

Supplementary Information

Molecular orientation transformation in initial growth stage of disk-like phthalocyanine during organic vapor deposition process

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Additional details about the simulation methods:

All MD simulations described in this work employ the COMPASS forcefield for all atom-atom interactions. Validation studies have shown that this force field can accurately predict the structural, conformational, vibrational, and thermophysical properties for molecules in isolation and in condensed phases.¹ Furthermore, it has been successfully applied to study the structure of molecular clusters,² self-assembly of molecules on graphite,³ and ordering of molecular nanocrystallites on α -SiO₂ substrate.⁴ The structural properties of bulk α -H₂Pc and α -SiO₂ were first simulated to test the force field and the non-bonded summation method. α -H₂Pc crystallizes in monoclinic system (space group C2/c) with unit-cell parameters of $a = 26.14$ Å, $b = 3.81$ Å, $c = 23.97$ Å, and $\beta = 91.10^\circ$.⁵ α -SiO₂ (with the density of 2.20 g cm⁻³)⁶ was imported from the structure database of Materials Studio software. Since the data of α -H₂Pc were obtained by x-ray diffraction at room temperature and ambient pressure,

where the thermal expansion and molecular motions may be important, we performed *NPT* simulation at 300 K and 1 atm for 3 ns on a $1\times 6\times 1$ supercell. The first 2 ns were taken for equilibrium, and the last 1 ns was used for data production. P was controlled by Parrinello-Rahaman algorithm.⁷ The same *NPT* simulation was also performed on bulk α -SiO₂. With the above setups, the simulation results for α -H₂Pc are $a = 25.32$ Å (−3.14%), $b = 3.95$ Å (+3.67%), $c = 23.38$ Å (−2.46%), and $\beta = 92.92^\circ$ (+2.00%), which correspond to the experimental results well.⁵ Moreover, the simulated density of α -SiO₂ is 2.33 g cm^{-3} , only 5.91% larger than the experimental result.⁶

α -SiO₂, a commonly used dielectric in OTFTs studies, was usually obtained by thermal oxidation of Si substrate. The gotten α -SiO₂ substrate was hydrophilic with water contact angle of $36\pm 1.5^\circ$ and surface energy of 58.7 mJ m^{-2} .⁸ Qualitatively, the surface character of α -SiO₂ is determined by surface concentration of silanols and siloxanes.⁹ As the surface concentration of silanols increases, the surface of α -SiO₂ becomes more hydrophilic.⁹ For simplicity, the completely hydrated α -SiO₂ surface, with water contact angle of about 0° and surface energy only slightly greater than that of liquid water,^{9,10} was used in this simulation work.

T_{sub} was chosen at 350 K, which lies in the range of typical OVD for planar phthalocyanine. Too low T_{sub} results in parallel molecular orientation and even amorphous OTFs,¹¹ while too high T_{sub} leads to obvious desorption and discontinuous OTFs.⁸ Furthermore, this chosen T_{sub} may reflect the temperature effect on the molecular orientation degree of OTFs. Except for the testing simulations described above, all simulations were performed in *NVT* ensemble.

Determination of $\gamma_{(100)}$, $\gamma_{(010)}$, $\gamma_{(001)}$, $\gamma_{i(010)}$, and $\gamma_{i(100)}$ values:

According to the calculating method in Ref. 12, $\gamma_{(100)}$, $\gamma_{(010)}$, and $\gamma_{(001)}$ at 0 K are determined as 106.30, 116.93, and 102.64 mJ m⁻², respectively. With the typical temperature coefficient of surface energy for organic materials (about -0.10 mJ m⁻² K⁻¹),¹³ $\gamma_{(100)}$, $\gamma_{(010)}$, and $\gamma_{(001)}$ at 350 K are determined as 71.30, 81.93, and 67.64 mJ m⁻². Based on the known $\gamma_{(010)}$, $\gamma_{(100)}$, and γ_{sub} values as well as the calculating method in Ref. 12, $\gamma_{i(010)}$ and $\gamma_{i(100)}$ are determined as 21.53 and 29.56 mJ m⁻², respectively.

