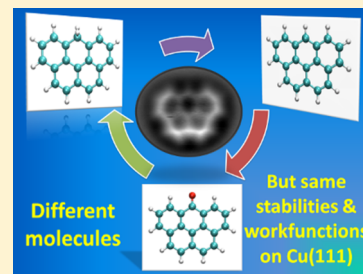


Identical Binding Energies and Work Functions for Distinct Adsorption Structures: Olympicenes on the Cu(111) Surface

Wei Liu,^{†,‡} Bruno Schuler,[§] Yong Xu,^{||,⊥,¶} Nikolaj Moll,[§] Gerhard Meyer,[§] Leo Gross,[§] and Alexandre Tkatchenko^{*,†,∇}[†]Nano Structural Materials Center, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, China[‡]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany[§]IBM Research, Zurich, 8803 Rüschlikon, Switzerland^{||}State Key Laboratory of Low Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, China[⊥]Collaborative Innovation Center of Quantum Matter, Beijing 100084, China[¶]RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan[∇]Physics and Materials Science Research Unit, University of Luxembourg, L-1511, Luxembourg

Supporting Information

ABSTRACT: Reliability is one of the major concerns and challenges in designing organic/inorganic interfaces for (opto)electronic applications. Even small structural differences for molecules on substrates can result in a significant variation in the interface functionality, due to the strong correlation between geometry, stability, and electronic structure. Here, we employed state-of-the-art first-principles calculations with van der Waals interactions, in combination with atomic force microscopy experiments, to explore the interaction mechanism for three structurally related olympicene molecules adsorbed on the Cu(111) surface. The substitution of a single atom in the olympicene molecule switches the nature of adsorption from predominantly physisorptive character [olympicene on Cu(111)], to an intermediate state [olympicene-derived ketone on Cu(111)], then to chemisorptive character [olympicene radical on Cu(111)]. Despite the remarkable difference in adsorption structures (by up to 0.9 Å in adsorption height) and different nature of bonding, the olympicene, its ketone, and its radical derivatives have essentially identical binding energies and work functions upon interaction with the metal substrate. Our findings suggest that the stability and work functions of molecular adsorbates could be rendered insensitive to their adsorption structures, which could be a useful property for (opto)electronic applications.



The interfaces between π -conjugated molecules and metal surfaces have high potential for applications in catalysis, light-emitting diodes, single-molecule junctions, molecular sensors and switches, and photovoltaics.^{1–6} The stability and performance of such hybrid interfaces are known to be critically influenced by their interface geometry. In particular, small changes in adsorption heights can lead to *qualitatively* different interfacial energy level alignment.^{7–9} For example, experiments clearly demonstrate that the lowest unoccupied molecular orbital (LUMO) of the PTCDA molecule is strongly involved in the formation of a bonding orbital with the Ag(111) surface, and charge transfer occurs from the metal to molecule upon adsorption.¹⁰ However, theoretical work has revealed that for the charge transfer process to occur, an accuracy of 0.1 Å is required in the calculation of the PTCDA/metal vertical adsorption height.^{11,12} Even small modification of the adsorbate, which can be caused by external perturbations or small distortions of the molecule, can strongly alter the interface electronic properties. In the search for reliable and robust functional interfaces, it is thus highly desirable to look

for systems whose stability and functions show a high degree of independence from their adsorption structures.

In this contribution, we demonstrate that these requirements are satisfied by recently synthesized olympicene molecule ($C_{19}H_{12}$), its radical ($C_{19}H_{11}$), and its ketone ($C_{19}H_{10}O$) derivatives adsorbed at the Cu(111) surface. Figure 1a shows the structures of these three olympicene molecules. The main difference between these three olympicene derivatives consists in the functional group bound to the central carbon ring. We employed density functional theory (DFT) calculations including van der Waals (vdW) interactions, in combination with noncontact atomic force microscopy (NC-AFM) experiments, to study the adsorption behaviors of the three structurally related molecules at the Cu(111) surface. Despite the fact that their chemical structure differs only by one atom, their adsorption geometries (adsorption height and tilt angle)

