Structural, electronic, electrochemical and electromechanical properties of new building blocks for nano-scale molecular electronics; DFT study of cumulenes and fulleroferrocene π-complexes

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As shown quite recently [1], the structural, chemical, optical, electrochemical, and molecular orbital properties of ferrocenyl-cumulenes make these molecular wires very promising objects for nano-scale molecular electronics in comparison with purely organic molecular wires. The structural stability and rigid molecular architecture of the cumulene chain is a key advantage in comparison with less rigid but more common polyene or polyphenyl chains, implying that such rigid molecular wires can sustain a large current density. Recent seminal work of E. Nakamura and M.Sawamura and their coworkers [2], who succeeded in functionalizing C_{60} regioselectively to a fivefold organo-substituted $C_{60}R_5H$ fulleroid Cp ligand, has opened exciting new possibilities for nano-scale molecular electronics.

A series of fulleroferrocenes containing one and two fullerocyclopentadienide ligands $C_{60}H_5$ and $C_{60}(CH_3)_5$ are studied by high level DFT calculations at the B3LYP/6-31gs level with full geometry optimization. Structurally, the coordination of iron enforces a break in symmetry with regard to the spherical shape of C_{60}, leading to considerable steric stress at the carbon atoms in the vicinity of the metal. Calculated dipole moments and electrochemical properties indicate that these nano-sized new metallofullerenes represent promising building blocks for future applications in materials science. The nano-scale electromechanical effect was studied on a series of polysubstituted cumulenes at the B3LYP/6-31gs level. Possible applications will be discussed. All calculations were performed with the Gaussian03 suite of programs [3].

[1] B. Bildstein, O. Loza, Y. Chizhov, Organometallics 2004, 23, 1825.
[2] M. Sawamura, H. Iikura, E. Nakamura, J. Am. Chem. Soc. 1996, 118, 12850.
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