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Description	

Highly polarized luminescence from aligned conjugated polymer electrospun nanofibers

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In this contribution we show highly polarized photoluminescence (PL) from aligned polyethyleneoxide: polyphenylenevinylene derivative composite nanofibers. We demonstrate PL polarization ratios (parallel to perpendicular) greater than 13. This ratio is further increased (up to ~25) by stretching the nanofibers. Stretching also results in an increase in conjugation length, fiber density, and PL lifetime. We argue that the effect of stretching is equivalent to applying a permanent and strong pressure. Our results open up the possibility for new optoelectronic devices and fundamental science studies based on polymer nanofibers. © 2008 American Institute of Physics. [DOI: 10.1063/1.2936998]

Conjugated polymers are attracting considerable attention as active materials in electronic and optoelectronic devices due to their unique photophysical properties and their potential for low cost fabrication and solution processability.¹ The intrinsic anisotropic nature of polymers can be exploited by uniaxially aligning the polymer chains in a specific direction.^{2,3} A variety of methods has been utilized in order to orient conjugated materials³ including mechanical alignment of thick films, Langmuir Blodgett deposition, liquid-crystalline self-organization, and alignment on specific substrates. Aligned films exhibit polarized luminescence and absorption,^{3,4} in-plane refractive index anisotropy,^{2,4} enhanced hole mobilities,^{5,6} and improved organic laser performance.^{7,8} The fabrication of electrospun polymer nanofibers (and nanowires) with diameters ranging from tenths of nanometers to several microns is a simple and versatile technique.⁹ Composite electrospun nanofibers containing a conjugated polymer and a non-conjugated more spinnable polymer have been also reported in recent years.¹⁰⁻¹⁵ Within the nanofibers, polymer chains have been found to be relatively aligned.^{11,14} It has been recently shown that the alignment of conjugated polymers within mesoporous silica (with porous sizes ranging between 2 and 20 nm) to form nanofibers yields polarized luminescence.^{16,17} These composite architectures are useful for the understanding of charge transfer and photoluminescence (PL) in one-dimensional systems. However, nanofibers fabricated by using electrospinning are more controllable since no template is needed for their production and they can be easily transferred to a wide range of substrates. Therefore, it seems interesting to explore the effects that chain alignment may have on the PL properties of electrospun fibers based on conjugated polymers. Compared to film geometry, the large aspect ratio (large active area) of nanofibers could be exploited in devices such as sensors and bulk heterojunction type solar cells and light emitting diodes. Moreover, aligned nanofibers hold promise as building blocks for nano-electronics.

In this work, we have electrospun composite nanofibers consisting of (1:2 in weight) poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and polyethyleneoxide (PEO) from chloroform solutions (total density 30 mg/ml). MEH-PPV was chosen as an archetypical light emitting polymer to prove the concepts. However, this technique is very general, and thus, could be used for most conjugated polymers, including those which do not show liquid-crystalline phases and, therefore, might not be oriented by using rubbed aligning layers such as polyimide.³ Details on the fabrication of aligned fibers are given elsewhere.¹⁸ Briefly, a two collector setup is used in which a negative voltage is switched between them and, as a result, aligned nanofibers are created in the middle. Nanofibers may, in the second step, be mechanically stretched in order to control their diameter.¹⁸ Spin coated films and random mats of nanofibers are used as references. In addition, we have fabricated two types of samples: (1) aligned during the electrospinning process and (2) aligned and subsequently stretched (two, three, and five times their original length). The aligned samples, which contained 1000 nanofibers, were transferred onto glass substrates for the optical studies. Figures 1(a) and 1(b) show representative scanning laser microscopy images (Keyence VK-9700) of a random mat and a bunch of aligned and stretched (three times) fibers. Corresponding scanning electron microscopy (SEM) (Hitachi, S-4500) images are shown in Figs. 1(c) and 1(d), respectively. As it can be seen, a high the degree of nanofiber alignment is achieved with this technique. Moreover, alignment and stretching reduces the average fiber diameter from around 600 nm (random mat) down to around 300 nm (Table I).¹⁸

Polarized emission was measured by using a Perkin Elmer LS55 Fluorescence spectrometer equipped with excitation and emission polarizers. The excitation wavelength was chosen around the absorption maximum for MEH-PPV (Refs. 13 and 16), i.e., 520 nm. Figure 2 shows the PL parallel (solid line) and perpendicular (dashed line) to the nanofiber direction for an aligned nonstretched sample under unpolarized¹⁹ excitation. A PL polarization ratio parallel to perpendicular (with respect to the alignment direction) of 13.3 is achieved for nonstretched samples. This is already

