

Electronic Supporting Information
for
Conducting poly(3,4-ethylenedioxythiophene) materials with
sustainable carrageenan counter-ions and their thermoelectric
properties

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Materials:

The following materials were purchased as indicated: Ethylene-3,4-dioxythiophene (EDOT) (Acros Organics; 99%), kappa-Carrageenan (κ -Carr) (Sigma), lambda-Carrageenan (λ -Carr) (SIGMA-ALDRICH), Iota-Carrageenan (ι -CGN) (Alfa Aesar; EINECS: 232-949-3), Iron chloride, FeCl_3 (SIGMA-ALDRICH; 97%), glass slides (Sigma Aldrich; VBS653/A). Silver conductive paint (RS Pro), polyimide film electrical (Kapton) tape was obtained from RS Pro.

Synthesis:

The synthesis of the **PEDOT- κ -Carr** polymer involves several steps. Firstly, (153.9 mg, 0.949 mmol, 1 equiv.) of FeCl_3 was added to 10 ml of deionized water. The mixture was sealed and sonicated at 40 °C for 20 minutes until a clear orange solution was obtained. In a separate round bottom flask, κ -Carr (366 mg, 0.949 mmol) was dissolved in 40 ml of deionized water of fast magnetic stirring (1400 rpm) at 70 °C, resulting in a clear, pale yellow viscous solution. Once κ -Carr was completely dissolved, the temperature was reduced to 50 °C. Then, (100 μL , 133 mg, 0.949 mmol) of EDOT was added dropwise over 10 minutes to the stirred solution. The mixture was continuously stirred at 1400 rpm, and argon gas was bubbled through it for 20 minutes to degas molecular oxygen. Subsequently, 10 ml of a 94 mM FeCl_3 aqueous solution was added dropwise to the mixture of EDOT and κ -Carr at 70 °C under argon over a period of 20 minutes. The addition of FeCl_3 caused the mixture to turn into a deep blue colour. The resulting mixture was then heated at 50 °C of constant stirring (1400 rpm) for 23 hours, followed by an additional heating step at 70 °C for 1 hour. Finally, a 50 ml dispersion of dark blue water dispersed **PEDOT- κ -Carr** was obtained. To produce more samples for further analysis, a scaled-up reaction with two-times and five times amount scale of reagents were performed. Different ratios of PEDOT to κ -Carr ranging from 1:1 to 4:1, 5:1, 7:1, 8:1, and 16:1 were used to observe the variations in morphology and conductivity.

For the synthesis of the 5:1 ratio, a solution of FeCl_3 (153.9 mg, 0.949 mmol, 1 equiv) was prepared by dissolving it completely in 10 mL of deionized water. The solution was then sealed and subjected to sonication at 40 °C for 20 minutes, resulting in the formation of clear solutions. Separately, κ -Carr (366 mg, 0.949 mmol) was dissolved in 40 mL of deionized water at 70 °C with vigorous stirring (1400 rpm), yielding a pale yellow viscous solution. After complete dissolution of κ -Carr, the temperature was lowered to 50 °C. Subsequently, EDOT (500 μL , 665 mg, 4.745 mmol) was added dropwise over a period of 20 minutes, leading to the formation of an aqueous mixture comprising EDOT and κ -Carr. In the same

conditions, 10ml 94 mM FeCl₃ solution was added to the mixture, resulting in the formation of a 50 ml dispersion of 5:1 **PEDOT-κ-Carr** in water. The synthesis procedure for other ratios followed a similar protocol.

The total yield of the 1:1 **PEDOT-κ-Carr** over many reactions was approximately 35%, and for 5:1 **PEDOT-κ-Carr** was approximately 25%.

The synthesis of **PEDOT-λ-Carr** involved the following steps: FeCl₃ (153.9 mg, 0.949 mmol) was added to 10 ml of deionized water, and the solution was completely dissolved by sonication at 40 °C for 20 minutes, resulting in two clear solutions with a concentration of 94 mM. Subsequently, λ-Carr (490 mg, 0.949 mmol) was dissolved in 40 ml of deionized water at 70 °C under argon with fast stirring (1400 rpm), leading to the formation of a clear, pale yellow viscous solution. Once complete dissolution of λ-Carr was achieved, the temperature was lowered to 50 °C. Next, EDOT (100 μL, 133 mg, 0.949 mmol) was added dropwise over a period of 10 minutes to the continuously stirred solution. The mixture was then subjected to bubbling of argon for 20 minutes while maintaining constant stirring (1400 rpm). This process helped to obtain identical 1:1 EDOT and λ-Carr aqueous mixture, which was degassed of molecular oxygen. Subsequently, 10 ml of 94 mM FeCl₃ (aq) was added dropwise to this mixture under argon at 70 °C for a period of 20 minutes. The mixture was heated at 50 °C under argon with constant stirring (1400 rpm) for an additional 23 hours, followed by heating at 70 °C for 1 hour. This resulted in the formation of 50 ml dark blue mixtures of water-dispersed **PEDOT-λ-Carr**.

Based on the phase inversion happened during the gel formation of the mix κ-Carr and λ-Carr, a 5:1 molar ratio for Mix-CGN (molar ratio of κ-Carr to λ-Carr =1) and EDOT reaction was attempted. FeCl₃ (153.9 mg, 0.949 mmol) was added to and wholly dissolved in deionised water (10 mL), sealed, and sonicated at 40 °C for 20 minutes to give clear solutions. κ-Carr (183 mg, 0.475 mmol) and λ-Carr (245mg, 0.475 mmol) (mole ratio=1) were added and dissolved in 70 °C deionised water (40 mL) to give a pale yellow viscous solution of fast stirring (1400 rpm). Once completed dissolution, the temperature was reduced to 50 °C. EDOT (500 μL, 665 mg, 4.75 mmol) was added dropwise over 20 minutes to give mix-CGN and EDOT aqueous mixtures. 94 mM FeCl₃ was added in the same condition to result 50 ml 5:1 **PEDOT-MIX-Carr** water dispersion.

General Methods:

Optical microscopy analysis was performed on the thin films on an Olympus BX51 Microscope with a Cool LED pE-100 LED Fluorescence Illuminator and SC100 Colour Camera. Borosilicate glass slides were sonicated in deionised water with Hellmanex III detergent solution from Ossila (10 minutes), acetone and then propan-2-ol 10 minutes each and dried under a flow of dinitrogen. Drop cast 60 μL **PEDOT-Carr** on a 18*2 mm, dried in air and then dry in a greenhouse-type atmosphere (high humidity).

Scanning Electron Microscopy (SEM) was performed on a JEOL 7000F FEG-SEM. The films for SEM are prepared by drop casting. The **PEDOT-Carr** suspension is drop-casted on cover glass as a thin strip and dry in sealed container with a high humidity. The dried films were then stuck on the stub using carbon tape and sputter coated with iridium (8nm) prior to SEM imaging.

Atomic Force Microscopy (AFM) The films used for AFM analysis were prepared using drop cast technique from solutions D and E sonicated for 10 minutes prior to deposition on pre-cleaned glass substrates; the samples were then left in a closed environment to allow a slow and controlled evaporation of the solvent. The dried films obtained as a thick black strip were then secured, before imaging, in the AFM chamber using a magnet as shown in Fig. S1.

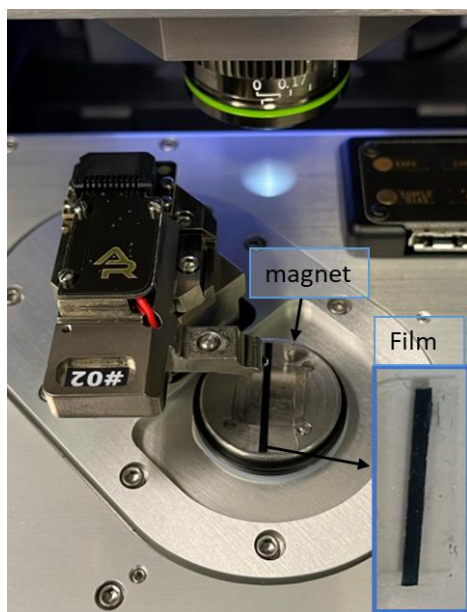


Fig. S1. Overview of the film and of the operating conditions for AFM. The material was deposited as a thick black strip on a pre-cleaned glass substrate (bottom-right corner). The sample is secured within the Cypher for AC-mode AFM using a magnet.

The morphology of the films was analysed using AFM performed in intermittent contact-mode (AC-mode). The measurements were carried out with an Asylum Cypher S microscope operating under ambient conditions using the natural resonance frequency of the oscillating cantilever (Nunano Scout 70 RAI, 70 kHz, Spring constant 2 N/m) and scanning at (512x512) pixels. Images were taken on different areas always in the middle of the films to ensure their homogeneity from microscale level, starting from 4 μm , zooming until 500 nm, details are reported in the captions. The PreEngage height was set at 100 μm to perform the approach carefully and, given the roughness of the samples, the images were acquired with a low scan rate [0.30; 1.50] Hz. The data were processed with Gwyddion, a modular program for SPM data visualization and analysis.

The morphological analysis was performed on the same samples prepared for the conductivity measurements. The roughness of the samples was investigated in terms of root mean square (RMS) as overall distribution of the heights over the surface of interest and lateral scale bars are also reported. The acquisition of the Phase channel was extremely challenging for all the samples even if the imaging was well performed, the recorded error associated to the analysis did not show any concern and there was a more than satisfactory overlap between trace and retrace. Knowing that the phase is particularly sensitive to small asperities over the surface investigated, it was not possible to totally eliminate “scratches” from the phase images at the different scan sizes analysed.

UV-visible-Near Infrared (UV-Vis-NIR) absorption spectroscopy was performed on a Cary 5000 UV-Vis-NIR spectrophotometer from Agilent Technologies. The UV-Vis spectras were obtained between 200 nm to 1200 nm. The water dispersion was sonicated before measurement to minimise aggregation during spectrum collection.

Electron Paramagnetic Resonance Spectroscopy (EPR) spectra were obtained from 2 ml of the 2 mM wet reaction mixture for **PEDOT-Carr** at 77 K using an X-band (9.5 GHz) with ER 041 XG Microwave Bridge under liquid nitrogen, both from Bruker.

Matrix-Assisted Laser Desorption-Ionization – Time of Flight Spectrometry (MALDI-TOF MS) was performed on a Bruker Autoflex Max MALDI-TOF. Samples were prepared by mixing the powder **PEDOT-Carr** with the matrix at around 1:5 ratio (w/w), then dissolved with 50 μl water, sonication for 30 seconds. Sinapinic acid and super-DHB (a 9:1 mixture (w/w) of 2,5-dihydroxybenzoic acid and 2-hydroxy-5-

methoxybenzoic acid) were both tried as the matrix, but the super-DHB gave better spectra for the **PEDOT-Carr** composites. Linear positive/negative MS modes were used, having calibrated.

Fourier-transform infrared spectroscopy (FT-IR) was performed on a Bruker Vertex 70 FTIR spectrometer with PLATINUM ATR accessory. The IR spectra of samples of **PEDOT-Carr** were obtained from dry samples transferred to the diamond window of the ATR attachment of the instrument as quickly as possible from a dry atmosphere to avoid moisture affecting the scans.

Raman Spectroscopy was performed on a HORIBA LabRAM HR Raman microscope, equipped with a 532 nm laser, a 600 lines/mm grating and a 100x objective, on solid powders of the materials.

X-Ray photoelectron spectroscopy (XPS) was performed using the Kratos AXIS ULTRA with a monochromated Al K α X-ray source (1486.6 eV) operated at 10 mA emission current and 12 kV anode potential (120 W). Spectra were acquired with the Kratos VISION II software. A charge neutralizer filament was used to prevent surface charging. Hybrid-slot mode was used for measuring a sample area of approximately 300 x 700 μm . The analysis chamber pressure was greater than 5×10^{-9} mbar. Three areas per sample were analysed. A wide scan was performed at low resolution (binding energy range 1400 eV to -5 eV, with pass energy 80 eV, step 0.5 eV, sweep time 20 minutes). High resolution spectra at pass energy 20 eV, step of 0.1 eV, and sweep time of 10 minutes each were also acquired for photoelectron peaks from the detected elements, and these were used to model the chemical composition. Sample loading to the XPS was performed in air. The spectra were charge corrected by setting the C 1s peak to 284.7 eV. Analysis was performed using the CasaXPS software.

Supporting data:

Optical microscopy

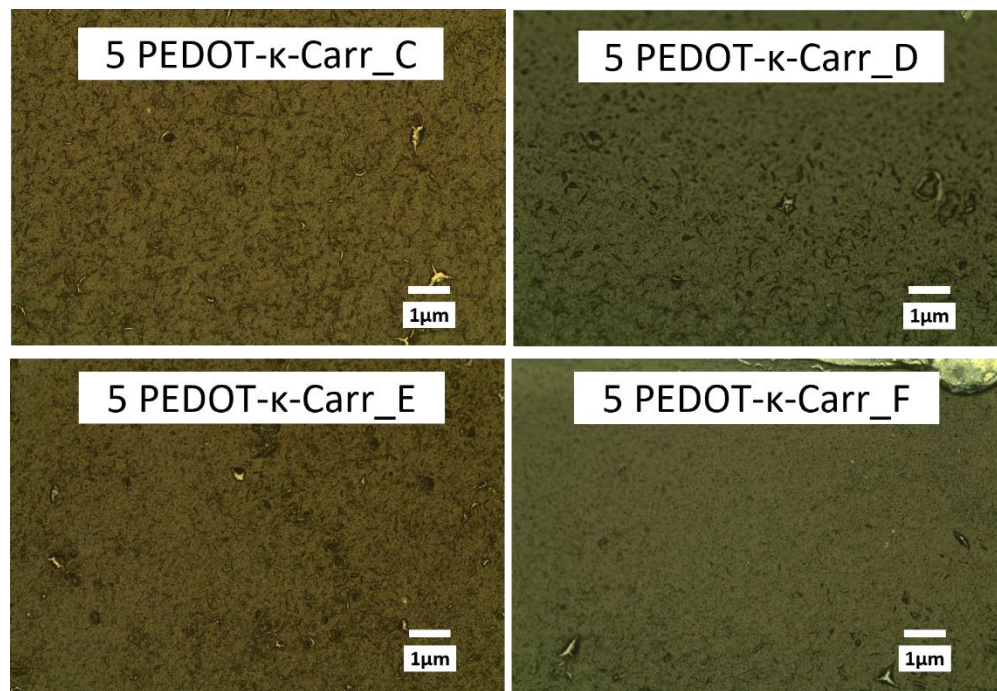


Fig. S2. *Optical micrographs (reflection mode) of the **PEDOT-κ-Carr** (C, D, E, F) deposited through drop casting ($V=60 \mu\text{L}$) on a $2 \text{ mm} \times 18 \text{ mm}$ glass from the water solution sonicated for 10 minutes.*

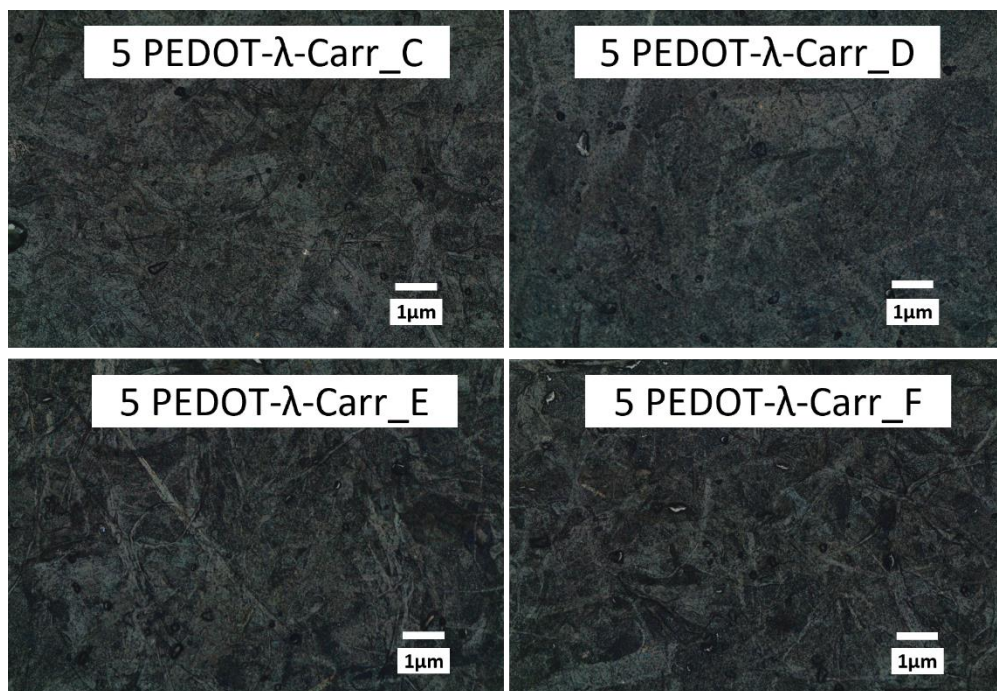


Fig. S3. Optical micrographs (reflection mode) of the **PEDOT-λ-Carr** (C, D, E, F) deposited through drop casting ($V=60 \mu\text{L}$) on a $2 \text{ mm} \times 18 \text{ mm}$ glass from the water solution sonicated for 10 minutes

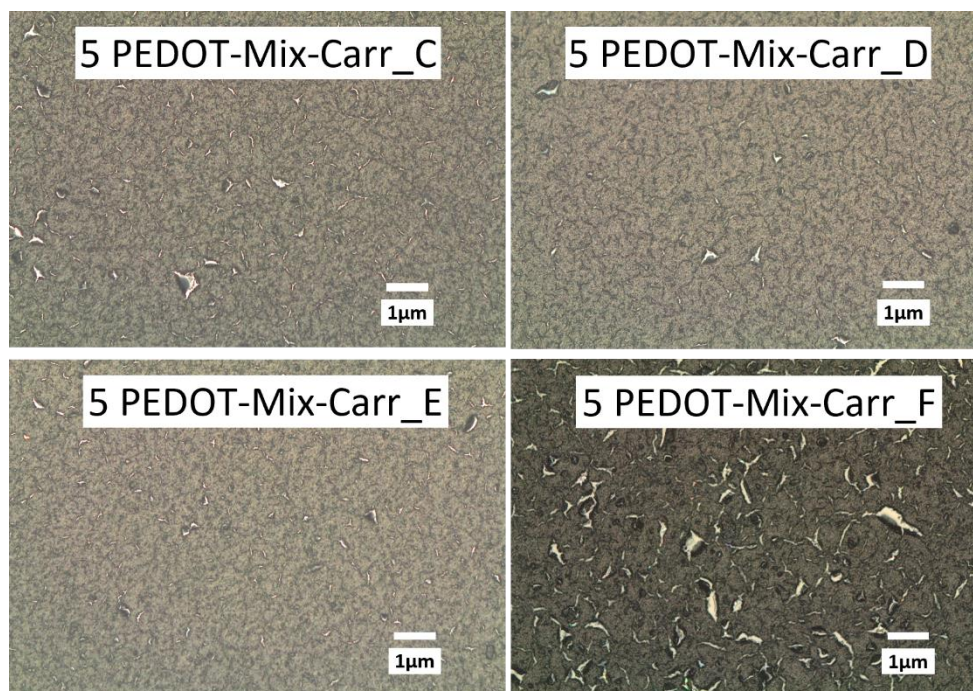


Fig. S4. Optical micrographs (reflection mode) of the **PEDOT-MIX-Carr** (C, D, E, F) deposited through drop casting ($V=60 \mu\text{L}$) on a $2 \text{ mm} \times 18 \text{ mm}$ glass from the water solution sonicated for 10 minutes

