

Improving photoluminescence of poly(9-vinylcarbazole)/4,7-diphenyl-1,10-phenanthroline/tris-(8-hydroxyquinoline) aluminum fibers via coaxial electrospinning

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ABSTRACT: Solutions of poly(9-vinylcarbazole)/4,7-diphenyl-1,10-phenanthroline (PVK/Bphen) and poly(9-vinylcarbazole)/tris-(8-hydroxyquinoline) aluminum (PVK/Alq₃) were individually delivered either to the inner or the outer needle of a coaxial spinneret for electrospinning to prepare green luminescent PVK/Bphen/Alq₃ composite fibers. The influence of both flow rate and applied voltage on the photoluminescence of the composite fibers was evaluated. Scanning electron microscopy showed ribbon-like fibers with uneven surfaces and thickness of about 5 μm. Raman spectroscopy and fluorescence microscopy revealed that Bphen was homogeneously dispersed in the PVK fibers; Alq₃ was not. Photoluminescence shows strong evidence that there are marked conditions where emission of the co-electrospun PVK/Bphen/Alq₃ fibers significantly improved as compared with those produced by simple electrospinning. It is suggested that the enhanced dispersion of the Alq₃ allowed a more efficient energy transfer from the PVK to the Alq₃. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44019.

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INTRODUCTION

In recent years considerable attention has been focused on manufacturing polymer fibers by coaxial electrospinning, not only because of their usefulness in numerous special applications, such as encapsulation of drugs into the polymeric matrix and preparation of nanofibers from materials lacking filament-forming properties, but also because of the improvement in their relative properties.^{1–5} Coaxial electrospinning is an innovative extension of electrospinning, in which two liquids are injected at appropriate flow rates through two electrified, aligned capillary needles, to enforce the formation of the fibers with a core-shell or core-sheath structure.^{6–8}

There have been several reports on the optical behavior, especially the photoluminescence, of co-electrospun light-emitting fibers made from conducting polymers. These reports include the use of easily spinnable polymers, carbon quantum dots, and mesoporous molecular sieves.^{5,9–12} Conducting polymers exhibit unique electronic, magnetic, and optical properties that are inherent to metals and/or semiconductors.¹³ Poly(9-vinylcarbazole) (PVK) is a light-emitting, easily-spinnable polymer, widely used for electronic and optoelectronic applications.^{14–16}

We recently reported the successful fabrication of green-emitting electrospun PVK/tris-(8-hydroxyquinoline) aluminum (PVK/Alq₃) and PVK/4,7-diphenyl-1,10-phenanthroline (PVK/Bphen) fibers from their blend solutions in 1,2-dichloroethane (DCE).¹⁷ Alq₃ is a green light-emitting molecule, mostly used as an electron-transporting material, while Bphen is commonly used as a hole-blocking material.^{18–20} The enhanced luminescence characteristics of the PVK/Alq₃ fibers, as compared with the corresponding spin-coated films, were attributed to an efficient energy transfer from PVK to Alq₃. In this study, we employed a dual-syringe electrospinning method to prepare luminescent, hole-blocking, electron-transporting, trifunctional fibers of (PVK/Bphen/Alq₃), which have potential application in single layered OLEDs.

EXPERIMENTAL

Materials

PVK ($M_w \sim 1,100,000$ g/mol), tris-(8-hydroxyquinoline)aluminum (Alq₃), Bphen, and DCE (99.8% HPLC grade) were purchased from Aldrich. All materials were used without further purification.

