

# **Are the Doping Anion Company Cations Influential in the Conducting Organic Polymers? The Case of the Popular PEDOT.**

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Conducting Organic Polymers (COPs) are made of a conjugated polymer backbone with a certain degree of oxidation. These positive charges are compensated by the doping anions that were introduced in the synthesis pot with their company cations. This work deals on the influence of these cations in the stoichiometry and physico-chemical properties of the resulting COPs, something that has been overlooked and as we prove, is highly relevant. As doping anion we have chosen the metallocarborane  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ , that acts as a thistle. This anion binds to the company cations with a distinct strength. If the strength is weak the more prone is the doping anion charge to compensate the positive charge of the polymer, the opposite is also true. Thus its ability

to compensate the polymer positive charges is tuned. This determines the stoichiometry of the polymer. As polymer we have studied PEDOT, and as cations  $\text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ . Noticeably  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  has grouped these cations in two sets,  $\text{Cs}^+$  and  $\text{H}^+$  in one and  $\text{Na}^+$  and  $\text{Li}^+$  in the second that have influenced the stoichiometry 2 EDOT: 1  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  for  $\text{Cs}^+/\text{H}^+$  and 3 EDOT: 1  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  for  $\text{Na}^+/\text{Li}^+$ . The distinct stoichiometries have been manifested in the physico-chemical properties of the COPs: electrochemical response, electronic conductivity, ionic conductivity, and capacitance.

## Introduction

Conducting Organic Polymers (COP) are outstanding materials that have received great attention since their discovery. Among the best studied are polypyrrole (PPy), polythiophene (PTh), polyaniline (PANI), polyphenylene vinylene (PPV), and polyethylene dioxythiophene (PEDOT). They are produced by chemical or electrochemical oxidation of the adequate monomer precursors. The synthesis process can be formally considered made of two oxidation stages: one leading to the construction of the polymer backbone (neutral polymer) and the second step leading to the oxidation of the polymer (formation of a semiconductor material). In the second step positive charges are generated in the polymer that require to be compensated by anions commonly known as doping agents. These anionic doping agents in the polymer synthesis medium are necessarily accompanied by cations. The significance of these company cations in the synthesis of the polymer, in its structure and in its final physico-chemical properties has been neglected; they were considered innocent, non-participating entities. There are several possible reasons for this. If small doping anions, e.g.  $\text{Cl}^-$ , are studied it could be contemplated that only them were required to compensate the positive charges on the polymer; further, in the reduction process of the charged polymer the anions would be driven out of the polymer bulk as would no longer be needed; conversely for large doping anions, e.g. polystyrene sulfonate, the reduction process would be different as the large doping anions are stuck within the polymer matrix and to maintain electroneutrality cations are driven in. Thus during the oxidation process of the COP with large doping

anions, cations are removed from the matrix and during the reduction process cations are taken in. This is the usual reference to cations when dealing with COPs. As said these COPs can be oxidized and reduced. They fall within the definition of redox polymers, to say polymers that alter their properties after gaining or losing electrons in a reversible way.<sup>1</sup> All the above mentioned polymers can have pendant arms, as is common with conventional organic polymers. The reversible redox reaction may occur in the polymer main-chain, as in the case of conducting organic polymers (COP) or in side-groups, mostly made of ferrocene,<sup>1-8</sup> and few examples with cobaltocene,<sup>9-11</sup> cobaltobis(dicarbonyl)<sup>12-16</sup> and cobaltopolypyridyl<sup>17, 18</sup> units. The redox process can become more complex but may provide more challenging properties if the redox centers are both in the conjugated backbone and in the side branches.<sup>1</sup> Polymers with optical, mechanical or chemical properties or displaying ionic or electrical conductivity may have these properties altered depending on their oxidation state. Because of their electrochemical tunability these polymers can find applications in batteries,<sup>19, 20</sup> supercapacitors,<sup>21</sup> biosensors,<sup>22</sup> electrochromic devices,<sup>23, 24</sup> and medical applications<sup>25, 26</sup> among others. Remarkably ferrocene has been the most common redox reversible organometallic moiety incorporated as pendant arm. It has also been part of polymer backbones both in conjugated and non-conjugated systems.<sup>2, 4</sup> Currently, the study of polymers incorporating transition metals is gaining momentum because of their inherent catalytic, magnetic, redox, light absorption and emission properties of the metals.<sup>27</sup> The electronic and electrochemical properties of the polymers containing transition metal atoms do not depend exclusively on the metal but also on the conjugation of the polymer main chain.<sup>28</sup>

