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Electronic Supplementary Information

# Synthesis of violet phosphorus with large lateral sizes to facilitate nano-device fabrications

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**Experimental Session**

**Single crystal X-ray diffraction.** The violet phosphorus single crystals with regular shape and without obvious crack were selected. The single crystal was then cut to 150 μm to fit the machine holder. The single crystal X-ray diffraction data were then collected on a Bruker D8 Venture Photon Ⅲ diffractometer with Mo Kα radiation (λ=0.71073 Å). The structures were solved by direct methods and refined against F2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. All calculations were carried out by the program package of and Olex2 ver 1.2.10. CSD-2160375 contains the supplementary crystallographic data in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

**Scanning electron microscopy (SEM).** The morphologies of the as-produced violet phosphorus were taken on a FEI Quanta 250F scanning electron microscope.

**Powder X-ray diffraction (XRD).** X-ray diffraction patterns were obtained from a Bruker D2 PHASER using Cu/Kαradiation (λ=1.5418 Å) at 40 kV and 30 mA.

**Raman spectroscopy.** Raman spectroscopy was taken in a back-scattering geometry using a single monochromator with a microscope (Reinishaw inVia) equipped with CCD array detector (1024×256 pixels, cooled to -70ºC) and an edge filter. A piece of violet phosphorus crystal was irradiated with a 633nm laser.

**TEM, HRTEM and SAED measurements.** TEM, HRTEM images and SAED patterns were acquired using Talos F200X electron microscope with an acceleration voltage of 200 kV. The violet phosphorus sonicated in ethanol for 15 min was dropped onto copper grids coated with ultrathin amorphous carbon films and then dried under ambient conditions.

**X-ray photoelectron spectroscopy (XPS).** The bulk violet phosphorus was tested using Thermo Fisher Xi+ with a dual anode Al/Mg target at 400 W.

**Inductively coupled plasma spectrometry (ICP).** The bulk violet phosphorus was tested using equipment model Pe Avio 200. A sample mass of 37.1 mg was taken and a volume of 100 ml was fixed.

**Lateral size measurements.** The image J software was used for size measurements.

**FET device fabrications and measurements.** The bulk violet phosphorus was mechanically exfoliated using blue adhesive tape and then transferred onto a silicon substrate with 300 nm $SiO_2$ as dielectric layer. An appropriate amount of poly(methyl methacrylate) (PMMA) resist was then drop coated onto sample-based silicon wafer and allowed to spread uniformly. The source and drain electrodes were patterned using a UPE 1102lu manual UV exposure system. Ti/Au (10 nm/50 nm) was then subsequently deposited using thermal evaporation (HHV, Auto-500e). The excess PMMA was then removed by a stripping process in warm acetone to form electrodes. The optoelectronic properties of the device were measured using a Keithley 4200A semiconductor parameter analyzer under ambient conditions. The combined light source was a 530 nm single-mode source, whose power was adjustable by a Thornlab LEDD1B driver. The incident power was measured by an optical power meter (Thorlabs PM130D).

