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Understanding the stability, bonding nature and chemical reactivity of $3d$-substituted heterofullerenes C$_{58}$TM (TM=Sc-Zn) from DFT study

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Abstract

The stabilities, bonding nature and reactivity of C$_{58}$TM (TM=Sc-Zn) heterofullerenes are investigated using DFT methods. The [6:6] structure is more stable than [5:6] isomer for all of studied heterofullerenes. Among titled heterofullerenes, C$_{58}$Zn has the largest heats of formation, and shows low thermal stability due to great expansion deformation of C$_{58}$ cage. For open-shell heterofullerenes, the spin densities are localized on TM atoms except C$_{58}$Sc and C$_{58}$Cu in which the spin densities are delocalized over C$_{58}$ cage. The QTAIM analyses indicate that the TM-C bonds show a partial covalent characteristic. The degree of covalence slightly increases from the left to the right in $3d$-block of Periodic Table. The chemical reactivity of

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studied heterofullerenes can be turned by substituted TM atoms from frontier molecular orbitals and Fukui function analyses. The Fukui function also shows that earlier TM-substituted $C_{58}Ti$, $C_{58}V$, $C_{58}Cr$ and $C_{58}Mn$ species are more active than other heterofullerenes. The adsorption of ethylene molecule on heterofullerenes is investigated to probe into the chemical reactivity of studied heterofullerenes, the fact that earlier TM atoms show the higher reactivity than later TM atoms is in excellent agreement with Fukui function prediction. Moreover, the adsorption energies (E_{ads}) of earlier TM-substituted heterofullerenes are comparable to that of the previous reported $C_{58}Ir(C_2H_4)$ complex.

Introduction

The heterofullerene molecules[1] in which one or more carbon atoms that form the fullerene carbon cage are replaced by a heteroatom are well known, as are endo- and exohedral fullerenes. So far, many heterofullerenes have been proved to successfully exist by experiments or theoretical predictions. The heteroatoms contain main-group elements, B,[2] N,[3] O,[4] etc. and metal atoms, Fe, Co, Ni, Pt, Ir[5] and so on.

The previous reports mainly paid attention to the heterofullerenes with even-number carbon and other atoms, probably due to the fact that the surface atoms in fullerenes and heterofullerenes tend to form three bonds with neighbor atoms. For example, Muhr et al.[6] reported on the preparation of monoborafullerenes $C_{59}B$, $C_{69}B$, and higher homologues by arc evaporation of doped graphite rods in a modified fullerene reactor. The density functional theory (DFT) study[5] of $C_{59}Pt$ and $C_{59}Ir$ had shown that the metal atoms were found in three coordinate sites on the fullerene surface. Computational study[7] of the structures of $C_{69}M$, where M=Co, Rh, and Ir, indicated that substitution sites at the more highly pyramidalized poles of the fullerene was energetically favored. A range of $C_{59}M$ compounds of group 6-8 metals were predicted by DFT studies of Jensen's group[8] to have sufficient stability for experimental observation. Campanera et al.[9] have performed a systematic search of the regioisomers of the heterofullerenes, $C_{57}Pt_2$ and $C_{56}Pt_2$, by means of density functional calculations to find the most stable structures. They found that the deformation

of the carbon framework was a general factor for governing the relative stabilities of the regioiso-mers. For the heterofullerenes with odd-number atoms, also many studies have been performed to probe into their existences. The ions $[C_{58}Pt]^-$ and $[C_{56}Pt]^-$ were produced from C_{60}/Pt film upon laser ablation.[10] The DFT calculations showed that the isomer with one Pt atom replacing the C_2 unit at a [6:6] ring junction of fullerene were more stable than the low symmetry isomer with the C_2 unit at a [5:6] ring junction replaced by metal atom. Liu has systematically investigated the structural and electronic properties of $C_{58}X$ (X=O, S, Se)[11] and $C_{58}Si$, $C_{58}Ge$[12] heterofullerenes using hybrid DFT functional. It is noteworthy that the $C_{58}Fe$ heterofullerene[5] was found in exper-iment of photoionization mass spectrum of C_{60}-Fe cluster. It is a direct proof for the existence of $3d$-substituted species. Unfortunately, no further theoretical investigations have been carried out to probe into the structures, electronic properties of $3d$-block (Sc-Zn) heterofullerenes. Therefore, we see a need for systematic theoretical studies on $C_{58}TM$ (TM=Sc-Zn) heterofullerenes.

In this paper, we will utilize DFT methods to investigate the structures, stability, bonding nature and reactivity of $C_{58}TM$, TM is the $3d$-block transition metals. The interaction nature between TM and neighbor C atoms is discussed with quantum theory of atom in molecule (QTAIM) analyses. The chemical reactivities of titled heterofullerenes are discussed with frontier molecular orbitals and Fukui function. The adsorption of ethylene molecule on heterofullerenes is investigated to compare the chemical active of studied heterofullerenes.

Computation detail

The three-parameter hybrid functional B3LYP[13] implemented in G09 program[14] was used in the geometry optimization and property calculations. The valence basis set CEP-121G[15] and all-electron basis set 6-31G* were adopted to describe the transition-metal and carbon atoms, respec-tively. The Quantum theory of atom in molecule (QTAIM)[16] topological analyses based on the wavefunction calculated at B3LYP/6-31G*(CEP-121G) level of theory were performed with mul-tiwfn 2.6 program.[17] For comparison, the revised PBE functional (revPBE) proposed by Hammer

et al.[18] in conjunction with the double numerical basis set augmented with polarization p-function (DNP)as implemented in Dmol^3 program[19] was also utilized to optimize the geometry structures of studied heterofullerenes.The reactivity of heterofullerenes was discussed by analyzing the interactions of ethylene molecules with heterofullerenes. The structures of ethylene-adsorption heterofullerenes were optimized at revPBE/DZP level of theory. The unrestricted methods were utilized for computing the open shell systems. All possible spin multiplicities were considered in geometry optimizations to obtain magnetic properties of studied heterofullerenes.The condensed Fukui function[20] was calculated to predict the local reactivity of heterofullerenes. The geometry parameters of pure C_{60} molecule were first obtained to test the reliability of both calculation schemes described above. The bond distances of C_2 unit at a 6:6 ring (6-6 bond) and a 5:6 ring (5-6 bond) junction of fullerene obtained at B3LYP/6-31G* level of theory are 1.395 and 1.453Å, respectively, which is excellently in agreement with the results of revPBE/DZP (1.404 and 1.458Å for 5-6 and 6-6 bonds, respectively). Both calculated values are in reasonable agreement with previous theoretical results[11] and experimental values.[21] Therefore, we believe that the selected methods are appropriate to describe heterofullerenes.

