Giant magnetoresistance through a single molecule

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GEOMETRY OPTIMIZATION

We used the quantum chemistry package TURBOMOLE [1] to find the atomic structure of the molecular junctions. We performed standard geometry optimization for H_2Pc on the Cu(111) surface, represented by a cluster of 65 atoms. The use of Co(111)-clusters for structure optimization is impaired by the very large number of energetically almost degenerate spin multiplets. The gradient corrected approximation (GGA [2, 3]) density functional theory (DFT) energy was amended by empirical corrections [4] to account for dispersive van der Waals interactions between the molecule and the surface. Our analysis suggests that hydrogen phthalocyanine (H_2Pc) prefers the "bridge" position (see main text, Figure 3a) with a binding energy -8.17 eV, relative to the "hollow" site position (binding energy -8.06 eV) and "atop" site position (binding energy -7.45 eV), which is consistent with earlier findings [5, 6].

ELECTRONIC STRUCTURE AND TRANSPORT CALCULATIONS THROUGH H_2PC.
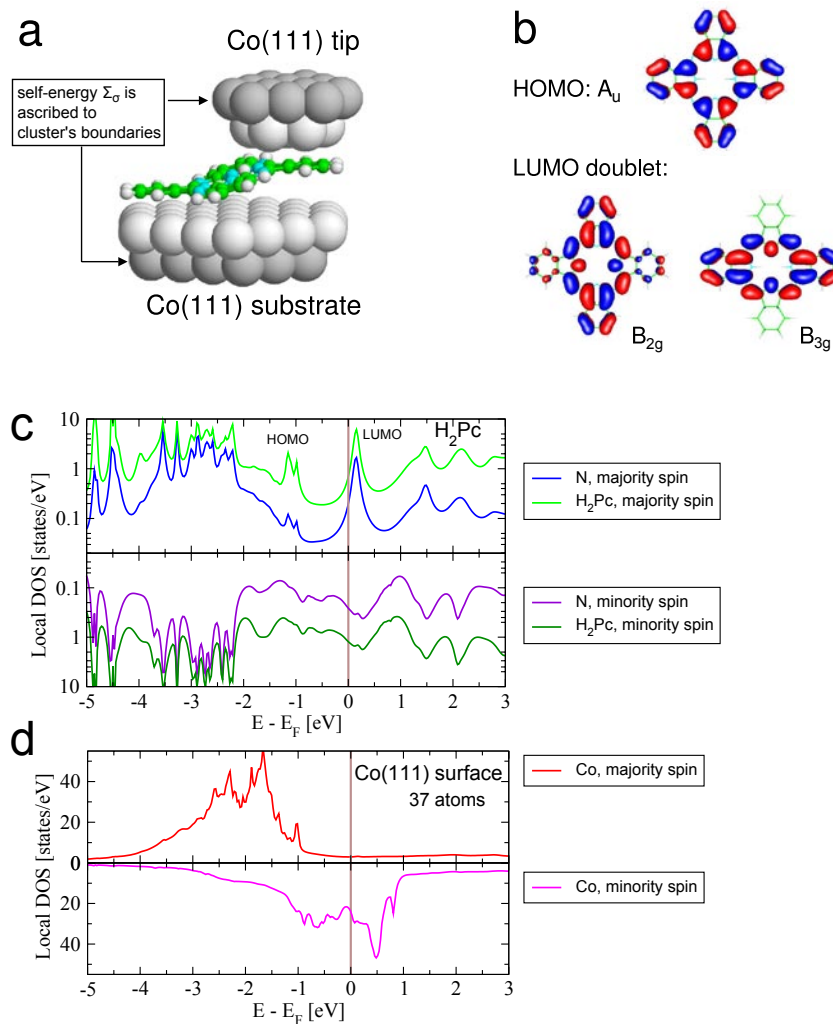
DFT based electronic structure and transport calculations through H_2Pc molecular junctions were performed within the non-equilibrium Green's function (NEGF) approach as implemented in a homemade simulation code [7] interfaced to the quantum chemistry package TURBOMOLE [1]. The atomic configuration of the "extended molecule" used to simulate the bottle-neck of the molecular junction is shown in Suppl. Fig. 1a ("contact" regime): H_2Pc is bound to the two Co(111) clusters with 51 and 19 atoms that represent the Co surface and the Co tip of the scanning tunneling microscope (STM), respectively. To establish this configuration, a free H_2Pc molecule was bent along the lowest-energy vibrational eigenmode that agrees with the experimental geometry. A similar atomic configuration with H_2Pc bound to the surface only was used for transport simulations in the tunneling regime. The GGA (BP86 functional [2, 3]) and a contracted Gaussian-type split-valence basis set with polarization functions (SVP) [8] were used for calculations.

