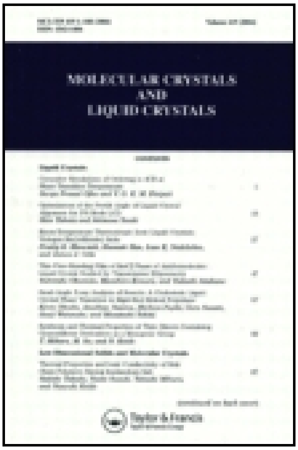

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# Electrospinning of Polycarbonate/ Tetrapyrazinoindoloporphyrazine Composite Fibers

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# Electrospinning of Polycarbonate/Tetrapyrazinoindoloporphyrazine Composite Fibers

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*We have fabricated polycarbonate/tetrapyrazinoindoloporphyrazine composite fibers using the electrospinning technique. The purpose of this research is to verify the capability of tetrapyrazinoindoloporphyrazines to maintain the optical and electronic properties when they are blended with polycarbonate to form spin-coated films and electro-spun fibers. X-ray photoelectron spectroscopy (XPS) confirms the chemical composition of composite films and fibers, and the N 1s peak indicates no significant interaction between polycarbonate and tetrapyrazinoindoloporphyrazine. UV-vis spectroscopy shows a strong Q band from the polycarbonate/tetrapyrazinoindoloporphyrazine composite film, and the Q band is almost identical with the Q band from tetrapyrazinoindoloporphyrazine itself. This is consistent with the XPS N 1s data indicating no interaction between polycarbonate and tetrapyrazinoindoloporphyrazine. Scanning electron microscopy (SEM) reveals the effect of solvent on the morphology of the electro-spun fibers. The diameters of fibers fabricated from chloroform solutions range from 5 to 20 μm. The fibers from cyclohexanone solutions have ultra-fine structures with diameters between 50 and 200 nm but contain droplets along their lengths.*

**Keywords:** electrospinning; nanofiber; phthalocyanine; polycarbonate; X-ray photoelectron spectroscopy

## INTRODUCTION

Electrospinning technology is a simple and low-cost method for making micro- and nanoscale fibers through the action of an external

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electric field imposed on a polymer solution [1,2]. An electrospinning setup consists of three major components: a high voltage power supply, a spinneret, and an electrically conductive collector. The spinneret is connected to a syringe in which a polymer solution is supplied. The syringe is connected to the syringe pump to be able to maintain a stable feeding rate of the solution. When a high voltage is applied to the spinneret, the pendent droplet of the solution at the aperture becomes highly electrified and is deformed into a conical shape due to electrostatic repulsion between surface charges. Once the voltage surpasses a threshold value, a liquid jet is ejected from the aperture and lands on the oppositely charged collector. The ejected jet experiences bending, whipping, stretching, and elongation leading to a long, thin, and uniform fiber during travel from the aperture to the collector.

A variety of materials, such as polymers, inorganic compounds, and polymer/inorganic composites have been used to prepare electro-spun fibers. Larsen *et al.* demonstrated the direct electrospinning of viscous inorganic sols and successfully fabricated fibers consisting of $TiO_2/SiO_2$ and $Al_2O_3$ [3]. Li and Xia demonstrated the electrospinning process to fabricate porous titania nanofibers from a $TiO_2$/poly(vinyl pyrrolidone) composite solution [4]. $TiO_2$ nanofibers can be fabricated via a template-directed method by dip-coating the surfaces of electro-spun polymeric fibers with sol-gel precursors followed by a photosynthesis treatment [5–7]. Xia and coworkers also prepared a variety of inorganic nanofibers including $V_2O_5$, $SnO_2$, indium tin oxide, $GeO_2$, $NiFe_2O_4$, $LiCoO_2$, $BaTiO_3$ by simply changing the sol-gel precursor [8,9].