Scanning electron microscope (SEM)

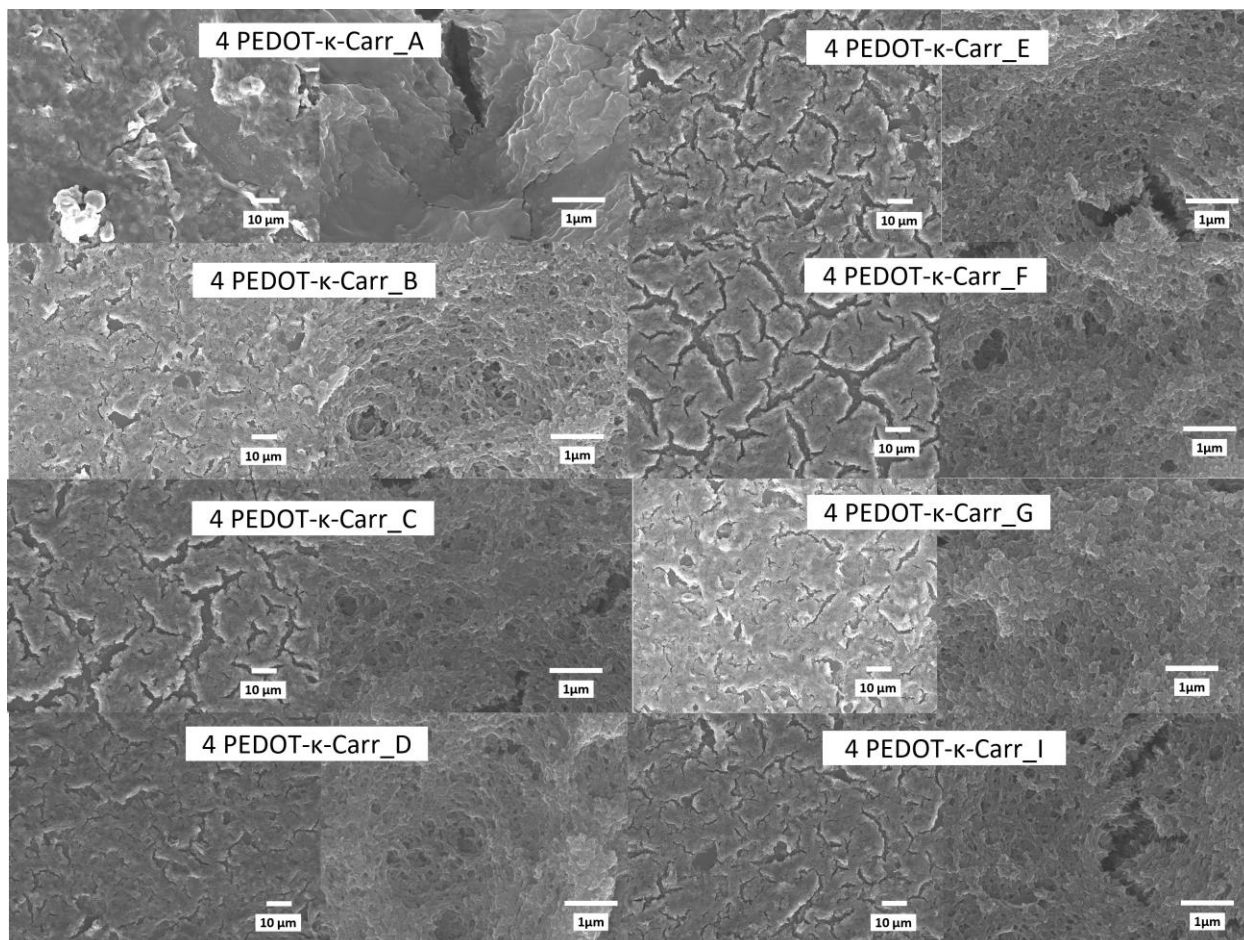


Fig. S5. Morphology of conducting polymers by SEM. *The images show scanning electron micrographs of iridium-coated films prepared using fractions A to G, I of 4:1 PEDOT-κ-Carr reaction.*

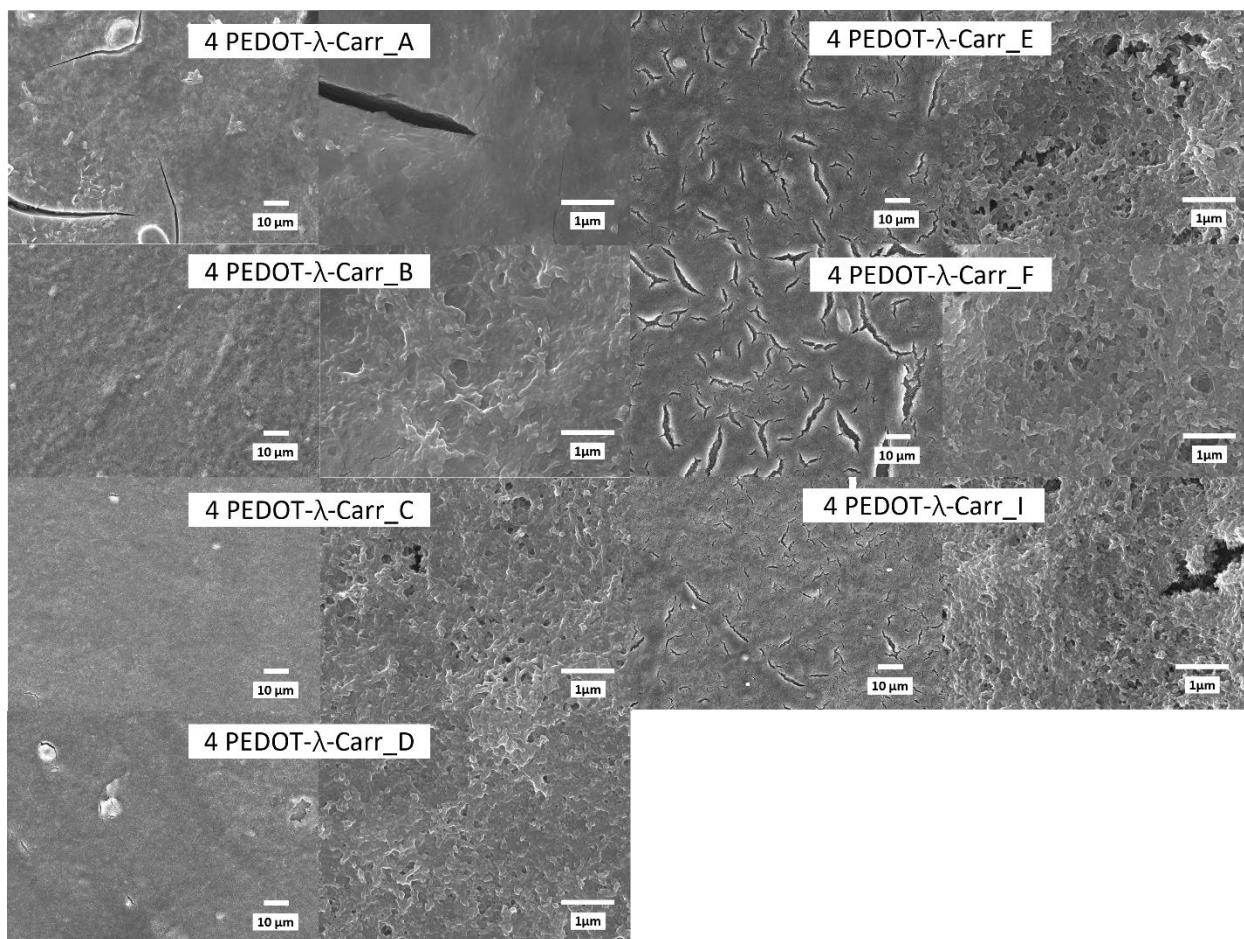


Fig. S6. Morphology of conducting polymers by SEM. *The images show scanning electron micrographs of iridium-coated films prepared using fractions A to F, I of 4:1 PEDOT-λ-Carr reaction.*

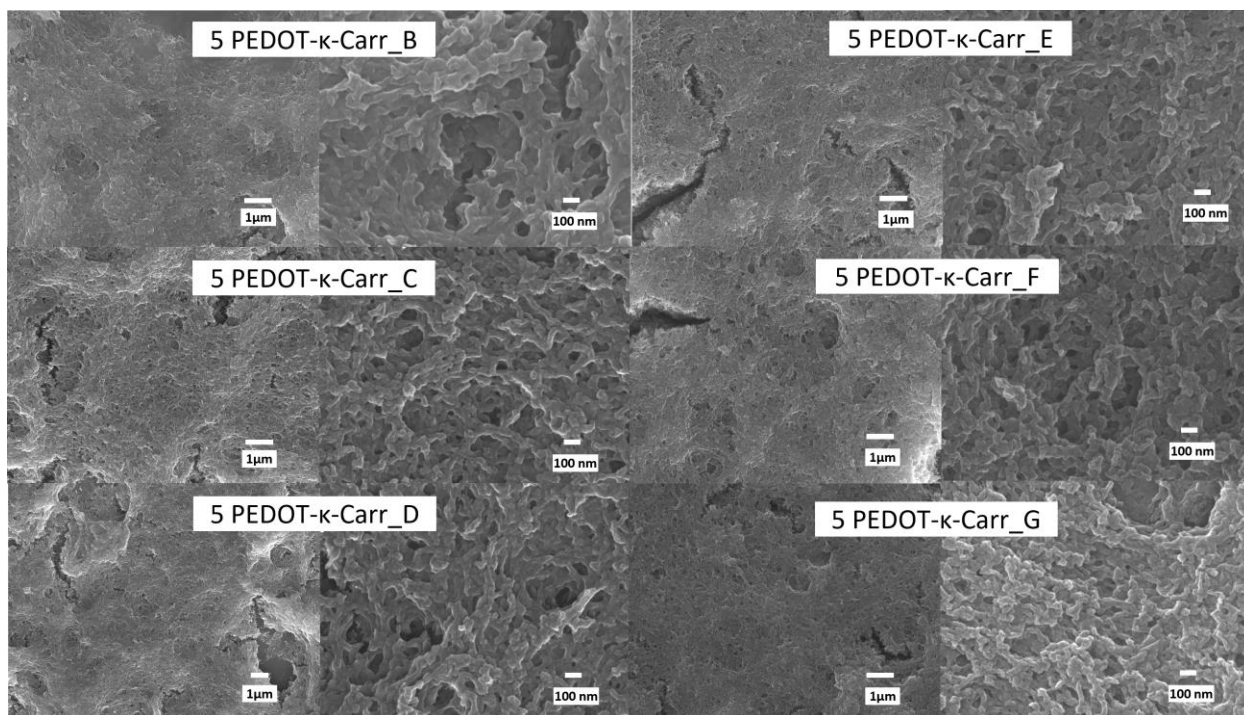


Fig. S7. Morphology of conducting polymers by SEM. *The images show scanning electron micrographs of iridium-coated films prepared using fractions B to G of 5:1 PEDOT-κ-Carr reaction.*

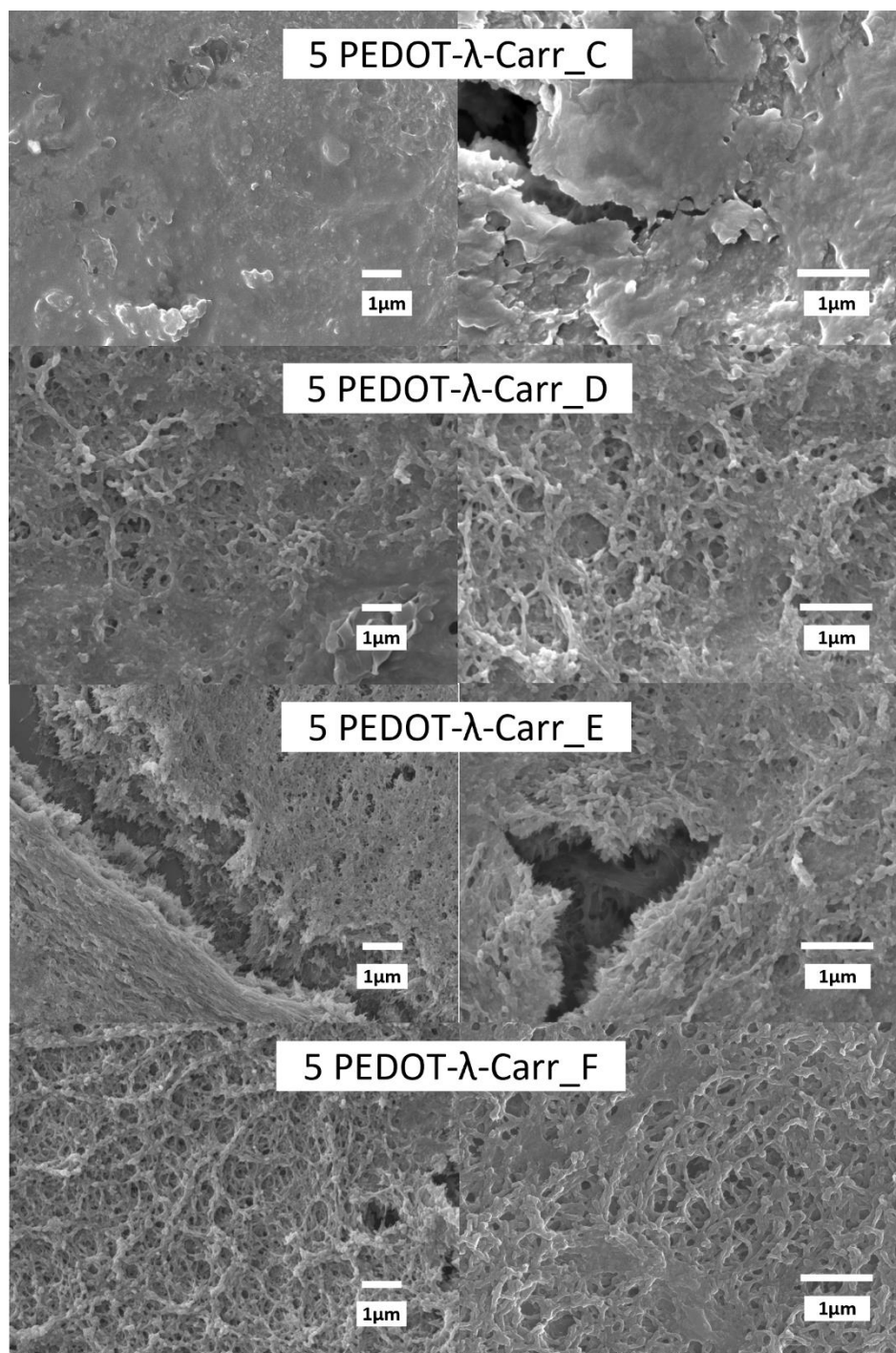


Fig. S8. Morphology of conducting polymers by SEM. *The images show scanning electron micrographs of iridium-coated films prepared using fractions C to F of 5:1 PEDOT-λ-Carr reaction.*

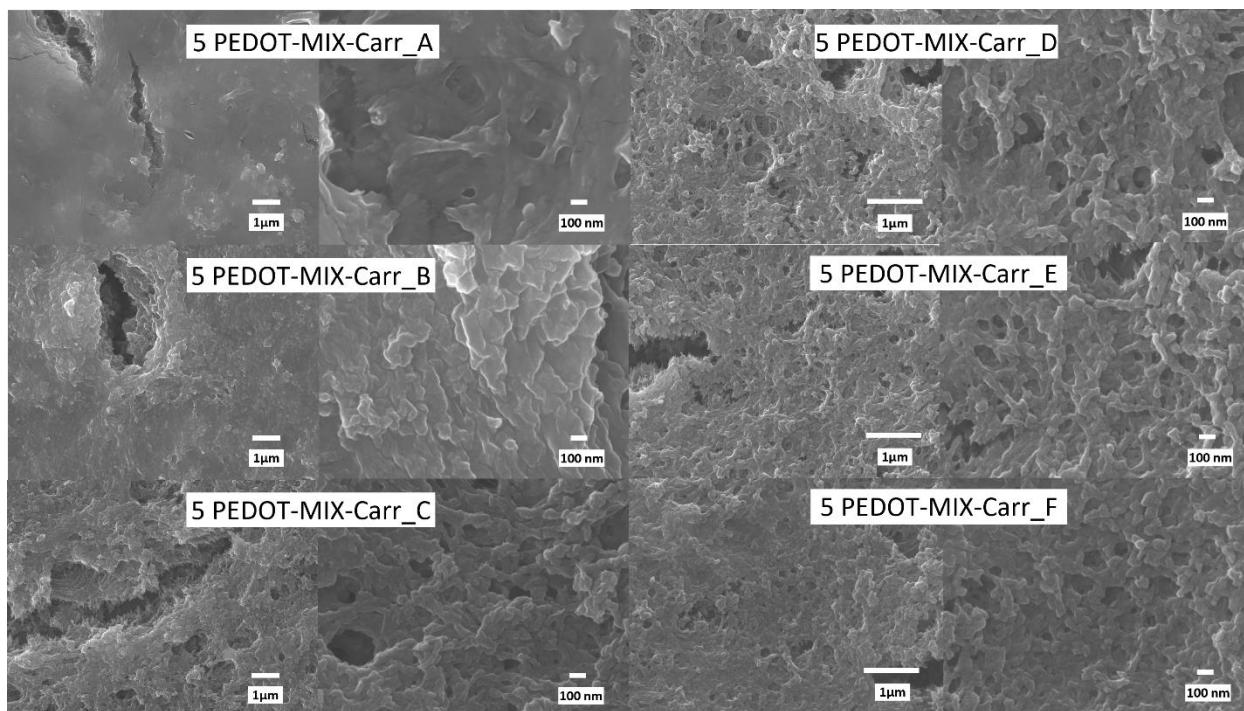


Fig. S9. Morphology of conducting polymers by SEM. *The images show scanning electron micrographs of iridium-coated films prepared using fractions A to F of 5:1 **PEDOT-MIX-Carr** reaction.*

Atomic Force Microscopy (AFM)

The optical micrographs in Fig. S10, taken using the lens available in the Cypher AFM machine, show the different films investigated by AFM. Considering the thickness and the colour of the strip, the aperture of the field diagram was modified in order to focus on the recognizable features on the surface of the samples.