First, a closed-shell (nonmagnetic) solution for the "extended molecule" comprising 2156 electrons was found. To account for infinite reservoirs with spin-polarized electrons, the spin-dependent ($\sigma = \pm 1/2$) local self-energies, $\Sigma_\sigma^{\text{surface/tip}}(\mathbf{x}, \mathbf{x}') = [\lambda + \sigma\Delta_{\text{ex}} - i\gamma]\,\delta(\mathbf{x} - \mathbf{x}')$, were ascribed to the outermost boundaries of the simulation cluster (dark gray atoms at Suppl. Fig. 1a). Here, a parameter $\Delta_{\text{ex}} = 1.6$ eV accounts for the exchange splitting of the bulk Co d-states [9]. The freedom to choose the sign of Δ_{ex} independently for the "surface" and "STM-tip" clusters allows us to assemble two solutions with a parallel and antiparallel alignment of the electrodes' magnetizations.

We apply the NEGF to evaluate the charge- and spin-density matrices in the presence of open boundaries, insuring a charge neutrality within the "extended molecule". The density matrices are returned to TURBOMOLE to find a modified set of Kohn-Sham orbitals, with a cycle to be repeated unless the self-consistent solution is reached. For a given value γ ($= 1.36$ eV in present calculations) of the level broadening, the contribution λ to the real part of the self-energy was defined by imposing the condition of spurious charge accumulation to be absent at the cluster's boundaries. Further details of the computational approach will be published elsewhere.

As an example, details of electronic structure for the molecular junction in the case of a parallel alignment of magnetizations are presented in Suppl. Fig. 1c,d. We have ascertained that, in our study, the electronic structure of the Co surface is properly reproduced. In particular, the electronic states at the Co-surface are spin-polarized with an exchange splitting ≈ 1.8 eV (Suppl. Fig. 1d), giving rise to an average magnetic moment $\approx 1.65\mu_B$ per a surface Co atom, in agreement with previously reported calculations [10].

Inspecting the H_2Pc local density of states (DOS) (see Suppl. Fig. 1c), we ascribe the majority spin resonance above the Fermi level (E_F) to the quasi-degenerate lowest unoccupied molecular orbital (LUMO), which is weighed significantly by nitrogen atoms (cf. Suppl. Fig. 1b). In contrast, no density is seen on nitrogen sites for the majority spin highest occupied molecular orbital (HOMO) resonance positioned at ~ 1.2 eV below E_F (Suppl. Fig. 1b). Furthermore, the minority spin H_2Pc LUMO level evolves into a broad peak due to a hybridization with the minority spin Co states, with a density near E_F that significantly exceeds that of majority spin electrons. It is the asymmetry in the LUMO level broadenings, i.e. $\Gamma^{\min} > \Gamma^{\text{maj}}$, that gives rise to the magnetoresistance effect (see main text for further details).

