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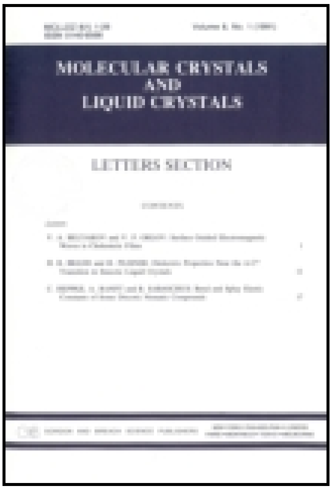

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Vertical Arrays of Photoluminescent Alq_3 Nanotubes on Flexible Substrates by Vapor Deposition

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In this work, one-dimensional (1D) nanomaterials were created from an organic semiconductor material via vapor deposition on flexible polyethylene terephthalate (PET) substrates. Tri-(8-hydrooxyquioniline) aluminum (Alq_3) molecules readily assembled into nanotubes under ambient pressure. Vertically grown Alq_3 nanotube arrays on PET substrates emitted green photoluminescent light after excitation at 380 nm. This extremely simple approach offers a straightforward pathway for creating and directing vertical arrays of organic semiconducting building blocks through molecular assembly, and can be used to assemble high-performance optoelectronic devices.

Keywords photoluminescence; Alq_3; nanotubes; vertical arrays; flexible substrates; vapor deposition

Introduction

One-dimensional (1D) nanomaterials made from organic semiconductors have numerous potential applications in optoelectronic, electromechanical, and biological devices [1–4]. In particular, vertically grown 1D nanoarchitectures have been demonstrated to have exceptional properties in light-emitting diodes, field-effect transistors, chemical sensors, and optical waveguides [5,6]. Despite the many advantages of organic nanostructures, a robust development process is still required for practical utilization of organic semiconducting nanomaterials in advanced devices. To date, 1D organic nanomaterials have been prepared by physical vapor transport or solution-based crystallization [7,8]. However, operational control for typical physical vapor deposition methods is relatively complicated, and hard substrates are required for the growth of nanostructures [7]. In addition, solvent-mediated strategies are disadvantageous for positioning organic nanomaterials at the desired sites and controlling array architecture [8]. Reports of direct vertical arrangements of organic nanostructures on flexible substrates are therefore rare.

Herein, we report a straightforward vapor deposition method to grow organic nanomaterials on flexible polyethylene terephthalate (PET) films. 1D nanotubes consisting of tri-(8-hydrooxyquioniline) aluminum (Alq_3) molecule were synthesized via molecular self-assembly under ambient pressure. Alq_3 is one of the most stable electron transport

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*Address correspondence to T. H. Han, Department of Organic and Nano Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul, 133-791, Korea (ROK). E-mail: than@hanyang.ac.kr and emitting materials, and is widely used in efficient organic light-emitting diodes [9–11] Prepared Alq_3 nanotubes emitted green photoluminescent (PL) light after excitation at 380 nm. The PL spectrum of the as-prepared tubes showed an obvious blue-shift compared to that of the Alq_3 monomers, indicating the presence of a molecular association effect. In addition, tunability of the vertical assembly of building blocks was achieved by controlling surface properties of the substrate, such as hydrophobicity. Our strategy represents a straightforward route to prepare vertical arrays of 1D nanostructure of organic semiconducting molecules on plastic substrates without complicated procedures.

Experimental

Materials

Commercial tris-(8-hydrooxyquioniline) aluminum (Alq_3) powder, acetone, ethanol, and (tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxysilane (FOTES) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification.