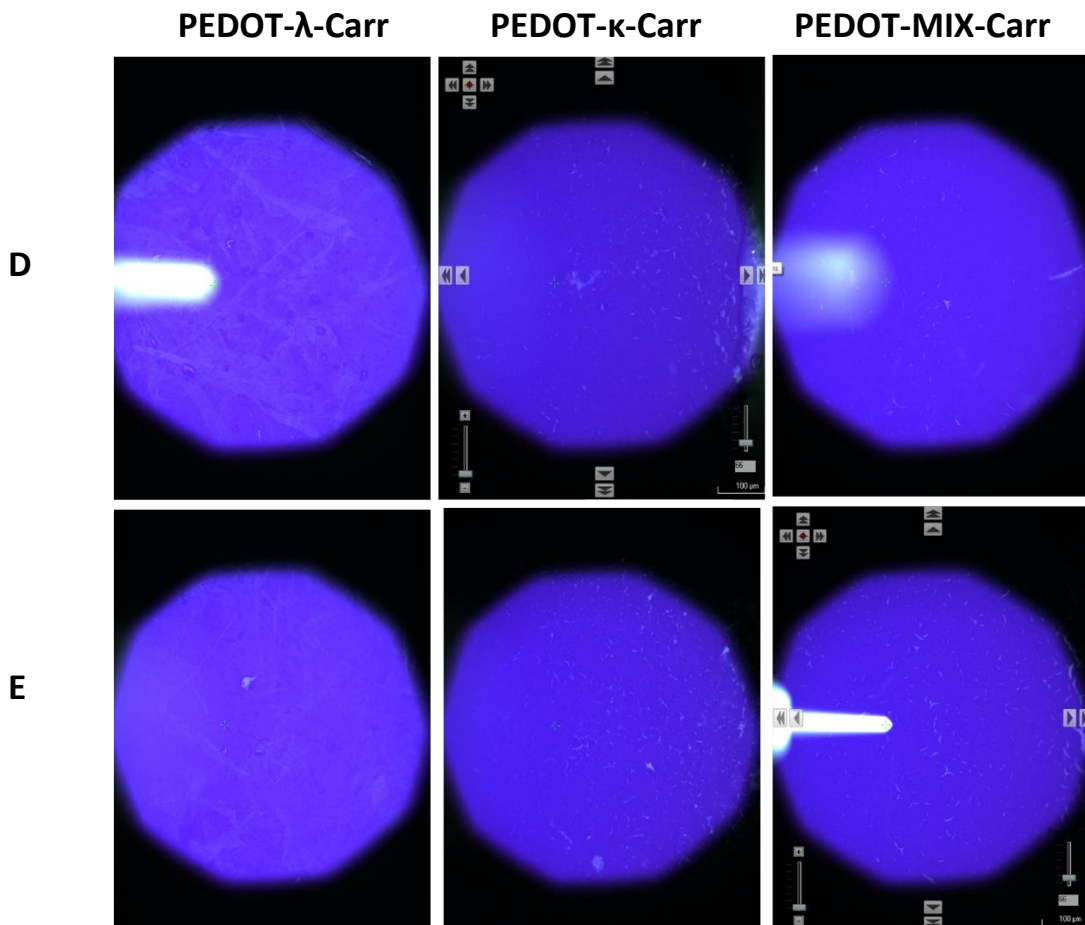


Fig. S10. Optical micrographs showing an example of investigated area of the films made of the different kind of **PEDOT-Carr** conductive material. The bright bar corresponds to the AFM cantilever.

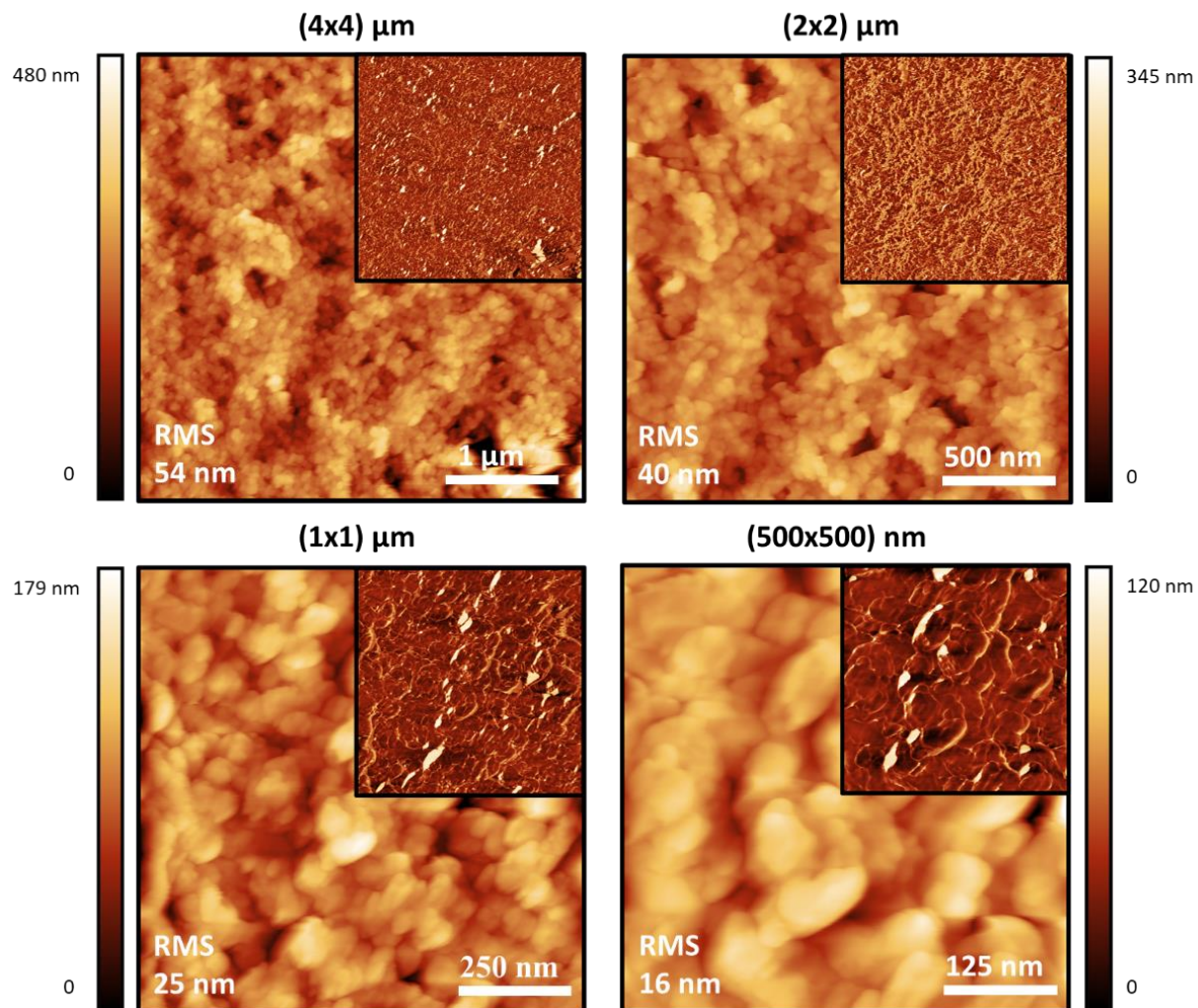


Fig. S11. Intermittent contact-mode atomic force microscopy (AFM) images of films prepared on glass substrates using the 5:1 PEDOT- κ -Carr (D) reaction, from aqueous solution after 10 minutes sonication time. Topographic AFM images at different scan sizes and corresponding phase images as top right inserts.

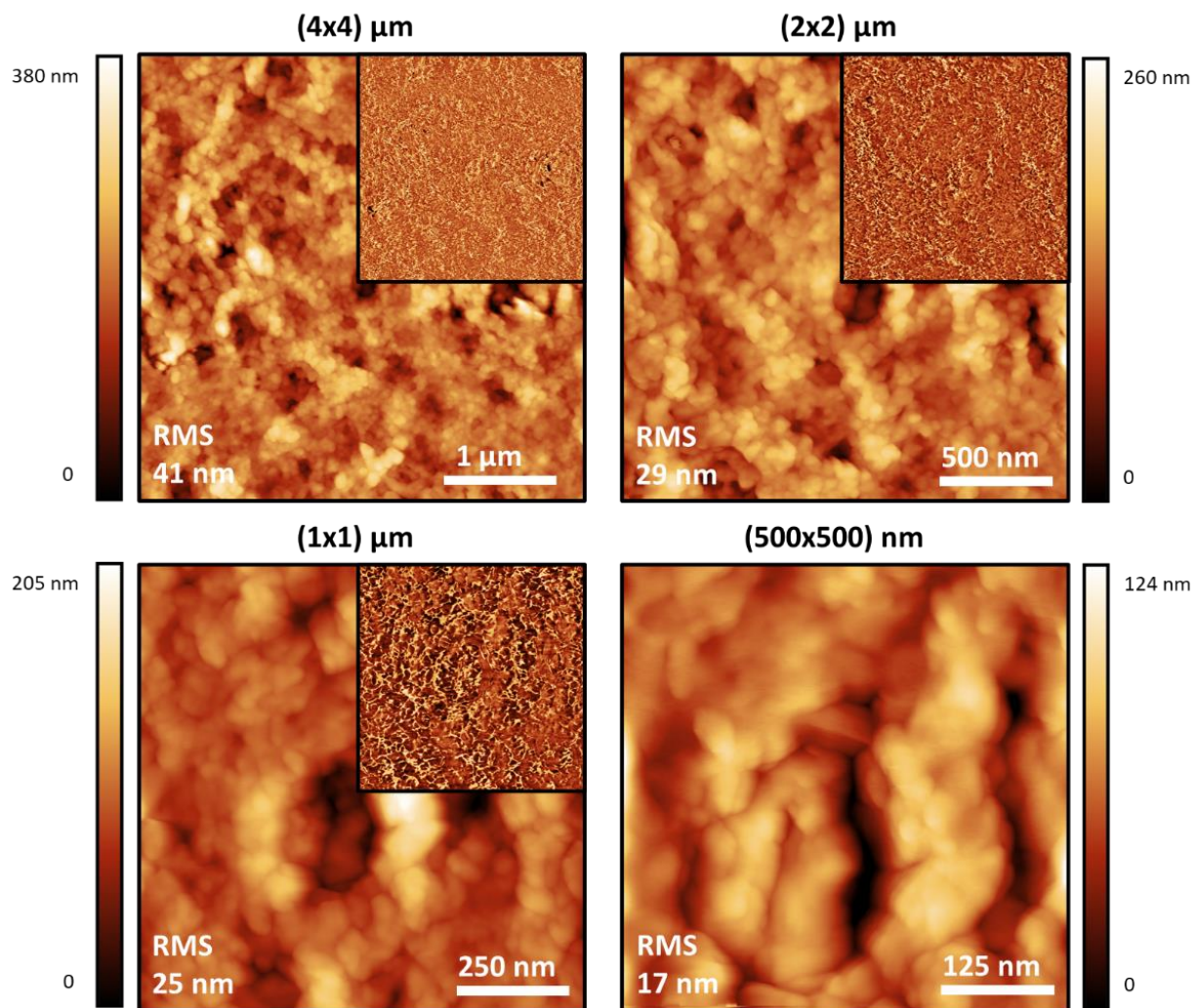


Fig. S12. AFM images of films prepared on glass substrates using the 5:1 PEDOT-λ-Carr (D) reaction from an aqueous solution after 10 minutes of sonication. Topographic AFM images at different scan sizes and corresponding phase images as top right inserts.

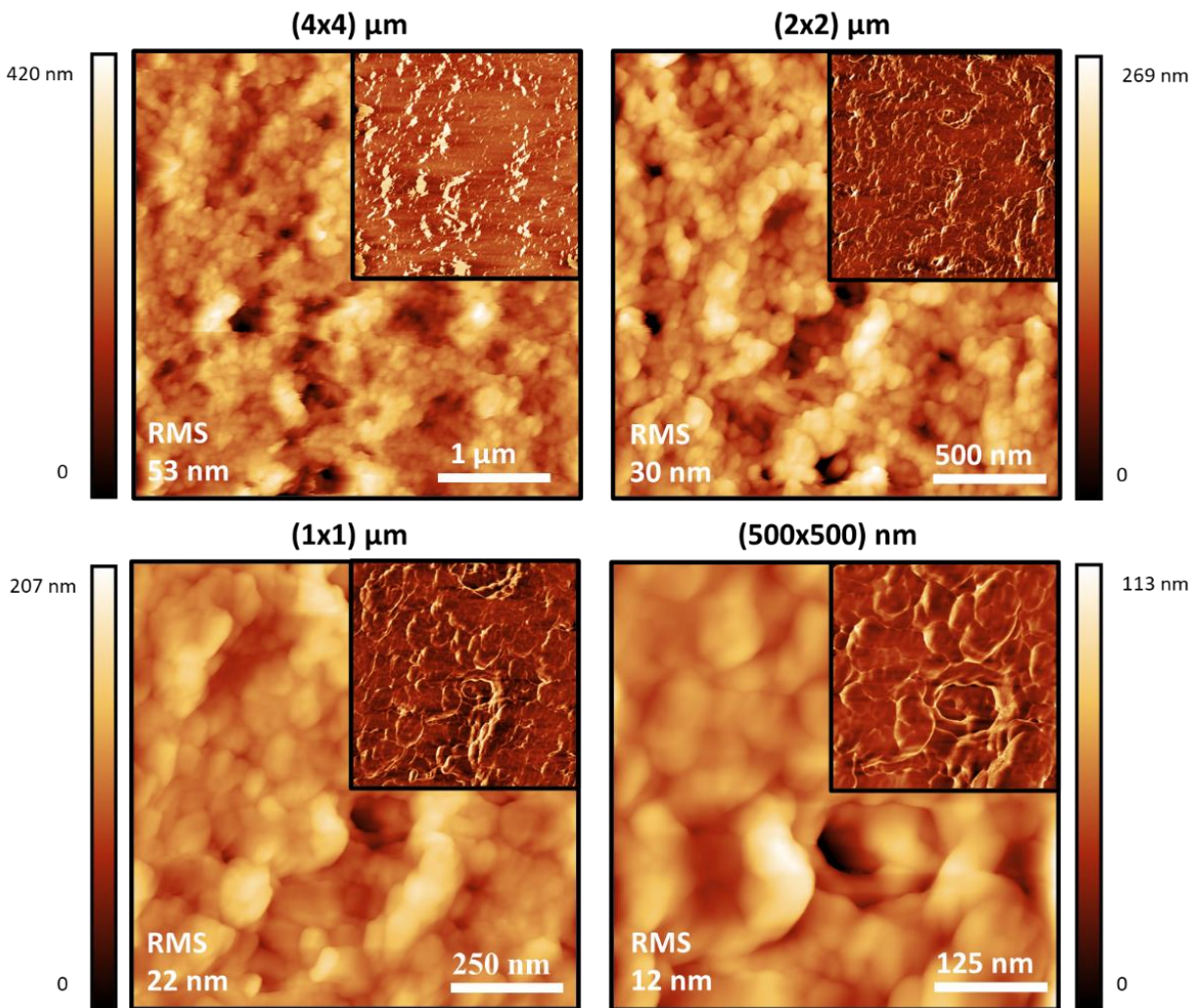


Fig. S13. AFM images of films prepared on glass substrates using the 5:1 *PEDOT-Mix-Carr (D)* reaction from aqueous solution after 10 minutes sonication time. Topographic AFM images at different scan sizes and corresponding phase images as top right inserts.

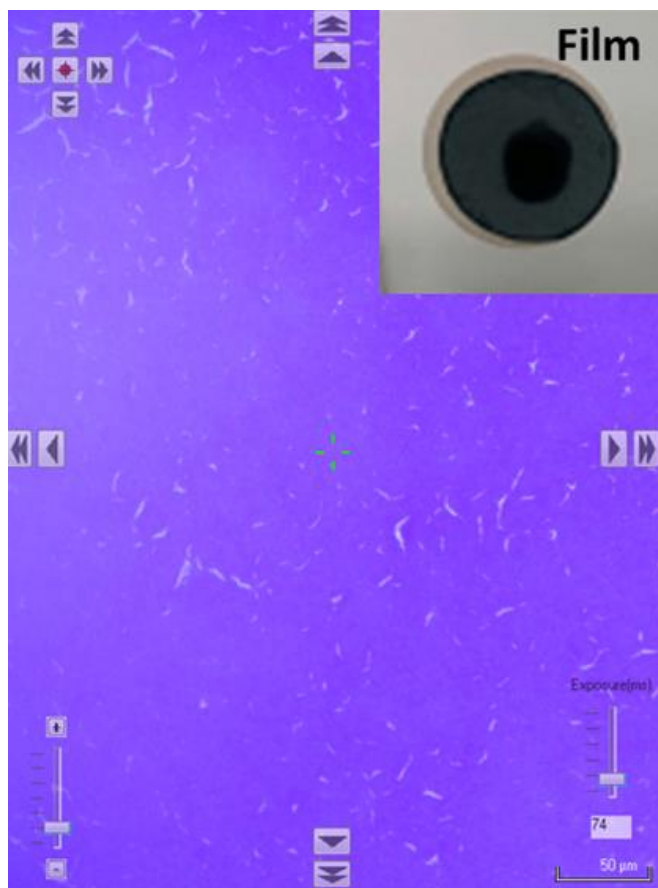


Fig. S14. Optical micrograph of the *PEDOT-Mix-Carr (E)* deposited through drop casting ($V=60 \mu\text{L}$) on a mica substrate from the aqueous solution sonicated for 10 minutes, top right insert shows the film.

