Electrostatic Mechanophores in Tuneable Light-Emitting Piezopolymer Nanowires

Luana Persano,* Andrea Camposeo, Aleksandr V. Terentjevs, Fabio Della Sala,* Eduardo Fabiano, Martina Montinaro, and Dario Pisignano*

Electromechanical coupling through piezoelectric polymer chains allows the emission of organic molecules in active nanowires to be tuned. This effect is evidenced by highly bendable arrays of counter-ion dye-doped nanowires made of a poly(vinylidenefluoride) copolymer. A reversible redshift of the dye emission is found upon the application of dynamic stress during highly accurate bending experiments. By density functional theory calculations it is found that these photophysical properties are associated with mechanical stresses applied to electrostatically interacting molecular systems, namely to counter-ion-mediated states that involve light-emitting molecules as well as charged regions of piezoelectric polymer chains. These systems are an electrostatic class of supramolecular functional stress-sensitive units, which might impart new functionalities in hybrid molecular nanosystems and anisotropic nanostructures for sensing devices and soft robotics.

In materials at the solid state, any mechanical action can induce chemicophysical changes which affect the overall or local properties. These variations may involve mass transfer, heating, mechanical stress generation/relaxation, or redistribution of electronic or ionic charges. In particular, the capability to control the optical properties of molecules by a mechanical stress can activate or deactivate chemical reactions, and enable new functionalities for monitoring and sensing. This is both a fundamental challenge in the broad field of nanosciences and a significant advantage for applications in medical diagnostics and for signal transduction in biointerfaces. Mechanophotoconversion has been reported, based on dynamic molecular recognition at the air–water interface. Recently, anisotropic compressive stresses at nN-scale have been found to induce photophysical changes in conjugate polymer nanoparticles and in single organic dye molecules. In another report, uniaxial tensile forces have been applied to polymer foils doped with an oligo-paraphenylenevinylene derivative, leading to a blueshift of the emission by 1.2 nm. With focus on practical applications, the capability to control electro-optical processes through the modification of a piezoelectric potential, in turn led by an external stress, has been introduced by the Wang’s group in 2010. This piezophototronic effect is based on the use of a strain-induced piezopotential at a metal–semiconductor interface, which tunes the charge transport across the junction and the quantum efficiency of nanostructured light emitting diodes. Piezophototronics is thus related to the simultaneous presence of piezoelectricity, emission excitation, and semiconducting behavior in the involved materials. Seeking for alternative platforms, extending further the control of optical properties through mechanical forces on flexible materials might not only help to elucidate the fundamental mechanisms of optomechanics at nanoscale but also open new perspectives for the development of next sensing and optoelectronic devices.

In this work, we introduce electromechanical coupling through piezoelectric polymer chains to tune the emission of organic molecules in active nanowires. Our system is made of highly bendable arrays of counter-ion dye-doped nanocomposite wires made of a poly(vinylidenefluoride) (PVDF) copolymer. A reversible redshift of the dye emission is found upon applying dynamic stress during highly accurate bending experiments. For purpose of comparison, no significant shift is found in either organic nanowires without counter-ions or a non-piezoelectric polymer. Using density functional theory (DFT) calculations, we show that these photophysical properties are...
associated with mechanical stresses applied to electrostatically interacting molecular systems, namely to counter-ion-mediated states involving the light-emitting molecules and the positively charged region of the piezoelectric polymer chain. This unveiled, electrostatic class of supramolecular mechanophores, as functional stress-sensitive units, might impart new functionalities in anisotropic, hybrid molecular nanosystems.

