SUPPLEMENTARY INFORMATION

B_{2g} mode

As reported in Reference [1], the Raman peak corresponding to the B_{2g} mode does not show any significant variation of its shape (splitting/appearance of additional Raman mode) or position with the number of black phosphorus layers. This is clearly seen in Figure S1 which shows representative spectra for thin and thick regions of flake 1 and flake 2. This result is further confirmed in figure S2 in which the evolution of B_{2g} mode as a function of number of layers for flake 2 and flake 3 is shown. The observed small changes in position of the B_{2g} mode are not systematic with the number of layers and are attributed to strain. Indeed, a similar shift with strain of the B_{2g} and A_g^2 modes is a prerequisite if the A_g^2 - B_{2g} splitting is to provide a reliable estimate of the number of layers present.

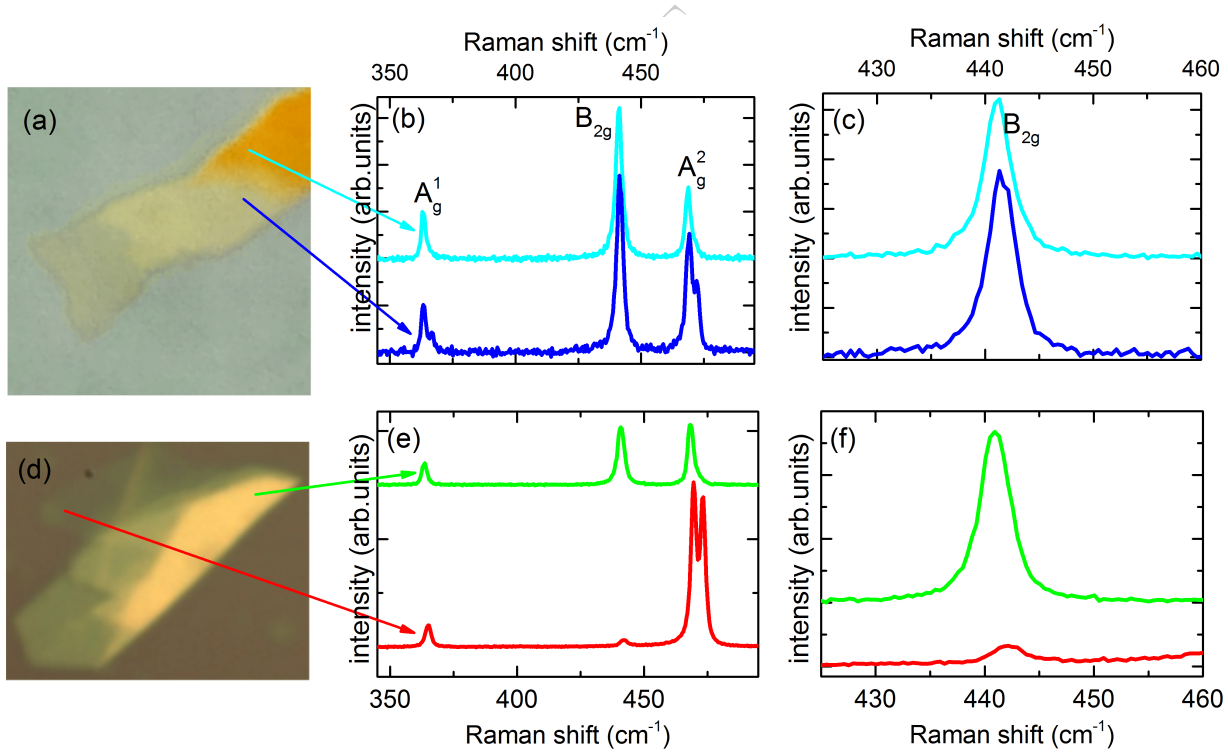

FIG. S1. (a) and (d) optical images of flake 1 and 2, (b) and (e) corresponding Raman spectra showing all observed BP Raman modes and (c) and (f) expanded view of the B_{2g} mode.

