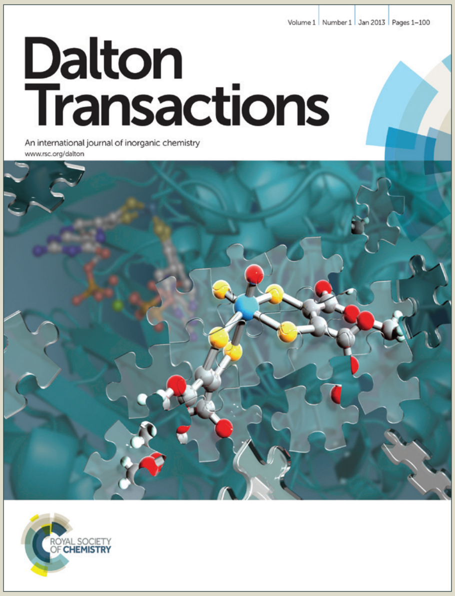

The V-shaped Polar Molecules Encapsulated into C_s (10528)-C_{72}: Stability and Nonlinear Optical Response

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Abstract:

Recently, a new sulfide cluster fullerene, $Sc_2S@C_s$ (10528)-C_{72} containing two pairs of fused pentagons has been isolated and characterized (*J. Am. Chem. Soc.* 2012, 134, 7851). Inspired by this investigation, we propose a question: what properties will be influenced by the interaction between the encapsulated V-shaped polar molecule and C_{72}? To answer this question, four encapsulated metallic fullerenes (EMFs) $M_2N@C_{72}$ (M = Sc or Y, N = S or O) along with pristine C_s-C_{72} (10528) were investigated by quantum chemistry methods. The results show that the the E_{gap} (3.01-3.14 eV) of $M_2N@C_{72}$ are significantly greater than that of pristine C_s-C_{72} (10528) (2.34 eV). It indicates that the stabilities of these EMFs increase by encapsulating the V-shaped polar molecule into the fullerene. Furthermore, the natural bond orbital (NBO) charge analysis indicates electron transfer from M_2N to C_{72} cage, which plays a crucial role in enhancing first hyperpolarizability (β_{tot}). The β_{tot} follows the order of 1174 au ($Y_2O@C_{72}$) ≈ 1179 au ($Sc_2O@C_{72}$) > 886 au ($Y_2S@C_{72}$) ≈ 864 au ($Sc_2S@C_{72}$) > 355 au (C_{72}). It indicates that the β_{tot} of $M_2N@C_{72}$ is more remarkable than that of pristine C_s-C_{72} (10528) due to the induction effect of the encapsulated molecule. Compared with sulfide cluster fullerenes ($Y_2S@C_{72}$ and $Sc_2S@C_{72}$), oxide cluster fullerenes ($Sc_2O@C_{72}$ and $Y_2O@C_{72}$) show much larger β_{tot} due to the small ionic radius and large electronegative of oxygen. In contrast, the metal element (scandium and yttrium) has a slight influence on the β_{tot}. Thus, oxide cluster fullerenes are candidate to become promising nonlinear optical materials with higher performance.

1. Introduction

The types of fullerenes have been largely expanded during the past few decades due to potential application in electronics[1-2] organic solar cell[3-5] and medicine.[6-7] It's well known that stable fullerenes strictly obey the isolated pentagon rule (IPR)[8] and IPR-violating fullerenes are too reactive to be isolated. However, a new family of endohedral fullerenes will be formed by encapsulating atoms, molecules or various metal clusters into hollow fullerenes.[9-15] IPR-violating fullerenes can be stable by the strong coordination and charge transfer from the encapsulated metal clusters to the fullerene cages. Encapsulated metallic clusters can be metal carbides,[16-18] nitrides,[13, 18-21] oxides,[22] especially, encapsulated metallic fullerenes (EMFs) containing metal elements Sc and Y have received more attention as a result of small ionic radii of them and the strong coordination with fullerene.[16-17, 21, 23-24] Recently, a new sulfide cluster fullerene, $Sc_2S@C_s(10528)\text{-}C_{72}$,[25] has been synthesized along with $Sc_2S@C_2(7892)\text{-}C_{70}$,[26] $Sc_2S@C_{82}(6 \text{ and } 8)$[27] and $M_2S@C_{3v}(8)\text{-}C_{82}$(M = Sc, Y, Dy and Lu).[28] Similarly, oxide cluster fullerenes $Sc_2(\mu_2\text{-}O)@C_s(6)\text{-}C_{82}$[29] has also isolated. It aroused our interest to investigate whether the other fullerene derivatives have the possibility to be synthesized and what properties do they possess, this information is essential for the further development of EMFs.

