Electronic Supplementary Material (ESI) for RSC Advances.

# Electronic supplementary information (ESI)

## N- and p-type doping of antimonene

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We examined the optimized configurations about co-adsorbed TTF and TCNQ lie in the one-side and two-side of the antimonene (8×8 supercell) are displayed on the Fig. S7. We find that these sites and directions of the TTF and TCNQ in the relaxed two systems are nearly invariable with the single molecule adsorbed systems (TTF/antimonene and TCNQ/antimonene), except the perpendicular distance between the molecules and antimonene. Supplementally, in order to avoid the interaction between two molecules, we set the nearest distance between TTF and TCNQ is ~10 Å. For the relaxed one-side configuration, the distance between TTF (TCNQ) and antimonene is 3.00 Å (3.16 Å). While the two-side configuration, the vertical distance between TTF and antimonene is larger than one-side counterpart with 3.32 Å, but the distance about TCNQ and antimonene shrinks to 3.08 Å. Intriguingly, regardless of one-side and two-side systems, the TTF molecule is a little bend with the value is 0.04 Å, but the twisting value of the TCNQ is larger than TTF and the maximal variation of the atoms in the TCNQ molecule is 0.14 Å. Notably, both of the two situation, the substrate antimonene is not twisting. By the way, the dipole correction is considered in the one-side doping. Furthermore, it has been known that bilayer antimony is metallic[1], thus, we guess that the adsorbed molecule will not change this property. We indeed confirm the conclusion that the metallic characteristic of co-adsorption of TTF and TCNQ on the bilayer Sb is unchanged. The optimized configuration and band structure are displayed in Fig. S8.

# Figure List

Figure S1. Top and side views of the optimized antimonene, with four possible chemical doing sites which are marked by different colored circles.

Figure S2. (a) The possible sites of the initial structures on TTF/antimonene are displayed. (b) The relaxed systems based on initial structures, and the corresponding total energy which compare with the most stable system are given.

Figure S3. (a) The possible sites of the initial structures on TCNQ/antimonene are displayed. (b) The relaxed systems based on initial structures, and the corresponding total energies are determined by comparing with the most favorable system.

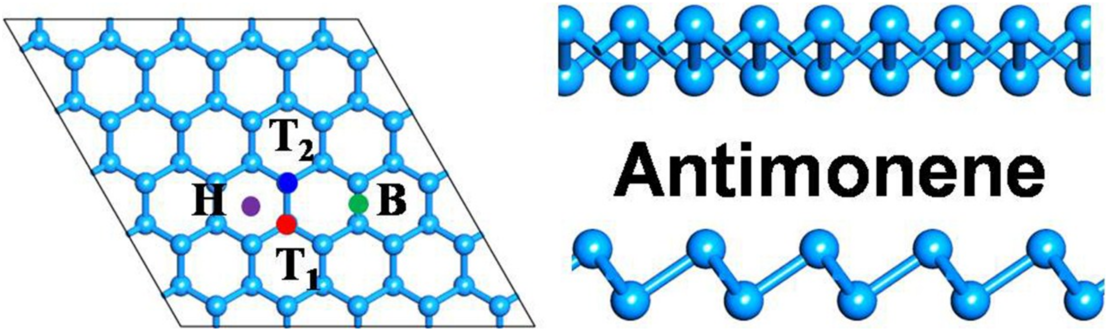
Figure S4. Partial charge density of CBM and VBM for (a) pristine antimonene, (b) TTF/antimonene, and (c) TCNQ/antimonene are displayed by the top views.

Figure S5. Electronic band structures of (i) initial antimonene and (ii) TCNQ/antimonene are calculated by (a) PBE and (b) HSE06 approaches, respectively. It is in well agreement with each other.

Figure S6. Partial density of states (PDOS) of TTF/antimonene (a) and TCNQ/antimonene (b) with p orbital are presented.

Figure S7. Structural schematics with the co-adsorption of TTF and TCNQ on the antimonene of (a) one-side and (b) two-side are shown in the form of top and side views, respectively. Additional, charge transfer between molecules and antimonene, meanwhile the twisting distance of molecules (the twisting distances of TTF and TCNQ are the same in the two situation) are displayed.

Figure S8. Structural schematics with the co-adsorption of TTF and TCNQ on the bilayer Sb are shown in the form of top (a) and side (b) views, respectively. Additional, the twisting distances of TTF and TCNQ are displayed, respectively.



