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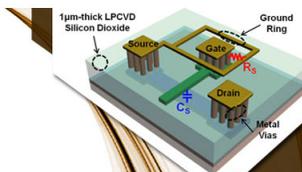
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Hierarchical assembly of light-emitting polymer nanofibers in helical morphologies

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Single electrospun nanofibers of light-emitting conjugated polymers hierarchically assemble at nano- to macroscopic lengthscales in various helical morphologies. At nanoscopic lengthscales, molecular chains follow the microscopic assembly, prevalently aligning along the fiber dynamic axis, as demonstrated by polarized photoluminescence spectroscopy. The role of molecular weight in the resulting assembling and optical properties is highlighted and discussed. Nanofibers based on the heaviest polymer exhibit the most stretched helical geometries and the highest suppression of the excitonic energy migration, resulting in the most blue-shifted photoluminescence with respect to thin films. © 2009 American Institute of Physics. [doi:10.1063/1.3275727]

The hierarchical assembly of molecules and nano-objects into well-ordered structures, at nanoscopic, microscopic, or higher scale, is a challenging research field.^{1–3} In particular, a large variety of organics and polymers are able to order in different hierarchical geometries, such as hexagonal,⁴ porous honeycomb,⁵ Kagomè,⁶ tubular,⁷ and helical structures,⁸ due to self-assembly induced by noncovalent intermolecular interactions. Among those geometries, helices are fascinating shapes which are observed at all scales in nature.

On the other hand, conjugated polymer one-dimensional nanostructures,^{9–11} raise an increasing interest because of their unique electronic and optical properties. These systems are expected to work as building blocks of forthcoming organic nanophotonics and electronics, and are already exploited in field-effect transistors,¹² energy storage units,¹³ and sensors.¹⁴ The possibility of organizing fluorescent polymer nanostructures in a hierarchical helical morphology (at micro- and nanoscale) remains widely unexplored, despite the possible applications for patterning organic semiconductors and light-emitting nanofibers and devices.¹¹ Recently, a few bottom-up approaches have been investigated to assemble polyaniline¹⁴ and oligo(*p*-phenylene)¹⁵ in helices. Differently from other methods, electrospinning is a low cost, high-throughput technology based on a jet of polymer solution, undergoing the bending instability which arises from the mutual repulsion of surface excess charges. This leads to depositing fibers coiled into macroscopic loops. In addition, upon impinging on the collector surface, the electrified jet undergoes short-length buckling patterns.¹⁶ For such unique features, the realization of light-emitting fibers in hierarchical helices by electrospinning certainly deserves to be investigated, possibly leading to organic photonic nanostructures.

In this letter, we report on submicrometers diameter optically active conjugated polymer fibers, hierarchically assembled from macro- to nanoscopic lengthscales. Fibers assemble in the most stretched helical geometry for the heaviest polymer, exhibiting the highest suppression of the excitonic energy migration and thus the highest blueshift

(BS) in the photoluminescence (PL) spectra with respect to thin films.

The light-emitting conjugated polymers poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (red-emitting, REP), poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(9-hexyl-3,6-carbazole)] (blue-emitting, BEP), and poly[9,9-dioctylfluorenyl-2,7-diyl)-co-1,4-benzo-{2,1'-3}-thiadiazole] (yellow-emitting, YEP) are dissolved in dimethyl sulfoxide and tetrahydrofuran with relative weight:weight concentration 1:4 between the two solvents. Conjugated polymer solutions are stored into a 1.0 mL plastic syringe tipped with a 27-gauge stainless steel needle, and injected at the end of the needle at a constant rate of 1 μ L/min by a syringe pump. The positive lead from a high-voltage supplier is connected to the metal needle applying a bias in the range 9.0–12.0 kV. Solid fibers assemble in a hierarchically helical morphology when collected on a grounded copper collector (10 \times 10 cm²) mounted on an isolating stand at a distance of 10–15 cm from the biased needle.

