



Theoretical Analysis of the Electronic Current at Au/PTCDA Interface

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Abstract

We have been studied and analysis the electronic current at the interfaces of Au/PTCDA system according to simple quantum mode for the electronics transition rate due to postulate quantum theory. Calculation of electronic current were performed at interface of Au/PTCDA as well as for investigation the feature of electronic density at this devices. The transition of electronic current study under assume the electronic state of Au and PTCDA were continuum and the states of electrons must be closed to energy level for Au at Fermi state, and the potential at interface feature depended on structure of Au and PTCDA material. The electronic transition current feature was dependent on the driving force energy that results of absorption energy by PTCDA dye and the transition energy for configuration.

Key World: Theoretical Analysis, Electronic Current and Au/PTCDA Interface.

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Introduction

In recently years, the charge transition in many devices such that metal-molecule devices has improvement to applying in more nanotechnology field devices. The nanotechnology devices effected by electron transfer mechanism such that: optoelectronics nano devices, dye-sensitized solar cells, photochemistry, photovoltaic cell, and single molecule or other group molecules [1]. R. Marcus investigation the charge transfer in two donor and acceptor states, it was a simple model for classical transition theory of charge transfer. Recently, this model had been extended to discussion the charge transfer from an electrode state to continuum accepting state [2]. The reaction of charge transfer is very simple processing that's happened at metal - molecule devices system. It's an important elementary reactions in physical chemistry and biophysical. Charge transfer is bases on transfer from donor to acceptor levels state [3]. In

heterogeneous system, the charge transfer has occur between metals electrode and molecule. Charge transport in nano scale material was essentially to some ordered processes naturally [4-5]. The cooperation between nano scientists and nanotechnology lead to solving much more energy problems in different countries at world[6]. In the field of nanotechnology, researcher were extended this field experimentally and theoretically in different material and applied devices.

Nanotechnology field has been introduce much information about the properties of materials [7]. On the other hand, the different of energy levels feature of metal and molecules made the treatment are difficult. The different in chemical and physical properties of molecule compare to metal effect on reaction at interface and potential structure.

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Quantum confinement phenomena was effected by nanomaterial properties and dependent strongly on size and geometrical effected with composition of material properties. Now, the research is pointed on morphology of nanoparticles and the particle size controlling specially in industrial as results of using amount of higher nanostructured material technology applications devices. Quantum mechanics helped to development and improvement nano devices and would be providing better knowledge to understanding the electronic structure and physical properties [8]. The controlling on nano materials scale have been crucial at many important advances in technological devices and science. Synthesis a new nanostructures and nano materials such that nano-hetero structures and/or nanowires have been suggested new methods to identify and evaluate [9]. Today, there are a huge research pointed at nanotubes materials depending on new topical nanostructures field, it's called molecular self-assembly (MSA). These structures have been investigation in applications under range from actuators to reinforce agents, and the MSAs should

became the famous tool in nano field [10].

Theory

For charge transfer we assume that two localized quantum states for Au metal $|\varphi_{Au}\rangle$ and PTCDA molecule $|\varphi_{PTCDA}\rangle$ that's given by complete set wave function

$$[1] |\varphi_{Au,PTCDA}\rangle = \sum_{k=0}^{\infty} C_k(t) |\varphi_k\rangle \exp\left(-\frac{i}{\hbar} E_k t\right) \quad (1)$$

where $C_k(t)$ is coefficients, $|\varphi_k\rangle$ is wave function in quantum space e, and E_k is Eigen energies and we could be adapted Anderson Hamiltonian operator given.

$$\hat{H} = \hat{H}_{Au} + \hat{H}_{PTCDA} + \hat{H}_{Au/PTCDA} \quad (2)$$

Where \hat{H}_{Au} is metal Hamiltonian operator, \hat{H}_{PTCDA} is PTCDA Hamiltonian operator and $\hat{H}_{Au/PTCDA}$ is the interaction Hamiltonian operator of Au metal and PTCDA dye, and Au-PTCDA system is illustrated in Figure(1)[13], then eigen values equation become.

$$\hat{H} |\varphi_{Au,PTCDA}\rangle = (\hat{H}_{Au} + \hat{H}_{PTCDA} + \hat{H}_{Au/PTCDA}) |\varphi_{Au,PTCDA}\rangle \quad (3)$$