Received: February 1, 2016

Accepted: February 29, 2016

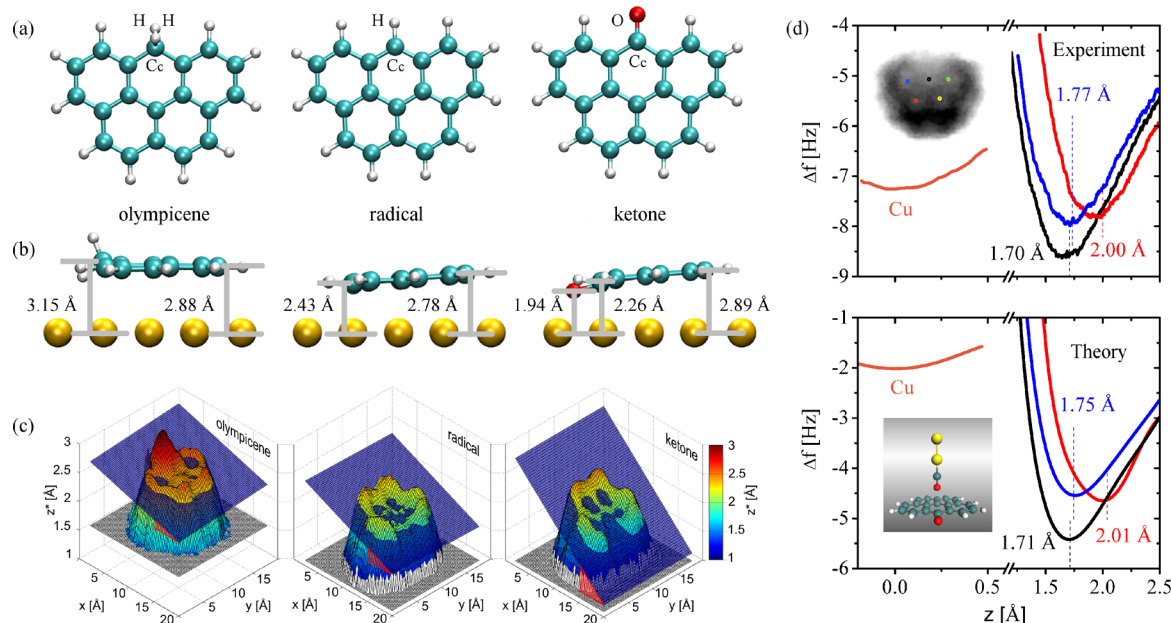


Figure 1. (a) Molecular structures of the olympicenes. (b) Adsorption geometries of the olympicenes/Cu(111) systems, all at the most stable hcp30° adsorption site. The indicated distances are referenced to the average positions of the relaxed topmost Cu atoms, obtained based on the PBE + vdW^{surf} optimized structures. (c) Map of the minima in the measured $\Delta f(z)$ spectra (z^*) with a fitted plane indicated in blue. The different tilting angles of the adsorbates (-2.6° , 2.5° , and 5.4° for the olympicene, radical, and ketone, respectively) are readily seen. (d) Frequency-shift curves for ketone on the Cu(111) surface from AFM experiments and DFT simulations. The inset in the top panel shows the respective positions of the spectra. The inset in the bottom panel shows the model for spectral calculations. Each computed frequency-shift curve was fitted to a polynomial. Note that we removed the Cu(111) surface but kept the atomic positions of the adsorbate fixed when calculating the frequency-shift curves above the molecules in order to reduce the computational time.

Table 1. Tilt angles θ in degrees, the binding energies E_b in electronvolts, and the work function changes $\Delta\phi$ in electronvolts for olympicenes/Cu(111) at the most stable hollow sites^a

molecule	site	θ^{DFT}	$\theta_{\text{CO}}^{\text{Exp}}$	$\theta_{\text{Xe}}^{\text{Exp}}$	E_b^{Total}	E_b^{PBE}	E_b^{vdW}	$\Delta\phi^{\text{Total}}$	$\Delta\phi^{\text{Bond}}$	$\Delta\phi^{\text{Mol}}$
olympicene	hcp30°	-0.4	-2.6	-1.1 ± 0.2	2.45	-0.39	2.84	0.85	0.81	0.04
	fcc30°	-0.3			2.42	-0.39	2.81	0.84	0.82	0.02
radical	hcp30°	3.4	2.5	3.3 ± 0.1	2.46	-0.78	3.24	0.71	0.63	0.08
	fcc30°	2.2			2.29	-0.84	3.13	0.71	0.67	0.04
ketone	hcp30°	5.9	5.4	4.9 ± 0.1	2.45	-0.74	3.19	0.74	0.58	0.16
	fcc30°	4.8			2.47	-0.60	3.07	0.70	0.47	0.23

^a $\theta_{\text{CO}}^{\text{Exp}}$ and $\theta_{\text{Xe}}^{\text{Exp}}$ denote the experimental tilt angles measured using AFM with CO- and Xe-decorated tips, respectively.¹³ $E_b = -(E_{\text{AdSys}} - E_{\text{Cu}} - E_{\text{Mol}})$, where the subscripts “AdSys”, “Cu”, and “Mol” denote the adsorption system, the clean Cu surface, and the free olympicene and ketone molecules, respectively. Because the free radical cannot stably exist we computed the radical/Cu(111) binding energy (or reaction enthalpy) as $E_b = -(E_{\text{AdSys}} + E_{\text{H/Cu}} - 2 \times E_{\text{Cu}} - E_{\text{Olym}})$, where the subscripts “H/Cu” and “Olym” indicate the H/Cu(111) system with H at the hollow site, and the intact olympicene molecule, respectively. The work function change $\Delta\phi^{\text{Total}}$ is divided into two components: one from the bond dipole $\Delta\phi^{\text{Bond}}$ and the other from the molecular dipole $\Delta\phi^{\text{Mol}}$. The calculated work function is 4.79 eV for the bare Cu(111), in good agreement with the experimental data (4.90 eV).¹⁴

