Electronic Supplementary Material (ESI) for Nanoscale
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Electronic Supplementary Information

Controlling the morphology of conductive PEDOT by in-situ electropolymerization: from thin films to nanowires with variable electrical properties

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Experimental details

3,4-Ethylenedioxythiophene, 97% (EDOT), acetonitrile anhydrous, 99.8% (MeCN) and anhydrous propylene carbonate, 99.7% (PC) were purchased from Sigma-Aldrich, and used without further purification. Gold electrodes on silicon dioxide (Fraunhofer Institute, Fig. S1) substrates were cleaned by subsequent ultrasonication bath in acetone and isopropanol prior to use. A Keithley 2636A source meter was employed for the polymerization in-situ and for the two probe current-voltage characteristics measurements. All the experiments were performed in ambient conditions. Atomic force microscopy (AFM) topographic images were obtained in tapping mode on a Dimension 3100 (Digital Instruments) microscope with a NanoScope IV controller, by employing commercial 125 μm long silicon cantilevers with a spring constant of 40 N/m. Torsion-resonance tunneling current (TR-TUNA AFM) images were obtained in a Multimode V (Veeco) microscope equipped with a Nanoscope V controller and Pt/Ir-coated Si tips with 225 μm long cantilever and spring constant in the range 0.5 – 9.5 N/m were used. The torsion amplitude was used as the feedback signal to measure surface morphology.

2 μL of EDOT 0.1M solution in MeCN or PC were dropped on top of the electrodes and a fixed bias was applied for 5 sec. During the process the current was recorded as a function of time.

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After the polymerization, the devices were washed with acetonitrile to remove residual monomers and dried in a stream of N_2, prior to two probe resistive characterization.

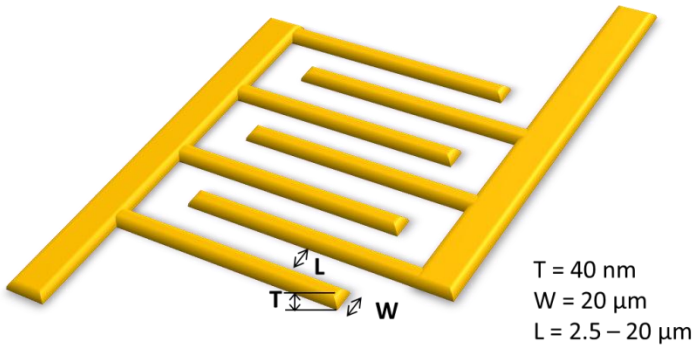

Figure S1. Scheme of the interdigitated electrode devices employed for the *in-situ* polymerization.

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Laser confocal microscopy

Fluorescence images were acquired with a Nikon Eclipse Ti scanning confocal fluorescence microscope, using continuous wave excitation at 405 nm, a 60x magnification 0.95 numerical aperture plan apo air objective, a 30 micron diameter confocal pinhole, and a 515 nm +/- 15 nm band pass filter before the detector. Spectra were taken at points of interest in the image via a fiber-coupled CCD/spectrograph combination (Princeton LN EEV/Acton SpectraPro 300i).

