Journal of Materials Chemistry C

REVIEW

Molecular doped organic semiconductor crystals for optoelectronic device applications

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Zhengsheng Qin,†[ab] Can Gao,†[a] Wallace W. H. Wong,[c] Moritz K. Riede,[d] Tianyu Wang,[a] Huanli Dong,*[ab] Yonggang Zhen[a] and Wenping Hu[ae]

Dedicated to celebrating Tobin Marks' 75th Birthday

For semiconductors, doping is an efficient approach to tune their energy bandgaps, charge transport, and optical properties which enable the improvement of corresponding performances and also the possibility of multifunction integration. Recently, significant advances have been achieved for molecular doped 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 review, we will give a summary of this exciting progress for molecular doped OSSCs from the aspects of selection criteria of molecular dopants, the general growth method, resulted in optoelectronic properties as well as their applications in optoelectronic devices. Finally, a brief conclusion is given with challenges and perspectives of molecular doped OSSCs in this field.

1. Introduction

In today's microelectronics industry, doping is a key strategy for modulating the electrical properties of inorganic semiconductors and tailoring their properties to meet the applications' demands. For example, doping inorganic semiconductors may allow changing energy level alignment at interfaces between the doped materials and the metal contacts, which can significantly increase their conductivities and reduce contact resistances even at ultralow doping ratios.[1,2] Similarly, doping organic semiconductors 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] The advantages and potential of molecular doping have been demonstrated for many applications including organic field-effect transistors (OFETs),[9-11] organic light-emitting diodes (OLEDs),[12,13] organic light-emitting transistors (OLETs),[8,14] organic thermoelectrics,[15-17] and other optoelectronic devices.[18-21] Based on the different effect of dopants induced in resulted doped organic semiconductors, the organic doping systems are further divided into electrical doping and host-guest doping without charge transfer process. The active materials used for electrical doping and host-guest doping are named in a unified way: the material with little content in the doping system is named dopant, and the material with large content is named as the host. As for electrical doping, there are two main models: ground state integer charge transfer (ICT) and host-dopant intermolecular hybridisation.[22,23] Both enable adding electrons to the lowest unoccupied molecular orbital (LUMO) of organic semiconductor (n-doping) or holes to the highest occupied molecular orbital (HOMO) of the organic semiconductor (p-doping), this process of ICT model is illustrated in Fig. 1a. Host-guest doping is another effective way which usually used for tuning the light emission characteristics of organic semiconductors *via* the radiation energy transfer and Förster and/or Dexter process (Fig. 1b). Förster energy transfer is considered a long-distance, non-contact energy transfer mode with an effective transfer distance of 3-10 nm due to the dipole-dipole interaction between donor and acceptor molecules. While efficient overlap of the molecular orbital of donor and acceptor molecules is required for Dexter energy transfer, which is a short energy transfer distance within a distance of 1-2 nm. The existence of energy transfer between donor and acceptor molecules is the fundamental reason for the change of optical properties such as luminescent emission-efficiency, emission color, and fluorescence lifetime of doped organic semiconductors.[24-26] Different from doping in inorganic semiconductors, dopants used in organic semiconductors can be atomic, ionic and molecular species, etc.[27-29] Atoms tend to diffuse in organic semiconductors, rendering the doping effect unstable and affecting device lifetime. This shortcoming can be overcome by

---

[a] *Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: dhl522@iccas.ac.cn (Huanli Dong)*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China.*
[c] *ARC Centre of Excellence in Exciton Science, School of Chemistry, Bio21 Institute, The University of Melbourne, Melbourne, Australia.*
[d] *Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, UK.*
[e] *Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Science, Tianjin University and Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China*

†These authors contribute equally to this work.

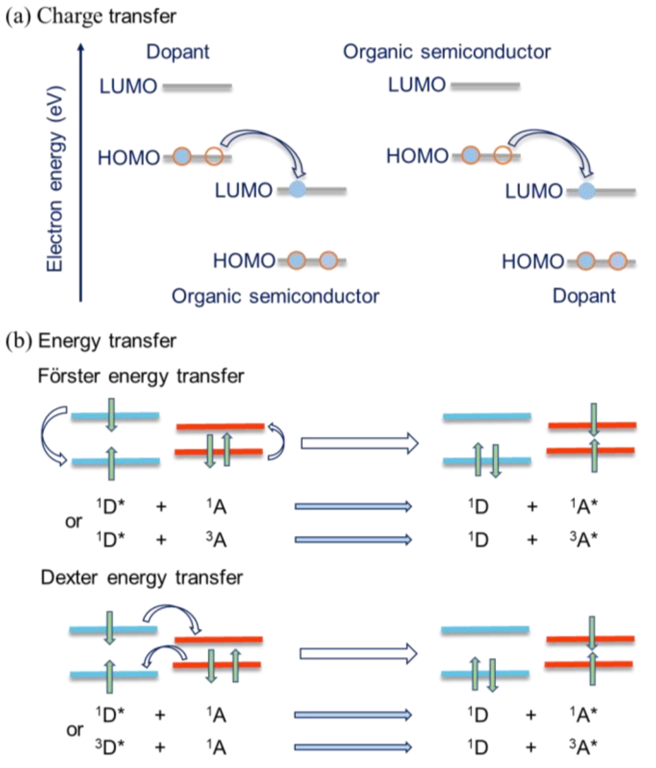

Fig. 1 (a) Simplified energetic relationships between organic semiconductors and dopants in electrical doping in the ICT mode. (b) Schematic illustration of Föster energy transfer and Dexter energy transfer in host-guest doping. The equations in the graph represent the corresponding energy transfer processes.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

using molecular dopants that are bulkier and difficult to diffuse into the host matrix, and thus molecular doped organic semiconductors have attracted increasing attention in recent years. Molecular doping has been shown to shift the Fermi levels and increase the conductivities of organic semiconductors by several orders of magnitude.[30-34] Some excellent reviews have summarized the progress of molecular doping in organic semiconductor thin films from different aspects, such as doping mechanisms, doping strategies, and functional devices.[3,35-38] In addition to research on organic thin films, currently some significant advances have also been achieved for molecular doped organic semiconductor single crystals (OSSCs).[4,8,26] Molecular doped OSSCs have been regarded as the ideal candidates for fundamental studies and improved optoelectronic properties for devices,[4,8,19,26] though this doping process is much more challenging in OSSCs systems.

In this review, we will give a timely summary of the exciting progress in the field of molecular doped OSSCs with special attention on their abilities to tune the charge transport, optical properties, and integrated optoelectronic properties of OSSCs and their applications in OFETs, OLEDs, and OLETs (Fig. 2). In this first section, we introduce a brief illustration of the basic selection criteria of molecular dopants for doped OSSCs 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 are 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.

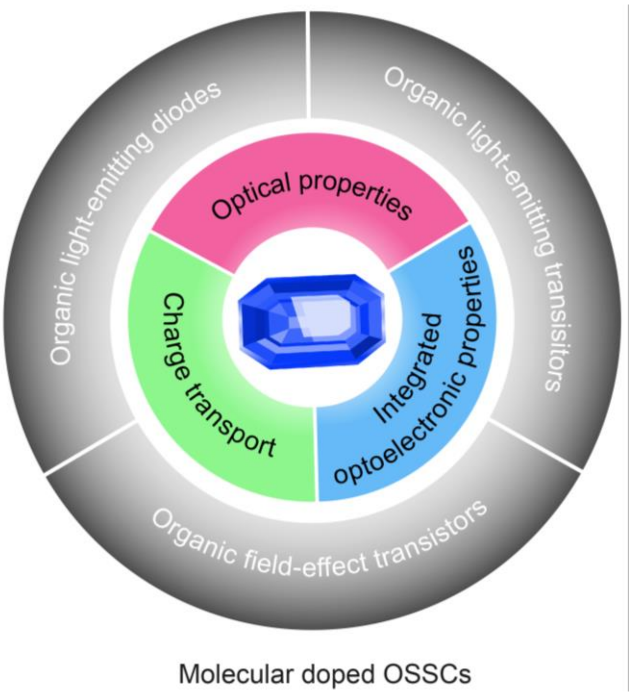

Fig. 2 Schematic illustration of some of the key optoelectronic applications of molecular doped OSSCs.

