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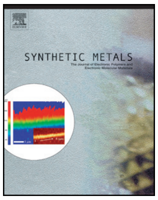

Charge transport in structural-ordering doped organic crystals: The effect of dye-doping concentration and crystal thickness on the mobility

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ABSTRACT

Doped organic crystals with structural-ordering retention expected to the integration of high carrier mobility and high luminescence efficiency could be as promising materials for the high-performance light-emitting devices even the electrically pumped laser. In this work, charge-transport characteristics in doped organic crystals based on distyrylbenzene (DSB) as the host and tetracene (Tc) or pentacene (Pc) as the guest have been discussed in detail, including the effect factors of the guest doping concentration and the crystal thickness by the field-effect transistor (FET) and space-charge limited current (SCLC) methods. In the FETs, the mobilities of doped crystals have the slight decrease compared with that of undoped crystal but all are in the same order of magnitude ($\sim 10^{-3}$–10^{-2} cm^2/Vs), which is attributed to the structural-ordering retention even when the concentration of guest molecules embedded into the host crystal is up to ~8%. Different with the lateral-configuration FET transporting the carriers inside several molecular layers of crystal surface, the vertical-configuration diode makes the carriers pass through the crystal body. The mobilities estimated by SCLC for doped and undoped crystals also present the similar variation with the FET's measurement. More significantly, the mobility increases with the crystal thickness at the same electrical field which indicates the negative influence of interfacial contact between the electrode and the crystal on the injected charges can be further suppressed by means of a relatively thicker crystal. Our primary results showcase that structural-ordering doped organic crystals have the comparable mobilities relative to their host sources, which is promising to extend to other doped crystal systems as well. Considering conveniently controllable properties of high efficiency and color-tunable emission by energy transfer, doped organic crystals are expected to be of interest for high-performance optoelectronic devices; moreover, it is verified that the increase of crystal thickness is beneficial for improving the utilization of injected charges in the vertical-configuration diode.

1. Introduction

Organic single crystals constructed by π-conjugated molecules have attracted great attention in the field of organic optoelectronic materials [1–4]. The academic motivation for organic single crystal research is their definite structures, which provides a model to investigate the basic interactions between the molecules (supramolecular interaction), and the relationship between molecular stacking modes and optoelectronic performance (luminescence and carrier mobility) [5,6]. In the meanwhile, the superiorities of organic crystals such as high thermal stability, high ordered structure and high carrier mobility make them attractive candidates for optoelectronic devices such as optically pumped lasers [7,8], field-effect transistors [9,10], electroluminescences [11,12], and photovoltaic cells [13,14]. For the traditional organic optoelectronic polycene materials such as tetracene, pentacene and rubrene extensively investigated in the aspect of mobility [9,10,15], it is difficult to obtain high luminescent-efficiency crystals because of their 'herringbone' intermolecular arrangements (H-aggregates) which limit the further application in electroluminescence or laser. The molecular stacking could be adjusted to J-aggregates or X-aggregates by introducing the special intermolecular interactions, to improve the luminescent efficiency of the crystal [5,16]; but in the view of supramolecular chemistry and crystal engineering, designing the intermolecular interaction by the chemical synthesis to control the molecular stacking mode in the crystal is usually complicated. As we know, doping dye

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molecules into certain host materials is a general method to increase the luminescent efficiency for the organic amorphous materials [17]. Another merit of doping is that it can shift the emission away from the absorption region of the host to decrease the absorption loss of lasers. Thus, achieving the high luminescence and desirable carrier mobility expected to be maintained simultaneously in the doped organic crystal is significant towards high-performance optoelectronic devices [18].

Doped organic molecular crystals have been paid much attention as early as 1970's and stimulated emissions in some systems were observed in succession [19–21]. Further in-depth photophysical characterizations of doped systems revealed the relationships between basic optoelectronic functions and molecular structures [22–26]. In our early work, we have succeeded to prepare the large-size and structural-ordering doped organic crystals based on distyrylbenzene (DSB) as the host and tetracene (Tc) or pentacene (Pc) as the guest by physical vapor transport (PVT) method [27], which is mainly attributed to the structural comparability of host and guest molecules (including molecular structures and their stacking modes) and their similar intermolecular edge-to-face arene-arene interactions. These doped crystals revealed the excellent properties of high efficiency and color-tunable emission by efficient energy transfer from the host to guest and the suppressing of the interaction among the guest molecules. Although the optical characteristics of steady-state and time-resolved fluorescences have been investigated detailedly, the basically electrical properties especially helpful for the further applications of crystal-based electronic devices such as field-effect transistors (FETs) and light-emitting diodes (LEDs) are still lack of enough understanding. Therefore, it is of great significance to explore the charge transport in doped organic crystals where the structural-ordering retention may benefit to obtain the desirable carrier mobility.

