Ferroelectricity in 2D metal phosphorus trichalcogenides and van der Waals heterostructures for photocatalytic water splitting†

Sheng Huang, Zhigang Shuai‡ and Dong Wang‡,*

Integration of ferroelectricity into van der Waals heterostructures offers additional opportunities to control over the properties and functionalities of heterostructures by switching the direction of polarization via an external electric field. To discover potential ferroelectric monolayers that exhibit out-of-plane electric polarizations, we screen a family of metal phosphorus trichalcogenides M1M2P2X6 with M1 = Cu/Ag, M2 = In/Bi, X = S/Se using density functional theory calculations. We predict room-temperature ferroelectricity in CuInP2S6 and CuBiP2S6 monolayers with out-of-plane polarizations (P) of 0.59 μC cm\(^{-2}\) and 0.35 μC cm\(^{-2}\) respectively. The strong metal-chalcogenide M1–X bond in the two Cu and S-based systems is responsible for their high phase transition temperatures. The polarizations in ferroelectric monolayers can persist in van der Waals heterostructures, and band gaps as well as band alignment of the heterostructures can be tuned by switching the polarization direction. Finally, we demonstrate that both visible light absorption and type-II band alignment facilitating fast charge separation can be realized in CuInP2S6/MnInP2S6 and CuInP2S6/ZnP2Se6 ferroelectric heterostructures, which are promising for applications in photocatalytic water splitting.

1. Introduction

Ferroelectric materials with spontaneous electric polarizations switchable by an external electric field have been widely applied in non-volatile memories, field-effect transistors, sensors and other devices.\(^1,2\) A large variety of ferroelectric materials are ferroelectric perovskites with the ABX\(_3\) type crystal structure, including BaTiO\(_3\), PbTiO\(_3\) and emergent organic–inorganic as well as metal-free organic perovskites.\(^3\) A serious issue associated with ferroelectric perovskites is that their thin films often suffer from interactions with the substrate, which can damage their intrinsic spontaneous polarizations, making them difficult to integrate into nanoscale devices.\(^4,5\) As a contrast, van der Waals (vdW) crystals\(^6–9\) with intrinsic layered structures lack dangling bonds when exfoliated into thin layers and they interact weakly with the substrate, which turn them into ideal candidates for ultrathin ferroelectric applications.\(^10\)

For materials to exhibit spontaneous electric polarizations, structures with no centrosymmetry in the polarization direction are a prerequisite. Room-temperature ferroelectricity in atomic thick layers is scarce, so far only a few ferroelectric monolayers have been reported experimentally, including the in-plane polarization observed in single-layer SnS and SnTe,\(^11,12\) the out-of-plane polarization in distorted 1T-MoTe\(_2\) (ref. 13) and both in-plane and out-of-plane polarizations observed in α-In\(_2\)Se\(_3\).\(^14\) Meanwhile, theoretical calculations have predicted a bunch of two-dimensional (2D) ferroelectric materials including PbTe, SbN, BiP and single-element As, Sb, and Te monolayers.\(^15–18\) Most of them have in-plane polarizations, and only a few show out-of-plane polarizations such as 1T-MoS\(_2\), oxide graphene and Sc\(_2\)CO\(_3\).\(^19–21\) We noticed that interesting ferroelectric or anti-ferroelectric orderings were previously discovered in bulk metal phosphorus trichalcogenides (MPTs) that possess vdW layered structures.\(^22,23\) And thin-layered CuInP\(_2\)S\(_6\) with about 20 nm thickness or even 4 nm thickness was shown to be ferroelectric at room temperature.\(^24,25\) Ferroelectric field-effect transistors based on CuInP\(_2\)S\(_6\) and MoS\(_2\) heterostructures and ferroelectric tunnel junctions using CuInP\(_2\)S\(_6\) as the ferroelectric barrier have been fabricated, which work at room temperature and show a large on-off ratio.\(^26,27\) To discover atomic thick ferroelectric materials with out-of-plane polarizations, we screen the family of MPTs, including M1M2P2X\(_6\) with M1 = Cu/Ag, M2 = In/Bi, X = S/Se, using density functional theory (DFT) calculations, and unveil how elemental substitutions at the metal and chalcogenide sites affect the ferroelectricity of 2D MPTs. We predict that all of these MPTs are ferroelectric except for AgInP\(_2\)S\(_6\), but only two of them, CuInP\(_2\)S\(_6\) and CuBiP\(_2\)S\(_6\), exhibit stable out-of-plane polarizations above room temperature. The ferroelectricity of CuInP\(_2\)S\(_6\) and CuBiP\(_2\)S\(_6\) monolayers is also