Poly(vinylidenefluoride-co-trifluoroethylene), P(VDF-TrFE) directly crystallizes from the melt or solution into the ferroelectric phase analogous to β-PVDF. It is characterized by high stability at room temperature and high achievable degree of crystallinity (>90%). PVDF and its copolymers have been largely investigated, and devices based on their nanofibers have shown enhanced piezoelectric properties, as well as highly flexible design and lightweight construction. Here light-emitting, composite nanowires are realized by electrospinning, using a fast rotating disk collector to generate free-standing arrays, and investigated under cyclic and dynamic stress conditions (schematics in Figure 1a,b). As reference, different molecular dyes as well as a plastic, nonpiezoelectric polymer (polymethymethacrylate, PMMA) are also tested. Prior to electrospinning, polymer solutions are doped with 1–1.5% w/w of light-emitting molecules (Figure 1c,d and Figure S1, Supporting Information). Scanning electron microscopy (SEM) images indicate that the nanocomposite P(VDF-TrFE) wires mostly have a cylindrical shape with smooth surfaces and average diameter of 150–180 nm (Figure 2a and Figure S2, Supporting Information). Photographs of the arrays of nanowires are shown in Figure 2b-e, where the different colors are indicative of the different used dyes, rhodamine 700 (LD700, Figure 2b,d), disodium-1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-difluoroborate complex (pyromethene, Figure 2c), and [2-[2-[4-(dimethylamino)phenyl]-ethenyl]-6-methyl-4H-pyran-4-ylidene]-propanedinitrile (DCM, Figure 2e). The obtained morphology of the nanowires is related to the solution concentration and entanglements, and to the properties of the solvent used.

Nanocomposite flexible wires are positioned on top of a 76 µm-thick Kapton (PI) film, and devices are built by establishing electrical contacts to the ends of the arrays of fibers (typical length ≈ 1.5 cm). Bending experiments are performed by using two synchronized linear stages, with the edges of the sample fixed with two stripes positioned on top of each stage. A high-speed camera precisely records the bending movement to determine the instantaneous values of the curvature radius and strain rate. The plot of the out-of-plane bending amplitude versus time for three bending cycles is reported in Figure S3 (Supporting Information). Each half-period (from flat to the maximum bent state and return) is well described by the laws of uniformly accelerated motion. The values of the bending radius (R) and strain rate (ε) at specific instant frames are reported in Figure 2f–j. At the maximum amplitude of bending, R is as low as 4 mm, and the strain rate zeroes. The instantaneous values of the bending radius and of the maximum exerted strain (εm) are displayed in Figure S4 (Supporting Information). During each bending cycle, εm approaches 1.5% and the corresponding tensile stress, σ, is ≈2.5 N mm⁻² (σ ≡ εmE, with E Young modulus, Figure S5, Supporting Information).

In addition, during bending cycles, the emission signal of the embedded dyes, photoexcited by a laser with wavelength 405 nm and power 0.2 mW, is acquired avoiding any spurious effect related to movement (spectra shown in Figure S7 in the Supporting Information, experimental details in the Supporting Information, Note 1 and in Figures S8–S10, Supporting Information). Briefly, the experimental system used to collect the light emitted by the samples is carefully implemented to be synchronous to the mechanical movement and to keep fixed the laser spot on the sample surface. A region of 3 × 10⁻² mm² is excited during each bending cycle. The applied strain is of tensile type, since the neutral strain position, where bending-induced compressive and tensile deformations cancel each other, is located within the Kapton layer. The effect of strain application is studied by repetitively recording the emission spectra with an integration time of 20 ms (<ε⁻¹>).

Figure 1. Schematics of free-standing arrays of nanofibers a) before and b) during bending. c,d) Molecular structure of LD700, and scheme of the counter-ion shift process leading to mechanotunable emission. The counter-ion ClO₄⁻ (orange ring) leads to a different configuration of the system during nanofiber bending, namely to reaching a different local minima of the potential energy surface. P indicates a piezodipole, roughly perpendicular to the nanofiber length. Colors in the molecular structures indicate different atoms. Red: oxygen; gray: fluorine; blue: nitrogen; green: carbon.
Figure 2. a) SEM image of the composite nanowires based on P(VDF-TrFE) doped with LD700. Scale bar: 10 µm. b–e) Photographs of the arrays of composite nanowires. From left to right: P(VDF-TrFE)/LD700, P(VDF-TrFE)/pyromethene, PMMA/LD700, and PMMA/DCM, respectively. f–j) Sequence of frames captured during bending of the nanowires. $R$ and $\dot{\varepsilon}$ are the bending radius and strain rate at each time, respectively.

