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**DOI:**

[10.1021/acsnano.7b05856](https://doi.org/10.1021/acsnano.7b05856)

**Document Version**

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

**Citation for published version (APA):**

Long, G., Zhang, T., Cai, X., Hu, J., Cho, C. W., Xu, S., Shen, J., Wu, Z., Han, T., Lin, J., Wang, J., Cai, Y., Lortz, R., Mao, Z., & Wang, N. (2017). Isolation and Characterization of Few-Layer Manganese Thiophosphite. *ACS Nano*, 11(11), 11330-11336. <https://doi.org/10.1021/acsnano.7b05856>

**Published in:**

ACS Nano

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# Isolation and Characterization of Few-Layer Manganese Thiophosphite

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**KEYWORDS:** MnPS<sub>3</sub>, Raman spectroscopy, antiferromagnetic, magnetic susceptibility, electronic transport

## ABSTRACT

This work reports an experimental study on an antiferromagnetic honeycomb lattice of  $\text{MnPS}_3$  that couples the valley degree of freedom to a macroscopic antiferromagnetic order. The crystal structure of  $\text{MnPS}_3$  is identified by high-resolution scanning transmission electron microscopy. Layer-dependent angle-resolved polarized Raman fingerprints of the  $\text{MnPS}_3$  crystal are obtained and the Raman peak at  $383\text{ cm}^{-1}$  exhibits 100% polarity. Temperature dependences of anisotropic magnetic susceptibility of  $\text{MnPS}_3$  crystal are measured in superconducting quantum interference device. Anisotropic behaviors of magnetic moment are explored on the basis of the mean field approximation model. Ambipolar electronic conducting channels in  $\text{MnPS}_3$  are realized by the liquid gating technique. The conducting channel of  $\text{MnPS}_3$  offers a platform for exploring the spin/valleytronics and magnetic orders in 2D limitation.

The magnetic order in 2D limitation is of boundless interest not only for fundamental condensed matter studies but also as a potential candidate in numerous technological applications.<sup>1-7</sup> Despite the extensive family of 2D crystals, only a few exhibit intrinsic magnetic orders.<sup>8-9</sup> Therefore, research has been mostly limited to the magnetic orders arising from extrinsic effects, such as vacancies, defects, edges or chemical dopants.<sup>10-15</sup> An emerging 2D crystal group, namely, transition-metal thiophosphate (TMT) ( $\text{MPX}_3$ ;  $\text{M}=\text{Fe, Ni, Mn, Cd, Zn, etc.}$ ;  $\text{P}=\text{P}$ ;  $\text{X}=\text{S, Se, etc.}$ ), offers possibilities because of the suitability of TMT as a platform for exploring intrinsic magnetic orders.<sup>16-18</sup> Different transition-metal ions in TMT accumulate different antiferromagnetic orders.  $\text{FePS}_3$  is best described by the Ising model, and  $\text{MnPS}_3$  by the isotropic Heisenberg model.<sup>5, 16</sup> The intrinsic degrees of electronic freedom, such as charge and spin, have been broadly explored in the last few decades in electronics and spintronics.<sup>19-22</sup> In recent years,

an electron-valley freedom has drawn much attention because of its immense potential for fundamental studies on quantum concepts and next-generation electronics.<sup>23-25</sup> This valley freedom is predicted to couple with antiferromagnetic order in MnPS<sub>3</sub> because of the latter's antiferromagnetic honeycomb lattice.<sup>26</sup> Coupling the micro-nature to the macro-phenomena renders MnPS<sub>3</sub> an ideal playground for exploring electronic degrees of freedom. In this work, we perform a systematic optical and electronic transport study of MnPS<sub>3</sub> in an atomically-thin level. In addition to identifying the crystal structure with high-resolution scanning transmission electron microscopy (HRSTEM), Raman fingerprints of MnPS<sub>3</sub> with different thickness are also determined through angle-resolved polarized Raman (ARPR) spectroscopy. Temperature dependence of magnetic susceptibility of MnPS<sub>3</sub> is measured by a superconducting quantum interference device (SQUID). Anisotropic behaviors of magnetic moment are studied based on the mean field approximation (MFA) model. Last, we develop a liquid gating (LG) technique and fabricate MnPS<sub>3</sub>-based electrical double-layer transistors (EDLTs) to determine its electronic transport properties. Benefiting from the high efficiency of LG,<sup>27</sup> an ambipolar conducting channel is observed with thickness-dependent carrier mobility of a few cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in MnPS<sub>3</sub>.

