Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2021

Supplemental information

Excavate the missing piece of unsaturated two-dimensional phosphorous: a theoretical approach

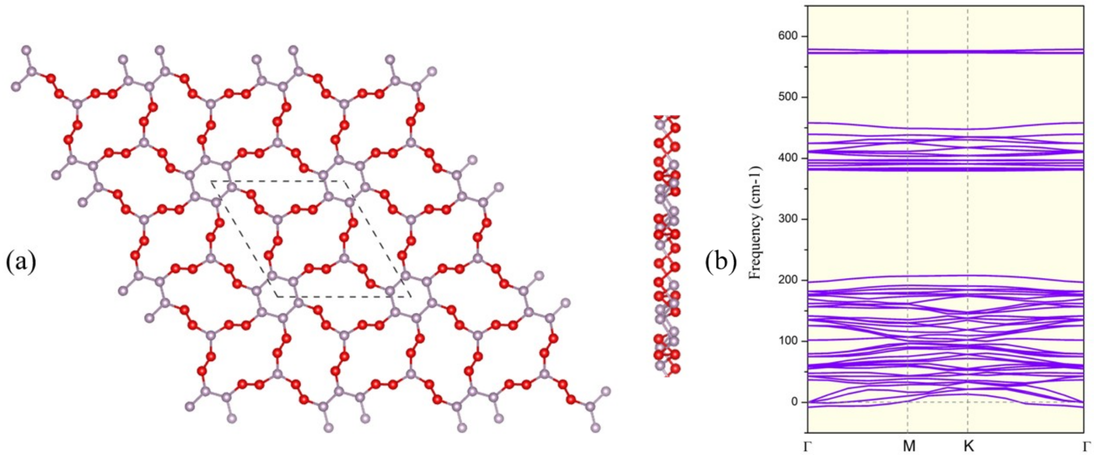

Figure S1. (a) optimized structure of *δ*-PY and (b) its phonon dispersion. The existence of inescapable soft modes illustrates its unstable nature, dynamically.

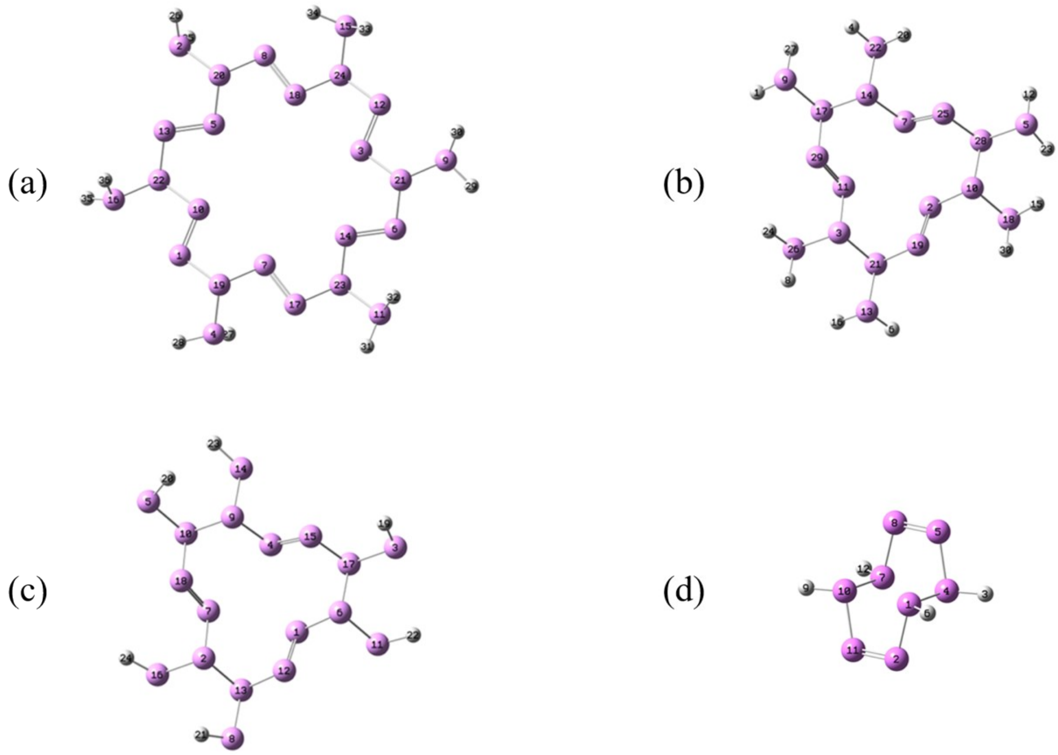

Figure S2. Smallest unit of (a) α-, (b) β-, (c) γ- and (d) P_{68}-PY used in NBO analysis

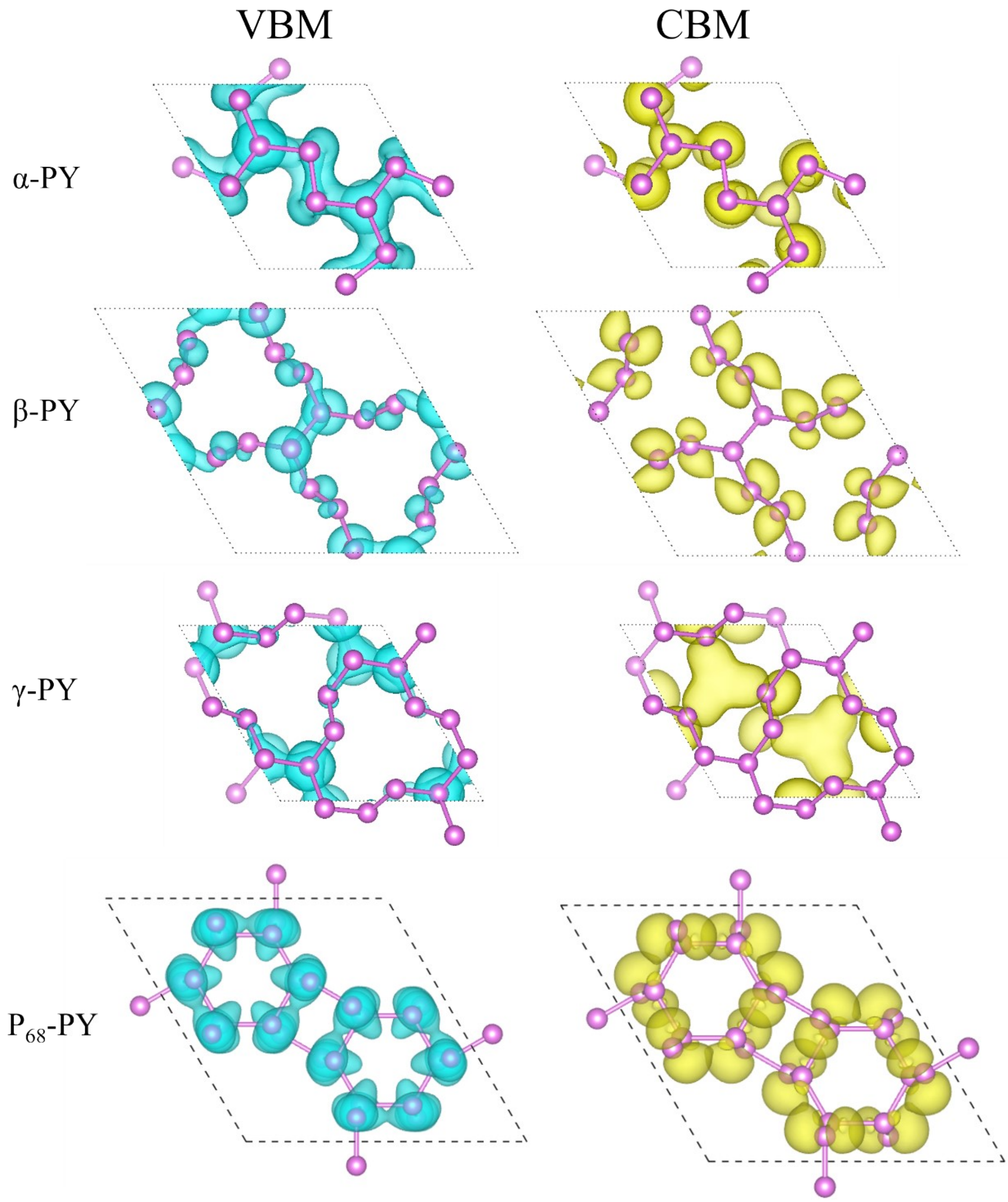

Figure S3. Density profile of the electron at valence band maximum and conduction band minimum for PY monolayers

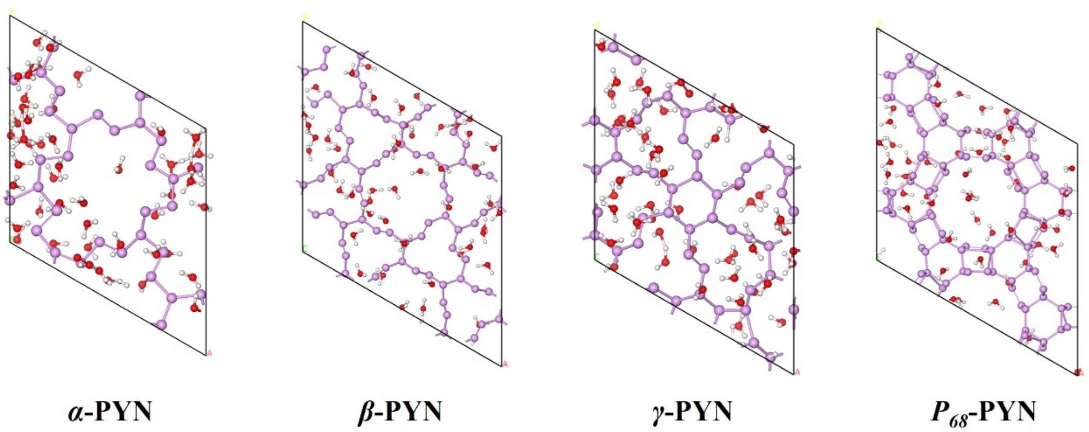

Figure S4. Snapshot of 5 ps AIMD simulations of PY in wet surroundings; water molecules are more favorable to approach *sp*^{2} phosphorous atoms, and some H atoms are dissociated from water molecules and bind to PY surface or even forming H_2.

Table S1 Structural parameters of phosphoryne allotropes

	Angle (°)			
	sp^2-sp^2-sp^3	*sp^2-sp^3-sp^2*	*sp^2-sp^3-sp^3*	*sp^3-sp^3-sp^3*
α-PY	99.26	104.71	/	/
β-PY	94.32	94.63	94.49	/
γ-PY	93.66	/	89.90	94.45
P_{68}-PY	103.12	/	94.45/100.12	109.99

Table S2 Second-Order Perturbation Theory Analysis of Fock Matrix in the NBO Basis corresponding to the intramolecular bonds of the unit of *β*-, *γ*- and P_{68}-PY at M062x/6-311G+(d, p) theoretical level

	donor(i)	acceptor (j)	$E^{(2)}$ Kcal/mol
β-PY	σ(P_3-P_{26})	π^*(P_{11}-P_{29})	3.71
	σ(P_3-P_{21})	π^*(P_2-P_{19})	3.54
	σ(P_{10}-P_{18})	π^*(P_2-P_{19})	4.03
	σ(P_{10}-P_{28})	π^*(P_7-P_{25})	3.52
	σ(P_{14}-P_{17})	π^*(P_{11}-P_{29})	3.57
	σ(P_{14}-P_{22})	π^*(P_7-P_{25})	3.70
γ-PY	σ(P_2-P_{13})	π^*(P_1-P_{12})	3.36
	σ(P_2-P_{16})	π^*(P_7-P_{18})	3.82
	σ(P_6-P_{11})	π^*(P_1-P_{12})	3.24
	σ(P_6-P_{17})	π^*(P_4-P_{15})	3.49
	σ(P_9-P_{10})	π^*(P_7-P_{18})	3.42
	σ(P_9-P_{14})	π^*(P_4-P_{15})	2.87
P_{68}-PY	σ(P_1-P_4)	π^*(P_2-P_{11})	2.54
	σ(P_1-P_4)	π^*(P_5-P_8)	2.54
	σ(P_7-P_{10})	π^*(P_2-P_{11})	2.54
	σ(P_7-P_{10})	π^*(P_5-P_8)	2.54

POSCAR of α-PY

```
1PY
   1.00000000000000
     8.5156002045000001    0.0000000000000000    0.0000000000000000
    -4.2578001022000000    7.3747261054999997    0.0000000000000000
     0.0000000000000000    0.0000000000000000   17.0466995238999992
   P
     8
Direct
  0.4480800259999995  0.3641400200000007  0.9908799889999997
  0.5519200430000026  0.6358600060000015  0.0091199880000019
  0.6358599280000021  0.0839400030000022  0.9908799889999997
  0.3641400129999965  0.9160599909999974  0.0091199880000019
  0.9160599630000021  0.5519200359999985  0.9908799889999997
  0.0839400099999992  0.4480800230000028  0.0091199880000019
  0.6666666759999984  0.3333333530000004  0.0429999999999993
  0.3333333200000013  0.6666666409999991  0.9570000379999968
```

POSCAR of *β*-PY

```
2PY
   1.00000000000000
     11.8448657177374006    -0.0000001601842046    -0.0000000000000006
     -5.9224327200895379    10.2579546960665411     0.0000000000000002
     -0.0000000000000004    -0.0000000000000007    24.5453769430127586
   P
     18
Direct
  0.7289198818701266  0.5481343437515349  0.5300306911785526
  0.2710800761298771  0.4518655732484618  0.4699692708214442
  0.4518655792484623  0.1807855431185956  0.5300306911785455
  0.5481343317515339  0.8192144468814035  0.4699692708214442
  0.8192144798814098  0.2710800791298666  0.5300306911785526
  0.1807855571185897  0.7289199108701325  0.4699692708214442
  0.1298144457666268  0.3929831234498806  0.5289430131141586
  0.8701855592333700  0.6070168665501186  0.4710569488858383
  0.6070168625501182  0.7368312933167473  0.5289430131141586
  0.3929831204498839  0.2631686726832569  0.4710569488858383
  0.2631686796832540  0.8701855382333719  0.5289430131141586
  0.7368313093167416  0.1298144387666227  0.4710569488858383
  0.5897847122136355  0.5738607996109977  0.4769332743992862
  0.4102152707863667  0.4261391653890030  0.5230667256007138
  0.4261391903890015  0.0159238776026385  0.4769332743992862
  0.5738608096109985  0.9840761213973650  0.5230667256007138
  0.9840760313973647  0.4102152727863668  0.4769332743992862
  0.0159238676026376  0.5897846932136375  0.5230667256007138
```

POSCAR of γ-PY

```
3PY
   1.00000000000000
     8.6417581362278817    0.0000000630528554    0.0000000000000000
    -4.3208791227193153    7.4839820478088788    0.0000000000000000
     0.0000000000000000    0.0000000000000000   21.4264348866011964
   P
    12
Direct
  0.0420249493563531  0.2392527660574473  0.0281467971946938
  0.9579751056436407  0.7607472149425476  0.9718531728053037
  0.7607472699425486  0.8027721682989082  0.0281467971946938
  0.2392527560574464  0.1972278577010940  0.9718531728053037
  0.1972278457010930  0.9579751176436417  0.0281467971946938
  0.8027721072989067  0.0420249463563565  0.9718531728053037
  0.5359889135362366  0.6037096993834297  0.9689993870638460
  0.4640111074637687  0.3962903416165702  0.0310006609361579
  0.3962903386165735  0.9322792831527948  0.9689993870638460
  0.6037096963834330  0.0677207358472032  0.0310006609361579
  0.0677207208472055  0.4640110704637692  0.9689993870638460
  0.9322792581527963  0.5359889405362352  0.0310006609361579
```

POSCAR of P_{68}-PY

```
4PY
   1.00000000000000
     12.0612790545750475    -0.0000000136799655    -0.0000000000000002
     -6.0306395154145083    10.4453740701894056     0.0000000000000002
     -0.0000000000000013     0.0000000000000000    30.3466732144643103
   P
    24
Direct
  0.4821721763218463  0.3323719812229982  0.0008853167870484
  0.5178278476781557  0.6676280027770005  0.9991147172129544
  0.6676280397770071  0.1498001650988670  0.0008853167870484
  0.3323719652229897  0.8501997809011357  0.9991147172129544
  0.8501998069011449  0.5178278376781336  0.0008853167870484
  0.1498001520988552  0.4821721453218615  0.9991147172129544
  0.9012994880273126  0.5577917159673120  0.9301272773173466
  0.0987005359726894  0.4422082670326830  0.0698726966826513
  0.4422082410326809  0.3435077160600102  0.9301272773173466
  0.5577916839673165  0.6564922299399925  0.0698726966826513
  0.6564922969400087  0.0987005239726741  0.9301272773173466
  0.3435077310599937  0.9012994690273288  0.0698726966826513
  0.8500266994207379  0.3322302865493114  0.9992710999610139
  0.1499732895792647  0.6677696594506912  0.0007289340389889
  0.6677696754506854  0.5177964018714007  0.9992710999610139
  0.3322303005493197  0.4822035811285943  0.0007289340389889
  0.4822035841285839  0.1499732945792829  0.9992710999610139
  0.5177964068714189  0.8500266884207122  0.0007289340389889
  0.9015605493449002  0.3437575464078577  0.0699927931147784
  0.0984394236550941  0.6562423995921449  0.9300072228852230
  0.6562424295921332  0.5578029819370514  0.0699927931147784
  0.3437575614078625  0.4421970010629508  0.9300072228852230
  0.4421970080629620  0.0984394446550922  0.0699927931147784
  0.5578029789370405  0.9015605293449127  0.9300072228852230
```