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Diradical Character and Nonlinear Optical Properties of Buckyferrocenes: Focusing on the Use of Suitably Modified Fullerene Fragments

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ABSTRACT

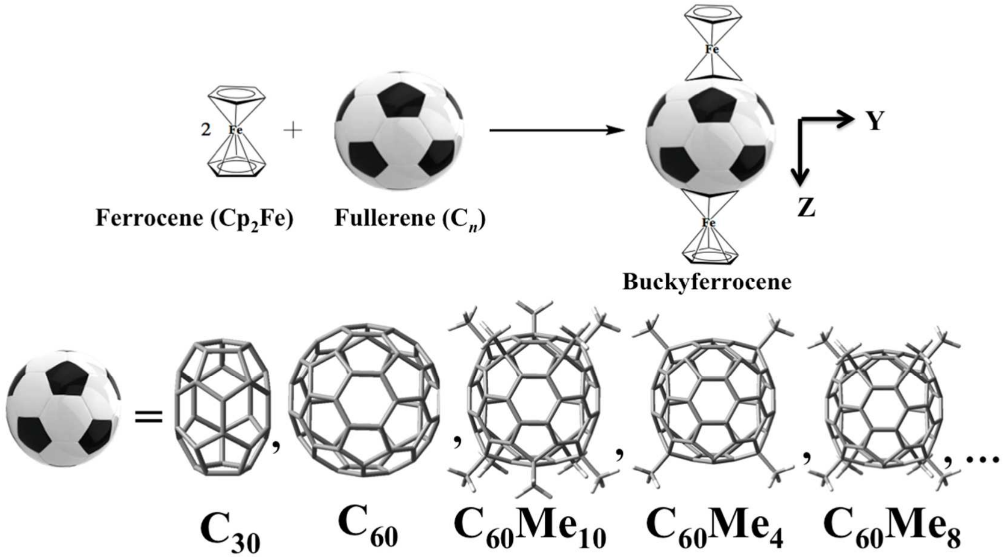
The buckyferrocenes, synthesized through face-to-face fusion of ferrocene and fullerene fragments ($C_{60}Me_{10}$), are expected to enjoy the rich scientific heritage of ferrocene and fullerene with extensively large π-conjugation network between the two Fe atoms [Matsuo, Y.; Tahara, K.; Nakamura, E., *J. Am. Chem. Soc.* 2006, *128*, 7154]. However, the addition of pentamethyl groups at each end of fullerene fragment breaks the π-conjugation path as well as metal-metal spin correlation between the two-ferrocene faces in a buckyferrocene. We found that the unblocking of π-

conjugation from different positions in fullerene fragments have substantial effects on their topologies, spin densities, diradical characters as well as nonlinear optical (NLO) properties of these buckyferrocenes. We study the topological dependence of open-shell diradical character and second hyperpolarizability (γ), the third-order NLO properties at the molecular scale, in several buckyferrocenes. On the basis of their different diradical characters (y_i), which are defined by the occupation number of the lowest unoccupied natural orbital (LUNO) + i ($i = 0, 1, \ldots$), these buckyferrocenes are categorized into three groups, i.e., closed-shell ($y_i = 0$), intermediate open-shell singlet ($0 < y_i < 1$), and almost pure open-shell singlet ($y_i = 1$) compounds. For example, we found that buckyferrocenes including $(CpFe)_2/_5C_{60}Me_{10}$ and $(CpFe)_2\eta^5C_{70}Me_{10}$ have closed-shell configurations. The buckyferrocenes $(CpFe)_2\eta^5C_{60}$, $(CpFe)_2\eta^5C_{70}$, $(CpFe)_2\eta^5C_{70}Me_8$, $(CpFe)_2\eta^5C_{70}Me_4$ and $(CpFe)_2\eta^5C_{30}$ are intermediate open-shell singlet, while $(CpFe)_2\eta^5C_{60}Me_4$ and $(CpFe)_2\eta^5C_{60}Me_8$ are pure open-shell singlet complexes. Interestingly, the γ_{zzzz} amplitude of $(CpFe)_2\eta^5C_{60}$, an open-shell intermediate diradical complex, is about 41 times and 13 times as large as those of its closed-shell ($(CpFe)_2\eta^5C_{60}Me_{10}$) and pure diradical ($(CpFe)_2\eta^5C_{60}Me_8$) counterparts, respectively. Similarly, the γ_{zzzz} amplitudes of $(CpFe)_2\eta^5C_{70}$, $(CpFe)_2\eta^5C_{70}Me_4$, and $(CpFe)_2\eta^5C_{70}Me_8$ with intermediate diradical character are about 36, 17, and 9 times as large as that of their closed-shell $(CpFe)_2\eta^5C_{70}Me_{10}$ counterpart. The fact that larger γ_{zzzz} values are obtained for buckyferrocenes with intermediate diradical characters is in line to the "y-γ correlation" obtained from the valence configuration interaction (VCI) results for a two-site diradical model [Nakano, M. *et al.*, *Phys. Rev. Lett.* 2007, *99*, 033001] as well as for fullerene and graphene systems. The γ_{zzzz} density analysis shows that the large positive contributions originate from the large γ_{zzzz} density distributions on the upper- and lower-extended edges of the buckyferrocenes, between which significant spin polarizations appear within the spin-unrestricted DFT level of theory. These results demonstrate that such buckyferrocenes are potential candidates for a novel class of open-shell singlet NLO systems, where γ_{zzzz} values are modulated tuning their diradical character through the use of suitably modified fullerene fragments.

1. INTRODUCTION

Over the past few decades, many types of π-conjugated nanomaterials have emerged as versatile and amazing functional materials with their applications ranging from light emitting diodes (LED), organic solar cells as well as spintronic to nonlinear optical (NLO) materials.[1] NLO active materials have the ability to generate new electromagnetic fields with new frequency, phase, or other physical properties by interacting with electric field of the incident laser light.[2] Among the modern functional materials, NLO materials have become the foundations for many interdisciplinary applications in optical computing, telecommunications, photonics, etc., where light is used to acquire, store, process, and transmit data.[3] Recently, intense research activity has been devoted to design and synthesize new NLO materials with larger amplitudes of their hyperpolarizabilities. Many research reports revealed that π-conjugated materials are the promising candidates to achieve desirably large NLO amplitudes.[4] In our previous studies,[5,6] it has been found that besides π-conjugation, the singlet diradical character is also a novel tuning parameter to enhance γ amplitudes: the singlet systems with intermediate diradical character give larger NLO properties than closed-shell and pure open-shell singlet systems. In this regard, we have studied several functional materials to establish structure-NLO property relationships using physical quantities associated with electronic excitations (excitation energy, transition moments and electronic dipole moments in ground and excited states) based on a two-site model in the framework of valence configuration interaction (VCI) scheme.[7] We have extended our findings ranging from the simplest hydrogen molecule dissociation[8] to polyaromatic hydrocarbons (PAHs),[9] graphene nanoflakes,[10] acetylene-linked phenalenyl based polyenes,[11] and more recently on a novel class of fullerenes,[12a] quinoidal oligothiophenes,[12b] 1,3-diradical compounds,[12c] transition metal compounds,[12d] phenalenyl radical aggregates,[12e] and four-membered-ring diradicals involving heavy main group elements.[12f] The interplay between diradical character and γ amplitudes in several fullerenes showed that diradical character has even larger impact on γ than π-conjugation. For example, it has been observed that the γ apmlitudes of C_{30} and C_{40} fullerenes (with intermediate diradical characters) in spite of their smaller π-conjugation are several times as large as that of C_{60}.[12a] It will be interesting to extend such findings from fullerenes to fullerene complexes (buckyferrocenes). Fullerenes are considered as ideal candidates for NLO applications due to their extensive π-conjugation. There have been several attempts to implement fullerenes as advanced functional materials into different disciplines by their substitutions, doping and complex formation (endohedral/exohedral) with different heteroatoms and metals.[13] It is well known that a ferrocene molecule is composed of a pair of 6π-electron pentagonal carbon rings and 6d electrons of Fe, which is equally bound to the all atoms of the ring through η^5 coordination bonds. Similarly, several fullerenes also bear such sp^2-hybridized pentagonal rings with excess negative charges on them.[14] In 2000, Jemmis *et al.*[15] reported the first theoretical framework for the possible exohedral complexes of fullerenes with ferrocene fragments. They proposed suitable transition metal fragments to overcome the unfavorable interaction arising from the spread out of π-orbitals of the five- and six-membered rings of C_{60} and C_{70} fullerenes.

