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Effect of isopropanol doped Poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate) on emission characteristics of organic light emitting diodes

Selin PIRAVADILI MUCUR[*]

The Scientific and Technological Research Council of Turkey (TÜBİTAK), Marmara Research Center,
41470 Gebze, Kocaeli, Turkey

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Abstract

The performance of polymer based organic light-emitting devices (OLEDs) that contained isopropanol (IPA) doped poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) utilized as positive charge carriers (hole) injecting electrode were investigated. In this study, morphological changes in PEDOT:PSS thin films have been analyzed with atomic force microscopy (AFM). The results of device performance with doped PEDOT:PSS were compared with the result of non doped PEDOT:PSS device. Fabricated OLED with the concentration 1:1 (PEDOT:PSS to IPA) shows the best performance among the others with almost 8000 cd/m^2 brightness and 1.75 cd/A efficiency. Additionally, effect of IPA doping mechanisms proposed in the literature have been surveyed.

Keywords: *Organic light emitting diodes, PEDOT:PSS, hole injection layer, IPA.*

İzopropanol katkılı Poli (3,4-etilen dioksitiyofen): poli (stirensülfonat) 'ın organik ışık yayan diyotların emisyon özellikleri üzerindeki etkisi

Öz

Pozitif yük taşıyıcılar (boşluk) enjekte eden tabaka olarak kullanılan izopropanol (IPA) katkılı Poli (3,4-etilen dioksitiyofen): poli (stirensülfonat) (PEDOT: PSS) içeren polimer bazlı organik ışık yayan cihazların (OLED) performans araştırılmıştır. Bu çalışmada, PEDOT:PSS ince filmlerindeki morfolojik değişiklikler atomik kuvvet

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[*] Selin PIRAVADILI MUCUR, selinpiravadili@tubitak.gov.tr, https://orcid.org/0000-0001-5030-6698

mikroskopisi (AFM) ile analiz edilmiştir. Katkılı PEDOT:PSS ile OLED aygıt performansı sonuçları katkısız PEDOT:PSS OLED aygıtı ile karşılaştırılmıştır. Konsantrasyon 1: 1 (PEDOT: PSS - IPA) ile üretilen OLED aygıt, neredeyse 8000 cd / m^2 parlaklık ve 1.75 cd / A verimliliği ile diğerleri arasında en iyi performansı göstermiştir. Ek olarak, literatürde önerilen IPA doping mekanizmalarının etkisi araştırılmıştır.

Anahtar kelimeler: *Organik ışık yayan diyotlar, PEDOT: PSS, boşluk iletim tabakası, IPA.*

1. Introduction

Elschner et al. published the history and technical details of poly (3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS) synthesis [1]. It was synthesized in 1988 [2] as a conducting polymer (**Fig. 1a**) that posses positive charge carriers in its all oxidized forms (**Fig. 1b**) [3,4]. Its stability feature has gained wide range of application area to PEDOT. Oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) is the synthetic route to PEDOT. PEDOT:PSS has become commercially the most popular and successful conductive polymer due to its stability, fine electrical and optical properties which is important for optoelectronic device technology.

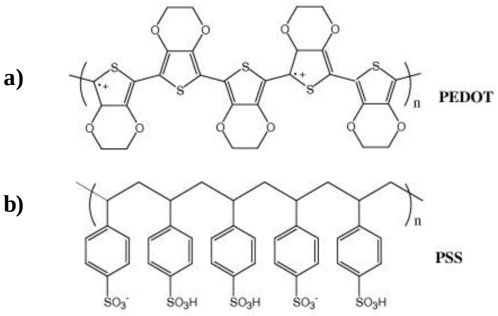

Figure 1. Chemical structure of a) PEDOT, b) polystyrene sulfonate.

From the point view of this work, PEDOT:PSS is used as a hole injection layer (HIL) in polymer based, organic light-emitting devices (OLEDs) and organic photovoltaics (OPV). [5,6]. In OLEDs and OPVs, PEDOT:PSS is used between the indium tin oxide (ITO) contact and an emissive layer (EL) (poly(p-phenylenevinylene) (PPV), polyfluorene (PF)) [5,6,7,8]. Utilization of PEDOT:PSS between the ITO and emissive layer provides contact therefore, notable rise in the lifetime of OLEDs due to preserving of the EL from migration of oxygen-involving species from the ITO contact [6] and balancing the energy difference between ITO and polymer.[9]. Groenendaal et al. published a review about applications, synthesis and characteristic properties of PEDOT:PSS [10].