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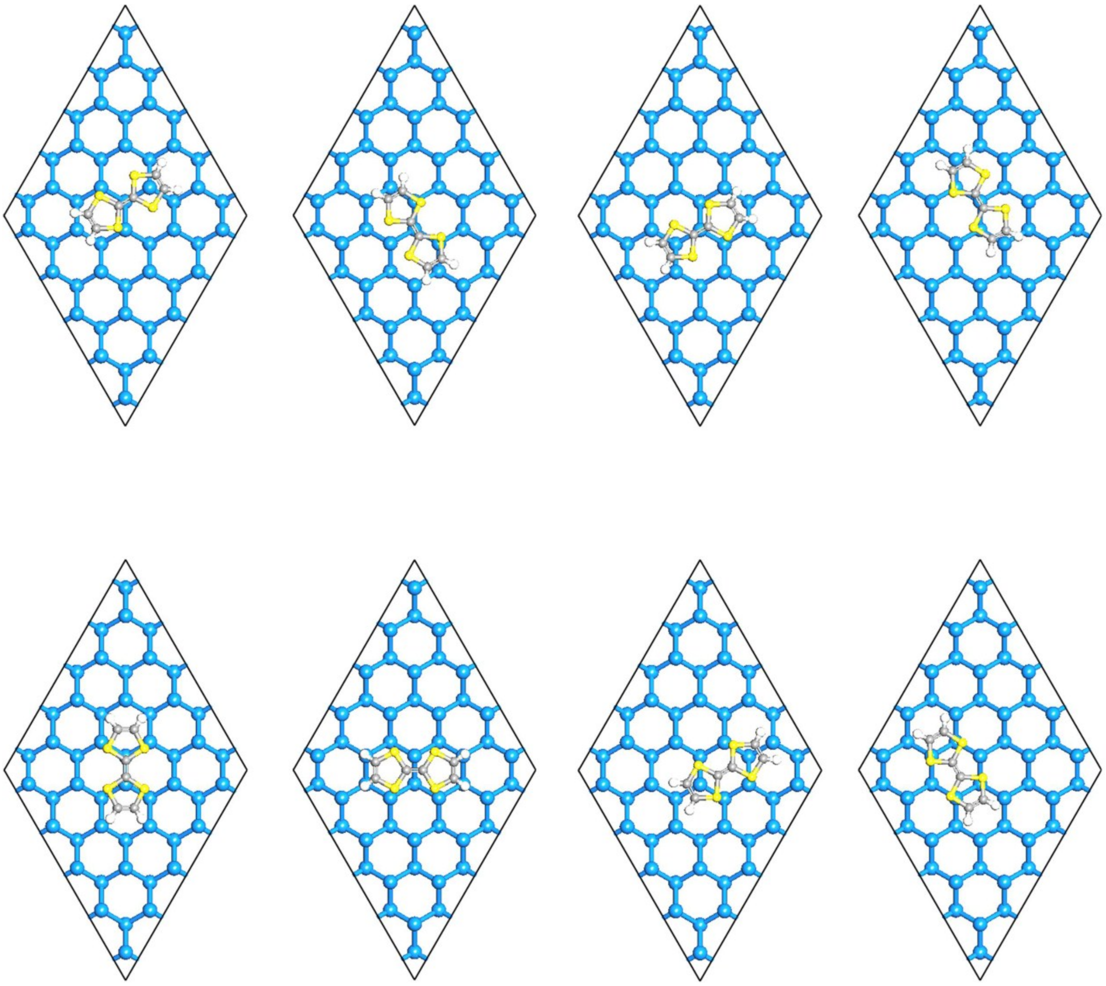
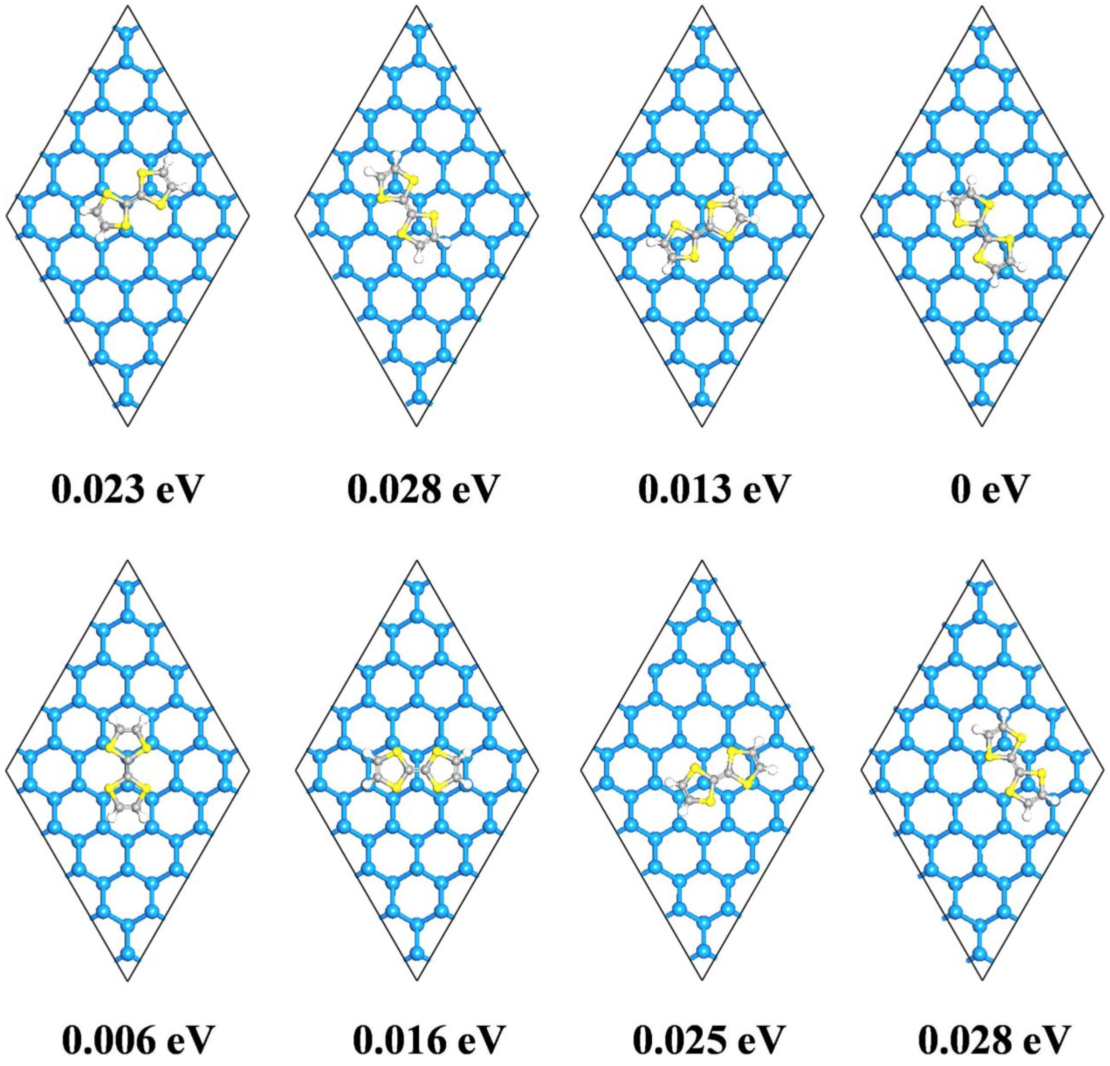