Among the different conducting polymers mentioned above, today poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is the most promising because of its high conductivity, easy processability and commercial availability. PEDOT:PSS is used as a transparent conductive oxide (TCO), as a hole-conducting layer or electrochromic layer for organic light-emitting diodes (OLEDs) and organic photovoltaic devices (OPVs). For application in biology PEDOT:PSS has some weaknesses mostly due to its low biofunctionality (PEDOT) and biocompatibility (PSS) replacing the latter with biopolymer.<sup>29</sup>

Metallacarboranes of which cobaltabisdicarbollide  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ ,  $[\text{COSANE}]^-$ , is the most researched, are redox reversible highly stable species with large possibilities for functionalization. They have been utilized both as components of pendant arms and as doping agents with PPy,<sup>12-15</sup> and as doping agents in a prospective PEDOT polymer.<sup>30</sup> Cobaltabisdicarbollide has been proven to generate hydrogen and di-hydrogen bonds highlighting their self-assembling in water generating micelles and vesicles,<sup>31, 32</sup> and their interaction with weakly acidic X-H units or with lone pair elements. Cobaltabisdicarbollide in its more common form is anionic, is an 18 electron obeying complex, has a sandwich structure, is redox reversible with 3 well documented redox couples and presents an outer sphere electron transfer mechanism. Because of its hydrogen bonding capacity it can easily form interactions with lone pair containing elements. Therefore it can be highly attractive assembling an outer sphere unique redox reversible tunable anion performing as a doping agent with a redox reversible PEDOT polymer. The metallacarborane offers a unique opportunity to do this task as there are few anions that have the chemical, physical and electrochemical properties described earlier. In this paper we will show that the interplay between the anionic doping metallacarborane and the PEDOT is existing despite the redox center is not in a pendant arm. This is assigned to the strong hydrogen bonding between the metallacarborane and the PEDOT. The electrochemical properties of the PEDOT: $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  in water, its capacitance, its electronic conductivity and its ionic conductivity compared to PEDOT:PSS will be described, enlightening the relevance of combining two non chemically bonded redox units. But very significant is the trace left by the doping agent counterions, the earlier indicated as company cations, in all aspects of the PEDOT: $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  material from the synthesis, to the structure, to the electrical properties to their applications. *Do not overlook company cations, they may be non-innocent. ; ; ;*

## **Experimental**

### **Materials.**

3,4-Ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich. Cs[COSANE] was obtained from Katchem Spol.sr.o. and H[COSANE],

Na[COSANE] and Li[COSANE] were synthesized from Cs[COSANE] as previously described.<sup>33</sup>

#### **Electropolymerization of PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>).**

The electropolymerization of PEDOT with metallocarboranes has been done by cyclic voltammetry (using a potentiostat/galvanostat Autolab PGSTAT302N) at room temperature in dry acetonitrile using a hand-made one compartment three electrode cell. A glassy carbon was used as the working electrode, a silver wire as the reference electrode and a platinum wire as the counter electrode. The glassy carbon was polished with 0.05  $\mu\text{m}$  alumina powder on Buehler felt pads and then cleaned with water and dried. The reference and counter electrodes were polished with sandpaper, cleaned with acetone and dried. The electropolymerization of PEDOT:M[COSANE] was done by using 10 mM M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>) and 10 mM EDOT in dry acetonitrile. The range of potential used was from -1.0 to 1.5 V vs Ag with a scan rate of 50 mV/s and 20 cycles. In each run about 0.2 mg of PEDOT:M[COSANE] were produced.

#### **Preparation of PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>) pellets.**

20-30 mg of powder PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>) were finely pulverized with a mortar and pestle and put into a pellet-forming device. A force of approximately 10 tons is applied for 2 minutes and the PEDOT:M[COSANE] pellets are formed.