Vertical Arrays of Nanotubes Using Thermal Evaporation

20 mg Alq_3 powder was dissolved in acetone in a glass vessel. Slow heating of the vessel resulted in evaporation of the acetone, leaving behind a uniform layer of Alq_3 film on the inner wall of the vessel. Then, the vessel was heated to the predetermined temperature of 370°C on a hot plate. Substrates were suspended above the source at a vertical distance of ~2 cm. The resulting products were collected on the downward-facing side of the substrates. Si wafers and PET films were prepared by sequential washing with methanol, ethanol, and deionized water. Hydrophilic Si and PET surfaces with a contact angle below 10^{o} were prepared through oxygen plasma treatment of cleaned substrates at 40 W for 5 min (Femto Science Cute). To obtain hydrophobic substrates, hydrophilic substrates were exposed to saturated FOTES vapor for 2 hours at 80°C in a sealed petri dish.

Characterization

The morphology of Alq_3 nanotubes was characterized by scanning electron microscopy (SEM; JEOL JSM-6710F) and transmission electron microscopy (TEM; JEOL JEM-2100F). To preparation TEM samples, nanotubes were detached from substrates by rinsing the substrates with water droplets and then placing the nanotubes on a lacey-carbon TEM grid (Ted Pella, Inc.). The thermal properties of Alq_3 powders were examined by thermogravimetric analysis (TGA; SDT Q600, TA Instruments). TGA measurements were carried out from 30°C to 600°C at a heating rate of $10^{\circ}C\ min^{-1}$ under an air environment. Fluorescent nanotube images were captured using an Olympus optical and fluorescence microscope (BX51W/DP70) with a U-MWB2 filter cube (Olympus). PL spectra were obtained from fluorescence spectra (Scinco, FS-2). Contact angles of water on the various substrates were measured with a Phoenix150 contact angle analyzer (Surface Electro Optics Co., Korea).

Results and Discussion

In this work, Alq_3 molecules (Fig. 1b) was used as building blocks to assemble 1D nanostructures. During typical synthesis (Fig. 1a), a thin coating of Alq_3 was obtained on the

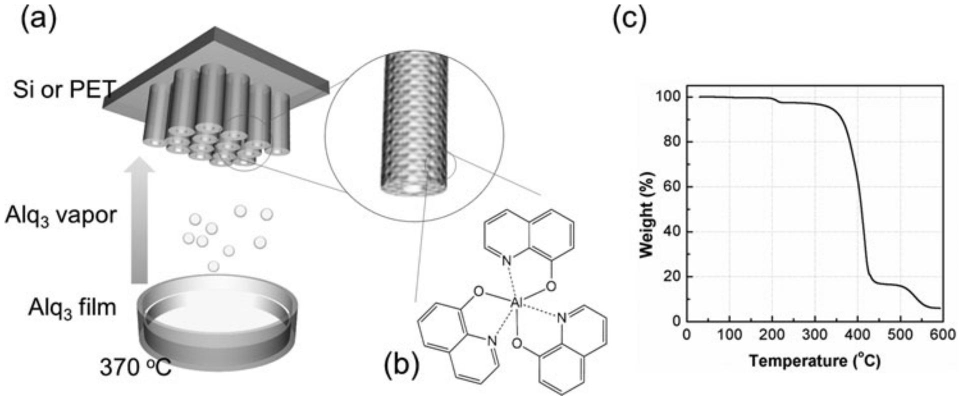

Figure 1. (**a**) Schematic diagram of the vapor deposition technique. Alq_3, heated to 370°C, assembled on a substrate to form ordered, vertically-aligned nanotubes. (**b**) Chemical structure of Alq_3. (**c**) Thermal behavior of Alq_3 molecules.

inner wall of a glass vessel by slow evaporation of acetone. The glass vessel was then heated to the predetermined temperature of 370°C. Evaporation temperature was beyond the point at which a large weight loss was observed on the thermogravimetric analysis (TGA) curve (Fig. 1c). The mass loss at around 200°C and 400°C in the TGA curve is ascribed to the loss of solvent molecules from the solvated phases and the major sublimation of Alq_3 molecules, respectively. Vaporized Alq_3 molecules were deposited on substrates. A uniform nanoarchitecture was obtaining using Alq_3 thin film because of the homogeneous effect of vaporization.