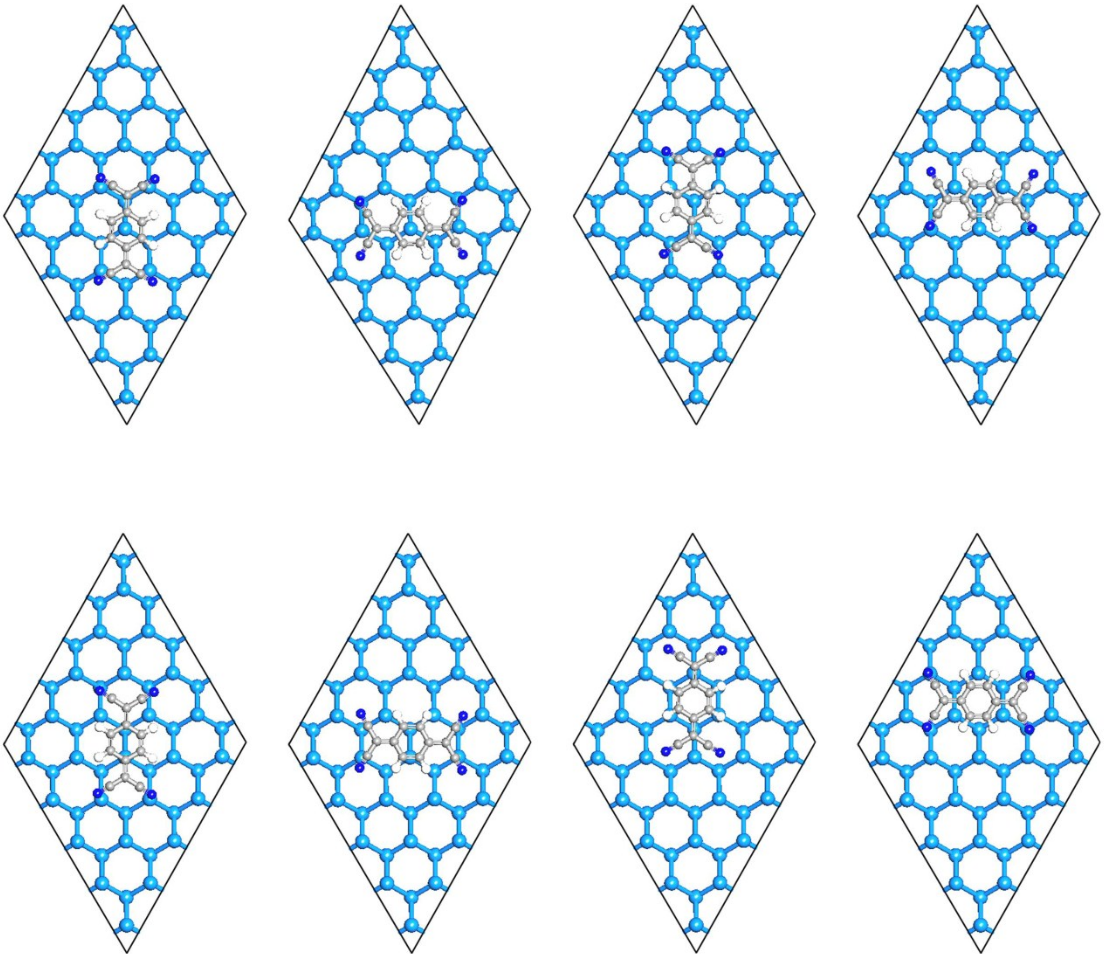