#### **Characterization of PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>).**

**Electrochemical properties.** The electrochemical performances of the polymers were explored by using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and square wave voltammetry (SWV) in a hand-made one compartment three electrode cell. The PEDOT:M[COSANE] polymer coated glassy carbon was used as the working electrode, Ag/AgCl electrode as reference electrode and platinum wire as counter electrode. Cyclic voltammograms of the polymers in water were recorded in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution between -1.8 V and 0.5 V vs Ag/AgCl with a scan rate of 100 mV/s. The linear sweep voltammograms were also run in 0.1 M Na<sub>2</sub>SO<sub>4</sub> in the potential range from 0 to 1.5 V vs Ag/AgCl with a scan rate of 0.5 mV/s and the square wave voltammograms were also recorded

in 0.1 M Na<sub>2</sub>SO<sub>4</sub> between -1.8 V and 0.5 V vs Ag/AgCl with a scan rate of 25 mV/s.

**Scanning electron microscopy (SEM).** The morphology of the polymers was examined using a scanning electron microscope (SEM) Quanta 200 FEG-ESEM (FEI Company) coupled to an Energy Dispersive X-Ray spectrometer (EDX) for elemental analysis of S and Co, operating at an acceleration voltage of 15 kV and low vacuum of 50 Pa. Samples were prepared by depositing few mg of powder polymer on top of a carbon support.

**Fourier transform infrared spectroscopy (FTIR) analysis.** Fourier transform infrared (FTIR) spectra of the polymers were recorded using a single-reflection ATR diamond crystal accessory in a JASCO FT/IR-4700 spectrometer between 600 and 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Backgrounds were acquired before each sample.

**Thermogravimetric analysis (TGA).** Thermal stability of the polymers was performed by thermogravimetric analysis (TGA) on a NETZSCH-STA 449 F1 Jupiter apparatus. All samples (3-6 mg) were weighed in alumina crucibles and were heated in a nitrogen flow (40 mL/min) at a heating rate of 10 K/min from 298 to 1173 K.

**Electrical conductivity by four probe method.** Electrical conductivity was measured using the four probe method. The measurements were done three times to test the reproducibility and the samples were electrodeposited in ITO substrate. Profilometer technique was used to know the thickness of the film.

**Electrochemical impedance spectroscopy (EIS).** Impedance measurements were carried out on PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>) samples at distinct temperatures in the range from 293 to 433 K and frequency window 10<sup>-1</sup> < f < 10<sup>7</sup> Hz. The experiments were performed with 100 mV amplitude, using a Novocontrol broadband dielectric spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface.

In measurements different voltages (0.1, 0.5 and 1 V) were considered with the intention to ensure the linear response. From the results observed we have chosen 1V as the most appropriate to get a linear response. For that purpose, two gold electrodes were

attached to both sides of the sample by co-pressing the made materials in a sandwich cell configuration. The measurements have been made following the usual procedures in EIS. Prior to the measurements the sample thickness was measured by a micrometer, observing that in all samples the thickness did not vary more than 5%, being the thickness of PEDOT:M[COSANE] ( $M = \text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ ) equal to  $147 \pm 4$ ,  $110 \pm 3$ ,  $98 \pm 3$ , and  $130 \pm 4$   $\mu\text{m}$ , respectively. Samples of 10 mm diameter were sandwiched between two gold circular electrodes coupled to the impedance spectrometer.

The assembly membrane-electrode was annealed in the Novocontrol setup under an inert dry nitrogen atmosphere previous to the start of the actual measurement. To ensure the measurements reproducibility two temperature cycles were studied. In the first one the temperature was gradually raised from ambient temperature to 473 K and then lowered to 293 K in steps of 20 K recording the dielectric spectra in each step. In the second cycle of temperature, the dielectric spectra were collected in each step from 293 to 433 K. During the conductivity measurements, the temperature was kept constant at each measuring step controlled by a nitrogen jet (QUATRO from Novocontrol) with a temperature error of 0.1 K, during every single sweep in frequency.

