

# Field Effects on the Statistical Behavior of the Molecular Conductance in a Single Molecular Junction in Aqueous Solution

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Received: 18 February 2010 / Revised: 21 March 2010 / Accepted: 21 March 2010

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## ABSTRACT

We have combined molecular dynamics simulations with first-principles calculations to study electron transport in a single molecular junction of perylene tetracarboxylic diimide (PTCDI) in aqueous solution under external electric gate fields. It is found that the statistics of the molecular conductance are very sensitive to the strength of the electric field. The statistics of the molecular conductance are strongly associated with the thermal fluctuation of the water molecules around the PTCDI molecule. Our simulations reproduce the experimentally observed three orders of magnitude enhancement of the conductance, as well as the temperature dependent conductance, under the electrochemical gates. The effects of the molecular polarization and the dipole rearrangement of the aqueous solution are also discussed.

## KEYWORDS

Molecular junction, field effect, solvent effect, temperature effect, statistical behavior

## 1. Introduction

The statistical behavior of molecular conductance has become one of most interesting aspects of recent studies of molecular electronics [1–7]. It is known that experimental current–voltage characteristics for single molecular break junctions are often obtained after statistical evaluation of large numbers of measurements. There are two major sources of the statistical uncertainty in current technology: the lack of precise control of molecule–metal bonding and the presence of solvent environments. The statistical behavior caused by the uncertainty of molecule–metal contact has been carefully analyzed recently by both experimental and theoretical studies [1–4], while for the effect of

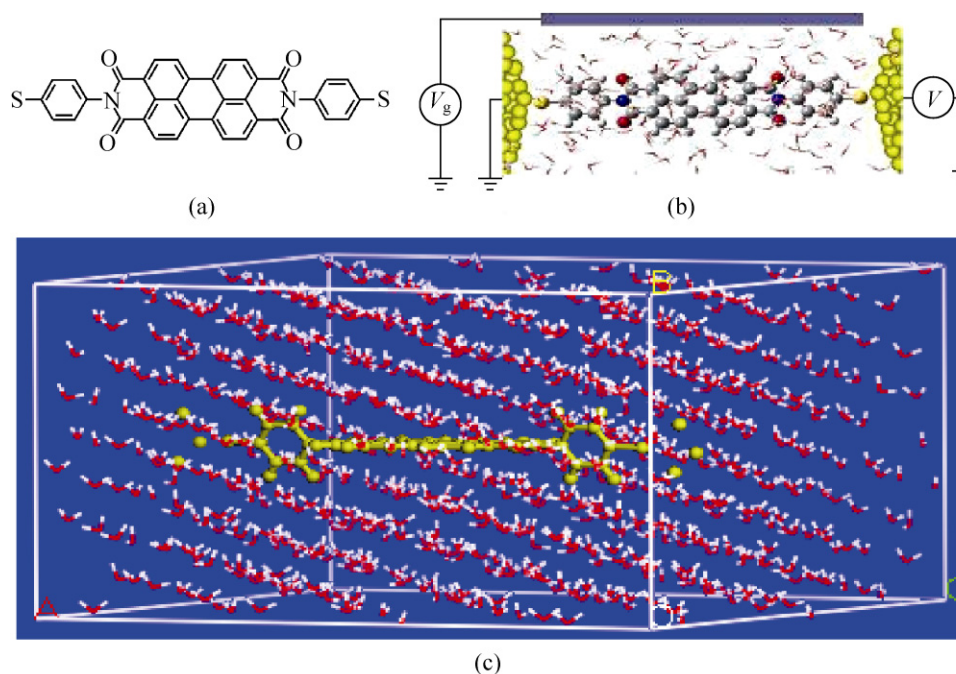
the solvent environment present in electrochemical molecular junctions [8–11] only a couple of theoretical studies are available [5]. In the latter, it was found that the experimentally adopted Gaussian function could not correctly describe the actual statistical distribution of molecular conductance [5, 11]. It was also found that the statistical conductance behavior in two-terminal molecular junctions is sensitive to changes in temperature of the aqueous solution. For a gate-controlled field effect transistor (FET), however, the effect of solvent on the statistical behavior of molecular conductance under an electric gate field is something that has been completely overlooked.