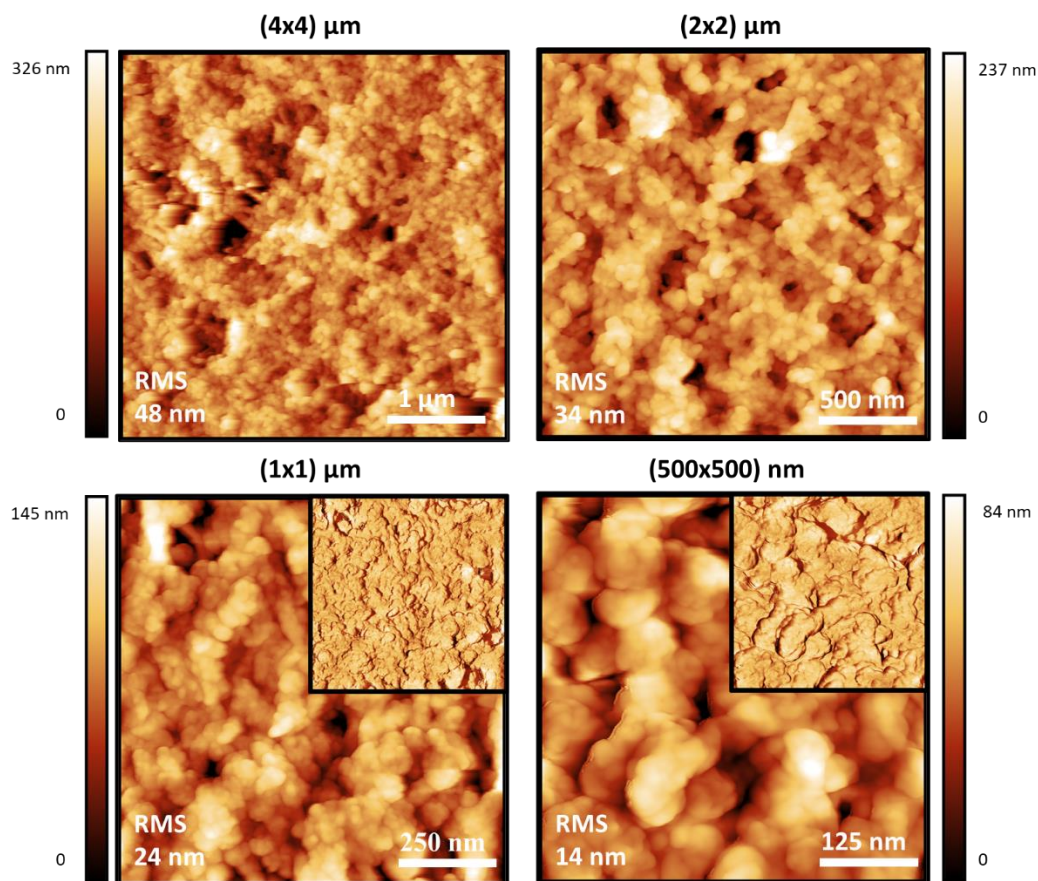


Fig. S15. AFM images of films prepared on mica substrates using the 1:1 *PEDOT-Mix-Carr (D)* reaction from the aqueous solution sonicated for 10 minutes. Topographic AFM images at different scan sizes and corresponding phase images as top right inserts.

UV-visible-Near Infrared (UV-Vis-NIR) absorption spectroscopy.

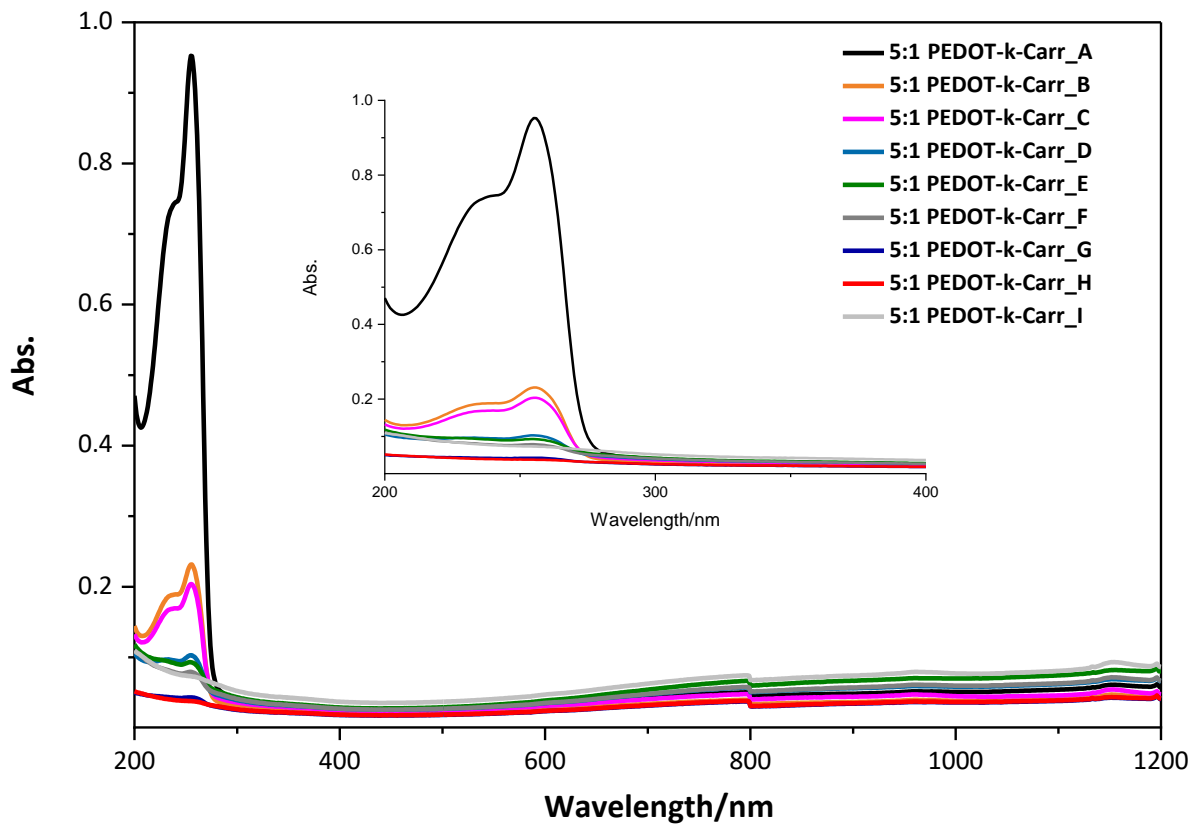


Fig. S16. UV-Vis absorption spectra of fractions A to I of 5:1 PEDOT-κ-Carr.

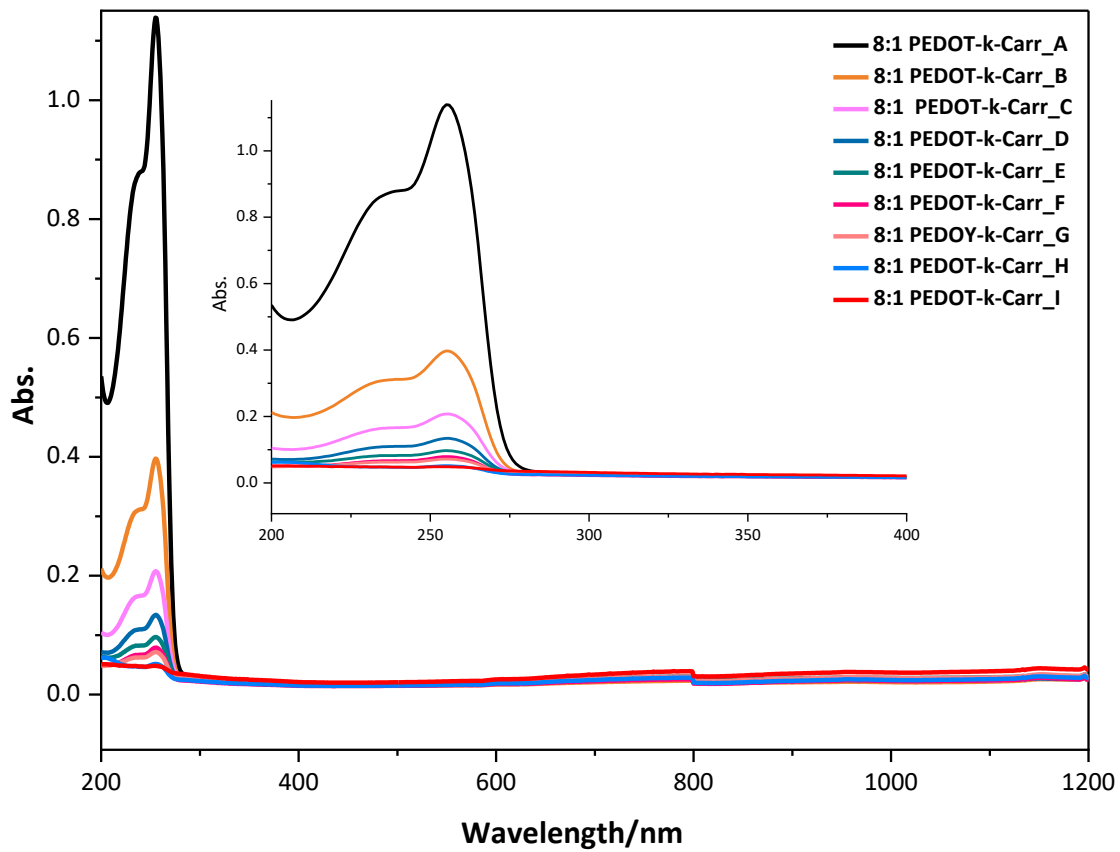


Fig. S17. UV-Vis absorption spectra of fractions A to I of 8:1 PEDOT-κ-Carr.

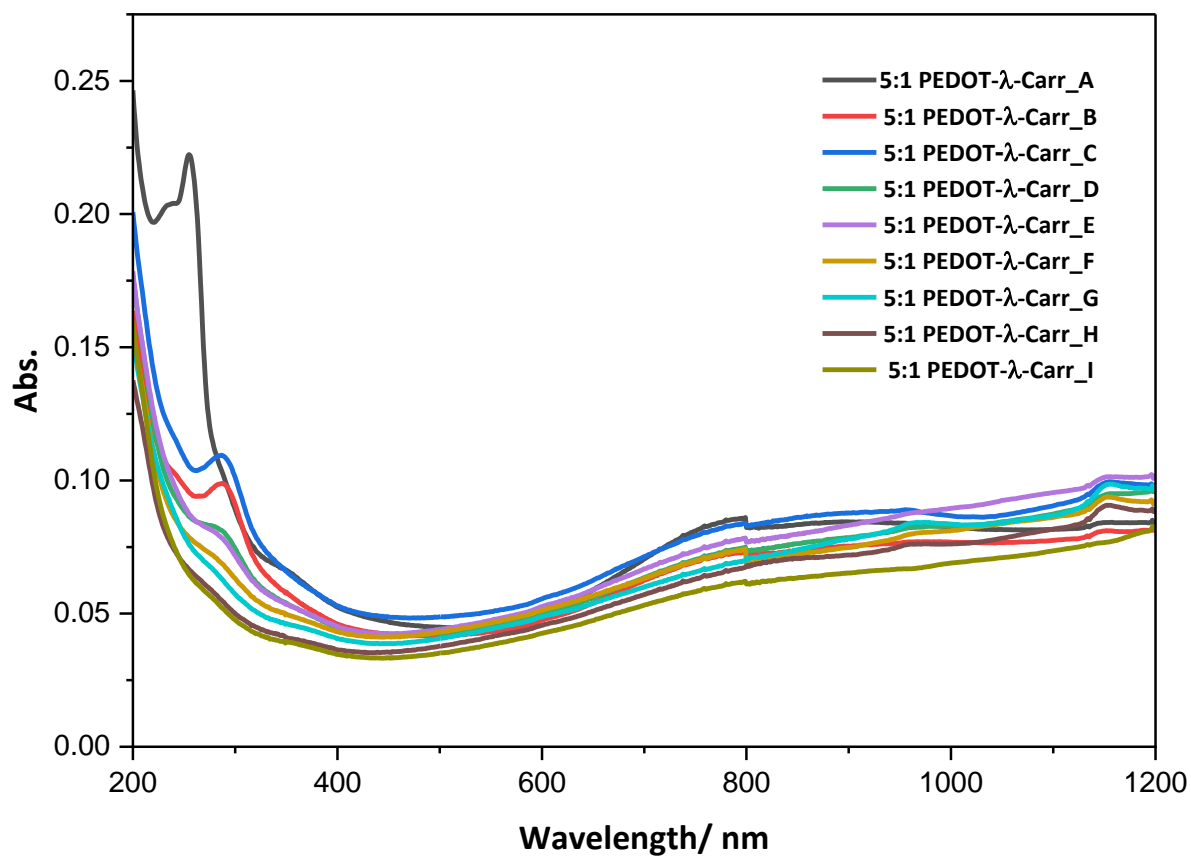


Fig. S18. UV-Vis absorption spectra of fractions A to I of 5:1 PEDOT-λ-Carr.

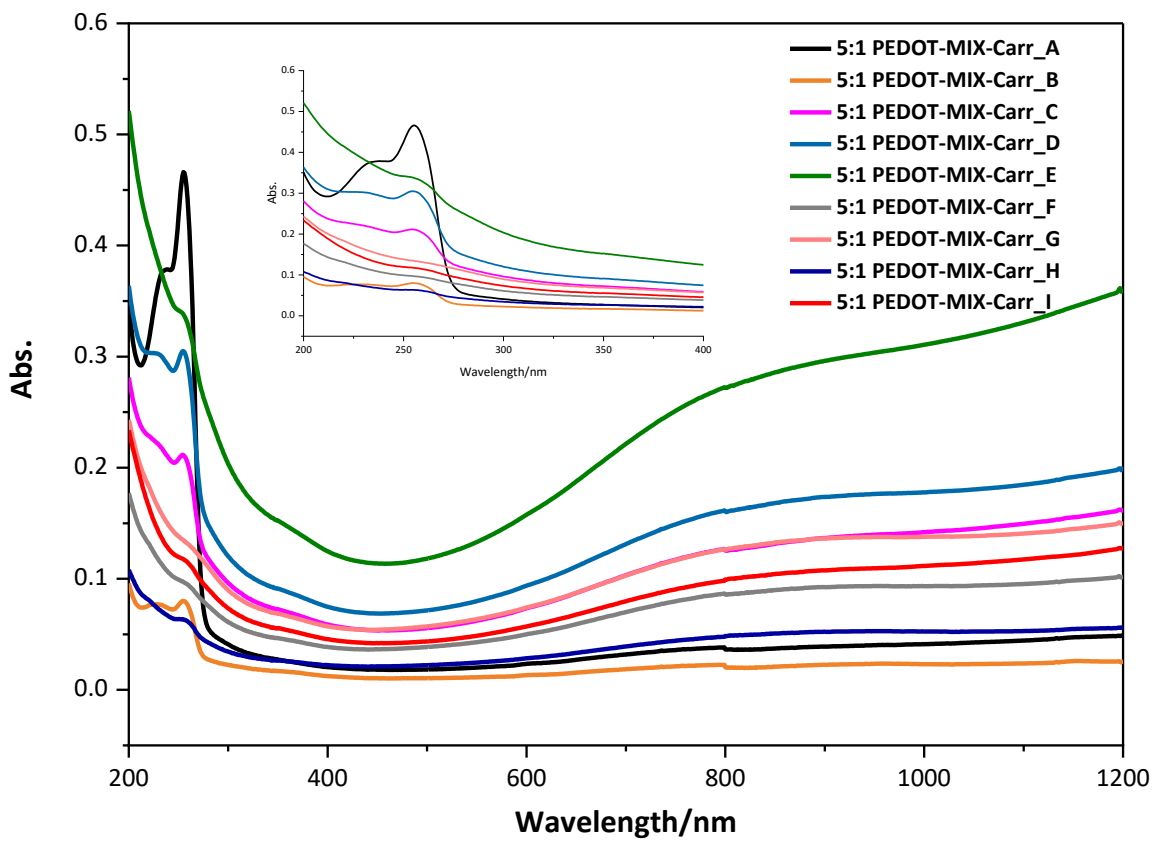


Fig. S19. UV-Vis absorption spectra of fractions A to I of 5:1 *PEDOT-MIX-Carr*.

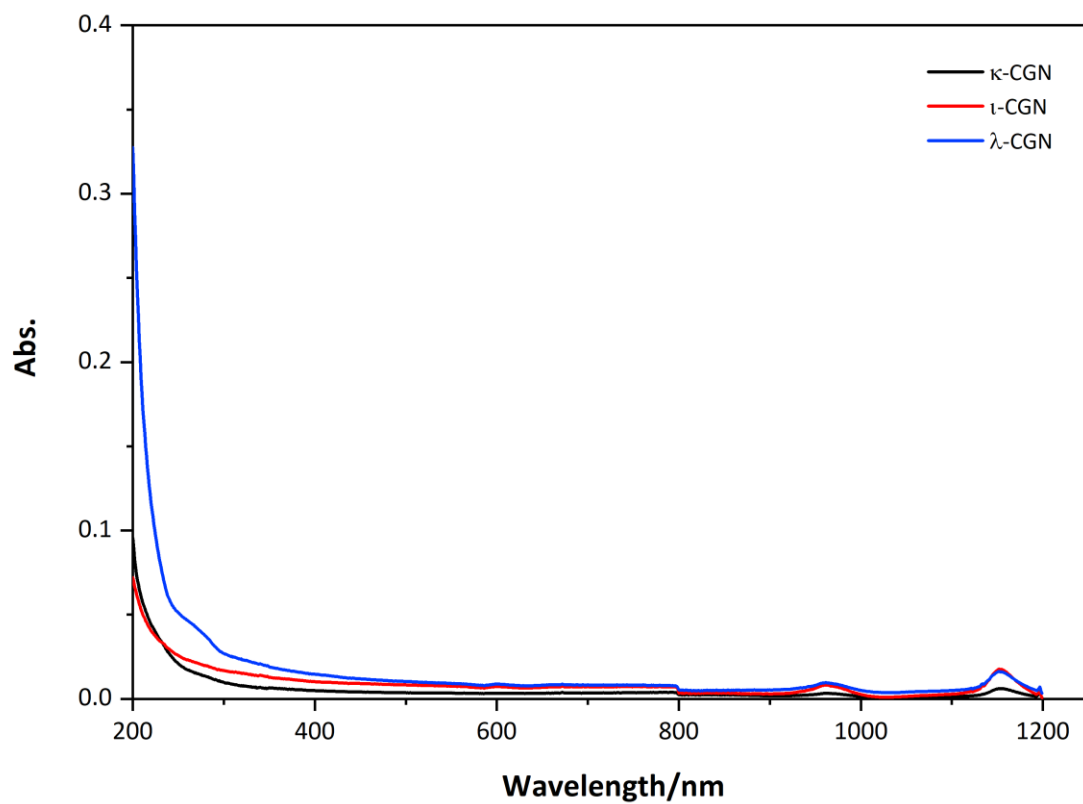


Fig. S20. UV-VIS absorption spectra of pure κ , λ and ι -Carr solutions.

