



In Silico understanding of the cyclodextrin–phenanthrene hybrid assemblies in both aqueous medium and bacterial membranes



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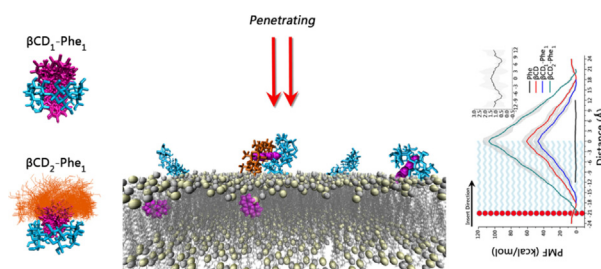
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HIGHLIGHTS

- Two hetero-assemblies, $\beta\text{CD}_1\text{-Phe}_1$ and $\beta\text{CD}_2\text{-Phe}_1$ were observed in water solution.
- Distinct membrane-binding patterns for βCD , Phe, and their complexes were found.
- Minor Phe *trans*-membrane energy barrier confirmed its membrane penetration ability.
- Huge energy barriers for βCD -involved assemblies denied their membrane penetration.
- Phe separation from $\beta\text{CD}_1\text{-Phe}_1$ was easier than that from $\beta\text{CD}_2\text{-Phe}_1$.

GRAPHICAL ABSTRACT



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ABSTRACT

The explicit-solvent molecular dynamic (MD) simulation and adaptive biased forces (ABF) methods were employed to systemically study the structural and thermodynamic nature of the β -cyclodextrin (βCD) monomer, phenanthrene (Phe) monomer, and their inclusion complexes in both the aqueous and membrane environments, aiming at clarifying the atomic-level mechanisms underlying in the CD-enhanced degradation of polycyclic aromatic hydrocarbons (PAHs) by bacteria. Simulations showed that βCD and Phe monomers could associate together to construct two distinctive assemblies, i.e. $\beta\text{CD}_1\text{-Phe}_1$ and $\beta\text{CD}_2\text{-Phe}_1$, respectively. The membrane-involved equilibrium simulations and the data of potential of mean forces (PMFs) further confirmed that Phe monomer was capable of penetrating through the membranes without confronting any large energy barrier, whereas, the single βCD and βCD -involved assemblies were unable to pass across the membranes. These observations clearly suggested that βCD only served as the carrier to enhance the bioavailability of Phe rather than the co-substrate in the Phe biodegradation process. The Phe-separation PMF profiles indicated that the maximum of the Phe uptake by bacteria would be achieved by the “optimal” βCD :Phe molar ratio, which facilitated the maximal formation of $\beta\text{CD}_1\text{-Phe}_1$ inclusion and the minimal construction of $\beta\text{CD}_2\text{-Phe}_1$ complex.

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1. Introduction

In the most recent years, soil and groundwater contaminations have attracted the huge attention due to their significant influences and potential risks on citizen's daily life and surroundings [1,2]. It has been widely reported that soil pollutions directly correlate to diverse diseases, such as, malignancy, elephantiasis, cancers, and so forth [3]. Many contaminants have been proved to be the causative agents for these environmental pollutions in the previous experiments [4]. As one type of the representative soil contaminants, polycyclic aromatic hydrocarbons (PAHs) sequestered in non-aqueous-phase liquids (NAPLs), are receiving increasing concerns, because of their ecotoxicities and continuous release through human activities and petroleum productions [5]. Phenanthrene (Phe), a small PAH composed of three fused benzene rings, widely exists in the soil and the groundwater. Due to the high hydrophobicity, Phe usually exhibits the low solubility and bioavailability, but a large magnitude of soil sorption, which gives rise to its ineffective degradation and unsatisfied remediation in nature [6,7]. Hence, tremendous interest has been aroused to achieve its effective cleanup in the most recent decades. Recent research has supported the possibility of enhancing the bioavailability and solubility of the hydrophobic molecules by adding the surfactants to the system [8–12]. However, the introduction of surfactants into the environments usually arouses the contamination concerns, because of its eco-toxicity and negative environmental side-effects, largely separating the surfactants from the potential candidate for the in situ bioremediation [13,14]. Consequently, the development of non-toxic and environmental-friendly alternatives achieves increasing interest in both industrial and scientific society.

