Theoretical Study of the Effects of Electron Density Distribution in Frontier Orbitals with Open-Shell Graphene Fragments

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Abstract

Open-shell fragments of graphene have attracted increased attention in recent years because of their unique spin carrier property.[1] Through the experimental efforts, these neutral π-radicals could be stabilized by steric protection or delocalized π-conjugated system, such as the phenalenyl-based molecules.[2] Here, we use zero sum rule[3] to extend the molecular size and investigate their electronic properties. The molecules studied in this work can be categorized into two kinds of open-shell structures: the ones with even electron density distribution in the frontier orbitals and the ones with uneven distribution. These molecules afford small reorganization energies in our computational results, especially in the even distribution case (smaller than 19 and 34 meV for hole and electron transfer, respectively). These ultra-low values can be interpreted with the strong nonbonding character in the frontier orbitals, so that the bond length alteration is small during charge transfer.[4],[5] Considering the overlap of bilayer open-shell graphene fragments, the even distribution molecules exhibit larger electronic coupling and binding energy than the uneven. Therefore, we propose that open-shell graphene fragments with uniform electron density distribution in the frontier orbitals would be better charge transfer materials than the ones with uneven electron density distribution.

References

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Figures

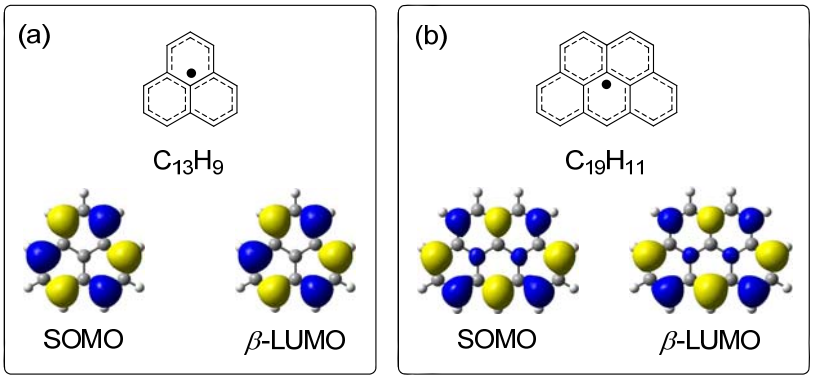

Figure 1. Example of a molecule with (a) even or (b) uneven electron density distribution in the frontier orbitals.