Supporting Information

Charge Transfer at the PTCDA/Black Phosphorus Interface

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1 XPS full spectrum

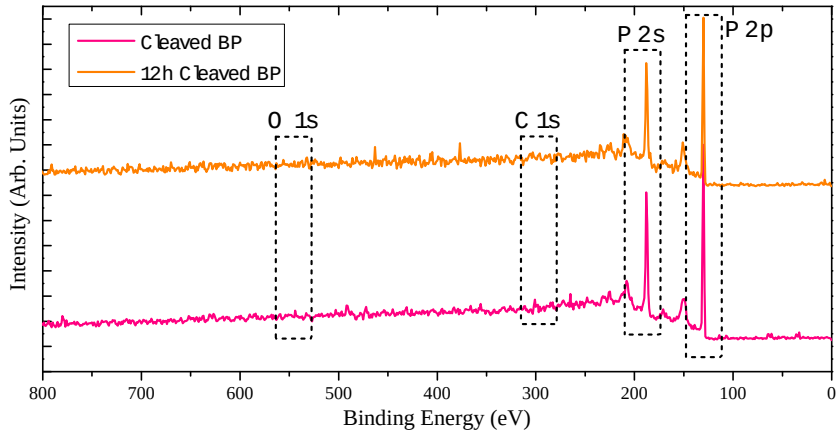

Figure S1: The survey XPS spectrum of the cleaved BP (red line) and 12h cleaved BP (yellow line). No observed O and C peaks are observed due to the BP is cleaved at UHV condition, even afther 12 hours in our main chamber.

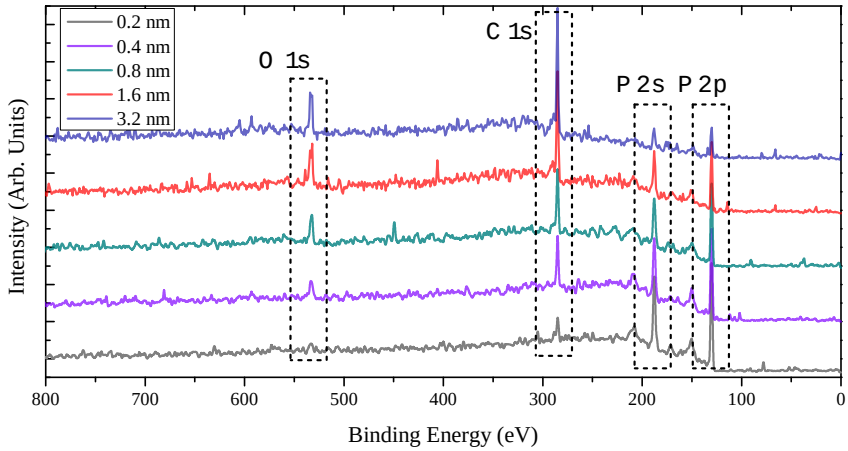

Figure S2: The survey XPS spectrum of the different thickness PTCDA on cleaved BP. It is found that the intensity of P $2p$ and $2s$ decrease monotonically with increasing PTCDA coverage from 0.2 nm to 3.2 nm. Inversely, the intensity of C $1s$ and O $1s$ increase with increasing PTCDA coverage.

