Designing Cyclophane-Based Molecular Wire Sensors

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Received: August 1, 2006; In Final Form: September 14, 2006

We propose a model molecular wire sensor that can detect zerovalent chromium by a strong increase in conductance when included in a metal−molecule−metal junction. An essential part of the sensor is a paracyclophane unit that binds to the metal atom. The nature and the energies of the molecular orbitals change drastically after the complex is formed, resulting in a 10- to 12-fold increase in conductance.

Introduction

Development of sensors capable of recognizing and sensing ions or neutral molecules of various types is very challenging, not only from the viewpoint of inorganic and supramolecular chemistry but also due to their importance in industrial and clinical applications. Sensors based on molecular recognition processes have been studied in great detail and there is a vast amount of literature available in this field. Most methods measure an optical, electrochemical, or mechanical signal that arises due to sensing of a large number of molecules.[1,2] But, studies of single molecule sensing based on conductance changes are not as plentiful. Interesting sensing studies of nanowires have been reported,[3−5] where the basis of sensing activities have been conductance changes based on copper nanowires, carbon nanotubes, or doped silicon nanowires which detected neutral molecules due to adsorption. A theoretical study[6] a few years later reported the possibility of recognition of alkali metal ions by a crown ether based metal−molecule−metal junction. This is important because the recognition process occurred at a single molecular level. It was reported that conductance decreases significantly due to complexation of the ions in the crown ether moiety. In a more recent study, a 2,2′-bipyridine unit incorporated into a π-conjugated system was used as a single-molecule device, in which the conductance change was used as a function of proton coordination.[7] Metal ion sensing was reported for peptide host molecules wired between two gold electrodes.[8] The host formed a 1:1 complex with the metal ions thereby increasing the conductance of the peptides. The length and conformation of the peptide molecule was found to be important in such a situation.

In the present theoretical study we use a paracyclophane (pCp) based molecule for metal ion sensing using change in conductance as the sensing parameter. Cyclophanes are a large class of host molecules known to recognize a variety of guests[9] hence there exists no doubt about its potential in the field of molecular sensing. Theoretical studies in this field in predicting new, efficient sensors can be very important. All types of systems ranging from inorganic and organic cations and anions to neutral molecules have been complexed by using tailor-made cyclophanes. Also in the recognition process all known modes of binding have been exploited, like hydrogen bonding, donor acceptor properties, cation−π interactions, and coordinate bonding.[9,10] Cyclophanes have also drawn much attention lately, for the synthesis of [2]rotaxane and [2]catenane group of molecules[11,12] in connection with the emerging field of nanotechnology. In this study, however, only the binding of metals to simple pCp-s is relevant. Many studies describe metal cyclophane complexes from very old times.[10,13−16] Traditionally cyclophanes have been used for recognition of metal ions by cation−π interaction. The complex formation of a metal ion with cyclophane depends on the size of the cavity, if the cavity permits an inclusion complex is formed. For larger metal atoms or smaller cavities the metal atom is coordinated at the outer face of the cyclophane. The close proximity of the benzene rings in smaller cyclophanes leads to a strong interaction of the π systems. This results in a repulsion of the π clouds, which forces the planar benzene rings to take a boatlike structure. We explicitly address the issue of metal ion binding by a [3.3]pCp-based molecular wire (pCp-wire) in free conditions and then included in a molecular junction and explore the changes in electronic properties due to the binding.

Recently, Seferos et al. probed π-coupling in metallic junctions in molecular wires with pCp cores.[17,18] The authors synthesized a phenylene vinylene oligomer (OPV) with a paracyclophane (pCp) core and studied it along with simple OPV molecules using electrochemical methods. It was demonstrated that the pCp unit yields a very conductive break in through-bond π conjugation and it was found a simple OPV molecule and OPV with a pCp core are almost equally conductive. But, the report did not include any research on how such a pCp-based molecule would behave in the presence of a suitable guest molecule to which pCp can bind. One can also think of other wire-like molecules with pCp cores, such as the one shown in Figure 1b. Here the wire is based on ethynylphenyl-based Tour wire[19] and a [3.3]pCp unit has been incorporated into it. The synthesis of polymers of similar molecules has been reported recently.[20] Since free [3.3]pCp is known to bind zerovalent chromium atoms,[10] the proposed molecule with the identical detection unit is likely to detect Cr(0). As different pCps are known to act as hosts for a wide variety of ions/molecules, one can think of a vast area of research in this direction.

