Supporting Information for the paper:

Complex Molecules on a Flat Metal Surface: Large Distortions Induced by Chemisorption Can Make Physisorption Energetically More Favorable

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Supporting Information includes:

1) Supporting figures and text
2) Computational Method
3) Relaxed coordinates attached at the end of this file
4) A movie for the MD simulation: separate file 'sm-MD_300K.mpg'

1) Supporting figures and text

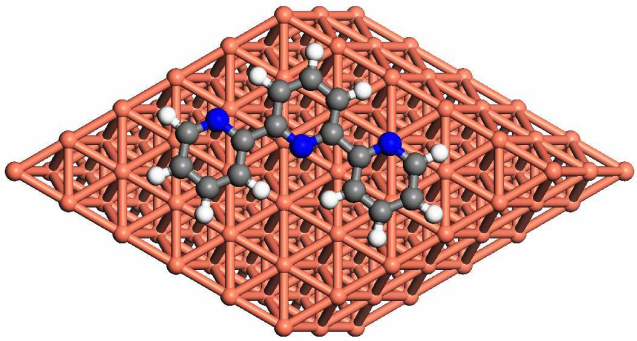

Figure S1. The simulation model: a single terpy molecule on Cu(111) in a (6x6) super-cell (here showing the most stable physisorption geometry with terpy in the trans-trans conformation).

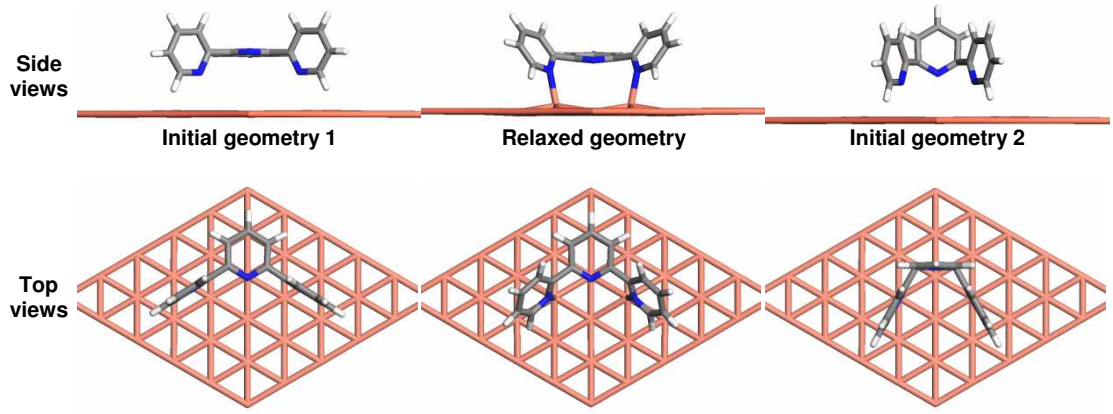

Figure S2. Middle panels: optimized chemisorption geometry for cis-cis terpy with two N-Cu bonds formed. Left and right panels: two very different initial geometries that relax to the same final geometry shown in the middle panels. The Cu atoms bonding to N are lifted up by 0.3 Å; the Cu atoms nearest to H are lowered by 0.09 Å due to the H-Cu surface repulsion.

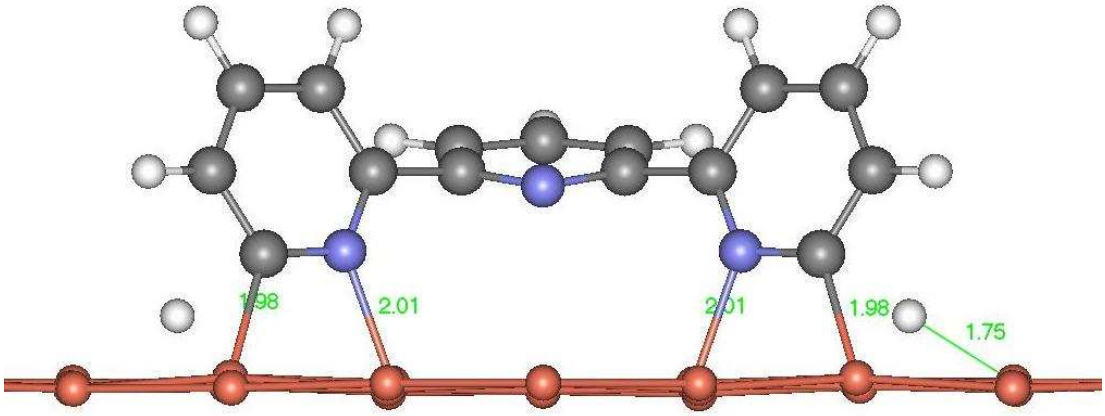

Figure S3. Double H dissociative adsorption of terpy on Cu(111), showing Cu-N, Cu-C and Cu-H bond lengths in Å.