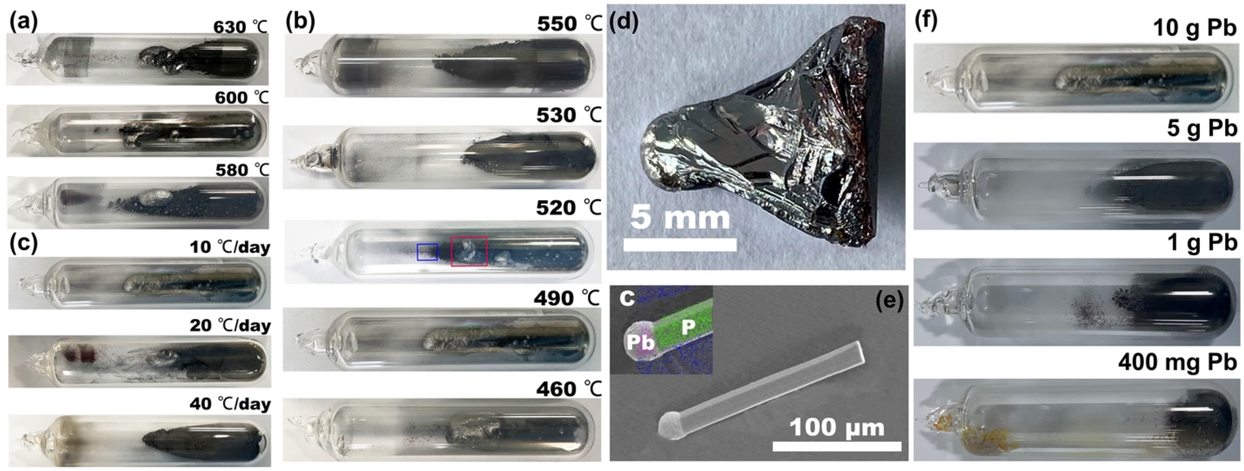


**Fig. S1.** Optical images of the quartz tubes after reactions with different (a) $T_{start}$, (b) $T_{end}$, (c) cooling rates, and (f) amount of Pd. (d) Optical image of the as-produced violet phosphorus wrapped inside molten lead (corresponding to the red box at 520 °C in Fig. S1b). (e) SEM image of partially grown violet phosphorus products on top of molten lead (corresponding to the blue box at 520 °C in Fig. S1b).

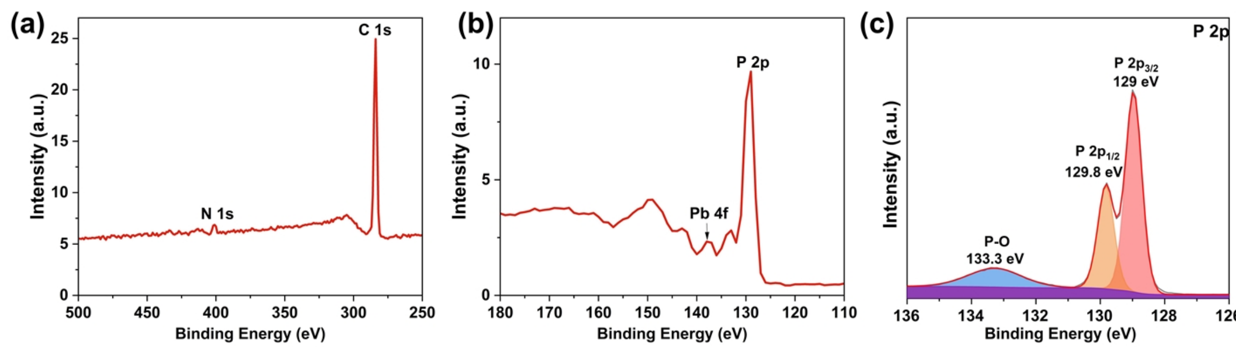


**Fig. S2.** XPS spectrum of violet phosphorus flakes after nitric acid treatments. (a) $N_{1s}$, (b) $Pb_{4f}$, and (c) high-resolution modes of $P_{2p}$.

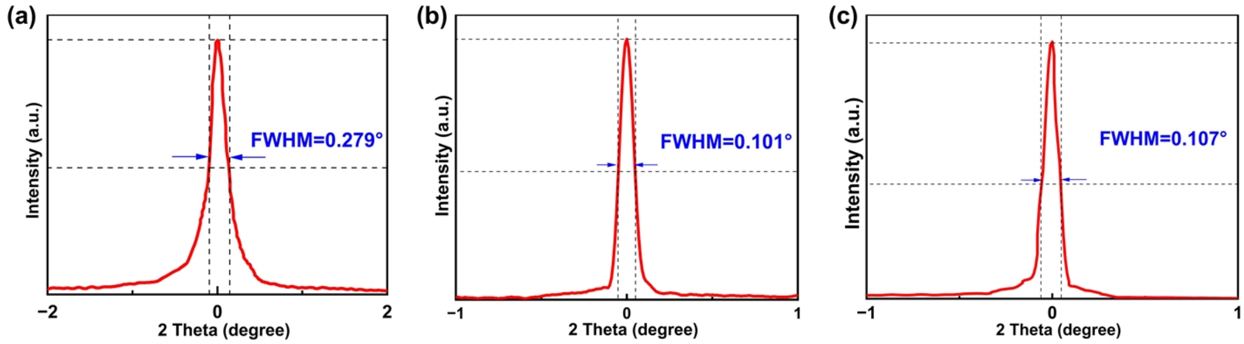


**Fig. S3.** X-ray rocking curve of violet phosphorus produced from a molten lead method. Peaks and FWHM at (a) {004}, (b) {006} and (c) {008} crystal planes.