are found to be qualitatively different on the metal substrate. Thus, we demonstrate that single-atom substitution can effectively control the bonding nature of large aromatic molecules on metal surfaces. Given the fact that the stability and electronic properties of hybrid systems are very sensitive to the adsorbate structure, one would expect significantly different binding energies and work functions for the three molecules. Remarkably, our theoretical calculations demonstrate that the complex interplay between weak and strong bonding can lead to identical binding energies and work functions.

We first explored the nature of bonding for the three molecules by calculating the geometric structure for olympicenes adsorbed at the Cu(111) surface. For all DFT calculations, we employed the recently developed DFT + vdW^{surf} method,¹⁵ coupled to the Perdew–Burke–Ernzerhof

(PBE) functional,¹⁶ which allows us to quantitatively treat both weakly and strongly adsorbed molecules on metal surfaces.^{17–22} For computational details, adsorption models, and convergence tests, refer to the [Methods](#) section. In order to obtain the most stable adsorption structure, we started by exploring the potential-energy surface for olympicenes on the Cu(111) surface. In analogy to benzene/Cu(111),²⁰ we relaxed a single olympicene molecule at the eight high-symmetry adsorption sites of the metal substrate. Note that the central carbon ring of olympicenes was taken as reference in the molecule, and for all starting geometries refer to the [Supporting Information](#). Consistent with observations from AFM experiments¹³ and vdW–DF calculations,²³ our PBE + vdW^{surf} results showed that the hollow adsorption structures are the most stable for all olympicenes on the Cu(111) surface, along with similar binding

energies at the hcp30° and fcc30° sites (c.f. Table 1). Their equilibrium structures at the hcp30° site are shown in Figure 1b, in which the carbon atom at the edge of the central ring, indicated as C_c, has very different adsorption heights *d*. More specifically, the olympicene has the largest C_c–Cu distance of *d* = 3.15 Å, because the saturated C–H₂ moiety hinders the interaction of the C_c atom with Cu surface. Dehydrogenation of olympicene by applying a voltage pulse of 1.6 V created a radical on the metal substrate.¹³ Due to high reactivity, the radical C_c adsorption height is significantly reduced by 0.72 Å compared to olympicene. The ketone is an intermediate in the synthesis of olympicene. For the ketone, the formation of the short O–Cu bond (1.94 Å in length) brings the C_c atom 0.89 Å closer toward the metal substrate than for the olympicene. Our PBE + vdW^{surf} structures justify the characteristically different contrast observed in the AFM images.¹³ In particular, the AFM images measured at the *same* set point also illustrate that the olympicene has a more intense contrast and thus is closer to the tip, that is, less closely adsorbed, than the radical.

In addition to the adsorption heights, the tilts of the molecular plane also clearly reflect the different bonding nature for the three molecules on Cu(111). In our calculations, the tilt angles were determined by a least-squares fitting of a plane to the carbon atoms in the optimized adsorption structures. As shown in Figure 1b, the olympicene adsorbs in a nearly flat-lying geometry on the Cu(111) surface, with a small tilt angle of –2.6°, whereas the ketone has the largest degree of tilt among the three molecules (5.4°). The computed sequence of tilt angles is consistent with the AFM experimental data shown in Figure 1c and Table 1, which were obtained from the spectra of three-dimensional force maps.¹³ Note that the tilt angles determined from the CO and Xe tips are slightly different, which was attributed to the distance dependent CO-tip tilting that affects the frequency shift versus distance spectra [$\Delta f(z)$]. In terms of the adsorption heights and tilt angles, we conclude that our DFT calculations are in excellent agreement with experiments.

The tilt of the adsorbed ketone can also be seen from individual $\Delta f(z)$ versus distance curves in AFM experiments. Experimentally, these curves were recorded with a CO-decorated tip approaching to different carbon-ring centers of the molecule (see Figure 1d). Analysis of these curves showed that different carbon-rings have different effective distances, defined as the difference between the Δf -minimum of the C-ring centers and Cu surface. To compare with experiments, we also used a CO-tip in our simulations, and computed the Δf -distance spectra by taking the second derivative of the binding-energy curve for the tip-molecule system.²⁴ We found that the computed effective distances shown in the bottom panel of Figure 1d (1.71, 1.75, and 2.01 Å) are in excellent agreement with experimental values (1.70, 1.74–1.77, and 1.97–2.00 Å). However, the computed frequency is slightly smaller than that of the AFM experiments, which is mainly because we used a small model for the tip (Cu₂CO). Notably, our tests for a similar, but smaller, benzene on Cu(001) system have shown that adding a Cu₅ cluster behind the CO tip increases vdW interactions, and rigidly shifts the Δf curves by about –1 Hz.

