# SUPPLEMENTARY INFORMATION

# Black or Red Phosphorus yield the same Blue

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deposition

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Figure S1 presents the Residual Gas Analyzer spectrum collected during red phosphorus evaporation at 320 °C in UHV conditions. Phosphorus vapor consists mainly of  $P_4$  molecules, with minor production of  $P_1$ ,  $P_2$  and  $P_3$ . Other residual gases were present. Intensity axis is in linear scale.



Figure S2: LEED I(V) curves of selected diffraction spots (indicated in blue). Red and black curves are acquired from BlueP/Au(111) grown by RedP and BlackP deposition, respectively. Both sets were extracted from a stack of energy-filtered LEED images acquired at room temperature over a 260 eV range of incident electron kinetic energy. The intensity is plotted in logarithmic scale to ease the comparison in the entire energy range.



Figure S3 shows a large-scale STM topographic image of BlueP-Au full monolayer grown on Au(111) from RedP precursor. The protrusions occurring in some pores of the BlueP-Au structures are additional P<sub>4</sub> clusters.<sup>S1</sup> The domain boundary separating two BlueP-Au islands with shifted unit cell is highlighted.

S1 S. Zhao, J. L. Zhang, W. Chen and Z. Li, *J. Phys. Chem. C*, 2020, **124**, 2024–2029.



Figure S4 is structured to offer direct comparison with Figure 4 in the main text. (a) ARPES map of clean Au(111) at binding energy of 1.2 eV, obtained by illumination with 65 eV photons. The high-symmetry points  $\Gamma$ , K and M are pinpointed with red dots, while the relative  $\Gamma$ -K and  $\Gamma$ -M axes are drawn with red lines. The electron intensity distribution appears asymmetrical and slightly affected by chromatic aberrations because of differences in the illumination and projection optics settings. The momentum distribution curves, extracted from a stack of ARPES maps measured at variable electron kinetic energy, are displayed for both samples along  $\Gamma$ -K (b) and  $\Gamma$ -M (c) axes. The Fermi energy is indicated by a white dashed line. The x-axis origin is fixed at the  $\Gamma$  position. The Au(111) surface state around  $\Gamma$  at low binding energy is clearly visible.