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Electronic Supplementary Information:

Chirality control of nonplanar lead phthalocyanine (PbPc) and its potential application for high-density storage: a theoretical investigation

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In the main body of this paper, we present the theoretical results of PbPc/M(001) at $Pb_{\downarrow}$ state since the $Pb_{\downarrow}$ is used as the initial structure in our calculations. For $Pb_{\uparrow}$ state, the corresponding results are given in this electronic supplementary information (ESI). We can find the main results of the $Pb_{\downarrow}$ and $Pb_{\uparrow}$ are similar and main conclusions are the same.

Fig. S1 shows the azimuthal orientations of PbPc at $Pb_{\uparrow}$ state. For PbPc/Cu(001), we can find two unequivalent stable states at $\theta=\pm26.6^{\circ}$. The PbPc molecular structures at +26.6° and -26.6° azimuthal orientations are enantiomorphous. There are also two metastable states at $\theta=0^{\circ}$ and $\theta=45^{\circ}$ azimuths. For PbPc/Pd(001), there are only three states. The stable state corresponds to 0° azimuth and PbPc keeps being four-fold symmetry just like free PbPc. For the metastable states, two structures are enantiomorphous and the azimuth θ is -24.8° for lefthand chirality and 24.8° for righthand chirality, respectively.

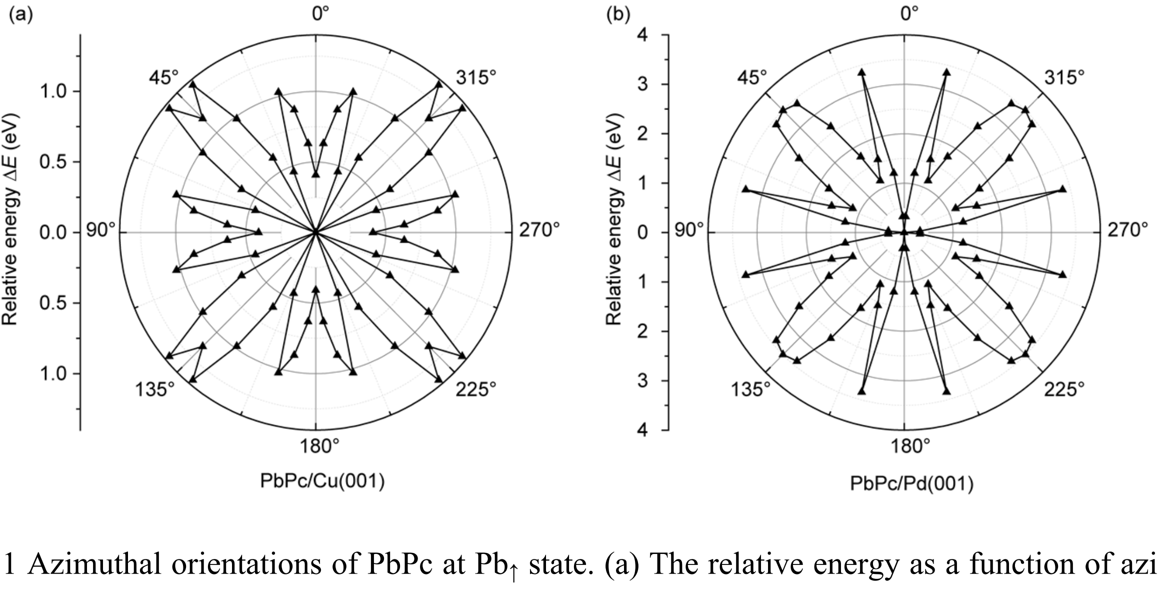

Fig. S1 Azimuthal orientations of PbPc at $Pb_{\uparrow}$ state. (a) The relative energy as a function of azimuth (θ) for (a) PbPc/Cu(100) and for (b) PbPc/Pd(100).

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Our study shows that PbPc would prefer to take achiral orientation on Pd(001). However, it is chiral on Cu(001), which is similar to the experimental result of CuPc on Ag(001) as shown in Fig. S2 (A) and (B). In adition, nonplanar PbPc can be used to store information by controlling central Pb atom up and down. Experimental study has also demonstrated this function of nonplanar MPcs, such as SnPc on Ag(111) as shown in Fig. S2 (C)-(F).

