Growth onset of perylene-based nanocrystals

U. Khalilov[*,1,2], M. Yusupov[1,2], A. Tojiboev[3,4], P. Nematollahi[2], D. Husanova[1], S. Mirzaev[1]

[1] Laboratory of Thermal Physics of Multiphase Systems, Arifov Institute of Ion-Plasma and Laser Technologies, Academy of Sciences of Uzbekistan, Durmon yuli str., 33, 100125, Tashkent, Uzbekistan
[2] Research Group PLASMANT, NANOLabCenter of Excellence, Department of Chemistry, University of Antwerp, Universiteits plein 1, 2610, Antwerp, Belgium
[3] University of Geological Sciences, Olimlar str. 64, 100041, Tashkent, Uzbekistan
[4] National University of Uzbekistan named after Mirzo Ulugbek, University str. 4, 100174, Tashkent, Uzbekistan

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* Corresponding author: e-mail: umedjon.khalilov@uantwerpen.be , Phone: + 998 93 803 0014

Широкое использование органических нанокристаллов требует более глубокого понимания механизмов их зародышеобразования. В частности, предстоит выяснить начало зародышеобразования, хотя были предприняты огромные усилия как в экспериментальных исследованиях, так и в исследованиях с использованием моделирования. В этом исследовании мы проводим моделирование молекулярной динамики (МД), подкрепленное квантово-механическими (DFT) расчетами, чтобы понять механизмы зарождения органических нанокристаллов перилена. Наши расчеты DFT показывают, что молекулярная укладка лицом к лицу и лицом к краю может в конечном итоге привести к образованию нанокристалла перилена типа елочки. С другой стороны, результаты моделирования методом МД показывают образование кластеров, которое продолжается с зарождением кристаллов в форме однонаправленного или разнонаправленного роста, в зависимости от скорости подачи молекулы перилена в вакууме. Это исследование поможет лучше понять процесс управления ростом органических нанокристаллов в современной нанотехнологии.

Ключевые слова: органический нанокристалл, механизм зародышеобразования, молекулярная динамика, квантово-механические расчеты, эффект кластеризации.

The wide application of organic nanocrystals requires a deeper understanding of their nucleation mechanisms. In particular, the onset of nucleation still needs to be elucidated, although tremendous efforts have already been made in both experimental and simulation studies. In this research, we conduct molecular dynamics (MD) simulations, supported by quantum-mechanical (DFT) calculations, to understand the mechanisms of the nucleation onset of organic perylene nanocrystals. Our DFT calculations indicate that face-to-face and face-to-edge molecular stacking can ultimately lead to the formation of a herringbone-style perylene nanocrystal. On the other hand, the results of MD simulations show the formation of clusters, which continues with the crystal nucleation in the form of unidirectional or multidirectional growth, depending on the feeding rate of perylene molecule in vacuum. This research helps to better understand the control of the growth of organic nanocrystals in modern nanotechnology.

Keywords: organic nanocrystal, nucleation mechanism, molecular dynamics, quantum-mechanical calculations, clustering effect.

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I. Introduction

Organic nanocrystals (ONCs) are being used for several technologies, including pharmaceuticals, agrochemicals, organic electronics, etc. [1, 2]. Because of

their importance, ONC synthesis has been studied for many decades [1, 3].

For the synthesis of ONCs, various fabrication techniques are used, such as the reprecipitation method, supercritical fluid crystallization method, etc [1]. Among these growth techniques, the reprecipitation method is a convenient method for synthesis of ONCs with controlled size and morphology [1]. In particular, in this method, the organic molecules are quickly exposed to the poor solvent surroundings, which induce the nucleation and subsequent growth of the molecules to ONCs. The size and morphology of resulting ONCs can be controlled by means of tuning some parameters, including temperature, stirring speed, etc [1, 2]. Several ONCs are widely fabricated using the reprecipitation method, such as nonlinear optical dyes, fullerene and some polymers and fluorescent dyes [1-3].

Recent studies showed that further successes in application of these nanocrystals require deeper understanding of ONC nucleation and consequent growth mechanisms [3]. Two main theories are used to explain the onset mechanisms of nanocrystal growth, i.e. classical and non-classical nucleation theories [4]. In classical nucleation theory, the crystal nucleation process is followed as single-step mechanism. Namely, crystal nuclei have the same structure as original crystal. On the other hand, non-classical theory explains the crystal nucleation process in two-step mechanisms: an emergence of initial liquid-like clusters followed by an appearance of the crystalline order.