## RESULTS AND DISCUSSION

Top view of monolayer MnPS<sub>3</sub> is illustrated in Fig. 1a (Upper left panel). Each [P<sub>2</sub>S<sub>6</sub>]<sup>4-</sup> unit is located at the center of a regular hexagon with six corners occupied by [Mn]<sup>2+</sup>. The dumbbell-shaped structure of [P<sub>2</sub>S<sub>6</sub>]<sup>4-</sup> is shown in Fig. 1b. All the [Mn]<sup>2+</sup> are arranged in a honeycomb structure, and each [Mn]<sup>2+</sup> is surrounded by six sulfur atoms. The zigzag direction of [Mn]<sup>2+</sup> is defined as the *a* direction, whereas the armchair direction (perpendicular to *a*) is defined as *b*. The

point group of monolayer  $\text{MnPS}_3$  is assigned to be  $\bar{3} 2/m$ .<sup>28</sup> The threefold inverse rotation symmetry results a valley degeneracy at the corner (K point) of the hexagonal first Brillouin zone (BZ). When stacked together along the  $c$  direction ( $\beta = 107.5^\circ$ ), the atomic layers break the threefold inverse rotation symmetry and render the bulk  $\text{MnPS}_3$  a monoclinic structure with a point group of  $2/m$  (Fig. 1a, right panel). We notice that single molecular layers of  $\text{Mn}_{0.8}\text{PS}_3$  and  $\text{Cd}_{0.8}\text{PS}_3$  in suspension in water has been obtained by the ion exchange method.<sup>29</sup> However the ion exchange leads to structure factor modulations and permits access to the intrinsic properties of few-layer  $\text{MnPS}_3$  crystal.<sup>29</sup> Given the weak van der Waals interaction between atomic layers, the mono- and few-layered  $\text{MnPS}_3$  flakes can be mechanically exfoliated from the bulk crystal by scotch tape method.<sup>30-31</sup> Fig. 1c shows a representative micro-optical image of  $\text{MnPS}_3$ , with different layers showing distinct optical contrasts due to light interference. To confirm the thickness of these flakes, we perform atomic force microscopy (AFM) measurement and a thickness  $h$  of 0.8 nm is obtained for one atomic layer (Fig. 1d), which agrees well with the layer space of 0.65 nm.<sup>32</sup>

While exfoliating the bulk crystal, we find that most of (>90%) the flakes exhibit hexagonal shapes with inner angles of  $\sim 120^\circ$  (Fig. 1c). To elucidate the mechanism behind the special angle, we compare between the selected-area electron diffraction (SAED) pattern and its defocused transmitted spot to index the edges of the exfoliated  $\text{MnPS}_3$  flakes. The  $\text{MnPS}_3$  flake is kept fixed along the  $c$  direction (Fig. 2a) and the focus is adjusted until the real space features are visible inside the transmitted spot (Fig. 2a, inset). The two edges forming  $60^\circ$  angle are indexed to be (110) and (020) according to the perpendicular relation between the reciprocal space and real space. The (110) and (020) directions correspond to the zigzag directions of  $[\text{Mn}]^{2+}$  in the  $\text{MnPS}_3$  structure. This result can be readily explained by the weakest breaking strength along the zigzag direction of  $[\text{Mn}]^{2+}$ .<sup>33</sup> To verify this conclusion, we obtain a high-angle annular dark field (HAADF)

HRSTEM image of the same sample along the  $c$  direction (Fig. 2b). Each bright spot corresponding to a single atom, the three elements are indicated by different colored balls, and primary unit cell is marked by a green-dashed parallelogram. The six-membered ring composed of manganese atoms is clearly visible. The variation in intensity along the dashed lines are displayed in the right bottom inset. The lattice parameters extracted from the image ( $a=6.08\pm 0.05$  nm;  $b=10.52\pm 0.05$  nm) agree with the values measured from neutron scattering experiment<sup>32</sup> and those obtained from X-ray analysis.<sup>28</sup>

Besides structural identification, we also examine the Raman fingerprints of MnPS<sub>3</sub> with different layer numbers. Fig. 3a shows the Raman spectra of MnPS<sub>3</sub> with different layers collected at room temperature. Two Raman peaks are apparent ( $P_{273}$ :  $273\text{ cm}^{-1}$ ;  $P_{383}$ :  $383.6\text{ cm}^{-1}$ ; the Raman peak at  $302\text{ cm}^{-1}$  is the second-order Raman peak of silicon substrate.<sup>34</sup>) in the 10-nm samples. The intensities of  $P_{273}$  and  $P_{383}$  decrease dramatically with decreasing layer number and disappear in the monolayer flake (Fig. 3b). The main Raman spectral features for the monolayer, bilayer, and trilayer flakes are summarized below. Monolayer flakes exhibit no observable Raman peaks. When layer number increases to two, both  $P_{273}$  and  $P_{383}$  emerge, and  $P_{383}$  is considerably weaker than  $P_{273}$ . For three-layer flakes, the two peaks at  $273\text{ cm}^{-1}$  and  $383\text{ cm}^{-1}$  exhibit similar intensities. The clear dependence of Raman peak intensities on layer number renders the Raman spectrum a reliable criterion for determining the thickness of a few-layer MnPS<sub>3</sub> sample.