In this article, we take the well-studied gate-controlled FET [8–12], constructed by a single perylene

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tetracarboxylic diimide (PTCDI) molecule covalently bonded to gold electrodes, as a model system to study the gate field induced change in the statistical distribution of molecular conductance. For this purpose, the computational scheme we proposed in our previous study is adopted [5], which combines molecular dynamics (MD) simulations and Green's function theory calculations with extra consideration of the influence of gate electric fields of  $2.0 \times 10^9$ ,  $3.5 \times 10^9$ , and  $5.0 \times 10^9$  V/m. It should be noted that the gate electric fields in the simulations are chosen according to experiment [9], where the electric field can reach about  $1.0 \times 10^{10}$  V/m. The molecular structure of PTCDI and a schematic drawing of the FET are given in Figs. 1(a) and 1(b), respectively. It should be noted from Fig. 1(b) that the gate electric field is imposed perpendicular to the  $\pi$ -conjugation plane of the molecule. Molecular conductance has been calculated for a PTCDI single molecular junction in aqueous solution at temperatures of 298 and 308 K. We use the Cerius<sup>2</sup> package [13] to perform all MD simulations employing the PCFF force field [14]. Each simulation takes 100 ps, with the first 50 ps as the pre-equilibrium stage and the latter 50 ps for sampling. We have

taken 200 snapshots over the latter 50 ps simulations, i.e., one snapshot per 0.25 ps, at each temperature and gate electric field. The quantum systems for electron transport calculations consist of the molecular junction and nearly 60 water molecules included in the first solvation shell [5] and are calculated using the generalized quantum chemical approach [15] implemented in the QCME program [16]. In the scattering region of the molecular junction, terminal sulfur atoms are placed at the hollow site of three gold atoms in the FCC (111) plane and the S–Au distance is set to 2.85 Å, which is an optimized distance in the gas phase and was adopted also in our previous work [5]. The use of a three-gold cluster was found to be adequate for investigation of the statistical distribution of molecular conductance. The electronic structure of each junction–water supermolecular cluster is calculated using density functional theory at the B3LYP level with the LanL2DZ basis set as implemented in the Gaussian 03 package [17]. As a requirement of consistency, a gate electric field with same direction as in the MD simulation is imposed on the scattering region in the computation of electronic structure. The gate is placed



**Figure 1** Structure of PTCDI (a) and a schematic view of the gate-controlled field effect transistor (b). When a gate electric field of  $3.5 \times 10^9$  V/m is imposed on the system (c), water molecules around PTCDI rearrange from a disordered to an ordered distribution