Results and discussions

Structures and stabilities

The substitution of heteroatoms for a C_2 dimer in fullerene can form two isomers because there are two different substitution ways which is depicted in Fig 1. When the C_2 unit at a [6:6] ring junction is replaced by metal atoms, one C_{2v} isomer can be formed, on the other hand, the remove of C_2 unit at a [5:6] ring junction results into one low-symmetry C_s structure. For the reason of simplicity, the [6:6] and [5:6] represent the C_{2v} and C_s isomers, respectively, in the followings of this paper. Our calculations show that the [6:6] structure is more stable than [5:6] isomer for all of studied heterofullerenes. The relative energies between these structures are in the range of 0.389-1.981eV, as shown in Table 1. Fig 2 shows the binding energies (E_b) of [6:6] and [5:6] structures

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(detailed values can be found in Table 1) vs substituted metals. The E_b values of [6:6] isomers are larger than those of [5:6] isomers for all studied species, again confirm the higher stabilities of [6:6] isomers. From Fig 2, one can see that the binding energies do not show strong dependence on substitution-metal, are around 6.80eV from Sc to Cu for [6:6] isomers. one dramatically drop with 6.64eV is found for $C_{58}Zn$, which reveals the lower stability of $C_{58}Zn$ relative to other species.
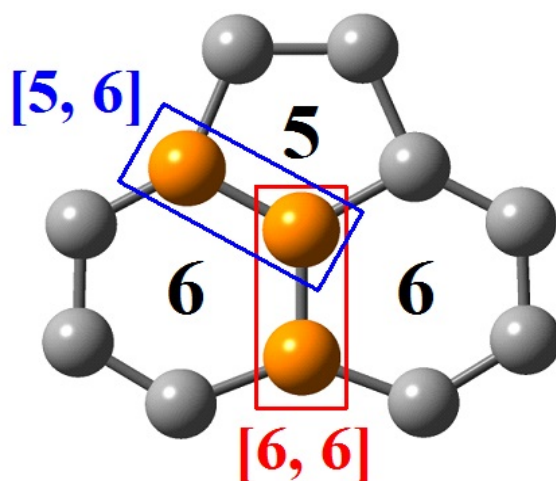

Figure 1: The scheme representation of different substitution patters.

For [6:6] isomers, the total energies of different spin multiplicities are listed in Table S1 in supporting information. All studied heterofullerenes, except $C_{58}Ti$, $C_{58}Ni$ and $C_{58}Zn$, favor open-shell ground states. The spin multiplicities,values of $\hat{S}^2$ and spin population of TM atoms are collected in Table 2 for open-shell species. The calculated $\hat{S}^2$ values are around expected eigenvalues, therefore, the spin-contaminant can be neglected in the spin-polarization systems. For the open-shell species, the unpaired electrons in $C_{58}Sc$ and $C_{58}Cu$ are delocalized over C atoms, whereas the rest heterofullerenes, $C_{58}V$, $C_{58}Cr$, $C_{58}Mn$, $C_{58}Fe$ and $C_{58}Co$ are characterized by spin densities localized on the TM atoms. Especially, the Cr, Mn, Fe atoms have large contribution for unpaired electrons.
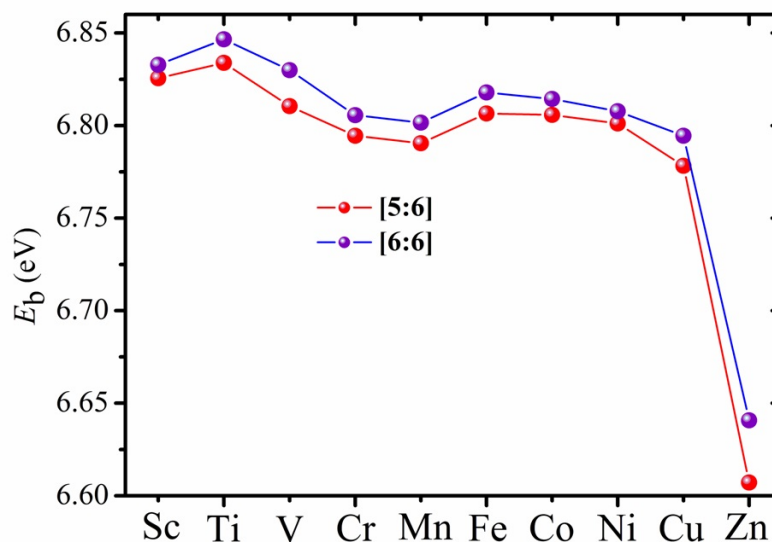
Figure 2: The binding energies of [5,6] and [6,6] isomers for studied $C_{58}TM$ (TM=Sc-Zn) hetero-fullerenes.

The optimized TM-C bond lengths of [6:6] structures listed in Table 2 are in the range of 1.929(Ni-C)-2.245Å(Sc-C) at B3LYP/6-31G*(CEP-121G) level of theory. These values are in agreement with the results of revPBE/DZP scheme which range from 1.951(Ni-C) to 2.284Å(Sc-C). It is noteworthy that the optimized TM-C distances in studied heterofullerenes are comparable with the values of Pt and Ir-substituted heterofullerenes ($C_{58}Pt$, $C_{58}Ir$)[10] reported previously. For comparison, the sum of covalent radius of C and TM atoms ($r_{TM}+r_C$) are also collected in Table 1. One can see that the distances of TM-C bonds (d_{TM-C}) in studied heterofullerenes are all close to sum of ($r_{TM}+r_C$), which implies that TM-C interactions in heterofullerenes show somewhat covalent characteristics. The Hirshfeld charges[22] of TM and bonded C atoms listed in Table 2 show that there are little charge transfers from TM to C atoms. This indicates that the ionic interaction is not preferred for studied TM-C chemical bonds. We note that the Zn-C bond length is 2.036Å, is comparable with other TM-C bond distances, but the molecular volume of $C_{58}Zn$ (shown in Table 2) is much larger than other studied heterofullerenes. Therefore, the low stability of $C_{58}Zn$ mentioned above is the result of great expansion deformation of C_{58} carbon cage not the expected weak Zn-C interaction. In fact, one can find that the Zn-C bonding strength is not obviously weaker than other TM-C interactions from the following QTAIM analyses.