Beta-cyclodextrin (β CD), one of the most accessible, low-priced, and nontoxic cyclodextrin, is the cyclic oligosaccharide consisting of seven cyclodextrins linked by α -(1,4)glucosidic bonds [15]. According to its crystal structure, β CD adopts the torus conformation with a hydrophilic outer shell and an apolar inner cavity [16]. Considerable experiments have demonstrated that β CD and its derivatives are capable of interacting with a wide range of low-polarity cargos to form the water-soluble hybrid inclusion complexes [17–23]. Their ability to bury the organic host molecules into the inner cavity offers the possibility of increasing the aqueous solubility of small organic molecules and enhancing their bioavailability [21,24–26]. Previous experiments have examined the capacity of β CD and its derivatives to promote the partitioning of PAHs from the NAPL to the aqueous solutions. The results consistently showed that β CD and its chemically-modified derivatives could effectively raise the aqueous concentration of PAHs in the NAPL-water systems in an environmental-friendly manner [2,27–32]. Moreover, the linear correlation between the β CD-induced equilibrium concentrations and biodegradation rate of PAHs was observed recently, implying that β CDs not only enhanced PAHs' solubility, but also promoted their biological uptake [27]. Furthermore, the reparability of the PAHs-polluting soil and ground water even directly correlates to their PAH extractabilities by CDs. However, the roles of CDs in the whole biodegradation-promoting process are still unclear to date.

Various chemical, physical, biological, and even the combined technologies have been attempted to investigate the properties of the CD-guest inclusions [33]. Germain monitored the solubility of pentachlorophenol by β CD and its derivatives, demonstrating that all kinds of CDs could form the 1:1 guest-host inclusion and their stabilities depended on the polarity of the compound [28]. Zhang, employing the synchronous fluorimetry method, investigated the effect of hydroxypropyl- β -cyclodextrin (HPCD) on the biodegradation of pyrene and proposed that the presence of HPCD can effectively raise the microbial degradation rate of pyrene due to the inclusion formation [21]. Semple, conducted the mineralization

assays to study the availability and bacterial degradation of Phe promoted by the CDs. Their results showed that the presence of CD in the soils increased Phe loss from the aged soil systems, especially at the high application rates [30]. Reid, studied the CD-enhanced biodegradation of polycyclic aromatic hydrocarbons and phenols in the slurries, supporting that the biodegradation of the hydrophobic molecules was not limited by the microbial catabolic activity, but depended on the target availability [34]. Complementary to the experiments, remarkable modeling and simulation efforts were also conducted [35]. Physics-based simulations offer a potent method to directly study the molecule-molecule interactions in atomic detail, allowing for the analysis in areas that are difficult, expensive, or unfeasible to probe experimentally [36]. Zhan, combining the quantum calculation and molecular dynamics simulation methods, studied the nature of polychlorinated biphenyls-CD complex at diverse stoichiometric ratios of 1:1, 1:2, 2:1, and 2:2. Their computational results supported the co-existence of the different inclusion patterns [37]. Bandyopadhyay, conducted the MD simulations of the β CD-phenylalanine assembly and found that the loss of the conformational entropy played the significant role in facilitating the formation of the inclusion [38]. Tan, performed the MD simulations of inclusions of puerarin and daidzin with β CD, observing the guest-induced structural adjustment of β CD and highlighting the significance of hydrogen bonds in separating puerarin from daidzin [39].

Herein, by means of the explicit-solvent molecular dynamics (MD) simulation and the adoptive biased forces (ABF) methods [40], the nature of the β CD monomer, Phe monomer, and their hybrid inclusion complexes in both aqueous and membrane environments were systematically studied. Our results suggested that β CD just acted as the carrier to enhance the bioavailability of Phe rather than the co-substrate in the whole degradation-promoting process. Phe was expected to separate from the β CD-Phe hybrid assemblies before the membrane insertion. Simulations also indicated that the maximum of the Phe uptake by bacteria would be achieved by the "optimal" β CD:Phe molar ratio, which facilitated the maximal formation of β CD₁-Phe₁ inclusion and the minimal construction of β CD₂-Phe₁ complex. This work provides the atomic-level understanding for CD-enhanced biodegradation of Phe.

2. Computational details

2.1. β CD-Phe mixture in the aqueous medium

The initial coordinates of Phe and β CD were obtained from the Cambridge structural database system [41]. The force fields for Phe and β CD molecules were developed in the CHARMM-compatible manner [42]. By means of the in-home program, individual five β CD and Phe monomers were put together with the random positions and orientations. The distances between each molecule were kept larger than 6.5 Å. Then, the whole system was solvent with a margin of 15 Å from any edge of the water box to any β CD and Phe atoms to construct the final cubic box of $55 \times 59 \times 58 \text{ \AA}^3$. The whole system was neutralized by adding Cl⁻ and Na⁺ ions.

2.2. β CD-Phe assemblies in the membrane environment

As the typical phospholipid in biological bilayers, phosphoethanolamine, consisting of a combination of glycerol esterified with two fatty acids and phosphoric acid is the principle lipid component of the membranes in common bacteria [43]. To construct the bacterial-mimic bilayers, the 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (POPE) lipids were employed to build the membranes. The monomer, β CD monomer, β CD₁-Phe₁, and β CD₂-Phe₁ complexes were placed on the top of the membranes with the z-distance of 15 Å. Four hybrid systems were solvent to

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