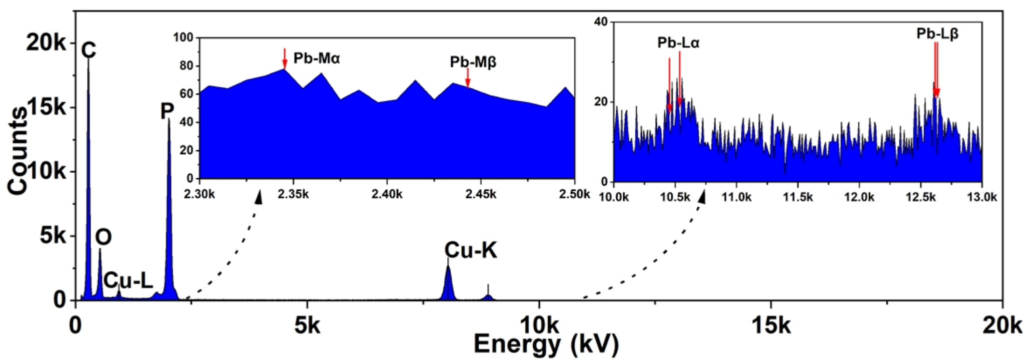


**Fig. S4.** EDS spectrum of violet phosphorus nanosheets (carbon and copper elements are from copper grid, and the red arrows mark the positions of the L and M line systems of lead elements).

