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Supporting Information

2*H*-Tetrakis(3,5-di-*tert*-butyl)phenylporphyrin on a Cu(110) Surface: Room-Temperature Self-Metalation and Surface-Reconstruction-Facilitated Self-Assembly

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The appearance of TTBPP molecules is usually dominated by the peripheral tert-butyl groups such that four of them form a rectangle. The geometric shape of the rectangle (perimeter and aspect ratio of long to short side) can be used to determine the intramolecular conformation of the molecules based on the geometric considerations shown in Fig. S1.

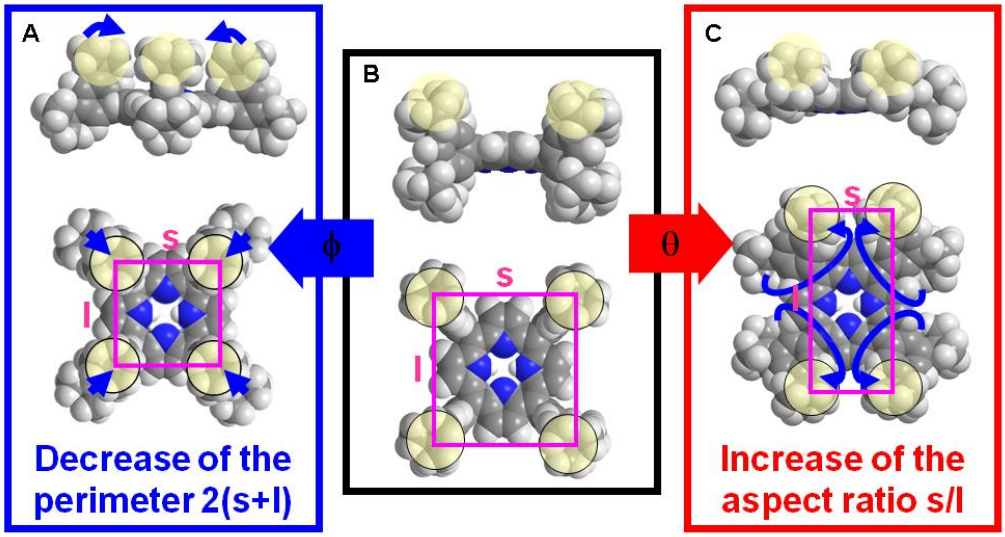

Figure S1. Scheme on how the intramolecular conformation 2HTTBPP (given by the twist angle θ and tilt angle ϕ of the peripheral phenyl groups) determines the geometry of a rectangle (purple) formed by four tert-butyl groups (yellow circles). (**B**) side view and top view of a space filling model of 2HTTBPP with the phenyl group oriented perpendicular to the plane of the poprhyrin macrocycle (rotation angle θ = 90°, tilt angle ϕ = 0°). In (**C**), a possible molecular deformation is shown, with the phenyl groups rotated out of the porphyrin macrocycle plane (rotation angle θ > 0°). Thereby, the quadratic arrangment of the upper tert-butyl groups (indicated by a yellow circle) changes to a rectangle, which effectively changes the aspect ratio, s/l, of the short and long sides of the rectangle. In (**A**), the phenyl groups are tilted upwards out of the plane of the poprhyrin macrocycle (tilt angle ϕ > 0°). Thereby, the distance between the upper tert-butyl groups is reduced, resulting in a decreased perimeter, 2(s+l), of the corresponing rectangle. By

comparing the experimental values s_{exp} and l_{exp} extracted from high-resolution STM images with the values s_{mod} and l_{mod} measured from corresponding space filling models (CambridgeSoft, Chem3D Pro 12.0.2.1076) an estimation of twist and tilt angle is possible.

Table S1. Overview of the intramolecular geometrical values for 2HTTBPP and CuTTBPP on Cu(110) and Cu(110)-(2×1)O at different temperatures, as extracted from STM data; θ: the rotation angle of the phenyl groups, φ: the corresponding tilt angle.

