SUPPLEMENTARY INFORMATION

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1. Energy stability, geometry and electronic parameters of Phosphorus allotropes

Table S1. Calculated relative energies (meV/atom) of main common bulk P structures using GGA-PBE coupled with two Grimme corrections and compared with values obtained at the same DFT level and beyond. All the numbers are given with respect to the β-white phase. The figures quoted for the Aykol study are approximate since they were extracted digitally from the plot in their paper.

	This work		Aykol *et al*[20]			
P allotrope	PBE+D2	PBE+D3	PBE+D2	PBE+D3	PBE+TS	RPA
Black	-198	-158	-190	-156	-143	-151
γ-white	-2.4	-1.0	-1.9	-0.3	-3.8	+5.0
Fibrous	-191	-163	-185	-159	-151	-155

Hittorf's	-191	-165	-185	-162	-155	-160

Table S2. PBE+D optimized unit cell lattice vectors and electronic band gaps of Hittorf's phosphorene (or hittorfene) compared with previous theory[46,54].

Ref.	Method	*a* (Å)	*b* (Å)	E_g (eV)
46	PBE	9.250	9.260	1.93
46	PBE+G06	9.150	9.210	-
46	PBE+TS	9.150	9.220	1.76
46	HSE	-	-	2.71
46	HSE+TS	-	-	2.52
54	PBE+D2	9.147	9.207	1.72
54	HSE	-	-	2.50
Present Work	PBE+D2	9.138	9.201	1.70
Present Work	PBE+D3	9.146	9.203	1.70

2. Electronic structures of Phosphorus allotropes

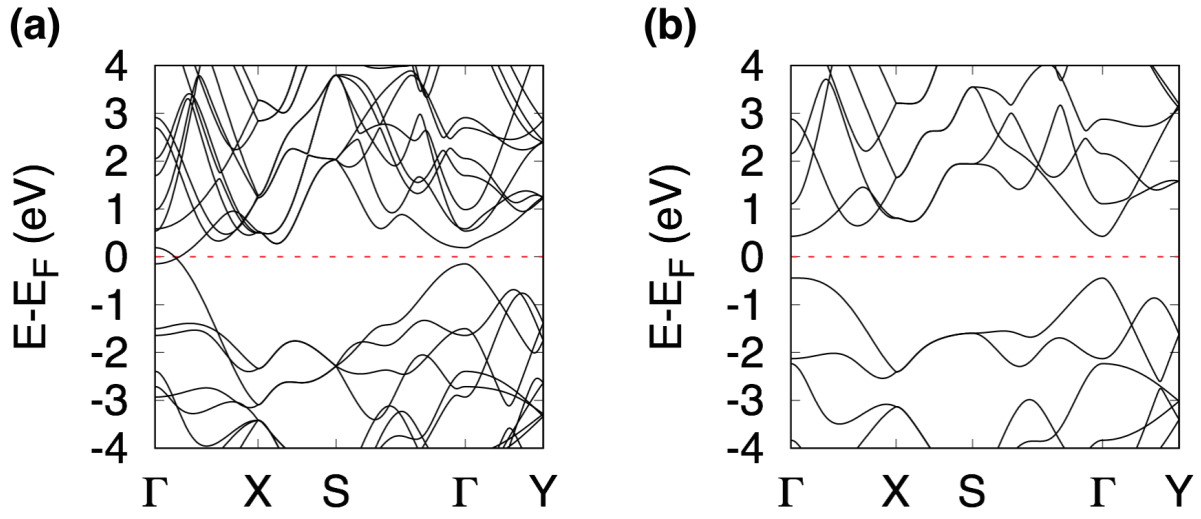

Figure S1: PBE+D2 electronic band structure of (a) bulk black phosphorus and (b) single-layer phosphorene calculated along Γ-X-S-Γ-Y path. Dashed red line represents the Fermi level position. DFT calculations have predicted for bulk and single-layer cases a metallic and semiconducting (~0.89eV) character, respectively.