Theoretical Methods

The main aspect of this study is to understand how the electronic properties and thereby the conductance of pCp-wire

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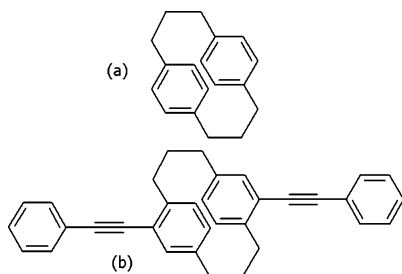* Address correspondence to these authors. E-mail: bidisa.das@aist.go.jp and s.abe@aist.go.jp.

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Figure 1. Schematic structures of (a) [3.3]pCp and (b) pCp-wire.

Figure 2. Optimized structure of [3.3]pCp. Anti and syn conformations of [3.3]pCp are shown.

changes in the presence of the target metal ion and then compare between the bound and unbound situations. Ab initio electronic structure methods are first employed to study the properties of the free and complexed pCp molecule. We have optimized unconstrained structures of the free molecule and the corresponding metal inclusion complex using Density Functional Theory (DFT) as implemented in Gaussian 03[21] software with 6-311G** basis set for carbon and hydrogen and 6-31G** for chromium. To mimic the two-probe situation in experimental conductance measurement systems, we have in some cases terminated the sensor molecules by gold (Au) atoms at the two ends. In these studies, we have used Lanl2DZ basis set and effective core potential[22] for Au. The studies use hybrid functional B3LYP formulated by Lee, Yang, and Parr.[23,24] The magnitude of the changes in energy levels of pCp after complexation with metal atom is analyzed as an essential factor that controls the change in conductivity. As a precautionary measure, we have also studied the geometries of the stable structures using Hartee−Fock (HF) methods using the same basis set in Gaussian 03 and GGA-PBE[25] using the DZP basis set in ATK 2.0 software.[26] We found the geometries are only marginally different from that predicted by B3LYP. The molecular orbital (MO) energies, however, are very different for HF, pure DFT, and hybrid DFT methods. To evaluate potential conductance channels, the nature of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule should be analyzed. The gap between the two (HOMO-LUMO gap or HLG) is an important factor controlling the tunneling current through the molecule. It is well-known that HF methods grossly overestimate the HLG of extended systems and DFT underestimates it slightly, but hybrid methods such as B3LYP, B3P86, and B3PW91 give a value close to experimental data.[27] Hence, our conclusions are based on the HLGs obtained with use of B3LYP method. All the stable geometries are characterized by vibrational frequency calculations. The binding energy of the complex formation reaction with metal atom reported here is determined by using the B3LYP method after basis set superposition error (BSSE) correction.[28,29]