Figure 3. a) PL spectra from arrays of P(VDF-TrFE)/LD700 fibers at different times during bending. Blue and red markers on the spectra highlight the position of the PL peak at each time, while photographs capture the corresponding mechanics. Spectra are vertically shifted for better clarity. Plots of the emission peak wavelength versus time for b) P(VDF-TrFE)/LD700 fibers and c) P(VDF-TrFE)/pyromethene fibers, respectively. Emission temporal profiles are shown for three different samples for each type of fiber. The shadow area indicates the first bending interval, and dashed horizontal lines highlight the initial wavelength peak for unperturbed samples. Finally, the dotted profiles in the top panel for each nanowire type are the calculated contributions to shifts coming from optical detection (namely, for the different distance of the sample and of the collection lens, under static conditions).
displays the PL spectra of a P(VDF-TrFE)/LD700 array collected during mechanical bending at different times. Data show that the emission of P(VDF-TrFE)/LD700 is reversibly redshifted, that is, optical transitions move toward lower energies, upon tensile strain (Figure 3a). Larger values of the redshift are recorded at $R = 5$ mm and $\varepsilon = 0.04$ both during the application ($t = 0.27$ s) and release ($t = 0.68$ s) of the buckling stress. Such behavior is cyclic and can be captured by measuring the PL response over periodic bending and unbending movements. In Figure 3b, the plot of the emission peak wavelength versus time (continuous lines) for three different P(VDF-TrFE)/LD700 samples is reported, evidencing a measured redshift by at least 2–5 nm compared to the emission wavelength measured in static and planar conditions (horizontal dashed lines in Figure 3b). Sample to sample variations (a few per mil) of the shifts are attributable to minor disuniformities in the incorporation of dyes during electrospinning, or possible local agglomerates of the emitters, which affect the initial conformation and local potential energy surface (PES) of the molecules. Also, effects of possible metastable states are appreciable through the $\varepsilon$-dependence of the optical redshifts, with maximum wavelength variations corresponding to higher strain rate values and slightly lower variations found at $\varepsilon = 0$ as shown in Figure 3a,b ($R = 4$ mm, $t = 0.45$ s). Local mechanisms for metastability could involve deconfocal reorientation of dyes in the polymeric host (up to a few nm within $\approx 0.1$ s, for typical diffusion coefficients of $10^{-13}$–$10^{-15}$ cm$^2$ s$^{-1}$). Several experiments are performed evidencing these results.

In addition, since during bending the vertical distance between the area excited on the sample and the optical collection system varies up to 1 cm, a calibration procedure is implemented to precisely determine the expected spectral shift due to changes of collection angle (orange dotted lines in Figure 3b and Supporting Information). In nanowires which are based on the same piezoelectric matrix but embedding a dye without counter-ions (pyrromethene), no significant modification of the transition energies is found, and only slight fluctuations of the emission peak associated with the optical detection during sample bending are measured (Figure 3c). In case of plastic, nonpiezoelectric samples, no substantial shift of the emission can be attributed to mechanical action during bending, and the observed spectral variations are always in line with those induced by the detection geometry variations for chromophores both with (LD700) and without (DCM) counter-ions (Figure S11, Supporting Information). These results suggest that a synergistic mechanism takes place in the nanocomposites, which is initiated by mechanical action, then being assisted by the electrostatic interaction between counter-ions and the positive region of piezio-dipoles at the sub-nanoscale.