Table 1. Binding energies (E_b) of [5,6] and [6,6] isomers and relative energies ($\triangle E$) between these two isomers calculated with B3LYP/6-31G*(CEP-121G).

	$C_{58}Sc$	$C_{58}Ti$	$C_{58}V$	$C_{58}Cr$	$C_{58}Mn$	$C_{58}Fe$	$C_{58}Co$	$C_{58}Ni$	$C_{58}Cu$	$C_{58}Zn$
E_b (eV) [6:6]	6.833	6.847	6.830	6.806	6.802	6.818	6.814	6.808	6.795	6.641
E_b (eV) [5:6]	6.826	6.834	6.811	6.794	6.790	6.807	6.806	6.801	6.778	6.607
$\triangle E$ (eV)	0.429	0.750	1.145	0.656	0.658	0.671	0.505	0.389	0.957	1.981

The energy levels of studied heterofullerenes are depicted in Fig 3, for the sake of comparison, the orbital energy level of C_{60} is also shown. As expect, the energy level of C_{60} is obviously discrete due to its high symmetry (I_h). The energy levels in studied C_{58}TM (TM=Sc-Zn) heterofullerenes are split for the reduction of symmetry from I_h to C_{2v}. From Fig 3, We also find that the gaps between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO)of titled heterofullerenes are observably smaller than that of C_{60}, this indicate that the chemical reactivity can be turned by substituted TM atoms.

Table 2. Multiplicities, values of $\hat{S}^2$, spin population, distances between TM and bounded C atoms (d_{TM-C}), molecular volumes and Hirshfeld charge of TM and bonded C atoms (C_B) for [6,6] isomer, the sum of covalent radius of isolated TM and C atoms ($r_{TM}+r_C$).

	$C_{58}Sc$	$C_{58}Ti$	$C_{58}V$	$C_{58}Cr$	$C_{58}Mn$	$C_{58}Fe$	$C_{58}Co$	$C_{58}Ni$	$C_{58}Cu$	$C_{58}Zn$
Multiplicities	2	1	2	3	4	5	2	1	2	1
$\hat{S}^2$	0.751	0	0.753	2.169	3.888	6.003	0.938	0	0.750	0
Spin population (TM)	0.020	-	1.188	3.176	4.152	3.584	1.870	0	0.008	0
d_{TM-C}(Å)	2.245	2.130	2.090	2.080	2.055	2.020	1.991	1.929	1.953	2.036
d_{TM-C}(Å)*	2.284	2.155	2.112	2.079	2.056	2.034	1.994	1.951	1.975	2.048
$r_{TM}+r_C$(Å)	2.21	2.13	2.02	2.04	2.16	2.02	2.03	1.98	2.15	2.08
Volume (Å^3)	639	635	634	631	633	631	629	626	627	656
Q (TM)	0.64	0.63	0.50	0.57	0.34	0.34	0.20	0.12	0.35	0.39
Q (C_B)	-0.12	-0.13	-0.10	-0.12	-0.09	-0.08	-0.06	-0.06	-0.09	-0.07

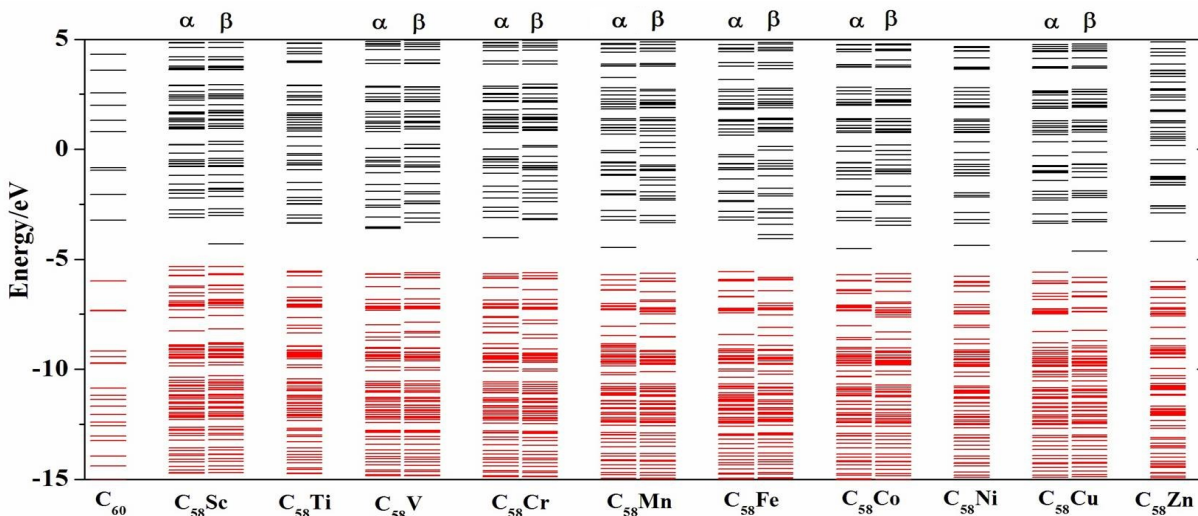*the optimized TM-C distances at revPBE/DZP level of theory.

Figure 3: The energy levels of [6,6] isomers for C_{60} and studied $C_{58}TM$ (TM=Sc-Zn) hetero-fullerenes.For open-shell species, the energy levels are split in spin-up (α) and spin-down (β) channals.

