INQUISITION INTO THE CONDUCTIVE BEHAVIOUR OF RARE EARTH METALS DOPED C_{20} FULLERENE DEVICE

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Abstract: The enticement of fullerene molecular devices for erratic number of electronic and conductive characteristics depending upon the genre of doping is becoming the most research preferred area. The smallest possible fullerene C_{20} is highly enriched with miscellaneous properties and is extremely doping subtle. A number of doping based studies have been done in order to enrich the conductive nature of fullerene but lanthanides have not been considered for this purpose before. In this paper, $1/5^{th}$ doping of capricious lanthanides in C_{20} molecular device have been studied. Doping effect of lanthanum, cerium, praseodymium, neodymium and promethium on C_{20} fullerene using a two probe device configuration has been delved. Transport properties were explored and compared which highlighted the superiority of Lanthanum doped device over cerium, praseodymium, neodymium and promethium doped C_{20} molecular devices. A careful sift has been made to study the effect of atomic radius and bonding strength on conductance of C_{20} doped devices. Differential conductive analysis highlighted the superconductivity feature of lanthanum doped C_{20} device over other doped devices.

1. Introduction

Lanthanides, the "Industrial Vitamins" of periodic table are considered to be the marvellous applicants for developing new materials in the field of science and technology. A family, known as rare earth elements, are considered to be the most versatile, attractive and necessary need for material sciences [1]. These rare earth elements show immense bonding properties with B, C and N thereby forming borides, carbides and nitrides which are high refractory compounds having melting points above 2300 K [2].Lanthanides have the tendency to provide physical (like magnetism and Luminescence), electronic and transportproperties of utmost interest. Advancement in experimental type of structuralized chemistry have freshened the interest in methodology of semi-emperical form of interpreting data. The affluent coordination chemistry offered by Lanthanides provides plausible application areas for designing intelligent complex compounds.

At the time when in 1913 Alfred Werner won Nobel Prize for his excellent work regarding coordination theory behind various transition metal chemistry, Lanthanides chemistry was still in the shadow of confusions and predictions [3]. Later in 1947 promethium lanthanide concluded its existence and full characterization [4-6]. The coordination chemistry related to the lanthanides displays ample of structural diversityin itself and also when linked with some other atoms or molecules. Because of high potential of lanthanides in influencing the electronic properties, many experiments demonstrated in the past suggested enhancement of fullerene cluster's chemical stability by encapsulating impurity atoms in it. Lanthanides proved themselves for showing immense conductive behaviour in case of carbon fullerenes. In 2006 the superconductive nature of rare-earth doped C_{60} fullerides was probed at two different transition temperatures which proves that when lanthanides are being linked up with C-atoms they alters the conductive nature of the pristine carbon molecule [7]. In 2012 a theoretical predictive study was done by Tapan. K. Ghanty and Debashree Manna on electronic and structural properties of endohedrally lanthanide doped C_{20} [8].

Later in the same year enhanced superconductivity was observed in case of Ln- and Sm- doped phenanthrene which suggested that lanthanides can affect the superconductive nature of molecules [9]. One study lead to the other and it was further proved that Ce- doped C_{60} fullerene significantly alters the total energy of the fullerene by various structural variations [10]. Zuowan Zhou and his team later in 2014 investigated the effect of f-block atoms/ions encapsulation on the stability of C_{20}, smallest fullerene having I_h symmetry[11]. Through these investigations, stability of C_{20} fullerene using lanthanides was totally proved. C_{20} which is considered to be the

smallest known fullerene has three hybridization states because of which various allotropes are possible making carbon a basal element in nature. Studies in past suggested that fullerenes along with their derivatives possess wide variety of properties including electronic, structural and conductive. The centre of attraction among smaller fullerenes is there higher values of curvature, superconductivity and steric strain [12-14].

