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REVIEW

Molecular doped organic semiconductor crystals for optoelectronic device applications

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As for semiconductors, doping is an efficient approach to tune their energy bandgap, charge transport and optical properties which enables the improvement of corresponding performances and also the possibility of multifunction integration. Recently, significant advances have been achieved for molecularly doping organic semiconductors, especially doped organic semiconductor single crystals (OSSCs) which have features of well-defined packing structure, long-range molecular orders and low-density defects for fundamental studies and improved properties. In this miniRev, we will give a summary of these exciting progress for molecular doped OSSCs from the aspects of selection criteria of molecular dopants, the general growth method, resulting in optoelectronic properties and their applications in optoelectronic devices. Finally, a brief conclusion is given with challenges and perspectives of molecular doped OSSCs and some possible promising research directions in this field.

1. Introduction

In today's microelectronics industry, doping is a key strategy for modulating the electrical property of inorganic semiconductors, thus to meet the application demands. Doping an inorganic semiconductor may allow changing energy level alignment at interfaces between the doped materials and the metal contacts, which can significantly increase their conductivity even with ultralow doping ratio.[1,2] In organic optoelectronic devices that have unique features of lightweight, low cost as well as large-area production ability, similarly, doping organic semiconductor has also been shown as a valuable approach to improve their electrical and optical properties,[3-5] and also with the possibility of integrating multi-functionalities simultaneously while that is difficult to be achieved from simple chemical synthesis.[4,6-8] Currently, various doped organic semiconductors have been developed and demonstrated potential applications in devices of organic field-effect transistors (OFETs),[9-11] organic light-emitting diodes (OLEDs),[12,13] organic light-emitting transistors (OLETs),[8,14] organic thermoelectricity,[15-17] and other optoelectronic devices.[18-23] Basically, doping in organic semiconductors can be distinguished into two different aspects based on their induced effects: electrical doping and host-guest doping. In the electrical doping system, charge transfer occurs between dopants and organic semiconductors. As shown in Fig. 1a, n-type doping is a dopant added into the organic semiconductor which donates an electron to the lowest unoccupied molecular orbital (LUMO) of organic semiconductor, while p-doping dopant extracts an electron from the highest occupied molecular orbital (HOMO) of the organic semiconductor. It has been shown that the conductivity of organic semiconductors can be improved via electrical doping with the increase of conductivity in several orders of magnitude.[24-26] Host-guest doping is another effective way which is usually used for tuning the light emission characteristics of organic semiconductors through the energy transfer from the host molecules to guest molecules via Förster and/or Dexter process (Fig. 1b). Förster energy transfer is a long-distance, non-contact energy transfer mode with an effective transfer distance of 3-10 nm due to the dipole-dipole interaction between host and guest molecules. Overlap of the molecular orbital of host and guest molecules is required for Dexter energy transfer, which results in a short energy transfer distance of 1-2 nm. The existence of energy transfer between host and guest molecules is the basis and fundamental reason for the change of optical properties such as luminescent emission-efficiency, emission color and fluorescence lifetime of doped organic semiconductor.[27-29] Different from the doping in inorganic semiconductors, dopants used in organic semiconductors can be atomic, ionic and molecular species, etc.[30-32] Atoms tend to diffuse in organic semiconductors, rendering the doping effect unstable. This shortcoming can be overcome by using molecular dopants that are bulkier and do not diffuse in the host matrix, that is molecular doping in organic semiconductors, which has attracted increasing

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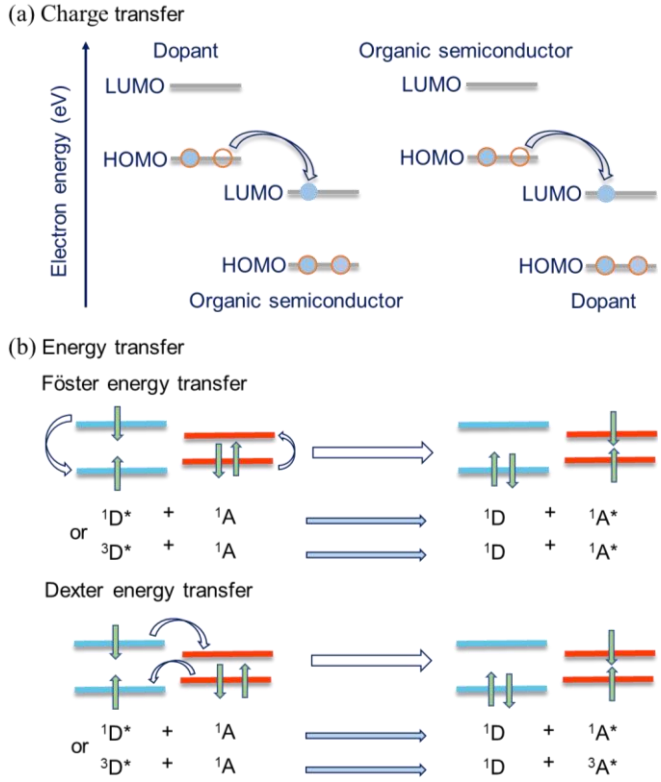

Fig. 1 (a) Energetic relationships between organic semiconductors and dopants in electrical doping. (b) Schematic illustration of Föster energy transfer and Dexter energy transfer in host-guest doping. The equations in the graph represent the corresponding energy transfer processes. A = acceptor; D = donor.

attention in recent years. Some excellent reviews have summarized the progress of molecular doping in organic semiconductor thin films from different aspects, such as doping mechanism, doping strategy and functional devices. [3,33-36] Except for organic thin films, currently some significant advances have also been achieved for molecular doped organic semiconductor single crystals (OSSCs)[4,8] which have been seen as the best candidates for fundamental studies and improved optoelectronic properties,[37-40] though this doping process is much difficulty in OSSCs systems.

