

Supporting Information

Temperature Depended Statistical Behavior of Single Molecular Conductance in Aqueous Solution

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1. Effects of size of extended molecule

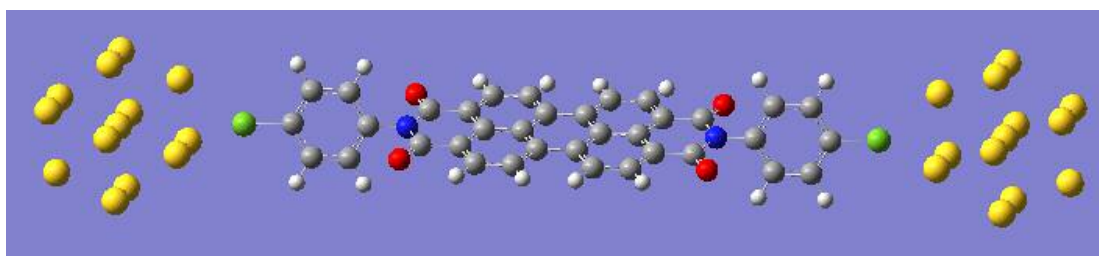


Figure S1. Extended molecules in the Au-PTCDI-Au junction with three layers of Au (13 atoms) at each end. Oxygen atoms are marked in red, gold atoms in yellow, nitrogen atoms in blue, sulfur atoms in green, carbon atoms in grey, and hydrogen atoms in white, respectively. The Au cluster follows along FCC (111) surface.

The use of triangle gold cluster for the extended molecule is mainly because of the limited computational resources we have had. In order to obtain meaningful statistic behavior of the conductance, 100 snapshots for each temperature have been taken. This has already required huge computational time for the small extended molecule used. However, our earlier studies have shown that the use of triangle gold cluster can give quite accurate results for many junctions. Test calculations have also shown that the use of large extended molecule does not change the major conclusion of the present study.

In Figure S1, an extended molecule with 13 Au atoms on each end of the molecule is given. The 13 Au atoms are arranged in three layers. We have performed molecular dynamic (MD) simulations for the extended molecule in water. The radial distribution functions (RDF) for oxygen-oxygen distance between the oxygen atoms in PTCDI molecule and the surrounded water molecules at 298 and 308 K are shown in Figure S2. It is found that the peak positions (3.67 and 3.90 Å at 298 and 308 K respectively) of the first solvation shell in the RDFs are nearly the same as those (3.69 and 3.87 Å at 298 and 308 K respectively) obtained for the small extended molecule. Moreover, the over-all distributions of RDF are very similar for two different systems. This shows

that the size of the gold cluster does not have strong impact on the hydrogen bonding network within the first solvation shell.

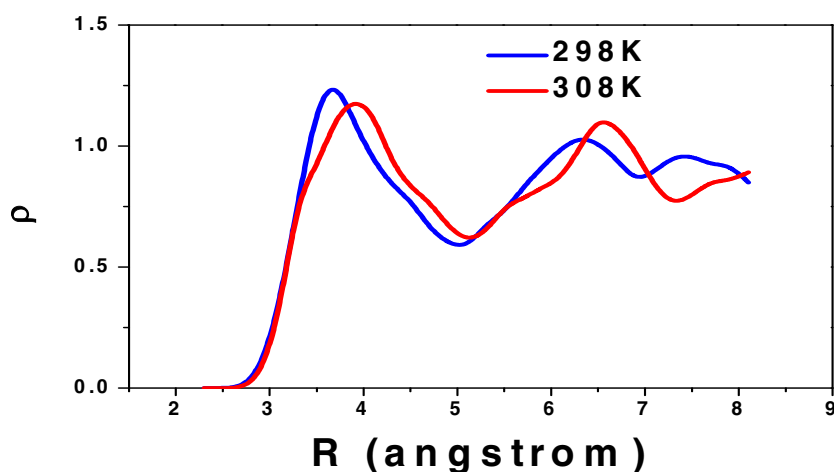


Figure S2. Radial distribution functions of O-O distance between the oxygen atoms in PTCDI molecule and the surround water molecules at 298 and 308 K.