To probe further into symmetry properties, we perform ARPR spectral measurements on a 4-layer MnPS<sub>3</sub> flake at room temperature. The ARPR measurement configuration is shown in the top right inset of Fig. 4a. The  $a$  direction (green arrow) runs along one of the edges of the exfoliated MnPS<sub>3</sub> flakes (zigzag direction of MnPS<sub>3</sub>), and the  $b$  direction (blue arrow) is perpendicular to  $a$  direction. The linear polarization direction of the incident laser (purple arrow) and scattered light

(light blue arrow) was illustrated as well. The definitions of angles  $\alpha$  and  $\theta$  are shown in the inset. Fig. 4a presents the ARPR spectra varying with  $\alpha$  when  $\theta$  is fixed at  $0^\circ$ .  $P_{273}$  remains unchanged with increasing  $\alpha$ , whereas the peak at  $383\text{ cm}^{-1}$  vary periodically with  $\alpha$ . Moreover,  $P_{383}$  reaches its maximum at  $0^\circ$  and  $180^\circ$ , and disappears at around  $90^\circ$ . This pattern demonstrates a 100% polarity of Raman peak at  $383\text{ cm}^{-1}$ .<sup>35-36</sup> We perform a fine  $\alpha$  (every  $10^\circ$ ) dependent ARPR measurement and the extracted intensities of the two peaks are shown in Fig. 4b. The black solid line implies  $I(\alpha) = I(\alpha = 0) * \cos^2(\alpha)$ , as expected and measured in varying systems. By contrast, the red dashed line confirms the depolarized feature of  $P_{273}$ .<sup>36</sup> The polarized and depolarized behaviors of Raman peaks demonstrate different symmetry properties of the corresponding phonon modes. Specifically, the polarized behavior of the Raman peak signifies that the peaks arise from totally symmetric variations. Fig. 4c presents the observed ARPR spectra at a few different  $\theta$  with  $\alpha$  fixed at  $0^\circ$ . The independence of the ARPR spectrum on  $\theta$  demonstrates that the crystalline orientation hardly affects the Raman spectrum of  $\text{MnPS}_3$ . The same anisotropic behaviors of the two Raman peaks are also observed in a 10-nm thick  $\text{MnPS}_3$  flake (supporting information). The phonon spectrum and corresponding Raman susceptibilities at the center of the first BZ are calculated through the density function perturbation theory (DFPT)<sup>37-40</sup> to assign the Raman modes and phonon frequencies (supporting information). The bulk crystal of  $\text{MnPS}_3$  belongs to the  $C2/m$  symmetry group. The 30 irreducible phonon modes at the first BZ center are expressed as  $\Gamma = 8A_g + 6A_u + 7B_g + 9B_u$  and confirmed by the calculation results. Our calculation result agree well with the reported one.<sup>41</sup> Polarized peak at  $383\text{ cm}^{-1}$  is assigned to the  $A_g$  mode, whereas the depolarized peak at  $273\text{ cm}^{-1}$  is assigned to the  $B_g$  mode according to the symmetry elements of the  $A_g$  and  $B_g$  modes.<sup>41-42</sup>

The electronic transport properties of MnPS<sub>3</sub> flakes with thickness ranging from 2-layer to 60-layers (around 50 nm) are probed. A large MnPS<sub>3</sub> band gap of more than 3 eV disables chemical potential tuning between the conduction and valence bands by using a field effect with SiO<sub>2</sub> or boron nitride as a dielectric layer.<sup>3</sup> Hence, an LG technique is applied to fabricate the EDLTs, which exhibit increased efficiency (about two orders of magnitude) in tuning the carrier density with respect to that of 300 nm-thick SiO<sub>2</sub>.<sup>27</sup> The high efficiency of LG enables the observation of an ambipolar conducting channel in MnPS<sub>3</sub>. The two-terminal output curves (Fig. 5a) of a MnPS<sub>3</sub> EDLT device of 2-layer channel thickness show large current modulations by both positive and negative LG voltages V<sub>LG</sub>. The channel current I<sub>ds</sub> exhibits super linear dependences on the excitation voltage V<sub>ds</sub>, which is likely caused by a large contact resistance. The improved contact quality is therefore enhance the device performance. The top-left inset shows the optical image of a typical EDLT device, and the top-right inset presents the magnified image of the same device. Fig. 5b reveals the transfer curve and the dramatic increase in channel conductance G when V<sub>LG</sub> is higher (lower) than the positive (negative) threshold voltage demonstrates the ambipolar conducting operation of our EDLTs. When V<sub>LG</sub> varies from +4 V to -3.5 V, the channel switches from n-type “on” state to “off” state and changed to p-type “on” state with an on/off ratio more than 10<sup>4</sup>. The on/off ratio is comparable with the values in widely studied TMDCs. The “off” state roughly ranges from V<sub>LG</sub>=-2.7 V to V<sub>LG</sub>=2.2 V resulting in a “gap” of 4.9 V, and this value of 4.9 V is in consistence with the calculated band gap of MnPS<sub>3</sub> crystal.<sup>4, 43-44</sup> The field effect carrier

mobility  $\mu = \frac{1}{C} \frac{dG}{dV_{LG}} \frac{L}{W}$ , where  $C = 8.4 \mu F cm^{-2}$  is the equivalent capacitance of LG,<sup>27</sup> and L and

