PRE-NUCLEATION MECHANISMS OF FLAT PERYLENE-BASED ORGANIC NANOCRYSTALS

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Abstract. Although perylene-based organic nanocrystals are used in various fields, understanding their pre-nucleation processes (considered the first steps of the synthesis) is still elusive. In this work, the nature of pre-nucleation processes of organic crystal synthesis based on two types of flat perylene molecules is studied using reactive molecular dynamics simulations. The obtained results indicate that the additional methoxy group significantly affects the clustering rate of molecules and the structure of the formed clusters. In addition, the cluster formation behavior for both molecules is explained by Ostwald ripening theory. The analysis, which is based on the Gibbs free energy of formation, clarifies that this phenomenon depends on the volume-dependent stability of clusters. In general, this study contributes to a better understanding of the onset of synthesis of organic nanocrystals based on flat perylene molecules for modern nanotechnology.

***Keywords**: organic nanocrystals, pre-nucleation mechanism, reactive molecular dynamics, clustering, flat perylene molecules*

Introduction

Organic nanocrystals (ONCs) are widely used in pharmaceuticals [1], topochemical polymerization [2], biological applications [3], and other promising areas that require thorough research in the control of their synthesis.

For this purpose, several methods, including, the reprecipitation method [4], supercritical fluid crystallization method [5], recovery method [6] and other techniques are being widely implemented [7]. Among these methods, the reprecipitation method is convenient for the synthesis of ONCs with a certain size and morphology, which can be tuned by the choice of synthesis parameters such as temperature, molecular mixing rate, and other control parameters [5]. In particular, in the reprecipitation method, organic molecules are initially nucleated in solution and subsequently grow as crystals.

Recent studies indicate that a deeper understanding of the mechanisms of organic molecule nucleation and subsequent crystal growth is essential for the successful selective synthesis of ONCs [6]. In general, two main theories are used to explain the mechanisms of the initial stage of nanocrystal growth: classical [8] and non-classical [9] nucleation theories. According to the classical theory, the crystal nuclei are assumed to have the same structure as the original crystal. However, non-classical theory explains the crystal nucleation process as consisting of two-stage mechanisms, i.e., (i) the appearance of liquid-like initial clusters, and then (ii) a crystal-ordered nucleus within these clusters. Although both theories have successfully explained experimental results to some extent, there are still two different views on the explanation of the crystal nucleation process [10]. A positive solution to this problem requires a better understanding of pre-nucleation processes [10].

Therefore, in this research, we aim to understand the mechanisms of pre-nucleation processes of ONCs consisting of aromatic hydrocarbon molecules, applying computer simulations considering the available experimental evidence and theoretical hypotheses. In particular, we study the nature of the pre-nucleation process of ONC synthesis from selected flat perylene molecules using reactive molecular dynamics (MD) simulations.

Simulation details

Two types of flat perylene molecules, i.e., polycyclic aromatic hydrocarbons, are chosen to study ONC pre-nucleation (Fig. 1). As a first model molecule, we choose a perylene ($C_{20}H_{12}$) that is formed by joining two naphthalene ($C_{10}H_6$) molecules (see Fig. 1*a*). Second model molecule is a perylene molecule containing a methoxy group, i.e., 1-methoxyperylene ($C_{21}H_{14}O$) (see Fig. 1*b*). According to the Cambridge Structural Database (CSD), perylene and 1-methoxyperylene molecules are named as PERLEN08 [11] and WUFJEM [12], respectively.

