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Size-dependent optical properties of 9,10-bis(phenylethynyl) anthracene crystals

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ABSTRACT

The optical properties of 9,10-bis(phenylethynyl)anthracene (BPEA) were studied for various states: nanoparticles (~100 nm), microcrystals (~1 μm), bulk crystals (~1 mm), and vacuum-deposited film. The absorption spectra showed a red shift from ethanol solution to bulk crystals with an increase in crystal size. The vacuum-deposited film seemed to have mixed spectral characteristics of nanoparticles and bulk crystals. The fluorescence of BPEA showed two peaks for the various crystals. The fluorescence of the shorter wavelength peak was shifted toward the blue from 556 to 527 nm from the bulk to nanoparticles. On the other hand, the position of the longest wavelength peak changed little, staying around 596 nm. The relative intensity of the former and latter increased with a decrease in the crystal size. The time-resolved fluorescence spectra clearly confirmed the existence of two emissive sites in the bulk crystals. These sites are probably located at the peripheral and inner positions of the crystals. Change in the relative proportions of the two sites could be the main reason for the size-dependent fluorescence.

1. Introduction

In recent years, organic nanoparticles have attracted much interest, because they are expected to have different chemical and physical properties from isolated molecules and corresponding bulk crystals [1–6]. Size-dependent optical properties are one of particularly interesting topics [6–14]. The size dependence of organic nanoparticles is observed when their particle size is larger than several tens of nanometers [6,15]. For example, perylene nanocrystals ranging from several tens to a few hundreds of nanometers in size showed the following fluorescence characteristics; the excimer fluorescence peak clearly showed a blue-shift with a decrease in the particle size, while the monomer fluorescence peak was little changed [6,7,11,15]. One reason suggested was lattice softening due to microcrystallization, which reduces the Coulombic interactions between molecules, resulting in wider bandgaps [7]. The size dependence was also ascribed to a change in the elastic properties of nanocrystal with size [6,15]. Another explanation could be the different location of the perylene molecules in the peripheral edges and in the center of the crystals [9].

Phenylene-ethynylene-based oligomers are expected to act as molecular switches because of their unique chemical structures [16]. Nano/micrometer sized single crystals of 9,10-bis(phenylethynyl) anthracene (BPEA, Fig. 1) exhibited high photoswitching performance [17,18]. BPEA is also well known for its remarkably high emission efficiency [19,20]. Optical properties of BPEA of nanocrystals are thus intriguing and worthy of study. In our previous study on nanoparticles (83–122 nm) dispersion in water by the reprecipitation method [21], two fluorescence peaks were observed at around 525 and 600 nm. The former and latter bands were assigned as being intrinsic to the BPEA nanocrystals and the bulk crystals. However, there still remain questions on the details of the fluorescence characteristics of BPEA nanocrystals and bulk crystals. Here the evolution of their optical properties was studied for BPEA from nano/microcrystals to bulk crystals.

2. Experimental

BPEA (Tokyo Chemical Ind. Co., Ltd.) was used as-received. BPEA nanoparticles were prepared by the reprecipitation method; 600 μL of an acetone solution of BPEA (1 mM) was injected into 10 mL of stirred water, which was further stirred for 1 h. BPEA microcrystals were made by the injection of 10 mL of an acetone solution of BPEA (1 mM) into 10 mL stirred water. Yellow microcrystals floated in water were collected by a paper filter. BPEA bulk crystals were grown in a saturated BPEA solution of acetone. Films were deposited on glass plates in a vacuum deposition chamber evacuated to 10^{-2} Pa.

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Samples were characterized via a scanning electron microscope (SEM, JEOL JSM-6510). The particle-size distribution of the BPEA dispersion was determined by the dynamic light scattering method using an Otsuka electronics FPAR-1000. Absorption and diffuse reflectance spectra were measured using a JASCO V-570 spectrometer for ethanol solution and dispersion, and film, microcrystals and powdered bulk crystals, respectively. The absorption spectra of film, microcrystals, and powdered crystals were obtained by a Kubelka–Munk function analysis. Fluorescence spectra were taken with a JASCO FP-6500 spectrometer and at room temperature and 77 K. Fluorescence lifetime and time-resolved fluorescence spectra were measured using a Fluorolog-TCSPC (Horiba). The lifetime was fitted with a triple-exponential function with the estimated errors about 10%. The measurements were done at room temperature unless otherwise specified.

