Challenges of organic “cocrystals”

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Organic cocrystal (also “co-crystal”), formed with two or more different components via non-covalent intermolecular interactions, possesses novel, unpredicted and unique properties, which are not the simple sum of those molecular components, e.g., with effect of $1+1>2$. In this regard, organic cocrystals provide a distinctive strategy for the synthesis of novel multifunctional materials, and an important platform for exploring new fundamental physicochemical phenomena in molecular systems, such as high conductivity [1,2], ambipolar charge transportation [3], photovoltaic behavior [4–6], white light-emitting [7], room-temperature phosphorescence [8], nonlinear optics [9–12] and ferroelectricity [13] etc., with potential application even in liquid crystal engineering [14,15] and drug industry [16].

Probably, the first cocrystal could be tracked back to 1844 assigning to the discovery of “quinhydrone” by Wöhler [17], while the conception of “cocrystal” was firstly used by Schmidt and Snipes [18] to describe the crystal of pyrimidine and purine complex in 1967. However, the widely acceptance of this concept is still progressing, since the definition of a cocrystal has been debated in the crystallography field. Another terminology of “molecular complex” was also proposed by Patrick and Prosser [19] to define the mixture of benzene and hexafluorobenzene in 1960, and then became another word to describe crystals with multi-components. The word cocrystal re-attracted attention since 2003, and a generally accepted definition is a structurally homogeneous crystalline material that contains two or more neutral building blocks that are present in definite stoichiometric amounts [20,21]. We have gathered and analyzed all reported organic cocrystals, and divided them into four types according to the intermolecular interactions responsible for the co-crystallization: halogen-bonded [22], hydrogen-bonded [23], π - π packing [24,25] and charge transfer (CT) [26]. Using this kind of division, a much clear image of organic cocrystals could be given. Molecules in cocrystal pack general in two modes: i) mixed-stacking, wherein different molecules alternative-

ly pack in a DADA...DADA fashion with sufficient D-A π -electron overlap, ii) segregated-stacking, wherein molecules pack in a DDDD...AAAA fashion with D-D and A-A π -overlap.

As a novel research area, there are full of challenges for organic cocrystals. The first challenge is the basic mechanism of co-crystallization, because not any two types of materials can recognize each other and self-assemble into a cocrystal. Hence, a question is what kind of material is suitable for co-crystallization, and how different molecules co-assemble, nucleate and crystallize. This is also related to the method applied for co-crystallization, including solution [24], vapor-phase [6,27–29] and mechanochemical techniques [16,30]. In our experience, some fundamental conditions are also essential for solution co-crystallization, such as strong intermolecular interactions, planar molecular structure and similar solubility of donor (D) and acceptor (A). In order to reveal the nucleation and growth mechanism of organic cocrystals and further control the self-assembling process of co-crystallization, we used perylene-tetracyanoquinodimethane (TCNQ) CT cocrystal as an example [31], and found that the morphology and phase of cocrystals mainly depend on the concentration of perylene (C_{perylene}) rather than TCNQ (C_{TCNQ}), and high C_{perylene} is favourable for the formation of (perylene)₃TCNQ (P3T1) microblocks, while low C_{perylene} facilitates the formation of (perylene)₁TCNQ (P1T1) nanowires (Fig. 1). More importantly, we demonstrate that the formed D-A complex is regarded as a new material species, because the solubility of the formed P3T1 in acetonitrile is obviously lowered than that of any single components. It actually allows us to define the cocrystal as a new molecular species. The structure-function relationship of these cocrystals is further investigated. P1T1 cocrystals exhibit n-type behavior with electron mobility of $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while P3T1 cocrystals display ambipolar behavior with high hole mobility of $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and low electron mobility of $2.1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Moreover, white light responsivity of P1T1 is higher than

