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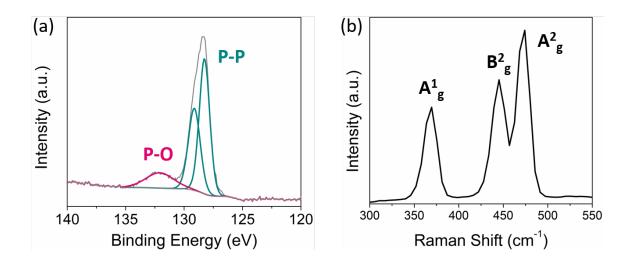


## Chemistry-A European Journal

## **Supporting Information**

## Stabilization of Black Phosphorus by Sonication-Assisted Simultaneous Exfoliation and Functionalization

Maart van Druenen, [a, b, c] Timothy Collins, [a, b, c] Fionán Davitt, [a, b, c] Jessica Doherty, [a, b, c] Gillian Collins, [a, b, c] Zdeněk Sofer, \*[d] and Justin D. Holmes\*[a, b, c]



**Figure S1**: (a) P 2p core level of bulk BP displaying P-P peaks at 128.3 and 129.1 eV and P-O shoulder at 132.1 eV. (b) Raman analysis shows peaks at 369, 444 and 473 which correspond to the  $A_g^1$ ,  $A_g^2$  and  $B_g^2$  modes, indicating the synthesis of crystalline BP.

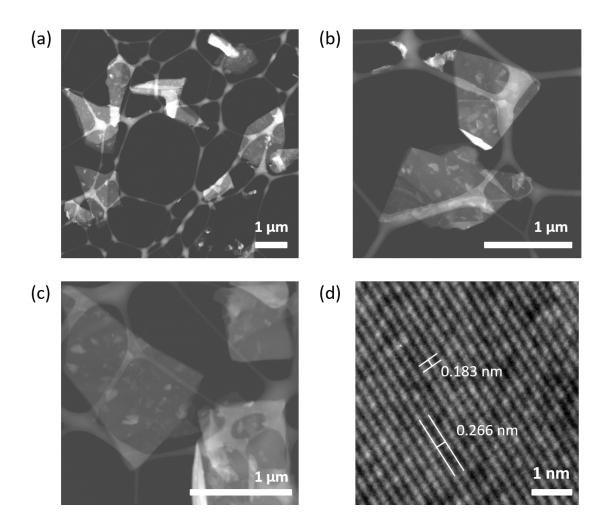
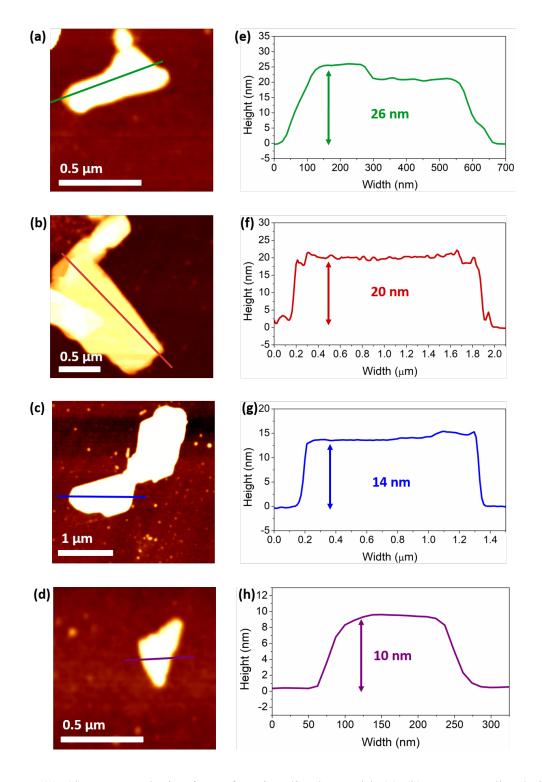
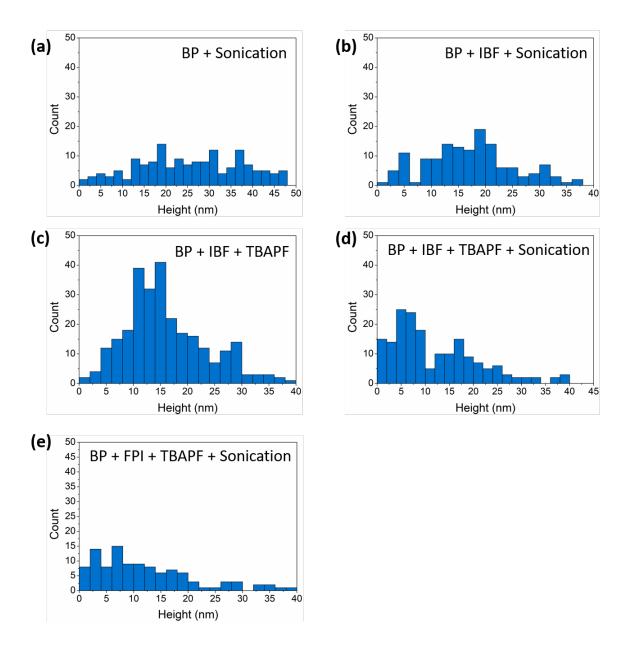


Figure S2: (a)-(c) STEM and (d) TEM analysis of exfoliated and IBF-functionalized BP.