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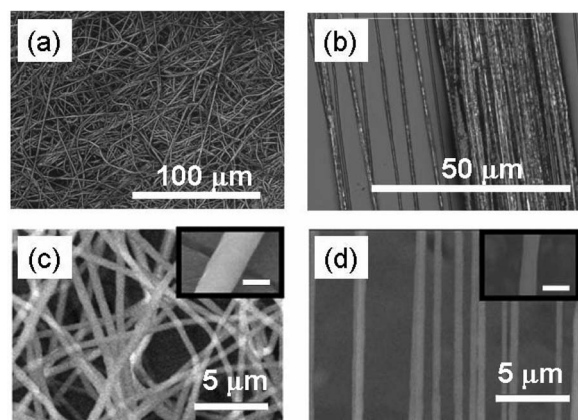


FIG. 1. [(a) and (b)] Scanning laser microscopy and [(c) and (d)] SEM for [(a) and (c)] a random MEH-PPV:PEO (1:2) nanofiber mat and [(b) and (d)] an aligned and stretched three times sample. The white scale bars for the images are (a) 100 μm , (b) 50 μm , and [(c) and (d)] 5 μm for the SEM images [600 nm for the insets in (c) and (d)].

higher than the recent reports which make use of mesoporous silica templates to form MEH-PPV nanofibers,^{16,17} where a maximum polarization ratio of 12.2 was obtained. This high polarization ratio for aligned nanofibers is consistent with a recent report by Bianco *et al.*¹⁴ on aligned polythiophene:PEO nanofibers, where polarized infrared spectroscopy showed a high degree of polymer chain alignment along the nanofiber axis. As it might be expected from the existing work on mechanical alignment (see, e.g., Ref. 4 and the references therein), stretching of the nanofibers may result in enhanced chain orientation. This is exactly what was experimentally observed. There is a gradual increase in the polarization ratio upon stretching (Table I and the inset of Fig. 2), with the sample stretched three times having a perpendicular PL component almost as small as detectable with our setup (hence the larger uncertainty). This demonstrates that the two step process consisting of alignment and stretching can be used to fine tune the desired degree of polarization in a controllable manner. We would like to note that the observed blueshifts in the PL maximum upon alignment and stretching (Table I) are an experimental artifact due to scattering effects (see supplemental information²⁰).

In order to address the morphology of the aligned and stretched nanofiber samples, we have used a nonresonant confocal Raman scattering (Nanofinder 30, Tokyo Instruments, Solar TII). The 632.8 nm line of a HeNe laser was used as the excitation wavelength. The spectra were analyzed

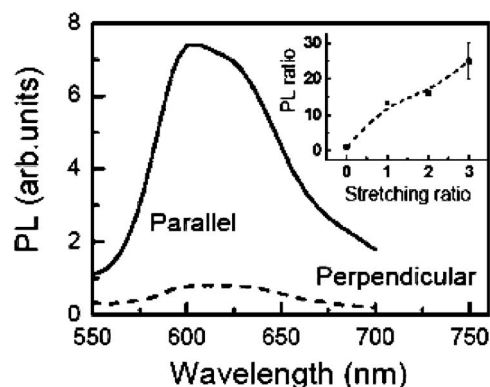


FIG. 2. (a) Polarized PL emission parallel (solid line) and perpendicular (dashed line) to the nanofiber axis for an aligned nonstretched MEH-PPV:PEO (1:2) sample. The inset shows the PL ratio as a function of stretching ratio, where 0 and 1 stand for a random mat and an aligned nonstretched sample, respectively.

by using a Voigt functions, i.e., mixed Lorentzian and Gaussian peaks. Figure 3 compares the Raman spectra for a MEH-PPV film and that of an aligned and three times stretched nanofibers sample. The 1589 cm^{-1} mode is the strongest component among a triplet of carbon-carbon stretching modes in the 1500–1600 cm^{-1} range and is identified as a stretching mode of the phenyl rings.^{21,22} As it can be seen in Table I, the 1589 cm^{-1} peak redshifts upon alignment, which go to even lower energies after stretching. Equivalent shifts of this mode occurring for other PPV systems have been assigned to increases in conjugation length.^{21–23} In relative terms, the observed 2 cm^{-1} shift upon stretching, although seemingly small, is equivalent to the 2 cm^{-1} peak shift measured when varying oligomer length from 4 to 6 phenylenevinylene repeat units,²¹ and thus, it can be associated with large enhancements in conjugation length. This is fully consistent with our polarized PL studies. The 1314 cm^{-1} mode is one of the doublet of modes that is assigned to in-plane vibrations involving a mixture of C—C/C=C stretching and C—H bending motions.^{21,22} We have recently reported for another PPV derivative that the intensity ratio between this peak and the 1589 cm^{-1} transition is a measure of the (micro-) density of the material.²³ As it is clearly illustrated in Fig. 3 and Table I, the intensity ratio increases when the nanofibers are aligned, and even further upon stretching. This may suggest that the aligned and stretched fibers are denser than the random mat and the pristine film. An increase in film density, as obtained by ap-

TABLE I. Summary of the parameters of interest derived in this study for composite nanofibers; PL polarization ratio (parallel to perpendicular), wavelength at the PL maximum collected at grazing angles, Raman shift for the $\sim 1589 \text{ cm}^{-1}$ peak, its width, two ratios between the Raman peak intensities, the PL lifetime at 625 nm, and fiber diameters (from 100 points in SEM images).