The commercially purchase PEDOT:PSS solution has dark-blue opaque color. Thin film deposition tecniques of PEDOT:PSS are spin casting, spray deposition doctor blade, inkjet printing, slot die coating, etc. The PEDOT:PSS thin film shows less than 5 nm a surface roughness. It has good photo and electrical stability in air. These superior characteristics make room for PEDOT:PSS with wide applications in opto-electronic area, energy conversion and storage fields [11]. PEDOT:PSS conductivity can be enhanced twice times due to inclusion of alcohol and its additives (ethylene glycol, mesoerythritol, 2-nitroethanol, sorbitol) or DMF and DMSO [12-20]. Due to positive side of organic polymers like ease of fabrication, flexibility and weightlessness. They are also usually chemically inert. In many PEDOT study, it was applied with an alcohol [21-29]. In the J. G. D'Angelo *et al.* study, acid type PEDOT chemistry was investigated with the addition of alcohols but without any additional reagents. PEDOT reacts with the alcohol, PEDOT facilities the chemical reaction [30].

Associated with the evolvement of organic electronics research, PEDOT:PSS has been commonly used because of their superior electrical, optical, and mechanical properties, that ensure them advantageous in the area of optoelectronic devices and also in applications of OLEDs. The purpose of our study that PEDOT could react with an isopropyl alcohol (IPA) to create ether and H_2O. Produced H_2O as a byproduct was evaporated by the annealing procedure. Therefore, in connection with these aspects of this polymer, isopropanol (IPA) was doped into PEDOT:PSS with varying (1:1,1:0.5,1:0.2,1:0.1) concentrations. This study was performed to inspect the effect of PEDOT:PSS characteristics on OLEDs performances. Therefore, the aim of this work was to show the concentration dependence of isopropanol to HTL on the light output property of the OLEDs.

2. Materials and methods

The ITO coated glass substrates (ITO thickness 120nm, 10 ohms/sq.) were purchased from Kintec Company. Aluminum (Al), Calcium (Ca) were purchased from Kurt J. Lesker Company. PEDOT:PSS and Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (were purchased from Heraeus Clevios GmbH and Sigma-Aldrich, respectively. IPA (99.5%) was supplied from Sigma-Aldrich.. The MEH-PPV solution was prepared in toluene with 10 mg/cm^3 concentration. PEDOT:PSS and MEH-PPV were filtered through a 0.45 μm PVDF and PTFE membrane filter respectively. Patterned ITO-patterned substrates were cleaned ultrasonically in an acetone, de-ionised water and IPA.

Hamamatsu PMA-12 C10027 Photonic Multichannel analyzer and digital multimeter (2427-C 3A Keithley) were utilized to measure performances of all fabricated devices. A profiler (KLA Tencor P-6) determined thickness of organic layers and an Atmic Force Microscopy (AFM,Park Systems XE-150) was used to investigate the morphology of thin films. FS5 Edinburg Spectrophotometer was used to determine UV-Vis absorbance of the thin films.

Prior to the device fabrication, the glass substrates for thin film characterization measurement were ultra-sonicated for 10 min each in de-ionized water and isopropyl alcohol. IPA doped PEDOT:PSS with 1:1,1:0.5,1:0.2,1:0.1 and non-doped PEDOT:PSS were spin coated on glass substrates having the same spin rates. They were annealed at 120 °C for 20 min. Thickness, roughness and Current (I) – potential(V) measurements were carried out, the datas obtained from characterization process were in summarized Table 1.

For the device fabrication;doped/non-doped PEDOT: PSS layer was spin-coated onto the ITO at 4000 rpm for 60 s and then annealed at 120 °C for 20 min. The emissive layer (MEH-PPV; 90 nm) was spin coated with 1500 rpm and annealed at ~120 °C for 10 min. Finally, Ca (25 nm) and Al (100nm) were growth for the cathode electrode of the devices. During thermal depositions, the chamber pressure was keeped under $3x10^{-6}$ mbar. The emission area ot he devices was 9.0 mm^2. The architecture of the device was ITO /doped or non doped PEDOT:PSS/MEH-PPV/Ca/Al, as seen in Figure 2a.

