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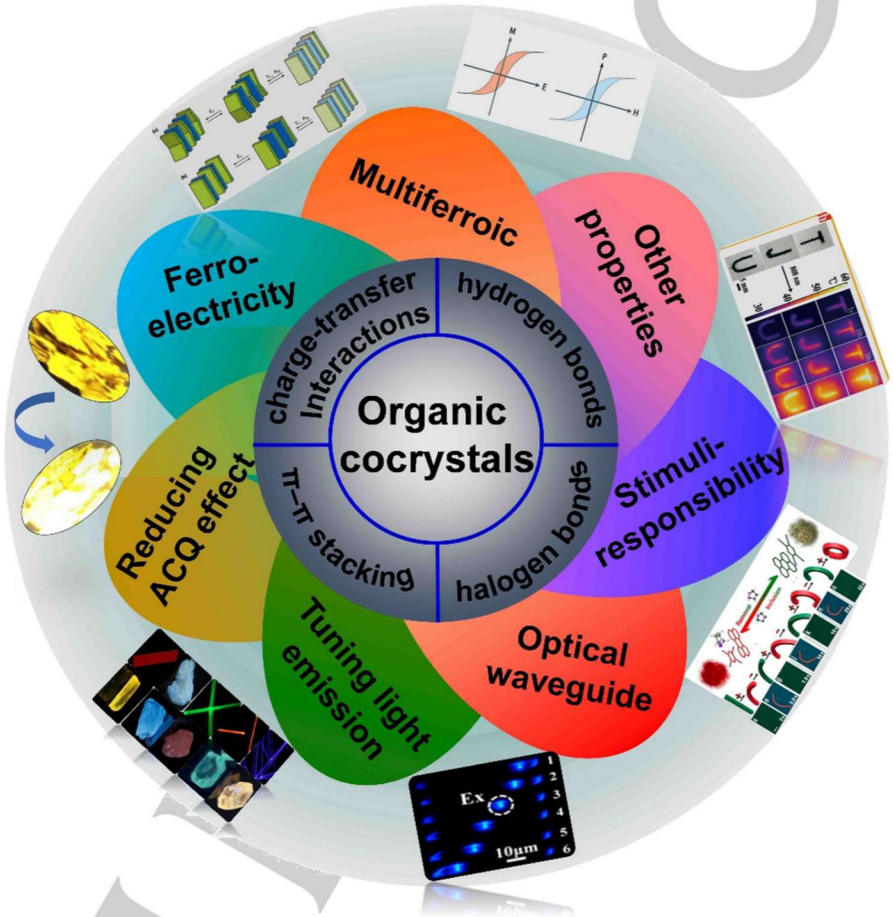
MINIREVIEW

Towards Emerging Properties and Applications of Organic Cocrystals Beyond Electrical Conductivities and Field-Effect Transistors (FETs)

Yinjuan Huang[+], Zongrui Wang[+], Zhong Chen, Qichun Zhang*



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MINIREVIEW

Abstract: *Organic cocrystals based on noncovalent intermolecular interactions (week interactions) have aroused enormous interest due to their unpredicted and versatile chemicophysical properties and charming applications. In this review, we highlight recent emerging researches of organic cocrystals on reducing aggregation-caused quenching (ACQ) effect, tuning light emission, ferroelectricity and multiferroics, optical waveguide, and stimuli-responsibility. We also summarize great progresses made in this field including revealing the structure-property relationships and developing unusual exciting properties. Moreover, we provide a discussion on current achievements, limitations and perspectives as well as some directions and inspiration for further investigation on organic cocrystals.*

1. Introduction

Compared with inorganic materials, organic multifunctional electronic semiconductors may be more suitable for photoelectric applications with benefits from excellent molecular designable capability, flexibility, solution processability, and lightweight. Although some successes in traditional structure-tailoring for obtaining tunable properties have been achieved for single-component organic materials, such processes are time-consuming and very tedious. Recently, co-crystallization strategy has been demonstrated to be an effective way towards tunable physicochemical properties,[1-3] luminescence,[4,5] phase and morphology,[6] optical switches,[7] and p–n junctions,[8] as well as novel properties[9] of molecular systems. Generally, organic cocrystals assemble from two or more different chemical species via noncovalent intermolecular interactions, such as charge-transfer (CT) interactions, π–π stacking, halogen and hydrogen bonds,[7, 10-12] which associate with designable multi-functional synergistic effects and an ordered stacking of donors (D) and acceptors (A).[13]

Organic cocrystal was discovered by Wöhler in 1844,[14] but began to attract much attention till 1973 when the cocrystals (charge-transfer complexes) formed from tetrathiafulvalene/7,7,8,8-tetracyanoquinodimethane (TTF–TCNQ) [15] presented high conductivity over a wide range of temperature, which aroused great research interest in organic optoelectronics.[16] Later on, organic cocrystals become a hot field and most researches focused on their electrical properties (e.g. insulators, semiconductors, and superconductors) and magnetic properties. Until 2004, since the first case of ambipolar charge-transport behavior under low temperature based on organic cocrystal Bis(ethylenedithiolo)tetrathiafulvalene(BEDT-TTF)-TCNQ was reported,[17] the door to charge carrier-transport area of organic cocrystals was opened. Especially, very recently, organic cocrystals, which are regarded as an efficient but facial way to prepare multifunctional and high performance optoelectronic materials, have attracted increasing attention due to their unpredicted and versatile chemicophysical properties and charming applications, such as high electrical conductivity,[15] photoconductivity,[18] photovoltaics properties,[19] nonlinear optics (NLO),[3,20,21] optical waveguide,[1,22a] ambipolar charge carrier transportation,[23,24] tunable luminescent features,[3,4,25,26] ferroelectrics,[27,28] stimuli-responsibility,[10,29] light-driven actuators,[10] liquid crystal materials,[30] and pharmaceutics.[31]

In this context, organic co-crystallization really provides an ideal way to design and achieve new organic solid-state materials with desirable and multiple-function molecular solids.[4] However, there are long-standing critical problems existing in this new research field.[4] Firstly, the basic interaction mechanism and principles during co-crystallization are not very clear: since not every pairs of donor and acceptor can self-assemble together, how to rationally select appropriate molecules for efficient co-crystallization,[32] and how to make diverse co-formers structurally match, co-assemble and crystallize together[5] need to be addressed. Secondly, the relationships between crystal structures and the resulting performance, and the CT degree within cocrystals connecting to lattice stability,[33] optoelectronic and photophysical properties,[34,35] as well as the mechanism of electronic interaction between building blocks remain elusive,[5] which greatly impedes the properties regulation of the cocrystals. In this case, effective tuning of cocrystals properties for the desirable functions via designing and controlling the definite stoichiometric ratio, molecular stacking mode, orientation, crystal phase and morphology is still in an early stage and remains a long-standing challenge.[5, 36]

Although there have already existed some excellent reviews about organic D-A complexes for novel organic electronics[37] and techniques/methods of the preparation and characterization of organic cocrystals, as well as some applications of cocrystals before 2016,[38a] in this review, we only make a brief summary focusing on recent development and applications (except electrical conductivities and field-effect transistors (FETs)) of organic cocrystals including reducing ACQ effect, tuning light emission, ferroelectricity and multiferroic, optical waveguide and stimuli-responsibility. We also provide a discussion on current achievements, limitations and perspectives. Finally, we try to aim at providing something useful instructions for further investigation on organic cocrystals.

2. Preparation of organic cocrystals

2.1 Interactions

Cocrystals are formed from two or more kinds of molecules, which can co-crystallize via one or more noncovalent interactions, such as π–π interactions, halogen bonds, hydrogen bonds and charge transfer (CT) interactions (Figure 1). Actually, CT interactions (Figure 1d), in which the CTs from the highest occupied molecular orbital (HOMO) of the electron-rich donor to the lowest unoccupied molecular orbital (LUMO) of the electron-deficient acceptor, [38a] exist in most of the organic cocrystals and act as the main driving force for the formation of cocrystals when a strong charge acceptor assembles with an suitable charge donor, such as TCNQ-perylene, TCNQ-TTF, and tetracyanobenzene(TCNB)-dibenzotetrathiafulvalene (DBTTF), and so on.[15,16,39] The strength of CT interaction depends on the electron affinity energy of the acceptors, the ionization potential of the donor and the electrostatic Coulomb forces between the D-A pairs,[38a] which can be characterized by IR and Raman measurements.[40]

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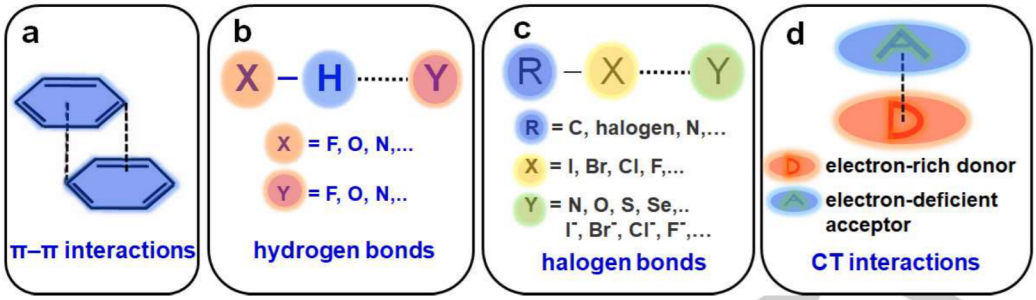

Figure 1. Schematics of π-π stacking (a), hydrogen bond (b), halogen bond (c) and CT interaction (d).