Determination of the supersaturation Δg :

During an OVD process, $\Delta g = \Delta H_{\text{subl}} + RT_{\text{sub}} \left[\ln \left(\sqrt{\frac{2\pi RT_{\text{sub}}}{M}} \Phi \right) - \frac{\Delta S_{\text{subl}}}{R} \right]$, where

ΔH_{subl} , ΔS_{subl} , R , and M denote the enthalpy of sublimation, entropy of sublimation, gas constant, and molecular weight, respectively.¹⁴ For H₂Pc molecules deposited on α -SiO₂ substrate at 350 K under typical Φ of 0.5~2.0 ML min⁻¹, Δg can be determined as $\Delta g = 1.29 \sim 1.33$ eV H₂Pc⁻¹ by the known ΔH_{subl} and ΔS_{subl} values.¹⁵

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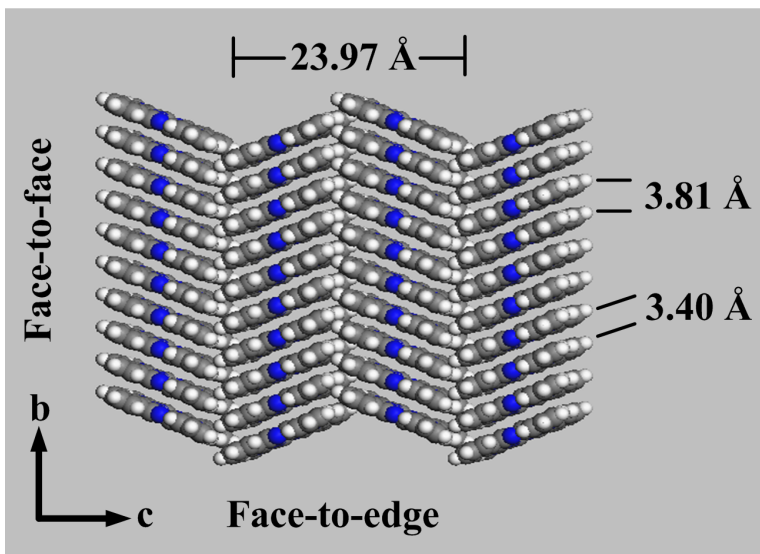


Fig. S1. Schematic diagram of α -H₂Pc's herringbone structure projected on the (100) plane.

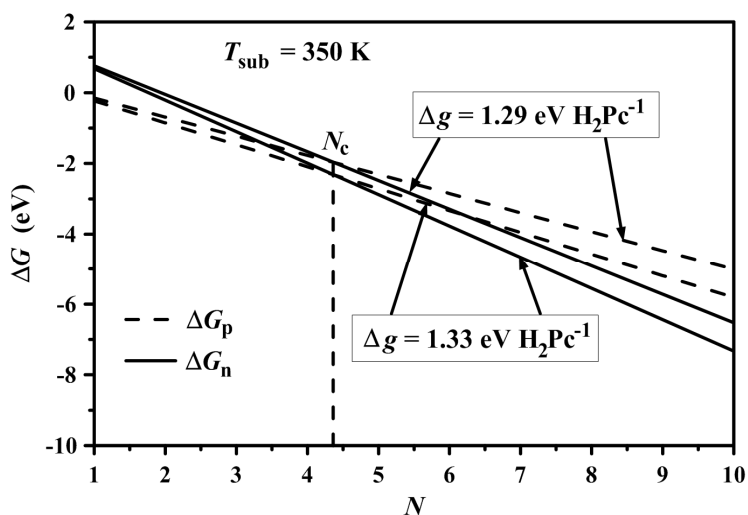


Fig. S2. ΔG_p and ΔG_n functions in light of Eqs. (5a) and (5b) under the typical experimental condition of $T_{\text{sub}} = 350$ K and $\Delta g = 1.29\sim 1.33$ eV H₂Pc⁻¹.

