Photophysical and electrical properties of organic waveguide nanorods of perylene-3,4,9,10-tetracarboxylic dianhydride

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ABSTRACT
The single crystalline nanostructure of organic semiconductors provides a very promising class of materials for applications in modern optoelectronic devices. However, morphology control and optoelectronic property modulation of high quality single crystalline samples remain a challenge. Here, we report the morphology-controlled growth of single crystalline nanorod arrays of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). We demonstrate that, unlike PTCDA film, PTCDA nanorods exhibit optical waveguide features, enhanced absorption, and Frenkel excitation emission in the visible region. Additionally, we measured the electrical properties of PTCDA nanorods, including the conductivity along the growth direction of the nanorod, which is roughly 0.61 S·m⁻¹ (much higher than that of pure crystalline PTCDA films).

1 Introduction
Because of their weak intermolecular forces (the π–π interaction, the charge-transfer (CT) interaction, the van der Waals force, and H-bands), organic semiconductors offer many unique advantages such as relative ease of chemical doping [1, 2], good processability [2], high reactivity [3], and high flexibility [4, 5]. These features make these materials complementary to their inorganic counterparts [6, 7] and allow them to be widely applied in the fabrication of modern optoelectronic devices, for example, organic light-emitting diodes [8, 9], organic field-effect transistors [10, 11], and organic solar cells [12].
Previously, researchers have noted the size-dependent photophysical properties [13, 14] and the dielectric anisotropy of quasi-epitaxial crystalline organic semiconductor films [15, 16]. However, during the growth process of organic films, lattice mismatch originating from the substrate is inevitable and results in the generation of molecular disorder and increased grain boundaries. In the preparation process of one-dimensional (1D) organic nanomaterials using vapor deposition [17] or organic molecular beam deposition (OMBD) methods [18], once the initial nuclei are formed, the organic molecules will be epitaxially deposited on the nuclei and form single crystalline 1D nanomaterials with an oriented growth direction. Moreover, the vacuum environment can reduce doping in organic nanomaterials. These properties effectively decrease the amount of molecular disorder and grain boundaries [18]. Consequently, the photophysical and electrical properties of single crystalline organic 1D nanomaterials might be superior to those of quasi-epitaxial organic films. To our knowledge, the correlation between morphology and optoelectronic properties has not yet been systematically studied [13, 15].

To investigate the morphology-dependent photophysical and electrical properties of organic 1D nanomaterials, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) was selected as the model molecule. Because the PTCDA molecule has a planar structure, elements of perylene, and peripherally rich oxygen atoms (as shown in Fig. 1(a)), they favor \( \pi-\pi \) stacking between the layer-stacked molecules, which creates a basis of well-defined growth. The unique electronic structure of the planar \( \pi \)-electron system is usually used as the model example to investigate interfacial charge transfer dynamics [19, 20]; PTCDA crystalline films have already attracted attention and have been used in light-emitting diodes, where they were reported to improve charge injection efficiency at the anode [21, 22]. Herein, we successfully prepared vertically aligned PTCDA nanorod (NR) arrays and modulated their morphologies using the OMBD method. We found that the photophysical properties, especially the fluorescence feature, strongly depend on NR morphologies. We have also measured the current versus voltage (\( I-V \)) characteristics of individual NRs and found that the electrical conductivity along the epitaxial direction of PTCDA NRs was roughly 0.61 S·m\(^{-1}\), which is much higher than that of pure crystalline PTCDA films. Our experiments provide important information regarding the fabrication of optoelectronic devices based on \( \pi \)-conjugated planar organic semiconductors.

![Figure 1](https://example.com/figure1.png)  
**Figure 1** Chemical structure of PTCDA molecule (a). SEM images of PTCDA NR arrays prepared by setting \( t_g = 5 \) min (b), 20 min (c), 45 min (d), and 90 min (e); the insets show enlarged images. Top-view fluorescence microscopy images of the NR array grown for 90 min (f); the inset shows a side-view image of the NRs. All SEM images were taken at a 45° angle (tilted relative to the substrates).