The resulting macro- and micro-oscopic assembly is investigated by fluorescence stereomicroscopy. For instance, at macroscopic lengthscales (10²–10⁴ μ m), individual REP fibers, long up to a few mm, are coiled in different shapes including straight lines [Fig. 1(a)] and circles (of diameter of a few millimeters) [Fig. 1(b)]. At microscopic lengthscales (1–10 μ m), the same light-emitting fibers exhibit helical morphologies [insets of Fig. 1(a) and Fig. 1(b)]. The investigated polymers assemble in different microscopic helical morphologies (Table I), with the polymer nanofiber loops approximately elliptical and having the minor axis parallel to the fiber axis. BEP fibers assemble into distant, small loops [Fig. 1(c)], having period of a few times the minor axis, whereas REP fibers helices exhibit larger and overlapping loops [Fig. 1(d)]. YEP single nanofibers undergo instead an intermediate helical assembly [Fig. 1(e)], where both the morphologies are present.

Pioneering studies¹⁷ attribute the helix formation to the competition between viscoelasticity and Coulombic repulsion in composite fibers, highlighting the importance of charge transfer from the conductive polymer component to the collecting substrate. However, more recent investigations find evidence of helix formation also in nonconducting polymers,^{16,18} and even in melt electrospun blends.¹⁹ There-

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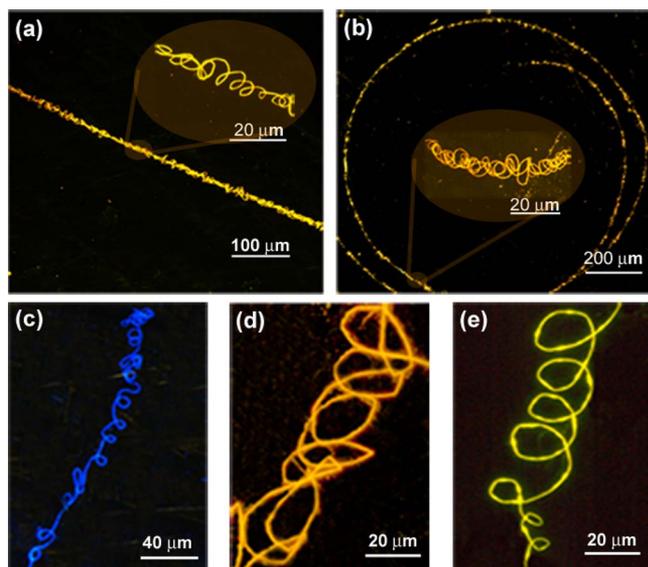


FIG. 1. (Color online) Top: macroscopic assembly of REP fibers (a), (b). Insets highlight the corresponding microscopic geometry for the selected regions. Bottom: Microscopic assembly of (c) BEP, (d) REP, and (e) YEP fibers.

fore, the macro/microscopic lengthscales of hierarchical assembly of nanofibers have to be attributed mainly to (i) the tensional forces due to bending instability and (ii) the local buckling of electrified jets occurring nearby collector, respectively. These effects can be strongly influenced by the different chemico-physical properties^{20–22} of the particular polymer and solutions.¹⁶

The different assemblies exhibited by the here studied light-emitting polymers (Table I) provide further evidence of a direct role played by the compound in the buckling phenomena, with highest loop periods being observed in fibers made of the light-emitting material (REP) with highest steric hindrance and molecular weight (MW). In addition, at nanoscale, the conjugated polymer chains are expected to tightly coil to minimize the number of aromatic repeating units interacting with the nonaromatic solvent molecules, like those of tetrahydrofuran.²³ This is in agreement with the investigation of the fiber surface morphology by Tapping™ mode atomic force microscopy (AFM), which reveals features of about 130–180 nm (Fig. 2) attributable to agglomerations of coiled chains.²⁴

To investigate the nanoscale organization more in depth, polarized PL spectroscopy²⁵ is carried out on different regions along a single helix. Excitation of a single YEP nanofiber loop is carried out through the unpolarized light of a mercury lamp coupled in a 20× magnification objective of an inverted microscope. A fiber-connected monochromator is used to collect photons emitted from single regions of the

TABLE I. Average polymer MW, characteristics of the helical geometries, and emission BS with respect to corresponding reference films, for the three investigated light-emitting nanofibers. Data on geometries are averages calculated over at least ten helix loops, on ten different fibers.