Soon after the theoretical prediction of transition metal complexes of fullerene, Matsuo *et al.*[16] have reported the synthesis of buckyferrocenes $(CpFe)_2\eta^5C_{60}Me_{10}$, through face-to-face fusion of ferrocene and modified fullerene fragment ($C_{60}Me_{10}$). After the synthesis of the buckyferrocenes, several experimental attempts have been made to clarify their electromagnetic and spin properties[17] along with further structural modifications in this novel class of material.[18] It has been expected that these buckyferrocenes could enjoy the rich scientific legacy of ferrocene and fullerene with extensively large π-conjugation network between the two Fe atoms. However, the buckyferrocenes synthesized by the decamethyl substituted fullerene are attracted much attention as a possible synthetic route of such compounds rather than as advanced functional material because the addition of pentamethyl groups at each end of fullerene break not only the π-conjugation path but also metal-metal spin correlation between the two ferrocene faces. The modification of fullerene C_{60} by the addition pentamethyl groups on each end might be considered as a necessary evil for the formation of buckyferrocenes.[16] In addition to $(CpFe)_2\eta^5C_{60}Me_{10}$, there are several possible buckyferrocenes that can be synthesized by the fusion of ferrocene and modified fullerenes. In the present study, we aim to design new members of buckyferrocenes using the modified fragments of fullerenes including fullerene C_{30}, C_{60}, $C_{60}Me_4$, $C_{60}Me_8$, $C_{60}Me_{10}$, C_{70}, $C_{70}Me_4$, $C_{70}Me_8$, and $C_{70}Me_{10}$. The buckyferrocenes designed by the above mentioned fullerene fragments will have completely blocked, partially blocked and completely unblocked π-conjugation paths between the two-ferrocene fragments. It is expected that blocking/unblocking central π-conjugation path will affect significantly their diradical characters as well as nonlinear optical responses.

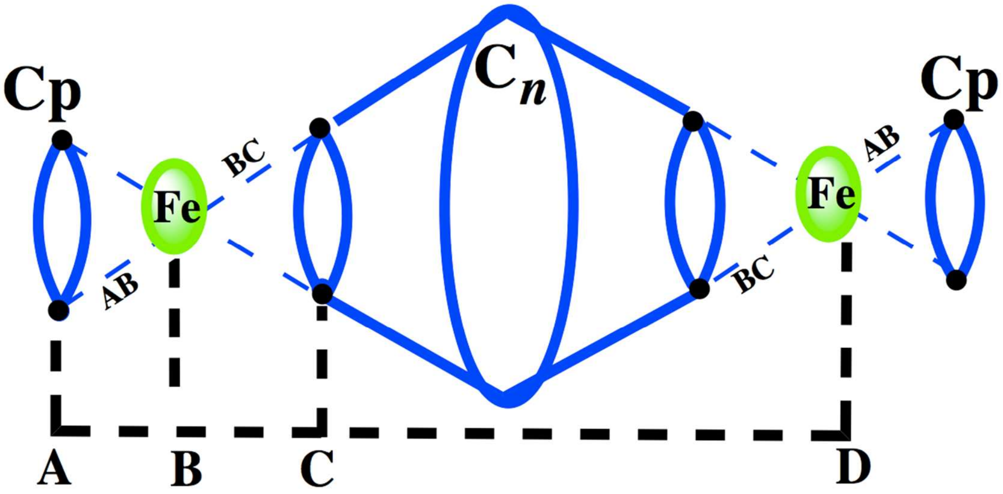


Scheme 1. Schematic representation of buckyferrocene systems where fullerenes and modified fullerene fragments are symbolized by football.

2. Methodology and Model Systems

2.1. Structures of Buckyferrocene Systems

We employed the spin-unrestricted (U) B3LYP/6-31G* method to get the optimized structures of singlet ground states for ferrocene and buckyferrocenes. The B3LYP exchange-correlation function has been used in present investigation because it is found to reproduce the experimental structures of conjugated diradical singlet systems.[19] A general sketch about the designing strategy of buckyferrocenes has been illustrated in Scheme 1. According to experimentally reported structure of $(CpFe)_2\eta^5C_{60}Me_{10}$ buckyferrocene and other ferrocene/fullerene hybrid molecules,[20] all buckyferrocene structures in their singlet ground states[21] are assumed using a general formula of $(CpFe)_2\eta^5C_n$ where Cps at both ends are cyclopentadienes containing -1 charge each, Fe(II) is transition metal with η^5-coordination and C_n denotes the central fullerene and modified fullerene fragments that can act as 6π-electron donor ligand to 6d-electron of Fe(II) atoms and/or might be locally charged as -2.[21] In several experimental syntheses buckyferrocenes, the fullerenes are usually converted into methylated anion ligands to form stable transition metal η^5-complexes.[22] Herein, the football symbolizes the individual fragments of fullerene and modified fullerene molecules including C_{30}, C_{60}, $C_{60}Me_4$, $C_{60}Me_8$, $C_{60}Me_{10}$, C_{70}, $C_{70}Me_4$, $C_{70}Me_8$, and $C_{70}Me_{10}$ as shown in Scheme 1. In present investigation, based on previous experimental reports, the overall charge[16] and total spin multiplicity $(2S+1)$[22] of all buckyferrocenes are assumed to be 0 and 1, respectively. We have also checked the stability of triplet states with spin (2S+1)=3 and the total energies have been compared with singlet states as given in Table S1 of supporting information. All the adopted open-shell buckyferrocenes show stable singlet structures except for $(CpFe)_2\eta^5C_{70}Me_4$ and $(CpFe)_2\eta^5C_{70}Me_8$ that have 1.136 and 2.438 kcal mol^{-1} less energy than their respective singlet states. The structural parameters for these compounds have been compared to each other (see Table 1 and Scheme 2).



Scheme 2 Schematic representation of buckyferrocene systems where Cp is cyclopentadiene ring and C_n represents C_{30}, C_{60} and C_{70} fullerenes and their fragments

To check the interaction among cyclopentadiene rings, Fe metal atoms and fullerene fragments, four different types of distances have been measured on these optimized buckyferrocenes as given in Table 1. The AB indicates the bond distance between the terminal atom of cyclopentadiene (Cp) and Fe metal atom, while BC does the bond distance between Fe metal and terminal atom of pentagonal ring of fullerene. It is important to mention here that AB and BC are not the same distances because these are between two different interfaces, i.e., BC between metal atom and fullerene fragments. The AC indicates the distance between cyclopentadiene and pentagonal ring of fullerene, while BD does the distance between two Fe metal atoms of buckyferrocene molecules as shown in Scheme 2.

