Electrospun Supramolecular Hybrid Microfibers from Conjugated Polymers: Color Transformation and Conductivity Evolution

Wei Xue\textsuperscript{a}, Man Xu\textsuperscript{a}, Meng-Na Yu\textsuperscript{a}, Hua-Min Sun\textsuperscript{a}, Jin-Yi Lin\textsuperscript{b,c}, Rong-Cui Jiang\textsuperscript{a}, Ling-Hai Xie\textsuperscript{a}, Nai-En Shi\textsuperscript{a,}\textsuperscript{c}, and Wei Huang\textsuperscript{a,b,c}\textsuperscript{*}

\textsuperscript{a} Center for Molecular Systems and Organic Devices (CMSOD), Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China
\textsuperscript{b} Center for Supramolecular Optoelectronics (CSO), Key Laboratory of Flexible Electronics (KLOFE) and Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China
\textsuperscript{c} Frontiers Science Center for Flexible Electronics (FSCE), Shaanxi Institute of Flexible Electronics (SIFE) & Shaanxi Institute of Biomedical Materials and Engineering (SIBME), Northwestern Polytechnical University (NPU), Xi’an 710072, China

Abstract A type of novel electrospun supramolecular hybrid microfibers comprising poly(9-(4-(octyloxy)-phenyl)-2,7-fluoren-9-ol) (PFPOH) and poly(N-vinylcarbazole) (PVK) are successfully prepared for intriguing multi-color emission properties. The supramolecular tunable PFPOH aggregation in PVK matrix endows the complex with a smart energy transfer behavior to obtain the multi-color emissions. In stark contrast to PVK fibers, the emission color of PFPOH/PVK fibers with an efficient dispersion of PFPOH fluorophores at a proper dope ratio can be tuned in a wide spectrum of blue (0.1%), sky blue (0.5%), nearly white (1%), cyan (2%), green (5%) and yellow (10%). Besides, conductive behaviors of the microfiber were demonstrated in accompany with the increment of the doping ratio of PFPOH to PVK. Successful fabrication of polymer light-emitting diode (PLED) based on the blended electrospun fiber provided a further evidence of its excellent electrical property for potential applications in optoelectronic devices.

Keywords Supramolecular approach; Electrospinning π-conjugated fibers; Multi-color emissions; Conductivity; Polymer light-emitting diodes

INTRODUCTION

With the rapid development of flexible molecular optoelectronics, light-emitting conjugated polymers (LCPs) have recently emerged as an important class of luminescent materials for the potential applications in polymer light-emitting diodes, chemical modification.\textsuperscript{[1−7]} In contrary to the complicated chemical synthesis based on the p-n (also called Donor-Acceptor) strategy,\textsuperscript{[8,9]} the nanoscale supramolecular aggregation is a convenient and effective strategy to the amplification of energy transfer, the tuning of charge separations and further modulating photophysical and electrical behavior in condensed structures.\textsuperscript{[10−15]} Generally, in order to achieve multi-color emissive polymer nanostructures, the most effective approach is to precisely tune fluorescence resonance energy transfer (FRET) process in a multi-component emitting systems.\textsuperscript{[16−22]} However, abundant experiments have revealed that the mixed emissive systems consisting of Red-Green-Blue (RGB) emitters are accompanied by unexpected electronic coupling, resulting in an undesirable energy transfer from the “host” dye to the “guest” dye, and thus causing unstable emission behaviors.\textsuperscript{[23−25]} Compared to traditional chemical synthetic method for fabricating RGB or white lighting emitters, supramolecular assembly technique allows for not only affording abundant non-covalent interactions to fabricate superstructures, but also manipulating FRET behaviors by modulating the molecular arrangements and packing models in condensed structures.\textsuperscript{[26]} Therefore, diverse supramolecular interactions can induce the formation of condensed-state microstructures which may serve as a “guest” of the energy transfer process from high-band emissive LCPs backbone chain “host” and thus effectively tune LCPs emissions.\textsuperscript{[27−32]} Herein, we focus on the preparation of multi-color emissive and conductive LCPs by fabricating supramolecular hybrid fibers of conjugated polymer.

