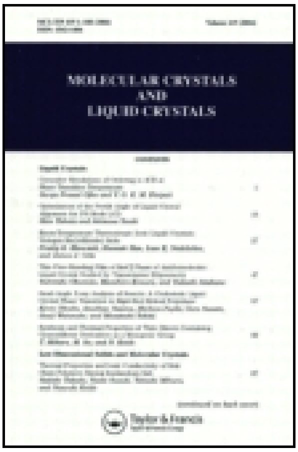

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[a] Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto, Japan

[b] Department of Applied Chemistry and Biochemistry, Kumamoto University, Kurokami, Kumamoto, Japan

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Highly Oriented Donor-Acceptor Molecules within Electrospun Nanofibers

HIROYUKI NOMOTO,[1,2] SURAWUT CHUANGCHOTE,[1] TAKASHI SAGAWA,[1] HIROSHI SAKAGUCHI,[1] SUSUMU YOSHIKAWA,[1] MAKOTO TAKAFUJI,[2] AND HIROTAKA IHARA[2]

[1]Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto, Japan
[2]Department of Applied Chemistry and Biochemistry, Kumamoto University, Kurokami, Kumamoto, Japan

*Poly(vinylpyrrolidone) (PVP) nanofibers containing 2,9,16,23-tetra-*tert*-butyl-29H,31H- phthalocyanine free base (H_2TTBPc) and fullerene (C_{60}) were prepared by electrospinning. The nanofibers were characterized by scanning electron microscopy, UV-visible absorption spectroscopy, and photoluminescence (PL) spectroscopy. Under the various conditions of electrospinning such as the concentrations of PVP and an organic volatile salt, and the sizes of the nozzle, we could find good conditions to obtain as-spun nanofibers of which average diameter was 429 nm. The incorporated H_2TTBPc in the nanofibers shows highly oriented α -type crystalline state in the presence of C_{60} as compared with that of the film prepared by a casting method.*

Keywords Charge transfer; electrospinning; nanofibers

1. Introduction

Nanofibers have been attracted much attention for their wide applicability to mechanics, electrodynamics, and optoelectronics, because of their specific properties: e.g., flexibility, crystallinity, high aspect ratio, small pore size, and high surface area [1]. While regulation of molecular orientation of donor (D) and acceptor (A) molecules is one of the most important strategies for highly efficient electron transfer. When D-A molecules are included inside nanofibers, 1D aligned (*viz.* highly oriented) and densely packed D-A molecules within the nanofibers will be formed effectively.

Electrospinning is a simple method for fabrication of nanofibers. PVP has good electrospinnability because of good solubility to various solvents [2,3]. H_2TTBPc also performs better solubility against nonpolar solvent than that of pristine

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Address correspondence to Hirotaka Ihara, Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555, Japan. Tel.: +81-96-342-3661; Fax: +81-96-342-3662; E-mail: ihara@kumamoto-u.ac.jp

phthalocyanine. On the other hand, H_2TTBPc and C_{60} form charge transfer (CT) complex [4]. In this context, we report herein fabrication and characterization of electrospun nanofibers of PVP including H_2TTBPc as D and C_{60} as A in order to design a D-A bicontinuous molecular wire within the polymer nanofibers.

2. Experimental Details

2.1. *Materials*

H_2TTBPc, C_{60}, PVP ($M_W = 1{,}300{,}000$), and formic acid were purchased from Sigma-Aldrich Co. Ltd. 1,2-Dichloroethane (DCE), chlorobenzen (CB), and pyridine were purchased from Wako pure chemical Co. Ltd.

2.2. *Preparation of Nanofibers by Electrospinning*

To prepare ultrafine fibers by electrospinning, the concentrations of PVP and pyridinium formate (PF) solution, and the sizes of the nozzle were optimized according to the previously reported procedures with slight modification [5–9].

H_2TTBPc and C_{60} were dissolved in DCE and CB, respectively. Equimolar amounts (1.4 mM) of H_2TTBPc and C_{60} solutions were mixed together followed by the addition of 0.5% (w/v) – 4.0% (w/v) PVP under vigorously stirring at 70°C. PF, a voltaic organic salt, was prepared by mixing of equimolar pyridine and formic acid. 1.0% (v/v) – 3.0% (v/v) PF was added to H_2TTBPc/C_{60}/PVP solution.

Electrospinning was carried out as follows. Solution of H_2TTBPc/C_{60}/PVP or H_2TTBPc/C_{60}/PVP/PF was loaded into plastic syringe. The temperature of the syringe was kept at 80°C with thermostatic chamber. The nozzle was made of stainless-steel needle with a blunt and smooth end (22 or 27 gauge). The collector was made of a sheet of aluminum foil on a plastic board. The high voltage power supply (Gamma High Voltage Research Co. Ltd.) was used to charge the solution across an electrode in solution. The collection distance was fixed at 15 cm and the applied electric potential was 15 kV. The flow rate of the syringe pump was 1 mL h^{-1}.