Despite these well-known nucleation theories that explain the ONC synthesis, as well as a number of experimental and simulations studies trying to understand the underlying mechanisms [5], the nature of the onset of nucleation of these functional ONCs is still elusive.

In this study, to support the experimental evidences, we conduct computer simulations, namely, molecular dynamics (MD) simulations together with quantum mechanical (DFT) calculations to understand the mechanisms of the nucleation onset of ONCs from cyclic aromatic hydrocarbon molecules. In particular, using DFT calculations we study initial molecular packing steps of perylene molecules, whereas applying MD simulations, we investigate subsequent clustering mechanisms of perylene molecules in vacuum in order to elucidate the sintering behavior of these organic molecules, thereby considering non-environmental effect.

II. Computational methodology

In this study, we perform MD simulations based on the ReaxFF reactive potential [6]. The latter is applied to properly describe the interactions between atoms of the system, allowing the MD to simulate both physical and chemical processes, including chemical reactions [7]. In our simulations perylene ($C_{20}H_{12}$) molecules are consecutively inserted into a simulation box at random positions. Initial distance between inserted molecule and already existing (i.e. already added) molecules exceeds 10 Å, so that there are no molecular interactions. The formation ONC clusters from perylene molecules is simulated at room temperature (300 K) using Bussi thermostat (i.e. NVT ensemble) [8]. Prior to thermal equilibration, the energy of the simulation system is minimized using the conjugate gradient method [9]. To support our classical MD results, the DFT calculations are performed using the VASP software [10]. All DFT optimizations are carried out in the generalized gradient approximation (GGA), employing the revised Perdew-Burke-Ernzerhof (RPBE) functional [11].

III. Results and discussion

Our quantum mechanical calculations reveal that the perylene molecules (Fig. 1, single) initially form into dimer (Fig. 1, dimer) with cofacial (face-to-face) stacking interactions, due to the presence of π-electrons in the inner (or central) part of these adjacent molecules [12].

At the edjes of the perylene molecule, where C-H bonds exist, the electrons are closer to the more negative C atoms [3]. Thus, noncovalent interactions such as electrostatic, induction and London dispersion interactions as well as exchange-repulsion forces lead to the formation of non-bonding C···H links with neighbor molecules [3, 13]. Consequently, such weak attractive non-bonding interactions allow third molecule to be located perpendicular (face-to-edge) to the dimer, thus forming a trimer (Fig. 1, trimer) [12]. The results show that such a packing of molecules (i.e., the formation of trimer) is energetically more favorable, since the interaction energy in the trimer structure is higher than in the dimer structure, i.e., –0.75 eV and –0.38 eV, respectively (see Fig. 1). Note that the interaction energy E_{int} is obtained as a difference between energies of the packed n molecules or cluster E_{clus} and isolated molecules (E_1, E_2, E_n) that belong to the cluster:

$$E_{\text{int}} = E_{clus} - (E_1 + E_2 + \ldots + E_n)\,. \qquad (1)$$

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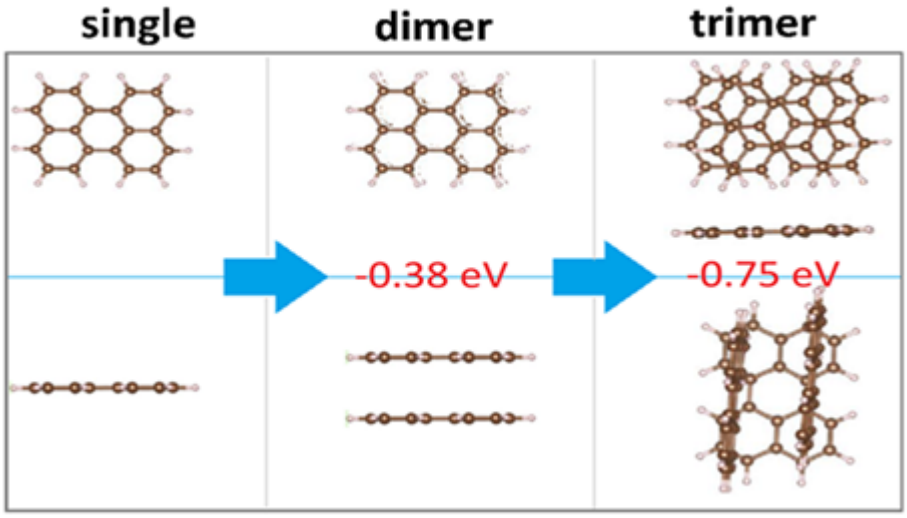


Figure 1. The initial steps of the sequential stacking of perylene molecules, shown in the top view (upper panels) and side view (bottom panels).