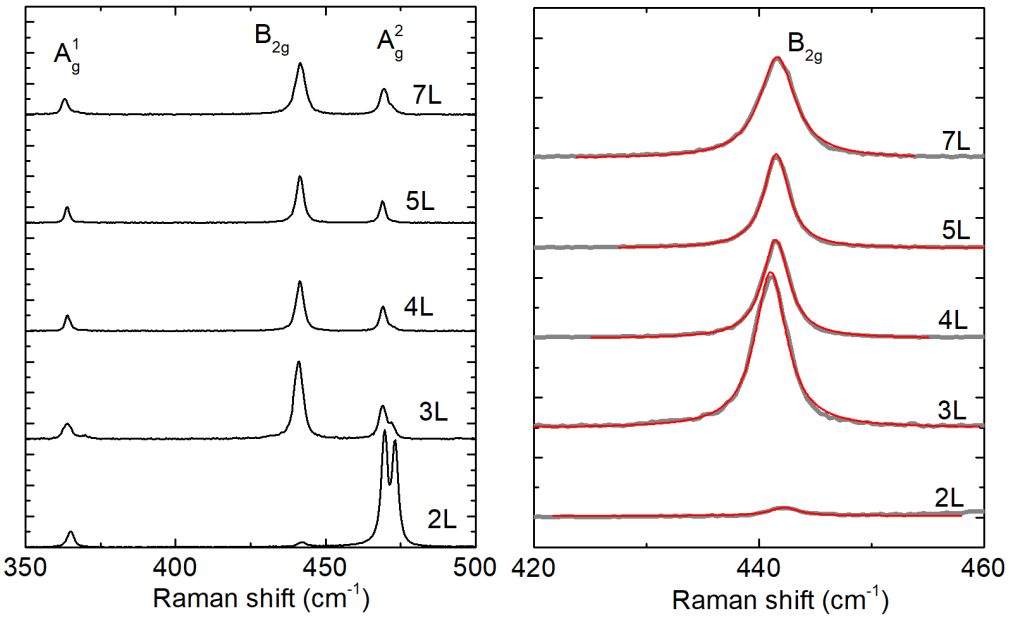

FIG. S2. The observed BP Raman modes (left) and an expanded view of the B_{2g} mode (right) for different numbers of layers. The spectra are normalized by the A_g^1 peak intensity.Red curve represents fits with single Lorentz curve

Thickness estimation

A precise determination of the black phosphorus thickness is complicated by the h-BN encapsulation which makes AFM measurements difficult to interpret. Several approaches have been suggested in the literature for estimating the number of black phosphorus layers based on Raman data. The number of layers can be estimated based on (i) the A_g^2 - B_{2g} splitting[1], (ii) intensity ratio of $I(A_g^2)/I(A_g^1)$[1] or (iii) ratio of the intensity of the silicon Raman peak (at 520 cm^{-1}) to the $I(A_g^2)$ intensity[1,2]. Here we use the first method (schematically presented in fig. S3(a)), as the second method suffers from the fact that the intensity ratio $I(A_g^2)/I(A_g^1)$ depends on the degree of phosphorus oxidation (degradation)[3] and the third method requires an appropriate orientation of the silicon substrate with respect to the laser polarization[2].

The A_g^2 - B_{2g} splitting versus the number of layers taken from reference [1] is plotted (closed red circles) in fig. S3(b). A functional fit (broken line) is used to reproduce the

