

Magnetic configurations of open-shell molecules on metals: The case of CuPc and CoPc on silverElisabeth Wruss,^{1,2} Georgia Prokopiou,³ Leeor Kronik,³ Egbert Zojer,² Oliver T. Hofmann,² and David A. Egger^{1,4,*}¹*Institute of Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany*²*Institute of Solid State Physics, NAWI Graz, Graz University of Technology, 8010 Graz, Austria*³*Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel*⁴*Department of Physics, Technical University of Munich, 85748 Garching, Germany*

(Received 6 May 2019; revised manuscript received 14 July 2019; published 30 August 2019)

For nanostructured interfaces between open-shell molecules and metal surfaces that involve charge transfer upon adsorption, the investigation of molecular magnetic properties is an interesting yet difficult task, because in principle different magnetic configurations with distinct properties can be found. Here, we study the magnetic properties of CuPc-Ag and CoPc-Ag interfaces, which constitute interesting test cases because charge is transferred to the initially open-shell Pc molecules upon adsorption. Using hybrid density functional theory, we examine the stability of the various magnetic configurations occurring at these nanoscale interfaces, as well as for the corresponding gas-phase anions, and compare our findings to those of previous experimental studies. For CuPc-Ag, we identify a high-spin triplet configuration as the most likely configuration at the interface, whereas for CoPc-Ag a quenching of the total magnetic moment is found. Interestingly, such quenching is consistent with two distinctly different interfacial electronic configurations. These important differences in the magnetic properties of CuPc and CoPc on Ag are rationalized by variations in the interaction of their central metal atoms with the substrate. Our work facilitates a deeper understanding of the magnetic configuration and interlinked electronic-structure properties of molecule-metal interfaces. Furthermore, it highlights the necessity of an appropriate choice of methodology in tandem with a detailed evaluation of the different emerging magnetic properties.

DOI: [10.1103/PhysRevMaterials.3.086002](https://doi.org/10.1103/PhysRevMaterials.3.086002)**I. INTRODUCTION**

An in-depth understanding of the electronic structure and magnetic properties of surface-adsorbed organic molecules is of direct relevance for and key to molecular spintronics [1–11]. Naturally, the deposition of nonmagnetic, closed-shell molecules on magnetic substrates can result in a magnetic polarization of the molecule [12–17]. Conversely, for molecules which are already spin polarized in the gas phase, adsorption on a nonmagnetic surface can also result in interesting molecular magnetic properties, e.g., via charge-transfer processes from/towards the molecule and screening effects [16,18–21]. The intrinsic magnetic moment of molecules is often quenched upon adsorption, especially in the case of strong hybridization [22–24]. However, some cases exist for which the molecular magnetic moment endures the deposition on the surface or is even enhanced upon adsorption [19]. To understand the driving forces behind such phenomena, two interesting examples are studied in the present work, namely, the molecules copper phthalocyanine and cobalt phthalocyanine (CuPc and CoPc, respectively), adsorbed on the Ag(111) surface. Despite their similarities in the gas phase, experimental results indicate that for CuPc-Ag the intrinsic $S = 1/2$ molecular magnetic moment is enhanced upon adsorption, whereas it is quenched for CoPc-Ag [18,19,25–27].

In this study, we aim to examine the appearance of different magnetic configurations, along with the electronic properties of surface-adsorbed open-shell molecules. This question can be addressed with various experimental techniques, for example, by using spin-polarized scanning tunneling microscopy (STM) or photoemission spectroscopy. Applying theoretical approaches allows one to obtain additional insights that are relevant to the interpretation of experimental data, especially because in principle different magnetic configurations can be tested with regard to their energetic stability. This would allow one to attain a thorough understanding of the magnetic properties of nanostructured molecule-metal interfaces. In practice, the necessary calculations are, however, highly non-trivial. In fact, the theoretical survey of magnetic properties is already challenging for gas-phase molecules, for which different spin solutions can be stabilized in the calculations to assess their relative energies. This would be equally needed for nanoscale molecule-metal interfaces to examine the possible existence of different spin solutions. There, the situation is, however, complicated by the molecule-metal interactions, i.e., hybridization and charge-transfer effects have to be taken into account. An additional complication arises from the system size, which can easily be on the order of several hundred atoms per unit cell. This calls for computationally tractable theoretical methods that can provide (i) an adequate evaluation of the amount of charge transferred between substrate and molecule, (ii) a correct description of the electronic structure in the adsorbed molecule, and (iii) a proper accounting of the exchange coupling between spins, in order to be

*Corresponding author: david.egger@tum.de

able to describe high- and low-spin configurations equally well.

Molecule-metal interfaces are usually computed using density functional theory (DFT), which has been shown to describe geometries of interface systems reliably, especially once conventional DFT functionals are augmented by dispersive corrections [28–32]. However, its description of electronic and magnetic properties is often not straightforward [33–35]. Specifically, in situations where the electronic potential energy surface has several local minima, the nature of the magnetic (or nonmagnetic) configuration obtained in a given calculation can depend on several factors, including the initialization of the self-consistent cycle used when solving the Kohn-Sham equations and the approximate density functional employed. A further complication arises from the fact that semilocal functionals, which are typically used for interface calculations [18,19,25,28,36–38], can have difficulties with all three of the above-listed demands needed to describe magnetic properties of molecule-metal interfaces: these functionals may fail at describing charge transfer [34,39–41] and the correct orbital configurations [28,42–53], which can (in part) be traced back to errors arising from self-interaction [39,43,44,48,54–56], and often do not allow for a proper description of exchange coupling [57–63]. A common approach to mitigate these shortcomings of semilocal DFT is the use of “higher-rung” methods, such as hybrid DFT functionals, which can partially reduce the unwanted consequences of these issues. This is relevant for the molecule-metal interfaces considered here, because in previous work some of us have reported that different magnetic solutions are stabilized when different DFT functionals are used for the CuPc-Ag(111) interface [28]. Notably, such differences in the obtained theoretical solutions may strongly impact the rationalization of experimental data by means of first-principles calculations. In this work, we investigate this aspect in considerable detail, demonstrating that an inadequate method can fail to capture the full complexity of such systems and in particular, the existence of certain magnetic configurations can be easily overlooked. This bears the risk of missing the relevant spin configurations, preventing a reliable interpretation of experimental findings and, even more so, standalone theoretical predictions of surface-adsorbed open-shell molecules.

We study CuPc and CoPc molecules adsorbed on Ag(111), with a focus on disentangling the different magnetic configurations appearing at these interfaces by means of hybrid DFT. These systems are perfectly suitable case studies for the present survey: they have been studied extensively both theoretically and experimentally and, despite their $S = 1/2$ configuration in the gas phase, they have been shown to exhibit distinctly different magnetic properties upon surface adsorption [18,19,25–27,64,65]. However, the full picture of the appearance of different magnetic configurations, to our knowledge, has not been captured to date. We show that in contrast to semilocal DFT, the use of a hybrid functional allows us to obtain more comprehensive insights into the various magnetic configurations, also for surface-adsorbed molecules, and to investigate their electronic properties in detail. By comparing the resulting magnetic configurations appearing at the interfaces, and by considering them also for the molecular anions in the gas phase, we can analyze various

effects that impact their relative stability, including charge transfer from the substrate and the role of the central metal atom.

II. COMPUTATIONAL METHODOLOGY

First-principles calculations of the molecule-metal interfaces were performed with the FHI-AIMS simulation package [66] using the HSE06 [67,68] and Perdew-Burke-Ernzerhof (PBE) [69] exchange-correlation functionals. The HSE06 functional, which applies exact exchange of 25% in the short range, has been chosen as it has been shown to perform well for phthalocyanine molecules in the gas phase [42,43,70]. In addition, for transition-metal complexes it has been shown that the spin-state energetics depend mainly on the percentage of short-range exchange, while long-range exchange and the exact value of the range-separation parameter are of less importance for this property [57,71]. To check whether this is the case also for the Pc molecules considered here, we performed additional calculations with long-range corrected functionals, elaborated below. Dispersive corrections were added to the self-consistently calculated DFT total energies via the vdW^{surf} method suggested by Ruiz *et al.* [29,72]. The repeated slab approach was applied using a Γ -centered k grid of $3 \times 3 \times 1$ points, and the electronic states were broadened by a Gaussian scheme using a width of 0.1 eV. At least 20 Å of vacuum were included above the slab, and a dipole correction was applied in the z direction in order to decouple the interface from periodic replicas in that direction [73]. Predefined FHI-AIMS “tight” settings were used for the CuPc interface calculations for all atomic species, which includes basis sets, integration grids, and the numerical accuracy of the Hartree potential. For the CoPc interface calculations, “light” settings were used because of numerical convergence issues. We have, however, tested for the case of CuPc-Ag(111) that neither the relative energies nor the electronic structure of the various magnetic configurations were affected by switching from “light” to “tight” settings. To assign charges and spins to individual atoms in the system, the Hirshfeld partitioning scheme was applied [74].

Monolayers of CuPc and CoPc molecules were calculated with one molecule in a $(5 \times 3\sqrt{3})$ Ag(111) surface unit cell (see Supplemental Material [75], Sec. 1) that also contained three layers of Ag to represent the metal substrate; note that this packing density is slightly smaller than the experimental one [76]. The bulk Ag lattice constant was optimized and found to vary by $\sim 0.2\%$ when HSE06 was used instead of PBE [77]. Therefore, the PBE-optimized Ag lattice constant of 4.15 Å was applied throughout. The geometry optimizations with the PBE + vdW^{surf} approach (force threshold 0.01 eV/Å) considered the relaxation of the adsorbed molecule and of the topmost Ag layer (see Supplemental Material [75], Sec. 1). The average optimized molecule-metal distances were 3.1 Å (CuPc) and 2.9 Å (CoPc) from the unrelaxed Ag(111) surface, in good agreement with previous experimental results [28,76,78,79].

For both systems, we performed extensive tests (see Supplemental Material [75], Secs. 2–4) of different initializations of the electronic self-consistency cycle, broadening widths, and choice of density functional, in order to examine whether

other stable magnetic configurations on the surface can be obtained. To check whether the geometries influence the final results of the calculations, we performed geometry optimizations of all CuPc and CoPc configurations on the surface (selected cases of the interface system were converged to a lesser stringent force threshold) and in the gas phase, see Supplemental Material [75], Secs. 2 and 5, respectively. In none of the cases did a relevant modification of the electronic structure or relative energetics appear. Therefore, the geometries optimized with PBE + vdW^{surf} were applied to obtain the three configurations for CuPc-Ag(111) and the two configurations for CoPc-Ag(111), as presented below.

