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Tunable Magnetic Anisotropy in 2D Magnets via Molecular Adsorption

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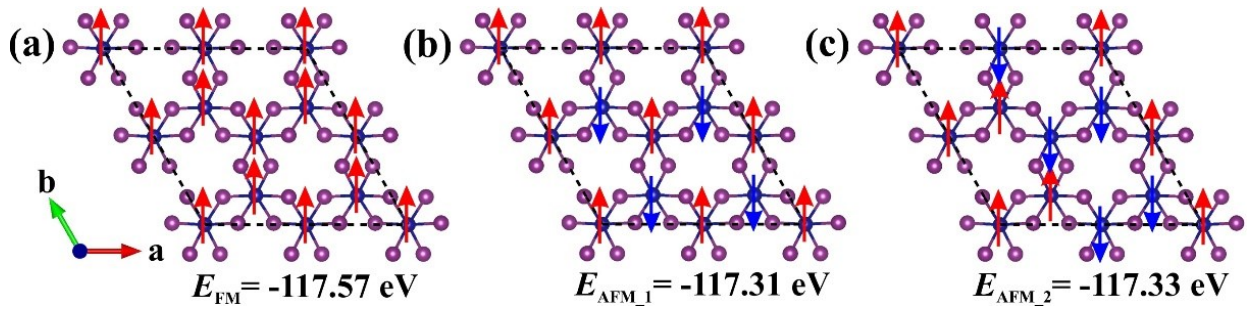

Figure S1. 2×2 supercell of CrI_3 monolayers under (a) FM, (b) AFM_1 and (c) AFM_2 configurations. The total energies of each magnetic state are displayed in the figure.

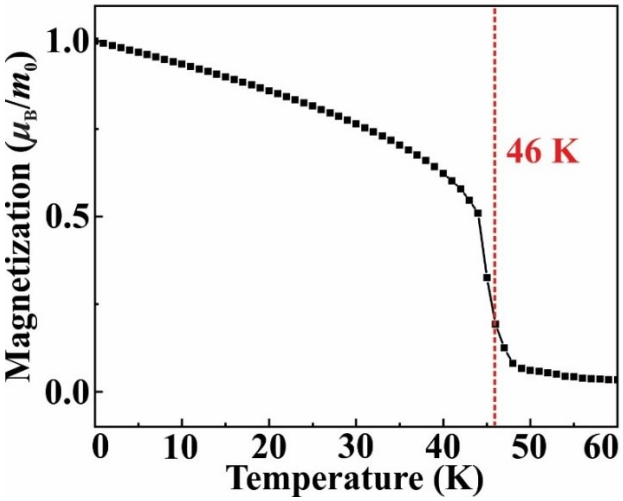

Figure S2. The average magnetic moment as a function of temperature in CrI_3 monolayer obtained by the Monte Carlo simulation. The Curie temperature of CrI_3 is estimated to be around 46 K.

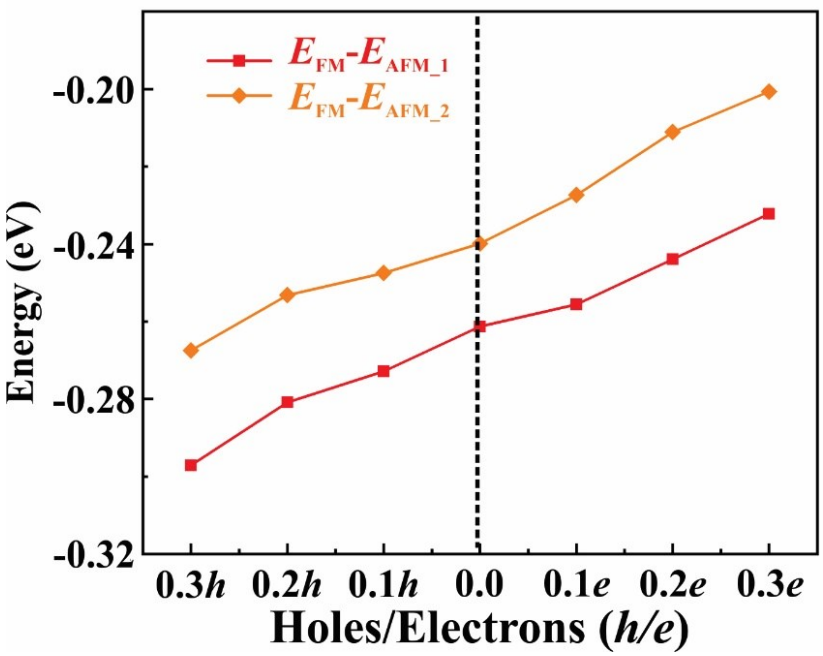

Figure S3. The energy difference between FM and AFM states of charge carrier doped monolayer CrI_3 supercell.