The HOMO and LUMO isosurfaces of titled heterofullerenes are depicted in Fig 4 to analyze the chemical reactivity. The corresponding orbital compositions are collected in Table 3. The spatial distributions of HOMO orbitals of titled heterofullerenes, except for $C_{58}V$, exhibit similar character. More specifically, the HOMOs are predominantly consist of $2p$ orbitals of surface carbon atoms. As for $C_{58}V$, the HOMO arises from $3d$ orbital of V atom and $2p$ orbitals of neighboring carbon atoms. The LUMO of $C_{58}Sc$ shows signally $C(2p)$ orbitals contribution. For the LUMO of $C_{58}Ti$, the electron density is predominantly built from $3d$ orbital of Ti atom. The LUMO of $C_{58}V$ is similar to that of $C_{58}Cr$, is built from $3d$ orbital and $2p$ orbitals of neighboring carbon atoms. $C_{58}Mn$ shows similar spatial distribution of LUMO to $C_{58}Co$, the $C(2p)$ orbitals contribution is predominantly. The LUMOs of $C_{58}Fe$ and $C_{58}Cu$ are absolutely composed of $2p$ orbitals of surface C atoms. $C_{58}Ni$ features non-ignorable $Ni(3d)$ contribution to the LUMO. The LUMO of $C_{58}Zn$ is composed of $Zn(3d)$ orbitals and $2p$ orbitals of neighboring C atoms. In general, the frontier MOs of studied $3d$-block heterofullerenes show some degree of difference, therefore they may behave different chemical reactivities.
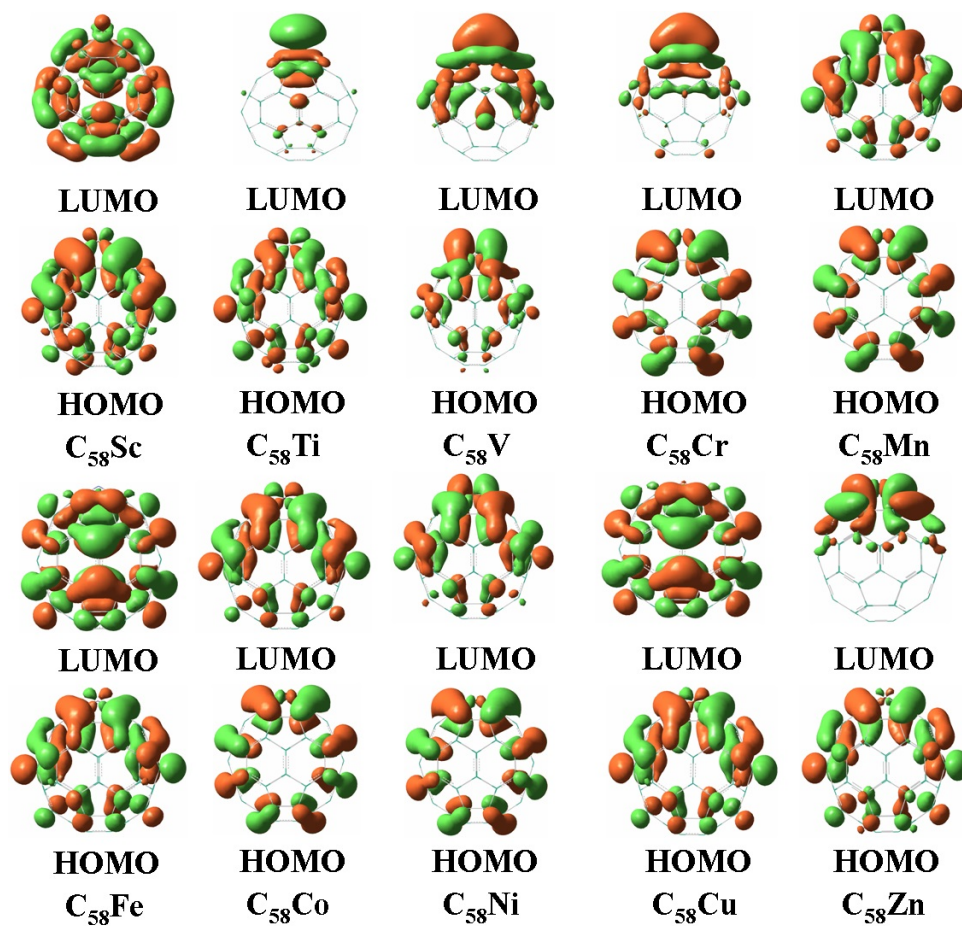
Figure 4: The frontier molecular orbitals of [6,6] isomers for studied heterofullerenes.

Table 3. The HOMO and LUMO orbitals composition for studied [6,6] heterofullerenes.

Species	Orbitals	Orbital compositions			
$C_{58}Sc$	HOMO	Sc (3d)	2.4%	C (2p)	86.7%
	LUMO	Sc (3d)	3.9%	C (2p)	88.4%
$C_{58}Ti$	HOMO	Ti (3d)	4.0%	C (2p)	81.2%
	LUMO	Ti (3d)	65.4%	C (2p)	7.9%
$C_{58}V$	HOMO	V (3d)	19.3%	C (2p)	49.4%
	LUMO	V (3d)	32.4%	C (2p)	43.5%
$C_{58}Cr$	HOMO	Cr (3d)	2.4%	C (2p)	90.0%
	LUMO	Cr (3d)	32.0%	C (2p)	34.6%
$C_{58}Mn$	HOMO	Mn (3d)	1.4%	C (2p)	94.6%
	LUMO	Mn (3d)	3.4%	C (2p)	86.1%
$C_{58}Fe$	HOMO	Fe (3d)	1.0%	C (2p)	90.8%
	LUMO	Fe (3d)	0.6%	C (2p)	93.2%
$C_{58}Co$	HOMO	Co (3d)	1.0%	C (2p)	92.3%
	LUMO	Co (3d)	1.9%	C (2p)	87.5%
$C_{58}Ni$	HOMO	Ni (3d)	0.6%	C (2p)	92.4%
	LUMO	Ni (3d)	13.5%	C (2p)	74.4%
$C_{58}Cu$	HOMO	Cu (3d)	1.3%	C (2p)	86.7%
	LUMO	Cu (3d)	<0.5%	C (2p)	91.1%
$C_{58}Zn$	HOMO	Zn (3d)	<0.5%	C (2p)	89.5%
	LUMO	Zn (3d)	7.7%	C (2p)	81.5%