2. Molecular doping in organic semiconductor crystals

2.1 Selection criteria of molecular dopants for doped OSSCs

Considering the long-ranged molecular features of organic single crystals, in principle, the similar physical properties between host and dopant molecules such as solubility for solution process and sublimation temperature for PVT method is better for the growth of high-quality doped OSSCs. There are several requirements for molecular dopants[26,39] for doping in OSSCs: i) The selected host and dopant 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 dopant only requires one heating source in the preparation process. With solution processing, the similar solubility of host and dopant materials in a common solvent is beneficial for the preparation of molecular doped OSSCs, because it is easy to obtain a uniform solution of dopant and host mixture. ii) In principle, the selected host and dopant molecules generally should have similar molecular configuration and size, which is favorable for the dopant 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 leading to the failure of doping. Of course, there are also some exceptional examples, such as OPV/C_{60}[40] and C_8-BTBT/F_4-TCNQ[9], the chemical

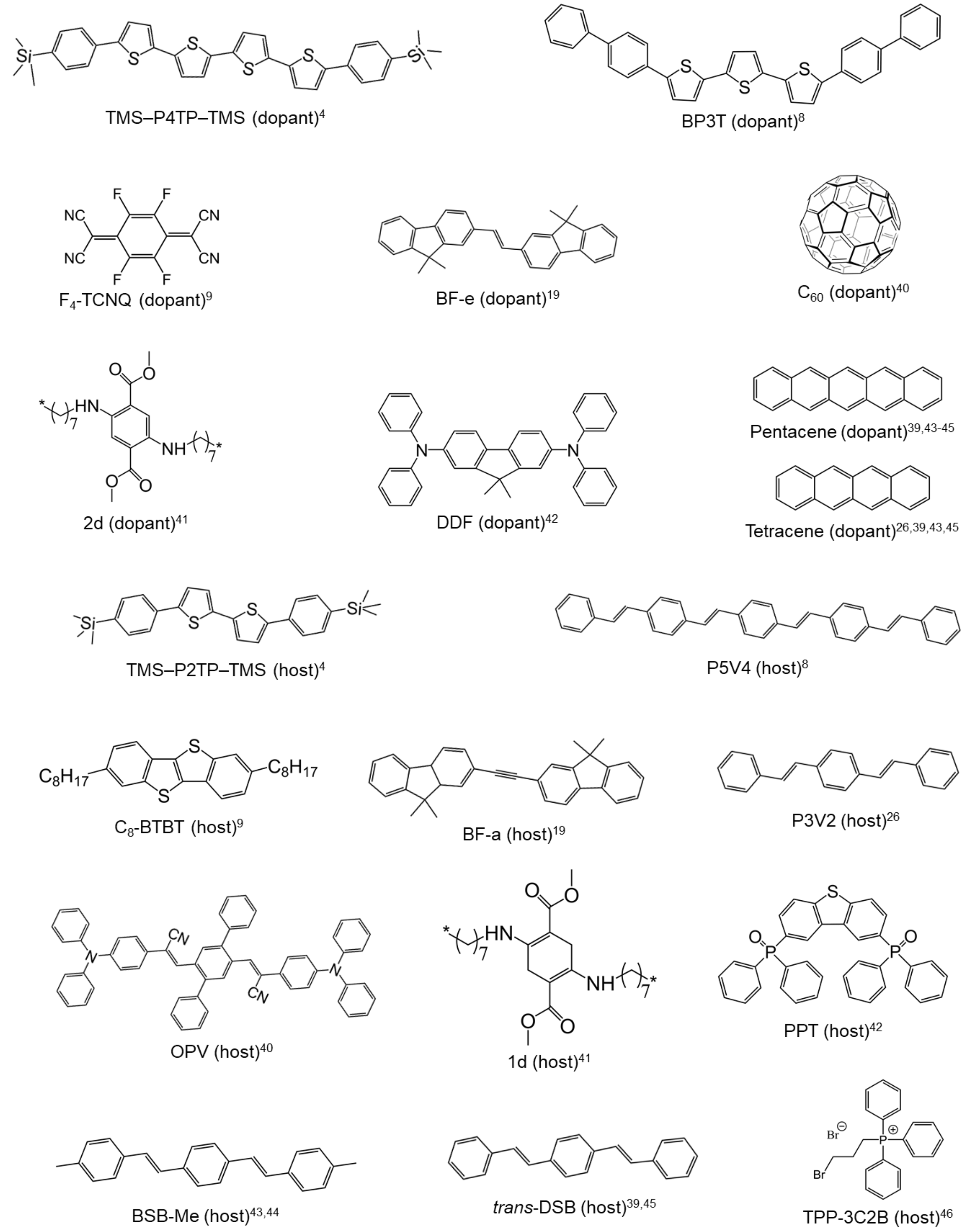

Fig. 3 Some host and dopant materials commonly used for molecular doped OSSCs in literature.

structures of them are shown in Fig. 3. iii) For host-guest doping, the emission spectrum of the host molecule is required to overlap well with the absorption spectrum of the dopant molecule to enable efficient energy transfer from host to dopant molecules. (iv) As for electrical doping, one of the main requirements for molecular dopants is that they should have appropriate energy levels with that of host molecules for efficient charge transfer. According to these above criteria, many molecules have been developed and used in molecular doped OSSCs,[26,39] some of them are summarized in Fig. 3, and some of these are discussed in this review. There is no doubt that the selection of the host and dopant materials has a crucial fluence on the preparation and property control of the molecular doped OSSCs. In fact, the lack of suitable host and dopant materials combinations and the difficulty in preparation of doped OSSCs have so far restricted the wide applications of molecular doped OSSCs in optoelectronic devices.

2.2 General growth methods for molecular doped OSSCs

Over the past decades, OSSCs possessing long-range molecular orders and absence of grain boundaries have received considerable attention and investigation due to their superior optoelectronic properties and advantages for fundamental studies.[47-51] To date, various approaches including physical vapor transport (PVT), solution assembly process, and other approaches derived from these two methods have been developed for the growth of high-quality OSSCs. Not only micro-nano crystals but also two-dimensional crystals, monolayer crystals, as well as large-area crystal arrays can be produced by these methods.[6,52,53] In principle, these methods could also be applied for the growth of doped OSSCs but with special considerations of the physicochemical properties for host and dopant materials, such as their molecular structure and sizes, the solubility and sublimation property, and so on. Fig. 4a-c shows the schematic of two type methods widely used for growing doped OSSCs in literature.

The PVT method is an effective method used for the growth of high-quality OSSCs,[54] 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. By controlling the time of growth, the flow rate of the carrier gas (typically N_2 or Ar), the temperature of crystals growth, and other conditions, the thickness and size of the crystals prepared by the PVT method are relatively controllable. At high temperatures, the molecules have higher kinetic energy, which is conducive to the insertion of dopant molecules into the crystal lattice of the host molecules, resulting in a high-quality molecular doped OSSCs with a small lattice mismatch.[45] 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 optoelectronic devices. The choice of preparation method for molecular doped OSSCs depends on the properties of the organic material. If the sublimation temperature of the dopant and host is close, their powder samples can be evenly mixed and placed in the sublimation region for the preparation of molecular doped OSSCs, as shown in Fig. 4a.[26] In the case of the sublimation temperature of the dopant and host is different, they can be placed in the sublimation zones with different temperatures respectively, as shown in Fig. 4b.[45] However, when the difference of sublimation temperatures between the dopant and host is quite considerable, the distance between the two sources should be large enough, which is not conducive to the growth of the two materials in the same growth zone, and need to carry on certain transformation to the equipment, Therefore, when the sublimation temperature of the host and dopant is close to each other, it is advantageous to prepare the doped crystal simply and successfully. PVT method is an effective growth technology for materials with poor solubility but good thermal stability. The alternative growth technology for materials with good solubility is to grow the OSSCs from the solution. The solution method is an efficient and relatively easy way to prepare molecular doped OSSCs. Here we describe a common double solution method to grow crystals as an example, as shown in Fig. 4c.[40] The mixed solution containing the host and dopant molecules are 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.

