Electronic Supplementary Material (ESI) for ChemComm.

# Massive conformational changes during thermally induced self-metalation of 2H-Tetrakis-(3,5-di-tert-butyl)-phenylporphyrin on Cu(111)

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# Supporting Information

### Determination of the internal conformation of 2HTTBPP on Cu(111)

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. S2. A detailed description of the estimation procedure can be found in[1].

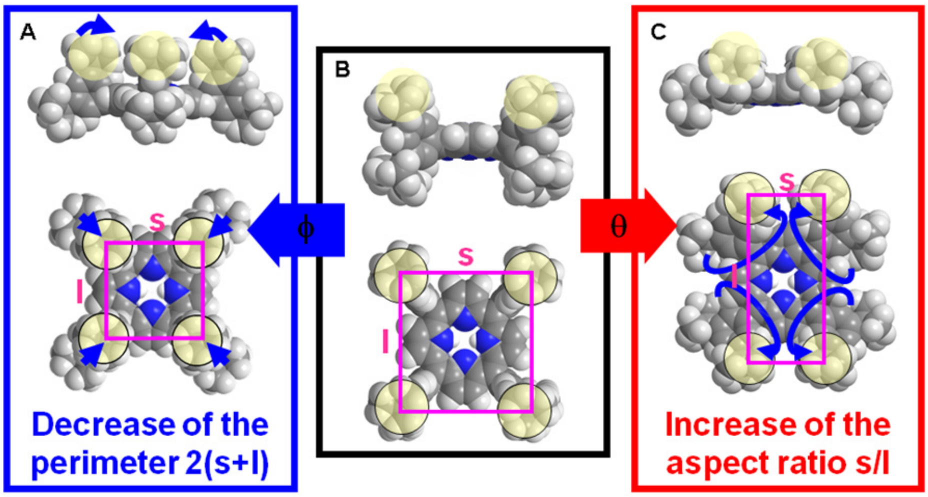

**Figure S1:** Scheme on how the intramolecular conformation 2HTTBPP (given by the twist angle θ and tilt angle ϕ of the peripheral phenyl groups) determines the geometry of a rectangle (purple) formed by four tert-butyl groups (yellow circles). (**B**) side view and top view of a space filling model of 2HTTBPP with the phenyl group oriented perpendicular to the plane of the poprhyrin macrocycle (twist angle $\theta = 90°$, tilt angle $\phi = 0°$). In (**C**), a possible molecular deformation is shown, with the phenyl groups rotated out of the porphyrin macrocycle plane (twist angle $\theta > 0°$). 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 $\phi > 0°$). 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.

### Reference

(1) Buchner, F.; Comanici, K.; Jux, N.; Steinrück, H.-P.; Marbach, H. *J. Phys. Chem. C* **2007**, *111*, 13531.