To rationalize these findings, we analyze the P(VDF-TrFE)/LD700 system by first-principles calculations. In the ground-state (zero stress), a given LD700 molecule with its ClO$_4^−$ counter-ion is fully surrounded by the P(VDF-TrFE) polymer chains due to the low dye density. Figure 4a shows the molecular structure, in the case of a single chain, obtained from DFT geometry optimization (computational details in the Experimental Section). Fourier-transform infrared (FTIR) measurements for light polarized parallel to the length of the composite fibers highlight dye features (at about 1500 and 1600 cm$^{-1}$) which well-compare with computed IR absorption spectra polarized along the long molecular axis for LD700 (Figure S12, Supporting Information). This indicates substantial orientation of the dopants parallel to the fibers, namely to the P(VDF-TrFE) backbones. The counter-ion strongly interacts with the positively charged hydrogen of the P(VDF-TrFE) piezio-dipoles (see the electrostatic potential map in Figure 4b) as well as with the LD700 molecules (dotted lines in Figure 4a highlight the shortest distances to ClO$_4^−$). The interaction is mainly electrostatic. DFT calculations show that the PES of the LD700/ClO$_4^−$ coupled system is rich of local minima, also affected by neighbor chains. When strain is applied, it induces a spatial shift between the polymer chains and the LD700/counter-ion. Hence, the relative orientation between LD700 and ClO$_4^−$ will dynamically change, i.e., the system will likely transit into other local minima of the calculated PES. For instance, Figure 4c shows the absorption spectra of LD700 for the two different positions of the counter-ion (displayed in the inset), as computed from time-dependent DFT. The two configurations correspond to two PES local minima with a total energy difference of 0.21 eV, and exhibit a significant difference in their optical properties, with a maximum achievable theoretical shift of the main absorption peak of 20 nm (Figure 4b). The mechanically tuneable electrostatic interaction so provides the P(VDF-TrFE)/LD700 system with so-called mechanophore units making the nanowire emission sensitive to tensile stress. Instead, for the P(VDF-TrFE)/pyrromethene system no significant changes of the optical properties can be expected upon applying the mechanical stress, because different P(VDF-TrFE) arrangements do not modify the electronic distribution of the light-emitting molecule. The DFT-optimized supramolecular organization of the P(VDF-TrFE)/pyrromethene complex is shown in Figure S13 (Supporting Information). For this ground-state conformation, a lowest singlet excited state ($S_1$, with the strongest oscillator strength) is predicted at 3.04 eV. This is almost unmodified by an external stress, leading to a relatively rigid spatial shift between the pyrromethene and the polymer along its main chain axis (Figure S14, Supporting Information).

The here presented mechanisms involve a soft mechanochemical actuation, namely the influence of the directional, tensile stress on weak, electrostatic forces mediated by the coupled counter-ion in the almost periodic and anisotropic structure of the P(VDF-TrFE) nanowires. Largely studied as tool to selectively form and break covalent bonds,[15,16,27] mechanophores making optical properties sensitive to strain or stress can also rely on electrostatic coupling. In this respect, stress and deformation act as stimuli to redirect optically active units, and make their localization in a specific PSE minimum more likely, thus affecting the nanowire emission properties.

The investigated correlation between a stress and the emission properties of the LD700/ClO$_4^−$ coupled system suggests an important role played by the mechanical properties of the nanowire array at macroscale. For instance, with stiffer arrays, comparable levels of applied stress can entail lower values of the associated strain and consequently, a reduced spatial shift between the polymer chains and the LD700/counter-ion. Also, stiffer arrays might increase the stability of mechanophore units in the involved PES local minima. Tuning of
the mechanical properties can be achieved through properly addressing the electrospinning parameters to increase the number of the inter-fibers joints[28] or to tailor the overall porosity in nanocomposites.[29]

In summary, the effect of tensile bending strain on the optical properties of dye-doped nanocomposite wires made of a PVDF copolymer is significant. Results indicate a redshift up to the scale of 5 nm in counter-ion dye-doped piezoelectric wires. Consistent with the results of first-principles DFT simulations, this effect can be rationalized with the formation of mechanically tunable electrostatic interaction, namely mechanophore units making nanowire emission sensitive to tensile stress. These electrostatic mechanophores might provide anisotropic, hybrid molecular systems with novel functionalities, including mechanochromisms and the consequent optical sensing capability to monitor local mechanical stress and damage also in transparent samples and soft robots.