To facilitate a comparison with the interface electronic properties, the molecular geometries obtained in the interface optimizations were also used for the gas-phase calculations of the anions of CuPc and CoPc presented in the main text. Note that because of the symmetry of the Ag(111) surface, both molecules in their surface-adsorbed geometry do not exhibit the symmetry properties known for gas-phase CuPc and CoPc in our gas-phase calculations [80,81]. We focused on the anionic species in the gas phase, because a charge transfer amounting to approximately one electron occurs at the interface, and performed two types of gas-phase calculations: first, we performed HSE06 calculations using FHI-AIMS with “tight” settings as described above for the interface calculations. Second, we performed optimally-tuned range-separated hybrid (OT-RSH) calculations, since this method has previously been found to describe the electronic structure of CuPc and CoPc in their neutral form particularly well [80,81]. OT-RSH calculations were performed with the Q-CHEM code 5.1 [82] using a cc-pVTZ basis set [83] for all the atoms. The OT-RSH functional was based on the PBE description of exchange-correlation and for both molecules applied 20% of exact exchange in the short range. The optimal range-separation parameter, γ , was determined to be 0.119 Bohr^{-1} for CoPc and 0.120 Bohr^{-1} for CuPc, which were tuned for the neutral molecules as in Refs. [80,81].

III. RESULTS AND DISCUSSION

A. Magnetic configurations of surface-adsorbed CuPc and CoPc

CuPc and CoPc exhibit an unpaired spin in the neutral gas-phase configuration (see Refs. [80,81] for a detailed description of the gas-phase configuration) and for both molecules, adsorption on the Ag surface results in charge transfer towards the molecule [19]. Hence, different magnetic configurations of each surface-adsorbed molecule are in principle possible. Metal-Pc interfaces were already studied in great detail experimentally and therefore allow for a comparison between our theoretical results to previous experimental data. One useful

way to achieve this comparison is by considering the interface electronic structure, specifically, the density of states (DOS) related to the molecule, which can be compared to data measured in, e.g., spin-dependent photoemission spectroscopy or STM [17,84–86].

First, we focus on the CuPc-Ag system, for which several experimental surveys indicated interesting magnetic properties of the surface-adsorbed molecule [18,19,25,37,87–90]. We find charge transfer of about one electron from the surface to the molecule. Importantly, depending on the magnetic initialization of the calculation (see Supplemental Material [75], Sec. 4.2), three different configurations can be obtained. In the first, the magnetic moment due to the localized spin-polarized state present in the gas phase is effectively quenched when CuPc is charged upon adsorption (see Table I). It has been suggested that this spin-polarized state has significant weight on the central metal atom [43]. Hence, a large amount of the transferred charge ought to be transferred to this region of the molecule. This is confirmed by the projected DOS (PDOS) and local DOS (LDOS) at the relevant energies in Fig. 1(a) [see peak 2 in Fig. 1(a) and the corresponding LDOS]. Since this configuration closely resembles a (gas-phase) singlet, we denote it as such in the following.

In the second configuration, the magnetic moment due to the localized spin-polarized orbital present in the gas phase is preserved, as can be inferred from the occupied Cu-based PDOS at $\sim -3 \text{ eV}$ in Fig. 1(b). One can also see that a second occupied spin-polarized state appears close to the Fermi energy, which is mainly distributed on the ligand part of CuPc [see peak II in Fig. 1(b) and the corresponding LDOS]. Therefore, a large amount of the transferred charge is accumulated in the ligand region in this case. From the spin-splitting of the ligand orbitals [see peaks I and II in Fig. 1(b) and the corresponding LDOS] and the molecular magnetic moment (see Table I), one sees that the transferred charge adds an extra spin to the system. This spin aligns parallel to the one localized in the vicinity of the Cu atom. Indeed, the spin density [see Fig. 2(a)], defined as $n_{\uparrow}(\vec{r}) - n_{\downarrow}(\vec{r})$, where $n_{\uparrow,\downarrow}(\vec{r})$ is the charge density of the spin-up and spin-down electrons, respectively, shows the coexistence of two occupied spin-polarized orbitals. They are centered on the Cu atom and distributed over the ligand region, respectively, and are aligned in parallel to give rise to a total magnetic moment of the molecule of $\mu \approx 1.7 \mu_B$. This configuration is therefore denoted as a triplet configuration, as it approximately resembles a gas-phase triplet. Note a deviation from the ideal $\mu = 2 \mu_B$ magnetic moment of the triplet configuration, owing to hybridization of molecular orbitals with the substrate electronic states, as well as to the fact that we assigned the molecular magnetic properties via a charge-partitioning scheme.

TABLE I. HSE06 calculated total energy differences ΔE , Hirshfeld charges on the molecule Q , magnetic moment on the molecule μ , and work-function modification $\Delta\Phi$ of CuPc-Ag(111) in the different configurations. ΔE is reported with reference to the lowest energy configuration found in our calculations. For comparison, the PBE-calculated values of $\Delta\Phi$ are also reported.

	ΔE (eV)	Q (e^-)	μ (μ_B)	$\Delta\Phi$ HSE06 (eV)	$\Delta\Phi$ PBE (eV)
CuPc singlet	+0.83	0.77	0.00	-0.35	-0.40
CuPc doublet	+0.05	0.70	0.96	-0.44	-0.41
CuPc triplet	0.00	0.77	1.74	-0.34	-

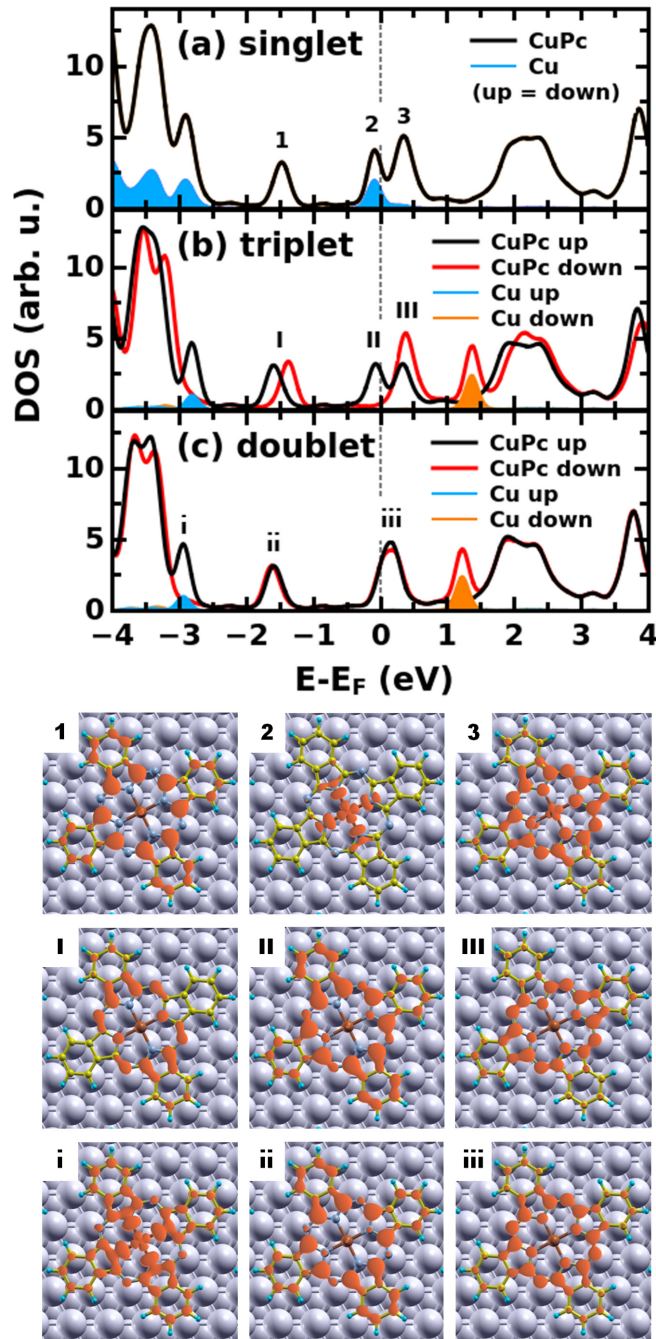


FIG. 1. Density of states projected onto the molecule (PDOS) of the different magnetic configurations of CuPc-Ag(111): the singlet (a), triplet (b), and doublet (c) configuration. For relevant features in the PDOS, an isosurface representation of the molecular contributions to the local density of states (LDOS) is shown below. Energy regions (integration window 0.5 eV) corresponding to the schematic representations of the LDOS are marked by numbers in the respective PDOSs.

For the third configuration, the localized spin-polarized Cu-centered orbital is again preserved [see peak i in Fig. 1(c) and the corresponding LDOS] and the transferred charge is found again mainly in the ligand region of the molecule [see peaks ii and iii in Fig. 1(c) and the corresponding LDOS]. In contrast to the triplet scenario, no extra magnetic moment is

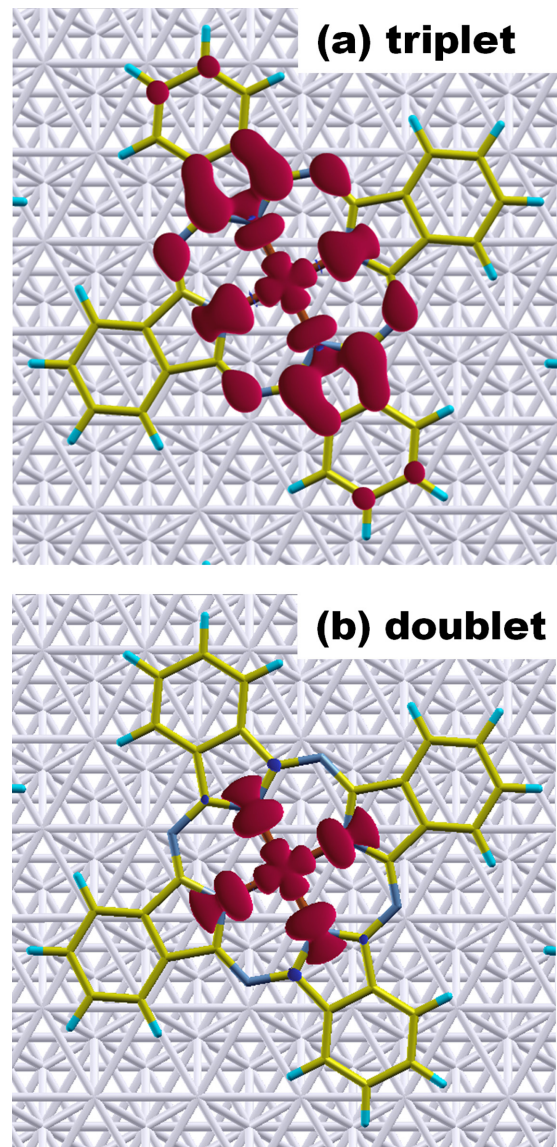


FIG. 2. Isosurface representation of the spin density for the triplet (a) and doublet (b) configuration of CuPc-Ag(111), see text for details. Regions of positive sign are plotted in red, and regions of negative sign are plotted in blue.

added to the system by the transferred charge (see Table I), and the spin density of this configuration [Fig. 2(b)] shows only the unpaired spin-polarized Cu-centered orbital. As the spin configuration of this scenario is equivalent to the one known for the neutral molecule, we denote this configuration as a doublet. Comparing the energies of these three configurations, we find that the triplet is by about ~ 0.8 eV more favorable than the singlet and by ~ 0.1 eV more favorable than the doublet (see Table I); note that the energy difference between triplet and doublet reaches the limits of the numerical accuracy of our calculations.