Nature of TM-C bond

The quantum theory of atom in molecules (QTAIM)[16] is a powerful theory for characterizing chemical bondings of metal complexes, clusters. In the present work, the QTAIM analyses are performed to discuss the TM-C bonding natures in [6:6] isomer of $C_{58}TM$ (TM=Sc-Zn). Within the QTAIM framework, a critical point (CP), where the gradient of electron density vanishes, allows us to classify atoms and chemical bondings. The molecular graph for [6:6] isomer of $C_{58}TM$ is depicted in Fig 5. In studied heterofullerenes, we first locate 58 attractors, i.e., nuclei shown as cyan ball in Fig 5. There exist 89 (3, -1) bond critical points (BCP) connecting C-C or C-TM in the fullerene. One ring critical point (RCP) is located in every 5 ring or 6 ring, total 32 RCPs are found as shown in Fig 5. Moreover, one cage critical point is situated in the cage of studied
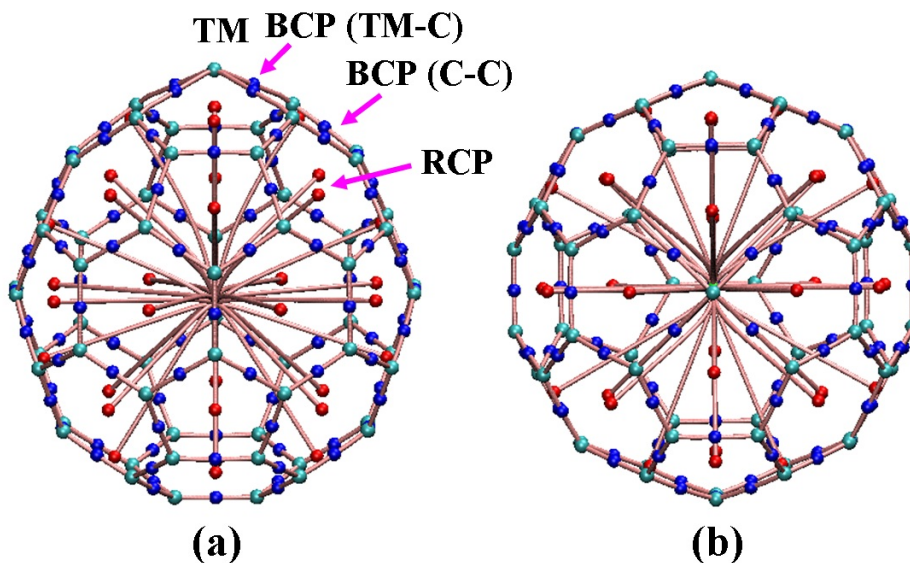
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heterofullerenes.

Figure 5: Molecular graphs of [6,6] isomers for studied heterofullerenes with sideview (a) and topview (b). The colour scheme identifying critical points is as followings: cyan ball for attractors, blue ball for bond critical points (BCP), red ball for ring critical points (RCP), green ball for cage critical points (CCP).

The topological properties collected in Table 4 allow an analysis of TM-C bonding characteristics in studied heterofullerenes. According to QTAIM theory, two types of interactions, i.e., shared interaction and closed-shell interaction can be identified by analyzing the values of electronic charge density (ρ) and its Laplacian ($\nabla^2\rho$) at critical points. Shared interactions generally correspond to high values of density and negative values of Laplacian, show covalent nature. Closed-shell interaction is characterized by low density and positive values of Laplacian, is typical of ionic and van del Waals bondings. However, this criterion has been proved to be not sufficient to describe bond natures of heavy atoms in previous works.[23] Another property, the total energy density $H(r)$(defined as the sum of local kinetic energy density $G(r)$ and local potential energy density $V(r)$) proposed by Cremer and Krala[24] is proved to be very appropriate to characterize the degree of covalency of a bond. The negative $H(r)$ is the indicator of a covalent bond. The C-C bonds show strong covalent nature. We now pay our attention to the bonding characteristics of TM-C bonds. As Fig 5 shows, there are four BCPs connecting TM and neighboring C atoms in [6:6] (C_{2v}) structures, and the corresponding parameters in Table 4 are similar for the four

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BCPs for a given species, so one TM-C BCP parameter is listed in Table 4. We can see that all of TM-C bondings have positive values of Laplacian and negative $H(r)$ values. Therefore, the natures of TM-C bondings in studied heterofullerenes can be described as closed-shell interactions with a partially covalent character. The covalent character can also be quantitively described by the $-V(r)/G(r)$ ralationship. The $-V(r)/G(r)$ value is greater than 2 for covalent bonds, smaller than 1 for closed-shell interactions and in the range of 1-2 for partially covalent interactions. The $-V(r)/G(r)$ ralationship is generally used to measure the degree of covalency of one chemical bonding. The calculated $-V(r)/G(r)$ values are all larger than 1, which indicate that all of TM-C bondings in studied heterofullerenes show some degree of covalent character. Based on the values of $H(r)$ and $-V(r)/G(r)$, one can obtain that the degree of covalence slightly increases from the left to the right in $3d$-block of Periodic Table. It is noteworthy that the Sc-C bond corresponds to smaller $H(r)$ value and lower $-V(r)/G(r)$ ralationship relative to other TM-C bonds. This indicates that the Sc-C bond is weaker than other TM-C bonds, which is also reflected by long Sc-C bond length and large charge transfer between Sc and bonded C atoms. So the ionic nature is suggested for Sc-C interaction. Moreover, we can obtain that the Zn-C bond show obvious partially covalent character by analyzing the values of $H(r)$ and $-V(r)/G(r)$. Therefore, low stability of $C_{58}Zn$ stems from the high deformation of C_{58} cage not the weak Zn-C interaction as analyzed in above section.

Table 4. Topological properties of (3,-1) critical point of various TM-C bonds in [6,6] isomers of titled heterofullerenes.

Species	BCP	ρ	$\nabla^2\rho$	$H(r)$	$-V(r)/G(r)$	$G(r)/\rho(r)$
$C_{58}Sc$	Sc-C	0.066	0.141	-0.011	1.244	0.707
$C_{58}Ti$	Ti-C	0.099	0.096	-0.032	1.570	0.566
$C_{58}V$	V-C	0.104	0.123	-0.032	1.511	0.606
$C_{58}Cr$	Cr-C	0.100	0.148	-0.030	1.444	0.667
$C_{58}Mn$	Mn-C	0.100	0.184	-0.030	1.396	0.759
$C_{58}Fe$	Fe-C	0.108	0.143	-0.038	1.519	0.682
$C_{58}Co$	Co-C	0.108	0.210	-0.035	1.400	0.808
$C_{58}Ni$	Ni-C	0.119	0.196	-0.054	1.524	0.860
$C_{58}Cu$	Cu-C	0.112	0.148	-0.054	1.592	0.811
$C_{58}Zn$	Zn-C	0.091	0.131	-0.036	1.527	0.756

Thermal properties and infrared spectra

In order to probe into the thermal stability of [6:6] isomer of $C_{58}TM$ (TM=Sc-Zn), the heats of formation $\triangle H_f^0$ are calculated at B3LYP/6-31G*(CEP-121G) level of theory. The energy change of following reaction with zero-point energy (ZPE) correction is considered to estimate the enthalpy changes $\triangle H_r$ and heats of formation $\triangle H_f^0$:

$$C_{60} + TM = C_{58}TM + C_2 \tag{1}$$

The enthalpy change $\triangle H_r$ of above reaction is calculated as followings:

$$\triangle H_r = (E + ZPE)_{C_{58}TM} + (E + ZPE)_{C_2} - (E + ZPE)_{C_{60}} - E_{TM,atom} \tag{2}$$