**(a) Initial-TTF/antimonene**



**(b) Relaxed-TTF/antimonene**

Figure S2. (a) The possible sites of the initial structures on TTF/antimonene are displayed. (b) The relaxed systems based on initial structures, and the corresponding total energies which compare with the most stable system are given.



**(a) Initial-TCNQ/antimonene**

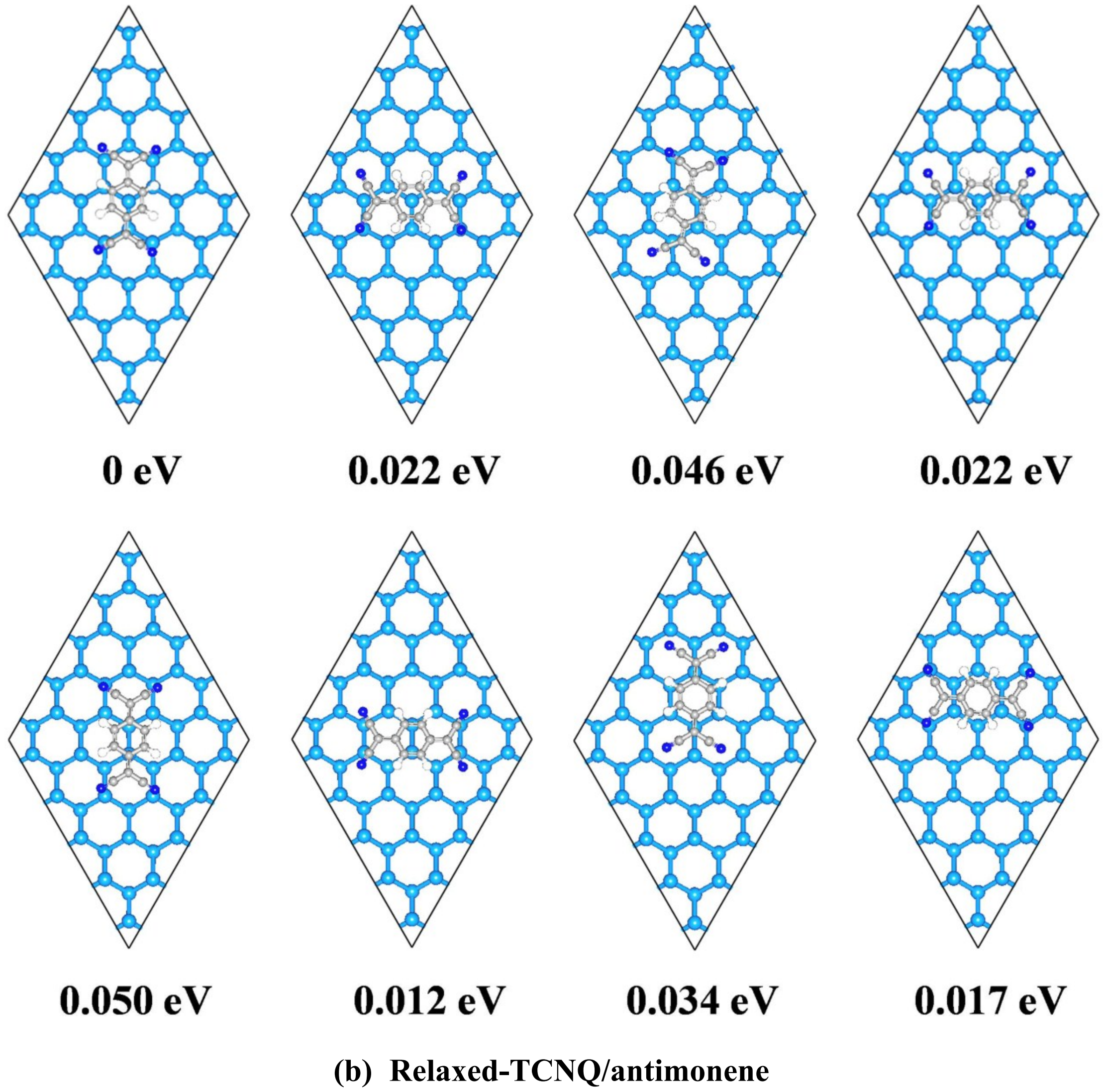


Figure S3. (a) The possible sites of the initial structures on TCNQ/antimonene are displayed. (b) The relaxed systems based on initial structures, and the corresponding total energies are determined by comparing with the most favorable system.