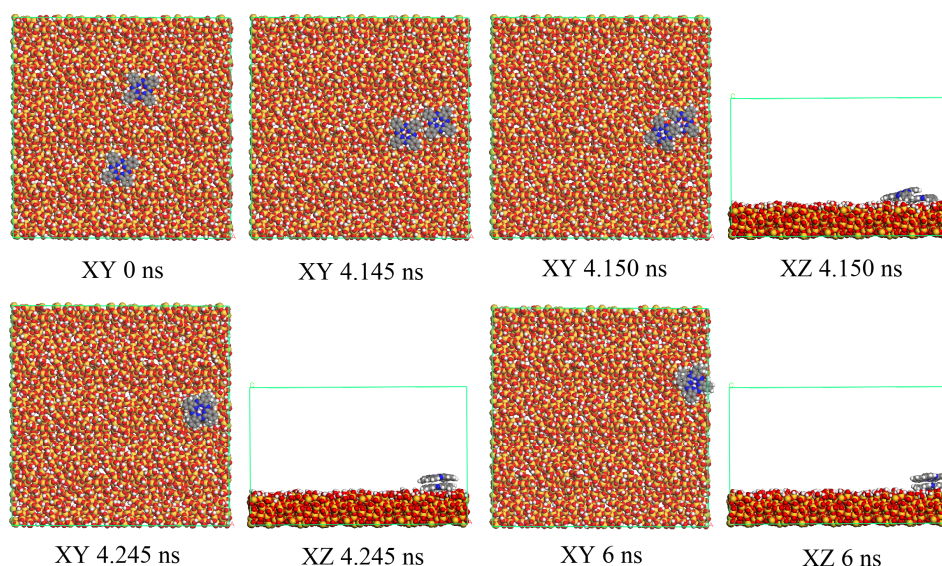


Fig. S3. Snapshots from simulation of two H₂Pc molecules deposited on *a*-SiO₂ substrate at 350 K. XY and XZ denote the corresponding projective planes.

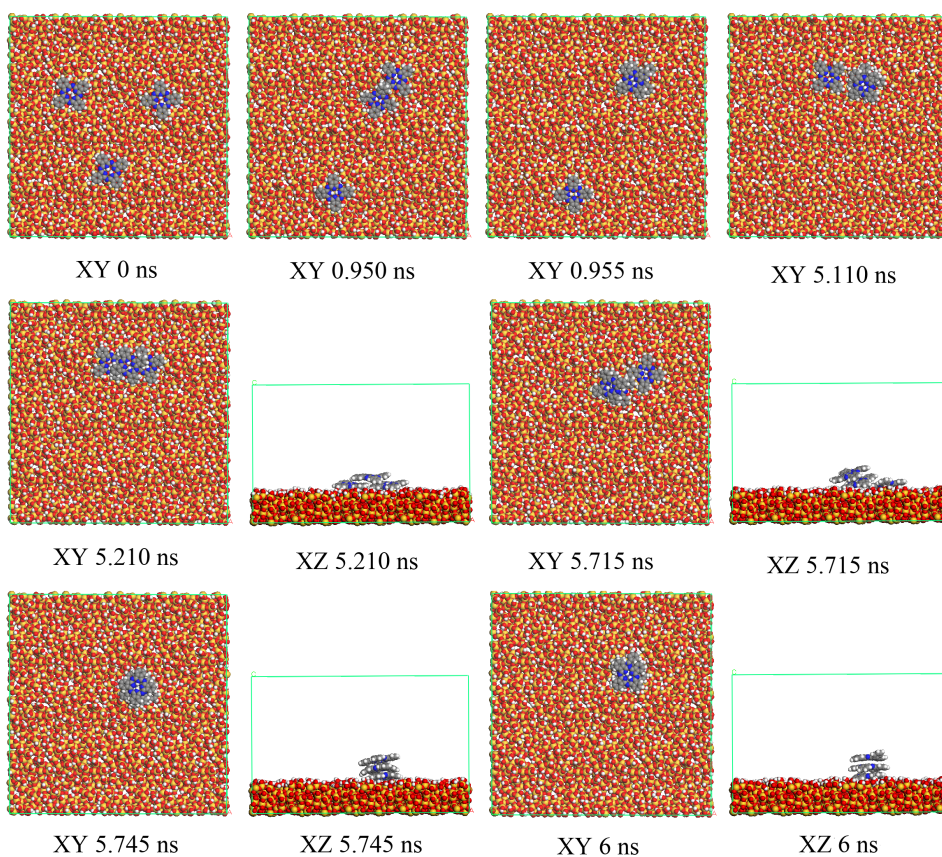


Fig. S4. Snapshots from simulation of three H₂Pc molecules deposited on *a*-SiO₂ substrate at 350 K.