Fullerenes were widely investigated as nonlinear optical materials owing to extensive π-electron conjugated along with charge delocalization.[30-33] Compared with pristine fullerenes, endohedral fullerenes show remarkably nonlinear optical (NLO) response as a result of strong coordination interaction bringing about the electron transfer from the encapsulated V-shaped polar molecule to fullerene cages.[30, 34-41] For sulfide cluster fullerenes (SCFs) and oxide cluster fullerenes (OCFs), most reports are relevant to their structures characterized by mass spectroscopy, UV-vis-NIR, absorption spectroscopy and X-ray diffraction.[25-27, 29, 42] However, there is very few information available about the NLO properties, which evoke our interest to obtain this knowledge. Thus, the structures, stability and nonlinear optical properties of the encapsulated fullerenes $M_2N@C_{72}$ (M = Sc or Y, N = S or O) and the pristine cage C_s-C_{72} (10528) were investigated to obtain this knowledge.

2. Computational details

The density functional theory (DFT) method has been widely used to optimize fullerene systems, considering the accuracy and computational costs, two exchange-correlation functionals, B3LYP and BHandHLYP were used to obtain geometry optimizations of the studied compounds. The Lanl2dz basis set was selected for Sc and Y and 6-31G* for the C and S atoms. It was found that the structure parameters made by the BHandHLYP functional were in good agreement with experimental X-ray structure. As shown in Table 1, the experimental Sc-S-Sc angle is 124.6º, the calculations in this paper is 124.8 º. Thus, BHandHLYP functional was chosen to optimize the geometry structures of C_s-C_{72}(10528) and $M_2N@C_{72}$. Besides, the E_{int} between encapsulated metal cluster and the fullerene cage was calculated to explore the stability of these complexes. To correct the basis set superposition error (BSSE) and the counterpoise (CP) procedure was used to calculate the interaction energies qualitatively.[43-44] Furthermore, the electronic properties of studied system were evaluated, the vertical electron affinity (VEA), vertical ionization potential (VIP) and the natural bond orbital (NBO) charge of them were computed at the BHandLYP/6-31G*-Lanl2dz level.

To evaluate the NLO properties of studied complexes, it is necessary to choose a proper method. The traditional B3LYP method has been reported to overestimate the (hyper)polarizabilities for some large systems,[45] the second-order Møller–Plesset perturbation (MP2) method is more reliable than DFT methods in the (hyper)polarizability calculations, but it costs much resources and time for large systems. Recently, the new hybrid functional CAM-B3LYP, and BHandHLYP were also employed to evaluate the static first hyperpolarizabilities for the endohedral fullerene dimers (Na@C60C60@F).[36] Results show that the static first hyperpolarizabilities calculated by CAM-B3LYP[46] and BHandHLYP functional are close to those of MP2 method. Besides, Champagne and Nakano pointed out that for a medium-size system, the BHandHLYP method can also reproduce the (hyper)polarizability values from the more sophisticated single, double, and perturbative triple excitation coupled-cluster [CCSD(T)] method.[47-48] Thus, the linear and nonlinear optical properties of studied complexes were evaluated at the BHandHLYP/6-31+G(d)-Lanl2dz level. In order to verify the reliability and accuracy of this method in this work, we compared the CAM-B3LYP and BhandHLYP methods. The results show that the β_{tot} values obtained by the CAM-B3LYP method are close to that obtained by the BhandHLYP method. At the same time, the transition energy was calculated by time-dependent density functional theory (TD-DFT)/6-31+G. The mean dipole moment (μ_0) and polarizability (α_0) can be defined as follows.