3. Results and discussions

Doping effect of PEDOT:PSS with IPA on the role of hole-injecting layer in polymer-based OLEDs and thin film properties were investigated systematically. Effect of IPA doped PEDOT:PSS with varying concentrations 1:1,1:0.5,1:0.2,1:0.1 and non-doped PEDOT:PSS for reference device were studied with regard to thin film properties and OLED device performances.

In Figure 2b, the highest occupied molecular orbital (HOMO) energy level of MEH-PPV polymer was good matched with the PEDOT:PSS HOMO energy level therefore the positive charge transfer from ITO to emissive layer becomes effortless. PEDOT:PSS thin films have high work function value ~5.2 eV. The good conductivity and high work function cause quicker charge transfer spontaneously under electrical field. The lowest unoccupied molecular orbital (LUMO) energy level (~2.7 eV) of MEH-PPV was high enough to conduct negative charge carriers between the cathode and anode. This supported efficient recombination of charge carriers in the emissive zone of the OLEDs.

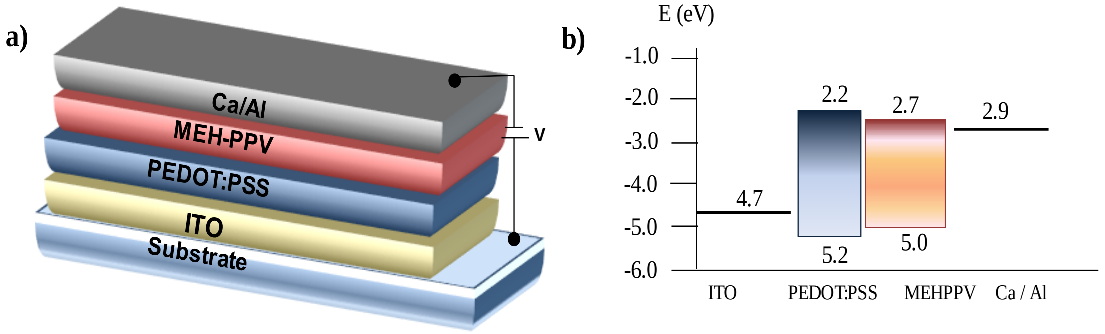

Figure 2. a) Schematic architecture of OLED, b) Band energies of the materials.

Current (I) – potential(V) measurements were carried out of thin films spin coated on glass substrates (1cm x 1cm) and the graph can be seen from Figure 3. As it can be seen from Table 1 the resistance was increasing with decreasing concentration of IPA in PEDOT:PSS. Doping with IPA enhances the conductivity of PEDOT:PSS thin films, thus this result positively reverberates the device performances.

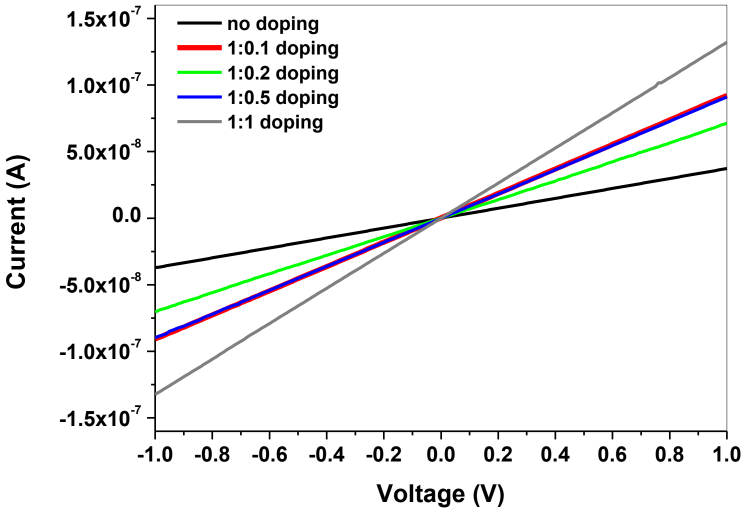

Figure 3**.** I-V characteristics of doped PEDOT:PSS

Table 1. Summary of resistance values of thin film of PEDOT:PSS.