In this paper, we'll be digging out the new aspects regarding the effect of lanthanides namely, Lanthanum, cerium, praseodymium, neodymium and promethium, on the transport properties of C_{20} fullerene which has never probed before. All the past researches related to structural and electronic features of lanthanides increases the thirst to know about how it will affect the conductivity of C_{20} the smallest known fullerene when doped randomly in it. The idea of $1/5^{th}$ doping came from the research done before based on the study of conductivity enhancement by alkali metals doped C_{20} fullerene by G. Singh [15] which concludes that random $1/5^{th}$ doping alters the pristine characters of fullerenes to a greater extent . Endohedral and Exohedral doping of lanthanides shows notable fluctuations in molecules but random doping has not been done before and moreover according to this context it is momentous to mention that the electronic and transport properties of fullerenes are highly doping dependent.

2. Computational Details

C_{20}, a pentagonal dodecahedron has a molecular geometry fulfilling three major isomeric shapes namely bowl, cage and ring. A total of 30 bonds and 12 pentagons are formed by all the carbon atoms inside the C_{20} cage. The smallest fullerene having full icosahedral point group I_h symmetry is C_{20}. We have regarded non-interacting Huckel Hamiltonian, an approximation to the real Hamiltonian as effective method that captures the geometric character of the cage molecule including C_{20} fullerene cage [16]. C_{20}, a polyhedral structural molecule consists of totally de-localised two 2p electrons and rest two 2s electrons which are indulged in molecular bonding phenomenon.

In order to investigate the effects of lanthanide doping on C_{20} fullerene device we have used quantum chemistry semi-empirical approach popularly known as Extended Huckel Theory (EHT). This theory provides good accuracy levels and speedy calculation analysis for molecular devices. A careful probe has been made on the current dependent characteristics of doped C_{20}fullerene devices. In our simulations C_{20} cage was brought in contactwith left and right gold electrodes (noble choice for electrode material) having single connections on both sides. A nano-scale molecular device has been created which is also considered to be as two – probe device configuration. In this molecular device system we have a central scattering region sandwiched between two electrodes of any material either metal or non-metal. This device creates an analogous electrical circuit path for the current transport from one electrode to the other through the molecule in between. This sort of set up is regarded to be as two region partitioned system suggested by Landauer, ultimately forming a central region here consisting of C_{20} fullerene molecule and electrodes on both sides (fig 1). This type of two probe

molecular device is best suited for studying transport properties of fullerene molecular junctions. The highly effective connections among all the regions are totally electrical and mechanical dependent.
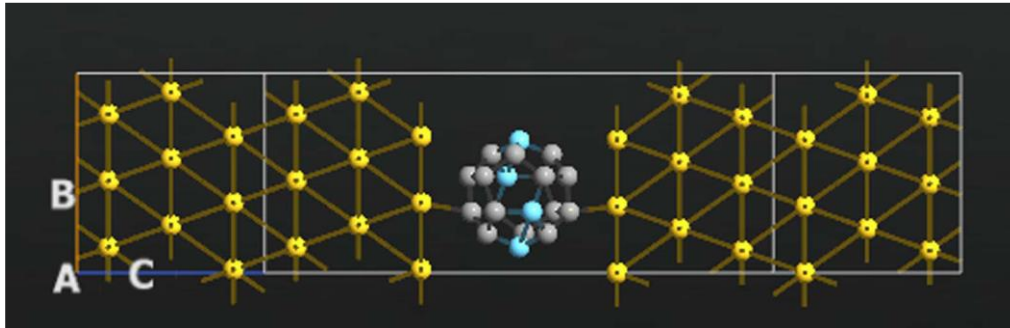

Fig.1.Doped C_{20} fullerene molecular device.

The blue colored atoms represent the doped atoms and Grey colored atoms represent Carbon atoms whereas atoms in yellow are gold atoms which comprises of left/right electrodes and some part of scattering region.

