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Facile synthesis of single-crystalline microwires based on anthracene derivative and their efficient optical waveguides and linearly polarized emission

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ABSTRACT

The well-defined single-crystalline microwires of a solid-emissive organic functional molecule, 2-(anthracen-9-yl)-4, 5-diphenyl-1H-imidozole (ADPI) were successfully prepared by a facile solution process without the use of surfactant or additional templates. In addition, the optical loss coefficient is as low as 0.1 dB μm^{-1} for the as-prepared ADPI microwires, which is lower than most previous reported organic optical waveguides. Meanwhile, these microwires also show optically uniaxial properties as demonstrated by the linearly polarized emission, providing potentially orientation-sensitive applications as optical waveguides with low optical loss.

1. Introduction

In recent years, one-dimensional (1D) functional micro/nanoscale materials have attracted a surge of interest due to their unique properties and various potential applications in photonics, electronics, high-density storage, chemo- and biosensors [1–4]. Among them, optical waveguides are important interconnectors in the miniaturized optical circuits and extensive studies in this fascinating field have so far been mainly focused on 1D inorganic semiconductor [5–8]. However, most of these optical materials are difficult to produce, which often need high-temperature processes, complicated chemical reactions, or precise physical vapor deposition. Compared to their inorganic counterparts, few 1D organic materials had been used to construct the optical waveguides, though they can offer better flexibility, greater variety, easier optical tunability and lower cost [9–11]. This is mainly because the conventional luminophores usually have planar π-conjugated structures and thus suffer from the notorious effect of aggregation-caused quenching in the condensed phase [12]. On the other hand, 1D nano/microscale materials based on polymers or organic small molecules are found to serve as a better media to generate or propagate light in a pre-defined way with low optical loss and more functionality [13,14]. Therefore, the exploration of new luminogens that are not only suitable for fabrication of 1D structures, but also even more importantly, enable strong fluorescence in the solid state remains a formidable challenge.

In this work, we designed and synthesized an anthracene derivative, namely 2-(anthracen-9-yl)-4,5-diphenyl-1H-imidozole (ADPI, Scheme 1). In this compound, anthracene fluorophore shows a highly planar structure, while the polar imidazolium unit may be prone to the formation of intermolecular hydrogen bonds. In particular, the two terminal phenyl groups can provide valuable steric hindrance to promote non-parallel packing, and facilitate visible luminescence in the condensed solid. We found that the targeted molecule could easily self-assemble into ultralong microwires by a facile solution process without the assistance of added surfactant or template under ambient conditions. Additionally, these wires exhibited excellent optical waveguide properties and the corresponding propagation loss coefficient is ca. 0.1 dB μm^{-1}. Meanwhile, the rotating microscopy imaging and polarized photoluminescence spectra of the ADPI microwires revealed typical characteristics of light emission anisotropy. These results indicate that the as-prepared ADPI microwires have potentially orientation-sensitive applications as optical waveguide with low optical loss.

2. Experimental

ADPI was conveniently synthesized in a straightforward manner by a simple one-step reaction, which was similar to that reported in the literature [15]. The ^1H NMR (400 MHz, $CDCl_3$): 8.54 (s, 1H), 8.02 (m, 2H), 7.77 (m, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.53 (m, 9H),

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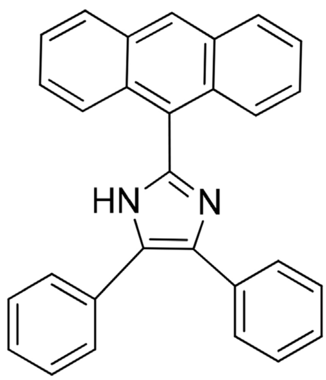

Scheme 1. Chemical structure of ADPI molecule.

7.24 (d, J = 7.6 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 3.09 (s, 3H). The typical preparation of ADPI microwires was performed through a facile reprecipitation method: the ADPI powder was dissolved in ethanol at a concentration of 8 mg ml^{-1} by sonication for 10 min. The resulting solution was then injected rapidly into a large volume of hexane ($V_{ethanol}$:V_{hexane} = 1:60). The final mixture was agitated by manual shaking and kept at room temperature without any further agitation for about 20 h for stabilization. The obtained precipitates could be transferred and cast onto a precleaned Si or quartz substrate by pipetting. The as-prepared samples were then characterized by scanning electron microscopy (SEM, Quanta 400 FEG), transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin), X-ray diffraction (XRD, Bruker D8 Advance X-Ray Diffractometer) and polarized photoluminescence spectra (PL, Varian Cary Eclipse fluorescence spectrophotometer).