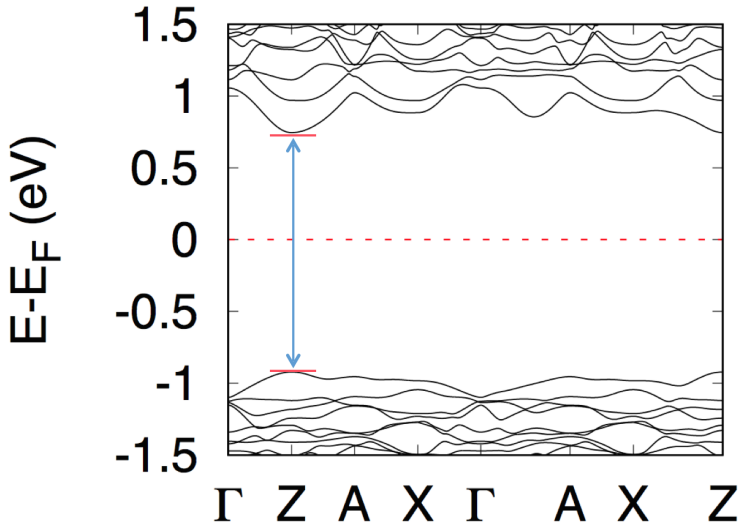

Figure S2: PBE+D2 electronic band structure of blue single-layer hittorf phosphorene (or equivalently, hittorfene) calculated along Γ-Z-A-X-Γ-A-X-Z path. Dashed red line represents the Fermi level position. DFT calculations have predicted a direct band gap of about ~1.70eV.

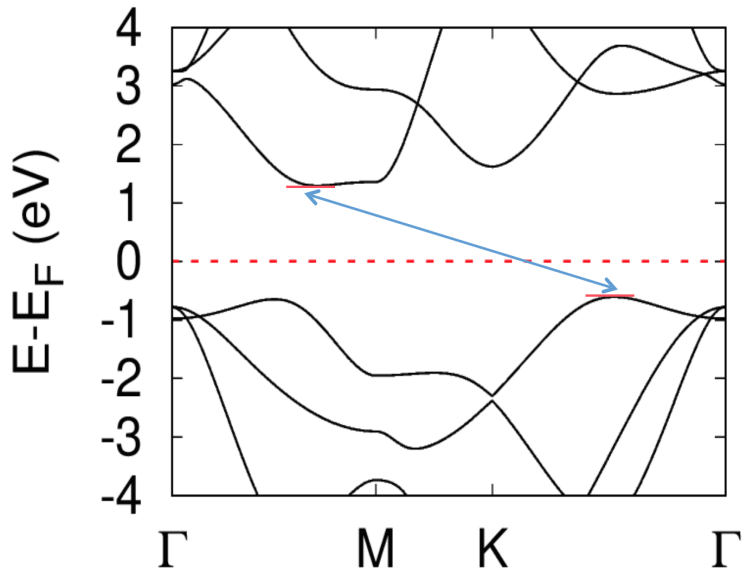

Figure S3: PBE+D2 electronic band structure of blue single-layer phosphorene calculated along Γ-M-K-Γ path. Dashed red line represents the Fermi level position. DFT calculations have predicted an indirect band gap of about ~1.91eV.

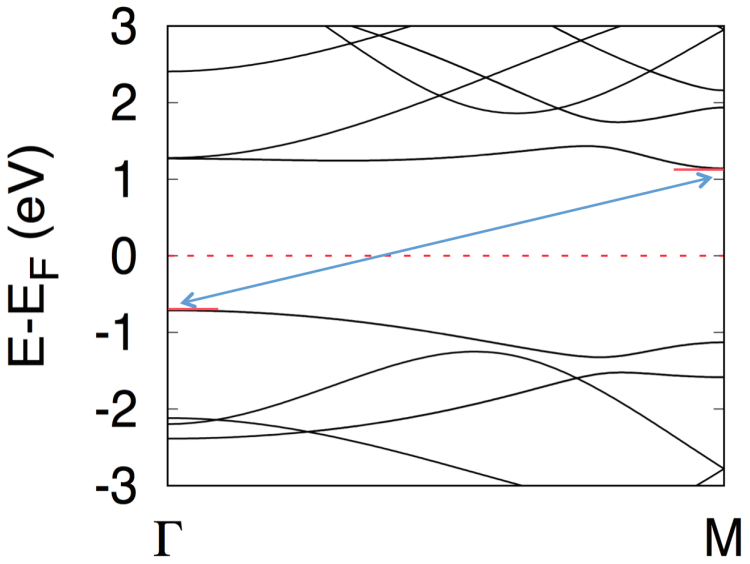

Figure S4: PBE+D2 electronic band structure of twisted square columnar phosphorus allotrope calculated along Γ-M path. Dashed red line represents the Fermi level position. DFT calculations predict an indirect band gap of about ~1.88eV.

