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Nonlinear optical and electronic properties of Cr-, Ni-, and Ti- substituted C_{20} fullerenes: A quantum-chemical study

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ABSTRACT

Density functional theory calculations have been performed for structures, electronic and non-linear optical properties of C_{20} fullerene and transition metals (chromium, nickel, and titanium) doped fullerene. The NBO charge distribution analysis reveals that doping with transition metal alters the charge distribution of C_{20} fullerene. The changes are more pronounced on doping with Ti followed by Cr and Ni, respectively. The dipole moment for TiC_{19} is higher than Cr C_{19} and NiC_{19} and it decreases monotonically across the period. The first hyperpolarizability of C_{20} fullerene is remarkably increased by transition metal doping. The first hyperpolarizability of Ti C_{19} is 2.5×10^3, three orders of magnitude higher than that of pure fullerene. The density of states (DOS), and frontier molecular orbital analyses confirm significant orbital hybridization upon metal doping in C_{20} fullerene, which suggest potential application of new clusters which may be important for the future development of fullerene-based nanodevices.

1. Introduction

Lately, many theoretical reports have appeared in the literature to advance the geometric, electronic properties of nanosystems [1–13]. Among these nano-clusters, cage-like systems were the subject of significant interest [14–21]. Fullerene (C60) is the prototype cage like structure. Discovery of fullerene and its isolation in large quantities has triggered an immense investigation to improve the electronic structure of fullerene [22]. C_{60} is also a primary model of a sphere-shaped aromatic molecule. However, C_{60} and all fullerene families have chemical properties resembling more close to reactive alkene molecules compared to aromatic systems [23]. All carbon fullerenes exist in other structures besides C_{60}. Among these, the structures of particular interest are C_{20}, C_{26}, C_{70} and C_{82}.

A fullerene C_n is a tri-valence polyhedral cage composed of precisely twelve pentagonal and $(n/2 - 10)$ hexagonal looks (Euler's theorem) that could be created in principle for all even values $n \geq 20$, however Considering the massive computational cost, in the present study, we chose the smallest fullerene C_{20} as the model for investigation that contains exclusively of pentagons, and it has been recognized in gas phase production by Prinzbach et al. [24].

Prinzbach et al. [13] synthesized the gas phase C_{20} fullerene by replacing the hydrogen atoms of dodecahedrane ($C_{20}H_{20}$) with bromine followed by debromination. Moreover, two groups [25,26] demonstrate effective syntheses of C_{20} fullerenes in solid phases independently. By using an ion beam irradiation method, Wang et al. [25] produced a hexagonal close-packed crystal, which has a lattice spacing of 4.6 Å, whereas Iqbal et al. [26] utilized laser ablation to deposit C_{20} fullerenes within an fcc frame.

C_{20} has also been the subject of several investigations. C_{20} is expected to have larger vibronic coupling compared to C_{60}. Therefore, the solid form of this fullerene is a potential super-conductor [27]. Domene et al. [28] studied the energetics of C_{20} and C_{22} fullerenes and near-fullerene carbon cages using quantum consistent force field and density functional tight binding methods. They showed that the C_{20} dodecahedral fullerene has the lowest energy of all mathematically possible polyhedral cages. An et al. [29] studied through the stabilization of C_{20} fullerene cage through density functional theory by employing interstitial atoms at the middle of the fullerene. In addition, they studied theoretically the transport properties of the fullerene C_{20} and the *endo*-hedral Li@C_{20} metallofullerene coupled to a 3-D electrode system [30]. A DFT study by Tian et al. [31] revealed chemisorption of H_2 molecule on Boron-doped fullerene ($C_{19}B$) while physisorption of this molecule was found by using C_{20} fullerene. Baei et al. [32] studied the modification of the electronic properties of C_{20} fullerene by encapsulating transition metals in the nano-cages. Recently, we investigated on the electronic structure of Cr- and Ni- doped fullerene [33]. We found the potential of transition metal substituted C_{20} as a strong carrier for

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adenine molecule.

The specific nonlinear change plays an imperative role in optical quantum computing [34]. The hyperpolarizability [35], as nonlinear-optical property of a molecule, is the second-order electric vulnerability per unit volume. In the present paper, we want to study effect of substitutional doping C_{20} with different transition metals (chromium (Cr), nickel (Ni), and titanium (Ti)) for electronic and non-linear optical properties. These doped nano-structures are expected to have interesting non-linear optical properties. The C_{20} fullerene is centrosymmetric with the hyperpolarizability almost zero that is expected to enhance significantly with transition metal doping. The literature reveals many examples where exohedral, endohedral and substitutional doping of cage like structures with alkali metal increases the hyperpolarizability by several orders of magnitude. The increase in hyperpolarizability is attributed to the generation of excess diffuse electrons. Doping of alkali metals in these nano-structures is an effective strategy to improve NLO properties [34–36].

The application of transition metal doping in nano-structures is rather limited. The only application of transition metal doping is for $Mg_{12}O_{12}$ where substitution of an atom with Sc results in remarkable increase in hyperpolarizability. In this study, substitution of an atom of C_{20} with Cr, Ti and Ni ($C_{19}Cr$, $C_{19}Ni$, and $C_{19}Ti$) is studied for NLO properties, which illustrates potential of these materials for the future development of fullerene-based nanodevices.

We have performed structural optimization of pristine C_{20} fullerene along with Cr-, Ni-, and Ti-doped clusters and changes in the electronic properties are evaluated through NBO charge analysis, Frontier molecular description, dipole moment, density of states, molecular electrostatic potential (MEP), and global indices of reactivity of resulted structure. To the best of our knowledge, this is the first investigation of fullerene family by tacking into account substitution of a carbon atom by transition metals.