Table I. Co-electrospinning Conditions

Set A				Set B			
Run	Core solution PVK/Bphen (6% w/v)	Shell solution PVK/Alq ₃ (4% w/v)	Voltage (kV)	Run	Core solution PVK/Alq ₃ (6% w/v)	Shell solution PVK/Bphen (4% w/v)	Voltage (kV)
A1	1	1	16	B1	1	1	16 ^a
A2	1	1	17	B2	1	1	17 ^a
A3	1	1	19	B3	1	1	19
A4	1	1	20	B4	1	1	20
A5	0.5	1	16	B5	0.5	1	16 ^a
A6	0.5	1	17	B6	0.5	1	17 ^a
A7	0.5	1	19	B7	0.5	1	19
A8	0.5	1	20	B8	0.5	1	20
A9	1	0.5	16	B9	1	0.5	16 ^a
A10	1	0.5	17	B10	1	0.5	17 ^a
A11	1	0.5	19	B11	1	0.5	19
A12	1	0.5	20	B12	1	0.5	20
A13	0.5	0.5	16	B13	0.5	0.5	16 ^a
A14	0.5	0.5	17	B14	0.5	0.5	17 ^a
A15	0.5	0.5	19	B15	0.5	0.5	19
A16	0.5	0.5	20	B16	0.5	0.5	20

^aNo fibers could be obtained at these conditions.

Preparation of Spinning Solutions

PVK/Alq₃ and PVK/Bphen (at a fixed blend ratio of 80:20) were prepared at 4 and 6% (w/v) using DCE. Bphen or Alq₃ were first dispersed in DCE by stirring at 25 °C for 1 h, followed by sonication in an ultrasonic bath for another 1 h. The appropriate amount of PVK was then dissolved in these solutions and dispersed by mechanical stirring for 12 h. Additional solutions of PVK/Bphen/Alq₃ (at a fixed blend ratio of 80:20:20) were prepared similarly at a concentration of 6% (w/v) using DCE.

Electrospinning/Co-electrospinning Process

For the electrospinning process, the PVK/Alq₃, PVK/Bphen, or PVK/Bphen/Alq₃ solution was placed into a 5-mL glass syringe connected to a metallic 21 gauge needle. The needle was connected to a high-voltage power supply (Gamma High Voltage Research RR30-5P), and the applied voltage was varied from 16 to 20 kV. The solutions were fed at 0.5 and 1 mL/h by a syringe pump (Fisher Scientific 78-0100I). The materials were collected for about 3 min on a grounded aluminum foil, which was placed 17 cm from the needle tip. The samples were then dried for 2 h at 60 °C in an oven. All solutions were processed under the same conditions.

For the co-electrospinning process, a commercial coaxial spinneret with style A hub (Ramé-Hart Instrument Co) was used. The outer needle has an inside diameter of 1.19 mm; the inner one has outside and inside diameters of 0.559 and 0.305 mm, respectively. The PVK/Alq₃ and PVK/Bphen solutions were placed in two 5-mL glass syringes and connected to the outer and inner needles, respectively. Another different set of samples

was prepared where the PVK/Alq₃ solution was connected to the inner needle and the PVK/Bphen solution to the outer needle. The outer needle was connected to the high-voltage power supply, and the applied voltage was varied from 16 to 20 kV. The flow rates of the solutions in the outer and inner needles were controlled by two syringe pumps. The electrospun fibers were collected for about 3 min on grounded aluminum foils, which were placed 17 cm from the outlets of the needles. The concentrations and flow rates of the solutions in the outer and inner needles were varied (Table I).

Characterization of As-Spun Fibers

Electrospun and co-electrospun fibers were observed with a JEOL JSM-7800F scanning electron microscope (SEM). Specimens were coated with gold and SEM micrographs were obtained using 5 kV secondary electrons. Fluorescent images were also taken with a fluorescence microscope (Nikon Eclipse-Ti-U), using an 870 nm wavelength LED and a blue excitation filter block B-2A (Ex450-490; DM505; BA520). Room-temperature micro-Raman measurements were performed with a Jobin Yvon LabRam HR800 system in backscattering geometry, using 784 nm laser excitation. Photoluminescence emission (PL) and excitation (PLE) spectra were measured using a SHI-MADZU RF-5301PC.