Usually, the size of organic crystals grown by the solution method and PVT method is limited (usually under millimeter size) and difficult to control accurately. Many strategies have been used for the preparation of large-area organic semiconductor films, such as spin-coating, dip-coating, inkjet printing, etc.[55-57] However, most of the films prepared by these methods are amorphous or polycrystalline. As a controllable preparation strategy, solution-shearing has unique advantages in the preparation of large-area organic crystalline films.[58] A schematic diagram of crystalline organic semiconductor film produced by solution shearing is shown in Fig. 4d. 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. The movement of the blade relative to the substrate exposes the

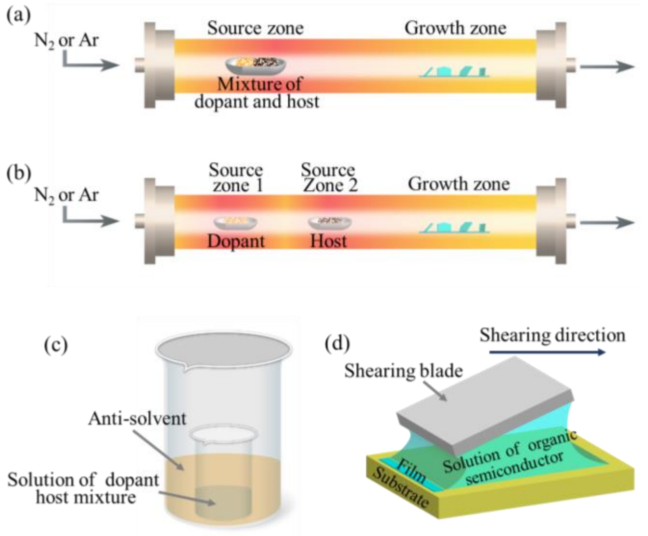

Fig. 4 Schematic diagram of crystal growth by PTV method for molecular doped OSSCs (a) single-source sublimation zone in case host and dopant materials exhibit similar sublimation temperature and (b) double-source sublimation zone, where the sublimation temperatures of host and dopant materials are largely different. (c) Schematic illustration of the solution method with double solvent (c) and the solution shearing method (d) for the growth of molecular doped OSSCs.

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. Recently, Hu et al. fabricated centimeter-scale highly aligned organic crystalline films by solution shearing for the construction of high-performance field-effect transistor arrays.[56] Therefore, from this point of view, solution shearing, as a potential technology, should also have certain advantages in the preparation of large-area doped organic crystalline films, which is difficult to achieve by the PVT and solution method.

3. The optoelectronic properties and device applications of molecular 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,[59] but it is usually difficult. Through the strategy of molecular doping, it is easy to realize the energy transfer from the host molecules to dopant 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 molecular doped crystals with *trans*-1,4-distyrylbenzene (*trans*-DSB) as the host and tetracene or pentacene as the dopant.[45] The similar crystal lattice structure of host and dopant material was considered to be the key to prepare doped crystals with high doped concentration (10%), as shown in Fig. 5a. The obtained photoluminescence quantum yield of the tetracene-doped *trans*-DSB crystal and the 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 dopant molecules were well dispersed in the host molecules, which effectively restrained the quenching caused by aggregation; ii) the efficient energy transfer between host molecules and dopant 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.[26,39,43]

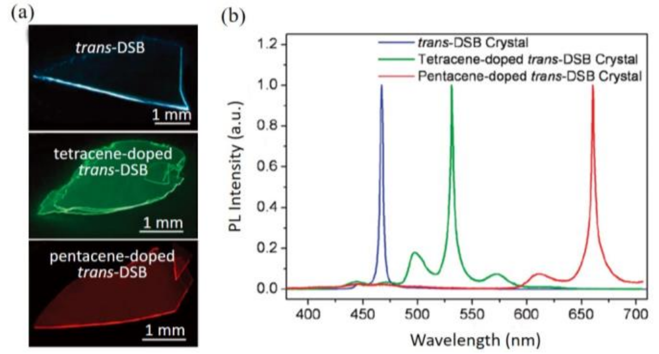

Fig. 5 (a) Representative fluorescence images and (b) ASEs spectra of *trans*-DSB crystal, tetracene-doped *trans*-DSB crystal, and pentacene-doped *trans*-DSB crystal. The chemical structures of *trans*-DSB, tetracene, and pentacene are shown in Fig. 3. Reprinted with permission from ref. 45. Copyright 2009 American Chemical Society.

Optically pumped organic lasers have emerged in the recent year thanks to the rapid development of organic semiconductor materials with high modifiability.[60-62] 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.[63,64] Molecular doped organic semiconductor materials have attracted increasing research interest recently due to their tunable ASE property and emission color.[65,66] In 2019, Zhao and co-workers prepared doped OSSC using C_{60} as a dopant and cyano-substituted oligo-(α-phenylenevinylene)-1,4-bis(R-cyano-4-diphenylaminostyryl)-2,5-diphenylbenzene (OPV) as a host,[40] as shown in Fig. 6a and 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 and d. The color-tunable laser emission from C_{60}@OPV crystal can be tailored by controlling doping concentration precisely (Fig. 6e). The achievement of laser emission from C_{60}@OPV crystal was attributed to the formation of charge-transfer (CT) complexes from host-guest materials. CT complexes with narrow bandgap can harvest the energy of the surrounding host molecules.

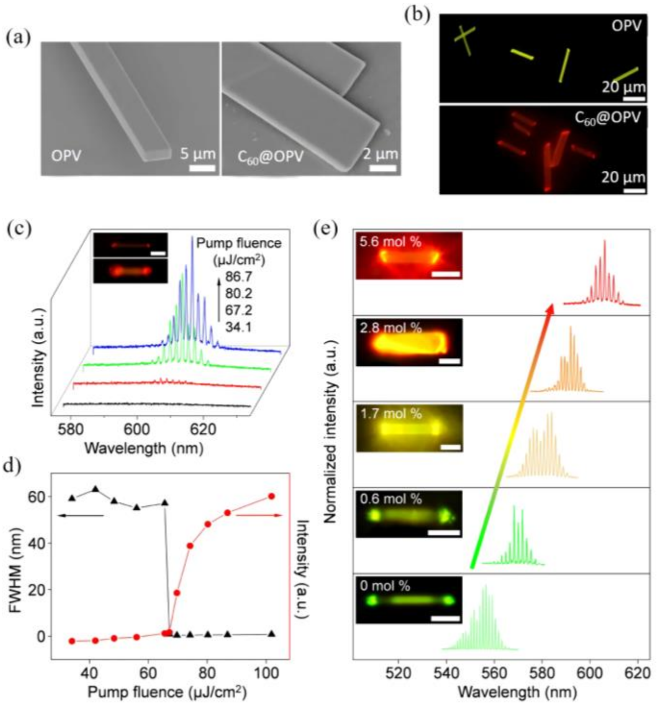

Fig. 6 (a) Representative SEM images of OPV crystals and C_{60}@OPV crystals. (b) Representative fluorescence image of OPV crystals and C_{60}@OPV crystals. (c) PL spectra of a typical C_{60}@OPV crystal. Scale bars, 10 µm. (d) Emission intensity and full width at half maximum (FWHM) as a function of 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. 40. Copyright 2019 American Association for the Advancement of Science.