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investigated in the presence of domain walls, an external electric field and strain, which provides further evidence for the device potential of these 2D ferroelectric materials. Finally, we demonstrate that both the band gaps and band alignment of ferroelectric vdW heterostructures can be modulated by switching the direction of polarization via an electric field, and show that CuInP$_2$S$_6$/Mn$_2$P$_2$S$_6$ and CuInP$_2$Se$_6$/Zn$_2$P$_2$Se$_6$ heterostructures with visible light absorption and type-II band alignment can be applied to photocatalytic water splitting.

2. Computational methods

All the calculations were performed by using the Vienna Ab initio Simulation Package (VASP version 5.4.1). A vacuum layer of 25 Å was added in the out-of-plane direction to avoid interactions between periodic images. The projected augmented wave (PAW) method and Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) were adopted. The cutoff energy of 600 eV for the plane-wave basis combined with Γ-centered $k$-mesh of $9 \times 9 \times 1$ was used in self-consistent calculations. The convergence criterion was $10^{-6}$ eV for the total energy, and $10^{-3}$ eV Å$^{-1}$ for forces during structural optimizations. To account for van der Waals interactions, Grimme’s D3 dispersion correction to the total energy was applied throughout the calculations. After structural optimizations with the PBE-D3 functional, a hybrid functional developed by Heyd, Scuseria and Ernzerhof (HSE06) was used in the electronic band structure and density of states (DOS) calculations for all the systems. To consider the on-site Coulomb interactions of transition metal Mn, the DFT+U method was applied with an effective U of 4 eV according to the literature to optimize the structure of Mn$_2$P$_2$S$_6$ and CuInP$_2$S$_6$/Mn$_2$P$_2$S$_6$. Spin-polarized calculations were performed for all the systems, with an initial spin of 1 on each atom and 5 on Mn atom. The results show that all the MPTs are non-magnetic except for Mn$_2$P$_2$S$_6$ and heterostructures based on it.

To examine the stability of the monolayer ferroelectric structure, phonon spectra were obtained with the finite-displacement method by combining the VASP and Phonopy code. The ab initio molecular dynamics simulations were carried out in a $4 \times 4 \times 1$ supercell at the Γ-point only. Ferroelectric polarizations were obtained using the Berry phase approach, and both ionic and electronic contributions were taken into account. The energy barrier for the polarization reversal process was obtained with the nudged-elastic-band (NEB) method. The external electric field in the out-of-plane direction was applied by inserting a dipole layer in the middle of the vacuum region. The LOBSTER code was used to analyze the bond strength (pCOHP) and projected density-of-states (pDOS) based on the PAW calculations of solids.

3. Results and discussion

3.1 Structure of MPTs

Bulk metal phosphorus trichalcogenides adopt a hexagonal lamellar structure. In each lamella of MPTs, metal atoms occupy 2/3 of the octahedral holes defined by the chalcogenide framework, while P–P dimers occupy the remaining 1/3. Each S/Se atom is bonded to a single P atom and coordinated by two metal atoms, forming an MPX$_3$ type structure. The crystal structures of bulk MPTs were taken from the ICSD database (Table S1†). Bulk MPTs have weak interlayer vdW interactions; actually thin layered MPTs such as CuInP$_2$S$_6$ and CuCrP$_2$S$_6$ have been recently fabricated by mechanical exfoliation methods, and we expect a monolayer can be easily cleaved from the bulk. The cleavage energy of all eight MPTs was calculated and it is smaller than that of graphite, manifesting the feasibility of fabricating single-layer and few-layer MPTs by exfoliations (Fig. S1†).

