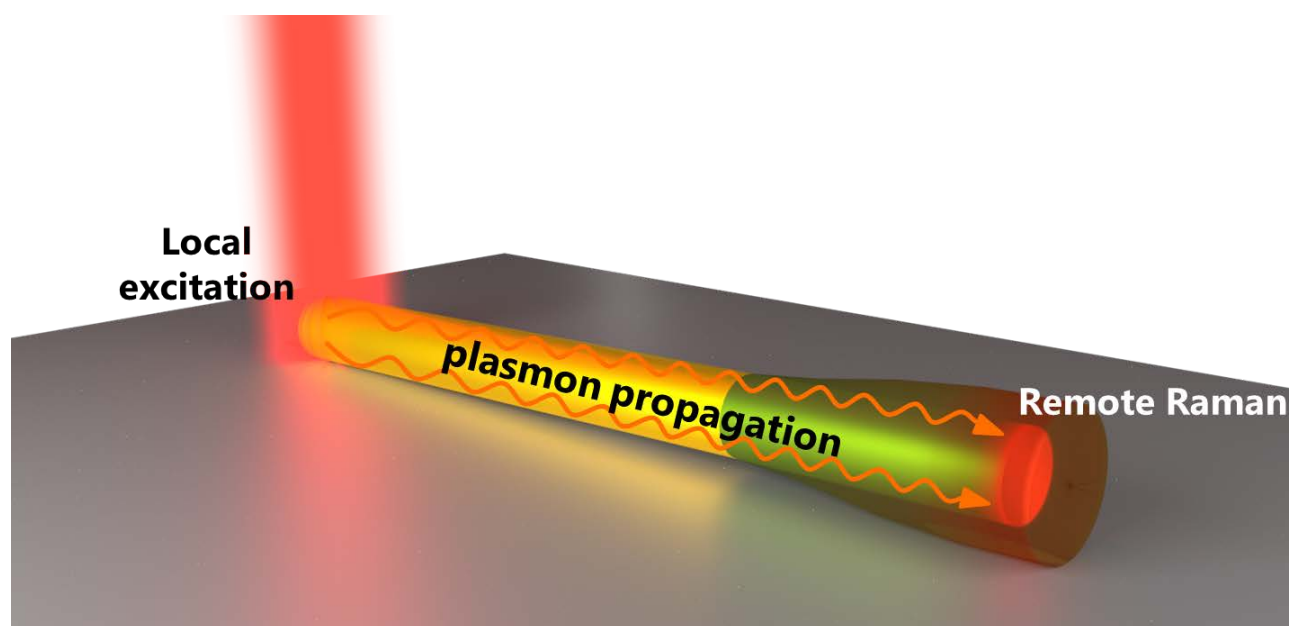


Electronic Supplementary Information (ESI)



Supplementary information

1. Experimental part

All the liquid-phase processes are carried out in Teflon “glassware” as it is observed that normal glassware could give some SiO₂ nanoparticles pollution. All the materials and substrates used are cleaned with piranha solution, aqua regia and MilliQ water under sonication to remove any organic or metallic impurities.

Synthesis of gold core and poly(3,4-ethylenedioxythiophene) shell (Au@PEDOT) nanowires was carried out by a hard-template method in a homemade electrochemical cell. Anodic aluminum oxide (AAO) membranes were purchased from InRedox with nominal pore diameter equal to 20, 40, 80 and 120 nm.

A thin layer of gold was sputtered onto the more homogenous face of the anodic aluminum oxide (AAO) membrane by physical vapor deposition in a radiofrequency magnetron sputtering system. Its thickness was typically five times the size of the pore diameter.

