Organic halogen-bonded co-crystals for optoelectronic applications

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ABSTRACT Organic halogen-bonded co-crystals assembled from two or more components *via* halogen bonds, have attracted significant attention due to their unpredictable and outstanding chemical and physical properties, which make them potential candidate materials for organic optoelectronic applications. This paper briefly summarizes the recent progress in terms of the developed fabrication methods for organic halogen-bonded co-crystals and their multifunctional optoelectronic applications. Based on the current research on organic halogen-bonded co-crystals, we further discuss the achievements as well as the existing challenges. Finally, we provide our outlooks for further studies and applications of organic halogen-bonded co-crystals.

Keywords: organic semiconductor molecules, single crystals, self-assembly, non-covalent interaction, organic optoelectronic

INTRODUCTION

The synthesis of organic co-crystals has been recognized as an efficient approach for designing functional organic solids, for the applications in organic field-effect transistors [1–4], organic light-emitting diodes [5–7], organic solid-state lasers [8–11], optical waveguides [12–16], organic light-emitting transistors [17–20], and sensors [21–23]. Organic co-crystals comprise at least two types of components formed through noncovalent intermolecular interactions, such as π – π stacking interaction, charge-transfer (CT) interaction, hydrogen bonds (HBs), and halogen bonds (XBs) [24–26]. Noncovalent interactions regulate the molecular packing pattern and crystallinity of organic solid-state materials, which, in turn, affect their optoelectronics performance [27–30]. Especially, halogen bonds are regarded as highly oriented bonds. They give rise to intermolecular transport of electrons [31], which is

a thriving strategy for designing multifunctional and high-performance optoelectronic organic solid-state materials [32–35]. The International Union of Pure and Applied Chemistry (IUPAC) defines the term “halogen bonding” as follows: “it occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity” [36]. As shown in Scheme 1, an HB can be represented by $R-X\cdots Y$ (the three dots denote the bond), where X is a halogen atom with an electrophilic area with which it covalently attaches to R; R–X denotes the XB donor; and Y is the XB acceptor with a nucleophilic area, which can be an anion or a neutral component [37,38].

In 1814, Colin [39] discovered the adducts between iodine and ammonia. In 1863, Guthrie *et al.* [40] purified and formulated the above adducts as a $NH_3\cdot I_2$ complex. In 1954, Hassel *et al.* [41], for the first time, described the solid-state structure of $Br\cdots O$ short-distance contact (2.71 Å) between dibromine and 1,4-dioxane through the crystal X-ray diffraction (XRD) experiment, and confirmed the existence of electrostatic attraction, which was a landmark in the understanding of the XB [42]. In 1968, Bent [43] verified that the distance between the halogen atom and the electron donor atom was smaller than the sum of their respective van der Waals radii, and in energy

Scheme 1 Schematic diagram of halogen bond.

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the interaction was equivalent to a strong HB. Clark *et al.* [44], through theoretical calculations, discovered that the electron density surrounding a XB was anisotropic in distribution, and thus, proposed the concept of σ -hole. In 1998, Resnati *et al.* [45,46] reported the tendency of iodine and bromoperfluorocarbons to form noncovalent interactions with neutral and anionic nitrogen as electron donors [47]. In addition, they indicated that the XB interaction force can be regulated by altering the halogen atoms and the covalently bonded groups [48]. Resnati *et al.* [49,50] also demonstrated that the strongest complex can be formed between nucleophilic nitrogen atoms and iodine atoms, whose electrophilicity can be enhanced by covalently bonding to an electron-poor perfluorocarbon group. When the environment around the halogen is sufficiently electron-withdrawing, the resulting intermolecular interaction will become strong enough to affect the crystal packing in the organic solid [51,52]. Meanwhile, there are many reports on the theoretical calculations of XBs [53,54,55]. For example, Wang *et al.* [54] investigated a series of blue-shifting halogen-bonded complexes, through which they further confirmed the CT interactions in XBs and noted that the large dipole moments of interacting monomers were important for multiple halogen bonding systems.

Currently, halogen bonding is widely employed as an effective strategy by crystal engineers for designing

functional solid-state architectures [56–58]. However, the challenge in the syntheses of organic halogen-bonded co-crystals lies in the selection of the co-formers and regulation of the molecular packing mode [59,60]. Until now, stilbene derivatives and cyanostilbene-based positional isomers, such as 1,4-bis(4-cyanostyryl) benzene (*p*-BCB), 1,2-bis(4-pyridyl)ethylene (Bpe), 4-(1-naphthylvinyl)pyridine (DPEpe), (Npe)4,4'-((1*E*,1*E'*)-2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl)dipyridine, 4-styrylpyridine (Spe), and (*E*)-2-(((5-methoxypyridin-2-yl)imino)methyl)phenol (MPI), are commonly used as halogen acceptors (Scheme 2a) [7,61,62]. Besides, fluorine and perfluorinated co-formers, such as 1,3,5-trifluoro-2,4,6-triiodobenzene (IFB) and 1,4-diiodotetrafluoro benzene (F4DIB), are commonly employed as halogen donors, which promotes the tendency of the iodine atoms to behave as electron acceptors in XB networks (Scheme 2b) [63–65].

