White-graphene sections confined in Graphene nano-flakes.
Toward a novel class of 2-D systems bearing extraordinary first order dipolar/octupolar non-linear optical responses

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Abstract

A proof-of-concept about a novel way of designing two dimensional based systems of exceptionally large first order non-linear optical (NLO) activity is presented. The proposed route has been inspired by the recent advances in synthesis of a novel type of graphene hybrid in which finite sections of "white graphene" (c.c hexagonal boron nitride, *h*-BN) are confined in larger sections of pure graphene. The so called graphene/*h*-BN hybrids have been grown already as a part of numerous attempts to open the zero band gab of graphene at the Fermi level by creating asymmetric electron and hole conduction with simultaneous negative-type (with Nitrogen) and positive-type (with Boron) chemical doping [1-3].

In this communication it is demonstrated by means of quantum chemical methods, (Ab initio, Density Functional) that finite sections of such hybrids can be utilized to assemble a very handy toolbox of 2-dimensional graphene based nanoobjects characterized by extraordinary first order hyperpolarizabilities. In particular, it will be revealed that such two dimensional architectures, are extremely promising for applications where high rated octupolar first hyperpolarizabilities are required. Octupolar molecules, bearing large octupolar NLO responses have been the subject of intense studies in the past mainly by Lehn, Zyss and co-worker[4-5] as very promising candidates for NLO materials allowing one to optimize the trade of between transparency and efficiency, achieving at the same time a non symmetric crystallization due to the absence of permanent electric dipole moment.

A representative collection of the model systems to be discussed is given in Fig. 1. Among them one can distinguish *h*-BN-C_{222} which in its pristine form can be obtained from cyclodehydrogenation of polyphenylenes. Such systems containing small $B_{24}N_{24}$ domains embedded in graphene are feasible to synthesize using a single step CVD route [2]. As it will be shown, their NLO properties may reach easily an order of magnitude of 10^5 atomic, while, with the proper modification, the threshold of 10^6 atomic units can be crossed. The resolved polarization mechanism points out that the charge transfer process in the excited states, responsible for the predicted responses, relies heavily on the particularities of the BN-graphene hetero-junction. What is more, the outcomes of extended structure-property investigation in systems up to 4.5 nm performed in our lab expose a remarkable correlation between of the position and the shape of the BN section in the hybrid flake and the delivered NLO response. Secondary parameters (but also important) are the total shape and size of the flake itself.

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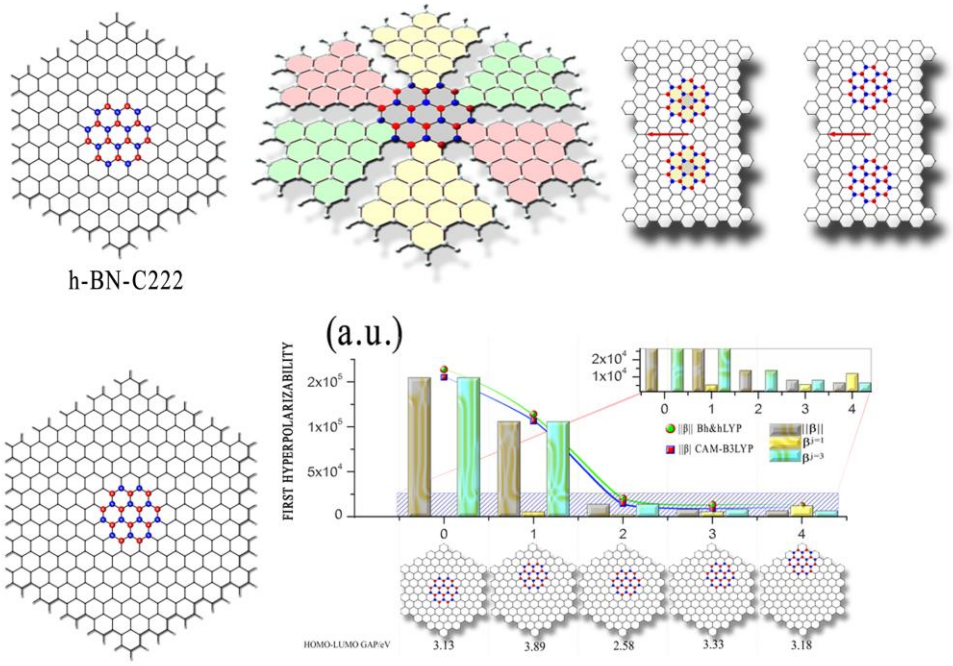

Figure. 1. Structures of hybrid *h*-BN/graphene flakes and correlations between structure and first hyperpolarizability.