In this miniRev, we will give a timely summary of these exciting progress on molecular doped OSSCs with special attention on their ability to tune the charge transport, optical property and integrated optoelectronic properties of OSSCs and their applications in OFETs, OLEDs and OLETs (Fig. 2). In this first section, we will give a brief illustration of the basic selection criteria of molecular dopants in organic semiconductors and the most widely used molecular dopant materials in this field, which is followed by the second part of the general growth methods for molecular doped OSSCs. Then, some representative examples will be shown to demonstrate the resulting tunable and improved optoelectronic properties of molecular doped OSSCs and their applications in devices. Finally, challenges and perspectives of molecular doped OSSCs and the promising research directions in this field are also discussed.

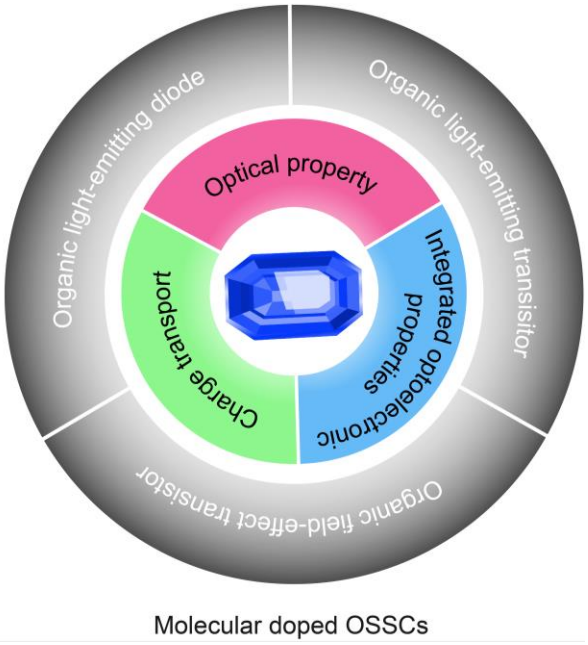

Fig. 2 Schematic illustration of the optoelectronic applications of molecular doped OSSCs.

2. Molecular doping in organic semiconductor crystals

2.1 Selection criteria of molecular dopants for OSSCs

There several requirements regarding the molecular dopants[29,41] for doping in OSSCs: i) The selected host and guest materials need to have similar physical properties, such as solubility or sublimation temperature. For the physical vapor transport (PVT) method, the similar sublimation temperature of the host and guest only requires one heating source in the preparation process. With solution processing, the similar solubility of host and guest materials in a common solvent is beneficial for the preparation of molecular doped OSSCs, because it is easy to obtain the uniform solution of donor and acceptor mixture. ii) The selected host and guest molecules need to have similar molecular configuration and size. This is favorable for the doping molecules to enter the host materials without lattice mismatch and loss of crystal mass. In the case of high doping concentration, the influence of molecular configuration and size is greater, even lead to the failure of doping. iii) The emission spectrum of the host molecule is required to overlap well with the absorption spectrum of the guest molecule to enable efficient energy transfer from host to guest molecules; In the charge transfer system, the energy levels between the host and guest should match well. For example, it is ideal that the LUMO level of the acceptor is above the HOMO level of the donor. According to these above criteria, many molecules have been developed and used in molecular doped OSSCs,[29,41] some of them are summarized in Fig. 3, and some of these are discussed in this miniRev. There is no doubt that the selection of the host and guest materials has a crucial