Next, we consider a monolayer of CoPc on Ag(111), as it has been reported that its magnetic properties are different from those of CuPc-Ag [19,27,64,79,91]. We find that again about one electron is transferred to the CoPc molecule upon adsorption on Ag(111) (see Table II). The situation of the

TABLE II. HSE06 calculated total energy differences ΔE , Hirshfeld charges on the molecule Q , magnetic moment on the molecule μ , and work-function modification $\Delta\Phi$ of CoPc-Ag(111) in the different configurations. ΔE is reported with reference to the lowest energy configuration found in our calculations. For comparison, the PBE-calculated values of $\Delta\Phi$ are also reported.

	ΔE (eV)	Q (e^-)	μ (μ_B)	$\Delta\Phi$ HSE06 (eV)	$\Delta\Phi$ PBE (eV)
CoPc closed-shell singlet	+0.02	0.83	0.0	-0.32	-0.30
CoPc open-shell singlet	0.00	0.81	0.2	-0.37	-

interface magnetic configuration turns out to be similarly complicated as for CuPc-Ag: two different configurations are found, both exhibiting a quenching of the gas-phase molecular spin such that the interface magnetic moment is essentially zero. The corresponding PDOSs and LDOSs of the relevant energy regions are shown in Fig. 3.

Despite their similar net magnetic moments, these two configurations differ significantly in their electronic structure (see PDOS data in Fig. 3). The first one closely resembles a (closed-shell) singlet scenario in the gas phase, since no unpaired spin remains in the system [see Fig. 3(a)]. In the other

configuration, the unpaired Co spin prevails upon adsorption [see occupied Co-based PDOS at ~ -2 eV in Fig. 3(b)] and a second spin appears in the ligand region of the system. However, in contrast to the triplet scenario of CuPc-Ag, the ligand spin aligns antiparallel to the Co spin, as can be seen in the spin density of this configuration (see Fig. 4). Therefore, the molecular magnetic moment is reduced to a low value of $0.2 \mu_B$, which resembles an open-shell singlet scenario. For the CoPc-Ag(111) system, the PDOS and LDOS indicate that the charge transfer involves electronic states from both the central Co atom and the molecular ligand in both configurations [see peaks 1 and 2 in Fig. 3(a), and I and II in Fig. 3(b), as well as the corresponding LDOS data]. This is in contrast to the situation of CuPc-Ag(111), where the case involving charge transfer to the central Cu region (singlet scenario) can be clearly distinguished from cases of charge transfer to the ligand region (triplet and doublet scenario), discussed in detail below. The singlet and the open-shell singlet configuration are essentially isoenergetic (see Table II).

B. Magnetic configurations of surface-adsorbed CuPc and CoPc—Implications for experimental observables

In view of our finding that for each molecule on Ag(111) two different magnetic configurations are isoenergetic (within the numerical accuracy of the calculations), it is interesting

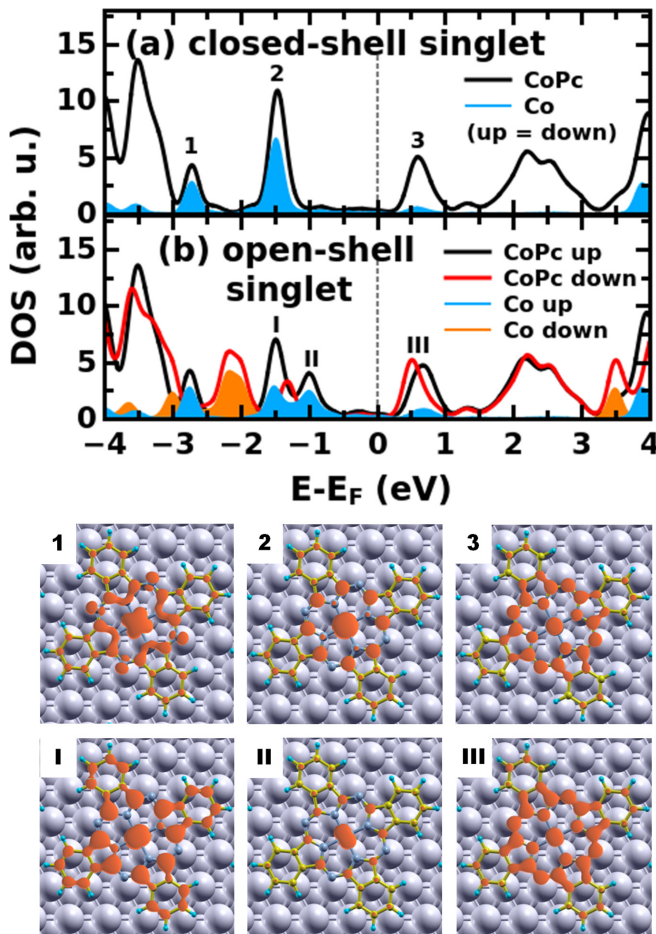


FIG. 3. PDOS of the different magnetic configurations of CoPc-Ag(111): (a) closed-shell and (b) open-shell singlet configurations. The molecular contributions of the LDOS corresponding to relevant features in the PDOS of the two configurations are shown below. Energy regions (integration window 0.5 eV) corresponding to the schematic representations of the LDOS are marked by numbers in the respective PDOSs.

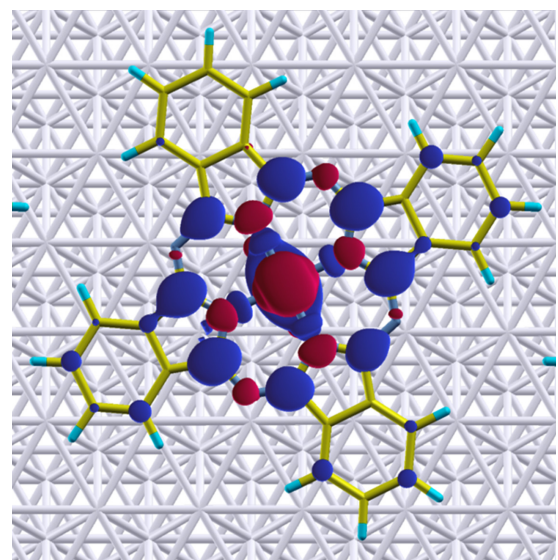


FIG. 4. Isosurface representation of the spin density for the open-shell singlet configuration of CoPc-Ag(111), see text for details. Regions of positive sign are plotted in red and regions of negative sign are plotted in blue.

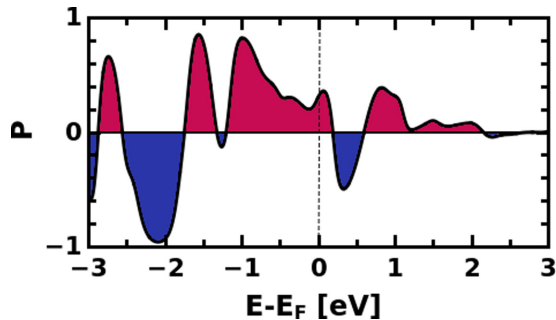


FIG. 5. Spin polarization, $P(E)$, for the open-shell singlet configuration of CoPc-Ag(111), calculated using Eq. (1).

to ask how the presence of a specific configuration would impact experimental observations. A standalone theoretical identification of the most stable configuration is complicated by the fact that the relative energies of the different spin states depend on the applied DFT functional, as discussed in detail below. To address these questions, we first consult previous experimental findings for the two interfaces.

For CuPc-Ag, Mugarza *et al.* have observed that about one electron is transferred from the Ag surface to the molecule upon adsorption [19,25]. They have also discussed the appearance of a ligand spin-polarized state for CuPc upon adsorption on Ag(100), which was found to be delocalized over the inner ligand atoms of the molecule and to be unrelated to the Cu spin. In addition, they described the appearance of a double-peaked structure around the Fermi energy, seen in the electronic structure of the molecule-metal interface recorded by scanning tunneling spectroscopy, which was assigned to a spin-split ligand orbital. These findings are fully consistent with the triplet configuration that was also obtained as the most stable one found in our work. It should, however, be kept in mind that a certain degree of uncertainty remains in this comparison, as the experiments were performed on the (100) surface, whereas our calculations considered the (111) surface of Ag.

For CoPc-Ag, several experimental studies found a quenching of the molecular magnetic moment upon adsorption [19,27,92]. We have discussed above that both configurations found in our calculations imply such a quenching. Our result that the two competing magnetic configurations show a very different PDOS and LDOS (see Fig. 3) provides a prediction that can be tested experimentally: both occupied and unoccupied states around the Fermi level are strongly spin-split only in the open-shell configuration. Specifically, the spin polarization P is an experimental observable that can be probed by spin-polarized STM [17] and can also be calculated from the spin-polarized DOS as follows [86]:

$$P(E) = \frac{\text{DOS}_{\uparrow}(E) - \text{DOS}_{\downarrow}(E)}{\text{DOS}_{\uparrow}(E) + \text{DOS}_{\downarrow}(E)}. \quad (1)$$

While this value is trivially always zero for the closed-shell singlet, the corresponding $P(E)$ curve calculated for the open-shell scenario (see Fig. 5) shows rich features around the Fermi energy. Therefore, we have explicitly established how the presence of a specific spin configuration directly impacts an experimental observable for the case of CoPc-Ag.