Conducting polymers including polyaniline, polythiophene, polypyrrole, and polyfluorene are not suitable for electrospinning because of limitations caused by their molecular weight and/or solubility. One of the most effective methods to solve this problem is to blend the conductive polymers with other polymers well-suited for electrospinning. MacDiarmid and coworkers fabricated electro-spun nanofibers of a doped polyaniline/polyethylene oxide blend with sub-30 nm diameter and observed field-effect transistor behavior in the electro-spun nanofibers [10,11]. Greiner *et al.* investigated the process to fabricate core-shell nanofibers of poly(ethylene oxide) (PEO) and poly(dodecylthiophene) by co-electrospinning [12]. Electro-spun nanofibers of polypyrrole [13–15], poly(3-hexylthiophene) [16] and polyphenylene vinylene [16,17] were also successfully fabricated by blending them with PEO.

Porphyrazine is composed of a central conjugated C8N8 ring with four pyrrole groups. The properties of the porphyrazine can be adjusted by tailoring the basic molecule, such as by substitution in a controlled manner with electron-withdrawing or -donating groups to the macrocycle, or extension of the $\pi$-electron system [18]. Phthalocyanines are the most studied molecules among porphyrazine derivatives due to their advantageous properties such as chemical and thermal stability, optical and electronic properties, and ordered crystal film growth [19]. Phthalocyanines have found potential applications in the field of organic light emitting diodes, organic field effect transistors, organic solar cells and sensors. In these applications, phthalocyanines have been mostly applied as thin films. Phthalocyanine thin films can be fabricated by several methods such as spin-coating, thermal evaporation and Langmuir-Blodgett (LB) techniques. Thermal evaporation and LB techniques have been widely used because of their simplicity in the control of the crystal structures of the molecules and film thickness. The spin-coating technique has been less frequently used since phthalocyanine tends to crystallize and exhibits difficulty in film formation by the spin-coating technique. The thermal evaporation method can cause thermal degradation of the molecules, and the LB technique is a very delicate and time-consuming process. Spin-coating is more rapid and convenient compared to the LB and thermal evaporation techniques.

In this study, we aim to fabricate polymer/tetrapyrazinoindoloporphyrazine composite films and fibers using the spin-coating and the electrospinning techniques, respectively. X-ray photoelectron spectroscopy has been used to verify the structural compositions of the composite films and fibers. UV-vis spectroscopy has been used to characterize the electronic transitions of the polycarbonate/tetrapyrazinoindoloporphyrazine composite films and fibers. The uv-vis spectra of the composite films and fibers have been compared to that of tetrapyrazinoindoloporphyrazine to investigate the change in the Q band of tetrapyrazinoindoloporphyrazine when it is blended with polycarbonate. Scanning electron microscopy has been used to reveal the morphology of the electrospun composite fibers.

## EXPERIMENTAL

### Materials

Tetra(5-*n*-nonyl-8-tert-butyl-2,3-pyrazino[2,3-*b*]indolo)porphyrazinato copper(II) was synthesized by substituting an indole group at the 2,3 position of the pyrazine [20]. This phthalocyanine hereafter is referred to as Cu-Pc-C8. Amorphous polycarbonate (PC, Mn = 100,000) was purchased from Sigma Aldrich Co. Figure 1 shows the chemical structures of Cu-Pc-C8 and amorphous PC. Chloroform and cyclohexanone (special grade) were purchased from Samchun Pure Chemical Co. and