Another important driving force is hydrogen bond (Figure 1b), which is stable and can present good orientation to help us predict the structural consequences much easier.[41] π-π interactions are also the common interactions in organic cocrystals (Figure 1a), which can be formed between π-donors such as acene-based derivatives and porphyrins, and π-accepting molecules, such as fullerenes.[1,37,42,43] Recently, cocrystals with halogen bonds were reported frequently. Halogen bonds, discovered in 1863,[44] are a kind of noncovalent interactions between halogen atom (donor) and nucleophilic region (acceptor) (Figure 1c),[45, 38] and present unique characters, like being excellent directional, hydrophobic, strength-tunable, and more effective than a hydrogen bond in cocrystal formation,[38] which is regarded as a thriving tool for cocrystal constructions. Strictly speaking, CT complexes involve two kinds of CT interactions: π and σ. The co-crystals containing halogen bonds are σ complexes, in which the lone electron pair in an electron-rich atom (e.g. N, O, S, Se, I^-, Br^-, Cl^-, and F^-) are donated to the halogen (I, Br, Cl, F) acceptor (n→σ* donation, halogen bond).[46] While in a π CT complex, a π electron cloud can greatly delocalize from a donor to an acceptor, resulting in a strong effect on optoelectronic properties of the as-prepared cocrystals.[1]

Except for controlling the self-assembly process and structures of cocrystals, more remarkable noncovalent interactions also govern the stability as well as the properties of the resulting cocrystals.[47] For example, cocrystals based on CT interactions have been reported to display various properties including high-temperature superconductivity, high room-temperature conductivity, photoconductivity, ferroelectricity, ambipolar transport and magnetic properties.[47a,b] The hydrogen bonds in cocrystals are closely related to the properties of the corresponding cocrystals.[41] π-π interactions can endow cocrystals with new optoelectronic properties (e.g. ambipolar charge-transport properties),[23] while halogen bonds can facilitate cocrystals with promising properties such as conductivity, light emission and magnetism.[38a] Indeed, the driving forces for co-crystallization are usually the simultaneous combination of several kinds of above-mentioned interactions.[38] Therefore, further investigation on the relationships between interactions and properties are highly desirable in order to achieve ideal cocrystals with desirable functional properties.

2.2 Preparation Methods

Up to now, there are three main reported strategies for preparing organic co-crystals, including vapor-phase (Figure 2a),[36] liquid-phase (Figure 2b)[25] and solid-phase (mechanochemical, grinding the mixture of donor and acceptor) methods.[31] As we all know, the solution-based technique is widely used, because it is the simplest way (convenient, fast, and low cost) to prepare uniform organic cocrystals with regular morphology, which is essential for further characterization and application. Liquid-phase techniques include liquid–liquid interfacial precipitation,[48] solvent vapor annealing,[49] reprecipitation,[25] drop-casting, and diffusion, which can produce cocrystals from a donor–acceptor mixed solution. However, it should be noted that this method for the preparation of organic cocrystals always requires planar molecular structure of both donor and acceptor blocks, strong intermolecular interactions, and similar solubility of the donor and acceptor molecules.[1] In comparison, vapor-phase methods are reported seldomly,[36] although they are essential for co-crystallizing of the organics with poor solubilities. In these methods, both co-sublimation and co-deposition should be performed, therefore the insoluble molecules with similar sublimation points can be used.[38] Solid-phase methods, which have been reported for a long time, mainly include grinding and solvent-assisted grinding.[31] Although such methods require no solvent and are relatively cheaper and easier to carry out, which are widely used in pharmaceuticals, the resulting materials are labeled with amorphous phases and should exhibit different properties comparing to the crystalline phases.

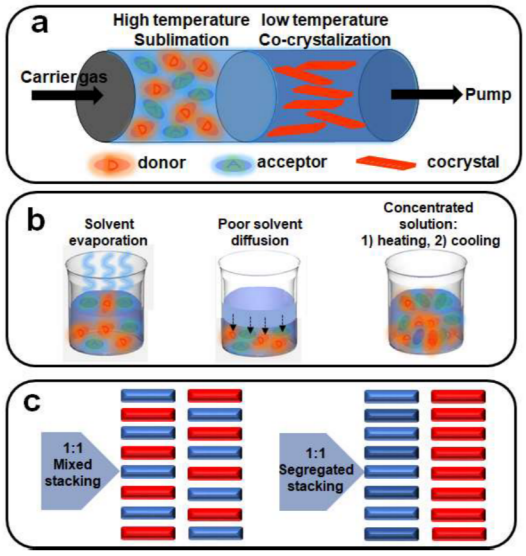

Figure 2. Preparations methods and stacking modes. a) vapor-phase method, b) liquid-phase method, c) packing modes of cocrystals formed via 1:1 stoichiometric ratio.

3. Properties and applications

3.1 Tuning the properties of organic cocrystals

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The ultimate purpose to prepare a cocrystal is to investigate its properties and realize its potential applications. It is well-known that cocrystals can exhibit new properties rather than a simple combination of the properties of each co-former. Thus, it is essential to make it clear which factors mainly affect the properties of cocrystals before achieving functional desirable complexes.

The types of donors and acceptors are the most important factors that determine the properties of cocrystals, because different co-formers can not only introduce intrinsic characteristics of each component into cocrystals but also lead to different crystal stacking structures, different degree of charge transfer, and different band structure, eventually affecting the properties of cocrystals.[38a] Specifically, although cocrystals usually exhibit different properties from that of their co-formers, they do retain the intrinsic properties of the donor and the acceptor to some extent. For example, cocrystals based on TCNB usually present good optical properties similar to the bright blue fluorescence of pure TCNB,[50] while the cocrystals formed from TCNQ or fullerene could demonstrate excellent electrical properties in line with one-component TCNQ or fullerene.[51] In this text, the characteristic properties of both donors and acceptors should be considered during the design of cocrystals with specific desired properties. In addition, different D-A arrangement can also lead to different properties. At present, the most common arrangement is 1:1 complexes, which include two packing modes, mixed stacking (…DADA…),[6] and segregated stacking (DDDD…AAAA) (Figure 2c).[15] Segregated-stacking cocrystals usually displays high electrical conductivity, by comparison, mixed-stacking complexes are semiconductors even insulators.[2] Other packing ratios (except for 1:1) are unusual in cocrystals, cocrystal formation with such ratios need to select appropriate donor, acceptor as well as the preparation conditions.[38a] In these cocrystals, the extra donor or acceptor compounds can either exist within the co-stack or form a new stack.[52] Moreover, the degree of charge transfer, a feature of CT cocrystals, is defined as q (0≤q≤1), which can be related to lots of physical properties.[34] Specifically, the cocrystals (larger q value) dominated by CT interactions normally possess high conductivity, while the ones (smaller q value) with weak CT interactions show potentially smaller conductivity.[34] Besides that, q value is also related to the molecular packing.[53] For example, the cocrystals dominated by CT interactions display strong ionic character, leading to segregated stacking, otherwise, resulting in mixed stacking.

In addition, the band structure of a cocrystal, depending on the kinds of donors and acceptors, is relate to lots of optoelectronic properties. It was proved that the HOMO of donors makes the largest contribution to that of the cocrystals, while the LUMO of acceptor is most correlated with that of cocrystals.[54] Similarly, the band structures can affect not only the stacking structure but also the charge-transfer behaviors of the cocrystals. Therefore, it is crucial to make a deep understand and suitable tailoring for the band structure, in order to obtain a cocrystal with particular desired properties.

