## Electronic Supplementary Information (ESI)

## Anomalous polarization dependence of Raman scattering and crystallographic orientation of black phosphorus

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Fig. S1 Orientation dependence of color of a BP crystal on a  $SiO_2/Si$  substrate in reflection mode. (a-d) Optical images taken with reflected light in cross polarization. (e) The RGB values of the sample image with respect to that of the substrate as a function of the angle between the incident polarization and the long straight edge. There is a small difference between 45° and 135°.



Fig. S2 Orientation dependence of color of a BP crystal on slide glass in reflection mode. (a-d) Optical images taken with reflected light in cross polarization. (e) The RGB values of the sample image with respect to that of the substrate as a function of the angle between the incident polarization and the long straight edge. There is a small difference between 45° and 135°.



Fig. S3 Orientation dependence of color of a BP crystal on slide glass in transmission mode. (a-d) Optical images taken with transmitted light in cross polarization. (e) The RGB values of the sample image with respect to that of the substrate as a function of the angle between the incident polarization and the long straight edge. There is no appreciable difference between 45° and 135°.



Fig. S4 Polarization dependence of Raman modes in cross polarization. Each row shows polarization dependence of  $A_g^1$ ,  $A_g^2$  and  $B_{2g}$  modes, respectively, taken with excitation wavelengths of 441.6, 514.5, 632.8 nm as indicated.



Fig. S5 Raman spectra corresponding to data in Fig. 5(e-p). The spectra are shown in 20degree increments. (e-h) and (i-l) are taken with the excitation wavelengths of 514.5 and 441.6 nm, respectively.

Wavelengt h (nm)	<b>BP</b> (zigzag) <sup>1</sup>	<b>BP (armchair)</b> <sup>1</sup>	SiO <sub>2</sub> <sup>2</sup>	Si <sup>3</sup>
441.6	4.10-0.21i	3.92-0.94i	1.47	4.79-0.10i
449.1	4.06-0.15i	3.88-0.65i	1.47	4.70-0.090i
450.6	4.05-0.14i	3.87-0.64i	1.47	4.68-0.087i
488.0	3.76-0.064i	3.66-0.45i	1.46	4.36-0.035i
497.1	3.72-0.060i	3.64-0.43i	1.46	4.30-0.027i
499.1	3.71-0.060i	3.64-0.43i	1.46	4.29-0.025i
514.5	3.67-0.050i	3.60-0.40i	1.46	4.21-0.016i
524.6	3.65-0.050i	3.58-0.37i	1.46	4.17-0.012i
526.8	3.64-0.050i	3.57-0.37i	1.46	4.15-0.011i
532.0	3.62-0.050i	3.57-0.37i	1.46	4.21-0.010i
542.8	3.61-0.050i	3.54-0.36i	1.46	4.10-0.0077i
545.1	3.60-0.050i	3.53-0.37i	1.46	4.22-0.0075i
632.8	3.46-0.044i	3.50-0.39i	1.46	4.14-0.0010i
648.1	3.43-0.040i	3.48-0.36i	1.46	4.16-0.0015i
651.4	3.43-0.040i	3.48-0.37i	1.46	4.09-0.0016i

Table S1 Refractive indices used in the calculation.

## REFERENCES

- 1 H. Asahina and a Morita, J. Phys. C Solid State Phys., 2000, 17, 1839–1852.
- 2 I. H. Malitson, J. Opt. Soc. Am., 1965, 55, 1205.
- G. Vuye, S. Fisson, V. Nguyen Van, Y. Wang, J. Rivory and F. Abelès, *Thin Solid Films*, 1993, **233**, 166–170.