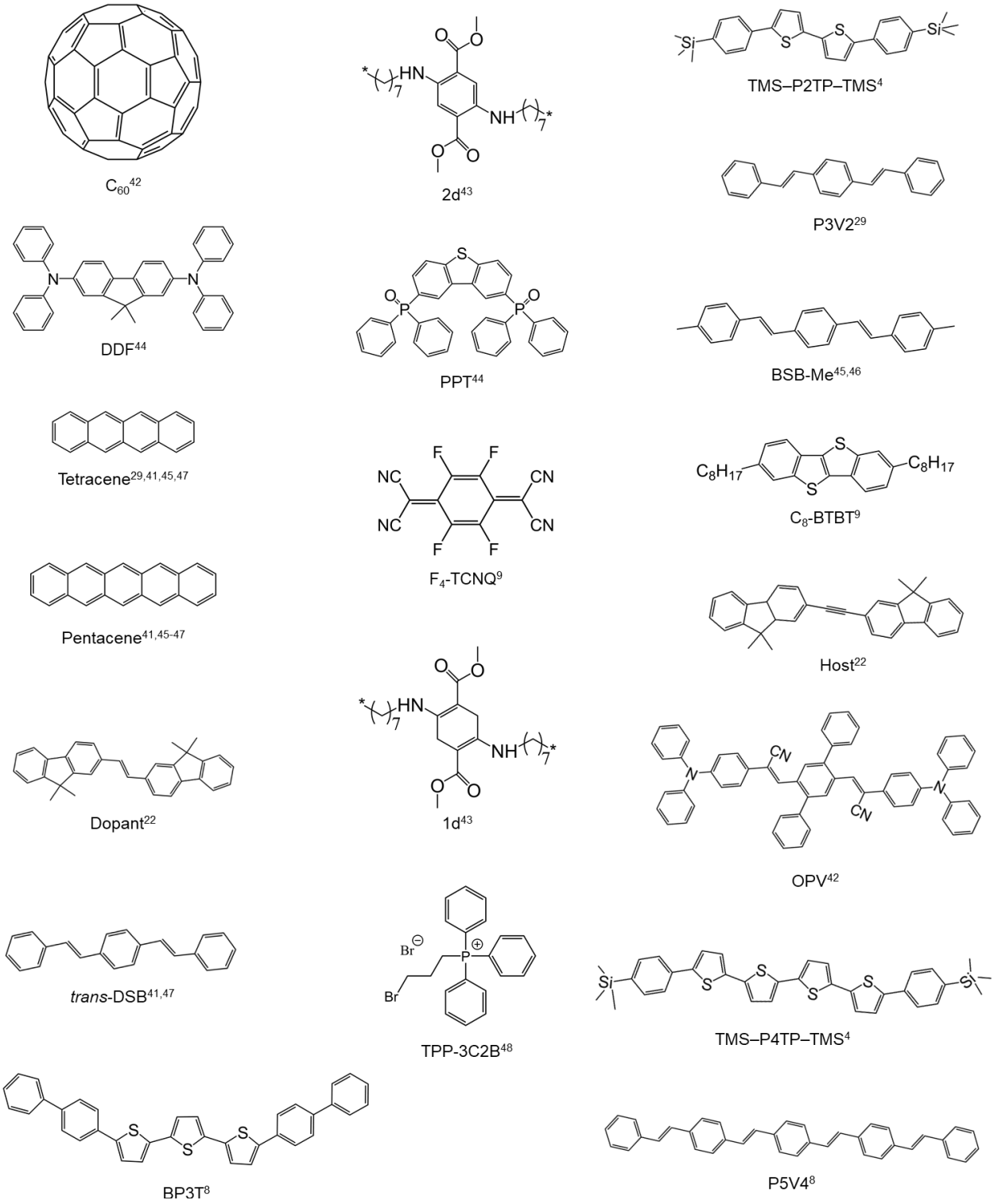

Fig. 3 The host and guest materials commonly used for molecular doped OSSCs in the literature.

influence on the preparation and property control of the molecular doped OSSCs. In fact, the lack of suitable host-guest materials and the difficulty in preparation of doped OSSCs restrict the wide applications of molecular doped OSSCs in optoelectronic devices.

2.2 General growth methods for molecular doped OSSCs

The choice of preparation method for doped OSSCs depends on the properties of the organic material. For example, organic materials with good solubility prefer solution methods to

prepare crystals, while materials with poor solubility but good thermal stability prefer the PVT method. Apparently, there are some differences in the quality, size and thickness of the molecular doped OSSCs prepared by different preparation methods. Here, we summarize the commonly used preparation technologies of molecular doped OSSCs in the literature.

The PVT method was first reported by Kloc et al. in 1997,[49] the principle of this method is to sublime the organic materials in the region with high temperature and transfer the gas-phase molecules to the low-temperature region by inert gas for crystals growth. Under the condition of high temperature, the molecules have higher kinetic energy, which is conducive to the impaction of guest molecules into the crystal lattice of the host molecules, resulting in a high-quality molecular doped OSSCs with a small lattice mismatch.[47] By controlling the time of growth, the flow rate of carrier gas, the temperature of crystals growth and other conditions, the thickness and size of the crystals prepared by the PVT method are relatively controllable. More importantly, the surface of the crystal prepared by PVT is very smooth. Therefore, the PVT method has been widely used in the preparation of active layers of various photoelectric devices. When the sublimation temperature of the acceptor and the donor is close, their powder samples can be evenly mixed and placed in the sublimation region for the preparation of doped crystals, as shown in Fig. 4a. In the case of the sublimation temperature of the acceptor and the donor is quite different, the acceptor and donor can be placed in the sublimation zone with different temperatures respectively, as shown in Fig. 4b. PVT method is an effective growth technology for materials with poor solubility but good thermal stability.

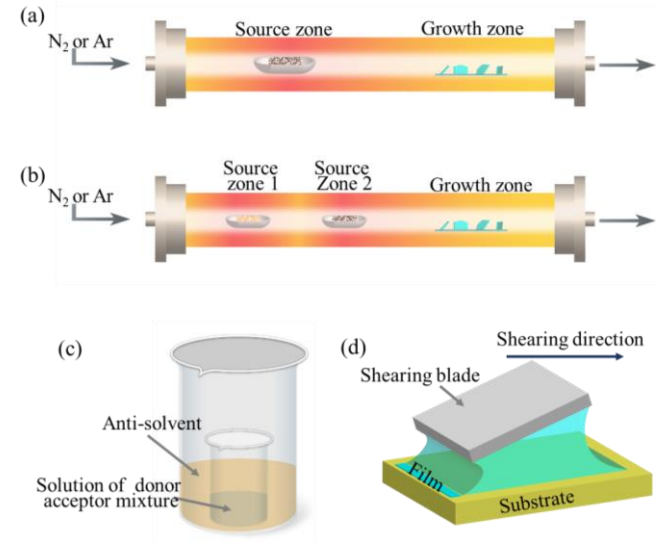

Fig. 4 Schematic diagram of crystal growth by PTV method with (a) the single-source zone and (b) the double-source zone. (c) Schematic illustration of crystal growth by solution method with double solvent. (d) Schematic diagram of crystalline organic semiconductor film produced by solution shearing.

There is an alternative growth technology for materials with good solubility. The principle of the solution growth method is to separate the precipitate from its solution to form the crystal. Here we take a common double solution method to grow crystals as an example, as shown in Fig. 4c. The mixed solution containing the host and guest molecules is placed in a closed beaker containing the anti-solvent. Through the exchange of good solvent and anti-solvent atmosphere, the solution will be supersaturated and the crystal grows up gradually.

