Section S1. Experimental Details

3-Hydroxyphenalenone (3-HPLN) of 98% purity was purchased from Acros Organics. The Cu (111) single crystals used for this study were obtained from Princeton Scientific, had a purity of more than 99.99% and were polished with orientation accuracy of better than 0.5%. All experiments were carried out under ultrahigh vacuum (UHV) in a UHV chamber system with a base pressure better than 1 x 10^{-10} mbar. The Cu surface was routinely cleaned following a procedure that is standard in the literature, consisting of repeated cycles of Ar+ ion sputtering at room temperature and annealing the crystal to 850K. 3-HPLN molecules were deposited by molecular beam epitaxy from a home-built Knudsen-Cell-type evaporator with a base pressure of 10^{-9} mbar during the evaporation. Following deposition, the samples were transferred in-situ to a chamber that houses the low-temperature scanning tunneling microscope (STM). The STM is an Omicron low temperature STM, which we operated at liquid nitrogen temperature for this study.

When deposited at room temperature on Cu(111), 3HPLN molecules typically form rows two or three molecules wide at sub-monolayer coverage (figure S1). These rows are oriented along 6 distinct directions, as can be seen in figure S1. While we were not able to simultaneously resolve 3-HPLN and the Cu substrate atoms, we attribute such an alignment to the epitaxial orientation of the molecular rows with the substrate's close-packed directions, under consideration of the chirality of the molecules. Annealing the molecular layer to 390K causes Oswald ripening where the rows transform into islands consisting of double rows, as described in the main text. At considerably higher coverage, such as above 2 ML nominal coverage, further annealing to 470K results in the extended honeycomb and linear chain networks, which are described in the main text.

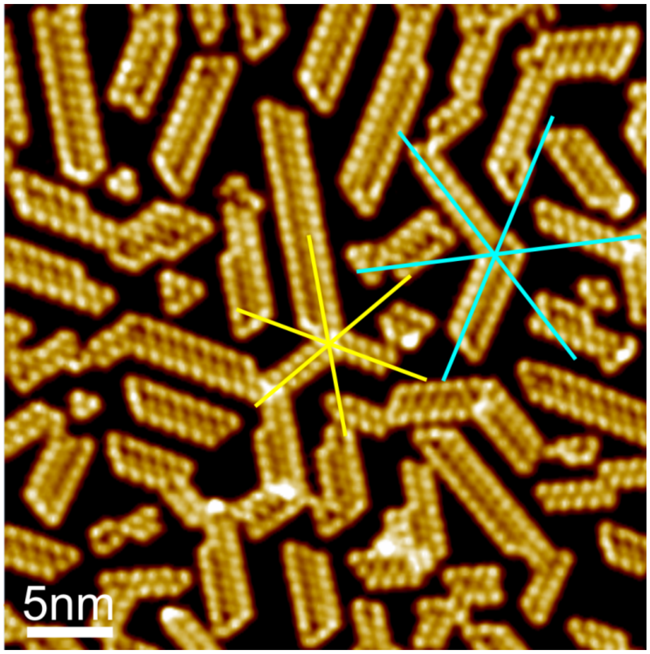
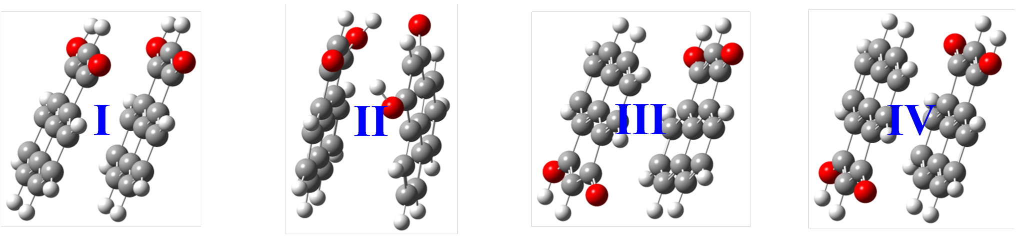


Figure S1: Scanning tunneling microscopy image of a sub-monolayer of 3-HPLN deposited on Cu(111) at room temperature. Highlighted are 6 distinct direction of island orientation. $I_T=500pA$, $V_b=1V$.