Table 1. Structural Parameters with Bond Lengths (Å) of Ferrocene and Buckyferrocenes according to Scheme 2

Systems	AB	BC	AC	BD
Ferrocene (Cp_2Fe)	2.082	2.082	3.404	--
$(CpFe)_2\eta^5C_{30}$	2.057	2.228	3.526	9.119
$(CpFe)_2\eta^5C_{60}$	2.066	2.173	3.445	10.201
$(CpFe)_2\eta^5C_{60}Me_4$	2.065	2.150	3.473	10.179
$(CpFe)_2\eta^5C_{60}Me_8$	2.079	2.118	3.406	10.053
$(CpFe)_2\eta^5C_{60}Me_{10}$	2.083 (2.050) [a]	2.115 (2.087)	3.425 (3.373)	10.048 (9.911)
$(CpFe)_2\eta^5C_{70}$	2.064	2.185	3.474	11.542
$(CpFe)_2\eta^5C_{70}Me_4$	2.074	2.116	3.406	11.473
$(CpFe)_2\eta^5C_{70}Me_8$	2.083	2.116	3.462	11.353
$(CpFe)_2\eta^5C_{70}Me_{10}$	2.080	2.114	3.422	11.334

[a] The experimental values have been taken from Ref. 16

A comparative analysis of geometrical parameters shows that the AB bond distances of all the buckyferrocenes are nearly equal to AB distance (2.082 Å) in ferrocene molecule. A further comparison of the most important bond distance BC among all the adopted systems shows that the interaction between fullerene pentagonal ring and ferrocene moiety are effective in modified buckyferrocenes because these are in the range of 2.114 Å to 2.228 Å, which is similar to that of 2.082 Å of ferrocene molecule as calculated at the B3LYP/6-31G* level of theory. It is also interesting to mention that the interaction between ferrocene moiety (CpFe) and fullerene are more effective in modified buckyferrocenes than those of C_{60} and C_{70} buckyferrocenes. For example, BC distances of 2.150 Å and 2.118 Å of $(CpFe)_2\eta^5C_{60}Me_4$, and $(CpFe)_2\eta^5C_{60}Me_8$ buckyferrocenes are shown to be shorter than 2.173 Å of $(CpFe)_2\eta^5C_{60}$ parent buckyferrocene. A similar trend of shorter BC distances is also observed for modified buckyferrocenes ($(CpFe)_2\eta^5C_{70}Me_4$, and $(CpFe)_2\eta^5C_{70}Me_8$) and their parent $(CpFe)_2\eta^5C_{70}$ buckyferrocene. A comparison of experimental bond lengths[16] with calculated bond lengths of $(CpFe)_2\eta^5C_{60}Me_{10}$ buckyferrocene shows a good semi-quantitative agreement with each other, the feature of which gives us the confidence about the reliability of our adopted computational methodology. Furthermore, a charge partition analysis of total neutral charge into the buckyferrocene moieties has been performed for $(CpFe)_2\eta^5C_{60}$, $(CpFe)_2\eta^5C_{60}Me_{10}$, $(CpFe)_2\eta^5C_{60}Me_8$ and $(CpFe)_2\eta^5C_{70}Me_8$ based on their natural bond orbital (NBO) charges as given in Figure S1 of supporting information. It can be seen from Figure S1 that locally fullerene fragments carry partial negative charges, while Fe metal atoms carry partial positive charges. On the other hand, Cp rings have slightly negative charges in optimized ground states of buckyferrocenes. The ground state structures of buckyferrocenes are found to be different from their assumed formal charges with significantly delocalization of charges, which is probably due to their extensive π-conjugation.

2.2. Calculation Methods of Diradical Character and Second Hyperpolarizability

The diradical character and second hyperpolarizability γ (only the dominant longitudinal component γ_{zzzz}) of buckyferrocenes have been calculated, respectively, using the LC-UBLYP method and the finite field (FF) approach that consists in the fourth-order differentiation of energy with reference to applied external electric field.[23] It is well known that (hyper)polarizabilities increase with the increase of π-electron conjugation in the conjugation direction.[4a, 24] In the present investigation, the influence of diradical on γ_{zzzz} (herein after referred to as γ) has been investigated, because it is the major charge transfer axis in our designed buckyferrocenes. The γ has been defined so-called B convention with the following numerical differentiation procedure:[25]

$$\begin{aligned}\gamma = \{&E(3F) - 12E(2F) + 39E(F) - 56E(0) \\ &+39E(-F) - 12E(-2F) + E(-3F)\}/36F^4.\end{aligned} \qquad (1)$$

Here, the $E(F)$ relates to the total energy in the presence of field F applied in longitudinal direction of z-axis. The field amplitude of 0.001 a. u. has been selected carefully to get accuracy within the range of 3% error in γ values. In the present investigation, the exchange-correlation functional LC-UBLYP has been used to calculate γ amplitudes. In LC-UBLYP functional, a range-separating parameter $\mu = 0.33$ bohr^{-1} has been adopted because it is found to semi-quantitatively reproduce the γ values calculated with spin-unrestricted coupled cluster methods for several open-shell organic molecules.[26] All the calculations were performed by the GAUSSIAN 09 program package.[27]

The calculation of diradical character (y_i) of a chemical system gives the quantitative evaluation of its open-shell singlet nature. The diradical character is originally defined by twice the weight of doubly excited configuration[28] in multi-configuration self-consistent-field theory. The diradical character of chemical systems is related to the highest occupied natural orbital (HONO) – i and the lowest unoccupied natural orbital (LUNO) + i, where i = 0, 1, etc. In single determinant scheme, the diradical character is defined using the occupation number (n_i) of natural orbital (NO) as given by

$$y_i = n_{\mathrm{LUNO}+i} = 2 - n_{\mathrm{HONO}-i}, \qquad (2)$$

The y_i takes a value ranging from 0 (closed-shell) to 1 (pure diradical). Thus, in the spin-restricted (R) single-determinant treatments like RHF or RDFT, the diradical character is all 1 or 0, while it takes fractional values when using spin-unrestricted (U) schemes like UHF or UDFT.[29] The wavefunction can be expanded in the form of a limited configuration interaction when considering different orbitals for different spins and that leads to fractional occupation numbers other than 0, 1, or 2. For example, in the dissociated H_2 molecule model,[5a,8] as the H–H bond stretches in a homolytic single-bond breaking process, H_2 becomes more and more diradical-like, eventually becoming a pure diradical at complete separation. Actually, the diradical character, which is not a physical observable like aromaticity, represents the number of unpaired electrons and their distribution in the chemical system as it has been explained in our several previous papers based on odd electron number and spin density.[5b, 6, 9b, 10a, 10b, 12, 30] Furthermore, it is important to stress here that the spin contamination effects, which are usually accompanied with spin-unrestricted single-determinant schemes like UHF and UDFT, on the y and γ values lead to incorrect results in principle, while they depend on the exchange-correlation functionals in the

UDFT method.[31] As shown in our previous studies,[12, 32] we have confirmed that the LC-UBLYP (μ = 0.33 bohr^{-1}) method gives semi-quantitative y-γ relationships for polycyclic aromatic hydrocarbons, and fullerene systems by comparing the results obtained by the approximate spin projection scheme,[28c] which can approximately correct the spin-contamination effect.

