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Supplementary Information

Sample Preparations; We have grown a SLG on a 6H-SiC(0001) substrate (Cree Inc.) by annealing the sample at temperature 1250 °C.[42,43] We confirmed the formation of SLG first by observing the characteristic changes in the low-energy electron diffraction (LEED) pattern, and then more convincingly the presence of a well-defined linear Dirac band in the valence band together with the C 1s core level spectrum unique only to SLG. The annealing temperature (T_a) was measured by using an optical pyrometer. Deposition of Cs^+ ions on graphene was made by using a low-energy alkali metal ion gun (Kimball Physics), and the ion beam current density measured from the sample was 1.7 nA cm^{-2}. Considering the relatively low desorption temperature (200 K) of Cs atoms,[40] we have kept our sample at 150 K while depositing Cs^+ ions on graphene. We also have used a Cs getter source (SAES) to adsorb neutral Cs atoms on graphene, and the Cs coverage, ϑ_{Cs}, was determined by using a quartz oscillator (0.2 Å min^{-1}), which was cross-checked by measuring the intensity ratio (I_{Cs}/I_C) of the main Cs 4d and C 1s core levels.

***Valence Band and Core Level Data*;** Our ARPES and HRCLS data were obtained with the sample maintained at 85 K at the beamline 4A2 of the Pohang Accelerator Laboratory (PAL) in Korea using synchrotron photons of energy 34 eV and 510 eV, respectively. Our UHV chamber kept under 1×10^{-10} Torr during the measurements was equipped with an electron analyser (R4000, VG-Scienta) that provides an overall energy resolution of 40 meV. We have obtained STM images with the sample at room temperature by using a low-temperature STM (UNISOKU) under a base pressure of 1×10^{-10} Torr.

***DFT Calculations*;** We have performed the first-principles calculations based on DFT implemented in Vienna Ab-initio Simulation Package to understand the changes in the π-band of graphene induced by Cs^+ ions.[44] We used the projector augmented wave pseudopotentials[45] as atomic potentials and the generalized gradient approximation (GGA) of Perdew, Burke and Enzelhof[46] to treat the exchange-correlation interaction of electrons. A kinetic energy cutoff of 420 eV was chosen for the expansion of the plane-wave basis set. Epitaxial graphene on SiC was emulated by 2×2 graphene supercells on SiC substrate that consists of two SiC bilayers with a √3×√3 in-plane supercell and hydrogen termination at the bottom. The irreducible Brillouin zone integration was done by 15×15×1 k-point sampling and structural optimizations were done by minimizing the Hellmann-Feynman force on ions less than 0.01 eV $Å^{-1}$. To adjust the error of GGA the van der Waals interactions, we employed the Tkatchenko-Scheffler correction method.[47]