With the enthalpy change and heats of formation of C_{60},[25] TM atoms[26] and C_2[27] molecule from previous experimental reports, the heats of formation of $C_{58}TM$ can be evaluated with following equation:

$$\triangle H_f^0 = \triangle H_{f,C_{60}}^0 + \triangle H_{f,TMatom}^0 + \triangle H_r - \triangle H_{f,C_2}^0 \tag{3}$$

The estimated heats of formation collected in Table 5 are in the range of 718-908Kcal/Mol, and are all larger than that of C_{60}, 609.6 Kcal/Mol. Therefore the thermal stabilities of studied heterofullerenes are lower than C_{60} fullerene. The values of heats of formation are also depicted in Fig 6, one can see that $C_{58}Zn$ corresponding to the largest heats of formation possesses the lowest thermal stability among all of studied heterofullerenes, which is in excellently agreement with binding energy results. Like the trends of binding energies, the heats of formation of other heterofullerenes do not show evident element-dependence. Comparing with previous reported $C_{58}Ge$, [12] $C_{58}X$ (X=O, S, Se) [11] heterofullerenes, our studied $3d$ species except $C_{58}Zn$ have lower heats of formation, and are more stable.
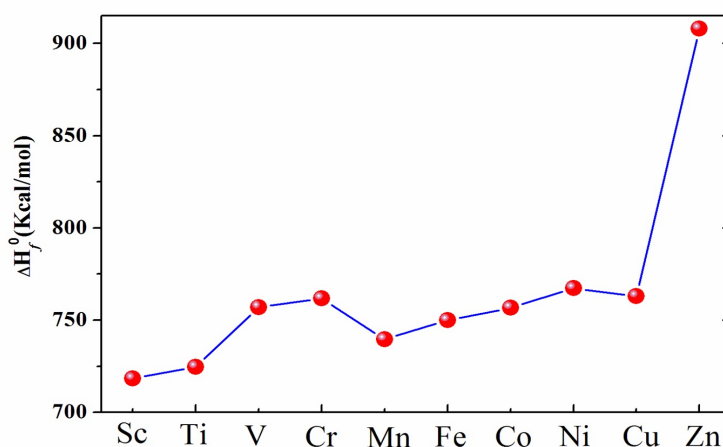

Figure 6: The heat of formation of [6, 6] isomers for studied $C_{58}TM$ (TM=Sc-Zn) heterofullerenes.

Table 5. The heats of formation for [6:6] isomer of studied $C_{58}TM$ heterofullerenes.

	$C_{58}Sc$	$C_{58}Ti$	$C_{58}V$	$C_{58}Cr$	$C_{58}Mn$	$C_{58}Fe$	$C_{58}Co$	$C_{58}Ni$	$C_{58}Cu$	$C_{58}Zn$
$\triangle H_f^0$(Kcal/Mol)	718	725	757	762	740	750	757	767	763	908

The infrared (IR) spectra of studied heterofullerenes are simulated to be accessed for further experimental assignment. Fig 7 shows the unscaled IR spectra of heterofullerenes and C_{60}. One can see that C_{60} only presents four peaks due to its high I_h symmetry, on the other hand, all of titled heterofullerenes show complicated absorption peaks due to reduction of symmetry from I_h to C_{2v}. There are two dominant absorption bands, corresponding to 400-600cm^{-1} and 1200-1600cm^{-1} in IR spectra of heterofullerenes. For all of studied heterofullerenes, some weak IR spectroscopic

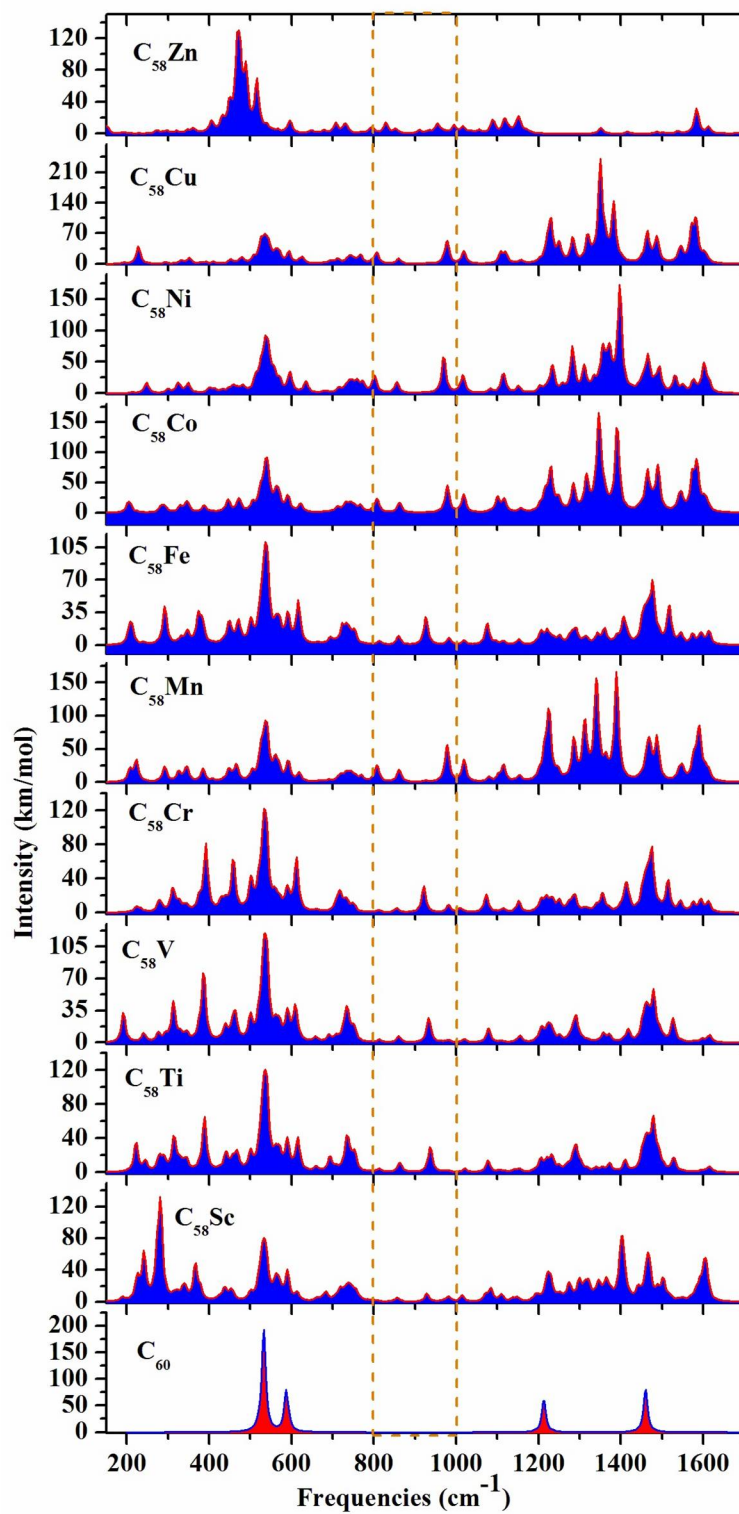signals can be found in the range of 800-1000cm^{-1}, which is assigned to TM-C bond stretching.