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \qquad (1)$$

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (2)$$

The first hyperpolarizability is defined as follows.

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad (3)$$

In which

$$\beta_i = \beta_{iii} + \beta_{ijj} + \beta_{ikk}(i, j, k = x, y, z) \qquad (4)$$

E_{int} is shown in the following expression

$$E_{\text{int}} = E_{\text{M}_2\text{N@C}_{72}}(X_{ab}) - [E_{\text{M}_2\text{N}}(X_{ab}) + E_{C_{72}}(X_{ab})] \qquad (5)$$

All calculations were performed by using the Gaussian 09 program package.[49]

3. Results and discussion

3.1 Optimized geometries and stability

Optimized structures of the studied complexes are shown in Figure 1. C_s-C_{72} (10528) is unstable because of the local strain originating from two pairs of fused pentagons, and the V-shaped polar molecules M_2N (M = Sc or Y, N = S or O) are also unstable even invisible without fullerene cages.[28] Interestingly, stable $M_2N@C_{72}$ were obtained by encapsulating the M_2N into IPR-violating C_s-C_{72} (10528), the four $M_2N@C_{72}$ complexes were classified as two groups: the OCFs ($Y_2O@C_{72}$ and $Sc_2O@C_{72}$) and SCFs ($Y_2S@C_{72}$ and $Sc_2S@C_{72}$). It is necessary to compare the structures of C_s (10528)-C_{72} and $M_2N@C_{72}$. As shown in Table 1, the bond length and bond angle of $Sc_2S@C_{72}$ in this work are close to that values obtained from the X-ray single-crystal structure, which means the BhandHLYP methods has good accuracy. For these EMFs, the Sc or Y reside close to adjacent pentagons of C_s-C_{72} (10528) and the C-C bonds locating in two pairs of fused pentagons of $M_2N@C_{72}$ change obviously compared with that in pristine C_s-C_{72} (10528), and the shortest M-C distances (between the metal and carbon atoms) involve the carbon atoms in 5:5 junctions of C_s-C_{72} (10528) (see Figure 2). The M-N bond length (between the metal and central non-metal) follows the order of 1.922 Å (Sc-O) < 2.006 Å (Y-O) < 2.332 Å (Sc-S) < 2.432 Å (Y-S). However, the M_1-N-M_2 angle (ɵ) shows the opposite trend with the order 163.0° (Sc_2O) > 135.8° (Y_2O) > 124.8° (Sc_2S) > 102.9° (Y_2S). The angles in oxide ($Sc_2O@C_{72}$ and Y_2O) are larger than that of sulfide (Sc_2S and Y_2S). Besides this, in order to investigate the kinetic stability of these complexes, the energy gaps (E_{gap}) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of them are presented in Table 2. The E_{gap} of $M_2N@C_{72}$ ranging from 3.01 to 3.14 eV are slightly larger 2.34 eV of C_{72} (10528). It indicates that these EMFs have higher stability than pristine C_{72} (10528), in which the $Sc_2S@C_{72}$ has been successfully isolated. Meanwhile, the E_{int} of $M_2N@C_{72}$ are all negative and varies from -179.5 to -224.0 kcal mol^{-1}, meaning the endohedral reactions are exothermic. Thus, the synthesis of these EMFs seems feasible. Furthermore, in order to investigate the electronic properties of studied systems, the vertical electron affinity (VEA) and vertical ionization potential (VIP) were also computed and listed in Table 2. The corresponding values of EMFs are in the range of 6.12 - 6.24 eV for VIP and 2.00 - 2.17 eV for VEA, respectively. Compared with C_s-C_{72} (10528) (6.48 eV for VIP and 3.18 eV for VEA), these EMFs possesses lower VIP and VEA values. Therefore, the $M_2N@C_{72}$ are easy to lose an electron but difficult to accept an electron, which mean that $M_2N@C_{72}$ possess enhanced reduction and reduced oxidation than pristine C_{72} (10528).