The types of halogen donors and acceptors modulate the stacking patterns of organic co-crystals, which affect the properties of the co-crystals. Thus, an urgent problem associated with organic halogen-bonded co-crystals is to broaden the molecular systems. However, XBs have been confirmed to regulate the photoluminescence (PL) and intermolecular electron transport in organic co-crystals. Thus, organic co-crystals do not simply combine the properties of the constituent molecules, which usually

Scheme 2 Structures of the typical (a) halogen donors and (b) halogen acceptors applied in organic halogen-bonded co-crystals.

exhibit unique optoelectronic properties. To date, most reported studies have focused on modulating the optical and photoelectronic properties of organic halogen-bonded co-crystals [17,50,66,67]. On one hand, owing to the heavy-atom effect, the organic halogen-bonded co-crystals can be promising phosphorescent materials. Bolton *et al.* [68] first fabricated bright and color-tunable organic phosphors by taking advantage of the heavy-atom effect of XBs, and recorded a PL quantum efficiency of up to 55%. On the other hand, XB-based co-crystals can also be used to tune the fluorescence properties of solid-state materials. Yan *et al.* [69] designed and fabricated a series of organic co-crystals employing a stilbene-type derivative, 1,4-bis-*p*-cyanostyrylbenzene, to form co-crystals with perfluorocarbon compounds, which were commonly used as XB donors. By introducing co-formers, a series of co-crystals with distinct crystal structures were obtained, which exhibited multi-color emission besides strong two-photon luminescence. These phenomena were attributed to the difference between the geometric configurations of the co-crystals, which influenced the formation of the excimers in the organic co-crystals. This demonstrated a new insight into the structure-performance relation of organic co-crystals. Also, we have realized the regulation of the crystallinity and optical properties of organic halogen-bonded co-crystals, which is expected to prompt the development of organic integrated optoelectronic devices [70].

Recently, despite many excellent reported reviews on organic co-crystals [58,71,72], only a few have focused on

the organic halogen-bonded co-crystals. In this review, we summarize various reported studies that focus on the fabrication strategies and optoelectronic applications of organic halogen-bonded co-crystals. We also provide perspectives for further investigations on organic halogen-bonded co-crystals and their potential applications in high-performance organic optoelectronic devices.

PREPARATION STRATEGIES

The main strategies for synthesizing organic halogen-bonded co-crystals include solution evaporation, mechanochemical, and liquid-assisted grinding methods. The preparation methods significantly affect the stacking pattern and crystal morphology, which in turn, affect the optical and optoelectronic properties of the organic co-crystals.

Solution evaporation

Currently, the solution evaporation method is a universal method for fabricating organic co-crystals with low defect and uniform morphology, which are desired for further optoelectronic characterization [6,73,74]. Meanwhile, the solution evaporation method is greatly affected by external conditions such as the type and proportion of the solvent, concentration of the precursor, and the temperature of crystallization. For instance, the microcrystals of DPEpe-F4DIB with different one-dimensional (1D) structures can be controllably synthesized *via* simple solvent evaporation based on different solvent systems, as shown in Fig. 1 [75]. The precursors of DPEpe and F4DIB

Figure 1 (a) Fabrication procedure for DPEpe-F4DIB microcrystals by solution-evaporation method. (b) SEM image of the DPEpe-F4DIB microrods. (c) SAED pattern of the DPEpe-F4DIB microrods. (d) SEM image of the DPEpe-F4DIB microtubes. (e) SAED pattern of the DPEpe-F4DIB microtubes. The inset: transmission electron microscopy (TEM) images. Reprinted with permission from Ref. [75]. Copyright 2018, Royal Society of Chemistry.

are bonded *via* the XBs between nitrogen and iodine (Fig. 1a). The procedure is as follows: DPEpe and F4DIB are first dissolved in dichloromethane (DCM), and then dropped directly onto a quartz substrate to obtain 1D co-crystal microrods, with a smooth surface and uniform diameter, after complete evaporation of the solvent (Fig. 1b). The scanning electron microscopy (SEM) image and the corresponding selected area electron diffraction (SAED) pattern indicate that the DPEpe-F4DIB co-crystal microrods belong to the triclinic space group, which grows along the [001] direction (Fig. 1c, d). In contrast, when DPEpe and F4DIB are dissolved in a mixed solvent of DCM and ethanol ($V_{\text{DCM}}:V_{\text{ethanol}} = 2:1$), the above procedure yields 1D microtubes (Fig. 1d). The microtubes follow the same crystal growth direction as that of the organic microrods (Fig. 1d). In addition, the obtained organic microrods in pure DCM can evolve into microtubes in the abovementioned solvent mixture, which is attributable to the etching effect of ethanol. The obtained molecular packing structures of DPEpe-F4DIB indicate that the molecules are separated and stacked along the *c*-axis, which facilitates the formation of 1D morphology. This paper proposes a beneficial strategy for a simple fabrication of multifunctional organic co-crystal optoelectronic devices based on identical molecule systems.