### **PEDOT:M[COSANE] ( $M = \text{Cs}^+$ , $\text{Na}^+$ , $\text{Li}^+$ and $\text{H}^+$ ) in aqueous asymmetric supercapacitors.**

Supercapacitors were constructed using 2-electrode Swagelok cells with an asymmetric configuration. PEDOT:M[COSANE] ( $M = \text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ ) was used as a positive electrode and activated carbon YP50F (Kuraray Chemical, Japan) as a negative electrode. The different polymers were electropolymerized on top of stainless steel electrode of 4 mm diameter and the carbon electrode sheet was manually cut into a circular shape of 4 mm diameter and put on top of stainless steel electrode by pressure. The weight of both electrode materials is approximately 0.5 mg for each supercapacitor. A wetted nylon membrane (pore size 450 nm) with 0.5 M  $\text{Na}_2\text{SO}_4$  has been employed to separate both electrodes.

Electrochemical experiments, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD), were performed in a VSP potentiostat (Biologic). The specific capacitance was calculated from the GCD curves by following the equation:

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V}$$

where  $I$  is the applied current for the charge-discharge testing,  $m$  is the mass of the active composite materials,  $\Delta t$  is the discharging time and  $\Delta V$  is the voltage excluding the  $iR$  drop.

## Results and discussion

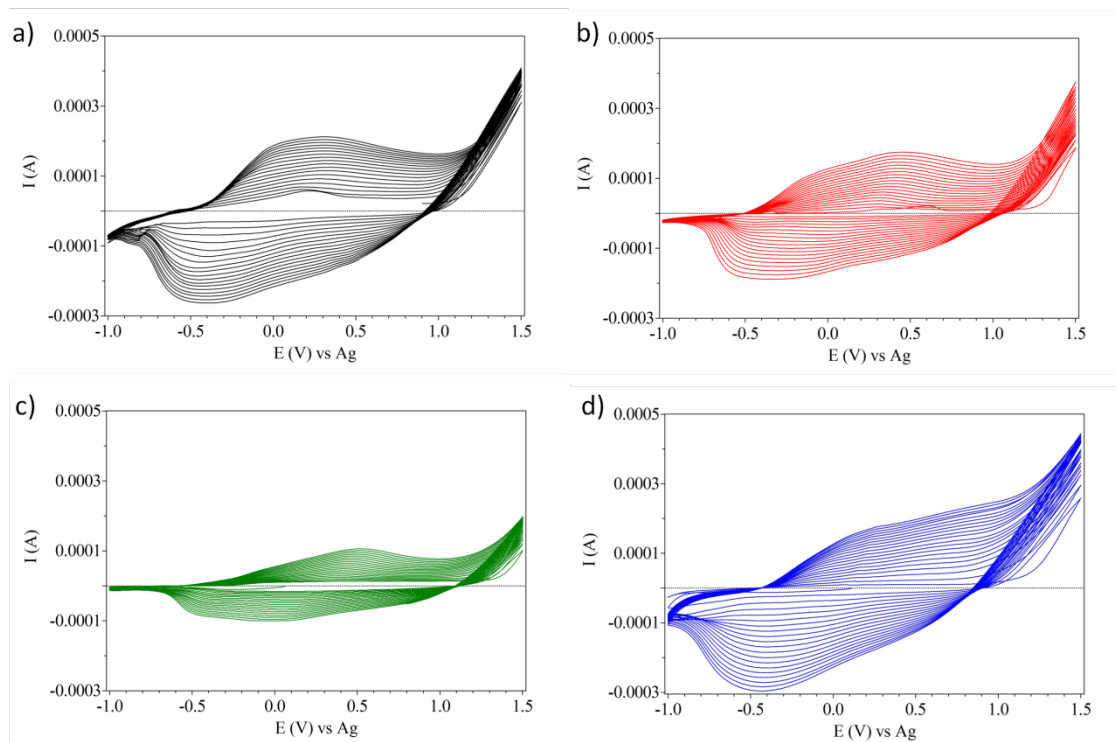
### Electrochemical polymerization of PEDOT:M[COSANE] ( $M = \text{Cs}^+$ , $\text{Na}^+$ , $\text{Li}^+$ and $\text{H}^+$ ).