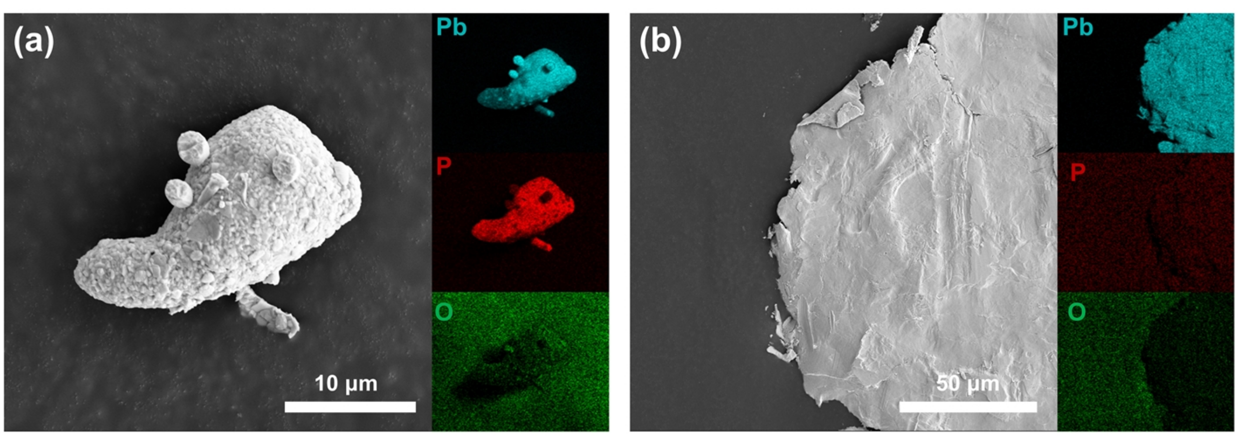


**Fig. S5.** SEM and elemental mapping analysis of (a) grey powder (b) silver-grey bump after reactions.

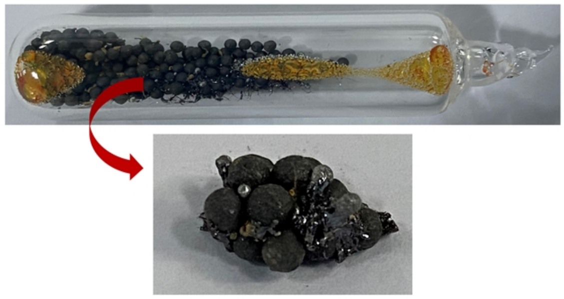

**Fig. S6.** Optical image of quartz tube after synthesis using lead granules instead of powder.

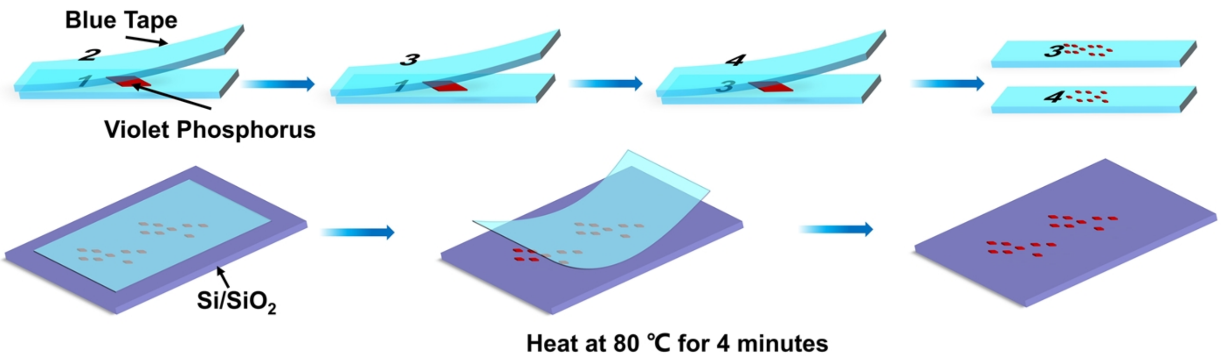


**Fig. S7.** Exfoliation of violet phosphorene and transference to substrate.

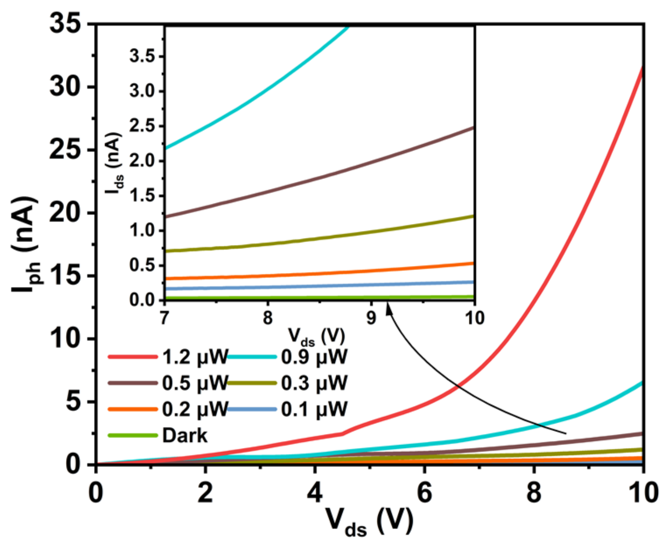


**Fig. S8.** Current-voltage characteristic of violet phosphorene nanosheet ($V_g$=0 V) under dark conditions and the irradiation of 530 nm laser with different power at room temperature (inset shows an enlarged part of the lower right corner).

**Table S1.** Crystal data of the as-produced violet phosphorus (T= 300 K)

| | |
|---|---|
| Identification code | 2160375 |
| Empirical formula | $P_{21}$ |
| Formula weight/g mol$^{-1}$ | 650.37 |
| Space group | P2/n (No. 13) - monoclinic |
| Cell parameters | a=9.1997(3) Å<br>b=9.1235(3) Å<br>c=21.9062(8) Å<br>β=97.727(1)° |
| Volume/Å$^3$ | 1821.97(11) Å$^3$ |
| Z | 4 |
| $\rho_{calc}$/g cm$^{-3}$ | 2.37084 |
| μ/mm$^{-1}$ | 1.890 |
| F(000) | 1260 |
| Crystal size/mm$^3$ | 0.174×0.152×0.11 |
| Radiation | MoKα(λ= 0.71073) |
| 2θ range for data collection/° | 4.464 to 49.442 |
| Index ranges | -10≤h≤10, -10≤k≤10, -25≤l≤25 |
| Reflections collected | 10959 |
| Independent reflections | 3088 [$R_{int}$ = 0.0294, $R_{sigma}$ = 0.0298] |
| Data/restraints/parameters | 3088/0/190 |
| Goodness-of-fit on F$^2$ | 1.064 |
| Final R indexes [I>=2σ(I)] | $R_1$= 0.0271, $wR_2$= 0.0512 |
| Final R indexes [all data] | $R_1$= 0.0385, $wR_2$= 0.0562 |
| Largest diff. peak/hole/e Å$^{-3}$ | 0.47/-0.37 |