Considering the large differences in the adsorption structures of the three molecules, one would expect significant renormalization of adsorption energies and electronic properties of the olympicenes/metal systems. However, this is not the case, as we will demonstrate below.

Table 1 shows that the olympicene, its ketone, and its radical have essentially identical binding energies on the Cu(111) surface. To understand this remarkable finding, we calculated the binding energy as a function of the C_c–Cu adsorption height for the three molecules at the hcp30° site. For each point in Figure 2, we constrained the molecular conformation at its

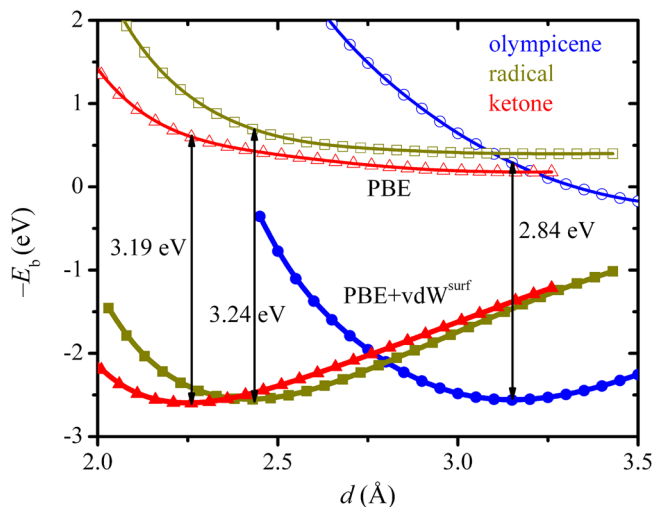


Figure 2. Binding energy $-E_b$ as a function of the C_c atom adsorption height *d* from both the PBE and PBE + vdW^{surf} methods. Note that the radical PBE curve will not converge to zero at large distance, because the single hydrogen atom always stays at the equilibrium distance at the Cu(111) surface.

equilibrium state but changed the adsorption height *d* that is evaluated relative to the C_c atom and the position of the unrelaxed topmost Cu layer. As discussed before, we found the radical and ketone significantly closer adsorbed compared to the olympicene. This can be rationalized by the half-filled HOMO of the radical and the unsaturated C=O bond that both increase the interaction with the Cu surface substantially. The closer adsorption distance leads to considerably larger vdW energies (3.24 and 3.19 eV for radical and ketone vs. 2.84 eV for olympicene). This somewhat unconventional result has also been observed for benzene and water adsorption on transition metal surfaces.^{19,20,25} On the other hand, the closer adsorption distance for the radical and ketone increases the Pauli repulsion compared to olympicene. This behavior can be seen from the PBE + vdW^{surf} curves shown in Figure 2, by comparing the energies at the equilibrium distances of the respective molecules. Especially, the binding energies for the ketone and the radical rise less steeply near their minima compared to the olympicene, which in turn explains the significantly larger adsorption height for the latter. As a result, the increased vdW energy and the increased Pauli repulsion compensate each other, which leads to nearly identical adsorption energies for the three systems.

Having explained the equal stability for olympicenes on Cu(111), we will discuss next the charge redistribution at the surface-molecule interface and its effect on the electronic work function. We first projected the total density of states (DOS) of the full adsorption system onto the HOMO and the LUMO of the free molecule,²⁶ and analyzed their different electronic features. As shown in Figure 3a, for olympicene/Cu(111), there is a very weak overlap of the HOMO and LUMO, with an absence of any noticeable charge transfer. In contrast, the

