Electronic Supplementary Information

Adsorption of PTCDA and C$_{60}$ on KBr(001): electrostatic   interaction versus electronic hybridization

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Part 1: PTCDA vertically adsorbed on KBr(001) substrate

Vertically stand PTCDA configurations were fully considered in this part, as shown in Figure S1, in comparison of the lie-flat configurations discussed in our manuscript. In our structural relaxation, the initial Br-O length was set to 2.5 Å, according to the values of 1.7 to 2.5 Å for Br-O covalent bond in the literature[1, 2]. Among them, the configuration shown in (c) is the most stable one with an adsorption energy of 0.34 eV, substantially smaller than the most stable configuration Br-top (1.30 eV) presented in Table 1 in our manuscript. In the fully relaxed structure, the Br-O bond length, however, enlarges from the initial length of 2.5 Å to over 3.5 Å, roughly 1 Å larger than the typical Br-O covalent bond length. Both results indicate non-covalent bonding between Br and O in a vertically adsorbed PTCDA on KBr.
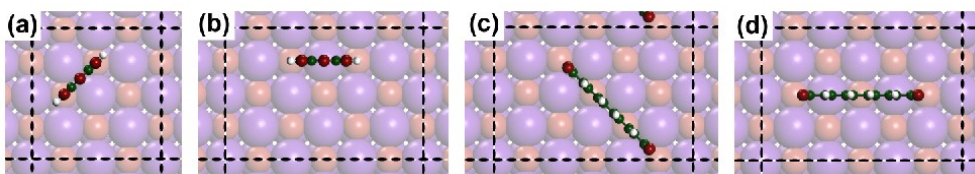

Figure S1   Top views of single PTCDA molecule adsorption on KBr substrate. $p(2\times2)$ and (2×3) Supercells are marked by the write dashed lines. Four configurations of the short and long axis of PTCDA along KBr [100] and [110] are presented in (a), (b), (c) and (d), respectively.

There is more evidence to suggest the lie-flat configurations are more stable than the vertically-stand PTCDA adsorbed on alkali halides. Burke *et al.* the demonstrated the most energetically favorable configuration for monolayer PTCDA on NaCl(001) is a $p(2\times3)$ structure [3], with a small tilt from the surface plane by using non-contact Atomic Force Microscopy (nc-AFM) and density functional theory (DFT). All those results are consistent with our theoretical predictions on the most stable configuration. We want to emphasize all the possible

configurations have been fully considered and the Br-top and ML-Btop are the most stable for the single and monolayer PTCDA on KBr(001), respectively.

Part 2: Role of vdW correction to LPDOS

In this part, further comparison on the differences for LPDOSs computed with RPBE-D, PBE-D and vdW-DF[4] were discussed. Single-molecule configurations were employed in our discussion for simplification. Table S1 shows the optimized angles and molecule-substrate distances for the Br-top configuration using four functionals. Apparently, the structural difference between them are rather small. We plotted the local density of state performed by these four methods for a single PTCDA adsorbed on KBr substrate in Figure S2 with the energy zero shifted to the vacuum level (a) and the valence band maximum (b). According to the benchmark and the methodology set by Grimme *et al.*, the dispersion correction of empirical DFT-D method does not affect electronic structures,[5] which is consistent with our PBE and PBE-D results. It shows that the features of LDOSs obtained with RPBE-D and vdW-DF2 coincide with each other, except a collective shift of ~+0.1 eV for RPBE-D and ~-0.3 eV for vdW-DF2 compared with that of PBE. In light of our results, the difference is qualitatively negligible.

