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Effects of electric field on a copper–dioxolene complex adsorbed on a gold surface

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ABSTRACT

A model of a copper–dioxolene complex linked to Au(1 1 1) surface with butanethiol linker is investigated using first-principles methods. It is shown that the complex adsorbed at the surface may appear in various locally stable structural forms differing in electron charge and spin density distribution, the symmetric high spin (HS) one and the twisted low spin (LS) structure. The electric field directed perpendicular to the surface controls the amount of the charge transfer between the complex and the substrate, starting from the zero-field value of $Q = +0.18\,|e|$ up to the value of $Q = +0.94\,|e|$ for the field strength of $E = 0.5$ V/Å. The field modifies also the mutual stability of the two structural forms, reducing the energy gap between the more energetically stable LS twisted form and the symmetrical HS one, from a value of $\Delta \sim 0.29$ eV in absence of the field to $\Delta \sim 0.11$ eV for the field strength of $E = 0.35$ V/Å.

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1. Introduction

The dioxolene complexes with transition metals for quite a time remain a rich field of studies in chemistry, physics and biology (for the reviews, see Refs. [1–3]). The special role of dioxolenes derivatives in metalorganic systems follows from the fact that they can behave as noninnocent ligands [4], coordinating to metal atoms in multiple oxidation states. Under favorable conditions the transfer of charge from the dioxolene ligand to the coordinated metal atom is possible because of a small energy difference between different valence states, and it is a manifestation of the valence tautomerism [5,6]. This easiness of changing the oxidation as well as the spin state of the coordinated metals is crucial for biochemical activity of these ligands [7], moreover it may be important for nanotechnological applications of these compounds. An interesting case is the Co–dioxolene complex where a transfer from the low-spin (LS) Co(III) state to the high-spin (HS) Co(II) state of the cobalt atom is observed with a rise of temperature or under influence of soft X-rays [8,9]. Another example is a Cu–dioxolene complex where a transfer from the Cu(II)-catecholate to the Cu(I)-semiquinone form is indicated by a change of the EPR signal with temperature [10]. Relatively recently, the studies stressing the potential of using the specific properties of dioxolene complexes in the technology of spintronics and molecular electronics [11–15] began to appear. In these works various dioxolene compounds interacting with surfaces of solids were studied [16–20].

A general understanding of the electronic and magnetic structure of the dioxolene complexes is supported by numerous first principles calculations [21–27]. So far the analyses were dealing mostly with free complexes either in the electrically neutral state or in the ionic one, corresponding to the situations in a solvent or in a solid state. Relatively less attention was devoted to investigations of dioxolene complexes at surfaces [18] or forming molecular junctions [28].

Recently we theoretically studied a simplified model of a Cu–dioxolene complex connected to a gold surface with alkanethiol linkers of various lengths [29], investigating the modifications of the molecule's properties by the contact with the metallic solid. Here we extend the previous work by considering the effects of the electric field perpendicular to the surface. We aim to evaluate a possibility of controlling the electron charge transfer between the molecule and the metallic substrate with the accessible electric field. We expect that using the field one may determine the charge redistribution within the functional group, possibly inducing the tautomeric changes within the molecule, modifying its molecular structure and the magnetic moment. The ability of changing these properties with the field is of central importance for application of the complex in molecular electronic devices, such as memory cells or molecular switches [30,31].

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2. The model of the system and details of calculations

We consider here a model of a Cu–dioxolene complex in which Cu atom is bound to a dioxolene unit by means of two oxygen atoms (Fig. 1). Two ammonia groups are connected to Cu atom on the opposite side of the dioxolene. They make a simplified representation of a co-ligand group, typically a derivative of bipyridine, binding to Cu atoms by means of two nitrogen atoms. The reference structure of the complex belongs to C_{2v} symmetry group and its electronic and spatial structure was studied earlier by other authors [22]. The model system studied here may be considered as a simplified representation of bipyridynium-Cu-di-*t*-3,5-butyl-benzoquinone studied in experiment.

Starting from the free form of the complex we subsequently create a model of the Cu–dioxolene molecule bound to the gold (1 1 1) surface with a butanethiol linker. The butanethiol chain is connected with its end carbon atom at position 3 of the benzene ring of the dioxolene part. The sulfur head of the linker is initially placed at the Au(1 1 1) surface near a hollow position and we observe that it gradually moves into the bridge position in the course of the structure optimizations. Such binding to the surface is typical to self-assembled monolayers (SAM) [33] where the complex play a role of a functional group. A SAM with a related Cu–dioxolene complex is also known from an experiment [34].

The computations were performed using the density functional theory (DFT) method with a help of SIESTA package [35]. The advantage of the code in analysis of the nanostructures comes from the fact that it uses finite range basis function and implements pseudopotential to reduce number of the electronic degrees of freedom. In the computations we used generalized gradient approximation (GGA) in the Perdew–Burke–Erzenhof (PBE) parametrization [36]. The PBE model works fairly well in metalorganic systems, as it was shown by the extensive computational tests comparing effectiveness of many exchange–correlation (XC) potential models [37]. However GGA, as a quasilocal approximation to the XC potential, is known to suffer from the so-called self-interaction (SI) error. This inaccuracy is particularly severe in magnetic systems with strongly interacting electrons, where it often leads to underestimation of the quasiparticle energy gaps at the Fermi level and too small results for the local magnetic moments. Various orbital-dependent hybrid functionals, including proper admixtures of the Fock exchange, are commonly applied to reduce the SI error. Alternatively, one can use the GGA+U method [38] to the similar effect [40,41]. In the SIESTA implementation the latter method is not much more computationally demanding than the regular GGA one, and for this reason we use GGA+U approach in the present paper. This method consists in dividing the electrons in the system into weakly correlated (usually *s*, *p* electrons) and strongly correlated (in our case: *d* electrons) ones. The XC potential for the strongly interacting electrons are next corrected with a Hubbard-type term treated in the HF approximation and takes a form:

$$E_{\mathrm{GGA+U}}[\rho(\vec{r})] = E_{\mathrm{GGA}}[\rho(\vec{r})] + E_{\mathrm{Hubbard}}[\{n^{\sigma}\}] - E_{\mathrm{DC}}[\{n^{\sigma}\}] \tag{1}$$

where $\rho(\vec{r})$ is the electron charge density and $\{n^{\sigma}\}$ is the reduced density matrix for *d*-electrons, E_{GGA} is the GGA functional, E_{Hubbard} denotes the Hubbard-like functional, and E_{DC} is the double-counting correction, eliminating the contribution from the *d* electrons already included in E_{GGA}. The contribution of the Hubbard term to the XC potential results in the shift of one-particle energy levels of the strongly interacting electrons [39]:

$$\epsilon^{\mathrm{GGA+U}}_{m\sigma} = \epsilon^{\mathrm{GGA}}_{m\sigma} + U\left(\frac{1}{2} - n_{m\sigma}\right) \tag{2}$$

where $n_{m\sigma}$ is the GGA+U orbital occupation. The effective Hubbard-*U* parameter can be obtained from a constrained DFT computations [41]. Another common approach consists in adjusting *U* to reproduce experimental data for studied systems. In the present paper we resort to the latter option, using results of GGA+U computations for a series of binuclear copper complexes of Ref. [40]. This study showed that the value $U = 6$ eV provided a good fit of the magnetic coupling constant in the studied compounds, and ensured a good agreement with the results based on B3LYP hybrid XC potential. For this reason we use $U = 6$ eV value in all our GGA+U computations.

We applied Troullier–Martins [43] norm conserving pseudopotential in scalar relativistic version for core electrons and with nonlinear core corrections [29]. For all the atoms in the system we used a double-zeta polarized (DZP) basis functions with a splitting norm 0.5 for hydrogen atoms and 0.15 for other atoms. The radius of basis functions was determined by energy shift parameter equal to 0.005 Ry. The calculations were performed using mesh cutoff parameter equal to 600 Ry and we applied grid cell sampling to reduce the egg-box effect. The convergence parameter for the density matrix was set to 10^{-4} and the electronic temperature was assumed equal to 300 K. The considered structures were relaxed with a help of the conjugate gradient (CG) method until the forces were smaller than 0.04 eV/Å.

The surface supporting the complex was represented by a gold slab consisting of four Au planes including 25 (5 × 5) Au atoms each, making 100 Au atoms in the unit cell. The structure of the slab corresponded to the one of Au FCC lattice with GGA optimized lattice constant equal to 4.18 Å. In the subsequent structure optimization we relaxed only the outermost plane of the slab and we applied the periodic transverse boundary condition. The length of

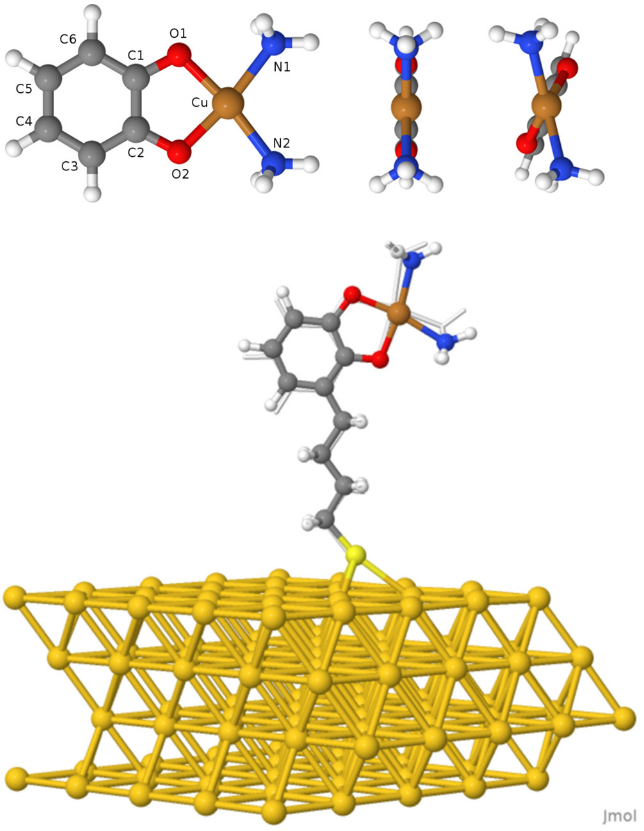

Fig. 1. Upper row: the perspective view of the spatial structure of the model of Cu–dioxolene complex in the projection perpendicular to the dioxolene plane and in the direction parallel to the plane. The first two structures in the upper row correspond to the complex in the symmetric state, the third one is for the twisted structure. Lower row: the complex adsorbed at Au(1 1 1) surface in the planarly symmetric state. With a light gray contour the structure modified by application of the electric field $\mathbf{E} = z \times 0.5$ V/Å directed perpendicular to the Au surface is shown [32].

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