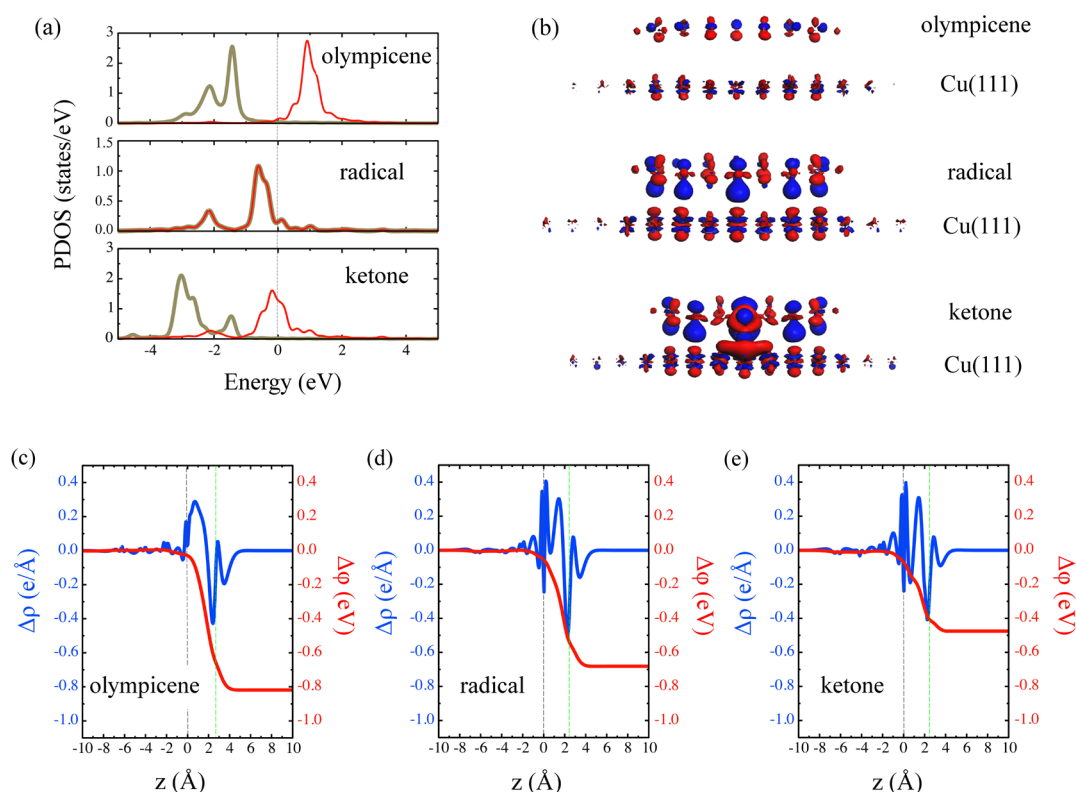


Figure 3. (a) Projected density of states (PDOS) onto the HOMO and LUMO of free olympicene, radical, and ketone molecules for the olympicenes/Cu(111) systems. The spin polarization was taken into account for the radical. The zero of energy corresponds to the Fermi level. (b) Side view of the electron density difference for olympicenes on Cu(111) at equilibrium distances. Plots were obtained by subtracting the electron density of an isolated molecule and clean surface from an electron density plot of the entire adsorption systems, using the same value of the isosurface (0.02 \AA^{-3}). The red and blue indicate the electron loss and gain, respectively. (c–e) Adsorption-induced electron density redistribution integrated over the x - y plane ($\Delta\rho$, left) and the generated bond dipole ($\Delta\phi$, right) for the olympicenes/Cu(111) systems as a function of z coordinate (perpendicular to the surface). $z = 0$ represents the position of the first Cu layer, and the green dashed lines denote the average position of carbon atoms of the adsorbates.

LUMO of the chemisorbed radical is shifted below the Fermi level and is occupied by 0.81 electrons upon interaction with the Cu(111) surface (Figure 3a, middle). Similarly, the LUMO level of the adsorbed ketone is noticeably broadened, accompanied by a back-donation of 1.62 electrons from the metal to the empty bands (LUMO and above) of the molecule (Figure 3a, bottom). Notably, the number of electrons was calculated by integrating the projected density of states (PDOS) of molecular orbitals, such as the HOMO and LUMO of the adsorbates, up to the Fermi level. To better understand the electron density changes upon adsorption, we further subtracted the electron density of the isolated olympicenes and that of the clean metal surface from that of the olympicenes/Cu(111) system. Figure 3b shows the electron density difference plots for the three adsorption systems at each equilibrium distance. For the same value of the isosurface (0.02 \AA^{-3}), the charge rearrangement for the olympicene on Cu(111) is weak (see Figure 3b, top), whereas significant charge redistribution occurs when the O–Cu bond is formed in the ketone/Cu(111) system (Figure 3b, bottom). The electronic structure analysis (the PDOS and the electron density difference), in combination with the molecular height on the substrate, highlight the different adsorption modes for the three olympicenes on the metal substrate.

In spite of the very different PDOS and charge transfer properties, we found that the adsorption decreases the work function of the clean Cu(111) surface by 0.85, 0.71, and 0.74

eV for olympicene, radical, and ketone, respectively (cf. Table 1), at the molecular coverage of 1.99 nm^{-2} . The magnitude of the work function decrease is essentially the same for the three cases, but the underlying mechanism differs, as we will explain below.

In general, molecular adsorption changes the work function of the bare surface by generating an interface dipole. The interface dipole can be partitioned into two components: the bond dipole and the molecular dipole perpendicular to the surface.²⁷ The bond dipole is caused by the electron redistribution. For weakly bound molecules, the bond dipole is predominantly attributed to the effect of Pauli repulsion, or “push-back” effect.²⁸ For strongly bound systems, in addition to the Pauli repulsion, the charge transfer between molecule and metal also creates a potential that shifts the molecular levels relative to the Fermi level of the clean metal surface.²⁹ Any deformation of the molecular structure can induce a molecular dipole that also contributes to the observed changes in the interface work function.

