Electronic structure and magnetic properties of endohedral metallofullerenes based on mixed metal cluster within fullerene cage with trifluoromethyl groups

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Abstract. Endohedral metallofullerenes based on encapsulated nitride scandium cluster within C$_{80}$ fullerene cage with trifluoromethyl group of CF$_3$ were characterized as a candidate model for controlling nuclear spin gate in NMR quantum computers. Effects of yttrium in nitride scandium cluster of Sc$_3$N within the fullerene cage with trifluoromethyl group on electronic structures and magnetic properties were investigated. Electronic structure and chemical shifts in $^{45}$Sc, $^{89}$Y, $^{19}$F, $^{13}$C and $^{14}$N atoms were calculated by quantum calculation using density functional theory. Addition of yttrium in nitride scandium cluster of Sc$_3$N within the fullerene cage provided a different position of chemical shift in $^{45}$Sc, $^{89}$Y, $^{19}$F, $^{13}$C and $^{14}$N atoms. This result was originated in magnetic interaction with spin-local interaction, dipole-dipole interaction and nuclear quadrupole interaction based on nuclear quadrupole moment and asymmetry of electron field gradient with a bias value of charge and spin density distribution of spd-hybrid orbital by inductive effect.

1. Introduction

Electronic structure and magnetic parameters of principle g-tensor, A-tensor for hyperfine coupling constant (hfc) of nitrogen, phosphorus, scandium atoms, and isotropic chemical shift of $^{13}$C in $^{14}$N@C$_{60}$, $^{31}$P@C$_{50}$ and $^{35}$Sc@C$_{82}$ within SWCNT as peapods for chiral index had been studied by electron spin resonance (ESR), electron nuclear double resonance (ENDOR), NMR and density functional theory (DFT) [1-4]. Recently, electronic structure and magnetic properties of endohedral fullerene based on encapsulating mixed metal cluster with several varieties of the modified fullerene cage and the mixed metal cluster have considerably been studied [5-8]. Trimetallic nitride endohedral fullerene derivatives based on asymmetric nitride scandium clusters within modified fullerene cage has been investigated by NMR, ESR and ultra-visible-near-infrared (UV-vis-NIR) absorption spectrometry using DFT [9-11]. For instant, synthesis and spectroscopic studies of a family of Sc$_3$N@C$_{80}$(CF$_3$)$_n$ (n=2-16) and their radical anion have been reported [9]. Spectroscopic (Mass spectrometry, $^{19}$F-NMR, UV-vis-NIR, ESR), structural, electrochemical studies revealed that addition of substitution CF$_3$ groups in Sc$_3$N@C$_{80}$(CF$_3$)$_n$ leaded to be easier to reduce than Sc$_3$N@C$_{80}$ [10]. The experimental and computational studies of the CF$_3$-addition motifs to Sc$_3$N@C$_{80}$
reported a special role played by the endohedral metal cluster in determining electronic structure of Sc$_2$N@C$_{80}$ [11]. In addition, effect of encapsulating mixed metal cluster in a series of endohedral fullerenes, ScYErN@C$_{80}$, ScLuN@C$_{80}$ and Sc$_2$YN@C$_{80}$ (x=0-3) on their electronic structure and reactivity have been investigated [12, 13]. The size of the endohedral moiety of mixed metal cluster in Sc$_2$YN@C$_{80}$ and ScY$_2$N@C$_{80}$ as similar geometric structure played an important role in affecting the electronic properties and chemical properties of endohedral fullerenes. In this work, effect of yttrium in nitride scandium cluster with modified fullerene cage of trifluoromethylated metallofullerene, Sc$_2$N@C$_{80}$(CF$_3$)$_2$ on electron structure and magnetic properties will be investigated by quantum calculation using DFT. The electronic structure and magnetic interaction will be discussed on the basis of quantum consideration using spin density distribution. Theoretical consideration based on Ramsey theory will be performed to reveal the factors determining the magnitude of chemical shifts in nitride mixed metal cluster fullerenes.