3.2 The natural bond orbital (NBO) charge and the interaction of the encapsulated M_2N and the C_{72}

To further evaluate the nonlinear optical properties of studied complexes, it is essential to research the electron transfer from the metal clusters to the fullerene. The NBO charge is listed in Table 1. The order of NBO charge of M_2N follows 2.308 (Y_2O) > 2.046 (Y_2S) > 1.837 (Sc_2O) > 1.430 (Sc_2S). We can conclude that the NBO charge of the V-shaped polar molecule in oxide cluster fullerenes is larger than that in the sulfide cluster fullerenes because oxygen possesses larger electronegative and smaller ionic radius than sulfur. Furthermore, the difference of electron density of $Sc_2S@C_{72}$ is shown in Figure 3, which can clearly reflect the interaction between the inner Sc_2S cluster and the external cage C_{72} (10528). The blue surface means electron density decrease in two Sc atoms. However, the corresponding purple regional means electron density increase in two pairs fused pentagon of carbon cage. It is clearly demonstrated the charge transfer from Sc_2S to the pentagon adjacencies region of C_{72} (10528), which is consistent with the NBO analysis. According to previous work, we know that the charge transfer plays an important role in determining the hyperpolarizability.[50-52] According to these analyses, it is reasonable to infer that the non-linear optical properties of the oxide cluster fullerenes are more significant than that of the sulfide cluster fullerenes.

3.3 The liner and nonlinear optical properties

The electric properties of studied complexes evaluated by the BHandHLYP function are listed in Table 4. Here, we focus on the first hyperpolarizability (β_{tot}). The order of β_{tot} value from BHandHLYP functional is 1174 au ($Y_2O@C_{72}$) ≈ 1179 au ($Sc_2O@C_{72}$) > 886 au ($Y_2S@C_{72}$) ≈ 862au ($Sc_2S@C_{72}$) > 355 au (C_{72}) Obviously, encapsulating the metal cluster into C_{72} cage can obtain larger β_{tot}. For EMFs, the β_{tot} mainly comes from the contribution of β_y, which means charge transfer in the direction of y coordinate axis (See Figure 1). More specifically, the OCFs ($Y_2O@C_{72}$ and $Sc_2O@C_{72}$) show large β_{tot} value than SCFs ($Y_2S@C_{72}$ and $Sc_2S@C_{72}$) (See Figure 4). It's obvious that small ionic radius and large electronegative of oxygen plays an important role in enhancing β_{tot} value of EMFs, while the metal atom (Sc or Y) has slightly effect to the β_{tot} value.

Furthermore, in revised manuscript, we compare the calculated transitions for $Sc_2S@C_{72}$ obtained by BHandHLYP/LANL2DZ/6-31G* level with the experimental results. The present calculated method overestimates transition energies. The μ_{ge} values, which were calculated as the differences of dipole between ground–state and excited-state, were inconsistent with the change of β_{tot}, which means that there are some other influence factors for β_{tot} of EMFs in addition to charge transfer. Meanwhile, it is found that the transition is composed of many components but not in terms of single pairs of molecular orbitals and the NLO properties of $M_2N@C_{72}$ are the result of configuration interaction. As seen in Figure 5, the dominant transition are $S_0 \rightarrow S_1$ transition and $S_0 \rightarrow S_5$ transition, which have larger oscillator strength ($f = 0.0363$ and $f = 0.0623$). Furthermore, we focus on the frontier molecular orbitals, the similar surfaces were found in these EMFs. For the $S_0 \rightarrow S_1$ transition, the electron transition from HOMO to LUMO. For $S_0 \rightarrow S_5$ electron transition from HOMO-2 to LUMO.

Conclusions

In summary, the high stability has been found in $M_2N@C_{72}$ after the M_2N was encapsulated into the C_s-C_{72} (10528), which indicates the strong interaction in EMFs lead to the enhancement stability. It is consistent with the syntheses of $Sc_2S@C_{72}$. Furthermore, it is discovered that the first hyperpolarizabilities of EMFs are larger than that of hollow fullerene C_{72} (10528), which can be explained by the induction effect of the encapsulated molecule. Meanwhile, the first hyperpolarizabilities of OCFs are larger than that of SCFs as result of much larger electronegative of oxygen than sulfur. In contrast, metal element scandium and yttrium influence slightly on the NLO response of studied systems. On the base of this investigation, we expect that it can encourage researcher to further explore promising nonlinear optical materials with higher performance based on EMFs.

