

Exploring the crystal energy landscapes of polycyclic aromatic hydrocarbons via crystal structure prediction and Monte Carlo threshold algorithm

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Polycyclic aromatic hydrocarbons (PAHs), although they are environmental pollutants with carcinogenic effects [1], exhibit electronic properties that make them attractive for use in organic electronics applications [2]. The performance of these materials is influenced by their molecular geometries and crystal packing arrangements [3, 4]. Computational screening, particularly crystal structure prediction (CSP), offers a valuable approach to explore the vast crystal packing space and identify thermodynamically stable structures [5]. However, CSP alone does not fully characterize the crystal energy landscape. Information regarding the energy barriers between different crystal structures and the depth of the potential energy surface (PES) minima is crucial for understanding polymorph stability and accessibility.

Our group recently extended the Monte Carlo threshold (MCT) algorithm to be used with molecular crystals [6, 7]. This method can be used to calculate the energy barriers between crystal structures, which can then be visualised using disconnectivity graphs [8].

In this study, we combine CSP with the MCT algorithm to conduct a comprehensive analysis of the crystal PES for three PAHs: phenanthrene, pyrene, and perylene. We employ three distinct potential energy models – FIT [9], PAHAP [10], and isoPAHAP [11] – to assess the influence of the intermolecular potential on the predicted landscapes. To achieve high energy barrier resolution and comprehensive coverage of the PES, we utilize a multistage sampling scheme, initiating MCT trajectories from a large set of the low energy CSP-generated structures. We discuss how CSP and the MCT algorithm combine to give a global view of the crystal energy landscapes of the selected PAH molecules.

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