Table S1   Structural details and adsorption energy ($E_{s\text{-}ads}$) of configuration Br-top. Molecular tilting angles of O2-Ctr-O2 and averaged Ol-Ctr-O1 of single PTCDA are denoted as $\alpha_{s\text{-}1}$ and $\alpha_{s\text{-}2}$, respectively. Distances $d_{s\text{-}O1\text{-}K}$, and $d_{s\text{-}Ctr\text{-}surf}$ indicate the averaged distance between overall four O1 atoms and K underneath, and the distance between the center of a PTCDA between the surface. $d_{C\text{-}K}$ indicates the absolute averaged distance between the lowest carbon and potassium atom underneath. The lowest pentagon in $C_{60\text{-}DB}$ rotates α from the KBr surface.

	Br-top PTCDA					$C_{60\text{-}Hex}$		$C_{60\text{-}DB}$		
DF	$\alpha_{s\text{-}1}$ (°)	$\alpha_{s\text{-}2}$ (°)	$d_{s\text{-}O1\text{-}K}$ (Å)	$d_{s\text{-}Ctr\text{-}surf}$ (Å)	$E_{s\text{-}ads}$	$d_{C\text{-}K}$	E_{ads}	$d_{C\text{-}K}$	α	E_{ads}
PBE	175.7	171.6	3.09	3.59	-0.60	3.74	-0.02	3.57	10.8	-0.04
PBE-D	178.5	173.8	2.96	3.29	-1.88	3.43	-0.40	3.20	10.5	-0.39
RPBE-D	177.9	173.7	3.07	3.47	-1.30	3.53	-0.63	3.28	10.4	-0.56
vdW-DF2	175.6	171.1	2.97	3.50	-1.97	/	/	/	/	/

The structure details of the two most stable configurations for C_{60}/KBr were also discussed. We didn't perform vdW-DF2 calculations since RPBE-D already gives the correct hybridization features as PBE does, namely a collective shift as shown in Fig 4 (b) in the main text. Therefore, as the case of PTCDA/KBr, the same conclusion of qualitatively negligible difference can be drawn for C_{60}/KBr case.
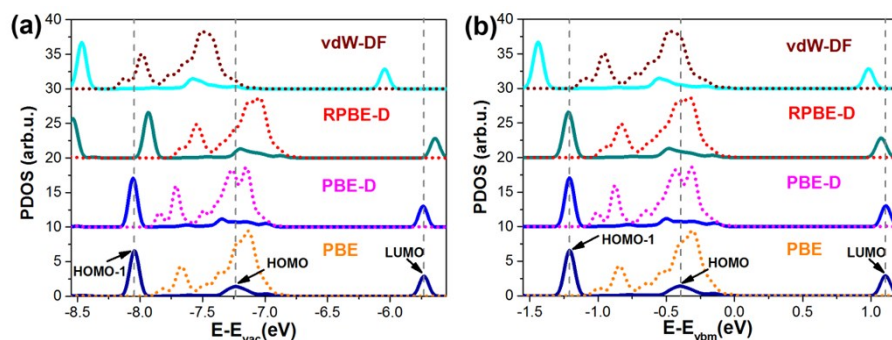
Figure S2 From bottom to top, LPDOSs for carboxylic oxygen O1 (solid lines) and Br1 anion (dotted lines) underneath calculated by PBE, PBE-D, RPBE-D and vdW-DF for PTCDA Br-top configuration. The grey dashed lines are set to the PTCDA molecular orbital levels of PBE for comparison.

Part 3: The electronic structure of PTCDA/ and C_{60}/ 2ML-KBr(001)/Cu(001)

2×3 and 4×4 supercells were employed for PTCDA and C_{60} monolayer adsorbed on two-monolayer-KBr-covered Cu(001). Four Copper layers, with a lattice compression of around 6% in comparison to KBr, were adopted as substrate. A $2 \times 2 \times 1$ k-point grid sampled the Brillouin Zone of both supercells.

