Charge transport mediated by d-orbitals in transition metal complexes†

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This communication reports an asymmetric charge transport with a large rectification ratio and finely featured NDR (negative differential resistance) by d-orbitals of a neutral ruthenium(II) complex with a C_2 axis of symmetry.

An extensive research effort in the area of molecular electronics is to synthesize and characterize new molecules with designed physical properties, such as switch, rectification and storage.[1] Numerous molecular systems have been explored for mediating charge transport in metal–molecule–metal junctions.[2] Among these molecules, transition metal complexes received attention only recently. Interesting phenomena such as the Kondo effect and electrochemically gated charge transport were observed.[3] This paper reports an asymmetric charge transport through a molecular wire ligand with a chelated transition metal complex. In the past years, our group has described the rectification effect in molecular diodes based on conjugated diblock co-oligomer structures.[4] We have unambiguously shown that the origin of the rectification effect in these molecules is from the existence of a permanent dipole moment. However, the rectification effect described in this work is imparted by the chelated transition metal complex.

The molecule studied is shown in the inset of Fig. 1 and contains a conjugated macromolecular bipyridine ligand chelated to a ruthenium(II) complex. It was synthesized according to a procedure developed in our lab.[5] The compound contains two thiols protected with different groups (acetyl, Ac and methoxymethyl, MOM). The complex exhibits a UV/Vis spectrum red-shifted from the corresponding molecular wire ligand (Fig. 1(a)). Metal to ligand charge transfer (MLCT) bands can be clearly observed in the wavelength range from 500 to 600 nm. The results indicate that the π-electronic system of the macromolecular ligand is coupled with d-orbitals.

In order to immobilize the compound on the Au(111) surface, the acetyl protection group of the compound was cleaved by aqueous NH_4OH in THF. The resulting complex with free thiol at one end was inserted into the defect sites of dodecanethiolate self-assembled monolayers (DDT SAM). Afterward, the MOM protection group was cleaved with trifluoroacetic acid (TFA) to free the top thiol group that was further reacted with a gold nanoparticle (Au NP) solution. Finally, an assembly with a gold–molecule–gold structure was formed and used for scanning tunneling spectroscopy (STS) measurements on charge transport behaviors.[6] The stepwsie immobilization process is needed in order to prevent the formation of mulitlayer assemblies.

Cyclic voltammetric measurements confirmed the immobilization of the Ru(II) complex. A quasi-reversible half-wave redox potential ($E_{1/2}$) at 0.45 V (*vs.* Fc/Fc^+) from the monolayer was observed and is attributable to the oxidation from Ru(II) to Ru(III) (Fig. 1(b)). The plot of anodic and cathodic current density against the scan rate is linear, indicating the existence of a surface confined faradaic reaction due to Ru(II) complex.[7] These results prove that the Ru(II) complex is intact after all of these chemical manipulations. STM images provide further evidence for the immobilization of complex in DDT SAM.[8]

The STS technique was used to investigate the charge transport behavior through the single molecular junction. Under the conditions of set point of 1 pA and 1000 mV bias voltage, the current was taken as the bias voltage scanned between −2.0 V to 2.0 V. A typical *I–V* curve is shown in Fig. 2. As a comparison, the charge transport through the molecular wire ligand was also investigated and is shown as an inset in Fig. 3. The results show several unique features. First of all, the *I–V* curve is asymmetric, identical to the *I–V* curves observed in a typical molecular diode.[4] The average rectification ratio ($RR = I(+2.0\ V)/I(-2.0\ V)$) is 3.53. Over 85% of the measured Ru(II) complexes showed higher tunneling current at positive bias voltage than at negative bias while the rest of them had the opposite rectifying behavior. The inset histogram shows the statistical distribution of RR for the different Ru(II) complexes measured, indicating the reproducibility of charge transport behaviors of different Ru(II) complexes.

