Theoretical study of functional carbon nanomaterials based on tetraazaporphyrin subunits

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The realization of the uniform nanomaterials with specific topology useful for high-performance nanoscale devices is currently one of the main challenges in nanotechnology. Thermally and chemically robust carbon materials, such as fullerenes and carbon nanotubes, are very exciting molecular-level building blocks for nanoscale materials design [1-2]. However, the separation of a synthetic mixture into mono-disperse or single chirality components is still challenge for researchers and hence provides some limitations to access the pure carbon nano-materials for technological applications.

The organic supramolecular assemblies, which consist of covalently or non-covalently bounded functional monomeric building blocks materials, can be rival to the pure nanocarbon-based systems. Porphyrins and phthalocyanines may consider as one of the most interesting building blocks. These molecules found a variety of applications ranging from traditional dyes and pigments to more contemporary cancer therapies, environmental and biochemical sensors, nonlinear optics and light-harvesting.

Here, we have presented a general design for functional 3D tetraazaporphyrin-based nanostructures, which would bridge the gap between the well-known fullerenes and nanotubes and a new class of the multifunctional nanomaterials. We have explored three major motifs for functional nanostructures which vary by three- or four-fold topology, porosity, degree of conjugation, and electronic structures [3]. The stability of proposed nanocages, nanobarrels and nanotubes generated by conversion from nanobarrels was revealed on the basis of density functional (DFT) and molecular dynamics (MD) calculations, whereas their optical properties were assessed using a time-dependent density functional (TDDFT) approach. It was shown that the electronic structures and optical properties of studied structures could be easily tuned via their size, topology, and the presence of bridging sp^3 carbon atoms. Based on DFT and TDDFT calculations, the optical properties of the new materials can rival those of known quantum dots. The ability to store large quantities of methane was observed in all cases with several compounds being close to or exceeding the DOE target of 180 $cm^3(STP)/cm^3$.

References:

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