W are the length and width of the conducting channel respectively, is estimated for both electrons and holes. The mobility values for electrons and holes are obtained to be  $\sim 1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $\sim 1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. Besides the measurements of bilayer MnPS<sub>3</sub> flakes, we obtain the flake-



thickness dependence of electronic transport behaviors (supporting information). In Fig. 5c, we plot the charge carriers mobilities as a functions of flake thickness. The electron mobility is rather weakly dependent on flake thickness which can be ascribe to combination of three factors. Firstly, the induced charge carrier are confined on the first one or two layers of MnPS<sub>3</sub> flakes due to the static screening effect. The confinement effect has been reported in different layered materials<sup>27, 45</sup> and the confined charge carriers distributions is independent on the flake thickness. Secondly, the flake thickness barely exhibits an impact on the conduction band of MnPS<sub>3</sub> flakes as predicated by theoretical literatures.<sup>43-44</sup> Thirdly, the 3D MnPS<sub>3</sub> bulk has been demonstrated as a high resistor which exhibits a high resistivity of 10<sup>13</sup> Ωcm.<sup>46-47</sup> The intrinsic layers below the biased ones contribute no parallel conducting channels to prohibit the access to the intrinsic properties to the biased one or two layers. As a contrast, the charge mobility of holes gradually increases when the MnPS<sub>3</sub> flake get thicker and thicker, and finally saturates when the flake is thicker than five layers. The saturated mobility is roughly twice of that of bilayer flakes. The saturating behavior of hole mobility for flake thicker than 5 layers arising from the similar sources with the thickness independent electron mobility. When flake is thinner than 5 layers, the thickness dependence of hole mobility may indicate that the magnetic orders in MnPS<sub>3</sub> is modified by the thickness. Firstly, the highest valence band is occupied by the 3d<sup>5</sup> electrons of [Mn]<sup>2+</sup> which construct the magnetic moment of MnPS<sub>3</sub> crystal.<sup>26, 43-44</sup> The same electrons also carry the channel current of P-type MnPS<sub>3</sub> conducting channels. Hence the change of charge carrier mobility of P-type channels indicate the modification of magnetic orders in MnPS<sub>3</sub> crystal thinner than 5 layers. More theoretical and experimental studies are needed to address the complicated dependences of carrier mobility, magnetic orders, and flake thicknesses. 2D MnPS<sub>3</sub> flakes are interesting material because their properties can be modified in-situ by applying V<sub>LG</sub>. It is noticeable that the efficiency of our

LG to modify the conductance of 2D MnPS<sub>3</sub> flakes (on/off ratio = 10<sup>4</sup>) is 10<sup>3</sup> higher than that of light illustrating on 3D MnPS<sub>3</sub> bulks (photo/dark ratio < 10).<sup>46, 48</sup> The ambipolar performance, as well as the high on/off ratio, render MnPS<sub>3</sub> a promising material for low-energy consuming devices with complementary logic. These desirable attributes are crucial to a superb noise margin and robust operation. The creation of an ambipolar conducting channel opens an avenue for exploring the magnetic order in 2D antiferromagnetic systems. This channel also supplies an ideal terrace for probing valleytronics coupled to antiferromagnetic orders.

Figure 6a reveals the temperature dependences of mass magnetic susceptibilities  $\chi_m$  of MnPS<sub>3</sub> bulk crystal for two directions, in-plane  $\chi_{m//}$  and out-plane  $\chi_{m\perp}$  magnetic fields, measured in SQUID. When temperature is above 200 K, the isotropic  $\chi_{m//}$  and  $\chi_{m\perp}$  demonstrate a Heisenberg-type magnetic order in MnPS<sub>3</sub>.<sup>49</sup> In the high temperature paramagnetic phase,  $\chi_m$  follows the Curie-Weiss law  $\chi_m = C / (T - T_C)$ , where  $C = 2.65 \pm 0.05 \times 10^{-4} \text{ m}^3 \text{ K kg}^{-1}$  is the Curie constant and  $T_C = -390 \text{ K}$  is the Curie temperature. According to the MFA model when temperature is sufficiently high, the effective magnetic moment  $\mu_{eff}$  of [Mn]<sup>2+</sup> could be extracted from the Curie constant

according to  $C = \frac{2\mu_0 N \mu_{eff}^2}{3k_B}$ , where  $\mu_0$  is the vacuum permeability,  $N$  is the primitive unit cell

number per unit mass (also the number of [Mn]<sup>2+</sup> pairs per unit mass),  $k_B$  denotes the Boltzmann constant.<sup>50-51</sup> The derived  $\mu_{eff} = 5.6 \mu_B$  agrees well with the total magnetic moment of 3d<sup>5</sup> electron

system in high spin state ( $S=5/2$ )  $\mu_{3d5} = 5.9 \mu_B$ .<sup>16</sup> To confirm the obtained electronic state of Mn element in MnPS<sub>3</sub> crystal, we performed the electron energy-loss spectroscopy (EELS) of few-layer flakes (Fig. 6c). The Mn-L<sub>2,3</sub> edge energy-loss near-edge structures (ELNES) and the chemical shift agree well with the reported [Mn]<sup>2+</sup> spectrum.<sup>52</sup> The value of  $\mu_{eff}$  demonstrates that

manganese is in the form of ions rather than atomic form in MnPS<sub>3</sub>. An large hump at 120K can be described by the critical fluctuation model.<sup>9,53</sup> As temperature cools down, the Curie-Weiss law fails to describe the behavior of  $\chi_m$ . Further cooling down the sample,  $\chi_{m\perp}$  sharply decreases to 0 while  $\chi_{m\parallel}$  remains essentially constant singling the antiferromagnetic order in MnPS<sub>3</sub> with  $T_N=77\text{K}$ .  $T_N$  is in consistence with the report value of 78K.<sup>49</sup>

