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Communication

Long-range ordering of composites for organic electronics: TIPS-pentacene single crystals with incorporated nano-fibers

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ABSTRACT

Multi-component active materials are widely used for organic electronic devices, with every component contributing complementary and synergistic optoelectronic functions. Mixing these components generally leads to lowered crystallinity and weakened charge transport. Therefore, preparing the active materials without substantially disrupting the crystalline lattice is highly desired. Here, we show that crystallization of TIPS-pentacene from solutions in the presence of fluorescent nanofibers of a perylene bisimide derivative (PBI) leads to formation of composites with nanofiber guest incorporated in the crystal host. In spite of the binary composite structure, the TIPS-pentacene maintains the single-crystalline nature. As a result, the incorporation of the PBI guest introduces additional fluorescence function but does not significantly reduce the charge transport property of the TIPS-pentacene host, exhibiting field-effect mobility as high as 3.34 $cm^2 V^{-1} s^{-1}$ even though 26.4% of the channel area is taken over by the guest. As such, this work provides a facile approach toward high-performance multifunctional organic electronic materials.

Organic semiconductors are widely used in a variety of electronic devices such as organic field-effect transistors (FETs) [1–6], organic solar cells (OSCs) [7–10], and organic light-emitting diodes (OLEDs) [11–15]. For these devices, high charge mobility is typically desired and organic single-crystals are, thus, ideal materials. In principle, organic single crystals have the potential to achieve superior charge transport performance, as they have the highest degree of order in long range compared with their amorphous and polycrystalline counterparts [16–19]. In addition to the function of charge transport, other optoelectronic functions are needed to construct a working device, such as exciton generation for emission [11] and exciton dissociation for photovoltaics [7]. Only a few materials (including organic and organic-inorganic hybrid materials) have good performance in multiple aspects, like charge transport, luminescence, light absorption and so on [20–25]. For example, high-mobility organic crystals typically exhibit very weak fluorescence due to the aggregation-induced quenching effect [26]. As such, multifunction is often achieved by mixing multi-components with varied functions [27–30]. Examples include chemical sensors with various composites [31–34], memory devices containing embedded nanoparticles [35,36], photo detectors incorporated with quantum dots [37,38], light-emitting devices based on multiple components [39–41] and solar cells with heterojunctions [8,42,43].

Although mixing is effective to realize multifunction, it generally reduces the crystallinity of active materials and leads to the reduction of charge mobility. Therefore, maintaining the ordered molecular packing within the multi-component active materials is needed. Efforts have been made to the fabrication of multifunctional composites based on single crystals. For example, functional nanoparticles and nanorods have been incorporated into well-ordered inorganic single crystals, organic single crystals and metal-organic framework single crystals to get materials with multiple functions [44–48]. However, design of single crystal composites where foreign materials are distributed inside single crystals to achieve multiple functions has not been appreciated in

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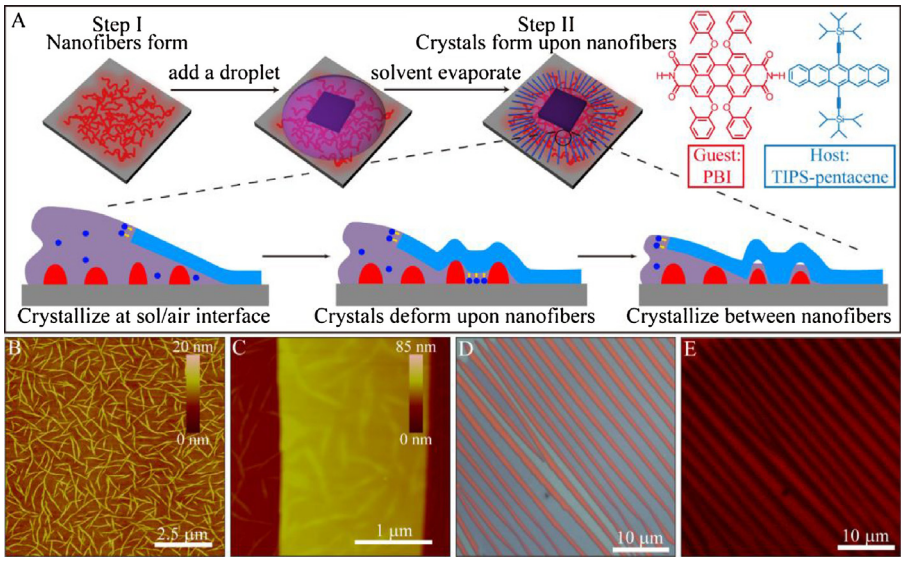

