Supporting Information

Effect of Net Charge on the Relative Stability of 2D Boron Allotropes

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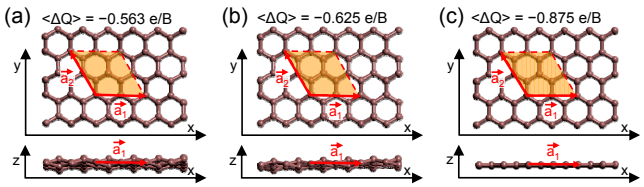

Figure S1: Electron doped 2D borophene structures obtained by optimizing a distorted boron honeycomb superlattice with 32 atoms per unit cell. The average excess charge $\langle \Delta Q \rangle$ per boron atom, specified in the panels, increases from (a) to (c). The structures are shown in top view (upper panels) and side view (lower panels). The lattice vectors $\vec{a}_1$ and $\vec{a}_2$, shown in red, delimit the highlighted unit cells.

Structure of 2D borophene at Intermediate Electron Doping

Results for 2D borophene structures carrying an extra charge of −5 e, −10 e, −13 e, −16 e, −24 e and −32 e in the 32-atom unit cell have been provided in Figure 2 of the main manuscript. Additional results at the doping levels of −18 e, −20 e and −28 e in the 32-atom unit cell and the corresponding average charge per boron $\langle \Delta Q \rangle$ are shown in Figure S1.

Charge Redistribution in Heterostructures of ϵ_3-B, ϵ_6-B and Ca_2N bilayers

Electron flow from the Ca_2N electride bilayer towards ϵ_3-B is shown in Figure S2(a) and towards ϵ_6-B is shown in Figure S2(b). The net

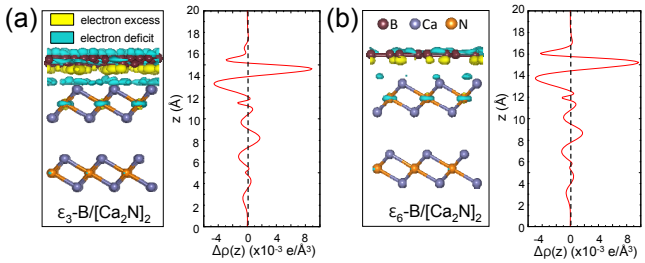

Figure S2: Electron flow between borophene and bilayers of the Ca_2N electride. Charge density redistribution $\Delta\rho = \rho(\mathrm{B}/[\mathrm{Ca_2N}]_2) - \rho(\mathrm{B}) - \sum \rho(\mathrm{Ca_2N})$ in (a) ϵ_3-$\mathrm{B}/[\mathrm{Ca_2N}]_2$ and (b) ϵ_6-$\mathrm{B}/[\mathrm{Ca_2N}]_2$ triple-layer heterostructures. $\Delta\rho$ is shown by isosurfaces bounding regions of electron excess at $+7\times10^{-3}$ e/Å^3 (yellow) and electron deficiency at -2×10^{-3} e/Å^3 (blue). $\langle \Delta\rho(z) \rangle$ is averaged across the $x-y$ plane of the layers.

electron transfer results are similar to those for Ca_2N monolayers in Figure 3 of the main manuscript, namely $\langle \Delta Q \rangle = -0.15$ e/B in ϵ_3-B and $\langle \Delta Q \rangle = -0.20$ e/B in ϵ_6-B. This indicates that the number of Ca_2N layers does not affect the charge transfer to borophene.

Electronic Band Structure of Doped Borophene

The electronic band structure has been shown only for selected doped borophene systems in Figure 6 in the main manuscript. Corresponding results for other structures are shown in Figure S3. These are band structures for the