For olympicene molecules, we calculated the electron density difference before and after adsorption, averaged it over the x - y plane (parallel to the surface), and solved a one-dimensional Poisson equation that gives an electron-redistribution induced potential change, an approximation to the bond dipole (see Figure 3).

In the case of olympicene, the adsorption proceeds without formation of chemical bonds. Upon adsorption, the electron

density between the adsorbate and the substrate is depleted in the region near the adsorbate and accumulated in the region close to the substrate. As illustrated in Figure 3c, the generated bond dipole resulting from the Pauli repulsion reduces the work function by 0.81 eV.

Despite the push-back effect being stronger for a smaller adsorption distance, we noticed that the smaller adsorption distances do not induce larger bond dipoles in the cases of radical and ketone compared to the olympicene (Figure 3c–e). Thus, there must be another mechanism that compensates the work function decrease driven by Pauli repulsion. Compared to the olympicene, the radical has a dangling bond and receives charge from the substrate, evidenced by the fact the previous empty LUMO orbital is now almost fully occupied (Figure 3a, middle). The charge transfer from substrate to adsorbate creates a dipole that increases the work function, which compensates the contribution of Pauli repulsion and decreases the total bond dipole. The same scenario applies to the ketone, although it has a larger electronegativity than the radical and thus exhibits increased charge transfer (Figure 3a, bottom). Consequently, the bond dipoles of the radical and the ketone are 0.18 and 0.23 eV smaller than that of the olympicene.

The molecular dipole also contributes to the change in the interface dipole. Here, all the isolated adsorbates have vanishing dipole moments, the molecular dipoles thus come from the structural deformation upon adsorption. From olympicene to ketone, the adsorption-induced distortions get increasingly larger, which decreases work function by 0.04, 0.08, and 0.16 eV, respectively. As shown in Table 1, the molecular dipole shows an opposite trend and reduces the differences in the bond dipole.

Therefore, it is the delicate balance between the push-back effect, charge transfer, and molecular dipole that gives similar work functions for all the three systems. Such a feature is highly favorable for reliable and robust devices, such as Schottky barrier diodes, considering that the work function determines the energy level alignment and plays a crucial role in defining the electronic properties at the interface.

In summary, we find that substitution of one atom in olympicene molecules significantly modifies the nature of bonding for the adsorbates on the Cu(111) surface. Despite the adsorption heights being significantly different among the three molecules, our calculations show that the delicate balance between the Pauli repulsion and vdW interactions leads to the identical binding energies, whereas the competition among the push-back effect, charge transfer, and molecular dipole gives rise to similar work functions.

METHODS

Density functional theory calculations employed the numeric atom-centered basis set all-electron code FHI-aims,³⁰ together with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional.¹⁶ We used the PBE + vdW^{surf} method¹⁵ to account for the van der Waals (vdW) interactions and collective response effects. The PBE + vdW^{surf} method extends pairwise vdW approaches to modeling of adsorbates on surfaces by a synergetic combination of the PBE + vdW method³¹ for intermolecular interactions with the Lifshitz–Zaremba–Kohn theory^{32,33} for the nonlocal Coulomb screening within the bulk. We used the scaled zeroth-order regular approximation³⁴ to treat relativistic effects for Cu atoms. The “tight” settings including the “tier2” standard basis set in the FHI-aims code were used for H, C, and O, and “tier1” for Cu. All atomic

positions were relaxed until the maximal force on each atom was smaller than 10^{-2} eV/Å. For all computations, the convergence criteria of 10^{-5} electrons per unit volume for the charge density and 10^{-6} eV for the total energy of the system were utilized. In slab calculations, we used a $3 \times 3 \times 1$ Monkhorst–Pack mesh for the sampling of the Brillouin zone of the (6×6) surface. Less than 50 meV difference was obtained for olympicene/Cu(111) when we further increased the k -point mesh to $6 \times 6 \times 1$. The radical was treated with spin-unrestricted DFT formalism. The dipole correction was taken into account for slab calculations. The Cu(111) surfaces were modeled by six-layer slabs. For geometry relaxations, the molecule and the two uppermost metal layers were allowed to fully relax, whereas the four bottommost layers were constrained at their bulk positions. Different slabs were separated by 30 Å of vacuum. Our extensive tests confirmed that our computational settings guarantee convergence of the calculated adsorption energy within 0.05 eV.

We computed the frequency-shift spectra for the olympicene ketone based on the fully relaxed ketone/Cu(111) structure, at the most stable hcp30° adsorption site. We only kept the atomic positions of the deformed ketone fixed, but removed the underlying metal substrate. In accord with previous studies,²⁴ we used a Cu-dimer tip functionalized with a CO molecule. To compare with AFM experiments, we placed the tip above the center of each carbon ring of the ketone molecule. Then, by using the PBE + vdW^{surf} method and the standard “safe” settings in the FHI-aims code, we calculated the total energy of the adsorbate interacting with the Cu₂CO tip as a function of vertical distance. Once the total energies were obtained, we took the second derivative with respect to the z direction, and finally obtain the frequency shift.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.6b00223.