These results provided valuable references and guidance for the design and synthesis of organic laser materials.

Generally, there are two active centers in long-persistent luminescence (LPL) materials: emitters and traps. As a radiation center, emitters can be emitted after excitation, while traps can be used for store energy and slowly release energy via physical stimulations. The traps in inorganic LPL materials can be formed by doping rare-earth ions, which is a research focus at present.[67,68] However, the high fabrication temperatures of traditional inorganic LPL materials (>1000 °C) and the use of rare earth elements which are non-renewable resources greatly limit their applications.[69,70] In this sense, much attention has been focused on organic LPL materials. The radiative transitions of organic molecules from photoexcited states usually produce only fluorescence, phosphorescence and delayed fluorescence, which cannot be compared with the long-life luminescence of inorganic LPL. In order to obtain charge-separated (CS) states for long-life luminescence of organic molecules, the host materials and dopants that can obtain CS states are selected.[71] Recently, Hu and co-workers successfully prepared a case of molecular doped OSSC with the dopant of 2,7-di-(N,N-diphenylamino)-9,9-dimethyl-9H-fluorene (DDF) and the host 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 and b.[42] The existence of a CS state with delayed fluorescence were confirmed by the nonexponential decay LPL emission which (Fig. 7b) different from the single-order exponential decay of RTP emission. The LPL emission was explained as a synergistic effect of delayed fluorescence from the CS state and persistent RTP from the DDF triplet state. This 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 OSSCs 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 OSSC with the host of N,N-dimethylaniline and the dopant 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 emission from CS states of TPP-3C2B: DMA is attributed to the simultaneous use of TPP-3C2B as a p-dopant and multiple protective traps.[46]

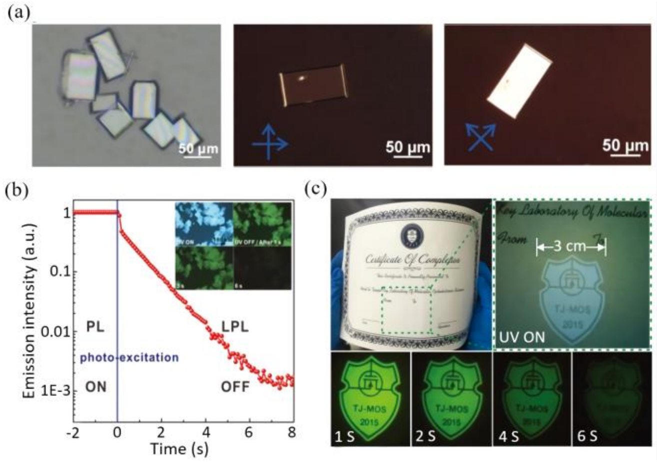

Fig. 7 (a) Optical microscope image and polarized microscope images of the PPT: DDF crystals. (b) Emission intensity map of PPT: DDF crystals over time (Inset: photographs of LPL from the PPT: DDF crystals under fluorescence microscope). (c) Photographs of LPL from the film based on PPT: DDF crystals. The chemical structures of PPT and DDF are shown in Fig. 3. Reprinted with permission from ref. 42. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Spectral upconversion could become 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.[72,73] TTA upconversion is essentially a process that creates high energy photons under low photon-energy excitation. Sensitizer (dopant) molecule which can absorb low energy photons is usually doped into an annihilator (host) molecule, which emits high energy photons after two or more triplets annihilated. Several attempts have been made to prepare crystalline upconversion systems.[74-78] The doping ratio of the dopant molecule in the host matrix plays a significantly important role in upconversion efficiency. With a low doping ratio, limited amounts of triplets are generated as the low absorptivity of the dopant molecules. In contrast, dopant molecules aggregate easily under high doping concentration, which results in low triplet energy transfer efficiency from dopant to host. In 2016, a near-infrared (NIR)-to-visible upconversion was obtained by Kimizuka and co-workers.[76] Upconversion nanoparticles containing osmium complex as the triplet sensitizer and rubrene as the triplet annihilator with the ratio of 1:270 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 palladium(II) meso-tetraphenyltetrabenzoporphyrin and 9,10-distyrylanthracene as the sensitizer and annihilator with the ratio of 1:800, respectively.[74] 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 sensitizer, and 9,10-diphenylanthracene (DPA) and its derivatives as triplet annihilators (Fig. 8a) with the ratio of 1:800.[79] 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. An upconversion efficiency of 0.92% of PtOEP-bDPA crystals was obtained, which was almost 50 times higher compared to that of PtOEP-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

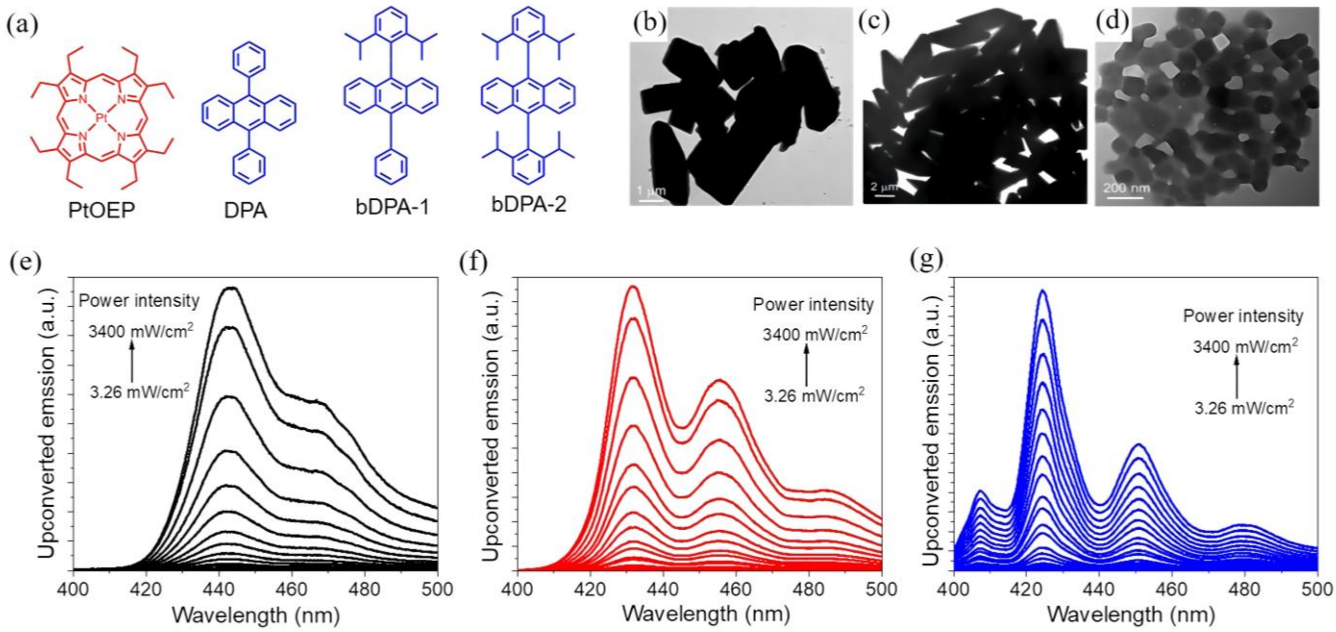

Fig. 8 (a) Molecular structures of the sensitizer (PtOEP) and annihilators (DPA, bDPA-1, bDPA-2); TEM images and upconverted emission as a function of excitation intensity at 532 nm of upconversion crystals of (b and e) DPA/PtOEP, (c and f) bDPA-1/PtOEP, (d and g) bDPA-2/PtOEP. Reprinted with permission from ref. 79. Copyright 2020 Owner Societies.