Another interesting question is how the work function, which is another important observable for molecule-metal interfaces, is impacted by the appearance of different magnetic configurations. First, we note that the HSE06 functional used here is known to perform reasonably well in calculating the properties of metals [93]. Indeed, the Ag(111) work function is found to be 4.42 eV when calculated with HSE06, which is in good agreement with the experimental value of 4.46 eV [94]. Adsorption-induced work-function modifications, $\Delta\Phi$, are listed in Tables I and II for both interfaces for their various magnetic configurations. Interestingly, they are within 0.1 eV for all obtained configurations, although the charge transfer does not always involve the same orbitals in each case. I.e., $\Delta\Phi$ is hardly affected by the appearance of a specific magnetic configuration despite their different electronic structures. The computed values vary between -0.34 and -0.44 eV for CuPc-Ag (experimental value -0.44 eV [28]) and between -0.32 and -0.37 eV for CoPc-Ag (experimental value -0.52 eV [64]). We consider this agreement between theory and experiment to be reasonable given that the packing density considered in the calculations is somewhat lower than that one typically occurring in experiments. Taken together, this comparison to experimental data shows that the distinctly different configurations obtained for both surface-adsorbed molecules are physically relevant, which motivates us to study their origin in more detail.

C. Magnetic configurations of gas-phase CuPc and CoPc

To examine whether the appearance of different magnetic configurations for surface-adsorbed CuPc and CoPc is due to an intrinsic “molecular” effect or a consequence of molecule-metal interactions, we first consult gas-phase calculations of both anions. Gas-phase properties of molecules are often used as a foundation to discuss electronic properties for surface-adsorbed molecules [19,25,27], because the chemical identity of the molecule is often preserved to a large degree upon interaction with the substrate, and also because interface calculations are often forbiddingly expensive when methods beyond semilocal DFT are used. In view of the different magnetic solutions obtained for both molecules on Ag(111), it is important to clarify whether the electronic structure of the respective anions in the gas phase is still a good approximation to the surface-adsorbed situation.

Our gas-phase calculations are based on two methods: First, using the HSE06 functional, which has been shown to accurately describe the relative alignment of the electronic orbitals in neutral CuPc and CoPc molecules [28,43,95], and which has also been employed in the interface calculations discussed above. Second, we also perform gas-phase calculations of the CuPc and CoPc anions with an OT-RSH functional [71,80,81,96], which uses a system-dependent but nonempirical tuning of the range-separation parameter and can produce highly accurate valence-electron spectra for molecules. In particular, the excellent performance of OT-RSH has been demonstrated for metal Pcs [80,81] and for other metallorganic complexes [71,97].

Again, we start with the eigenvalue spectrum and orbitals of the CuPc anion in selected magnetic configurations (see Fig. 6) and compare them to the electronic structure of the

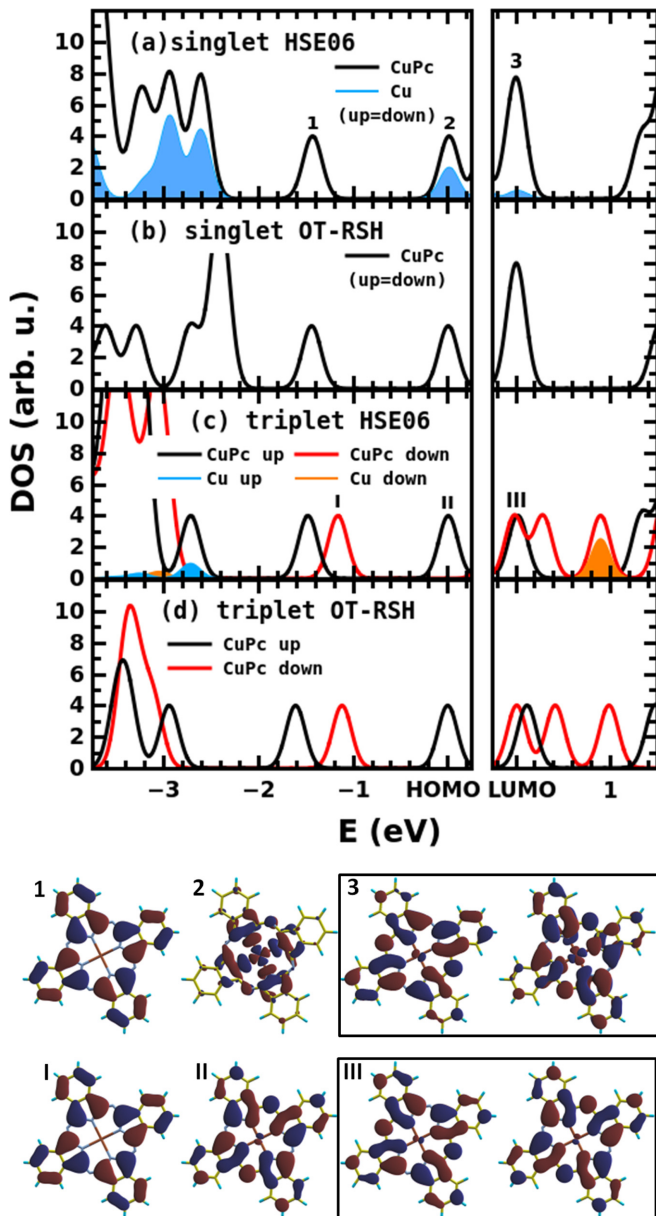


FIG. 6. Broadened eigenvalue spectrum (using a Gaussian with $\sigma = 0.1$ eV) of the singlet and triplet configuration of the CuPc anion in the gas phase, calculated with HSE06 (panels a and c) and OT-RSH (panels b and d). Relevant HSE06-calculated orbitals are also shown. The regions corresponding to the schematic representations of the orbitals are marked by numbers in the respective spectra. We note that, as expected, the OT-RSH energy gap is larger than the one calculated with HSE06, owing to the different description of the long-range exchange interaction. Therefore, the energies of the occupied and unoccupied orbitals are aligned separately to the HOMO (left panels) and LUMO (right panels).

surface-adsorbed molecule by means of the LDOS of Fig. 1. We find that with HSE06 and OT-RSH, for both the singlet and the triplet solution, the orbital ordering is preserved upon surface adsorption. This suggests that for this system the gas-phase anion serves as a good model for the electronic structure of the metal-organic interface. Considering the relative energetics of the different configurations in the gas phase,

TABLE III. HSE06 and OT-RSH calculated total energy differences ΔE of different configurations of CuPc and CoPc anions in the gas phase. ΔE is reported with reference to the lowest energy configuration found in our calculations.

	ΔE HSE06 (eV)	ΔE OT-RSH (eV)
CuPc closed-shell singlet	+0.74	+0.64
CuPc open-shell singlet	+0.02	+0.00
CuPc triplet	0.00	0.00
CoPc closed-shell singlet	+0.09	+0.05
CoPc triplet	+0.04	+0.09
CoPc open-shell singlet	0.00	0.00

we find that the singlet and triplet solutions differ by about 0.7 (HSE06) and 0.6 (OT-RSH) eV, with the triplet solution being more stable (see Table III). This is consistent with the triplet being more stable by 0.8 eV in the surface calculations discussed above. Note that a quantitative difference between HSE06 and OT-RSH is not surprising, as the latter method involves an adaption of the amount of exact exchange in the short range as well as of the range-separation parameter optimized for the given molecule (see Methods section for details).

The eigenvalue spectra and orbitals obtained with the HSE06 and OT-RSH functionals of the gas-phase CoPc anion, in the two different configurations obtained on the surface, are given in Fig. 7. Comparing these data to the CoPc-Ag(111) results (see Fig. 3), we find that the gas-phase CoPc anion also serves as a good starting point to discuss the surface-adsorbed situation, as the electronic structure is similar in both cases. This is in line with previous work showing that the strong reordering of the CoPc electronic states upon charging is similar on the surface and in the gas phase [19,27]. As for the surface-adsorbed molecule, the gas-phase results show the energies of the two CoPc anion configurations to differ only slightly (within 0.1 eV, see Table III).

The observation that the results for the gas-phase anions largely reproduce the electronic-structure and energetic ordering of the different configurations obtained for surface-adsorbed CuPc and CoPc implies that the charging of the molecules, occurring upon surface adsorption, is the crucial factor determining the stability of the magnetic configurations. Therefore, it is interesting to consider also the gas-phase results for the open-shell scenarios that have not been found on the surface, namely, the open-shell singlet of CuPc and the triplet of CoPc (see Table III). The open-shell singlet is essentially isoenergetic to the triplet for the CuPc anion, and the open-shell singlet is only slightly lower in energy (~ 0.1 eV) than the triplet for the CoPc anion. To understand why these alternative configurations did not appear on the surface, one needs to consider the interactions of CuPc and CoPc with Ag.