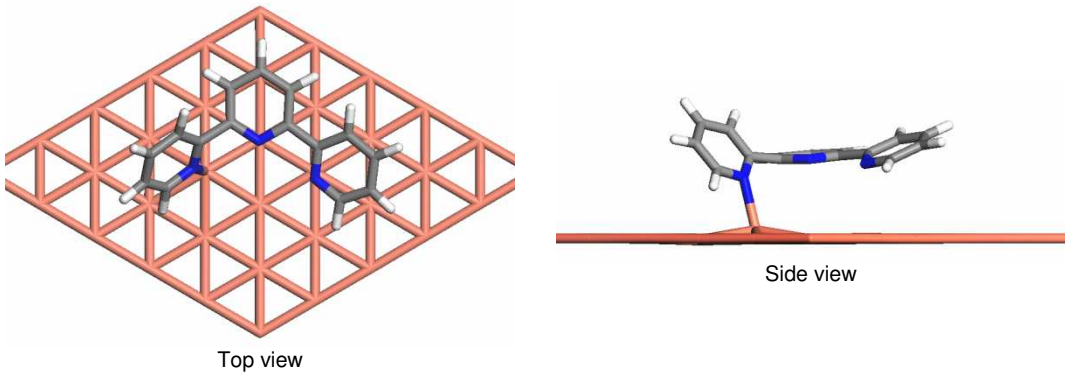

Figure S4. Another relaxed chemisorption geometry with only one N-Cu bond, obtained from three initial geometries with the different rings rotated by 40° from the cis-cis coplanar geometry (see text for details of the three initial geometries).

In order to obtain the energetically most favorable configurations discussed above, we have considered many adsorption geometries. For non-parallel adsorption, we also considered adsorption configurations with the outer rings rotated by 40° and 120° from the cis-cis coplanar geometry. After relaxation, initial adsorption geometries with the 120° rotation become the trans-trans parallel adsorption geometry. For the 40° rotation geometries, after relaxation, three different initial structures lead to the same final adsorption geometry in which one N atom bonds to the Cu surface (Figure S4). The three initial geometries are, starting from the cis-cis coplanar geometry: the two outer rings rotated by 40° and -40°, resp.; the two outer rings rotated by 40° and 40°, resp.; and all the three rings rotated by 40° (a negative angle means rotation away from the Cu surface).

2) Computational Method

In the current study, using total-energy calculations (with and without Van der Waals corrections) we illustrate such competition between chemisorption and physisorption for the adsorption of the terpy molecule on a Cu(111) surface. Most of our calculations are performed using the Vienna *ab initio* simulation package (VASP) [1] with the PBE density functional [2]. For the correction to the adsorption energies with Van der Waals (VdW) interactions, the VdW density functional (VdW-DF) [3,4] as implemented in the grid-based real-space code GPAW [5] is adopted. Both VASP and GPAW are implementations of the projector augmented wave (PAW) method of Blöchl [6,7], which is an all-electron full-potential method within the frozen core approximation. The simulation model contains a single terpy on Cu(111) in a (6x6) supercell, as shown in Figure S1 [8]. The nearest H-H distance between periodic repeats of terpy molecules is larger than 5 Å, so there is practically no inter-molecular interaction. We use four Cu layers to simulate the Cu(111) surface, which has been proved sufficient for our study [9-11]. For all possible adsorption geometries, the whole molecule and the top two Cu layers are relaxed via a conjugate gradient optimization procedure until the maximum force on all the atoms is smaller than 0.04 eV/Å.

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3) Relaxed Coordinates: coordinates and supercell for chemisorption

SuperCell: Cu(111) p(6x6), slab model with VASP; Coordinates are given in Angstrom units

15.3358799999999995	0.0000000000000000	0.0000000000000000
-7.6679399999999998	13.2812616699999992	0.0000000000000000
0.0000000000000000	0.0000000000000000	22.0000000000000000

Coordinates (173 atoms, one terpy molecule on four Cu layers):

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C	3.902782126000000	4.382093306000000	13.637211077000000
C	4.567613098000000	5.609979383000000	13.491460310000001
C	2.572406406000000	6.776638478000000	13.492275960000001
C	1.828388312000000	5.595321643000000	13.638223345000000
C	1.948287106000000	8.116009420999999	13.647986088000000
C	6.041401328000000	5.722395464000000	13.644358532000000
C	6.627279821000000	5.153371339000000	14.783368407999999
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C	8.040708070999999	6.769059575000000	13.116649410999999
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C	1.145104907000000	10.680781334000001	14.260852094000001
C	0.765154595000000	9.643165399000001	15.108167554000000
C	1.181336051000000	8.350158222999999	14.797134253999999
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