Supporting Information

Visualizing Tilted Binding and Precession of Diatomic NO Adsorbed to Co-porphyrin on Au(111) using Scanning Tunneling Microscopy

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Identification of CoTPP and H$_2$TPP molecules on Au(111)

The two different molecules randomly occupied sites in the square grids of molecular islands. The height of each molecule is influenced by the herringbone corrugation of Au(111). Both molecules have four bright dots at the locations of the phenyl groups which have dihedral rotations about the C-C bonds connecting the phenyls to macrocycles. In Fig. S1, we provide the STM images of mixed CoTPP and H$_2$TPP on Au(111) obtained after NO exposure, without and with grid lines and molecular marks to help identify individual TPP molecules. In Fig. S2, we provide more enlarged images of Fig. 1(a).

**Figure S1.** The STM images of mixed CoTPP and H$_2$TPP on Au(111) obtained after NO exposure, without (Left - the same as in Fig.1(b)) and with (right) grid lines and molecular marks to help identify individual TPP molecules. CoTPP, H$_2$TPP, and NO-CoTPP are denoted by red, blue, and green marks, respectively.
Figure S2. The STM images of mixed CoTPP and H₂TPP on Au(111) obtained after NO exposure. Lower four images are the enlarged images of four regions of upper one denoted with dotted squares. In all images, bright ring structures are visible.
Spontaneous NO bindings at CoTPP molecules

Before NO exposures, CoTPP and H₂TPP molecules are mixed in the two dimensional islands on Au(111) surfaces (Fig. S3). They showed three-lobed structures for CoTPP and dark depression at the center for H₂TPP in typical filled state STM images. After NO exposures at around 300 L, some of CoTPP molecules change their appearances in STM images from original three-lobed structures to bright ring structures. Most of CoTPP molecules change to NO-CoTPP after 900 L NO exposures. NO molecules do not have any influence to H₂TPP molecules.

Figure S3. Series STM images before (left) and after exposures 300 L (middle) and 900 L (right). The tunneling conditions for all images are $I_T = 0.1$ nA and $V_S = -0.5$ eV

Double tip induced STM image for NO-CoTPP

The state of our tip sometimes changes. Figure S3 shows examples of STM images which were obtained with double tip or asymmetric tip. The image obtained with double-tip effect still shows double ring structures similar to the number 8. The image obtained with asymmetric-tip effect shows the shape of paired beans or alphabet C. In all cases, the centers of the NO-CoTPP showed depression.
**Figure S4.** STM images of NO-CoTPP with (a) Double-tip and (b) and (c) asymmetric-tip effects. (Insets) Individual NO-CoTPP was zoomed-in. Regardless of double or asymmetric tip effects, the center of NO-CoTPP show depression. The tunneling conditions are $I_T = 0.1 \, \text{nA}$ and $V_S = -0.5 \, \text{eV}$ for (a), (b) and $V_S = -0.6 \, \text{eV}$ for (c).

**Thermal desorption mass spectroscopy of NO-CoTPP**

The adsorbed NO molecules could be desorbed by thermal annealing. We performed mass spectroscopy measurements for NO-CoTPP. While keeping the temperature of a NO-CoTPP sample at 500 K for 200 s, we measured the partial pressures of N, O, NO, and NO$_2$ using a quadrupole residual gas analyzer (Stanford Research RGA 200), as shown in Fig. S5. A clear signature of NO molecules is visible, whereas no trace of the other molecules is detected. From this measurement, it was confirmed that the adsorbed species was NO molecule, not others.

**Full Scale Fourier transform infra-red spectroscopy of NO-CoTPP**

A full scale Fourier transform infra-red spectroscopy (FTIR) that spans from 500 to 4000 cm$^{-1}$ is shown in Fig. S6. Two additional vibration modes 1680 and 1283 cm$^{-1}$ are visible at the spectrum obtained from CoTPP with NO exposure.
Figure S5. Mass spectroscopy measurement results. The mass spectroscopy signals were measured from NO-CoTPP while it was kept at 500 K. The dashed line indicates the beginning of annealing. The graphs were shifted vertically for clarity.
Figure S6. Fourier transform infra-red spectroscopy results obtained from CoTPP with and without NO exposure.