3. Results and Discussion

3.1. Diradical Character and Spin Polarization

The calculated diradical characters (y_0) for buckyferrocenes are given in Table 2. Based on their diradical characters (y_0), there are three types of buckyferrocenes including closed-shell ($y_0 \cong 0$), intermediate diradical ($0 < y_0 < 1$) and almost pure diradical systems ($y_0 \cong 1$). It is found that $(CpFe)_2\eta^5C_{60}Me_{10}$ and $(CpFe)_2\eta^5C_{70}Me_{10}$ are closed-shell systems with $y_0 \cong 0$, while that $(CpFe)_2\eta^5C_{60}$, $(CpFe)_2\eta^5C_{70}$, $(CpFe)_2\eta^5C_{30}$, and $(CpFe)_2\eta^5C_{60}Me_8$ are open-shell intermediate diradical systems with y_0 values of 0.419, 0.451, 0.338 and 0.778, respectively. In $(CpFe)_2\eta^5C_{30}$, a tetraradical value of $y_0 = y_1 \cong 0.338$ can be seen, the feature of which is due to more than one pair of degenerate orbitals obtained for relatively smaller and symmetrical structure of $(CpFe)_2\eta^5C_{30}$. This kind of degeneracies is not present on other buckyferrocenes due to their relatively larger size and the lower symmetry structures. The third group includes $(CpFe)_2\eta^5C_{60}Me_4$, $(CpFe)_2\eta^5C_{60}Me_8$, $(CpFe)_2\eta^5C_{70}Me_4$ with diradical y_0 values of 0.891, 0.920, and 0.802, respectively. In a semi-quantitative way, the categorization of buckyferrocenes based on their diradical characters is shown to be further correlated to their HOMO-LUMO (H-L) energy gaps calculated at the RB3LYP/6-31G* level of theory. It turns out that the closed-shell systems have the higher values of their energy gaps, and nearly pure open-shell systems have lower values of their energy gaps, while those intermediate diradical systems have intermediate range of H-L energy gaps. For example, the H-L energy gaps of closed-shell ferrocene (Fc) as well as $(CpFe)_2\eta^5C_{60}Me_{10}$ and $(CpFe)_2\eta^5C_{70}Me_{10}$ buckyferrocenes are shown to be 5.262, 3.389 and 1.833 eV, respectively, while those for open-shell $(CpFe)_2\eta^5C_{60}Me_4$ and $(CpFe)_2\eta^5C_{60}Me_8$ buckyferrocenes are found to be 0.790 and 0.727 eV, respectively. The remaining buckyferrocenes with intermediate diradical character are found to approximately stand in between these two ranges as shown in Table 2.

Table 2. Diradical Character (y_i), HOMO-LUMO Energy Gaps (eV), and Second Hyperpolarizability (γ_{zzzz}) of Ferrocene and Buckyferrocenes Calculated at the LC-UBLYP/6-31G* Level of Theory

Chem. Models	y_0	y_1	$\Delta E_{\text{H-L}}$[a]	$\gamma_{zzzz} \times 10^4$
Ferrocene (Cp_2Fe)	0.000	0.000	5.262	0.076
$(CpFe)_2\eta^5C_{30}$	0.338	0.338	1.863	12.38
$(CpFe)_2\eta^5C_{60}$	0.419	0.041	0.830	113.75
$(CpFe)_2\eta^5C_{60}Me_4$	0.891	0.036	0.790	10.07
$(CpFe)_2\eta^5C_{60}Me_8$	0.920	0.024	0.727	8.33
$(CpFe)_2\eta^5C_{60}Me_{10}$	0.000	0.000	3.389	2.78
$(CpFe)_2\eta^5C_{70}$	0.451	0.047	0.821	130.71
$(CpFe)_2\eta^5C_{70}Me_4$	0.802	0.050	0.835	31.74
$(CpFe)_2\eta^5C_{70}Me_8$	0.778	0.018	0.836	60.39
$(CpFe)_2\eta^5C_{70}Me_{10}$	0.000	0.000	1.833	3.60

[a] Calculated using the RB3LYP/6-31G* method

It is very important to trace the origin of these diradical characters, which can help the experimentalists to modify the structure of these buckyferrocenes to get their optimal functional properties. To have an overview of spin polarization effects in open-shell buckyferrocenes, we have first performed the partition analysis of Mulliken atomic spin densities for three selected open-shell molecules including $(CpFe)_2\eta^5C_{60}$ $(CpFe)_2\eta^5C_{60}Me_8$, $(CpFe)_2\eta^5C_{70}Me_8$ buckyferrocenes. The unpaired spin density distributions of these buckyferrocenes are shown in Figure 1, where positive (blue font) and negative (red font) values of unpaired spin densities represent the spatial distributions of α and β spins, respectively. Spin densities are partial numbers of electrons in terms of the difference between α and β electron populations (Mulliken Scheme). From the Figure 1, it can be seen that the main portions of unpaired spin densities arise from fullerene fragments in all the buckyferrocenes. The unpaired spin densities on Fe metal atoms are shown to correlate with respective side of fullerene fragments. The central belt of 10 carbon atoms in $(CpFe)_2\eta^5C_{70}Me_8$ buckyferrocene is fond to be spin free part, which is due to its central spatial position effect between α and β spin containing carbon atoms. The contributions of cyclopentadiene rings at both ends are found to be negligible in all three buckyferrocenes. On the other hand, in case of $(CpFe)_2\eta^5C_{60}$ buckyferrocene, the Fe metal spin density is found to be 2.2 times larger than those of others, [e.g., Fe spin density amplitude = 0.086($(CpFe)_2\eta^5C_{60}Me_8$) vs. 0.187($(CpFe)_2\eta^5C_{60}$ buckyferrocene) due to the relatively larger interaction of Fe metal with non-substituted C_{60} fullerene fragment because of less spin interactions between metal dz^2 orbital and π-orbitals of substituted fullerene fragments as seen from corresponding orbitals in Figure 2[a] and as it will be further explained in succeeding section based of their structural distortions. The spin density distributions of open-shall buckyferroces are also shown in Figure S3 of supporting information, where the spatial distributions of α and β spins are represented by positive and negative spin densities, respectively. In the spin-unrestricted solutions, the symmetry broken spatial distributions of α and β spins are usually interpreted to approximately indicate the feature of spatial correlation between α and β spins. These spin density distributions are primarily different in different open-shall buckyferrocene systems representing variable extend of spatial correlation between α and β spins as shown in Figure S3, while such kind of spin polarization are not present in decamethyl-substituted closed-shall buckyferrocenes.

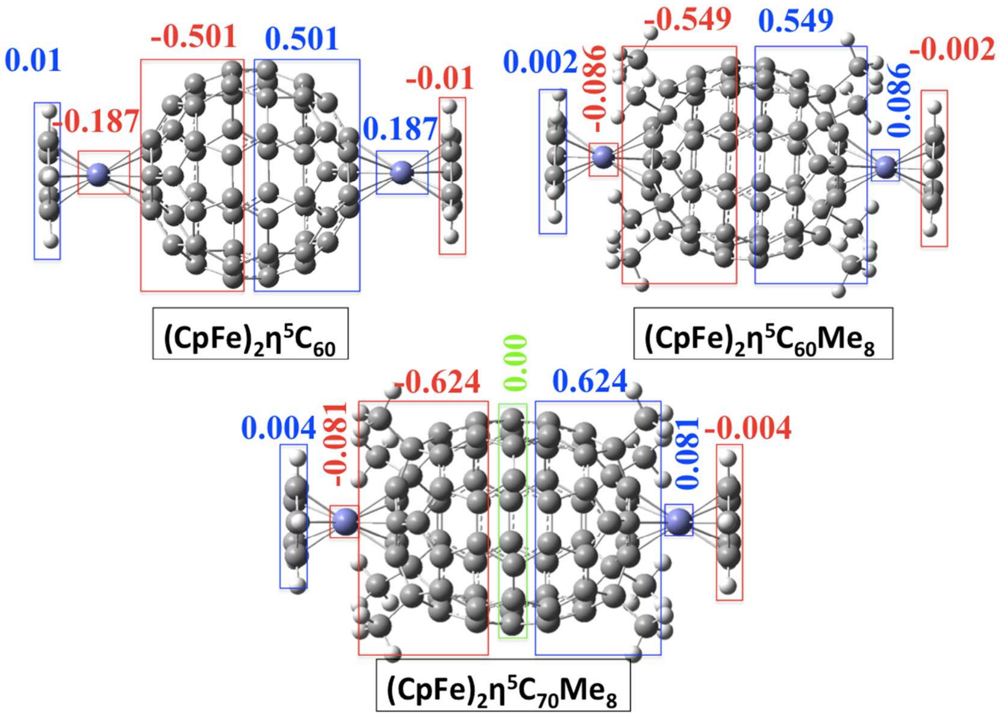


Figure 1. Approximate partitioning of unpaired spin density distributions [α (positive, blue) and β (negative, red) spins] in different open-shell buckyferrocenes