RESULTS AND DISCUSSION

Fiber Morphology

Figure 1 shows the SEM images of the PVK/Bphen, PVK/Alq₃, and PVK/Bphen/Alq₃ electrospun fibers produced at a flow rate

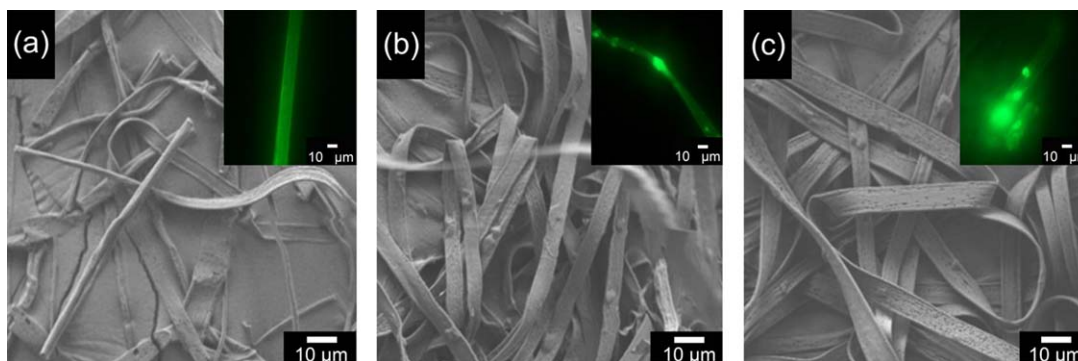


Figure 1. SEM images of: (a) PVK/Bphen, (b) PVK/Alq₃, and (c) PVK/Bphen/Alq₃ electrospun fibers. The insets are the corresponding fluorescence microscope images. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 1 mL/h and applied voltage of 19 kV. The inset figures are the corresponding fluorescence microscopy images. All exhibit ribbon-shaped structures. The rapid removal of the solvent from the surface of the jet in the early stage of electrospinning forms a skin. This skin causes the formation of hollow tubes, which subsequently collapse to form ribbons.²¹

PVK/Bphen fibers have a width in the range of 3–5 μm and present rough surfaces [Figure 1(a)]. The uniformity of their green fluorescence is indicative of the good solubility of Bphen

and PVK in DCE. However, PVK/Alq₃ fibers are wider (~5–7 μm), thicker, and their surface is rough with protuberances ascribed to in-homogeneously incorporated Alq₃ [Figure 1(b)].¹⁷ The small-greener domains observed in its fluorescence image corroborates that Alq₃ is poorly dispersed in the PVK matrix. One main drawback in the application of Alq₃ is the phase separation that occurs when it is blended with polymers to enhance its limited processability.²² Likewise, there seems to be an increase in the size and number of protuberances on the surface of the PVK/Bphen/Alq₃ electrospun fibers, as well as an increase in the size of the bright-greener domains, caused by poorer dispersion of the Alq₃ in the PVK matrix [Figure 1(c)].

Figure 2 shows the SEM images of co-electrospun fibers obtained from the A7 and B7 solutions. The inset figures are the fluorescence microscopy images of the corresponding co-electrospun fibers.

Ribbon-like fibers are formed, as in the simple electrospun fibers (Figure 1), but with more widely varying widths (~3–7 μm). For fibers processed from the PVK/Bphen solutions connected to the inner needle and the PVK/Alq₃ solutions connected to the outer needle, rough surfaces are observed with some protuberances either in the center or border of the fibers [Figure 2(a)]. For fibers processed from the solutions connected