Section S2. Computational Details

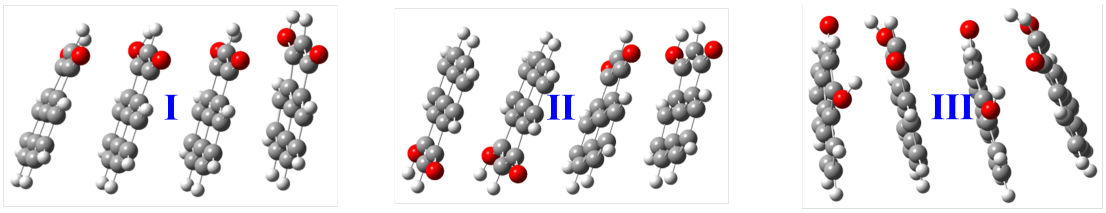
For the top layer of the honeycomb-like bilayer, the constituent unit can be treated as a π–π stacked dimer. As shown in Fig. 1e of the main text, three π–π stacked dimers can further form the junction (i) and two π–π stacked dimers can further assemble the linear segment (ii). In order to obtain possible structures of pinwheel junction (i) and linear segment (ii), different free dimers, tetramers, and hexamers are optimized at the level of M06-2X/6-31G(d) in the Gaussian 09 software package.[1] Their optimized structures and relative energies are summarized in Figs. S2, S3, and S4, respectively. Different from the dimers, tetramers, and hexamers in the top layer, 3-HPLN molecules can just assemble through hydrogen bonding to form the constituent unit, trimer, in the bottom layer of the honeycomb-like bilayer. The stable 3-HPLN trimer can easily locate through formation of three hydrogen bonds as indicated by Fig. S5 (**I**). We cannot consider all possible free trimers, and six typical trimers are constructed to make energy comparison. Without the Cu(111) substrate, direct M06-2X/6-31G(d) geometry optimization of trimers would fail or obtain some partially $\pi-\pi$ stacked trimers. The BLYP functional with the Gaussian plane-wave (GPW) method implemented in the CP2K software package[2] is employed to optimize different 3-HPLN trimers. To better describe the long-range electron correlations that are responsible for the van der Waals (vdW) interactions between 3-HPLN molecules, the Grimme's correction (D3)[3] is adopted. The core electrons are described by the Goedecker-Teter-Hutter (GTH) norm-conserving pseudopotential,[4, 5] and the wave functions of valence electrons are expressed by the combination of the polarized double-ξ quality Gaussian basis[6] and a plane-wave basis set (with an energy cutoff of 280 Ry). After geometry optimization in the CP2K software, the single-point energies of these trimers are further computed at the level of M06-2X/6-31G(d) method in the Gaussian 09 software. Of course, the more hydrogen bonds the trimer (**I**) has, the lower its energy is, as indicated by Fig. S5.

As shown in Fig. S2, the lowest-energy $\pi-\pi$ stacked dimer (**II**) is aligned so that the carbonyl group of one 3-HPLN molecule is in juxtaposition with the hydroxyl group of the other molecule, which is beneficial to formation of two hydrogen bonds to further stabilize the dimer. When this stable dimer is used to assemble linear $\pi-\pi$ stacked tetramers, the lowest-energy tetramer (**IV**) in Fig. S3 have two such dimers with O- and OH-containing ends pointing opposite directions. The tetramer (**II**) should be mentioned since it can be found in the experimental 3-HPLN crystal.[7] However, its relative energy is 0.18 eV/molecule larger than that of the tetramer (**IV**). For the free hexamers in Fig. S4a, eight configurations are considered, including (**I**) with six all "upward" molecules, (**II**) with two “downward” molecules in the big sky-blue circle, and (**III~VIII**) with certain horizontally reversing molecules in the small sky-blue circles. The “upward” and “downward” indicate the orientation of O- and OH-containing ends. The horizontally reversing action would drive the carbonyl of one 3-HPLN molecule in juxtaposition with hydroxyl of the other molecule. Although the hexamer (**IV**) (Fig. S4b) has the lowest energy, two π−stacking 3-HPLN molecules in this hexamer lie down, which would be not energy-favorable as the pinwheel junction (i) in the honeycomb-like structure. The second-lowest-energy hexamer (**I**) (Fig. S4b) is not directly assembled by the lowest-energy dimer (**II**). The hexamer (**I**) includes three dimers with O- and OH-containing ends pointing the same direction, and 3-HPLN molecules in each dimer are identically aligned. This alignment induces three energy-favorable hydrogen bonds between neighboring carbonyl and hydroxyl groups.