3. Results and discussion

Fig. 2 shows the SEM images of samples: (a) single crystals recrystallized from saturated acetone solution, (b) microcrystals prepared by injecting 10 mL of acetone (BPEA 1 mM) into 10 mL of water, (c) a vacuum-deposited film on a glass plate, and (d) nanoparticles prepared by the reprecipitation method and dried on a polymer film. The single crystals (a) had a hexagonal columnar structure with a diameter about 160 μm and length about 2 mm, which is attributed to a monoclinic rod structure named α phase [18]. The precipitated crystals (b) consisted of rods and rectangular solid about 300 nm–1 μm in diameter and 2 μm in length. The deposited films that were a few μm in thickness (c) showed a granular structure of particles of about 400 nm diameter. The SEM photograph of nanoparticles (d) was not clearly resolved, but they seemed to be aggregated structures consisted of submicrometer particles. The average diameter of nanoparticles in water was determined by the dynamic light scattering method to be approximately 90 nm, which is essentially similar to the previous result [21]. Thus the BPEA nanoparticles must be aggregated during the drying process on polymer film.

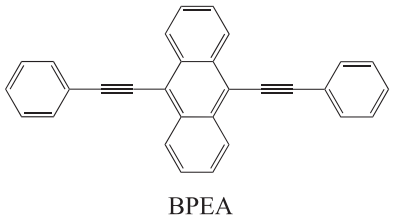

Fig. 1. Structure of 9,10-bis(phenylethynyl)anthracene (BPEA).

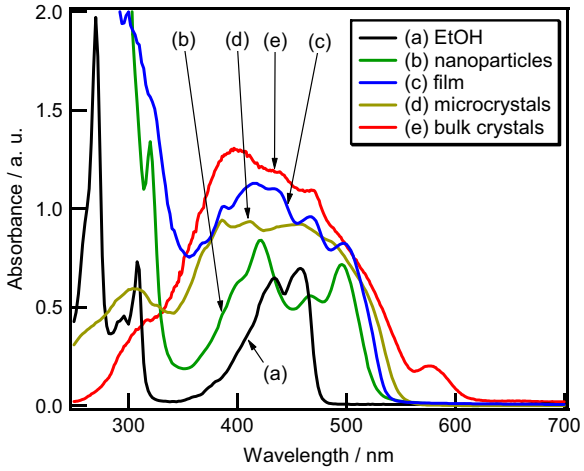

Fig. 3. Absorption spectra of BPEA in various states: (a) ethanol solution, (b) nanoparticles, (c) vacuum-deposited film on a glass plate, (d) microcrystals, and (e) bulk crystals.

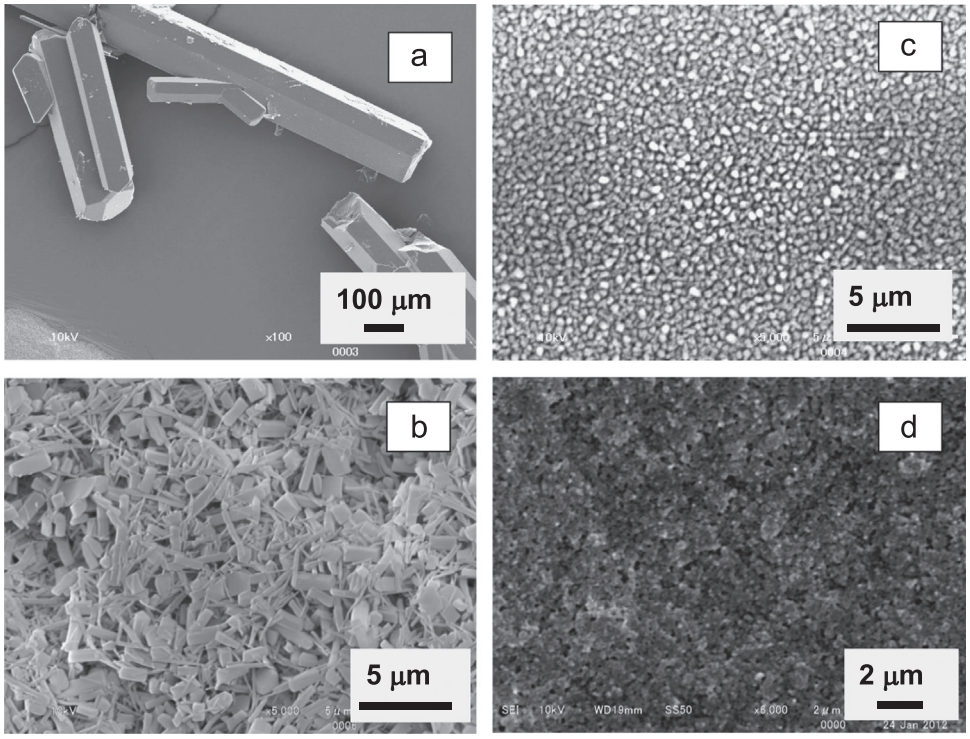

Fig. 2. SEM photographs of BPEA crystals: (a) single crystals recrystallized from a saturated acetone solution, (b) microcrystals prepared by injecting 10 mL of acetone (BPEA 1 mM) into 10 mL of water, (c) vacuum-deposited film on a glass plate, and (d) nanoparticles prepared by injecting 600 μL of an acetone solution of BPEA (1 mM) into 10 mL of water and dried on a polymer film.