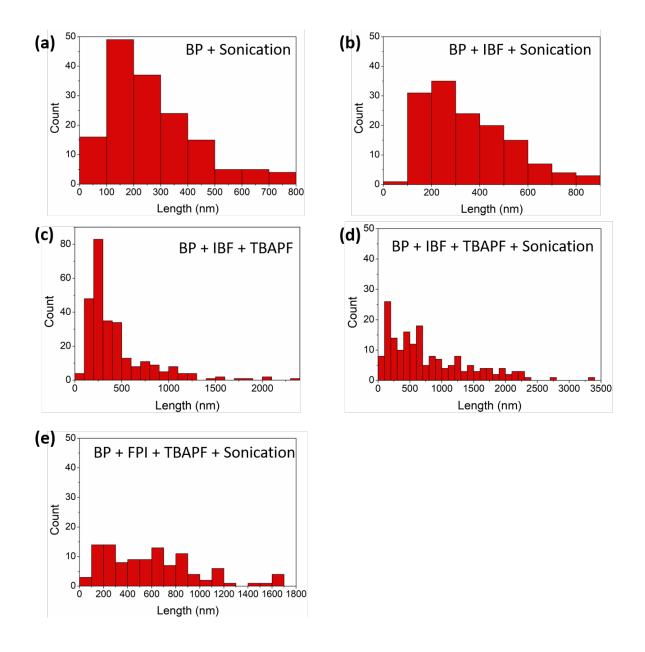
**Figure S3**: (a)-(d) AFM analysis of IBF-functionalized BP with (e)-(h) corresponding heights in the 10-26 nm range.



**Figure S4**: AFM analysis displaying the range of heights obtained when exfoliating BP (a) under sonication, (b) in IBF under sonication (without TBAFP), (c) in IBF and TBAFP with minimal sonication (10 min) (d) in IBF and TBAFP under continuous sonication and (e) in FPI and TBAFP under sonication.

 Table S1: Heights of exfoliated flakes.

Sample	<10 nm (%)	<20 nm (%)
BP + Sonication	11	37
BP + IBF + Sonication	19	67
BP + IBF + TBAFP	19	74
BP + IBF + TBAFP + Sonication	54	82
BP + FPI + TBAFP + Sonication	50	84



**Figure S5**: AFM analysis displaying the flake lengths obtained when exfoliating BP (a) under sonication, (b) in IBF under sonication (without TBAFP), (c) in IBF and TBAFP with minimal sonication (10 min) (d) in IBF and TBAFP under continuous sonication and (e) in FPI and TBAFP under sonication.

 Table S2: Lengths of exfoliated flakes.

Sample	>0.5 μm (%)	>1 μm (%)
BP + Sonication	9	0
BP + IBF + Sonication	21	0
BP + IBF + TBAFP	26	9
BP + IBF + TBAFP + Sonication	59	30
BP + FPI + TBAFP + Sonication	56	14

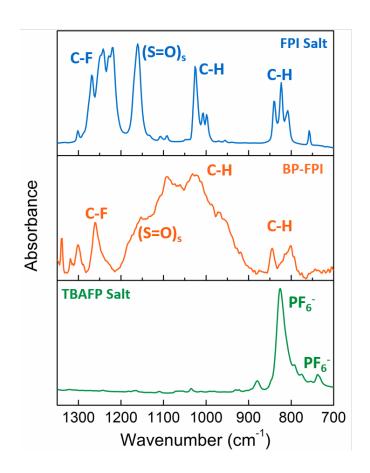
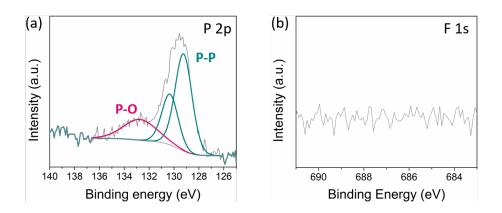
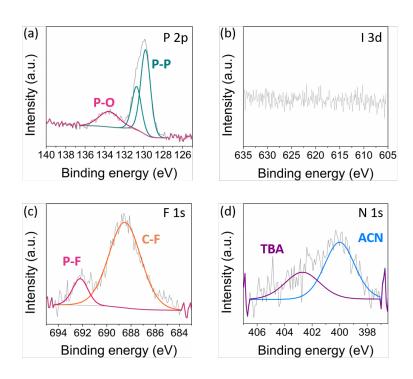


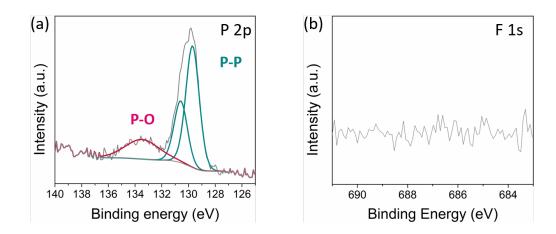
Figure S6: ATR-FTIR analysis of FPI-functionalized BP.



