Electronic Supplementary Material

Inversion symmetry broken 2D SnP_2S_6 with strong nonlinear optical response

Yue Zhang[1], Fakun Wang[1], Xin Feng[1], Zongdong Sun[1], Jianwei Su[1], Mei Zhao[1], Shuzhe Wang[1], Xiaozong Hu[2] (✉), and Tianyou Zhai[1] (✉)

[1] *State Key Laboratory of Materials Processing and Die & Mould Technology, and School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China*
[2] *Henan Key Laboratory of Crystalline Molecular Functional Materials, Henan International Joint Laboratory of Tumor Theranostical Cluster Materials, Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, China*

Supporting information to https://doi.org/10.1007/s12274-021-3806-0

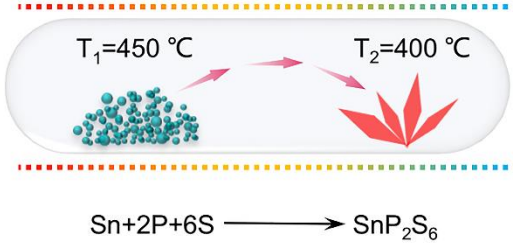

Figure S1 Schematic illustration of the CVT synthesis SnP_2S_6 single crystals.

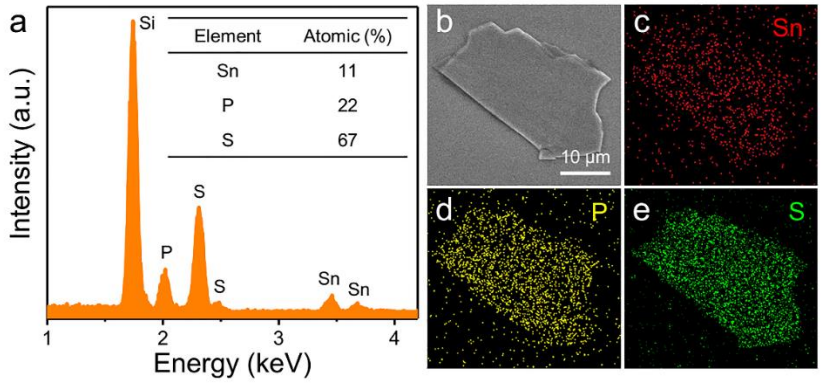

Figure S2 (a) EDS results of an exfoliated SnP_2S_6 flake. (b) SEM image of exfoliated SnP_2S_6 flake. (c-e) Sn, P and S element mapping of exfoliated SnP_2S_6 flake.

Address correspondence to Xiaozong Hu, huxz@zzu.edu.cn; Tianyou Zhai, zhaity@hust.edu.cn

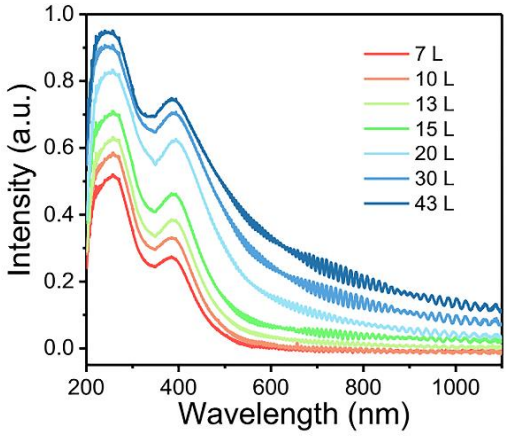

Figure S3 The absorption spectrum of SnP_2S_6 flakes with different thickness. It can be seen that the thicker flakes have the stronger absorption ability, which is consistent with the variation of Raman intensities of 2D SnP_2S_6.