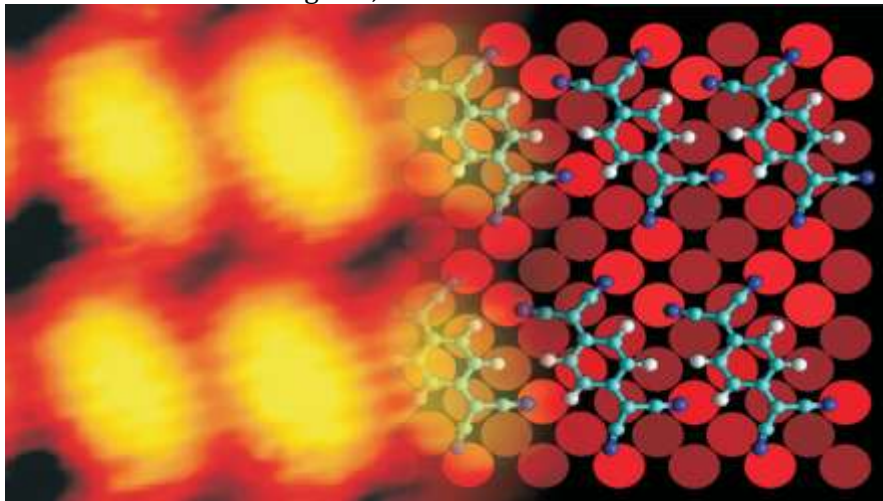


Figure 1. Illustrated schematic of the Au/PTCDA interface

The Hamiltonian in Eq. (2) obey the Eigen values of Schrödinger equation to results.

$$(\hat{H}_{Au} + \hat{H}_{PTCDA}) |\varphi_{Au,PTCDA}\rangle + \hat{H}_{Au/PTCDA} |\varphi_{Au,PTCDA}\rangle = i\hbar \frac{d}{dt} |\varphi_{Au,PTCDA}\rangle \quad (4)$$

According to some mathematical treatment, we can find.

$$i\hbar \frac{d}{dt} C_k(t) = \sum_{k=0}^{\infty} C_k(t) \hat{H}_{Au/PTCDA} \exp\left(-\frac{i(E_{Au} - E_{PTCDA})}{\hbar} t\right) \quad (5)$$

Then probability of the transition current is given by [14].

$$P(t \rightarrow \infty) = \sum_k^n |C_k(t)|^2 \quad (6)$$

The results of Eq.(6) lead to.

$$P_n(t) = |C_k(t)|^2 = \frac{C_{Au-PTCDA}^2}{\hbar^2} \left| \frac{\exp\left(-\frac{i(E_{Au} - E_{PTCDA})}{\hbar} t\right) - 1}{\frac{(E_{Au} - E_{PTCDA})}{\hbar}} \right|^2 \quad (7)$$

Where $\hbar w_{Au/PTCDA} = E_{Au} - E_{PTCDA}$ Eq.(7) reduced to.

$$P_n(t) = \frac{|C_{Au-PTCDA}|^2}{\hbar^2} \left| \frac{\exp\left(-\frac{i(E_{Au} - E_{PTCDA})}{\hbar} t\right) - 1}{w_{Au/PTCDA}} \right|^2 \quad (8)$$

From $|\exp ix - 1|^2 = 4(\sin \frac{x}{2})^2$, and $\left. \frac{(\sin xt)^2}{x^2} \right|_{t=\infty} =$



$\pi t \delta(x)$ [15] the Eq.(8) can be written as.

$$P_{n(t)} = \frac{|C_{Au-PTCDA}|^2 (\sin \frac{W_{Au/PTCDA}}{2})^2}{\hbar^2 (\frac{W_{Au/PTCDA}}{2})^2} = \frac{|C_{Au-PTCDA}|^2}{\hbar^2} \pi t \delta(\frac{W_{Au/PTCDA}}{2}) \quad (9)$$

Where δ is the delta Dirac function and due to $\frac{1}{|a|} \delta(x) = \delta(ax)$ [16] the probability in Eq.(9).

$$P_{n(t)} = \frac{2\pi t}{\hbar} \left| C_{\frac{Au}{PTCDA}} \right|^2 \delta(E_{Au} - E_{PTCDA}) \quad (10)$$

The rate of transition current is.

$$\kappa_{Au}^{PTCDA} = \frac{2\pi}{\hbar} \left| C_{\frac{Au}{PTCDA}} \right|^2 \int D(E) \delta(E_{Au} - E_{PTCDA}) dE \quad (11)$$