In general, electrospinning (ES) is a convenient and univer-
sal technique to manufacture a series of one-dimensional polymeric superstructures with diameters ranging from micrometers to tens of nanometers. As is well-known, high viscosity of polymer precursor solution is a prerequisite to construct micro- and nano-fibers via ES technology, which is driven by a strong electrostatic force. However, considering low-viscosity of rigid conjugated backbone structures in LCPs, the key factors should be considered, such as high molecular weight, suitable solvents or blending polymer matrix. A common approach to enhancing viscosity is to blend LCPs with high-molecular-weight non-conjugated insulated polymers. In general, the insulating linear vinyl polymers are chosen as matrix, such as poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(vinyl pyrrolidone) (PVP), and poly(vinyl alcohol) (PVA). But these polymers always seriously deteriorate the charge transport and conductive properties. Herein, we have exploited electrospinning to prepare multi-color emissive blending fibers using light-emitting polymers, a kind of π-conjugated polymer named poly(9-(4-(octyloxy)-phenyl)-2,7-fluoren-9-ol) (PPFOH) as emitter, and π-stacked poly(N-vinylcarbazole) (PVK) as matrix (Scheme 1). Significantly, wide spectra of multi-color emissive ES composite fibers are successfully realized, and their conductivity is found to be enhanced by increasing the doping ratio of PPFOH to PVK. Moreover, the successful fabrication of PLEDs based on the ES fiber further pave the way to obtain organic light emitting diode by means of electrospinning. The electrospun polymer fibers with tunable emissions via controlling energy transfer in the supramolecular system would be potentially exploited in fibrous PLEDs, organic waveguide or lasers.

**EXPERIMENTAL**

**Materials**

Poly(9-vinylcarbazole) (PVK, $M_n=1.1\times10^5$), poly(3,4-ethyl-enedi-oxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) were offered by Sigma-Aldrich Trading Co., Ltd. Chloroform, 2-propanol, acetone, LiF and Al were offered by Sinopharm Group Chemical Reagent Co., Ltd. Poly(9-(4-(octyloxy)-phenyl)-2,7-fluoren-9-ol) (PPFOH) is obtained according to the method reported in our previous work with $M_n$ and PDI of 2.4×10^4 and 2.2, respectively.

**Characterization**

FESEM images were taken on a Hitachi S-4800 field emission scanning electron microscope. Fluorescence microscopy (FLM) images were taken on an Olympus IX71 ($\lambda_{ex}=365$ nm) optical microscope. The electrosynipped fibers were fabricated by a FM1301 electrospinning apparatus (Beijing Future Materials Sci-tech. Co., Ltd, China). Absorption spectra (1 μmol/L in toluene) were measured with a Shimadzu UV-3600 spectrometer at 25 °C, and photoluminescence spectra were recorded on a Shimadzu RF-5301 PC luminescence spectrometer. PL quantum yields ($\Phi_{PL}$) were carried out at room temperature on Edinburgh FLSP920 fluorescence spectrophotometer. Current-voltage (I-V) measurements were performed by Keithley 4200. The current-voltage luminescence characteristics of the devices were recorded using a combination of a Keithley source meter (model 2602) and a luminance meter. The electroluminescent (EL) spectra and chromaticity (CIE) coordinates of the devices were analyzed with a spectra-scan PR655 spectrophotometer. All the devices were characterized without encapsulation, and all the measurements were carried out in the ambient condition at room temperature (R.T.). The emission area of the devices is 12 mm² or 40 mm×40 mm as defined by the overlapping area of the indium tin oxide (ITO) films and top electrodes.

**Preparation of PPFOH/PVK Electrospun Microfibers**

The preparation of PPFOH-doped PVK electrospun fibers was performed as follows. The electrospun precursor solutions were initially prepared by dissolving PPFOH and PVK (m_{PPFOH}/m_{PVK}=0.1%, 0.5%, 1%, 2%, 5% and 10%) into CHCl₃. The prepared solution was transferred into a 2 mL syringe mounted on the electrospinning apparatus of FM1301. A high-voltage power supply provided DC voltage up to 19 kV. The working distance between the syringe tip and collector was 15 cm. The electrospun solution was fed at a constant rate of 0.005 mm/s by a syringe pump. Microfibers were collected on glass slides (0.5 cm×2.5 cm) mounted on aluminum foil with a collection time of 5 min.
**PLEDs Device Fabrication**

The PLEDs devices were fabricated on ITO-coated glass whose sheet resistance is 10 Ω/square. The ITO-glass were ultrasonic cleaned sequentially with detergent, 2-propanol, acetone and demonized water, then dried in an oven, and treated in an ultraviolet-ozone chamber for 5 min. PEDOT:PSS was spin-coated onto the ITO-glass at a speed of 3000 r/min for 60 s and then annealed at 120 °C for 20 min. Next, the ES fibers are collected on the film of PEDOT:PSS, and then transferred into the glovebox filled of N₂ for annealing at 80 °C for 20 min. Finally, TPBi (20 nm), LiF (0.8 nm) and Al (100 nm) were deposited onto the active polymer layer successively using thermal evaporation in vacuum through a shadow mask under a base pressure of 5.33×10⁻² Pa.

