Covalent-Like Pi-Pi Bonding between Graphene Layers Enabled by Electron or Hole Dopings

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Regardless of the stacking motifs, neighboring graphene layers are known to be separated at a distance corresponding to van der Waals (vdW) interactions. Herein we show that interlayer covalent-like pi-pi bonding between AA-stacked graphene layers can be realized by electron or hole dopings through N- or B-substitutions, respectively, by using rigorous theoretical calculations with density functional theory (DFT) containing empirical vdW corrections or self-consistent vdW functional methods, nonlocal many-body dispersion (MBD) method, and adiabatic-connection fluctuation-dissipation theorem (ACFDT) used in the direct random phase approximation (RPA). The pi-pi bonding manifests in the significantly enhanced interlayer binding energy and the correspondingly reduced interlayer separation. Such an unusual chemical bonding arises from the pi-pi overlap across the vdW gap while the individual layers maintain their in-plain pi-pi conjugation and therefore planarity. The presence of the interlayer pi-pi bonding is corroborated by electronic structure calculations and crystal orbital overlap population (COOP) analyses. Due to the interlayer pi-pi bonding interactions, AA-stacked bulk structures exhibit metallic characteristics both in the in-plane and along the stacking directions.