The density of state for system is given by [17].

$$D(E) = (4\pi \Theta_{Au}^{PTCDA} k_B T)^{-\frac{1}{2}} \exp \frac{-(\Theta_{Au}^{PTCDA} + \Delta U)^2}{4\Theta_{Au}^{PTCDA} k_B T} \quad (12)$$

By substituting Eq.(12) in Eq.(11) is.

$$\kappa_{Au}^{PTCDA} = \frac{2\pi}{\hbar} \left| C_{\frac{Au}{PTCDA}} \right|^2 (4\pi \Theta_{Au}^{PTCDA} k_B T)^{-\frac{1}{2}} \int \exp \frac{-(\Theta_{Au}^{PTCDA} + \Delta U)^2}{4\Theta_{Au}^{PTCDA} k_B T} \delta(E_{Au} - E_{PTCDA}) dE \quad (13)$$

Where ΔU the difference potential relate to (E) by equation [18].

$$\Delta U = \Delta U^\circ - E \quad (14)$$

Here (ΔU°) is driving force energy of reaction. The electron transfer rate constant be further written as.

$$\kappa_{Au}^{PTCDA} = \frac{2\pi}{\hbar} \left| C_{\frac{Au}{PTCDA}} \right|^2 (4\pi \Theta_{Au}^{PTCDA} k_B T)^{-\frac{1}{2}} \int \exp \frac{-(\Theta_{Au}^{PTCDA} + \Delta U)^2}{4\Theta_{Au}^{PTCDA} k_B T} F(E) \delta(E_{Au} - E_{PTCDA}) dE \quad (15)$$

Where $C_{\frac{Au}{PTCDA}}$ is the coupling matrix element, and

$F(E) = \frac{1}{1 + \exp \frac{E}{k_B T}}$ is the Fermi-Dirac probability

distribution given by [19]. Inserting $F(E)$, and Eq.(14) in Eq.(15) to results.

$$\kappa_{Au}^{PTCDA} = \frac{2\pi}{\hbar} \left| C_{\frac{Au}{PTCDA}} \right|^2 (4\pi \Theta_{Au}^{PTCDA} k_B T)^{-\frac{1}{2}} \int \exp \frac{-(\Theta_{Au}^{PTCDA} + \Delta U^\circ - E)^2}{4\Theta_{Au}^{PTCDA} k_B T} F(E) \delta(E_{Au} - E_{PTCDA}) dE \quad (16)$$

Solving Eq.(16) using higher mathematical physics to simply.

$$\kappa_{Au}^{PTCDA} \approx \frac{2\pi}{\hbar} \left| C_{\frac{Au}{PTCDA}} \right|^2 (4\pi \Theta_{Au}^{PTCDA} k_B T)^{-\frac{1}{2}} \exp \frac{\Theta_{Au}^{PTCDA}}{4k_B T} \left[1 - \frac{1}{4\Theta_{Au}^{PTCDA} k_B T} \left(\frac{\pi k_B T}{4} \right)^2 \right] \quad (17)$$

The transition energy due to charge transfer reaction for Au metal and dye interface is [20].

$$\Theta_{Au}^{PTCDA} = \frac{e^2}{8\pi \epsilon_0} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \left(\frac{1}{R} - \frac{1}{2D} \right) \quad (18)$$

Where e is the electron charge, ϵ_0 and ϵ are the vacuum permittivity and dielectric constant, D and R are the distance between the complex and electrode and the radius of the molecule. The radius can be approach [21].

$$R = \left(\frac{3M}{4\pi N \rho} \right)^{\frac{1}{3}} \quad (19)$$

Where M , N and ρ are molecular weight, Avogadro's number, mass density. On the other hand the driving force energy is given by [22].

$$\Delta U^\circ = \Theta_{abs} - \Theta_{Au}^{PTCDA} \quad (20)$$

Where Θ_{abs} is the absorption energy by electron, h is Planck constant, f is the frequency, $f = \frac{c}{\lambda}$ where c is the velocity of light, λ is the wave length and Θ_{Au}^{PTCDA} is the reorientation energy.

