

Supporting information for

Two-dimensional polyphenylene: experimentally available porous graphene as hydrogen purification membrane

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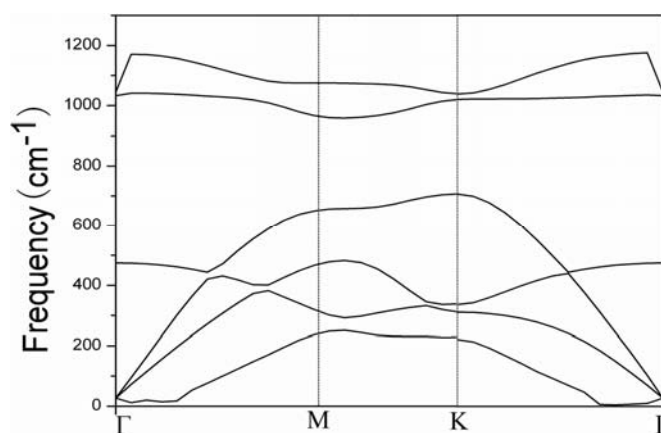
Computational Details

First-principles computations were carried out by using the density functional theory (DFT) method implemented in DMol³ package.¹ The generalized gradient approximation (GGA) in the PW91² form as well as all-electron double numerical basis set with polarized function (DNP) were chosen for the spin-unrestricted DFT computations. The real-space global cutoff radius was set to be 3.70 Å. The Brillouin zone was sampled with a 6×6×1 Γ centered k -point grid, and Gaussian seaming with a width of 0.05 eV was used for the occupation of the electronic levels. We used a supercell with the length of 15 Å in the z direction to avoid the interaction between polyphenylene layer and its periodic images. The structures were fully optimized with no constrain, and the forces on atoms were less than 0.05 eV · Å⁻¹ after geometric optimization. The transition state search was performed through the synchronous transit method³ with conjugated gradient refinements implemented in the DMol³ package. This method involves linear synchronous transit

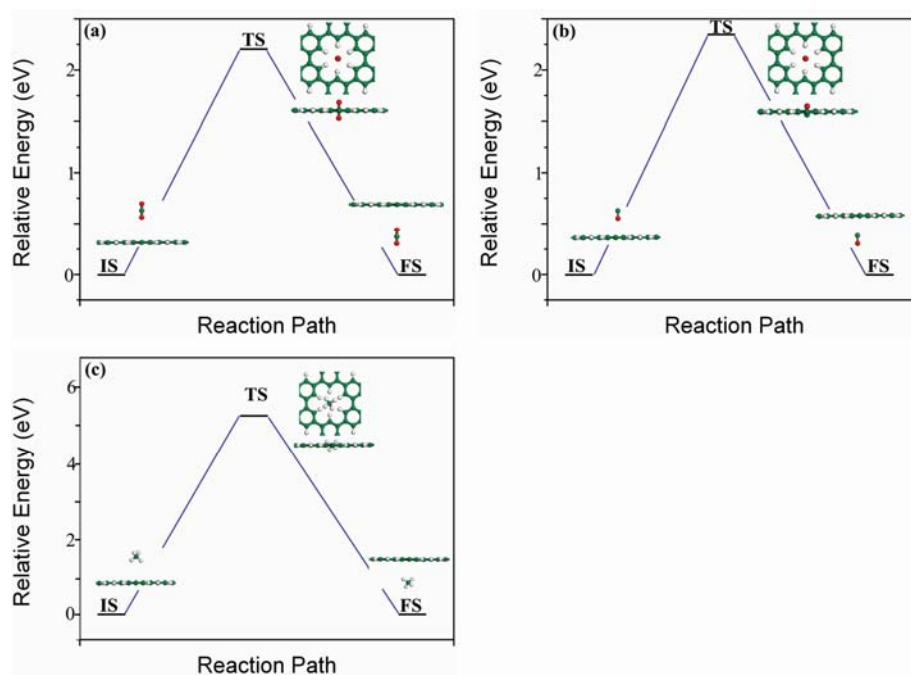
(LST) maximization, followed by repeated conjugated gradient (CG) minimizations, and then quadratic synchronous transit (QST) maximizations and repeated CG minimizations until a transition state is located.

References

1. B. Delley, *J. Chem. Phys.* 1990, **92**, 508–517; *J. Chem. Phys.* 2000, **113**, 7756–7764.
2. J. P. Perdew and Y. Wang, *Phys. Rev. B* 1992, **45**, 13244–13249.
3. N. Govind, M. Petersen, G. Gitzgerald, D. King-Smith and J. J. Andzelm, *Comput. Mater. Sci.* 2003, **28**, 250–258.



S-Fig. 1 The phonon band structure of 2D polyphenylene. All phonon-dispersion curves without imaginary frequency confirm that the 2D planar polyphenylene is a stable structure.



S-Fig. 2 Energy profiles for (a) CO₂, (b) CO, and (c) CH₄ passing through the pore of polyphenylene. The insets are the corresponding configurations of **IS**, **TS**, and **FS**. Especially for **TS**, both top and side views are given. The gas adsorption energies at IS are -0.09 , -0.05 and -0.12 eV for CO₂, CO, and CH₄, respectively.

S-Table 1 Energy barriers (eV) of four molecules passing through the pore of 2D polyphenylene computed from both PW91 and BLYP functional. Compared with BLYP functional, PW91 functional slightly underestimates the energy barriers.

	H ₂	CO ₂	CO	CH ₄
PW91	0.61	2.21	2.35	5.19
BLYP	0.68	2.32	2.47	5.62