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.[9-13] Despite the excellent advantages, molecular doped OSSCs received much less attention compared to the molecular doped organic semiconductor films due 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.[80-86] In 2011, Takeya and co-workers prepared a solution-processed OFET 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 the dopant 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 the crystalline films before and after the dipping process. Owing to inducing moderate oxidization in the C_8-BTBT channel, the obtained OFET 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-OFET. The carrier transport properties of organic semiconductors can also be switched by doping, which is similar to that of silicon. In 2016, Zhang and co-workers prepared a “molecular doped” OSSC with a host of 2,7-di-*tert*-butyl-10,14-di(thiophen-2-yl)phenanthro[4,5-*abc*][1,2,5]thiadiazolo[3,4-*i*] phenazine (DTPTP) and a dopant of tetracyanoquinodimethane (TCNQ).[87] After doping TCNQ, the original p-type carrier transport characteristics of the host (0.3 cm^2 V^{-1} s^{-1}) switched to n-type carrier transport characteristics (3 × 10^{-3} cm^2 V^{-1} s^{-1}). The TCNQ-doped DTPTP crystal adopts a dense one-dimensional mixed π–π stacking mode was proved by the single-crystal X-ray studies. These results revealed that molecular doping provides a new strategy for switching and improving transport characteristics of organic electronics.

Despite the obvious advantages of organic crystals with high carrier mobility, low impurities, and defects,[88,89] the development of OLEDs based on organic crystals has been lagged due to the difficulty in device preparation. Organic crystal prepared by molecular doping strategy was successfully used as an active layer for the preparation of white OLED (WOLED) was reported by Sun et al. for the first time.[43] Double-doped organic crystal with white emission was prepared with a host of 1,4-bis(4-methylstyryl)-benzene (BSB-Me) and dopants (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 OLED 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 OLED was approaching 80~90, which is the highest value of crystal-based WOLEDs so far. The International Commission on Illumination (CIE) coordinates of this WOLED were varied from (0.32, 0.36) to (0.32, 0.34) with the change of the current

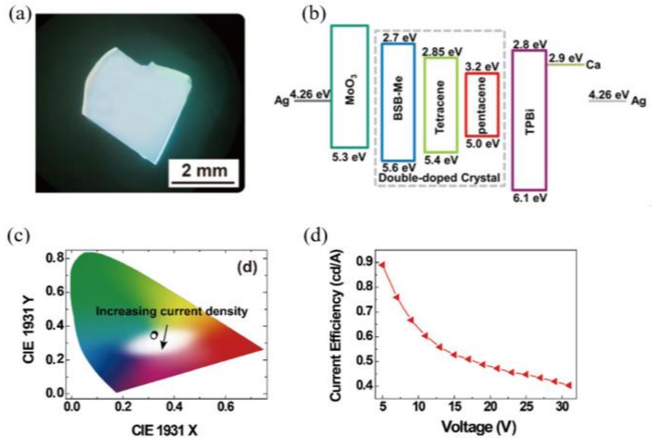

Fig. 9 (a) Representative fluorescence image of double-doped organic crystal. (b) Energy level diagram of white OLED (WOLED) based on the double-doped organic crystal. (c) The current efficiency of WOLED. (d) CIE coordinates of WOLED with the change of the current density (from 3.3 to 196.7 mA cm^{-2}). The chemical structure of BSB-Me is shown in Fig. 3. Reprinted with permission from ref. 43. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

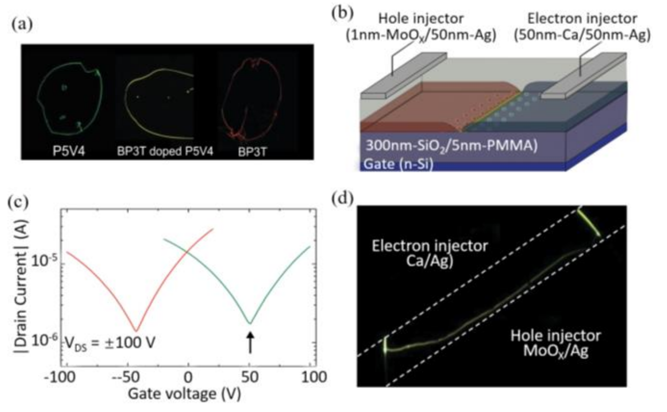

Fig. 10 (a) Representative fluorescence images of P5V4 crystal, BP3T crystal, and BP3T-doped P5V4 crystal. (b) Schematic illustration of OLET based on BP3T-doped P5V4 crystal with a bottom-gate top-contact configuration. (c) Transfer characteristics of OLET based on BP3T-doped P5V4 crystal. (d) Microscope 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.

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.[44,90]

OLETs are integrated optoelectronic devices that combine the electrical switching abilities of OFETs and the light generation properties of OLEDs, showing great potential for next-generation of revolutionary flexible displays and electrically pumped lasers.[91-93] High mobility emissive organic semiconductors are the key to fabricate high-performance OLETs.[94-96] Although many achievements have been made in this area,[97-99] 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 OSSC with p-bis[(p-styryl)styryl]benzene (P5V4) as a host and α,ω-di(biphenyl)-terthiophene (BP3T) as a dopant, as shown in Fig. 10a.[8] As described in Section 3.1, due to the energy transfer between host and dopant molecules and the good dispersion of the dopant 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 OLET. Ambipolar charge transport of OLET based on BP3T-doped P5V4 crystal was realized by the construction of asymmetric electrodes (Fig. 10b), and the electron and hole mobilities were approaching 0.11 cm^2 V^{-1} s^{-1} and 0.06 cm^2 V^{-1} s^{-1}, 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 transport layer and the light-emitting layer in the construction of OLET.[14] They successfully prepared a bilayer OLET 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 transport layer (Fig. 11a and 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 OLET was realized by the construction of asymmetric electrodes (Fig. 11b). The electron and hole mobilities were approaching 0.99 cm^2 V^{-1} s^{-1} and 3.17 cm^2 V^{-1} s^{-1}, 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

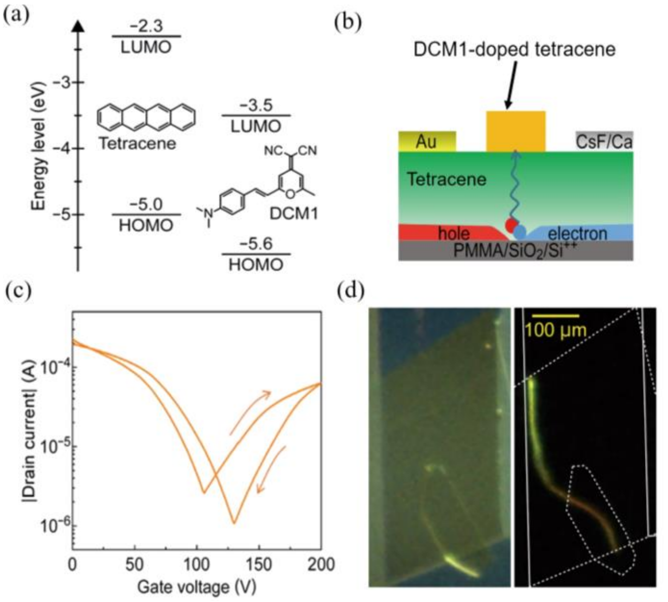

Fig. 11 (a) Molecular structures and energy levels of the tetracene and DCM1. (b) Schematic illustration of OLET based on tetracene and DCM1-doped tetracene crystal with a bottom-gate top-contact configuration. (c) Transfer characteristics of bilayer OLET based on tetracene and DCM1-doped tetracene crystal.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

