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Crystalline oligopyrene nanowires with multicolored emission†

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Highly crystalline oligopyrene nanowires have been prepared by template-assisted electropolymerization of pyrene in boron trifluoride diethyl etherate medium, which can emit strong blue, green or red fluorescence as excited at 405, 488 or 543 nm, respectively.

One-dimensional (1-D) nanostructures of conjugated polymers are expected to possess the advantages of both low-dimensional systems and organic conductors.[1] Many synthetic methods including chemical and electrochemical polymerizations in the presence or absence of a solid template have been developed to prepare nanostructured conjugated polymers.[2] Nanowires and fibers of conjugated polymers prepared by electrospinning[3] and mechanical stretching[4] have also been reported.

Conjugated polymers such as polyphenylenevinylene (PPV) and its derivatives are known as visible light emitters and have been widely used in the fabrication of light-emitting devices.[5] However, to date, few studies have concerned the optical properties of 1-D nanostructures of conjugated polymers and the multicolor emitting behavior of the conjugated polymers or oligomers has not yet been reported. On the other hand, highly crystalline conjugated polymers are very important for efficient charge carrier transport, and a crystalline structure of the polymers will effectively enhance the performances of their electronic or optical devices.[6] Several crystalline conjugated polymers have been synthesized through chemical routes.[7] However, it is believed that the conjugated polymers obtained *via* the electrochemical routes are rather non-crystalline materials with broad amorphous halos in the wide-angle X-ray diffraction regions, and with a weak small-angle peak corresponding to periodic structure from the planar configuration of the polymer backbone.[8] Herein, we report oligopyrene (Fig. 1) nanowires generated by using template-assisted electrochemical polymerization of pyrene. It was found that the nanowires not only have high crystallinity, but also can emit strong multicolor fluorescence.

The oligopyrene nanowires were fabricated by electropolymerization of pyrene using a porous alumina membrane (Anodisc, Whatman) with a pore diameter of 200 nm as the template. Pyrene was chosen as the monomer mainly because it is a good fluorescent indicator with a large π conjugated structure, a large Stokes shift, high quantum yield, strong absorbance and excellent photostability and long fluorescence lifetime.[9] The electrolyte was boron trifluoride diethyl etherate (BFEE) containing 0.1 M pyrene. A template membrane with a thin layer gold coating (formed by vapor deposition) served as the working electrode in a three-electrode configuration.[10] The counter electrode was a stainless steel sheet (AISI 304) and all the potentials were referred to a saturated calomel electrode (SCE). The polymerization was carried out potentiostatically at 1.2 V. The nanowires were released from the alumina membrane by dissolving the template in 1 M KOH aqueous solution for 24 h and were then collected and washed repeatedly with deionized water. They were dispersed into a free-standing state by ultrasound vibration in ethanol.

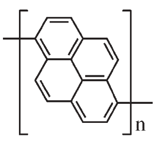

Fig. 1 Chemical structure of oligopyrene.

Fig. 2 shows the scanning (SEM) and transmission (TEM) electron microscope images of the oligopyrene nanowires. As can be seen from Fig. 2a, the resulting product has aligned wire-like nanostructures with lengths of *ca.* 50 μm. Their diameters are fairly uniform and were measured to be close to *ca.* 200 nm, which concides with the pore size of the alumina template (Fig. 2a, insert). The aspect ratio of the nanowires is calculated to be about 250. The transmission electron microscopy (TEM) picture also indicates that the solid nanowires have smooth surfaces and uniform diameters (Fig. 2b). The microscopic electron diffraction (ED) pattern of a nanowire represents a series of bright diffraction spots, revealing the multicrystalline nature of the organic polymer nanostructures (Fig. 2b, insert).

MALDI-TOF MS results demonstrated that the resulting product was oligopyrene with chain lengths of 4–13 repeat pyrene units (see supporting information). The oligomer has a linear structure with few structural defects. This is mainly due to the oxidation potential of pyrene in BFEE ($\sim$ 1.0 V, *vs.* SCE) being much lower than that in a neutral medium such as acetonitrile ($>$ 2 V, *vs.* SCE).[8e] Therefore, oligopyrene can be grown at a fairly low applied potential (*e.g.* 1.2 V, *vs.* SCE) in BFEE, which supports the formation of linear conjugated polymers. The conductivity of the pressed pallet of as-prepared polypyrene nanowires was measured to be $\sim$ 0.1 S cm^{-1}. The wide angle X-ray diffraction (XRD) pattern of the oligopyrene nanowires exhibits a series of sharp lines in the region of $5^\circ < 2\theta < 30^\circ$ (Fig. 3b). In comparison to the XRD pattern of the monomer (Fig. 3a), Fig. 3b showed fewer diffraction lines at different positions. A well-developed progression of diffraction lines appear at 5.5°, 11.2°, 16.4° in 2θ, indicating the samples possess a layered structure with an interlayer spacing of *ca.* 16.1 Å. To the best of our knowledge, most electrosynthesized organic conjugated polymers or oligomers including poly(*para*-phenylene), poly(naphthalene), polyaniline, polypyrrole are amorphous materials.[8] However, the polypyrene electrodeposited in the BFEE medium has a high crystallinity close to 100% according to Fig. 3b.