PEDOT:M[COSANE] ( $M = \text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ ) were electropolymerized using cyclic voltammetry in anhydrous acetonitrile in which EDOT and M[COSANE] are soluble. The different voltammograms recorded during the potentiodynamic synthesis are presented in **Fig 1**. The electrochemical reactions that lead to the polymer formation occur between 1.0 and 1.5 V for all samples. The onset potential of the monomer oxidation was 1.1 V PEDOT:Cs[COSANE] and PEDOT:H[COSANE] and 1.2 V PEDOT:Na[COSANE] and PEDOT:Li[COSANE] in the anodic scan of the first cycle.

The oxidation/reduction process of the different polymers takes place between -0.8 and 0.8 V for all samples and the voltammetric profile is very similar for all the polymers; however, some differences can be observed. Depending on the cations of the [COSANE]<sup>-</sup>, the value of the anodic peak potential of the PEDOT:M[COSANE] varies as it does the number of peaks. For PEDOT:Cs[COSANE] there is a broad anodic peak at 0.2 V, but for PEDOT:Na[COSANE] and PEDOT:Li[COSANE] two anodic peaks are observed for each sample at -0.2 and 0.5 V, and -0.1 and 0.5 V, respectively, with a potential shift of the second peak of 0.3 and 0.2 V from the first cycle to the last one, respectively. PEDOT:H[COSANE] has an anodic peak potential at 0.2 V followed by a high and relatively constant albeit rising current from 0.2 to 0.8 V. The broad cathodic peaks of the different polymers take place at -0.40, -0.35 and -0.45 V for polymers with  $\text{Cs}^+$ ,  $\text{Na}^+$  and  $\text{H}^+$  cations respectively, without any potential shift. However, PEDOT:Li[COSANE] has two cathodic peaks at -0.45 and 0 V without potential shifting with the cycling. Therefore, the redox potentials of the EDOT electropolymerizations in the first cycle are -0.100, -0.075, 0.150 and -0.125 V for PEDOT:Cs[COSANE], PEDOT:Na[COSANE], PEDOT:Li[COSANE] and PEDOT:H[COSANE], respectively. This behavior suggests that the cations show key role during the electrochemical polymerization of EDOT and that the sample



PEDOT:H[COSANE] should have different conducting properties due to the high capacitive current from 0.2 to 0.8 V.



**Fig. 1** Cyclic voltammograms of the electropolymerization of 10 mM EDOT and 10 mM of M[COSANE]. a) Cs[COSANE]; b) Na[COSANE]; c) Li[COSANE] and d) H[COSANE] from -1.0 to 1.5 V vs Ag, 20 cycles at 50 mV/s in anhydrous acetonitrile.

### **Electrochemical properties of PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>).**

The electrochemical properties of PEDOT:M[COSANE] were investigated in 0.1 M Na<sub>2</sub>SO<sub>4</sub> in water. **Fig 2** shows the voltammograms of the different polymers in a solution free of monomers. The redox processes of the couple Co<sup>3+/2+</sup> of M[COSANE] appear in the four samples at -1.56, -1.36, -1.51 and -1.36 V for the polymers with the cations Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup> respectively, confirming that the metallocarborane is present in the polymeric matrix and, importantly that the counter cations are within the bulk of the polymer too, despite the high Na<sup>+</sup> concentration in the electrolyte. This implies that, most probably, the cation exchange occurs only in the outer part of the film and not very extensively, that is in agreement with the large potential separation

between the anodic and cathodic peak waves of the COPs. Pristine Cs[COSANE] has a redox potential of -1.27 V vs Ag/AgCl in acetonitrile corresponding to the couple  $\text{Co}^{3+/2+}$  (the redox potential of [COSANE]<sup>-</sup> is independent of the cation). With no exception there is a shift of  $E^\circ$  for  $\text{Co}^{3+/2+}$  to more negative values proving the higher difficulty to produce the reduction  $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$  process. Moreover, the intensity of the  $\text{Co}^{3+/2+}$  peak varies with the different polymers. Notable is that the two PEDOT polymers with smaller company cations ( $\text{Li}^+$  and  $\text{H}^+$ ) are the ones that induce less free [COSANE]<sup>-</sup> redox intensity. One possible explanation is that the signal for the  $\text{Co}^{3+/2+}$  couple is shifted to the wide PEDOT wave for PEDOT:M[COSANE] ( $M = \text{Li}^+$  and  $\text{H}^+$ ), see **Fig 2** .