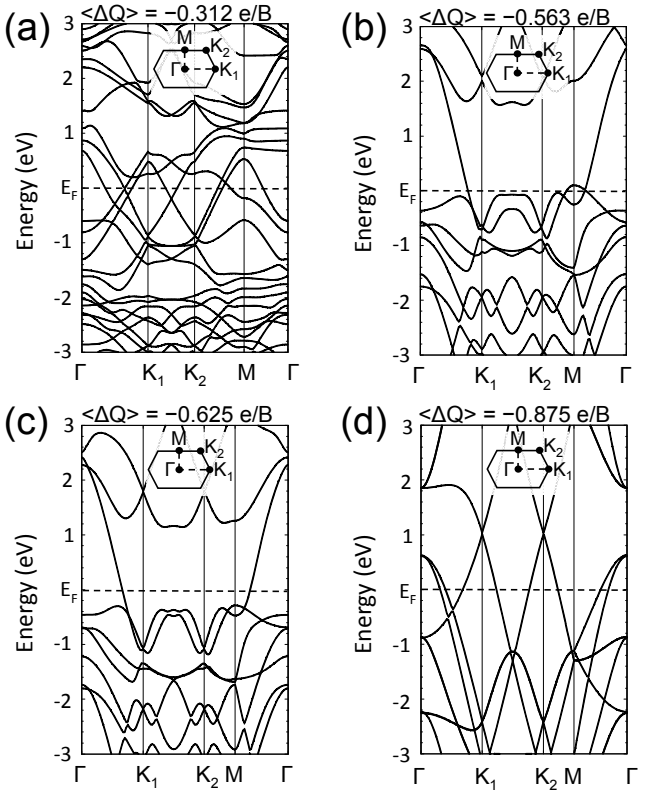

Figure S3: Electronic band structure of selected borophene allotropes. (a) ϵ_2-B of Figure 2(b) in the main manuscript with $\langle \Delta Q \rangle = -0.312$ e/B, (b) structure of Figure S1(a) with $\langle \Delta Q \rangle = -0.563$ e/B, (c) structure of Figure S1(b) with $\langle \Delta Q \rangle = -0.625$ e/B, and (d) structure of Figure S1(c) with $\langle \Delta Q \rangle = -0.875$ e/B.

system ϵ_2-B of Figure 2(b) in the main manuscript with $\langle \Delta Q \rangle = -0.312$ e/B, shown in Figure S3(a), the system of Figure S1(a) with $\langle \Delta Q \rangle = -0.563$ e/B, shown in Figure S3(b), the system of Figure S1(b) with $\langle \Delta Q \rangle = -0.625$ e/B, shown in Figure S3(c), and the system of Figure S1(c) with $\langle \Delta Q \rangle = -0.875$ e/B, shown in Figure S3(d). These results confirm the trend that a Dirac cone at the K_1 point appears only in honeycomb structures carrying more than half, but less than one excess electron per boron, and is located well above the Fermi level.

Effect of strain on the electronic structure of ϵ-B

The neutral ϵ-borophene monolayer is an indirect-gap semiconductor, as seen in Figure 6(a) of the main manuscript. Its electronic structure changes, however, significantly, when it is subject to in-layer strain, as shown in Figure S3. The effect of strain along the softer $\vec{a}_1$ direction is shown in Figures S4(a)-S4(d). Our results indicate that compression exceeding 4% closes the gap and turns ϵ-B metallic. Stretching opens the gap and, when in excess of 4%, turns the gap direct. The effect of strain along the harder $\vec{a}_2$ direction is shown in Figures S4(e)-S4(h). The trend is opposite in this case, since it is compression that opens the gap and turns it direct, and stretching beyond 3% turns the system metallic. Ability to tune very narrow band gaps by moderate strain appears very interesting for Terahertz applications.

Spatial Distribution of Excess Electrons in Doped Borophene

In parallel to Figure 3(a) and 3(b) of the main manuscript, where we showed the spatial distribution of extra electrons added to two borophene structures, we present in Figure S5 corresponding results for the distribution of extra two electron charges added to the 32-atom unit cell of borophene, equivalent to $\langle \Delta Q \rangle = -0.0625$ e/atom. We considered negatively charged structures ϵ_1-B in Figure S5(a), ϵ_2-B in Figure S5(b), ϵ_3-B in Figure S5(c), and ϵ_4-B in Figure S5(d). In addition to these structures described in Figure 2 of the main manuscript, we present results for the structure depicted in Figure S1(b) in Figure S5(e), and for that of Figure S1(c) in Figure S5(f). Our results indicate that the electrons are initially occupying p_z (or π) states, causing increasing buckling, which is evident when comparing the side views in Figures S5(a)-S5(c). After transition to an all-hexagon lattice in Figure S5(d), electrons begin gradually occupying σ states, causing flattening of the honeycomb lattice, until the excess charge of one electron per B atom is reached in Figure S5(f). Occupation of the σ-states in the bond region even at doping levels as low as half an electron per boron is facilitated by the fact that the σ band lies much closer to the π band and to the Fermi level than in graphene.