Unfortunately, the size of organic crystals grown by the solution method and PVT method is limited and difficult to control accurately. Thus, the prepared crystals are not suitable for large-area optoelectronic devices fabrication as active layers. In 2008, the solution shearing method was first developed by Bao et al., showing great advantages of preparing large-area crystalline organic semiconductor film on the substrate surface.[40] The basic working principle of this technology is that the growth of crystalline organic semiconductor film on the substrate surface is controlled by the guidance of a shearing blade, as shown in (Fig. 4d). The movement of the blade relative to the substrate exposes the meniscus of the solution, allowing the solvent to evaporate, which is accompanied by the formation of crystalline organic semiconductor films. A large area of the crystalline organic semiconductor film can be obtained by controlling the size of the blade, optimizing the moving speed of the blade and substrate temperature. The operation procedure and application of this technology was described in detail in literature .[51-53]

3. The optoelectronic properties and device applications of doped OSSCs

3.1 The tunable properties of molecular doped OSSCs

From the point of view of molecular design and synthesis, the optical properties of materials can be tuned by the introduction of different kinds of functional groups,[54] but it is usually hard. Through the strategy of molecular doping, it is easy to realize the energy transfer from the host molecules to guest molecules for regulating optical properties, such as emission color, emission efficiency and exciton harvesting efficiency, etc. For instance, in 2009, Ma and co-workers successfully prepared the

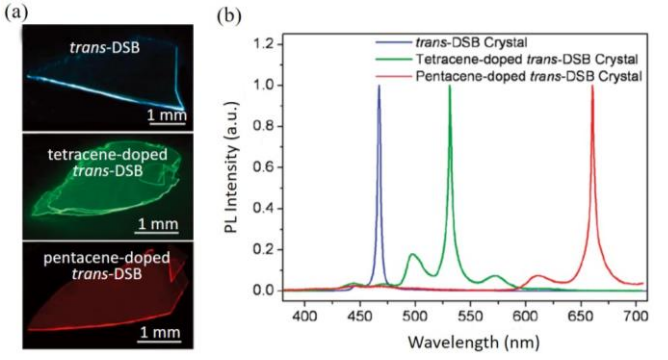

Fig. 5 (a) Representative fluorescence images and (b) ASEs spectra *trans*-DSB crystal, tetracene-doped *trans*-DSB crystal and pentacene-doped *trans*-DSB crystal. The chemical structures of *trans*-DSB, tetracene and pentacene are shown in Fig. 3. Reprinted with permission from ref. 47 Copyright 2009 American Chemical Society.

molecular doped crystals with *trans*-1,4-distyrylbenzene (*trans*-DSB) as the host and tetracene or pentacene as the guest.[47] The

similar crystal lattice structure of host and guest material was considered to be the key to prepare doped crystals with high doping concentration (10%), as shown in Fig. 5a. The obtained photoluminescence quantum yield of the tetracene-doped *trans*-DSB crystal and pentacene-doped *trans*-DSB crystal was up to 74 ± 4% and 28 ± 4%, respectively. The successful preparation of color-tunable doped crystals with high luminescent efficiency was attributed to: i) the guest molecules were well dispersed in the host molecules, which effectively restrained the quenching caused by aggregation; ii) the effective energy transfer between host molecules and guest molecules. Interestingly, these two doped crystals possessed the characteristic of amplified spontaneous emission (ASE), suggesting the potential application of molecular doped OSSCs in the laser devices, as shown in Fig. 5b. Inspired by this work, many organic crystals with color-tunable emission and high efficiency based on molecular doped OSSCs were reported.[29,41,45]

The organic laser has emerged in the recent year thanks to the rapid development of organic semiconductor materials with high modifiability.[55-57] However, the design and synthesis of efficient organic laser materials are still facing great challenges, even with the great efforts that have been made in this field.[58,59] Molecular doped organic semiconductor materials have attracted increasing research interest recently due to their tunable ASE property and emission color.[60,61] In 2019, Zhao and co-workers prepared doped organic crystals using C_{60} as host and cyano-substituted oligo-(*α*-phenylenevinylene)-1,4-bis(R-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene (OPV) as a guest,[42] as shown in Fig. 6a,b. The characteristic of broad spontaneous emission of C_{60}@OPV crystal was realized under low pump fluence. At the higher pump fluence, stimulated emission was realized, as shown in Fig. 6c,d. The color-tunable laser emission from C_{60}@OPV crystal can be tailored by controlling doping concentration precisely (Fig. 6e). These results provided valuable references and guidance for the design and synthesis of organic laser materials.

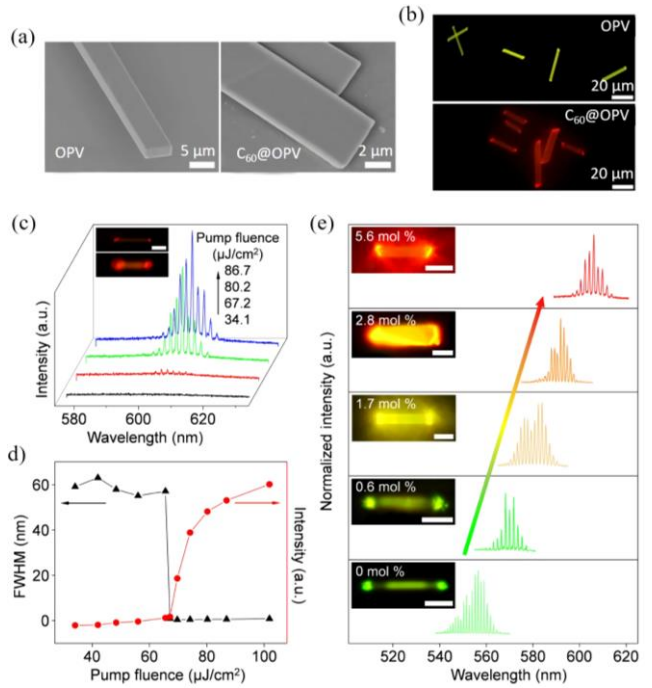

Fig. 6 (a) Representative SEM images of OPV crystal and C_{60}@OPV crystals. (b) Representative fluorescence image of OPV crystals and C_{60}@OPV crystals. (c) PL spectra of a typical C_{60}@OPV crystal. Scale bars, 10 μm. (d) Emission intensity and full width at half maximum (FWHM) as a function of pump fluence. (e) Normalized lasing spectra recorded from the C_{60}@OPV crystals with different doping concentrations. Scale bars, 10 μm. The chemical structures of OPV and C_{60} are shown in Fig. 3. Reprinted with permission from ref. 42 Copyright 2019 American Association for the Advancement of Science.