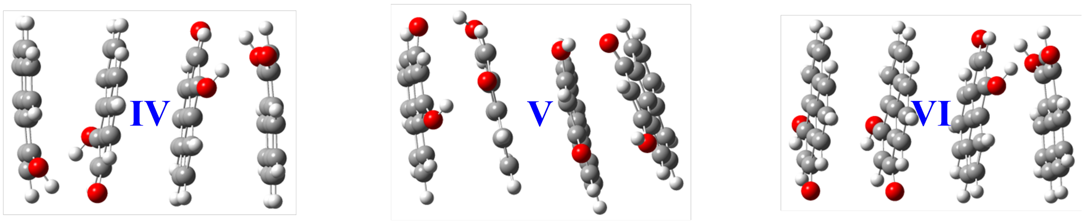


Relative Energy (eV/molecule)	**0.18**	**0.00**	**0.14**	**0.15**

Fig. S2 Optimized free dimers (**I~IV**) with their relative energies at the level of M06-2X/6-31G(d).



Relative Energy (eV/molecule)	0.20	0.18	0.02



Relative Energy (eV/molecule)	0.00	0.04	0.09

Fig. S3 Optimized free tetramers (**I~VI**) with their relative energies at the level of M06-2X/6-31G(d).

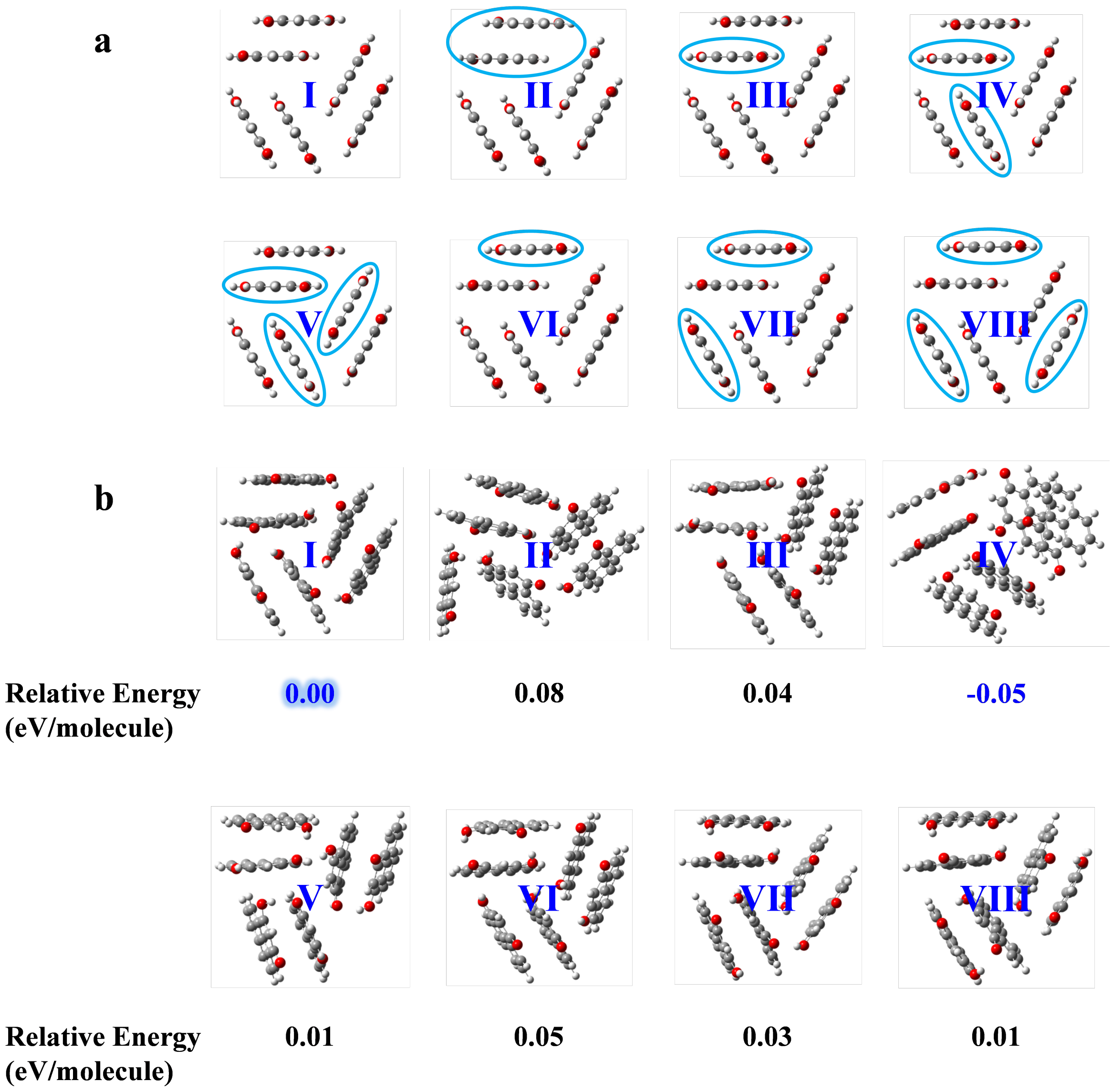


Fig. S4 (a) Initial generation of different hexamers (**I~VIII**) for possible pinwheel junction (i) in the top layer of the honeycomb-like bilayer. For the hexamer (**I**), O- and OH-containing ends of all the 3-HPLN molecules point the same direction ("upward" orientation). For the dimer in the big sky-blue circle of the hexamer (**II**), these two molecules have "downward" orientation. For the hexamers (**III~IV**), molecules in the small sky-blue circles have horizontally reversing orientation to let carbonyl of one molecule in juxtaposition with hydroxyl of the other molecule.

(b) Optimized free hexamers (**I~VIII**) with their relative energies at the level of M06-2X/6-31G(d).