2. Quantum calculation

Isolated molecular structures were optimized by ab-initio quantum calculation using restricted Hartree–Fock (RHF) and DFT using B3LYP with hybrid function LANL2DZ and STO-3G*, 3-31G* and 6-31G* as basis set because of computational limitations (Gaussian 03 Inc.). The highest occupied molecular orbital (HOMO), HOMO-1, the lowest unoccupied molecular orbital (LUMO), LUMO+1 and the HOMO-LUMO band gap (E$_g$) were calculated. Mulliken atomic charges and spin density distribution were estimated by Mulliken population analysis. Continuously, isotropic chemical shift (δ) of $^{13}$C, $^{14}$N and $^{89}$Y and $^{19}$F atoms were calculated by DFT using NMR/GIAO with hybrid function B3LYP and 3-31G* as basis set. Nuclear quadrupole interactions were estimated on basis of multiplication of nuclear quadruple moment and the electro field gradient (EFG) tensor generated by charge distribution around nucleus. Excited energy level at state and wavelength in UV-vis-NIR spectra of Sc$_2$N@C$_{80}$(CF$_3$)$_2$, Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ and ScY$_2$N@C$_{80}$(CF$_3$)$_2$ as referred to Sc$_2$N@C$_{80}$, Sc$_2$YN@C$_{80}$, ScY$_2$N@C$_{80}$, Sc$_3$N, Sc$_2$YN and ScY$_2$N were calculated by time-dependent DFT (TD-DFT) with B3LYP and RHF using 3-21G* as basis set.

3. Results and Discussion

Figure 1 show DFT-computed spin densities at HOMO and LUMO of trifluoromethylated metallofullerenes: (a) Sc$_2$N@C$_{80}$(CF$_3$)$_2$, (b) Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ and (c) ScY$_2$N@C$_{80}$(CF$_3$)$_2$. Electron spin density distribution of s, p and 3d-orbital in $^{14}$N, $^{45}$Sc and $^{13}$C atoms at HOMO was delocalized on the carbon cage around trifluoromethyl group. Electron spin density distribution at LUMO was delocalized on surface of carbon cage near trifluoromethyl group. Addition of yttrium in scandium cluster of Sc$_3$N as mixed metal cluster within fullerenes cage influenced orbital-phase with electron spin density distribution. Calculated energy levels and band gap of metallofullerenes and metal clusters are listed in Table 1. In the case of Sc$_2$N@C$_{80}$(CF$_3$)$_2$, energy levels at LUMO and HOMO and the energy gaps (E$_g$) between HOMO and LUMO were estimated to be -3.7 eV, -5.9 eV and 2.2 eV, which was corresponded to π→π* excited transition. Addition of only two CF$_3$ groups as electron-withdrawing group caused inductive effect to result a considerable bias of hybrid spin density distribution on the fullerene surface. Addition of yttrium in nitride scandium cluster of Sc$_3$N within the fullerene cage will provide effect of a slight different position of chemical shift, which based on nuclear quadrupole interaction with nuclear quadrupole moment and asymmetry of electronic field gradient (EFG) with a bias value
The nuclear quadrupole interaction in Sc, Y, and metal clusters. The nuclear quadrupole interaction in Sc, Y, and metal clusters.

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of charge and spin density distribution of spd-hybrid orbital. For instant, the nuclear quadrupole interaction in ScY2N@C80(CF3)2 is depending on nuclear quadrupole moment to be -588~593 Debye-Ang. with a bias value of EFG of 89Y. 45Sc and 14N atoms, asymmetry parameter (\(\eta\)) to be 0.36~0.38, 0.58 and 0.20, Mulliken atomic charge of ScY, 45Sc and 14N atoms to be 2.03~2.04 e, 2.02 e, -0.92 e. The nuclear quadrupole interaction in ScY2N@C80(CF3)2 is caused by nuclear quadrupole moment to be -573~577 Debye-Ang. with a bias value of EFG of 89Sc and 14N atoms with \(\eta\) to be 0.59~0.64 and 0.11, Mulliken atomic charge of 45Sc and 14N atoms to be 1.85~1.92 e and -0.87 e. The nuclear quadrupole interaction of 45Sc and 14N based on nuclear quadrupole moment with a bias of EFG will provide a different position of the chemical shift in 45Sc and 14N atom with multicity at I=7/2 and 1.

