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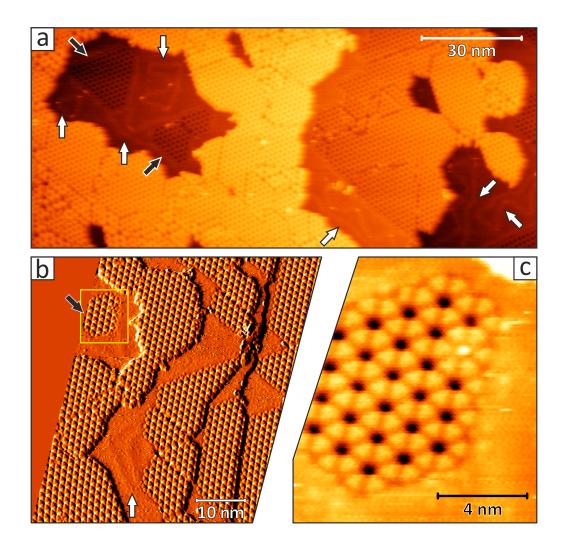


Figure S1: STM visualization of (4 x 4)-BlueP patches incorporated into the top-most Au layer. (a) large-scale image, patches of (4 x 4)-BlueP are marked with black arrows. On areas free from P one can see lines and loops of a modified herringbone reconstruction (marked with white arrows). (b) Large-scale current channel STM image of a different region showing a (4 x 4)-BlueP patch and islands connected to the step edges of Au(111). Details of the phosphorus-gold border region are similar in both cases. A close-up of the (4 x 4)-BlueP patch in the yellow rectangle is shown in panel (c). Tunneling parameters were: (a)  $I_t = 0.5$  nA,  $U_t = 1$  V; (b), (c)  $I_t = 0.6$  nA,  $U_t = 1$  V.

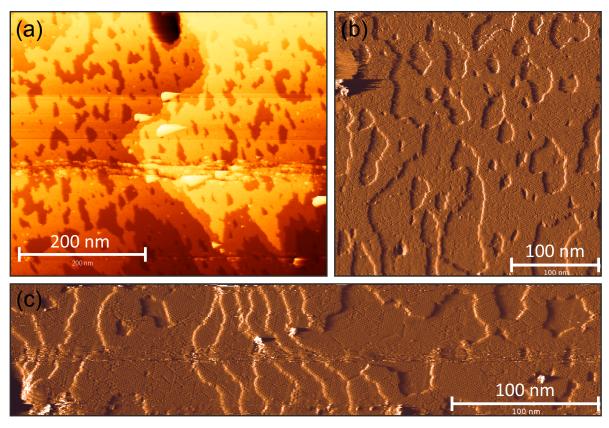


Figure S2: (a), (b) and (c) Large-scale STM images of BlueP on Au(111) prepared after P deposition with the substrate held at room temperature and a post-deposition annealing step at  $250^{\circ}$ C.

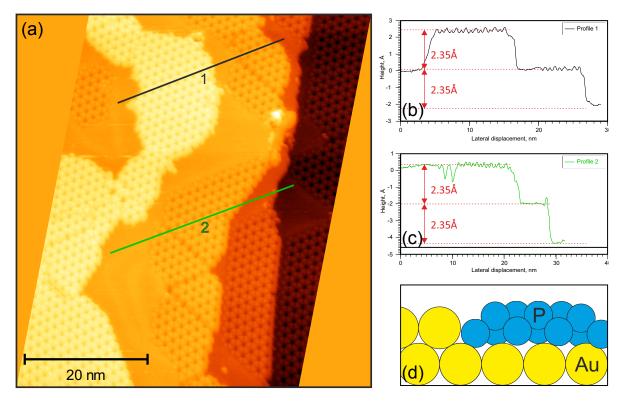


Figure S3: (a) STM image of BlueP on Au(111) after room temperature deposition and post-deposition annealing at 250°C. (b), (c) Line profiles along the marked segments in (a). (d) Ball and stick model representation corresponding to (b), (c).