We calculated the change in conductance of the system after complex formation of the pCp-wire with metal atom. The electronic transport properties are calculated with ATK 2.0 software,[26] which combines the nonequilibrium Green's function (NEGF) formalism and density functional theory. The DFT implementation uses a numerical atomic basis set to solve the Kohn−Sham equations.[30−32] We use the DZP basis set with GGA-PBE[25] functional for the exchange correlation functional for this study. In NEGF theory, the molecular junction is divided into three regions: left electrode (L), contact region (C), and right electrode (R). The contact region includes part of the physical electrodes where screening effects take place, to make sure that the charge distributions in the L and R region correspond to the bulk phases of the same material. The semi-
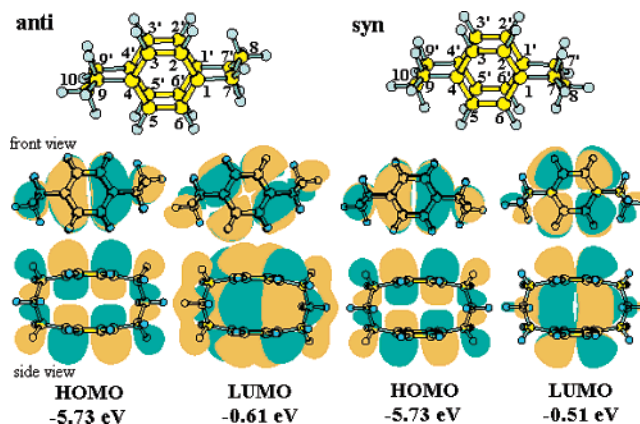
infinite electrodes are precalculated separately to obtain the bulk self-energy. The nonlinear current at an applied bias voltage V_b through the contact is calculated by using Landauer formula,[33,34]

$$I(V_b) = G_0 \int_{\mu_L}^{\mu_R} T(E,V_b)\, \mathrm{d}E$$

where $G_0 = 2e^2/h$ is the quantum unit of conductance, $\mu_{L/R}$ are the electrochemical potentials of the left and right electrodes, and h is Planck's constant. The left and the right electrodes in our study are modeled by two Au(111)−(5 × 3) surfaces. The unit cell for electrodes contains three Au layers and two Au layers at both the left and the right sides are included in the contact region. Although it is known that in the case of a large molecule for the screening approximation to hold accurately one must include many layers in the contact region, our layers being 5 × 3 including just two layers make the calculations sufficiently heavy. The sensor molecule, pCp-wire, is bonded to the two electrodes with −S−Au (thiol) bonds. The structure of the central molecule is preoptimized by using the same basis set and DFT functional (DZP/GGA-PBE), using ATK 2.0. We note that the optimized geometry is similar to the structure obtained with the B3LYP method. The structure of the metal− molecule−metal system has not been relaxed due to the huge computational times required. With these structures, we calculated the transmission spectra and current−voltage (I−V) characteristics for the free pCp-wire and metal pCp-wire complex.

Results and Discussions

Free [3.3]Paracyclophane. We first consider the free [3.3]-pCp molecule in more detail. The reason for choosing [3.3]-pCp instead of [2.2]pCp is its larger cavity size and smaller strain energy in comparison to the later. The optimized structure of [3.3]pCp is shown in Figure 2. As shown in the figure the structures can be "syn" or "anti" with respect to the methylene bridges between the two phenyl rings. The two structures are equally stable with the syn structure being more stable by only 0.2 kcal/mol. The optimized bond distances are also similar (see the Supporting Information). The two phenyl rings facing each other are distorted from planarity. Near the bridges the distances (see 1−1′ and 4−4′) are somewhat smaller (3.22 Å) than the other inter-ring nonbonded distances (3.40 Å on average). The overall shape of the rings resembles boatlike structures facing each other. For the double decker phenyl rings in the case of syn and anti isomers, intra-ring bond distances are similar. We have plotted the HOMO and LUMO for both structures in Figure
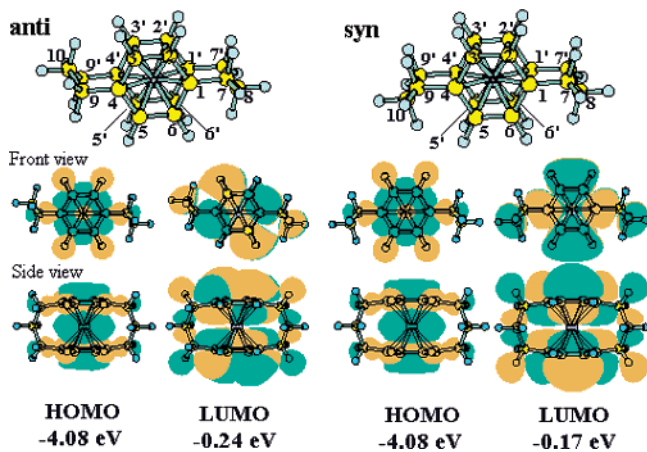
Figure 3. Optimized structure of the Cr(0)-complex of [3.3]paracyclophane. Anti and syn conformations of [3.3]pCp are shown.