For all samples the voltammetric profiles are very different from each other. This suggests that the company cations are non-innocent during the electropolymerization and induce different properties to the polymeric material. The specific capacitance values of the different polymers were calculated based on the equation given below:

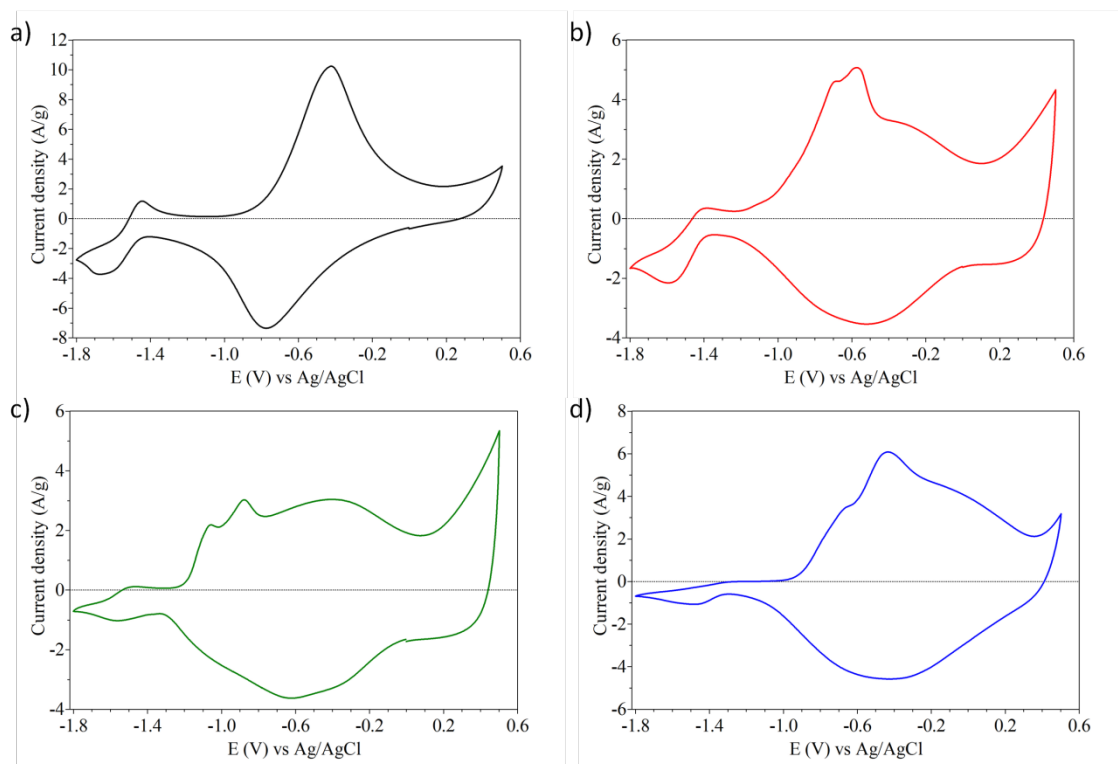
$$C_g = \frac{S}{\Delta V \cdot v \cdot w} \quad (1)$$

where  $C_g$  is specific capacitance,  $S$  is the enclosed area in the CV curve,  $\Delta V$  is the potential window,  $v$  is the scan rate and  $w$  is the weight (g) of the polymer.