Figures 2a and 2b show SEM images of nanotubes grown vertically on Si wafers for 5 min. The TEM images in Figs. 2c and 2d clearly demonstrate that the nanostructures were tubular in shape, whereas conventional methods, such as annealing of amorphous films, recrystallization through poor-solvent diffusion, or condensation of saturated vapor, yield nanostructures with wire-like morphologies [12–14]. Nanotubes shown in Figs. 2c and 2d were grown for 5 min and 10 min, respectively. As the deposition time increased, the ratio of the inner space to the tube diameter decreased from 0.25 to 0.17. Diffused ring of electron diffraction in the TEM image (Fig. 2d, inset) indicated that the nanotubes were almost amorphous, in contrast to the crystalline Alq_3 nanowires reported previously [12–15].

Alq_3 nanotubes grew from the seed particles, similar to typical vapor-grown methods for 1D nanomaterials [16]. The early stage of vapor deposition was observed at the termination of evaporation within 30 sec. Alq_3 first deposited to form nanoparticles of ~100 nm in diameter on the substrates, as marked by the white arrows in Fig. 3a, indicating that the tubes were grown on these seed nanoparticles [16]. The resulting Alq_3 nanotubes had broad, polydisperse diameters and lengths. Nanotubes grown for 5 min had an average length of 1.03 μm, with diameters ranging from 40 to 220 nm (Fig. 3c). Although precise control of the average length, thickness, and surface density of these nanotubes was not achieved due to fast vapor deposition and subsequent tube growth, the average length of the nanotubes increased to approximately 1.73 μm with a large expansion in the diameter as the deposition time was increased from 5 min to 10 min (Fig. 3d). Assembly of the Alq_3 molecules sometimes resulted in branched and interconnected structures as shown in Fig. 3b, after a long deposition time. Morphological observations (Figs. 3c and 3d) revealed that

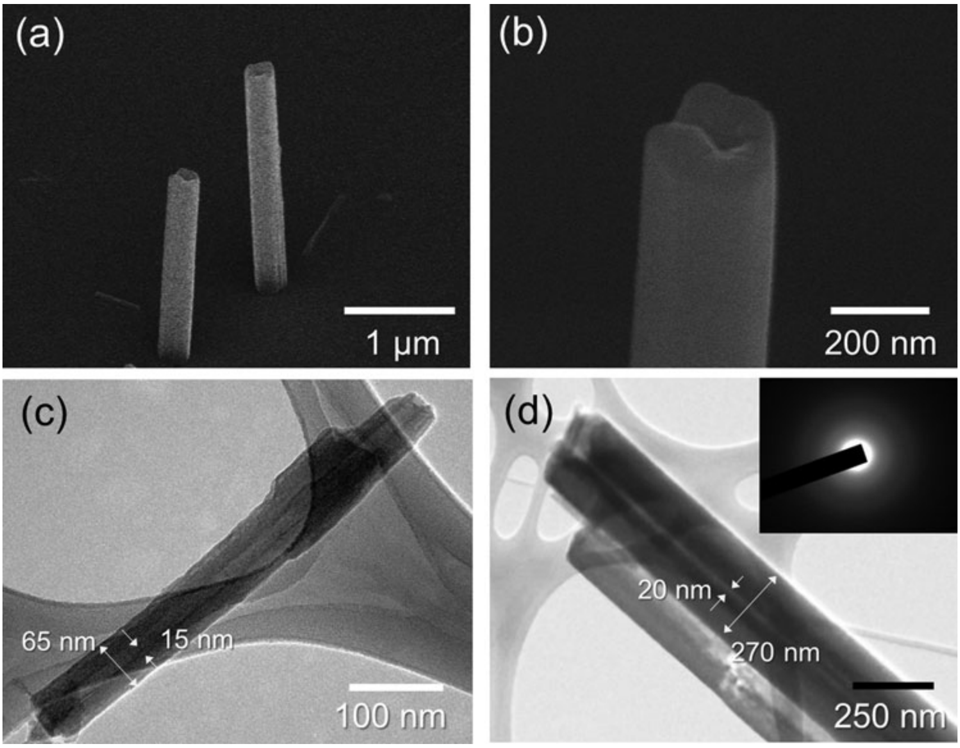

Figure 2. SEM images of tubes grown for 5 min at (**a**) low and (**b**) high magnifications. (**c**, **d**) TEM images of tubes deposited for 5 min and 10 min, respectively. Inset: electron diffraction pattern of nanotubes grown for 10 min, indicating the almost amorphous nature of the nanotubes.