2. The nature of the HOMO is similar for the syn and anti structures and both are at −5.73 eV. The nature of the LUMO is also similar but it is affected by the symmetry of the bridges. The HLG for the anti structure is 5.12 eV and that for the syn structure is 5.22 eV.

The inclusion complex of [3.3]pCp with zerovalent chromium gives an 18 electron system (6 electrons from two phenyl rings each and 6 electrons from the Cr atom) that gives rise to a stable complex.[35] Cr atom brings the two phenyl rings slightly nearer (see Supporting Information). The phenyl rings remain boat-like but the bonds within the rings are elongated, which indicates a slight expansion of the two phenyl rings. The MOs are shown in Figure 3 and we find that, after complex formation, the HOMO energy goes up by 1.65 eV and the electron density becomes localized mainly on the transition metal atom. But there is not too much change in the nature of the LUMO after complex formation. The HLG also goes down after complex formation (HLG values are 3.84 eV for the anti and 3.91 eV for the syn structure). We have also studied complex formation when the Cr atom is symmetrically on top of one benzene ring, instead of occupying its place inside the cavity. Such an outer face Cr-complex, though a minima in the potential energy surface, is nearly 80 kcal/mol higher in energy than an inclusion complex.

Paracyclophane Wire and Its Chromium Complex. Next we consider a molecular wire with a [3.3]pCp core as shown schematically in Figure 1. Due to the presence of the pCp unit the molecular wire is a double decker type with the OPE fragments arranged in para positions of two different rings of the pCp core. Cyclophane-based molecular wires such as this can be used in molecular junctions for conductance studies where the cyclophane moiety acts as the detection unit. When the detection unit recognizes the target, conductance of the system changes drastically. The pCp considered here is equipped with a conductive molecular wire unit that can translate the electronic changes due to complex formation in terms of the change in conductance of the system, which would then detect the target electrically. Similar molecular systems with OPV wire have been studied electrochemically.[17,18] However, the complex formation of such a wire system and the consequent changes in electronic properties are being studied for the first time.

Figure 4 shows the optimized structure for the pCp-wires. Though there can be syn and anti structures for the pCp portion (as shown for [3.3]pCp) of the wire, we discuss only the anti structure. We have analyzed the syn structures as well, but they are very similar to the anti structures without any special character. The wire fragments of the pCp-wire are nearly linear.
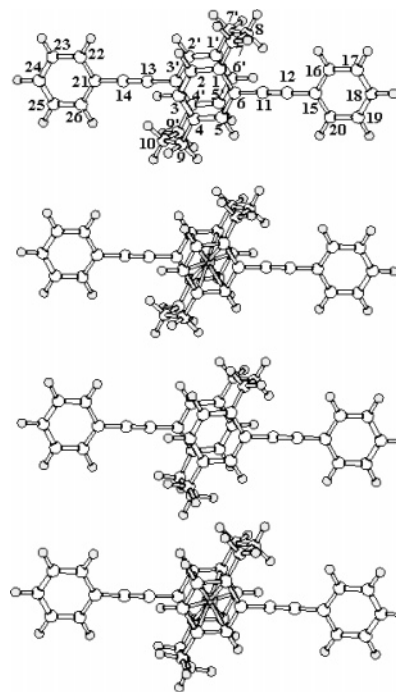

Figure 4. Optimized structure of pCp-wire. Anti and syn structures are shown along with the respective Cr-complex. The central atom represents Cr. Numberings are the same for all four structures given here.