The contrasting behaviors between  $\chi_{m\perp}$  and  $\chi_{m\parallel}$  in the low temperature regime agree well with the MFA model. The left (right) panel of Fig. 6d present the magnetic susceptibility measurement configuration with an applied magnetic field  $H$  perpendicular (parallel) to the spin orientations. When  $H$  is perpendicular to the spin orientations, the system energy density can be expressed as:  $U = -\mu_0\lambda M^2(1-0.5(2\alpha^2)) - 2\mu_0^2HM\alpha$ , where  $\lambda$  is the Weiss constant,  $M=|M_A|=|M_B|$  is the magnetization strength for the  $[\text{Mn}]^{2+}$  with unit orientation,  $\alpha$  is the orientation of  $M_A$  and  $M_B$  caused by  $H$ .  $U$  reaches its minima at  $\alpha = \mu_0 H / 2\lambda M$ , hence the magnetic susceptibility with  $H$  perpendicular to spin orientations (in-plane magnetic field)

$\chi_{\parallel} = \frac{2M\alpha}{H} = \frac{\mu_0}{\lambda}$  is a constant. The observed slight increase of  $\chi_{m\parallel}$  when cooling down (Fig. 6a)

signals the onset of long-ranged antiferromagnetic order arising from a combination of dipole-dipole anisotropy with inter planar coupling when temperature is lower than  $T_N$ .<sup>18, 32, 53-54</sup> When  $H$  is normal to the layers (right panel of Fig. 6d),  $M_A$  and  $M_B$  make equal angles with  $H$  and the magnetic field is not changed and the  $\chi_{\parallel}(T=0) = 0$  which agrees well with the measured results.

Fig. 6b presents the mass magnetization accompanied with the derivative mass magnetic

susceptibility defined as  $\chi_{md} = \frac{1}{m} \frac{dM}{dH}$  with magnetic field perpendicular to the layer plane at

$T=5\text{K}$ . The mass magnetization exhibits a spin-flop transition feature at  $H_C=3.8\times 10^6 \text{ A/m}$

corresponding to the peak of  $\chi_{md}$ <sup>55-56</sup> as illustrated by the three insets. It is worth noting that the exchange energies of  $[\text{Mn}]^{2+}$  have been accurately measured using neutron scattering technique.<sup>57</sup>

## CONCLUSIONS

In summary, few-layer  $\text{MnPS}_3$  crystal offers a productive platform for exploring antiferromagnetic order and valley degree of electron freedom in 2D limitation. Fundamental crystal parameters, such as lattice constants, layer-dependent Raman fingerprints and Raman peak anisotropy are measured by HRSTEM and ARPR techniques. Identifying the crystal structure and obtaining the Raman spectrum of  $\text{MnPS}_3$  flakes lay a solid foundation for follow-up research. The Heisenberg-type antiferromagnetic order in  $\text{MnPS}_3$  is confirmed by SQUID measurement. Anisotropic behaviors of magnetic moments of  $\text{MnPS}_3$  crystal are discussed based on the MFA model. The confirmation of ambipolar conducting channels in an antiferromagnetic semiconductor opens an avenue for exploring fundamental correlated phenomena, *i.e.* spin/valleytronics coupled to an antiferromagnetic order.

## METHODS

### Crystal Synthesis

The  $\text{MnPS}_3$  single crystals were prepared by a chemical vapor transport method. The stoichiometric mixture of Mn, P, and S powder was sealed in an evacuated quartz tube. Plate-like single crystals can be obtained *via* the vapor transport growth with a temperature gradient from 650 °C to 600 °C. The composition and structure of  $\text{MnPS}_3$  single crystals were checked by X-ray diffraction and Energy-dispersive X-ray spectrometer.

## **TEM Characterization**

The TEM samples are prepared by direct transfer from scotch tapes to 400-mesh copper grids after mechanical exfoliation. The SAED and EELS are carried out with a JEM 2010F (JEOL, Japan) under 200 kV while the HRSTEM is performed with a JEM ARM 200CF (JEOL, Japan), equipped with a CEOS probe corrector and a cold field-emission gun, also at an acceleration voltage of 200 kV for its highest resolution. A low probe current (less than 75 pA) is chosen to reduce electron radiation and a convergence semiangle of around 35mrad and an inner acquisition semiangle of 79 mrad were used in the HAADF STEM. The HRSTEM image is filtered through the standard Wiener deconvolution to increase its signal-noise ratio for a better display. The zero-loss peak in the EELS data is aligned to exact 0 eV and the Mn-L<sub>2,3</sub> edge spectrum go through the power-law background subtraction after that.