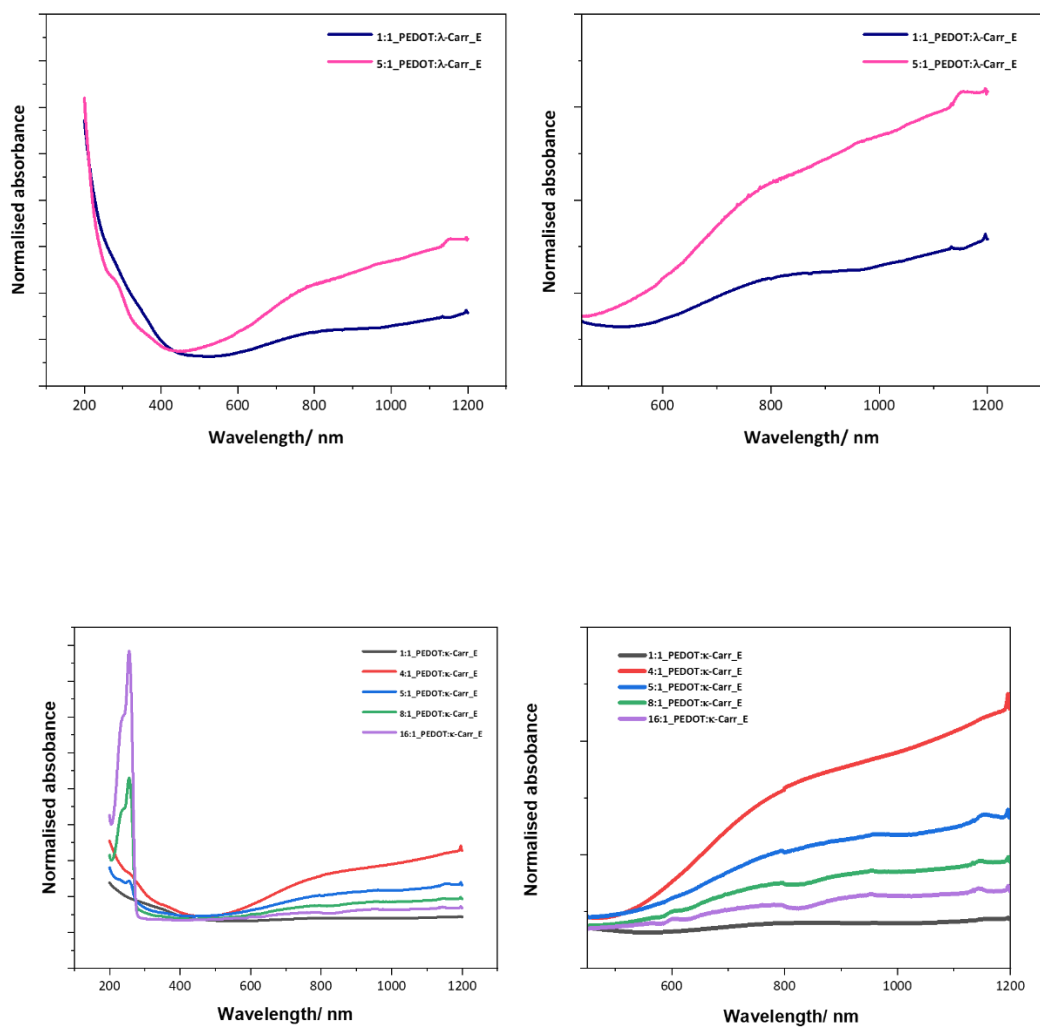


Fig. S21. Normalised UV-Vis absorption spectra of the **PEDOT** κ and λ -Carr products made with different proportions of oxidant to EDOT.

Electron paramagnetic resonance (EPR)

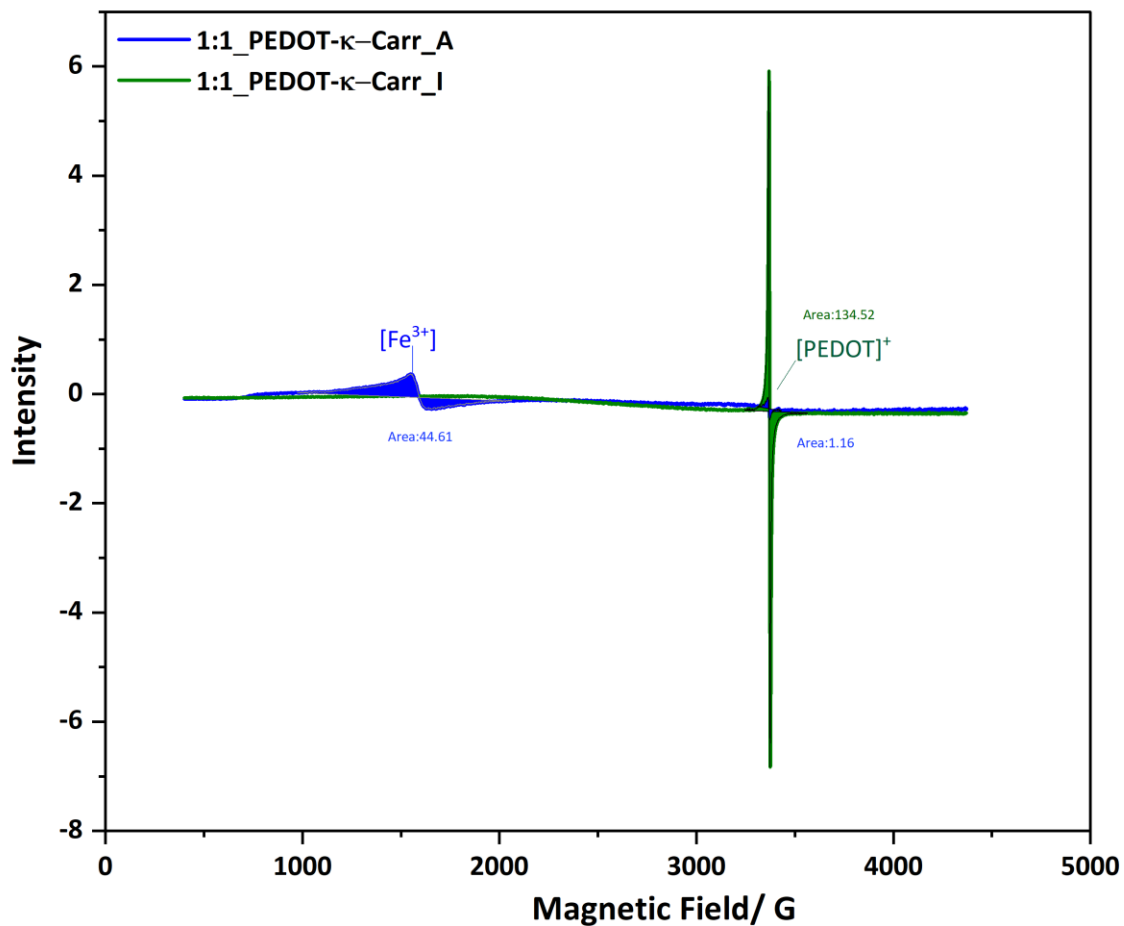


Fig. S22. EPR spectra of two representative samples from the iron(III) catalysed reaction recorded at 77 K, and the area of the different peaks.

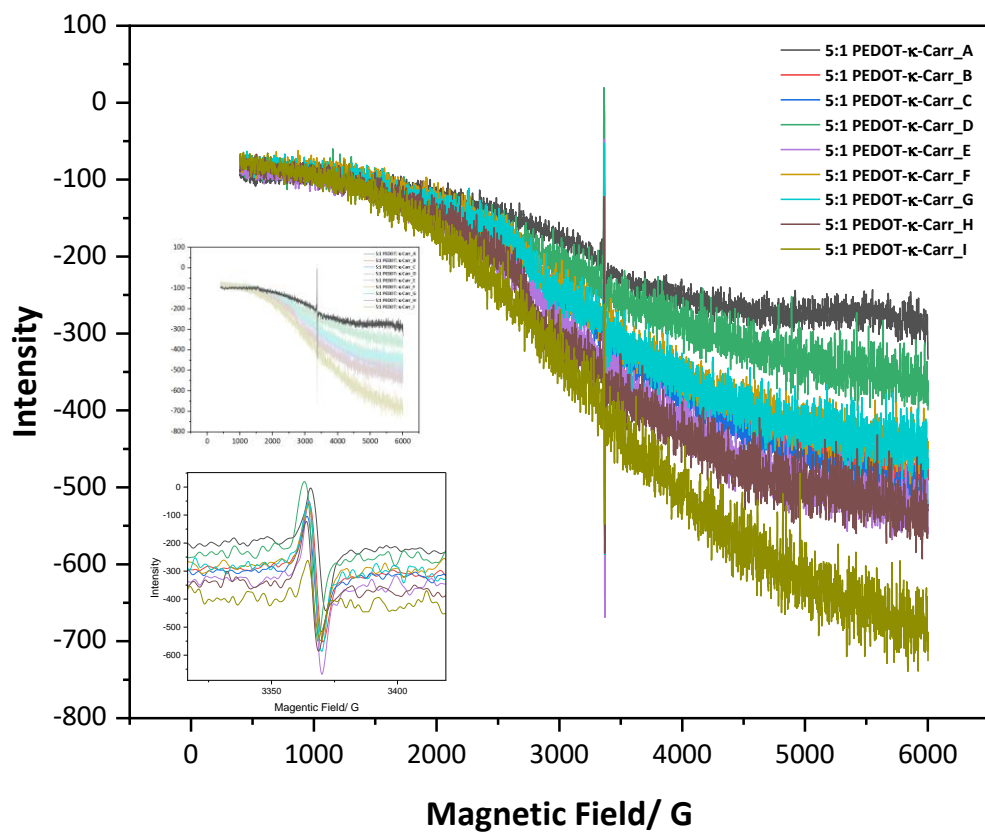


Fig. S23. EPR spectra of nine representative samples from the iron(III) catalyzed of 5:1 PEDOT-κ-Carr reaction recorded at 77 K.

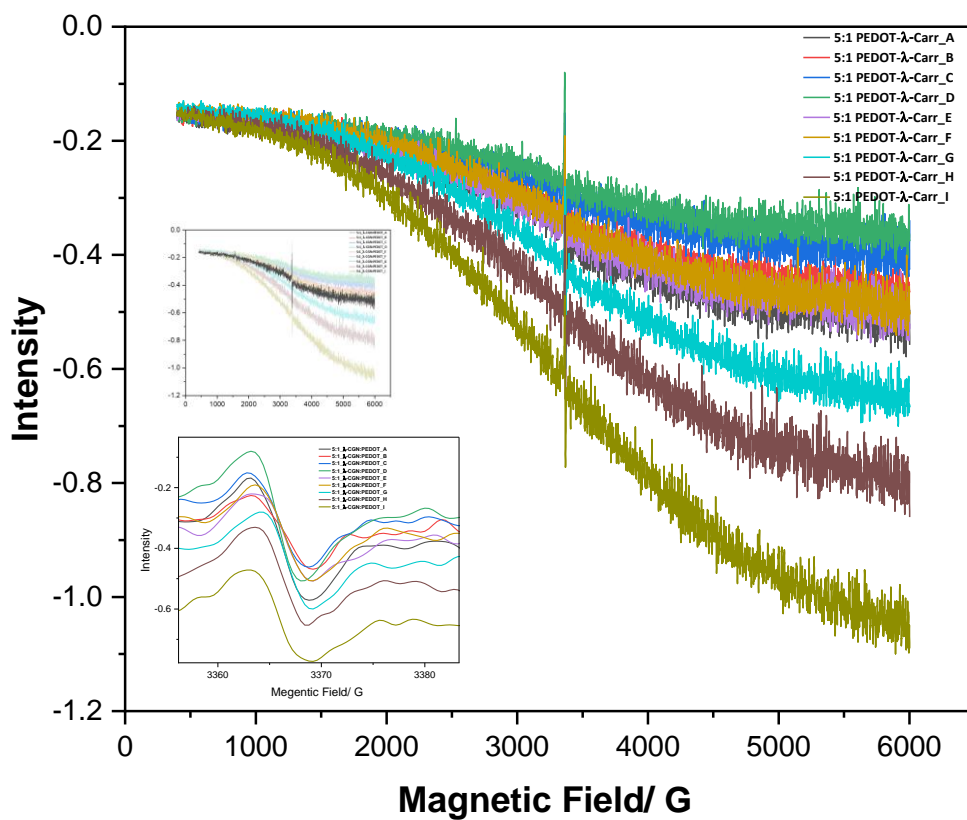


Fig. S24. EPR spectra of nine representative samples from the iron(III) catalyzed of 5:1 PEDOT- λ -Carr reaction recorded at 77 K.

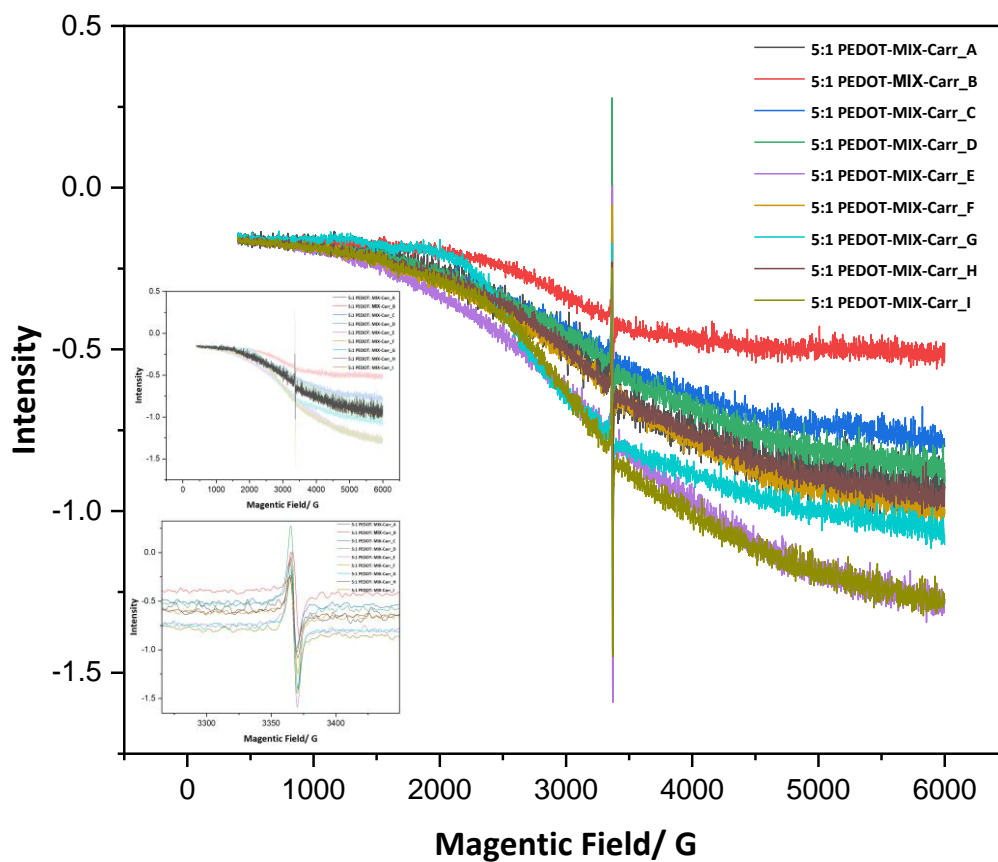


Fig. S25. EPR spectra of nine representative samples from the iron(III) catalysed of 5:1 PEDOT-MIX-Carr reaction recorded at 77 K.

MALDI-TOF mass spectrometry (MALDI-TOF MS)

κ -Carr

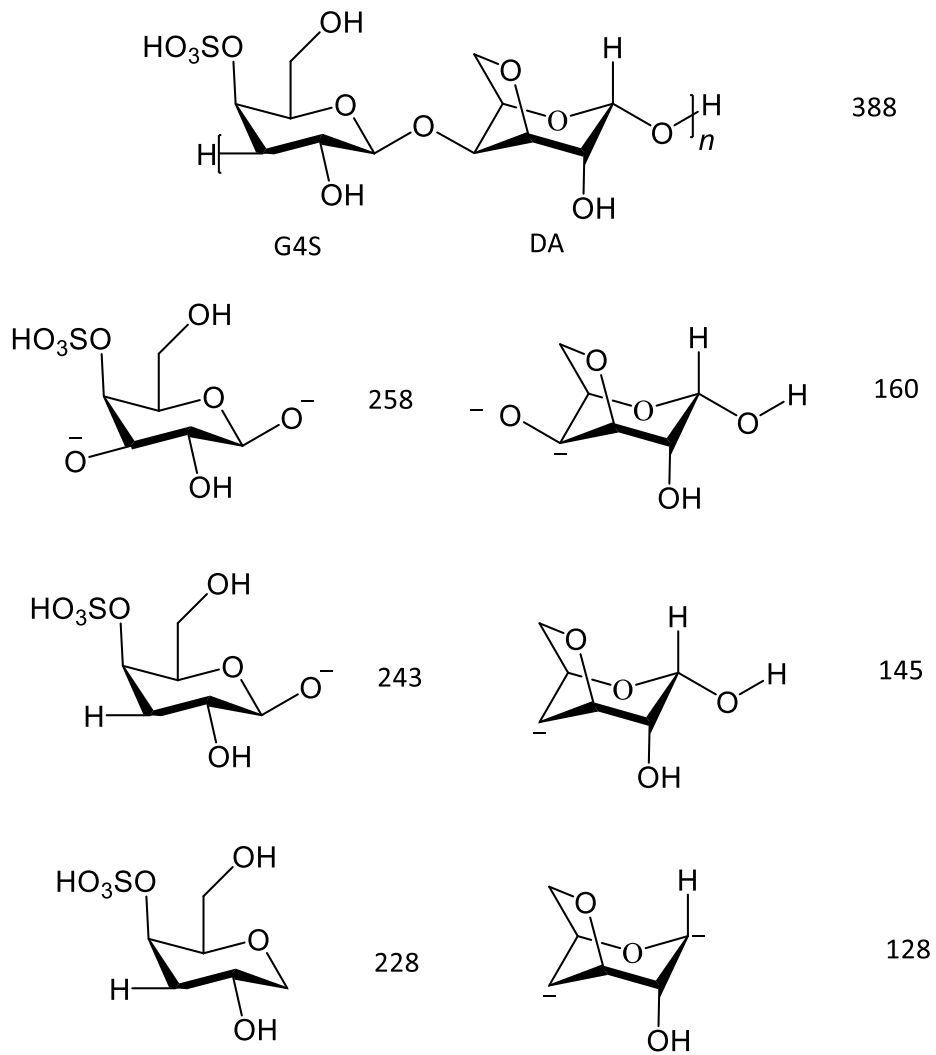


Fig. S26. MALDI-TOF MS structures of the fragments of PEDOT- κ -Carr.