**Table S2.** Fractional atomic coordinates (×10[4]) and equivalent isotropic displacement parameters (Å$^2$×10$^3$) of the as-produced violet phosphorus. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| P1 | 8078.6(9) | 2778.1(9) | 3834.6(4) | 18.80(19) |
| P1' | 7060.5(9) | 4055.1(9) | 4559.2(3) | 17.26(18) |
| P2 | 8934.9(9) | 4488.0(9) | 3276.9(4) | 19.50(19) |
| P2' | -2614.4(9) | -3627.3(8) | 4338.6(4) | 18.08(18) |
| P3 | 10802.7(9) | 5153.2(8) | 3959.2(3) | 17.44(18) |
| P3' | -250.0(9) | -3528.1(9) | 4667.8(3) | 17.06(18) |
| P4 | 11210.9(9) | 6788.7(9) | 3261.2(4) | 19.78(19) |
| P4' | -327.5(9) | -1271.5(8) | 4314.9(4) | 18.17(19) |
| P5 | -730.7(9) | -1752.4(9) | 3306.4(4) | 20.84(19) |
| P5' | 7506.6(9) | 6458.6(9) | 3324.5(4) | 20.65(19) |
| P6 | 6196.0(9) | 2010.7(9) | 3186.2(4) | 20.11(19) |
| P6' | 4687.6(9) | 3910.7(8) | 4276.1(3) | 17.02(18) |
| P7 | 15572.8(9) | 10326.0(9) | 3831.1(4) | 19.17(19) |
| P7' | 4542.6(9) | 1589.0(9) | 4551.5(3) | 17.67(18) |
| P8 | 4734.8(9) | 3890.6(9) | 3277.1(3) | 18.72(19) |
| P8' | 1867.4(9) | 1006.9(9) | 3264.1(3) | 18.34(19) |
| P9 | 2451.8(9) | 3226.6(8) | 2992.6(3) | 16.77(18) |
| P10 | 13699.5(9) | 9472.2(9) | 3196.6(3) | 18.47(19) |
| P10' | 2149.7(9) | 1383.5(8) | 4264.9(3) | 16.97(18) |
| P11 | 13080.9(9) | 7808.3(9) | 3837.6(4) | 18.88(19) |
| P11' | 2038.2(9) | -908.6(9) | 4554.2(3) | 17.60(18) |

**Table S3.** Anisotropic displacement parameters (Å$^2$×10$^3$) for the as-produced violet phosphorus. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| P1 | 13.2(4) | 15.3(4) | 28.2(4) | -0.9(3) | 3.9(3) | -3.5(3) |
| P1' | 14.2(4) | 17.3(4) | 20.1(4) | -0.3(3) | 1.7(3) | -4.7(4) |
| P2 | 18.1(5) | 18.5(4) | 23.0(4) | -4.6(3) | 6.6(3) | -6.5(4) |
| P2' | 14.4(4) | 15.9(4) | 24.6(4) | -2.3(3) | 5.1(3) | -3.3(3) |
| P3 | 13.5(4) | 14.3(4) | 25.3(4) | -0.1(3) | 5.3(3) | -2.3(3) |
| P3' | 15.2(4) | 16.7(4) | 19.7(4) | -0.9(3) | 3.9(3) | -5.0(4) |
| P4 | 20.5(5) | 17.4(4) | 22.8(4) | -2.5(3) | 7.8(3) | -6.0(4) |
| P4' | 15.4(4) | 13.9(4) | 26.1(4) | -2.4(3) | 6.1(3) | -3.5(3) |
| P5 | 19.5(5) | 18.2(4) | 24.5(4) | 4.2(3) | 1.7(3) | -3.4(4) |
| P5' | 16.4(5) | 20.9(5) | 24.0(4) | 1.5(3) | 0.2(3) | -4.2(4) |
| P6 | 18.5(5) | 19.4(4) | 23.5(4) | -3.9(3) | 7.1(3) | -6.4(4) |
| P6' | 13.4(4) | 16.6(4) | 21.2(4) | -3.0(3) | 3.1(3) | -3.4(3) |
| P7 | 13.4(4) | 15.1(4) | 29.2(4) | 0.4(3) | 3.7(3) | -1.8(3) |
| P7' | 15.8(4) | 17.5(4) | 19.7(4) | 1.0(3) | 2.1(3) | -4.9(4) |
| P8 | 17.6(5) | 17.8(4) | 20.3(4) | 1.1(3) | 0.5(3) | -4.3(4) |
| P8' | 16.1(4) | 18.1(4) | 20.6(4) | 0.7(3) | 1.7(3) | -3.3(4) |
| P9 | 16.0(4) | 16.2(4) | 17.9(4) | -0.5(3) | 1.7(3) | 0.7(3) |
| P10 | 18.0(5) | 16.3(4) | 22.1(4) | -2.5(3) | 6.1(3) | -5.0(4) |
| P10' | 16.2(4) | 14.5(4) | 21.2(4) | -1.0(3) | 6.0(3) | -3.8(3) |
| P11 | 15.7(5) | 13.8(4) | 27.6(4) | 0.1(3) | 5.0(3) | -2.5(3) |
| P11' | 16.9(4) | 16.6(4) | 19.7(4) | 0.2(3) | 3.7(3) | -4.8(4) |

