

Graphene induced molecular flattening of neutral and cationic porphyrins

V.A. Karachevtsev¹, S.G. Stepanian¹, M.V. Karachevtsev¹, L. Adamowicz²

¹ *B. Verkin Institute for Low Temperature Physics and Engineering, , Natl. Acad. of Sci. of Ukraine, 47, Nauky Ave., Kharkiv, 61103, Ukraine.*

E-mail: karachevtsev@ilt.kharkov.ua

² *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, USA.*

Unique structural, mechanical and electronic properties of graphene (Gr) make this material promising for creating various miniature devices. Noncovalent functionalization of Gr with different organic molecules greatly extends the areas of effective Gr using in nanotechnology. Such important chromophores as porphyrins with the conjugated π -system play important role in functionalization of Gr or nanotubes as they form stacking structures with the graphene surface that have great opportunities for their practical applications in different areas.

In the present contribution the results of the quantum-chemical calculations and molecular dynamics simulation of the adsorption of two porphyrins with similar structures; neutral meso-5,10,15,20-tetraphenyl porphyrin (TPP) and cationic meso-5,10,15,20-tetras-(N-methyl-4-pyridyl) porphyrin (TMPYP4) on graphene are presented. Structures and the interaction energies between porphyrins and graphene are determined. We determined the interaction energies with values of -111 and -23 kcal/mol for cationic TMPYP4 and the neutral TPP, respectively. It was shown that in addition to the van der Waals stacking interaction of porphyrins with graphene the essential contribution to the total binding energy is due to the cation- π attraction of four cationic methylpyridinium (MPYP) rings of TMPYP4.

The strong π - π stacking interaction of porphyrin core of TMPYP4 or TPP with graphene leads to the twisting of the back-side rings. In contrast to the structure of the unbound porphyrin, when four cationic MPYP (or phenyl) moieties are nearly perpendicular to the plane of porphyrin core, on graphene these groups are rotated toward the coplanar conformation with respect to the flattened porphyrin core. As a result the molecular structure of these porphyrins on graphene becomes flatter. We show that the cation- π interaction of MPYP rings of TMPYP4 with graphene results additional rotation of these rings.

In the UV-visible spectra of TMPYP4 the Soret band shows a large bathochromic shift (28 nm) after binding to graphene oxide sheets. This observation is attributed in part to the flattening of TMPYP4 structure, which was caused by twisting of the cationic MPYP groups.

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