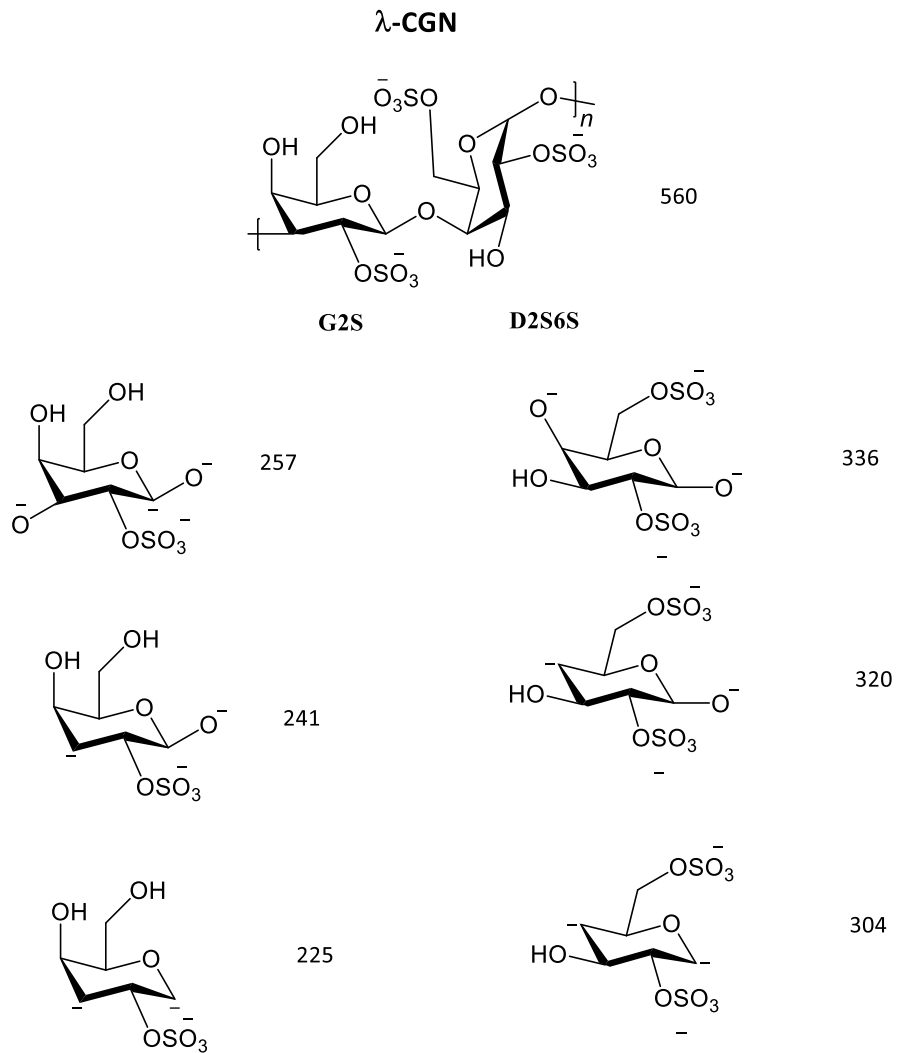


Fig. S27. MALDI-TOF MS structures of the fragments of *PEDOT- λ -Carr.*

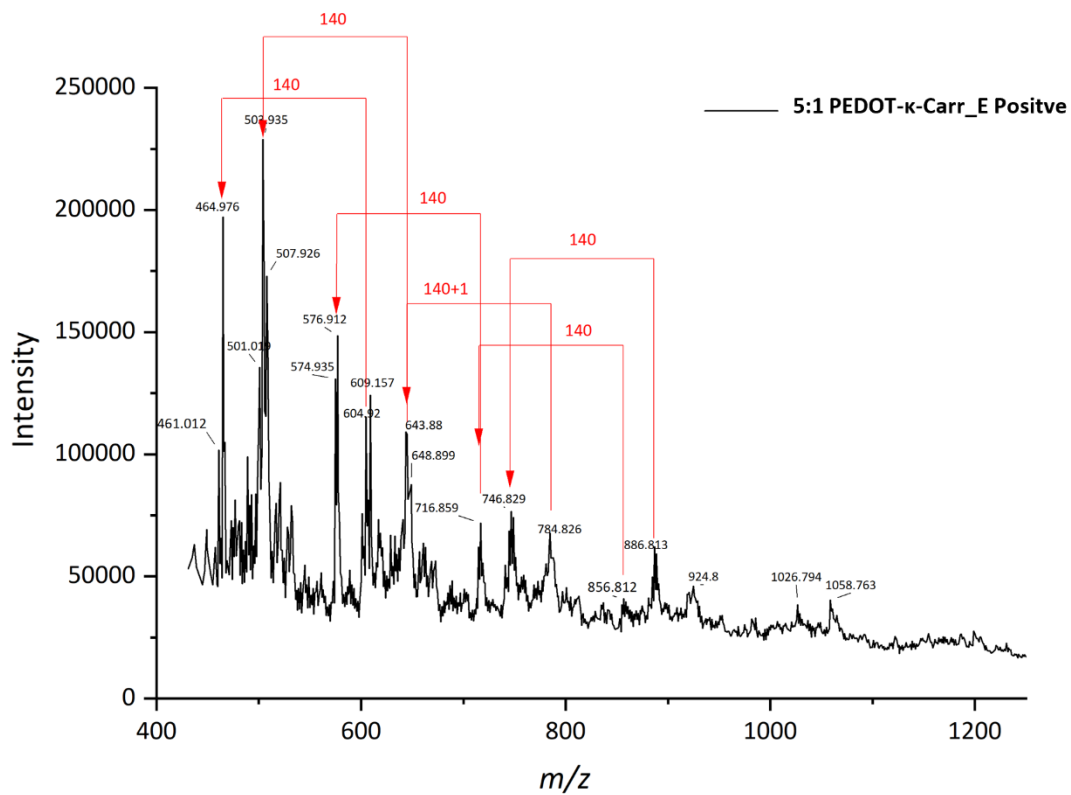


Fig. S28. MALDI-TOF MS spectra of 5:1 **PEDOT- κ -Carr (E)** in linear positive MS mode. With one repeat fragment unit (140 molecular weight fragment from PEDOT)

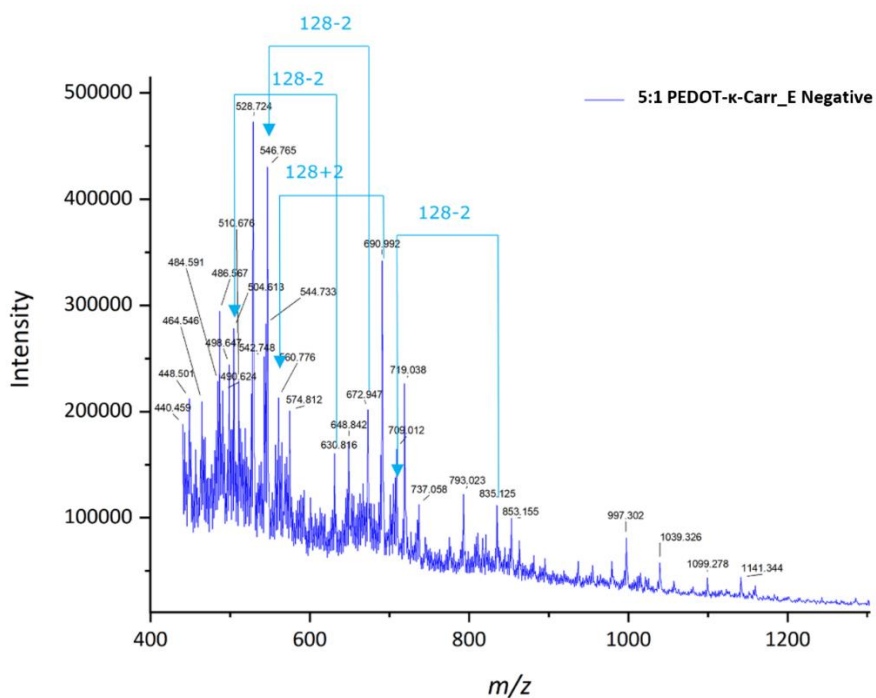
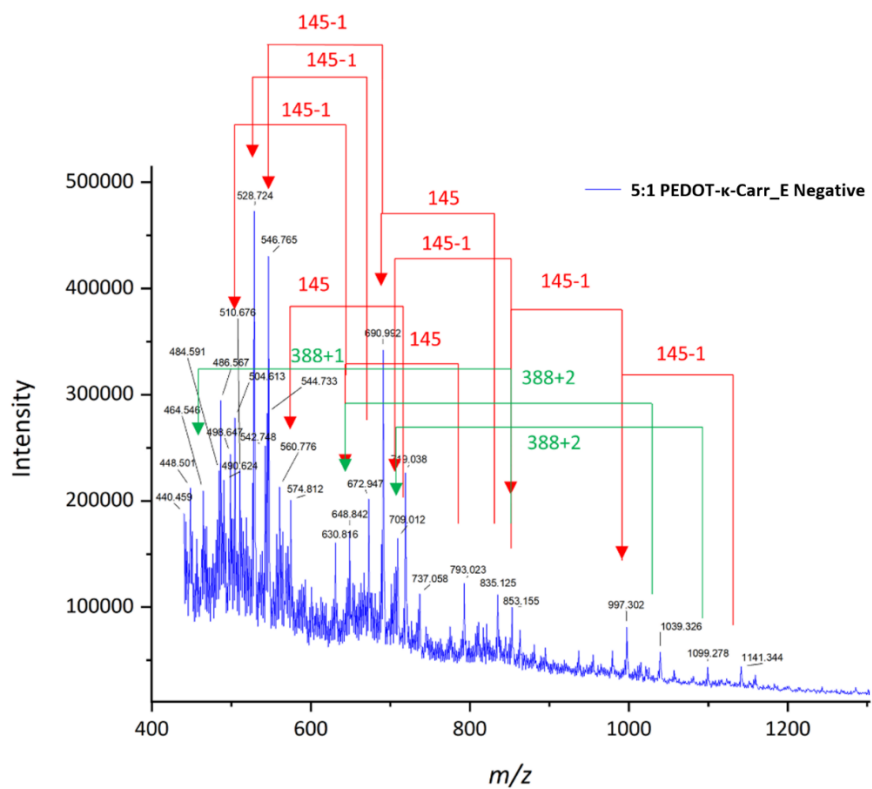


Fig. S29. MALDI-TOF MS spectra of 5:1 **PEDOT- κ -Carr** (E) in linear negative MS mode. With three repeat fragment units (128, 145, 388 molecular weight fragment from κ -Carr)

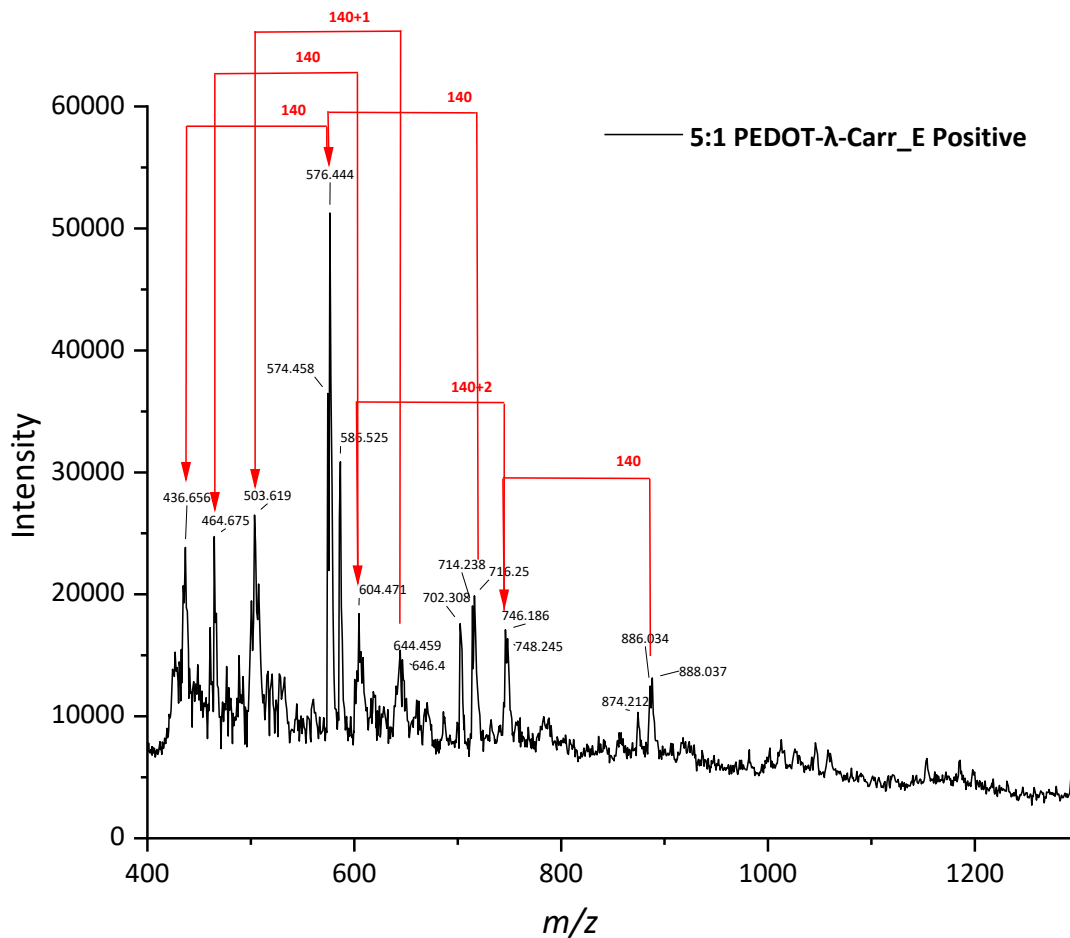


Fig. S30. MALDI-TOF MS spectra of 5:1 **PEDOT-λ-Carr (E)** in linear positive MS mode. With one repeat fragment unit (140 molecular weight fragment from PEDOT)

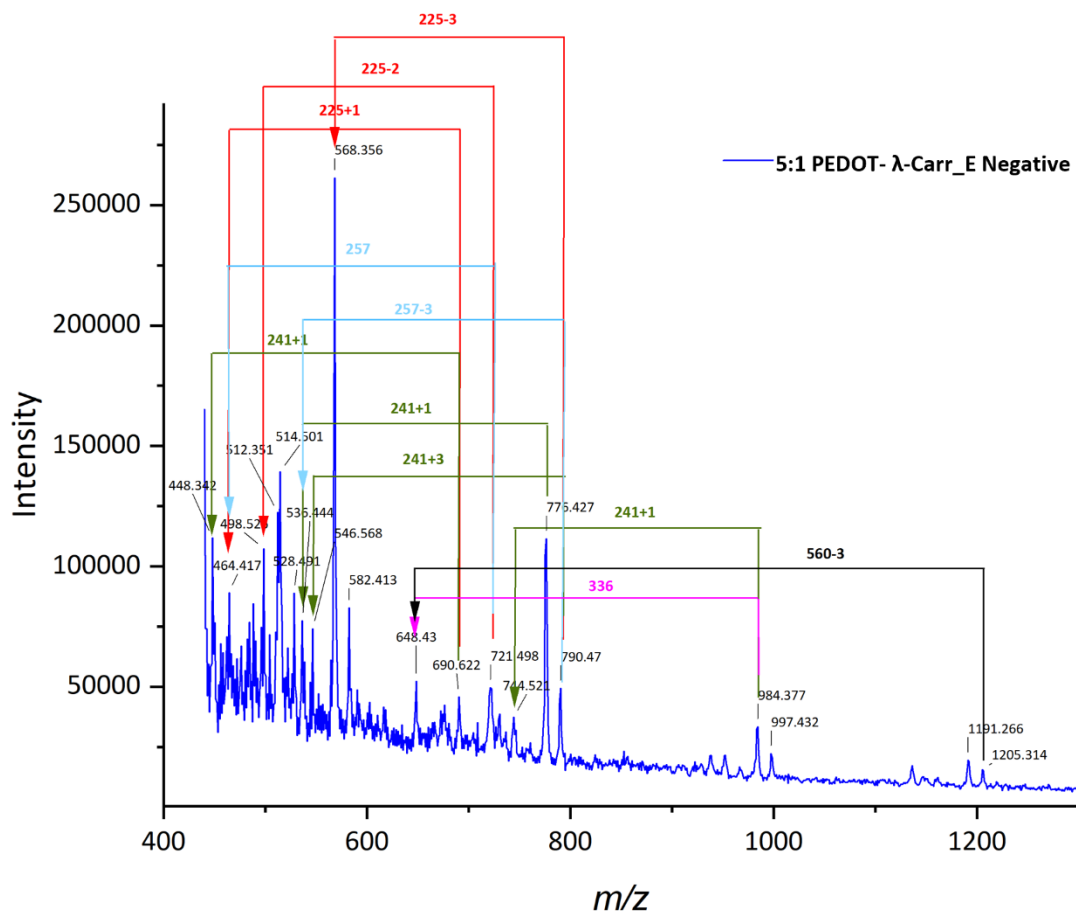


Fig. S31. MALDI-TOF MS spectra of 5:1 PEDOT-λ-Carr (E) in linear negative MS mode. With three repeat fragment units (128, 145, 388 molecular weight from λ-Carr)