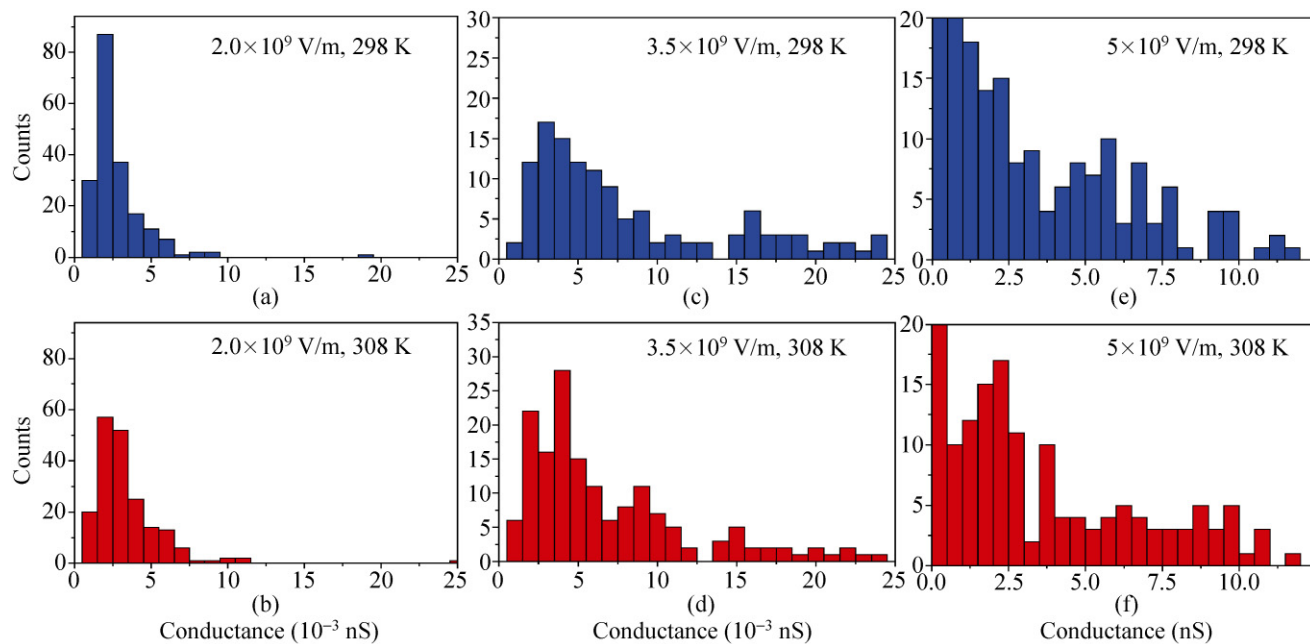
at about 1 nm away from the PTCDI molecular plane and is assumed as the reference point of electric potential.

Under the external electric field, it is observed from MD simulations that a phase transition of water from a disordered arrangement to an ordered arrangement takes place at around 35 ps. Figure 1(c) shows a typical snapshot of molecular dynamics simulations under a gate field of  $3.5 \times 10^9$  V/m. The phase transition under the external electric gate field completely changes the short-range ordered and long-range disordered microscopic distribution behavior of the water molecules. The dipole moment of the whole system, which is anti-parallel to the external electric gate field, increases from zero to about 1800 Debye. Such a rearrangement of water molecules could have a drastic effect on the electron transport of the PTCDI molecule. In this case both the hydrogen bonding interactions between oxygen atoms in the PTCDI molecule and the surrounding water molecules, and the electrostatic interactions between all the molecules are important factors in controlling the conductance behavior of the molecular junctions.

The statistical behavior of the molecular conductance of the PTCDI molecular junction at a bias of 0.1 V

under electric gate fields of  $2.0 \times 10^9$ ,  $3.5 \times 10^9$ , and  $5.0 \times 10^9$  V/m at 298 and 308 K are presented in Fig. 2. It can be seen that the maximal peak conductance at 308 K is larger than that at 298 K in general. The temperature dependent statistical histograms of conductance in Figs. 2(a) and 2(b) corresponding to a smaller gate field of  $2.0 \times 10^9$  V/m are, however, different from those given in Figs. 2(c) and 2(d) with a gate field of  $3.5 \times 10^9$  V/m and those in Figs. 2(e) and 2(f) with a gate field of  $5.0 \times 10^9$  V/m. The temperature dependent statistical conductance shown in Figs. 2(a) and 2(b) is similar to the case without the gate field [5], i.e., the intensity of the main peak at 308 K is lower and its width is greater than that of the corresponding peak at 298 K. The statistical histograms obtained for higher electric gate fields, as given in Figs. 2(c)–2(f) show more complicated temperature dependent behavior. It seems that the statistical distributions are composed of more peaks. In general, none of the conductance histograms can be described by a simple Gaussian function, as is often used in analyzing experimental data.