The bond distances of the pCp unit are almost unaffected after it is incorporated into an elongated molecular wire structure. The acetylenic bonds (11−12 and 13−14) are 1.22 Å with the connecting bonds between pCp and wire (6−11 and 3′−13) being 1.42 Å long. The bond distances in the benzene rings in the wire portion are 1.39−1.40 Å on average. More dramatic changes are seen when one analyzes the nature of the MOs. The MOs for the pCp-wires with anti structured pCp units are given in the Supporting Information. MOs of the syn form are very similar in nature and also in terms of energy hence we do not show them here. The pCp-wire has orbitals which are extended over the entire molecule. HOMO, HOMO−1, and LUMO, LUMO+1 are fully extended over the entire wire and they make excellent channels for electronic conduction despite the double decker structure in the pCp unit. This has already been found for OPV wires with a pCp core.[17] The HLG for the wires that we study are 3.97 (anti pCp) and 4.0 eV (syn pCp). Comparing the HLG for the [3.3]pCp molecule with the HLG of pCp-wire clearly shows that extended delocalization in the wire reduces the energy gap.

After complex formation with Cr(0) the pCp portion of the wire resembles the complexed [3.3]pCp molecule. The binding energy for complex formation is 170 kcal/mol after BSSE correction. The interplane distances between the two phenyl rings change only marginally if compared with the Cr(0)-[3.3]-pCp complex. This indicates the incorporation of the wire portion does not really affect the geometry and the recognition properties of cyclophanes. The optimized structures are shown in Figure 4 and the detailed MOs are given in the Supporting Information. Similar to the case of complexation of [3.3]pCp, HOMO at −4.41 eV for the pCp-wire complex is localized on the metal atom. But HOMO−1 at −4.70 eV is extended over the wire. Also we find LUMO and LUMO−1 to be extended over the entire molecule. So these MOs can serve as conduction channels after complex formation occurs. After complex formation the HLG for the anti structure is 2.88 eV, which is 1.10

eV less than the HLG of uncomplexed pCp-wire. This large change in HLG may have resulted from the drastic charge redistribution in the pCp portion of the wire where Cr(0) binds. For the syn case HLG is 2.92 eV in comparison to 4.0 eV for the uncomplexed case. This huge change in HLG is expected to change the conductance of the system significantly in the case of molecular junction experiments.

The metallic electrodes considered in this study are Au(111) surfaces. Since thiol gold bonds are strong and well studied, in the present case thiol endgroups (−S−Au) bonded to the pCp-wire have been studied. In such cases, the hydrogen atoms at the two ends of the molecules are replaced by −S−Au groups. Though attaching two isolated gold atoms at the two ends of the molecule hardly depicts the real situation, it can still give an idea about how the molecular orbitals may shift due to the presence of metal electrodes. It is found that after −S−Au groups are bonded at the two ends of the free sensor molecule the energy levels indeed change and HLG becomes much smaller (2.21 eV for anti and 2.22 eV for syn pCp-wires). After complex formation the HLG for the anti pCp-wire is 1.17 eV and that for the syn cyclophane-based wire is 1.19 eV. The MO of the gold-terminated molecule also confirms that there is a reasonable amount of charge density in the contact region, which suggest that the contacts are well defined with strong covalent bonds. Such studies are useful for understanding the nature of the bonding of the molecule with the metallic electrodes and have been used before.[17,33,36,37] Examination of atomic charges in the pCp-wire and the corresponding complex with the −S−Au bond shows that drastic changes occur only near the pCp unit, but the remaining wire portion and the S or Au atoms at the two ends undergo minor changes. So complex formation is not expected to cause strong charge redistribution near the contact region.