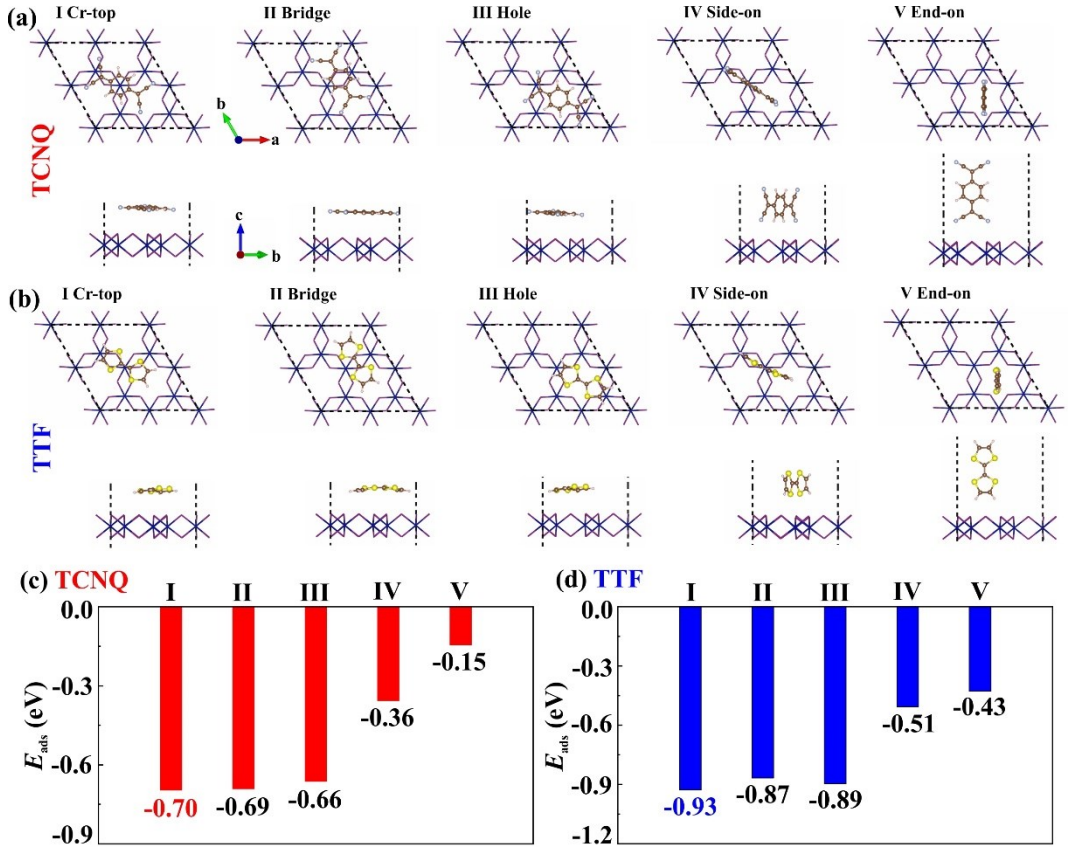

Figure S4. Different adsorption configurations for (a) TCNQ and (b) TTF molecules. (c, d) Corresponding adsorption energies for each configuration. The most stable one is the Cr-top configuration for both TCNQ- and TTF-CrI_3.

Table S1. The total energies (eV) of molecules adsorbed CrI_3 monolayers under different magnetic configurations. AFM_1 represents the Néel AFM configuration. The adsorption energy E_{ads} (eV) of each case under their magnetic ground states.