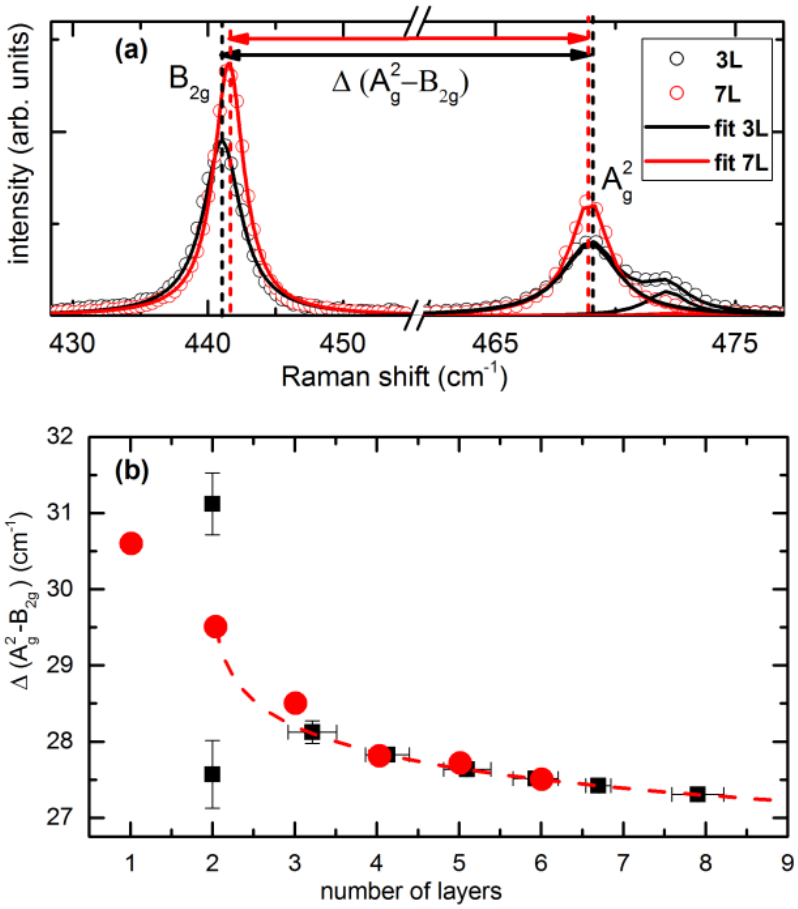

FIG. S3. (a) Raman spectra (symbols) acquired at two different locations on flake 3 on regions approximately 3 and 7 layers thick. Lorentzian fits to the B_{2g} and A_g^2 modes (solid lines) are used to extract the B_{2g}-A_g^2 splitting which establishes that the regions are 3 and 7 layers thick. (b) B_{2g}-A_g^2 splitting from[1] (red circles), fit used to approximate these data points (red dashed line) and our experimental data, collected from all flakes and averaged for a given number of layers (black squares).

dependence of the A_g^2 - B_{2g} splitting versus the number of layers. This function is then used to identify 3 layer and thicker parts of the sample. This approach is not reliable in the case of two layers due to the strong additional Raman mode on the high energy side of the A_g^2[3,4]. For two layers the data point from reference[1] lies exactly between the positions of the two peaks observed here (black closed squares) and in other works[3,4]. This suggests that the two Raman modes were not resolved in the earlier investigations of black phosphorus[1]. In practice, two layer black phosphorus is easily identified from its characteristic Raman

spectrum[3,4] *i.e.* the presence of a strong Raman mode just above A_g^2 accompanied by a significant weakening of the B_{2g} mode.

To demonstrate the validity of our approach we compare the maps of the calculated number of layers with number of layers estimated from the intensity ratio of the A_g^1 mode to the Si Raman mode and the Si mode intensity (figures S4-S7). In general all these methods lead to qualitatively the same result, with the exception that the intensity ratio does not provide a reliable estimate close to the edge of the sample, where the laser spot and phosphorus layer do not completely overlap. It should be noted however, that while the intensity ratio provides a useful indication of regions with different thickness, it does not provide an absolute value of the number of layers.

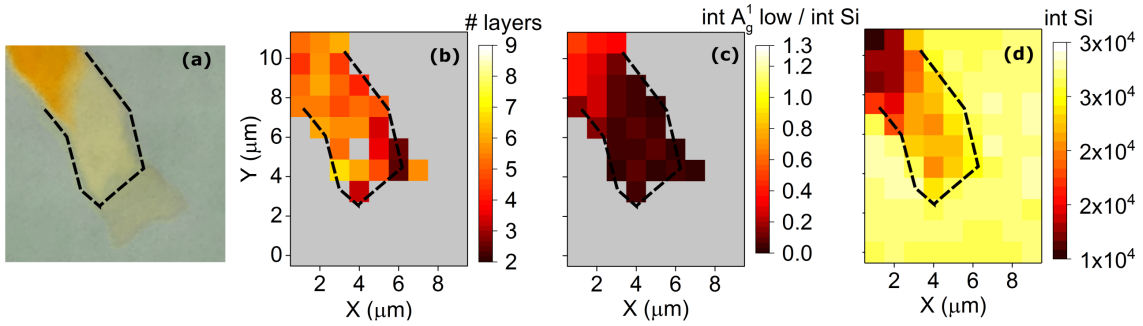

FIG. S4. Micrograph of flake 1 (a), the calculated number of layers (b), A_g^1/Si peak intensity ratio (c) and Si peak intensity (d). The thinnest part of the flake visible in the optical image was not detected in Raman mapping. The optical image was taken prior to h-BN encapsulation, so a possible explanation is that the flake has been damaged in the transfer process. The dashed lines outline the flake boundaries.