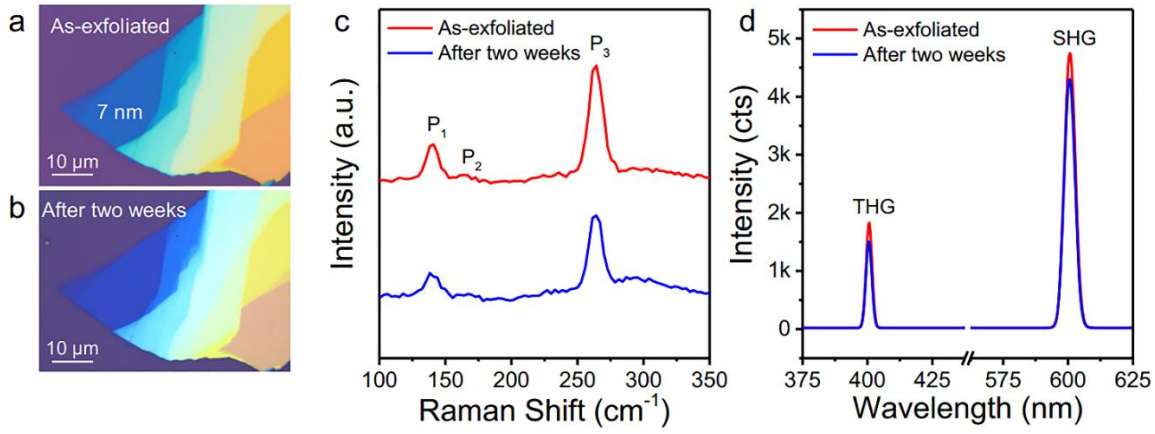

Figure S4 (a) The OM image of as-exfoliated SnP_2S_6 flakes. (b) The OM image of SnP_2S_6 flakes after being placed in air for two weeks. (c) Raman spectra and (d) NLO signal of 7 nm SnP_2S_6 flake at different times.

Calculation of Second-order nonlinear susceptibility

$$P_{2\omega} = \frac{8\pi^2 d^2}{\varepsilon_0 c \lambda^2 A} \cdot \frac{[\chi^{(2)}]^2}{n_\omega^2 n_{2\omega}} \cdot P_\omega^2 \quad \text{(S1)}$$

Where P_ω and $P_{2\omega}$ are excitation laser power and SHG power, respectively; $\chi^{(2)}$is the second-order susceptibility; ε_0 and c are dielectric constant and the speed of light in vacuum, respectively; A is the area of the incident laser spot; d is the thickness of the sample to be measured; n_ω and $n_{2\omega}$ are the refractive index of SnP_2S_6 under excitation wavelength and SHG wavelength, respectively. Due to the SHG power cannot be measured directly, we will estimate the second-order susceptibility $\chi^{(2)}_{SnP2S6}$ of SnP_2S_6 by comparing with monolayer MoS_2 in the same test conditions (like same excitation power, wavelength, environment, etc.) [1, 2]. And the second-order susceptibility $\chi^{(2)}_{MoS2}$ of monolayer MoS_2 has been measured previously. According to formula (S1), we can deduce the following formula

$$\frac{\chi^{(2)}_{SnP2S6}}{\chi^{(2)}_{MoS2}} = \sqrt[2]{\frac{P_{2\omega-SnP2S6}}{P_{2\omega-MoS2}}} \cdot \frac{d_{MoS2}}{d_{SnP2S6}} \cdot \sqrt[2]{\frac{n_{2\omega-SnP2S6}}{n_{2\omega-MoS2}} \frac{n^2_{\omega-SnP2S6}}{n^2_{\omega-MoS2}}} \quad \text{(S2)}$$

The SHG power is proportional to SHG intensity, so we can obtain formula (S3)

$$\chi^{(2)}_{SnP2S6} = \sqrt[2]{\frac{I_{2\omega-SnP2S6}}{I_{2\omega-MoS2}}} \cdot \frac{d_{MoS2}}{d_{SnP2S6}} \cdot \sqrt[2]{\frac{n_{2\omega-SnP2S6}}{n_{2\omega-MoS2}} \frac{n^2_{\omega-SnP2S6}}{n^2_{\omega-MoS2}}} \cdot \chi^{(2)}_{MoS2} \quad \text{(S3)}$$

Fig. S5 shows the SHG signal of 8 nm SnP_2S_6 and monolayer MoS_2 (prepared by chemical vapor deposition) under the same test environment. The incident wavelength is 810 nm, and $n_{2\omega-MoS2}$ =3.4, $n_{\omega-MoS2}$ =4.12, $n_{2\omega-SnP2S6}$ =3.26 and $n_{\omega-SnP2S6}$ =2.8, respectively. According to previous report, the second-order susceptibility $\chi^{(2)}_{MoS2}$ of monolayer MoS_2 is about 10^{-7} m V^{-1} at 810 nm excitation wavelength [3]. Therefore, we can estimate the second-order susceptibility $\chi^{(2)}_{SnP2S6}$ is approach 4.06×10^{-9} m V^{-1} for 8 nm SnP_2S_6 flake from formula (S3).