Polymer	MW	Average fiber diameter (μm)	Average loop minor axis (μm)	Average loop period (μm)	Blueshift (nm, ± 0.5 nm)
BEP	10000–40000	0.69 ± 0.12	5 ± 2	14 ± 5	1.0
YEP	10000–40000	0.72 ± 0.13	9 ± 7	15 ± 6	2.5
REP	374000	0.39 ± 0.10	18 ± 5	21 ± 6	5.5

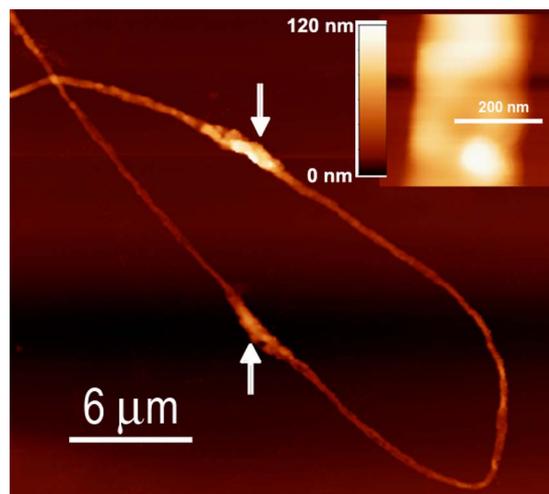


FIG. 2. (Color online) AFM micrograph of a REP fiber (average diameter 470 nm). Inset: Magnification of a straight segment of nanofiber with 130–180 nm features attributable to local agglomerations.

fiber loop, and the light anisotropy is studied by orienting the axis of an optical polarizer parallel and perpendicular to the nanofiber dynamic axis. The overall spectral response of the detection system does not present a significant dependence on polarization.

The PL spectra for each loop region of the YEP fiber, highlighted in the fluorescence micrograph in Fig. 3(a), clearly show that the signal collected with the polarization axis parallel (PL_{\parallel}) to the fiber dynamic axis is always more intense than that collected with the polarization axis perpendicular (PL_{\perp}) to the axis (Fig. 3). The resulting polarization ratio, $\chi_{\text{PL}} = \text{PL}_{\parallel} / \text{PL}_{\perp}$ are (1.5 ± 0.4) , (1.4 ± 0.2) , and (1.4 ± 0.2) for fiber segments at the loop sides [labeled as “A” in Fig. 3(a)], for segments at the outer edge of the elliptical loops (“B”) and for the straight regions connecting ad-

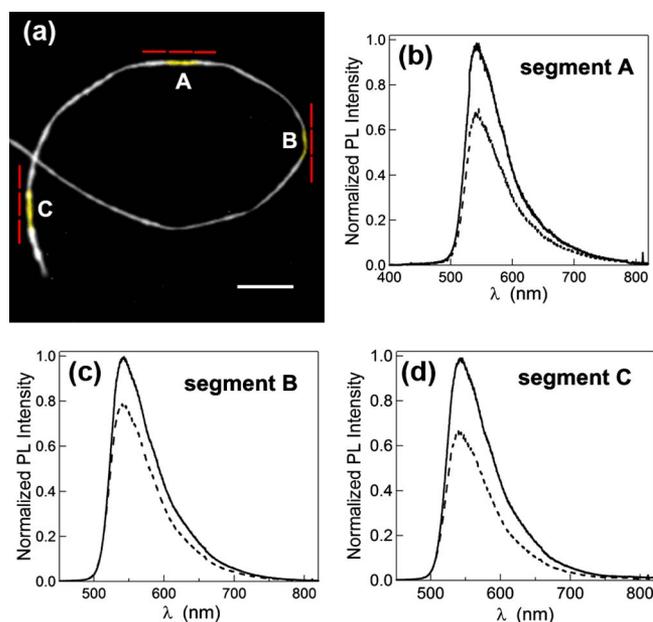


FIG. 3. (Color online) Polarized PL spectroscopy of single nanofiber. (a) Fluorescence micrograph of a YEP helix loop: The highlighted fiber segments, labeled as “A,” “B,” and “C” are individually investigated. The dashed lines indicate the nanofiber dynamic axes in the three probed regions. Scale bar = 2 μm . (b)–(d) PL_{\parallel} (continuous lines) and PL_{\perp} (dotted lines) spectra by segment “A” (b), “B” (c), and “C” (d), respectively.