## **EDLT Fabrication**

Thin flakes of MnPS<sub>3</sub> are prepared by micro-mechanical exfoliation of a single bulk crystal. The thickness of MnPS<sub>3</sub> flakes is verified by atomic force microscopy. Then the flakes are transferred on the top of another prepared boron nitride flake. Electron-beam lithography (EBL) is then applied to define Hall patterns on the MnPS<sub>3</sub> flakes followed by electron-beam evaporation and lift-off techniques to deposit contact metals in the defined Hall patterns. Finally standard Hall devices with side gate electrodes are fabricated. The contact metal electrodes consist of Ti/Au/SiO<sub>2</sub> (5 nm/60 nm/30 nm) while the side electrodes are not covered by SiO<sub>2</sub>. The contact metal electrodes are covered by SiO<sub>2</sub> to isolate the electrodes from direct contact with the ionic liquid. The sizes of the side-gate electrodes are much larger (area ratio >10<sup>3</sup>) than those of the MnPS<sub>3</sub> flakes. The large area ratio is designed to make sure that the voltage drop is effectively applied at the interface between MnPS<sub>3</sub> flakes and the ionic liquid instead of between the side gate

electrode and ionic liquid. Thanks to the thin electric layer ( $\sim 1$  nm) formed between the ionic liquid and graphene surface, an extremely strong electric field ( $\sim 5 \times 10^9$  V/m) is generated to introduce an extremely high density of charge carriers to the samples ( $\sim 5.23 \times 10^{13}$  V<sup>-1</sup>cm<sup>-2</sup>). The ionic liquid is N, N-diethyl-N-(2-methoxyethyl)-N-methyl ammonium bis-(trifluoromethylsulfonyl)-imide (DEME-TFSI).

## ASSOCIATED CONTENT

### **Supporting Information**

Supporting Information is available free of charge *via* the Internet at <http://pubs.acs.org>. Supporting Information shows an elemental analysis of MnPS<sub>3</sub> flake, the anisotropic Raman peaks of 10 nm-thick MnPS<sub>3</sub> flake, the assignment of MnPS<sub>3</sub> Raman modes and phonon frequencies, electronic transfer curves of MnPS<sub>3</sub> flakes with different thicknesses, and the instability of MnPS<sub>3</sub> flakes.

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### **Author Contributions**

The manuscript was drafted with contributions from all authors. All authors have approved the final version of manuscript.

### **Funding Source**

Research Grants Council of Hong Kong (Project Nos. 16302215, 16300717, GRF16307114 and HKU9/CRF/13G).

U.S. Department of Energy (Grant No. DE-SC0014208)

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGEMENTS

Technical support of the Raith-HKUST Nanotechnology Laboratory for the electron-beam lithography facility at MCPF are acknowledged.