3.2 Reducing ACQ effect

Organic luminescent materials, that can present higher photoluminescence efficiency in the aggregated state than in solution (defined as aggregation induced emission (AIE) behaviors), are attracting increasing interest recently, because this type of materials have great potential for the applications in the real world, such as optoelectronic devices, biomedical probes, chemical sensors, and so on. Therefore, a variety of AIE-active organic molecules have been developed and widely used in many fields.[55] However, there are still some problems remained in these materials. Firstly, some AIE-active molecules are not easy to synthesize and purify, thus resulting in a higher cost. Furthermore, most of them mainly are single-component materials, which is difficult to create excellent characters that can be displayed by multicomponent complexes.

Thus, a facile low-cost strategy, co-crystallization, has been developed to create a new family of efficient luminescent materials based on multicomponent systems.[22, 25, 43, 57, 58] For example, in 2011, a pyrene derivative (1,3,6,8-tetramethylpyrene, TMPY)

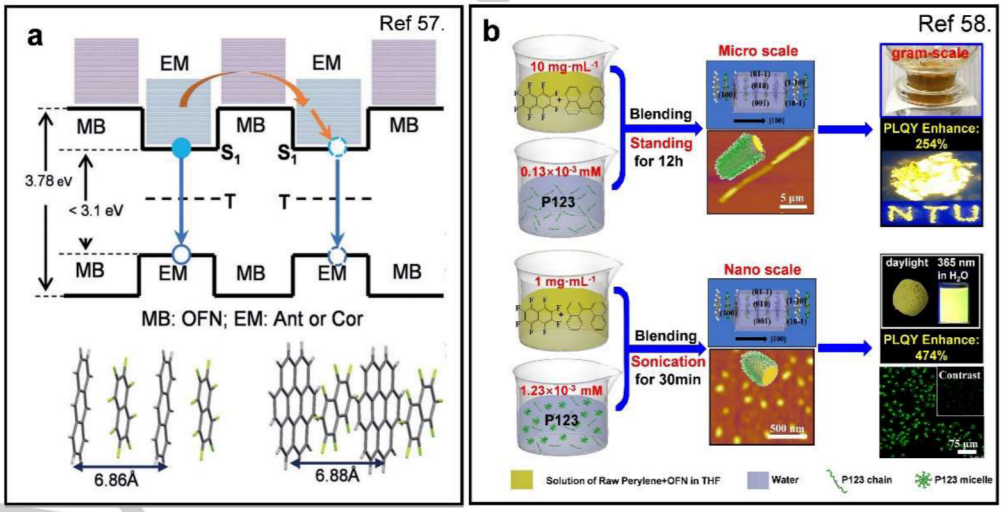

Figure 3. (a) Schematic of the electronic energies within the periodic co-crystalline structures. The blue arrows represent the transition of the singlet emission. The orange arrows represent singlet trapping via singlet–singlet annihilation. Reproduced with permission from [57]. Copyright 2018 Wiley-VCH. (b) Illustrations of preparation processes and morphologies (middle) and the emission enhancement as well as cell imaging results (right side) for the micro/nano Per/OFN cocrystals. Reproduced with permission from [58].

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a high quantum yield of 0.94 in dilute solution but can self-quench in aggregated states.[56] After doping with perylene, the photoluminescence quantum yield (PLQY) was enhanced due to the effective energy transfer to the molecules with high PLQY. Moreover, a naphthalene–TCNB CT complex with single-crystalline microtubes has been prepared via low-cost etching-assisted self-assembly driven by weak CT interaction.[25] Remarkably, the naphthalene–TCNB microtubes present highly efficient blue emission owing to AIE effect. The PLQY for the microtubes suspension of the blue-emissive naphthalene–TCNB complex is 17.5% (higher than that of naphthalene–TCNB in acetonitrile solution), which is because a solid environment can reduce the rapid internal conversion and recombination in solution. Recently, octafluoronaphthalene (OFN) with a higher band energy gap (ca. 3.78 eV) is chosen as a molecular barrier to improve the emission of coronene and anthracene, where coronene and anthracene possess band gaps of ca. 2.76 eV and ca. 3.10 eV, respectively (Figure 3a).[57] The molecular barriers (OFN) are intercalated in a periodic π-stacked molecular complex, which effectively block the interaction and electron exchange between the two adjacent fluorophores and cut off the pathway from singlet state to triplet state (intersystem crossing, ISC), leading to the absence of triplet states. Surprisingly, the PLQYs of OFN-anthracene and OFN-coronene increased from 81% to 100% and 5% to 100%, respectively. This work opens an exciting direction for organic emitting materials with high PLQY in the solid state.

Encouraged by this work, more polycyclic aromatic hydrocarbon (PAH) chromophores with ACQ effects have been investigated.[58] Specifically, a facile emulsion method is employed to regularly co-assemble two different conformers into well-ordered aggregates, where coronene, perylene and pyrene are used as ACQ chromophores, OFN is used as molecular barrier, and P123 (PEO_{20}-PPO_{70}-PEO_{20}) was chosen to improve the water dispersibility as well as decease the dimensions of the resulting cocrystals to micro/nano scale (Figure 3b).[58] All PLQYs of the micro/nano cocrystals have been improved, especially for coronene-OFN and perylene-OFN nano cocrystals, the PLQYs have been enhanced by 582% and 474%, respectively. More importantly, the nano cocrystals display excellent cellular permeability, biocompatibility and wonderful bioimaging. Such results provide novel avenues for the applications of PAHs with ACQ effect in bioimaging.

Very recently, 4-(1-naphthylvinyl)pyridine (NP)-based co-crystals, such as NP-1,4-diiodotetrafluorobenzene, NP-4-bromotetrafluorobenzoic acid and NP-4-benzoylbenzoic acid also present higher fluorescence properties compared with the pristine NP solid, among which the cocrystal based on NP and 4-bromotetrafluorobenzoic acid present a high PLQY (more than 50%).[43] This research could further enrich the AIE families, and new kinds of two-photon emission materials can be developed based on this strategy. Another work confirmed that co-crystallization could be an alternative method to achieve greatly enhanced electrochemiluminescence (ECL) signal via selecting rational intermolecular interactions and molecular recognition.[22a] Here, 9,10-diphenylanthracene (DPA) with high ECL efficiency in solution but much lower efficiency in solid electrode is selected to form cocrystals with appropriate co-assembling acceptors. The ECL signal of the resulting cocrystals is highly improved compared with the pure DPA, because the enhanced donor-acceptor and π-π stacking interactions could accelerate electron transfer and then result in the change of oxidation potential.

Although such researches based on decreasing ACQ effect of several chromophores have been reported, this research is still in its early stage and more efforts are required to explore more co-crystalized systems for the further applications in optoelectronics.

3.3 Tuning light emission

Recently, tuning the optical/luminescence properties of molecular crystals, especially multi-component ones, has gained many scientists' interests because it is really a facial and effective way to realize tunable multicolor emission of organic materials.[59] As highlighted in the news entitled "Co-crystals Give Light a Tune-up" published in Nature Chemistry, which is a good highlight for the importance of co-crystallization engineering in tunable emission of organic materials.[5] There have been lots of works have been reported to achieve tunable optical properties in supramolecular systems via co-crystallization methods.[21-22, 25-26, 56, 60-64]

The halogen bonds as a good strategy to achieve controllable multifunctional co-crystals are widely used. For example, a stilbene derivative, cyanostilbene-based positional isomers (CS) are chosen as a fluorescent donor system, the haloperfluorobenzenes with different potential hydrogen or halogen bond interactions with cyano groups in CS are selected as acceptors, resulting in various cocrystal systems (Figure 4, AE', AH', AC', BB' and CG').[4,5,65-66] The resulting co-crystals can be tuned to present multi-color emission from yellow through green to blue as well as strong two-photon luminescence. Another stilbene derivative, 1,2-bis(4-pyridyl)ethylene (Bpe) is also employed to tune its optical properties through co-crystallization with different acceptors.[1] When 1,3,5-trifluoro-2,4,6-triiodobenzene (IFB) and 1,4-diiodotetrafluorobenzene (F4DIB) are selected as acceptors, a segregated stacking form with CT interactions or a mixed stacking form without CT interactions are obtained (Figure 4, DD' and DB'). These factors make Bpe-IFB and F4DIB-IFB show different properties, e.g. strong violet-blue photoluminescence for Bpe-IFB, and interesting white-light emission and optical waveguide property for F4DIB-IFB. Supramolecular co-crystals of solid UV/blue luminescent materials are also obtained based on 2,5-diphenyloxazole (DPO) and four typical co-assembled co-formers (4-bromotetrafluorobenzene carboxylic acid, F4DIB, OFN, and pentafluorophenol) (Figure 4, RB', RG' and KC').[21,67] Compared with the single-component DPO crystals, the resulting DPO-based co-crystals exhibit tunable optical properties and multi-color polarized emission within the UV/blue region, and also present reversible mechano-chromic fluorescence (MCF) properties. These new properties make DPO-based co-crystals to be potential candidates for applications in solid UV/blue opto-electronics. Non- or poor fluorescent 3-ring-N-heterocyclic hydrocarbons (Figure 4, VB', WB', XB', SB', TB', UB, and TP') [68-71] and fluoranthene (Figure 4, KD', KK', KP' and KN') [72] in the solid-state can be endowed with different emissions such as pink, orange, orange yellow, green, or blue light after co-crystalized with haloperfluorobenzenes. The emitting colors of (naphthylvinyl)pyridine can also be adjusted via co-crystallizing with HFB or 4-bromo-2, 3,5,6-tetrafluorobenzoic acid (Figure 4, EB' and EI').[43] The two-photon emission with adjustable wavelengths can be achieved in this work, which helps the co-crystals to be promising candidates as up-conversion materials.