3. Results and discussion

For organic solid-state materials, the optical and electronic properties are governed by the whole collective rather than by the individual molecules, because the constituent molecules may form strong intermolecular interactions and thus assemble into packed structures. Solution-based self-assembly of ADPI may use a non-solvent nucleation or reprecipitation method, where the ADPI molecules are transferred from an ethanol solution into a poor solvent (e.g., hexane) to induce aggregation. The intermolecular π–π stacking between anthryl chromophore directed by the stronger intramolecular N—H. . .N hydrogen bonding can be utilized to achieve ordered self-assemblies. Large anisotropy in surface energy leads to the spontaneous growth of ADPI microwires.

Figure 1a shows typical SEM image of the obtained microwires, which are several hundred microns in length and several microns in diameter. These micowires are smooth and clean in surface, suggestive of a uniform arrangement of the luminogenic molecules. XRD pattern were recorded to further investigate the crystal structure of the microwires and starting powder materials as shown in Figure 1c. Both XRD patterns can be readily indexed by a monoclinic system with the space group $P2_1/n$. Moreover, the preferential growth of microwires also induces the more distinctive, highly crystalline XRD pattern. The TEM image of an individual microwire and its corresponding selected area diffraction (SAED) pattern were shown in Figure 1b and d. Well-defined array of sharp spots and no change in the SAED pattern was observed for the different parts of the same microwire, indicating that the whole microwire had single crystalline structure. These results further prove that the assembly morphology of ADPI is determined by its molecular interactions.

The fluorescence microscopy images of the ADPI microwires are shown in Figure 2a. It can be clearly seen that these microwires exhibit bright luminescence spots at both ends of each wire as well as the intersections of crossed wires and relatively weaker emission from the bodies of the wires, which is a typical characteristic of an optical waveguide. That is, following optical excitation at location along the wire, resulting PL emission propagated to the end of the wire where the bright spot observed at the tip arose due to out-coupling of the PL by diffraction. The waveguide effect is usually observed in an optically anisotropic system, such as

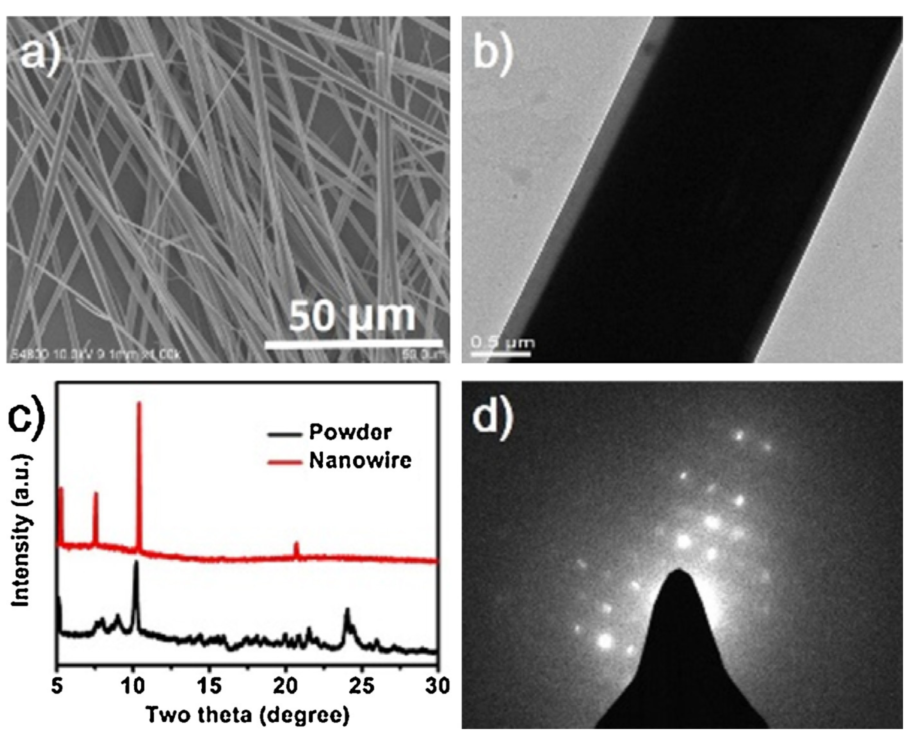

Figure 1. (a) Typical SEM image of ADPI microwires, (b) TEM image of a single ADPI microwire, (c) XRD pattern of the microwires and source powder of ADPI and (d) the corresponding SAED pattern recorded with a single microwire.