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Supplemental Information for

Giant Manipulation of Thermal Conductivity Anisotropy in Black Phosphorene Under External Electric Fields

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The atomic displacement, dipole moment, and structural energy variation as a function of the external electric field's intensity are depicted in **Figure S1**. In **Figure S1(a)**, the displacement of the phosphorus atom (P) remains largely invariant until the external electric field surpasses a threshold of $E_{(f\_xx)}$ = 0.05 V/Å, beyond which all structural parameters exhibit an exponential increase relative to the electric field strength. At an electric field of $E_{(f\_xx)}$ = 0.2 V/Å, the displacement of the P atom is marginally altered by 4.2×10^{-7} Å, indicating that the buckled configuration of black phosphorene is maintained robustly. Consequently, this correspondence disregards variations in structure induced by differing electric fields. Moreover, **Figure S1(b)** illustrates a linear escalation in the dipole moment with increasing electric field intensity. Furthermore, as the electric field strength intensifies, the total energy of black phosphorene diminishes, corroborating a thermodynamically more stable structure under external influence, which forms the foundational basis for subsequent phonon transport calculations, as referenced in **Figure S1(c)**.

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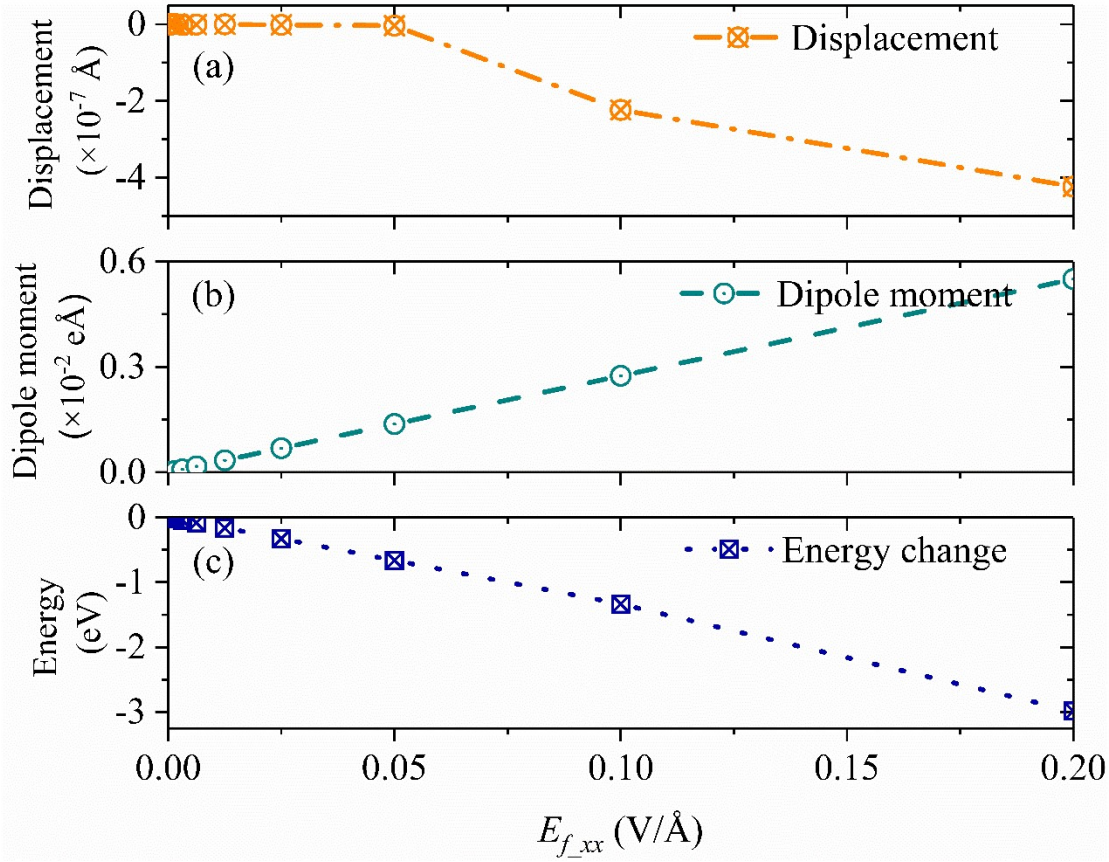

Figure S1. The changes of (a) atomic displacement (b) dipole moment (c) structural energy as a function of the strength of *Zigzag* electric field.