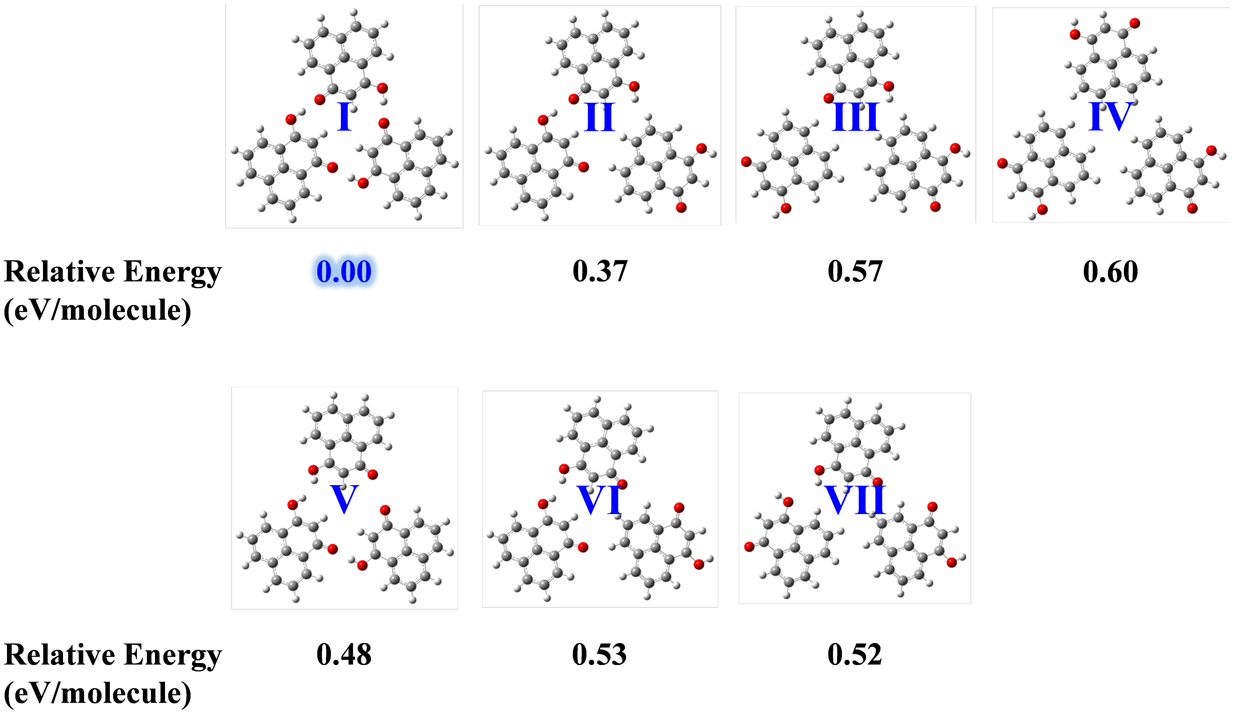


Fig. S5 BLYP-D3 optimized free trimers (**I~VII**) in CP2K and their relative energies calculated at the level of M06-2X/6-31G(d) in Gaussian.

In order to reveal the influence of the bottom layer of honeycomb-like bilayer and substrate on orientation choice of π−π stacked 3-HPLN molecules in the top layer, the periodic density functional theory (DFT) calculations are performed in the Vienna ab Initio Simulation Package (VASP 5.3)[8, 9] by using the Perdew-Burke-Ernzenhof (PBE)[10] form within the framework of generalized gradient approximation (GGA). The Grimme's correction (D2)[11] is also adopted to account for weak van der Waals (vdW) interactions among 3-HPLN molecules. The different periodic surface models in consideration of orientation-different 3-HPLN molecules in the linear chains of the top layer are built, and their optimized structures are shown in Fig. S6a. For the surface model (**I_{up}**), its top view is also present in insets. Because of the computational consume, the surface models (**I_{up}**, **I_{down}**, and **III)**, have three-layer Cu(111) substrate, and the surface models (**II** and **IV**) have one-layer Cu substrate. These surface models all have the more-than-20-Å vacuum layer. For geometry optimization of different surface models, the electron-ion interaction is described by the projector augmented wave (PAW) potentials[12, 13] with an energy cutoff of 500 eV. The Brillouin zones are sampled using a 3×3×1 k-point mesh in the Monkhorst-Pack scheme.[14] The total energy change is required to be less than 10^{-5} eV, and the magnitude of the largest force acting on the atoms should be less than 0.05 eV/Å. For the direction perpendicular to the substrate, the dipole correction is added. In order to make their single-point energies comparable between orientation-different surface models, the new surface models are rebuilt in Fig. S6b. For the surface models (**I_{up}**, **I_{down}**, and **III**), they are rebuilt by enlarging their corresponding optimized unit cells (Fig. S6a) twice along *b* axis. For the surface models (**II** and **IV**), they are rebuilt by directly depositing 3-HPLN molecules on three-layer Cu(111) substrate. For the single-point energy calculations, the energy cutoff for electron-ion interaction becomes 600 eV and the convergence of the self-consistent field iteration is set to be less than 10^{-6} eV. As shown in Fig. S6b, upon attachment of the linear chains to a flat-lying bottom layer on Cu(111) surface, the configuration (**III**) has the lowest energy with the O- and OH-containing ends of all dimers pointing towards the bottom layer. In addition, in each dimer, 3-HPLN molecules are aligned so that carbonyl of one molecule is in juxtaposition with hydroxyl of the other molecule.