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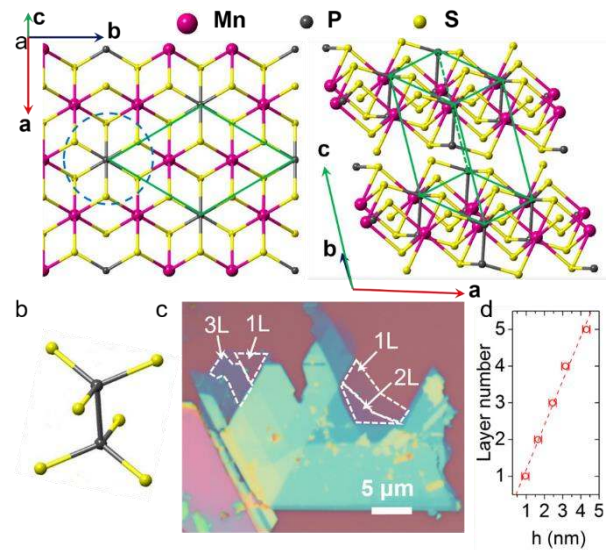
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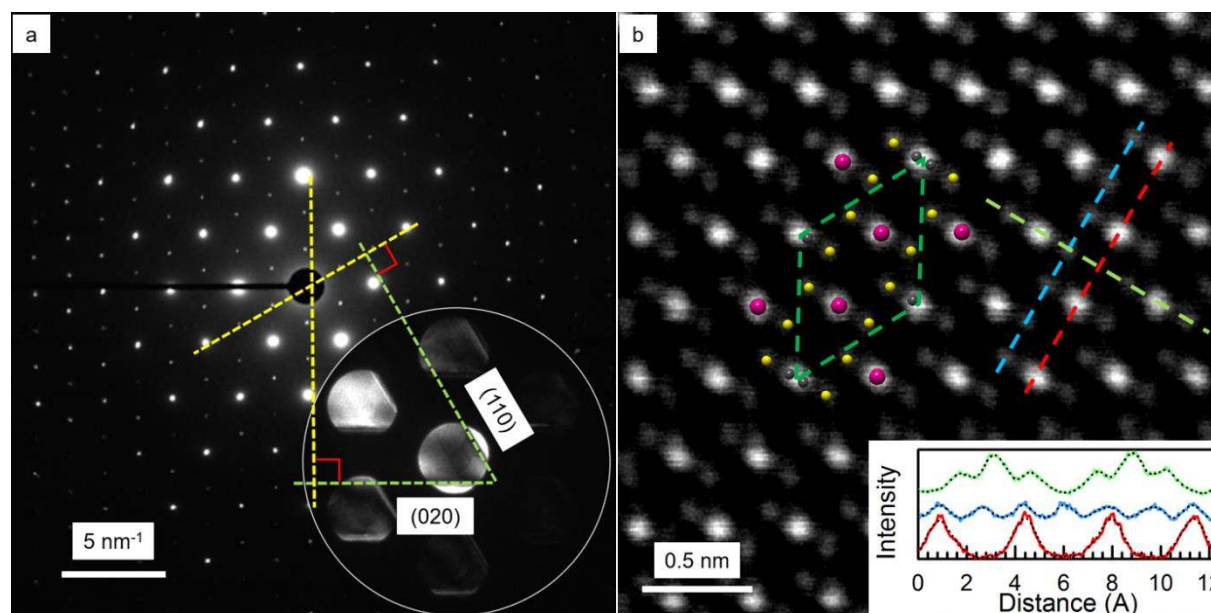
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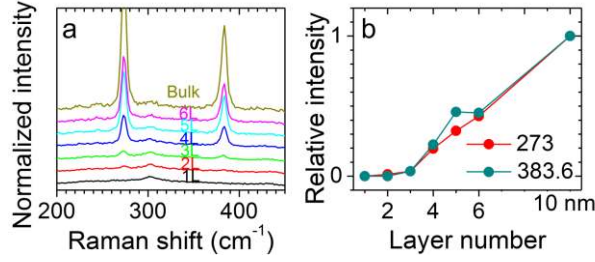
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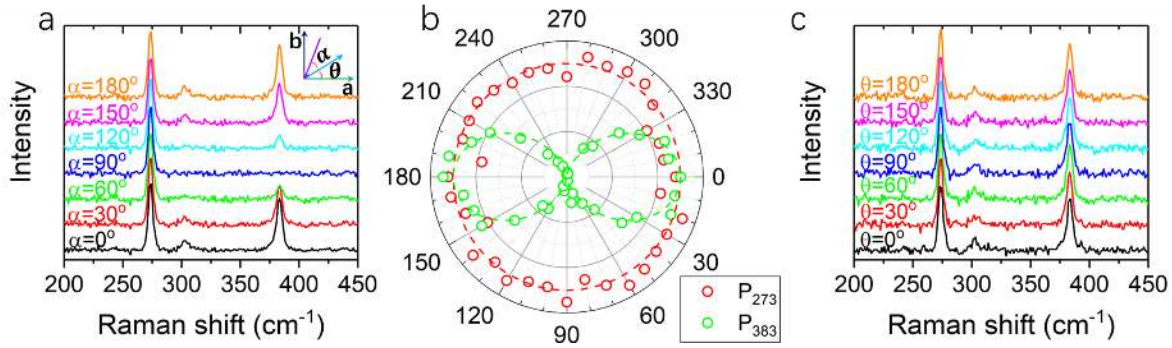
**Figure 1. Crystal structure of MnPS<sub>3</sub>.** (a) Ball-and-stick model of the MnPS<sub>3</sub> crystal structure. The left panel shows the top view of the monolayer model. The green parallelogram indicates the primary unit cell. The arrows show the crystalline orientations (red: a; blue: b; green: c). The right panel displays the side view of the bilayer model, and the green parallelepiped indicates the primary unit cell of the MnPS<sub>3</sub> bulk crystal. (b) The dumbbell-shaped structure of the [P<sub>2</sub>S<sub>6</sub>]<sup>4-</sup> unit is marked by the dashed light blue circle in (a). (c) Micro-optical image of an exfoliated few-layer MnPS<sub>3</sub>. The scale bar denotes 5 μm. (d) Measured thicknesses  $h$  and corresponding layer numbers. The red dashed line represents the linear fitting result.



**Figure 2. Transmission electron microscopy (TEM) images of MnPS<sub>3</sub>.** (a) SAED pattern of MnPS<sub>3</sub>. The scale bar represents 5 nm<sup>-1</sup>. The inset shows the defocused diffraction pattern at the same site. The real space features are apparent in the defocused transmitted spot. The light green dashed lines indicate the two edges of the MnPS<sub>3</sub> sample, whereas the yellow dashed lines show the directions perpendicular to the two edges. A magnetic declination of 3° is corrected. The two edges are indexed to be (110) and (020) according to the diffraction patterns. (b) HAADF STEM image of MnPS<sub>3</sub> sample along c direction. The scale bar represents 0.5 nm. The colored balls indicate the different elements in the image (purple: Mn; black: P; yellow: S). The dashed green parallelogram denotes the primary unit cell. The inset indicates that the intensities vary with distance along the directions, as marked by the dashed lines with the same colors. A constant offset between different lines is introduced for a clear display.

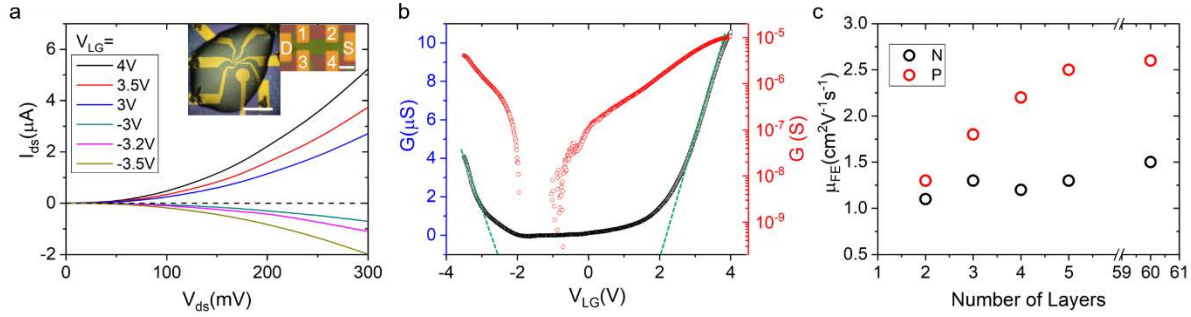


**Figure 3. Thickness-dependent Raman spectrum of MnPS<sub>3</sub>.** (a) Raman spectra of MnPS<sub>3</sub> with different thicknesses (monolayer to 10 nm (~12 layers)). The Raman intensities are normalized to the peak intensity of substrate Si. (b) MnPS<sub>3</sub> Raman peak intensities change with thickness. The peak intensities of the 10 nm sample is regarded as one unit.