Doping ratio	Resistance (MΩ)
No doping	26.8
1:0.1	10.9
1:0.2	14.2
1:0.5	11.0
1:1	7.5

IPA concentration effect on photophysical properties of PEDOT:PSS thin films was investigated by UV-Vis absorption and transmittance (Figure 4). A strong transmittance at visible region was observed. In this range, PEDOT:PSS thin film has above 90 % at 550 nm transmittance. When the transmittance values were compared amog themselves, transmittance values were almost the same and no shift to blue/red region can be seen. Besides, absorption characteristics were very low in the visible range. This property was compatible for OLEDs as it should be.

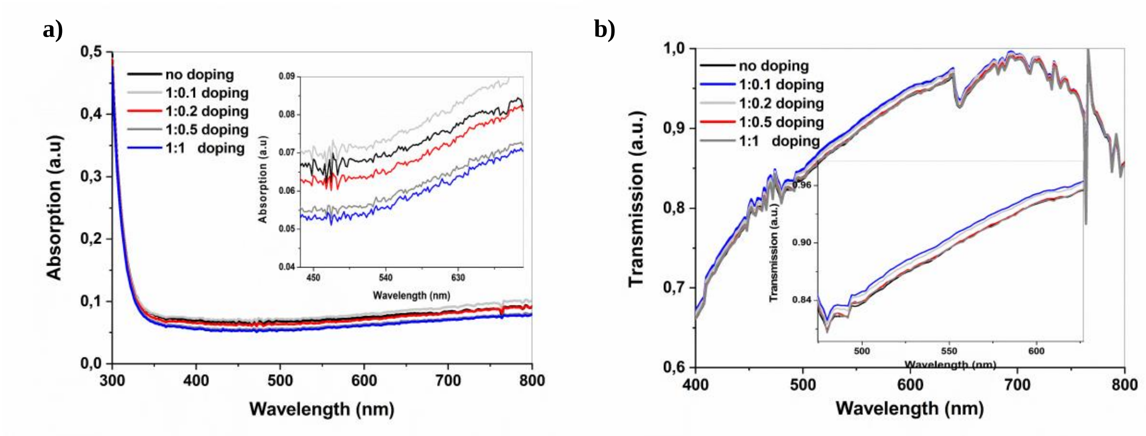

Figure 4. a) UV absorbance and b) Transmittance% spectra of ipa doped PEDOT:PSS films. (inlet shows detailed zoom of the graphs)

Table 2. Doping ratio depence of the film thickness and surface roughness of thin film PEDOT:PSS.

Doping ratio	Film Thickness (nm)	Surface roughness (nm)
No doping	65.2	0.97
1:0.1	62.1	1.37
1:0.2	54.1	1.01
1:0.5	59.2	0.92
1:1	61.8	1.33

An atomic force microscopy (AFM) was used to reveal morphological changes effected by doping ratios. Prior to the doped/non-doped PEDOT:PSS thin film deposition on the glass substrates, de-ionized water and isopropyl alcohol were used for cleaning the substrates for 5 min in ultrasonic bath. Thin fims were spin coated and annealed as the same conditions of PEDOT:PSS used in OLEDs. From the AFM images in Figure 5a-Figure 5e, surface roughnesses were almost the same (~1.0 nm). Doping ratios do not effect the thin film roughness values. Roughness values were too small < 2 nm. Stylus Profiler was used to measure the thin fim thicknesses coated with the same spin rate. Doping was not significant effect on the thickness. All the films have nearly 60-65 nm thickness values as summarized in Table 2.