It was found experimentally that the maximal conductance becomes less sensitive to the change in temperature when the gate field is increased [11]. This

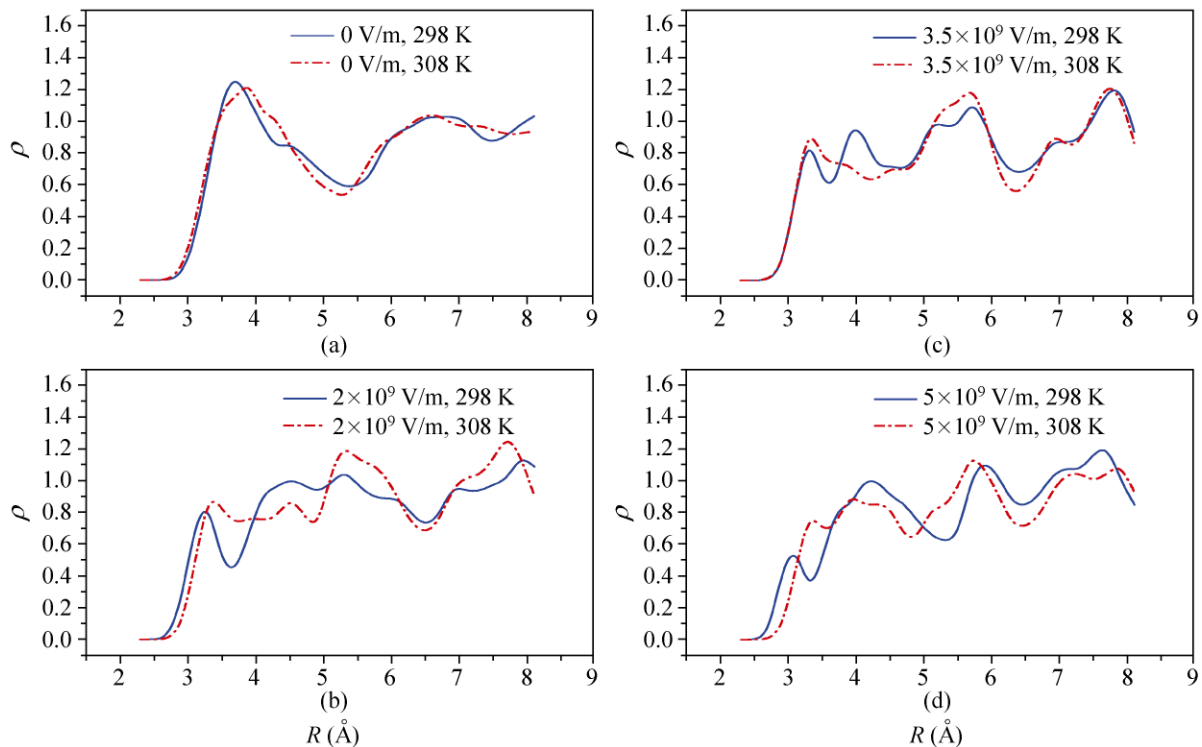


**Figure 2** Statistical distribution of the conductance for PTCDI molecular junctions in aqueous solution at 298 (top) and 308 K (bottom) under external electric gate fields of (a), (b)  $2.0 \times 10^9$  V/m, (c), (d)  $3.5 \times 10^9$  V/m, and (e), (f)  $5.0 \times 10^9$  V/m, respectively

observation can be well reproduced by our calculated results as shown in Fig. 2. The ratio between the calculated maximal conductance at 298 and 308 K is found to be 1.20, 1.10, and 1.05 under gate fields of  $2.0 \times 10^9$ ,  $3.5 \times 10^9$ , and  $5.0 \times 10^9$  V/m, respectively. In other words, the difference in conductance at temperatures of 298 and 308 K becomes quite small under the highest electric field of  $5.0 \times 10^9$  V/m, which is consistent with the experimental observation. However, it should be noted that the overall distribution of the conductance is still sensitive to the temperature even under such a high electric field.