First, the growth of Au nanowires was carried out in a homemade three-electrode electrochemical cell placing the non-Au-coated face of the AAO membrane in contact with a 0.1M KCl, 0.1M K₂HPO₄, 0.03M HAuCl₄ aqueous solution (chemicals provided by Sigma Aldrich). The sputtered Au thin layer acted as working electrode and a platinum foil was used as counter-electrode. For gold electroplating, a cyclic voltammetry was performed in the range 0.75-0.00V against saturated calomel electrode (SCE) at a sweeping rate of 50 mV/s.¹ The number of cycles determined the length of the nanowires in a directly proportional relationship. The Au nanowires embedded in the AAO membrane were rinsed thoroughly with ultrapure water ($\rho \approx 18.2 \text{ M}\Omega \cdot \text{cm}$) to remove any residue of the Au saline solution. A pore-widening process was carried out immersing the membrane in an 8.1 wt% H₃PO₄ solution for a controlled duration, typically 90 minutes.² In the case of the asymmetric Au@PEDOT nanowires, the immersion time was reduced to 5 minutes to get a smaller space around the Au core. Then, the pore-widened membrane was rinsed thoroughly with ultrapure water again. The PEDOT shell was electropolymerized around the Au nanowires by placing the membrane in the homemade cell in contact with an aqueous solution containing 0.05 M 3,4-ethylenedioxythiophene, 0.07 M sodium dodecyl sulfate, 0.1 M LiClO₄.³ A fixed potential of 0.80 V vs SCE was then applied for 50 seconds to electropolymerize PEDOT onto the surface of the Au nanowires. This electropolymerization time was reduced to 30 seconds in the case of the asymmetric Au@PEDOT nanowires. The membrane was then rinsed thoroughly with milliQ water. Finally, in order to remove the alumina template, the membrane was immersed in a 4.9 M H₃PO₄ solution for 48 hours. The fragile membrane was then rinsed with ultrapure water and stored as an array of self-standing Au@PEDOT nanowires on Au film. We revealed a yield of 90% for the symmetric Au@PEDOT nanowires respect to the total number of nanowires dispersed, and a yield of 70% for the asymmetric nanowires. In the latter case we found that the unsuccessful 30% corresponded to uncovered nanowires and, in rare cases, nanowires with PEDOT at both tips.

A similar process was used to electropolymerize pure PEDOT nanowires, using the electrolyte and the electropolymerization conditions described above.

Raman spectroscopy characterization was performed with a Renishaw InVia® Raman spectrometer. The samples were prepared by sonicating during 0.5 s the Au@PEDOT nanowires array anchored on the Au electrode immersed in ultrapure water. Then the dispersion is drop-casted on a boron-doped silicon wafer or on different types of TEM grids and allowed to dry for one day. Single nanowires were located with an optical microscope (objective: x100, long focal distance) on a grid imprinted on the silicon wafer by laser ablation (collaboration with M-Solv). Four excitation wavelengths were available: 488, 514, 633 and 785 nm. The experimental conditions (laser power, time acquisition) were adjusted to get a good signal-to-noise ratio and to prevent the degradation of the polymer in the configuration of a direct excitation of PEDOT by the laser, i.e. to measure a stable and reproducible Raman spectrum.

Scanning electron microscopy (SEM) characterization was performed in a JEOL JSM 7600F equipped with secondary electrons imaging (SEI) by in-lens detector and back-scattered electrons imaging (BEI) detector. A 5kV acceleration voltage was used. The Au@PEDOT nanowires solid dispersions on boron-doped silicon

wafers made for Raman spectroscopy were mounted on brass stabs using Ag paste. The same preparation was used for studying the Au@PEDOT nanowires array on Au. In the case of the TEM grids, they were mounted in a special stab for SEM study of TEM grids.