Suppl. Fig. 1: (a) Atomic cluster representing the bottle-neck of the H_2Pc molecular junction, as used for the electronic structure and transport calculations. The outermost boundaries of the Co cluster (dark gray) are subject to the absorbing boundary conditions modeled by the self-energy Σ_σ. (b) Frontier molecular orbitals of H_2Pc (D_{2h} symmetry): an A_u HOMO and a quasi-degenerate LUMO doublet, B_{2g} and B_{3g}. (c) and (d): spin-polarized local density of states of the H_2Pc molecule and Co(111) surface, respectively.
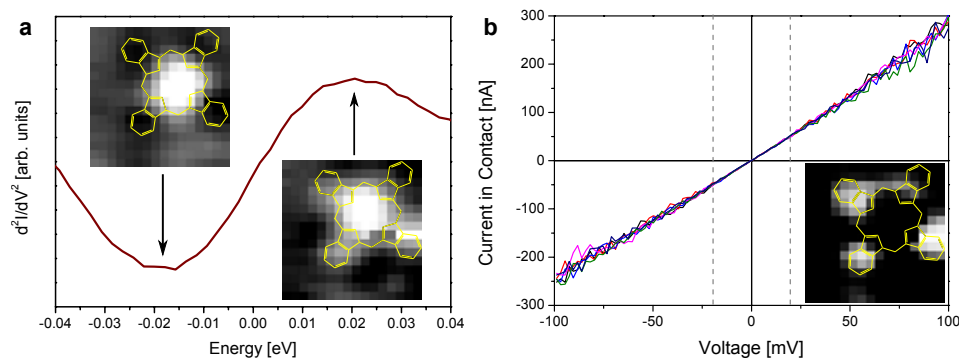
Suppl. Fig. 2: (a) d^2I/dV^2 curve for Pc [11] taken in the tunneling regime. One observes an excitation located at around 20 meV. The insets shows the d^2I/dV^2 map taken at these energies. The dip-peak structure is clearly constrained to the side groups of the molecule, visualized in the inset of (b) showing the difference of the two images. (b) $I(V)$ conductance curves measured in the contact regime, when the molecules bridge the tunnel gap. At 20 mV the noise of the curve strongly increases, indicating that the soft vibron of the molecule is excited.

SOFT VIBRON EXCITATION

We calculated the junction's geometry before and after contact. These two geometries correspond to two local minima in the energy landscape separated by an energy barrier. The transition between these two states is expected to follow the lowest energy path between the two states. Thus, the transition is related to the softest vibration mode of the molecule agreeing with the geometry. As shown in our previous work [11], the lowest-lying vibron of the molecule is at around 20 meV (see Suppl. Fig. 2a). Spatially resolved inelastic tunneling spectroscopy is also consistent with the theoretical observation, namely, that the excitation is located on the sidegroups of the molecule, indicated by a dip and peak in the spectroscopy data of the two insets of Suppl. Fig. 2a. To extract the spatial distribution of the vibron, the difference signal was taken, resulting in bright spots on the four sidegroups (inset Suppl. Fig. 2b). This soft vibron is not only responsible for forming the contact but also for breaking it. When taking the $I(V)$ in the contact geometry (see Suppl. Fig. 2b), one notices a strong increase of the current noise when exceeding the excitation threshold of 20 mV (dashed lines). This is an additional reason to acquire the giant magneto-resistance (GMR) data at voltages below 20 mV so as to reduce the current noise.

TRANSPORT MEASUREMENTS ACROSS MAGNETIC PHTHALOCYANINE MOLECULES

We also carried out GMR measurements across Co-Phthalocyanine molecules on Co thin films with Co coated tips. In contract to the case of H_2Pc molecules, we were not successful to observe any GMR effect. This may be due to two effects. First, the magnetic molecules posses a local spin on the molecule that can cause substantial spin scattering of the transport electrons destroying the spin polarization of the current. Second, if the Co molecular site is coupled ferromagnetically to both the substrate and tip as observed [12, 13] for related interfaces, it may be difficult to achieve a simple antiparallel alignment. In this case, a tunneling regime across two Co/CoPc interfaces that are decoupled by additional CoPc monolayers [14] or by vacuum [5] appears more promising.

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