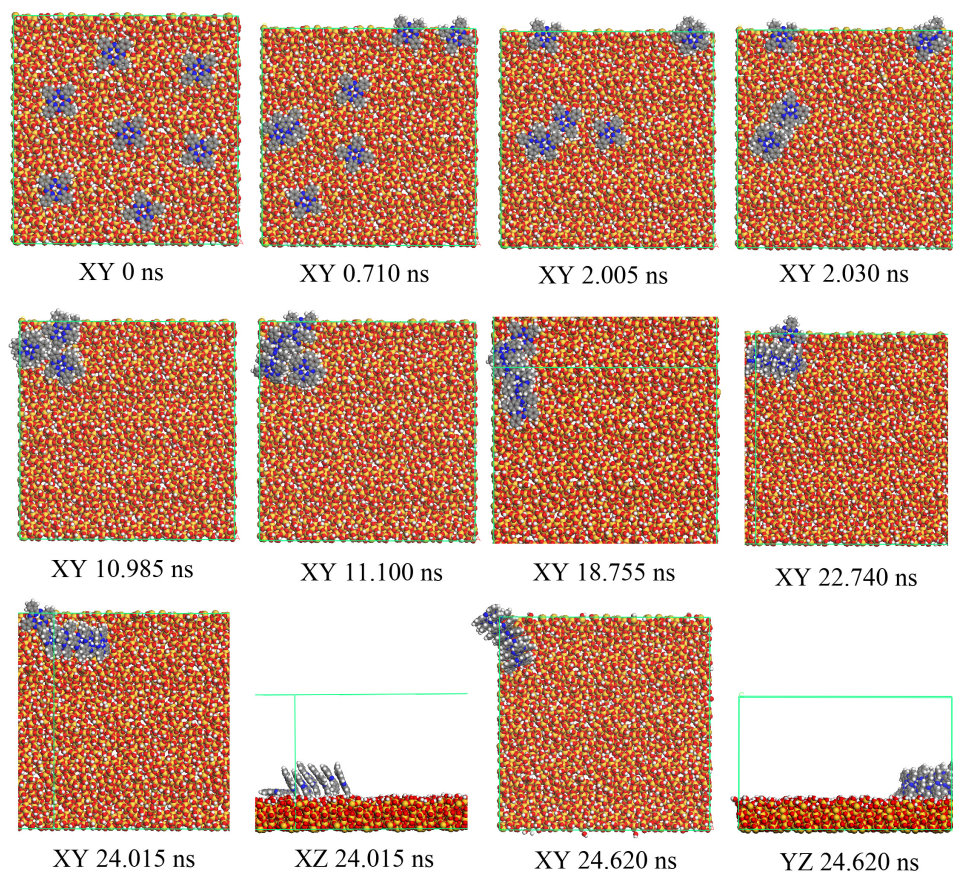


Fig. S5. Snapshots from simulation of seven H₂Pc molecules deposited on *a*-SiO₂ substrate at 350 K.