longer deposition times induced the formation of dense arrays, including some branched nanotubes, with thicker and longer tubes.

To directly fabricate flexible fluorescence films, vertical arrays of Alq_3 nanotubes were prepared on PET substrates via the same procedure described above (370°C for 10 min). A top view of the nanotube arrays under a fluorescence microscope upon excitation is shown in Fig. 4a. Bright light was emitted from each tube under excitation. The relatively large dots may have originated from branched or interconnected nanotubes. Inset image in Fig. 4a shows that Alq_3 nanotubes grown at the edge of the PET film emitted green fluorescent light. White dotted line represents the edge line of the PET film. It should be noted that the PET film was thermally and mechanically stable during deposition of Alq_3 vapor, even when the source was heated to a high temperature. Figures 4b shows that vertical arrays of Alq_3 nanotubes/PET hybrid film were stable and undamaged, even after repeated bending.

PL spectra of the Alq_3 monomers in ethanol, Alq_3 tubes on the PET film, and bare PET film excited at 380 nm are shown in Fig. 4c. The peak at 424 nm is the response of the PET films to the light source of a fluorospectrometer. PL spectra of the Alq_3 monomer and nanotubes had a symmetric peak in the 450–600 nm range, with a maximum intensity at 512 and 499 nm, respectively. Compared with Alq_3 monomer emission, that of the nanotubes showed a blue-shift of approximately 13 nm. This observed shift appears to be related to intermolecular interactions and the presence of crystalline structures [10,13–15,17]. According to the literature, Alq_3 nanostructures demonstrate blue-shifts due to wider