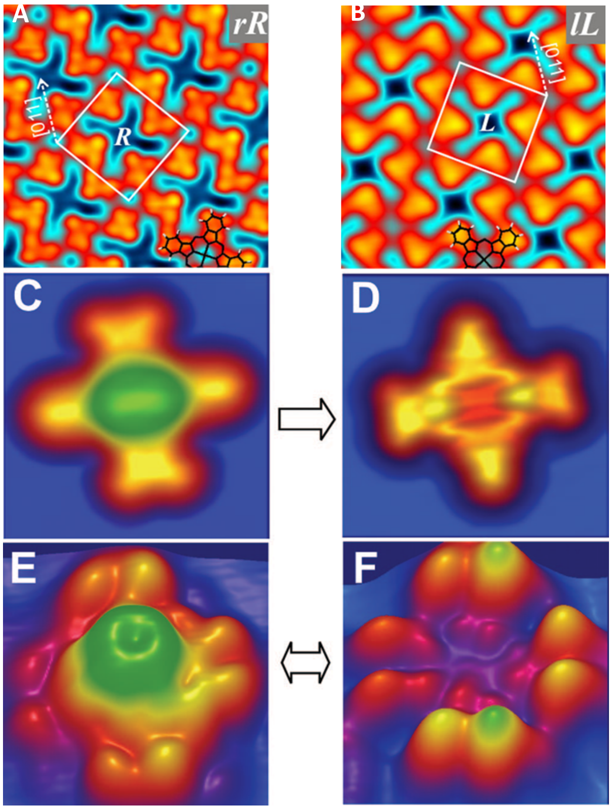

Fig. S2 (A) and (B) show the chirality of CuPc on Ag(001) from Mugarza et al. Reprinted (adapted) with permission from Phys. Rev. Lett. 105, 115702 (2010). Copyright © 2010 American Physical Society. (C)-(F) demonstrate the information storage by controlling central metal atom up and down. Reprinted with permission from Wang et al., J. Am. Chem. Soc. 2009, 131, 3639. Copyright © 2009 American Chemical Society.

At $\mathrm{Pb}_{\uparrow}$ state, the charge density difference (CDD) shows that the charge transfer between molecule and substrate mainly results from the carbon atoms of benzene group and the first layer Pd atoms below molecules as shown in Fig. S3 (a)-(d). Taking a typical carbon atom marked by a red circle in Fig. S3 (c) and the corresponding carbon atom in Fig. S3 (d), we evaluate the difference in hybridization electron by integrating the PDOS in Fig. S3 (e) and (f). The results show that 0.28 p_z electron (h_e) takes part in the hybridization at 0° azimuth but the h_e is 0.26 p_z electron at 24.8° azimuth in the mainly hybridization region from (E_f-5 eV) to E_f. Therefore, the hybridization interaction between molecule and substrate at 0° azimuth is stronger than that at 24.8° azimuth. And the symmetry axis of PbPc tends to be parallel to Pd[110].