Results

The dynamics of charge transfer can be understanding due to transition theory for metal/molecule system. It has been evaluation electronic current rate according to the transition parameters, one can assume continuum energy levels for different structure material that illustrated in figure (1). Study the electronic current rate κ_{Au}^{PTCDA} in *Au/PTCDA* systems depending on dynamic simple model that supply much more knowledge. The electronic current rate is evaluated due to solve Eq.(17) by MATLAB program at different temperature $T=300, 350$ and 400 k. However, the evaluation of electronic current rate of system and investigation the transition mechanisms were needing to calculation the transition energy Θ_{Au}^{PTCDA} and effective electronic coupling $C_{\frac{Au}{PTCDA}}$ between metal and molecule states. Transition energy of system must has reform to transition, it has calculation using Eq.(18) according to estimation radii of PTCDA molecule from Eq.(19) by substituting the density $\rho_{PTCDA} = 1.764 \text{ g/cm}^3$ [23] and molecular weight $M_{PTCDA} = 392.3 \text{ molecule/mole}$ [25] of PTCDA molecule, results is $r_{PTCDA} = 4.450 \text{ \AA}$ and $r_{Au} = 1.413 \text{ \AA}$ respectively. However, the transition energy of *Au/PTCDA* is calculation due to Eq.(18) for inserting the refractive index and dielectric constant of solvent that listed in tables (1) and solving Eq.(18) mathematically to results are showing in table(1) *Au/PTCDA* system.



Table 1. Physical characteristic of solvent and transition energy θ_{Au}^{PTCDA} (eV)

Solvent	$\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right)$	Refractive index [25]	Dielectric constant [25]	Transition energy θ_{Au}^{PTCDA}
Methanol	0.538	1.3265	32.70	0.535
Ethyleneolamine	0.397	1.4513	12.90	0.399
Dimethylsulfoxidl	0.437	1.4773	46.68	0.438

Driving force energy ΔU° was a good factor that refers to magnitude of transition. It could be calculation as function of absorption energy θ_{abs} due to spectrum of PTCDA in figure (2) and

transition energy θ_{Au}^{PTCDA} from table (1), results are listed in table (2).

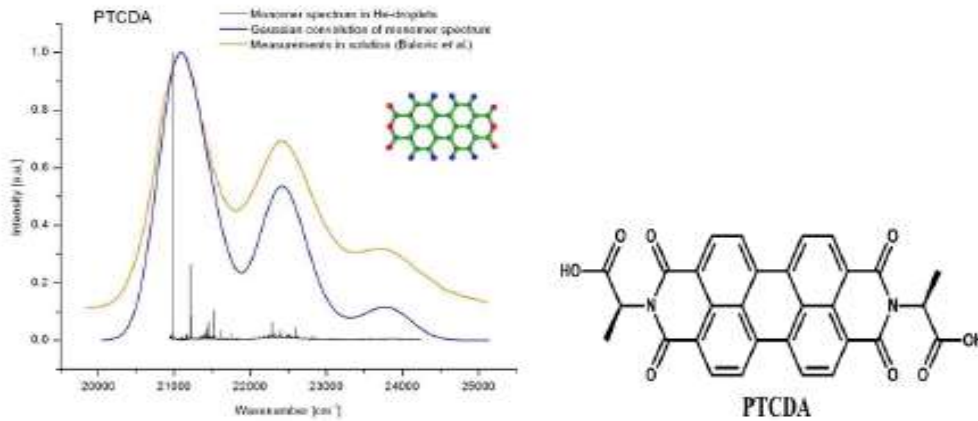


Figure 2. A) Spectral absorbance and B: Chemical structure and PTCDA -dye.

Table 2. Results calculation of driving force energies for PTCDA molecule at Methanol, Ethyleneolamine, and Dimethylsulfoxidl solvents

Wave length λ (nm)	Absorb tion energy (eV)	The driving force energy ΔU° (eV)		
		<i>Au/PTCDA</i>		
		Meth anol	Ethyleneol amine	Dimethylsu lfoxidl
350	3.535	2.996	3.139	3.099
400	3.093	2.550	2.696	2.656
450	2.750	2.208	2.351	2.311
500	2.475	1.932	2.076	2.035
550	2.250	1.706	1.850	1.810
600	2.062	1.518	1.662	1.622
650	1.904	1.359	1.503	1.463
700	1.767	1.223	1.367	1.326

On the other hand the evaluation of the electron current rate, we could be using Eq.(17) with coupling coefficient $C_{\frac{Au}{PTCDA}}$ for the metal/molecule are taken from typical values $C_{\frac{Au}{PTCDA}} = 0.010, 0.020, 0.030,$ and 0.040 eV and transition energy results from table (1) with temperature $T=300, 350$ and 400 . The results of electrons current rate are evaluation by MATLAB program and results are shown in table(3).

