

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

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ABSTRACT Normally, chemisorption will give stronger bonding to a surface than physisorption. However, if chemisorption induces large distortions of the adsorbate that are energetically costly, physisorption may become more favorable. We illustrate this second, anomalous behavior through theoretical modeling of a 2,2':6',2''-terpyridine (terpy) molecule on a flat metal surface. Terpy exhibits rich intra-molecular ring-ring interactions mainly due to the N heteroatoms; in addition, the single C-C bonds linking rings allow the molecule to be twisted into quite different conformations. On a Cu(111) surface, the flat physisorption of terpy is energetically more favorable than its strongest chemisorption in a twisted and strongly distorted conformation. We may expect in general that intra-molecular ring-ring interactions which control distortions like molecular twisting can become important in the adsorption of molecules with N-heterocyclic rings linked by twistable bonds.

Keywords Physisorption, chemisorption, DFT calculations, Van der Waals interactions

The interaction of molecules with metal surfaces ^{1,2} has attracted renewed interest in the context of molecular electronics and spintronics ³⁻⁵. This is due partly to the study of larger and especially more complex molecules on surfaces. In particular, molecules containing heterocycles (such as phenyl rings with one CH group replaced by N) connected by C-C single bonds, exhibit rich intra-molecular ring-ring interactions mainly due to the heteroatoms (e.g. N). In addition, for these molecules, torsional rotations around the single-bond axes are possible, so the molecule can be twisted relatively easily into several quite different conformations. For such molecules on surfaces, the twistable single bonds and the heteroatoms with electron lone pairs give rise to many possible adsorption geometries even on a flat metal surface such as Cu(111). These adsorption configurations include both physisorption of the rings parallel to the surface and chemisorption through heteroatom-metal bonds.

Of special interest is the question whether the physisorption and chemisorption energies can become comparable, or even reversed so that physisorption becomes more favorable than chemisorption⁶. Generally, we expect that when chemical bonds are formed after adsorption, chemisorption will be energetically more favorable than physisorption ^{7,8}, even though chemisorption will normally induce larger distortions in both the adsorbate and the substrate and hence cost some energy: this energetic argument actually serves to define chemisorption vs. physisorption. In this work, through the study of a single 2,2':6',2''-terpyridine molecule (terpy) adsorbed on a Cu(111) surface, we show that physisorption may even become energetically more stable than chemisorption: the strong distortions induced by chemisorption both in the molecule and in the substrate (especially torsion between neighboring aromatic rings within the molecule) can result in an energy cost that exceeds the energy gain from forming new chemical bonds, thus making untwisted flat physisorption more favorable. Another possibility is dissociative chemisorption, which may avoid large molecular distortions in the chemisorbed fragments and thus avoid the energetic cost of such distortions; this may be more favorable than either physisorption or chemisorption of the intact molecule, but may require overcoming a large dissociation barrier.

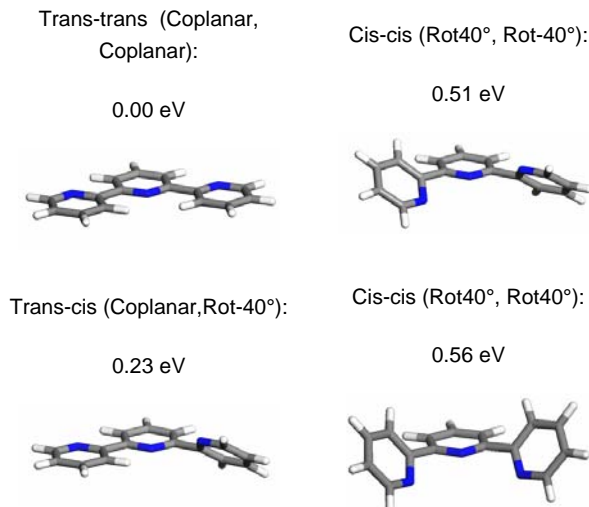


Figure 1. Possible nonequivalent geometries after relaxation of the free terpy molecule in the trans-trans, trans-cis, and cis-cis conformations and the energy for each geometry (C, N and H atoms are shown gray, blue and white, resp.). The perfectly planar trans-trans conformation is the most stable, and serves as the energy reference (energy zero) for the other metastable conformations. A positive/negative rotation angle means rotating an end ring counterclockwise/clockwise from the coplanar orientation as seen from the central ring; the first angle is for the left ring and the second angle is for the right ring.