High-symmetry adsorption sites for olympicenes on the Cu(111) surface. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: tkatchenko@fhi-berlin.mpg.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.T. acknowledges support from the European Research Council (ERC Starting Grant VDW-CMAT). W.L. acknowledges support from the National Natural Science Foundation of China (no. 21403113), the Fundamental Research Funds for the Central Universities (no. 30915011330), the Natural Science Foundation for Distinguished Young Scholars of Jiangsu Province (no. BK20150035), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions. B.S., N.M., G.M., and L.G. acknowledge financial support from the EU project PAMS (agreement no. 610446), and the ERC Advanced Grant CEMAS. We thank Anish Mistry and David Fox for providing the molecules studied in this paper.

REFERENCES

- (1) Temirov, R.; Soubatch, S.; Luican, A.; Tautz, F. Free-Electron-Like Dispersion in An Organic Monolayer Film on A Metal Substrate. *Nature* **2006**, *444*, 350.
- (2) Heimel, G.; Duhm, S.; Salzmann, I.; Gerlach, A.; Strozecka, A.; Niederhausen, J.; Bürker, C.; Hosokai, T.; Fernandez-Torrente, L.; Schulze, G.; et al. Charged and Metallic Molecular Monolayers through Surface-Induced Aromatic Stabilization. *Nat. Chem.* **2013**, *5*, 187–194.
- (3) Cao, L.; Gao, X.-Y.; Wee, A. T. S.; Qi, D.-C. Quantitative Femtosecond Charge Transfer Dynamics at Organic/Electrode Interfaces Studied by Core-Hole Clock Spectroscopy. *Adv. Mater.* **2014**, *26*, 7880–7888.
- (4) Aradhya, S. V.; Frei, M.; Hybertsen, M. S.; Venkataraman, L. van der Waals Interactions at Metal/Organic Interfaces at the Single-Molecule Level. *Nat. Mater.* **2012**, *11*, 872.
- (5) Borca, B.; Schendel, V.; Pétuya, R.; Pentegov, I.; Michnowicz, T.; Kraft, U.; Klauk, H.; Arnau, A.; Wahl, P.; Schlickum, U.; et al. Bipolar Conductance Switching of Single Anthradithiophene Molecules. *ACS Nano* **2015**, *9*, 12506–12512.
- (6) Gomez-Romero, P. Hybrid Organic-Inorganic Materials-In Search of Synergic Activity. *Adv. Mater.* **2001**, *13*, 163.
- (7) Roman, T.; Groß, A. Periodic Density-Functional Calculations on Work-Function Change Induced by Adsorption of Halogens on Cu(111). *Phys. Rev. Lett.* **2013**, *110*, 156804.
- (8) Toyoda, K.; Hamada, I.; Lee, K.; Yanagisawa, S.; Morikawa, Y. Density Functional Theoretical Study of Pentacene/Noble Metal Interfaces with van der Waals Corrections: Vacuum Level Shifts and Electronic Structures. *J. Chem. Phys.* **2010**, *132*, 134703.
- (9) Morikawa, Y.; Ishii, H.; Seki, K. Theoretical Study of N-Alkane Adsorption on Metal Surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *69*, 041403.
- (10) Zou, Y.; Kilian, L.; Schöll, A.; Schmidt, T.; Fink, R.; Umbach, E. Chemical Bonding of PTCDA on Ag Surfaces and the Formation of Interface States. *Surf. Sci.* **2006**, *600*, 1240–1251.
- (11) Romaner, L.; Nabok, D.; Puschnig, P.; Zojer, E.; Ambrosch-Draxl, C. Theoretical Study of PTCDA Adsorbed on the Coinage Metal Surfaces, Ag(111), Au(111) and Cu(111). *New J. Phys.* **2009**, *11*, 053010.
- (12) Tkatchenko, A.; Romaner, L.; Hofmann, O. T.; Zojer, E.; Ambrosch-Draxl, C.; Scheffler, M. van der Waals Interactions between Organic Adsorbates and at Organic/Inorganic Interfaces. *MRS Bull.* **2010**, *35*, 435.
- (13) Schuler, B.; Liu, W.; Tkatchenko, A.; Moll, N.; Meyer, G.; Mistry, A.; Fox, D.; Gross, L. Adsorption Geometry Determination of Single Molecules by Atomic Force Microscopy. *Phys. Rev. Lett.* **2013**, *111*, 106103.
- (14) Duhm, S.; Gerlach, A.; Salzmann, I.; Bröker, B.; Johnson, R. L.; Schreiber, F.; Koch, N. PTCDA on Au(111), Ag(111) and Cu(111): Correlation of Interface Charge Transfer to Bonding Distance. *Org. Electron.* **2008**, *9*, 111.