D. The role of molecule-metal interactions for CuPc and CoPc

We now examine the molecule-metal interactions by calculating the charge-density rearrangements upon adsorption, defined as the difference in charge density of the interacting Pc-Ag system and the isolated subsystems. They are shown in Figs. 8(a)–8(c) for the various configurations of CuPc on Ag(111). The results corroborate the above-discussed finding,

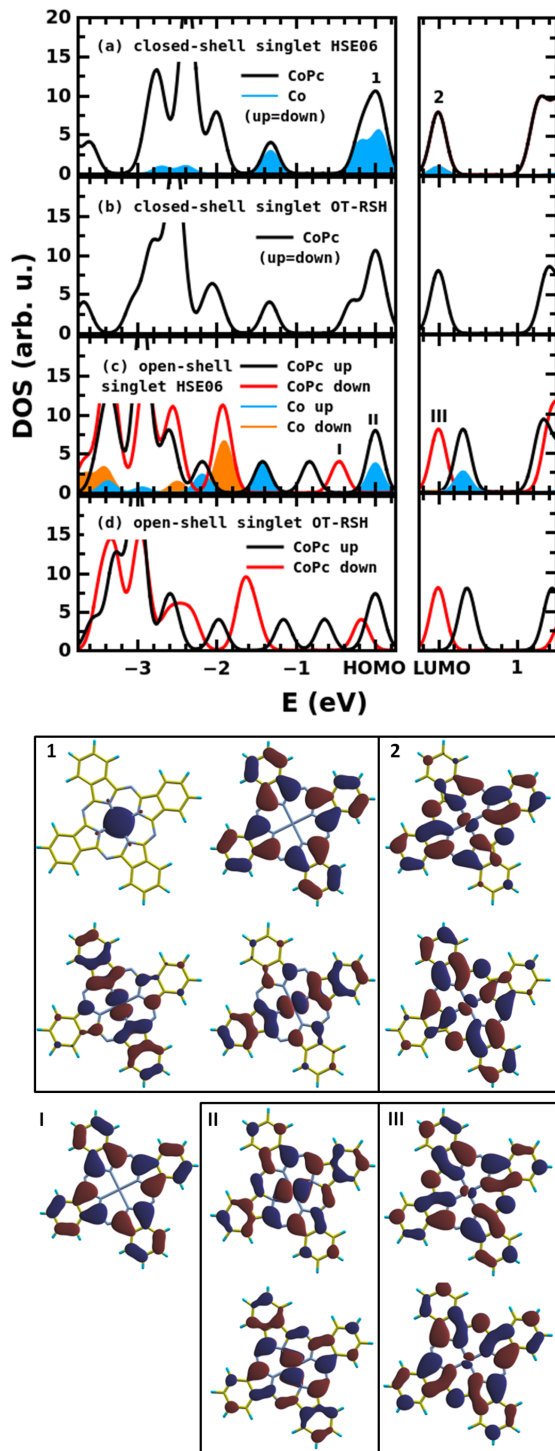


FIG. 7. Broadened eigenvalue spectrum (using a Gaussian with $\sigma = 0.1$ eV) of the closed-shell singlet and open-shell singlet configuration of the CoPc anion in the gas phase, calculated with HSE06 (panels a and c) and OT-RSH (panels b and d). Relevant HSE06-calculated orbitals are also shown. The regions corresponding to the schematic representations of the orbitals are marked by numbers in the respective spectra. We note that, as expected, the OT-RSH energy gap is larger than the one calculated with HSE06, owing to the different description of the long-range exchange interaction. Therefore, the energies of the occupied and unoccupied orbitals are aligned separately to the HOMO (left panels) and LUMO (right panels).

namely, that in case of the singlet configuration charge is transferred mainly to the region of the centering Cu atom, whereas it is transferred to the ligand region in the triplet and doublet case. The situation is very different for the two obtained configurations of CoPc-Ag(111) [see Figs. 8(d) and 8(e)]. For the closed- and open-shell singlet configurations, the rearrangements look virtually identical in that charge is transferred mainly to the central region of the molecule and a pronounced charge accumulation around the central Co atom appears. These features can be associated with the frontier Co d -orbital and indicate a strong hybridization between Co and the Ag substrate. This is in contrast to the situation for CuPc-Ag(111), where even for the singlet, for which charge is transferred mainly into the region of the central Cu atom, no such strong features protruding from the molecular backbone appear [cf. Figs. 8(a), 8(d), and 8(e)]. These findings are in line with previous studies, which argued that the hybridization between the frontier orbital which is localized mostly on the central metal atom and the substrate plays a more dominant role for CoPc than CuPc [22,26,27,87,88]. The reason for this difference lies in the metal d -orbitals: in the case of CoPc, the Co-centered frontier orbital has d_{z^2} character, while for CuPc this is not the case for the frontier orbitals. The Co-centered d_{z^2} orbital is sticking out of the molecular plane towards the metallic surface and hence promotes a stronger interaction of the central metal with the surface for CoPc [22,26,27,87,88,98,99].

For additional insights, we again consider the gas-phase data of the respective anions. The most prominent difference in the gas-phase data of the two molecular anions is that in the CuPc triplet case no filled Cu orbitals lie close to the frontier orbitals, whereas for both CoPc anion configurations an orbital with strong Co contribution is the highest occupied one. Furthermore, the gas-phase results show that for both molecules the open-shell singlet and the triplet are very close in energy (see Table III). And yet, on the surface we could not find the open-shell singlet in case of CuPc and the triplet in case of CoPc. Tentatively, we ascribe this to the different nature of the molecule-metal interaction. In CoPc, the d_{z^2} orbital (which is oriented perpendicular to the surface) is a main source of the molecule-metal interaction. But the d_{z^2} orbital can only participate in the charge transfer for the singlet and not for the triplet scenario (cf. the gas-phase situation shown in the Supplemental Material [75], Sec. 6). In contrast, for the CuPc molecule the orbitals associated with the ligand region are the main source of molecule-metal interactions. Therefore, it can be concluded that the qualitative difference in the obtained magnetic configurations of CuPc and CoPc on the surface is a consequence of the above-discussed more pronounced interaction between CoPc and Ag(111) that is mediated by the Co d -states.

E. Impact of the DFT functional

The results reported above were obtained with the hybrid-functional HSE06. Because for both CuPc-Ag(111) and CoPc-Ag(111) the theoretical data are in line with previous experimental findings for similar interfaces (see above), it appears that DFT is a suitable tool to investigate the properties of magnetic configurations at molecule-metal interfaces.

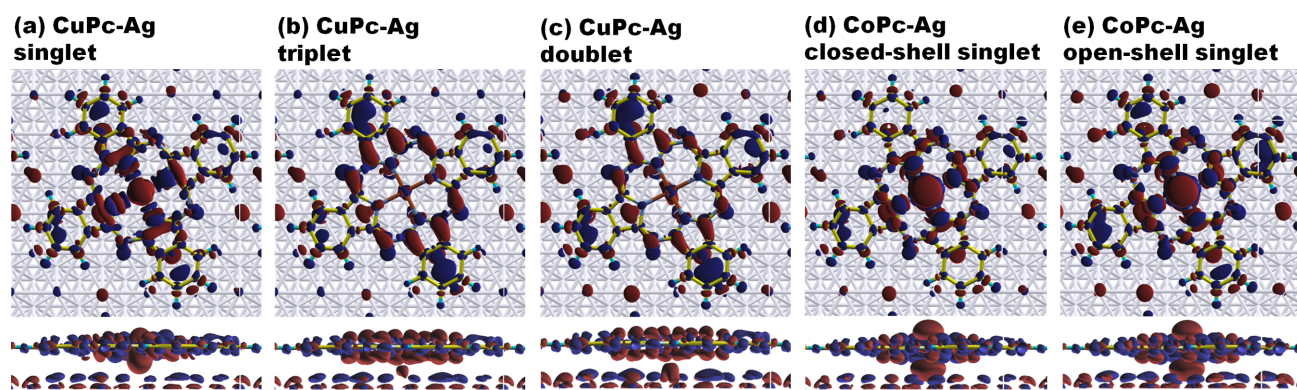


FIG. 8. Three-dimensional representation of the charge-density rearrangements occurring upon adsorption of CuPc and CoPc on Ag(111) for their various magnetic configurations. Regions of electron accumulation are plotted in red, and regions of electron depletion are plotted in blue. For each configuration, a top and a side view are shown.

We now examine whether an equally successful analysis of the magnetic configurations would have been possible with the computationally more efficient PBE functional, which is the most frequently used functional for molecule-metal interface calculations. Similar to the HSE06 results, PBE calculations of CuPc-Ag(111) and CoPc-Ag(111) find charge transfer of about one electron from the substrate to the molecule in both cases. While it has been reported that the applied DFT functional can have some impact on the amount of charge transfer between molecule and metal [100], this is clearly not the case here. Hence, the $\Delta\Phi$ values calculated with PBE are comparable to those obtained for the various magnetic configurations with HSE06 (see Tables I and II).

However, in contrast to the HSE06 results, the number of magnetic configurations we could obtain for both molecules when using the PBE functional was smaller. For CuPc-Ag(111), only the singlet and the doublet were obtained with PBE (see PBE-PDOS in the Supplemental Material [75], Sec. 3). This is an important difference to the HSE06 findings, which provided (almost isoenergetic) triplet and doublet scenarios that are both energetically substantially favored compared to the singlet. Interestingly, none of the solutions obtained with PBE for CuPc on Ag(111) resulted in an enhanced spin moment upon surface adsorption, which was discussed for CuPc on Ag(100) in Refs. [18,19]. Furthermore, the energy difference between singlet and doublet is much smaller when using PBE instead of HSE06 (see Supplemental Material [75], Sec. 3). For CoPc-Ag(111), when the PBE functional is used, only one magnetic configuration, namely, the closed-shell singlet, was found (see PBE-PDOS in the Supplemental Material [75], Sec. 3). In principle, this would already agree with the experimental results that the gas-phase molecular magnetic moment is quenched upon adsorption and could lead one to believe that PBE is sufficient to describe the magnetic properties of the CoPc molecule upon adsorption on Ag. However, the HSE06 results indicate that the situation of the magnetic configurations at the CoPc-Ag interface may be more complicated.

These findings show that PBE fails to describe more complex spin configurations and therefore does not capture the full complexity of molecule-metal interfaces with possibly interesting magnetic configurations. This is consistent with the

notion that higher-level methods, such as hybrid functionals, or the use of “DFT+U” or “DFT+Anderson impurity” methods [90,101–103], are necessary to properly capture magnetic properties of molecular systems [58–62,104,105]; note that the latter two methodologies are also known to have their own intrinsic limitations for describing theoretically the properties of these systems [90,106]. Precedent for this statement can be found for the case of gas-phase transition-metal complexes, where it has been shown that with increasing amount of exact exchange, the ground-state charge density within the complexes localizes more in the ligand region than on the metal and the splitting between low- and high-spin states increases [107]. Indeed, due to the inclusion of exact exchange, hybrid functionals are able to better describe exchange-coupling effects between spin-parallel electrons, which are not fully captured by semilocal DFT functionals such as PBE [57–61,63].