This study originated in such a case: we have observed experimentally with scanning tunneling microscopy (STM) that molecules containing terpy groups on a Cu(111) surface adopt an intact flat-lying physisorbed geometry at low temperatures^{9,10}, while this same molecule should have the possibility to also bend itself into a distorted non-planar configuration that allows chemisorption through strong N-Cu bonds. We here explain this situation with total-energy calculations of the critical part of these molecules, terpy, composed of three C₅N rings connected by twistable C-C single bonds (Figure 1 shows our calculated stable and metastable conformations of free terpy). Our results show that physisorption of terpy in its most stable trans-trans phase through the delocalized π -like orbitals is energetically more favorable than its most stable chemisorption, which occurs in a distorted cis-cis phase through N-Cu σ -like localized bonds. The energy cost induced by distortion is analyzed in detail in terms of the intra-molecular (ring-ring) and molecule-substrate interactions of the free molecule and

of the adsorbed system, respectively. These interactions contain both attractive (mainly covalent) and repulsive (mainly Van der Waals) contributions.

The terpy molecule contains three pyridine units connected by twistable C-C single bonds. Pyridine itself is a heterocyclic molecule and the role of the heteroatom N on the adsorption of pyridine on the Cu(110) surface is reported in recent work¹¹. Terpy is used as a ligand in coordination chemistry through its nitrogen lone pair electrons. It may act as a monodentate, bidentate or terdentate ligand for metal atoms¹². Complexes containing two terpyridines, i.e. $[M(\text{terpy})_2]^{n+}$, are common. Besides metal atoms, terpy also tends to form complexes with other molecules like water. Many studies exist of terpy in coordination chemistry and of its potential use in molecular spintronics⁵, but no theoretical studies appear to exist of terpy adsorbed on metal surfaces, although there are some studies of pyridine and bipyridine on metal surfaces¹³⁻¹⁵. An experiment studied a close-packed terpy monolayer on Au(111)¹⁶: from the measured STM images, adsorption perpendicular to the surface (chemisorption) is proposed and attributed to inter-molecular interaction through π -stacking between molecules. No low-coverage studies appear to have been conducted. A single adsorbed terpy and a terpy incorporated in a close-packed adsorbed monolayer could have quite different adsorption geometries, owing to the relative weakness of the molecule-surface interaction¹⁴ and the inter-terpy interactions present only in the close-packed monolayer, as occurs with benzene, pyridine and other molecules on metal surfaces^{4,15}.

Before studying the possible adsorption geometries, we first need to find the possible conformations of a free terpy molecule. To this end, we tried many initial geometries in structure relaxations: these included terpy in the coplanar trans-trans conformation and terpy in non-planar geometries with the two outer rings rotated by 40°, 80°, 120° and 160° from the trans-trans coplanar conformation. After relaxation, we obtain four non-equivalent possible optimized geometries, shown in Figure 1. Note that for the relaxed non-planar geometries, the torsion angle of the outer ring(s) is always approximately 40° relative to the plane of the central ring. This may be compared with structures of free 2,2'-bipyridine where possible conformations are trans and twisted cis with a torsion angle also close to 40°¹³. Among

the four favored conformations of free terpy, the trans-trans coplanar geometry is the most stable for a free terpy molecule, while the cis-cis(Rot40°, Rot40°) twisted geometry is the least stable with an energy increase of 0.56 eV relative to the trans-trans geometry. It is known that this conformational preference is caused by steric repulsion between hydrogen atoms in adjacent rings, and *possibly* by electron–electron repulsion between the lone pairs in the nitrogen atoms ^{12,17}. To explore whether a repulsion between the N lone pair electrons does exist, we compare the projected density of states (PDOS), for terpy in trans-trans and in cis-cis coplanar geometries. The cis-cis coplanar geometry is adopted since the N-N distance becomes the nearest between N in the central ring and in the outer rings. The PDOS analysis of nitrogen revealed that a lone pair electron repulsion between N-N does indeed exist and is strong.