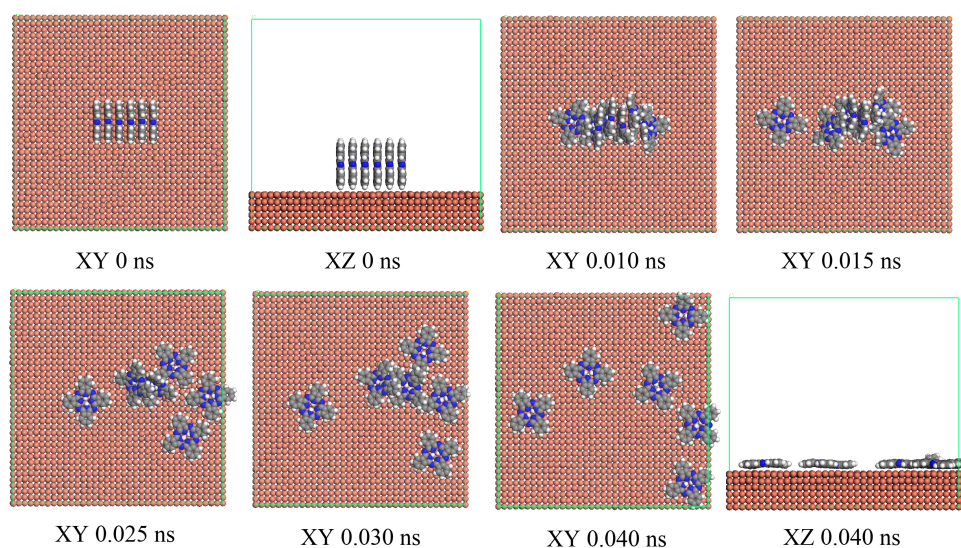


Fig. S6. Snapshots from simulation of a normal six-H₂Pc cluster on Cu(100) at 300 K.

The orange spheres denote Cu atoms.

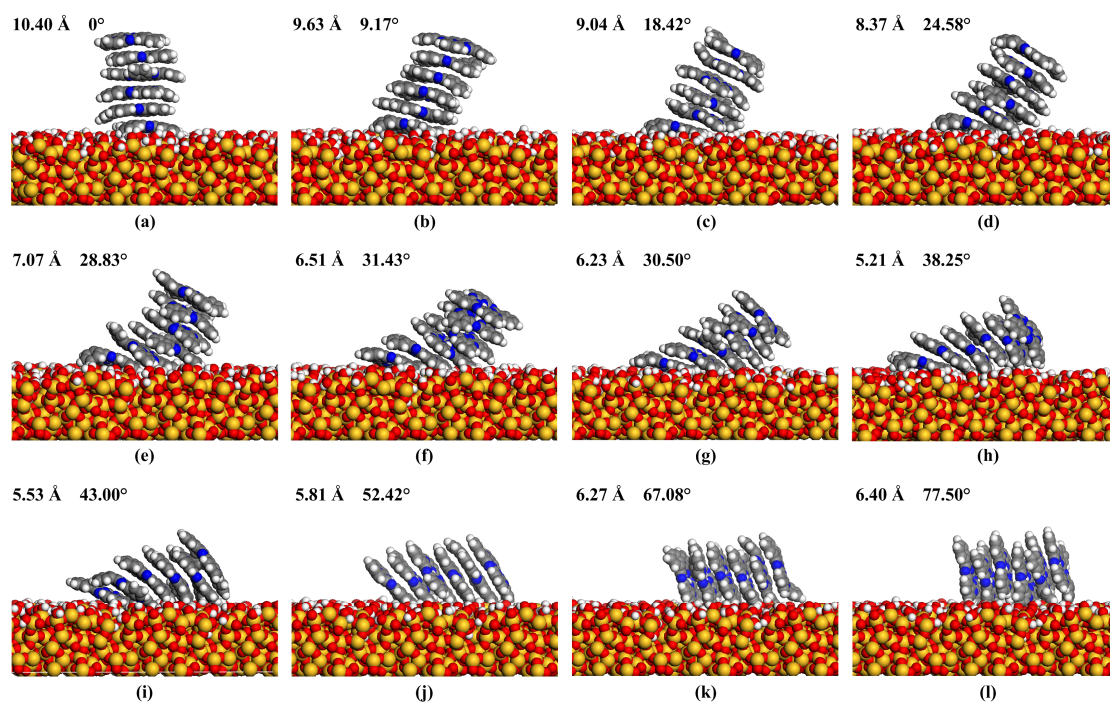


Fig. S7. Snapshots from the parallel-normal transformation of a parallel six-H₂Pc. (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), (k), and (l) correspond to the data points in the insert of Fig. 5b.