The optimized structures of single-layer MPTs are shown in Fig. 1a. All of them, except for AgInP$_2$Se$_6$, share similar structures with no centrosymmetry. Instead of locating at the...
octahedral site, M1 = Cu/Ag atoms shift predominantly in the out-of-plane direction. As a result of the large off-center shift of M1 atoms, three short metal-chalcogenide (M1–X) bonds and three long metal-chalcogenide (M1–X) bonds are formed, instead of six equivalent bonds. Meanwhile, there exists a smaller shift of M2 = In/Bi atoms in the opposite direction. The dynamical stability of single-layer structures was confirmed by phonon spectra lack of imaginary frequencies and molecular dynamics simulations (Fig. S2†). The structural parameters of single-layer MPTs are summarized in Table S2,† in which ZM1 and ZM2 represent the off-center displacement of metal atoms in the out-of-plane direction. The shift of M1 in CuInP2S6 (1.37 Å) is larger than that in CuInP2Se6 (1.29 Å) and AgInP2S6 (1.17 Å), indicating that the shift in Cu and S-based systems is the largest. As a result, the polarization in CuInP2S6 is the largest among all MPTs.

Several previous theoretical studies predicted that single-layer CuInP2S6 and CuInP2Se6 are anti-ferroelectric based on PBE-D3 and PBE-D2 calculations.42–44 They also showed that in the presence of compressive strain or an electric field, the ground state of single-layer CuInP2S6 and CuInP2Se6 can be tuned to the ferroelectric state. To ascertain that the ferroelectric (FE) monolayers of MPTs can exist, we also calculated the energy of anti-ferroelectric (AFE) configuration in a 2 × 1 × 1 supercell. It turned out that the ferroelectric structure is more stable than the anti-ferroelectric one in CuBiP2S6, CuBiP2Se6, and all Ag-based MPTs. However, the energy of anti-ferroelectric CuInP2Se6 is 0.4 meV per formula unit lower than the ferroelectric one, and that of anti-ferroelectric CuInP2S6 is 23.6 meV lower (Table S3†). The energy of ferroelectric and anti-ferroelectric CuInP2Se6 is almost degenerate. Actually, both anti-ferroelectric and ferroelectric in-plane domains were recently observed in bulk CuInP2Se6.45 We further calculated the transition energy path between anti-ferroelectric and ferroelectric structures in the absence of as well as in the presence of an electric field. Our results show that the minimum energy pathway between AFE and FE CuInP2S6 is 145.7 meV, much larger than the energy difference of 23.6 meV. And, applying an electric field of 0.35 V Å⁻¹ can turn the ground state of CuInP2S6 ferroelectric. The same result holds for monolayer CuInP2Se6 (78 meV energy switching barrier between AFE and FE states versus a 0.4 meV energy difference between them, as shown in Fig. S3†). As a result, it is possible to prepare the ferroelectric CuInP2S6 and CuInP2Se6 monolayers by the application of an electric field and the ferroelectric structures remain stable even after the electric field is removed. In the following, we will only discuss the ferroelectric MPT monolayers.

### 3.2 Ferroelectricity in single-layer MPTs

The off-center displacement of metal atoms breaks centrosymmetry, so the electric polarization in the out-of-plane direction arises. The polarization of single-layer M1M2PₓXₘ falls within a range of 0.35–0.59 μC cm⁻² (Table 1) by assuming an effective thickness of 6.5 Å for the monolayer. The polarization in single-layer CuInP2S6 is the largest, and it is two orders-of-magnitude lower than that in prototypical bulk ferroelectric BaTiO₃ (≈26 μC cm⁻²). The small polarizations in MPTs mainly arise from displacements of metal atoms M1 and M2 in opposite directions, whose contributions to overall polarization cancel out to some extent, forming the so-called ‘ferroelectric’ pattern.

Below we take two Cu and S-based systems, CuInP2S6 and CuBiP2S6 as examples, to unravel the polarization reversal behavior of 2D MPTs. Firstly, minimal energy pathway (MEP) mapping between two stable ferroelectric phase structures with opposite polarizations is constructed by the nudged-elastic-band (NEB) method. As shown in Fig. 1b and 2a, the high-energy structure is centrosymmetric with all metal atoms located at the octahedral center, which represents the paraelectric structure. A typical ferroelectric–paraelectric–ferroelectric transition pathway is identified, with an activation barrier of 335 meV per unit cell in CuInP2S6 and 326 meV in CuBiP2S6. Along the structural phase transition path, metal atoms exhibit large off-center displacement perpendicular to the atomic plane, resulting in the polarization of 0.59 μC cm⁻² in CuInP2S6 and 0.35 μC cm⁻² in CuBiP2S6 (Fig. 2b). Subsequently, ab initio molecular dynamics simulations at temperatures between 50 K and 800 K were performed. Taking the out-of-plane z-coordinate difference between metal atom M1 and M2 (ZM1 – ZM2) as the