Substrate	Molecule	Temperature	θ (°)	φ (°)
Cu(110)	2HTTBPP	200 K	10 ± 5	30 ± 5
	CuTTBPP		90 ± 5°	45 ± 5°
		RT	0± 5°	0± 5°
Cu(110)-(2×1)O			20/10 ± 5	30 ± 5

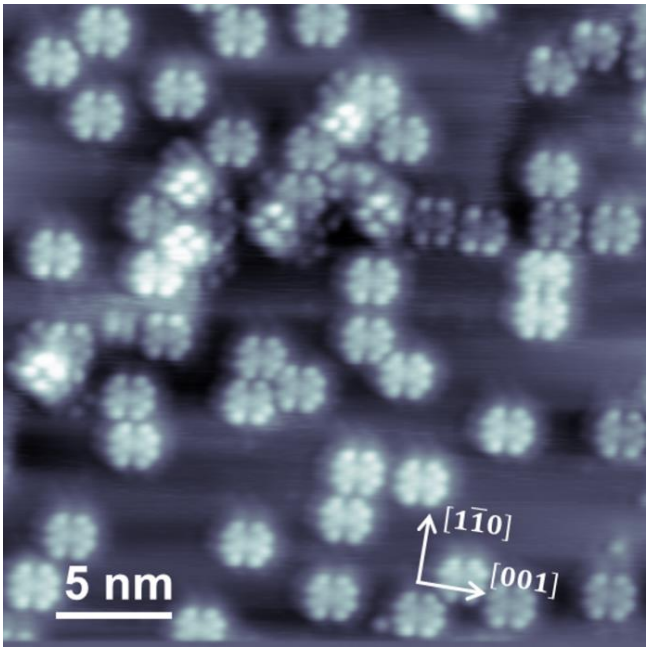

Figure S2. Constant current STM image measured at RT after depositing 2HTTBPP on Cu(110) surface at 180 K (U = -1.0 V, I = 25 pA).

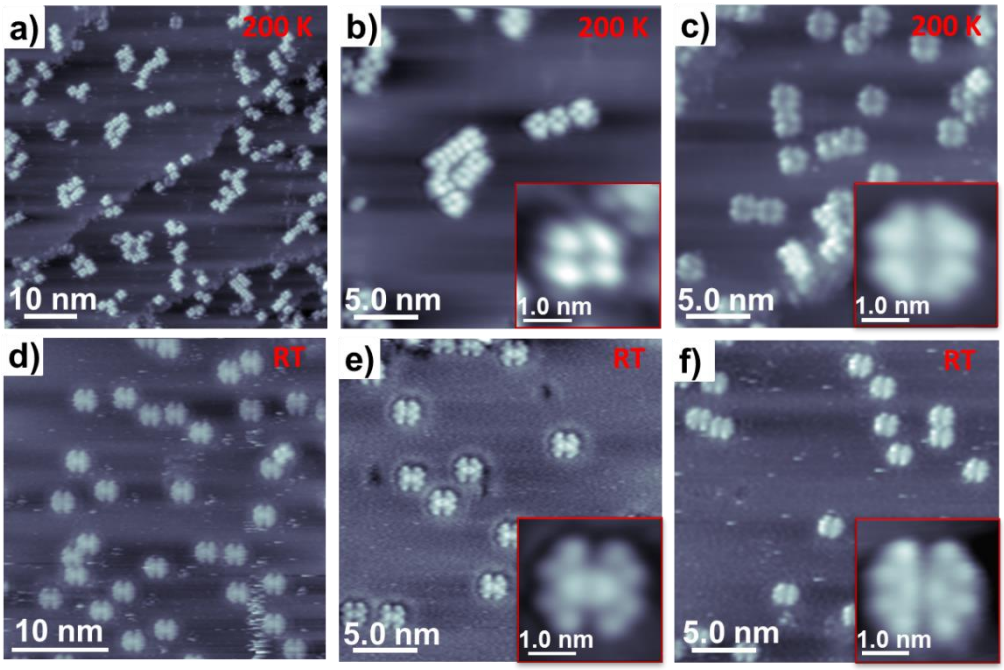

Figure S3. (a) and (b) Constant current STM images measured at 200 K after depositing CuTTBPP on Cu(110) at 180 K (U = -1.0 V, I = 29 pA). (c) Constant current STM image measured at 200 K after depositing 2HTTBPP on Cu(110) at 180 K (U = -1.1 V, I = 30 pA). (d) and (e) Constant current STM images of CuTTBPP molecules on Cu(110) with deposition and measurement temperatures both at RT (U = -1.2 V, I = 30 pA). (f) Constant current STM image of 2HTTBPP on Cu(110) with deposition and measurement temperatures both at RT (U = -1.3 V, I = 30 pA). The inserts are the molecularly resolved images of single molecule. For CuTTBPP on Cu(110) measured at 200 K, each molecule has an intramolecular conformation with $\theta = 90 \pm 5°$ and $\varphi = 45 \pm 5°$.