2.3. *Spectroscopic Characterization*

As-spun products were dried overnight at 60°C in a vacuum oven before characterization. The morphologies of the as-spun products were observed by a scanning electron microscope (SEM, JEOL JSM-6500FE), operating at an acceleration voltage of 10 kV. UV-visible absorption spectroscopy (SHIMADU, UV-2450) was carried out for structural studies. The PL spectroscopy was performed using a He-Cd laser operating at wavelength of 325 nm and with an incident power on the sample surface of about 5 W/cm^2. The PL spectra have been recorded with a monochromator fitted with 1800 grooves/mm grating and a photomultiplier tube (PMT).

3. Results and Discussions

3.1. *Preparation of Nanofibers by Electrospinning*

Figure 1 shows the SEM images of as-spun products from the solutions of 2.0% (w/v) PVP containing H_2TTBPc and C_{60}. Ultrafine fibers were prepared from the

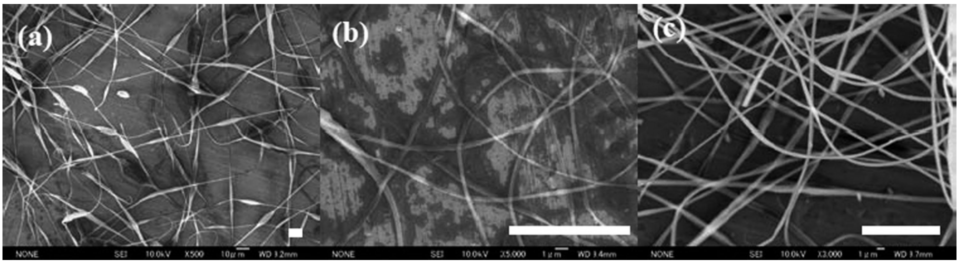

Figure 1. SEM images of as-spun products from the solution of (a) $H_2TTBPc/C_{60}/PVP$ with a 22 G nozzle, (b) $H_2TTBPc/C_{60}/PVP/PF$ with a 22 G nozzle and (c) $H_2TTBPc/C_{60}/PVP/PF$ with a 27 G nozzle. The scale bar in each images equal 10 µm.

solution of H_2TTBPc and C_{60} including 2.0% (w/v) PVP and 2.0% (v/v) PF with a 27 G nozzle. The average diameter of the finest nanofibers was 429 nm and standard deviation (S.D.) of the average diameter of the finest nanofibers was 0.11 (See also Fig. 1c).

3.2. *UV-vis Absorption and PL Spectroscopic Characterization of the Nanofibers*

Figures 2 and 3 show that the UV-vis absorption spectra of the as-spun fibers and the cast films of $H_2TTBPc/C_{60}/PVP$. As shown in Figures 2a and 3a, PVP film has a strong absorption peak in the range of 200–300 nm. H_2TTBPc/PVP and C_{60}/PVP as compared with pristine H_2TTBPc and C_{60} films also show a remarkably strong absorption of PVP in the same range (Figs. 3b and 3c). On the other hand, Figures 2c and 3c do not show clear peak at around 600 nm. The peak at around 600 nm as shown in Figures 2a, 2b, 3a, and 3b is ascribed to the α-type crystalline form of H_2TTBPc [10–11]. In particular, it is clear that the electrospinning of $H_2TTBPc/C_{60}/PVP$ increased the absorption peak at around 600 nm as shown in Figure 2a.

Though extent of crystalinity of the electrospun nanofibers is still not so high (*viz*. amorphous), which was confirmed by XRD patterns observation (data not shown), incorporation of H_2TTBPc in the nanofibers promotes the generation of

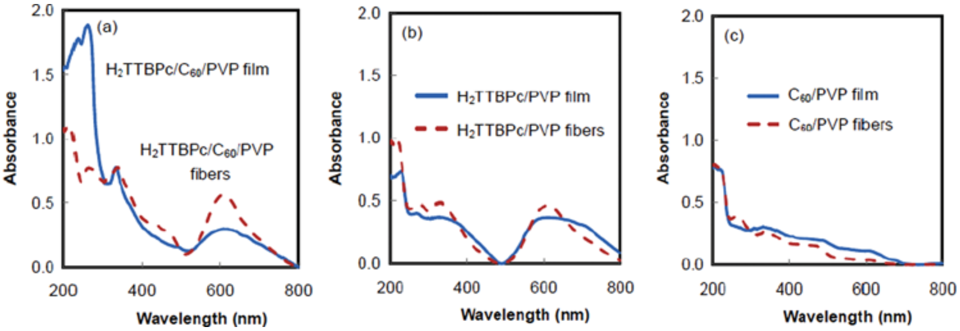

Figure 2. UV-visible absorption spectra of film (solid) and fibers (broken) composed of (a) $H_2TTBPc/C_{60}/PVP$, (b) H_2TTBPc/PVP, and (c) C_{60}/PVP.