2 LEED pattern

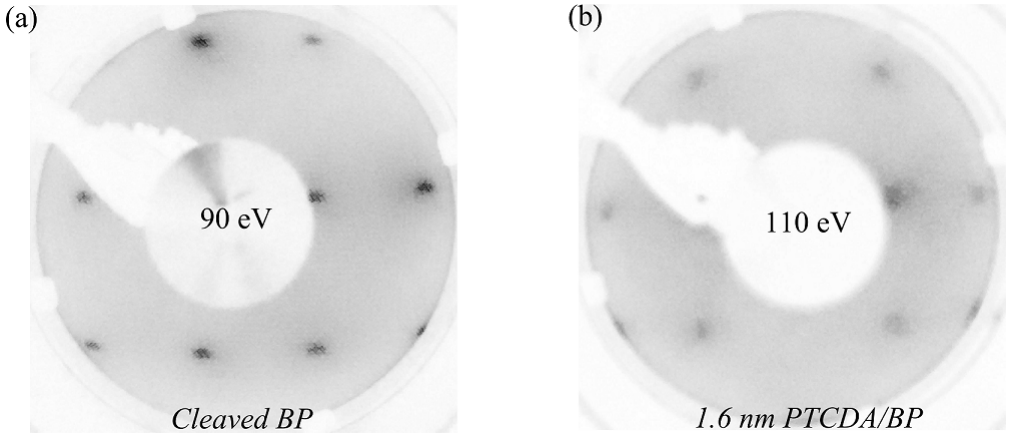

Figure S3: LEED images of (a) the clean cleaved BP surface, recorded at $E_{kin} = 90$ eV; (b) a 1.6 nm thin film PTCDA/BP, recorded at $E_{kin} = 110$ eV. As the diffraction spots are weak and diffuse, the LEED pattern also indicates that there is a rather weak ordering relative to the substrate and with relatively small domain sizes.

3 Atomic force microscopy

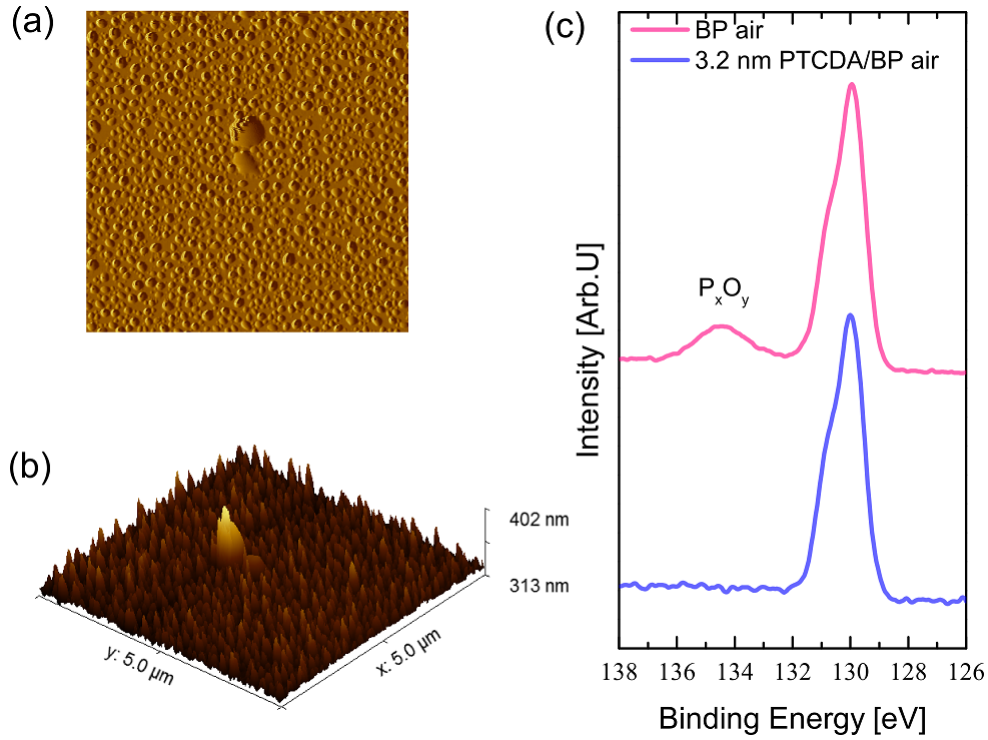

Figure S4: (a) and (b) AFM image of cleaved BP substrate in ambient conditions for 3 hours, 5×5 micrometer. (c) P 2p core-level X-ray photoelectron spectra of a bulk BP crystal and 3.2 nm PTCDA/BP sample upon 3 hours exposure in ambient air.