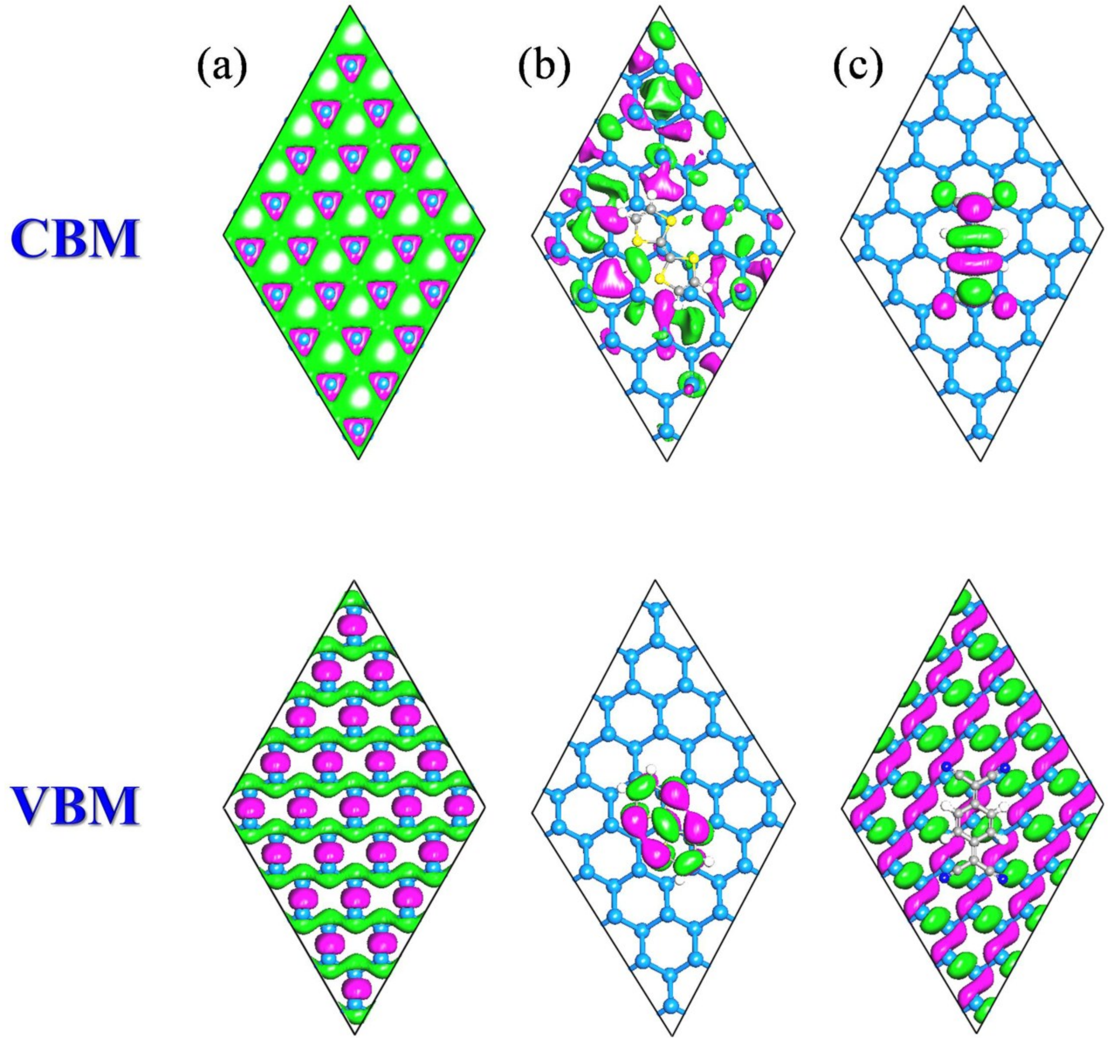
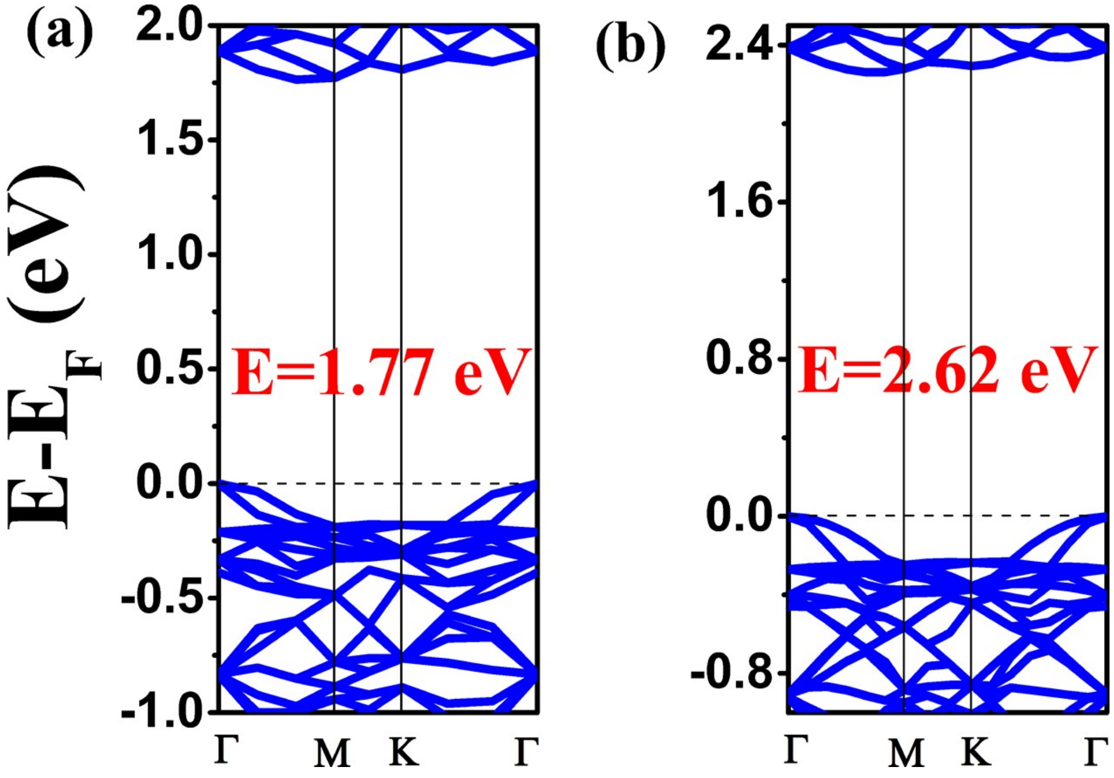