Table 3. Data results of calculation the charge flow rate κ_{Au}^{PTCDA} for Au/PTCDA at at Methanol, Ethyleneolamine, and Dimethylsulfoxidl solvents.

solvent	$\kappa_{Au}^{PTCDA} \times 10^{11} (sec)$									
	T=300K			T=350K			T=400K			
	$C_{\frac{Au}{PTCDA}}(eV)$									
	0.	0.	0.	0.0	0.	0.	0.	0.	0.	0.
	0	0	0	40	0	0	0	0	0	0
	1	2	3		1	2	3	4	1	2
	0	0	0		0	0	0	0	0	0
Methanol	0.	0.	0.	1.6	0.	0.	2.	3.	0.	1.
	1	4	9	65	2	9	1	8	3	5
	0	1	3		3	5	4	0	8	5
	4	6	7		8	2	2	7	9	7
Ethyleneolamine	0.	1.	4.	7.9	0.	3.	7.	1.	1.	5.
	4	9	4	18	8	5	9	4	2	0
	9	8	5		8	5	9	2	5	2
	5	0	4		9	6	9	2	5	1
Dimethylsulfoxidl	0.	1.	2.	5.0	0.	2.	5.	9.	0.	3.
	3	2	8	82	6	4	4	7	8	5
	1	7	5		1	4	9	7	9	9
	8	0	9		1	2	6	0	8	5



Discussion

The electric properties of Au/PTCDA system was effected by electrons current rate $\kappa_{Au}^{PTCDA} (sec^{-1})$ as the function of transition energy $\Theta_{Au}^{PTCDA} (eV)$ and overlaping coupling coefficient $C_{\frac{Au}{PTCDA}} eV$ at different temperature $T(K)=300,350$ and 400 K for PTCDA dye molecule bounded to Au metal, that's means the energy state at Fermi levels assuming to be a continuum energy levels of PTCDA. The electrons current rate has been calculated due to transition energy $\Theta_{Au}^{PTCDA} (eV)$, that's energy enough to reorientation before transition and the overlapping coupling energy at interface. However, the driving energy force is most important energy factor to drive more electrons to transfer out of potential at interfaces and it has been supplied from absorbtion of PTCDA dye at figure (2). Driving energy in table (2) has been supplied more energy the electrons in Au/PTCDA system to cross the potential and drive more electrons from Au metal to PTCDA molecule cross interface. Table (2) show that driving force energy for system are is increasing with decreasing wave length and increasing absorbtion energy and vice versa. The potential at interface depending on the material structure and characteristic of HOMO-LUMO energy levels at for PTCDA and levels energy at Fermi levels for Au metal. Results of transition energy in table (1) refers that Au/PTCDA system with Ethyleneolamine needed low energy to reorientation to transfer than system with methanol and Dimethylsulfoxidl solvent and the system has low transfer energy has large electronic current rate and vice versa for three solvents. It can be showing that electrons current rate are increasing with increasing temperature for all solvent

Table (3) show that the current rate with Ethyleneolamine solvent is larger than systems with the Methanol, and Dimethylsulfoxidl solvents.

Results in table (3) show that system with ethyleneolamine solvent have fast current rate to transfer and give large flow charge transfer cross interface and Propanol was active media surrounding to transfer than other solvent. Solvent Ethyleneolamine with Au/PTCDA system is good media surrounding for transfer as function of polarity of system comparing with each other two solvent. Table (3) show that the electronic current rate are increasing with coupling coefficient and

Au/PTCDA with faster than solvent, its indicate that solvent is active media for Au/PTCDA system. Furthermore, the results in tables (3) refers to charge flow rate increases for increases coupling for all system.

Conclusion

In conclusion that from evaluation of electrons current rate the transition was a function of transition energy, temperature and coupling coefficient. The electrons current rate at Au/PTCDA are increasing with decreasing the transition energy and increases with increases the coupling coefficient and temperature. The potential at interface indicate the charstristic feature of material. The electrons current rate at Au/PTCDA system was dependent on polar media and was active for more polar solvent comparing with the other two solvents. The electrons current rate increases with increases temperature and Au/PTCDA system at solvent matching to transfer of electrons.

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