**RESULTS AND DISCUSSION**

In general, polyfluorene is a widely investigated LCPs owing to their applications in PLED and organic laser, associated with deep-blue luminescence and high emission efficiency. According to previous reports, incorporation of hydroxyl unit at 9-position of polyfluorene empower it to obtain excellent gelation processing and self-assembly behaviors, which provide a self-dopant property to obtain multi-color emission behavior in diluted solution, nanodispersion and solid films. Compared with the condensed states above, one-dimensional nano/microstructures manufactured via electrospinning technology may present amplified energy transfer due to the chain conformations arising from the elongation process of electrospinning. Considering the relatively low viscosity of PPFOH, we firstly blended the PPFOH into linear vinyl polymers, PVK, to enhance the viscosity of precursor solution for electrospinning process. The ratios of PPFOH in PVK matrix are precisely tuned to modulate the energy transfers in these doped microfibers.

Fig. 1 shows the FESEM images of the PPFOH/PVK electrospun fibers. It is found that all electrospun fibers are belt-like with several micrometers in width and ca. 500 nm in thicknesses. It is observed that there are a series of porous structures with a diameter of 50–100 nm in all doped ES fibers (Fig. S1 in the electronic supplementary information, ESI), which is attributed to the rapid evaporation of the CHCl₃ molecules and a subsequent rapid solidification during the electrospinning process. In general, this surface morphology of ES fiber is dominated with the solvent evaporation and viscosity of the precursor solution. Consideration of a low dopant ratio of PPFOH/PVK, it is reasonably observed that there is no significant difference among all PPFOH/PVK composite electrospun fibers. Whereas the morphology of the prepared PPFOH/PVK composite electrospun fibers (Fig. 1) and pristine PVK electrospun fibers (Fig. S2 in ESI) are obviously different, indicating that the addition of PPFOH has a significant influence on the morphology of the microfibers, due to the slight phase separation of PVK and PPFOH in the hybrids. Fluorescence microscope (FLM) images of PPFOH/PVK composite ES fibers displayed in Fig. 2 show that the emission colors of PPFOH/PVK can be tuned from deep-blue (0.1%), sky blue (0.5%), nearly white (1%) to cyan (2%), green (5%) and yellow (10%). An efficient dispersion of PPFOH fluorophores in PVK matrix can also be demonstrated via the uniform FLM images. Moreover, in this regard, multi-color emissive electrospun polymer composite fibers have been constructed via tuning interchain energy transfer by controlling the doping content of PPFOH to PVK. Considering the low emission efficiency of PVK in solid state, these multi-color emissions of PPFOH/PVK composite ES fibers should mainly derive from modulated energy transfer in PPFOH nanoaggregates in the fibers.

In order to investigate the interchain energy transfer, PL spectra of a series of PPFOH/PVK ES fibers are collected and compared in Fig. 3(a). The optical properties of PVK ES fibers are shown in Fig. S3 (in ESI). PVK ES fibers show weak deep-blue emission bands at the peak of 420 nm, associated with the emission of carbazolyl aggregation. The PL spectra of PPFOH/PVK ES fibers consist of two obvious emission bands at 440–460 and 520–550 nm, similar to the PL spectra of pristine PPFOH spin-coated film (Fig. S4 in ESI). The former band is attributed to the polyfluorene main chains, and the latter derives from interchain aggregation-induced excimer emission, which evidences the formation of supramolecular aggregates in the ES fibers. With the increasing ratio of PPFOH to PVK, the low energy band emission (520–550 nm) was enhanced greatly and deep-blue emission was reduced. This indicates that the energy transfer from deep-blue band to the low energy green band is enhanced. Furthermore, green band emissions exhibit double-exponential (1A*, 2A*), contributing to the singlet transitions of single-chain and molecular aggregation (or excimer). The life time at 530 nm
It should be noted that there is hydrogen-bonding interaction in PPFOH aggregate, which will cause a strong aggregation-induced excimer emission at 500–600 nm. Meanwhile, by increasing the ratio of PPFOH to PVK, a relative distance among the polymer chains in the ES fibers may become shorter, thus inducing a more efficient energy transfer from PPFOH single chain (blue emission) to chain aggregate or excimer (green emission). As a result, the intensity of green-yellow emission increased and concomitantly blue emission decreased as PPFOH content increased in the PPFOH/PVK composite ES fibers, which led to different fluorescence colors of the PPFOH/PVK composite ES fibers. As shown in Fig. 3(b), emission color can be tuned from deep blue (0.18, 0.17), sky blue (0.24, 0.26), nearly white (0.26, 0.30), to cyan (0.31, 0.32), green (0.30, 0.37), yellow (0.42, 0.40). The PL quantum yields (ΦPLQY) of pristine PVK fibers are ~10%. In contrast, the ΦPLQY values of PPFOH/PVK composite ES fibers are calculated to be 38%, 34%, 30%, 26%, 22% and 20% at the doping ratios of 0.1%, 0.5%, 1%, 2%, 5% and 10%, respectively. The supramolecular highly-fluorescent color-tunable fibrous LCPs herein utilize the PPFOH aggregation successfully and benefit efficient energy transfer in the ES fibers.