In this work, lateral-configuration FETs and vertical-configuration diodes based on undoped DSB, Tc-doped DSB (DSB⊂Tc) and Pc-doped DSB (DSB⊂Pc) crystals have been fabricated to investigate the influences of the guest doping concentration and the crystal thickness on the carrier mobility. The primary results indicate that structural-ordering doped organic crystals have the comparable mobilities relative to the undoped crystal, which provides an effective strategy to design the integration of high mobility and tunably high luminescence in a doped system of organic crystal extremely urgent for the electrically pumped laser [28].

2. Experimental section

Fluorescence spectra were recorded on RF-5301PC spectrophotometer. The wide-angle X-ray diffraction was detected with a Rigaku X-ray diffractometer (D/Max-rA, using Cu-Kα radiation of wavelength 1.542 Å), and in the test the slice crystal was flatted parallel to the single-crystal Si substrate.

2.1. FET fabrications

A 200-nm-thick SiO_2 layer on a highly doped silicon wafer was used as an insulator. A 100-nm-thick poly(methylmethacrylate) (PMMA) layer was spin-coated from a toluene solution (30 mg/mL) onto the wafer. After the PMMA deposition, the substrates were maintained overnight in an oven at 70 °C and were subsequently annealed at 100 °C for 3 h in a N_2 atmosphere. Next, the crystals were carefully placed on the substrate. The 50-nm-thick top-contact gold electrodes were thermally evaporated on the crystal surface at a rate of 0.1 nm/s through a shadow mask under a background pressure of 1×10^{-6} mbar. The channel length and width were checked with an optical microscope. The FET measurements were carried out in the glovebox without exposing the substrate to air.

2.2. Diode fabrications

Firstly, the poly(3,4-ethyl-enedioxythiophene): polystyrenesulfonate (PEDOT: PSS) layer on the indium tin oxide (ITO) substrate was obtained by spin-coating at 1000 rpm for 60 s. Then, the sample was dried by heating at 110 °C for 180 min in a glove box. The thickness of PEDOT: PSS film was $\sim$100 nm, as measured by α-step. The very thin crystals were chosen, displaying better interfacial contact for electrical properties. The thinness of the crystals made them naturally bendable and electrostatically bonded (van der Waals forces) to the PEDOT: PSS/ITO substrate. A 150-nm-thick aluminum (Al) layer was thermally evaporated on the crystal surface at a rate of 0.3 nm/s under a background pressure of 1×10^{-6} mbar. But for Time of Flight (TOF) measurement, a 30-nm-thick semitransparent Al layer required as the cathode was used instead.

2.3. Electrical measurements

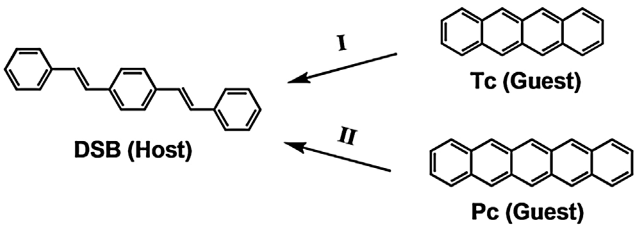
I/V measurements were done using semiconductor parameter analyzer (SPA) HP4155C (Agilent Technologies) in a glove box.

Time of Flight (TOF) measurement were perform using a pulse generator (Agilent 8110A), and a $50\,\Omega$ input of an Oscilloscope (Tektronix TDS 3012). The light excitation was done using the third harmonic (355 nm) of a Nd:YAG laser (PASSAT Ltd. Naples) at a repetition rate of $\sim$100 Hz with pulse width $<$3.5 ns. In order to attenuate the beam intensity a neutral density filters were used (Thorlabs BK7 Reflective Neutral Density Filters).

3. Results and discussion

3.1. Materials and structure information

Scheme 1 shows host and guest molecular structures in the doped system where both DSB and Tc/Pc are the linear configurations and the molecules in the crystals are arranged in similar "herringbone" type structure in *ab*-plane, as proved in previous work [29–31]. Fig. 1a–c shows the optical photographs of DSB, DSB⊂Tc and DSB⊂Pc crystals under the ultraviolet lamp. Other doped crystals with different host/guest mol ratio and their photoluminescence (PL) spectra are also shown in Figs. S1 and S2. Fig. 1d shows the diffraction patterns of X-ray diffraction (XRD) on above slice crystals. According to Bragg equation ($2d\sin\theta = n\lambda$) the average layer spacing of DSB, DSB⊂Tc and DSB⊂Pc crystals are calculated to be 1.72, 1.74 and 1.75 nm, respectively. The results indicate that the ordered structures of doped crystals are retained but a slight increase of the molecular layer spacing compared with DSB crystal after the guest molecules embedded occupy the lattice locations of host molecules during the crystal growth process. Fig. 1e and f represents the proposed molecular stacks of DSB⊂Tc



Scheme 1. (a) Doped crystal system of DSB as the host, and Tc (I) and Pc (II) as the guest, respectively.