Calculation of CO adsorption capacity of single iron(II)-porphyrin and related electron transfer behavior by DFT theory

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Abstract

The effect of CO adsorption on the electron transport behavior of single iron(II)-porphyrin molecular wire with sulfur end groups bonded to two gold electrodes is investigated using nonequilibrium Green's function formalism combined with first-principles density functional theory. The current-voltage characteristics of the single Fe-porphyrin molecular wires with and without CO adsorption are calculated. The results demonstrate that Fe-porphyrin molecular wire shows a negative differential resistance (NDR) at 2.0 V.

1. Introduction

As silicon technology approaches its technological and physical limits, molecular electronics has been envisioned as a promising candidate for nano-electronics in the future.¹⁻⁴ Currently, many potentially useful molecular electronic devices, such as molecular wires, molecular rectifiers, molecular resonant tunneling rectifiers, molecular switches,⁵⁻⁷ and molecular storage devices have been proposed and studied extensively at molecular level.⁸⁻¹³ Most of these molecular electronic devices consist of conjugated structure, which contain alternating single and double (or triple) bonds and facilitates the electron transport.

Protoporphyrin and its derivatives are the most promising materials for future applications in nano-electronics because of the rigid geometric configuration, highly conjugated structure, and good chemical stability.¹⁴⁻¹⁷ They can coordinate with different metal ions which could affect the electron transport through the porphyrin molecule. The Fe-porphyrin molecule is a haem of haemoglobin in human blood, which is famous for its role in carrying oxygen to our body. But, the FeP molecule binds with carbon monoxide (CO) more strongly than with oxygen. Therefore, in the presence of CO, oxygen-carrying Fe-porphyrin is disturbed.¹⁸ At present, the electron transport of porphyrin molecular system have been investigated theoretically by several groups.¹⁹⁻

²⁷ Most of these works focus on the protoporphyrin, multiporphyrin, and metal-porphyrin complexes. There are few reports on the electron transport behavior of the metal-porphyrin coordinated to diatomic ligands, such as CO, O₂, and NO. To give a further insight of the electron transport mechanism of the molecules, the molecular projected self-consistent Hamiltonian (MPSH) states and transmission coefficients of the single Fe-porphyrin molecular wires with and without CO adsorption under various external voltages are analyzed in detail.

2. Computational methods

The calculations for the present work follow two main processes. First, we perform geometric optimizations for the thiol ended Fe-porphyrin (abbreviated as FeP) and thiol ended CO adsorbed Fe-porphyrin (abbreviated as FeP(CO)) using Gaussian 03 software. Two small gold clusters, each consisting of three atoms, are used to mimic the Au(1 1 1) electrodes. These gold atoms form an equilateral triangle with sides of 2.88 Å. Each sulfur atom connected to the gold cluster is confined at the center of the triangle, i.e., the hollow site (see Fig. 1a). The relative positions of the gold atoms are frozen in each triangle, but the distance between the two clusters is relaxed during the geometric optimization. The optimizations are carried out at the B3LYP/LanL2DZ level of theory. The spin multiplicity is specified according to the lowest energy of the isolated bridge molecules, which is 3 for FeP and 1 for FeP(CO).

Fig. 1. (a) The optimized structure of FeP molecule attached to two gold clusters. (b) Top view of the FeP(CO) junction structure by periodic boundary condition and the contour indicates the unit cell. (c) Schematic illustration of the computational cell for determining the I - V characteristic of a molecule coupled to a (3×3)-gold (1 1 1) electrode. The structure is repeated periodically in the x and y directions, and the gold electrodes extends to $z=\pm\infty$.

After the geometric optimization, the molecule, except the two gold clusters (-S-M-S-), is translated into the gold junction with (1 1 1) surfaces as shown in Fig. 1c. Each layer of gold electrodes is represented by a (3×3) supercell with the periodic boundary conditions so that it imitates bulk metal structures (see Fig. 1b). Then the electron transport properties of the molecular junctions are calculated by fully self-consistent non-equilibrium Green's function formalism combined with first-principles density functional approach (NEGF-DFT). In the NEGF-DFT approach, the molecular junction is divided into three regions, left electrode (L), scattering region (S), and right electrode (R) as shown in Fig. 1c. The scattering region includes the molecule itself as well as part of each electrode where the screening effect takes place. Two layers of gold from the left electrode and three layers of gold from the right electrode are included in the scattering region (see Fig. 1c). Atoms in the Scattering region are included in the self-consistent cycle, while the remainder of the electrodes are modeled as self-energy operators.

3. Results and discussion

The optimized structure of isolated FeP exhibits a perfect planar configuration. However, when CO molecule coordinates with the Fe center of FeP, the porphyrin core is found to be domed. The Fe atom is 0.21 Å out of the plane toward the CO molecule. The Fe-C and C-O bond lengths in the FeP(CO) are 1.74 and 1.18 Å, respectively. The Fe-C-O angle is 180°. Fig. 2a shows the calculated I - V curves of the FeP and FeP(CO) molecular junctions by NEGF-DFT method. For FeP system, with the increase of applied bias the molecular current increases initially and then reaches maximum at about 1.2 V. Further increasing the bias the molecular current decreases. For FeP(CO) system, the molecular current monotonously increases with the increase of the applied bias. In addition, the molecular current increases almost linearly with the applied bias in the range 0.0–1.4 V. Further increasing the bias voltage the molecular current increases faster. Comparing the I - V curves of the two molecular systems, one can see that the molecular current of FeP is much higher than that of the FeP(CO). For example, the molecular current for the FeP at 1.0 V is 36.36 μA, which is 26 times higher than that (1.32 μA) of the FeP(CO) at the same bias voltage. Such a significant I - V difference indicates that FeP has the potential to be used as a molecular sensor and/or a molecular switch.