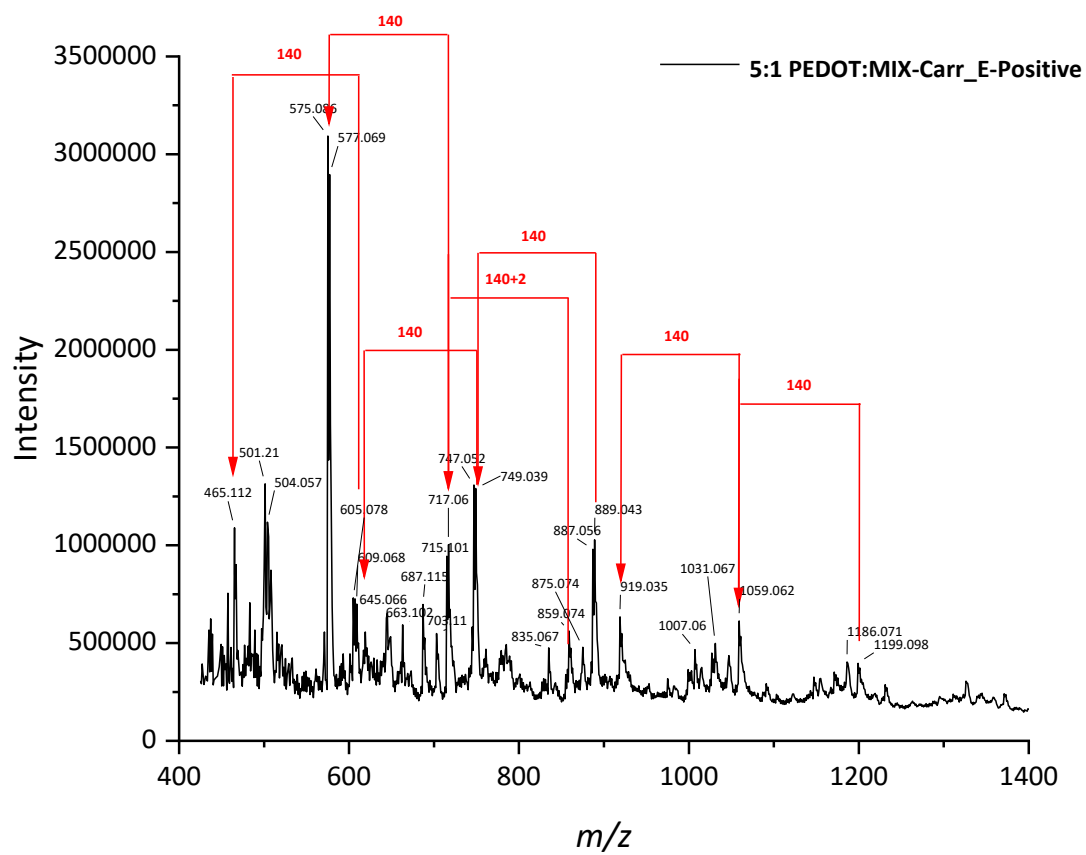


Fig. S32. MALDI-TOF MS spectra of 5:1 PEDOT-MIX-Carr (E) in linear positive MS mode. With one repeat fragment unit (140 molecular weight fragment from PEDOT)

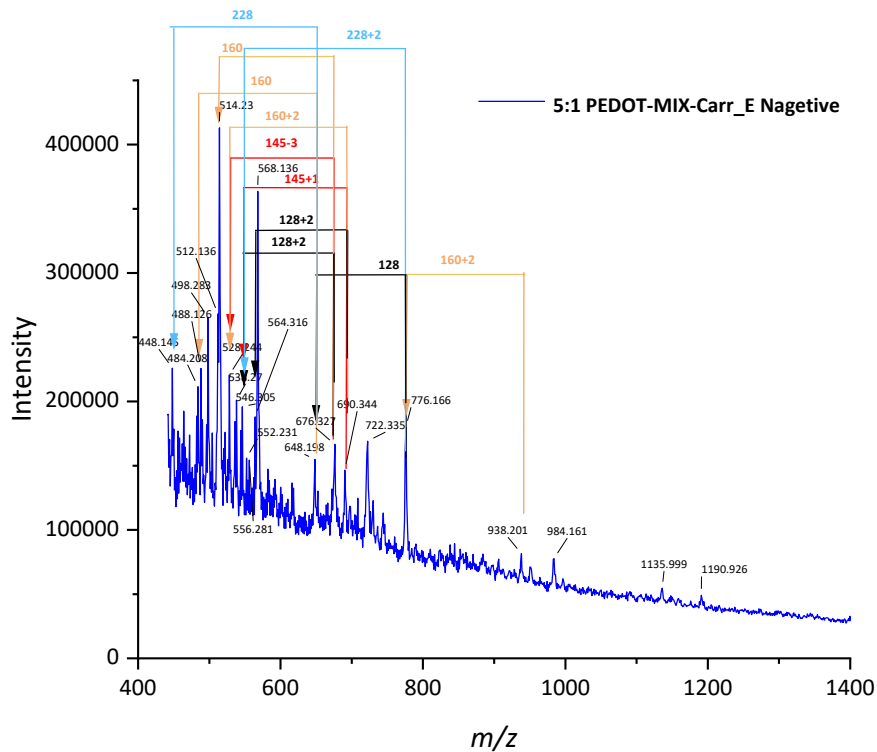
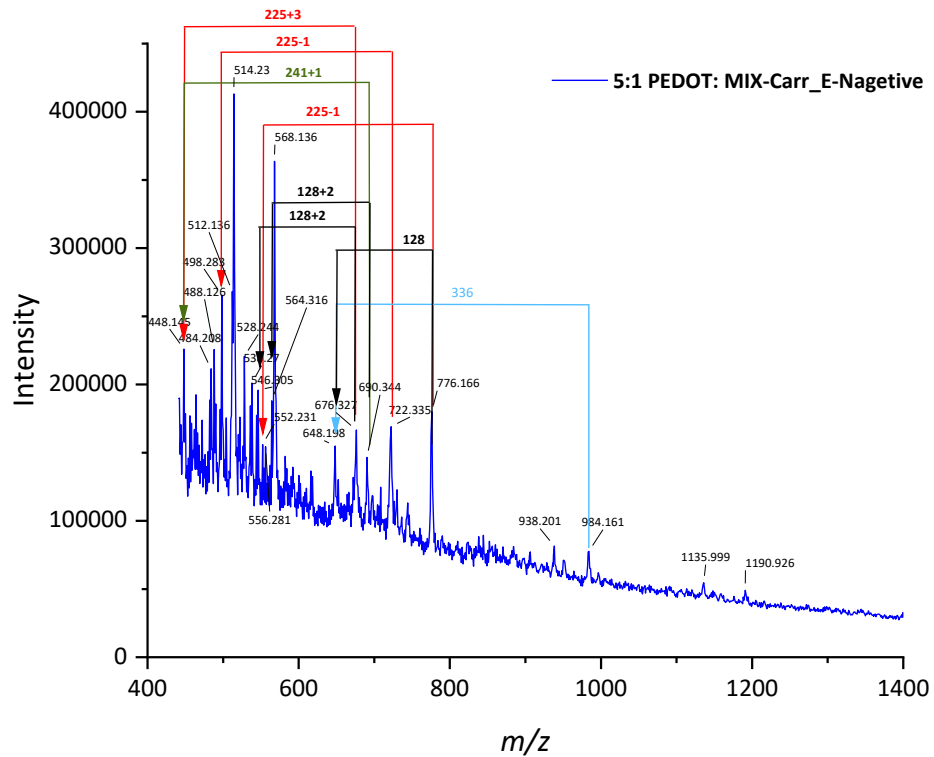


Fig. S33. MALDI-TOF MS spectra of 5:1 *PEDOT-MIX-Carr* (E) in linear negative MS mode. With seven repeat fragment units (128, 145, 388 molecular weight from λ -Carr)

XPS

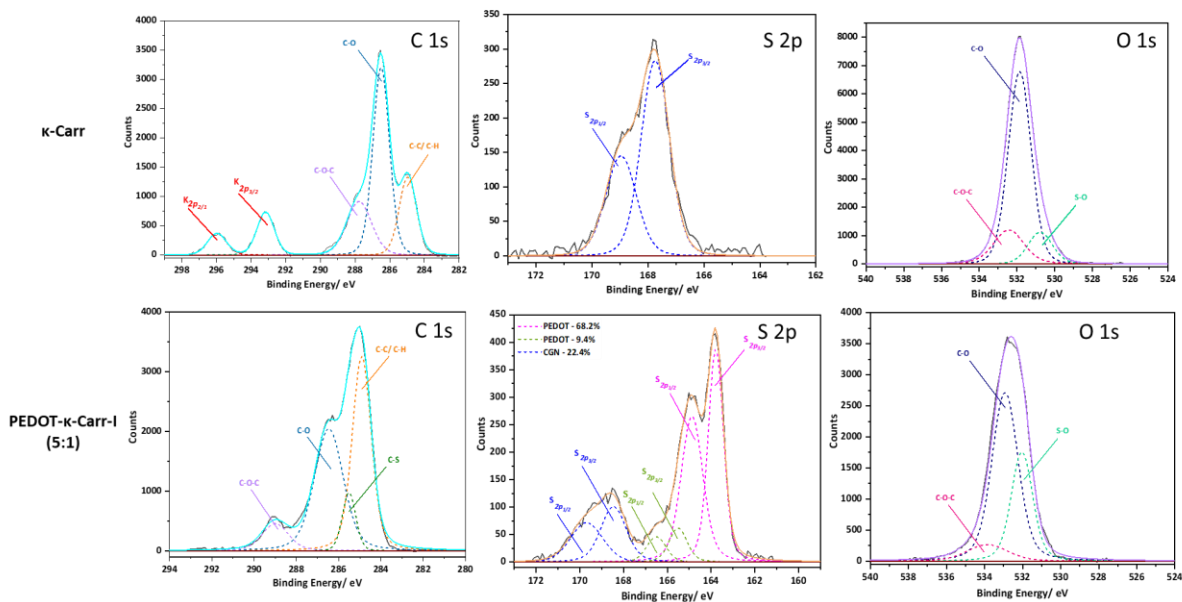


Fig. S34. Relevant regions of the XPS spectra of κ -carrageenan (top) and PEDOT- κ -Carr (I) (bottom). In the C1s region, the as-used κ -carrageenan shows peaks from potassium that is present as a counter-ion

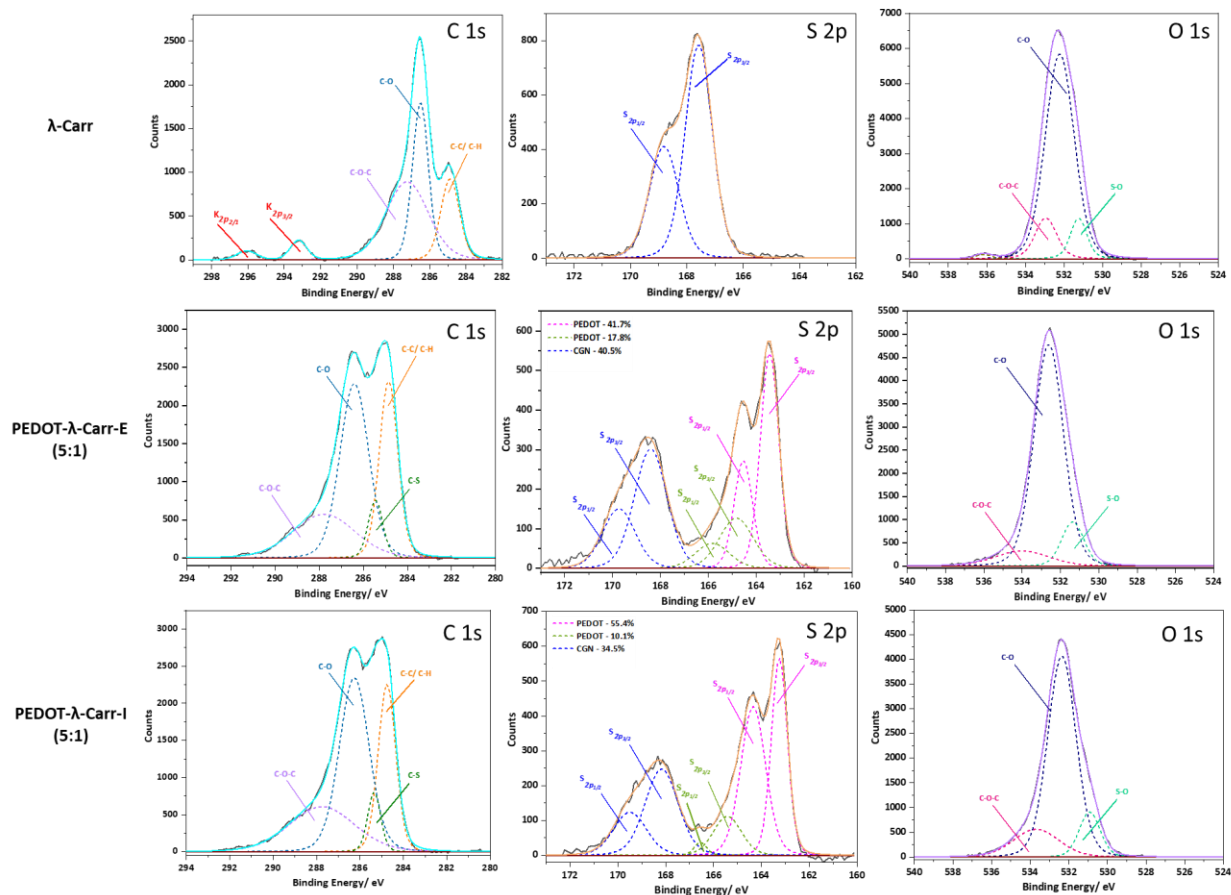


Fig. S35. Relevant regions of the XPS spectra of pure λ -carrageenan (top), *PEDOT- λ -Carr (E)* (middle) and *PEDOT- λ -Carr (I)* (bottom). In the C1s region, the as-used λ -carrageenan shows peaks from potassium that is present as a counter-ion

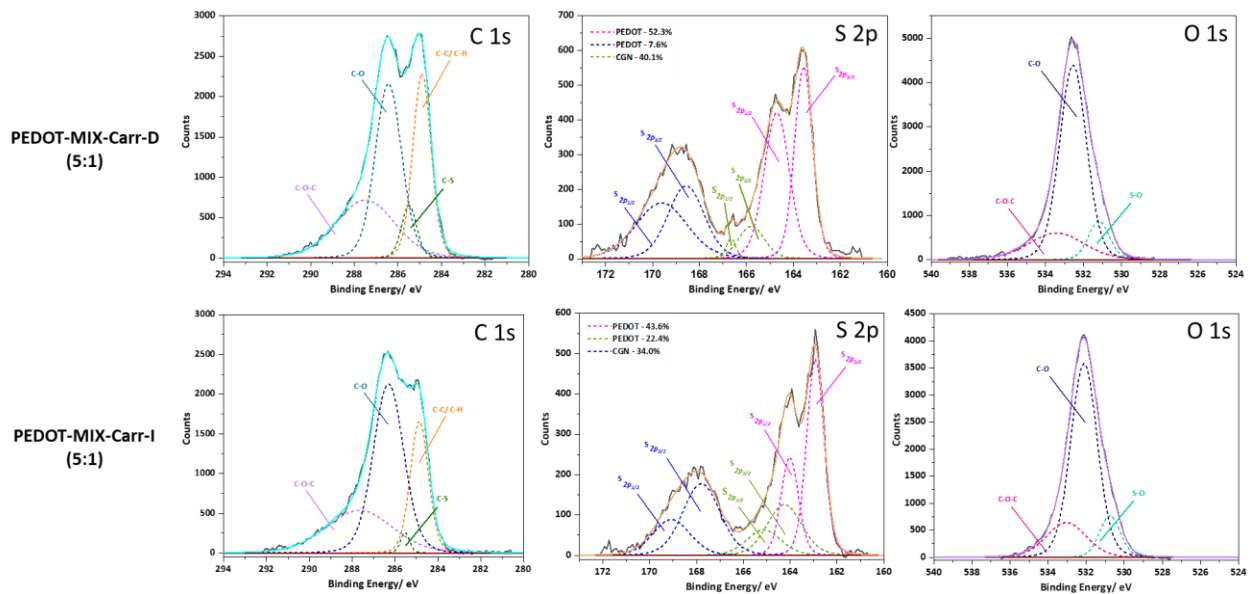


Fig. S36. Relevant regions of the XPS spectra of *PEDOT-MIX-Carr (D)* (top) and *PEDOT-MIX-Carr (I)* (bottom).

Raman Spectroscopy

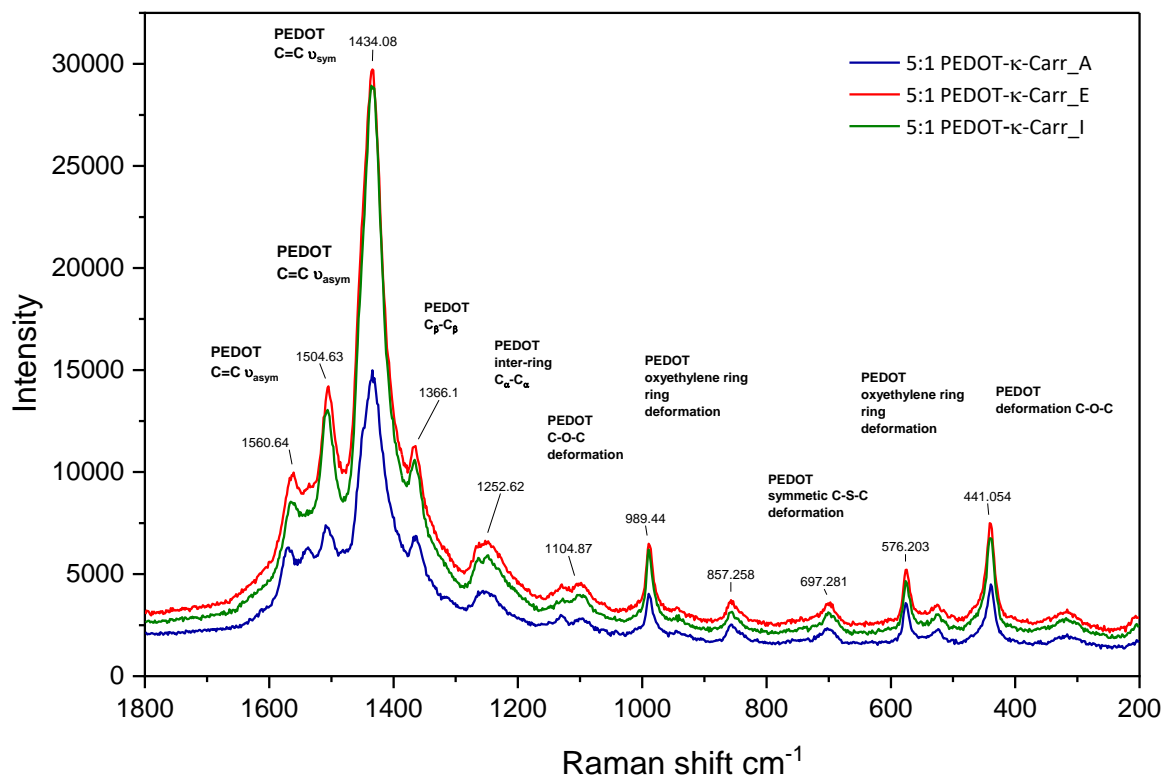


Fig. S37. Raman spectra of films of fractions A, E and I of the PEDOT- κ -Carr materials.