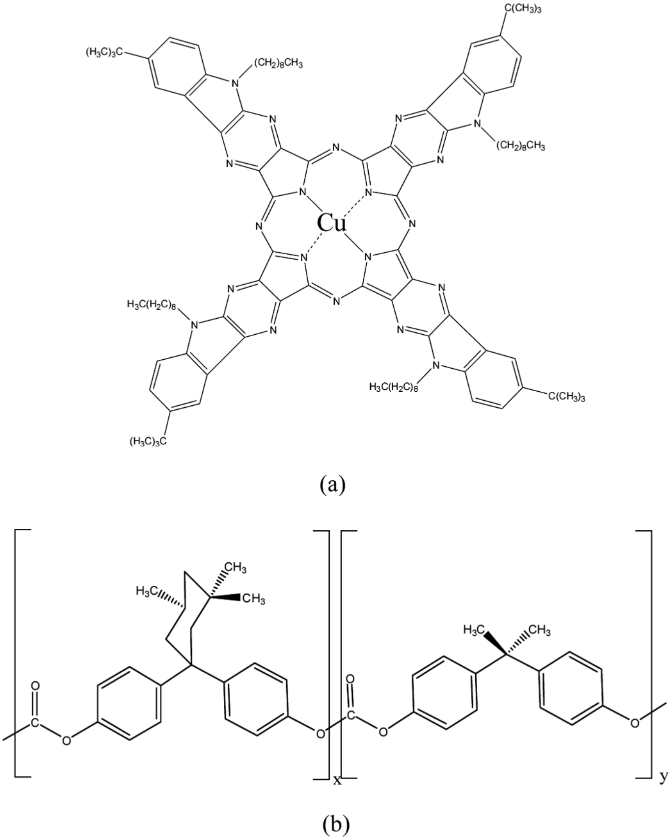

**FIGURE 1** The chemical structures of (a) tetra(5-*n*-nonyl-8-tert-butyl-2,3-pyrazino[2,3-*b*]indolo)porphyrazinato copper(II) (Cu-Pc-C8) and (b) poly [Bisphenol A carbonate-co-4,4′-(3,3,5-trimethyl cyclohexylidene)diphenol carbonate] (PC).

used as received without additional purification. The PC solution (20 wt.%) and Cu-Pc-C8 solution (0.05 wt.%) were prepared by dissolving them in chloroform and cyclohexanone at room temperature. The Cu-Pc-C8/PC solution was prepared by mixing two solutions (20 g of PC solution and 2 g of Cu-Pc-C8 solution) while stirring.

## Electrospinning Set-Up

In a typical procedure, the Cu-Pc-C8/PC solution was loaded into a plastic syringe equipped with a 30 gauge needle made of stainless steel. The needle is connected to a high voltage power supply that is capable of generating DC voltages up to 30 kV. The solution was continuously supplied using a syringe pump (KDS-200, Stoelting, Wood Dale, IL) at a rate of 0.01 mL/h. Voltages of 6, 9, 12, 15, and 20 kV were applied for electrospinning. The distance between the needle tip and the collector was between 15 and 28 cm. The needle, electrode, and grounded target are all enclosed in order to reduce the effect of air currents on the trajectory of the electro-spun jet. The collected Cu-Pc-C8/PC composite fiber was dried at 70°C for one day to evaporate any remaining solvent.

## Characterization

Electro-spun Cu-Pc-C8/PC composite fiber was collected on Si(111) for XPS and SEM experiments and quartz substrates for UV-vis spectroscopy. XPS measurements were carried out in a VG ESCALAB 220-I photoelectron spectrometer equipped with a concentric hemispherical analyzer. MgK$\alpha$ X-rays ($h\nu = 1253.6$ eV) were used as an excitation source. To minimize charging during the experiments, silver paint was used to make electric contact from the edges of the sample surface to the sample stub. The sample stubs were held at electrical ground during XPS measurement. All of the measured binding energies are referenced to the C 1s peak at 284.9 eV. UV-visible spectroscopy was performed using a Shimadzu UV-1650PC spectrophotometer. SEM images were taken using a field-emission scanning electron microscope (JSM-6700F FE-SEM, JEOL) operated at accelerating voltages of 5 and 15 kV, and the samples were coated with Au/Pd before imaging. The diameters of these fibers were quantitatively measured from their high-magnification SEM images.