In total 1/5th doping was done by replacing four C-atoms with lanthanides, fig 1. Using Landauer-Buttiker formulism, transmission coefficients were used to calculate current,

$$I = \frac{e}{h} \sum_{\sigma} \int T_{\sigma}(E) \left[f\left(\frac{E - E_F^L + eV_R}{T_R k_b} \right) - f\left(\frac{E - E_F^L + eV_L}{T_L k_b} \right) \right] dE \tag{1}$$

Where f =Fermi energy level function

E_F^L =Fermi energy

T_R/T_L = Right and Left electrode's electron temperature.

$T_{\sigma}(E)$ = Transmission coefficient for σ spin.

Calculations of differential conductance from transmission was performed using

$$\sigma(V_{bias}) = \frac{I\left(V_{bias}^1, T_L, T_R\right) - I\left(V_{bias}^2, T_L, T_R\right)}{V_{bias}^1 - V_{bias}^2} \tag{2}$$

Calculative analysis and simulations has been actualized using Atomistix Virtual Nano lab (ATK-VNL) [17-18].In our study the parameters which have been considered for conductive properties calculations are shown in table 1.

Table 1. Parameters considered for conductive properties calculations.

K-point sampling	1:1:100
Miller indices	1:1:1
Density mesh cut-off	10 Hartree
Length along c-axis	45Å
Electrode length	7.06Å

3. Conductance Properties

3.1 *Transmission Analysis*

Calculations have been done by critically analysing the relationship of charge transfer and energy using a two probe device configuration. Total transmission spectrum informs regarding transfer of chargeacross HOMO-LUMO gap at zero bias. A transmission spectrum indicates the strength and flow of current across fermi level. From fig 2 it is clear that conductance in lanthanum doped C_{20} device is more than that of other doped devices.
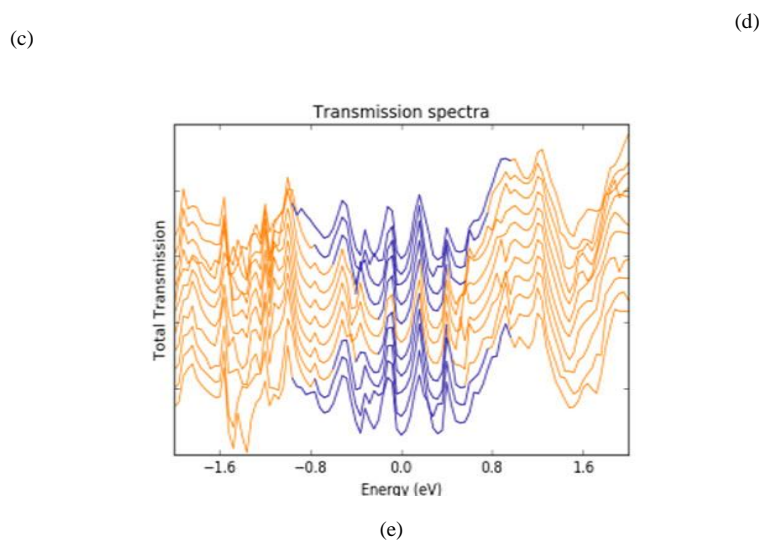

(a)

(b)

(c)

(d)