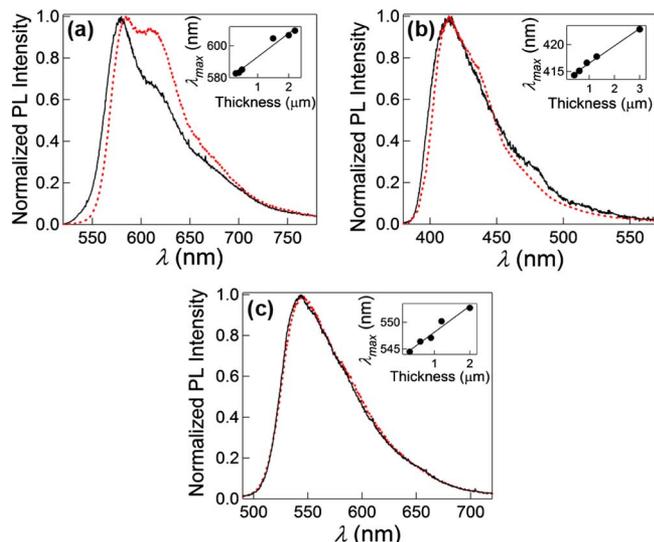


FIG. 4. (Color online) PL spectra from electrospun nanofibers (continuous lines) and reference spin-cast films (dotted lines) with same thickness, for (a) REP, (b) BEP, and (c) YEP. Insets: PL peak wavelength vs film thickness. Superimposed lines are guides for the eye.

adjacent loops (“C”), respectively. Therefore, at nanoscale the prevalent orientation of the polymer chromophores is parallel to the micrometers-scale nanofiber local direction, thus following the helix morphology along the dynamic nanofiber axis, and determining polarized micro-PL emission. Though the here found χ_{PL} is about one order of magnitude lower than values desirable for light-emitting devices applications,²⁶ higher polarization ratios may be achieved by suitable composite materials, and by stretching after deposition.²⁷

We find a BS up to about 5.5 nm of the PL from fibers mats excited using a He–Cd laser (325 nm) with respect to corresponding spin-cast films (Fig. 4 and Table I). We employ reference films of comparable thickness as the fiber diameter to properly evaluate the BS. This is needed because of the thickness-dependent self-absorption in the material, as highlighted by the dependence of the PL peak wavelength λ_{max} on the thickness of the light-emitting films (insets of Fig. 4). The observed BS can be attributed to the different packing geometry induced in the fibers by electrospinning, on its turn determining conjugation breaks along the emitting molecules or the suppression of exciton migration toward chromophore sites of lower energy. Similar mechanisms are observed in other spatially confined organic semiconductor systems.^{28–30} The emission BS is indeed characteristic of molecular systems exhibiting less dense packing and reduced π – π overlaps between different conjugated segments. The supramolecular organization of the conjugated polymer chains in the light-emitting fibers, as indicated by the PL spectra, determines therefore a suppression of the excitonic energy migration. Interestingly, we find that significant BS, together with a change in the vibronic structure [Fig. 4(a)] compatible with a relative reduction of interchain species formation by the light-emitting polymer,²⁴ are associated with more stretched helical geometries in our fibers (Table I).

The mechanical response of the electrospun material is ruled by its elastic and viscous forces, and long-range molecule motions, such as the plastic flow of the materials, mainly occur upon weakening the intermolecular entanglements. On the contrary, stiffer conformational states can be

favored by the steric hindrance provided by larger side groups and higher MWs. The mechanisms, which determine suppressed exciton migration and higher-energy emission from the polymer chromophores, can also result in less contracted helical assemblies because of different viscoelastic, restoring forces at the microscale.

In perspective, single optically active polymer nanofibers hierarchical assembled at macro-to nanoscopic length-scales by electrospinning open the way to the low cost, high throughput realization of light-emitting structures, and architectures for nanoelectronics and nanophotonics based on conjugated polymers.

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