

# OPTICAL SIGNATURES OF THE STRONG 3D ANISOTROPY IN BLACK PHOSPHORUS

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After reports of high mobility and a tunable bandgap covering a wide spectral range from the visible to the mid-infrared region, layered black phosphorus (BP) has emerged as a promising 2D material for high performance electronic and optoelectronic devices [1]. Owing to its orthorhombic crystallographic structure, black phosphorus expresses strong anisotropic properties [2,3]. While recent investigations on few-layers crystals have extensively explored the in-plane anisotropy, much less attention has been given to the out-of-plane direction.

In this work, we use polarization-resolved photoluminescence (PL) and Raman spectroscopies to investigate the band structure anisotropy of bulk BP along the in-plane (zigzag, armchair) and out-of-plane directions. An unexpected room-temperature luminescence is detected in the visible, and strongly polarized in the out-of-plane direction. This emission, detected at 1.75 eV far above the band gap (0.3 eV), is surprising as it violates Kasha's rule which favors light emission from the lowest energy states. To elucidate its origin, we have systematically examined the characteristics of this luminescence as a function of polarization, temperature and excitation energy. These results reveal an unreported out-of-plane resonance at 2.3 eV in both the PL and Raman responses. Polarization selection rules and density functional theory (DFT) calculations of the complex dielectric permittivity are used to understand the origin of the strongly polarized optical response and demonstrate the remarkable extent to which the anisotropy influences the optical properties and carrier dynamics in black phosphorus.

## References

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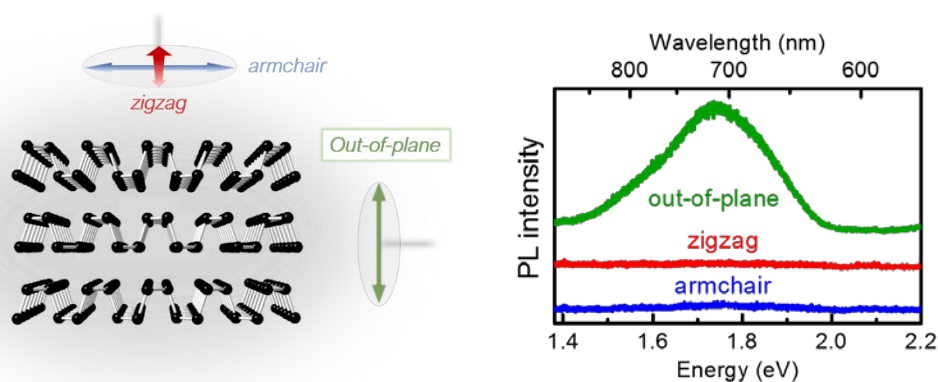


Figure 1: Left: Schematic illustration of the polarization-resolved spectroscopy experiments on bulk BP. Right: Room temperature PL spectra recorded along the out-of-plane (green), zigzag (red) and armchair (blue) directions.