

Design of Polar Assemblies with Bowl-shaped π -conjugated Molecules and Their Bulk Photovoltaic Effect

Daigo Miyajima¹

Center for Emergent Matter Science, RIKEN

daigo.miyajima@riken.jp

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A solar power system is indispensable technology for the realization of a sustainable society. In general, solar energy is generated with a photovoltaic effect using a donor-acceptor heterojunction, while a totally different type of photovoltaic effect, known as the bulk photovoltaic effect (BPVE)¹, has been attracting broad research interest. The BPVE is observed in principle in non-centrosymmetric single-crystalline materials and possesses unique features such as being ultrafast responsive and dissipationless and enabling a low noise photocurrent, which are not accessible with conventional photovoltaics. To date, the BPVE has been studied mainly for inorganic materials, possibly because the number of reported polar organic assemblies is limited due to the lack of rational synthetic strategies for them. Although rapid advances in the fields of supramolecular chemistry and crystal engineering have provided a profound understanding of molecular assembly, perfectly predicting and controlling the crystal structures of molecules is still difficult. To the best of our knowledge, no strategy and guiding principle for designing polar single crystals suitable for optoelectronic applications have been reported. Recently, we reported a rational strategy to form polar assemblies with bowl-shaped π -conjugated molecules and a molecular design principle for this strategy². Based on this design principle, we successfully developed more than 12 polar crystals. Furthermore, we unveiled that the BPVE observed in these polar assemblies is generated in the shift current mechanism. This presentation will overview the design principle and discuss the relationship between excitation and photocurrent generation³.

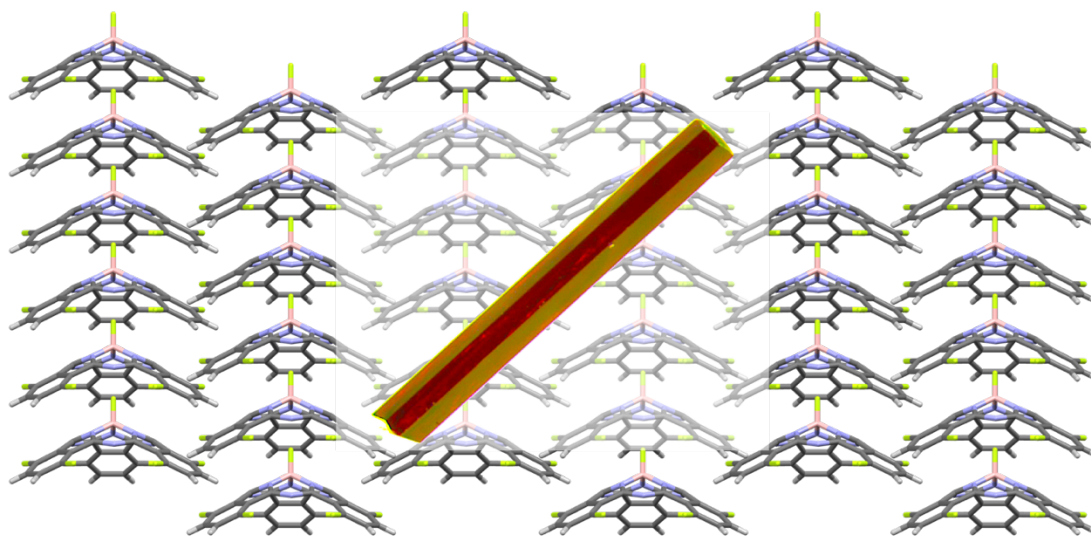


Figure 1. Schematic illustration of a polar assembly with bowl-shaped π -conjugated molecules.

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Organic semiconductor crystals: from low dimensional crystals to cocrystals

Wenping Hu^{1,2}

Tianjin Key Laboratory of Molecular Optoelectronics, Tianjin University, Tianjin 300072, China

(E-mail: huwp@tju.edu.cn)

The fundamental advantages of organic semiconductors have attracted the world's attention at recent decades and resulted in the rapid development and progress of organic electronics (or called molecular electronics). However, there remain some key challenges in this field such as the low mobility, the not fully understanding structure-properties relationship, the absence of techniques for the fabrication of high performance devices and circuits etc. It is prospective that high-quality single crystals of organic semiconductors could answer these questions and further advance the development of this field. However, the growth, characterization, and application of organic semiconductor crystals are full of challenges. Here we will focus on organic micro- and nanocrystals, two dimensional crystals and cocrystals for a brief introduction.