**Table S4.** Bond lengths for the as-produced violet phosphorus.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| P10' | P7' | 2.2144(11) | P10 | P11 | 2.1943(11) |
| P10' | P11' | 2.1915(11) | P10 | P7 | 2.2056(11) |
| P10' | P8' | 2.1997(11) | P1 | P2 | 2.1922(11) |
| P9 | P9$^{1}$ | 2.1720(15) | P1 | P6 | 2.2013(11) |
| P9 | P8' | 2.1977(11) | P8' | P10$^{2}$ | 2.2115(12) |
| P9 | P8 | 2.1943(11) | P11 | P11'$^{3}$ | 2.2715(11) |
| P6' | P7' | 2.2113(11) | P11 | P4 | 2.1989(11) |
| P6' | P1' | 2.1916(11) | P2 | P3 | 2.2055(11) |
| P6' | P8 | 2.1946(11) | P2 | P5' | 2.2375(12) |
| P3' | P2' | 2.1996(12) | P7 | P7'$^{3}$ | 2.2623(11) |
| P3' | P4' | 2.1969(11) | P7 | P6$^{3}$ | 2.2147(11) |
| P3' | P3$^{2}$ | 2.2801(11) | P8 | P6 | 2.2046(12) |
| P7' | P7$^{2}$ | 2.2624(11) | P6 | P7$^{2}$ | 2.2147(11) |
| P11' | P4' | 2.1942(11) | P4 | P5$^{3}$ | 2.2405(12) |
| P11' | P11$^{2}$ | 2.2715(11) | P4 | P3 | 2.2046(11) |
| P1' | P2'$^{3}$ | 2.1984(11) | P5 | P4$^{2}$ | 2.2405(12) |
| P1' | P1 | 2.2702(11) | P5 | P5'$^{2}$ | 2.3050(12) |
| P2' | P1'$^{2}$ | 2.1984(11) | P3 | P3'$^{3}$ | 2.2801(11) |
| P2' | P5'$^{2}$ | 2.2404(11) | P5' | P2'$^{3}$ | 2.2404(11) |
| P4' | P5 | 2.2338(11) | P5' | P5$^{3}$ | 2.3050(12) |
| P10 | P8'$^{3}$ | 2.2115(12) | | | |