<table>
<thead>
<tr>
<th>System</th>
<th>ZM1 – ZM2 (Å)</th>
<th>Pₑ (μC cm⁻²)</th>
<th>E₀ (meV)</th>
<th>Tₐ (K)</th>
<th>Length of M1–X bond (Å)</th>
<th>IpCOHP of M1–X bond (eV)</th>
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<tr>
<td>CuInP2S6</td>
<td>1.63</td>
<td>0.59</td>
<td>335</td>
<td>486</td>
<td>2.23</td>
<td>–5.77</td>
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<tr>
<td>CuBiP2S6</td>
<td>1.62</td>
<td>0.35</td>
<td>326</td>
<td>394</td>
<td>2.25</td>
<td>–5.95</td>
</tr>
<tr>
<td>CuInP2Se6</td>
<td>1.57</td>
<td>0.44</td>
<td>166</td>
<td>254</td>
<td>2.36</td>
<td>–5.57</td>
</tr>
<tr>
<td>CuBiP2Se6</td>
<td>1.56</td>
<td>0.39</td>
<td>160</td>
<td>194</td>
<td>2.38</td>
<td>–5.71</td>
</tr>
<tr>
<td>AgInP2S6</td>
<td>1.45</td>
<td>0.46</td>
<td>31</td>
<td>143</td>
<td>2.48</td>
<td>–4.66</td>
</tr>
<tr>
<td>AgBiP2S6</td>
<td>1.54</td>
<td>0.35</td>
<td>62</td>
<td>268</td>
<td>2.51</td>
<td>–4.86</td>
</tr>
<tr>
<td>AgInP2Se₆</td>
<td>1.38</td>
<td>0.34</td>
<td>25</td>
<td></td>
<td>2.64</td>
<td>–4.81</td>
</tr>
</tbody>
</table>

* Monolayer AgInP2Se₆ adopts a stable centrosymmetric structure without off-center displacement of metal atoms and ferroelectricity. * Monolayer AgBiP2Se₆ doesn’t show first-order transition with an obvious transition temperature (see Fig. S4c).
order parameter, its time evolution clearly shows that single-layer ferroelectric CuInP$_2$S$_6$ and CuBiP$_2$S$_6$ can maintain their polarizations at temperatures up to 350 K, while at further higher temperatures polarizations diminish gradually, which is manifested by the disordered positions of Cu metal atoms. The statistical average of $Z_{M1} - Z_{M2}$ as a function of the temperature demonstrates phase transition to occur at $T_C$ of 486 K and 394 K (Fig. 2c and Table 1), suggesting stable ferroelectricity in these Cu and S-based MPTs against room temperature. The results of other MPTs are provided in Fig. S4 and S5,† suggesting stable ferroelectricity in these MPTs against room temperature. The results of Fig. 2c and Table 1), suggesting stable ferroelectricity in these MPTs against room temperature. The results of Fig. 2c and Table 1), suggesting stable ferroelectricity in these MPTs against room temperature. The results of Fig. 2c and Table 1), suggesting stable ferroelectricity in these MPTs against room temperature. The results of Fig. 2c and Table 1), suggesting stable ferroelectricity in these MPTs against room temperature. The results of Fig. 2c and Table 1), suggesting stable ferroelectricity in these MPTs against room temperature. The results of Fig. 2c and Table 1), suggesting stable ferroelectricity in these MPTs against room temperature. The results of Fig. 2c and Table 1), suggesting stable ferroelectricity in these MPTs against room temperature.