The local partial density of states of PTCDA monolayer adsorbed on two-monolayer-KBr-covered Cu(001) substrate is shown in Figure S3, where solid lines refer the DOSs of the whole system and dotted line refers to PTCDA monolayer adsorbed on KBr substrate without Copper. It is suggested that no hybridization is found between PTCDA and Cu or Br, but Br-Cu covalent bonds are formed when 2ML KBr sits on Cu substrate. The HOMO-1 and lower molecular orbitals of PTCDA locate similarly as the system without the Cu substrate. For higher orbitals, the energetic value of LUMO minus HOMO is 0.2 eV smaller than that of PTCDA/KBr(001), due to the bending of PTCDA differs from the system without Cu substrate. The parameters describing how much PTCDA molecules bend are α_1, α_2 and α_3 (see Figure 2 in the main text), which are 172.0°, 177.7°, 174.3°, respectively, indicating PTCDAs have a larger bending than that without Cu substrate.
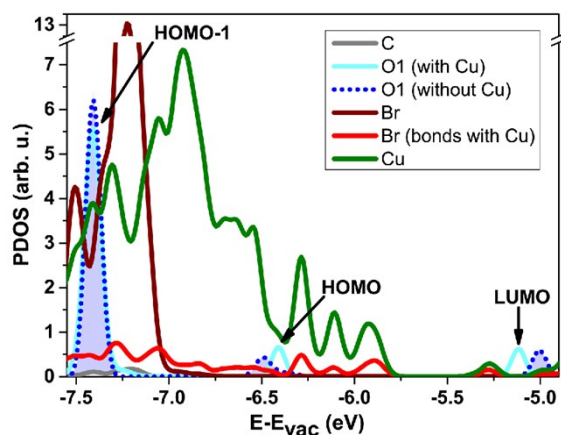

Figure S3 Local partial density of states for a carboxylic oxygen (O1) and an "averaged" C atom in PTCDA, a Br anion under C atoms, a Cu atom and a Br atom that forms a covalent bond in PTCDA/2ML-KBr/Cu. All energies are reference to the Vacuum Level. HOMO-1, HOMO, LUMO are indicated by the black arrows.
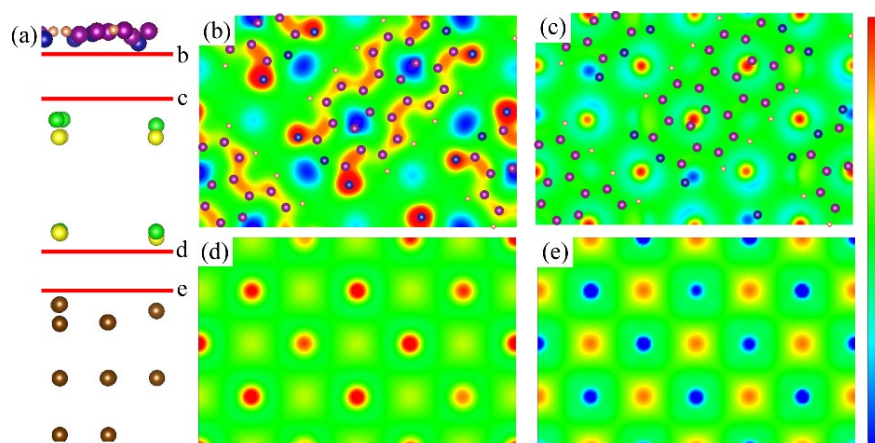
Figure S4   (a) Side view of the sketch of PTCDA/2ML-KBr(001)/Cu. Alphabet letter *b, c, d* and *e* represent slabs close to PTCDA and KBr for the PTCDA/KBr interface, close to KBr and Cu for the KBr/Cu interface, respectively. (b), (c), (d) and (e) are top views of DCDs of slabs b, c, d and e.
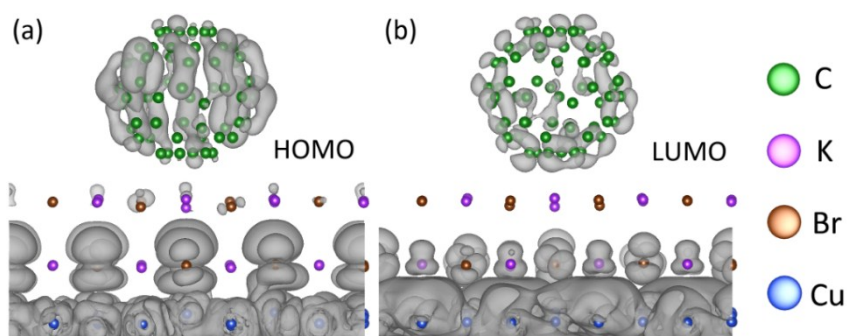