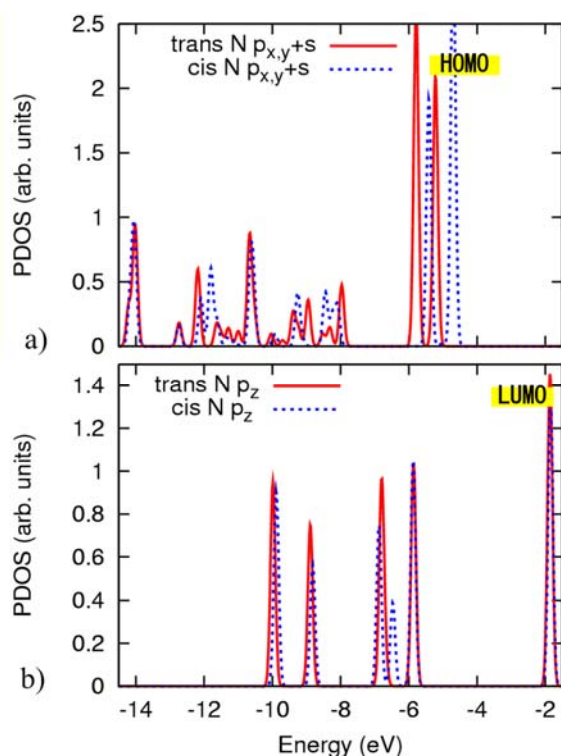


Figure 2. PDOS of N for terpy in trans-trans and cis-cis coplanar geometries -- the up-shift of HOMO in cis-cis geometry is due to the repulsion between N lone pairs: a) the sum of the PDOS of the $p_{x,y}$ and s orbitals in the molecular plane including HOMO; b) PDOS of the p_z orbital perpendicular to the molecular plane including LUMO.

The highest occupied molecular orbital (HOMO) of terpy represents the N lone pair distributed in the molecular plane (p_x and p_y) hybridizing with the s orbital^{14,15}. From the PDOS of nitrogen for terpy in the trans-trans and cis-cis conformations, shown in Figure 2(a), we learn that the HOMO energy level for cis-cis terpy is shifted upward by about 0.5 eV relative to that for trans-trans terpy. Since the HOMO (for cis-cis terpy) represents the anti-bonding combination of the N lone pairs, the upward shift of the HOMO in cis-cis geometry is a direct evidence for the N lone pair repulsion -- for cis-cis the repulsion between N shifts the HOMO up. Note that Figure 2 exhibits the PDOS of N in the central ring, while the PDOS of N in the outer rings gives the same conclusion: from trans-trans to cis-cis, the HOMO shifts up. Also note that the energy levels of terpy in the cis-cis conformation have been shifted a little according to the small difference in the vacuum level between trans-trans and cis-cis.

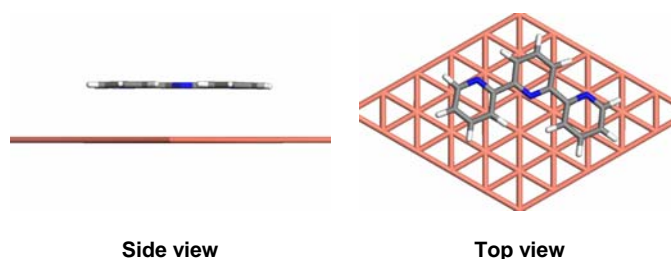


Figure 3. The most stable adsorption geometry of terpy on Cu(111): physisorption in trans-trans conformation with an adsorption height of about 3.5 Å. The side view (with only the outermost Cu layer) emphasizes the lack of significant relaxations of atomic positions; the molecule can almost freely move laterally across the substrate.

For pyridine on the Au(111) surface, the most stable adsorption geometry is the atop configuration in which pyridine stands perpendicularly to the surface with its nitrogen bonded to a single Au atom. The adsorption energy is small, about 0.3 to 0.5 eV (7.3 to 11 kcal mol⁻¹)¹⁴. For bi-pyridine on Au(111) both parallel and perpendicular adsorption may occur, depending on the charge state or bias voltage on the surface^{13,18}. For adsorbed terpy, we are aware of only one STM study: it concerns a close-packed monolayer of terpy on Au(111); a perpendicular adsorption geometry from the measured STM images is proposed and attributed to the inter-molecular interaction through π -stacking¹⁶. As discussed above, two kinds of adsorption are expected for a single terpy: a) perpendicular or tilted (non-parallel)