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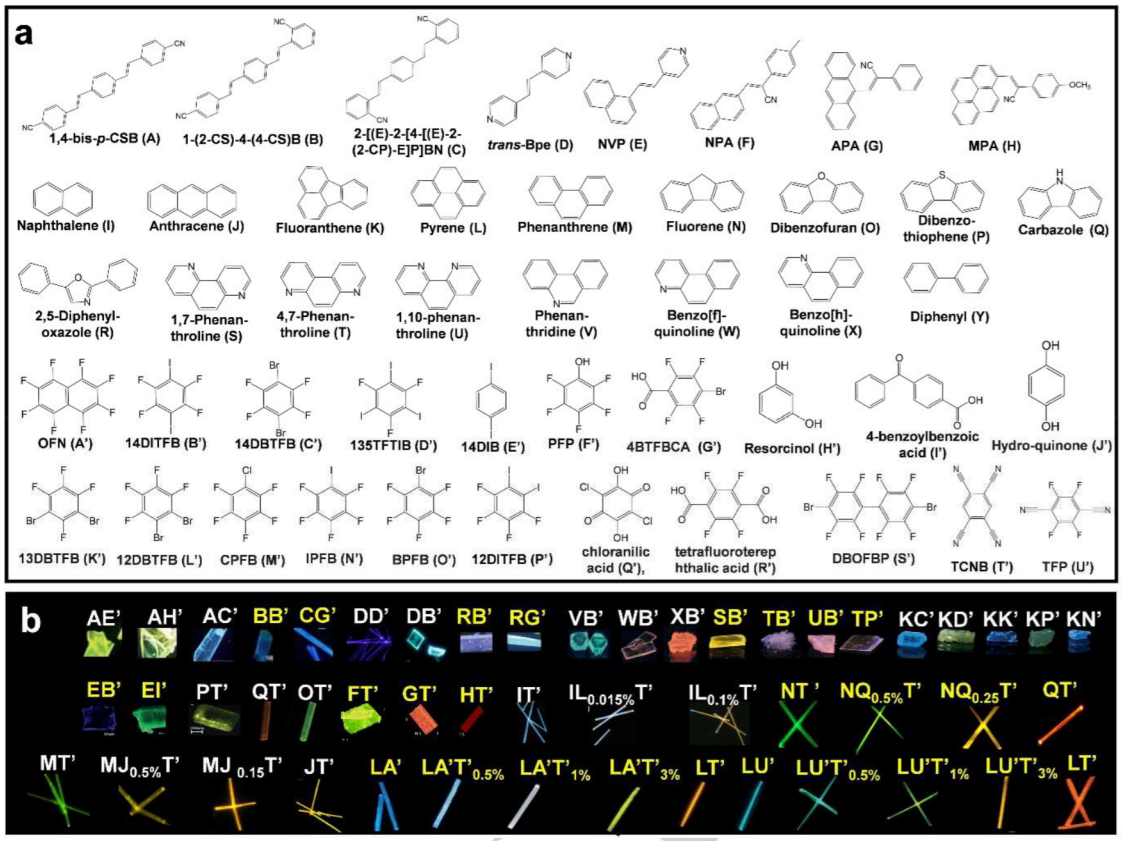

Figure 4. (a) Structures of the reported donors and acceptors used in tuning tunable multicolor emission. (b) The fluorescence microscopy images of the cocrystals formed from the donors and acceptors in (a). Reproduced with permission from [74], [1], [26], [4], [21], [43], [60], [25], [65], [70], [68], [72] and [73]. Copyright 2018, 2015, 2015, American Chemical Society, 2011, 2013, 2018, 2017, 2012, Wiley-VCH, 2014 Springer Nature and 2016 Elsevier, 2014, 2017, 2017, the Royal Society of Chemistry, respectively.

Another kind of acceptor, TCNB, is also commonly used to tune optical properties of organic solid materials through CT interactions, not only for two-component compounds [73-75] but also for three-component complexes.[25,26,60] He and the coworkers[74] reported excellent fluorescent tunability of three novel binary D-A cocrystals with strong CT interactions, in which TCNB and three derivatives of PAH (naphthalene, anthracene and pyrene) are selected as the acceptor and donor, respectively (Figure 4, FT', GT' and HT'). The tunable emission is associated with the ionization potential of the polycyclic donors and the CT interactions within the cocrystals. A simple two-step CT induced co-assembly method with solvent-etching process was developed to prepare various multi-component CT crystalline microtubes based on $(anthracene)_x(phenanthrene)_{1-x}(TCNB)$ $(0 \leqslant x \leqslant 1)$ (Figure 4, MT', $MJ_{0.5\%}T'$, $MJ_{0.15}T'$ and JT').[26] The structural compatibility and CT interactions of anthracene-TCNB and phenanthrene-TCNB motivate the formation of $(anthracene)_x(phenanthrene)_{1-x}(TCNB)$ complexes. The emission colors of the resulted cocrystals can be changed from green to yellow to orange at low dopant concentrations ($x \leqslant 5\%$), whereas the hexagonal cross sections can change to square ones gradually at $0.15 < x < 1$. Moreover, such solvent-processed synthetic method can further be extended to other CT pairs, such as $(carbazole)_x(fluorene)_{1-x}(TCNB)$, based on structural compatibility (Figure 4, NT', $NQ_{0.5\%}T'$, $NQ_{0.25}T'$ and QT'), which offers an excellent platform to explore structural and energy-transfer relationship between two different organic CT complexes.

More surprisingly, white-light emitting (WLE) of multi-component organic CT complexes was discovered by Liang and his coworkers [25] based on naphthalene (donor), pyrene (donor) and TCNB (acceptor). After 5 years, Hu and his coworkers [60] reported another multi-component WLE materials (Figure 4, LA', $LA'T'_{0.5\%}$, $LA'T'_{1\%}$, $LA'T'_{3\%}$, LT', LU', $LU'T'_{0.5\%}$, $LU'T'_{1\%}$, $LU'T'_{3\%}$ and LT'). They prepared two typical kinds of organic luminescent cocrystals with tunable emission colors and comprising pyrene–OFN and pyrene–TCNB. Interestingly, the cocrystals demonstrate distinct optical properties due to different intermolecular interactions, arene–perfluoroarene (AP) and CT interactions. Unexpectedly, a pyrene–TCNB complex with strong CT interactions can generate WLE when doped into a pyrene–OFN host. In these supramolecular systems, an efficient energy-transfer behavior from pyrene–OFN to pyrene–TCNB occurred due to the well-matched spectra of the precursors and a suitable energy D/A distance. In addition to above-mentioned two kinds of acceptors, there are other acceptors that have been reported for tuning optical properties more recently.[76-78]

Remarkably, Yan et al.[42] experimentally and computationally illustrated how the formation of two-component crystals can tune and control the solid-state emission via changing the intermolecular interactions and aggregation structures. Introduction of suitable co-formers generates excited-state potential energy profiles and then results in highly reduced or enhanced excited-state intramolecular proton transfer (ESIPT) emission. Although a great amount of cocrystals with tunable

emission have been reported (Figure 4), we still should apply the design and construction principles of multi-component cocrystals (with tunable molecular packing mode and orientation, intermolecular interactions and crystal symmetry) to investigate more novel mixed crystalline systems, comprising two and more diverse organic molecules, and to further enrich the fluorescent material families. More significantly, it will be a great challenge to make such solid fluorescent semiconductors applicable in in optoelectronic devices, which needs more efforts from our researchers.