The above results are based on MPTs with an ideal ferroelectric structure of infinite size. In experiment, domain walls between oppositely polarized states were observed in thin-layered CuInP$_2$S$_6$. To explore the polarization reversal process in the presence of domain walls, we built an ideal ferroelectric structure ($\uparrow \uparrow \uparrow \downarrow$) and two possible domain wall structures ($\uparrow \uparrow \uparrow \downarrow$ and $\uparrow \uparrow \downarrow \downarrow$) in a $4 \times 1 \times 1$ supercell (Fig. S6a†). The energy of domain wall structures is very close to that of the ideal ferroelectric structure, indicating that these domain walls are easy to form. A similar MEP mapping between two degenerate ferroelectric states ($\uparrow \uparrow \uparrow \downarrow$ and $\downarrow \downarrow \downarrow \downarrow$) through domain wall structures ($\uparrow \uparrow \uparrow \downarrow$ and $\uparrow \uparrow \downarrow \downarrow$) has been calculated (Fig. S6b†). It shows that the energy barrier for polarization reversal is substantially lowered in the presence of domain walls. In CuInP$_2$S$_6$, it decreases from 335 meV per unit cell to 70 meV per unit cell in the transition from the $\uparrow \uparrow \uparrow \uparrow$ to $\uparrow \uparrow \uparrow \downarrow$ state, and 73 meV per unit cell in the transition from the $\uparrow \uparrow \uparrow \uparrow$ to $\uparrow \uparrow \downarrow \downarrow$ state. These results manifest that the presence of domain walls between oppositely polarized domains actually facilitates the reversal of electric polarization along the kinetic pathway.

### 3.3 Ferroelectricity modulated by an electric field and strain

The electric polarization of ferroelectric materials can be reversed by the application of an external electric field. After an electric field is applied in the out-of-plane direction, the two oppositely polarized ferroelectric states are no longer degenerate. Their energy difference increases linearly with the electric field, as shown in Fig. S7,† so the population difference increases exponentially with the electric field. Meanwhile, the activation barrier decreases linearly with the electric field. At an electric field of 0.3 V Å$^{-1}$, the energy difference between the two oppositely polarized ferroelectric states of CuInP$_2$S$_6$ is as large as 47 meV per unit cell and the activation barrier is lowered by 26 meV per unit cell. On the other hand, ferroelectric materials are also piezoelectric, which means ferroelectricity can be tuned by the application of strain. We show that after a uniaxial strain is applied along the in-plane $x$ direction, both the activation barrier and the electric polarization are modulated to some extent. The activation barrier decreases in the presence of a compressive strain (Fig. S7†). The polarization decreases too, but the variation in the polarization is less dramatic than that in the activation barrier. An opposite trend has been observed when a tensile strain is applied. We attribute the decreased polarization with the application of the compressive strain to the decreased distance between M1 and M2, and the increased polarization with the tensile strain to the increased distance between M1 and M2.

### 3.4 Elemental substitution effect on the ferroelectricity of 2D MPTs

The ferroelectric properties of all single-layer MPTs, M$_1$M$_2$P$_2$X$_6$ with M$_1$ = Cu/Ag, M$_2$ = In/Bi, X = S/Se have been shown in Table 1. Among them, CuInP$_2$S$_6$ and CuBiP$_2$S$_6$ exhibit the highest Curie temperature above 300 K and the highest energy barrier of polarization reversal (>300 meV per unit cell), while...
CuInP$_2$Se$_6$ and CuBiP$_2$Se$_6$ exhibit the Curie temperature around 200 K and a moderate energy barrier (~160 meV). Ag-based systems have the lowest energy barrier (~100 meV). Clearly, elemental substitutions at the M1 metal site and X chalcogenide site significantly affect their polarization stability, while that at the M2 metal site has a marginal effect. Overall, we found superior ferroelectricity in Cu and S-based systems compared to Ag and Se-based ones.

To explain the substitution effect on the ferroelectricity of MPTs, we analyzed the partial density-of-states (pDOS) and projected crystal orbital Hamilton population (pCOHP) (Fig. 3) of both ferroelectric and paraelectric phase structures. pCOHP analysis can decompose energy of an electronic state in extended systems into contributions from chemical bonds. The negative and positive values of pCOHP indicate bonding and anti-bonding features of a certain bond, respectively. In the paraelectric phase of all single-layer MPTs, the valence band is featured predominantly by the metal-chalcogenide M1–X antibond while the conduction band is featured by the M2–X antibond. In the ferroelectric phase, a significant change is identified near the Fermi level (0 eV): accompanying the ferroelectric distortion and off-center displacement of M1, the anti-bonding feature of M1–X bond is remarkably diminished. The reduction of M1–X anti-bonding strength is observed in all ferroelectric MPTs (Fig. S8†), so we conclude that the M1–X (Cu/Ag–S/Se) bond plays a key role in stabilizing the ferroelectric structure. Since Cu and Ag atoms, as well as S and Se atoms are in the same group in the periodic table, and the atomic radius of Cu is smaller than that of Ag, and the atomic radius of S is smaller than that of Se, the Cu–S bond is shorter than the Cu–Se, Ag–S and Ag–Se bonds as shown in Table 1, which leads to a more stable ferroelectric structure in Cu and S-based MPTs. Indeed, integrated pCOHP (IpCOHP) of the M1–X bond over the entire energy range below the Fermi level shows that IpCOHP of the Cu–S bond is most negative, which implies that the Cu–S bond is the strongest, followed by Cu–Se, Ag–S and Ag–Se. The strength of the M1–X bond correlates positively with the ferroelectric stability of M1M2P$_2$X$_6$. In contrast, the M2 (In/Bi) metal atom contributes little to the DOS near the Fermi level (Fig. 3), so substitution at the M2 site has little effect on the ferroelectric stability, but substitution of In with Bi does affect the magnitude of electric polarization.