Conductance Studies. We now consider a molecular electronic system consisting of a molecule coupled to two electrodes with the same or different electrochemical potentials. The transmission properties of such systems are determined by the electronic structure of the combined molecule and electrodes in a two-probe setup. In simple terms, one can think of a metal−molecule−metal junction as a finite potential well between two infinite metal electrodes. When a molecule bridges the interelectrode gap with a well-defined molecule−metal bond, extended π-MOs of the molecule can act as channels for the flow of electrons in the two-probe system. In such a system the transport is assumed to occur via scattering states which are Bloch-like states in the electrodes and extended MO-like states in the molecular bridge region. Under low bias voltages and at low temperatures, transport properties of a molecular junction are successfully described by the Landauer picture.[34]

The two-probe system for free pCp-wire and the Cr(0)-complex is shown in Figure 5. Au(111) electrodes on the either side of the molecule were modeled as (5 × 3) surfaces. The metal−molecule−metal system has not been optimized in this study. We expect only minor changes in geometry and recognition properties after optimization, because the metal electrodes are far away from the detection part. We have positioned the central molecule (or the Cr-complex) between two electrodes in such a way that the sulfur atoms in both the termini are bonded to gold atoms. The Au−S bond has been very well studied for self-assembled monolayers and we have used bond lengths similar to such studies.[38,39] We have considered situations for two adsorption sites fcc-hollow and bridge on Au-(111) as it has been reported[40,41] that the molecule−metal
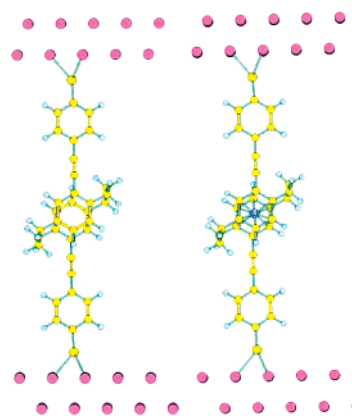

Figure 5. Two-probe setup for transport studies. Both the electrodes are 5 × 3 Au(111) slabs.
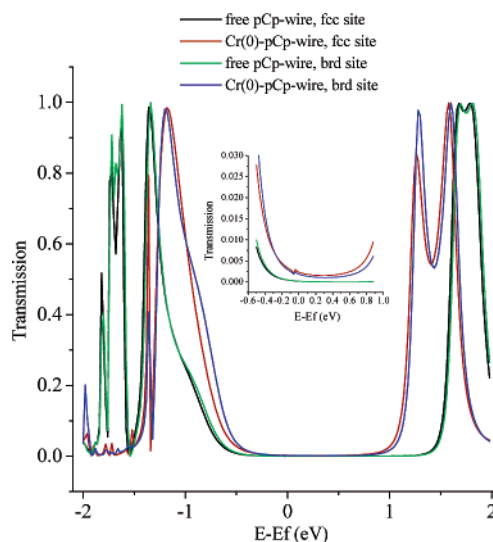

Figure 6. Calculated transmission spectra. Results for the fcc bonded central molecule and the bridge bonded central molecule are shown. Enlarged view of the plot around the electrode Fermi energy is shown in the inset.

contacts are very important aspects of a two-probe systems. The central molecule is assumed to be perpendicular to both electrodes.

The transmission spectra for the pCp-wire and its chromium complex are shown in Figure 6. This clearly shows that the HLG decreases strongly in the two-probe setup and drastically after complex formation. In the case of the fcc-bonded central pCp-wire, all S−Au distances are 2.55 Å. After complex formation with Cr(0), pCp-wire is slightly distorted, which decreases the length of the molecule by 0.1 Å. Since in the two-probe setup the interelectrode distances are fixed (at 24.6 Å), the shrinkage of the molecular length causes the S−Au distances to increase to 2.61 Å on both sides. In the case of the bridge-bonded central pCp-wire, all S−Au distances are 2.50 Å, which increases to 2.52 Å after complex formation. The value of conductance for the free sensor and the complexed sensor can be calculated from the transmission at the Fermi energy. The conductance of the free pCp-wire is 0.015 μS in comparison to 0.18 μS for the fcc-bonded wire. Thus there is a 12-fold increase in the conductance after complex formation. For the bridge-bonded case, free pCp-wire has almost the same conductance, but the Cr-complex has a conductance of 0.14 μS, which is nearly a 10-fold increase in conductance. The nature of the transmission spectra for the fcc- and bridge-bound cases is similar.
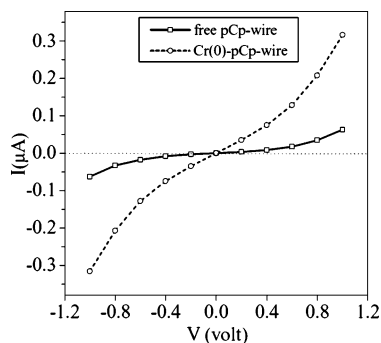
Figure 7. Calculated $I-V$ curve. Results for the fcc bonded pCp-wire and the corresponding Cr(0)-complex are shown.