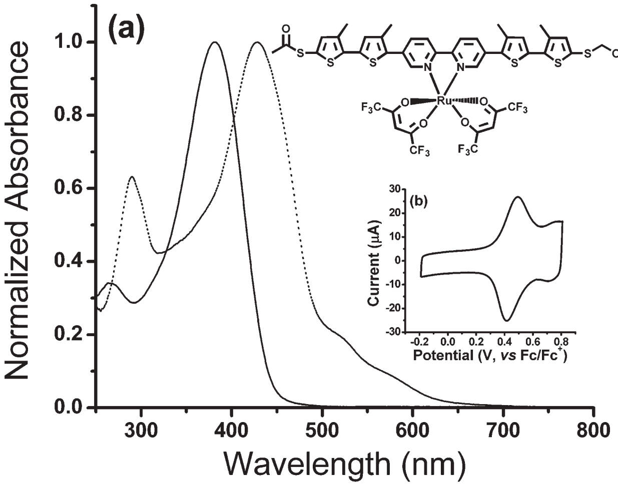

Fig. 1 (a) UV/Vis spectra of the ruthenium(II) complex (dotted line) and molecular wire ligand (solid line). Inset: Molecular structure of the ruthenium(II) complex. (b) Cyclic voltammogram of a monolayer of the ruthenium(II) complex on the Au(111) substrate. Scan rate 0.5 V s^{-1}.

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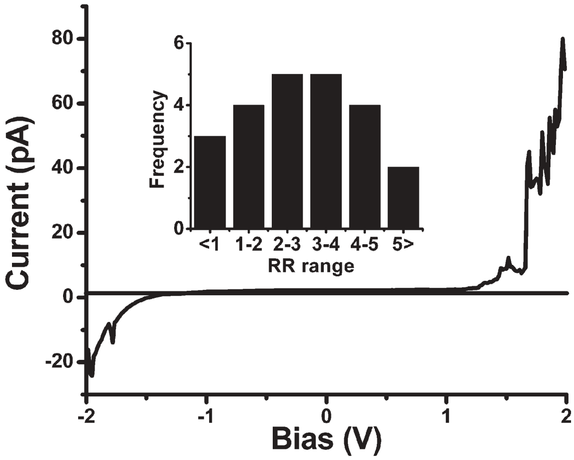

Fig. 2 *I–V* characteristics of the ruthenium(II) complex (set point conditions: 1 pA and 1000 mV). Inset: Histogram of RR range for different Au NP–Ru complex–Au assemblies measured.

Second, there were a few fine features of the conductance in the positive bias region, which is shown more clearly in Fig. 3 as the differential conductance (d*I*/d*V*). Third, the *I–V* curve of the molecular wire ligand is almost symmetric and has no fine features, at least at room temperature as shown, in the inset of Fig. 3. The resistance of the complex is much smaller than that of the ligand, which is caused by the forced planarity in the ligand conjugation system. These are unprecedented results; the rectification effect is especially unusual, considering that the complex has a C_2 axis of symmetry. These results can be explained if we consider the relative line-up of the Fermi energy levels of the gold electrodes to the molecular orbitals (MOs) of the complex and a resonant tunneling mechanism.[9] We calculated the electronic structure of the Ru(II) complex by using B3PW91 hybrid density functional theory (DFT) with the LANL2DZ basis set. As shown in Fig. 4, HOMO, HOMO-1, HOMO-2, HOMO-3, and HOMO-4 are closely located. HOMO, HOMO-3, and HOMO-4 orbitals are derived from the ruthenium d-orbitals (d_{xy}, d_{yz}, d_{zx}) with the π* contribution from the molecular wire and the acetoacetate (acac) ligands. It seems that HOMO-1 and HOMO-2 orbitals are made of the π-orbitals of bithiophene molecular wire because the major electron density is located on the electron-rich bithiophene segment.[8] When no bias voltage is applied to the assembly, the Fermi energy level of electrodes can be assume to line up at the middle of the gap between the HOMO and LUMO of the molecule.[10] This will lead to a symmetric *I–V* curve if the molecular wire ligand is free of metal complexes. However, the compound is a heteroligand complex and exhibits a permanent dipole moment perpendicular to the molecular wire ligand. Theoretical calculations indicated a dipole moment of 11.3 Debye along the direction from acac to the bipyridine ligand.

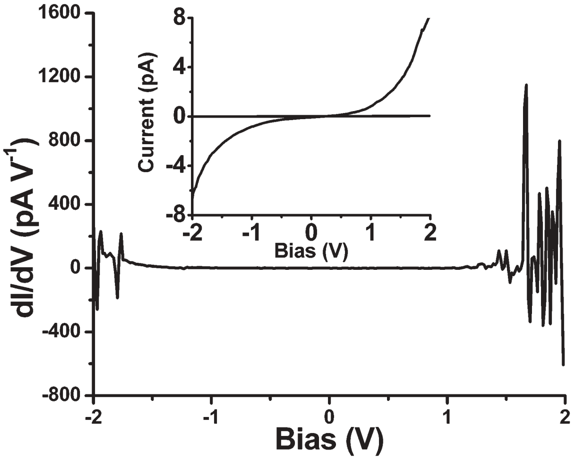

Fig. 3 Differential conductance (d*I*/d*V*) *versus* applied bias relationship for the ruthenium(II) complex. Inset: *I–V* characteristics of the molecular wire ligand.