	FM	AFM_1	AFM_2	E_{ads}
CrI_3	**-117.56832**	-117.30706	-117.32848	-
TCNQ-2×2 CrI_3	**-269.73011**	-269.45045	-269.47686	-0.70
TTF-2×2 CrI_3	**-201.27020**	-201.01587	-201.03414	-0.93
TCNQ-1×2 CrI_3	**-211.12401**	-211.00834	-	-0.89
TTF-1×2 CrI_3	**-142.48854**	-142.34428	-	-0.95
TCNQ-1×3 CrI_3	**-240.52857**	-240.37934	-	-0.87
TTF-1×3 CrI_3	**-171.83927**	-171.65479	-	-0.92
TCNQ-2×3 CrI_3	**-328.49014**	-328.16058	-	-0.71
TTF-2×3 CrI_3	**-259.99528**	-259.64512	-	-0.93

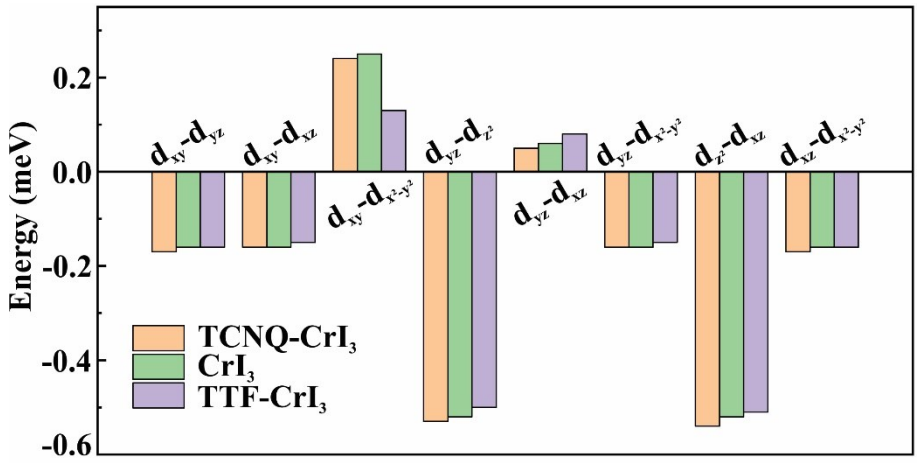

Figure S5. The orbital-resolved MAE of the same Cr atom in CrI3 monolayer with and without organic molecular adsorption.

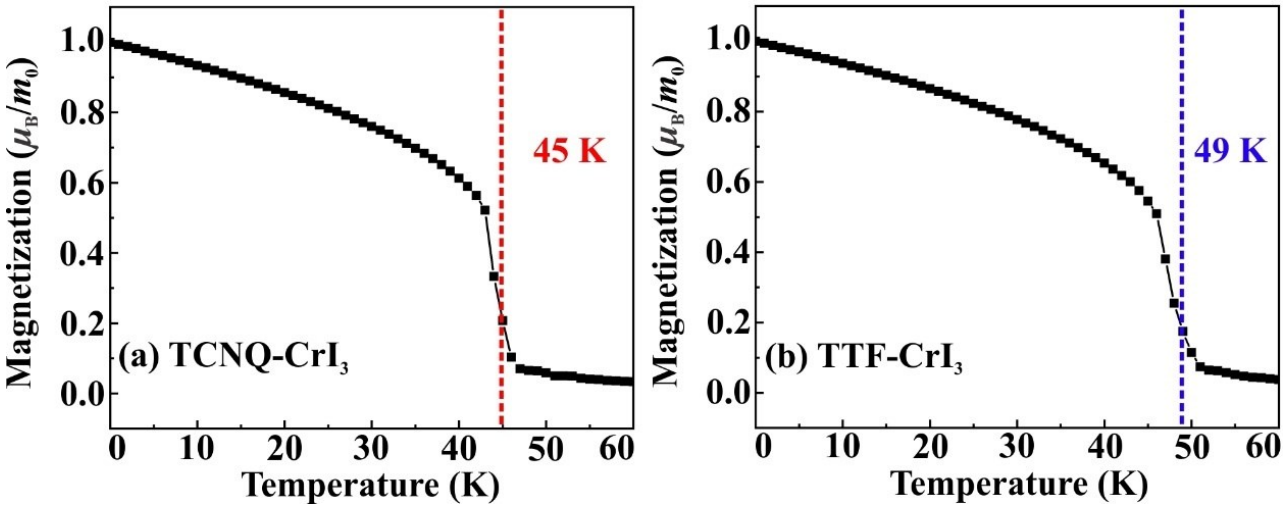

Figure S6. The estimated Curie temperature T_C (K) of TCNQ- and TTF-CrI_3 monolayers through Monte Carlo simulations.

