Enhanced and Selective Unidirectional Proton Transport via Covalent Benzenesulfonic Functionalized Nanoporous and Pristine Graphene

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The fundamental understanding of the proton transport mechanism through graphene-based proton exchange membranes (PEMs) is crucial to develop novel and advanced two-dimensional (2D) separation materials for energy conversion devices. [1] We computationally investigate ways to enhance the balance between proton permeability and selectivity using a combination of ReaxFF molecular dynamics (ReaxFF-MD), Density Functional Theory (DFT), and metadynamics. In both the cases of graphene nanopore and pristine graphene, covalent benzenesulfonic functionalization introduces significant improvements in proton permeability and selectivity compared to other moieties. [2,3] For the graphene nanopore scenario, the benzenesulfonic functionality dynamically acts as a proton trap and proton shuttle by establishing a favourable hydrogen-bond network, resulting in an effective proton channel through the nanopore (Figure 1a). [2] In the pristine graphene case, the benzenesulfonic functionality guides the proton hopping toward the distorted basal plane, enabling successive proton tunnelling to the other side of the graphene monolayer (Figure 1b). [3,4] Notably, in these systems we achieve estimated proton diffusion coefficients that are comparable to or higher than the current state-of-the-art PEM, Nafion. [2,3] The mechanisms exhibited by these benzenesulfonic functionalized graphene-based systems set the ground for designing new 2D-PEMs with efficient unidirectional proton transport features.

References

[1] Liu, X. et al. Nat. Nanotechnol. 15, 307–312 (2020).
[2] Calvani, D. et al. J. Phys. Chem. C. 128, 8, 3514–3524 (2024).
[3] Zhang, W. et al. arXiv:2308.16112.
[4] An, Y. et al. Adv. Mater. 32 (37), 2002442 (2020).

Figures

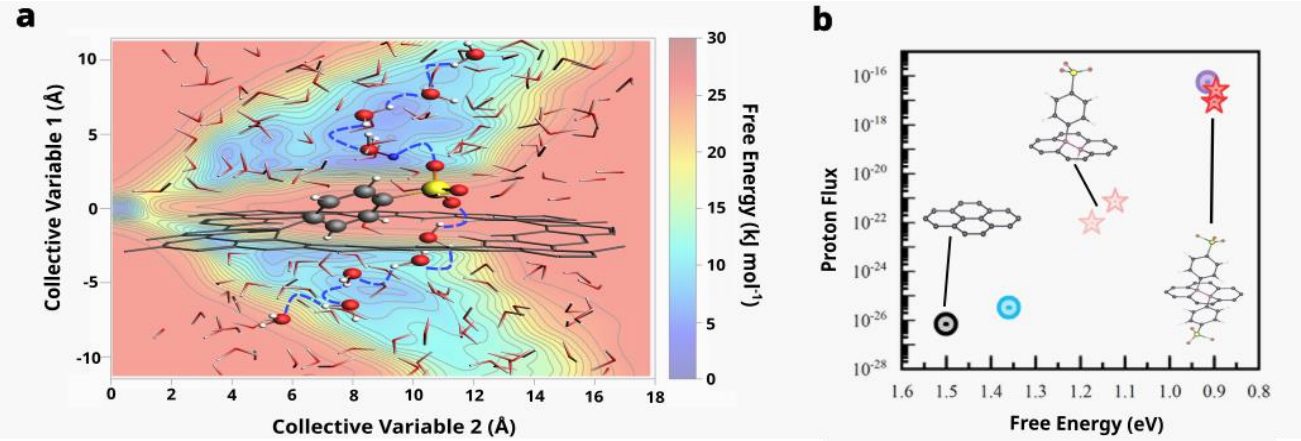

Figure 1: a, Free energy profiles (kJ mol^{-1}) along two collective variables (Å) from ReaxFF-MD metadynamics simulations for a graphene nanopore functionalized with benzenesulfonic group. **b**, Transmembrane transport proton flux with different benzenesulfonic functionalized pristine graphene monolayers *vs* corresponding DFT free energy barriers (eV). The flux was simulated using the Wentzel–Kramers–Brillouin (WKB) tunneling approximation.