The phonon transport characteristics of black phosphorene are assessed utilizing the ShengBTE computational package[1]. The requisite second-order (harmonic) and third-order (anharmonic) interatomic force constants (IFCs) are determined via the method known as compressive sensing lattice dynamics (CSLD)[2]. An exhaustive analysis of the thermal conductivity's convergence concerning the cutoff energy and *Q-grid* is presented in **Figure S2**. As depicted in **Figure S2(a)**, with an increment in the cutoff energy, the structural energy initially decreases and subsequently stabilizes beyond a threshold of 50 Ry. Similarly, **Figure S2(b)** illustrates that the thermal conductivity of black phosphorene exhibits a well-converged profile once the *Q-grid* exceeds dimensions of 50×50×1. Consequently, to balance computational efficiency and accuracy, the cutoff energy is established at 50 Ry and the *Q-grid* configuration at 50×50×1 for subsequent calculations of thermal conductivity.

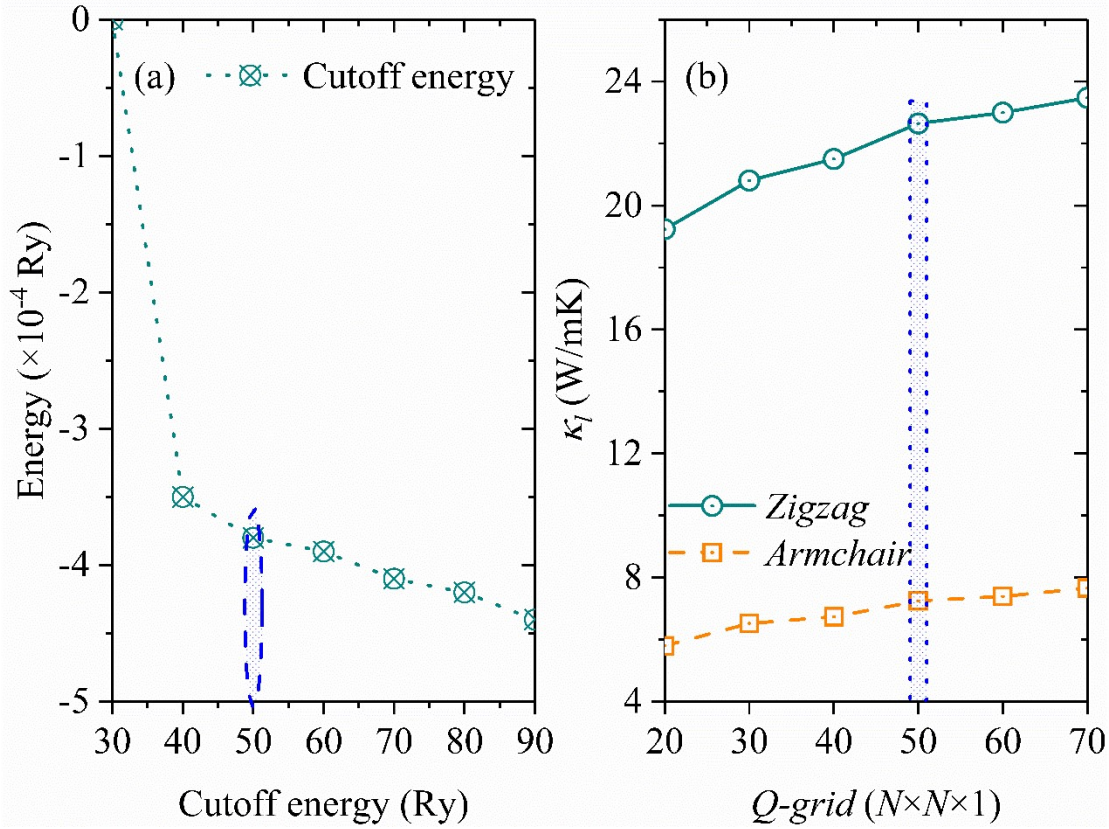

Figure S2. (a) The structure energy as a function of cutoff energy. (b) The thermal conductivity as a function of *Q-grid*.