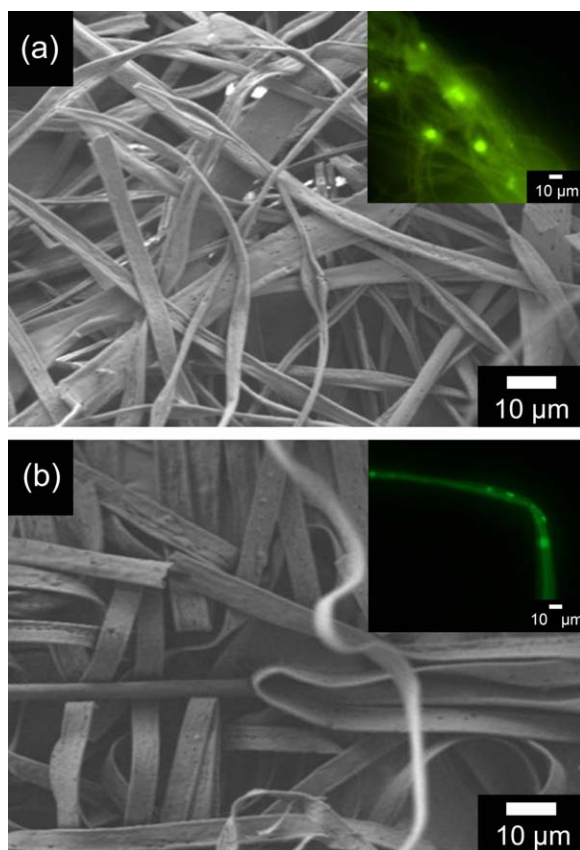


Figure 2. SEM images of co-electrospun (PVK/Bphen)/(PVK/Alq₃) fibers obtained from the (a) A7 and (b) B7 solutions. The insets are the corresponding fluorescence microscope images. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

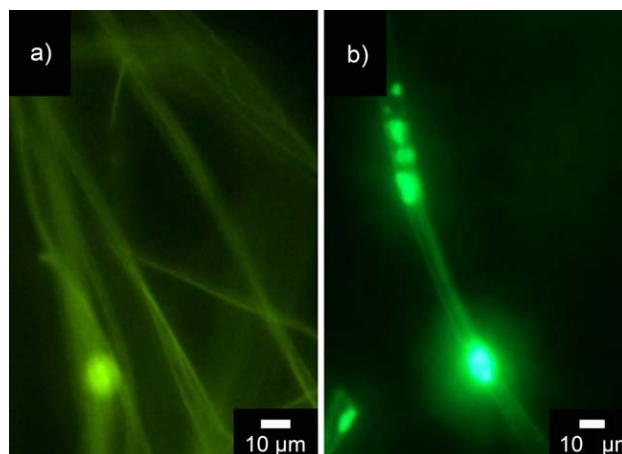


Figure 3. Fluorescence microscope images of co-electrospun (PVK/Bphen)/(PVK/Alq₃) fibers obtained from the (a) A11 and (b) B11 solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