chemisorption through the N lone pair electrons and b) parallel physisorption through the delocalized π orbitals. Our calculations indicate that the energetically most favorable adsorption geometry is parallel physisorption with terpy in its most stable trans-trans conformation with an adsorption height of about 3.5 Å (Figure 3). In contrast, the most stable chemisorption geometry (Figure 4, bottom panels) is less favored than physisorption because chemisorption induced distortions in both the terpy molecule and the metal surface cost too much energy (as discussed in detail in the following). Table 1 lists adsorption energies for the most stable physisorption and chemisorption geometries. The adsorption energy, E_{ads} , is defined as the difference between the energy of the adsorbed molecule-metal system and the separated systems:

$$E_{ads} = E^{\text{terpy/Cu(111)}} - (E^{\text{Cu(111)}} + E^{\text{trans-trans terpy}}) \quad (1)$$

Thus, a negative adsorption energy corresponds to bonding. Note that the energy of terpy in the most stable trans-trans conformation is used as reference in the calculation of adsorption energies.

Table 1. Adsorption energies E_{ads} for the most stable parallel physisorption and non-parallel chemisorption configurations without VdW correction (DFT) and with VdW correction (DFT+VdW). The energy of terpy in the most stable trans-trans phase is used as reference. If we use the energy of cis-cis (Rot40°, Rot40°) terpy as reference for the tilted chemisorption (this geometry is closest to the chemisorption geometry), the adsorption energy is -0.60 eV rather than -0.04 eV (DFT result).

E_{ads}	DFT	DFT+VdW
Parallel physisorption (Figure 3)	-0.10 eV	-0.94 eV
Tilted chemisorption (Figure 4)	-0.04 eV	-0.42 eV

From the adsorption energy listed in Table 1, with or without VdW interaction, the parallel physisorption is always more stable than the tilted chemisorption. We further checked lateral movements of terpy across the substrate in the parallel adsorption with the VdW-DF: this gives only minor changes in the adsorption energy; the maximum variation in energy is only 0.02 eV. The size of the VdW energy correction (~0.8 eV) can be put in perspective by comparison with benzene (C₆H₆) adsorbed on Au(111), among other examples: this single aromatic ring physisorbed on the weakly

bonding Au(111) surface has a measured desorption energy of 0.64 eV vs 0.42 eV calculated with the RPBE-VdW-DF approximation⁴; terpy having three rather than one ring and being adsorbed on the more strongly bonding Cu(111) surface can thus well have a considerably stronger physisorption energy, as we calculate.

For non-parallel chemisorption, the most stable geometry after relaxation is the tilted adsorption with the two N atoms in the two outer rings bonding to two Cu surface atoms -- two N-Cu bonds are formed, as shown in the bottom panels of Figure 4. It is interesting to note that two initial geometries with 90° rotation in the rings, as shown in the top left and top right panels of Figure 4 (also see Supporting Information, Figure S2), after relaxation give the same final adsorption geometry as shown in the bottom panels. We can understand why chemisorption is not favored in this system by analyzing the chemisorption induced distortion and energy cost in both the substrate and the adsorbate. Regarding the substrate, the Cu atom bonding to N is pulled out of the surface plane by 0.3 Å due to a strong chemical bond, while the Cu atom nearest to H is pushed in by 0.09 Å due to the H-Cu surface repulsion (the height changes are measured relative to the average height of the other Cu atoms in the top layer). Regarding the adsorbate, chemisorption forces terpy into the unfavorable cis-cis geometry and induces an additional distortion from cis-cis (Rot40°, Rot40°). All the above distortions in both the Cu surface and the terpy molecule cost considerable energy. The energy increase for the Cu surface under distortion is 0.56 eV; the energy increase is even larger for the distorted cis-cis terpy, 0.77 eV, relative to terpy in the trans-trans geometry (0.21 eV relative to terpy in cis-cis (Rot40°, Rot40°)). The 0.77 eV energy increase comes from both the changing intra-molecular ring-ring interaction (trans-trans to cis-cis) and the additional bonding-induced distortion from the cis-cis conformation. We have performed a molecular dynamics simulation at 300K for the non-parallel chemisorption geometry, which also shows it to be unstable: after about 1200 femtoseconds (covered in 1200 1-femtosecond time steps, cf. movie in Supporting Information) one of the N-Cu bonds breaks and the affected ring rotates to the trans conformation seen in physisorption.