To have more intuitive view about the origin of diradical character as well as the direct contribution of frontier orbitals to y_0 value, we have calculated the corresponding orbitals for selected $(CpFe)_2\eta^5C_{60}$, $(CpFe)_2\eta^5C_{60}Me_8$, $(CpFe)_2\eta^5C_{70}Me_8$ buckyferrocenes as shown in Figure 2[a]. Among these selected open-shell systems, $(CpFe)_2\eta^5C_{60}$ and $(CpFe)_2\eta^5C_{70}Me_8$ exhibit intermediate diradical value, while $(CpFe)_2\eta^5C_{70}Me_8$ system does nearly pure diradical character. Usually, the corresponding orbitals whose overlaps are directly related to the balance between ionic and neutral character in the broken symmetry (BS) wavefunction and can be used to define a physically transparent diradical character.[28,33] For buckyferrocene $(CpFe)_2\eta^5C_{60}Me_8$ having large diradical character of 0.920, its corresponding orbitals are shown to be distributed on opposite sides of $C_{60}Me_8$ fragment in $(CpFe)_2\eta^5C_{60}Me_8$ complex as shown in Figure 2[a]. The larger distance between the two corresponding orbitals (α- and β-orbitals) provides less overlap resulting in large/pure diradical character. On the other hand, for $(CpFe)_2\eta^5C_{70}Me_8$ and $(CpFe)_2\eta^5C_{60}$ buckyferrocenes, their corresponding orbitals (α- and β-orbitals) are seen to be situated on the same sides of $C_{70}Me_8$ fragment, which leads to relatively larger overlap or intermediate diradical character. The distribution of the corresponding orbitals of $(CpFe)_2\eta^5C_{60}$ buckyferrocene is shown to be different from others, where the electronic density, i.e., α- and β-orbitals are distributed over the whole C_{60} fullerene fragment with larger amplitudes towards both ends of C_{60} fullerene fragments. In $(CpFe)_2\eta^5C_{60}$ buckyferrocene, the contributions from Fe metal atoms is also shown to be larger, which can be assumed from the larger overlap of dz^2 type of orbitals with sp^2 hybridized fullerene fragment as seen from corresponding orbitals diagram (see Figure 2). There is no and smaller metal commutations with modified fullerene fragments in deca- and octa-methyl substituted buckyferrocenes, respectively. This is because of the presence of sp^3 hybridized carbon atoms at each methyl substituted position, which results in breaking the π-conjugation network of fullerene fragments in these buckyferrocenes. We have also checked the structural deformations in fullerene fragments of $(CpFe)_2\eta^5C_{60}$ and $(CpFe)_2\eta^5C_{60}Me_8$ buckyferrocenes. As seen from Figure S2, the structural distortions at both ends of $C_{60}Me_8$ fullerene fragment are significantly larger than C_{60} fullerene fragment. Unlike the C_{60} fullerene fragment, the structural distortions or/and the orientation of π-orbitals at both ends of $C_{60}Me_8$ fullerene fragment results in less spin interactions between metal dz^2 orbital and π-orbitals of substituted fullerene fragments as seen from corresponding orbitals in Figure 2[a].

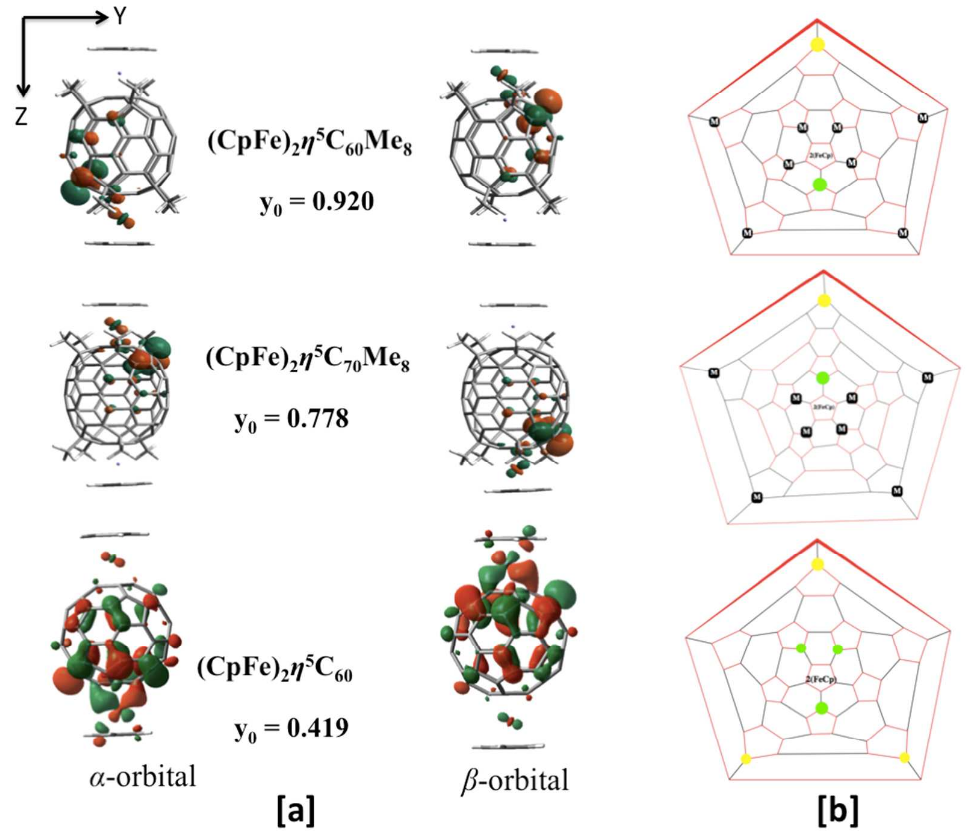


Figure 2. [a] Corresponding orbitals at the isosurfaces of ± 0.02 a.u. [positive (green) and negative (red)] and [b] Schlegel projection of $(CpFe)_2\eta^5C_{60}Me_8$ and $(CpFe)_2\eta^5C_{70}Me_8$ with $(FeCp)^2$ in center of each projection, where green and yellow circles represent the approximate positions of α- and β- orbitals, respectively.

The similar trends about the origin of diradical characters can also be comprehended by using the Schlegel projections as shown in Figure 2[b]. In Schlegel projections of $(CpFe)_2\eta^5C_{60}Me_8$, $(CpFe)_2\eta^5C_{60}$ and $(CpFe)_2\eta^5C_{70}Me_8$ complexes, the green and yellow spots represent the *α*- and *β*-orbitals, respectively, while octamethyl groups have also been represented with black squares as well. Interestingly, from these projections it can be seen that the magnetic orbitals stand on sp^2 hybridized carbon atoms of fullerenes in buckyferrocene complexes, which cause their diradical characters depending on their overlap. In contrast, for decamethyl substituted buckyferrocene complexes, these sp^2 hybridized carbon atom sites are absent, resulting in their closed-shell configurations. It can be concluded that the extent of diradical character can be tuned by changing the position and the number of methyl substitutions of open-shell buckyferrocenes.