(e)
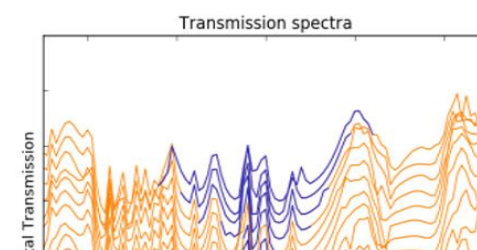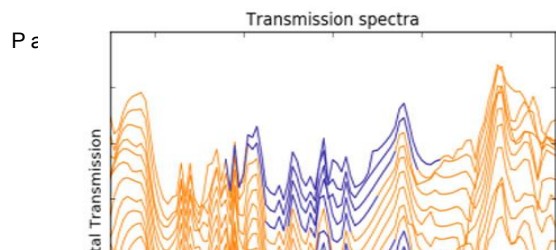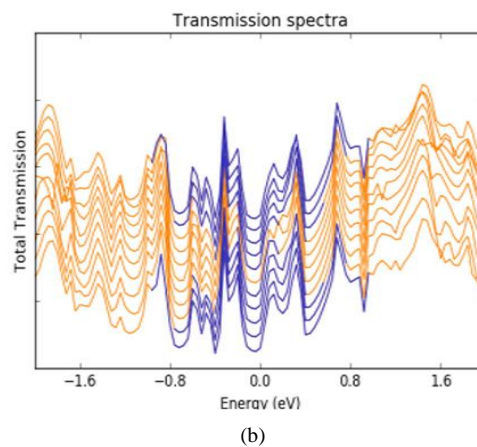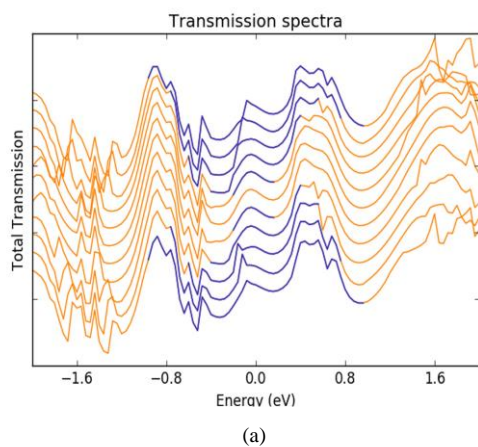
Fig. 2.Total transmission spectra of (a) lanthanum, (b) cerium, (c) praseodymium, (d) neodymium and (e) Promethium doped C_{20} devices.

Highest conductance among La@C_{20} device is followed by Pr@C_{20} device. Later in this series, places are reserved by Nd@C_{20}, Ce@C_{20} and Pm@C_{20} devices. Peakfrequency of occurrence, shifting around fermi level and strength totally influence the current carrying capacity of a fullerene device.

3.2   I-V Curve Analysis

After transmission spectra, next we outspreaded the comparative study of IV characteristics of lanthanide doped C_{20} molecular device. Conductivity among fullerenes depends upon concentration of doping and genre of bonding between dopant atoms and fullerene atoms. Our results proved the high conductivity of La@C_{20}

and least conductivity of Pm@C_{20} fullerene device. Rare earth elements are considered to be most reactive ones but at the same time they have high degree of unpredictability. The electronic configuration of lanthanides was experimentally established. Basic difference between these elements and other elements in periodic table is the electrons of former in f-orbitals. The energy of 4f sub-shell starts to fall below the energy levels of 5d sub-shell after lanthanum.4f and 5d sub-shells are very similar energy levels. Lanthanide contraction starts because of penetration of 5s and 5p orbitals into 4f sub-shell. This indicates the non-shielding character of 4f orbitals from increasing nuclear charge which causes decrease in atomic radius throughout the series. The atomic radius contributes the extent of conductivity through atomic bonding mechanism and charge transfer process between the atoms.

