Interplay between Diradical Characters and Third-Order Nonlinear Optical Properties in Fullerene Systems

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In the modern era, nonlinear optical (NLO) and spintronic materials are the two types of hi-tech and the smartest materials.[1] As a pioneering attempt towards understanding of the interplay between these two properties, we proposed a new structure-property relationship between the diradical character (y_i), which is a chemical index of the bond nature, and the third-order NLO polarizability (second hyperpolarizability, γ) of open-shell singlet systems. We studied the topological dependence of diradical character and second hyperpolarizability (γ) in fullerenes. We found that the large differences between the geometry and topology of fullerenes have a significant effect on the diradical character of each fullerene as elucidated by their odd electron density distributions (see Fig.1a). On the basis of their different diradical character, these fullerenes were categorized into three groups, that is, closed-shell ($y_i = 0$), intermediate open-shell ($0<y_i<1$), and almost pure open-shell compounds ($y_i \cong 1$). This categorization has been found in accordance with Clar's sextet rule that has been applied on Schlegel projections of these fullerenes. For example, we found that closed-shell fullerenes include $\mathbf{C_{20}}$, $\mathbf{C_{60}}$, and $\mathbf{C_{70}}$, whereas fullerenes {$\mathbf{C_{26}}$, $\mathbf{C_{36}}$} and {$\mathbf{C_{30}}$, $\mathbf{C_{40}}$, $\mathbf{C_{42}}$, $\mathbf{C_{48}}$} are pure and intermediate open-shell compounds, respectively. Interestingly, the γ_{zzzz} enhancement ratios between $\mathbf{C_{30}}$/$\mathbf{C_{36}}$ and $\mathbf{C_{40}}$/$\mathbf{C_{60}}$ are 4.42 and 11.75, respectively, regardless of the smaller π-conjugation size in $\mathbf{C_{30}}$ and $\mathbf{C_{40}}$ than in $\mathbf{C_{36}}$ and $\mathbf{C_{60}}$, respectively. Larger γ_{zzzz} values were obtained for other fullerenes that had intermediate diradical character that is in line to our previous valence configuration interaction (VCI) results for the two-site diradical model.[2] The γ_{zzzz} density analysis shows that the large positive contributions originate from the large γ_{zzzz} density distributions on the right- and left-extended edges of the fullerenes, between which significant spin polarizations (related to their intermediate diradical character) appear within the spin-unrestricted DFT level of theory (see Fig.1b). On the bases of this structure-property relationship, we have further constructed bucky ferrocenes with robust second hyperpolarizabilities that can be switched *on* and *off* in their *singlet* and *triplet* ground states, respectively.

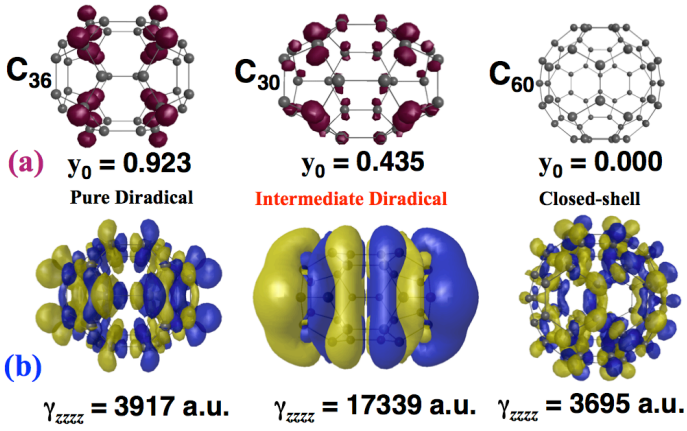

Fig.1 Odd electron densities in maroon color with isosurfaces of 0.001a.u.(a) second hyperpolarizability densities yellow and blue meshes of ±10 a.u. (b)

References (1) S. Kawata, *et al. Chem. Rev.,* **2000**, *100*, 1777 (2) M. Nakano, *et al. Phys. Rev. Lett.*, **2007**, *99*, 033001