We have also calculated conductance for Au₁₃-PTCDI-Au₁₃ junction in gas phase and in water solution. For the latter case, two snapshots from MD simulations have been used. The calculated results are given in Table S1 together with those for Au₃-PTCDI-Au₃ junction for comparison. We have calculated the conductance (see Table S1) of the molecular junctions containing these extended molecules. It can be seen that the use of large cluster has uniformly increased the conductance in comparison with the small cluster, but not the statistic behavior.

Table S1. Comparison between calculated conductances of Au₃-PTCDI-Au₃ and Au₁₃-PTCDI-Au₁₃ junctions at the bias of 0.1V in gas phase and water (nS).

Extended molecules	Snapshots from MD	Conductance of junctions	
		In water	In gas phase
Au ₃ -PTCDI-Au ₃	54ps	2.23×10 ⁻³	3.17×10 ⁻¹
	68ps	2.22×10 ⁻³	
Au ₁₃ -PTCDI-Au ₁₃	54ps	2.41×10 ⁻²	3.67×10 ⁰
	68ps	2.65×10 ⁻²	

We have also exemplified another extended molecule with Au₁₃ cluster of two layers, in which the first layer is with 3 Au atoms and the second with 10 Au atoms. The conductance of this extended molecule in gas phase is found to be 3.55 nS, which is very close to the value of 3.67 nS for the extended molecule with three layers Au atoms. It illustrates that the shape of the metal cluster does not play an important role in determination of the conductance.

2. Band gap of the extended molecule in water

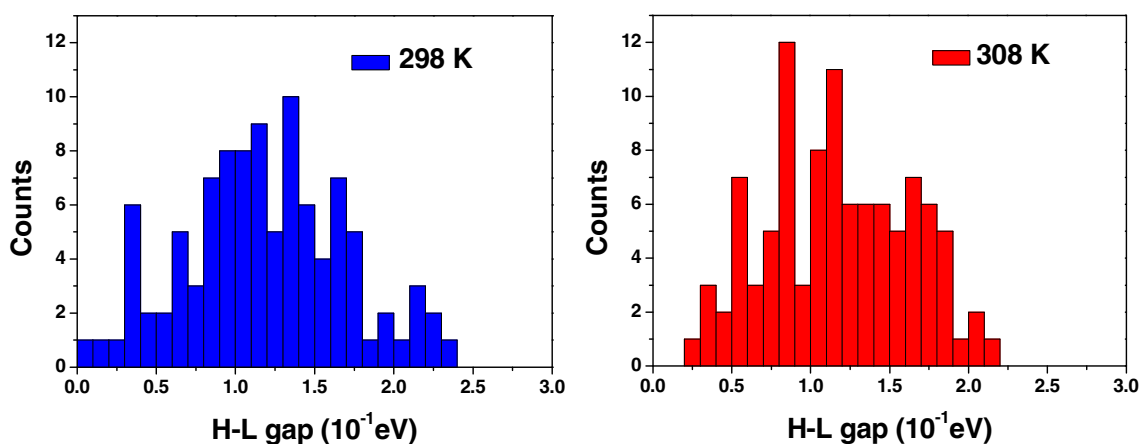


Figure S3. Distributions of band gap for the extended molecule Au₃-PTCDI-Au₃ at 298 and 308 K respectively.

The band gap is defined as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest molecular orbital (LUMO). In Figure S3, the statistic distribution of band gap for extended molecule Au₃-PTCDI-Au₃ is given. Although the averaged band gap is all around 1.2 eV at both temperatures, the actually distributions of band gap are very different. Moreover, it is difficult to directly associate the band gap distribution to the statistic behavior of the conductance.