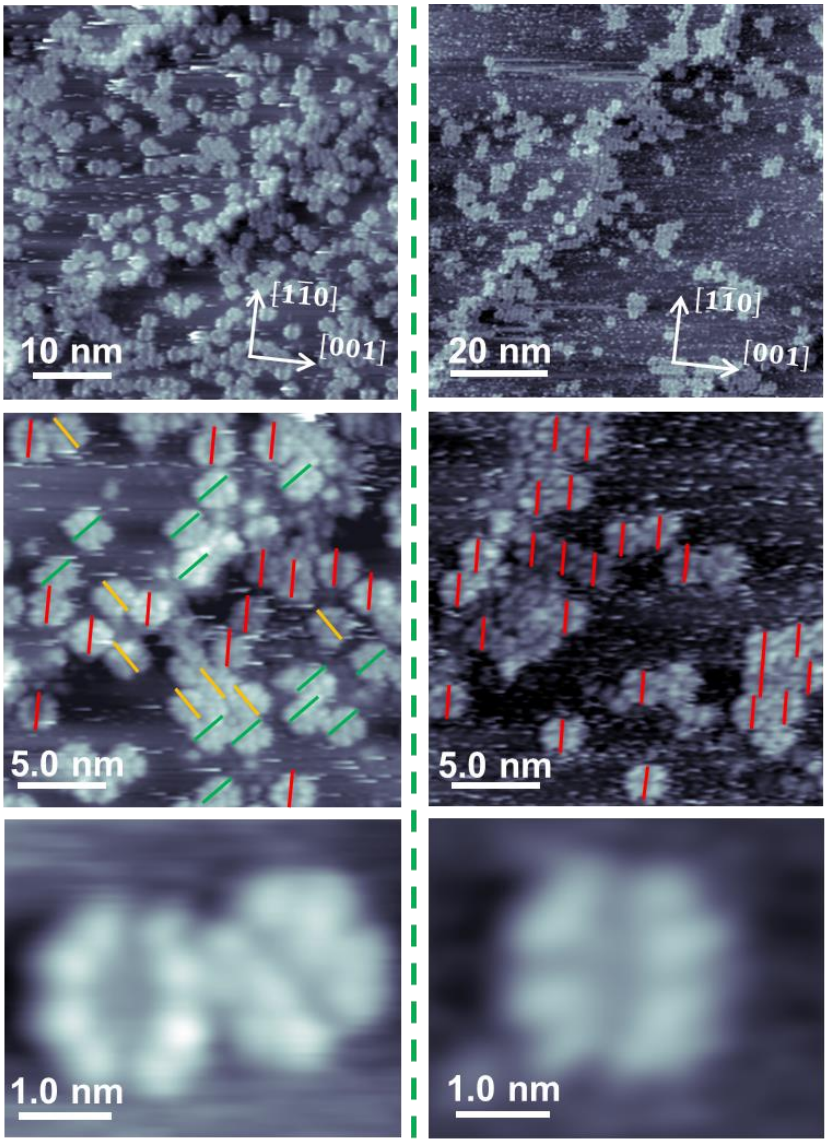

Figure S4. Constant current STM images of 2HTTBPP (left column; U = -1.0 V, I = 30 pA) and CuTTBPP (right column; U = +1.0 V, I = 30 pA) on Cu(110)-(2×1)O surface with a deposition temperature of 180 K and a measurement temperature of 200 K. Note that the orientations of individual molecules are marked with lines in different colors. For 2HTTBPP molecules, they are randomly distributed on the surface with three different molecular orientations with the substrate. In contrast, the CuTTBPP molecules prefer to form small clusters along the step edges with only one molecular orientation with the substrate.