In our earlier study [5], it was shown that the statistical distribution of conductance is closely related to a radial distribution function (RDF) that describes the number of water molecules in a small shell corresponding to the distance between the oxygen atoms ( $O-O$ ) in the PTCDI molecule and the surrounding water molecules, i.e., the hydrogen bonding network around the oxygen atoms in the PTCDI molecule. Figure 3 shows different RDFs under various electric gate fields at two different temperatures, 298 and 308 K. The RDFs for the system without the

gate are also given in Fig. 3(a) for comparison. It can be seen that without the gate field, the water molecules around the oxygen atoms in PTCDI are short-range ordered, but long-range disordered. The first solvation shell can be clearly defined by RDFs with a width of around 5.3 Å. The most probable  $O-O$  distance is found to be around 3.6 Å. Under a gate field, the RDFs show significant changes. The most noticeable difference is the presence of multi-peak structures in the RDFs, indicating that the surrounding water molecules have a multilayered structure. Another interesting observation is the location of the first peak in the RDFs. On increasing the electric field, this distance gets shorter, implying that the electric field has fixed the water molecules closely around the PTCDI molecule and significantly enhanced the hydrogen bonding strengths. In general, an increase in temperature can slightly smear out the multi-peak structures in the RDFs, i.e., thermal fluctuation can still play a role in the single molecular FET, but become less significant with increasing electric gate field. The distributional change of the water molecules around the PTCDI molecule is also reflected by the



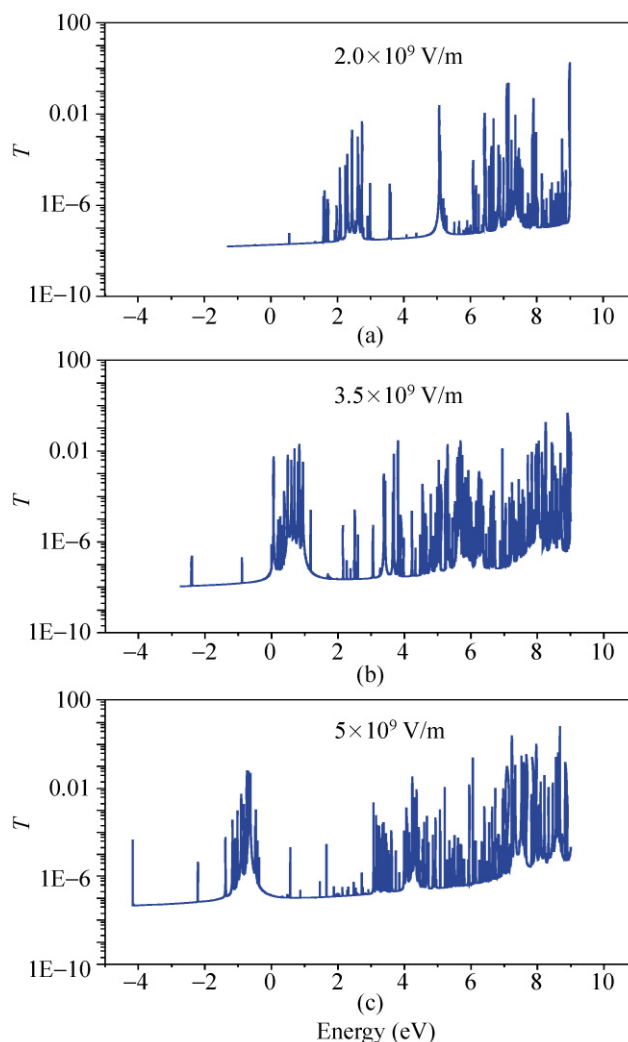
**Figure 3** Radial distribution functions of water molecules around the oxygen atoms in PTCDI at 298 (blue solid lines) and 308 K (red dashed lines) under gate electric fields of (a) 0 V/m (Ref. [5]), (b)  $2.0 \times 10^9$  V/m, (c)  $3.5 \times 10^9$  V/m, and (d)  $5.0 \times 10^9$  V/m