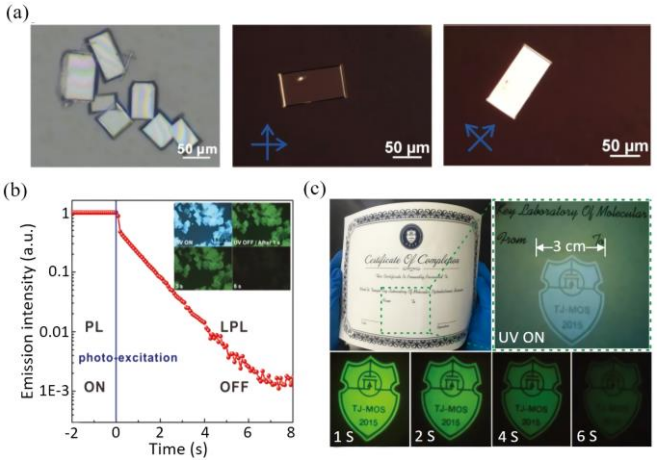

Fig. 7 (a) Optical microscope image and polarized microscope images of the PPT: DDF crystals. (b) Emission intensity map of PPT: DDF crystals over time (Inset: photographs of LPL from the PPT: DDF crystals under fluorescence microscope). (c) Photographs of LPL from the film based on PPT: DDF crystals. The chemical structures of PPT and DDF are shown in Fig. 3. Reprinted with permission from ref. 44 Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Generally, the preparation temperature of traditional inorganic long-persistent luminescence (LPL) materials is more than 1000 °C, and rare earth elements which are non-renewable resources are used, which greatly limits their applications.[62,63] Recently, Hu and co-workers successfully prepared a case of molecular doped OSSCs with the donor of 2,7-di-(N,N-diphenylamino)-9,9-dimethyl-9H-fluorene (DDF) and the acceptor of 2,8- bis(diphenylphosphoryl)dibenzo[b,d] thiophene (PPT), which possessed the characteristic of LPL with a continuation of more than 6 s under the excitation of low energy light, as shown in Fig. 7a,b.[44] The film based on doped crystal was prepared by screen-printing technology, and the visible light was still emitted from the film for up to 6 s after the excitation light was turned off, as shown in Fig. 7c. It implies that the great application prospect of molecular doped crystals with the characteristic of LPL in fields of bioimaging and anti-counterfeiting. More recently Tang and co-workers successfully prepared a case of molecular doped OSSCs with the electron donor of *N,N*-dimethylaniline and the acceptor of TPP-3C2B (Fig. 3). The as-synthesized TPP-3C2B: DMA possessed the characteristic of LPL with a continuation of up to 7 h which remarkably long than other reported organic LPL systems. The excellent LPL performance of TPP-3C2B: DMA is attributed to the simultaneous use of TPP-3C2B as a strong electron acceptor and multiple protective traps.[48]

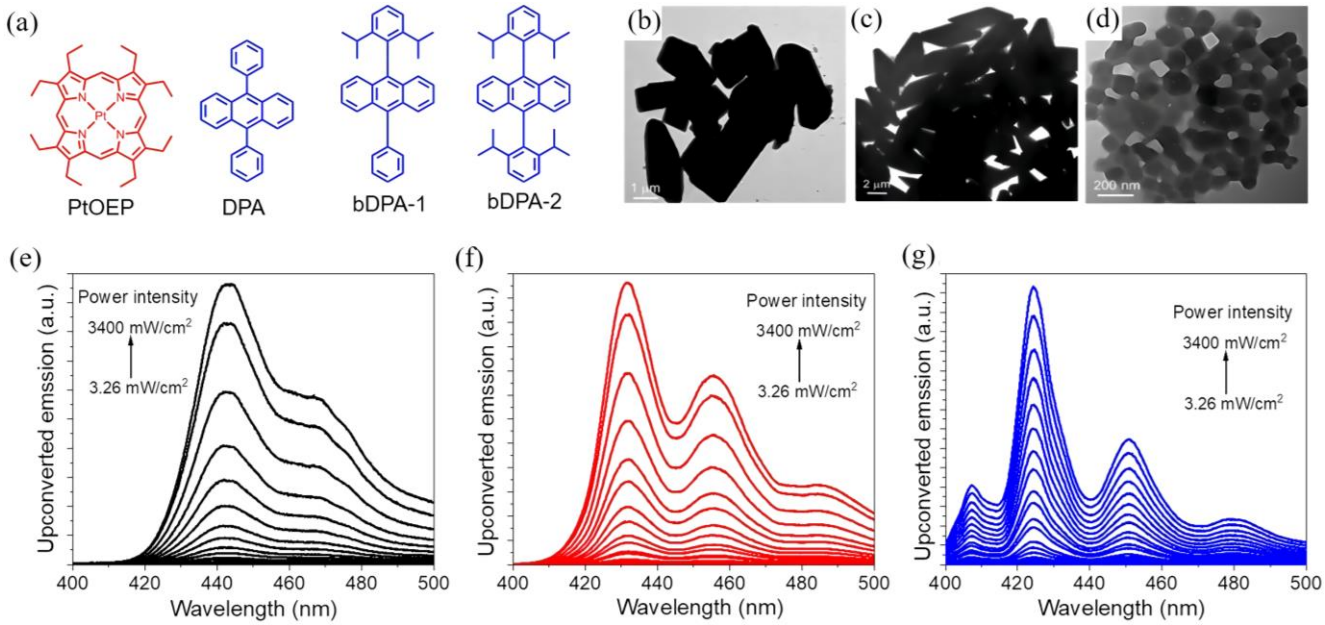

Fig. 8 (a) Molecular structures of the donor (PtOEP) and acceptors (DPA, bDPA-1, bDPA-2); TEM images and upconverted emission as a function of excitation intensity at 532 nm of upconversion crystals of (b and e) DPA/PtOEP, (c and f) bDPA-1/PtOEP, (d and g) bDPA-2/PtOEP. Reprinted with permission from ref. 71 Copyright 2020 Owner Societies.