![Figure 1](image)

**Figure 1** DFT-computed spin densities at HOMO and LUMO of trifluoromethyl metallofullerenes: (a) Sc3N@C80-Ih(CF3)2, (b) Sc2YN@C80(CF3)2 and (c) ScY2N@C80(CF3)2.

Calculated excited states and wavelength of mixed metallofullerenes of Sc3N@C80-Ih(CF3)2, Sc2YN@C80(CF3)2 and ScY2N@C80(CF3)2 as calculated by TD-DFT with B3LYP using 3-21G* as basis set are shown in Fig. 2 and Table 2. Energy levels and wavelengths of mixed metallofullerenes were calculated to 2.28 eV, 2.43 eV and 2.36 eV, which converted to be 544 nm, 511 nm and 526 nm. The calculated excited states corresponded to HOMO to LUMO+3 excited transition. As shown in Fig. 2, there were multi levels of energy between HOMO, LUMO, LUMO+1, LUMO+3 and band gaps, which would be assigned as multi states as exited transition, suggesting a wide range of wavelength. This result would be originated in s, p, and d-hybridization at d-d* and \(\pi-\pi^*\) exited-transitions near HOMO and LUMO+3. Addition of yttrium in nitride scandium cluster within trifluoromethylated fullerene cage of C80(CF3)2 provided a slight change of band gap with a slight blue shift of wavelength, as compared with those of Sc2Y@C80, ScY2@C80, Sc2Y and ScY2 as listed in Table 1 [13].

**Table 1** Calculated energy levels and band gaps of metallofullerenes and nitride metal clusters.

|        | LUMO+1 (eV) | LUMO (eV) | HOMO (eV) | HOMO-1 (eV) | E_g (eV) |
|--------|-------------|-----------|-----------|-------------|---------|
| Sc3N@C80(CF3)2 | -3.4 | -3.7 | -5.9 | -6.2 | 2.2 |
| Sc2YN@C80(CF3)2 | -3.5 | -3.9 | -6.0 | -6.2 | 2.1 |
| ScY2N@C80(CF3)2 | -3.5 | -3.7 | -5.9 | -6.2 | 2.2 |
| Sc3N@C80 | -3.5 | -3.6 | -6.1 | -6.1 | 2.5 |
| Sc2YN@C80 | -3.3 | -3.5 | -6.1 | -6.2 | 2.6 |
| ScY2N@C80 | -3.2 | -3.5 | -6.1 | -6.2 | 2.7 |
| Sc3N | 0.4 | 0.4 | -5.6 | -7.1 | 6.0 |
| Sc2YN | 0.4 | 0.3 | -5.2 | -5.5 | 5.5 |
| ScY2N | 0.4 | 0.3 | -5.0 | -5.3 | 5.3 |
Figure 2 UV-vis-NIR spectra of metallofullerenes.

Table 2 Calculated excited states and wavelength of metallofullerenes.

| Sample                           | Excited states          | Energy (eV) | Wavelength (nm) |
|----------------------------------|-------------------------|-------------|-----------------|
| Sc$_3$N@C$_{80}$(CF$_3$)$_2$     | HOMO → LUMO+3           | 2.28        | 544             |
| Sc$_2$YN@C$_{80}$(CF$_3$)$_2$   | HOMO → LUMO+3           | 2.43        | 511             |
| ScY$_2$N@C$_{80}$(CF$_3$)$_2$   | HOMO → LUMO+3           | 2.36        | 526             |