	Random mat	Aligned	Stretched (twice)	Stretched (three times)
$PL_{\text{par}}/PL_{\text{per}}$	1.0 ± 0.2	13.3 ± 0.5	16.2 ± 0.5	25 ± 5
λ at PL_{max} (nm)	621 ± 1	604 ± 1	588 ± 1	588 ± 1
Raman shift (cm^{-1})	1590.16 ± 2.12	1589.95 ± 1.77	1588.10 ± 0.32	1588.96 ± 0.32
Raman full width at half maximum (cm^{-1})	17.5 ± 1.8	17.0 ± 0.8	15.8 ± 0.2	16.8 ± 0.6
I_{1314}/I_{1589}	0.333 ± 0.034	0.339 ± 0.029	0.365 ± 0.017	0.371 ± 0.012
I_{1286}/I_{1589}	0.157 ± 0.018	0.173 ± 0.018	0.199 ± 0.012	0.201 ± 0.011
τ ($\lambda = 625 \text{ nm}$) (ns)	1.54 ± 0.05	1.52 ± 0.05	1.92 ± 0.07	1.76 ± 0.07
Average diameter (nm)	574 ± 107	498 ± 115	423 ± 89	329 ± 81

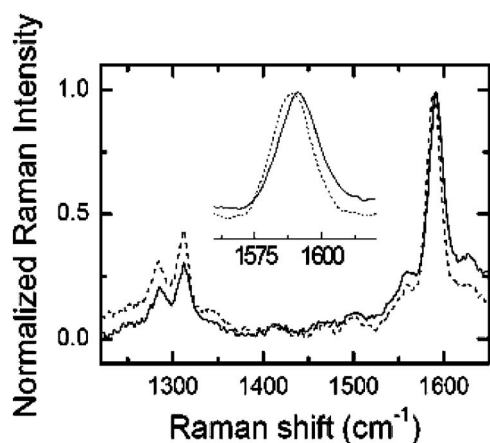


FIG. 3. Nonresonant confocal Raman spectra for a neat MEH-PPV film (solid line) and an aligned and three times stretched nanofiber sample (dashed line). The spectra have been normalized to the maximum of the peak centered at around 1589 cm^{-1} .

plying high pressure to spin coated MEH-PPV films, has been found to result in higher conjugation lengths.²⁴ The suggested increase in density by alignment and stretching is then consistent with the observed redshifts in the Raman peaks, as well as the increase in the polarization ratio.

Pressure does also increase the PL lifetime in neat and blend MEH-PPV films due to enhanced conjugation length.²⁴ Following with the analogy, we have measured the lifetime of our composite fibers. For this purpose, we have used a Horiba JovinYvon setup (FluoroCube 3000-U SP) exciting with a pulsed (1 MHz repetition rate, 200 ps pulse duration) diode laser emitting at 378 nm. The data (see Fig. S2 in supplemental information²⁰) were analyzed by using two exponential fits and the results are summarized in Table I. Composite nanofibers have longer lifetimes than neat films, mainly due to the isolation of MEH-PPV polymer chains by blending.²⁴ The lifetimes for random mat and aligned (non-stretched) samples are comparable but they considerably increase upon stretching. The increase in PL lifetime from 1.54 to 1.92 ns upon aligning and stretching the nanofibers for three times is comparable to the increase in lifetime (from 1.49 to 1.75 ns, collected at 610 nm) observed in MEH-PPV films blended (0.05%) with polymethylmetacrylate which was exposed to 64 kbar.²⁴ Our results suggest then that stretching has an equivalent effect as applying high pressures, with the important difference that the process of stretching is irreversible, i.e., the longer lifetimes will remain after the stretching has finished (cf. application of pressure). Longer lifetimes are also in agreement with longer conjugation lengths, both of which could be beneficial for optoelectronic devices.²⁵

In conclusion, we have demonstrated highly polarized PL from aligned electrospun MEH-PPV:PEO nanofibers with a controllable degree of polarization via mechanical stretching.

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- ¹⁹Very similar results were obtained when both excitation and emission polarizers were set in the same direction. This might be due to a fast energy transfer from the less aligned chain segments towards those with more extended conjugation lengths (see Ref. 17) or might be related to scattering effects (see Ref. 20).
- ²⁰See EPAPS Document No. E-APPLAB-92-079821 for fluorescent microscope images, angular dependent PL spectra and PL lifetime of an aligned and stretched nanofiber sample which are presented in the supplemental information. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
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- ²⁵Longer lifetimes could be beneficial for efficient exciton dissociation in organic solar cells, especially when a certain degree of phase separation is desirable in order to improve charge mobility and percolation. Moreover, since the mobility of aligned chains is enhanced with respect to that of nonaligned films (Refs. 5 and 6), electrospun aligned and stretched nanofibers may be an interesting fabrication protocol for single nanofiber photodetectors and solar cells.