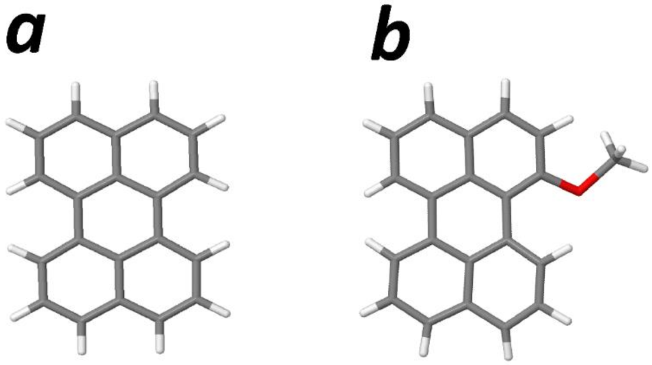

Fig. 1. Structural representation of (a) PERLEN08 (C20H12) and (b) WUFJEM (C21H14O) molecules. C, H, and O atoms are shown in gray, white, and red colors.

As mentioned above, we use reactive MD simulations [13] where the interactions between atoms in the system are represented by the ReaxFF potential using the parameter set introduced by Zhang et al. [14, 15]. The MD simulations are performed using the LAMMPS package [16].

The NVT ensemble is used to simulate the clustering process of perylene molecules, ensuring that all thermodynamic parameters (i.e., N, V, and T) remain constant during the process. The number of both perylene molecules in the simulation box is chosen to be 27, 64 and 125, the corresponding number of atoms (N) of which is 864, 2048 and 4000 for PERLEN08 and 972, 2304 and 4500 for WUFJEM molecules, respectively. Molecules are isotropically distributed/placed through the entire volume of the simulation box with periodic boundary conditions applied to its boundaries. A Nose-Hoover thermostat is used to control the temperature of the thermodynamic system at 300 K with a coupling constant of 100 fs [17]. The time step selected in the simulations is 0.5 fs, and the simulations are run up to 2.5 ns. The trajectory of atoms is provided at every 1 ps. All simulations are repeated 5 times for each case, and the obtained parameters are averaged over these cases.

Results and discussion.

Figure 2 shows the evolution of the cluster formation for PERLEN08 and WUFJEM molecules. During cluster formation, the number of clusters containing different numbers of molecules gradually increases and eventually turns into a single cluster. In cluster formation processes, larger clusters grow further, while small clusters shrink until they disappear, according to the Ostwald ripening rule [18]. This phenomenon depends on the stability of clusters, which can be explained by the Gibbs free energy of formation (ΔG). ΔG is equal to the sum of surface and volume terms (i.e. $\Delta G = 4\pi r^2\gamma + \frac{4}{3}\pi r^3 \Delta\mu_V$ [20]), where r is the cluster radius, γ is the surface free energy per area and $\Delta\mu_V$ is the bulk free energy per volume. The surface energy term is always positive, and the volume energy term is always negative. Consequently, as the cluster in the system becomes larger, the volume energy term increases and the cluster becomes more stable. On the other hand, smaller clusters are composed mostly of surface molecules, resulting in more surface energy than bulk energy, resulting in increased instability and size reduction.

During the clustering process, both flat perylene (i.e., PERLEN08 and WUFJEM) molecules inserted in a vacuum, form mainly two types of configurations, i.e., face-to-face (parallel) and face-to-edge (T-shaped), as a result of non-bonded interactions [19]. In particular, as shown in Figure 2, flat perylene molecules initially form a dimer, then a trimer (see Fig.2, stage 1), a tetramer, small molecular assemblies (see Fig. 2, stage 2), and finally a whole cluster (see Fig. 2, stage 3).