3. Hydrogen networks.

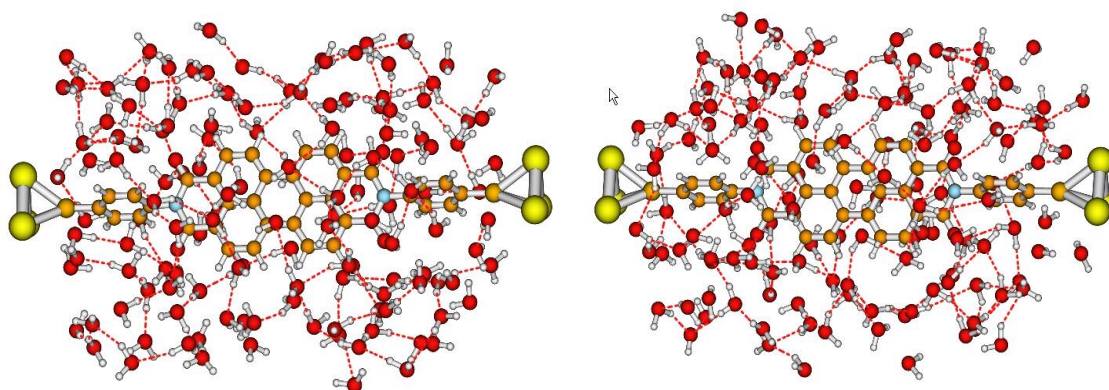


Figure S4. Different hydrogen networks for Au₃-PTCDI-Au₃ extended molecule in water at 298 K, taken from MD simulations at 62.5 (left) and 72.5 (right) ps respectively, with band gaps of 2.20 and 1.63 eV respectively.

4. Brief descriptions of the methodology on ME transport

Our approach for the electron transport is based on the general Green's function formalism of Mujica, Kemp and Ratner¹. It considers a system that consists of two semi-infinite electron reservoirs, namely the source (S) and the drain (D), connected by a molecule (M). The transition matrix element from the source to the drain is written as²:

$$T(E_i) = \sum_J \sum_K V_{JS} V_{DK} \sum_{\eta} \frac{\langle J|\eta\rangle \langle \eta|K\rangle}{z_i - \varepsilon_{\eta}} \quad (1)$$

where J and K run over all atomic sites, which are denoted as $1, 2, \dots, N$, where site 1 and N are two end sites of molecule that connect with two electron reservoirs. V_{JS} (V_{DK}) represents the coupling between atomic site J (K) and reservoirs S (D). Orbital $|\eta\rangle$ is the eigenstate of the Hamiltonian H_f of a finite system with the molecule sandwiched between two clusters of metal atoms:

$$H_f |\eta\rangle = \varepsilon_{\eta} |\eta\rangle \quad (2)$$

The product of two overlap matrix elements $\langle J|\eta\rangle \langle \eta|K\rangle$ represents the delocalization of orbital $|\eta\rangle$. Here parameter z_i is a complex variable, $z_i = E_i + i\Gamma_i$, where E_i is the energy at which the scattering process is observed, and therefore corresponds to the energy of the transmitting electron when it enters the scattering region from reservoir S . This is the same energy at which the electron is collected at time $+\infty$ by reservoir D , e.g., an elastic-scattering process. Γ_i is the escape rate. All parameters presented in Eq. (1) are obtained directly from the solutions of the finite system. Assume that the molecular device is aligned along the z direction. The tunneling current density from state k of source to some state q of drain is

$$i_{SD} = \frac{2\pi}{\hbar} \sum_{k,q} f(E_k) \times [1 - f(E_q)] |T|^2 \times \delta(E_k - E_q) \quad (3)$$

where $f(E)$ is the Fermi distribution function, which is dependent to the applied voltage. The net current through the molecular junction can then be computed out in regard to applied bias.

Reference:

¹ Mujica, V.; Kemp, M.; Ratner, M. A.; *J. Chem. Phys.* **1994**, 101, 6849.

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6. QCME program:

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