Comparison between chemical shifts of $^{45}$Sc, $^{89}$Y, $^{14}$N, $^{13}$C and $^{19}$F in Sc$_3$N@C$_{80}$(CF$_3$)$_2$, Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ and ScY$_2$N@C$_{80}$(CF$_3$)$_2$ were investigated for accumulating on the principle of quantum superposition of nuclear spin, $^{45}$Sc, $^{89}$Y and $^{14}$N with multiplicity at I=7/2, 1/2 and 1. As shown in Fig. 3 (a), chemical shift of $^{45}$Sc, $^{14}$N, $^{13}$C and $^{19}$F atoms inside Sc$_3$N@C$_{80}$(CF$_3$)$_2$ was individually separated and identified on a high magnetic field in a wide range from -300 ppm to 1000 ppm. As shown in Fig. 3 (a)-(c), chemical shifts of $^{45}$Sc in nitride scandium cluster within the fullerene cage were placed near 950 ppm. A detail of chemical shift of $^{45}$Sc in Sc$_3$N@C$_{80}$(CF$_3$)$_2$ is listed in Table 3. This result indicates anisotropic behavior as similar to those of $^{45}$Sc in S$_2$YN@C$_{80}$(CF$_3$)$_2$ and ScY$_2$N@C$_{80}$(CF$_3$)$_2$. The chemical shifts of $^{45}$Sc in Sc$_3$N@C$_{80}$(CF$_3$)$_2$, S$_2$YN@C$_{80}$(CF$_3$)$_2$ and ScY$_2$N@C$_{80}$(CF$_3$)$_2$ compared with nitride scandium cluster of Sc$_3$N to be -1831 ppm was considerably shifted by cage effect on magnetic interaction in $^{45}$Sc with multiplicity at I=7/2. A slight change of chemical shifts of $^{45}$Sc in the nitride scandium cluster with addition of $^{89}$Y would be explained by asymmetrical spin density distribution with synergistic effect on nuclear quadrupole interaction with nuclear quadrupole moment and EFG.

The chemical shift of $^{89}$Y atom in mixed metal cluster within the trifluoromethylated fullerene cage of Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ and ScY$_2$N@C$_{80}$(CF$_3$)$_2$ was considerably shifted in a low magnetic field near 3000 ppm as shown in Fig. 3 (b) and (c). Influence of $^{89}$Y atom in mixed metal cluster of Sc$_3$N on chemical shift of $^{14}$N is listed in Table 3. A slight change of the $^{14}$N chemical shifts in the series of nitride cluster would be explained by magnetic interaction in the nitrogen nuclei with metal nuclei of $^{45}$Sc and $^{89}$Y atoms in Sc$_3$N$^{6+}$ clusters within the fullerene cage. Encapsulation of the nitride metal cluster into the carbon cage dramatically influenced nitrogen shielding constants. Similarly, chemical shift in $^{89}$Y atoms was based on magnetic interaction between $^{45}$Sc, $^{89}$Y and $^{14}$N atoms with nuclear quadrupole moment of $^{45}$Sc and $^{14}$N atoms with asymmetry of EFG based on a bias value of charge and spin density distribution of $^{45}$Sc, $^{89}$Y and $^{14}$N atoms by inductive effect.

The chemical shifts of $^{13}$C atom with splitting in $^{13}$C-NMR spectra are shown in Fig. 3 (d)-(f). The chemical shift of $^{13}$C atom in Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ were similarly identified to those of

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**Journal of Physics: Conference Series** 433 (2013) 012004

doi:10.1088/1742-6596/433/1/012004
ScY$_2$N@C$_{80}$(CF$_3$)$_2$ near 100 ppm. A detail of chemical shifts of $^{13}$C on the modified fullerene cages of (a) Sc$_3$N@C$_{80}$(CF$_3$)$_2$, (b) Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ and (c) ScY$_2$N@C$_{80}$(CF$_3$)$_2$ are shown as remarked in Fig. 4. The chemical shifts of $^{13}$C in pentagon and hexagon aromatic ring near nitrogen atom on the modified fullerene cages in Sc$_3$N@C$_{80}$(CF$_3$)$_2$, Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ and ScY$_2$N@C$_{80}$(CF$_3$)$_2$ were differed slightly. Addition of yttrium in scandium cluster within the fullerene cage influenced the chemical shift of $^{13}$C around $^{89}$Y atom. This result would be explained by a magnitude of magnetic interaction based on s, p, and 3d hybrid orbital with a bias value of charge and spin density delocalization on hexagon aromatic ring on the fullerene cages by induction effect. Addition of yttrium in nitride mixed metal cluster within the modified fullerene cage with trifluoromethyl groups played an important role in affecting the electron structure and magnetic interaction.