With the facile solvent evaporation method, we mod-

ulate the yellow-emissive *p*-BCB polyhedral microcrystals to the blue-emissive *p*-BCB-DIFB co-crystals formed by using XBs (Fig. 2a, c) [70]. The typical synthesis procedure involves dissolving *p*-BCB and DIFB in chloroform in a molar ratio of 1:1, and then, dropping the solution onto a substrate. The XRD pattern demonstrates that the *p*-BCB-DIFB co-crystal belongs to the monoclinic system, whereas the *p*-BCB organic microwire belongs to the triclinic system. In addition, the intermolecular distance of *p*-BCB is 0.71 nm in the *p*-BCB-DIFB co-crystals, which is much larger than the required distance for the excimer formation (0.35 nm). Comparing the PL spectra of *p*-BCB microcrystals with that of *p*-BCB-DIFB co-crystals, it is found that the orange emission of the *p*-BCB microcrystals turns into blue emission of *p*-BCB-DIFB co-crystals, and the PL spectra of the co-crystals exhibit a fine electronic-vibrotational structure (Fig. 2d). This indicates that the growth morphology and light emission can be modulated *via* the co-crystal strategy.

Mechanochemical approach

In the solution method, the components are required to have similar solubility. In comparison, the mechanochemical approach does not involve the solvent, and thus, can be easily performed. It has been demonstrated to be a clean, green, and effective method for the synth-

Figure 2 (a) The schematic of halogen bond force between *p*-BCB and DIFB molecule. (b) The PL spectra of *p*-BCB solution and organic microcrystals (top panel) and the *p*-BCB and DIFB mixed solution and *p*-BCB-DIFB co-crystals (bottom panel). Inset: the photographs of *p*-BCB microcrystals (top panel) and *p*-BCB-DIFB co-crystals (bottom panel) under UV lamp. (c) Fluorescence microscopy image of *p*-BCB-DIFB co-crystals. (d) The CIE chromaticity diagram of the co-crystals and solution. Reprinted with permission from Ref. [70]. Copyright 2018, Wiley-VCH.

Figure 3 Synthetic schematic and the corresponding fluorescence photographs of co-crystals (a) DPA [DPA·I₂F₄ (1) and DPA·(I₂F₄)₂ (2)], (b) tS·I₂F₄ (3) and tS·(I₂F₄)₂ (4). Reprinted with permission from Ref. [77]. Copyright 2015, American Chemical Society.

eses of organic halogen-bonded co-crystals [72,76–78]. For instance, d'Agostino *et al.* [77] synthesized four types of organic co-crystals, denoted as DPA·I₂F₄ (1), DPA·(I₂F₄)₂ (2), tS·I₂F₄ (3), and tS·(I₂F₄)₂ (4) *via* the mechanochemical method. The procedure for the co-crystal synthesis was as follows: I₂F₄, DPA, or tS were ground in a molar ratio of 1:1, and the obtained products were divided into two portions (Fig. 3). One portion was used for single crystal growth by seeding in methanol (1-crystals), while the other portion further reacted with an additional equal amount of I₂F₄ co-former. The freshly obtained solid product was grown into single crystals by seeding in a mixture of solvents (CHCl₃/n-hexane) (2-crystals). I₂F₄ and tS were subjected to the same treatments as those stated above, to obtain two other single crystals (3-crystals and 4-crystals). As shown in Fig. 3a, b, the 1- and 3-crystals, with a co-former molar ratio of 1:1, are blue-emissive crystals, exhibiting fluorescence and phosphorescence emission properties. Meanwhile, the other two co-crystals with a molar ratio of 1:2 exhibit reddish-brown emission crystals, which are verified to be triplet emitters with the highest phosphorescence quantum efficiency of 0.06 at room temperature.

From the X-ray analysis of the single-crystal structures, it is found that the DPA·I₂F₄ (1) and tS·I₂F₄ (3) co-crystals are intercalation solids. The co-former of the I₂F₄ molecule is almost perpendicular to the benzene ring in an alternating consecutiveness in the 1D structure of DPA or tS, where the C–I... π interactions play a more important role than C–H... π interactions in pure DPA and tS crystals (Fig. 4). As shown in Fig. 5, DPA·(I₂F₄)₂ (2) and tS·(I₂F₄)₂ (4) are arranged in a 2D network. However,

Figure 4 Space filling representation of (a) crystalline 1 and (b) crystalline 3. Reprinted with permission from Ref. [77]. Copyright 2015, American Chemical Society.

Figure 5 Space filling representation of (a) crystalline 2 and (b) 4. Reprinted with permission from Ref. [77]. Copyright 2015, American Chemical Society.

attempts to synthesize the above co-crystals *via* the solution method are unsuccessful. This mechanochemical method provides a new strategy for regulating the photophysical properties of organic co-crystals by varying the stoichiometric ratio of the halogen donor and acceptor.