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 OLET 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 review, the recent progresses for molecular doped OSSCs have been summarized including their corresponding 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 inherent properties of dopants, such as molecular shape, size, and energy levels, play important roles in optoelectronic properties of molecular doped crystals. However, the detailed understanding of the inherent doping mechanism (especially for host-guest doping mode) for rational selection and design of more efficient dopants and thus the resulting properties are still unclear. ii) The design and synthesis of host and dopant materials is an enormous challenge. Generally speaking, there are few host and dopant materials for the preparation of molecular doped OSSCs. Different functional devices have different requirements for active materials. Thus, it remains a great challenge to design and synthesize function-oriented appropriate host and dopant materials for desired application demand. iii) Technologies of crystal preparation and post-processing are limited so far. At present, molecular doped OSSCs are mostly prepared by the PVT method and solution method. However, the preparation of uniform and large-area crystals for large-area optoelectronic devices is challenging. The advantages of the described approaches are that 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.[8,14,26] More efforts are expected for a much better optoelectronic property with the current development of a series of high mobility emissive organic semiconductors,[6,7,96-99] 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 raise of organic electronics is ascribed to the discovery of conducting polymer of doped polyacetylene.[5] The main challenge here is due to the intrinsic difficulty of obtaining high quality conjugated polymer crystals, including polymer materials with one-dimensional and two-dimensional conjugation.[100-105] We hoped that further advances can 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 due to the highly delocalized π-conjugation structures.

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.

Acknowledgements

The authors acknowledge financial support from the Ministry of Science and Technology of China (2018YFA0703200, 2017YFA0204503 and 2016YFB0401100), the National Natural Science Foundation of China (91833306, 61890943, 51725304, 51733004, 21875259), the Strategic Priority Research Program (XDB12000000) of the Chinese Academy of Sciences, the Youth Innovation Promotion Association of the Chinese Academy of Sciences, the National Program for Support of Top-notch Young Professionals, the Beijing National Laboratory for Molecular Sciences (BNLMS- CXXM-202012) and the CAS President's International Fellowship Initiative (PIFI). W. W. H. Wong is supported by the ARC Centre of Excellence in Exciton Science (CE170100026).

Notes and references

1 S. Q. Shi, L. J. Liu, C. Y. Ouyang, D. S. Wang, Z. X. Wang, L. Q. Chen and X. J. Huang, *Phys. Rev. B*, 2003, **68**, 195108.

2 K. Kim, G. Kim, S. I. Kim, K. H. Lee and W. Lee, *J. Alloy. Compd.*, 2019, **772**, 593-602.

3 B. Lussem, C. M. Keum, D. Kasemann, B. Naab, Z. Bao and K. Leo, *Chem. Rev.*, 2016, **116**, 13714-13751.

4 O. D. Parashchuk, A. A. Mannanov, V. G. Konstantinov, D. I. Dominskiy, N. M. Surin, O. V. Borshchev, S. A. Ponomarenko, M. S. Pshenichnikov and D. Y. Paraschuk, *Adv. Funct. Mater.*, 2018, **28**, 1800116.

5 C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. Macdiarmid, *Phys. Rev. Lett.*, 1977, **39**, 1098-1101.

6 X. Zhang, H. Dong and W. Hu, *Adv. Mater.*, 2018, **30**, 1801048.

7 Z. Xie, D. Liu, Y. Zhang, Q. Liu, H. Dong and W. Hu, *Chem. J. Chinese U.*, 2020, **41**, 1179-1193.

8 H. Nakanotani and C. Adachi, *Adv. Opt. Mater.*, 2013, **1**, 422-427.

9 J. Soeda, Y. Hirose, M. Yamagishi, A. Nakao, T. Uemura, K. Nakayama, M. Uno, Y. Nakazawa, K. Takimiya and J. Takeya, *Adv. Mater.*, 2011, **23**, 3309-3314.

10 S. Lan, Y. Yan, H. Yang, G. Zhang, Y. Ye, F. Li, H. Chen and T. Guo, *J. Mater. Chem. C*, 2019, **7**, 4543-4550.

11 Y. Kim, S. Chung, K. Cho, D. Harkin, W. T. Hwang, D. Yoo, J. K. Kim, W. Lee, Y. Song, H. Ahn, Y. Hong, H. Sirringhaus, K. Kang and T. Lee, *Adv. Mater.*, 2019, **31**, 1806697.

12 H. L. Smith, J. T. Dull, E. Longhi, S. Barlow, B. P. Rand, S. R. Marder and A. Kahn, *Adv. Funct. Mater.*, 2020, **30**, 2000328.

13 M. Gross, D. C. Muller, H. G. Nothofer, U. Scherf, D. Neher, C. Brauchle and K. Meerholz, *Nature*, 2000, **405**, 661-665.

14 H. Shang, H. Shimotani, T. Kanagasekaran and K. Tanigaki, *ACS Appl. Mater. Interfaces,* 2019, **11**, 20200-20204.

15 Y. Lu, J. Y. Wang and J. Pei, *Chem. Mater.*, 2019, **31**, 6412-6423.

16 D. Huang, H. Yao, Y. Cui, Y. Zou, F. Zhang, C. Wang, H. Shen, W. Jin, J. Zhu, Y. Diao, W. Xu, C.-a. Di and D. Zhu, *J. Am. Chem. Soc.*, 2017, **139**, 13013-13023.

17 J. Guo, G. Li, H. Reith, L. Jiang, M. Wang, Y. Li, X. Wang, Z. Zeng, H. Zhao, X. Lu, G. Schierning, K. Nielsch, L. Liao and Y. Hu, *Adv. Electron. Mater.*, 2020, **6**, 1900945.

18 B. Maennig, J. Drechsel, D. Gebeyehu, P. Simon, F. Kozlowski, A. Werner, F. Li, S. Grundmann, S. Sonntag, M. Koch, K. Leo, M. Pfeiffer, H. Hoppe, D. Meissner, N. S. Sariciftci, I. Riedel, V. Dyakonov and J. Parisi, *Appl. Phys. A*, 2004, **79**, 1-14.

19 P. Baronas, G. Kreiza, M. Mamada, S. Maedera, P. Adomėnas, O. Adomėnienė, K. Kazlauskas, C. Adachi and S. Juršėnas, *Adv. Opt. Mater.*, 2019, **8**, 1901670.

20 C. Falkenberg, K. Leo and M. K. Riede, *J. Appl. Phys.*, 2011, **110**, 124509.

21 I. D. W. Samuel and G. A. Turnbull, *Chem. Rev.*, 2007, **107**, 1272-1295.

22 I. Salzmann, G. Heimel, S. Duhm, M. Oehzelt, P. Pingel, B. M. George, A. Schnegg, K. Lips, R. P. Blum, A. Vollmer and N. Koch, *Phys. Rev. Lett.*, 2012, **108**, 035502.

23 H. Mendez, G. Heimel, S. Winkler, J. Frisch, A. Opitz, K. Sauer, B. Wegner, M. Oehzelt, C. Rothel, S. Duhm, D. Tobbens, N. Koch and I. Salzmann, *Nat. Commun.*, 2015, **6**, 8560.

24 C. Gao, S. K. K. Prasad, B. Zhang, M. Dvořák, M. J. Y. Tayebjee, D. R. McCamey, T. W. Schmidt, T. A. Smith and W. W. H. Wong, *J. Phys. Chem. C*, 2019, **123**, 20181-20187.

25 L. Xiao, Y. Wu, J. Chen, Z. Yu, Y. Liu, J. Yao and H. Fu, *J. Phys. Chem. A*, 2017, **121**, 8652-8658.

26 H. Nakanotani, M. Saito, H. Nakamura and C. Adachi, *Adv. Funct. Mater.*, 2010, **20**, 1610-1615.

27 A. S. Komolov, S. N. Akhremtchik and E. F. Lazneva, *Spectrochim. Acta A*, 2011, **79**, 708-711.

28 X. Wu, A. Surendran, J. Ko, O. Filonik, E. M. Herzig, P. Mueller-Buschbaum and W. L. Leong, *Adv. Mater.*, 2019, **31**, 1805544.