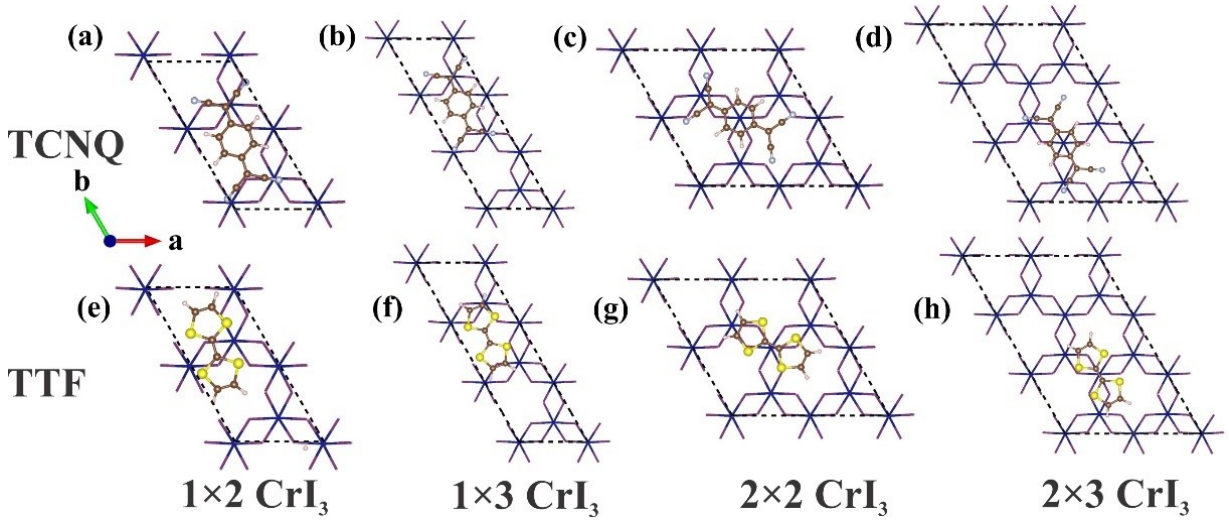

Figure S7. The geometries of (a-d) TCNQ and (e-h) TTF adsorbed CrI_3 monolayer under different concentrations.

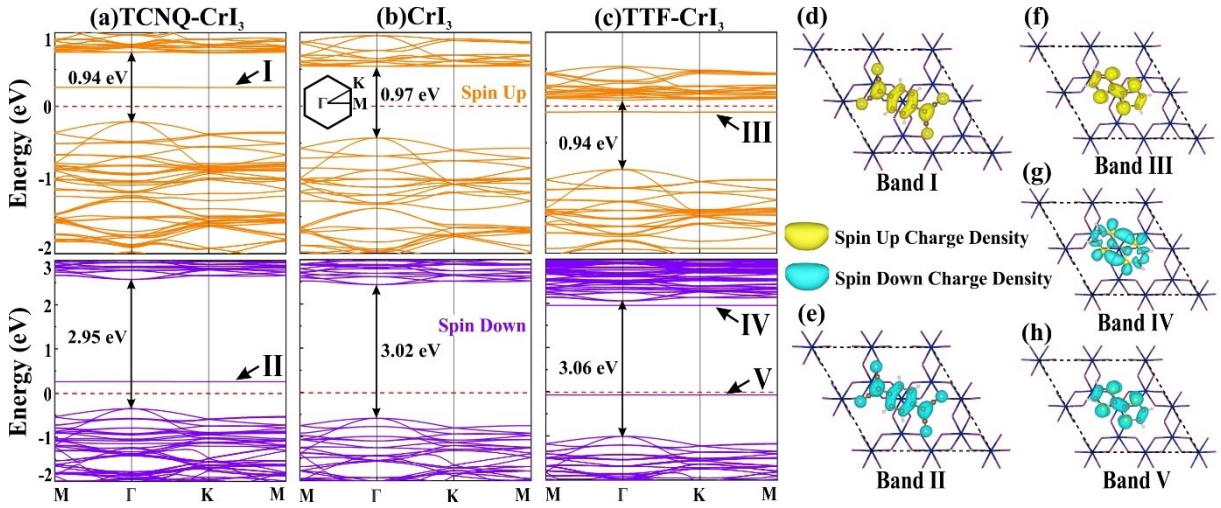

Figure S8. Spin-polarized band structures for (a) TCNQ-CrI_3, (b) CrI_3 and (c) TTF-CrI_3 nanosheets. The geometry of 2×2 supercell CrI_3 substrate is used. (d-h) Band decomposed charge density for marked impurity states.