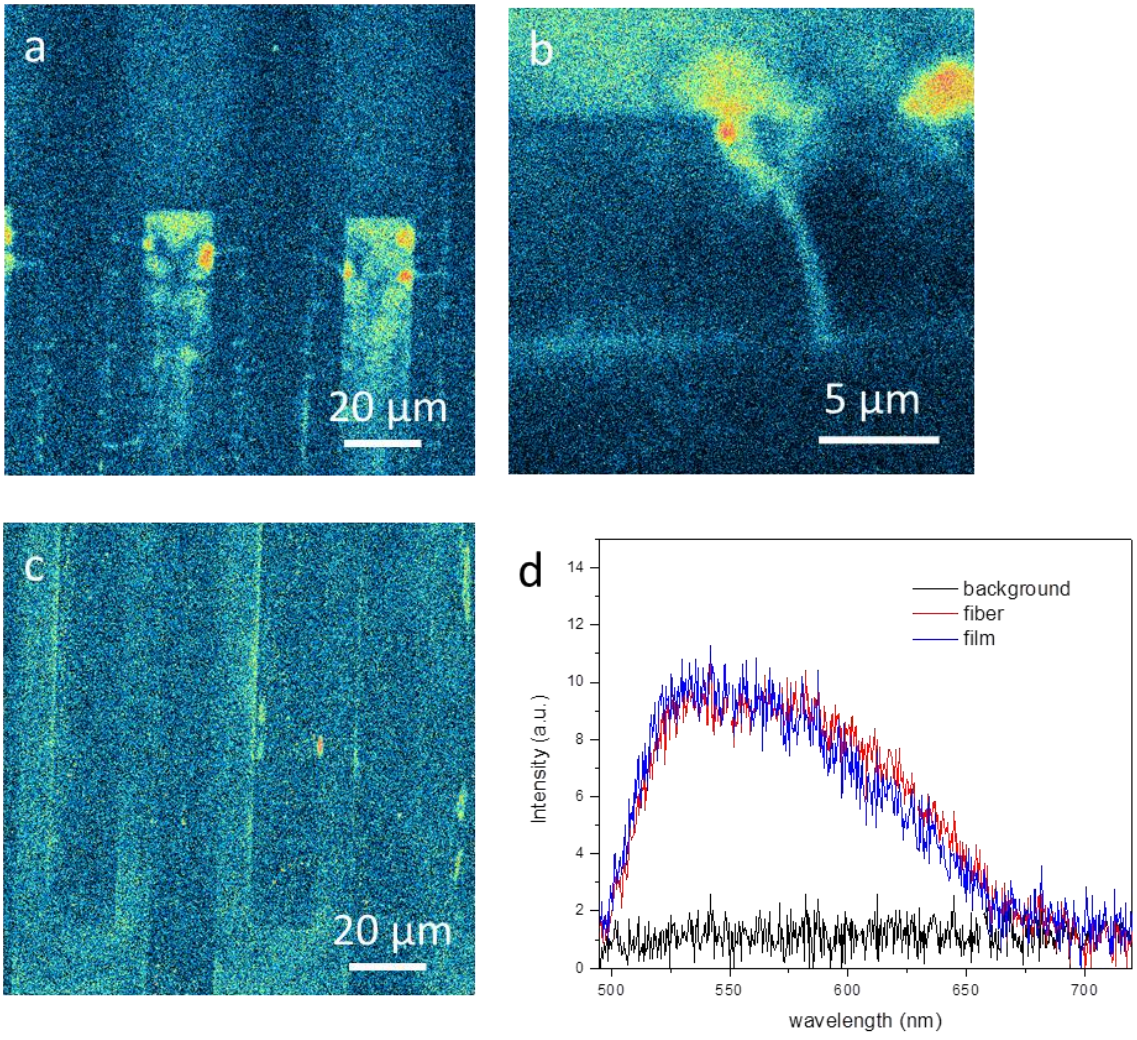

Figure S2. Confocal fluorescence microscopy images of fibers (a, b) and film (c) based devices, (excitation at 405 nm, emission 500 to 530 nm). The brightest (red/yellow) areas correspond to higher emission. (d) Emission spectra recorded on a single PEDOT fiber, a PEDOT film, and on the bare substrate.

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Electropolymerization of EDOT in propylene carbonate solution

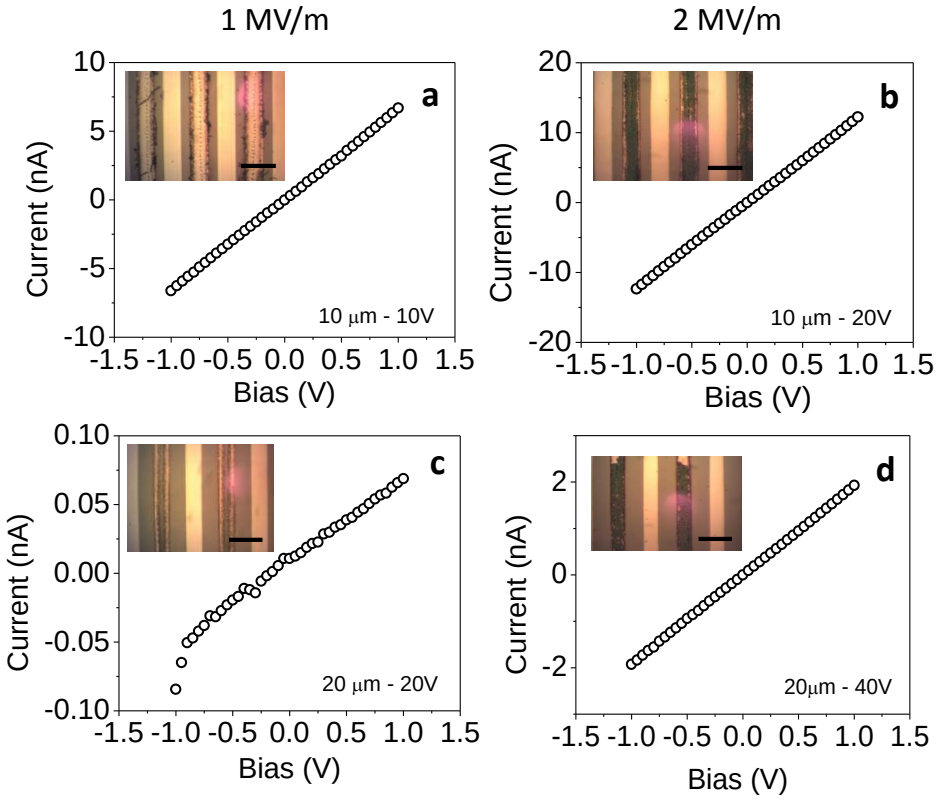

Figure S3. Current *vs.* voltage characteristics of PEDOT obtained by electropolymerization in propylene carbonate at electric field intensities of 1 MV/m (a, c); and 2 MV/m(b, d). In the insets optical images show the presence of thick films growing in 3D fashion over the electrodes (scale bar 40 μm). The films over the electrodes are thicker whereas higher electric fields are used.