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Crystal Structure Manipulation by Methylchalcogenation and In Silico Crystallization of Brickwork-related Structures

Kirill Bulgarevich¹, Kazuo Takimiya^{1,2,3}

¹RIKEN CEMS, Hirosawa 2-1, Wako-shi, Saitama 351-01, Japan. ²Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, Japan 980-8577. ³Tohoku University IMR, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

kirill.bulgarevich@riken.jp

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Organic semiconductors with crystal structures that enable two-dimensional charge transport, hold great promise for achieving high carrier mobility. Examples of such structures include herringbone, pitched- π , and brickwork. Many acenes and heteroacenes such as pentacene, [1]benzothieno[3,2-*b*]benzothiophene (BTBT), and benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) crystallize in herringbone structures, while pitched- π and brickwork structures are less common and have only been observed in materials like rubrene and 6,13-bis(triisopropylsilyl)ethynyl)pentacene (TIPS-pentacene). Recently, we discovered a way to “manipulate” the crystal structure of organic semiconductors by selectively introducing methylchalcogeno groups. For instance, by introducing methylthio or methylseleno groups at β -positions of the thiophene rings in BDT, we were able to change its herringbone structure to a pitched- π or brickwork structure.^{1,2} Furthermore, we found that introducing four methylthio groups into pyrene at 1,3,6,8- positions (MT-pyrene) resulted in a change from a dimeric herringbone structure to a brickwork structure (Fig. 1a), leading to very high carrier mobility of over $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in single-crystal organic field-effect transistors.³ However, the selenium replacement of sulfur atoms in MT-pyrene, MS-pyrene, resulted in two structural polymorphs (Figs. 1b and 1c) with low two-dimensionality and mobility inferior to MT-pyrene (up to $7.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).⁴ Similarly, with the core replacement to perylene from pyrene, two brickwork-related structure polymorphs were observed, but mobility was low ($0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This highlights the need for accurate predictions of crystal structures with the precision to discuss differences in electronic structure in the solid state.

To address this issue, we developed an “*in silico* crystallization (ISC)” algorithm. Unlike traditional crystal structure prediction algorithms that consider a large number of candidate structures from a vast search range, ISC simplifies the search by limiting it to systems in which a brickwork structure is expected. The algorithm determines the mutual positions of molecules in the crystal by optimizing their mutual interaction through quantum chemical calculations. In brickwork structures, the molecular interactions are hierarchical with the strongest interaction being in the π -stacking (face) direction, followed by the interlayer (side) direction and the molecular long axis (end) direction. This makes it possible to determine the molecular mutual positions in an orderly manner, rather than determining the overall structure at once (Fig. 1d). Using ISC, we were able to accurately simulate the crystal structures of MT-, MS-pyrene, and MT-perylene, including the fine differences in the two-dimensionality between the structures. Our algorithm even predicted the existence of a related polymorph of MT-pyrene, which was later confirmed experimentally. This demonstrates the potential of ISC for aiding the search for high-mobility organic semiconductors.

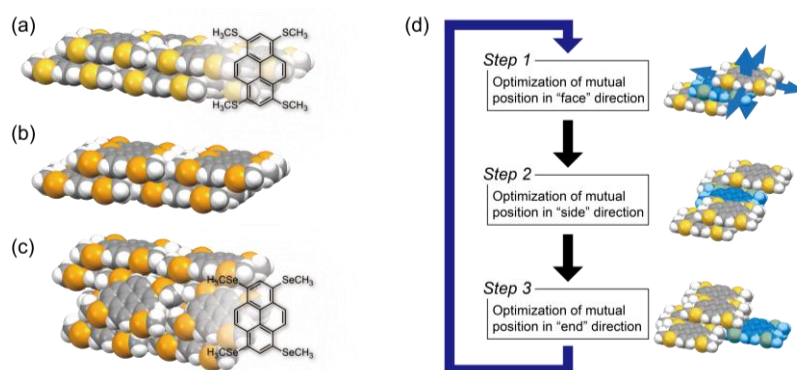


Figure 1. Brickwork structure of (a) MT-pyrene and (b) MS-pyrene. (c) Inclined brickwork structure of MS-pyrene. (d) Protocol for crystal structure simulation by “*in silico* crystallization”.

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Computational prediction of dynamics and structure of organic semiconductor crystals

Go Watanabe^{1,2}

¹ Kitasato University, 1-15-1 Kitasato Minami-ku, Sagami-hara 252-037, Japan,

² Kanagawa Institute of Industrial Science and Technology, 705-1 Shimoizumi, Ebina 243-0435, Japan

go0325@kitasato-u.ac.jp

Keywords: organic semiconductors, molecular dynamics simulation, crystal structure prediction

Organic semiconductors (OSCs) have attracted much attention because they have a potential to be applied to flexible and printed electronic devices. In general, when developing a new organic molecule, it requires much time and effort to design and synthesize the molecule and perform X-ray diffraction analysis of its single crystal. To create new OSCs with innovative functions and physical properties, it is necessary to establish a novel method utilizing computational science for predicting crystal structure and dynamics of OSCs.