The main feature of the transmission spectra of pCp-wire is a transmission peak near -1.22 eV, which has a broad shoulder near -0.97 eV in the negative region (values are relative to Fermi energy of gold) and a double peak between 1.55 and 1.75 eV. The transmission peaks in the negative regions stand for the HOMO and the HOMO-1 orbital of the molecule. This has been confirmed by the study of molecular projected self-consistent Hamiltonian (MPSH) states. In the positive energy region the twin peaks stand for LUMO and LUMO$+1$ orbitals which are nearly degenerate. For the complexed pCp-wire the transmission peak in the negative region is near -1 eV, which is uniformly broadened. This corresponds to the HOMO-1 orbital, as HOMO is localized and does not conduct. Another sharp peak is at -1.46 eV, which corresponds to the HOMO-3 orbital as HOMO-2 is localized. In the positive region the double peaks have separated around 1.3 and 1.6 eV and correspond to LUMO and LUMO$+1$ orbitals.

To obtain the current versus voltage characteristics we have done self-consistent calculations at a bias voltage range -1.0 to 1.0 V. Since the electronic structures in the contact region are symmetric in this case and the molecule is also symmetric, we expect a symmetric $I-V$ curve with respect to the reversed bias. The calculated $I-V$ curve is shown in Figure 7. It is nonlinear in nature and current increases with increased applied bias voltage for the free wire and after complex formation. However, the extent of increase is much more after complex formation occurs.

Conclusion

We have proposed a model metal sensor that can detect a Cr atom. The molecule forms an inclusion complex with Cr(0) and this binding causes the electronic properties of the systems to change drastically. Huge changes take place in the MO energies and the HLG after complex formation. This also results in a 10- to 12-fold increase in conductance of the sensor after detection. The main aspect of this study is the large change in HLG of the host molecule after binding to the guest atom. Upon complex formation, the HOMO of pCp-wire becomes localized on the Cr atom and HLG decreases drastically. This large change in turn affects the conductance of the system after the binding occurs. Since the [3.3]pCp unit is built into the wire the change taking place in the detection part of the molecule is very easily read by the conducting wire portion of the system.

As far as conductance studies are considered, we stress the changes in conductance rather than those in the individual absolute values. There can be numerous microscopic details of a metal molecule contact during device operation, such as the binding site, the metal$-$molecule bond distance, the orientation angle, etc., which can dynamically change during the current flow. Hence a theoretical estimate of current transport though

such a molecular junction is likely to differ from real values as they are too ideal in nature. Our studies have an advantage of being relative, hence the percentage difference in the conductance after complex formation is likely to be reliable. In this example only [3.3]paracyclophane is taken into account and only Cr binding to it was studied. However, one can think of other targets if the appropriate host moiety could be incorporated into the wire. We believe that a variety of efficient sensors can be developed in this manner.

Supporting Information Available: Optimized bond distances of [3.3]pCp and the corresponding Cr-complex are available, as well as molecular orbitals of pCp-wire and the corresponding Cr-complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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J. Phys. Chem. B, Vol. 110, No. 47, 2006 **23811**

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