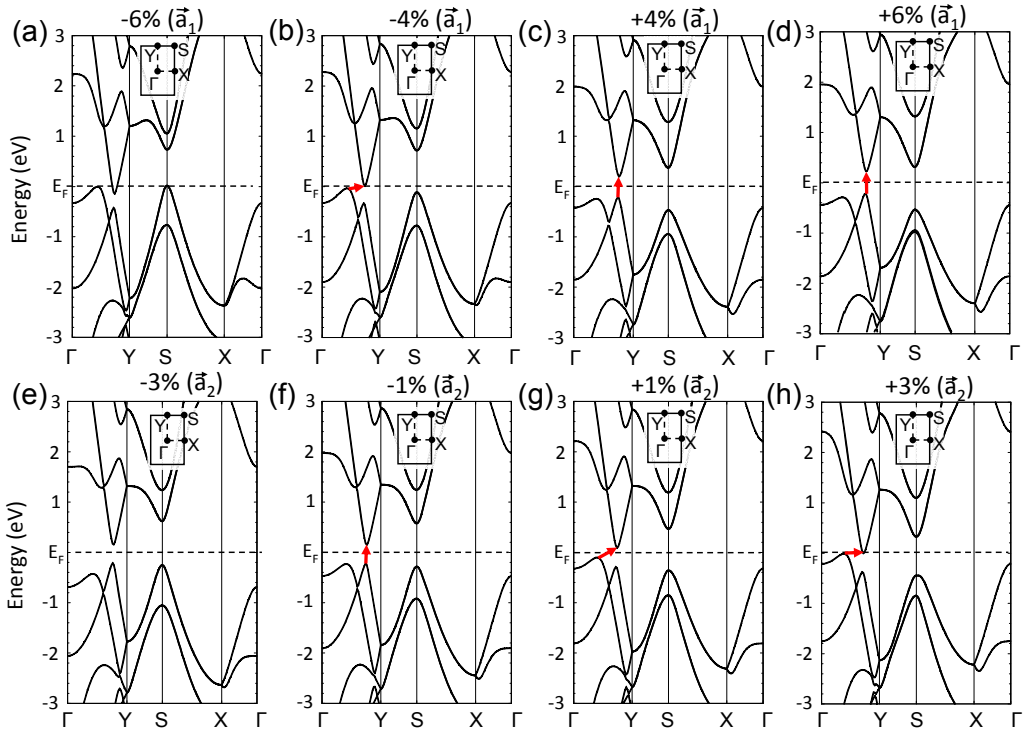

Figure S4: Electronic band structure of ϵ-B subject to in-layer strain of (a) -6%, (b) -4%, (c) +4%, and (d) +6% along the $\vec{a}_1$ direction, and (e) -3%, (f) -1%, (g) +1%, and (h) +3% along the $\vec{a}_2$ direction. The fundamental band gap is indicated by the red arrows in semiconducting systems.

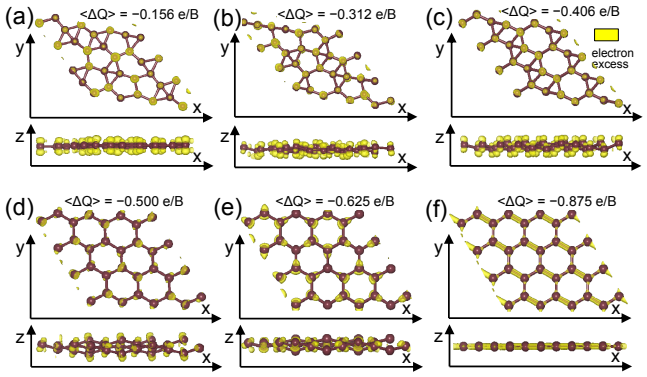

Figure S5: Charge density difference $\Delta\rho$ caused by placing an excess charge $\langle\Delta Q\rangle = -0.0625$ e/atom on selected borophene structures characterized in Figure 2 of the main manuscript and in Figure S1. (a) ϵ_1-B of Figure 2(a), (b) ϵ_2-B of Figure 2(b), (c) ϵ_3-B of Figure 2(c), (d) ϵ_4-B of Figure 2(d), as well as B structures shown in (e) Figure S1(b) and (f) Figure S1(c). $\Delta\rho$ is shown by isosurfaces bounding regions of electron excess at $+2.5\times10^{-3}$ e/Å^3 (yellow).