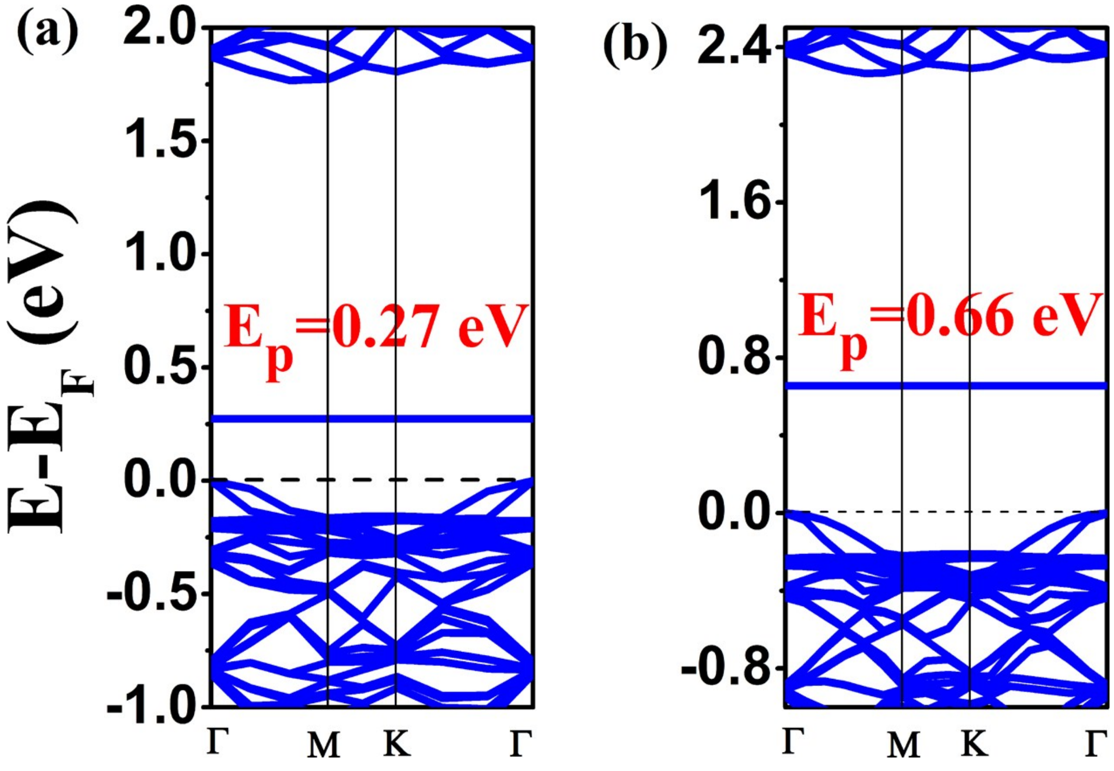


