

# Supplementary Information: Understanding Enantioselective Interactions by Pulling Apart Molecular Rotor Complexes

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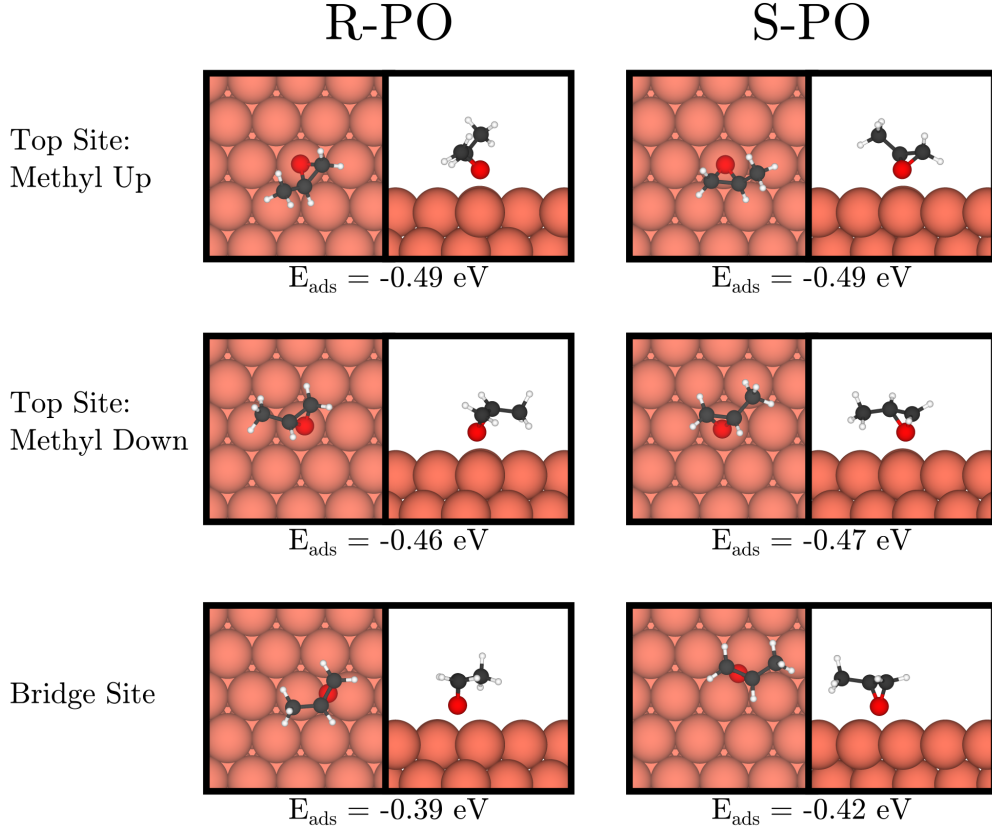
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# 1. Adsorption Sites of Propylene Oxide on Cu(111)



**Figure S1.** Possible adsorption sites on Cu(111) for both enantiomers of propylene oxide (PO) and their respective adsorption energies.

We tested all possible adsorption sites for propylene oxide (PO) on the Cu(111) surface prior to performing the calculations shown in the main text, Figure S1. PO binds to the surface through a dative bond with its lone electron pairs and can bind to a top site or a bridge site. The adsorption energy for each configuration was obtained by computing:

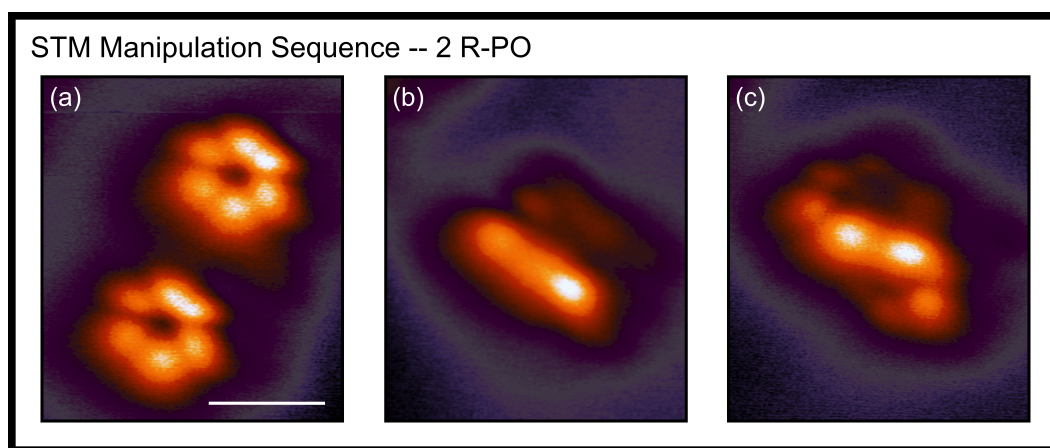
$$E_{\text{ads}} = E(\text{PO/Cu(111)}) - E(\text{PO(g)}) - E(\text{Cu(111)}) \quad (\text{S1})$$