4 Optimization calculations

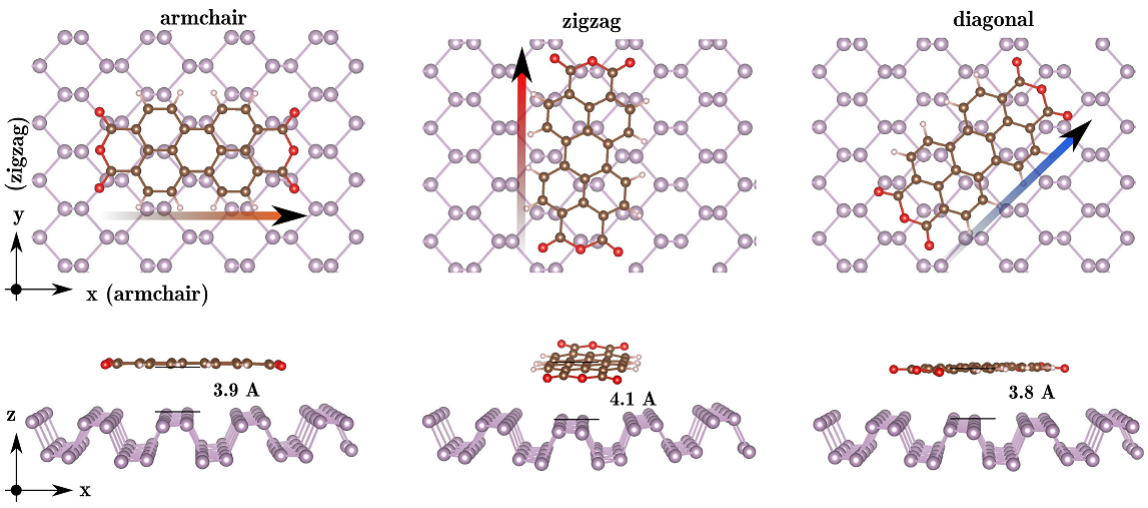

Figure S5: Top and side views of the optimized structures of PTCDA/BP along armchair direction (a), zigzag direction (b), and diagonal direction (c). The PTCDA/BP along diagonal direction own the lowest energy.

Table S1: Structural parameters and total energy of PTCDA/BP systems.

	a	b	c	h	Total Energy
Armchair	19.66 Å	13.49 Å	23.77 Å	3.93 Å	-720.65 eV
Zigzag	19.69 Å	13.50 Å	23.37 Å	4.15 Å	-720.47 eV
Diagonal	19.69 Å	13.49 Å	23.91 Å	3.81 Å	-720.74 eV

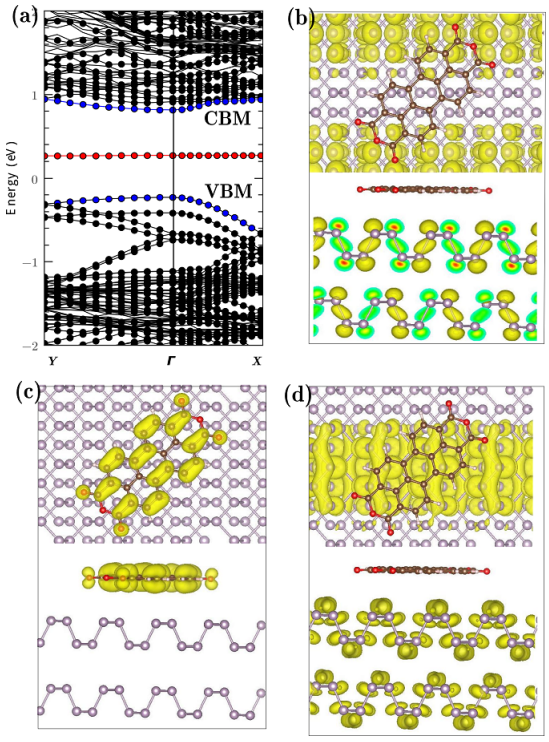

Figure S6: (a) Band structure of PTCDA on bilayer BP composite and the optimized structure of PTCAD molecule along the diagonal direction. The electronic wave function of (b) VBM, (c) Flat-band, and (d) CBM from top view (up) and side view (down), respectively.