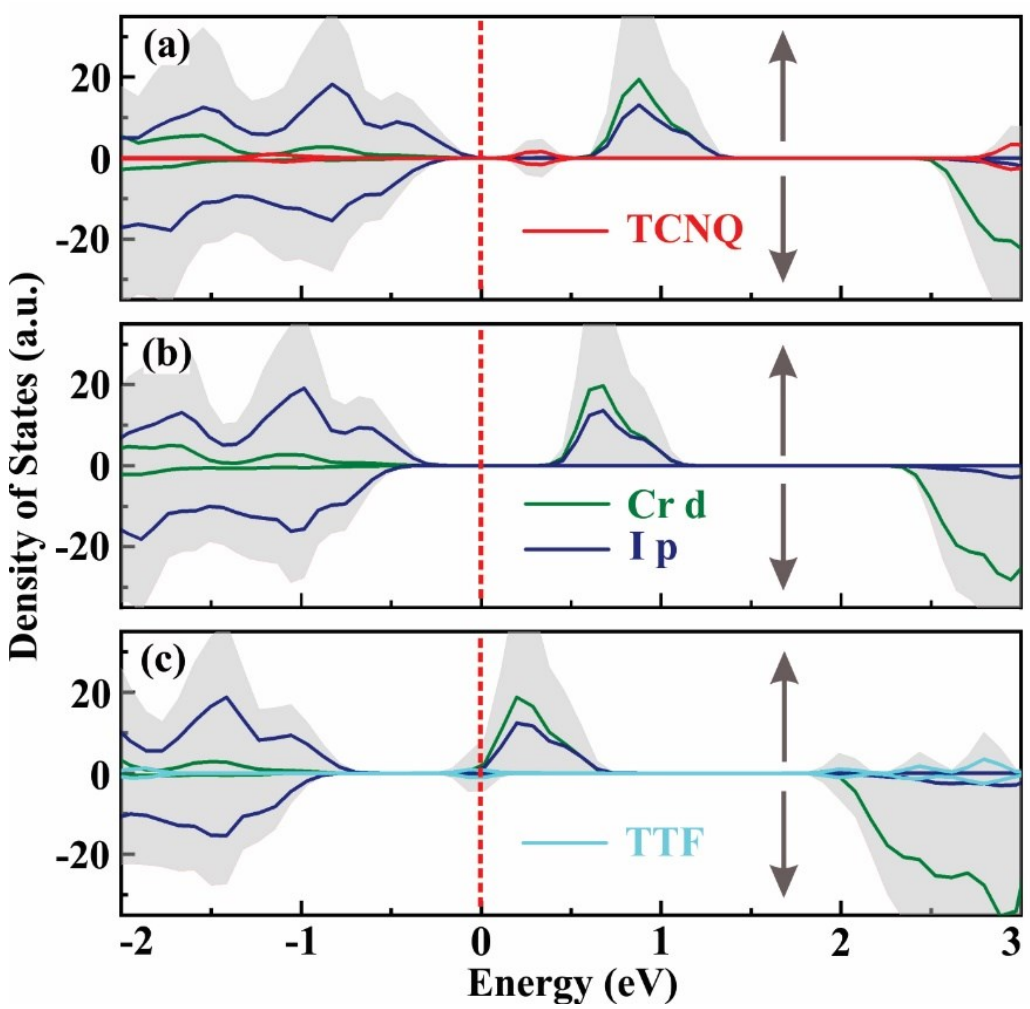

Figure S9. Orbital-resolved density of states of FM (a) TCNQ-CrI_3, (b) CrI_3 and (c) TTF-CrI_3. The grey area represents the total density of states.