Spectral upconversion is an essential way to assist photovoltaic devices to harvest sub-bandgap photons. Photon upconversion based on triplet-triplet annihilation (TTA) has attracted significant attention due to its advantages of working with non-coherent and low-power excitation, intense absorption of the excitation light and high upconversion quantum yield.[64,65] TTA upconversion is essentially a process that creates high energy photons under low photon-energy excitation. Sensitizer (donor) molecule which can absorb low energy photons is usually doped into an emitter (acceptor) molecule, which emits high energy photons after two or more triplets annihilated. Several attempts have been made to prepare crystalline upconversion systems.[66-70] The doping ratio of the donor molecule in the acceptor matrix plays a significantly important role in upconversion efficiency. With a low donor ratio, limited amounts of triplets are generated as the low absorptivity of the donor molecules. In contrast, donor molecules aggregate easily under high doping concentration, which results in low triplet energy transfer efficiency from donor to acceptor. In 2016, a near-infrared (NIR)-to-visible upconversion was obtained by Kimizuka and co-workers.[68] Upconversion nanoparticles containing osmium complex as the triplet donor (sensitizer) and rubrene as the triplet acceptor (emitter) were prepared by the reprecipitation method. NIR light (918 nm) was successfully upconverted to visible light (570 nm) with an efficiency of 1.5%. In 2017, Li et al. prepared red-to-green upconversion nanocrystals using 9,10-distyrylanthracene and palladium(II) meso-tetraphenyltetrabenzoporphyrin as the emitter and sensitizer, respectively.[66] An upconversion efficiency of 0.29% was obtained under the excitation at 640 nm with a laser intensity of 120 mW cm^{-2}. Very recently, Wong et al. prepared upconversion crystals using platinum octaethylporphyrin (PtOEP) as the triplet donor, and 9,10-diphenylanthracene (DPA) and its derivatives as triplet acceptors (Fig. 8a) with the ratio of 1:800.[71] Bright blue upconverted emission from PtOEP-DPA and PtOEP-bDPA crystals were observed under the excitation of 532 nm, and the emission intensity increased as increasing the excitation power intensity (Fig. 8e-g). Compared to PtOEP-DPA crystals, PtOEP-bDPA crystals showed more efficient triplet energy transfer and TTA upconversion efficiencies due to the better distribution of PtOEP in bulky-DPA crystals. In addition, the crystalline TTA upconversion system is relatively air-stable as the tight molecular packing can block oxygen well, showing potentials in integrating into solar cell devices to harvest sunlight. All the above examples fully demonstrate the great potential of molecular doped organic crystals in the regulation of optical properties.

3.2 Device applications of molecular doped OSSCs

Molecular doped organic semiconductor films are widely used in the field of optoelectronics, such as OFETs and OLEDs.[9,10,12,13] Despite the excellent advantages, molecular doped OSSCs received much less attention compared to the molecular doped organic semiconductor films duo to its complex preparation procedure. In this part, we summarized some representative examples of molecular doped OSSCs including crystalline films as active layers in kinds of optoelectronic devices, such as OFETs, OLEDs and OLETs. As the basic unit of integrated circuits, OFETs have attracted significant attention with potential applications in display drivers, radio frequency identification tags, and logic circuits.[72-78] In 2011, Takeya and co-workers prepared a solution-processed OFETs based on crystalline organic semiconductor films composed of the host of 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzo-thiophene (C_8-BTBT) and guest of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane

(F_4-TCNQ).[9] The doped crystalline film was achieved by dipping the active layer in the solution of the dopant. There is no obvious change in the morphology of crystalline films before and after the dipping process. Owing to inducing moderate oxidization in the C_8-BTBT channel, the obtained OFETs with the active layer of F_4-TCNQ-doped C_8-BTBT showed the characteristics of lower threshold voltage and higher $I_{ON/OFF}$ compare with that of C_8-BTBT-OFETs.

Despite the obvious advantages of organic crystal with high carrier mobility, low impurities and defects,[73,74,79,80] the development of organic light-emitting devices (OLEDs) based on organic crystals has been retarded due to the difficulty in device preparation. Organic crystals prepared by molecular doping strategy was successfully used as an active layer for the preparation of WOLED, was reported by Sun et al. for the first time.[45] Double-doped organic crystal with white emission was prepared with a host of 1,4-bis(4-methylstyryl)-benzene (BSB-Me) and guests (tetracene and pentacene), as shown in Fig. 9a. The doped organic crystal with white emission possessed high photoluminescence efficiency (70 ± 4%). It was introduced into the construction of OLEDs as the active layer subsequently, as shown in Fig. 9b. Due to the precise control of dopant concentration, the color-rendering index (CRI) of obtained OLEDs was approaching 80~90, which is the highest value of crystal- based WOLEDs so far. The International Commission on Illumination (CIE) coordinates of this OLEDs were varied from (0.32, 0.36) to (0.32, 0.34) with the change of the current density, as shown in Fig. 9c. Moreover, the high current efficiency of 0.89 cd A^{-1} was also achieved for this crystal-based WOLED (Fig. 9d). Similarly, some other color-tunable OLEDs with molecular doped OSSCs as the active layer have also been reported.[46,81]