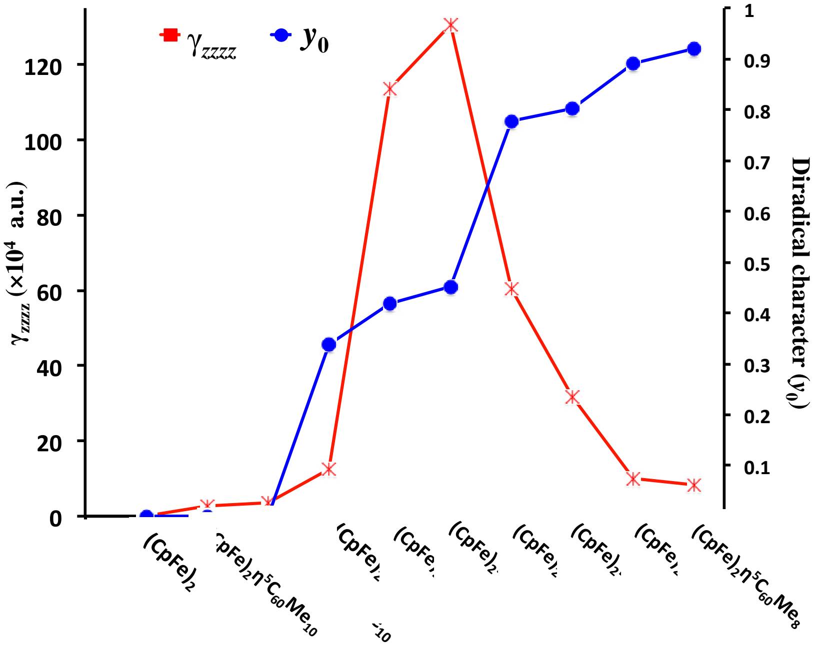


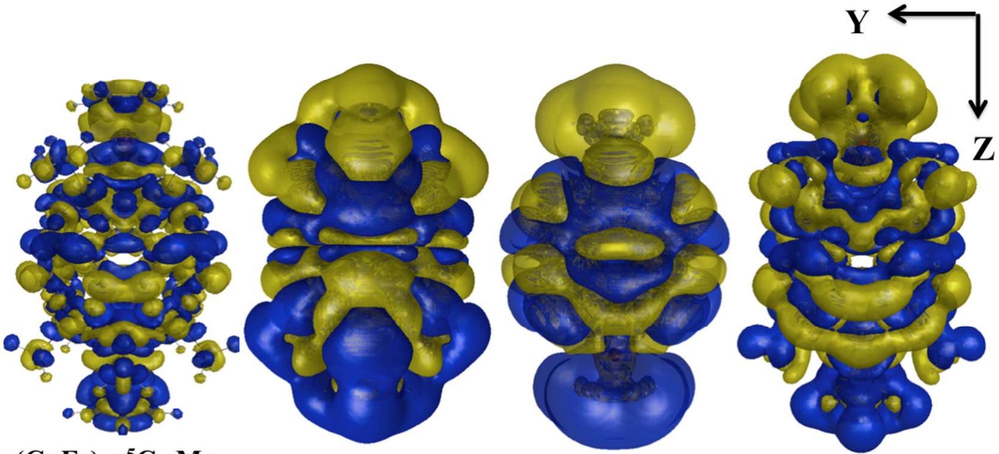
Figure 3. Second hyperpolarizability (γ_{zzzz}) vs. diradical character (y_0) of different chemical systems

3.2. Diradical Character Dependence of Second Hyperpolarizability

The amplitudes of γ_{zzzz} are given in Table 2 for different classes of buckyferrocenes calculated at the LC-B3LYP/6-31G* level of theory. The buckyferrocenes $(CpFe)_2\eta^5C_{60}Me_{10}$, $(CpFe)_2\eta^5C_{70}Me_{10}$ and ferrocene molecule itself have closed-shell configurations, which possess small amplitudes of γ_{zzzz} values, i.e., 0.076×10^4, 2.78×10^4 and 3.60×10^4 a.u., respectively. Similarly, buckyferrocenes $(CpFe)_2\eta^5C_{60}Me_4$ and $(CpFe)_2\eta^5C_{60}Me_8$ with relatively larger or pure diradical character also possess smaller amplitudes of γ_{zzzz} values of 10.07×10^4, and 8.33×10^4 a.u., respectively. In particular, the third class of buckyferrocenes with almost intermediate diradical values including $(CpFe)_2\eta^5C_{60}$, $(CpFe)_2\eta^5C_{70}$, $(CpFe)_2\eta^5C_{70}M_8$, $(CpFe)_2\eta^5C_{70}M_4$ and $(CpFe)_2\eta^5C_{30}$ show remarkably larger amplitudes of γ_{zzzz}, which reach into 113.75×10^4, 130.71×10^4, 60.39×10^4 and 31.74×10^4 a.u., respectively. Interestingly, the γ_{zzzz} amplitudes of $(CpFe)_2\eta^5C_{60}$, an open-shell intermediate diradical complex, is about 41 times and 13 times larger than its closed-shell ($(CpFe)_2\eta^5C_{60}Me_{10}$) and pure diradical ($(CpFe)_2\eta^5C_{60}Me_8$) counterparts, respectively. A similar trend is also observed for buckyferrocenes of C_{70} fullerene complexes, where the γ_{zzzz} amplitudes of $(CpFe)_2\eta^5C_{70}$, $(CpFe)_2\eta^5C_{70}Me_4$, and $(CpFe)_2\eta^5C_{70}Me_8$ systems with intermediate diradical characters are about 36, 17, and 9 times larger than that of their counterpart closed-shell $(CpFe)_2\eta^5C_{70}Me_{10}$ system. The γ_{zzzz} amplitudes of intermediate diradical buckyferrocenes (hybrid of ferrocene and fullerene) are also shown to be remarkably larger than those of ferrocene (0.076×10^4 a.u.) and fullerenes C_{60} (3.79×10^4 a.u.) and C_{70} (9.72×10^4 a.u.) as calculated in our previous study at the same LC-BLYP/6-31G* level of theory.[12a] Using valence configuration interaction (VCI) method, we have previously traced the fundamental origin of γ amplitude of a symmetric two-site model ($A^\bullet$-$B^\bullet$ two electrons in two orbitals),[7] which gives three singlet states including the ground state (g), the first excited state (e1) and second excited state (e2). Based on perturbation theory, the expression for static γ value of symmetric molecules only contains the contributions of type-II (negative) and type-III-2 (positive) as given by[34]

$$\gamma = \gamma^{\mathrm{II}} + \gamma^{\mathrm{III-2}} = 4\left[-\frac{(\mu_{\mathrm{g,e1}})^4}{E_{\mathrm{e1,g}}^3} + \frac{(\mu_{\mathrm{g,e1}})^2(\mu_{\mathrm{e1,e2}})^2}{(E_{\mathrm{e1,g}})^2 E_{\mathrm{e2,g}}}\right], \qquad (3)$$