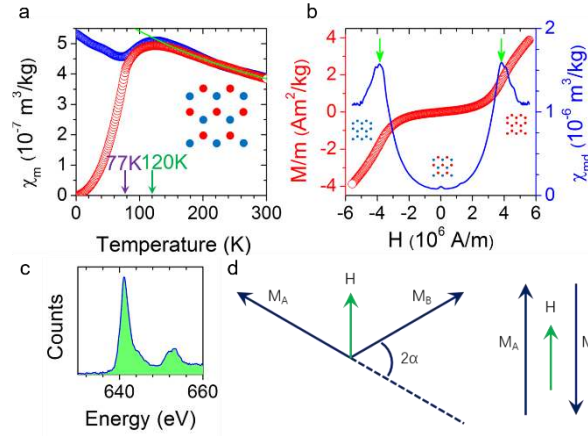
**Figure 4. Angle-resolved polarized Raman spectrum of 4-layer MnPS<sub>3</sub>.** (a) Polarized Raman spectra of MnPS<sub>3</sub> with  $\theta = 0$ . The top-right inset shows the ARPR spectrum measurement configuration. The green and blue arrows indicate the a and b directions, respectively. The purple and light blue arrows indicate the linear polarization directions of the incident and scattered lights, respectively. Angle  $\alpha$  is the angle between the incident and scattered lights, whereas angle  $\theta$  is the angle between the scattered light and the a direction. (b)  $\alpha$ -dependent polarized Raman peak intensities with  $\theta = 0$  (Red: P<sub>273</sub>; green: P<sub>383</sub>). The peak intensities at  $\alpha = 0$  is considered as one unit. The red and green dashed lines display the fitting results of constant intensity and  $\cos^2(\alpha)$ , respectively. (c)  $\theta$ -dependent polarized Raman spectrum with  $\alpha = 0$ .





**Figure 5. Transport features of electrical double layer transistor (EDLT) based on MnPS<sub>3</sub>.**

(a) Output curves of MnPS<sub>3</sub> at different LG voltages. Current of electrons (positive LG voltage) are shown with positive indices, and those of electrons (negative LG voltage) are shown with negative indices. The two insets show the micro-optical images of an EDLT in different ratios. The scale bars denote 300  $\mu m$  (left) and 3  $\mu m$  (right). (b) Room temperature transfer characteristics in linear (black dots) and log (red dots) scales of the MnPS<sub>3</sub> EDLT. The green dashed lines show the linear fitting result of transfer characteristics. (c) Field effect mobilities of holes (red) and electrons (black) of MnPS<sub>3</sub> flakes with thickness ranging from 2 layers to around 60 layers.



**Figure 6. Magnetic susceptibility of MnPS<sub>3</sub>.** (a) Temperature dependences of mass magnetic susceptibility  $\chi_m$  with in-plane (blue) and out-plane (red) magnetic fields of 1600 A/m. The green line shows the fitting result of Curie-Weiss formula. The purple arrow indicate the critical temperature between paramagnetic and antiferromagnetic orders. The green arrow indicate the temperature corresponding to the peak value of  $\chi_m$ . The inset displays the magnetic order of MnPS<sub>3</sub> in antiferromagnetic order regime (blue: spin up; red: spin down; or inverse). (b) Mass magnetization (red) and derivate mass susceptibility (blue) as functions of out-plane magnetic field at T=5K. The three inset patterns display the magnetic orders at magnetic field ranges (blue: spin up; red: spin down; or inverse). The green arrows indicate the peak positions of derivate mass susceptibility. (c) Electron energy loss spectrum (EELS) of the few-layer sample shows characteristic peaks from [Mn]<sup>2+</sup>. (d) Mean field approximation (MFA) model for in- plane (left) and out-plane (right) field magnetic susceptibility in antiferromagnetic regime.  $M_A$  and  $M_B$  indicate the magnetizations with opposite orientations,  $H$  is the applied magnetic field.

TOC:

Raman spectroscopy magnetic susceptibility, and the electronic transport properties of the hexagonal antiferromagnetic lattice in  $\text{MnPS}_3$  are studied. Raman fingerprints of  $\text{MnPS}_3$  with different thicknesses are obtained. Temperature-dependence of anisotropic magnetic susceptibility is obtained to extract critical magnetic parameters like effective magnetic moment of  $[\text{Mn}]^{2+}$ . A liquid gating technique is applied to probe the ambipolar transport properties of  $\text{MnPS}_3$ .