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Table 1. The important bond lengths (Å) and angles (°) and the selected NBO charge of important atoms of this system calculated by BHandHLYP/6-31g*- Lanl2dz function.

	$Sc_2S@C_{72}$ Theo (Expe)[a]	$Y_2S@C_{72}$	$Sc_2O@C_{72}$	$Y_2O@C_{72}$
Sc(Y)-C	2.234, 2.271, 2.283, 2.316 (2.230, 2.258, 2.287, 2.301)	2.421, 2.431 2.442, 2.496	2.335, 2.340 2.377, 2.429	2.475, 2.490 2.524, 2.533
Sc(Y)-S(O)	2.332(2.344)	2.432	1.922	2.006
M-N-M (ɵ)	124.8 (124.6)	102.9	163.0	135.8
$q_{Sc(Y)}$	0.958	1.402	1.445	1.779
$q_{O(S)}$	-0.486	-0.758	-1.053	-1.250
q_{M2N}	1.430	2.046	1.837	2.308

[a] the experimental data were obtained from the crystal structure in the reference of 25

Table 2. The interaction energy E_{int} (kcal/mol), total energy E_{tot} (au), the HOMO-LUMO energy gap E_{gap} (eV), the vertical ionization potebtials VIP (eV) and the vertical electron affinities VEA (eV) for studied systems at B3LYP/6-31G*- Lanl2dz

	C_{72}	$Sc_2S@C_{72}$	$Y_2S@C_{72}$	$Sc_2O@C_{72}$	$Y_2O@C_{72}$
E_{int}		-216.1	-179.5	-211.4	-190.3
E_{tot}	-2742	-3233	-3216	-2910	-2893
E_{gap}	2.34	3.14	3.07	3.01	3.03
VIP	6.48	6.24	6.23	6.12	6.22
VEA	3.18	2.17	2.06	2.00	2.09

Table 3. The mean dipole moment μ_0 (Debye), polarizability α_0 (au), the first hyperpolarizabilities β_{tot} (au) and transition energy ΔE (eV) of the studied complexes

		C_{72}	$Sc_2S@C_{72}$	$Y_2S@C_{72}$	$Sc_2O@C_{72}$	$Y_2O@C_{72}$
μ_0		2.30	1.29	1.23	1.44	3.53
α_0		738	686	693	684	690
β_x		143	783	770	1081	1021
β_y		325	360	439	470	579
β_z		1	0	0	0	3
β_{tot} (BHandHLYP)		355	862	886	1179	1174
β_{tot} (CAM-B3LYP)		339	826	869	1131	1140
β_{tot} (BP86)		688	911	960	1130	1125
$S_0 \rightarrow S_1$	μ_{ge}	0.01	0.02	0.34	0.36	2.96
	f	0.0136	0.0363	0.0359	0.0313	0.0319
	E_{ge}	0.979	1.63	1.58	1.52	1.55
$S_0 \rightarrow S_5$	f	0.0157	0.0623	0.0722	0.0652	0.0747
	E_{ge}	1.28	2.47	2.48	2.50	2.43