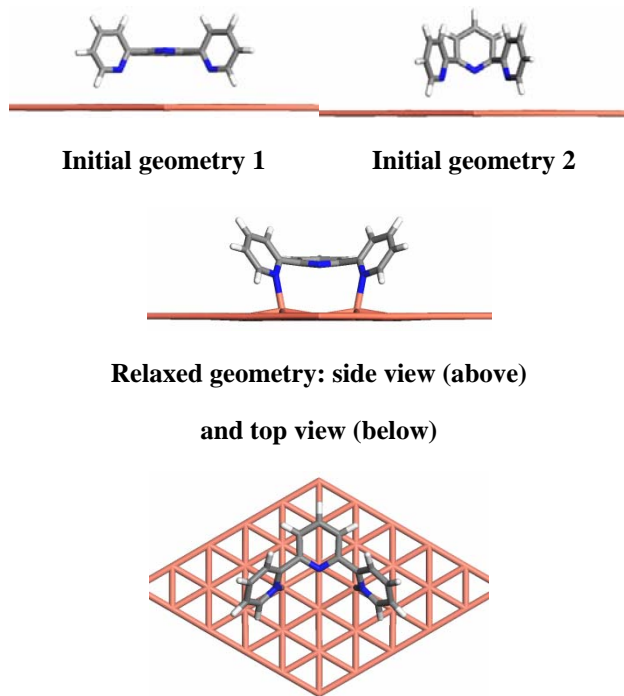


Figure 4. Bottom: side and top views of the optimized chemisorption geometry for cis-cis terpy with two N-Cu bonds formed. Top left and top right: two very different initial geometries that relax to the same final geometry shown at bottom. The Cu atoms bonding to N are lifted up by 0.3 Å; those nearest to H are lowered by 0.09 Å.

Further analysis reveals that the Cu-N bond is weakened due to the repulsion between H and the Cu metal surface. The relaxed geometry gives a Cu-N bond length of 2.17 Å, which is larger than the sum of the covalent radii of Cu and N by about 0.14 Å (Cu 1.32 Å, N 0.71 Å, adding to 2.03 Å). This elongation in the N-Cu bond is due to the H-Cu surface repulsion (the Cu atom nearest to H is lowered by 0.09 Å due to the H-Cu surface repulsion as discussed above). So the H-Cu repulsion stretches the Cu-N bond, or equivalently the Cu-N bond cannot take its preferred length because that would force H too close to Cu. To find the preferred N-Cu bond length without H-Cu repulsion, we relaxed the chemisorption geometry with the two lowest hydrogen atoms removed to the surface (double H dissociative adsorption, H on the surface and far from terpy, Supporting Information, Figure S3). This configuration gives a N-Cu bond length of 2.01 Å, which is 0.16 Å shorter than the N-Cu bond length with H-Cu repulsion, and close to the sum of covalent radii 2.03 Å. The relaxed C-Cu bond length is 1.98 Å, shorter than the relaxed N-Cu bond length of 2.01 Å, but we expect the C-Cu bond length to be

larger than the N-Cu bond length because the atomic radius of C is larger than for N and the electronegativity of N is larger -- this is further evidence for the relative weakness of N-Cu bonding.

For the most stable parallel physisorption geometry we also considered the effect of the VdW interaction on the adsorption height. The adsorption height with the PBE functional is 3.52 Å. With the VdW density functional, the adsorption height is reduced to 3.48 Å, a very small change for terpy on this relatively unreactive surface. The adsorption height and its small change between PBE and VdW functionals are in good agreement with recent studies of physisorption of molecules on closed-packed less-reactive (111) surfaces of metals^{4,19,20}. Interestingly, we further find that the adsorption height of the physisorption geometry is rather insensitive to the number of Cu layers: one Cu layer gives virtually the same adsorption height as 4 Cu layers (the height difference is less than 0.01 Å between 1 and 4 Cu layers with the PBE functional).