3.4 Ferroelectricity properties

Ferroelectricity is a characteristic of some materials with a spontaneous electric polarization that can be reversed by an external electric field [79] and has long been a very important field not only in condensed-matter science but also for the technical applications.[49,79] However, most investigated ferroelectric materials are focused on inorganic or organic-inorganic hybrid compounds (such as lead zirconate titanate (PZT)). For organic ferroelectrics, despite with the superiorities of lightness, flexibility and non-toxicity in industrialization, they are rare and has once been limited to the well-known polymers (such as Polyvinylidene fluoride (PVDF)) and a few specific compounds (such as thiourea). Nevertheless, the emergence of the co-crystallization strategy in very recent years has aroused an alternative route for the new organic ferroelectrics exploration, because assembling multifunctional components through non-covalent interactions allows scientists to tailor their final materials with the unique and desired physicochemical properties.[38a] Normally, for the conventional inorganic and organic ferroelectrics, the typical mechanisms of the ferroelectricity achievement can be categorized as: (i). *Order-disorder* type, where the polar molecules or ions with permanent diploes can generate the spontaneous electric polarization, and aligning them causes the ferroelectricity, i.e., the ordered orientations of dipole moments below a critical temperature (Curie temperature, Tc) are in the ferroelectric state, whereas the random directions indicate the paraelectric state (such as $NaNO_2$, Figure 5a. i). (ii) *Displacive* type, where the spontaneous electric polarization can be induced by the relative displacement of ions. That is, an ion can be slightly displaced from the equilibrium position due to the subtly unbalanced electrostatic attractive and pulsion force between ions for structure instability, which produces the spontaneously lattice deformation with an asymmetrical shift and leads to a permanent dipole moment (such as $BaTiO_3$, Figure 5a. ii).(iii) *Proton transfer* type, where the ferroelectricity of the lattice is triggered by the collective-ordering proton dynamics on hydrogen bonds. For example, in the KH_2PO_4 (KDP) family, the spontaneous polarization can be reversed by the protons transferring from site to site on the O-H···O bonds along one direction (Figure 5a. iii). In the supramolecular ferroelectrics with two or more components, the *displacive* and *proton-transfer* mechanisms have been successfully applied and two types of multicomponent compounds have been designed and well explored: charge-transfer complex and proton donor-acceptor compounds with intermolecular hydrogen bonds.

Charge-transfer complex. A CT complex with a partially transferred electron between donor and acceptor has provided an effective route to organic ferroelectrics by displacing oppositely charge species. The ferroelectricity is always found in a mixed stack motif, because it can form one-dimensional chains with donors (D) and acceptors (A) assembled in an alternatingly face-to-face stack. The originally nonpolar DA DA DA… sequence with equally spaced apart (centrosymmetric) can be distorted by a reversible Peierls instability, where the symmetric periodicity can be broken by the movement of donors and acceptors relative to one another along the stacked axis and the macroscopic polarization can be emerged with the formation of the dipolar DA dimers (such as DA. DA. DA…). The external field can further induce the dynamic switching of the dimerization pairs (such as D. AD. AD. A…) and trigger the polarity reversal of the crystal (Figure 5b).

The most systematically investigated ferroelectric CT complexes are the TTF-quinone-based system, for example, the complex based on TTF and CA (*p*-chloranil, CA).[53, 80] In this system, a valence transformation between the neutral and ionic (NI) solid phases is happened when decreasing the temperature and induces the formation of DA dimers (room temperature: neutral, paraelectric; below 81K, ionic, ferroelectric). The dimerization process is also accompanied with the lattice transition from monoclinic $P2_1/n$ group to the polar one (space group Pn). The molecular displacement and rearrangement of the molecular-charge distribution have polarized the CT chain into the ionic/ferroelectric phase (Figure 5b. ii). Besides, molecular deformation with one of the components spontaneously bent can also break the symmetry and trigger to dipolar DA chains (Figure 5b. i).[81a] In addition, very recently, a cocrystal of acenaphthene (AN) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) has been reported to be room-temperature ferroelectricity by forcing the lattice from centrosymmetric $P2_1/c$ phase into a polar Pc space group (Tc = 341K).[81b] Interestingly, the lattice shift is a result of the AN rotation but not the NI transition. Although it has been well manifested the advantages of the supramolecular design in its modularity to form new CT ferroelectrics, there still exist many challenges for the CT complex. The most severe drawback is the electric leakage of the CT compounds as the narrow charge gap for NI transition induces the large dielectric loss, which would degrade the spontaneous polarization and hamper ferroelectric applications. Nevertheless, it has been found that hydrogen-bonding interactions can well alleviate the dielectric loss and thus incorporating other non-covalent interactions (such as hydrogen bonding) instead of CT interaction to trigger non-centrosymmetric structures is vital and promising.[27]

Hydrogen bonded compounds. The proton transfer between alternating acid and base mediated by intermolecular hydrogen bonds can create a dipole along the linear chain and play a crucial role in crystal ferroelectricity. In this approach to induce ferroelectricity, there have been reported two well-designed and -studied prototypical cases. The one is the neutral system with the simply hydrogen-bonded nonpolar molecules and a prominent example is the binary cocrystal based on chloranilic acid or bromanilic acid (H_2ca or H_2ba) with phenazine (Phz).[13] In Phz-H_2xa compounds (Figure 5c. i), the molecules are structurally symmetric and electrically neutral without the acid-base proton transfer at room temperature, which owes to the equivalent pKa of the acid and base to ensure the hydrogen equally shared (Phz: pK_1 = 1.20; H_2ca: pK_1 = 0.73, H_2ba: pK_1 = 0.80). Whereas at temperature below Tc, the ferroelectric lattice is produced with the elongation of the thermal ellipsoid of O-H···N and the spontaneous polarization is triggered accompanying with the lattice symmetric change from space group $P2_1/n$ to polar $P2_1$ group. But note that, instead of the proton transfer from site (O) to site (N), the protons all retain the neutral O-H···N. It is the

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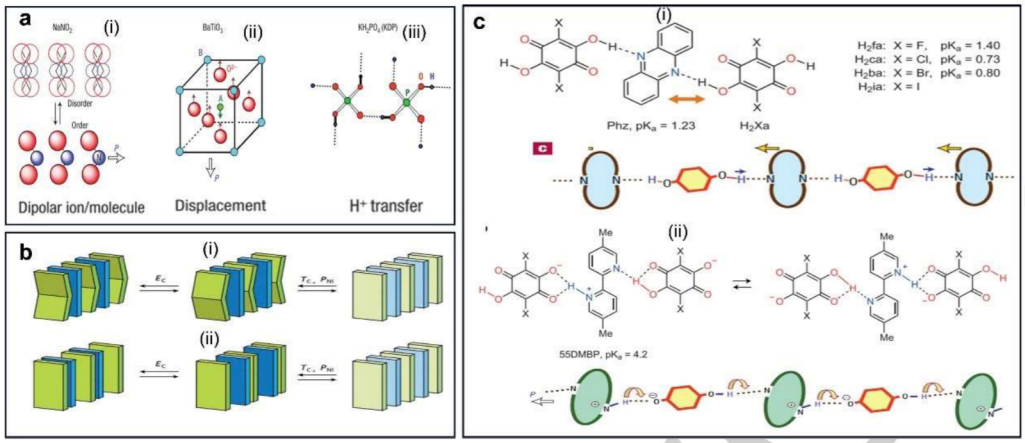

Figure 5. (a) Conventional mechanisms in designing the ferroelectricity and the correspondingly typical examples of inorganic materials (*P*: dipole moment or polarization) Reprinted with permission from Ref.[79a]. Copyright 2008 Springer Nature. (b) Two typical mechanisms of displacive ferroelectricity in CT complex: (i) molecular deformation, (ii) molecular displacement. The polarization can be reversed by applying an external electric field (*E*c: coercive electric field; P_{NI}: NI transition pressure). Reprinted with permission from Ref.[81b]. Copyright 2018 Wiley-VCH. (c) (i) A neutral system with the simply hydrogen-bonded nonpolar acid-base cocrystal, such as Phz-H_2xa compounds. (ii) An ionic supramolecular system of 55DMBP-H_2xa. The protonation of acid and base from the proton transfer in hydrogen bond can trigger the ferroelectricity. Reprinted with permission from Ref.[79a] and Ref.[79b]. Copyright 2008 and 2015 Springer Nature.

disproportionation of hydrogen bonds through hydrogen atom deviating the central position of O–H···N to elongate O-H bond and reduce H···N distance that generates the molecular displacement and thus results in the displacive-type ferroelectricity. In contrast, when the pKa of components is significantly distinct, the site-to-site proton transfer reaction would occur, and it can induce the polarization of the chain in the hydrogen-bonded direction. This ionic supramolecular system can be afforded a ferroelectricity as in the case of 55 DMBP (pKa = 4.2) and H_2ia (Figure 5c. ii).[82] In this case, the proton transfer from acid to base generates a polar chain with alternating O-H···N and N-H^+···O^- bonds in the same direction at temperature below Tc. When applied an external electric field, the chain can reverse the polarity with the simultaneously proton-transfer process. Whereas, at temperature above Tc, the disordered state of the protons in the O-H···N and N-H^+···O^- forms makes it paraelectric. Therefore, the ferroelectricity is derived from the order-disorder dynamics of protons.