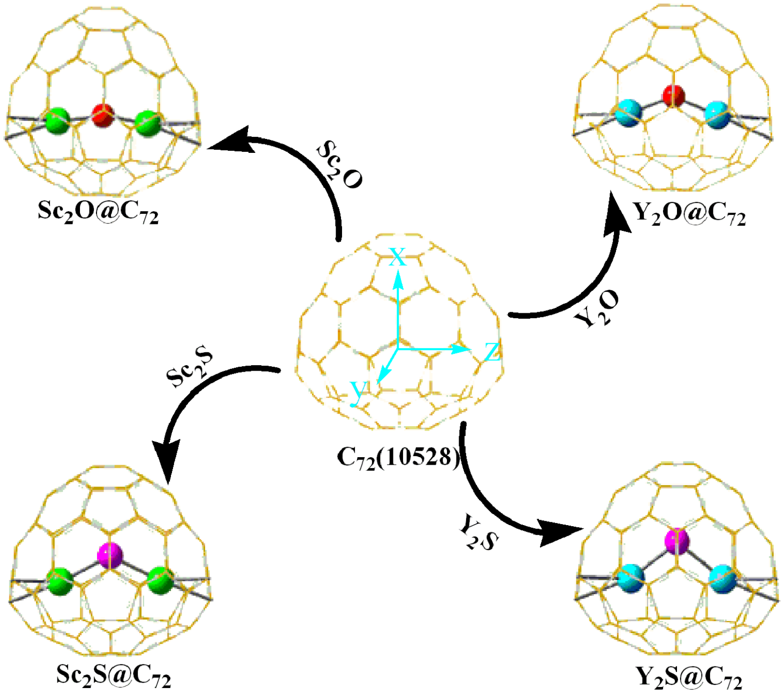

Figure 1. The optimized structures of the $M_2N@C_{72}$ (M = Sc, Y; N = O, S) and pristine C_s-C_{72} (10528).

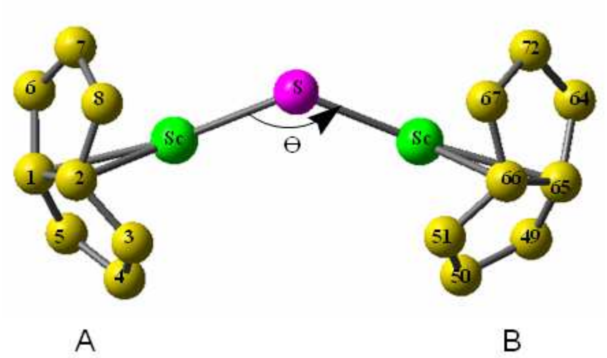

Figure 2. The two pairs of fused pentagons of $Sc_2S@C_{72}$ are recorded numbers and the closest Sc-C distance containing the 5:5 adjacent carbon atoms.

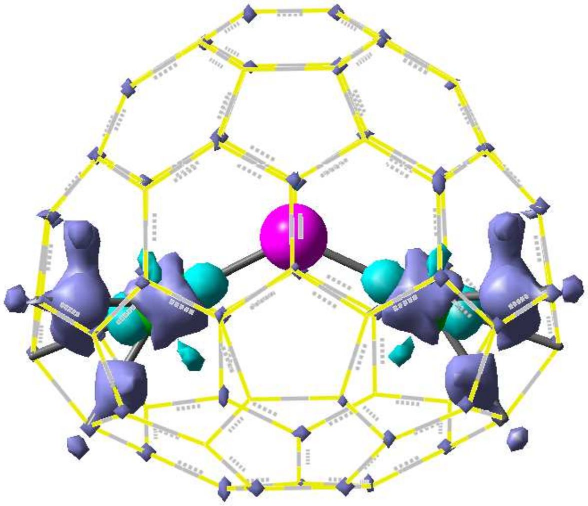

Figure 3. The difference of electron density of $Sc_2S@C_{72}$ is shown in purple and blue.

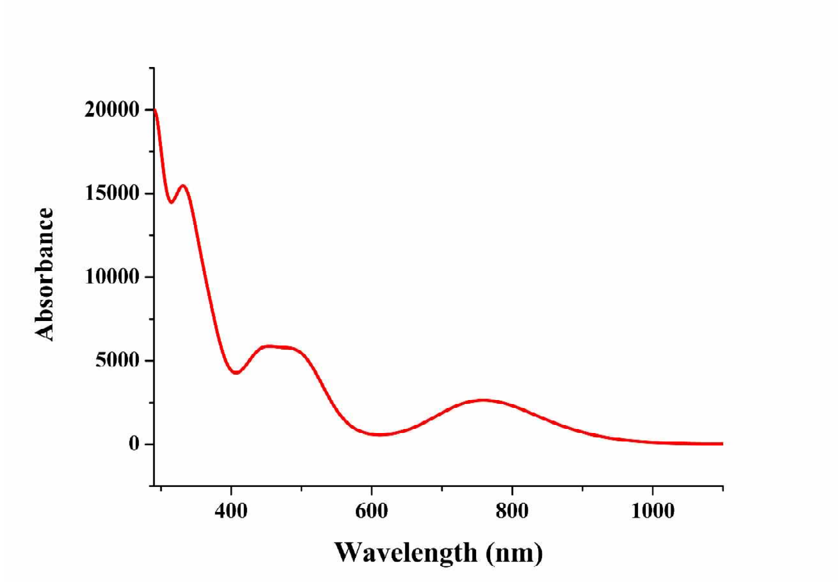

Figure 4. UV-vis-NIR absorption spectra of $Sc_2S@C_{72}$ obtained by BHandHLYP functional