Transmission electron microscopy (TEM) characterization. Preliminary characterization was performed with a Hitachi H-9000 NAR at an acceleration voltage of 300 kV at IMN, Nantes. Then, further TEM investigations were developed at the Laboratorio de Microscopias Avanzadas (LMA) of the Instituto de Nanociencia de Aragon (INA)-Universidad de Zaragoza (Spain). A FEI Titan Low-Base aberration-corrected TEM microscope operated at 80 kV has been employed. This TEM is equipped with a Cs probe corrector, a monochromator, an ultrabright X-FEG electron source and a Gatan Tridiem ESR 865 EELS spectrometer. The convergence angle was 25 mrad and the inner and outer angles for HAADF imaging were 70 and 200 mrad, respectively. EELS studies have been conducted in STEM mode, using spectrum image and line scan modes. The EELS datasets were then de-noised with the open-source program Hyperspy by using principal component analysis routines.⁴

2. Complementary results

- **Evidence of the coaxial morphology by SEM: secondary electrons versus backscattered electrons**

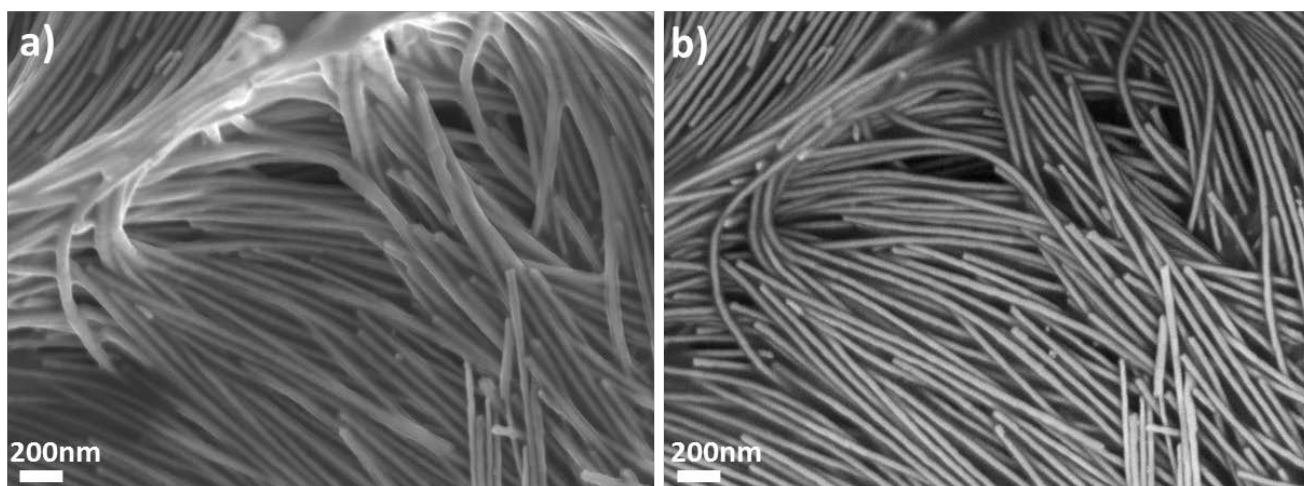


Figure S1. (a) SEM-secondary electrons image (SEI) and (b) SEM-backscattered electrons image (BEI) of Au@PEDOT nanowires array (initial pore diameter: 42 nm) after total etching of the AAO membrane.

- **Study of the preferential orientation of the PEDOT chains**

The dichroic ratio is defined as $R = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$ where I_{\parallel} and I_{\perp} are the Raman intensity of the C=C symmetric stretching band for parallel and perpendicular polarizations, respectively. A value of $R = 1$ indicates that the conjugated segments are fully oriented parallel to the wire axis. On the contrary, a dichroic ratio of -1 indicates that the conjugated segments are fully oriented perpendicular to the wire axis.

Case of the pure PEDOT nanowires:

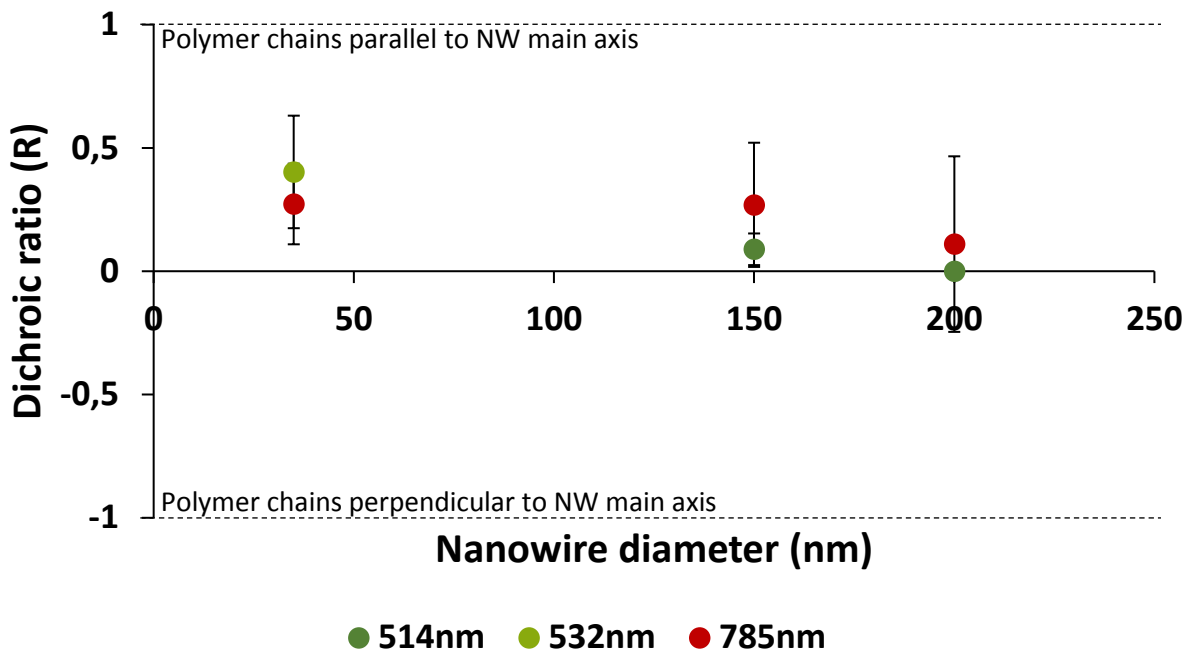
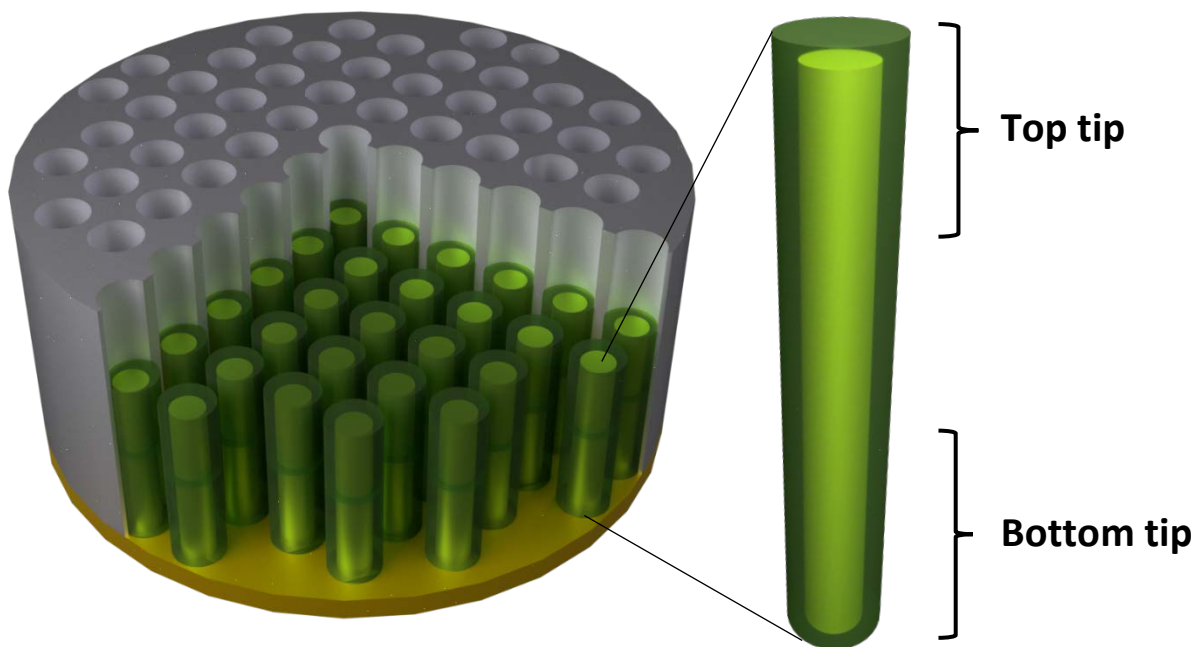
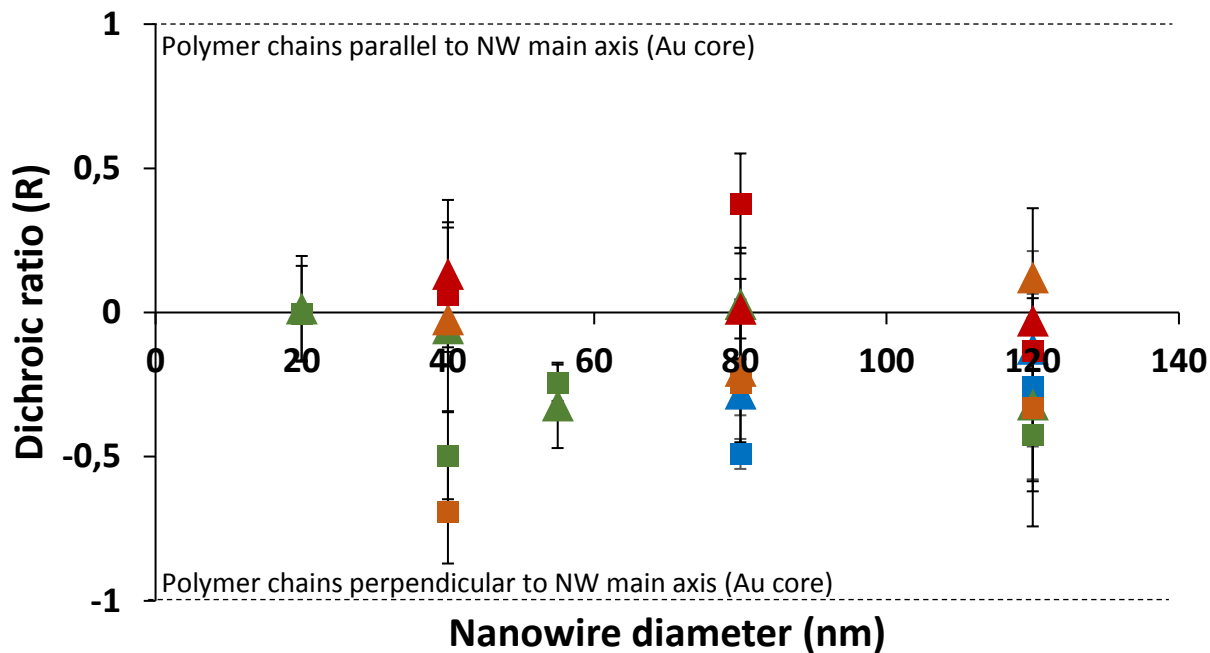


Figure S2. Dichroic ratio scheme from the study of polarized Raman spectroscopy for pure PEDOT nanowires of different diameters and at different $\lambda_{excitation}$.

Case of the coaxial Au@PEDOT nanowires:





▲ 488nmBottom ■ 488nmTop ▲ 514nmBottom ■ 514nmTop
 ▲ 633nmBottom ■ 633nmTop ▲ 785nmBottom ■ 785nmTop

Figure S3. Dichroic ratio scheme from the study of polarized Raman spectroscopy for Au@PEDOT NWs at their bottom tip (triangles) and their top tip (squares) of different diameters and at different $\lambda_{excitation}$.

References

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