Figure 7: IR spectra of [6, 6] isomers for studied C$_{58}$TM (TM=Sc-Zn) heterofullerenes.

Local site reactivity

In this section, the local reactivity of [6:6] isomer of $C_{58}TM$ (TM=Sc-Zn) heterofullerenes is analyzed by means of Fukui indices[28] to predict the local reactivity sites. This method relates the reactivity of one chemical species with respect to nucleophilic/electrophilic attack to the charge density, and is a successful way of measuring the reactivity of regions of molecules and clusters.[29–31] Parr and Yang[28] define the Fukui function (FF) as the partial derivative of the electron density with respect to the total number of electrons at a constant potential:

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} \tag{4}$$

Owing to the discontinuity of the derivative of above equation, two different Fukui functions can be defined by applying the finite difference approximation:

$$f^+(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)^+_{v(\vec{r})} \tag{5}$$

$$f^-(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)^-_{v(\vec{r})} \tag{6}$$

The $f^+(r)$ and $f^-(r)$ Fukui functions measure the reactivity towards a nucleophilic and electrophilic attacks, respectively. The FF for radical attack, $f^0(r)$, is simply the average of these two. The condensed Fukui function proposed by Yang[20] can be obtained with the following expression:

$$f_k^+ = q_k(N+1) - q_k(N) \tag{7}$$

$$f_k^- = q_k(N) - q_k(N-1) \tag{8}$$

where q_k is the electronic population of atom k in a certain chemical species. The values of q_k can be calculated from a numerical integration procedure such as Hirshfeld charge.[22] In the present work, the Hirshfeld partial scheme is utilized.

Table 6. The calculated Fukui indices of TM and bonded C atoms (C_B) in studied $C_{58}TM$ heterofullerenes.

	$C_{58}Sc$	$C_{58}Ti$	$C_{58}V$	$C_{58}Cr$	$C_{58}Mn$	$C_{58}Fe$	$C_{58}Co$	$C_{58}Ni$	$C_{58}Cu$	$C_{58}Zn$
$f^-(TM)$	0.059	0.057	0.063	0.049	0.064	0.036	0.051	0.067	0.027	0.028
$f^+(TM)$	0.064	0.152	0.115	0.087	0.064	0.056	0.048	0.045	0.028	0.054
$f^0(TM)$	0.061	0.105	0.089	0.068	0.064	0.050	0.049	0.056	0.028	0.041
$f^-(C_B)$	0.025	0.019	0.018	0.023	0.024	0.023	0.020	0.027	0.025	0.022
$f^+(C_B)$	0.024	0.018	0.020	0.023	0.021	0.018	0.021	0.021	0.019	0.046
$f^0(C_B)$	0.024	0.019	0.019	0.023	0.023	0.021	0.020	0.024	0.022	0.034

The calculated Fukui indices (FI) of TM atoms for studied heterofullerenes are listed in Table 6, from which one can see that the TM atoms in $C_{58}Ti$, $C_{58}V$, $C_{58}Cr$, $C_{58}Fe$ and $C_{58}Zn$ corresponding to the higher $f^+(r)$ values, favor nucleophilic attack such as CO molecule. The Ni atom in $C_{58}Ni$ heterofullerenes shows the feasibility of electrophilic attack. The TM sites in $C_{58}Sc$, $C_{58}Mn$, $C_{58}Co$ and $C_{58}Cu$ have comparable $f^+(r)$ and $f^-(r)$ values, and are favorable in front of any chemical attacks. All of bonded carbons in studied heterofullerenes show "amphiphilic" characteristics. It is important to note that all of bonded C atoms have the lower FI values relative to TM atoms, which indicate that the TM atoms are more active than carbons in front of chemical attacks. Moreover, later $3d$ TM atoms may be less active than earlier TM atoms which is revealed by their low $f^0(r)$ values. Fig 8 shows the radial Fukui function mapped onto an isosurface of the total electron density (isovalue=0.017 au) for studied heterofullerenes. One can see that the high density accumulation is found on TM atoms sites. Therefore, the TM atoms possess the higher chemical activities than all C atoms. By comparing studied $3d$ series, earlier TM atoms correspond to high density accumulation, and are more active.
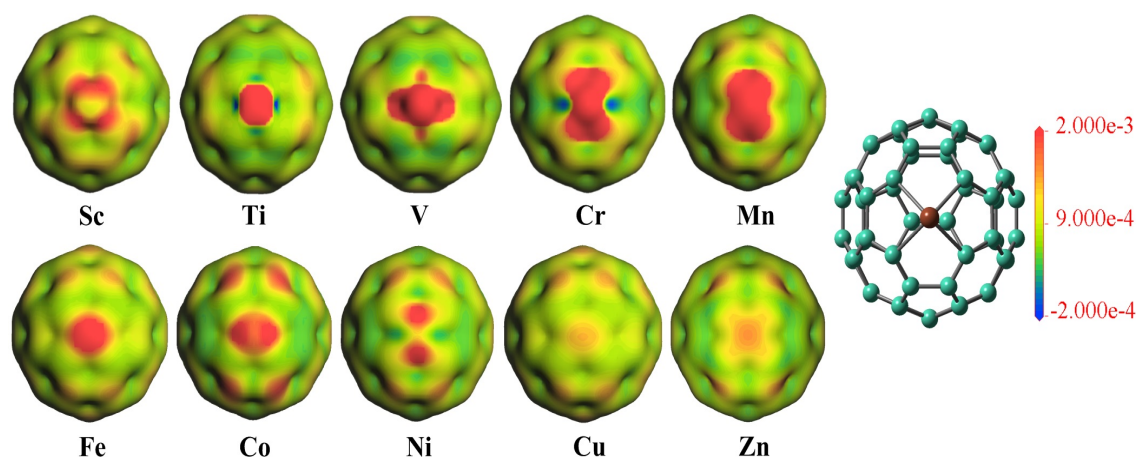
Figure 8: Radial Fukui function mapped onto an isosurface of the total electron density (isovalue=0.017 au) for studied heterofullerenes.