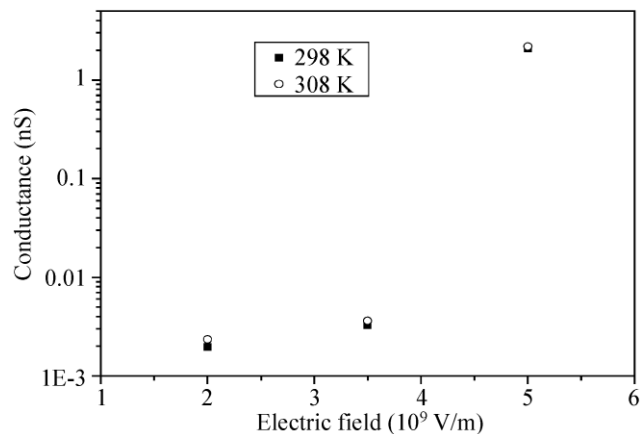
changes in dipole moment. It is found that the difference between the calculated peak dipole moments of the surrounding water molecules at the two different temperatures is about 6.2, 2.5, and 1.1 Debye under electric gate fields of  $2.0 \times 10^9$ ,  $3.5 \times 10^9$ , and  $5.0 \times 10^9$  V/m, respectively, which clearly demonstrates that the thermal fluctuation is compressed more under higher gate fields.

We have seen that the electric gate field can significantly change the hydrogen bonding network in the junction, which in turn can alter the statistics of the molecular conductance. However, there is another important aspect of the electric gate field, namely changing the electronic structure of the junctions. In Fig. 4, zero-bias transmission coefficients of a typical molecular junction (one snapshot) at 298 K under different electric gate fields are given. Under a gate field of  $2.0 \times 10^9$  V/m (Fig. 4(a)), the electron transport is in the off-resonance region while in the case of fields of  $3.5 \times 10^9$  (Fig. 4(b)) and  $5.0 \times 10^9$  V/m (Fig. 4(c)) the electron transport is mainly controlled by a near-resonance tunneling. In the off-resonance region, the thermal fluctuation is the dominant factor affecting the statistical behavior of the conductance, which is similar to the case of a two-terminal junction. In the resonance region, however, the small thermal fluctuation can cause a bigger variation in the number of electronic states that come into the bias window, and consequently have a drastic effect on the conductance, as well as its statistical distribution. This might explain why under the high electric gate field, the statistical distribution of the conductance becomes so irregular.

It was found experimentally that the current through the molecular junction could be reversibly controlled with a gate electrode over nearly three orders of magnitude at room temperature [11]. In Fig. 5, we have given the maximal peak value in the statistical distribution of the conductance for different fields and temperatures. It can be seen that under a gate field of  $5.0 \times 10^9$  V/m, the molecular conductance shows three orders of magnitude increase in comparison with that under electric fields of  $2.0 \times 10^9$  and  $3.5 \times 10^9$  V/m. The sudden change in the conductance results from the major changes in molecular electronic structure induced by the strong polarization of the external



**Figure 4** Transmission coefficients ( $T$ ) of a typical molecular junction at 298 K under electric gate fields of (a)  $2.0 \times 10^9$  V/m, (b)  $3.5 \times 10^9$  V/m, and (c)  $5.0 \times 10^9$  V/m, respectively. The zero point on the horizontal axis is the Fermi energy level



**Figure 5** Field effects of PTCDI molecular junctions in water under electric fields of  $2.5 \times 10^9$  V/m,  $3.5 \times 10^9$  V/m, and  $5.0 \times 10^9$  V/m at 298 and 308 K

electric gate field, since these push a significant number of conducting orbitals into the transport window [12].

In summary, we have presented the first theoretical study of the electric-gated field-dependent statistical behavior of molecular conductance in aqueous solution. It is shown that the statistical distribution of the conductance is very sensitive to changes in the electric gate field. The electric gate field can significantly change the hydrogen bonding network of the water molecules around the conducting molecule to form multilayered water structures. It can also drastically alter the electronic structure of the molecular junction through strong polarization.

## Acknowledgements

This work was supported by the Swedish Research Council (VR), the Swedish National Infrastructure for Computing (SNIC), the Natural Science Foundation of China (No. 20825312), and the Fok Ying Tong Education Foundation (No. 111013).

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