The theoretical calculation of Pc molecules is further complicated by the fact that they exhibit a fairly complex electronic structure already as neutral compounds in the gas phase, which has been studied in great detail by some of us [42,43,70,80,81,95]. For example, the CuPc molecule exhibits strongly localized metal-centered Cu orbitals that lie close in energy to delocalized ligand π orbitals [43,95], which implies that the orbital self-interaction error strongly impacts the ordering of frontier orbitals. Therefore, the calculated electronic structure of Pc molecules is strongly corrupted already in the gas phase when the PBE functional is used [28,42,43,70,95]. Of course, the orbital ordering of the neutral molecule cannot be expected to fully predict the electronic structure of the anionic species in the gas phase or that of the charged one on the surface. However, the consequences of PBE self-interaction errors, including an incorrect orbital ordering, are still carried over to some extent from the gas phase to the interface calculation. Since hybrid functionals can also partially correct for the orbital self-interaction error [28,49,50], it makes sense that HSE06 provides a better description of the interface electronic structure than PBE for the cases considered here. Of course, when one aims for a full quantitative assessment of the energetics of different configurations of a larger pool of molecule-metal interfaces, conventional hybrid functionals cannot be expected to perform well for all cases [49,108,109]. In particular, our findings

that multiple solutions are energetically close implies that configurational mixing may well play a role in determining the interface properties, which is not taken into account in an approximate single-determinant method such as hybrid DFT. Additionally, it should be noted that the description of potentially important phenomena, notably the Kondo effect, are not possible with conventional DFT functionals.

IV. SUMMARY AND CONCLUSIONS

In this work, our goal was to identify the magnetic configurations appearing at nanostructured interfaces between open-shell molecules and metal surfaces by applying hybrid DFT calculations using the HSE06 functional. The presence of different magnetic configurations in a specific DFT calculation can impact important observables for such systems, which is significant because such calculations are often used to support the interpretation of experimental results. To this end, we studied CuPc and CoPc molecules adsorbed on Ag(111), which are interesting cases to address this question. First, these Pc molecules bear an unpaired spin already in their gas-phase ground-state configuration. Second, adsorption on Ag results in charge transfer to the molecule, where it is *a priori* unclear which magnetic configuration will be stabilized at the interface.

For CuPc on Ag, we obtained three different configurations for which the intrinsic magnetic moment of the molecule was either quenched, preserved, or enhanced upon the charging of the molecule by the transfer of about one electron upon adsorption. We analyzed these configurations and compared the results to gas-phase calculations and to previous experimental data. The most stable solutions found at the surface were a triplet and a doublet scenario. For CoPc on Ag, we also found two stable configurations, both of which imply quenching of the total magnetic moment of the molecule, again in agreement with previous experiments. Notably, their electronic structures were found to be very different, since the charge transferred from the substrate of about one electron resulted either in a closed-shell or an open-shell singlet scenario. In the latter, the spins on the Co and ligand aligned antiparallel to each other, which is in contrast to the triplet situation of CuPc-Ag. While both configurations exhibited very similar total energies, it was found that the experimentally accessible spin polarization is vastly different for the two configurations. These important differences in the configurations appearing for CuPc and CoPc on Ag were explained in terms of differences in the microscopic mechanism of molecule-metal interactions, mediated by the Co-centered *d* orbitals, which

promoted strong interactions of the central metal atom with the substrate in case of CoPc. This suggests that different types of orbitals are involved in the molecule-metal interactions in the two cases, which leads to different magnetic configurations appearing for CuPc and CoPc when adsorbed on Ag.

Finally, the question raised initially, as to whether DFT calculations can be used to disentangle the different magnetic configurations of surface-adsorbed open-shell molecules, has to be addressed with care. For the specific cases considered in our work, a hybrid functional was found to be a suitable approach for calculating magnetic observables, especially since the theoretical data were found to be in broad agreement with experimental findings. However, we also observed that using the PBE functional did not provide the full picture of interface magnetic properties. While it provided results very similar to those of HSE06 for the calculated work function, it omitted one of the spin configurations for each of the systems. Furthermore, at the level of both PBE and HSE06 the description of correlation effects in the electronic structure is achieved by means of a semilocal approximation, which could be insufficient for other cases of open-shell molecules on metals. Therefore, whether or not DFT is suitable for reliably calculating magnetic properties of certain molecule-metal interfaces not only depends on the specifics of the system, but also on the approximate density functional in use as well as on the specific observable one is interested in. Careful investigations of these aspects are especially relevant for more complicated cases such as transition-metal phthalocyanines, where several unpaired spins can coexist on one molecule.

ACKNOWLEDGMENTS

Fruitful discussions with Peter Puschnig, Daniel Lüftner (both at the University of Graz), and Achim Schöll (University of Würzburg) are acknowledged. We acknowledge support from the Deutsche Forschungsgemeinschaft within SFB 1277 (Project B01). Financial support through FWF Project P27868-N36 is also gratefully acknowledged. Funding provided by the Alexander von Humboldt Foundation within the framework of the Sofja Kovalevskaja Award, endowed by the German Federal Ministry of Education and Research, is also acknowledged. D.A.E. is further supported by the Technical University of Munich – Institute for Advanced Study, funded by the German Excellence Initiative and the European Union Seventh Framework Programme under Grant Agreement No. 291763. The presented computational results were obtained in part using the Vienna Scientific Cluster VSC3.

-
- [1] L. Bogani and W. Wernsdorfer, Molecular spintronics using single-molecule magnets, *Nat. Mater.* **7**, 179 (2008).
 [2] N. Ishikawa, Phthalocyanine-based magnets, in *Functional Phthalocyanine Molecular Materials*, edited by J. Jiang, Structure and Bonding Vol. 135 (Springer-Verlag Berlin Heidelberg, 2010), pp. 211–228.
 [3] A. Stróżecka, M. Soriano, J. I. Pascual, and J. J. Palacios, Reversible Change of the Spin State in a Manganese

Phthalocyanine by Coordination of CO Molecules, *Phys. Rev. Lett.* **109**, 147202 (2012).

- [4] L. Liu, K. Yang, Y. Jiang, B. Song, W. Xiao, L. Li, H. Zhou, Y. Wang, S. Du, M. Ouyang *et al.*, Reversible single spin control of individual magnetic molecule by hydrogen atom adsorption, *Sci. Rep.* **3**, 1210 (2013).
 [5] C. Nistor, C. Krull, A. Mugarza, S. Stepanow, C. Stamm, M. Soares, S. Klyatskaya, M. Ruben, and P. Gambardella,

- Exchange bias of TbPc₂ molecular magnets on antiferromagnetic FeMn and ferromagnetic Fe films, *Phys. Rev. B* **92**, 184402 (2015).
- [6] F. A. Ma'Mari, T. Moorsom, G. Teobaldi, W. Deacon, T. Prokscha, H. Luetkens, S. Lee, G. E. Sterbinsky, D. A. Arena, D. A. MacLaren *et al.*, Beating the Stoner criterion using molecular interfaces, *Nature (London)* **524**, 69 (2015).
- [7] D. E. Bürgler, V. Heß, T. Esat, S. Fahrenndorf, F. Matthes, C. M. Schneider, C. Besson, K. Y. Monakhov, P. Kögerler, A. Ghisolfi *et al.*, Spin-hybrids: A single-molecule approach to spintronics, *e-J. Surf. Sci. Nanotechnol.* **14**, 17 (2016).
- [8] D. van Vörden, M. Lange, J. Schaffert, M. C. Cottin, M. Schmuck, R. Robles, H. Wende, C. A. Bobisch, and R. Möller, Surface-induced dechlorination of FeOEP-Cl on Cu(111), *ChemPhysChem* **14**, 3472 (2013).
- [9] T. Esat, T. Deilmann, B. Lechtenberg, C. Wagner, P. Krüger, R. Temirov, F. B. Anders, M. Rohlfing, and F. S. Tautz, Transferring spin into an extended Pi orbital of a large molecule, *Phys. Rev. B* **91**, 144415 (2015).
- [10] D. Rakhmievitch, S. Sarkar, O. Bitton, L. Kronik, and O. Tal, Enhanced magnetoresistance in molecular junctions by geometrical optimization of spin-selective orbital hybridization, *Nano Lett.* **16**, 1741 (2016).
- [11] S. Sanvito, Molecular spintronics, *Chem. Soc. Rev.* **40**, 3336 (2011).
- [12] C. Iacovita, M. V. Rastei, B. W. Heinrich, T. Brumme, J. Kortus, L. Limot, and J. P. Bucher, Visualizing the Spin of Individual Cobalt-Phthalocyanine Molecules, *Phys. Rev. Lett.* **101**, 116602 (2008).
- [13] E. Annese, J. Fujii, I. Vobornik, G. Panaccione, and G. Rossi, Control of the magnetism of cobalt phthalocyanine by a ferromagnetic substrate, *Phys. Rev. B* **84**, 174443 (2011).
- [14] Y.-S. Fu, Q.-K. Xue, and R. Wiesendanger, Spin-Resolved Splitting of Kondo Resonances in the Presence of RKKY-Type Coupling, *Phys. Rev. Lett.* **108**, 087203 (2012).
- [15] E. Annese, C. E. ViolBarbosa, G. Rossi, and J. Fujii, CoPc 2D and 1D arrangement on a ferromagnetic surface, *Langmuir* **32**, 5300 (2016).
- [16] I. R. Reddy, P. M. Oppeneer, and K. Tarafder, Interfacial spin manipulation of nickel-quinonoid complex adsorbed on Co(001) substrate, *Magnetochemistry* **5**, 2 (2019).
- [17] N. Atodiresei, J. Brede, P. Lazić, V. Caciuc, G. Hoffmann, R. Wiesendanger, and S. Blügel, Design of the Local Spin Polarization at the Organic-Ferromagnetic Interface, *Phys. Rev. Lett.* **105**, 066601 (2010).
- [18] S. Stepanow, A. Mugarza, G. Ceballos, P. Moras, J. C. Cezar, C. Carbone, and P. Gambardella, Giant spin and orbital moment anisotropies of a Cu-phthalocyanine monolayer, *Phys. Rev. B* **82**, 014405 (2010).
- [19] A. Mugarza, R. Robles, C. Krull, R. Korytár, N. Lorente, and P. Gambardella, Electronic and magnetic properties of molecule-metal interfaces: Transition-metal phthalocyanines adsorbed on Ag(100), *Phys. Rev. B* **85**, 155437 (2012).
- [20] H. Wende, M. Bernien, J. Luo, C. Sorg, N. Ponpandian, J. Kurde, J. Miguel, M. Piantek, X. Xu, P. Eckhold *et al.*, Substrate-induced magnetic ordering and switching of iron porphyrin molecules, *Nat. Mater.* **6**, 516 (2007).
- [21] J. Brede, N. Atodiresei, S. Kuck, P. Lazić, V. Caciuc, Y. Morikawa, G. Hoffmann, S. Blügel, and R. Wiesendanger, Spin- and Energy-Dependent Tunneling Through a Single Molecule with Intramolecular Spatial Resolution, *Phys. Rev. Lett.* **105**, 047204 (2010).
- [22] A. Zhao, Q. Li, L. Chen, H. Xiang, W. Wang, S. Pan, B. Wang, X. Xiao, J. Yang, J. G. Hou *et al.*, Controlling the Kondo effect of an adsorbed magnetic ion through its chemical bonding, *Science* **309**, 1542 (2005).
- [23] L. Gao, W. Ji, Y. B. Hu, Z. H. Cheng, Z. T. Deng, Q. Liu, N. Jiang, X. Lin, W. Guo, S. X. Du *et al.*, Site-Specific Kondo Effect at Ambient Temperatures in Iron-Based Molecules, *Phys. Rev. Lett.* **99**, 106402 (2007).
- [24] Y.-S. Fu, S.-H. Ji, X. Chen, X.-C. Ma, R. Wu, C.-C. Wang, W.-H. Duan, X.-H. Qiu, B. Sun, P. Zhang *et al.*, Manipulating the Kondo Resonance through Quantum Size Effects, *Phys. Rev. Lett.* **99**, 256601 (2007).
- [25] A. Mugarza, C. Krull, R. Robles, S. Stepanow, G. Ceballos, and P. Gambardella, Spin coupling and relaxation inside molecule—Metal contacts, *Nat. Commun.* **2**, 490 (2011).
- [26] S. Stepanow, P. S. Miedema, A. Mugarza, G. Ceballos, P. Moras, J. C. Cezar, C. Carbone, F. M. F. de Groot, and P. Gambardella, Mixed-Valence Behavior and Strong Correlation Effects of Metal Phthalocyanines Adsorbed on Metals, *Phys. Rev. B* **83**, 220401 (2011).
- [27] E. Salomon, P. Amsalem, N. Marom, M. Vondracek, L. Kronik, N. Koch, and T. Angot, Electronic structure of CoPc adsorbed on Ag(100): Evidence for molecule-substrate interaction mediated by Co 3d orbitals, *Phys. Rev. B* **87**, 075407 (2013).
- [28] Y. L. Huang, E. Wruss, D. A. Egger, S. Kera, N. Ueno, W. A. Saidi, T. Bucko, A. T. S. Wee, and E. Zojer, Understanding the adsorption of CuPc and ZnPc on noble metal surfaces by combining quantum-mechanical modelling and photoelectron spectroscopy, *Molecules* **19**, 2969 (2014).
- [29] V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, Density-Functional Theory with Screened van Der Waals Interactions for the Modeling of Hybrid Inorganic-Organic Systems, *Phys. Rev. Lett.* **108**, 146103 (2012).
- [30] D. A. Egger, V. G. Ruiz, W. A. Saidi, T. Bučko, A. Tkatchenko, and E. Zojer, Understanding structure and bonding of multi-layered metal—Organic nanostructures, *J. Phys. Chem. C* **117**, 3055 (2013).
- [31] M. Willenbockel, R. J. Maurer, C. Bronner, M. Schulze, B. Stadtmüller, S. Soubatch, P. Tegeder, K. Reuter, and F. Stefan Tautz, Coverage-driven dissociation of azobenzene on Cu(111): A route towards defined surface functionalization, *Chem. Commun.* **51**, 15324 (2015).
- [32] W. Liu, F. Maaß, M. Willenbockel, C. Bronner, M. Schulze, S. Soubatch, F. S. Tautz, P. Tegeder, and A. Tkatchenko, Quantitative Prediction of Molecular Adsorption: Structure and Binding of Benzene on Coinage Metals, *Phys. Rev. Lett.* **115**, 036104 (2015).
- [33] R. J. Maurer, C. Freysoldt, A. M. Reilly, J. G. Brandenburg, O. T. Hofmann, T. Björkman, S. Lebègue, and A. Tkatchenko, Advances in Density-Functional Calculations for Materials Modeling, *Annu. Rev. Mater. Res.* **49**, 1 (2019).
- [34] C. Draxl, D. Nabok, and K. Hannewald, Organic/inorganic hybrid materials: Challenges for ab initio methodology, *Acc. Chem. Res.* **47**, 3225 (2014).
- [35] L. Kronik and Y. Morikawa, Understanding the metal-molecule interface from first principles, in *The*