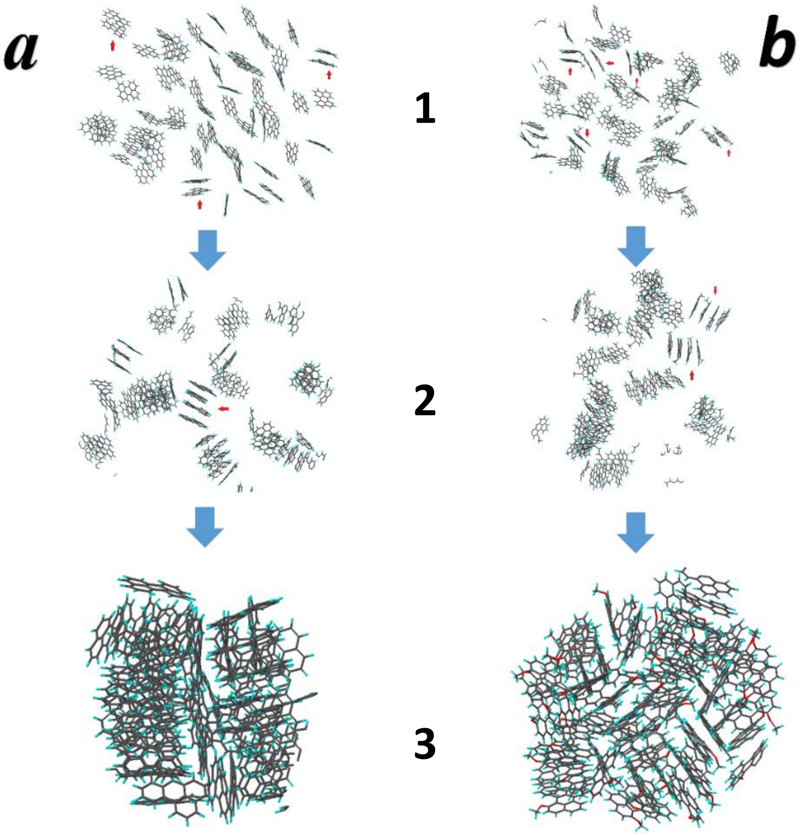

Fig. 2. Evolution of (a) PERLEN08 and (b) WUFJEM clusters' formation. Stages 1-3 indicate the formation of dimer/trimer, tetramer/small molecular assembly and whole cluster, respectively.

The results show that due to π-π stacking [20] between adjacent perylene molecules, dimers are formed with a face-to-face arrangement of molecules and subsequently trimer is formed by attaching the next molecule, and so on. MD results also show that the interaction energy of PERLEN08 tetramer is lower than that of the trimer, and the interaction energy of the trimer is lower than that of the dimer, which are -0.7005, -0.7027 and -0.7137 eV for the face-to-face dimer, trimer, and tetramer, respectively (see Table 1). This drop in energies indicates that the formation of larger PERLEN08 clusters with face-to-face configuration is more favorable than the smaller ones. In the case of WUFJEM clusters with the face-to-face configuration of dimer, trimer, and tetramer, the interaction energies are -0.8195, -0.7429 and -0.8959 eV, respectively (see Table 1). This distribution of energies leads the WUFJEM trimer to turn back into a dimer and a monomer, and then this dimer attaches face-to-face to the neighboring dimer to form a tetramer (i.e., dimer-to-tetramer transformation).

Table 1.

The face-to-face interaction energy of dimers, trimers, and tetramers.

	E_{dimer}, eV	E_{trimer}, eV	$E_{tetramer}$, eV
PERLEN08	-0.7005	-0.7027	-0.7137
WUFJEM	-0.8195	-0.7429	-0.8959

The partial charges of atoms in flat perylene molecules are in the range of 0.042 *e* and -0.032 *e* for the PERLEN08 molecule and 0.0523 *e* and -0.0108 *e* for the WUFJEM molecule, respectively. These non-zero partial charges result in electrostatic and London dispersion interactions, thereby leading to the formation of non-covalent C---H bonds between neighboring molecules [21]. This causes molecules to be assembled in face-to-edge (T-shaped) configurations in addition to their face-to-face counterparts [19]. Although this nature of molecular assembly applies to both perylene molecules, in the case of the WUFJEM molecule, their assembly is also facilitated by hydrogen bonds (H---O) formed between H and O atoms of neighboring molecules, thereby favoring their face-to-face assembly [22]. In particular, the interaction energies of PERLEN08 tetramer in the face-to-face (IIII) and face-to-edge ($\overline{\text{III}}$) stackings are -0.7137 eV and -0.7528 eV, respectively, which leads to an increase in the number of face-to-edge molecules in the cluster. On the contrary, in the case of WUFJEM, these energies are -0.8959 eV and -0.8244 eV, respectively, which causes more face-to-face arrangement of molecules in the cluster. In general, the obtained results indicate that during the clustering process, T-shaped clusters are formed less in the case of WUFJEM than in the case of PERLEN08 (see Fig. 2, stage 2).