## RESULTS AND DISCUSSION

XPS was performed to verify the chemical compositions of the electro-spun Cu-Pc-C8/PC composite fiber. Figure 2 shows XPS spectra of the electro-spun Cu-Pc-C8/PC composite fiber, the spin-coated Cu-Pc-C8/PC film, and an electro-spun PC fiber on silicon substrates. In the case of the XPS spectrum for electro-spun Cu-Pc-C8/PC composite fibers, Si 2p, C 1s, N 1s, O 1s, and Cu $2p_{3/2}$ peaks appeared at 99.6, 285.5, 400, 532, and 935.8 eV, respectively. The intensity of the XPS N 1s and Cu $2p_{3/2}$ peaks are very weak (not observed in XPS survey, Fig. 2(a)) due to the very low density of the nitrogen and copper atoms on the fiber compared to the film. These two peaks are detected by scanning with higher resolution and clearly shown in Figures 3(a) and 4(a). For comparison, XPS was performed for electro-spun PC fiber without

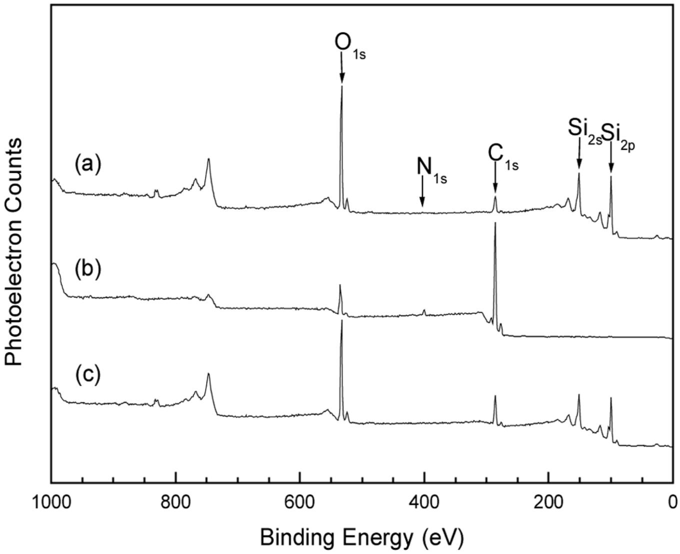

**FIGURE 2** MgK$\alpha$ XPS of (a) electro-spun Cu-Pc-C8/PC composite fiber, (b) spin-coated Cu-Pc-C8/PC composite film, and (c) electro-spun PC fiber on silicon substrates.

the Cu-Pc-C8 compound. In this case, the XPS spectrum does not show an N 1s peak, consistent with pure PC electro-spun fibers. These results clearly confirm the formation of a Cu-Pc-C8/PC composite.

Figure 3 shows N 1s XPS spectra of an electro-spun Cu-Pc-C8/PC composite fiber, an electro-spun PC fiber, and a spin-coated Cu-Pc-C8/PC composite film on silicon substrates. For comparison, the N 1s peak of a Cu-Pc-C8 LB film on a gold-coated silicon substrate is shown in the figure. The N 1s peak is present only for the electro-spun fiber, spin-coated film of Cu-Pc-C8/PC composite, and Cu-Pc-C8 LB film. In the case of the spin-coated Cu-Pc-C8/PC composite film and Cu-Pc-C8 LB film, the N 1s peak centered at 400 eV with a shoulder at 401.5 eV corresponds to the nitrogen atoms in the phthalocyanine ring and indoloporphyrazine group. Compared with the intensity of the N 1s peaks for a spin-coated Cu-Pc-C8/PC composite film and a Cu-Pc-C8 LB film, the peak intensity for the electro-spun Cu-Pc-C8/PC composite fiber is relatively weak due to very low density of the electro-spun fiber web on the silicon substrate.