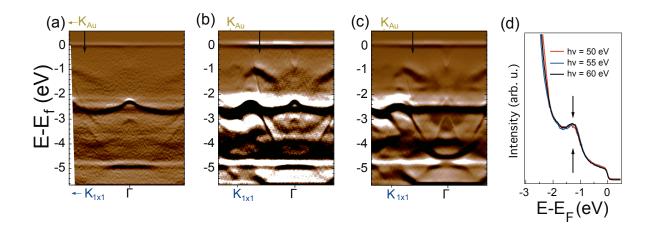


Figure S4: (a) ARPES spectra along the  $\Gamma$ K high-symmetry direction for excitation energies of (a) 50, (b) 55, and (c) 60 eV. (d) Energy distribution curves at  $k_{\parallel}=0.8~{\rm \AA}^{-1}$ , marked with black arrows in (a)-(c), of the (4 x 4)-BlueP on Au(111).

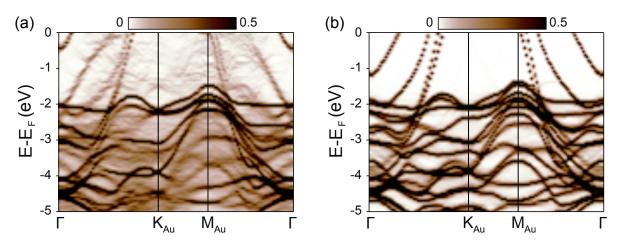


Figure S5: Effective band structure of (a)  $(4 \times 4)$ -BlueP on  $(5 \times 5)$ -Au(111) and (b) pristine  $(5 \times 5)$ -Au(111), unfolded to the BZ of  $(1 \times 1)$ -Au(111)

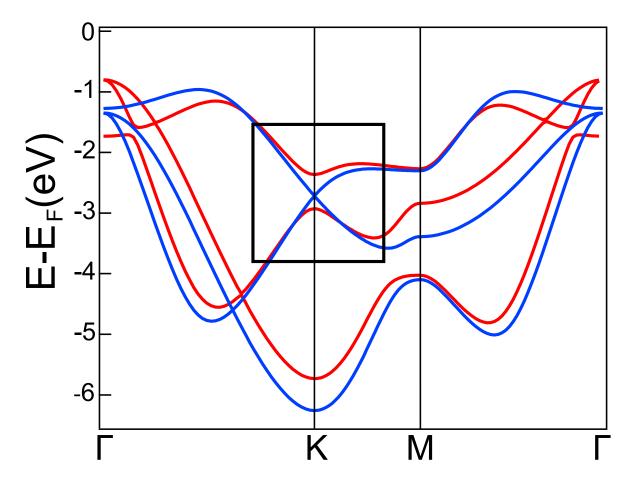


Figure S6: Freestanding band structure calculation of pristine BlueP (blue line) and BlueP with a Li atom on top of one of BlueP's unit cell atoms (red line). The Li atom breaks the sublattice symmetry and a gap opens at the K point — region highlighted by black frame.

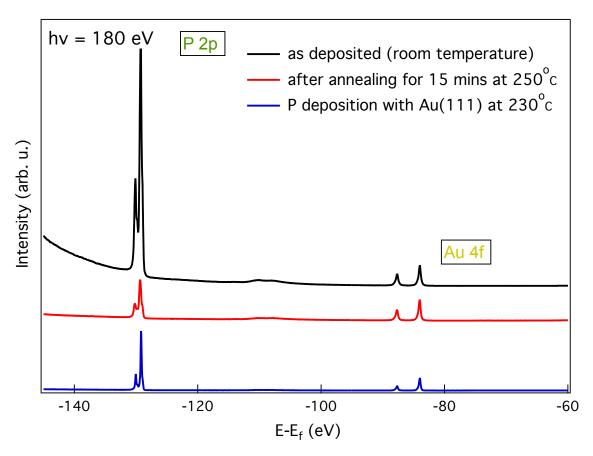


Figure S7: P 2p and Au 4f core levels of  $(4 \times 4)$ -BlueP on Au(111) under different preparation conditions (see legend).