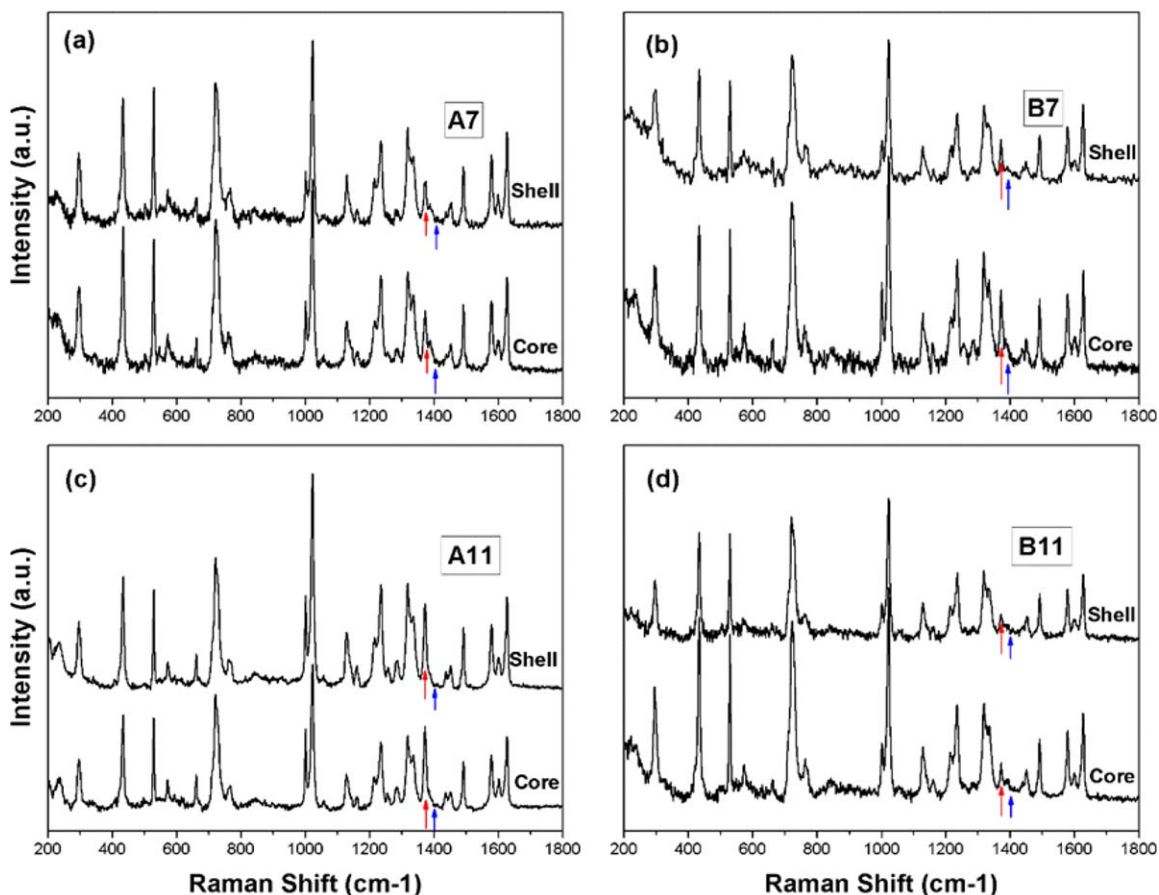


Figure 4. Raman spectra of (PVK/Bphen)/(PVK/Alq₃) single-strand co-electrospun fibers obtained from the (a) A7, (b) B7, (c) A11, and (d) B11 solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

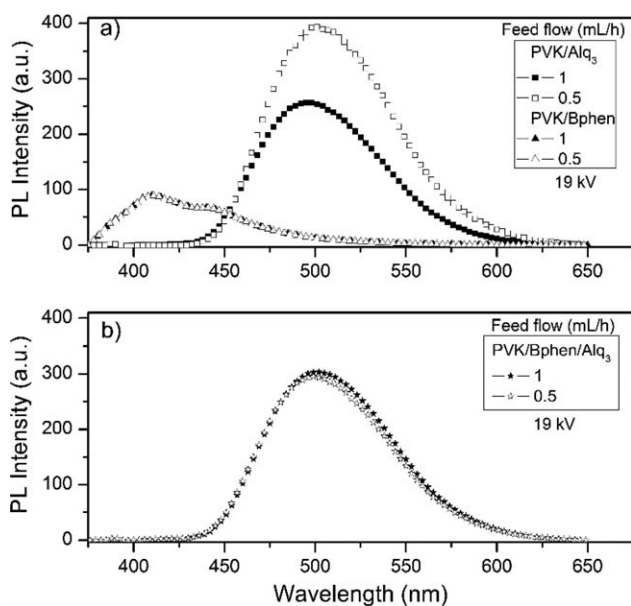


Figure 5. PL spectra of (a) PVK/Bphen and PVK/Alq₃ electrospun fibers and (b) PVK/Bphen/Alq₃ electrospun fibers, produced with an applied voltage of 19 kV.

inversely, marked protuberances could also be observed throughout all the fibers [Figure 2(b)].

It is worth noting that a relatively uniform green fluorescence is observed in the co-electrospun fibers processed from the PVK/Bphen solutions connected to the inner needle [A7: Figure 2(a) and A11: Figure 3(a)], similar to the fluorescence of the electrospun PVK/Bphen fibers [Figure 1(a)], with sparse, small, bright-green domains associated with the poorly dispersed Alq₃.