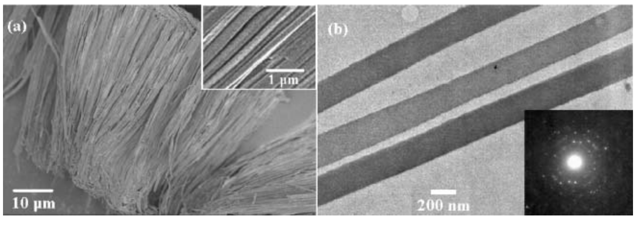

Fig. 2 A SEM image of aligned polypyrene nanowires (a, insert: a regional magnified view) and a TEM image of polypyrene nanowires (b, insert: an electron diffraction pattern of a nanowire).

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† Electronic supplementary information (ESI) available: MALDI-TOF mass spectrum of oligopyrene. See http://www.rsc.org/suppdata/cc/b4/b412638f/

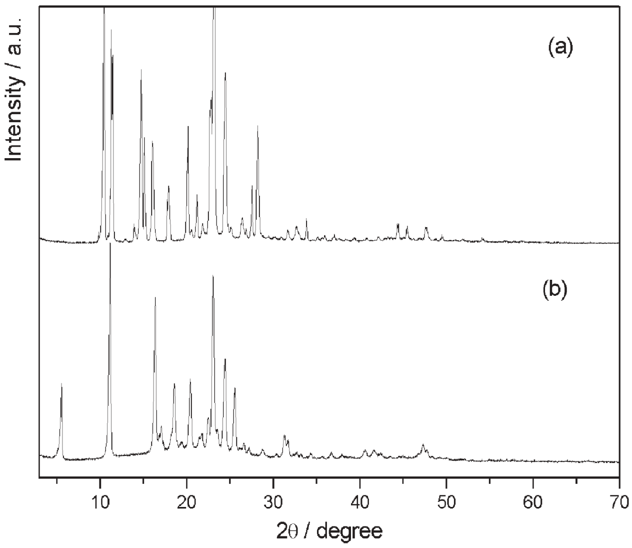

Fig. 3 XRD patterns of pyrene monomer (a) and polypyrene nanowires (b).

It is interesting that the oligopyrene nanowires excited at different wavelengths emit multicolored fluorescence light. As shown in Fig. 4, excited at 405, 488 or 543 nm, the nanowires emit blue, green or red fluorescence light, respectively. The emission spectra of nanowires dispersed in ethanol by ultrasound vibration also show narrow fluorescence peaks consistent with the observed colors. This is mainly because the oligopyrene has broad chain dispersity, and longer conjugated chains have lower energy gaps and emit light with longer wavelengths. In this case, the 405 nm light has the highest energy among these 3 excitation sources and can excite the polymer components with relatively short conjugated chain lengths, while the 543 nm light can excite only the components with relatively long conjugation sequences. Thus, the wavelength of fluorescence emission increased with the wavelength increase of the excitation source. Although emission with a full range of colors by using different conjugated polymers has been reported,[11] this is the first example of homopolymers that emit multicolors.

In conclusion, we have achieved the preparation of crystalline oligopyrene nanowires by template-assisted electropolymerization of pyrene in BFEE medium. This material is a strong blue, green and red nanometer scaled fluorescence emitter, depending on the wavelength of the excitation source. Like other organic semiconductor materials, they can be easily functionalized to allow for tailoring their optical, electronic, and chemical properties. The highly crystalline nature and multicolored emission property of oligopyrene nanowires provide potential applications in multicolor fluorescent labeling in bioscience[12] and the fabrication of nanodevices.

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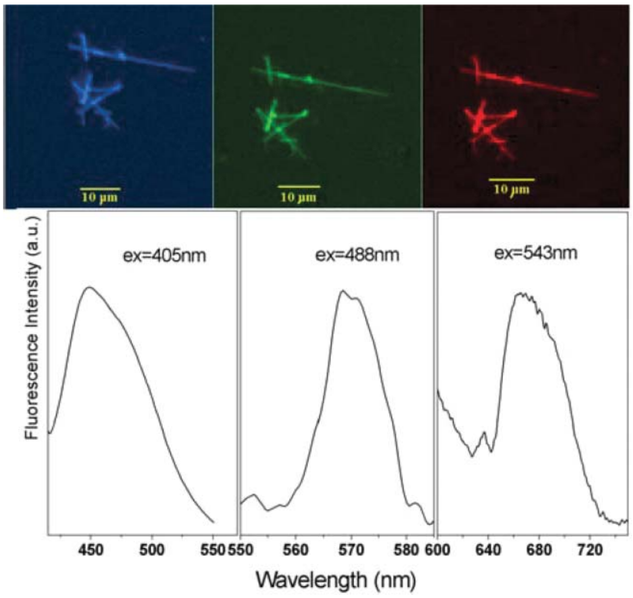

Fig. 4 Confocal fluorescence images of nanowires excited at 405, 488 and 543 nm, respectively (nanowires were sonicated to disperse in ethanol and then dropped on a glass sheet), and the corresponding emission spectra of the nanowires dispersed in ethanol.

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