where  $E(\text{PO/Cu(111)})$  is the total energy of an isolated PO adsorbed on the Cu(111) surface within a  $p(6 \times 6)$  unit cell,  $E(\text{PO(g)})$  the total energy of a PO in the gas phase and  $E(\text{Cu(111)})$  is the total energy of a clean  $p(6 \times 6)$  unit cell. Both types of hollow sites (HCP and FCC)



were tested, but the molecule moved to a top site or bridge site during the optimization indicating that adsorption over these sites is not favorable. When adsorbed on a top site, the molecule has two possible orientations. In the “methyl up” position, the vector representing the methyl group is pointed out of the plane parallel to the surface. Conversely, the “methyl down” position has the vector representing the methyl group pointed into the plane parallel to the surface. Interestingly, the oxygen’s surface induced chirality in the “up” position is identical to the intrinsic to the molecular chirality while it is opposite in the “down” position. Although the energetic differences between these two methyl orientations are small, there is a slight preference for the surface-induced and molecular chirality to be the same when PO is adsorbed on this surface.

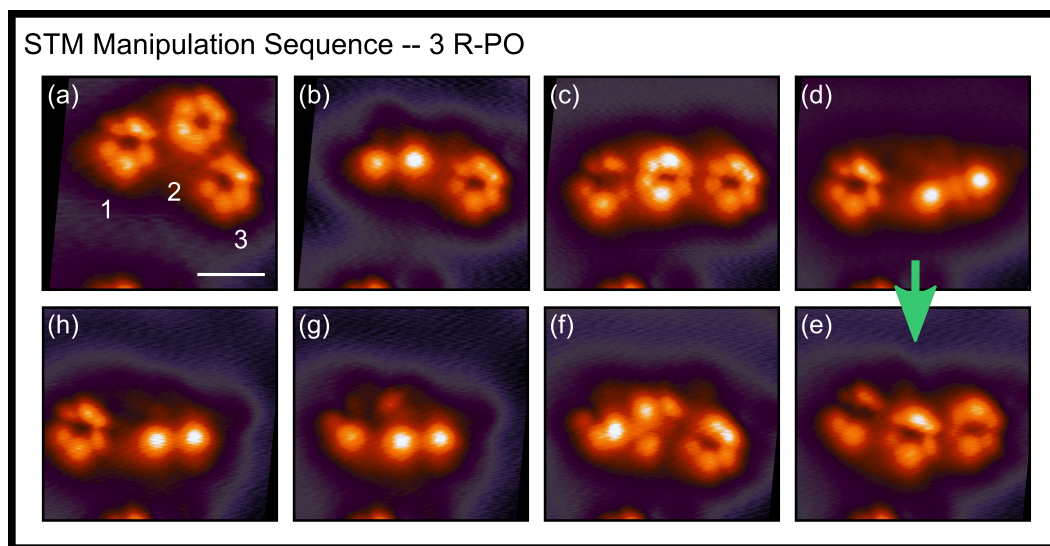
## 2. Molecular Manipulation of Propylene Oxide on Cu(111)



**Figure S2.** Manipulation of two PO molecules (a) brought together in an unstable configuration (b), which results in perturbed rotation (c). Scale Bar = 1 nm. 10-20 mV, 4 pA (scanning); 4 mV, 4.5 nA (manipulation).

While lone PO molecules rotate, the PO-PO interaction stops the rotation of both molecules when in close proximity, a reversible process in which STM manipulation is used to move PO together as well as apart, as demonstrated in Figure S2. When two PO molecules are forced to interact the resulting structure is not necessarily stable, as was found directly

after the imaging of (b), where the perturbation of rotational lobes seen in (c) suggests that the molecules would preferably rotate. Most PO molecules are dispersed across the surface, with annealing (80 K) increasing this dispersion, suggesting weak repulsive forces between PO molecules, but these forces are too small to be quantified within the error of our DFT calculations.

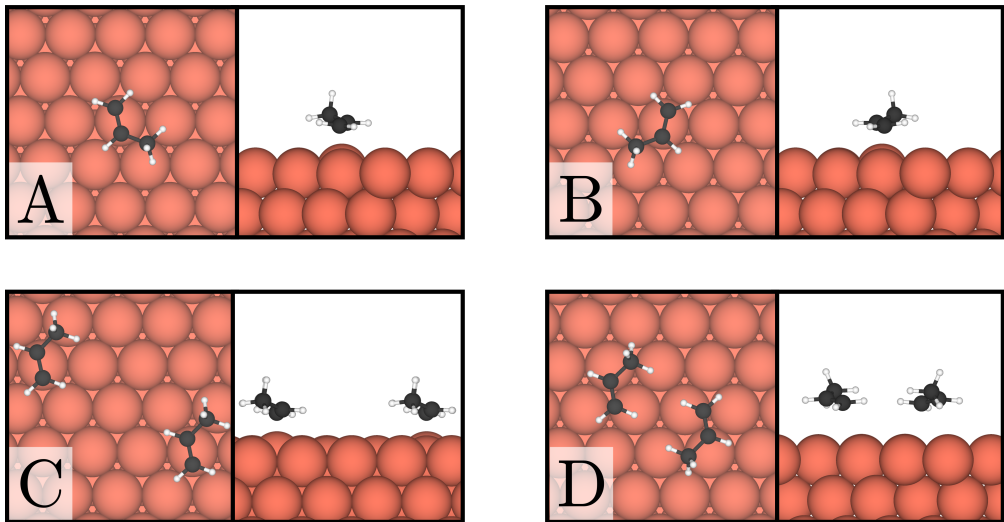


**Figure S3.** (a) Three distinct rotating PO molecules are numbered from left to right. (b) Molecule 2 is brought close to molecule 1, stopping the rotation of both molecules. (c) Molecule 1 is pulled away; all molecules rotate. (d) Molecule 2 is pushed towards molecule 3, stopping the rotation of both molecules. BELOW: (e) Molecule 2 is moved away from molecule 3; all molecules rotate. (f) Molecule 2 is moved to molecule 1 resulting in perturbed rotation of both molecules. (g) Molecule 3 is moved toward the other molecules; no molecules are rotating. (h) Molecule 1 is moved away from the cluster, allowing its rotation. Scale bar = 1 nm. 25 mV, 10 pA (scanning); 4 mV, 4.5 nA (manipulation).

Besides pushing the molecules together, it is possible to pull the interacting molecules apart. PO molecules can be reproducibly pushed together and pulled apart with the STM tip. In Figure S3, three R-PO molecules are manipulated into a row where small manipulations of the molecules causes adjacent molecules to either interact and stop rotating or rotate without interference. This can be seen in the sequence of images in Figure S3 where PO molecules are sterically hindering each other's rotation. Of note is panel (g) where the three PO molecules are all stationary.

### 3. Adsorption of Propene on Cu(111)

The adsorption of propene was tested in a variety of sites on the Cu(111) surface as well. Particularly, we examined whether the molecule adsorbed to two Cu sites, where the electrons in its double bond form two sigma bonds to the surface, or one Cu site, where the overlap between the  $\pi$ -orbital electrons and surface is responsible for the binding. Although propene prefers adsorption through forming two sigma bonds on Pt(111),<sup>1</sup> adsorption on Cu(111) only occurs through  $\pi$ -orbital overlap with the surface. From there, we proceeded to adsorb the propene molecule in this configuration over bridge, hollow, and top sites of the Cu(111) surface. All of these calculations optimized propene to be adsorbed over a top site. Therefore, the adsorption site presented in the main text is the only possible site for propene to adsorb at based on our calculations.



**Figure S4.** Adsorption of (A) R'-Py and (B) S'-Py on Cu(111). The adsorption energy for both chiralities is  $-0.4$  eV. A repulsive interaction energy of  $0.21$  eV is obtained when computing the total energy difference between two neighboring Py molecules as shown in (D) with respect to two well-separated molecules as shown in (C).

The adsorption geometry where the C=C double bond is approximately parallel to the surface with the methyl angled away is similar to what is calculated for propene chemisorbed on Pt(111)<sup>2</sup> and propyne on Cu(111);<sup>3,4</sup> albeit with 2-fold bridging and bridging across 3-fold hollow adsorption sites preferred. Atop adsorption was observed and calculated for Py on

Cu(211) where the C=C bond is bound on top of a copper atom in the step edge, with the methyl group following the geometry of the nearest terrace.<sup>5</sup> Free rotation of the propene molecule is not predicted or seen in these studies, but rotation and chiral inversion could be induced on Cu(211). For the Py molecule on Cu(111), the carbon-copper bond distances for each carbon in the double bond vary slightly (2.35 Å and 2.48 Å). As expected on a less reactive surface, these values are larger than the 2.12 Å and 2.14 Å distances for Py calculated on Pt(111).<sup>2</sup> The corresponding binding energy for Py on Cu(111) is  $-0.4$  eV on a top site using Equation S1 ( $-0.5 \pm 0.1$  eV on the Pt(111) bridge site<sup>2</sup>). We also obtained an repulsive interaction energy between two Py molecules of 0.21 eV, by calculating the total energy difference between a configuration with two neighboring Py molecules (shown Figure S4 (D)) and a configuration with two well-separated Py molecules (shown Figure S4 (C)).

#### 4. 3-fold Symmetry of Propene Rotation

Simple rotation of the Py molecule on top of the Cu atom would result in a six-lobed structure with the methyl group imaging brightly;<sup>5,6</sup> however, unless the methyl group images differently depending on its geometry or the molecule’s surface-bound chirality, we cannot account for the alternating brightness of the lobes, Figure 2 (d). As compared to PO adsorption on Cu(111), the binding energy of Py is 0.1 eV weaker; however the distance between the methyl group and the surface is shorter by  $\sim 1$  Å, but DFT calculations have not revealed significant adsorption height differences for the methyl group of Py during rotation, ruling out a geometric explanation for the alternating brightness. Manipulation with the STM tip rules out the possibility of this lobed structure containing more than one Py molecule (demonstrated in Figure 2 (e)). With two surface-bound enantiomers of propene, two structures for each adsorption site must be found on the achiral surface in equal concentrations. We see only two structures seemingly commensurate with the underlying symmetry of the lattice; there is no mirrored rotational offset as is seen with PO, only a contrast in the brightness of the lobes to distinguish orientations. Most translations of Py

molecules across the surface, as demonstrated in Figure 2 (e), do not change the orientation of the contrast in the brightness of the lobes. As such, these two structures relate directly to the two surface-bound enantiomers of Py, but are unattributed to a specific chirality experimentally. With calculations determining small probability differences between the six rotational positions of the propene molecules, the surface-bound chirality can be defined to a specific lobe-brightness pattern.

## 5. Propene Translations

Experiments were performed at 5 K, where as deposited PO and Py were manipulated with the STM tip. Over 115 images, the positions and orientations of 102 Py molecules were tabulated: noting translation, complex formation/separation and rotation. Of 124 translations, most preserve Py orientation, there is only a 3.3 % chance of translation flipping the molecule to the other surface-bound chirality when voltages are below 200 mV. Non-perturbative scanning conditions of 60 mV, 40 pA were used with manipulation conditions of 150-200 mV and 1.7-3 nA. The tip conditions used were found to ‘pull’ the Py molecules.

## 6. Molecular Manipulations

STM examination of this PO and Py system allows for direct manipulation of the molecular adsorbates. Previously, Ernst *et al.*, has used STM manipulation to manually separate helicene dimers to analyze their chiral composition.<sup>7,8</sup> This decomplexation required modification and reconditioning of the tip for manipulation vs. imaging;<sup>7</sup> as opposed to this study which does not require such tip preparation. The dimer formation energy of PO/Py is a fifth of what is seen for the heterochiral heptahelicene dimers<sup>7</sup> formed by attractive van der Waals interactions.

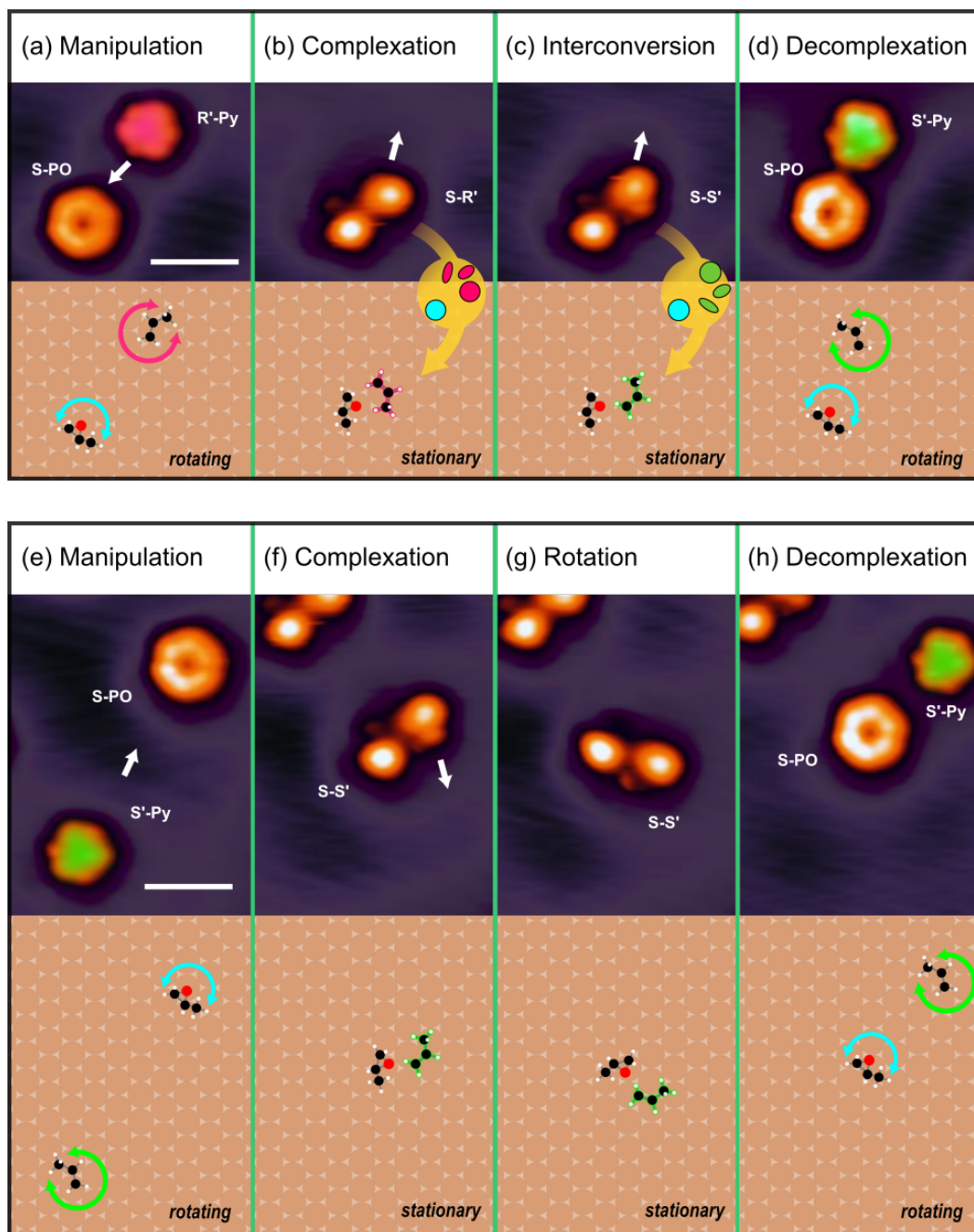
As deposited on the surface at 5 K, translation of the Py molecules near to the rotating PO molecules with the STM tip results in the formation of chemisorbed dimer complexes;

Figure S5 (a) and (e). The two complexes in Figure S5 (b) and (f) are visually different in the orientation of the larger lobe corresponding to the Py molecule in the complex (diastereomers); the S-PO molecule is in the same exact orientation in both complexes. It is relatively easy to rotate the complexes from one high-symmetry direction to another while preserving the internal complex structure; a  $60^\circ$  rotation occurs for the complex seen in Figure S5 (g). It is possible to interconvert between the complexation structures, such that the orientation of the propene molecule switches; the complex in Figure S5 (c) has converted to the other complexation configuration. Decomplexation occurs when the Py molecule is removed from the complex leaving PO minimally disturbed. Rotation, inversion and separation of complexes were achieved at the same manipulation conditions in Figure S5 with differing probabilities of occurring; an exploratory series of manipulations concluded that complex rotations occur more easily than separation with inversion of the Py in-complex rare. Chirality is preserved in translation of Py and complexation with PO, but can be changed after complexation. In manual decomplexation with the STM tip, it is possible that separation of the molecules occurs simultaneously with Py inversion in some instances as there were seemingly no preservation of Py orientation in complex separation. We make no statistical claim as to the preservation of chirality in decomplexation due to more perturbative manipulation conditions being required to separate the molecules from a complex. However, in almost all instances of complex formation from molecules of known chirality, complexes of expected structure were formed.

## 7. Interaction Energy between 1:1 Py:PO Complexes

The DFT-based interaction energy between PO and Py was obtained from:

$$\Delta E_{\text{int,POPY}} = E_{\text{ads,POPy}} - E_{\text{ads,Py}} - E_{\text{ads,PO}} \quad (\text{S2})$$



**Figure S5.** These two sequences of 5 K STM images (1 nm scale bar; 60 mV, 40 pA) demonstrate STM tip manipulations (200 mV, 1.7 nA) to directly form and separate chiral complexes. Arrows demonstrate and highlight subsequent manipulations. (a) S-PO combines with R'-Py (highlighted pink) to form (b) the SR' complex. (c) The internal orientation of Py molecule changes by STM tip manipulation: interconversion to SS'. (d) The complex is then pulled apart revealing rotating Py with S'-surface bound chirality (highlighted green). The cartoons illustrate the change in rotation of the molecules and their orientations upon complexation. (e) S-PO and S'-Py combine to form (f) the SS' complex. (g) Rotation of this complex maintains internal propene chirality. (h) Decomplexation reveals the subsequently unchanged chiralities of the PO and Py molecules.

where  $E_{\text{ads,Py}}$  and  $E_{\text{ads,PO}}$  are obtained from Equation S1 and

$$E_{\text{ads,POPy}} = E(\text{POPy}/\text{Cu}(111)) - E(\text{Cu}(111)) - E(\text{PO}(\text{g})) - E(\text{Py}(\text{g})) \quad (\text{S3})$$

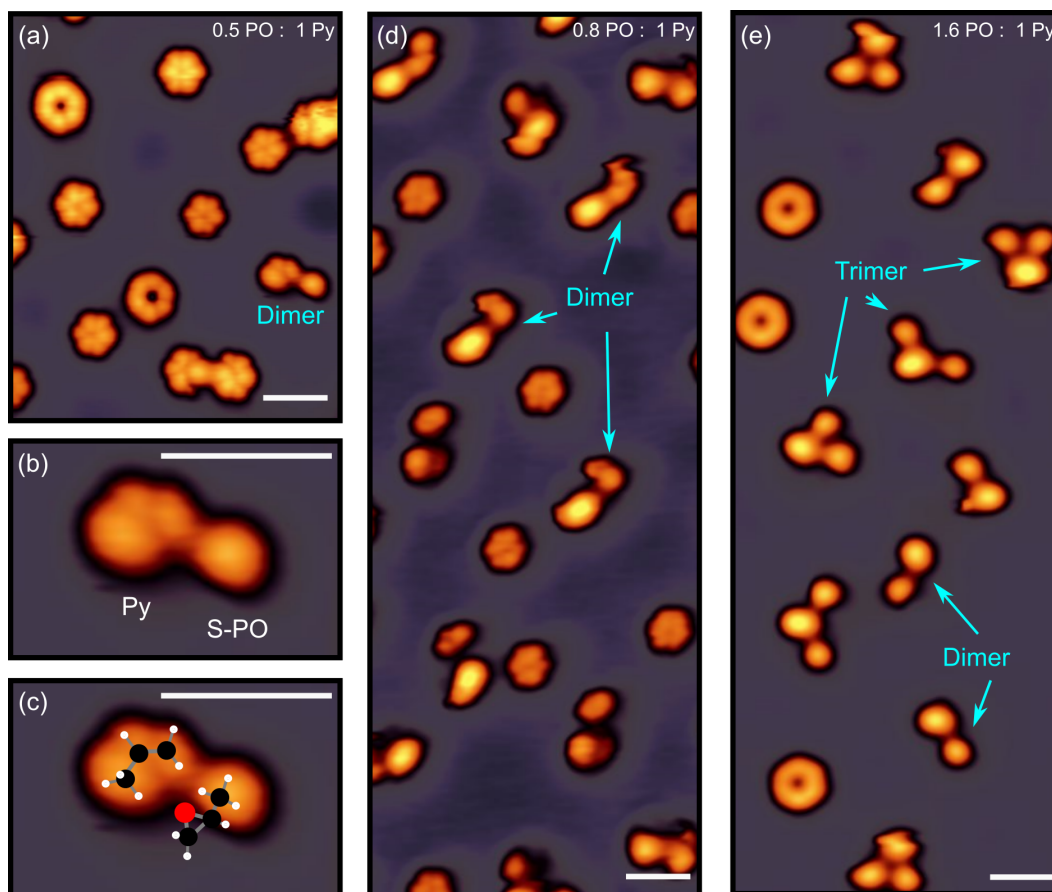
where  $E(\text{POPy}/\text{Cu}(111))$  is the total energy of the POPy complex that is adsorbed on a Cu(111) surface as shown in Figure 5 of the main text,  $E(\text{PO}(\text{g}))$  is the total energy of a PO molecule in the gas phase,  $E(\text{Py}(\text{g}))$  is the total energy of a Py molecule in the gas phase and  $E(\text{Cu}(111))$  is the total energy of a clean Cu(111) surface.

## 8. Forming Exclusively 1:1 Py:PO Complexes

At low surface coverage of PO and Py, properties of the molecules can be utilized to form one to one dimers between PO and Py. At 5 K we know PO and Py individually rotate, but the PO:Py interaction produces a non-rotating complex. These complexes can be formed by incorporating a small amount of energy into the system, such as by annealing to 40 K, or by direct manipulation with the STM tip. Figure S6 exhibits the subtlety of PO and Py complexation at low coverage and temperature. Forming 1:1 dimers is contingent on the correct ratio of PO to Py being on the surface; the amount of PO on the surface must be less than the amount of Py inhibiting the formation of larger complexes with 2 or more PO, Figure S6 (e). When the PO:Py ratio is 0.8:1, 1:1 dimers are almost exclusively formed with few rotating Py between, Figure S6 (d). Though ultimately dependent on STM tip shape and scanning conditions, intermolecular resolution of 1:1 complexes can be achieved, Figure S6 (b). Py images as three lobes, while PO images predominately image as one bright lobe in the complex. These brightest features correspond to the methyl groups of the two molecules, Figure S6 (c). The calculated adsorption configurations of the individual molecules in the complex are nearly identical to the isolated molecules.

The coverage seen in Figure S6 (e) was not conducive to statistical analysis. In this experiment, more PO on the surface resulted in complexes containing more than one PO





**Figure S6.** (a) STM image at PO : Py ratio of 0.5:1 (no anneal). Scale bar = 1 nm. (b) Close up of dimer complex in (a). The three left lobes correspond to the Py molecule; the right lobe is S-PO. (c) Cartoon of PO and Py molecules based on a DFT model overlaid on the STM image. (d) STM image at a PO:Py ratio of 0.8:1 after annealing to 40 K where predominately 1:1 complexes form with Py between. (e) STM image at a PO:Py ratio of 1.6:1 after annealing to 80 K. Larger complexes containing 2 or more PO with one Py molecule can form at this ratio; like the trimer complexes labeled here. (a - e) STM images have slightly different tip states and scanning conditions such that molecules and complexes look similar, but not identical. Intermolecular resolution can be achieved, but secondary features, particularly in PO, are faint and tip dependent.

for which the molecule orientations were too complicated to determine. For a PO:Py ratio of 1.6:1, 30 % of the structures formed were trimers, tetramers, or larger combinations; this greatly increases the error of any enantiospecific analysis. The 0.8:1 PO:Py coverage, Figure S6 (d), is used in Table 1 of the manuscript. This coverage resulted in <1 % formation of trimers on the surface, with a small number of rotating Py and a large number of 1:1 PO:Py complexes. Of the 1:1 complexes, only 4 % were unidentified. The statistics in Table 1 come from 8 distinct STM images in which a total of 621 complexes were seen.

## References

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