- Molecule-Metal Interface*, edited by N. Ueno and A. T. S. Wee (Wiley-VCH, Weinheim, Germany, 2013), pp. 51–89.
- [36] A. Mugarza, N. Lorente, P. Ordejón, C. Krull, S. Stepanow, M.-L. Bocquet, J. Fraxedas, G. Ceballos, and P. Gambardella, Orbital Specific Chirality and Homochiral Self-Assembly of Achiral Molecules Induced by Charge Transfer and Spontaneous Symmetry Breaking, *Phys. Rev. Lett.* **105**, 115702 (2010).
- [37] S. Stepanow, A. Lodi Rizzini, C. Krull, J. Kavich, J. C. Cezar, F. Yakhou-Harris, P. M. Sheverdyeva, P. Moras, C. Carbone, G. Ceballos *et al.*, Spin tuning of electron-doped metal–Phthalocyanine layers, *J. Am. Chem. Soc.* **136**, 5451 (2014).
- [38] C. Krull, R. Roberto, A. Mugarza, and P. Gambardella, Site- and orbital-dependent charge donation and spin manipulation in electron-doped metal phthalocyanines, *Nat. Mater.* **12**, 337 (2013).
- [39] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Insights into current limitations of density functional theory, *Science* **321**, 792 (2008).
- [40] Sala Fabio Della, Fabiano Eduardo, Laricchia Savio, D’Agostino Stefania, and Piacenza Manuel, The Role of exact-exchange in the theoretical description of organic-metal interfaces, *Int. J. Quantum Chem.* **110**, 2162 (2010).
- [41] V. Atalla, I. Y. Zhang, O. T. Hofmann, X. Ren, P. Rinke, and M. Scheffler, Enforcing the linear behavior of the total energy with hybrid functionals: Implications for charge transfer, interaction energies, and the random-phase approximation, *Phys. Rev. B* **94**, 035140 (2016).
- [42] N. Marom and L. Kronik, Density functional theory of transition metal phthalocyanines, I. Electronic structure of NiPc and CoPc—Self-interaction effects, *Appl. Phys. A* **95**, 159 (2008).
- [43] N. Marom, O. Hod, G. E. Scuseria, and L. Kronik, Electronic structure of copper phthalocyanine: A comparative density functional theory study, *J. Chem. Phys.* **128**, 164107 (2008).
- [44] N. Dori, M. Menon, L. Kilian, M. Sokolowski, L. Kronik, and E. Umbach, Valence electronic structure of gas-phase 3,4,9,10-perylene tetracarboxylic acid dianhydride: Experiment and theory, *Phys. Rev. B* **73**, 195208 (2006).
- [45] P. Puschnig, A. D. Boese, M. Willenbockel, M. Meyer, D. Lüftner, E. M. Reinisch, T. Ules, G. Koller, S. Soubatch, M. G. Ramsey *et al.*, Energy ordering of molecular orbitals, *J. Phys. Chem. Lett.* **8**, 208 (2016).
- [46] P. Puschnig, E.-M. Reinisch, T. Ules, G. Koller, S. Soubatch, M. Ostler, L. Romaner, F. S. Tautz, C. Ambrosch-Draxl, and M. G. Ramsey, Orbital tomography: Deconvoluting photoemission spectra of organic molecules, *Phys. Rev. B* **84**, 235427 (2011).
- [47] D. Lüftner, S. Refaely-Abramson, M. Pachler, R. Resel, M. G. Ramsey, L. Kronik, and P. Puschnig, Experimental and theoretical electronic structure of quinacridone, *Phys. Rev. B* **90**, 075204 (2014).
- [48] T. Körzdörfer, S. Kümmel, N. Marom, and L. Kronik, When to trust photoelectron spectra from Kohn-Sham eigenvalues: The case of organic semiconductors, *Phys. Rev. B* **79**, 201205 (2009).
- [49] D. A. Egger, Z.-F. Liu, J. B. Neaton, and L. Kronik, Reliable energy level alignment at physisorbed molecule–Metal interfaces from density functional theory, *Nano Lett.* **15**, 2448 (2015).
- [50] F. Rissner, D. A. Egger, A. Natan, T. Körzdörfer, S. Kümmel, L. Kronik, and E. Zojer, Collectively induced quantum-confined Stark effect in monolayers of molecules consisting of polar repeating units, *J. Am. Chem. Soc.* **133**, 18634 (2011).
- [51] B. Himmetoglu, A. Floris, S. de Gironcoli, and M. Cococcioni, Hubbard-corrected DFT energy functionals: The LDA+U description of correlated systems, *Int. J. Quantum Chem.* **114**, 14 (2014).
- [52] D. A. Scherlis, M. Cococcioni, P. Sit, and N. Marzari, Simulation of Heme using DFT + U: A step toward accurate spin-state energetics, *J. Phys. Chem. B* **111**, 7384 (2007).
- [53] H. J. Kulik and N. Marzari, Transition-metal dioxides: A case for the intersite term in Hubbard-model functionals, *J. Chem. Phys.* **134**, 094103 (2011).
- [54] J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B* **23**, 5048 (1981).
- [55] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Many-electron self-interaction error in approximate density functionals, *J. Chem. Phys.* **125**, 201102 (2006).
- [56] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Challenges for density functional theory, *Chem. Rev.* **112**, 289 (2012).
- [57] M. Reiher, O. Salomon, and B. Artur Hess, Reparameterization of hybrid functionals based on energy differences of states of different multiplicity, *Theor. Chem. Acc.* **107**, 48 (2001).
- [58] R. Poli and J. N. Harvey, Spin forbidden chemical reactions of transition metal compounds, New ideas and new computational challenges, *Chem. Soc. Rev.* **32**, 1 (2003).
- [59] A. Droghetti, D. Alfè, and S. Sanvito, Assessment of density functional theory for Iron(II) molecules across the spin-crossover transition, *J. Chem. Phys.* **137**, 124303 (2012).
- [60] E. I. Ioannidis and H. J. Kulik, Towards quantifying the role of exact exchange in predictions of transition metal complex properties, *J. Chem. Phys.* **143**, 034104 (2015).
- [61] M. Swart and M. Gruden, Spinning around in transition-metal chemistry, *Acc. Chem. Res.* **49**, 2690 (2016).
- [62] E. I. Ioannidis and H. J. Kulik, Ligand-field-dependent behavior of Meta-GGA exchange in transition-metal complex spin-state ordering, *J. Phys. Chem. A* **121**, 874 (2017).
- [63] J. J. Phillips and J. E. Peralta, The role of range-separated Hartree-Fock exchange in the calculation of magnetic exchange couplings in transition metal complexes, *J. Chem. Phys.* **134**, 034108 (2011).
- [64] M. Schmid, A. Kaftan, H.-P. Steinrück, and J. M. Gottfried, The electronic structure of cobalt(II) phthalocyanine adsorbed on Ag(111), *Surf. Sci.* **606**, 945 (2012).
- [65] S. Thussing and P. Jakob, Structural and vibrational properties of CuPc/Ag(111) ultrathin films, *J. Phys. Chem. C* **120**, 9904 (2016).
- [66] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, *Ab initio* molecular simulations with numeric atom-centered orbitals, *Comput. Phys. Commun.* **180**, 2175 (2009).
- [67] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, *J. Chem. Phys.* **118**, 8207 (2003).
- [68] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, *J. Chem. Phys.* **124**, 219906(E) (2006).