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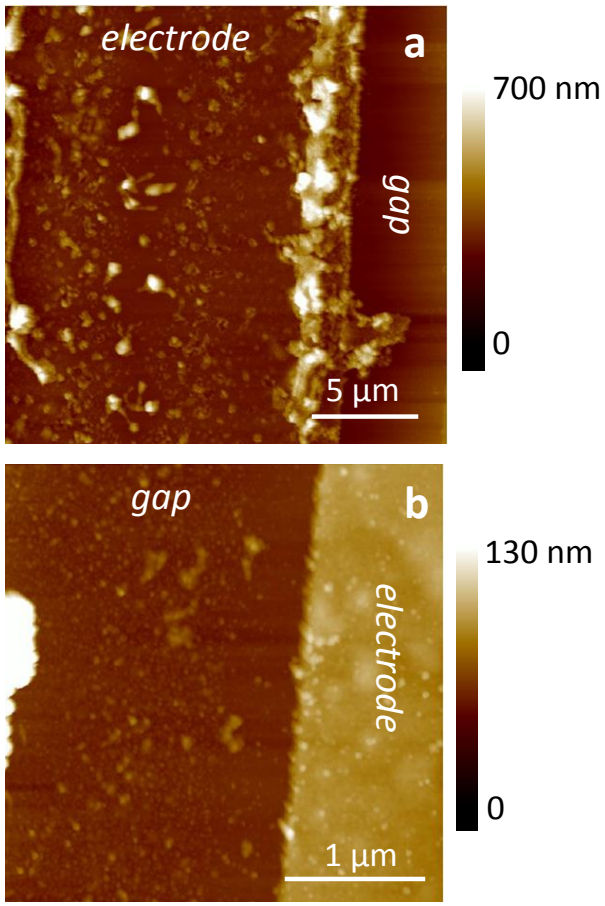

Figure S4. AFM images showing the morphology of the 10 µm gap devices polymerized at 10V (Fig. S2a). Nodular structures are present on the electrode which was positively biased (***a***) and a film is also visible inside the channel (***b***). With the propylene carbonate solution no fiber-like structures were observed after the polymerization process, seeming to produce only films mostly growing on the positively biased electrode but also covering the channels. So in this case a 3D growth type mechanism seems to be the prominent one under the employed conditions.

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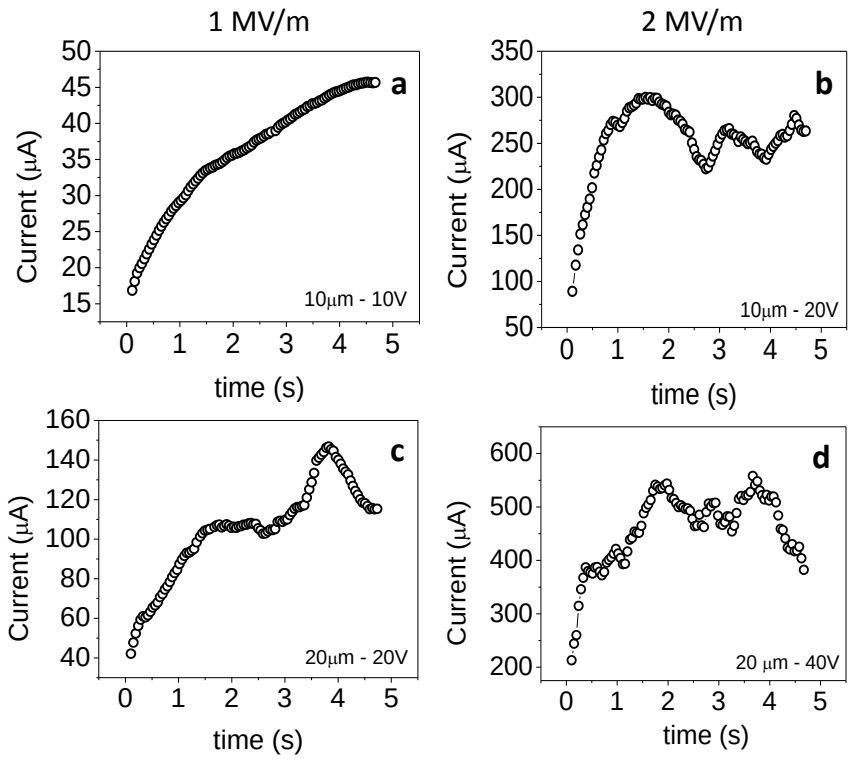

Figure S5. Current *vs.* time curves registered during the polymerization processes of EDOT in PC solution at electric field intensities of 1 MV/m (***a, c***) and 2 MV/m (***b, d***).