Fig. 2. (a) The current–voltage curves and (b) differential conductance–voltage curves of FeP and FeP(CO) molecular junctions.

Fig. 2b presents the differential conductance of FeP and FeP(CO) molecular junctions as a function of the bias voltage. It can be seen that the *zero* bias conductance of FeP (39.12 μS) is much higher than that (0.97 μS) of the FeP(CO). With the applied bias voltage increasing, the differential conductance of FeP first increases slightly, then decreases sharply after about 0.6 V and reaches minimum at about 1.4 V. Further increasing the applied bias, the differential conductance increases again. However, for FeP(CO) the differential conductance increases in the whole applied bias range. When the applied bias is less than 1.1 V, the differential conductance of FeP(CO) is lower than that of FeP. When the applied bias voltage is more than 1.1 V, the differential conductance of FeP(CO) is higher than that of FeP.

Fig. 3. Transmission spectra of FeP and FeP(CO) molecular junctions at different applied bias. The filled region represents the bias window and the dots correspond to the energy positions of the MPSH states of the FeP and FeP(CO) molecular wires.

For FeP(CO) system, no transmission peak enters the bias window with the applied bias increasing from 0.0 to 1.6 V and therefore the molecular current is rather small. When the applied bias increases to 2.0 V, the first peak above Fermi level enters the bias window and so the molecular current shows an obvious increment as shown in Fig. 2a. The transmission spectra in Fig. 3 can be further analyzed from the molecular orbitals of the bridge molecules.

Table 1 presents the MPSH states around Fermi level as well as their eigenvalues for the FeP and FeP(CO) junctions. The MPSH states are analyzed for bias voltage of *zero*, 1.0, and 2.0 V. In a common sense, the transmission peak height is mainly determined by the orbital delocalization. For FeP system, under zero bias, the two sharp peaks just above Fermi level can be assigned to the fully delocalized MPSH LUMO and LUMO+1; the first peak below Fermi level is due to the superposition of the MPSH HOMO and HOMO-1, which are close to alignment with each other. The small misalignment between the transmission peaks and the MPSH states can be related to the coupling with the electrodes. The zero bias MPSH HOMO–LUMO gap of FeP(CO) is 1.32 eV, which is much larger than that (0.27 eV) of FeP. For FeP(CO), a hybridization of

the σ orbital of CO with the dz^2 orbital of Fe is observed, as well as a more effective π -back bonding (the hybridization between the d_{xz} (or d_{yz}) orbitals and the π^* orbital of CO). The d_{yz} and d_{xz} orbitals of the Fe atom split into bonding and antibonding orbitals due to the adsorption of CO. Thus the MPSH HOMO–LUMO of FeP(CO) becomes larger.

Table 1. Comparison of the MPSH states as well as their eigenvalues for FeP and FeP(CO) molecular systems under different bias voltage. The isovalue of molecular orbitals is 0.02 e au^{-3} .

MPSH orbitals	FeP			FeP(CO)		
	0.0 V	1.0 V	2.0 V	0.0 V	1.0 V	2.0 V
LUMO+2	1.0130 eV	0.9180 eV	0.8555 eV	1.3462 eV	1.1396 eV	1.0909 eV
LUMO+1	0.4814 eV	0.4724 eV	0.5477 eV	1.2496 eV	0.9840 eV	0.9609 eV
LUMO	0.2296 eV	0.2603 eV	0.0009 eV	1.1989 eV	0.9473 eV	0.9045 eV
HOMO	-0.0355 eV	-0.4304 eV	-0.6395 eV	-0.1197 eV	-0.5709 eV	-0.7528 eV
HOMO-1	-0.0682 eV	-0.5154 eV	-0.9633 eV	-0.5184 eV	-0.7362 eV	-1.0451 eV
HOMO-2	-0.3194 eV	-0.5507 eV	-0.0054 eV	-0.5648 eV	-0.8694 eV	-1.0543 eV

For FeP(CO) system, under zero bias, the three sharp peaks above Fermi level can be assigned to the MPSH LUMO, LUMO+1, and LUMO+2; the first peak (very narrow) below Fermi level is due to the MPSH HOMO, which localizes in the central part of the FeP(CO). When bias voltage is applied, the MPSH states above Fermi level shift to low energy but their shapes almost remain and therefore their correlated transmission peaks seem insensitive to the applied bias; however, due to the large MPSH HOMO–LUMO gap, there is no MPSH states above Fermi level enter the bias window until the bias is up to 2.0 V. With the increase of applied voltage, the MPSH HOMO, HOMO-1, and HOMO-2 get localized and so their correlated transmission peaks decrease. Moreover, these MPSH states below Fermi level also move to low energy with the increase of the applied bias and hence almost no correlated transmission peak below Fermi level enters the bias window. Therefore, the molecular current of FeP(CO) is much smaller than that of FeP as shown in Fig. 2.

4. Conclusion

The electron transport behavior of Fe-porphyrin (FeP) and its complex with CO (FeP(CO)) have been investigated by the nonequilibrium Green's function approach in combination with density functional theory. The results demonstrate that the CO adsorption cause a significant decrease of molecular current through FeP molecular wire, which could potentially be used as molecular sensors and/or molecular switches. The great difference between the I - V curves of FeP and FeP(CO) is analyzed from the evolution transmission spectra and the molecular projected self-consistent Hamiltonian (MPSH) states close to Fermi level. It is found that the increase of HOMO-LUMO gap and the localized molecular orbitals of FeP(CO) are the essential reasons for generating this great difference of the electron transport behavior.

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