**Table S5.** Bond angles for the as-produced violet phosphorus.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| P11' | P10' | P7' | 94.72(4) | P6 | P1 | P1' | 104.57(4) |
| P11' | P10' | P8' | 97.77(4) | P10' | P8' | P10$^{2}$ | 100.18(4) |
| P8' | P10' | P7' | 105.98(4) | P9 | P8' | P10' | 97.21(4) |
| P9$^{1}$ | P9 | P8' | 108.25(3) | P9 | P8' | P10$^{2}$ | 110.42(4) |
| P9$^{1}$ | P9 | P8 | 96.71(5) | P10 | P11 | P11'$^{3}$ | 104.81(4) |
| P8 | P9 | P8' | 115.92(4) | P10 | P11 | P4 | 100.10(4) |
| P1' | P6' | P7' | 94.29(4) | P4 | P11 | P11'$^{3}$ | 104.15(4) |
| P1' | P6' | P8 | 97.48(4) | P1 | P2 | P3 | 97.11(4) |
| P8 | P6' | P7' | 105.90(4) | P1 | P2 | P5' | 106.77(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P2' | P3' | P3$^{2}$ | 104.29(4) | P3 | P2 | P5' | 98.99(4) |
| P4' | P3' | P2' | 86.52(4) | P10 | P7 | P7'$^{3}$ | 104.74(4) |
| P4' | P3' | P3$^{2}$ | 104.57(4) | P10 | P7 | P6$^{3}$ | 95.19(4) |
| P10' | P7' | P7$^{2}$ | 104.65(4) | P6$^{3}$ | P7 | P7'3 | 105.08(4) |
| P6' | P7' | P10' | 95.62(4) | P9 | P8 | P6' | 97.99(4) |
| P6' | P7' | P7$^{2}$ | 104.55(4) | P9 | P8 | P6 | 109.36(4) |
| P10' | P11' | P4' | 99.12(4) | P6' | P8 | P6 | 100.99(4) |
| P10' | P11' | P11$^{2}$ | 104.56(4) | P1 | P6 | P7$^{2}$ | 93.31(4) |
| P4' | P11' | P11$^{2}$ | 104.75(4) | P1 | P6 | P8 | 97.50(4) |
| P6' | P1' | P2'$^{3}$ | 98.94(4) | P8 | P6 | P7$^{2}$ | 105.60(4) |
| P6' | P1' | P1 | 105.08(4) | P11 | P4 | P5$^{3}$ | 106.86(4) |
| P2'$^{3}$ | P1' | P1 | 105.00(4) | P11 | P4 | P3 | 94.65(4) |
| P3' | P2' | P5'$^{2}$ | 98.33(4) | P3 | P4 | P5$^{3}$ | 99.22(4) |
| P1'$^{2}$ | P2' | P3' | 97.20(4) | P4' | P5 | P4$^{2}$ | 97.65(4) |
| P1'$^{2}$ | P2' | P5'$^{2}$ | 106.14(4) | P4' | P5 | P5'$^{2}$ | 98.38(4) |
| P3' | P4' | P5 | 99.04(4) | P4$^{2}$ | P5 | P5'$^{2}$ | 98.45(4) |
| P11' | P4' | P3' | 94.20(4) | P2 | P3 | P3'$^{3}$ | 104.06(4) |
| P11' | P4' | P5 | 107.06(4) | P4 | P3 | P3'$^{3}$ | 104.04(4) |
| P11 | P10 | P8'$^{3}$ | 97.45(4) | P4 | P3 | P2 | 84.61(4) |
| P11 | P10 | P7 | 95.10(4) | P2'$^{3}$ | P5' | P5$^{3}$ | 99.83(4) |
| P7 | P10 | P8'$^{3}$ | 105.79(4) | P2 | P5' | P2'$^{3}$ | 97.23(4) |
| P2 | P1 | P1' | 103.73(4) | P2 | P5' | P5$^{3}$ | 98.58(4) |
| P2 | P1 | P6 | 100.21(4) | | | | |

**Table S6.** Hole mobility of violet phosphorus.

| $V_{ds}$/V | $L_{ch}$/μm | $W_{ch}$/μm | $C_{ox}$/F*cm-2 | $dI_{ds}\backslash dV_g$ | Mobility($cm^2*V^{-1}*s^{-1}$) |
|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 0.5 | 11.24 | 5.16 | 1.15E-08 | 2.74E-09 | 1.03783 |
| 2 | 0.5 | 10 | 16.26 | 1.15E-08 | 8.22E-09 | 0.87829 |
| 3 | 1 | 12 | 5.2 | 1.15E-08 | 1.15E-08 | 2.307773 |
| 4 | 1.5 | 10.26 | 7.65 | 1.15E-08 | 6.49E-09 | 0.504375 |
| 5 | 3 | 20 | 10 | 1.15E-08 | 6.11E-09 | 0.353753 |