OLETs are integrated optoelectronic devices that combine the electrical switching abilities of OFETs and the light generation properties of OLEDs, showing great potentials for next-generation of revolutionary flexible displays and electrically pumped laser.[82-84] High mobility emissive organic

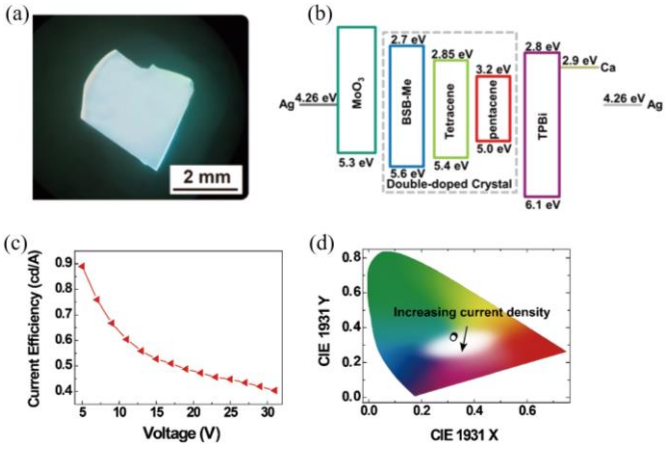

Fig. 9 (a) Representative fluorescence image of double-doped organic crystal. (b) Energy level diagram of WOLED based on the double-doped organic crystal. (c) The current efficiency of WOLED. (d) CIE coordinates of WOLED with the change of the current density (from 3.3 to 196.7 mA cm^{-2}). The chemical structure of BSB-Me is shown in Fig. 3. Reprinted with permission from ref. 45 Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

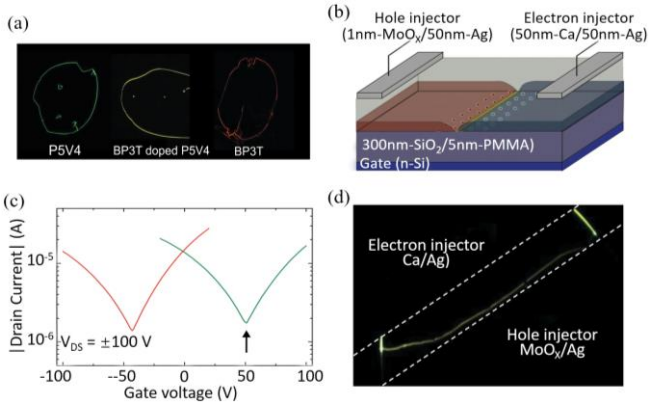

Fig. 10 (a) Representative fluorescence images of P5V4 crystal, BP3T crystal and BP3T-doped P5V4 crystal. (b) Schematic illustration of OLET based on BP3T-doped P5V4 crystal with a bottom-gate top-contact configuration. (c) Transfer characteristics of OLET based on BP3T-doped P5V4 crystal. (d) Microscope image of OLET based on BP3T-doped P5V4 crystal under operating condition. The chemical structures of BP3T and P5V4 are shown in Fig. 3. Reprinted with permission from ref. 8 Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

semiconductors are the key to fabricate high-performance OLETs devices.[85-87] Although much progress has been made in this area,[88-90] it is still a big challenge to develop new materials with high mobility and strong emission simultaneously. The Multi-component doping system is important for the construction of highly efficient OLETs as it can easily realize the integration of high mobility and strong emission, especially when the host material is a high mobility material. For instance, in 2013, Adachi and co-workers prepared a case of molecular doped OSSCs with p-bis[(p-styryl)styryl]benzene (P5V4) as a donor and α,ω-di(biphenyl)-terthiophene (BP3T) as an acceptor, terthiophene (BP3T) as an acceptor, as shown in Fig. 10a.[8] As described in Section 3.1, due to the energy transfer between host and guest molecules and the good dispersion of the guest material in the host material, BP3T-doped P5V4 crystals possessed high photoluminescence efficiency (80 ± 2%) and color-tunable emission. Subsequently, BP3T-doped P5V4 crystals were used to fabricate an OLETs. Ambipolar charge transport of OLETs based on BP3T-doped P5V4 crystal was realized by the construction of asymmetric electrodes (Fig. 10b), and the mobilities were approaching 0.11 $cm^2 V^{-1} s^{-1}$ and 0.06 $cm^2 V^{-1} s^{-1}$ for electron and hole, respectively (Fig. 10c). It is difficult for a single active layer to possess the characteristics of high mobility and strong fluorescence simultaneously. In this sense, Tanigaki and co-workers cleverly separated the charge transfer layer and the light-emitting layer in the construction of OLETs.[14] They successfully prepared a bilayer OLETs which composed of a 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM1)-doped tetracene crystal as a light-emitting layer and a tetracene crystal as a charge transfer layer (Fig. 11a,b). The HOMO-LUMO gap of DCM1 is smaller than that of tetracene, which ensures the effective energy transfer between them in the doped crystal (Fig. 11a). Ambipolar charge transport of this OLETs was realized by the construction of asymmetric electrodes (Fig. 11b). The mobilities were approaching 0.99 $cm^2 V^{-1} s^{-1}$ and 3.17 $cm^2 V^{-1}$