Although atomic radius decreases along the period but still there is fluctuation among its conductive performance probably because of concentration of doping and strength of bonding between lanthanide atoms and carbon atoms. The atomic radius is determined by both nuclear charge and number of electrons that are present in electronic shells. The degree of occupancy affects the size of atoms within those shells. Across lanthanide series, there is addition of electrons to 4f sub-shell. The first f-shell inside full 5s and 5p shells and well localised 4f shell near atomic nucleus has little effect on chemical bonding. The trend in atomic radius, valence electrons present, doping concentration and above all electronegativity differences does affect their chemistry and consequently affects the reactivity of Lanthanide doped devices.
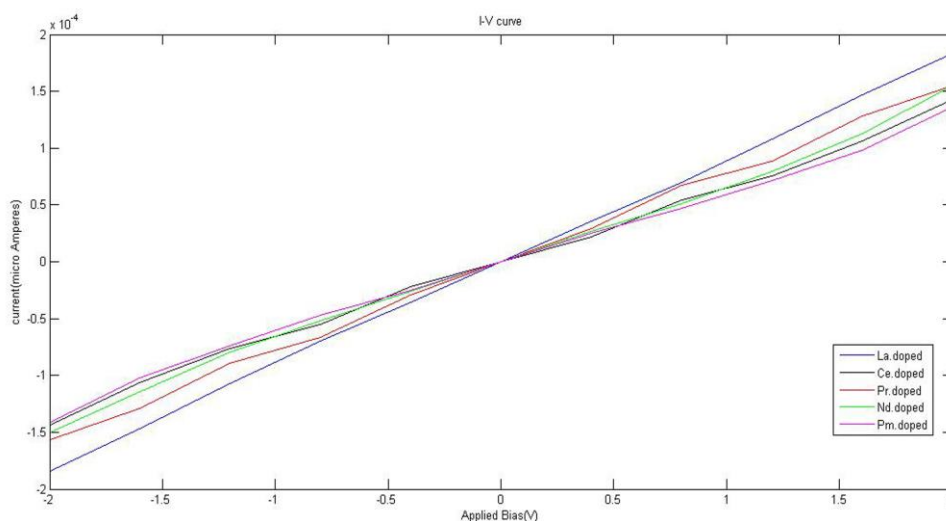

Fig. 3. Comparative I-V graph for lanthanides doped C_{20} devices.

Lanthanum among all lanthanides has higher atomic radius and indeed is considered to be more reactive than others. As we move across the period for our considered lanthanides, we will find that results found through I-V analysis and graphical representation of comparative study of I-V valuesas shown in fig 3are totally intact

with that of basic properties exhibited by lanthanides. Hence, the conductivity order thus garnered is La@C$_{20}$> Pr@C$_{20}$> Nd@C$_{20}$> Ce@C$_{20}$> Pm@C$_{20}$ molecular device.

3.3   *Differential Conductance Curve*

Our next step towards exploring more about transport properties of lanthanide doped C$_{20}$ molecular device was studying the differential conductance phenomenon. Using equation 1 differential conductive values were calculated at all considered voltages for each and every device. According to our calculated readings and fig 4, there is little variation among voltage levels ±0.8 volts and ±1.6 volts perhaps because of the un-predictive behaviour of lanthanides.
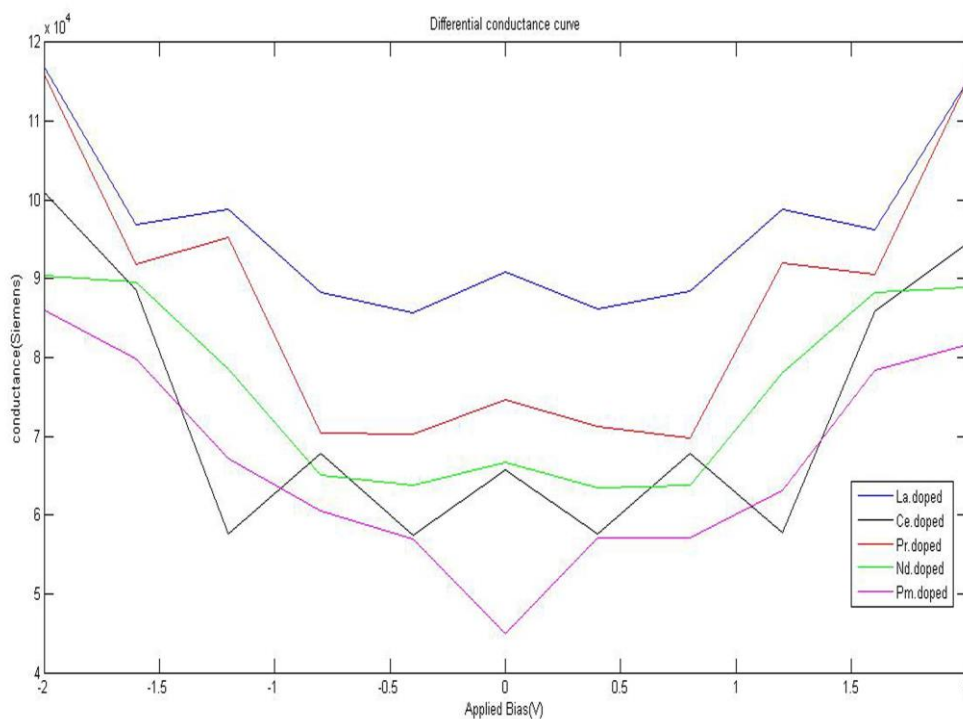