3. Raman spectra of Phosphorus allotropes

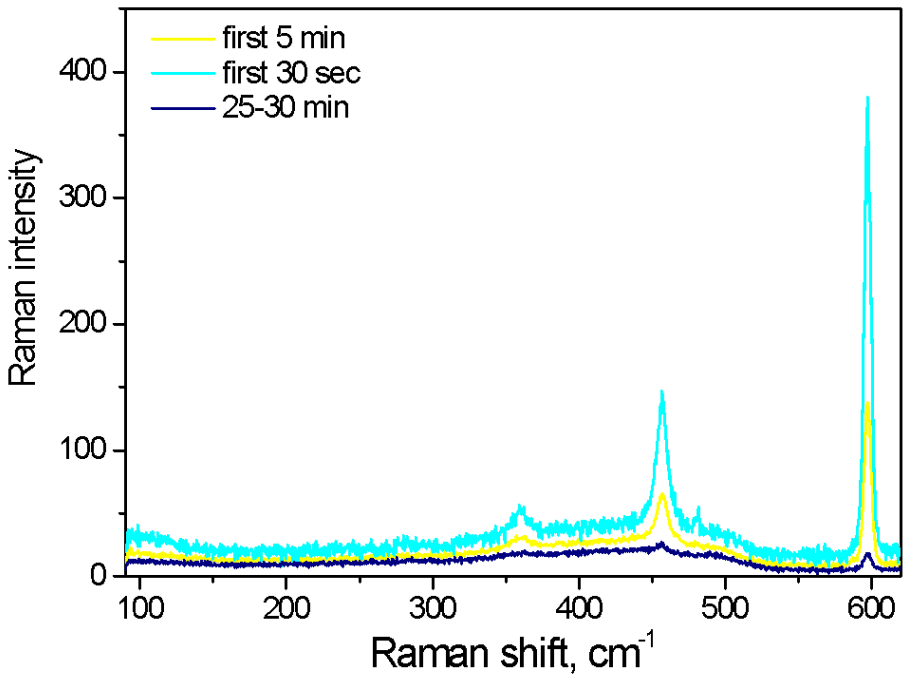

Figure S5: Spectra of white phosphorus, measured through the ampoule at a laser power of 8 mW. Different lines are measured at different times after the start of the first measurement. The lines characteristic of this material are very intense at the first moment of the measurement and then rapidly decrease. Reducing the intensity of the laser 12 times slows this process, but does not fully eliminate it. Consequently, the process of "burnout" of lines is associated with the phototransformation of the material, depending on the exposure.

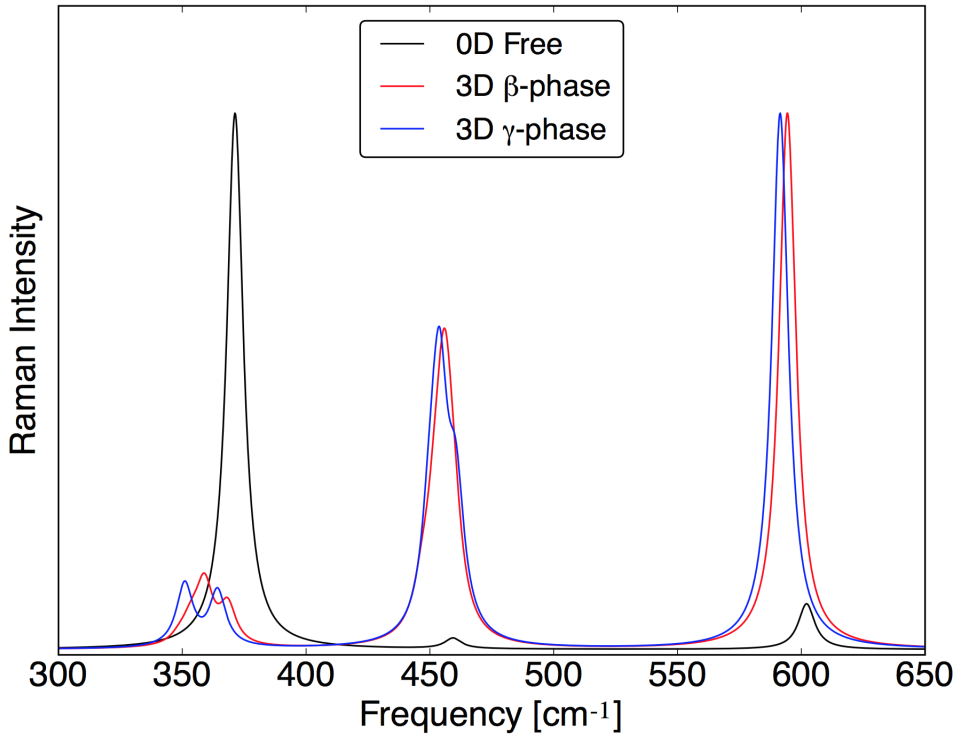

Figure S6: DFT-D2 simulated Raman spectra of white phosphorus in different configurations: 0D isolated P4 molecule (black line), 3D bulk β- (red) and γ-phase (blue) under 2.3eV excitation energy.