### 3.5 Ferroelectricity in vdW heterostructures

Finally, we demonstrate the device potential of 2D ferroelectric MPTs. A bilayer vdW heterostructure is constructed by stacking a monolayer of Zn$_2$P$_2$Se$_6$ or Mn$_2$P$_2$Se$_6$ on top of a monolayer of CuInP$_2$Se$_6$ which is in the polarization state +P or −P (Fig. 4a). We use these two examples to show the tunable electronic properties of ferroelectric heterostructures by means of polarization reversal. Both Zn$_2$P$_2$Se$_6$ and Mn$_2$P$_2$Se$_6$ monolayers are non-ferroelectric and they show little lattice mismatch with CuInP$_2$Se$_6$ (see Methods in the ESI†). The MEP mapping between +P and −P states in the CuInP$_2$Se$_6$/Zn$_2$P$_2$Se$_6$ heterostructure shows that the activation barrier is 438 meV from the +P to −P state and 342 meV from the −P to +P state (Fig. 4b). However the activation barrier in the CuInP$_2$Se$_6$/Mn$_2$P$_2$Se$_6$ heterostructure is 389 meV from the +P to −P and 299 meV from the −P to +P state. In both heterostructures, +P and −P states are no longer degenerate, due to the interlayer interactions. The activation barriers of polarization reversal are almost the same as those in the ferroelectric monolayer of CuInP$_2$Se$_6$ indicating that the room-temperature ferroelectricity of CuInP$_2$Se$_6$ can be retained in vdW heterostructures. As other MPTs, single-layer CuInP$_2$Se$_6$ is a semiconductor with an indirect band gap of 2.79 eV. Due to the presence of an intrinsic dipole in the monolayer, the vacuum energy at the opposite sides of CuInP$_2$Se$_6$ differs by 0.50 eV (Fig. S9†). After the direction of polarization is reversed by the external electric field, the band offset between Zn$_2$P$_2$Se$_6$ and CuInP$_2$Se$_6$ monolayers will be shifted by 0.42 eV (which is close to the vacuum energy difference), and the band gap of the heterostructure is reduced from 1.98 eV in the +P state to 1.56 eV in the −P state (Fig. 4c and d). In both cases, the band alignment is of type-II with the valence band maximum (VBM) from Zn$_2$P$_2$Se$_6$ and the conduction band minimum (CBM) from CuInP$_2$Se$_6$. However in the CuInP$_2$Se$_6$/Mn$_2$P$_2$Se$_6$ heterostructure, both the CBM and the VBM are from CuInP$_2$Se$_6$ in the +P state, giving rise to the type-I band alignment and a band gap of 2.86 eV close to that in monolayer CuInP$_2$Se$_6$. When CuInP$_2$Se$_6$ is in the −P state, the band alignment is of type-II with the VBM from Mn$_2$P$_2$Se$_6$ (only 0.06 eV higher than that of CuInP$_2$Se$_6$) and the band gap is 2.73 eV (Fig. 4e and f). Ferroelectric heterostructures based on CuInP$_2$Se$_6$ and g-C$_3$N$_4$ have been reported, which display substantially accelerated charge transfer and an enhanced photocatalytic H$_2$ evolution rate over paraelectric-phase CuInP$_2$Se$_6$. To demonstrate the potential of these ferroelectric
heterostructures for water splitting, the absolute band energy is obtained. Both heterostructures in both P+ and P− states show a valence band energy lower than the redox potential of O2/H2O (−5.67 eV) and the conduction band energy higher than the redox potential of H+/H2 (−4.44 eV), indicating their potential abilities of photocatalytic water-splitting. By switching the ferroelectric polarization, the band gap in the CuInP2S6/ Zn2P2Se6 heterostructure is tuned by 0.42 eV to the near-infrared region, while the band alignment in CuInP2S6/Mn2P2S6 is tuned from type-I to type-II, which can promote electron and hole separation.