In contrast, various small, bright-green domains are observed in the co-electrospun fibers processed from the PVK/Alq₃ solutions connected to the inner needle [B7: Figure 2(b) and B11: Figure 3(b)], similar to the PVK/Alq₃ electrospun fibers [Figure 1(b)]. The solidification of the shell polymer solution occurs faster than the solidification of the core polymer solution.²³ Thus, it is most likely that when the PVK/Alq₃ solution is connected to the inner needle, the diffusion of the Alq₃ is prevented by the low diffusion coefficients relative to the solidification process taking place in the shell, promoting the formation of bright-green domains.²⁴

Raman Spectroscopy Analysis

The dispersion of Bphen and Alq₃ in the PVK matrix was also studied using Raman spectroscopy (Figure 4).

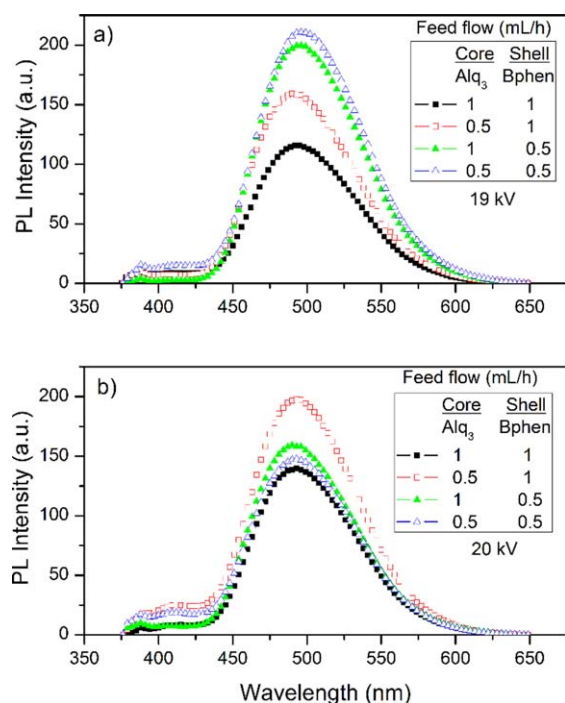


Figure 6. PL spectra of co-electrospun (PVK/Bphen)/(PVK/Alq₃) fibers processed at conditions where the PVK/Alq₃ solutions are connected to the inner needle, with applied voltages of 19 kV and 20 kV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