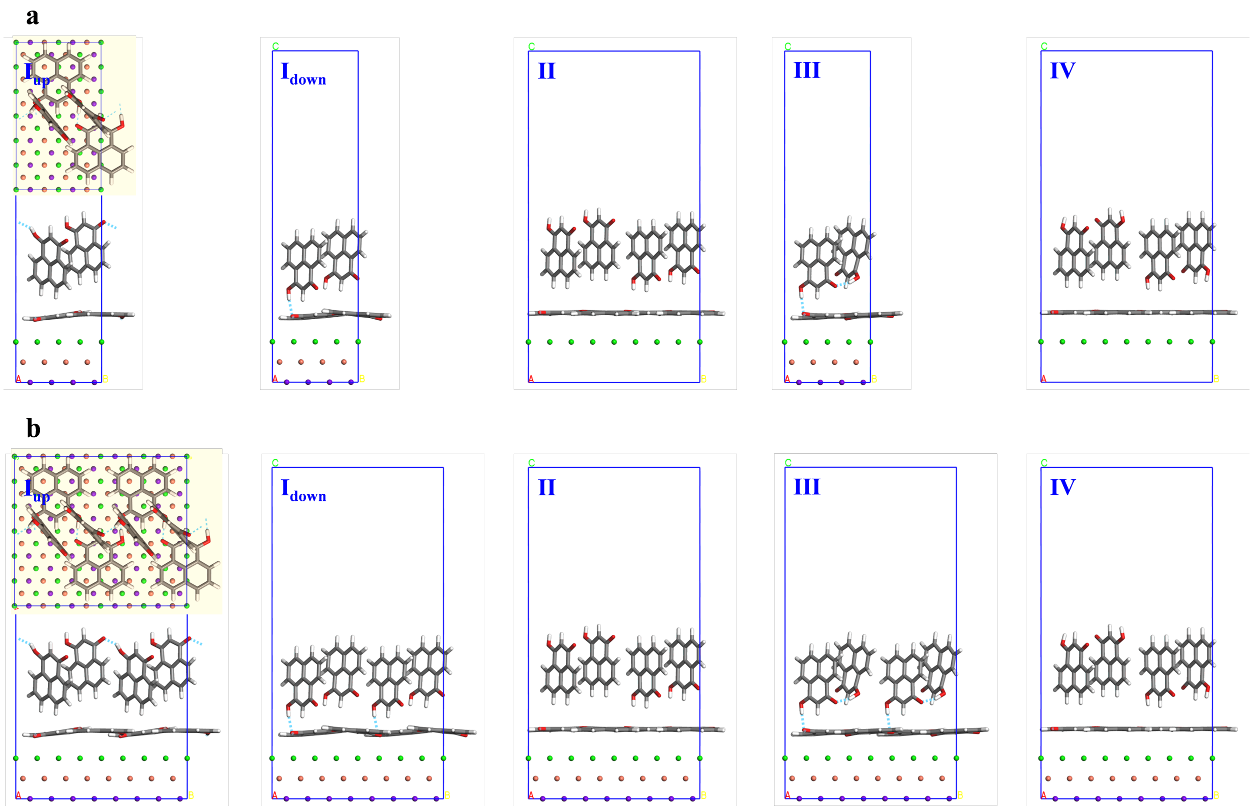


Fig. S6 (a) Optimized structures of different surface models (**I_{up}**, **I_{down}**, **II**, **III**, and **IV**) with orientation-different 3-HPLN molecules in the 2nd layer based on PBE-D2 calculations. (b) Rebuilt surface models (**I_{up}**, **I_{down}**, **II**, **III**, and **IV**) for single-point energy calculations. For two surface models **I_{up}**, their top views are also present in insets respectively. The hydrogen bonds are highlighted by the sky-blue dashed line. Cu atoms in three different layers are indicated in three different colors.

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