where g, e1 and e2 represents the ground, first excited, and second excited states respectively. It can be seen from the above equation that type-II composed of the product of transition moments in the numerator and the excitation energies in the denominator. It has been found in the VCI results[5b,7] that the ground state (g) involves the equal weight of its covalent (diradical) and ionic components at $y_0 = 0$ and with increasing y_0 value, its diradical component gradually increases. In contrast, for the second excited state (e2) which also involves similar components with equal weight at $y_0 = 0$ and correlates with the ground state, the ionic component increases comparatively with increasing y_0 value. On the other hand, the first excited state is present as pure ionic state during the variation of y_0 value. As the value of y_0 increases, these multi-state features cause the change in their excitation energies and transition properties: (i) the excitation energies of e1 and e2 states decrease and coincide with each other at $y_0 = 1$, (ii) transition amplitudes between e1 and e2 transition increases, while that of between e1 and g state decreases to zero value at $y_0 = 1$. These changes in transition energies and properties by increasing y_0 results in a bell-shaped variation of γ for y_0 with the systems of the same size: γ amplitude increases and attains a maximum value at an intermediate value of y_0 and then decreases again at large y_0 value. In the light of our previous finding and to comprehend the origin of diradical character dependence of large γ_{zzzz} amplitudes, we plot the γ_{zzzz} amplitudes vs. diradical character for all designed systems, which have similar size, as shown in Figure 3. Figure 3 shows a bell-shaped variation of γ_{zzzz} amplitudes for increasing y_0 values, i.e., γ_{zzzz} amplitudes at intermediate diradical characters are larger than those at smaller and larger diradical characters. The trends in the variation of γ_{zzzz} amplitude of buckyferrocenes with increasing y_i value are found to be inline with our previous VCI method studies.



$(CpFe)_2\eta^5C_{60}Me_{10}$
$y_0 = 0.000$

$(CpFe)_2\eta^5C_{70}Me_8$
$y_0 = 0.778$

$(CpFe)_2\eta^5C_{60}$
$y_0 = 0.419$

$(CpFe)_2\eta^5C_{60}Me_8$
$y_0 = 0.920$

Figure 4. γ density $[\rho^{(3)}(r)]$ distributions, where yellow and blue meshes represent positive and negative γ densities with iso-surfaces of ±10.00 a.u., respectively.

3.3. γ Density Analysis

The influence of intermediate diradical character in buckyferrocenes is further addressed by examining their spatial electronic contributions using γ density distributions. The γ density $\rho_{iii}^{(3)}(r)$ is numerically calculated from the third-order derivative of electron density with respect to an applied electric field:[25, 35]

$$\rho_{zzz}^{(3)}(\boldsymbol{r}) = \left.\frac{\partial^3 \rho(\boldsymbol{r})}{\partial F_z \partial F_z \partial F_z}\right|_{F=0}, \tag{4}$$

which gives γ_{zzzz} value by

$$\gamma_{zzzz} = -\frac{1}{3!}\int r_z \rho_{zzz}^{(3)}(\boldsymbol{r})\, d\boldsymbol{r}. \tag{5}$$

A pair of positive and negative distributions along the positive direction of *z*-axis contributes to γ_{zzzz} positively, where its contribution is proportional to the product of the density amplitudes and separating distance between them. The contributions obtained from a pair of positive and negative γ densities provide a description of local contributions of electrons, i.e., field-induced third-order dipole moment, to the total γ. The γ density plots for some selected buckyferrocenes are shown in Figure 4, which includes closed-shell, intermediate and pure diradical buckyferrocenes systems. A close observation of γ density plots of $(CpFe)_2\eta^5C_{60}$ and $(CpFe)_2\eta^5C_{70}Me_8$ buchkyferrocenes (with intermediate diradical character) shows that the primary contribution to their γ values come from π-electrons, which are delocalized over the whole buckyferrocene systems and have larger amplitudes of well-separated positive and negative γ densities, particularly of the positive and negative γ densities of two terminal fragments of ferrocene moieties. In contrast, $(CpFe)_2\eta^5C_{60}Me_{10}$ (closed-shell) and $(CpFe)_2\eta^5C_{60}Me_8$ (pure diradical) buckyferrocenes show relatively poor amplitudes of their positive and negative γ densities and their significant cancellation due to the alternant positive/negative distributions as shown in Figure 4. Thus, the γ density plots of closed-shell, intermediate open-shell and pure open-shell buckyferrocenes illustrate the relative amplitudes of their respective γ values.

3.4. Density of State (DOS) Analysis

Can the buckyferrocenes enjoy the rich scientific legacy of ferrocene and fullerene with extensively large π-conjugation network between the two Fe atoms as assumed in the synthesis of $(CpFe)_2\eta^5C_{60}Me_{10}$? To answer this question and to check the contribution of individual parts, we calculate the total (TDOS) and partial (PDOS) density of states[36] for selected buckyferrocene systems. For the calculation of TDOS and PDOS, we divide the buckyferrocene systems into three parts, i.e., fullerene, Fe metals and cyclopentadiene (Cp) rings. The TDOS and PDOS plots of $(CpFe)_2\eta^5C_{60}Me_{10}$, $(CpFe)_2\eta^5C_{60}$, $(CpFe)_2\eta^5C_{60}Me_4$, and $(CpFe)_2\eta^5C_{70}Me_8$ buckyferrocenes are shown in Figure 5. From Figure 5, it can be seen that $(CpFe)_2\eta^5C_{60}Me_{10}$ has relatively larger band gap with almost no contributions in its frontier orbitals from the metal atoms and Cp rings. Thus, the sp^3 hybridized carbon atoms containing decamethyl substituents cause the breakdown of its extensively large π-conjugation network between the two Cp edges. On the other hand, in our designed systems $(CpFe)_2\eta^5C_{60}$ (with no substituted fullerene) $(CpFe)_2\eta^5C_{60}Me_4$, and $(CpFe)_2\eta^5C_{70}Me_8$ (with partly substituted fullerenes), their bad gaps are relatively small with substantial contributions of the metal atoms and Cp rings in their frontier orbitals. Interestingly, the contributions of the two iron metal atoms are also significant in the low-energy bonding orbitals of all three modified buckyferrocenes, the feature of which is not present in $(CpFe)_2\eta^5C_{60}Me_{10}$ buckyferrocene due to blocking of π-conjugation network by the sp^3 hybridized decamethyl substituents. Thus, the DOS graphs show the importance of using suitably modified fullerenes (partially methyl substituted) in order to get the full advantage of large π-conjugation network and better electronic communication between ferrocene moieties at the two edges of the buckyferrocene as well as of tuning the diradical character.

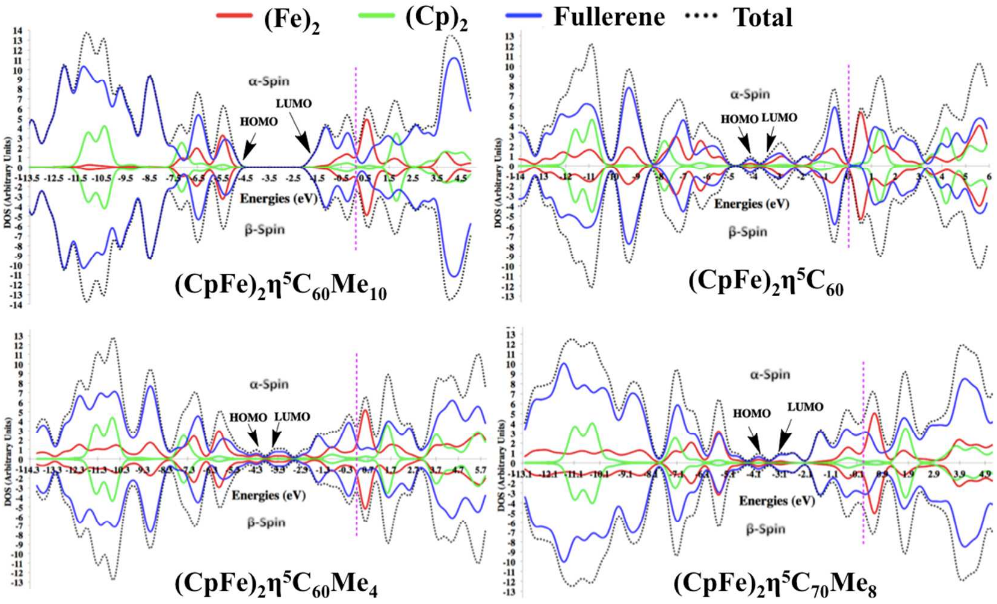


Figure 5. Total and partial [(Fe)$_2$, (Cp)$_2$ and fullerene fragments] densities of states in selected buckyferrocenes