Figure 4 displays Cu 2p XPS spectra of an electro-spun Cu-Pc-C8/PC composite fiber, an electro-spun PC fiber and a spin-coated Cu-Pc-C8/PC composite film on silicon substrates. The Cu 2p peaks

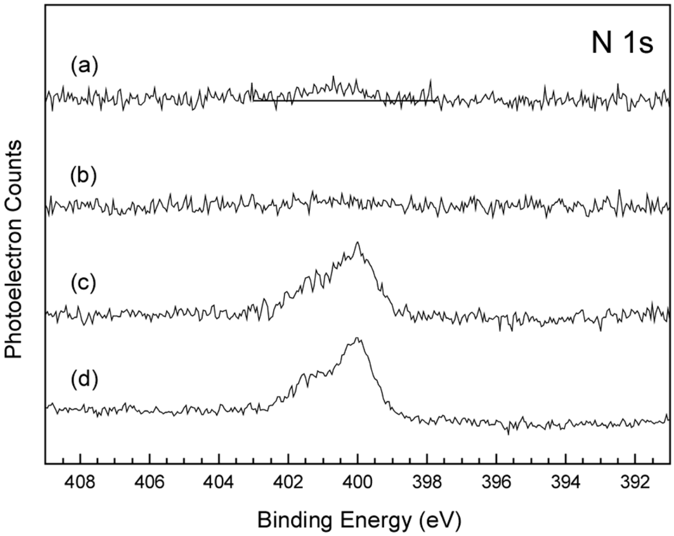

**FIGURE 3** MgK$\alpha$ XPS N 1s region of (a) electro-spun Cu-Pc-C8/PC composite fiber, (b) electro-spun PC fiber, and (c) spin-coated Cu-Pc-C8/PC composite film on silicon substrates and (d) Cu-Pc-C8 LB film on a gold-coated silicon substrate.

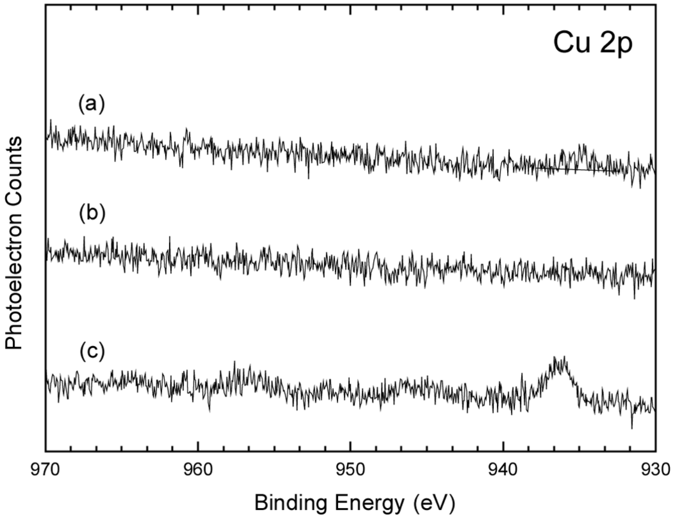

**FIGURE 4** MgK$\alpha$ XPS Cu 2p region of (a) electro-spun Cu-Pc-C8/PC composite fiber, (b) electro-spun PC fiber, and (c) spin-coated Cu-Pc-C8/PC composite film on silicon substrates.

are present only for the electro-spun fiber and spin-coated film of Cu-Pc-C8/PC composite samples. In the case of the spin-coated Cu-Pc-C8/PC composite film, the Cu 2p peaks appear at 936.2, 945.4, 956.2, and 964.2 eV, assignable to the copper captured inside the phthalocyanine ring. Electro-spun Cu-Pc-C8/PC composite fibers shows only one Cu $2p_{3/2}$ peak at 934.8 eV with very low intensity due to low density of the web.