In particular, the interaction energy of the cofacial (face-to-face) perylenes in the molecular dimers and trimers (with an intermolecular distance of 3.5 Å) is closer to the energy of pentacene dimers obtained from other quantum mechanical calculations, which ranges from –0.58 eV to –0.97 eV [13]. The formation of both cofacial (due to π-π stacking [12]) and edge-to-face stacking configurations (due to noncovalent interactions [13]) in the structure of packed molecules (or clusters) indicates that the structure of the growing perylene-based nanocrystal belongs to the herringbone arrangement [12].

The formation of clusters is observed in our classical MD simulations. The simulation results reveal that the number of clusters containing different number of molecules gradually increases during the process of molecular packing [14] (Fig. 2).

The results also indicate that the number of molecules in a single cluster is inversely proportional to the number of clusters in a vacuum. In addition, a shape of clusters is gradually transformed with an increase of the number of their molecules. Namely, while a cluster with a small number of perylene molecules expands in all three dimensions

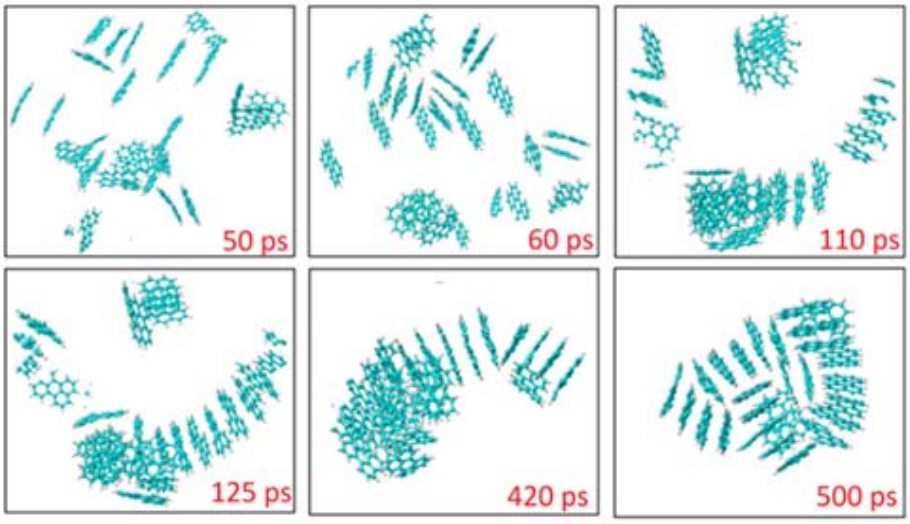


Figure 2. Clustering steps ofperylene molecules.

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(Fig. 2, 50–60 ps), an increase in the number of molecules in a cluster leads to its growth in only one direction (Fig. 2, 110–125 ps). This unidirectional layer-by-layer growth behavior was also experimentally observed when perylene molecules were inserted faster (i.e. in the case of a high chemical potential) [15]. However, due to the increasing instability of such a structure, the shape of a cluster gradually turns into a round-like form (Fig. 2, 420–500 ps). This process continues until crystal nuclei starts to appear [4].

The results of the MD simulations also show that after a rather long simulation time (i.e. few hundreds of ns), the perylene molecules in a given cluster can be arranged in an ordered manner, as in the crystal structure (cf. (*a*) and (*b*) in Fig. 3). Although the resulting final cluster structure is not the exact structure of the perylene crystal, both structures are quite comparable (Fig. 3). Such a small difference in these structures can be explained by a phase transition or structural transformation between the clustering process and crystal growth [16, 17], which will be studied in our further investigations.