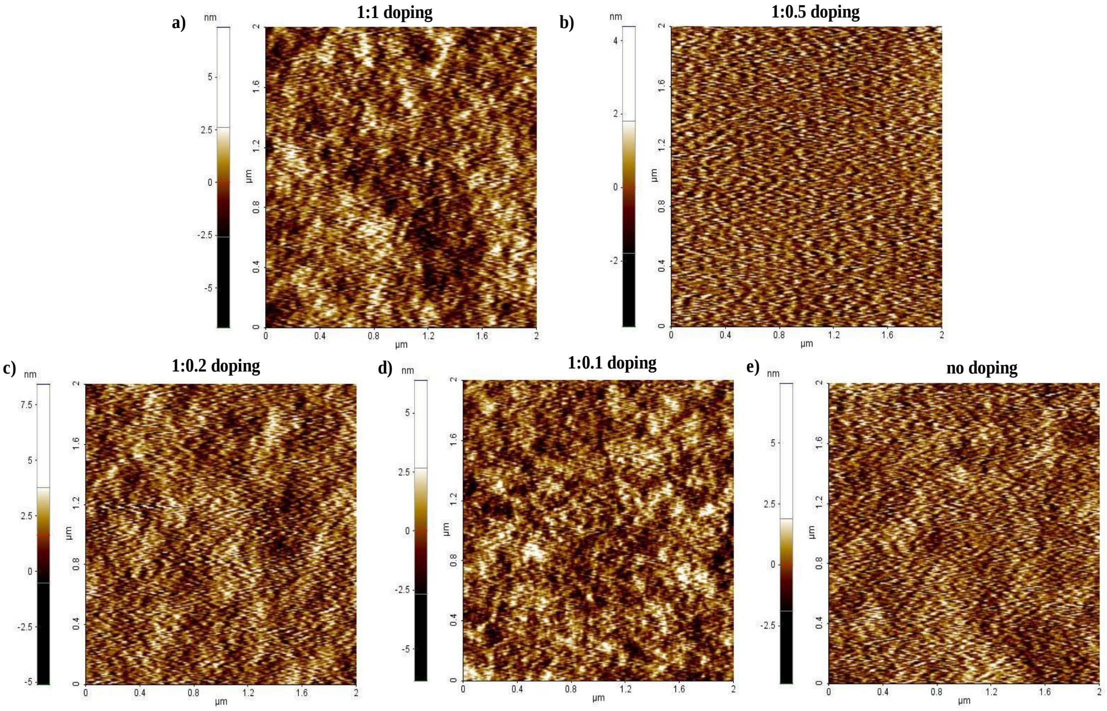

Figure 5. AFM images of PEDOT:PSS films with dopin ratio a) 1:1, b) 1:0.5, c) 1:0.2, d) 1:0.1 and e) no doping.

Figure 6a–Figure 6e represented the characteristics of the OLEDs fabricated with various concentarions of IPA:PEDOT:PSS. Device with 1:1 IPA:PEDOT:PSS concentration exhibited 7965 cd/m^2 maximum luminance (Figure 6a), maximum luminous efficiency 1.60 cd/A (Figure 6c) and maximum external quantum efficiency

(EQE) 0.91% (Figure 6e). In Figure 6b, J-V characteristics can be seen and from this graph, onset voltages can be determined. Here the onset voltage was the intersection of the tangent of the current density curve and the voltage axis. As it can be seen, onset voltages were nearly the same value (3.7 V) for all devices with different doping ratios. In Figure 6d normalized electroluminescence (EL) intensity characteristics can be seen. From the spectra, the emissions of devices were almost the same in shape and peak wavelength values (597 nm) with the MEH-PPV emission profile. As it was expected, doping of PEDOT:PSS does not change the emission properties of the system. In the A. De Girolamo Del Mauro et al. work, they realized transparent films of Dimethyl sulfoxide (DMSO) doped PEDOT:PSS used them as HIL in OLED devices. The device with DMSO-PEDOT:PSS had the lowest turn on voltage and their luminance values were higher than undopped PEDOT:PSS [31]. In another work, in order to improve the conductivity of PEDOT:PSS films methanol, ethanol, 2-propanol and ethylene glycol alcohol vapor treatment technique was applied and found that the sheet resistance of PEDOT:PSS thin films was decreased when treated with alcoholvapor [32]. In addition to this, A.K. Havare et al. investigated sorbitol (a polyalcohol carbohydrate) doped PEDOT:PSS the effect on the performance of OLED devices. The sorbitol doped PEDOT:PSS anode device showed the best performance in terms of luminous efficiency with respect to undopped PEDOT:PSS device [33].