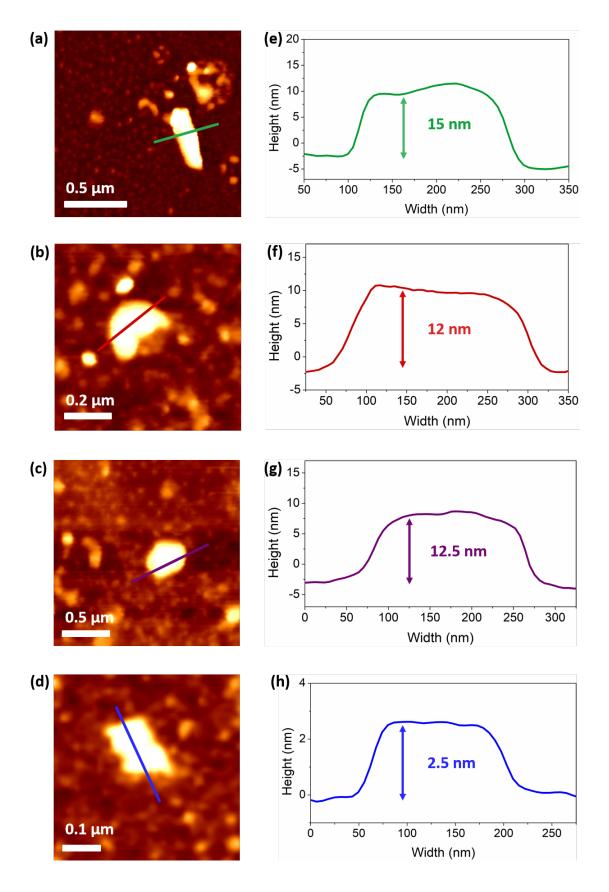
**Figure S7**: The (a) P 2p and (b) F 1s core levels of BP exfoliated in a solution of TBAFP without the presence of IBF did not result in a F 1s signal.



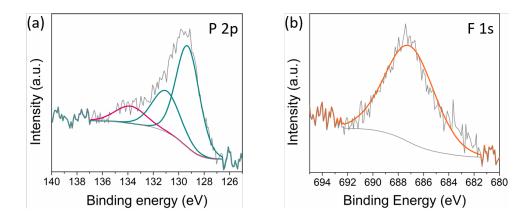
**Figure S8**: XPS analysis of FPI-functionalized BP showing the (a) P 2p, (b) I 3d, (c) F 1s and (d) N 1s peak.



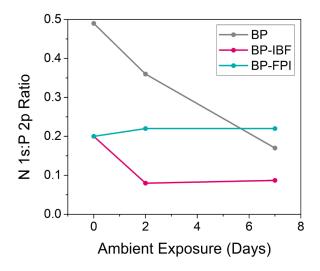
**Figure S9**: The (a) P 2p and (b) F 1s core levels of BP exfoliated in an IBF solution without the presence of TBAFP did not result in covalent attachment, as indicated by the absence of a discernible F 1s signal.



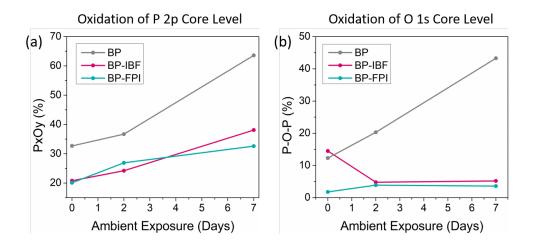
**Figure S10**: (a)-(d) AFM analysis and (e)-(h) corresponding line profiles display the formation of few-layer BP flakes through intercalation with minimal sonication.



**Figure S11:** (a) P 2p and (b) F 1s core levels for a sample prepared using stepwise intercalation using TBA, followed by minimal sonication (10 min) and exposure to an IBF solution also displayed signs of functionalization.



**Figure S12**: The N 1s:P 2p ratio as a function of ambient exposure displays the variation of solvent passivation for bare, FPI- and IBF-functionalized BP.



**Figure S13**: Evolution of the (a) P 2p and (b) O 1s core levels over a 1 week period show the superior ambient stability of functionalized BP.