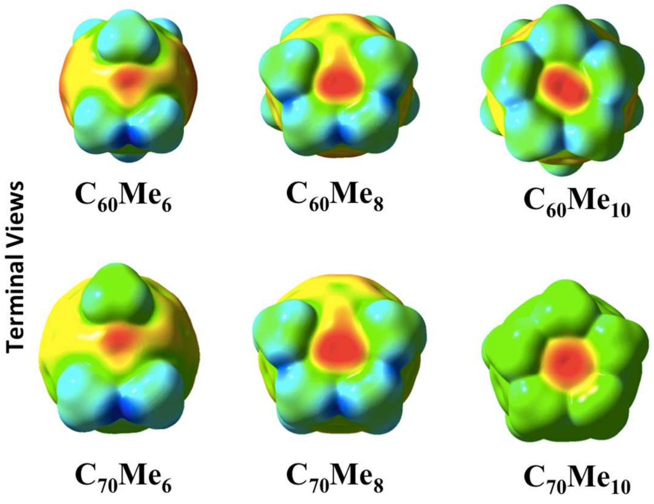


Figure 6. Molecular electrostatic potential (MEP) maps for modified fragments of C_{60} and C_{70} fullerenes with isovalue of 0.0030 a.u., where negative potential decreases in order of red > orange > yellow > green > blue.

3.5. Prospect of Design Strategy for Efficient Nonlinear Optical Materials

Matsuo et al.[16] have reported the synthesis of some buckyferrocenes through face-to-face fusion of ferrocene and modified fullerene (decamethyl-substituted) fragments. The fullerene fragments were prepared by pentamethyl substitutions on both edges of the C_{60} fullerene. Due to these pentamethyl substitutions, it is assumed that terminal pentyl ring achieve enough localized electron density, so that it can easily react with ferrocene moiety. What would be the electronic configuration in the case of tri- and tetra-methyl substituted fullerene fragments? To answer this question, we make the molecular electrostatic potential (MEP) maps of tri- and tetra-methyl substituted C_{60} and C_{70} fullerenes as illustrated in Figure 6. The MEP is the measurement of electrostatic potential on constant electron density surface. The MEP is a helpful property to investigate the reactivity of molecular species by predicting whether the approaching electrophile is attracted to a negative region of molecule, which are in the present case the terminal pentyl rings of fullerenes. In these plots, the maximum negative region, i.e., a preferred site for electrophilic attach, is indicated with red surface, while blue represents its vice versa. The decamethyl C_{60} and C_{70} fullerenes show significant negative electrostatic potential on their terminal pentyl ring for its possible η^5 coordination with ferrocene moieties. In the case of tri- and tetra-methyl C_{60} and C_{70} fullerenes, the relative intensity of the negative electrostatic potential is smaller but still it can be considered enough for η_5 coordination with ferrocene moieties as shown in Figure 6. These MEPs provide a semi-quantitative guess about the use of suitably modified fullerene fragments for the preparation of highly efficient buckyferrocenes that can act not only as preferred ligands for ferrocene moieties but also maintain sp^2-hybridized carbon skeleton of fullerene between the terminal fragments of ferrocene moieties (FeCp) and thus realize a wide range of the diradical characters. This feature can make the buckyferrocenes as excellent functional material for its outstanding nonlinear optical properties.

4. Conclusion

The diradical characters and third-order nonlinear optical properties of several buckyferrocenes have been investigated using density functional theory methods. The analysis of geometrical topologies, spin densities and γ densities of buckyferrocenes have been performed to achieve an uninterrupted π-electron network together with intermediate diradical characters, the feature of which causes remarkably large third-order nonlinear optical responses. It is found that the π-electrons in fullerenes C_{60}, C_{70} and their modified fragments, i.e., $C_{60}Me_4$, $C_{60}Me_8$, $C_{70}Me_4$ and $C_{70}Me_8$ play a crucial role to tune the open-shell character and third-order nonlinear optical responses in buckyferrocenes. A systematic study of buckyferrocenes shows that a significant spin polarization can be obtained by changing the number and position of methyl groups in fullerene π-conjugated fragments. The buckyferrocenes with intermediate diradical characters are found to possess significantly larger amplitudes of second hyperpolarizability as compared to their pure diradical and closed-shell counterparts. In particular, the γ_{zzzz} amplitudes of $(CpFe)_2\eta^5C_{60}$, an open-shell intermediate diradical complex, turns out to be about 41 times and 13 times larger than its closed-shell ($(CpFe)_2\eta^5C_{60}Me_{10}$) and pure diradical ($(CpFe)_2\eta^5C_{60}Me_8$) counterparts, respectively. The γ density distribution plots show that the field-induced π-electron transfer between two terminal fragments of ferrocene moieties provide the major positive contribution to the γ value in buckyferrocene systems with intermediate diradical characters. Thus, to get highly-efficient functional buckyferrocenes, it is important to use suitably modified fullerene fragments (having uninterrupted π-electron network together with intermediate diradical character) that can act not only as preferred ligands for ferrocene moieties but also maintain sp^2-hybridized fullerene skeleton between the two terminal fragments of ferrocene moieties (FeCp). This feature can make the open-shell singlet buckyferrocenes as excellent functional material for its efficient nonlinear optical properties. Finally, it is worthy to note that the electronic communication between the two terminal ferrocene moieties through the methyl-substituted fullerenes is also speculated to realize open-shell singlet systems with acceptor(A)-π-acceptor(A)-type charge distribution, which are recently predicted to further enhance the NLO properties as compared to usual diradicaloids with uniform charge distribution.[37] The investigation of the effects of the A-π-A nature on the diradical character and NLO properties of buckyferrocenes will be one of the next challenging themes.

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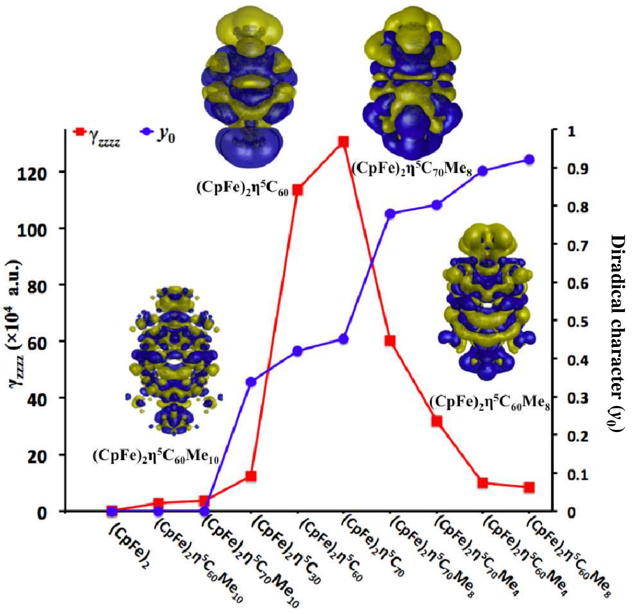
TOC



Buckyferrocenes, which are made up of suitably modified fullerenes fragments having an uninterrupted π-electron network, show intermediate diradical character and robustly large third-order nonlinear optical responses