Experimental Section

**Nanowires Fabrication and Characterization:** P(VDF-TrFE) (75/25 wt%, Solvay Solexis) was dissolved in a 3:2 volume ratio of dimethylformamide/acetone (DMF/acetone, Sigma-Aldrich) at a polymer/solvent concentration of 21% w/w. PMMA (120k, Sigma-Aldrich) was dissolved in chloroform at a polymer/solvent concentration of 25% w/w. LD700, pyromethene, and DCM were added to solutions with relative concentration 1–1.5% w/w with respect to the polymers. Electrospinning was performed by placing 1–1.5 mL of solution into syringes tipped with a 21–27 gauge stainless steel needles. The positive lead from a high voltage supply (EL60R0.6-22, Glassman High Voltage) was connected to the metal needle for application of bias values of 15–25 kV. The solution was injected into the needle at a constant rate of 1 mL h \(^{-1}\) with a syringe pump (33 Dual Syringe Pump, Harvard Apparatus). A cylindrical collector was placed at a distance of 6 cm from the needle and negatively biased for the fabrication of aligned arrays. All the fabrication steps were performed at room temperature with air humidity of about 40%. The morphological analysis was performed by a Nova NanoSEM 450 system (FEI), using an acceleration voltage around 5 kV and an aperture size of 30 mm. The mechanical properties were investigated by dynamic mechanical analysis (DMA Q800, TA Instruments, New Castle, DE), in tensile mode. Specimen dimensions were \(\approx 6.5 \text{ mm} \times 10.0 \text{ mm}\) (width \times length) with thicknesses between 20 and 30 \(\mu\text{m}\). FTIR measurements were carried out by a Spectrum 100 system (Perkin-Elmer Inc.), equipped with an IR grid polarizer (Specac Limited, UK), consisting of 0.12 mm wide strips of aluminum. The beam, incident orthogonally to the plane of the sample, was polarized alternatively parallel or orthogonal to the main axis of fiber alignment.

**Mechanotunable Emission:** Two synchronized linear stages (Physik Instrumente GmbH & Co. KG, Karlsruhe, Germany) were used to apply cyclic dynamic bending stress. A fast camera (FAST CAM APX RS Photron) was used to collect videos (1024 pixel \(\times\) 1024 pixel) at 250 fps, corresponding to acquisition times of 4 ms. The light emitted by the

---

**Figure 4.** a) Optimized conformation for the P(VDF-TrFE)/LD700 system, mediated by the \(\text{ClO}_4^-\) counter-ion. Dotted lines represent the shortest distances to \(\text{ClO}_4^-\). b) Color map of the electrostatic potential of the P(VDF-TrFE) chain. c) TD-DFT absorption spectra for two different conformations of LD700/\(\text{ClO}_4^-\), shown in the inset.
nanowires was collected synchronously with their mechanical movement, exciting samples by a diode laser with wavelength $\lambda_{\text{exc}} = 405$ nm and collecting continuous sequences of 26 photoluminescence spectra by a fiber-coupled monochromator equipped with a charged coupled device (Figure S8, Supporting Information) and careful calibration procedures on samples at rest were carried out to take into account contributions related to geometry-related photon collection efficiency and angle-modulated photon scattering (full details in Supporting Information).

**Computational Details:** The P(VDF-TrFE) copolymer was investigated using the plane-wave Quantum Espresso software package \cite{P Complete2013a} using the Perdew–Burke–Ernzerhof functional and ultrasoft pseudopotential with an energy (density) cutoff of 80 (800) Ry. A Gaussian smearing of 0.001 Ry was used to enhance convergence and the threshold for the Perdew–Burke–Ernzerhof functional and ultrasoft pseudopotential calculations for LD700 with ClO$_4^-$ with the same parameters but with the def2-TZVPD basis set. \cite{Rappoport2005}

**Keywords**

- The authors declare no conflict of interest.
- Laboratories WAFITECH (09) is also acknowledged. Maria Moffa is acknowledged for her support with mechanical measurements.

**Acknowledgements**

The research leading to these results received funding from the European Research Council under the European Union’s Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement No. 306357 (ERC Starting Grant “NANO-JETS”). The Apulia Network of Public Research Laboratories WAFITECH (09) is also acknowledged. Maria Moffa is acknowledged for her support with mechanical measurements.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

- electrospinning, light-emission, nanofibers, piezoelectricity

Received: February 21, 2017
Revised: March 31, 2017
Published online: