Easy and fast *in-situ* functionalization of exfoliated 2D black phosphorus with gold nanoparticles

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Supporting Information

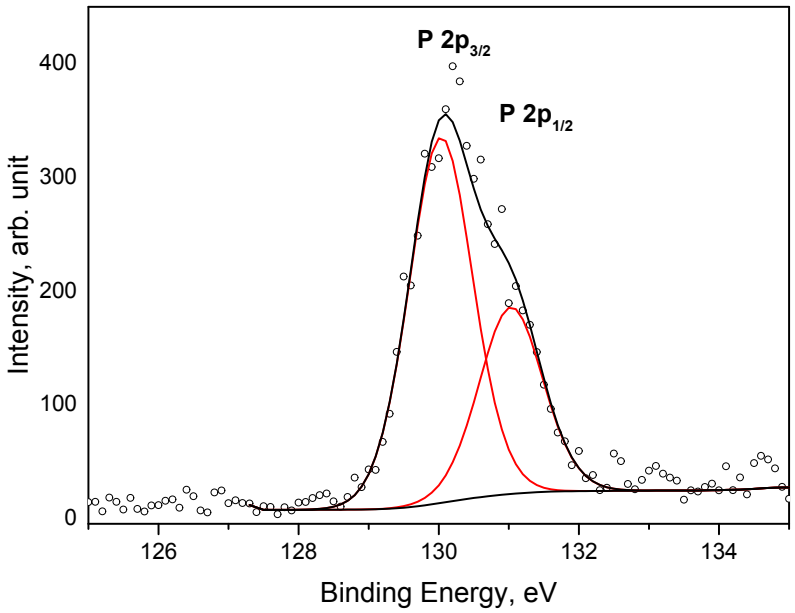

Figure S1. XPS spectra of bulk bP on a Si/SiO_2 substrate.

Table S1. Binding Energy (BE) and atomic concentration (atomic %), acquired on a bare 2D bP flake.

Name	Peak BE	Atomic %	Bond
C1s – 1	284.9	47.6	C – C
C1s – 2	286.7	5.3	C – O

O1s – 1	532.2	6.2	C – O
O1s – 2	533.8	3.5	
$P2p_{3/2}$	130.0	37.4	P^0

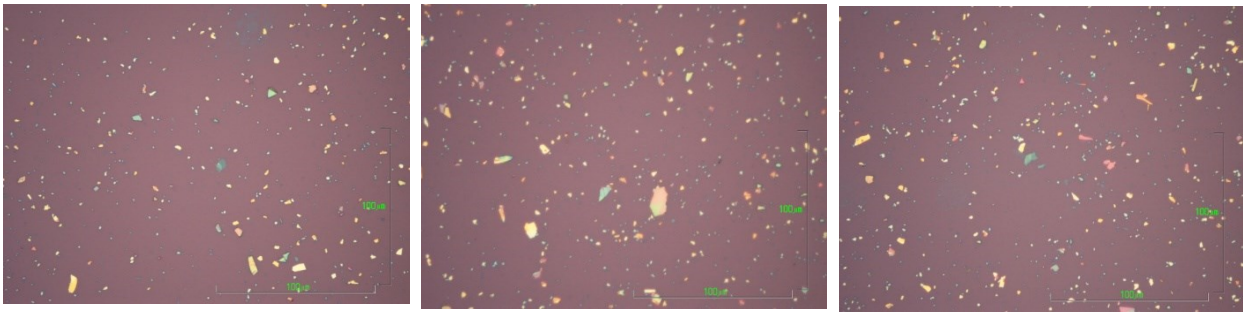

Figure S2. Optical microscopy images in different areas of a sample of mechanically exfoliated 2D bP on a Si/SiO_2 substrate.

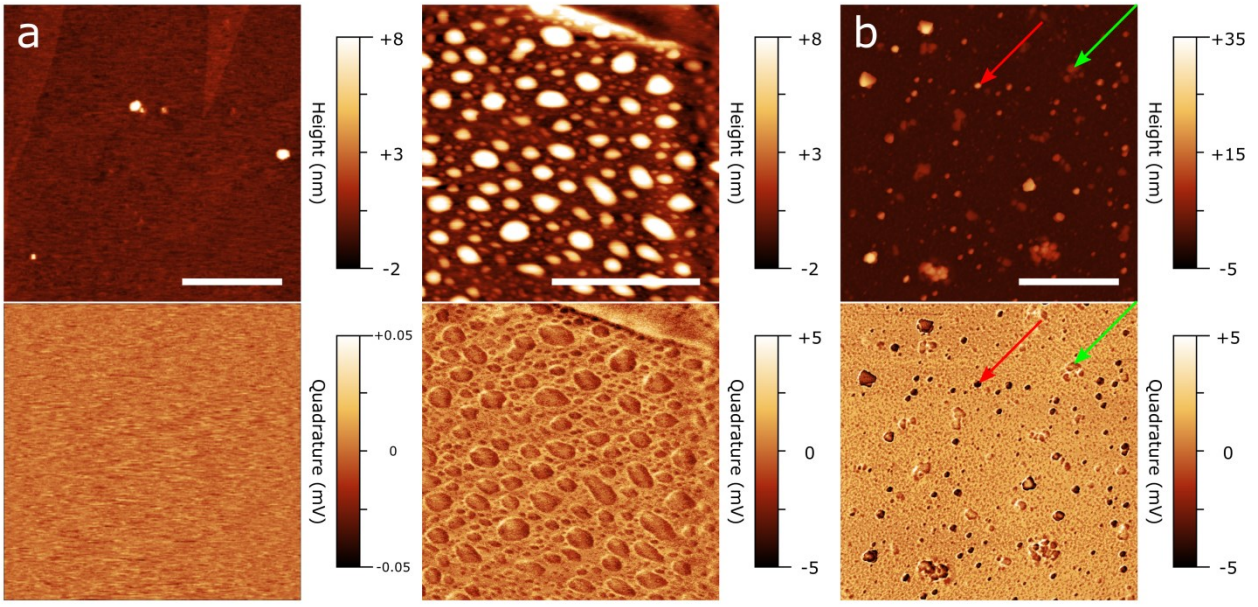

Figura S3. (a) Representative AFM topography (top row) and peakforce quadrature (bottom row) of 2D BP immediately after cleavage (left column) and after being exposed to air for 1h (right column). Oxidation leads to the formation of raised 'bubbles' which have markedly different mechanical characteristics wrt pristine BP. Scale bar = 500 nm. (b) AFM topography (top) and peakforce quadrature (bottom) of a 2D BP flake decorated with Au nanoclusters after several hours of AFM imaging under a gentle nitrogen flow. This zone is partially contaminated with solvent/inert gas impurities, and is beginning to show local oxidation. Nevertheless, Au clusters (e.g. red arrow) are still easily told apart from other features with similar morphology (e.g. green arrow) on the basis of their lower quadrature signal. Scale bar = 500 nm.

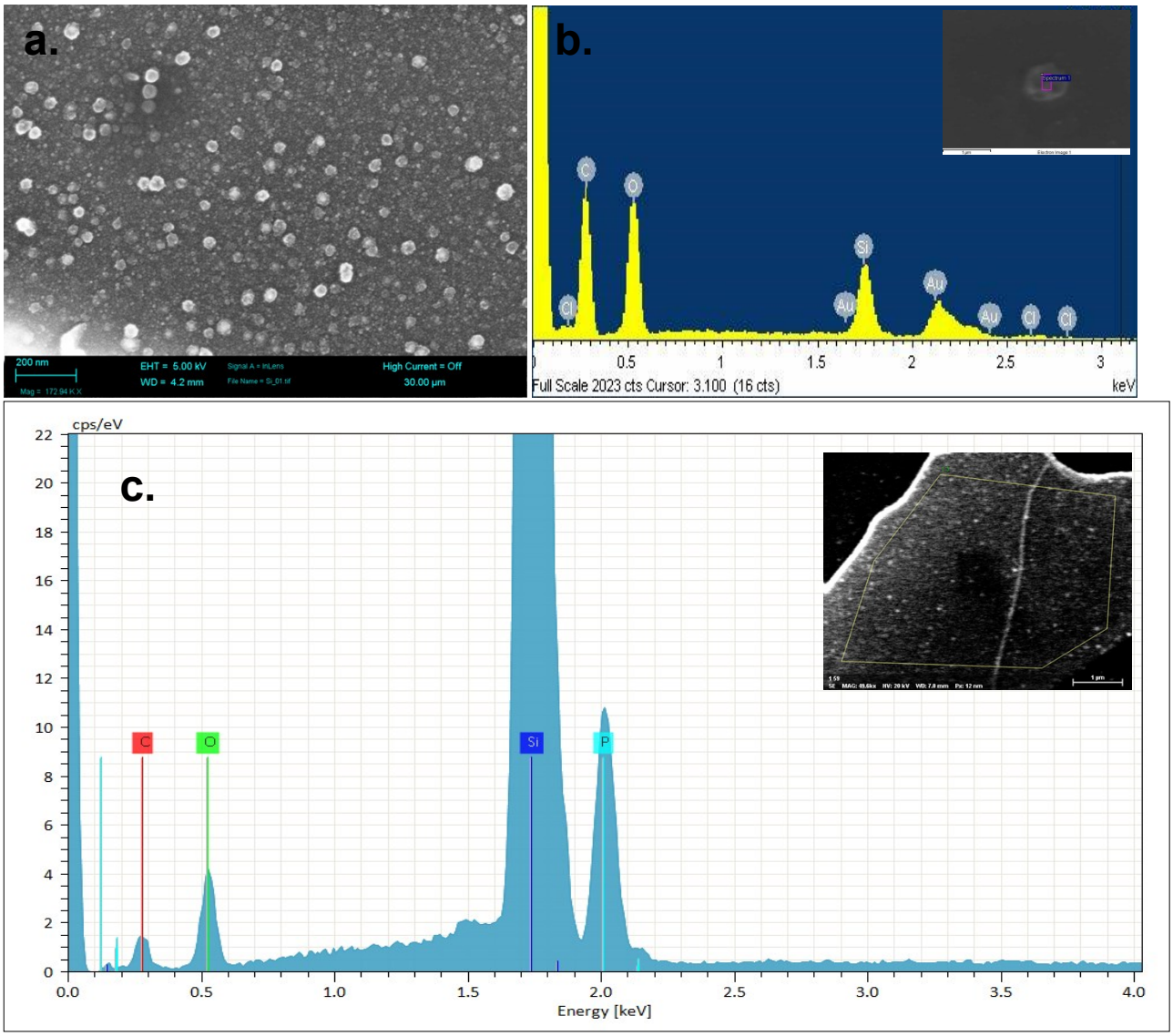

Figure S4. SEM images and relative EDX analysis on a Si/SiO_2/2D bP sample functionalized with gold NPs during 18h of reaction. (a) SEM image where gold NPs are visible as bright spots and spread all over the surface of the 2D bP flake (b) elemental analysis through EDX spectrum of a micrometric Au NPs adsorbed on the Si/SiO_2 substrate; (c) elemental analysis through EDX spectrum of an area of a 2D bP flake covered with Au NPs; the typical signal from Au is not evidenced here due to its relative low content (<1%).

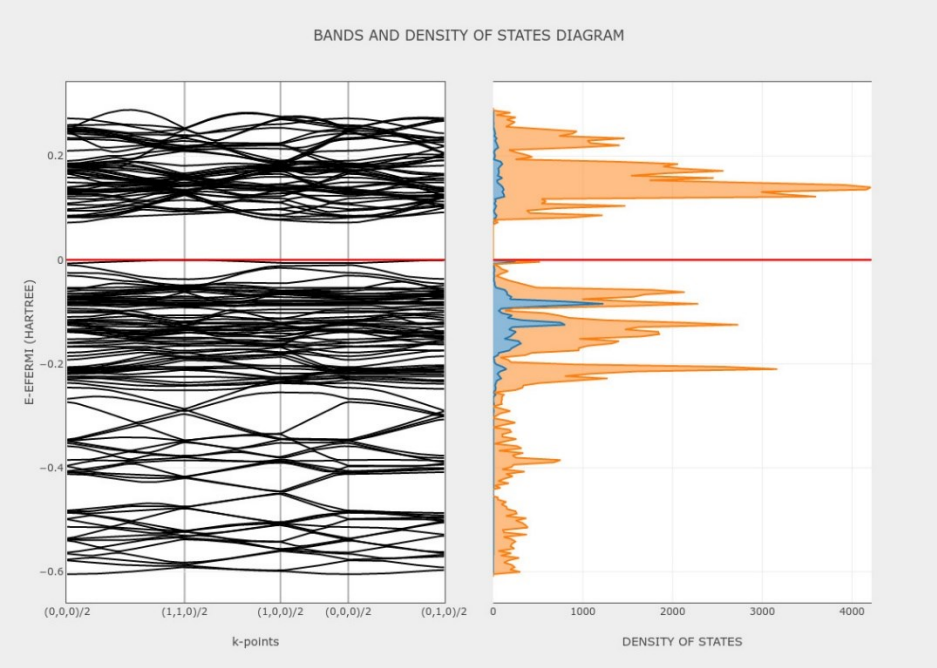

Figure S5. Band and DOS structures of the heterostructure of phosphorene and a Au_2 moiety. The contribution from gold in blue falls in between the valence and conducting bands with a consequent narrowing of band gap.

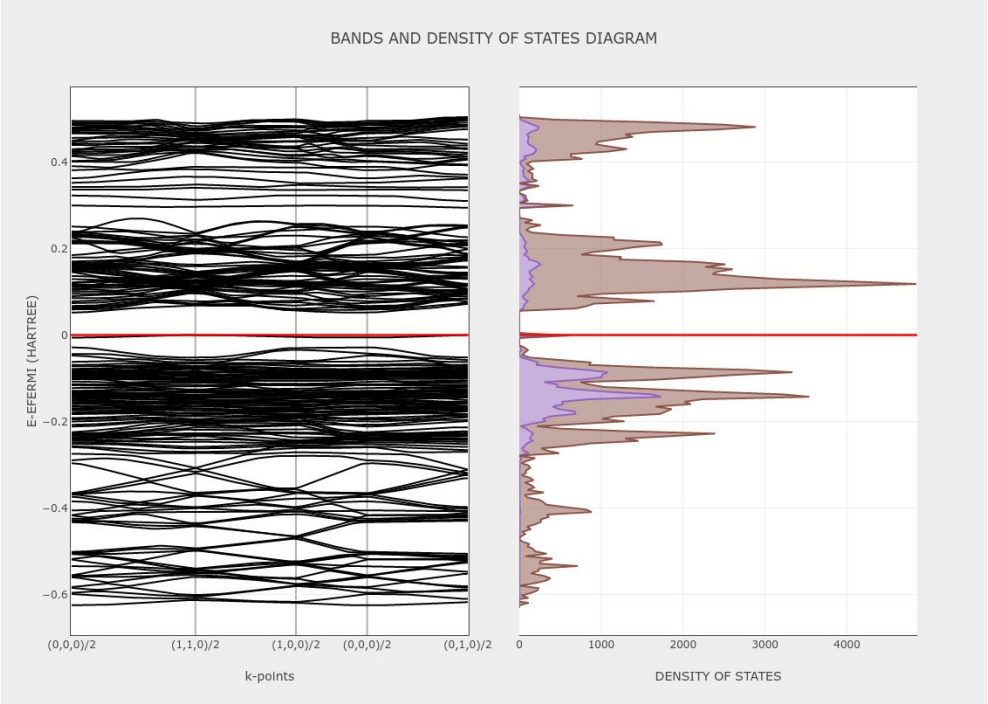

Figure S6. Band and DOS structures of the heterostructure of phosphorene and a Au_4 moiety. The contribution from gold in violet falls in between the valence and conducting bands with a consequent narrowing of band gap.

List of Coordinates and Energy parameters of Optimized Structures

Phosphorene, supercell of 32 atoms
Structural parameters
CELL 13.4084 9.4218 89.9991

P 0.125014 0.048968 1.094693
P 0.000011 0.207071 1.095026
P -0.000001 0.298947 -1.024510
P 0.125021 0.456998 -1.026356
P -0.124988 0.048976 1.094462
P 0.250011 0.207063 1.094954
P 0.250054 0.298941 -1.024543
P -0.124981 0.457068 -1.024263
P 0.125029 -0.451082 1.093039
P 0.000062 -0.292969 1.094767
P 0.000026 -0.201024 -1.024559
P 0.125025 -0.042950 -1.024729
P -0.124970 -0.451025 1.095204
P 0.250008 -0.292971 1.094798
P 0.250019 -0.201026 -1.024545
P -0.124972 -0.042944 -1.024965
P -0.374984 0.048961 1.094466
P -0.499982 0.207050 1.094576
P -0.499978 0.298968 -1.024819
P -0.374991 0.457072 -1.024407
P 0.375006 0.048964 1.094573
P -0.249989 0.207056 1.094578
P -0.249984 0.299002 -1.024763
P 0.375012 0.457059 -1.024325
P -0.374972 -0.451025 1.095061
P -0.499978 -0.292927 1.094727
P -0.499980 -0.201032 -1.024807
P -0.374976 -0.042947 -1.025010
P 0.375038 -0.451037 1.095155
P -0.249978 -0.292922 1.094634
P -0.249958 -0.201039 -1.024929
P 0.375026 -0.042941 -1.024886

Energy -10922.3367839 AU/CELL

Phosphorene with one gold atom
Structural parameters
CELL 13.39372594 9.55786828 89.999627

P 1.250236441839E-01 6.960022737075E-02 1.044869652918E+00
P -3.808682116868E-03 2.190658109243E-01 1.089258627397E+00
P -1.130580563399E-03 3.026844522494E-01 -1.040849578717E+00
P 1.250216452365E-01 4.581371937772E-01 -1.028672144265E+00
P -1.242894968668E-01 5.330448710344E-02 1.129598213450E+00
P 2.538549268754E-01 2.190679268408E-01 1.089320440973E+00
P 2.511764002959E-01 3.026865529854E-01 -1.040820903347E+00
P -1.285684215782E-01 4.559716417149E-01 -1.060695721786E+00
P 1.250223839398E-01 -4.565086540142E-01 1.104039276921E+00
P 2.412683254050E-03 -2.967067532424E-01 1.180946824034E+00
P 1.344049291881E-03 -1.984772920828E-01 -9.180161695524E-01
P 1.250202486879E-01 -4.069161976372E-02 -1.016537042161E+00
P -1.272590554680E-01 -4.577366219743E-01 1.060417920572E+00
P 2.476295303463E-01 -2.967039785150E-01 1.180958403358E+00
P 2.486990078826E-01 -1.984723687745E-01 -9.179928890088E-01
P -1.245830817342E-01 -4.454603028594E-02 -9.540566012173E-01
P -3.749770967178E-01 4.884227293511E-02 1.106226803143E+00
P -4.991026627534E-01 2.066820296553E-01 1.085522515507E+00
P -4.988571260098E-01 2.938952964842E-01 -1.053705565054E+00
P -3.749780931992E-01 4.513926648882E-01 -1.044132472439E+00
P 3.743358827289E-01 5.330499631502E-02 1.129595926997E+00
P -2.508525434649E-01 2.066815399926E-01 1.085508659635E+00
P -2.510995003405E-01 2.938916740583E-01 -1.053724991974E+00
P 3.786113103151E-01 4.559757321584E-01 -1.060705124982E+00
P -3.749780587217E-01 -4.540487993084E-01 1.077675704011E+00
P 4.997656019820E-01 -2.990754008242E-01 1.102708936887E+00
P 4.992490040075E-01 -2.017797673058E-01 -9.870430549456E-01
P -3.749779084802E-01 -4.597122636339E-02 -9.937556051221E-01
P 3.773015496557E-01 -4.577291261478E-01 1.060403328621E+00
P -2.497217440028E-01 -2.990778379703E-01 1.102726039993E+00
P -2.492050112055E-01 -2.017818544008E-01 -9.870265815394E-01
P 3.746257974311E-01 -4.454268245465E-02 -9.540681812515E-01
Au 1.249953971085E-01 -1.345344860252E-01 2.368225352949E+00

Energy -11057.660457649 AU/CELL

Phosphorene with two gold atoms parallel to the channel (Figure 6a in the text)
Structural parameters
CELL 13.38295710 9.68648254 90.022004

P 1.257112060372E-01 6.955488997194E-02 1.102071363479E+00
P 2.388297213415E-05 2.263286833989E-01 1.141827706132E+00
P 8.346912797902E-06 3.048088137532E-01 -9.927927566606E-01
P 1.279603648023E-01 4.561828331431E-01 -1.021572031758E+00
P -1.257350149849E-01 6.964747735129E-02 1.102847219437E+00

P 2.546973599648E-01 2.158486551063E-01 1.082308205675E+00
P 2.510416266342E-01 2.969084464422E-01 -1.067986694266E+00
P -1.277419781810E-01 4.564041392895E-01 -1.019713247008E+00
P 1.291053871211E-01 -4.601062944069E-01 1.097041358196E+00
P -2.114010403052E-06 -2.955713336840E-01 1.299706330827E+00
P -7.542884365770E-05 -1.963541219748E-01 -8.022670185380E-01
P 1.245757699657E-01 -4.205611696473E-02 -9.412658493853E-01
P -1.290065903296E-01 -4.597404530832E-01 1.099853509869E+00
P 2.498804200862E-01 -2.996670383593E-01 1.175822986990E+00
P 2.483218030498E-01 -1.982128525323E-01 -9.082799912693E-01
P -1.245991903370E-01 -4.196675377939E-02 -9.406525994579E-01
P -3.748326160987E-01 5.286422092217E-02 1.119117771588E+00
P -4.999793594539E-01 2.063661504598E-01 1.071420367486E+00
P -4.999517447245E-01 2.911063890215E-01 -1.079698750491E+00
P -3.769738849874E-01 4.494942885511E-01 -1.101242406576E+00
P 3.748331315483E-01 5.278143763597E-02 1.118659607173E+00
P -2.546393357867E-01 2.159830526744E-01 1.083468497001E+00
P -2.509479329503E-01 2.972536308599E-01 -1.066039535725E+00
P 3.770388772431E-01 4.493038387488E-01 -1.101718746745E+00
P -3.754594046079E-01 -4.582633487692E-01 1.008562184704E+00
P 4.999593551465E-01 -3.050887273476E-01 1.064127644918E+00
P 4.999845959468E-01 -2.003767485074E-01 -9.882238660221E-01
P -3.744863708798E-01 -4.602556046229E-02 -9.590496818712E-01
P 3.753628169307E-01 -4.583681187006E-01 1.008251146412E+00
P -2.499213851643E-01 -2.995256569207E-01 1.177287440996E+00
P -2.483773015852E-01 -1.981701142462E-01 -9.070889442459E-01
P 3.745126924701E-01 -4.606115900846E-02 -9.595990780587E-01
Au 1.160634473757E-01 -1.380569205845E-01 2.378655114358E+00
Au -1.155514312821E-01 -1.379256279987E-01 2.380262742839E+00

Energy -11193.01327626 AU/CELL

Phosphorene with two gold atoms over the channel (Figure 6b in the text)
Structural parameters
CELL 13.40868591 9.48997962 90.000747
P 1.249972931988E-01 6.440545114373E-02 1.022828104588E+00
P -3.772199787055E-03 2.132365824383E-01 1.090913751815E+00
P 2.362430726518E-03 3.029269561080E-01 -1.037645518623E+00
P 1.250057791857E-01 4.622570459590E-01 -9.433591096072E-01
P -1.249039396849E-01 4.901162601588E-02 1.104478655966E+00
P 2.537758178314E-01 2.132245319200E-01 1.091019306961E+00
P 2.476401741455E-01 3.029186445389E-01 -1.037566190585E+00
P -1.261636197706E-01 4.539065752109E-01 -1.079464728207E+00
P 1.250087818501E-01 -4.457318763998E-01 1.307287114514E+00
P -4.712251541618E-03 -2.927061568555E-01 1.174249150887E+00
P 9.958481675746E-04 -2.041406574211E-01 -9.724730809461E-01

P 1.250039689889E-01 -4.694820176820E-02 -1.034412365277E+00
P -1.264734887393E-01 -4.564243874834E-01 1.030273215796E+00
P 2.547260693501E-01 -2.927040680132E-01 1.174192685103E+00
P 2.490073884913E-01 -2.041424610506E-01 -9.728459979553E-01
P -1.236179010387E-01 -4.604139034027E-02 -1.004209711370E+00
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P -4.994576029183E-01 2.050231432100E-01 1.065891903656E+00
P 4.998596661440E-01 2.939293268112E-01 -1.067178200409E+00
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P -2.505406389803E-01 2.050305739420E-01 1.065940480635E+00
P -2.498576841018E-01 2.939356276040E-01 -1.067127675340E+00
P 3.761677589893E-01 4.539002817495E-01 -1.079365786595E+00
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P -3.749976725619E-01 -4.550460062078E-02 -1.032080273478E+00
P 3.764787509475E-01 -4.564316554874E-01 1.030361446967E+00
P -2.504429990542E-01 -2.991925650085E-01 1.068418727561E+00
P -2.494785394046E-01 -2.020268973221E-01 -1.026264336038E+00
P 3.736236910921E-01 -4.604281637114E-02 -1.004297275549E+00
Au 1.250297052198E-01 -1.041430360356E-01 2.656285171023E+00
Au 1.251955920813E-01 -3.377352419521E-01 3.865713103141E+00

Energy -11193.03924027 AU/CELL

Phosphorene with four gold atoms

Structural parameters

CELL 13.40268910 9.48211116 90.437818
P 1.118275872495E-01 6.207551921147E-02 1.188194940760E+00
P -1.267524142705E-02 2.205017879102E-01 1.221943245336E+00
P -7.862069710170E-03 3.075673549163E-01 -9.187958863663E-01
P 1.171077614259E-01 4.659992826666E-01 -9.334258094771E-01
P -1.349606323286E-01 5.666108021239E-02 1.180090495719E+00
P 2.424319746631E-01 2.098617342443E-01 1.158952773470E+00
P 2.395838706619E-01 3.057629897558E-01 -9.474763084305E-01
P -1.341664177212E-01 4.615206554731E-01 -9.801992378408E-01
P 1.166692019219E-01 -4.394056742470E-01 1.207650397666E+00
P -9.764623813792E-03 -2.830817171000E-01 1.189329986913E+00
P -8.667492021925E-03 -1.919475399277E-01 -9.369267923484E-01
P 1.166725327921E-01 -3.499313850030E-02 -9.873935927209E-01
P -1.342884420891E-01 -4.446720952205E-01 1.114869876600E+00
P 2.464001988277E-01 -2.842903964387E-01 1.210062441872E+00
P 2.378992901806E-01 -1.913040757818E-01 -1.049983192325E+00
P -1.332460314632E-01 -3.479866550798E-02 -9.449259163012E-01
P -3.841831098379E-01 5.256690599839E-02 1.167390759220E+00
P 4.912062440299E-01 2.091936739550E-01 1.168051385701E+00
P 4.918305420805E-01 2.970594551501E-01 -9.682544656367E-01

P -3.839981237176E-01 4.572166076736E-01 -9.801907446032E-01
P 3.657504054715E-01 4.995129080987E-02 1.190019031195E+00
P -2.598711801568E-01 2.122967516977E-01 1.167996956269E+00
P -2.588956672984E-01 3.019279196012E-01 -9.611693141148E-01
P 3.685800581908E-01 4.569343703367E-01 -9.457726242043E-01
P -3.843528794920E-01 -4.453120950597E-01 1.119459909012E+00
P 4.909351967965E-01 -2.901310820270E-01 1.119733416841E+00
P 4.890523411790E-01 -1.927888018512E-01 -9.768351003427E-01
P -3.841445684652E-01 -3.670785061214E-02 -9.576107397274E-01
P 3.690810273835E-01 -4.523823042524E-01 1.151547654430E+00
P -2.587105042288E-01 -2.888652713407E-01 1.127855105862E+00
P -2.588854949834E-01 -1.927636613788E-01 -9.681194285638E-01
P 3.640834529668E-01 -3.566071625250E-02 -9.732720626672E-01
Au 1.350741430753E-01 -1.189159545765E-01 2.790263288736E+00
Au 1.977031676525E-01 -3.509849971002E-01 3.817054864747E+00
Au 2.496424290206E-01 3.662074632758E-01 2.928031611039E+00
Au 2.664410531853E-01 4.503011942867E-01 5.348753074282E+00

Energy -11463.784640832 AU/CELL