Apparently, the co-crystallization engineering has provided an efficient route to design and synthesize new organic ferroelectrics. Moreover, it occupies an increasingly important role in both academic and technological development with the superior advantages in fabricating flexible, lightweight, large-area and low-cost organic devices.

3.5 Multiferroic properties

Multiferroics, firstly proposed by H. Schmidt in 1994,[83a] are a type of materials exhibiting more than one of the ferroic orders, like ferromagnetism, ferroelectricity and ferroelasticity in the same phase. In recent years, this term is always referred to magnetoelectric multiferroics simultaneously with ferroelectric and ferromagnetic states in single- or multicomponent materials, in which a proportional polarization (magnetization) can be induced by an external magnetic (electric) field (Figure 6a). Apparently, it has become a vital and burgeoning field because it is possible to exploit both states of magnetization and polarization in one material and their coupling effects can also trigger novel functionalities that do not exist in either state alone, which can facilitate the development of faster, smaller and energy-efficient data-storage technology. [83b] For conventional inorganic multiferroics, several mechanisms have been proposed to describe the coexistence of ferroelectricity and ferromagnetism as follows[83c, d]: (1) *Lone-pair active multiferroics*, in which the ferroelectricity comes from the spatial asymmetry induced by the anisotropic distribution of unbonded valence electrons (lone pairs or dangling bonds) around A sites. (2) *Geometric ferroelectricity*, where it is the steric effects (a rotational distortion of the polyhedra) rather than the bond chemistry that induces the ionic shifts and the polar ferroelectric state formation. (3) *Charge ordering*, where the valence electrons are non-uniformly localized on different cation sites in an ordered pattern to form a periodic superstructure. (4) *Spin-driven mechanism*, in which the interaction of spin and charges can drive the long-range magnetic order (non-centrosymmetric) to trigger the macroscopic electric polarization. In comparison, the research on organic multiferroics relatively lags, and the actual and systematic mechanism on the organic multiferroics is still in infancy although they have retained the remarkable progress and significantly potential impact. One very important route towards organic magnetoelectric multiferroics is through the charge-transfer behavior, where the spin polarization would be induced by the collectively intra- or inter-molecular charge transfer between donors or/and acceptors with ordered crystalline networks and noncovalent interactions in a specific direction. Here, we will describe several representative examples of the recently investigated all-organic multiferroics with magnetoelectronic coupling as follows.

The first predicted organic CT compound with magnetoelectric coupling is TTF-CA,[84a] which has been widely investigated in ferroelectric applications. Later, in 2010, Kagawa *et al* reported the first experimentally all-organic multiferroic material, TTF-BA (tetrathiafulvalene-*p*-bromanil), with one-dimensional quantum magnets, as a typical CT complex for the spin-driven ferroelectricity.[84b] Different from the well-known mechanism of emerged ferroelectricity induced by the specific magnetic order with spin-frustrated magnets, the magnetoelectricity is triggered by the spin-Peierls instability. As seen in Figure 6b, TTF-BA adopts two $D^+A^-D^+A^-$…mixed stacks along *a* and *b* axes

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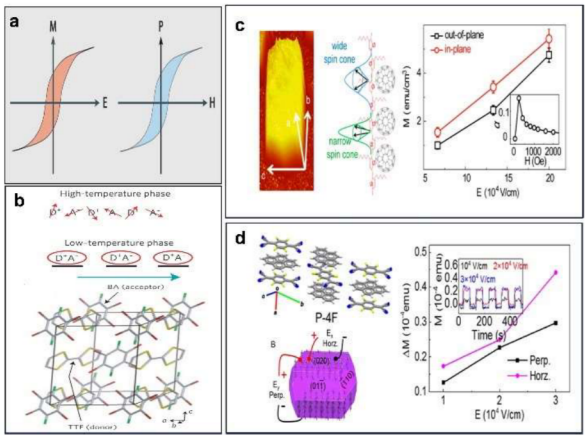

Figure 6. (a) Schematic of typical magnetoelectric multiferroics in multiferroics. Reprinted with permission from Ref.[83d]. Copyright 2016 Springer Nature. (b) Schematic of D+ A- … mixed stack of TTF-BA in high- and low-temperature phases (The arrow: spin -1/2, underline: a dimer, ellipsoid: a singlet state and P: electric polarization) (top); Crystal structure of TTF-BA (bottom). Reprinted with permission from Ref.[84b] Copyright 2010 Springer Nature. (c) Schematic of spin cone distribution due to the exciton-lattice coupling (left); Electric field dependent magnetization (M: magnetization; inset: magnetic field dependent magnetoelectric coupling coefficient; right). Reprinted with permission from Ref.[84d]. Copyright 2015 American Chemical Society. (d) Crystal packing and schematic of applied electric field on Pyrene-F4TCNQ cocrystal (left). Electric field dependent magnetization (inset: perpendicular electric field dependent magnetization; right). Reprinted with permission from Ref.[84e]. Copyright 2018 American Chemical Society

respectively with both dimerization occurrence and this ionic D^+A^- stack can be regarded as one-dimensional Heisenberg chain with 1/2 spin. When below Tc (53 K), a 1D polar chain would be realized *via* dimer-singlet formation with the space group change from nonpolar (P-1) to polar (P1). The vanish of spontaneous polarization with the suppression of singlet state by a magnetic field further proves that the D^+A^--dimerized ferroelectricity is primarily due to the spin-Peierls instability. Another typical organic multiferroics system is C_{60}-based CT complex, in which C_{60}, with characteristics of high-level electronic structure, low symmetry and essential polarizability,[84c] acts as an acceptor. Qin *et al* have explored a room temperature CT multiferroics with hierarchical thiophene crystalline nanowire and well-ordered fullerene (Figure 6c).[84d] The observed room-temperature magnetoelectricity comes from the tunable ratio of singlet and triplet charge transfer (with a small exchange interaction) by an external magnetic field. Namely, the external magnetic field can induce less spin mixing with more triplet excitons generation, which can effectively enhance the dipole density of the CT complexes due to their longer lifetime (more than microseconds). The magneto-dielectric effect is observed due to that the spin-triplet excitons can scatter the carriers in CT complex, which induces the decreased conductance. Besides, the strong exciton-lattice coupling generated from the molecular assembly and spin cone orientation can also result in the anisotropic magnetization. Note that, very recently, Yang *et al* have found that the F_4TCNQ-based CT complex can also afford a room temperature magnetoelectricity (Figure 6d).[84e] Investigation shows that Pyrene-F_4TCNQ owes anisotropic magnetoelectric coupling with the coupling coefficient along the π-π stacking direction is much stronger than others. Besides, the Cotton-Mouton effect is also obtained in the CT complex, indicating the potential application in optomagnetic devices.

Despite with substantial achievements on the organic multiferroics, there still exist a lot of problems, for example, the exploration of new charge-transfer systems with improved magnetoelectric coupling effect, the investigation and invention of the systematic mechanisms of magnetoelectricity in CT multiferroics to guide the synthesis of new compounds, and the application of organic multiferroics in the actual industrial production.