- (15) Ruiz, V. G.; Liu, W.; Zojer, E.; Scheffler, M.; Tkatchenko, A. Density-Functional Theory with Screened van der Waals Interactions for the Modeling of Hybrid Inorganic–Organic Systems. *Phys. Rev. Lett.* **2012**, *108*, 146103.
- (16) Perdew, J.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (17) Camarillo-Cisneros, J.; Liu, W.; Tkatchenko, A. Steps or Terraces? Dynamics of Aromatic Hydrocarbons Adsorbed at Vicinal Metal Surfaces. *Phys. Rev. Lett.* **2015**, *115*, 086101.
- (18) Liu, W.; Tkatchenko, A.; Scheffler, M. Modeling Adsorption and Reactions of Organic Molecules at Metal Surfaces. *Acc. Chem. Res.* **2014**, *47*, 3369–3377.
- (19) Liu, W.; Carrasco, J.; Santra, B.; Michaelides, A.; Scheffler, M.; Tkatchenko, A. Benzene Adsorbed on Metals: Concerted Effect of Covalency and van der Waals Bonding. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 245405.
- (20) Liu, W.; Ruiz, V. G.; Zhang, G.-X.; Santra, B.; Ren, X.; Scheffler, M.; Tkatchenko, A. Structure and Energetics of Benzene Adsorbed on Transition-Metal Surfaces: Density-Functional Theory with van der Waals Interactions Including Collective Substrate Response. *New J. Phys.* **2013**, *15*, 053046.
- (21) Al-Saidi, W. A.; Feng, H.; Fichthorn, K. A. Adsorption of Polyvinylpyrrolidone on Ag Surfaces: Insight into a Structure-Directing Agent. *Nano Lett.* **2012**, *12*, 997.
- (22) Wagner, C.; Fournier, N.; Tautz, F. S.; Temirov, R. Measurement of the Binding Energies of the Organic-Metal Perylene-Tetracarboxylic-Dianhydride/Au(111) Bonds by Molecular Manipulation Using an Atomic Force Microscope. *Phys. Rev. Lett.* **2012**, *109*, 076102.
- (23) Yildirim, H.; Kara, A. Effect of van der Waals Interactions on the Adsorption of Olympicene Radical on Cu (111): Characteristics of Weak Physisorption versus Strong Chemisorption. *J. Phys. Chem. C* **2013**, *117*, 2893–2902.
- (24) Moll, N.; Schuler, B.; Kawai, S.; Xu, F.; Peng, L.; Orita, A.; Otera, J.; Curioni, A.; Neu, M.; Repp, J.; et al. Image Distortions of Partly Fluorinated Hydrocarbons in Atomic Force Microscopy with Carbon Monoxide Terminated Tips. *Nano Lett.* **2014**, *14*, 6127–6131.
- (25) Carrasco, J.; Klimeš, J.; Michaelides, A. The Role of van der Waals Forces in Water Adsorption on Metals. *J. Chem. Phys.* **2013**, *138*, 024708.
- (26) Rangger, G. M.; Romaner, L.; Heimel, G.; Zojer, E. Understanding the Properties of Interfaces between Organic Self-Assembled Monolayers and Noble Metals-A Theoretical Perspective. *Surf. Interface Anal.* **2008**, *40*, 371–378.
- (27) Rangger, G. M.; Hofmann, O. T.; Romaner, L.; Heimel, G.; Bröker, B.; Blum, R.-P.; Johnson, R. L.; Koch, N.; Zojer, E. F4TCNQ on Cu, Ag, and Au as Prototypical Example for a Strong Organic Acceptor on Coinage Metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *79*, 165306.
- (28) Braun, S.; Salaneck, W. R.; Fahlman, M. Energy-Level Alignment at Organic/Metal and Organic/Organic Interfaces. *Adv. Mater.* **2009**, *21*, 1450–1472.
- (29) Koch, N.; Ueno, N.; Wee, A. T. S. *The Molecule-Metal Interface*; John Wiley & Sons: Weinheim, Germany, 2013.
- (30) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals. *Comput. Phys. Commun.* **2009**, *180*, 2175.
- (31) Tkatchenko, A.; Scheffler, M. Accurate Molecular van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (32) Lifshitz, E. M. The Theory of Molecular Attractive Forces between Solids. *Sov. Phys. JETP* **1956**, *2*, 73–83.
- (33) Zaremba, E.; Kohn, W. van der Waals Interaction between an Atom and a Solid Surface. *Phys. Rev. B* **1976**, *13*, 2270.
- (34) van Lenthe, E.; Baerends, E.-J.; Snijders, J. G. Relativistic Total Energy using Regular Approximations. *J. Chem. Phys.* **1994**, *101*, 9783.