2. Computation method

We have performed fully relaxed geometry optimizations of C_{20} and transition metal doped fullerenes ($C_{19}Cr$, $C_{19}Ni$, and $C_{19}Ti$) with *meta*-hybrid functionals (wB97XD) [37] at 6–311G (d,p) basis set, as implemented in Gaussian 09 suite of program [38]. We considered restricted spin for pristine C_{20} (singlet), and unrestricted spin for doped fullerenes. Different spin states were considered for transition metal doped fullerenes and the most stable spin states for transition metal doped fullerenes are triplet for C19Ti and C19Ni, and quintet for C19Cr. Optimization was carried out till the magnitude of the forces acting on each system reaches to 0.01 eV/Å. For all optimization, the global charge of system was neutral. The maximum force and RMS forces are 3×10^{-4} and 4.5×10^{-4} (Hartrees/Bohr and Hartrees/Radian) whereas maximum displacement and RMS displacement are 1.8×10^{-3} and 1.2×10^{-3}. Polarizability calculations are also carried out on same level of theory. First hyperpolarizability is calculated at LC-wB97XD/6–311 + G(d). The electrophilicity concept was stated for the first time in 1999 by Parr et al. [39]. Chemical potential (μ) is defined based the subsequent equation [40]:

$$\mu = -(E_{HOMO} + E_{LUMO})/2 \quad (1)$$

where E_{HOMO} is the energy of HOMO and E_{LUMO} is the energy of LUMO. In addition, hardness (ŋ) can be calculated using the Koopmans' theorem [40] as:

$$ŋ = (E_{LUMO} - E_{HOMO})/2 \quad (2)$$

Softness (S) [40] and electrophilicity (ω) [40] are explained as the subsequent equations, respectively.

$$S = 1/2\ ŋ \quad (3)$$

$$\omega = \mu^2/2\ ŋ \quad (4)$$

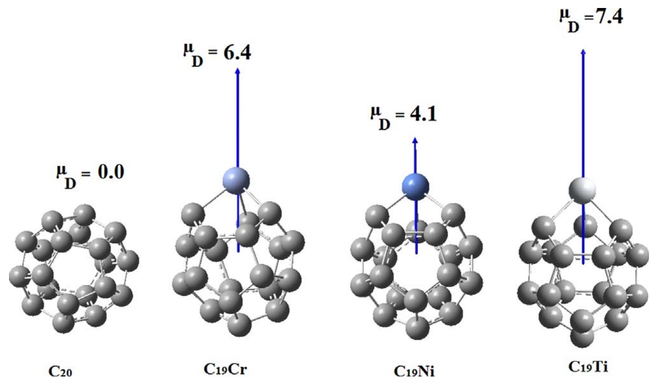

Fig. 1. Relaxed structure along with dipole moment for each system.

3. Results and discussion

Doping of an outside atom (particularly a transition metal atom) in fullerenes and its analogues bring significant changes in the geometric, electronic and optical properties of fullerenes. The endohedral doping of C_{20} fullerenes is reported in the literature however, exohedral and substitutional doping of C_{20} with transition metal atoms is very limited. Substitutional doping involves replacement of an atom of fullerene with a dopant (transition metal in our case). C_{20} fullerene is the smallest fullerene which breaks the "isolated pentagon rule" [24,25]. Replacement of a carbon atom of fullerene with a transition metal is expected to distort the geometry because of the large M—C bond. Indeed, this has been observed in the optimized geometries where metal atoms protrude out of the fullerene (see Fig. 1).

The titanium atom in Ti@C_{20} is not located symmetrically rather Ti—C bonds differ among themselves. The Ti—C bond lengths are 2.03, 2.03 and 2.07 Å. The unsymmetrical orientation of Ti in the fullerene also affects other C—C bond lengths. The C—C bond lengths in the vicinity of doping range from 1.43 to 1.48 Å. Such type of unsymmetrical orientation is not observed for Cr and Ni doping. The C—Cr bond lengths are 1.983–1.986 Å however; C—Ni bond lengths are 1.92 Å. The symmetrical orientation of Cr is demonstrated in C—C bonds in the vicinity of Cr. The C—C bond lengths are 1.44–1.46 Å.

3.1. Dipole moment and charge analysis

The doped nano-cages differ significantly among themselves for dipole moment and charges distributions. The amount of dipole moment depends on charge allocation of doped atom. Since each doped atom has different electronic nature, so it can be expected different results. The pristine fullerene (C_{20}) is Centro symmetric with 0.0 D dipole moment (see Fig. 1). The dipole moments are remarkably enhanced by doping with transition metal. The results in Fig. 1 illustrate that the order of dipole moment is Ti@C_{20} > Cr@C_{20} > Ni@C_{20}. The trend can be rationalized on the electropositivity of the doped metal. Titanium being more electropositive than Cr and Ni, loses more charge to the fullerene (gains more positive charge) which is responsible for high dipole moment (7.4 D). The charge on titanium in TiC_{19} is 1.349, which is higher than 1.249 and 1.227 for chromium and nickel, respectively. Chromium, being less electropositive than titanium, does not render as high dipole moment as TiC_{19}. The dipole moment of CrC_{19} is 6.4 D whereas the dipole moment of NiC19 is 4.1 D. The high value of dipole moment for Ti and Cr over Ni doped fullerenes can also be related to C—M bond. The dipole moment depends on the quantity of the charges as well as separation between them. The dipole moment in all doped cluster originates from the center of the nano-cage and points towards the metal atom.

NBO Charge analysis reveals that doping of metal brings prominent changes in the charge distribution of fullerenes (see Fig. 2). C_{20} is a symmetrical molecule with 0.0 D dipole moment however; there exist

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