![Figure 3](image)

Figure 3 NMR spectra of chemical shifts in (a)-(c) $^{14}$N, $^{19}$F, $^{45}$Sc and $^{89}$Y atoms in nitride scandium cluster within (d)-(f) $^{13}$C fullerene cage: Sc$_3$N@C$_{80}$(CF$_3$)$_2$, Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ and ScY$_2$N@C$_{80}$(CF$_3$)$_2$.

Table 3 Chemical shifts of $^{14}$N, $^{45}$Sc and $^{89}$Y atoms in mixed metal cluster within the fullerene cage.

| Chemical shift (ppm) | Sc$_3$N@C$_{80}$(CF$_3$)$_2$ | Sc$_2$YN@C$_{80}$(CF$_3$)$_2$ | ScY$_2$N@C$_{80}$(CF$_3$)$_2$ |
|----------------------|-----------------------------|-----------------------------|-----------------------------|
| $^{14}$N              | -209                        | -198                        | -191                        |
| $^{45}$Sc             | 944                         | 966                         | 979                         |
|                      | 953                         | 971                         | -                           |
|                      | 960                         | -                           | -                           |
| $^{89}$Y             | -                           | 2952                        | 2921                        |
|                      | -                           | -                           | 2944                        |
In Ramsey’s theory for nuclear magnetic shielding, the components of the shielding tensor are evolved as a sum of two terms: diamagnetic and paramagnetic terms [14]. The chemical shift will be mainly in dependence on paramagnetic effect based on spin-local interaction, the spin-dipole interaction and hybridization of molecular orbital between excited state and ground states. The chemical shift and multiplicity of $^{13}$C for optimized structure with paramagnetic moment could be explained by Karplus-Pople equation [15]. In this case, the chemical shift mainly depends on spin-local interaction, dipole-dipole interaction with nuclear quadrupole interaction in $^{45}$Sc and $^{14}$N atoms at nuclear multiplicity state, I=7/2 and I=1 on the basis of quantum consideration. The magnetic interactions determining the magnitude of chemical shifts in nitride metallofullerenes were related on hybridization of molecular orbital of s, p and 3d spin orbital with a magnitude of spin density distribution at multi-energy state. Addition of yttrium in nitride scandium cluster of Sc$_3$N within the modified fullerene cage with trifluoromethyl groups plays an important role in affecting the electronic structure and magnetic parameters in NMR, ESR and ENDOR spectra. The quantum consideration expect that the chemical shift of mixed metal cluster within the modified fullerene cage can be manipulated to control quantum spin gate with decoupling pulses in the NMR quantum computer. Molecular design of endohedral metallofullerenes based on mixed metal cluster within fullerene cage has a great advantage to quantum-calculate in the NMR quantum computer.

4. Conclusion

Electronic structure and magnetic properties of endohedral metallofullerenes based on nitride mixed metal cluster within the fullerene cage were studied for design of spin gate in the NMR quantum computer. Endohedral metallofullerenes based on encapsulated nitride mixed metal clusters within the fullerene cage with trifluoromethyl groups were characterized. Effects of modified fullerene cage and yttrium in scandium cluster on electronic structures and magnetic properties were investigated by quantum calculation using DFT. Addition of yttrium in scandium cluster within the fullerene cage resulted a slight different position of chemical shift in $^{45}$Sc, $^{89}$Y, $^{14}$N and $^{13}$C atoms. This result was originated in magnetic interaction with spin-local interaction, dipole-dipole interaction and nuclear quadrupole interaction based on nuclear quadrupole moment and asymmetry of EFG with a bias value of charge and spin densities distribution of spd-hybrid orbital by inductive effect. Addition of yttrium in nitride scandium cluster within the modified fullerene cage with trifluoromethyl groups as electron-withdrawn groups plays an important role in affecting chemical shift. Molecular design of mixed metallic nitride endohedral fullerenes has a great advantage to be a candidate model for controlling nuclear spin gate in the NMR quantum computers.
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