Water Passage through Graphynes' Pores: First-Principles Penetration Barrier and Force Field Optimization

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Abstract: Graphynes are novel two-dimensional carbon-based materials, naturally presenting a nanoweb-like structure characterized by triangular and regularly distributed pores[1]. These intriguing features make them appealing for molecular filtering, especially for water purification technologies. First principles calculations are carried out at the MP2C level of theory to properly assess the interaction between water and graphyne, graphdiyne and graphtriyne pores. The computed penetration barriers (see Figure) suggest that water transport is unfeasible through graphyne while being unimpeded for graphtriyne. Nevertheless for graphdiyne, which presents a pore size almost matching that of water, a low barrier is found which in turn disappears if an active hydrogen bond with an additional water molecule on the opposite side of the opening is taken into account (see Figure). These results confirm the possibility of an efficient use of graphtriyne (and larger pore homologues) membranes for water filtration and purification, as very recently suggested by molecular dynamics investigations[2-5]. Still, in contrast with these studies[2-5], present findings do not exclude graphdiyne since the related first principles penetration barrier leads to water permeation probabilities[6] which are at least two orders of magnitude larger than those estimated by employing generic force fields[2-5]. The computed energy profiles for graphdiyne have also served to build a new pair potential for the water--carbon non-covalent component of the interaction which better represents the water--pore behaviour[6] and it is recommended for molecular dynamics simulations involving graphdiyne and water.

Keywords: graphyne, graphdiyne, porous materials, nanofiltration, water purification, ab-initio calculations

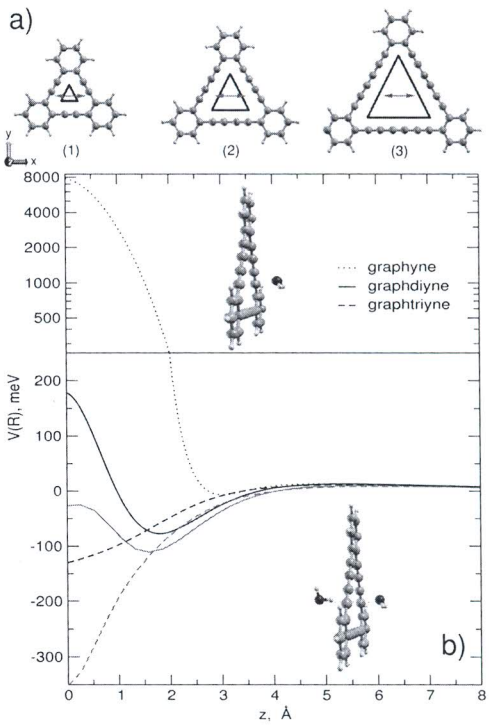

Figure: a) Annulenic molecular structures used to study the nano-pores of graphyne(1), graphdiyne(2) and graphtriyne(3). The black triangles depicted inside the pores represent their effective available area to be compared with the van der Waals diameter of the water molecule (red double-headed arrow).
b) Energy profiles obtained at the MP2C level of theory for water perpendicularly approaching the geometric center of graphyne, graphdiyne and graphtriyne pores. Black lines correspond to the case of a single water molecule approaching the pore. Red lines refer to the case in which a second water molecule fixed on the other side of the pore is added. A catalyzing effect is noticed due to the presence of an active hydrogen bond, which for graphdiyne leads to the suppression of the penetration barrier.

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