Figure S5 Real Space Distributions of wavefunctions of HOMO (a) and LUMO (b) of C_{60}/2ML-KBr/Cu.

Charge accumulations and reductions are found similarly to the slabs near the PTCDA monolayer and KBr for PTCDA/KBr in the differential charge density, as shown in Figure S4 (b) and (c). A charge accumulation in the DCD of slab d near Br atoms and a charge reduction in the slab e near Cu atoms, which bond with Br atoms, are found in Figure S4 (d) and (e), respectively. Typical Br-Cu covalent bonds are formed for the KBr/Cu interface, which is also illustrated by PLDOS above. The Cu atoms, under K atoms in the upper layer, gain electrons due to the positive potential of K atoms. Interestingly, much stronger dipoles are formed both within PTCDA and the whole system in consideration of metal substrate, which can be further approved in Part 5.

Visualized wavefunctions of the HOMO and LUMO of C_{60} were plotted to illustrate the electronic hybridization situation between C, Br and Cu in Figure S5. The LUMO of C_{60}, residing at -4.61 eV, does not hybridize with neither Br or Cu and keep its original shape as the case of C_{60} adsorbed on KBr substrate (see Figure S5 (a)). A new hybridized HOMO state between C, Br and Cu occurs, locating at -6.19 eV. It can be concluded that a hybridized state will be formed for molecules/2ML-KBr/Cu if there is a newly formed hybridized state for molecules adsorbed alkali halides substrate. Whether hybridization states are formed or not does not change when metal substrate is introduced. Two monolayer alkali halides are good candidates for electronically insulating organic functional molecules from the metal substrate for STM.

Part 4: STM simulation of PTCDA and C_{60} on Cu substrate covered by thin layer KBr (001)

Figure S6 shows the simulated STM images for configurations PTCDA- and C_{60}-covered 2ML-KBr thin films on copper surfaces. Our simulation is based on the Tersoff-Hanmann Approximation.[6] Two bias voltages, namely +1.0 V and -1.5 V, were considered according to a previous experimental work [7, 8], in which STM experiments of PTCDA/layered NaCl/Ag were conducted with sample bias of +1.0 V and -1.5 V to detect the molecular orbitals. We believe this new section is an important addition to our work and may attract considerable attention from experimental groups.

Figure S6   Constant-height mode STM simulations at different bias for PTCDA (a) and (b), and for C_{60} in (c) upper and lower panels, respectively. (a) V_b = -1.5, h = 1.3 Å and (b) V_b = +1.0, h = 1.3 Å for PTCDA; (c) V_b = -1.5, h = 1.0 Å and (d) V_b = +1.0, h = 1.0 Å for C_{60}.

Part 5: Bader analysis of molecules adsorbed on the 2ML-KBr-covered Cu substrate

A larger amount of electrons is transferred between PTCDA or C_{60}, two monolayer KBr and metal substrate compared to the case without thse metal substrate, indicating a stronger electrostatic interaction. Specifically, the KBr monolayer closed to PTCDA loses 0.87 e, while the PTCDA monolayer gains 0.91 e according to Bader analysis[9]. In terms of C_{60}, internal charge redistribution happens with an amount of 0.69 e transferred to C_{60}. The KBr monolayer close to C_{60} loses 0.13 e. All these evidences show that the electrostatic interaction is the primary mechanism for PTCDA adsorbed KBr(001).

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