3.6 Optical Waveguide

As we all know, organic crystals with distinctive shapes and smooth crystal planes can be used as active optical waveguide resonators, which provides a novel platform for the optical confinement.[85-93] Compared with 1D organic crystals, 2D crystals can transfer photons along different directions, making them much more suitable for applications in optical planar diodes,[85a,b] a whispering-gallery-mode (WGM) resonator including controlling directional waveguides[86] and organic crystal lasing.[87] While very limited organic molecules present 2D self-assembly behaviors for a single component material, greatly impeding the development of 2D organic photonics and electronics.[88] Therefore, multi-component cocrystals with 2D self-assembly crystallization behaviors have been developed, in which anisotropic noncovalent interactions (hydrogen/halogen bonds and D–A interactions) are introduced to finely tuning the cocrystal structures via choosing an suitable co-precursors.[1,89-92] On the other hand, as mentioned in the beginning, the cocrystals can also exhibit versatile optoelectronic properties that cannot be obtained in single component.[90]

Hu et al.[1] prepared 2D Bpe-F4DIB cocrystal, which stacks in a mixed stacking mode without CT interactions and are confirmed to be insulators. Moreover, the cocrystals demonstrate two-dimensional optical waveguide property and unique white light emission (Figure 7a and e). The same year, a CT Bpe-TCNB

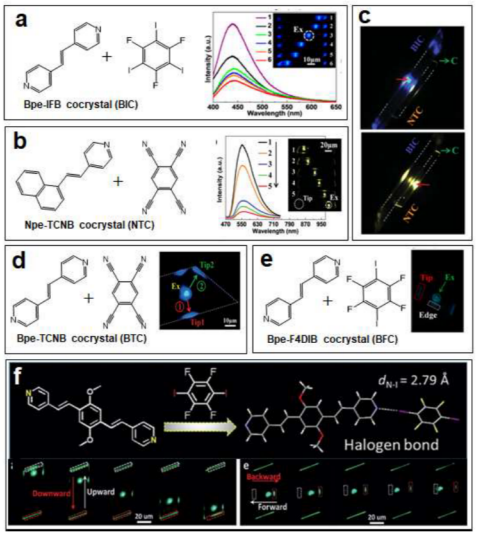

Figure 7. Optical waveguide properties of BIC (a), NTC (b), cocrystal waveguide couplers from BIC and NTC (c), optical waveguide properties of BTC (d) and DPEpe-F4DIB (f). Reprinted (adapted) with permission from [1], [90], [93], [91]. Copyright 2015 American Chemical Society, 2016, 2015, 2018 Wiley-VCH, respectively.

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cocrystal with unique 2D parallelogram-like morphology motivated by CT, π–π, -N···HC interactions was reported.[93] The excited PL can propagate in the 2D cocrystal without anisotropy, which means the optical waveguide property of Bpe-TCNB cocrystal is not related to the molecular packing structures (Figure 7d). Then, the authors changed Bpe to 4-(1-naphthylvinyl) pyridine (Npe) and obtained ribbon-like cocrystals Npe-TCNB (Figure 7b).[90] The weak CT_1 excitonic PL of Npe-TCNB can efficiently propagate along this ribbon optical waveguide with R = 0.040–0.11 dB μm^{-1}. More interestingly, and interfacial white emission made up of the ones from individual two-component cocrystals was found due to the energy transfer from Bpe-TCNB to Npe-TCNB induced by the spectroscopic matching, which is the first case that different photons are mixed in "cocrystal waveguide coupler" to generate white emission (Figure 7c). More recently, F4DIB and 4,4'-((1E,1'E)-(2,5-dimethoxy-1,4-phenylene)bis(ethene-2,1-diyl))dipyridine(DPEpe) were chosen to fabricate 2D halogen-bonded parallelogram cocrystals, which present asymmetric optical waveguide with optical-loss coefficients of $R_{Forward}$ = 0.0894 dBμm^{-1} and $R_{Backward}$ = 0.0346 dB μm^{-1} along the [010] direction (Figure 7f).[91] The 2D cocrystals are presented as micro optical logic gate containing multiple input/out channels based on their packing direction-oriented asymmetric photon transport, which may provide potential applications of the 2D cocrystals for the integrated organic photonics. Above contributions are an important step on the long way to organic optical computing and integrated photonic circuitry.

3.7 Stimuli-responsibility

Solid-state co-crystals assembled from multiple components can be served as good systems for controlling and switching the bulk properties by external perturbations,[94] because the photo-/solvent-/pH-/thermal-active co-components as well as the relative weak noncovalent interactions between the co-formers can be further tailored via grinding, mechanical and temperature stimuli.[4,95] Such dynamic materials can provide exiting advantages because selected properties (such as luminescence and shape) can be turned "on" and "off" reversibly, and may lead to applications in a broad range, e.g., electronic display and information storage systems, smart sensors/switches, optical switching devices, memory devices, and nonlinear optics.[96-98] Up to now, even if the co-crystals have been largely used to change their static properties,[99] how to further investigate dynamic multi-functional materials remains a challenge.

3.7.1 Stimuli-responsive luminescent cocrystals

Stimuli-responsive luminescent materials have recently attracted enormous attention due to their easy recognition, highly sensitive signal response, and visualization.[100,101] However, how to rationally tailor the environment of the molecules within molecular solids so as to obtain a desired stimuli-responsive photophysical properties remains a challenge.[102] In addition, the research of multiple-stimuli responsive luminescent crystals remains an early stages.[103] In this text, multi-component co-crystals can be served as an ideal system for the tailoring of dynamic non-covalent interactions.[4,95,104] Based on these points, the stimuli-responsive luminescent cocrystals are expected to be developed, which can present different emission under external stimuli.

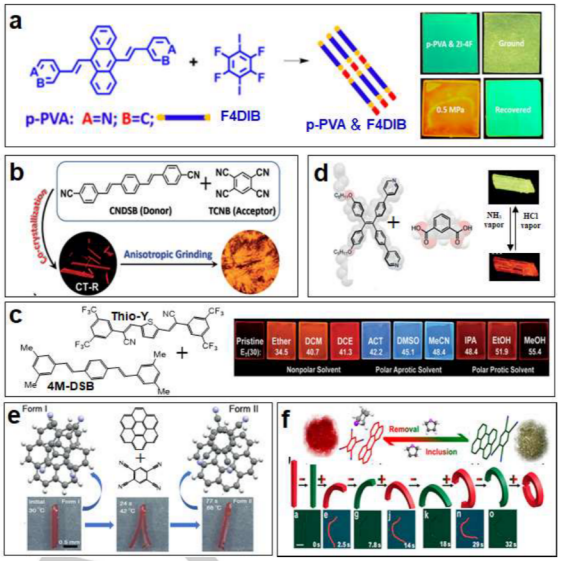

Figure 8. Stimuli-responsibility of organic cocrystals. (a) Piezochromic properties of p-PVA&F4DIB. (b) Grinding induced tuning emission of CNDSB-TCNB cocrystal, (c) solvent-responsive tuning emission of 4M-DSB &Thio-Y, (d) tunable emission of TPE-Py & m-phthalic acid cocrystal via acid or base. (e) Thermo-Mechanically Responsive behavior of coronene-TCNB cocrystal, (f) Solvato-mechanically bending behaviors of perylene-TCNB cocrystal. Reprinted (adapted) with permission from [98], [105], [108], [106], [29] and [113]. Copyright 2017 American Chemical Society, 2018, 2016, 2015, 2016, 2018 Wiley-VCH and 2018 American Chemical Society respectively.

The most commonly used stimuli are mechanical stimuli. Zhao et al.[98] developed two piezochromic assemblies based on pyridylvinylanthracenes (p-PVA) and F4DIB for haptic memory (Figure 8a). The change of the fluorescent color induced by different pressure is reversible, e.g. the piezo-chromic response can be recovered to the original state upon mild heating treatment. Very recently, an organic CT cocrystal CNDSB-TCNB (CNDSB, 1,4-bis-p-cyanostyrylbenzene) with different luminescent responses to different mechanical stimuli (isotropic compression and anisotropic grinding) was reported (Figure 8b).[105] Grinding leads to the structural rearrangement from segregated stacking to mixed stacking, and hence results in an enhanced and blue-shifted emission. While hydrostatic pressure results in a remarkable red-shifted emission, due to the closer stacking. Solvent vapor treatment can also initiate the change of luminescence of a crystalline mixture. For example, Park and coworkers [106] reported that the luminescence of a crystalline D-A mixed film (distyrylbenzene-based donor and dicyanodistyrylthiophene-based acceptor) can blue-shift from 658 nm to 472 nm attributed to the structural transformation from a mixed stacking into segregated phase when treated with solvent vapor annealing, which can recover the original color once grinding or thermal stimuli (Figure 8c).

In addition, acid-base stimuli-responsive behaviors have also been reported in cocrystals.[43,107,108] For instance, a cocrystal assembled by 4-[2-(4-quinolinyl)vinyl]phenol and tetrafluoroterephthalic acid with tunable luminescence and acid-base stimuli-responsive properties was reported.[107] The photoemission intensity of the cocrystal change from weak to strong upon acid fuming and can be reversible when exposed in base. Besides, Zheng et al.[108] reported cocrystals based on TPE derivatives bearing pyridine rings and m-phthalic acid. The

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emission of the co-crystals is reversible between red and yellow via alternating exposure to ammonia and HCl vapor (Figure 8d).