Liquid-assisted grinding approach

The liquid-assisted grinding method is considered to be superior to the solvent-free grinding method, which

Scheme 3 Chemical formula of the halogen acceptor (A) and halogen donors (B, C, D, E, F, G). Reprinted with permission from Ref. [69]. Copyright 2011, Wiley-VCH.

usually exhibits higher yields, better crystallinity, less likely deformation, and wider option scope of precursors [79,80]. For example, Yan *et al.* [69] synthesized six types of co-crystals *via* the liquid-assisted grinding strategy with 1,4-bis-*p*-cyanostyrylbenzene (A) as the fluorescent model system and compounds with a weak visible solid-state fluorescence as the co-formers (Scheme 3). However, co-crystals cannot be directly obtained *via* co-crystallization from the solution due to the difference in the solubilities of the co-formers. The co-formers B, C, E, F, and G afford functional groups commonly used in supramolecular synthesis, which can be assembled into 1D chain structures with A *via* XB or HB interactions. In addition, single crystals can be obtained *via* crystallization, by slowly evaporating the solvent from the chloroform solution of the co-crystal.

Observing the emission of co-crystals 1–6, their color under daylight illumination is different from that of pure A crystals, as shown in Fig. 6a. When irradiated with ultraviolet light, these co-crystals are found to exhibit multicolor luminescence, changing from blue to green, and to yellow (Fig. 6b). Fig. 6d shows the fluorescence images of the transparent co-crystals 1–6, where the luminescence of the single crystals is similar to that of the powder, whereas the co-crystals exhibit tunable emission (Fig. 6c). The two-photon emission of the prepared co-crystals at a single wavelength of 800 nm laser can be tuned to emit light from blue to yellow, and hence, it is a

candidate material for two-photon fluorescence. It is concluded that the liquid-assisted grinding method offers more possibilities for designing co-crystals, which have potential applications in luminescent materials.

OPTOELECTRONIC APPLICATIONS

Optical waveguide: 1D photon transport

Optical waveguides based on organic halogen-bonded co-crystals, especially the 1D organic solid-state materials,

Figure 6 Photographs of (a) the co-crystal samples (1–6) and A. (b) The corresponding powder under sunlight and 365 nm UV light. (c, d) The fluorescence microscope of co-crystal samples (1–6) and A under 365 nm UV and sunlight. (e) Two photon luminescence under 800 nm laser. Reprinted with permission from Ref. [69]. Copyright 2011, Wiley-VCH.

have recently attracted research interest due to their potential applications in organic photonic devices, sensors, light-concentrating devices, and waveguides [81–85]

As reported earlier [75], 1D microrods and microtubes of DPEpe-F4DIB co-crystals can be controllably fabricated *via* the solution-evaporation method by tuning the solvent system. The optical waveguide features of the as-prepared 1D microrod and microtube co-crystals were characterized to determine the structure–property relation for the micro/nanostructures. According to the micro-area fluorescence microscopy image of the as-prepared DPEpe-F4DIB microrods and microtubes excited at different positions with a 375 nm laser beam, the photons are restricted in two dimensions and travel in two opposite directions along the central axis of the microrod (Fig. 7a, c). The spatially resolved PL spectra record the fluorescence intensity in the excitation site along the 1D microcrystal (I_{body}) and the tip of the luminescence (I_{tip}) (Fig. 7b, d). A single exponential decay relation is observed for $I_{\text{tip}}/I_{\text{body}}$ (Fig. 7e), which indicates active

waveguide properties. The optical-loss coefficients (R) for the microrods and microtubes are 0.0341 and 0.0145 dB μm^{-1} at 525 nm, respectively, according to the equation $I_{\text{tip}}/I_{\text{body}} = A\exp(-RD)$. Compared with the previous reports, the R value is low enough for organic optical waveguides, which indicates fine photonic transmission property. In addition, the much lower optical-loss coefficient of the organic co-crystal microtubes, as compared with that of the microrods, can be attributed to the following: i) the hollow microtubes, which form circular microcavity, exhibit more efficient confinement effect on the photons than that of the microrods, due to the much smaller refractive index of air ($n_{\text{air}} = 1$), compared with that of the 1D organic crystal ($n_{\text{crystal}} \approx 2$); ii) the defect traps inside the organic microrods lead to much more optical loss as the light transmits along the axis of the organic microrods, which does not exist in the organic microtube; iii) the thin tubular walls of the microtubes also contribute to their much lower optical loss. These 1D organic co-crystals are promising building

Figure 7 (a, c) Bright-field and fluorescence micrograph images of a single DPEpe-F4DIB microrod and microtube excited at different sites with 375 nm laser beam. (b, d) Spatially resolved PL spectra from the tip of the microrod and microtube for different separation distances between the excitation site and the tip as shown in (a) and (c). (e) Ratios of $I_{\text{tip}}/I_{\text{body}}$ and the distance D corresponding to (a) and (c). Reprinted with permission from Ref. [75]. Copyright 2018, Royal Society of Chemistry.

blocks for optical waveguide devices.