- [69] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* **77**, 3865 (1996); **78**, 1396(E) (1997).
- [70] N. Marom and L. Kronik, Density functional theory of transition metal phthalocyanines, II. Electronic structure of MnPc and FePc—Symmetry and symmetry breaking, *Appl. Phys. A* **95**, 165 (2009).
- [71] G. Prokopiou and L. Kronik, Spin-state energetics of Fe complexes from an optimally tuned range-separated hybrid functional, *Chem. – Eur. J.* **24**, 5173 (2018).
- [72] A. Tkatchenko and M. Scheffler, Accurate Molecular Van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data, *Phys. Rev. Lett.* **102**, 073005 (2009).
- [73] J. Neugebauer and M. Scheffler, Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111), *Phys. Rev. B* **46**, 16067 (1992).
- [74] F. L. Hirshfeld, Bonded-atom fragments for describing molecular charge densities, *Theor. Chim. Acta* **44**, 129 (1977).
- [75] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevMaterials.3.086002> for structural representation of the surface unit cells and results from additional calculations performed for the interface and gas-phase systems.
- [76] I. Kröger, B. Stadtmüller, C. Stadler, J. Ziroff, M. Kochler, Andreas Stahl, F. Pollinger, T.-L. Lee, J. Zegenhagen, F. Reinert *et al.*, Submonolayer growth of copper-phthalocyanine on Ag(111), *New J. Phys.* **12**, 083038 (2010).
- [77] M. Marsman, J. Paier, A. Stroppa, and G. Kresse, Hybrid functionals applied to extended systems, *J. Phys.: Condens. Matter* **20**, 064201 (2008).
- [78] B. Stadtmüller, I. Kröger, F. Reinert, and C. Kumpf, Submonolayer growth of CuPc on noble metal surfaces, *Phys. Rev. B* **83**, 085416 (2011).
- [79] J. D. Baran, J. A. Larsson, R. A. J. Woolley, Y. Cong, P. J. Moriarty, A. A. Cafolla, K. Schulte, and V. R. Dhanak, Theoretical and experimental comparison of SnPc, PbPc, and CoPc adsorption on Ag(111), *Phys. Rev. B* **81**, 075413 (2010).
- [80] D. A. Egger, S. Weissman, S. Refaely-Abramson, S. Sharifzadeh, M. Dauth, R. Baer, S. Kümmel, J. B. Neaton, E. Zojer, and L. Kronik, Outer-valence electron spectra of prototypical aromatic heterocycles from an optimally tuned range-separated hybrid functional, *J. Chem. Theory Comput.* **10**, 1934 (2014).
- [81] I. E. Brumboiu, G. Prokopiou, L. Kronik, and B. Brena, Valence electronic structure of cobalt phthalocyanine from an optimally tuned range-separated hybrid functional, *J. Chem. Phys.* **147**, 044301 (2017).
- [82] Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng *et al.*, Advances in molecular quantum chemistry contained in the Q-Chem 4 program package, *Mol. Phys.* **113**, 184 (2015).
- [83] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations, I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* **90**, 1007 (1989).
- [84] J. Stöckl, A. Jurenkow, N. Großmann, M. Cinchetti, B. Stadtmüller, and M. Aeschlimann, Spin- and angle-resolved photoemission study of the Alq₃/Co interface, *J. Phys. Chem. C* **122**, 6585 (2018).
- [85] F. Djeghloul, F. Ibrahim, M. Cantoni, M. Bowen, L. Joly, S. Boukari, P. Ohresser, F. Bertran, P. Le Fèvre, P. Thakur *et al.*, Direct observation of a highly spin-polarized organic spinterface at room temperature, *Sci. Rep.* **3**, 1272 (2013).
- [86] N. Atodiresei and K. V. Raman, Interface-assisted spintronics: tailoring at the molecular scale, *MRS Bull.* **39**, 596 (2014).
- [87] I. E. Brumboiu, S. Haldar, J. Lüder, O. Eriksson, H. C. Herper, B. Brena, and B. Sanyal, Influence of electron correlation on the electronic structure and magnetism of transition-metal phthalocyanines, *J. Chem. Theory Comput.* **12**, 1772 (2016).
- [88] J. Kügel, M. Karolak, J. Senkpiel, P.-J. Hsu, G. Sangiovanni, and M. Bode, Relevance of hybridization and filling of 3d orbitals for the Kondo effect in transition metal phthalocyanines, *Nano Lett.* **14**, 3895 (2014).
- [89] B. Siegert, A. Donarini, and M. Grifoni, Nonequilibrium spin crossover in copper phthalocyanine, *Phys. Rev. B* **93**, 121406 (2016).
- [90] M. Rumetshofer, D. Bauernfeind, E. Arrigoni, and W. von der Linden, First-principles quantum transport simulation of CuPc on Au(111) and Ag(111), *Phys. Rev. B* **99**, 045148 (2019).
- [91] J. D. Baran and J. A. Larsson, Theoretical insights into adsorption of cobalt phthalocyanine on Ag(111): A combination of chemical and Van der Waals bonding, *J. Phys. Chem. C* **117**, 23887 (2013).
- [92] Z. Li, B. Li, J. Yang, and J. G. Hou, Single-molecule chemistry of metal phthalocyanine on noble metal surfaces, *Acc. Chem. Res.* **43**, 954 (2010).
- [93] J. Paier, M. Marsman, and G. Kresse, Why does the B3LYP hybrid functional fail for metals? *J. Chem. Phys.* **127**, 024103 (2007).
- [94] M. Chelvayohan and C. H. B. Mee, Work function measurements on (110), (100), and (111) surfaces of silver, *J. Phys. C: Solid State Phys.* **15**, 2305 (1982).
- [95] N. Marom, X. Ren, J. E. Moussa, J. R. Chelikowsky, and L. Kronik, Electronic structure of copper phthalocyanine from G₀W₀ calculations, *Phys. Rev. B* **84**, 195143 (2011).
- [96] S. Refaely-Abramson, S. Sharifzadeh, N. Govind, J. Autschbach, J. B. Neaton, R. Baer, and L. Kronik, Quasiparticle Spectra from a Nonempirical Optimally Tuned Range-Separated Hybrid Density Functional, *Phys. Rev. Lett.* **109**, 226405 (2012).
- [97] O. S. Bokareva, T. Möhle, A. Neubauer, S. I. Bokarev, S. Lochbrunner, and O. Kühn, Chemical tuning and absorption properties of iridium photosensitizers for photocatalytic applications, *Inorganics* **5**, 23 (2017).
- [98] P. Gargiani, M. Angelucci, C. Mariani, and M. G. Betti, Metal-phthalocyanine chains on the Au(110) surface: Interaction states versus d-metal states occupancy, *Phys. Rev. B* **81**, 085412 (2010).
- [99] Z. Hu, B. Li, A. Zhao, J. Yang, and J. G. Hou, Electronic and magnetic properties of metal phthalocyanines on Au(111) surface: A first-principles study, *J. Phys. Chem. C* **112**, 13650 (2008).
- [100] O. T. Hofmann, V. Atalla, N. Moll, P. Rinke, and M. Scheffler, Interface dipoles of organic molecules on Ag(111) in hybrid density-functional theory, *New J. Phys.* **15**, 123028 (2013).
- [101] D. Jacob, M. Soriano, and J. J. Palacios, Kondo effect and spin quenching in high-spin molecules on metal substrates, *Phys. Rev. B* **88**, 134417 (2013).
- [102] J. Kügel, M. Karolak, A. Krönlein, J. Senkpiel, P.-J. Hsu, G. Sangiovanni, and M. Bode, State identification and tunable

- Kondo effect of MnPc on Ag(001), *Phys. Rev. B* **91**, 235130 (2015).
- [103] A. Droghetti and I. Rungger, Quantum transport simulation scheme including strong correlations and its application to organic radicals adsorbed on gold, *Phys. Rev. B* **95**, 085131 (2017).
- [104] G. Ganzenmüller, N. Berkäine, A. Fouqueau, M. E. Casida, and M. Reiher, Comparison of density functionals for differences between the high- (T_{2g}) and low- (A_{1g}) spin states of iron(II) compounds, IV. Results for the ferrous complexes [Fe(L)(‘NHS4’)], *J. Chem. Phys.* **122**, 234321 (2005).
- [105] S. R. Mortensen and K. P. Kepp, Spin propensities of octahedral complexes from density functional theory, *J. Phys. Chem. A* **119**, 4041 (2015).
- [106] A. Calzolari, A. Ferretti, and M. B. Nardelli, Ab initio correlation effects on the electronic and transport properties of metal(II)-phthalocyanine-based devices, *Nanotechnology* **18**, 424013 (2007).
- [107] T. Z. H. Gani and H. J. Kulik, Where does the density localize? Convergent behavior for global hybrids, range separation, and DFT+U, *J. Chem. Theory Comput.* **12**, 5931 (2016).
- [108] A. Biller, I. Tamblyn, J. B. Neaton, and L. Kronik, Electronic level alignment at a metal-molecule interface from a short-range hybrid functional, *J. Chem. Phys.* **135**, 164706 (2011).
- [109] Z.-F. Liu, D. A. Egger, S. Refaely-Abramson, L. Kronik, and J. B. Neaton, Energy level alignment at molecule-metal interfaces from an optimally tuned range-separated hybrid functional, *J. Chem. Phys.* **146**, 092326 (2017).