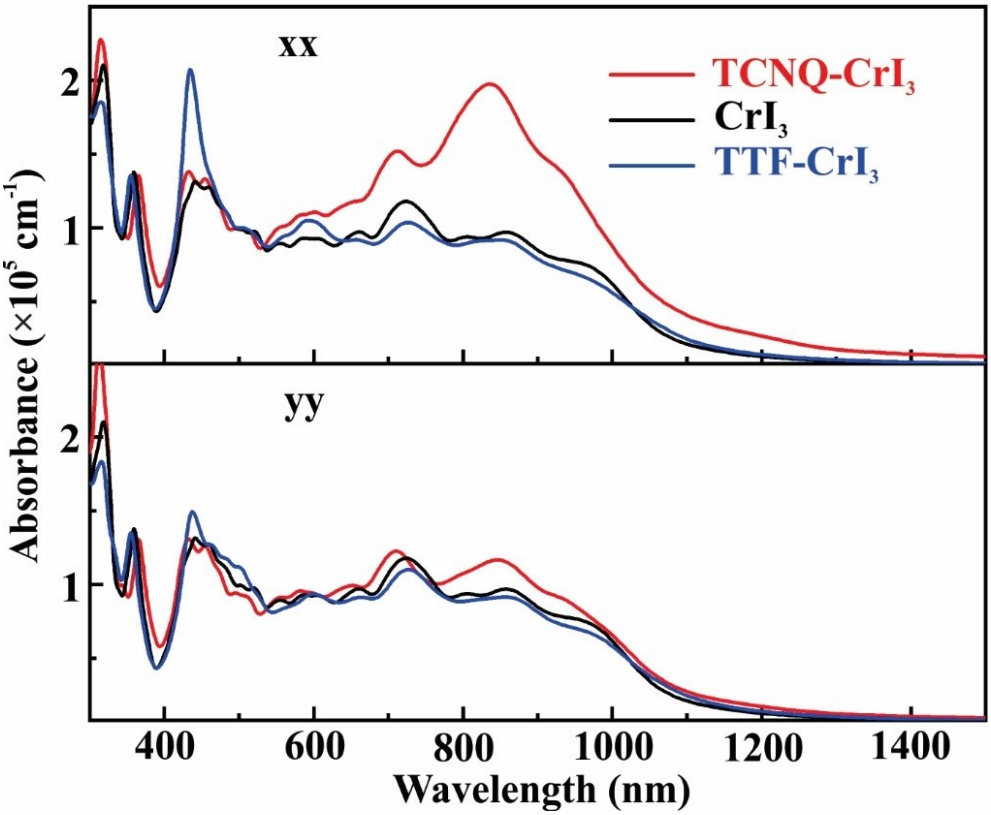

Figure S10. The optical absorption of organic molecules adsorbed CrI_3 monolayers.

Organic molecules adsorption on other 2D magnets

After realizing the modulation effect of organic molecules on CrI_3 monolayers, we expanded it to other representative 2D magnets, such as CrI_3 bilayer (BL-CrI_3) and $CrBr_3$ monolayer. As shown in Fig. S11, the supercells of 2×2 are used to reduce the interactions between neighboring molecules. The AB stack CrI_3 bilayer is adopted, due to its lowest total energy among all studied configurations[1]. All the calculations are performed with the DFT+U method. The magnetic ground state of these calculated magnets is FM by comparing the total energies of different magnetic configurations, and it remains FM after organic molecular adsorption. Notably, the calculated adsorption energies of these magnetic substrates are all negative (Fig. S12), indicating the stability of the molecular adsorption. When adsorbing on the 2D magnets, the TCNQ (TTF) molecule introduces the hole (electron) doping into the magnetic substrates through the interfacial electrostatic effects. Thus, the magnetic anisotropy of these carrier doped 2D magnets can be readily regulated in a large range, as in the case of the CrI_3 monolayer. It is worthy to note that the magnetocrystalline easy axis changes from out-of-plane to in-plane in the $CrBr_3$ monolayer

by TTF adsorption. Therefore, the organic molecular adsorption can be regarded as a universal method to modulate the magnetic anisotropy in 2D magnets.

