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Journal Name:	Physical Science International Journal
Manuscript Number:	2014_PSIJ_14438
Title of the Manuscript:	New metrology approach for single molecular device: probing of molecular energy gap by electrical and optical measurements
Type of the Article	

General guideline for Peer Review process:

This journal's peer review policy states that **NO** manuscript should be rejected only on the basis of '**lack of Novelty**', provided the manuscript is scientifically robust and technically sound.

To know the complete guideline for Peer Review process, reviewers are requested to visit this link:

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PART 1: Review Comments

	Reviewer's comment	Author's comment (if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)
<u>Compulsory</u> REVISION comments	The proposed and objectives of this manuscript are interesting. Some of results showed in this paper can be found in the references 10, 29, and 30, but the authors' analysis introduces a new point of view of these data. However to improve the manuscript quality, I recommend major revisions in the text. Some sentences need to be rewritten. Some experimental data need to be further detailed. Some Suggestions: Line 21 to 23: These complementary techniques that can provide some information about structure of molecular junction are barely accessible for many experimental groups. The present work proposes ... Line 31 to 35: Crossover between trapezoidal barriers regime and triangular barrier regime, in the Simons model was recently studied in the case of molecular junctions [7, 8, 9, 10, 11]. This methodology has potential to become a metrology tool for analysis of molecular nanojunctions, due to the correlation between the energy scale of transition point (V_{trans}) and optical offset between	Thanks for the comments and correction. We really appreciate your time and efforts. Submitted paper is indeed partly relies on our previous studies. We are making a baby steps in interpretation of our experimental results. There are still few aspects of the same research topic that pending for their adequate interpretation to build the consistent big picture. In my opinion, Molecular Nanoelectronics (at current stage of development, e.g. ref 1) does not suffer from lack of new experimental data. It is really the insight of the field, which is missing. Corrected correspondingly Corrected as: "Crossover between trapezoidal barriers regime and triangular barrier regime in the Simons model has been studied in the case of molecular junctions [7, 8, 9, 10, 11]. This crossover methodology has potential to become a metrology tool for analysis of molecular nanojunctions due to the correlation between energy scale of transition point (V_{trans}) and

	Fermi Energy Level (E_F), and nearest molecular orbital (MO). Line 38 to 40: The simultaneous analysis of electrical and optical properties is also a useful approach to study the transport.... Line 41 to 60: the sentences are too long, which difficult the comprehension of text. I recommend rewrite this text. Line 79: I suggest remove the expression “long time ago”	optical offset between Fermi Energy Level (E_F) and nearest molecular orbital (MO).” Corrected correspondingly These sentences are rewritten as following: We also assume that device with Au electrodes has a hole conductivity (since E_{FAu} is in the HOMO proximity) and device with Al electrodes has an electron conductivity (since E_{FAl} is in the LUMO proximity). Tunneling through HOMO and LUMO molecular orbitals is determined by values of Φ_{BLUMO} and Φ_{BHOMO} barriers between these molecular orbitals and E_F of electrodes. For device with Au and Al electrodes those barriers are designated as Φ_{BAu} and Φ_{BAl} correspondingly. Φ_{BAu} and Φ_{BAl} barriers can be derived from conductivity measurements by using Simmons model at low biases. Knowledge of Φ_{BAu} and Φ_{BAl} values and difference in workfunction, ΔWF, between Au and Al metal electrodes allows us to evaluate gap between HOMO and LUMO for single molecular junction by summation of Φ_{BAu} and Φ_{BAl} and ΔWF values. We designate the HOMO-LUMO gap that can be derived from electrical measurement as $\Phi_B\Sigma$. The same gap can be found by optical measurements. The goal of this paper is to compare the $\Phi_B\Sigma$ to the optical gap Δo [14]. Thanks, I remove this expression
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	Line 85: found	Corrected
	Line 90: Therefore the current amplitude also increases...	Corrected
	Line 117: It has been demonstrated [28, Error! Bookmark not defined]	Corrected
	Line 191 to 196: This concentration is typical for a single molecular device [29, 30, 31]. We denote this device as 'r=10⁻⁶ device'. In this report the conductive molecular channels are composed by Me-PET molecules. Similar studies were done using methylbenzene di-thiol (Me-BDT) molecules [29, 30]. The structure of Me-PET/PT and Me-BDT/PT 'r=10⁻⁶ devices' are very similar. Every Si chip was constituted by three different devices, each one with an active area of about 0.5 mm².	Corrected correspondingly
	Line 212: (...) molecular orbitals (...)	Corrected
	Line 340: 2.0 ± 0.1 eV	Corrected
	Line 353: 1.0 ± 0.1 eV	Corrected
	Line 354: 4.2 ± 0.3 eV	Corrected
	Table 1. It is unclear whether the parameters are related to r =0 or r=10⁻⁶ devices in Au or Al electrodes. This is explained only in the lines 341 and 342. Suggest that equations (1) and (2) are close to this Table. Perhaps the explanation of the Simmons equations can be done before these results.	Table 1 is specified for devices with Au electrodes. We shifted eq.(1) and eq.(2) in paragraph before Table 1 along with explanation of Simmons model. It really looks better this way thanks a lot.
	Figure 2: These graphics show the same results found in the reference [10]: Pakoulev, A, and Burtman, V. , J.	We include ref [40] in title of Figure 2. This reference state that "We used the same data for



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	Phys. Chem. C 2009, 113, 21413-21421. As recommended: "If author(s) are using any part of published paper, they should give proper reference" In Results and Discussion, it is recommended some comments about experimental measurements of optical gap.	analysis of crossover from direct to indirect tunneling in 'r=10⁻⁶' device in ref Error! Bookmark not defined. In this study we proved direct tunneling in 'r=10⁻⁶' device at room temperature. This observation enables us to study the <i>energy gap proximity</i>, $\Phi_B^Z \approx \Delta_o$, at room temperature." First we added more experimental details in Materials and Method section: "We have used a Keithley 236 electrometer for two terminal electrical measurements and Varian/Cary 5G spectrophotometer for recording surface reflectivity spectra. Varian/Cary 5G spectrophotometer was equipped with a custom design sample-holder for reflectivity measurement [Error! Bookmark not defined.]."; And in results and discussion section before figure 4: "Optical spectra of the surface reflectivity of 'r = 10⁻⁶' device at room temperature with a marked HOMO-LUMO optic resonance (λ_o) are summarized in figure 3. In figure 3 two peaks at 4.3 eV and 6.3 eV are assigned to HOMO-LUMO gap in Me-PET and PT molecules 'r = 10⁻⁶' device. 4.3 eV peak is stronger and wider than 6.3 eV, presumably, due to a larger cross-section of Me-PET molecule and rotation of Me-PET molecules on substrate at room temperature [Error! Bookmark not defined.], but both peaks are well distinguishable. Most commercial photometers are sensitive enough to record spectra of single molecules [Error! Bookmark not defined.], Error! Bookmark not defined.
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		defined.,Error! Bookmark not defined.]”
<u>Minor</u> REVISION comments		Thank you again for your comments
<u>Optional/General</u> comments		