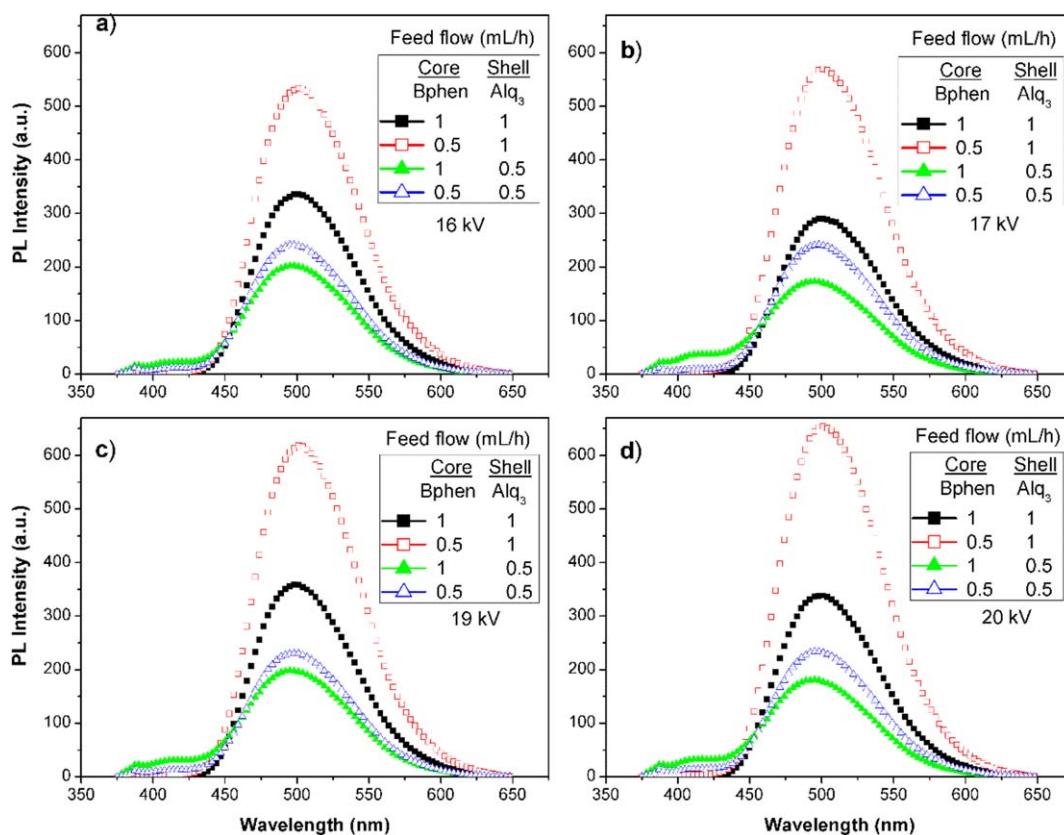


Figure 7. PL spectra of co-electrospun (PVK/Bphen)/(PVK/Alq₃) fibers processed at conditions where the PVK/Bphen solutions are connected to the inner needle, at different applied voltages. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

The characteristic Raman peaks of both PVK (434–529 cm⁻¹ and 1316 cm⁻¹) and Bphen (1368 cm⁻¹) appear in the core and shell spectrum of all of the selected co-electrospun fibers, indicating good diffusion of the Bphen throughout all the fibers [Figure 4(a–d)]. This may be attributed to the evaporation and diffusion of the solvent that drive the polymers and small molecules to mix together since the solutions contain the same solvent.²⁵ On the contrary, the major Raman band of the Alq₃ at 1400 cm⁻¹ was barely evident, even in the core spectrum of the co-electrospun fibers processed from the PVK/Alq₃ solutions connected to the inner needle [Figure 4(b,d)], implying that Alq₃ is not homogeneously distributed in the PVK matrix.

PL Spectroscopy Analysis

Figure 5 shows the PL spectra of the PVK/Bphen, PVK/Alq₃, and PVK/Bphen/Alq₃ electrospun fibers produced with an applied voltage of 19 kV.

The PL spectra of the PVK/Bphen fibers show peaks at 389, 409, and 447 nm ($\lambda_{exc} = 337$ nm) due to PVK [Figure 5(a)]. The emission at 447 nm has been ascribed to fully overlapping, sandwich-like configurations of the f-PVK excimers in electrospun PVK fibers and the band at 389 nm has been associated with the carbazole groups in the partially overlapping conformation of the p-PVK singlet excimers.^{14,26} The contribution of the Bphen is not apparent; its PL emission bands are very close to that of PVK.¹⁷ In contrast, the PL spectra of the PVK/Alq₃ fibers are dominated by the peak corresponding to the Alq₃

(~500 nm); the contribution of the PVK is not apparent [Figure 5(a)]. This result reveals efficient energy transfer from PVK to Alq₃ as reported for PVK/Alq₃ spin-coated thin films.¹⁹ Additionally, the position of the PL peak is red-shifted from 501 to 498 nm when the flow rate is changed from 0.5 to 1 mL/h, and the luminescence intensity is higher at a flow rate of 0.5 mL/h than at a flow rate of 1 mL/h. The PL peak position of dyes is influenced by the distance between their molecules.²⁷ Therefore, it can be deduced that the distance between Alq₃ molecules in the two types of fibers is different and leads to a more uniform dispersion of the Alq₃ in the PVK matrix when the flow rate is 0.5 mL/h, which in turn increases luminescence. The difference in spacing between Alq₃ molecules could be ascribed to the low diffusion coefficients of Alq₃ and the level of blend miscibility.^{24,28} The emission spectra of the PVK/Bphen/Alq₃ electrospun fibers are similar to that of the PVK/Alq₃ fibers, showing the same characteristic emission peak for the Alq₃ [Figure 5(b)].

