, which can be reduced by using larger supercells, and are often seen for the ZA mode of 2D materials, which should exhibit a parabolic dispersion.

Table S3 Total energy of monolayer antiferroelectric (AFE) and ferroelectric (FE) MPTs.  $E_{FE}$  and  $E_{AFE}$  are energies of FE and AFE structures per formula unit, calculated in a 2×1×1 supercell with  $\uparrow\uparrow$  and  $\uparrow\downarrow$  polarizations respectively (see Fig. S3d).  $\Delta E = E_{FE} - E_{AFE}$  is the energy difference between FE and AFE structures, and  $E_{barrier}$  is the transition energy barrier between FE and AFE structures along the minimal energy pathway, as shown below in Fig. S3

System	CuInP <sub>2</sub> S <sub>6</sub>	CuBiP <sub>2</sub> S <sub>6</sub>	CuInP <sub>2</sub> Se <sub>6</sub>	CuBiP <sub>2</sub> Se <sub>6</sub>	AgInP <sub>2</sub> S <sub>6</sub>	AgBiP <sub>2</sub> S <sub>6</sub> <sup>a</sup>	AgBiP <sub>2</sub> Se <sub>6</sub> <sup>a</sup>
E <sub>FE</sub> (eV/fu)	-46.8367	-47.5370	-42.0643	-42.8892	-45.6921	-46.4459	-41.9673
<i>E</i> <sub>AFE</sub> (eV/fu)	-46.8603	-47.5277	-42.0647	-42.8634	-45.6648	N.A.	N.A.
Δ <i>E</i> (meV/fu)	23.6	-9.3	0.4	-25.8	-27.3	N.A.	N.A.
<i>E</i> <sub>barrier</sub> (meV/fu)	145.7	163.3	78.0	86.7	33.1	N.A.	N.A.

<sup>a</sup>After the structural optimization, antiferroelectric monolayer AgBiP<sub>2</sub>S<sub>6</sub> and AgBiP<sub>2</sub>Se<sub>6</sub> will turn into ferroelectric structure.



**Fig. S3** Minimal energy pathway of the FE-AFE transition in single-layer MPTs with/without an external electric field. (a)  $CuInP_2S_6$ . (b)  $CuInP_2Se_6$ . (c) Energy difference between FE to AFE  $CuInP_2S_6$  and  $CuInP_2Se_6$  in the presence of an electric field. (d) Optimized structures of FE (upper panel) and AFE (lower panel)  $CuInP_2S_6$  in a  $2 \times 1 \times 1$  supercell.



**Fig. S4** Minimal energy pathway of the FE-PE-FE transition in single-layer MPTs. (a)  $CuInP_2Se_6$  and  $CuBiP_2Se_6$ . (b)  $AgInP_2S_6$  and  $AgBiP_2S_6$ . (c)  $AgBiP_2Se_6$ . Minimal energy pathway is shown on the left and polarization is given on the right.



**Fig. S5** Statistical average of  $Z_{M1}$  -  $Z_{M2}$  as a function of temperature from AIMD simulations of single-layer MTPs. (a) CuInP<sub>2</sub>Se<sub>6</sub> and CuBiP<sub>2</sub>Se<sub>6</sub>. (b) AgInP<sub>2</sub>S<sub>6</sub> and AgBiP<sub>2</sub>S<sub>6</sub>. (c) AgBiP<sub>2</sub>Se<sub>6</sub>. The ferroelectric transition temperature  $T_c$  is estimated by a sigmoid fitting of the data.



**Fig. S6** Domain wall calculations. (a) Side view of the supercell structure, three initial setups of polarization were constructed. (b) Minimal energy pathway of polarization reversal in the presence of domain walls in single layer Cu-based MPTs.



Fig. S7 Modulation of ferroelectric properties by out-of-plane electric field and uniaxial in-plane strain for single layer Cubased MPTs. (a)  $CuInP_2S_6$ . (b)  $CuBiP_2S_6$ . (c)  $CuInP_2Se_6$ . (d)  $CuBiP_2Se_6$ .