Optical waveguide: 2D photon transport

Few single-component organic molecules exhibit 2D self-assembly behavior, which greatly impedes the progress of 2D organic photonics and electronics [86]. Compared with 1D organic crystals, 2D organic crystals with good morphology exhibit excellent photon-confinement effect, which makes them more appropriate for the applications in a microscale planar photonics system [87–89]. Thus, by choosing appropriate co-formers, organic co-crystals held together by anisotropic XBs can be ideal candidates for achieving optoelectronic properties that cannot be achieved with a single component [89].

We have previously synthesized regular 2D organic halogen co-crystals using DPEpe and F4DIB molecules (Fig. 8) [90]. These as-prepared 2D organic co-crystals

exhibit asymmetric light propagation. To reveal the asymmetric transmission in the DPEpe-F4DIB 2D co-crystal, the properties of the optical waveguide were investigated. The results reveal symmetrical and asymmetric optical waveguides in two directions. The optical waveguides along the [100] direction are symmetrical, and exhibit similar optical loss coefficients ($R_{\text{Upward}} = 0.0344 \text{ dB } \mu\text{m}^{-1}$ and $R_{\text{Downward}} = 0.0333 \text{ dB } \mu\text{m}^{-1}$) (Fig. 9a–d). Interestingly, asymmetric optical waveguides along the [010] direction are also observed and the optical loss coefficients are $R_{\text{Backward}} = 0.0346 \text{ dB } \mu\text{m}^{-1}$ and $R_{\text{Forward}} = 0.0894 \text{ dB } \mu\text{m}^{-1}$. The difference in the optical loss coefficients is attributed to an anisotropic molecular stacking pattern of the 2D DPEpe-F4DIB co-crystals (Fig. 9e–h). We anticipate that these 2D organic co-crystals with asymmetric photon transport can be applied in optical logic gates and other organic photonics at micro/na-

Figure 8 The chemical structure of DPEpe-F4DIB halogen-bonded co-crystal. Reprinted with permission from Ref. [90]. Copyright 2018, Wiley-VCH.

Figure 9 (a, e) Fluorescence microscopy images of DPEpe-F4DIB co-crystal excited by 375 nm laser at different site along with [100] and [010] direction, respectively. (b, c) and (f, g) The corresponding spatially resolved PL spectra in (a) and (e). (d, h) Ratios of $I_{\text{tip}}/I_{\text{body}}$ and the distance D corresponding to (a) and (e). Reprinted with permission from Ref. [90]. Copyright 2018, Wiley-VCH.

noscale.

Organic solid-state laser

Organic solid-state lasers (OSSLs) have received substantial attention due to their potential application in some frontier optoelectronics [91–95]. Although the gained molecular systems that can be used in OSSLs are very limited, organic co-crystals broaden the range of options [96,97]. For instance, Chu *et al.* [98] designed the first organic halogen-bonded co-crystal microlaser using MPI as the halogen acceptor and F4DIB and IFB as the halogen donors. As shown in Fig. 10a, MPI can be self-assembled into a 1D structure *via* π - π stacking along the *c*-axis. However, the insertion of F4DIB molecules induces the formation of a 2D plate-like structure along the *a*-axis, as well as π ...O interactions, with the aid of the O...H bond (Fig. 10b). The formation of the 2D morphology co-crystal MPI-F4DIB is attributed to the strong halogen bond of N...I and I... π in the *bc*-plane between the MPI and F4DIB molecules (Fig. 10c). The CT between the N and iodine atoms among the halogen bond interactions makes the co-crystals potential candidates for stimulated emissions. To regulate the energy band and the molecular packing model of the co-crystal, IFB having one more iodine atom in its skeleton than F4DIB is used as the halogen bond donor. IFB is expected to have a stronger intermolecular interaction with the halogen bond acceptor, MPI, than F4DIB, which results in the formation of a ring-like MIC co-crystal (Fig. 10d). In the MIC co-crystals, the MPI and IFB molecules are held together by XBs, such as I... π , N...I, and I...O, which provides a more efficient CT in the MIC co-crystal than that in the MFC co-crystal (Fig. 10d).

To investigate the laser performance of the MPI co-crystal microwire and MFC microplate, optical-pump

laser measurements were performed. The MPI microwire shows green emission at its terminal while being excited by a 400 nm pulsed laser (inset in Fig. 11a). A sharp cavity-mode peak located at ~560 nm is also observed, as shown in the PL spectra in Fig. 11a. The specific knee signal at 116.5 $\mu\text{J cm}^{-2}$, as shown in Fig. 11b, indicates the laser behavior for the MPI microwire. As the pump fluence increases, the full width at half maximum (fwhm) at 551 nm becomes as narrow as 0.24 nm (Fig. 11b), which indicates distinct microcavity effects, and the *Q* (defined as λ/fwhm) value becomes as high as 2300. Moreover, the linear correlation between $\lambda^2/2\Delta\lambda$ and *L*, as shown in Fig. 11c, demonstrates a classical Fabry-Pérot-type resonance. The antinodes are confirmed by characterizing the electromagnetic field intensity distributions (inset in Fig. 11c). In addition, owing to the regular 2D defect-free facets, a self-waveguided edge emission for the MFI co-crystal microplate is observed, which is considered to be of great importance in light confinement. When the pump fluence is increased to over 12.74 $\mu\text{J cm}^{-2}$, the 2D MFI co-crystal microplate exhibits a long-wavelength laser with a high *Q* value (~1800) at ~580 nm (Fig. 11d, e). The MFC microplates of different sizes also show Fabry-Pérot-type microcavity effects, verified by the lasing spectra (Fig. 11f), and the simulated electric field intensity distribution characterization (inset in Fig. 11f). Remarkably, this is the first time that laser oscillation is realized through alleviating the intermolecular CT and modulating the energy-level structure in the organic halogen-bonded co-crystals. However, the stimulated emission of halogen-bonded co-crystal materials remains challenging due to the difficulty in designing and tuning the four-level system for the population inversion.