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Figure 1 Optical images of (a) P1T1 nanowires and (b) P3T1 microblocks. (c) The dependence of crystal morphology and material concentration in acetonitrile solution. (d) Schematic illustration of the formation mechanism of cocrystals. (e) The optical images of mixed solution ($C_{\text{perylene}} = 0.80 \text{ mmol L}^{-1}$, $C_{\text{TCNQ}} = 2.45 \text{ mmol L}^{-1}$) prepared immediately and after aging for one day. (f) The optical images of the obtained crystals from the corresponding solution after aging for different time. (g) The proposed mechanism for cocystal formation. The pictures are reprinted with permission from Ref. [31]. Copyright 2015, John Wiley & Sons, Inc.

that of P3T1 cocrystals, since the mixed-like packing structure in P3T1 is not favourable for exciton separation. These interesting results here pave the way for rational design and preparation of cocrystals with desired functions. It should be noticed, because of the limited reports on vapor-phase co-crystallization and lack of mechanism investigation on mechanochemical method, further research should focus on these issues as well as the extension of organic cocrystals into two-dimensional (2D) structures [32].

Another long-standing problem is to understand the CT interactions and exciton dynamics. It is key important

to confirm whether the CT interactions exist in cocrystal, which significantly affect the lattice instability [33] and bulk optoelectronic properties [34,35]. A puzzle we are encountering is to distinguish the ground and excited state [36,37]. Recently, we [38] found that both of ground and excited states of 1,2,4,5-tetracyanobenzene (TCNB) based cocrystals are actually CT state, as experimentally verified by spectroscopic studies, electron spin resonance (ESR) measurements and theoretical calculations (Fig. 2). Significantly, we demonstrated that the CT interactions in cocrystals are related to their molecular packing and can be

Figure 2 (a) The morphology and structure of Bpe-TCNB cocrystal. Bpe = 1,2-di(4-pyridyl)ethylene. (b) The confocal laser scanning microscope image of cocrystal. (c) The absorption spectra, (d) electron spin resonance spectrum, (e) photoluminescence (PL) spectra, and (f) PL lifetime measurement of cocrystals. The pictures are reprinted with permission from Ref. [38]. Copyright 2015, John Wiley & Sons, Inc.

triggered or suppressed by crystal engineering [39], thus resulting in distinct optoelectronic properties. And we proposed that the π -electron-rich circumstances in molecular columns of donor are helpful to promote the CT process from donor to acceptor.

In order to gain a deeper understanding of fantastic optoelectronics, the dynamics of excitons in cocrystals should be concerned, especially in those with a neutral ground but a CT excited state [24]. In these cocrystals, the generated singlet excitons are changed ultrafast into CT excitons, which is common but largely puzzled in organic photovoltaics [40]. Due to the limited studies on these, further investigations may be devoted to revealing the exciton dynamics and related molecular dynamics by applying advanced time-resolved spectroscopic techniques, as well as theoretical calculations. Moreover, both of the CT degree in the ground state and its influences on physicochemical properties are not yet well understood.

The third challenge is to explore new physicochemical properties and potential applications for organic cocrystals. Since the discovery of high conductivity in 1973 [1,2], the research on this area has gained enormous attention, but now the question is what kind of new properties which have not been revealed in today's molecular materials that co-crystallization will bring to us, and what kind of novel application could be expected. Like organic-inorganic perovskites [41,42], organic cocrystals are expected possessing not only ideal field-effect properties, but also photovoltaic, light-emitting and even magnetic properties. In our opinion, further research interests should mainly focus on ferroelectrics, nonlinear optics (such as two-photon absorption and fluorescence) and magnetic properties, as well as multifunctional and smart cocrystal materials. We believe that organic cocrystal is at the fundamental heart of molecular science and is now gaining a lot of attention. And we believe, in the near future, more and more research on this area will take us to a beautiful and fantastic "cocrystal world".

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Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 本文简明扼要地介绍了“有机共晶”这个重要研究领域的兴起和发展过程,在有争议的方面,如共晶定义和如何判定分子排布等,给出了作者独到的见解.特别重要的是,通过阐述该领域当前存在的问题和挑战,结合分析最新的研究进展和结果,使得人们对共晶的认识更为系统和深入.基于此,作者同时分析和指出了未来可能重点发展的研究方向.