Recently, we reported that thermal fluctuation of each atom and structural stability of organic crystals can be calculated by performing molecular dynamics (MD) simulations. The organic semiconductors with high carrier mobility showed significantly larger thermal fluctuations of each atom than those with low carrier mobility (Figure 1). It was also confirmed that the thermal fluctuations of OSC thin films could be analyzed and the larger fluctuations at the air interface resulted in the destabilization and surface roughness of self-assembled thin films of OSCs. The MD simulations would make it possible to estimate charge-carrier mobility.

To predict the crystal structure of a OSC molecule, we propose a new approach that combines molecular mechanics (MM) and molecular dynamics (MD) calculations. At first, candidate crystal structures from a 3D conformation of a target molecule are provided by using the software based on MM calculation. Followed by MD simulations for the predicted crystal structures, the most appropriate crystal structure of the molecule can be determined. The new method proposed was confirmed to predict crystal structure of typical n-type OSCs precisely. Our computational science approach based on molecular simulations would accelerate to create new innovative OSCs and lead to breakthrough in organic electronics.

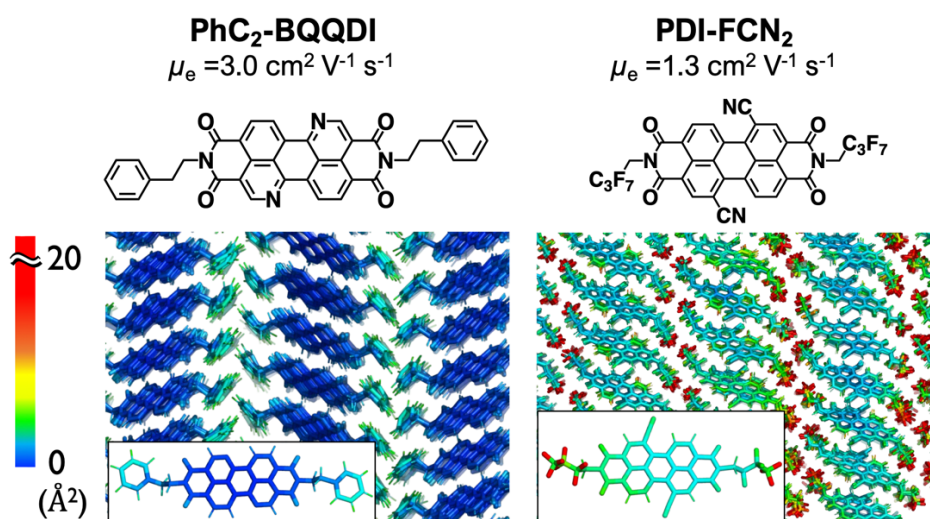


Figure 1. Color-coded thermal fluctuations obtained from the trajectories of the bulk single crystals of PhC₂-BQQDI and PDI-FCN₂ during the last 10 ns of 100 ns MD runs.

Transient delocalization in organic molecular semiconductors

David Beljonne

Laboratory for Chemistry of Novel Materials

University of Mons, Place du Parc 20, 7000 Mons (BELGIUM)

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There is compelling evidence that charge carriers in organic semiconductors (OSs) self-localize in nano-scale space because of dynamic disorder. Yet, some OSs, in particular recently emerged high-mobility organic molecular crystals, feature reduced mobility at increasing temperature, a hallmark for delocalized band transport. Here we present the temperature-dependent mobility in two record-mobility OSs: DNTT (dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]-thiophene), and its alkylated derivative, C8-DNTT-C8. By combining terahertz photoconductivity measurements with fully atomistic non-adiabatic molecular dynamics simulations, we show that while both crystals display a power-law decrease of the mobility (μ) with temperature (T), following: $\mu \propto T^{(-n)}$, the exponent n differs substantially. Modelling provides n values in good agreement with experiments, and reveals that the differences in the falloff parameter between the two chemically closely related semiconductors can be traced to the energy-dependent delocalization of the states thermally accessed by the charge carriers, which in turn depends on the specific electronic band structure of the two systems. The emerging picture is that of holes surfing on a dynamic manifold of vibrationally-dressed extended states with a temperature-dependent mobility that provides a sensitive fingerprint for the underlying density of states.