Figure S4. Partial charge density of CBM and VBM for (a) pristine antimonene, (b) TTF/antimonene, and (c) TCNQ/antimonene are displayed by the top views.



**(i) Freestanding antimonene**



**(ii) TCNQ/antimonene**

Figure S5. Electronic band structures of (i) initial antimonene and (ii) TCNQ/antimonene are calculated by (a) PBE and (b) HSE06 approaches, respectively. The horizontal dotted lines indicate the Fermi level.

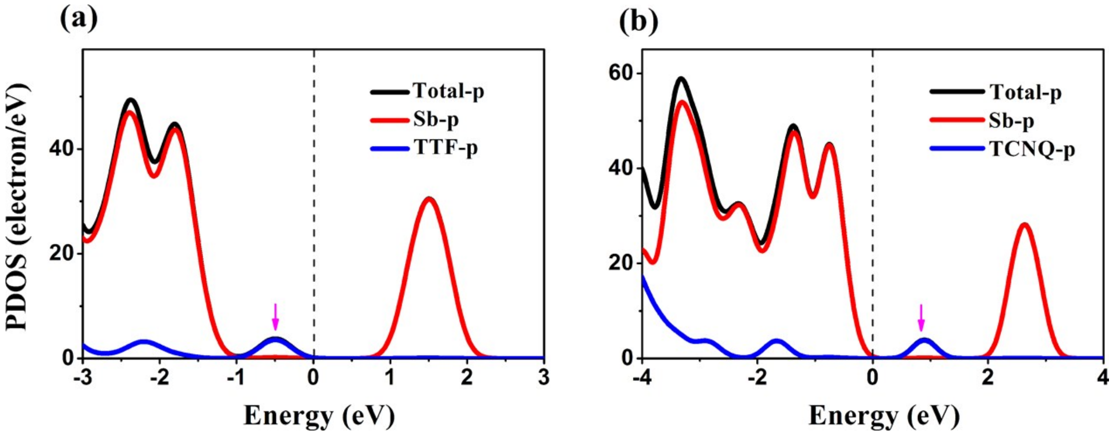


Figure S6. Partial density of states (PDOS) of TTF/antimonene (a) and TCNQ/antimonene (b) with p orbital are presented. For molecules (i.e., TTF and TCNQ), p orbital means the contribution set of every atom (p-orbital) in molecules. The vertical dotted lines indicate the Fermi level.

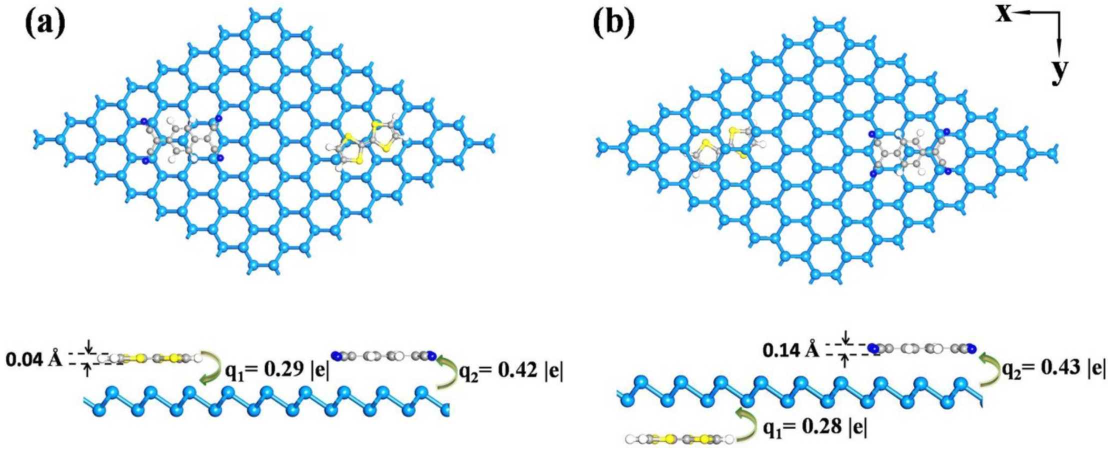
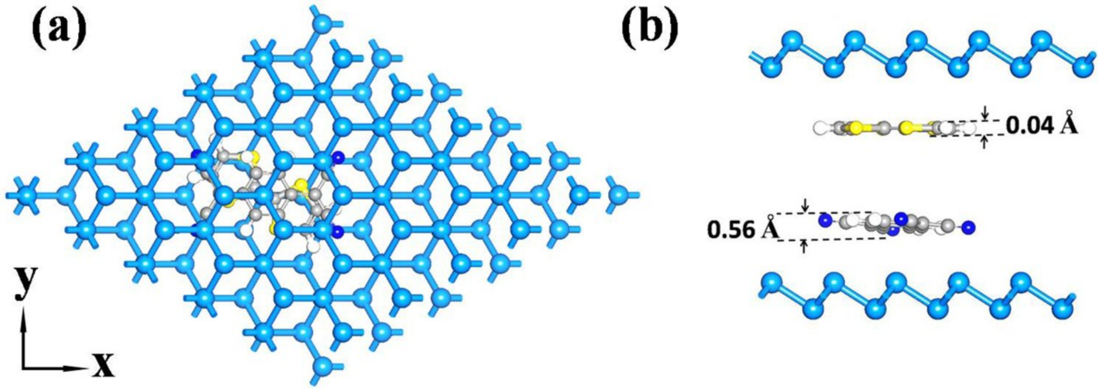


Figure S7. Structural schematics with the co-adsorption of TTF and TCNQ on the antimonene of (a) one-side and (b) two-side are shown in the form of top and side views, respectively. Additional, charge transfer between molecules and antimonene, meanwhile the twisting distance of molecules (the twisting distances of TTF and TCNQ are the same in the two situation) are displayed.



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