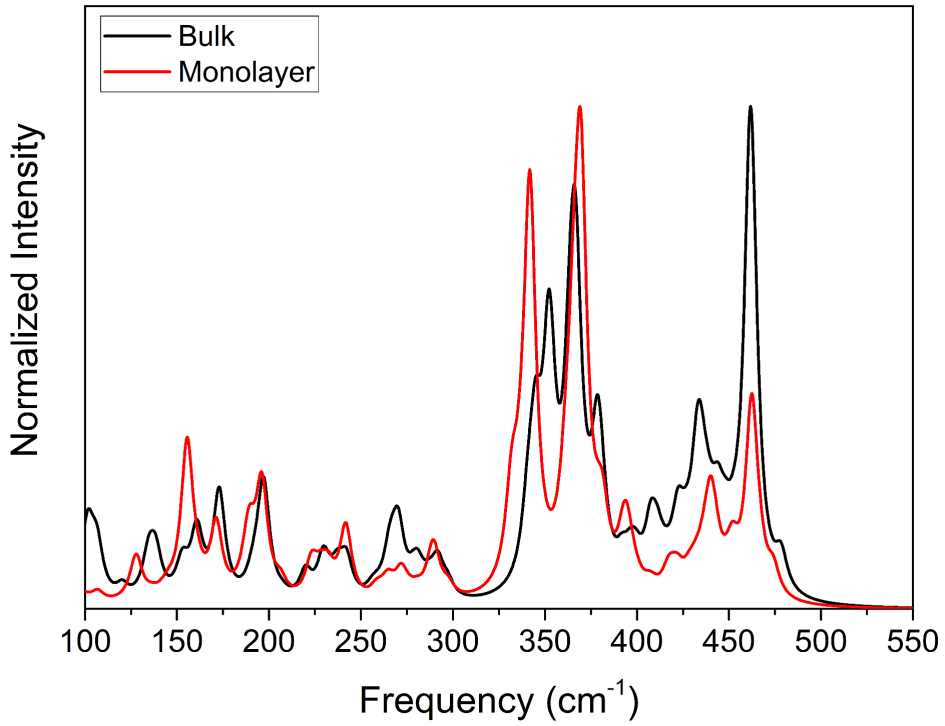

Figure S7: Comparison of the calculated DFT-D2 Raman spectra of (black line) bulk Hittorf's phosphorus and (red line) single-layer hittorfene at 2.3eV excitation energy (538 nm).

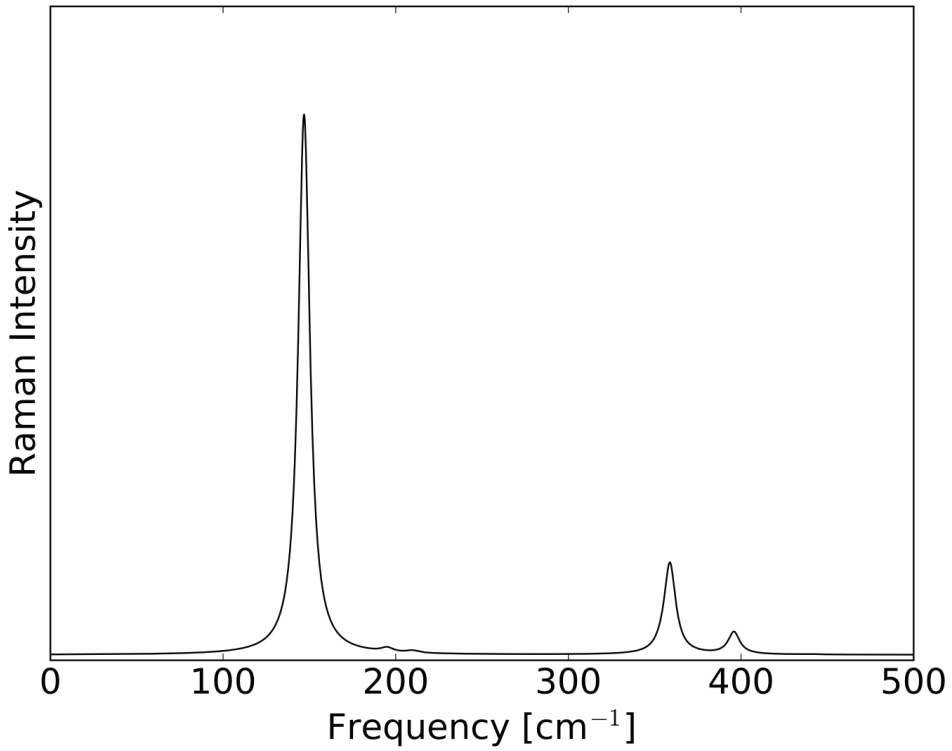

Figure S8: DFT-D2 simulated Raman spectra of the twisted square columnar phosphorus allotrope under 2.3eV excitation energy.