The differential charge density (DCC) of black phosphorene under representative electric fields is depicted in **Figure S3**. A comparative analysis between **Figure S3(a)** and **Figure S3(b)** reveals that the electric field induces a positive accumulation and a negative depletion of charges, leading to induced charges of opposite signs localized around the phosphorus cores. In **Figure S3(c)**, with an applied electric field of $E_{(f\_yy)}$ = 0.2 V/Å, there is a redistribution of charges along the *Armchair* direction, with a reduction in the number of ionic bonds compared to the configuration under $E_{(f\_xx)}$= 0.2 V/Å. Consequently, there is a minimal alteration in the lifetime and anisotropic thermal conductivity of black phosphorene. The DCC isosurface set at 1×10^{-5} (a.u.) in **Figure S3(d)**, significantly smaller than in other configurations, indicates a lesser induction of charges by $E_{(f\_zz)}$= 0.2 V/Å. This observation is consistent with a charge accumulation at the bottom of the lower plane and a depletion at the top of the upper plane, aligning

with findings reported in the previous reference[3].

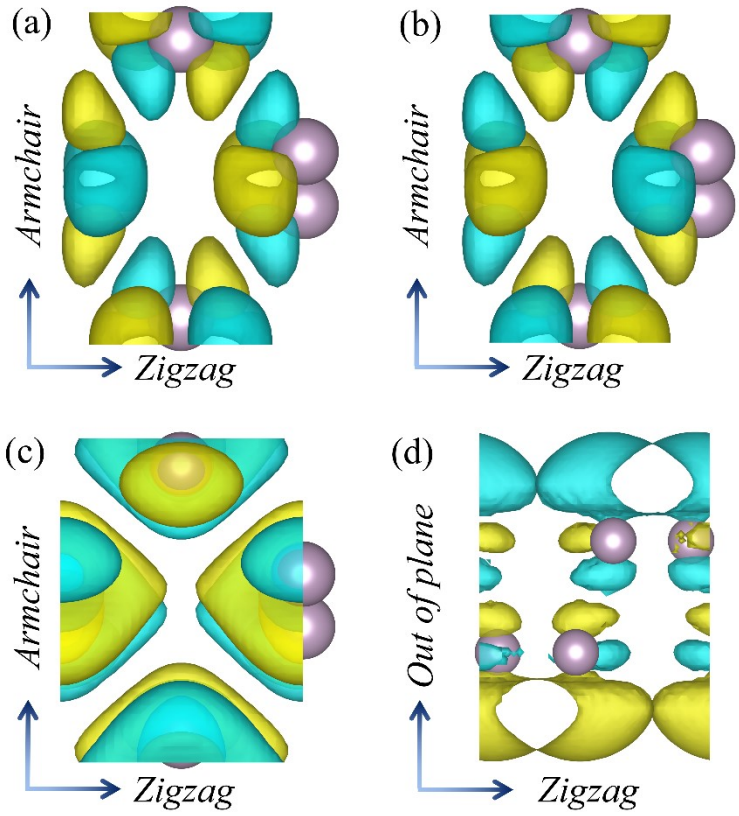

Figure S3. Top view of the charge density (yellow, positive; cyan, negative) under the electric field of (a) $E_{(f\_xx)}$= 0.2 V/Å, (b) $E_{(f\_xx)}$= -0.2 V/Å, (c) $E_{(f\_yy)}$= 0.2 V/Å. The isosurface is set as 1×10^{-4} (a.u.). (d) Side view of the charge density under the electric field of $E_{(f\_zz)}$ = 0.2 V/Å. The isosurface is set as 1×10^{-5} (a.u.).

Reference:

[1] Li W, Carrete J, Katcho N, Mingo N. ShengBTE: A solver of the Boltzmann transport equation for phonons. Computer Physics Communications, 2014, 185: 1747–1758.

[2] Zhou F, Nielson W, Xia Y, Ozoliņš V. Lattice Anharmonicity and Thermal Conductivity from Compressive Sensing of First-Principles Calculations. Physical Review Letters, 2014, 113(18): 185501.

[3] Wang X-P, Li X-B, Chen N-K, Zhao J-H, Chen Q-D, Sun H-B. Electric field analyses on monolayer semiconductors: the example of InSe. Physical Chemistry Chemical Physics, 2018, 20(10): 6945-6950.