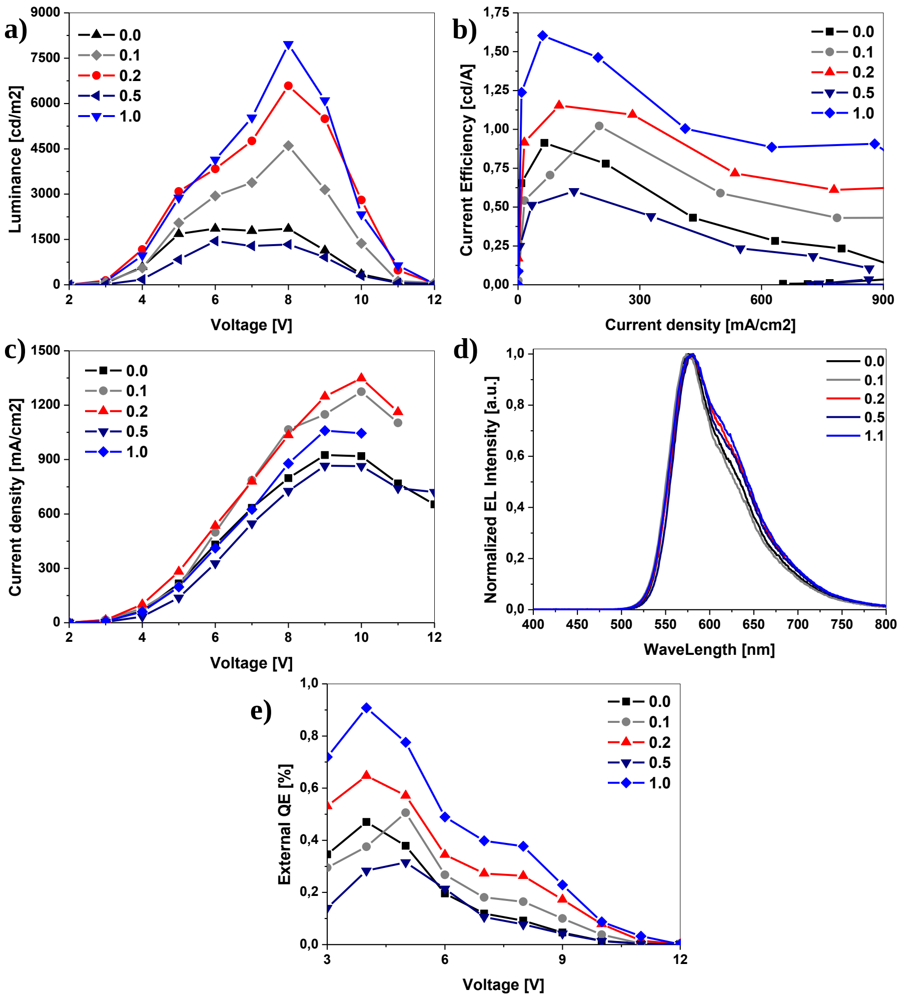

Figure 6. a) Luminance-voltage, b) current density-voltage, c) current efficiency-current density, d) normalized EL intensity-wavelength, e) EQE-voltage characteristics of OLEDs fabricated with doped PEDOT:PSS.

4. Conclusion

Doped/non-doped PEDOT:PSS thin films, spin-coated from solution, were used in polymer-based OLED device structure. The results of the work presented in this study have several significant properties that effect performance of the OLEDs.

Since the reaction mechanism has not yet been clear, PEDOT:PSS required a further investigation of the reactivity with functional groups. The effect of PEDOT:PSS chemical reactivity on the opto-electronic devices as the hole injection layer was not known, but it was obviously an important issue that requires more work and further study. However, it was clearly seen that doping with IPA enhanced the device performances due to increasing electrical conductivity of the thin film of PEDOT:PSS.Therefore charge transfer became easier and recombination probability was increasing in the emissive zone of the devices. In consideration of these obtained results, using doped PEDOT:PSS has the advantages for the future OLEDs applications. For our further research, the effect of doping on the charge transfer mechanism physics were going to realized with density functional theory (DFT) calculations using Gaussian program.

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