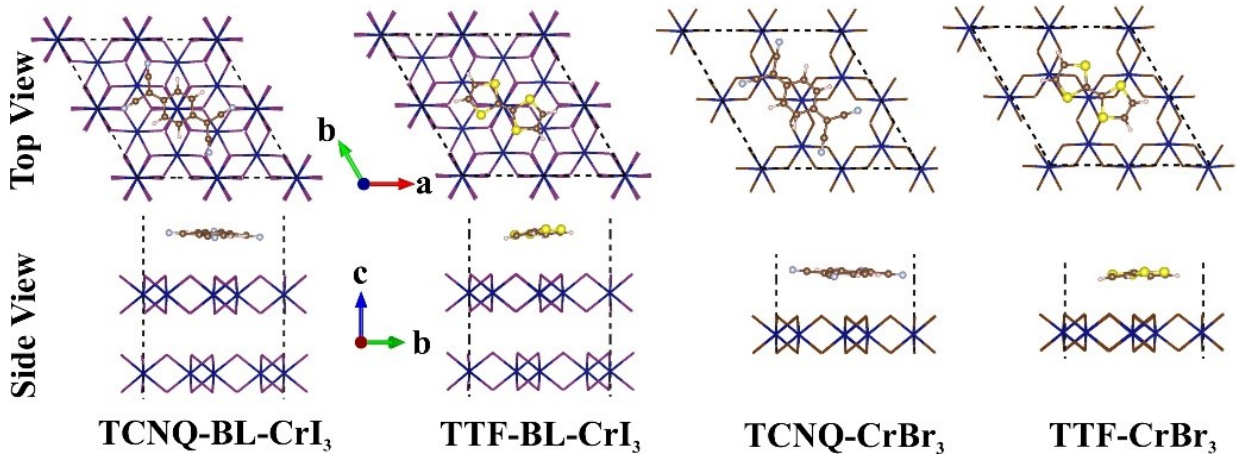

Figure S11. The top and side views of geometries of TCNQ-BL-CrI_3, TTF-BL-CrI_3, TCNQ-$CrBr_3$ and TTF-$CrBr_3$.

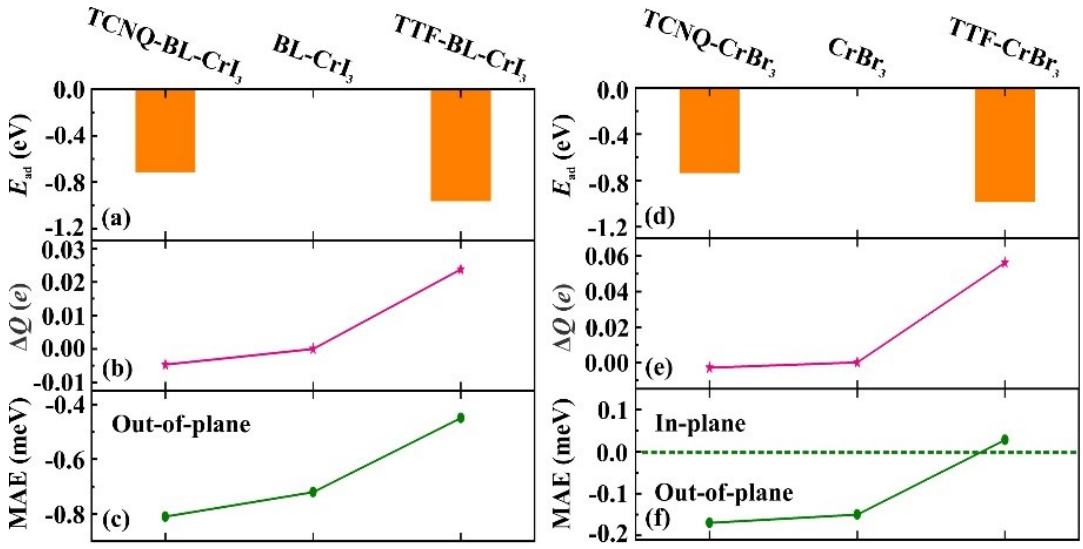

Figure S12. Adsorption energies E_{ad} (eV), charge difference ΔQ (e) and magnetic anisotropic energy MAE (meV) of molecular adsorption on (a-c) CrI_3 bilayer and (d-f) $CrBr_3$ monolayer, respectively.

References

1. N. Sivadas, S. Okamoto, X. Xu, C. J. Fennie and D. Xiao, *Nano Lett.*, 2018, **18**, 7658-7664.