Multiscale Simulation of PFOS and PFOA Capture Inside a Molecular 'Cage of Cages'

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Per- and polyfluoroalkyl substances (PFAS) have emerged as critical environmental contaminants due to their chemical stability, bioaccumulation potential, and resistance to conventional remediation strategies. This study explores the use of a hierarchical covalent organic structure - termed a "cage of cages" (Figure 1) - as an efficient host system for PFAS sequestration. Using an integrated computational approach involving density functional theory (DFT), molecular dynamics (MD), and nudged elastic band (NEB) calculations, we examine the adsorption characteristics and confinement behavior of two representative PFAS molecules: perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). DFT results reveal that PFOS forms stronger host–guest interactions (−33.07 kcal/mol) than PFOA (−24.63 kcal/mol), largely due to enhanced van der Waals and electrostatic interactions [1]. NEB simulations show higher desorption energy barriers for PFOS (109.18 kcal/mol) compared to PFOA (99.84 kcal/mol), indicating more persistent entrapment within the cage structure. MD simulations confirm the structural integrity and dynamic stability of the PFAS-loaded cage in aqueous environments. Additionally, QTAIM and Hirshfeld surface analyses provide detailed insight into the intermolecular forces governing these interactions, highlighting the dominant role of dispersion and hydrogen bonding [2]. Overall, these results support the potential of molecular cages as selective, reusable adsorbents for PFAS removal, paving the way for their application in advanced water purification technologies.

References

[1] S. Grimme, Chem. Eur. J., 18 (2012) 9955–9964
[2] M.A. Spackman et al., CrystEngComm, 4 (2002) 378–392

Figures

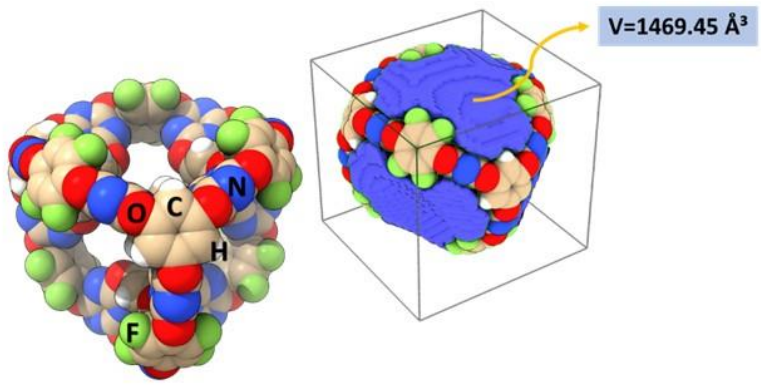

Figure 1: Optimized model of "cage of cage" and the calculation is cavity volume.