The nature of interactions between molecules also affects the rate of their aggregation or clustering. In particular, Figure 3 shows the degree of clustering as a function of cluster formation time for both perylene molecules.

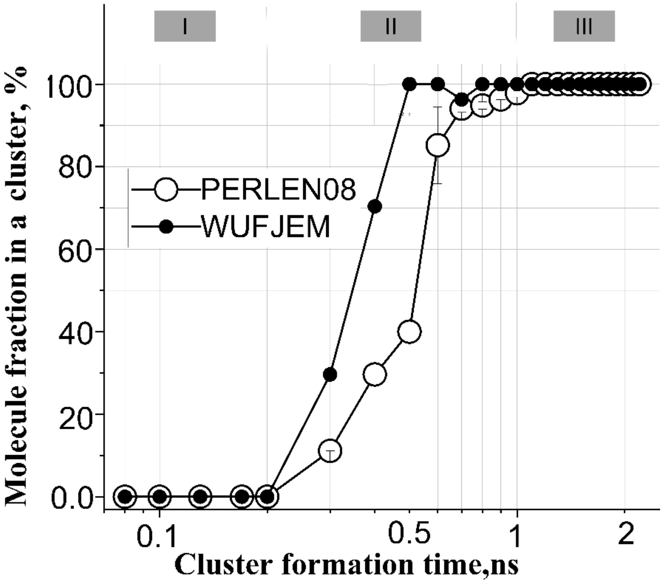

Fig. 3. Degree of clustering at three stages.

As is clear from the figure, the state of clustering is divided into three stages. The first stage of clustering lasts up to 0.2 ns, during which the molecules do not assemble (i.e., no formation of a dimer, trimer, tetramer, etc.). The first molecular aggregation occurs in the second stage (0.2-1.0 ns). At the period of 0.3-0.5 ns of the second stage, the fraction of assembled molecules relative to the whole PERLEN08 cluster is found to be between 11-40%, while in the case of the WUFJEM cluster, this percentage is between 30-100%. However, the formed WUFJEM cluster is not stable at this stage. The third stage (i.e., formation of a completely stable cluster) starts when the whole cluster is formed, which is 0.8 and 1.1 ns for WUFJEM and PERLEN08 clusters. The overall results show that the clustering rate of WUFJEM molecules is about 2 times higher than that of PERLEN08 molecules, and this is explained by the formation of hydrogen bonds between WUFJEM molecules.

Conclusions

In this work, the pre-nucleation (clustering) processes of ONCs consisting of PERLEN08 and WUFJEM molecules are studied using reactive MD simulations. The results show that in both cases, the process of clustering of molecules takes place based on the theory of Ostwald ripening, and it is shown that the initially formed clusters of different sizes turn into one single cluster. It is found that at the initial stages of clustering, PERLEN08 molecules assemble together according to the face-to-face and later on face-to-edge (T-shaped) configurations, while WUFJEM molecules assemble more in a face-to-face (parallel) configuration due to the formation of hydrogen bonds, in addition to the π-π stacking between adjacent perylene molecules. It was also found that the degree of clustering of WUFJEM molecules is about 2 times higher than that of PERLEN08 molecules due to the existence of hydrogen bonding. The obtained results help to better understand the mechanisms of the first steps of the synthesis of ONCs in a vacuum.

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