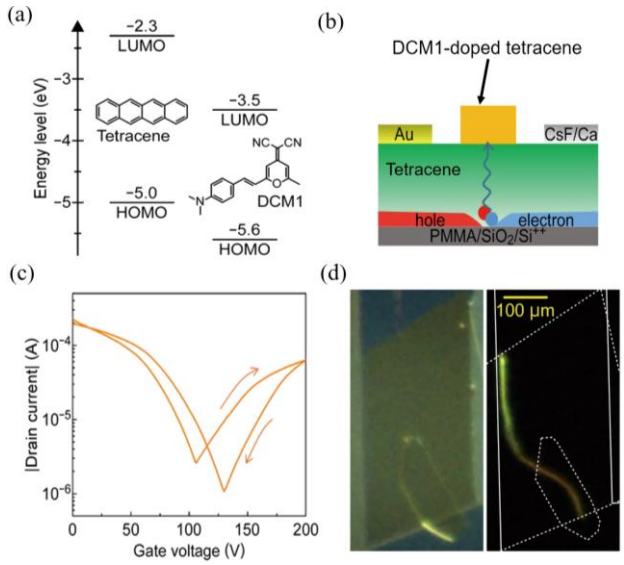

Fig. 11 (a) Molecular structures and energy levels of the tetracene and DCM1. (b) Schematic illustration of OLETs based on tetracene and DCM1-doped tetracene crystal with a bottom-gate top-contact configuration. (c) Transfer characteristics of bilayer OLET based on tetracene and DCM1-doped tetracene crystal. (d) Microscope image of bilayer OLETs in the light (left) and it's light emission in the dark (right). Reprinted with permission from ref. 14 Copyright 2019 American Chemical Society.

s^{-1} for electron and hole, respectively (Fig. 11c). The red electroluminescence of the upper layer is different from the green in the lower layer (Fig. 11d), which shows that the red electroluminescence comes from the DCM1-doped tetracene crystal. To confirm the excitation mechanism, a transparent insulator (tetratetracontane) with a HOMO−LUMO gap of 9.28 eV, was deposited between the tetracene crystal and DCM1-doped tetracene crystal. The electroluminescence of OLETs with tetratetracontane layer is green, which indicated that the DCM1-doped tetracene crystal was not excited. Therefore, it proved that the doped crystal at the top was excited by the exciton diffusion of the tetracene crystal at the bottom. These results successfully demonstrate that the strategy of molecular doping is an effective approach to improve the optoelectronic properties of organic semiconductors.

4. Conclusions and perspectives

In this miniRev, a series of progress for molecular doped OSSCs have been summarized and also discussed their doping process, resulting in optoelectronic properties and applications in devices. Molecular doping in OSSCs is particularly interesting and beneficial to improve electrical and optical properties, as well as the performance of the optoelectronic devices. However, there are still many challenges that remain as follows. i) The precise doping mechanism is unclear. The inherent properties of dopants, such as molecular shape, size and energy levels, play important roles in optoelectronic properties of molecular doped crystals. The detailed understanding of the inherent doping mechanism is essential to select and design more efficient dopants, as well as give a better prediction for resulting optoelectronic properties. ii) The design and synthesis of host-guest materials is an enormous challenge. Generally speaking, there are few host-guest materials for the preparation of molecular doped OSSCs. Different functional devices have different requirements for active materials. In addition, the preparation of doped OSSCs is very hard. Thus, it is also a great challenge to design and synthesize functional oriented appropriate host-guest materials for desired application demand. iii) Technologies of crystal preparation and post-processing. At present, the molecular doped OSSCs are mostly prepared by the PVT method and solution method. However, these methods are not suitable for the preparation of uniform and large-area crystals which are essential to fabricate large-area optoelectronic devices and their industrial applications. Thus, developing new technologies to facilitate the controllable preparation of large-area molecular doped OSSCs is urgent. On the other side, the crystal processing technology is also the key factor for the preparation and application of crystal in functional devices.[91] Doping indeed provides an alternative approach to chemical synthesis for new functional and multifunctional organic semiconductors, such as the integration of high charge transport and strong emission for OLETs applications,[8,14] more efforts are expected for much higher integrated optoelectronic property with the current development of a series-high mobility emissive organic semiconductors,[6,7,87-90] leading to the rapid progress of OLETs research field. In addition, and also very importantly, doping conjugated polymer crystals has been a research gap in this field although the open of organic electronics is ascribed to the discovery of conducting polymer of doped polyacetylene.[5] The main reason is due to the intrinsic difficulty of obtaining high quality conjugated polymer crystals, including polymer materials with one-dimensional and two-dimensional conjugation.[92-97] It is hoped that further advances would be achieved under the joint efforts of scientists for doped conjugated polymer crystals because they have unique features of giving high conductivity, superior optical properties as well as other interesting photophysical properties in polymers. In summary, molecular doping provides a new dimension to the design of high-performance OSSCs used for optoelectronic devices. More developments of molecular doping will not only address the fundamental questions about the doping mechanism but also yield new device concepts based on molecular doped OSSCs.

Conflicts of interest

There are no conflicts to declare.

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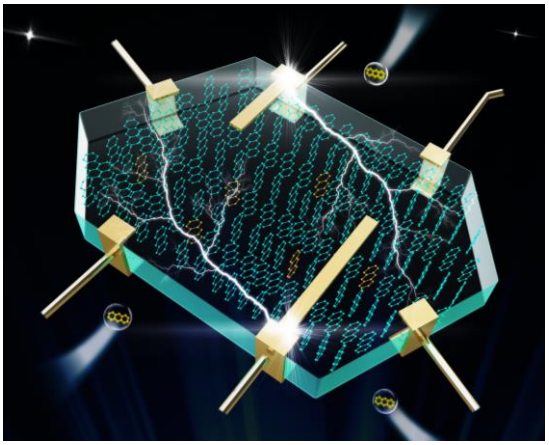

In this MiniRew, highlighted topics include selection criteria of molecular dopants, the general growth method, resulting in optoelectronic properties and their applications in optoelectronic devices are summarized. The brief conclusion of challenges and perspectives of molecular doped OSSCs and some possible promising research directions in this field are also given.