There also have been a few reports about multi-stimuli responsive solids materials. N-Salicilideneanilines are one of the most studied photo- and thermo-chromic systems in solid state.[109,110] Yan and coworkers[65] prepared three cocrystals (donor, cyanostilbene-based isomers, CS1, CS2, CS3; acceptor, 1, 4-bromotetrafluorobenzene carboxylic acid, OFN, and 1,4-diiodotetrafluorobenzene) with solvent-responsive luminescence. Moreover, CS2-OFN presents reversible fluorescence once alternating grinding and light illumination. More recently, Yan et al.[43] chose (naphthylvinyl)pyridine as donor, 1,4-diiodotetrafluorobenzene, 4-bromotetrafluorobenzoic acid and 4-benzoylbenzoic acid as acceptors. The as-prepared cocrystals present stimuli-responsive luminescent switches with reversible transformations upon external stimuli (such as base vapor and heating).

3.7.2 Stimuli-responsive mechanical -deformation of cocrystals

Stimuli-responsive mechanical -deformation of cocrystals are attracting increasing interest because their shape can be turned "on" and "off" reversibly (Figure 8 e and f),[10,29,111-113] which may lead to applications in smart sensors/switches and memory devices. Irie and coworkers [10] reported the photo-mechanical behaviors of rectangular cocrystal composed of OFN and a photochromic molecule, 1,2-bis(2-methyl-5-(1-naphthyl)-3-thienyl)perfluorocyclopentene. The cocrystal exhibits reversible bending behaviors upon alternate irradiation with visible light and ultraviolet (UV), which is motivated by the shape change of diarylethene molecules upon photocyclization and can be repeated over 250 times. The generated maximum stress by UV irradiation is ~ 44 MPa, which is 100 times larger than that of a muscle and even comparable to that of crystalized piezoelectric materials. Flexible molecular cocrystals with stimuli-responsive behaviors are highly desirable. Herein, Yan and coworkers [111] reported an elastic molecular crystal (based on naphthylvinylpyridine and tetrafluoroterephthalic acid) that present light-stimuli fluorescence changes as well as dynamic mechanical responses at a macro-scale level. Zhang et al.[29] amplified the molecular-level motions of CT cocrystals based on coronene and TCNB into macroscopic scale. The resulting cocrystals present remarkable thermo-mechanical responses and self-healing behavior during thermally motivated reversible single-crystal-to-single-crystal phase transitions due to the changes of molecular orientations and stacking sequence (Figure 8e). More recently, Hu et al.[113] reported a solvato-mechanical bending behavior for the first time (Figure 8f). In this work, a solvated (perylene-TCNB)·2THF cocrystal was used, which can reversibly transform into perylene-TCNB cocrystal upon successive desorption or absorption of THF vapor, resulting in a macroscopic mechanical bending. Another recent report is the first example of a smart cocrystal based on probenecid and 4,4'-azopyridine, which can reversibly respond to multiple stimuli (UV light, heat, and mechanical pressure) via elastic deformation, twisting, and bending without fracture.[112] Such results are attributed to reversible crystal-to-crystal phase transition and trans–cis isomerization of the azopyridine unit and interlocked crisscrossed molecular packing and isotropic intermolecular interactions lead to a high elasticity of the cocrystal. Inspired by above research works, we believe that more kinds of stimuli-responsive CT cocrystals may be designed and constructed via judiciously selecting donors and acceptors, which may further extend the applications of CT materials.

3.8 Other properties

In addition to above-mentioned performance, there are many other properties that have been reported for organic cocrystals, such as nonlinear optical (NLO) properties of Spe(4-styryl-pyridine)-F4DIB, Npe-F4DIB and Spe-TCNB cocrystals (Figure 9a and b),[89,114] energetic–energetic cocrystals based on 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and 2,4,6-trinitrotoluene (TNT) [115] as well as diacetone diperoxide and trihalotrinitrobenzene explosives,[116] elastic and bendable cocrystals formed by caffeine and 4-chloro-3-nitrobenzoic acid,[117] mechanical properties of cocrystals consist of resorcinol or 4,6-diX-res (X = Cl, Br, I) and Bpe,[118] near-infrared photothermal conversion and imaging of DBTTF-TCNB cocrystal (Figure 9c),[39] and so on.

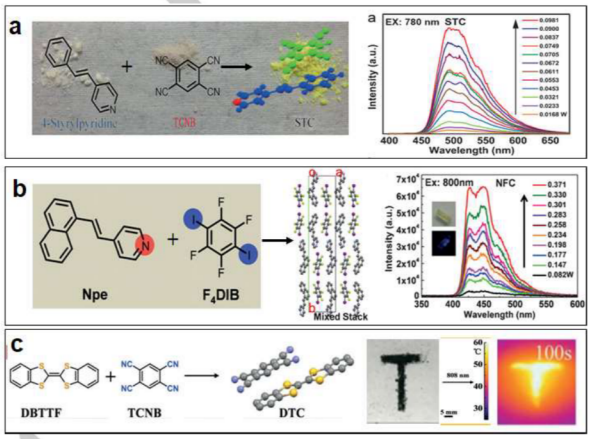

Figure 9. Other properties of organic cocrystals. Nonlinear optical properties of STC (a) and NFC (b), Near-Infrared photothermal conversion and imaging of DTC (c). Reprinted (adapted) with permission from [114], [89] and [39]. Copyright 2017, 2016, 2018 Wiley-VCH, respectively.

4. Summary and Outlook

Organic cocrystals based on noncovalent intermolecular interactions (such as CT interactions, π–π stacking, halogen and hydrogen bonds) have attracted increasing attention due to unpredicted and versatile chemicophysical properties and charming applications. In this review, we highlight several recent researches of organic cocrystals on reducing ACQ effect, tuning light emission, ferroelectricity, multiferroic, optical waveguide and stimuli-responsibility. We can draw a conclusion that great progresses including revealing the structure–property relationships and developing exciting properties have been made in this field. However, there are still long-standing critical challenges existing in this new field. Firstly, the basic interaction mechanism and principles during co-crystallization are not very clear, not every pairs of donor and acceptor can self-assemble together, and, how to rationally select appropriate molecules for efficient co-crystallization and how diverse co-formers structural match, co-assemble and crystallize need to be figured out. Secondly, the relationships between crystal structures and the resulting performance, the CT within cocrystals connecting with lattice stability, optoelectronic and photophysical properties, as well as the mechanism of electronic interaction between building

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blocks, remain elusive, which greatly impedes the regulation of cocrystals properties. In this case, effective tuning of cocrystals properties via designing and controlling the definite stoichiometric ratio, molecular stacking mode, orientation, crystal phase and morphology remains at an early stage and a long-standing problem. Thirdly, the investigations in reducing ACQ effect, optical waveguide properties, ferroelectricity, multiferroic, two-photon absorption properties are still in its infancy, which needs to be further explored. In addition, it is essential for researchers to break through the old donors or acceptors and find more novel molecules, which may introduce some novel properties. Lastly, based on the development of cocrystals, we should explore most of their properties and find their potential applications. We strongly believe that, with our joint effort, organic cocrystals will possess an excellent prospect.

Acknowledgements

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Keywords: Organic cocrystals • reducing ACQ effect • tuning light emission • ferroelectricity • multiferroic • optical waveguide • stimuli-responsibility.

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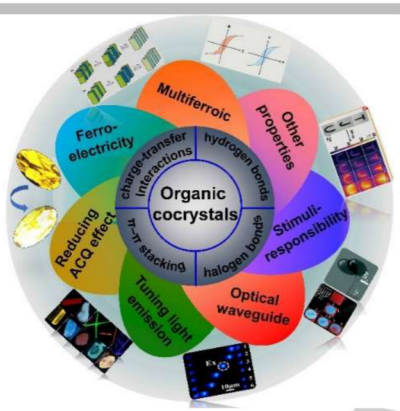
MINIREVIEW

Organic Cocrystals: This review provides a summary on current achievements (reducing ACQ effect, tuning light emission, ferroelectricity, multiferroic, optical waveguide and stimuli-responsibility) of organic cocrystals, limitations and perspectives as well as some directions and inspiration for further investigation on organic cocrystals.



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Towards Emerging Properties and Applications of Organic Cocrystals Beyond Electrical Conductivities and Field-Effect Transistors (FETs)

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