**Fig. S8** Partial density-of-states (pDOS) and projected crystal orbital Hamilton population (pCOHP) of single layer MPTs. (a)  $CuInP_2Se_6$ . (b)  $CuBiP_2Se_6$ . (c)  $AgInP_2S_6$ . (d)  $AgBiP_2S_6$ . (e)  $AgBiP_2Se_6$ . The dashed line denotes the Fermi level position. Those for the paraelectric structure are shown on the left, and for the ferroelectric structure are on the right.



**Fig. S9** CuInP<sub>2</sub>S<sub>6</sub>-based vdW heterostructures. (a) Side view of CuInP<sub>2</sub>S<sub>6</sub>/Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> heterostructures with CuInP<sub>2</sub>S<sub>6</sub> in two oppositely polarized states, +P and -P. (b) Electrostatic potential of CuInP<sub>2</sub>S<sub>6</sub>, polarization causes an energy difference of 0.5 eV on the two sides of the monolayer. (c) Partial density-of-states (pDOS) of CuInP<sub>2</sub>S<sub>6</sub>/Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> with CuInP<sub>2</sub>S<sub>6</sub> in the +P state. (d) pDOS of CuInP<sub>2</sub>S<sub>6</sub>/Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> with CuInP<sub>2</sub>S<sub>6</sub> in the -P state. (e) pDOS of CuInP<sub>2</sub>S<sub>6</sub>/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> with CuInP<sub>2</sub>S<sub>6</sub> in the +P state. (f) pDOS of CuInP<sub>2</sub>S<sub>6</sub>/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> with CuInP<sub>2</sub>S<sub>6</sub> in the -P state.



**Fig. S10** Optimized adsorption structures of different species on  $\text{CuInP}_2\text{S}_6$  (-P)/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> in the HER and OER. (a) H<sub>2</sub>O adsorbed on the P site of Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> layer. (b) OH adsorbed on the P site of Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> layer. (c) O adsorbed on the P site of Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> layer. (d) OOH adsorbed on the P-S bond of Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> layer. (e) H<sub>2</sub>O adsorbed on the Cu site of CuInP<sub>2</sub>S<sub>6</sub> layer. (f) One H adsorbed on the S site of CuInP<sub>2</sub>S<sub>6</sub> layer. (g) Two H adsorbed on the S site and P site of CuInP<sub>2</sub>S<sub>6</sub> layer, respectively.

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Species	E <sub>ZPE</sub> (eV)	<i>-TS</i> (eV)	<i>E</i> (eV)	<i>G</i> (eV)
H <sub>2</sub>	0.27	-0.41	-6.77	-6.91
H <sub>2</sub> O	0.56	-0.67	-14.22	-14.33
*			-104.06	-104.06
H*	0.21	-0.01	-106.04	-105.83
HH*	0.48	-0.01	-109.62	-109.15
OH*	0.37	-0.04	-113.62	-113.29
0*	0.09	-0.02	-108.90	-108.83
00H*	0.41	-0.14	-117.61	-117.35

Table S4 Zero-point energy correction ( $E_{ZPE}$ ), entropy contribution (-*TS*, *T* = 298.15 K), total energy (*E*), and Gibbs free energy (*G*) of molecules and adsorbates on CuInP<sub>2</sub>S<sub>6</sub> (-P)/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>

Gibbs free energy of  $O_2$  was calculated according to the experimental free energy change of  $O_2(g) + 2H_2(g) \rightarrow 2H_2O(l)$ , which is -4.92 eV. As a result, Gibbs free energy of  $O_2$  is -9.92 eV.



**Fig. S11** Free energy diagrams of HER (left panel) and OER (right panel) on  $CuInP_2S_6$  (-P)/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> under different pH conditions. (a) At pH = 2. (b) At pH = 3. (c) At pH = 7.

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