We developed an approach to form organic halogen-bonded co-crystal that transforms the nonlasing micro-

Figure 10 (a, b, d) The speculative growth pattern of MPI, MFC and MIC. (c, e) The halogen bond structures in the co-crystals. Reprinted with permission from Ref. [98]. Copyright 2018, American Chemical Society.

Figure 11 (a, d) Optically pumped lasing measurements for the single MPI wire and MFC plate. Insets: Bright-field and PL images for microwire and microplate. Scale: 20 and 5 μm . (b, e) Power-dependent profiles (blue) and fwhm (red) of the MPI and MFC. (c, f) Plots and fitted curves of $\lambda^2/2\Delta\lambda$ vs. the length of the co-crystal microwires and microplates. Insets: simulated electric field intensity distributions. Reprinted with permission from Ref. [98]. Copyright 2018, American Chemical Society.

crystals to the lasing co-crystals [99]. The as-prepared *o*-BCB microcrystals exhibit a green-emissive 1D microrod structure, which belongs to the triclinic crystalline lattice and grows along the [001] direction (Fig. 12b–d). Using the halogen bond between BFC and *o*-BCB, the *o*-BCB-BFC co-crystal microrods are synthesized, which exhibits a blue-emission and monocline crystalline structure growing along the [010] direction (Fig. 12f–h). The addition of the BFC co-former increases the intermolecular distance between *o*-BCB from 3.06 to 7.10 Å in the *o*-BCB-BFC co-crystal.

The optically pumped lasing characterization reveals that as the excitation intensity attains the maximum value of $20.2 \mu\text{J cm}^{-2}$, the PL intensity is enhanced, while fwhm remains at 80 nm (Fig. 13a). This indicates the absence of lasing action for *o*-BCB microwires. Relatively, the *o*-BCB-BFC co-crystals exhibit excellent lasing emission. As the excitation intensity increases from 0.8 to $4.1 \mu\text{J cm}^{-2}$, the *o*-BCB-BFC co-crystals show a broad blue emission centered at 450 nm. When the excitation intensity exceeds $4.4 \mu\text{J cm}^{-2}$, a series of peaks located at 447 nm appear and fwhm narrows from 22 to 0.4 nm (Fig. 13b), indicating the occurrence of lasing oscillation. In summary, with the aid of the XB between BFC and *o*-BCB, the intermolecular space of the nearby *o*-BCB molecule shortens from 3.06 to 7.10 Å, which prevents the excimer in the *o*-BCB microcrystals and offers a true four-level

energy level system in *o*-BCB-BFC co-crystals. This organic halogen-bonded co-crystal strategy expands the molecular options for solid-state laser-gain materials.

Nonlinear optics

Nonlinear optics (NLO) materials based on organic micro/nanocrystals have several practical applications in optoelectronics, such as frequency conversion, electro-optic modulation, and optical parametric oscillation [100,101]. However, the structure-property relation, especially for the photophysical and NLO properties, remains unclear in the reported organic halogen-bonded co-crystals [102–104], which hinders the further rational design and fabrication of the co-crystals for optoelectronic devices. In this context, Zhu *et al.* [105] designed two organic halogen-bonded co-crystals and investigated the molecule-packing-property relation. In the research, Npe and Spe were used as the halogen acceptor, because of their unique π -conjugated system and the strong halogen bond interaction of C–I...N with F4DIB (Scheme 4). These co-crystals display unique spectra and photophysical properties as compared with the single-component crystals.

The researchers compared the intermolecular interactions, self-assembling behavior, morphology, and crystal structure, as well as the spectroscopic, photophysical, and NLO properties, and found that the strategy of halogen-

Figure 12 (a) Halogen-bonded co-crystal of *o*-BCB-BFC. (b, f) Fluorescence microscopy images of the *o*-BCB microcrystals and *o*-BCB-BFC co-crystals. (c, g) TEM images of *o*-BCB microrod and *o*-BCB-BFC co-crystal microrod. (d, h) The corresponding SAED pattern. (e) Molecular stacking pattern in *o*-BCB crystal and *o*-BCB-BFC co-crystal. Reprinted with permission from Ref. [99]. Copyright 2019, American Chemical Society.