Figure 5 displays the electronic absorption spectra of the Cu-Pc-C8 Langmuir-Blodgett film, the spin-coated Cu-Pc-C8/PC composite film, and the spin-coated PC film on quartz substrates. In general, phthalocyanines exhibit absorption spectra with a Soret band at around 350 nm and Q bands at higher wavelengths (ca. 650 nm). The Soret and Q bands are due to $\pi$-$\pi^*$ transitions [21]. In the case of Cu-Pc-C8 Langmuir-Blodgett films, the Soret band appears at 363 nm with a broad shoulder centered at 460 nm. A broad Q band appears at 712 nm with two shoulders at 636 and 767 nm. Polycarbonate (PC) is one of the representative transparent polymers. As seen in Figure 5, the PC film is optically transparent down to 400 nm. It is interesting to study the change in the Q band of tetrapyrazinoindoloporphyrazine when it is mixed with PC. The Q band of tetrapyrazinoindoloporphyrazine in the composite appears at an almost identical wavelength with a similar shape, indicating almost no interaction between Cu-Pc-C8 and PC.

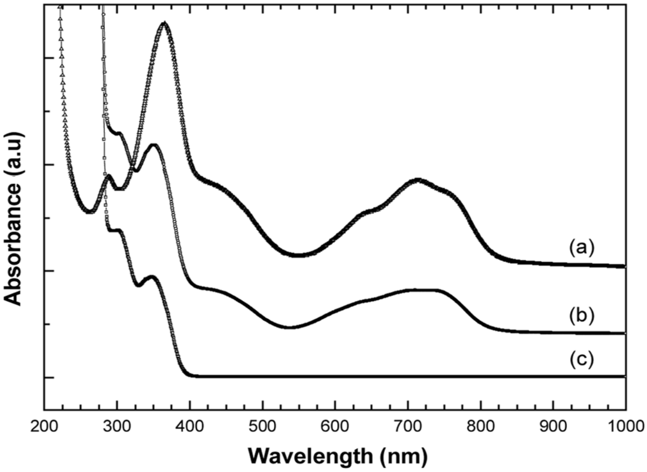

**FIGURE 5** UV-vis spectra of (a) Cu-Pc-C8 LB film, (b) spin-coated Cu-Pc-C8/PC composite film, and (c) spin-coated PC film on quartz substrates.

Figure 6 shows SEM images of electro-spun Cu-Pc-C8/PC composite fibers from a 20 wt.% solution in chloroform at 20 kV. The fibers were collected at distances of 15 and 20 cm from the needle to the collector to determine the influence of the distance on the morphology of the fibers. The diameters of the electro-spun fibers range from 5 to 20 μm. The morphology of the PC fibers is spaghetti-like. Changing the distance from 15 to 25 cm does not induce significant alterations in morphology of the fibers. Figure 7 displays SEM images of

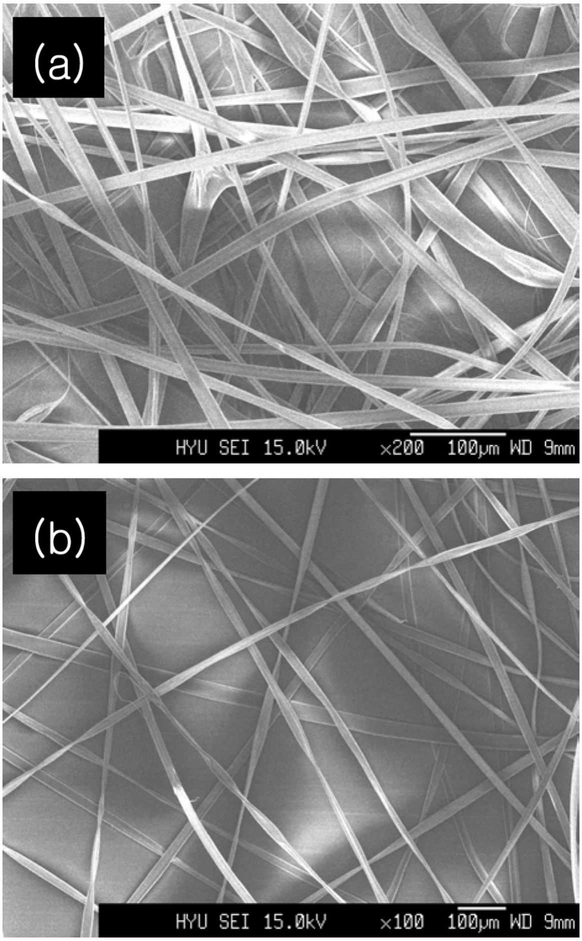

**FIGURE 6** SEM images of electro-spun Cu-Pc-C8/PC composite fiber dissolved in chloroform at 20 kV. The distance between the needle and the collector is (a) 15 and (b) 25 cm.