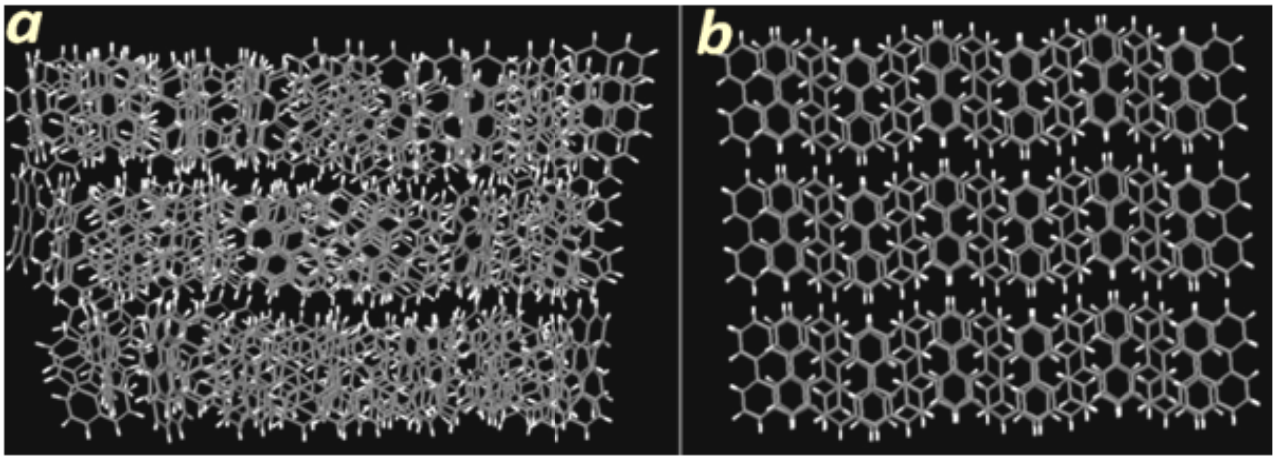


Figure 3. Structure of the obtained cluster (*a*) and perylene crystal (*b*).

IV. Conclusions

In this work, the nucleation mechanism of organic nanocrystals is revised using reactive molecular dynamics (MD) simulations and quantum-mechanical (DFT) calculations. In particular, the initial molecular packing and subsequent stages of clustering of the perylene molecules are interpreted using the DFT and MD, respectively. Specifically, we find that cofacial (face-to-face) and face-to-edge stacking modes as well as flux-dependent cluster formation can clarify the underlying mechanisms in the nucleation on set of perylene-based nanocrystals.

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Перилен асосидаги нанокристаллар ўсишининг илк босқичлари

У. Халилов[1,2], М. Юсупов[1,2], А. Тожибоев[3,4], П. Нематоллахи[2], Д. Хусанова[1], С. Мирзаев[1]

[1] Ўзбекистон Фанлар академияси Арифов номидаги Ионплазма ва лазер технологиялари институти, Дўрмон йўли кўчаси. 33, 100125, Тошкент, Ўзбекистон
[2] PLASMANT тадқиқот гуруҳи, Нано лаб. маркази, кимё бўлими, Антверпен университети, Universiteits plein 1, 2610, Антверпен, Бельгия
[3] Геология фанлари университети, Олимлар кўчаси 64-уй, 100041, Тошкент, Ўзбекистон
[4] МирзоУлуғбек номидаги Ўзбекистон Миллий университети, Университет кўчаси 4, 100174, Тошкент, Ўзбекистон

Органик нанокристаллардан кенг фойдаланиш уларнинг илк ҳосил бўлиш механизмларини яхшироқ тушунишни талаб қилади. Гарчи экспериментал ва моделлаштириш билан боғлиқ тадқиқотларда бу бўйича жуда ката ишлар амалга оширилган бўлсада, нишона структура ҳосил бўлишининг илк босқичлари ҳалигача мавҳумлигича қолмоқда. Биз ушбу тадқиқотларимизда органик перилен нанокристалларининг нуклеация (ядроланиш) механизмларини яхшироқ тушуниш мақсадида квант механик (DFT) ҳисоб-китоблари билан қўллаб-қувватланган молекуляр динамика (MD) моделлаштириш тадқиқотларини амалга оширдик. Хусусан, бизнинг DFT ҳисоб-китобларимиз шунга далолат қилдики, юзма-юз ва юз-ён молекуляр тўпланишлар охир-оқибатда арчасимон перилен нанокристалинингшаклланишига олиб келиши мумкин. Бошқа томондан эса, MD моделлаштириш натижалари вакуумдаги перилен молекулаларининг киритилиш тезлигига боғлиқ ҳолда бир томонлама ёки кўп йўналишли ўсиш шаклидаги нишона кристалларини акс эттирадиган кластерларнинг шаклланиши мумкинлигини кўрсатади. Ушбу тадқиқот замонавийнанотехнологияда органик нанокристал ўсиши бошқарувини яхшироқ тушунишга ёрдам беради.

Калит сўзлар: органик нанокристал, нуклеация механизми, молекуляр динамика, квант-механик ҳисоблашлар, кластерланиш эффекти

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