In order to obtain the energetically most favorable configurations discussed above, we have considered many other adsorption geometries (Supporting Information, Figure S4 and the related text). Another interesting finding from the geometry optimizations is that, for all chemisorption geometries, nitrogen can bind only with one Cu atom, i.e. N cannot bind with two (as in bridge sites) or three Cu atoms (as in hollow sites). This effect results from the fact that the axial direction of the σ lone pair electrons of N points toward a Cu atom, thus making a single N-Cu σ -like bond (as mentioned above, the HOMO orbital of pyridine is a σ -like orbital; see also the electronic structure analysis in the following).

We conclude here that, while pyridine can adsorb in a perpendicular geometry at the Au(111) surface, terpy is always tilted with respect to the surface normal of Cu(111) due to mainly two factors: 1) the molecule-substrate interactions favor tilting (N atoms of the molecule bind only with one surface Cu each; matching with the lattice constant of the metal is not favorable for perpendicular adsorption of the two outer rings) and 2) the intra-molecular ring-ring interaction prevents the two outer rings from rotating by 90° relative to the central ring (the central ring always tends to be parallel to the surface).

We have analyzed the energetic reasons why chemisorption can be less favorable than physisorption, based on strong chemisorption-induced geometrical distortions in both the terpy molecule and the Cu surface. A central component of this is the weakened N-Cu bond resulting from relatively strong Van der Waals Cu-H repulsion. We can gain further insight into the character of the weakened N-Cu bond by analyzing the electronic structure, particularly by considering the change of the charge density and of the PDOS of N before and after bonding to Cu. We define the differential charge density as the difference between the charge density in the whole system and in the sum of the separate adsorbate and substrate subsystems, which primarily reflects the charge redistribution due to N-Cu bonding. Figure 5 exhibits separately the electron accumulation and depletion for the most stable chemisorption geometry of this system.

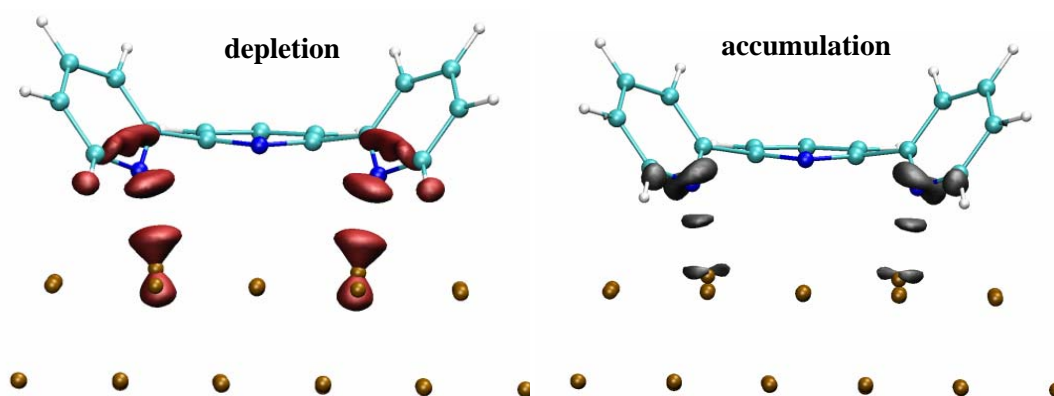


Figure 5. The differential charge density for the best chemisorption of terpy on Cu(111) (isovalue $0.025 \text{ e}/\text{\AA}^3$): the left panel shows electron depletion; the right panel shows electron accumulation.

Both electron accumulation and electron depletion are mainly confined to the binding N and Cu atoms, which indicates that the Cu(111)-terpy interaction is well localized. The differential charge density shows a minor net charge transfer from the substrate to the molecule, which is also confirmed by a Bader topological analysis of the charge density²¹ (the charge transfer is less than $0.1 |e|$ from the Bader analysis). The bond formation affects mainly the charge density on the N and Cu atoms

themselves, rather than in the middle of the N-Cu bond. This indicates that no strong covalent bond is formed between terpy and Cu¹⁴.