In experiment[10] the evidence for the ability of the Ir and Pt atoms in some of heterofullerenes to bind added ligands has been obtained by conducting the laser ablation studies in the presence of 2-butene. The $[C_{58}Ir(2\text{-butene})]^-$ adduct was observed in the mass spectrum obtained by laser ablation of a $C_{60}/Ir(CO)_2$ film in a butene atmosphere.[10] In order to compare the chemical reactivity of titled heterofullerenes with previous $C_{58}Ir$ and $C_{58}Pt$, the binding of ethylene molecule (to simply model the 2-butene ligand) on TM atoms of studied heterofullerenes is investigated. The geometries of C_2H_4-adsorption heterofullerenes were obtained at revPBE/DZP level of theory. The adsorption energies (E_{ads}) are obtained by evaluating the difference of energy between $C_{58}TM(C_2H_4)$ and free $C_{58}TM$ and C_2H_4 units. By comparing with bare heterofullerenes, the adsorption of ethylene molecule induces slight elongation of the distances between TM and neighboring C atoms of fullerene in all studied species as the values in Table 7 show,whereas the TM-ethylene bond lengths are obviously longer than TM-C (fullerene) distances. The C-C bonds in ethylene are slightly elongated relative to the free ethylene. The adsorption energies listed in Table 7 indicate that earlier TM atoms show the higher reactivity than later TM atoms. This result is in excellent agreement with Fukui function prediction. It is noteworthy that the E_{ads} values for earlier TM-substituted heterofullerenes are very close to the value of the previous reported $C_{58}Ir(C_2H_4)$ complex which was confirmed by the experimental observation of a peak in the mass spectrum that

may be associated with $[C_{58}Ir(2\text{-butene})]^-$.

Table 7. The geometry parameters and adsorption energies of ethylene-adsorption $3d$-sustituted heterofullerenes.[a]the distances between TM and neighboring C atoms of fullerene, [b]the distances between TM and neighboring C atoms of ethylene, [c]the C-C bonding lengths of adsorbed ethylene molecule.

	$C_{58}Sc(C_2H_4)$	$C_{58}Ti(C_2H_4)$	$C_{58}V(C_2H_4)$	$C_{58}Cr(C_2H_4)$	$C_{58}Mn(C_2H_4)$
$d_{TM-C}(\text{Å})^a$	2.294	2.161	2.114	2.078	2.053
$d_{TM-C}(\text{Å})^b$	2.898	2.683	2.280	2.270	2.360
$d_{C-C}(\text{Å})^c$	1.349	1.353	1.349	1.358	1.374
$E_{ads}(\text{eV})$	0.580	0.774	0.688	0.318	0.420
	$C_{58}Fe(C_2H_4)$	$C_{58}Co(C_2H_4)$	$C_{58}Ni(C_2H_4)$	$C_{58}Cu(C_2H_4)$	$C_{58}Zn(C_2H_4)$
$d_{TM-C}(\text{Å})^a$	2.045	2.003	2.015	1.988	2.080
$d_{TM-C}(\text{Å})^b$	2.401	2.297	2.097	2.760	2.613
$d_{C-C}(\text{Å})^c$	1.366	1.375	1.419	1.350	1.354
$E_{ads}(\text{eV})$	0.641	0.189	0.176	0.213	0.390

Conclusion

In this paper, the structures, thermal stability, bonding nature and reactivity of $C_{58}TM$ (TM=Sc-Zn) heterofullerenes are systemically investigated by using DFT methods. Our calculations show that the [6:6] structure is more stable than [5:6] isomer for all of studied heterofullerenes. For open-shell heterofullerenes, the spin densities are localized on TM atoms except $C_{58}Sc$ and $C_{58}Cu$ in which the spin densities are delocalized over C_{58} cage. The heats of formation are calculated to probe into the thermal stability of heterofullerenes. $C_{58}Zn$ has the largest heats of formation among all of studied $3d$ series. The low thermal stability of $C_{58}Zn$ can be explained as the great expansion deformation of C_{58} carbon cage. Moreover, the studied $3d$ heterofullerenes show the higher thermal stability relative to previous reported $C_{58}Ge$, $C_{58}X$ (X=O, S, Se) heterofullerenes. The HOMO-LUMO gaps of titled heterofullerenes are dramatically smaller than that of C_{60}, this

indicates that the chemical reactivity can be turned by substituted TM atoms. Moreover, the frontier MOs of studied $3d$-block heterofullerenes show some degree of difference, therefore they may behave different chemical reactivities. The QTAIM analyses indicate that the TM-C bonds show some degree of covalent characteristic. The weak IR spectroscopic signals in the range of 800-1000cm^{-1}, which is assigned to TM-C bond stretching, can be used for further identify of these studied $3d$ heterofullerenes. The surface reactivity is predicted with Fukui indices for studied $3d$ heterofullerenes, the TM atoms show high feasibility of chemical attack. The earlier TM-substituted $C_{58}Ti$, $C_{58}V$, $C_{58}Cr$ and $C_{58}Mn$ species are more active than other heterofullerenes. The binding of ethylene molecule on TM atoms of the studied heterofullerenes is investigated to probe into their chemical reactivity. The fact that earlier TM atoms show the higher reactivity than later TM atoms is in excellent agreement with Fukui function prediction. The ability of Fukui function to predict the local reactivity sites is confirmed. Moreover, the E_{ads} values for earlier TM-substituted heterofullerenes are very close to the value of the previous reported $C_{58}Ir(C_2H_4)$ complex which was confirmed by the experimental observation of a peak in the mass spectrum that may be associated with $[C_{58}Ir(2\text{-butene})]^-$.

Acknowledge

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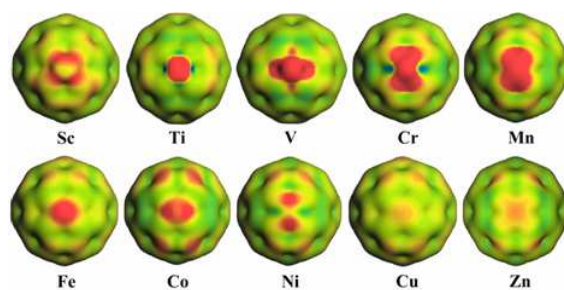
One systemic DFT study for stability, bonding nature and reactivity of 3d-substituted heterofullerenes $C_{58}TM$ (TM=Sc-Zn).