The spectra of the co-electrospun (PVK/Bphen)/(PVK/Alq₃) fibers processed from the PVK/Alq₃ solutions connected to the inner needle and the PVK/Bphen solutions connected to the outer needle with an applied voltage of 19 and 20 kV, are shown in Figure 6. No fibers could be obtained at 16 or 17 kV. The peak maximum associated with Alq₃ varies from 493 to ~498 nm depending on coelectrospun conditions, presumably due to changes in the distance between Alq₃ molecules.²⁷ The presence of the broad shoulder associated with PVK (375–430 nm) in all these spectra suggests that Alq₃ does not diffuse through the shell of the fibers resulting in no significant energy transfer from PVK to Alq₃ in that zone. The luminescence intensity of these co-electrospun fibers decreased, as compared to that of the simple electrospun PVK/Bphen/Alq₃ fibers, indicating a poor dispersion of the small molecules in the PVK matrix at these co-electrospinning conditions.

The PL spectra of the co-electrospun (PVK/Bphen)/(PVK/Alq₃) fibers processed from the PVK/Bphen solutions connected to the inner needle and the PVK/Alq₃ solutions connected to the outer needle are rather different (Figure 7). It is surprising that the relative intensity of the band associated with the Alq₃ in the blue-green spectral range (430–550 nm, $\lambda_{\text{exc}} = 371$ nm) increases up to two times compared with the intensity of the simple electrospun PVK/Alq₃ or PVK/Bphen/Alq₃ fibers, when the feed flow of the core solution is set at 0.5 mL/h and the feed flow of the shell solution (PVK/Alq₃) is set at 1 mL/h, at all applied voltages [Figure 7(a–d)].

At other co-electrospun conditions, the intensity of this band is similar to or less than the intensity of the electrospun fibers. An interesting feature is the decrease of the shoulder due to PVK as the band associated with the Alq₃ increases; no shoulder is observed at the conditions for maximum intensity of the Alq₃ band. These results indicate a good lateral diffusion of the Alq₃ from the shell to the core solutions during the coelectrospinning of fibers from the PVK/Bphen solutions connected to the inner needle and the PVK/Alq₃ solutions connected to the outer needle, which eventually leads to a very efficient energy transfer from PVK to Alq₃. It is interesting to note that these fibers do not have visible protuberances and present a more homogenous

emission than the fibers processed at conditions where the PVK/Alq₃ solution is connected to the inner needle, demonstrating that coaxial electrospinning can be used not only to achieve a good dispersion of small molecules into polymers but also to improve the quality of monolithic nanofibers, as previously reported.^{2,29}

CONCLUSIONS

Green luminescent PVK/Bphen/Alq₃ composite fibers with an average width of 5 μm were prepared by coaxial electrospinning. The dispersion of Alq₃ in the PVK matrix was greatly improved by coaxial electrospinning when the core fluid was a solution of PVK/Bphen at a flow rate of 0.5 mL and the outer fluid was PVK/Alq₃ at a flow rate of 1 mL/h, at all applied voltages. PL studies revealed that the improved dispersion of Alq₃ in the PVK matrix facilitated an increase of energy transfer from PVK to Alq₃ resulting in a significant increase of green emission over that for the simple electrospun PVK/Bphen/Alq₃ fibers. Thus, coaxial electrospinning can be used to achieve a good dispersion of small molecules into polymers. Furthermore, because of the better dispersion, the quality of monolithic nanofibers can also be improved. These green-emitting fibers have potential applications in producing higher efficiency white light or in medical applications, such as optogenetics and enhancement of fibroblast growth.

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