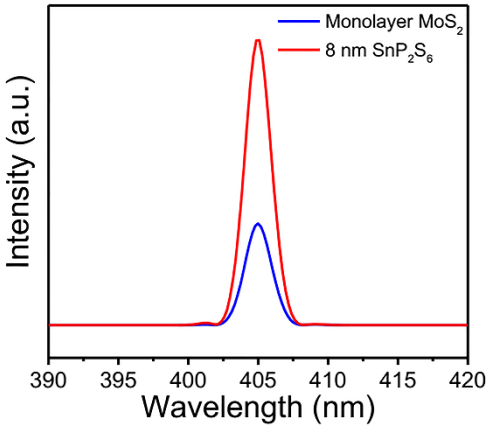

Figure S5 SHG signal for monolayer MoS_2 and 8 nm SnP_2S_6 flake under 810 nm excitation wavelength.

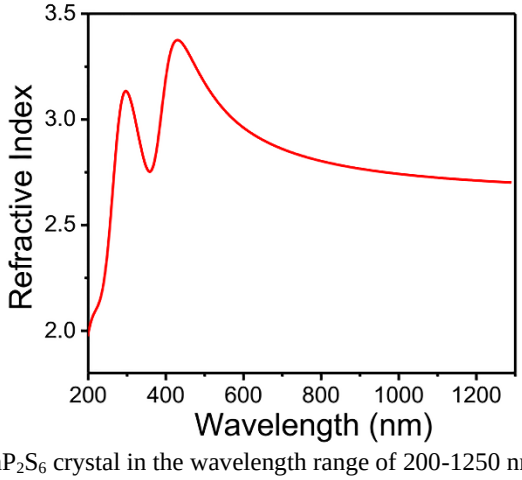

Figure S6 The refractive index of SnP_2S_6 crystal in the wavelength range of 200-1250 nm.

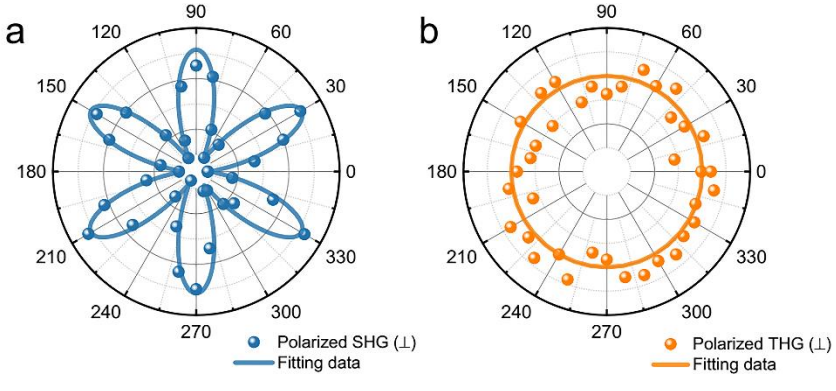

Figure S7 (a) and (b) are polarization-dependent SHG and THG intensity of SnP_2S_6 flake in perpendicular configuration.

References

[1] Yang, D.; Hu, X.; Zhuang, M.; Ding, Y.; Zhou, S.; Li, A.; Yu, Y.; Li, H.; Luo, Z.; Gan, L., et al. Inversion symmetry broken 2D 3R-$MoTe_2$. *Adv. Funct. Mater*. **2018**, *28*, 1800785.

[2] Shi, J.; Yu, P.; Liu, F.; He, P.; Wang, R.; Qin, L.; Zhou, J.; Li, X.; Zhou, J.; Sui, X., et al. 3R MoS_2 with broken inversion symmetry: a promising ultrathin nonlinear optical device. *Adv. Mater*. **2017**, *29*, 1701486.

[3] Kumar N., Najmaei S., Cui Q., Ceballos F., Ajayan P. M., Lou J., Zhao H. Second harmonic microscopy of monolayer MoS_2. *Phys. Rev. B* **2013**, *87*, 161403.