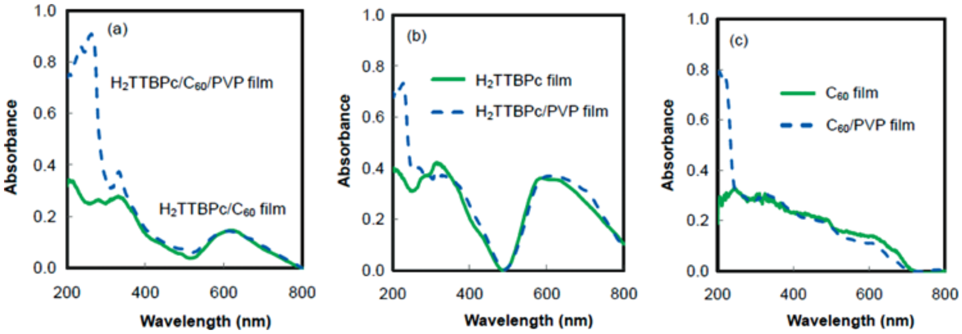

Figure 3. UV-visible absorption spectra of (a) H_2TTBPc/C_{60} and $H_2TTBPc/C_{60}/PVP$ films, (b) H_2TTBPc and H_2TTBPc/PVP films, and (c) C_{60} and C_{60}/PVP films.

α-type crystalline form in the presence of C_{60} as compared with that of the film prepared by a casting method.

A Sharp emission around 700 nm as shown in Figure 4 is assigned to $\pi_0 \leftarrow n\pi_2^*$ transition of PVP and broad emission around 450 nm is assigned to $\pi_0 \leftarrow n\pi_1^*$ of PVP [12]. H_2TTBPc film shows strong emission around 800 nm [13], while C_{60} film shows broad emission around 750 nm [14]. Addition of H_2TTBPc and/or C_{60} to PVP quenched the emission around 450 nm, remarkably. $H_2TTBPc/C_{60}/PVP$ fibers strongly quenched the PL around 700 nm as compared with that of the $H_2TTBPc/C_{60}/PVP$ film. Present electrospun nanofibers of $H_2TTBPc/C_{60}/PVP$ show remarkable PL-quenching of PVP around both 450 nm and 700 nm even though the predominant amount of PVP. This result implies that the densely packed state of the three components in the fibers affects electrostatically such as charge transfer complex formation.

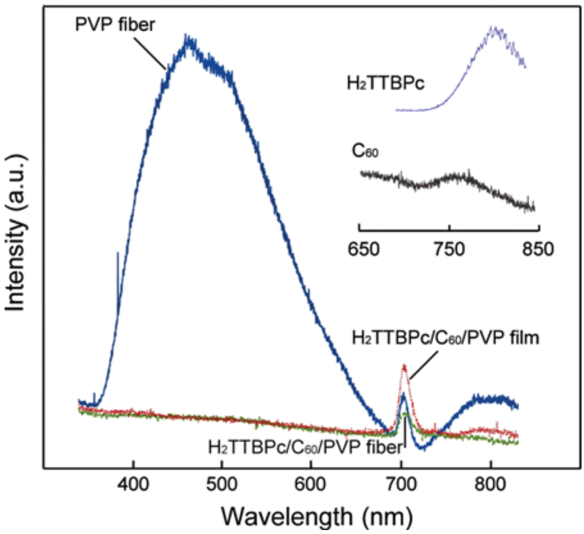

Figure 4. PL spectra of PVP fiber (blue), H_2TTBPc (cyan), C_{60}(black), $H_2TTBPc/C_{60}/PVP$ film (red), and $H_2TTBPc/C_{60}/PVP$ fiber (green).

4. Conclusions

Under the conditions when the continuous nanofibers were predominantly obtained, it was found that the incorporated H_2TTBPc in the fibers shows the existence of highly oriented α-type crystalline state in the presence of C_{60} as compared with that of the film prepared by a casting method. Remarkable PL-quenching of PVP nanofibers including H_2TTBPc and C_{60} was observed. Further investigation should be done to clarify the precise molecular interactions of the three components in the fibers and the dynamics of the PL quenching in future.

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