29 I. Salzmann and G. Heimel, *J. Electron Spectrosc.*, 2015, **204**, 208-222.

30 M. L. Tietze, J. Benduhn, P. Pahner, B. Nell, M. Schwarze, H. Kleemann, M. Krammer, K. Zojer, K. Vandewal and K. Leo, *Nat. Commun.*, 2018, **9**, 1182.

31 R. Warren, A. Privitera, P. Kaienburg, A. E. Lauritzen, O. Thimm, J. Nelson and M. K. Riede, *Nat. Commun.*, 2019, **10**, 5538.

32 X. Lin, B. Wegner, K. M. Lee, M. A. Fusella, F. Zhang, K. Moudgil, B. P. Rand, S. Barlow, S. R. Marder, N. Koch and A. Kahn, *Nat. Mater.*, 2017, **16**, 1209-1215.

33 H. Zhang, H. Dong, Y. Li, W. Jiang, Y. Zhen, L. Jiang, Z. Wang, W. Chen, A. Wittmann and W. Hu, *Adv. Mater.*, 2016, **28**, 7466-7471.

34 Y. Zhen, K. Inoue, Z. Wang, T. Kusamoto, K. Nakabayashi, S.-i. Ohkoshi, W. Hu, Y. Guo, K. Harano and E. Nakamura, *J. Am. Chem. Soc.*, 2018, **140**, 62-65.

35 B. Lüssem, M. Riede and K. Leo, *phys. Status Solidi A*, 2013, **210**, 9-43.

36 I. E. Jacobs and A. J. Moule, *Adv. Mater.*, 2017, **29**, 1703063.

37 I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler and N. Koch, *Acc. Chem. Res.*, 2016, **49**, 370-378.

38 J.-H. Lee and J.-J. Kim, *Phys. Status Solidi A*, 2012, **209**, 1399-1413.

39 H. Wang, Y. Zhao, Z. Xie, H. Shang, H. Wang, F. Li and Y. Ma, CrystEngComm, 2015, **17**, 2168-2175.

40 K. Wang, Z. Gao, W. Zhang, Y. Yan, H. Song, X. Lin, Z. Zhou, H. Meng, A. Xia, J. Yao and Y. S. Zhao, *Sci. Adv.*, 2019, **5**, eaaw2953.

41 R. Huang, C. Wang, Y. Wang and H. Zhang, *Adv. Mater.*, 2018, **30**, 1800814.

42 J. Han, W. Feng, D. Y. Muleta, C. N. Bridgmohan, Y. Dang, G. Xie, H. Zhang, X. Zhou, W. Li, L. Wang, D. Liu, Y. Dang, T. Wang and W. Hu, *Adv. Funct. Mater.*, 2019, **29**, 1902503.

43 R. Ding, F. X. Dong, M. H. An, X. P. Wang, M. R. Wang, X. B. Li, J. Feng and H. B. Sun, *Adv. Funct. Mater.*, 2019, **29**, 1807606.

44 R. Ding, X. P. Wang, J. Feng, X. B. Li, F. X. Dong, W. Q. Tian, J. R. Du, H. H. Fang, H. Y. Wang, T. Yamao, S. Hotta and H. B. Sun, *Adv. Mater.*, 2018, **30**, 1801078.

45 H. Wang, F. Li, B. Gao, Z. Xie, S. Liu, C. Wang, D. Hu, F. Shen, Y. Xu, H. Shang, Q. Chen, Y. Ma and H. Sun, *Cryst. Growth Des.*, 2009, **9**, 4945-4950.

46 P. Alam, N. L. C. Leung, J. Liu, T. S. Cheung, X. Zhang, Z. He, R. T. K. Kwok, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, C. C. S. Chan, K. S. Wong, Q. Peng and B. Z. Tang, *Adv. Mater.*, 2020, **32**, 2001026.

47 H. Jiang and W. Hu, *Angew. Chem. Int. Ed.*, 2020, **59**, 1408-1428.

48 J. Wu, Q. Li, G. Xue, H. Chen and H. Li, *Adv. Mater.*, 2017, **29**, 1606101.

49 Y. Yao, H. Dong, F. Liu, T. P. Russell and W. Hu, *Adv. Mater.*, 2017, **29**, 1701251.

50 C. Wang, H. Dong, L. Jiang and W. Hu, *Chem. Soc. Rev.*, 2018, **47**, 422-500.

51 D. Zhu, S. Shi and R. Qian, *Makromol. Chem., Rapid Commun*. 1986, **7**, 313-317.

52 J. Liu, L. Jiang, W. Hu, Y. Liu and D. Zhu, *Sci. China Chem.*, 2019, **62**, 313-330.

53 C. Xu, P. He, J. Liu, A. Cui, H. Dong, Y. Zhen, W. Chen and W. Hu, *Angew. Chem.Int. Ed.*, 2016, **55**, 9519-9523.

54 C. Kloc, P. G. Simpkins, T. Siegrist and R. A. Laudise, *J. Cryst. Growth*, 1997, **182**, 416-427.

55 Y. Diao, L. Shaw, Z. Bao and S. C. B. Mannsfeld, *Energy Environ. Sci.*, 2014, **7**, 2145-2159.

56 S. Duan, T. Wang, B. Geng, X. Gao, C. Li, J. Zhang, Y. Xi, X. Zhang, X. Ren and W. Hu, *Adv. Mater.*, 2020, **32**, 1908388.

57 T. Kawase, T. Shimoda, C. Newsome, H. Sirringhaus and R. H. Friend, *Thin Solid Films*, 2003, **438**, 279-287.

58 Y. Diao, B. C. K. Tee, G. Giri, J. Xu, D. H. Kim, H. A. Becerril, R. M. Stoltenberg, T. H. Lee, G. Xue, S. C. B. Mannsfeld and Z. Bao, *Nat. Mater.*, 2013, **12**, 665-671.

59 P. Wang, D. Liu, Y. Wang, P. Zhang, M. Wang, Y. Zhen, H. Dong and W. Hu, *Chi. Chem. Lett.*, 2020, DOI: org/10.1016/j.cclet.2020.02.012.

60 G. Tsiminis, Y. Wang, A. L. Kanibolotsky, A. R. Inigo, P. J. Skabara, I. D. W. Samuel and G. A. Turnbull, *Adv. Mater.*, 2013, **25**, 2826-2830.

61 Y. Jiang, P. Lv, J.-Q. Pan, Y. Li, H. Lin, X.-W. Zhang, J. Wang, Y.-Y. Liu, Q. Wei, G.-C. Xing, W.-Y. Lai and W. Huang, *Adv. Funct. Mater.*, 2019, **29**, 1806719.

62 D. Liu, J. De, H. Gao, S. Ma, Q. Ou, S. Li, Z. Qin, H. Dong, Q. Liao, B. Xu, Q. Peng, Z. Shuai, W. Tian, H. Fu, X. Zhang, Y. Zhen and W. Hu, *J. Am. Chem. Soc.*, 2020, **142**, 6332-6339.

63 X. Liu, M. Sang, H. Lin, C. Liu, J. Zhang, J. Yi, K. Gao, W.-Y. Lai and W. Huang, Chem.-Eur. J., 2020, **26**, 3103-3112.

64 X. D. Wang, Z. Z. Li, S. F. Li, H. Li, J. W. Chen, Y. S. Wu and H. B. Fu, Adv. Opt. Mater., 2017, **5**, 1700027.

65 H. Nakanotani, S. Akiyama, D. Ohnishi, M. Moriwake, M. Yahiro, T. Yoshihara, S. Tobita and C. Adachi, *Adv. Funct. Mater.*, 2007, **17**, 2328-2335.