In the other aspect, in the past several years, photophysical property and optoelectronic applications of ES fibers based on LCPs/insulated polymers have been extensively investigated, but these blended systems are always non-conductive because of electrical insulation of the matrix, which may hinder the expansion of their applications in optoelectronic devices. Therefore, upon the fabrication of these multi-color emissive PPFOH/PVK fibers, we attempted the construction of a new series of conductive blended ES fibers for light-emitting applications in organic electronics. In contrast to traditional composite ES fibers using insulated linear vinyl polymer as the matrix, the inherent semiconducting property of PVK endows our robust ES fibers with conductive behavior. We fabricated a diode as shown in the inset of Fig. 4. I–V measurement of the PPFOH/PVK ES fibers was performed, show-
ing typical semiconducting properties. However, the approach (applied voltage is measured from negative bias to positive bias) and retract curves of the I-V measurements are analyzed, which show slight hysteresis. Five to seven different locations are chosen by the I-V measurements, and the results are subsequently averaged. It is found that the conductivity of our ES composite fibers is associated with the doping ratio of PPFOH. With the increasing doping ratio of PPFOH in the ES fibers, the conductivity increased as compared to that of purified PVK ES fibers. We cannot precisely calculate the cross sectional area of ES fibers, so it is difficult to obtain an exact conductivity of the ES fibers. However, it is obvious that the conductive properties of blend ES fibers can be tuned by changing the doping amount of PPFOH in PVK, which may broaden the applications for this kind of semiconducting ES fibers in organic optoelectronics.

In order to confirm the potential application in light-emitting devices, we also fabricated a series of PLEDs based on PPFOH/PVK blended ES fibers. As discussed above, there are many microscaled aggregates in the ES fibers. Therefore, we set two samples, such as 0.1% and 10% ratio of PPFOH/PVK ES fibers as the emissive layer. Device performance is shown in Fig. 5 and Fig. 5S (in ESI). As expected, the EL spectra of the devices based on 0.1% ES fiber consist of two emission bands at 400–460 and 500–600 nm (Fig. 5a). It can be reasonably observed that there is a strong emission at 500–600 nm, which is associated with the stronger energy transfer from single chain (feature emission at blue band) to excimer emission (500–600 nm) under electrical field, compared with the optical excitation (as shown in Fig. 3). Similarly, only a broaden emission at 564 nm is observed in the EL spectrum of the device based on 10% PPFOH/PVK fiber, which is consistent with the discussion above, suggesting that the complete energy transfers to aggregation-induced green emission (Fig. 5b). The corresponding CIE coordinates of the 0.1% and 10% ES fibers are about (0.45, 0.45), (0.51, 0.45) at 2 mA/m², respectively. However, the performance is relatively worse than those of pure PPFOH-based PLEDs. Turn-on voltages (V_{on}) for device based on 0.1% and 10% ES fibers are about 7.50 and 8.50 V, respectively. Two devices exhibit the maximum brightness of 571 and 171 cd/m² with the maximum current efficiency (C. E.) of 0.40 cd/A at 10 V and 0.17 cd/A at 11 V, respectively. It can be confirmed that it is effective for the construction of supramolecular structure-enhanced conductive PVK-based hybrid ES fibers and the possible fabrication of hybrid fibrous optoelectronic devices.

CONCLUSIONS

In summary, we construct a series of semiconducting multicolor emissive PPFOH/PVK LCPs ES fibers with the supramolecular structures in the composite fibers. By controlling the interchain energy transfer, PPFOH/PVK emitting color can be precisely tuned in a wide spectrum from blue, sky blue, nearly white to cyan, green and yellow. Interestingly, in contrast to traditional insulated fiber, PPFOH/PVK composite ES
fibers have excellent conductive behaviors, which can be further improved via controlling the doping ratios of PFPPOH to PVK. Color-tunable PLEDs based on ES fibers are also fabricated successfully. Supramolecular electrospun fibers can be used as multifunctional materials, which may open a gateway towards the applications ranging from chemical sensors, organic light-emitting diodes to organic light-effect transistors.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-021-2542-y.

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