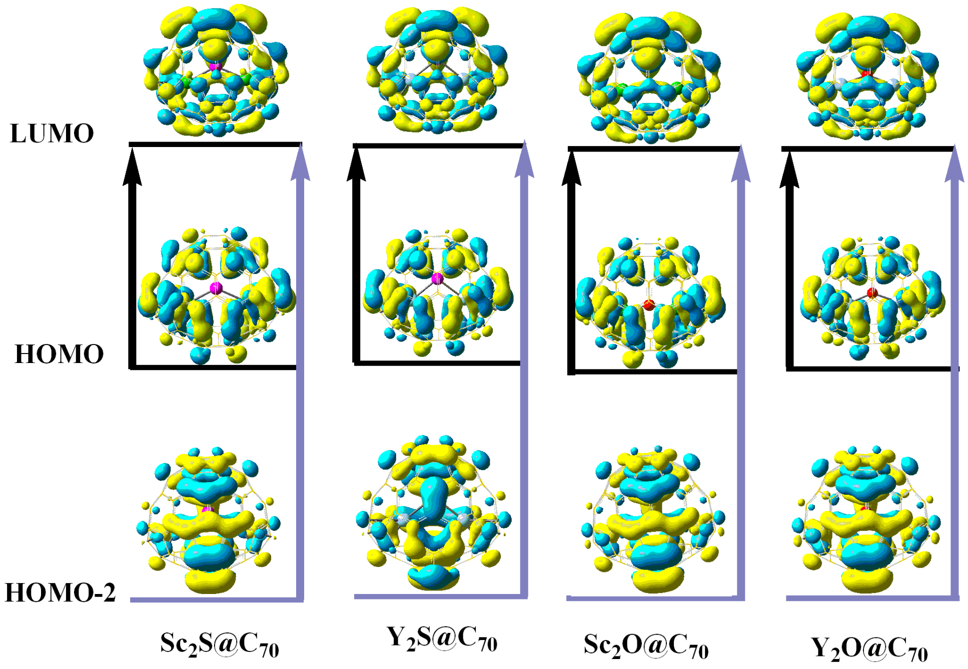

Figure 5. The crucial excited states for $M_2N@C_{72}$.

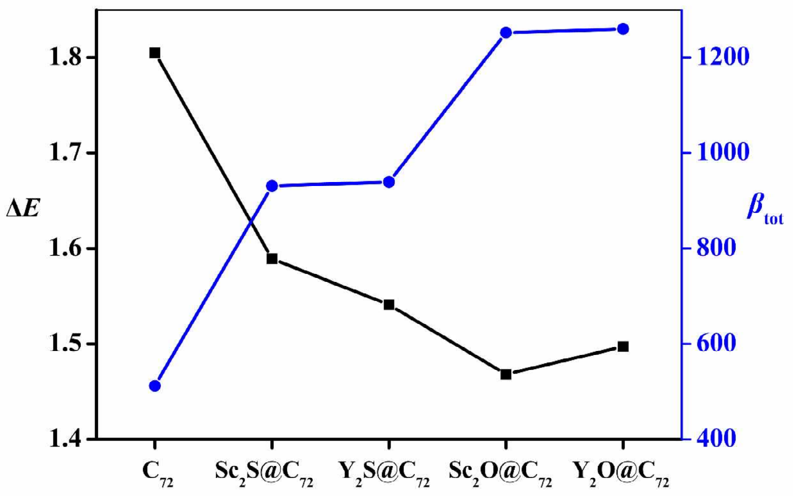

Figure 6. The relationship between first hyperpolarizabilities (β_{tot}) and the transition energy (ΔE) of C_{72}(10528) and $M_2N@C_{72}$.

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