## Bias voltage dependence of STM of 2HTTBPP and CuTTBPP on Cu(111)

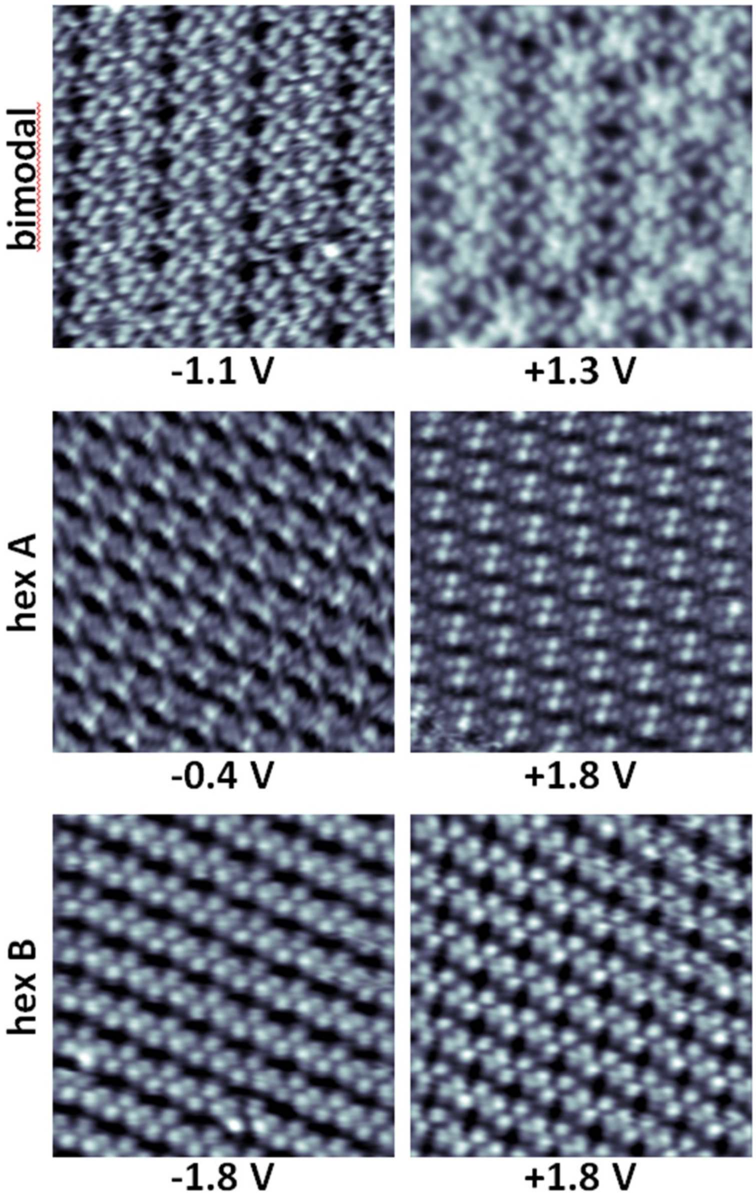

**Figure S2:** Set of images of bimodal, *hexA* and *hexB* domains at positive and negative bias. The appearance of the molecules is due to their upper tert-butyl groups and thus to a large extent independent of the bias voltage. All images were acquired in constant current mode with a tunneling current of 30 pA.

## C 1s XP spectra

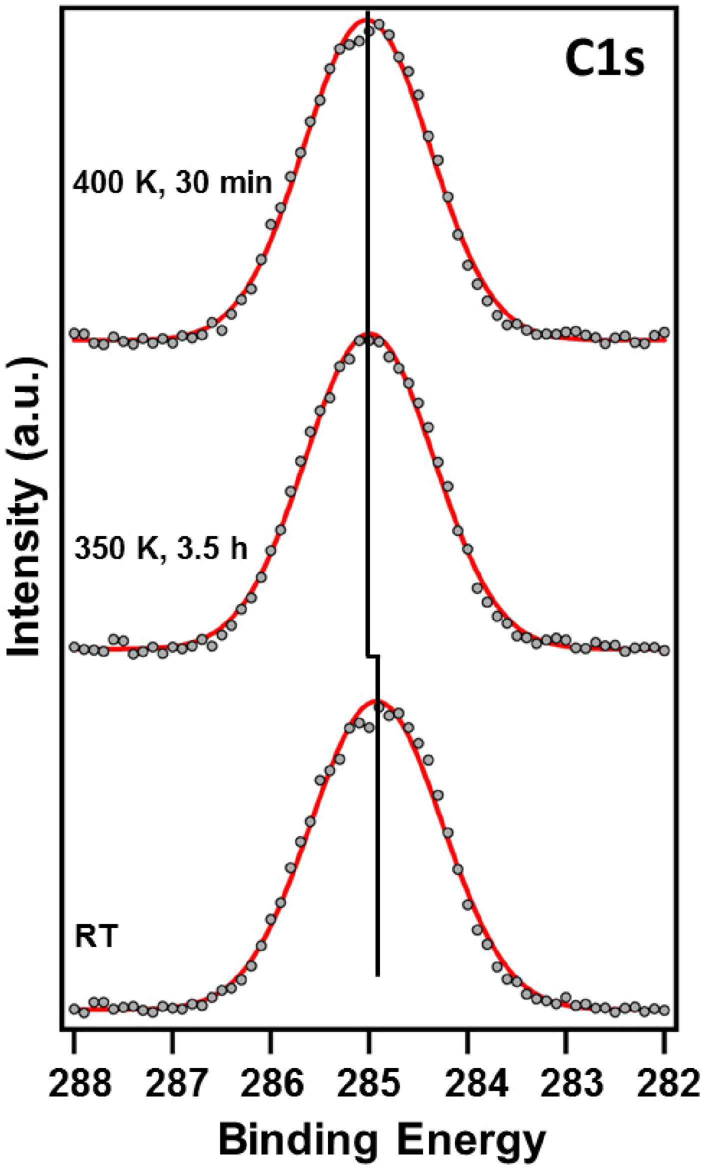

**Figure S3:** C 1s XP spectra of 2HTTBPP on Cu(111) for the as prepared layer (bottom) and after the indicated heat treatments; the topmost spectrum corresponds to almost fully metalated CuTTBPP (81 %, see Fig. 2). Upon metalation of 2HTTBPP, the C 1s peak shifts slightly by 0.1 eV to higher binding energies, in agreement with a reduced final state screening as the molecule moves away from the surface. The shift is accompanied by a slight narrowing of the FWHM from 1.57 to 1.51 eV.