Fig. 4. Differential conductance curve for Lanthanide doped C$_{20}$ device.

For such anomalous cases our prime approach is to evaluate differential conductance in terms of quantum fundamental conductance unit given as,

$$G_0 = 2e^2 / h = 77.27 \mu S \tag{3}$$

Table 2 shows calculated values of differential conductance as compared with quantum differential conductance unit for bias levels showing varying trend.

Table 2.Conductance in terms of Fundamental Quantum Conductance Unit for various applied bias.

Bias(V)	La doped C_{20}	Ce doped C_{20}	Pr doped C_{20}	Nd doped C_{20}	Pm doped C_{20}
-1.6	1.264	1.146	1.188	1.158	1.034
-0.8	1.142	0.878	0.910	0.880	0.784
0	1.176	0.830	0.966	0.863	0.622
0.8	1.145	0.879	0.902	0.885	0.738
1.6	1.245	1.111	1.171	1.141	1.014

The non-zero conductance value indicates the superconductive behaviour of considered lanthanide doped devices. Among La@C_{20}, Pr@C_{20}, Nd@C_{20}, Ce@C_{20} and Pm@C_{20} doped devices lanthanum doped C_{20} fullerene device makes itself capable of conductive electronics application at low bias values through its superior conductivity at zero bias.

4. Conclusion

Fullerene devices provide a big room for electronic and transport research purposes. Using a two probe system and placing lanthanide doped fullerene molecule in the central region surrounded by gold electrodes electronic as well as conductive properties are studied. Using smallest fullerene C_{20} device, doping it with lanthanides and studying its transport characteristics proved the tantalizing effect of atomic bonding strength and lanthanide contraction over conductance behaviour. The overall influence of atomic radius fluctuations on the current carrying behaviour of lanthanum, cerium, praseodymium, neodymium and promethium doped C_{20} fullerene device shows the superior conductivity behaviour of lanthanum doped C_{20} device followed by Praseodymium, neodymium, cerium and promethium doped C_{20} molecular device. Series of conductivity thus obtained was La@C_{20}> Pr@C_{20}> Nd@C_{20}> Ce@C_{20}> Pm@C_{20} molecular device. Using quantum differential conductive theory we laid a firm foundation about superconductivity of lanthanum as compared to other lanthanides considered and also its high conductance at zero bias values which make it a promising candidate for low bias   applications. This research work paves a fresh and new path for more interesting researches where more elements can be bonded up with C_{20}, C_{60} and other carbon fullerene molecules to create erratic number of diverse materials comprising of superconductors and insulators. Further sensor solid state designing is completely based on conductive nature of fullerene devices and the changes which can occur when our suggested lanthanides doped fullerenes interacts with the planar molecular geometric structure, it will provide

high degree of integrity and selectivity in IC's designing which is the need of the hour in our emerging nano-molecular based electronics industry.

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