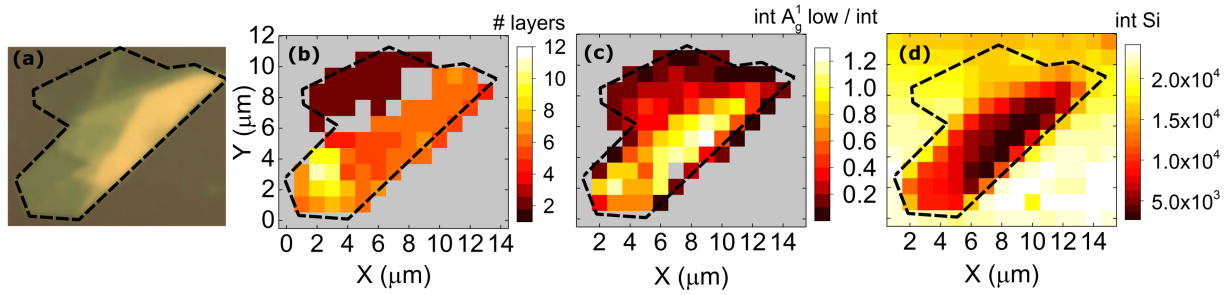

FIG. S5. Micrograph (a), the calculated number of layers (b), A_g^1/Si peak intensity ratio (c) and Si peak intensity (d) for flake 2. Missing data points on the number of layers map indicate areas where the laser spot covered regions of different thickness (bilayer and thicker regions) and a straightforward calculation was not possible.

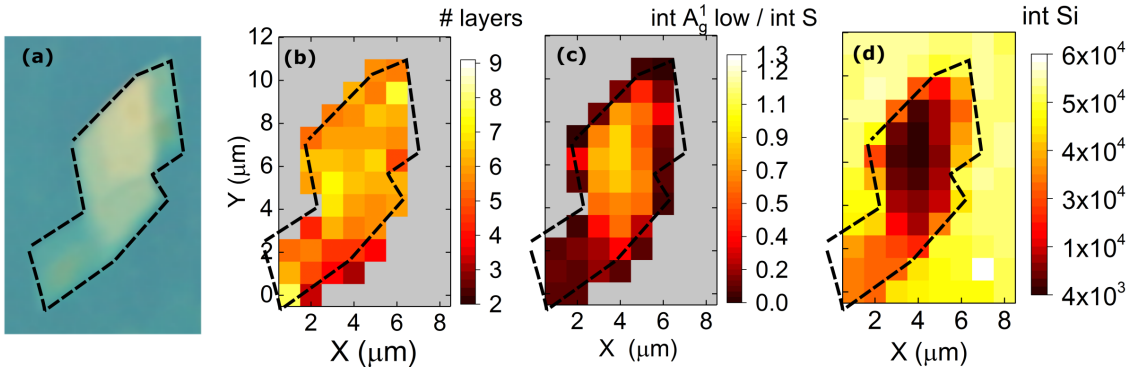

FIG. S6. Micrograph (a), the calculated number of layers (b), A_g^1/Si peak intensity ratio (c) and Si peak intensity (d) for flake 3.

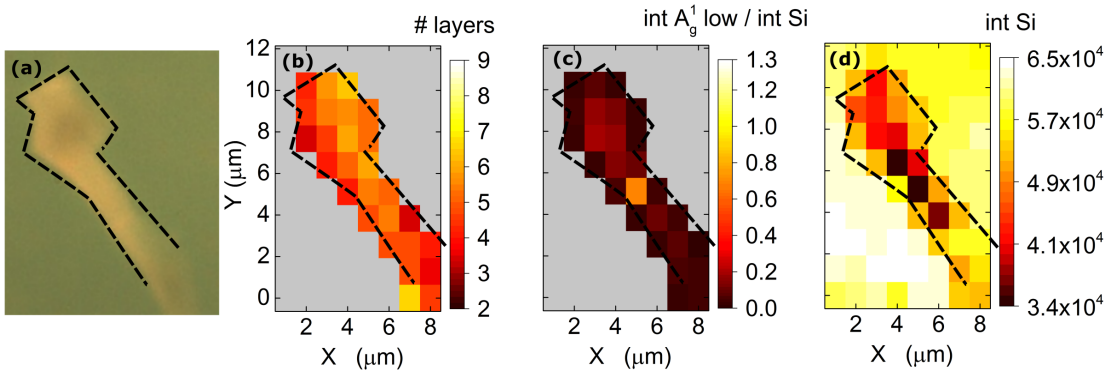

FIG. S7. Micrograph (a), the calculated number of layers (b), A_g^1/Si peak intensity ratio (c) and Si peak intensity (d) for flake 4.

[1] W. Lu, H. Nan, J. Hong, Y. Chen, C. Zhu, Z. Liang, X. Ma, Z. Ni, C. Jin, and Z. Zhang, Nano Research **7**, 853 (2014).

[2] A. Castellanos-Gomez, L. Vicarelli, E. Prada, J. O. Island, K. Narasimha-Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. Alvarez, *et al.*, 2D Materials **1**, 025001 (2014).

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[4] A.-L. Phaneuf-L' Heureux, A. Favron, J.-F. Germain, P. Lavoie, P. Desjardins, R. Leonelli, R. Martel, and S. Francoeur, Nano Letters **16**, 7761 (2016).