66 Y. Han, L. Bai, M. Xu, X. An, C. Wei, L. Sun, N. Sun, M. Yu, H. Zhang, J. Lin, C. Ou, L. Xie, C. Yin, C. Sun, X. Ding, J. Cabanillas-Gonzalez and W. Huang, *Adv. Opt. Mater.*, 2020, **8**, 1902163.

67 L. Liang, N. Chen, Y. Jia, Q. Ma, J. Wang, Q. Yuan and W. Tan, *Nano Res.*, 2019, **12**, 1279-1292.

68 J. Xu, D. Murata, J. Ueda and S. Tanabe, *J. Mater. Chem. C*, 2016, **4**, 11096-11103.

69 Y. Li, M. Gecevicius and J. Qiu, *Chem. Soc. Rev*., 2016, **45**, 2090-2136.

70 Z. Qiu, Y. Zhou, M. Lu, A. Zhang and Q. Ma, *Acta Mater.*, 2007, **55**, 2615-2620.

71 R. Kabe and C. Adachi, *Nature*, 2017, **550**, 384-387.

72 J. Zhao, S. Ji and H. Guo, *RSC Adv.*, 2011, **1**, 937-950.

73 J. Zhou, Q. Liu, W. Feng, Y. Sun and F. Li, *Chem. Rev.*, 2015, **115**, 395-465.

74 L. Li, Y. Zeng, T. Yu, J. Chen, G. Yang and Y. Li, *Chemsuschem*, 2017, **10**, 4610-4615.

75 L. Li, Y. Zeng, J. Chen, T. Yu, R. Hu, G. Yang and Y. Li, *J. Phys. Chem. Lett.*, 2019, **10**, 6239-6245.

76 S. Amemori, Y. Sasaki, N. Yanai and N. Kimizuka, *J. Am. Chem. Soc.*, 2016, **138**, 8702-8705.

77 C. Gao, J. Y. Seow, B. Zhang, C. R. Hall, A. J. Tilley, J. M. White, T. A. Smith and W. W. H. Wong, *Chempluschem*, 2019, **84**, 746-753.

78 T. Ogawa, N. Yanai, H. Kouno and N. Kimizuka, *J. Photon. Energy*, 2018, **8**, 022003.

79 C. Gao, B. Zhang, C. R. Hall, L. Li, Y. Chen, Y. Zeng, T. A. Smith and W. W. H. Wong, *Phys. Chem. Chem. Phys*., 2020, **22**, 6300-6307.

80 H. Dong, X. Fu, J. Liu, Z. Wang and W. Hu, *Adv. Mater.*, 2013, **25**, 6158-6182.

81 C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208-2267.

82 Y. Zhang and W. Hu, *Sci. China Ser. B-Chem.*, 2009, **52**, 751-754.

83 W. Deng, X. Zhang, H. Dong, J. Jie, X. Xu, J. Liu, L. He, L. Xu, W. Hu and X. Zhang, *Mater. Today*, 2019, **24**, 17-25.

84 S. Wang, J. Xu, W. Wang, G.-J. N. Wang, R. Rastak, F. Molina-Lopez, J. W. Chung, S. Niu, V. R. Feig, J. Lopez, T. Lei, S.-K. Kwon, Y. Kim, A. M. Foudeh, A. Ehrlich, A. Gasperini, Y. Yun, B. Murmann, J. B. H. Tok and Z. Bao, *Nature*, 2018, **555**, 83-88.

85 Z. Zheng, Z. Ni, X. Zhang, Y. Zhen, H. Dong, J. Zhang and W. Hu, *Sci. China Mater.*, 2019, **62**, 813-822.

86 Y. Zhang, J. Ye, Z. Liu, Q. Liu, X. Guo, Y. Dang, J. Zhang, Z. Wei, Z. Wang, H. Dong and W. Hu, *J. Mater. Chem. C*, 2020, DOI: 10.1039/D0TC01174F.

87 J. Zhang, P. Gu, G. Long, R. Ganguly, Y. Li, N. Aratani, H. Yamada and Q. Zhang, *Chem. Sci.*, 2016, **7**, 3851-3856.

88 G. Zhao, H. Dong, Q. Liao, J. Jiang, Y. Luo, H. Fu and W. Hu, *Nat. Commun.*, 2018, **9**, 4790.

89 M. Hu, J. Liu, Q. Zhao, D. Liu, Q. Zhang, K. Zhou, J. Li, H. Dong and W. Hu, *Sci. China Mater.*, 2019, **62**, 729-735.

90 R. Ding, J. Feng, F.-X. Dong, W. Zhou, Y. Liu, X.-L. Zhang, X.-P. Wang, H.-H. Fang, B. Xu, X.-B. Li, H.-Y. Wang, S. Hotta and H.-B. Sun, *Adv. Funct. Mater.*, 2017, **27**, 1604659.

91 C. Zhang, P. Chen and W. Hu, *Small*, 2016, **12**, 1252-1294.

92 C.-F. Liu, X. Liu, W.-Y. Lai and W. Huang, *Adv. Mater.*, 2018, **30**, 1802466.

93 M. U. Chaudhry, K. Muhieddine, R. Wawrzinek, J. Sobus, K. Tandy, S. C. Lo and E. B. Namdas, *Adv. Funct. Mater*., 2019, **29**, 1905282.

94 Z. Qin, H. Gao, J. Liu, K. Zhou, J. Li, Y. Dang, L. Huang, H. Deng, X. Zhang, H. Dong and W. Hu, *Adv. Mater.*, 2019, **31**, 1903175.

95 J. Li, K. Zhou, J. Liu, Y. Zhen, L. Liu, J. Zhang, H. Dong, X. Zhang, L. Jiang and W. Hu, *J. Am. Chem. Soc.*, 2017, **139**, 17261-17264.

96 A. Dadvand, A. G. Moiseev, K. Sawabe, W.-H. Sun, B. Djukic, I. Chung, T. Takenobu, F. Rosei and D. F. Perepichka, *Angew. Chem. Int. Ed.*, 2012, **51**, 3837-3841.

97 J. Li, L. Zheng, L. Sun, C. Li, X. Zhang, S. Cheng and W. Hu, *J. Mater. Chem. C*, 2018, **6**, 13257-13260.

98 J. Liu, H. Zhang, H. Dong, L. Meng, L. Jiang, L. Jiang, Y. Wang, J. Yu, Y. Sun, W. Hu and A. J. Heeger, *Nat. Commun.*, 2015, **6**, 10032.

99 Y. Zhao, L. Yan, I. Murtaza, X. Liang, H. Meng and W. Huang, *Org. Electron.*, 2017, **43**, 105-111.

100 H. Dong, Q. Yan and W. Hu, *Acta Polym. Sin.*, 2017, **8**, 1246-1260.

101 Z. Zhang, Q. Liu, H. Dong and W. Hu, *Sci. China Chem.*, 2019, **62**, 1271-1274.

102 Q. Li, Y. Yao, G. Qiu, P. Zhang, H. Dong and W. Hu, *Chinese Sci. Bull.*, 2016, **61**, 2688-2706.

103 Q. Yan, Y. Yao, H. Dong and W. Hu, *Sci. China Chem.*, 2016, **46**, 1007-1022.

104 D. H. Kim, J. T. Han, Y. D. Park, Y. Jang, J. H. Cho, M. Hwang and K. Cho, Adv. Mate., 2006, **18**, 719-723.

105 C. Li, Y. Wang, Y. Zou, X. Zhang, H. Dong and W. Hu, *Angew. Chem. Int. Ed.*, 2020, **59**, 9403-9407.