DFT methods have been widely applied to reveal the photocatalytic activity of 2D materials, including 2D ferroelectric materials.48–52 To show the catalytic activity of the ferroelectric heterostructure for water splitting, we calculated the free energy change of the HER and OER on CuInP2S6/Mn2P2S6 with CuInP2S6 in the −P state. In photocatalytic water splitting, the potential of photogenerated electrons for the HER (Uc) arises from the energy difference between the CBM and the absolute potential of the hydrogen electrode, while that of photogenerated holes for the OER (Uc) is taken as the energy difference between the absolute potential of the hydrogen electrode and the VBM. At pH = 0, Uc and U0 of CuInP2S6 (−P)/ Mn2P2S6 are 0.49 eV and 2.23 eV, respectively. More computational details can be found in Table S4 and Methods in the ESL† As shown in Fig. 4h for the HER, the free energy change of the first electron transfer step to form the H* intermediate is 1.68 eV. At the potential generated by photoexcitation (Uc = 0.49 eV), it is reduced to 1.19 eV, but still too high to activate the HER. However, when we consider a higher hydrogen coverage on the photocatalyst, such as the catalyst with one hydrogen already adsorbed to it as shown in Fig. S10,† the free energy change for the H* formation step is significantly reduced to 0.14 eV and the HER becomes energetically downhill with the help of photogenerated electrons (Uc = 0.49 eV). The OER follows a four-proton and four-electron pathway with the intermediates OH*, O*, and OOH*. The free energy profile for the OER on CuInP2S6 (−P)/Mn2P2S6 is shown in Fig. 4i. The third step in which O* is oxidized to OOH* is the rate-limiting step since the free energy change in this step is the highest. At the potential produced by photoexcitation (Uc = 2.23 eV), the free energy change of this step has been reduced to 0.13 eV. We further analysed the pH effect on the HER and OER processes catalysed by CuInP2S6 (−P)/Mn2P2S6. As we can see from Fig. S11,† with the help of photogenerated electrons and holes, both the HER and OER are energetically downhill at pH = 3. Based on these calculations, we conclude that the CuInP2S6 (−P)/Mn2P2S6 ferroelectric heterostructure with type-II band alignment could be a promising photocatalyst for the water splitting process. In addition to photovoltaic and photocatalytic applications, ferroelectric vdW heterostructures also offer unique opportunities for realizing ultrathin non-volatile memories, field-effect transistors and other ferroelectric devices with new functionalities.

4. Conclusions

To summarize, we report two room-temperature 2D ferroelectric materials, CuInP2S6 and CuBiP2S6, discovered in the family of metal phosphorus trichalcogenides M1M2P2X6 with M1 = Cu/Ag, M2 = In/ Bi, X = S/Se. Both phonon dispersion calculations and first-principles molecular dynamics simulations confirm that MPTs can be mechanically exfoliated down to a single layer. All of them, except for AgInP2Se6, exhibit ferroelectric
polarizations in the out-of-plane direction. The ferroelectric properties of Cu and S-based MPTs are superior to those of Ag and Se-based ones, because of the strong metal-chalcogenide bond M1–X, which plays an essential role in stabilizing the ferroelectric phase structure. CuInP2S6 and CuBiP2S6 monolayers exhibit a Curie temperature, $T_C$, of 486 K and 394 K, and the electric polarization, $P_e$, of 0.59 μC cm$^{-2}$ and 0.35 μC cm$^{-2}$, respectively. Room-temperature ferroelectricity of MPT monolayers can be well retained in vdW heterostructures constructed based on them. We demonstrate that these ferroelectric heterostructures are promising for photocatalytic water splitting, as well as for application in ultrathin nonvolatile memories, field effect transistors, and other ferroelectric devices of broad interest.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**