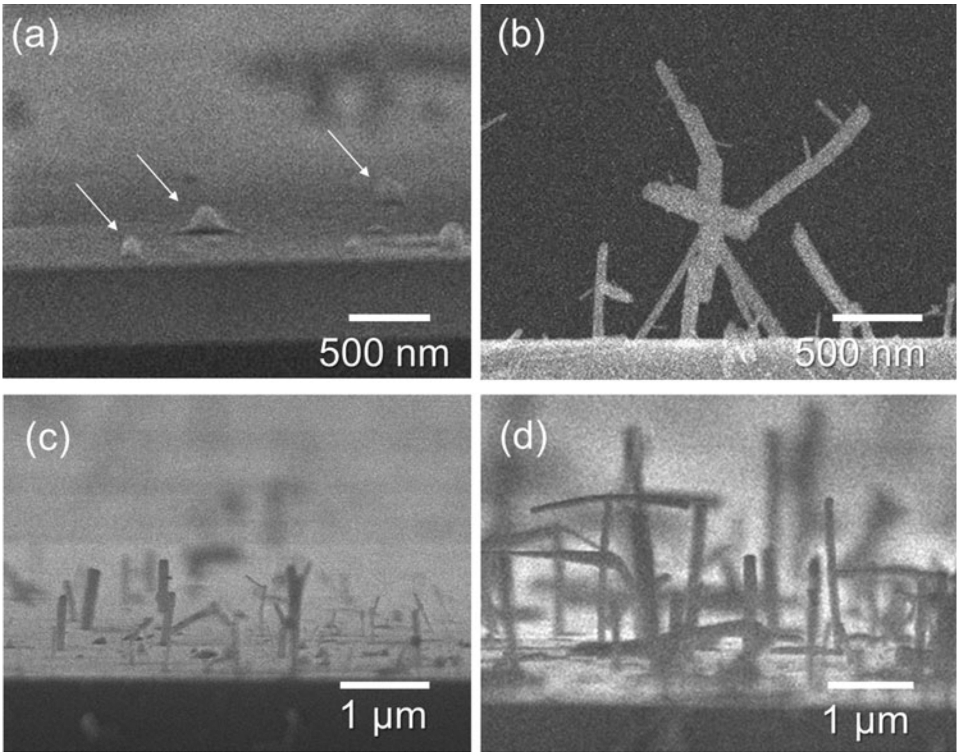

Figure 3. Vapor deposition of vertically-aligned Alq$_3$ nanotubes. (**a**) SEM image of Alq$_3$ nuclei at the early stage of nanotube growth on a Si wafer (30 sec). (**b**) Side view of Alq$_3$ nanotube branches (10 min). (**c**, **d**) Tilted view of vertically-aligned Alq$_3$ nanotubes after evaporation for 5 min and 10 min, respectively.

spacing of the quinoxaline ligands of neighboring Alq$_3$ molecules as a result of increased intermolecular interactions that reduce orbital overlap and finally induce a spectral blue shift [13–15]. Another reason for the observed blue-shift is the greater Rayleigh scattering of shorter wavelengths by Alq$_3$ crystalline grains [17]. We speculate that the blue-shift was caused by molecular association effects within the 1D morphology due to the presence of a crystalline phase, even though the electron diffraction pattern showed that the tubes were largely amorphous.

Deposition of Alq$_3$ molecules on the substrates was largely dependent on the surface properties of the substrates. Hydrophilic PET substrates were prepared by oxygen plasma treatment. Subsequent exposure to these substrates to saturated silane vapor afforded hydrophobic substrates with a water contact angle of 79°. As shown in Figs. 5a and 5b, more PL light was emitted from Alq$_3$ structures on the hydrophobic substrate than those on the hydrophilic substrate. Two images were obtained under the same conditions, such as exposure time, brightness, etc. This difference is likely due to different nucleation densities for Alq$_3$ deposition [5]. Hydrophobic Alq$_3$ molecules showed greater nucleation on FOTES-treated surfaces, resulting in a brighter hybrid film. Cleaned PET substrates, utilized in previous experiments, showed water contact angles of about 67°. Therefore, control of the surface properties of the substrates appears to have contributed to the formation of homogeneous and dense vertical arrays of Alq$_3$ tubes.