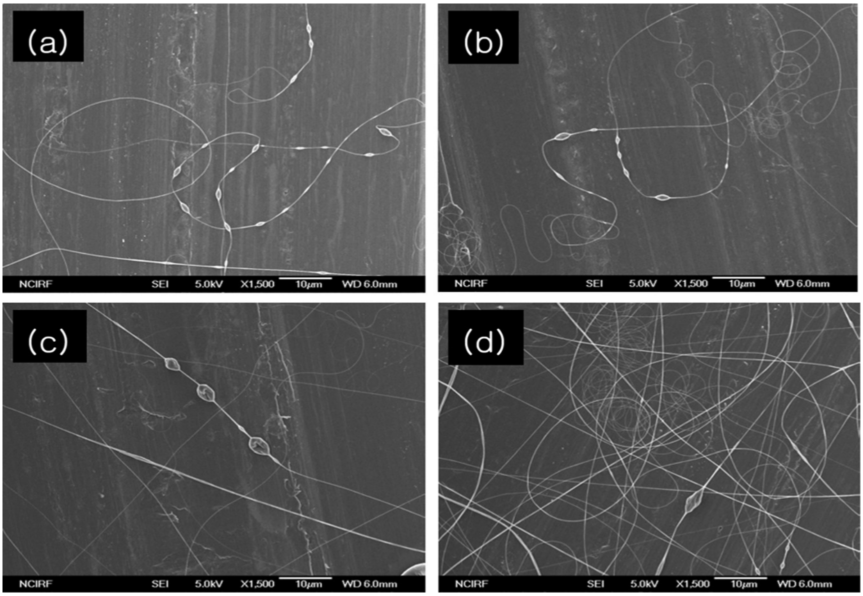

**FIGURE 7** SEM images of electro-spun Cu-Pc-C8/PC composite fiber dissolved in cyclohexanone at (a) 6, (b) 9, (c) 12, and (d) 15 kV. The distance between the needle and the collector is 20 cm for all of these images.

electro-spun Cu-Pc-C8/PC composite fibers from a 20 wt.% solution in cyclohexanone. Electrospinning was also performed at 6, 9, 12, 15 kV to examine the effect of the voltage difference between the needle and collector. In these studies, the distance from the needle to the collector was maintained at 20 cm. Compared to the electro-spun Cu-Pc-C8/PC composite fibers from a chloroform solution, significant difference in the diameter of the fibers is observed by changing the solvent from chloroform to cyclohexanone. The diameters of the electro-spun fibers from cyclohexanone solutions range from 50 to 200 nm. As seen in the figure, however, the fibers have beads (droplets) occasionally located along their lengths. As seen in the figures, the differences in the supply voltage do not change the morphology of the fibers.

## CONCLUSIONS

This study reports the fabrication and characterization of electro-spun polycarbonate/tetrapyrazinoindoloporphyrazine composite fibers. XPS N 1s and UV-vis spectroscopy confirm no significant interactions between polycarbonate and tetrapyrazinoindoloporphyrazine. The Q band of the tetrapyrazinoindoloporphyrazine is very sensitive to acidic and basic environments. In future research, we will fabricate sensors using composite films and fibers and characterize their pH sensing properties. The diameters of fibers fabricated from chloroform solution range from 5 to 20 μm. The fibers from cyclohexanone solution have ultra fine structures – diameters between 50 to 200 nm – but contain many droplets. Alteration of the distance between the tip and the collector and the supply potential do not induce significant differences in fiber morphology.

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