Figure 13 PL spectra obtained by exciting at varying energies for (a) one *o*-BCB microrod and (b) one *o*-BCB-BFC co-crystal microrod. Inset of (b): PL spectra of *o*-BCB-BFC co-crystal microrod with exciting energies below the lasing threshold. Reprinted with permission from Ref. [99]. Copyright 2019, American Chemical Society.

Scheme 4 Molecular structures of Npe, F₄DIB, and Spe. Reprinted with permission from Ref. [105]. Copyright 2016, Wiley-VCH.

bonded co-crystals can modulate the NLO properties. The NLO properties of Npe, Spe crystals, and Npe-F₄DIB co-crystal (NFC) were investigated independently. As shown in Fig. 14a, as the power of excitation laser increases, the PL intensity of the Npe crystal at $\lambda = 420$ nm is enhanced. The fitted linear correlation between the PL intensity and excitation power, as shown in Fig. 14b, demonstrates the two-photon absorption (TPA) process.

Figure 14 (a, c, e) The up-conversion PL spectra for Npe crystal, NFC co-crystal and Spe crystal. (b, d, f) The fitted linear correlation between the PL intensity and excitation power for Npe crystal, NFC co-crystal and Spe crystal. Reprinted with permission from Ref. [105]. Copyright 2016, Wiley-VCH.

Similarly, the linear relation for NFC co-crystals indicates the TPA process while excited with $\lambda_{\text{ex}} = 720\text{--}840\text{ nm}$ (Fig. 14c, d). The TPA process in NFC is attributable to the supramolecular electronic polarization, which results in the expansion of D- π -A configuration. Moreover, the Spe crystals show second harmonic generation (SHG) properties when excited by $\lambda_{\text{ex}} = 740\text{--}1000\text{ nm}$. Fig. 14e shows that when Spe is excited with the 740 nm laser, a weak and sharp peak at 370 nm appears, and a fitted linear correlation between the PL intensity and the excitation laser is obtained (Fig. 14f). These suggest that the D-A structure of the Spe molecule bearing intramolecular electronic polarization and the non-centrosymmetric media results in SHG properties of the Spe crystal. Thus, XB is beneficial to the NLO properties of the organic co-crystals, which can be advantageous in tuning the optical nonlinearities at the molecule level.

Photonic logic gate

Optical logic gates with multiple input/output channels have potential applications in optical components for integrated organic photonics [106,107]. 2D organic co-crystals with a regular morphology and isotropic/anisotropic molecular stacking pattern result in direction-oriented asymmetric photon transport, and hence, can be used as a microscale optical logic gate [108,109]. Owing to the anisotropic DPEpe-F4DIB co-crystals, which display direction-oriented asymmetric optical waveguide characteristics, we employ DPEpe-F4DIB co-crystals in the optical logic gate with multiple inputs and output channels, as shown in Fig. 15a1–a8 (the excited laser $\lambda_{\text{ex}} = 375\text{ nm}$) [90]. The PL intensity ratios of the four output terminals of the eight typical excitation positions in the same crystal are normalized and divided into four regions correspondingly, as shown in Fig. 15b. The information

Figure 15 (a1–a8) Fluorescence microscopy images for DPEpe-F4DIB co-crystal excited at eight typical sites with 375 nm laser beam. (b) The ratios of the intensity of four edges corresponding to the eight exciting sites in one co-crystal microplate. (c) Representation of the microcell edge and the exciting sites at the opposite edges. (d, e) Spatially resolved PL of the microcell edge corresponding to (c). Reprinted with permission from Ref. [90]. Copyright 2018, Wiley-VCH.

codes of (0, 1, 3, 0) can be read through the four output terminals, whereas the input position is located on the lower-right vertex (Fig. 15a, b). The same mechanism is applicable to the other input positions. On the other hand, accurate microcell emission properties are obtained by decomposing the luminescence edge of the organic crystal into eight parts along the [100] direction (Fig. 15c). The microcell emission intensity on the luminescence edge is related to the distance between each typical input position on the other side (Fig. 15d, e). Moreover, as the asymmetric photon is transported along the [010] direction, the intensity of the out-coupled light corresponding to the symmetric input site, especially that of B and D, demonstrates a unidirectional signal transmission performance. The above results indicate that the multi-channel emission of 2D DPEpe-F4DIB co-crystals displays encoding/decoding functions by using different excitation sites as the encryption keys, and a definite emission intensity model serves as the output signal.

Electrical properties

CT interactions, as well as CT exciton dynamics, between

the donor and acceptor groups in organic co-crystals play an important role in optoelectronic devices. As aforementioned, XBs have been confirmed to be a CT interaction where atoms with lone electron pairs, such as N, O, and S, delocalize to the halogen atom acceptor ($n \rightarrow \sigma^*$) [38,43]. Thus, organic halogen-bonded co-crystals are considered as the σ -complex. However, only a few studies have been conducted on CT interactions in organic halogen-bonded co-crystals [110,111], which has hindered further rational design and fabrication of organic optoelectronic devices. Zhu *et al.* [112] conducted an electrical investigation on the organic halogen-bonded co-crystals. They synthesized two types of organic co-crystals with distinct molecular packing modes and systematically investigated the “assembly-structure-CT interaction”. They demonstrated that the CT interactions can be tuned *via* the crystal engineering strategy in organic halogen-bonded co-crystals.