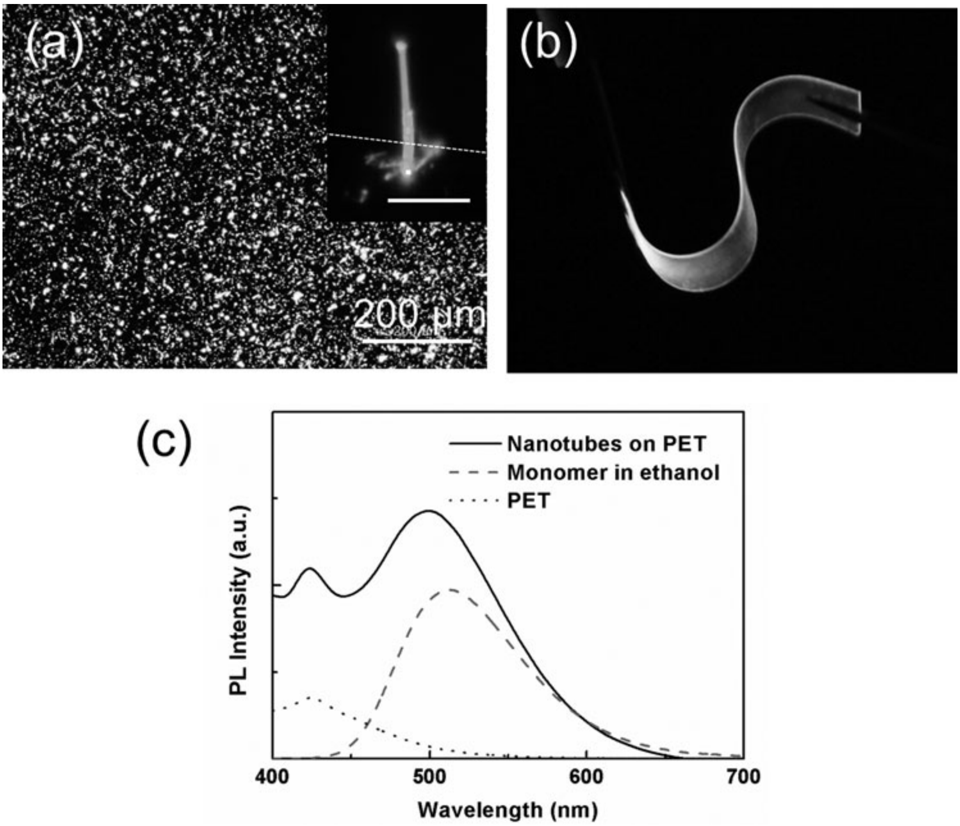

Figure 4. (**a**) Photoluminescent image of Alq$_3$ nanotube arrays over a large area on PET substrates. Inset image of a single nanotube was obtained from the edge of a PET film. Inset scale bar: 10 μm. (**b**) Photo image of bendable Alq$_3$ nanotubes/PET substrates after excitation at 365 nm with a portable UV lamp. (**c**) PL spectra of an Alq$_3$ monomer in ethanol, Alq$_3$ nanotubes and bare PET films excited at different wavelengths.

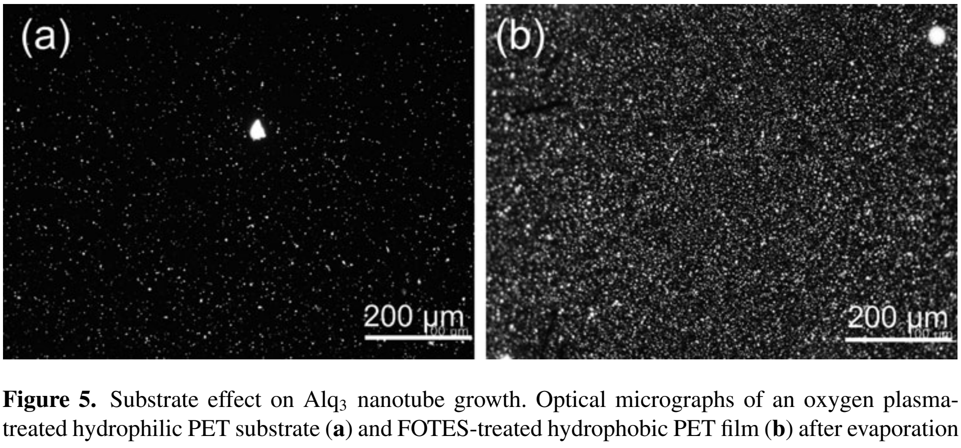

Figure 5. Substrate effect on Alq$_3$ nanotube growth. Optical micrographs of an oxygen plasma-treated hydrophilic PET substrate (**a**) and FOTES-treated hydrophobic PET film (**b**) after evaporation of Alq$_3$ at 370°C for 10 min.

Conclusions

We describe a simple vapor deposition method for the growth of organic nanotubes on flexible PET films. 1D nanotubes of Alq$_3$ molecules were synthesized by molecular self-assembly under ambient pressure. Prepared Alq$_3$ nanowires emitted green PL light after excitation at 380 nm, and showed a spectral shift, indicating a molecular association effect. This approach can be used to obtain vertical arrays of nanoarchitectures of a variety of organic semiconducting molecules on flexible substrates, and is also a versatile route to realize high-performance optoelectronic devices via the development of novel architectures for fast electron-transporting materials.

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