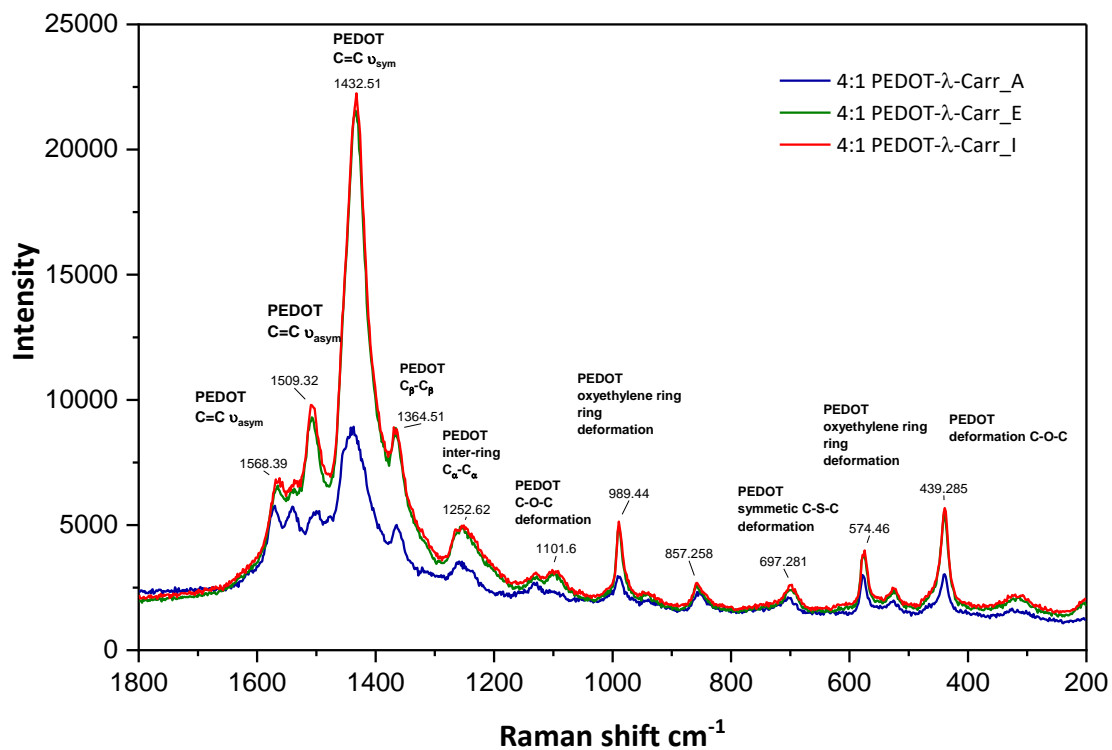


Fig. S38. Raman spectra of films of fractions A, E and I of the **PEDOT- λ -Carr** materials.

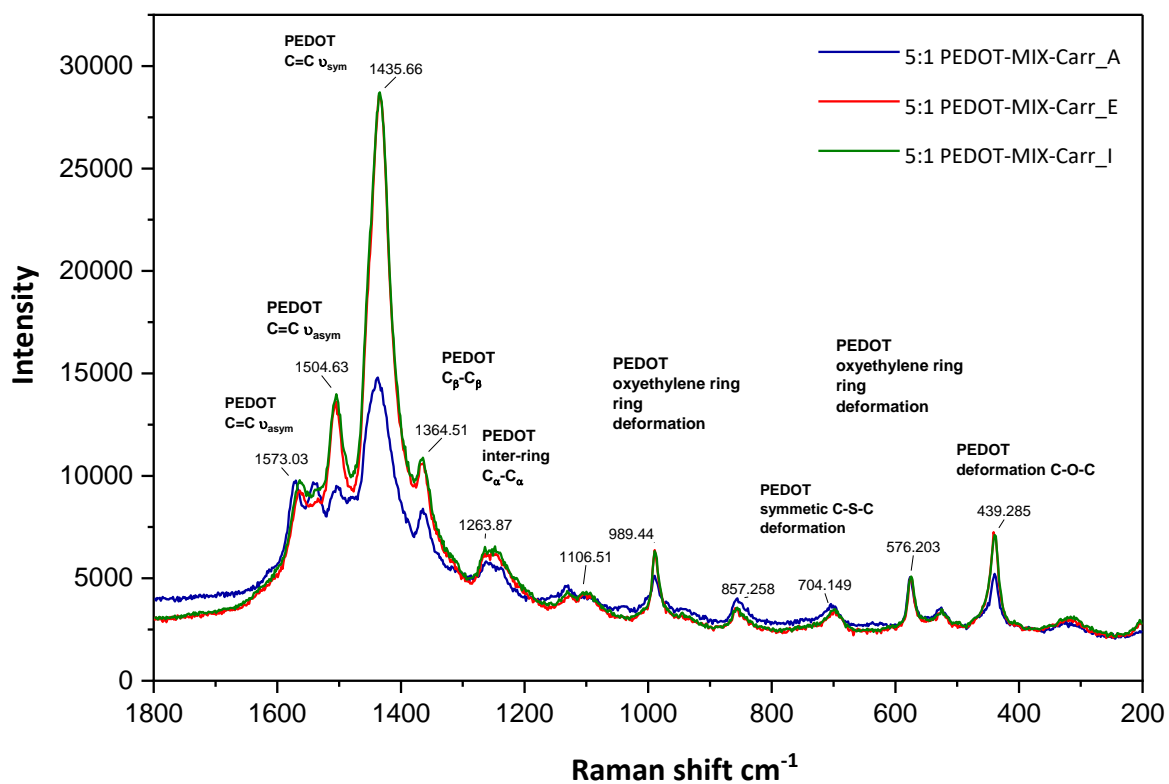


Fig. S39. Raman spectra of films of fractions A, E and I of the **PEDOT-MIX-Carr** materials.

ATR-FT-IR Spectroscopy

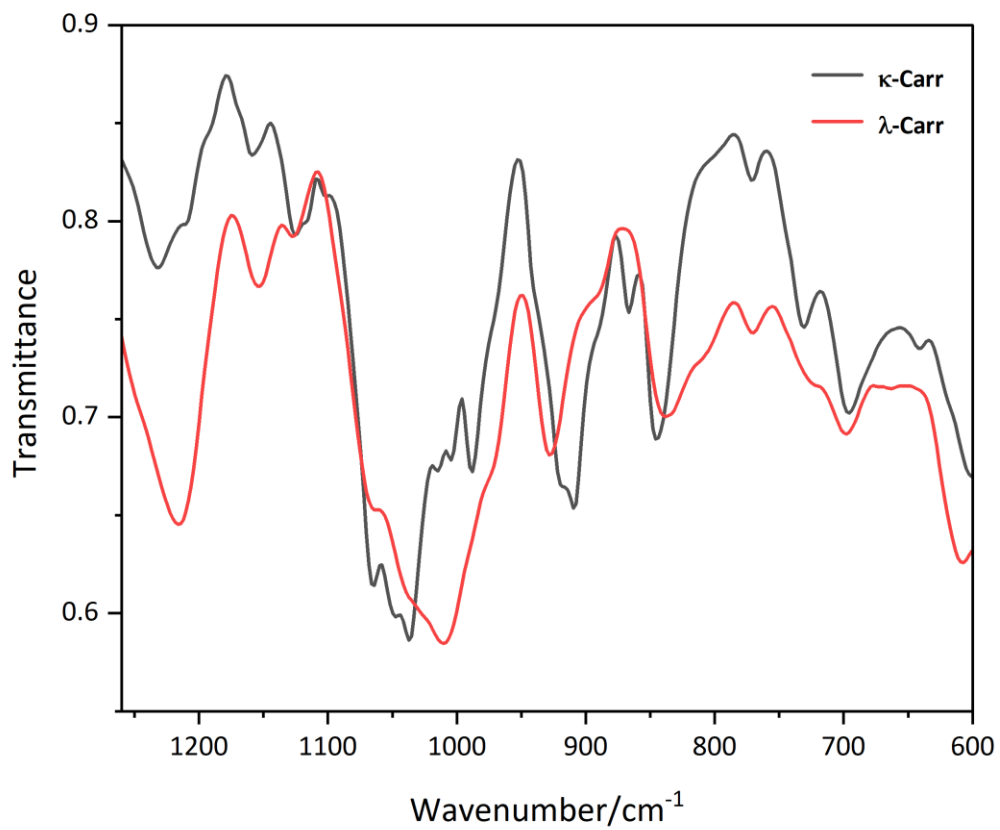


Fig. S40. FT-IR spectra of two pure carrageenans (κ -Carr and λ -Carr)

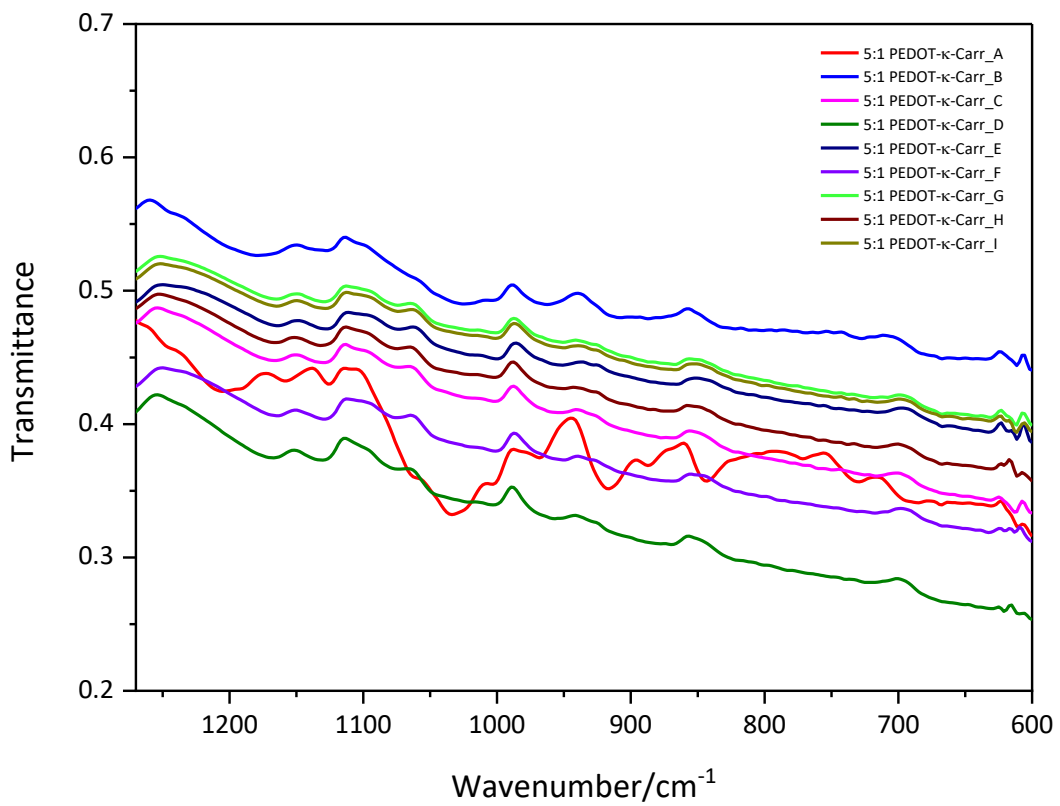


Fig. S41: FT-IR spectra of vacuum dried composites. FT-IR spectrum of 5:1_PEDOT-k-CGN A to I. Air background and measurement scans = 100

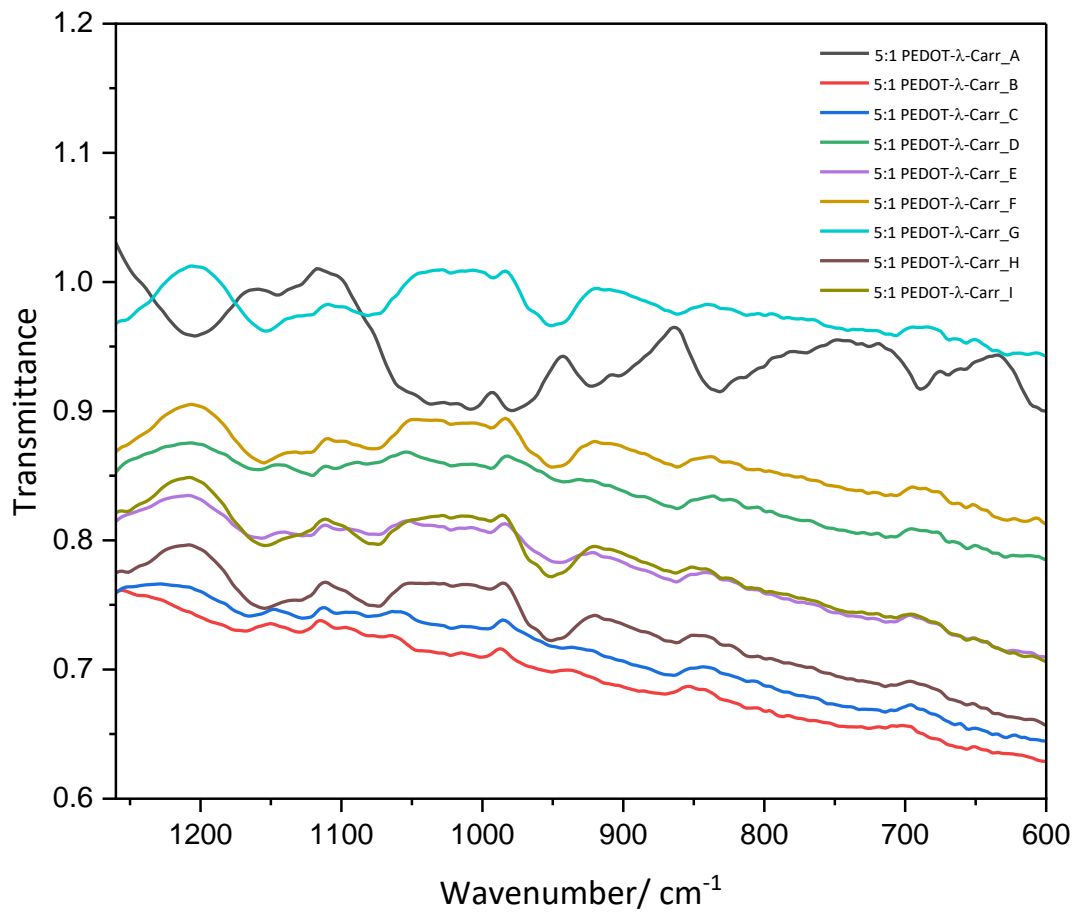


Fig. S42: FT-IR spectra of vacuum dried composites. FT-IR spectrum of 5:1_PEDOT-λ-CGN A to I. Air background and measurement scans = 100

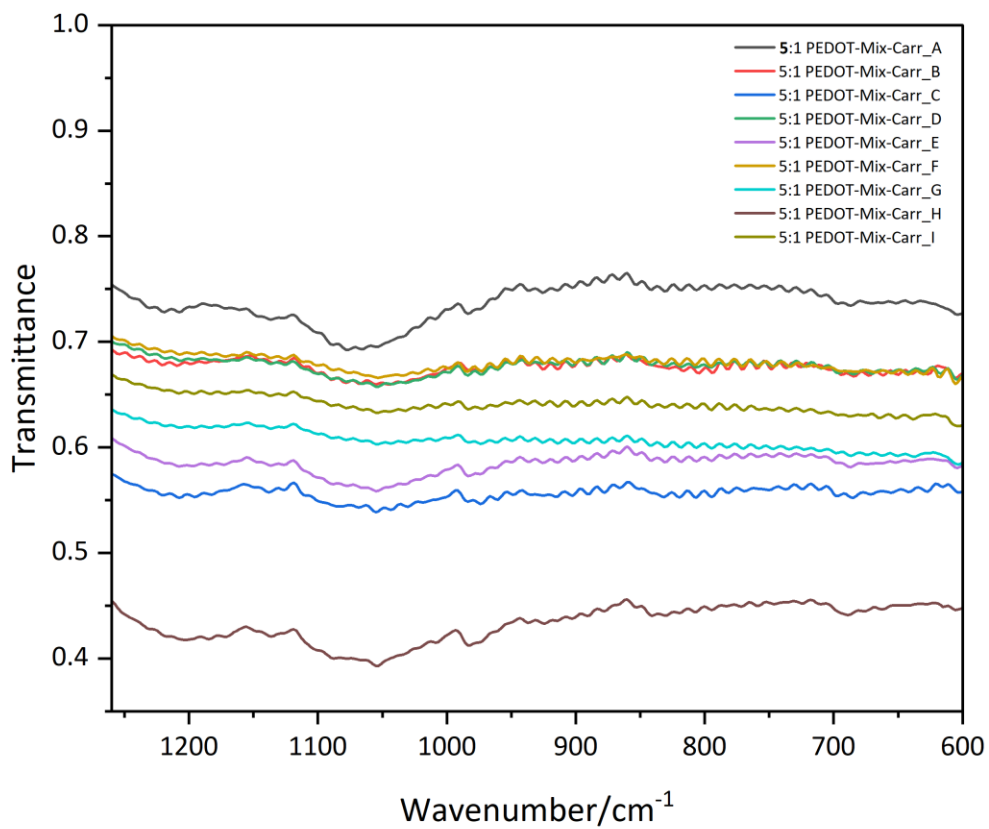


Fig. S43: FT-IR spectra of vacuum dried composites. FT-IR spectrum of 5:1 *PEDOT-Mix-Carr* A to I. Air background and measurement scans = 100

Seebeck Device Configuration

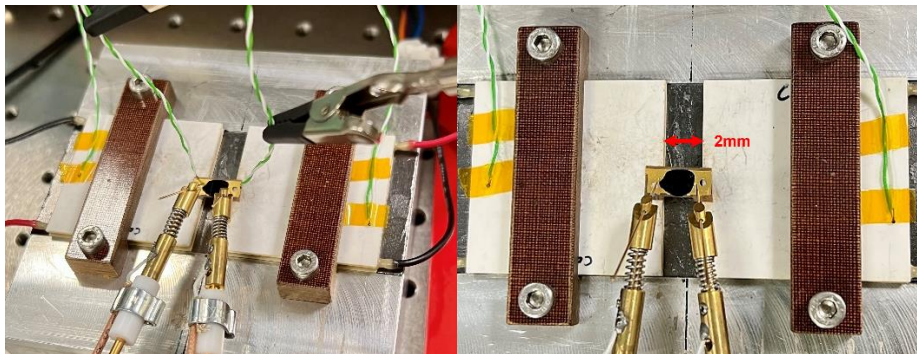


Fig. S44: The device for measuring Seebeck coefficient .

Elemental Analysis

Table. S1. The elemental analysis of different PEDOT-Carr A, E, I fractions

	1:1 PEDOT-κ-Carr			5:1 PEDOT-κ-Carr			8:1 PEDOT-κ-Carr			4:1 PEDOT-λ-Carr		
Fractions	A	E	I	A	E	I	A	E	I	A	E	I
%C	26.1	36.2	41.9	24.8	38.8	41.2	26.4	35.1	39.8	26.3	34.7	36.0
%H	2.8	3.0	3.2	3.8	3.6	3.9	3.6	3.7	3.7	2.7	3.4	3.8