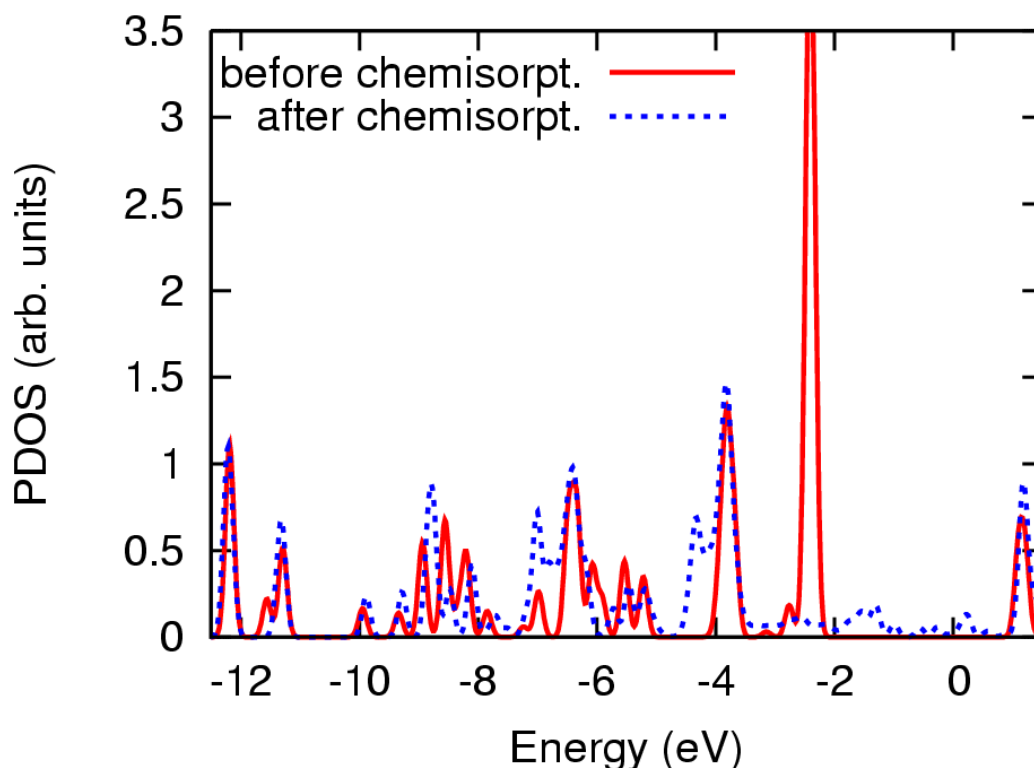


Figure 6. PDOS of the N atom before and after chemisorption of terpy to Cu(111) (Fermi energy set to zero).

Figure 6 shows the PDOS of the N atom before and after chemisorption of terpy to Cu. The most significant changes are the shape and position of the HOMO, which represents the N lone pair. The large peak at -2.4 eV corresponds to the HOMO and shifts to -4.3 eV. The strong interaction between adsorbate and substrate is apparent but this does not give rise to covalent bonding as the interacting orbitals are fully occupied¹⁴. Therefore, this interaction can only give rise to relatively weak, orientation-dependent, dispersive bonding¹⁴.

In summary, by theoretically studying the adsorption of a single terpy molecule on a Cu(111) surface in the low coverage limit, we find that strong distortions induced by chemisorption can cost so much energy that the net adsorption energy is actually smaller than that for physisorption in a different conformation of the molecule. The distortion-induced energy cost is analyzed in detail for terpy on

Cu(111) in terms of intra-molecular interactions (especially between rings) and molecule-substrate interactions. For terpy, the intra-molecular interactions in various conformations (cf. Figure 1) include: the repulsion between the lone pair electrons of N, the steric repulsion between H atoms in adjacent rings^{12,17}, and the conjugation between the central ring and the outer rings. Here the N-Cu bond at the surface is weakened substantially by strong H-Cu Van der Waals repulsion. The predominantly non-covalent Cu-N bonding character is obvious from the electronic structure analysis. The strong molecule-substrate interaction in the tilted cis-cis chemisorption conformation results in strong distortions of both the substrate and the molecule, and hence costs so much energy that it is less favored than physisorption. Based on our analysis, we expect that intra-molecular ring-ring interactions in adsorption situations will also be important for other molecules containing N-heterocyclic rings linked by twistable bonds.

SUPPORTING INFORMATION AVAILABLE: Supporting figures, text, computational method, coordinates, and a movie. These materials are available free of charge via the Internet at <http://pubs.cas.org>.

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