Fig. 1. Schematic representations of the two-step preparation method for single-crystal composites together with the morphologies of the products in each step. (A) Schematic representations of the method: TIPS-pentacene crystallizes from a receding droplet on a substrate containing preformed PBI nanofibers. Crystals first grow at the interface of solution and air. As the solvent separating the crystals and the nanofibers evaporates, crystals contact the nanofibers and deform. Further crystallization fills the space between the nanofibers. (B) An AFM image of spin-coated PBI nanofibers. (C) An AFM image of single-crystal composites, showing fibrous humps on the top surface. (D, E) Optical and fluorescence microscopy images showing the light blue crystal ribbons in (D) emit red fluorescence in (E).

the field of organic electronics. In this article, we demonstrate that fluorescent PBI nanofibers, the guest, can be incorporated into the solution-grown aligned 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) single crystals, the host, by a two-step method to form single-crystal composites (Fig. 1A). These single-crystal composites exhibit additional luminescence performance while maintaining high charge carrier mobility.

TIPS-pentacene [49] was selected as the host and a recently reported PBI gelator [50] as the guest (Fig. 1A). TIPS-pentacene crystallizes easily and has the potential to exhibit high mobility [51] while TIPS-pentacene films have very weak fluorescent emission [52]. On the other hand, the PBI molecules self-assemble through hydrogen bonding into highly fluorescent nanofibers [50]. The nanofiber guest and the crystal host were interfaced together using a two-step method as described in Fig. 1. First, PBI nanofibers formed after PBI solutions (0.1 mg/mL) were spin-coated on a substrate, as imaged by AFM (Fig. 1B). The nanofibers are 2–10 nm in height and 0.4–1.9 μm in length. Second, the TIPS-pentacene crystallizes in the presence of the PBI nanofibers. A droplet of TIPS-pentacene solution with an orthogonal solvent (hexane, 0.3 mg/mL) was added on the PBI fibers. As the solvent evaporated, crystals formed through a DPC process in which directional receding of a droplet leads to crystal alignment [53,54]. Interestingly, the obtained TIPS-pentacene crystals (Fig. 1D) exhibit well-aligned ribbon shapes similar to those of crystals grown in the absence of the PBI nanofibers [55,56] (Fig. S1 in Supporting information). The well-aligned long crystals have a width of 2.3–6.9 μm and a height of 27–57 nm, as measured from AFM images. As the crystals do not cover the substrate surface completely, the exposed PBI nanofibers between the crystals were easily washed away and those covered by the crystals can be imaged by fluorescence microscopy. In OM and fluorescence microscopy, red fluorescence emission was observed exactly at the locations of the crystals, indicating the coexistence of the fluorescent PBI and the TIPS-pentacene crystals (Fig. 1D and E).

Similarly, the coexistence of both components was directly imaged by TEM (Fig. 2A). Furthermore, how the PBI nanofibers distributed together with the TIPS-pentacene crystals was examined by imaging both the top and bottom surfaces of the crystals.

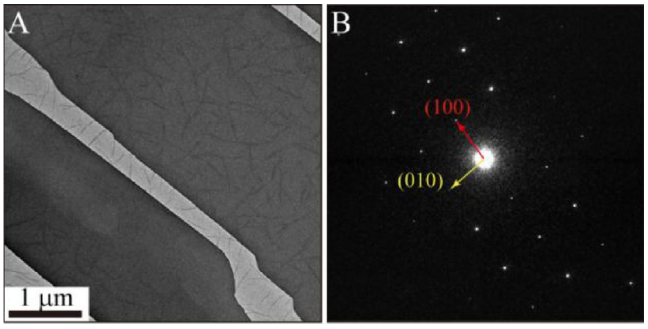

Fig. 2. (A) TEM image showing the coexistence of nanofibers and single crystals (dark ribbons). (B) SAED pattern showing the single crystallinity.

The AFM images show fibrous humps on the top surface (Fig. 1C) and fibrous pits on the bottom surface (Fig. 3A), instead of the typical smooth terraces [55]. The sizes and morphologies of these humps and pits are similar to those of the PBI nanofibers, indicating that the nanofibers penetrate into the crystals. Despite the presence of the nanofibers in the crystals, the host crystals still maintain their single-crystalline nature. Selected-area electron diffraction (SAED) of a large area (diameter of 6.5 μm, Fig. 2B), including fibers, gives a single set of diffraction spots consistent with those of TIPS-pentacene single crystals [57]. And the single-crystallinity was reconfirmed by polarized OM (Fig. S2 in Supporting Information). Therefore, the OM, TEM, AFM and SAED evidences demonstrate that we obtained the single-crystal composites with PBI nanofiber guest incorporated in the TIPS-pentacene crystal host.

Next, the mechanism of the single-crystal composites form is investigated. On one hand, the fibrous humps (Fig. 1C) observed on the top surface of the crystals indicate that the smooth crystalline terraces are deformed by the PBI fibers into rough surfaces when the crystals contact the nanofibers. On the other hand, the deep pits (Fig. 3A) on bottom surface of the crystals suggest that the

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