In that study, the selected co-formers are IFB, trans-Bpe, and F4DIB (Scheme 5). Two co-crystals of Bpe-IFB and Bpe-F4DIB were synthesized *via* solution drop-casting. The electrical conductivities of the obtained co-

Scheme 5 The molecule structures for Bpe, IFB and F₄DIB. Reprinted with permission from Ref. [112]. Copyright 2015, American Chemical Society.

crystals were determined by using a two-terminal microscale device. Each of the BIC microwires shows a typical *I*-*V* characteristic curve, as shown in Fig. 16a, and the linear correlation of the *I*-*V* behavior obeys ohm's law (Fig. 16b). The electric conductivity (σ) of BIC co-crystals is obtained to be $1.42 \times 10^6 \Omega^{-1} \text{m}^{-1}$, according to the equation: $\sigma = L/RWH$, where σ and R are the electrical conductivity and resistance of the microwire, respectively, and W , H , and L denote the width, height, and length of the device channel for the crystal. It indicates that the BIC co-crystals exhibit a quasi-1D semiconductor nature. The BFC co-crystals are obtained to be electrically insulating (Fig. 16c, d), which can be attributed to the mixed-stacking structure without CT interactions. Hu's group

[112] attributed the existence of the CT interaction in the separated BIC co-crystals to the π -electron-rich circumstances in the π - π stacking Bpe columns, which facilitates the CT interaction in co-crystals. However, in the BFC co-crystals, the Bpe molecules are scattered, thus resulting in a deficiency of π -electrons, and in turn, a poor CT interaction between Bpe and F₄DIB molecules. Therefore, the molecular packing mode in organic halogen-bonded co-crystals has a significant influence on the CT interaction, which in turn affects the optoelectronic properties of the organic co-crystals.

CONCLUSIONS

XBs have been confirmed to regulate intermolecular electron transport as well as the PL of organic co-crystals. Thus, organic co-crystals based on them have attracted increasing attention due to their unpredictable and outstanding chemical and physical properties, as well as their potential in optoelectronic applications. In this paper, we have systematically summarized the recent developments in organic halogen-bonded co-crystals with regard to their fabrication methods and optoelectronic properties. Some methods commonly employed in the fabrication of

Figure 16 Optical images of (a) BIC co-crystal (upper section) and the device (bottom section), (c) BFC co-crystal (upper section) and microblock-based device (bottom section). The scale bars are $10 \mu\text{m}$. (b, d) *I*-*V* curve and corresponding fitted relationship for BIC and BFC co-crystals. Reprinted with permission from Ref. [112]. Copyright 2015, American Chemical Society.

organic halogen-bonded co-crystals, including solution evaporation, mechanochemical, and liquid-assisted grinding methods, are summarized. Furthermore, the optoelectronic properties are discussed in detail with regards to various applications.

Among the fabrication methods, solution evaporation is the simplest and most efficient method, and is dependent on external conditions such as the solvent, concentration, and temperature. The morphology of the organic co-crystals can be modulated by adjusting the concentration of organic molecules. However, the fabricated micro/nanostructures exhibit random distribution, and thus, cannot form a large-scale array of ordered arrangements. Therefore, there is a need to extend the method to achieve structures with large-scale and highly ordered arrays for practical applications.

For optoelectronic applications, there is still much ambiguity and randomness in the choice of constituent materials for effective co-crystallization with expected functions. Thus, it is imperative to broaden material systems and develop high-performance halogen-bonded co-crystals for the corresponding applications. Taking organic solid-state lasers as an example, a stimulated emission of halogen-bonded co-crystal materials remains a challenge due to the difficulty in tuning of the four-level energy system for population inversion. Thus, the constituent materials, crystal structure, and energy-level structure of halogen-bonded co-crystals need further optimization and development. In addition, efforts are demanded to widen the application of organic halogen-bonded co-crystals in electronic fields (such as electrically pumped organic lasers or organic photoelectric detectors), thus boosting the multifunctional development.

In summary, not minding the challenges, there is a promising future for organic halogen-bonded co-crystals. As novel organic semiconductor crystals, we hope that organic halogen-bonded co-crystals would play an important role in the next-generation optoelectronics.

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Conflict of interest The authors declare no conflict of interest.

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有机卤素键晶体及其在光电子学中的应用

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摘要 有机卤素共晶是由两个或者更多不同组分通过碳卤键构成的。因其多样化的化学物理特性, 及在有机光电子学领域的潜在应用价值, 有机卤素共晶引起了研究者的广泛关注。本综述文章中, 我们简单总结了有机卤键共晶的制备方法和在光电子器件领域应用的最新进展。此外, 我们还讨论了目前有机卤键共晶的研究方向及面临的技术挑战, 同时对有机卤键共晶的进一步研究和应用前景进行了展望。