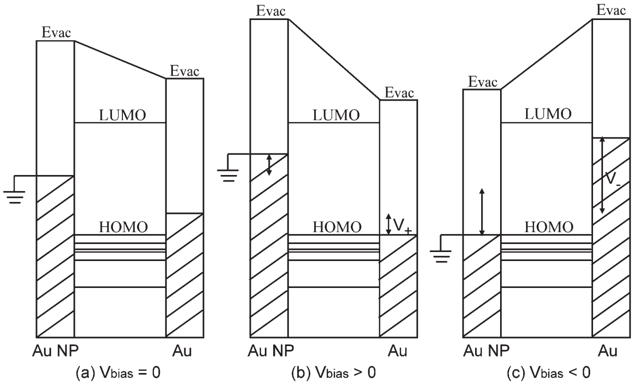

Fig. 4 Energy band diagrams for Au NP–Ru complex–Au assembly at (a) equilibrium, (b) positive applied bias, V_+, (c) negative applied bias, V_-.

When this molecule is immobilized into DDT SAM on the gold surface, it will be tilted due to the thiol–gold bond. There are two possibilities: the dipole moments of the complex will point either toward the grounded STM tip or the Au electrode. When the dipole moment of the complex has projected a component that is pointed toward the direction of grounded STM tip, the Fermi energy levels between electrodes relative to molecular orbital will show an uneven line-up (Fig. 4a) due to the dipolar field, E_d. Therefore, a small positive bias voltage (V_+) is needed to bring the Fermi energy level with the molecular orbital into resonance to allow charge transport (Fig. 4b). However, when a negative bias voltage is applied, a large voltage V_- is needed to overcome the dipolar field and bring the molecular orbital into resonance with the Fermi level of electrodes (Fig. 4c). This caused asymmetric charge transport to ensue. However, when the direction of dipole moments of the complex are pointed toward the Au electrode, the opposite rectifying behavior can be achieved. This explanation is in agreement with our observation that the complexes showed opposite rectifying behaviors although with less probability. We believe that there is a dominant orientation of the complex onto the Au electrode due to the electrostatic, van der Waals, or anchoring group interactions, leading to a preferred asymmetric charge transport. A more detailed characterization is needed to elucidate the orientation.

Differing from the charge transport through ligand, the d_{xy}, d_{yz}, and d_{xz} orbitals provide resonance channels for the charge transport *via* π* orbital in the complexes. A small positive bias is needed to push the Fermi level of the ungrounded electrode into resonance with these orbitals. When the Fermi level undergoes resonance with these orbitals, small negative differential resistance will be observed. The Fermi level will not have a resonance with the d_{z^2} and $d_{x^2-y^2}$ because they are not coupled with the π* orbital in the molecular wire and are spatially isolated from the electrodes. When a negative bias voltage is applied, electron tunneling will occur only when the bias voltage is negative enough to bring either the MOs containing *xy*, *yz*, *xz* or the LUMO MOs into resonance with electrodes. When the bias voltage passes the threshold for the tunneling through the first π* orbital, NDR peaks can be observed because the available state density is reduced.

These explanations provide several directions for further studies. First of all, the rectification should be a function of the relative energy levels between the d-orbitals and the ligand. It can be predicted that introducing an electron-withdrawing group into the ligand will change the rectification ratio. Second, the fine structures should depend on the d-orbital ordering. If a complex with different geometry is used, the fine structures must change correspondingly. Third, detailed theoretical calculations of molecular structure involving model gold electrodes will shed light into the detailed mechanism. Our further research effort will investigate these points.

In summary, we have synthesized molecular electronic components containing a neutral ruthenium(II) complex. STS studies revealed an interesting rectification effect with a large rectification ratio and finely featured NDR. A plausible explanation is offered to interpret the results. Much more detailed studies are needed to further explore this system.

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