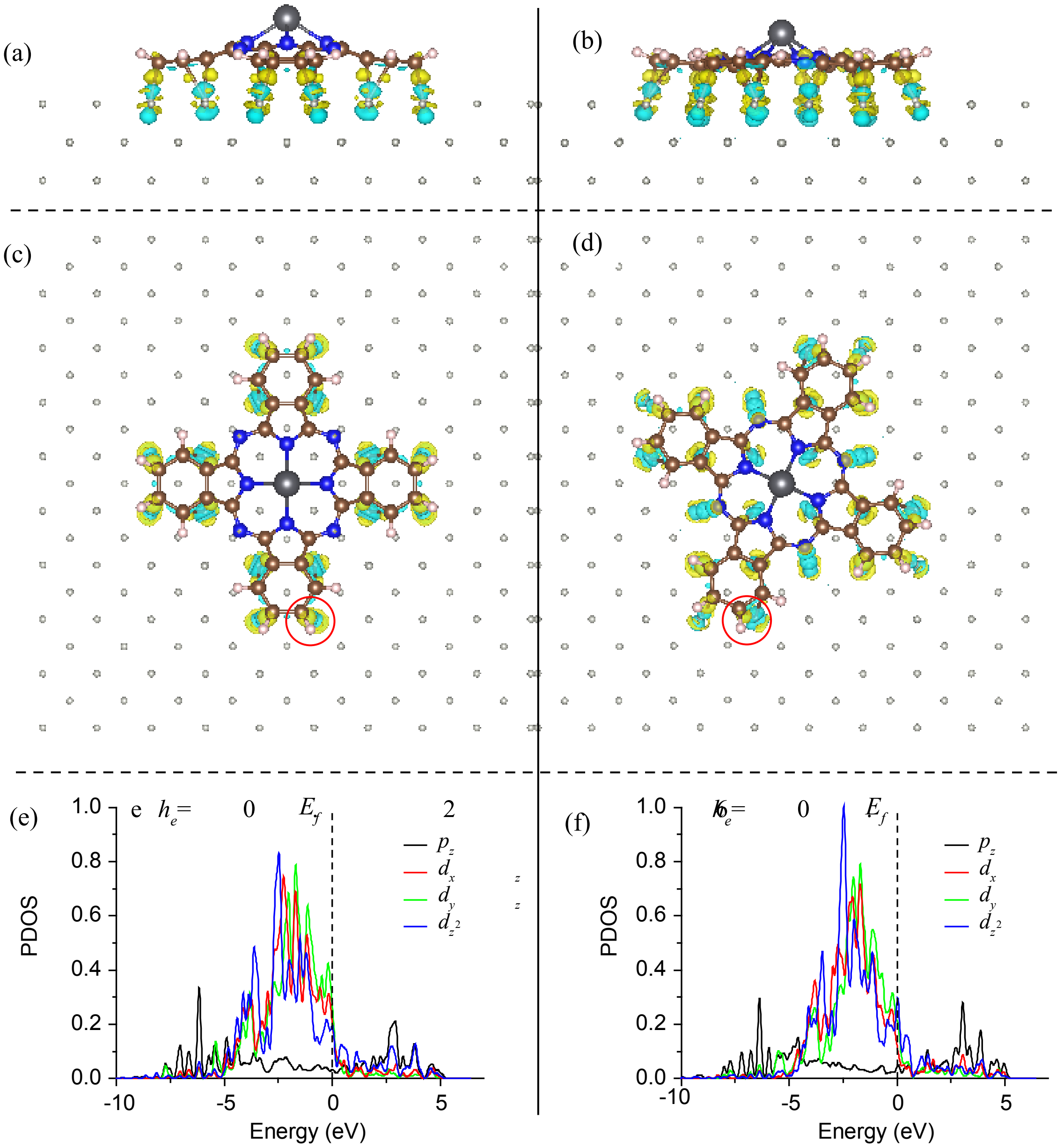

Fig. S3 Charge density difference (CDD) and projected density of state (PDOS) of PbPc/Pd(001) at Pb↑ state. (a) and (b) are the side views of CDD at 0° and 24.8° azimuth, respectively. (c) and (d) are the top views of CDD. (e) and (f) are PDOS.

From the adsorption energy per unit area in Fig. S4, we can find that PbPc at Pb↑ state also tends to form a (3×4) reconstruction on Pd (001), which is the same to the result at Pb↓ state.

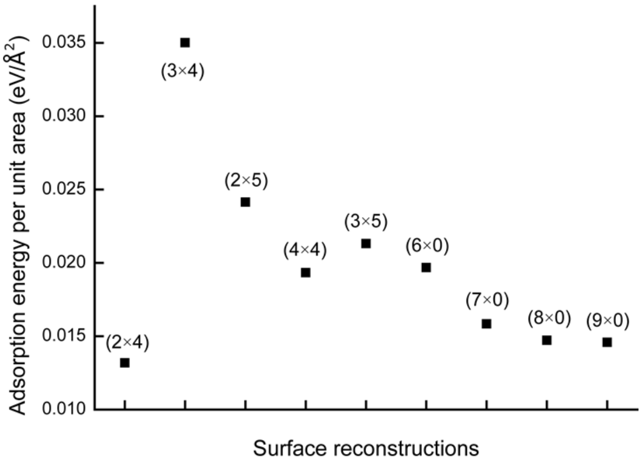

Fig. S4 Adsorption energies per unit area (E_A) of nine kinds of surface reconstructions for Pb↑ state. The (m×n) denotes [m n, -n m] reconstruction.

Due to molecule-substrate interaction, molecule adsorption will induce rearrangement of surface atoms. In generally, surface atoms and the adsorbed molecules have the same period, such as the (3×4) surface reconstruction in this study. Fig. S5 shows the height contour map of top Pd atoms before and after PbPc adsorption. It clearly demonstrates the (3×4) surface reconstruction induced by PbPc adsorption since the lattice constants of the top Pd atoms satisfy the relation of [b_1,b_1]=[3 4, 4 3]·[a_1,a_1], where the a_1 and b_1 are the lattice constants of two dimensional (2D) Pd surface before and after PbPc adsorption, respectively. In the main body of this paper, we use "surface reconstruction" to denote "surface reconstruction induced by PbPc adsorption". So the surface reconstruction characterizes the period of both two dimensional PbPc molecules and top layer Pd atoms.

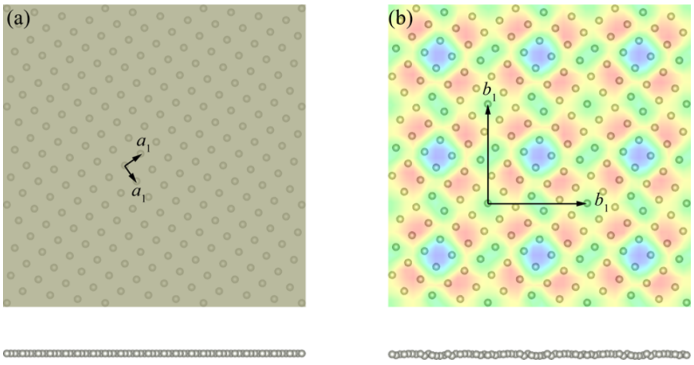

Fig. S5 The height contour map of top layer Pd atoms. (a) Ideal Pd(001) surface before PbPc adsorption and (b) (3×4) surface reconstruction induced by PbPc adsorption.