**Table 1** shows the specific capacitance values for PEDOT:M[COSANE] ( $M = \text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ ) with the potential window from -1.3 to 0.5 V ( $\Delta V$  1.8 V) without taking into account the redox process of  $\text{Co}^{3+/2+}$  and from -1.8 to 0.5 V ( $\Delta V$  2.3 V) with the redox process of  $\text{Co}^{3+/2+}$ . In all cases the capacitance values are higher for  $\Delta V$  1.8 V, which implies that the faradaic process of  $\text{Co}^{3+/2+}$  doesn't provide better values because there is no overlap with the capacitive process of PEDOT; but the  $\text{Co}^{3+/2+}$  process provides a larger stability window till -1.8 V vs Ag/AgCl.

**Fig 3** shows the linear sweep voltammograms of the PEDOT polymers in 0.1 M  $\text{Na}_2\text{SO}_4$  at 0.5 mV/s. The peak observed in the four samples was interpreted to be the overoxidation resistance limit (ORL), at which the material starts to become an insulator and loses their conductive properties.<sup>14</sup> The ORL values are 1.06, 1.06, 1.08 and 1.06 V for the PEDOTs with the company cations  $\text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ , respectively that implies no significant influence of the company cation in the overoxidation resistance in these samples.

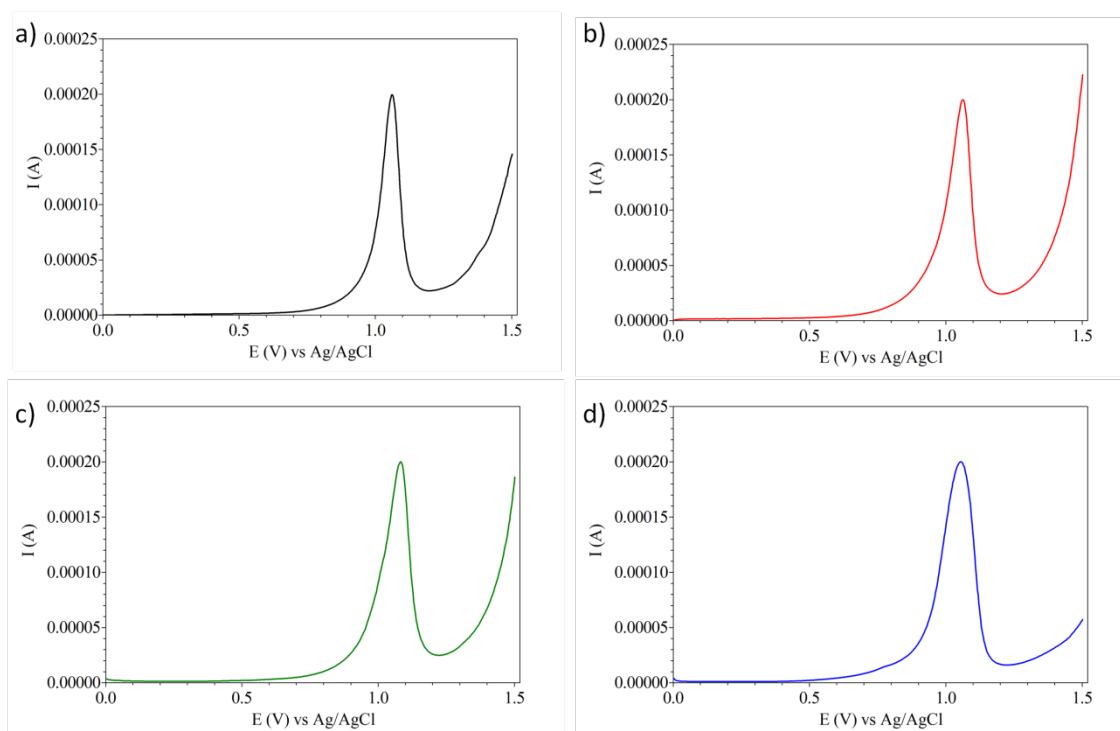
The square wave voltammograms (SWV) **Fig 4** have been studied to learn on the singular fact that the free [COSANE] redox wave for  $\text{Co}^{3+/2+}$ , left wave in the figure, is weakened in the sequence  $\text{Cs} > \text{Na} > \text{Li} > \text{H}$  whereas the width/complexity of the PEDOT wave, right wave in the figure, is increased in the reverse order. For this purpose **Fig 4** shows the deconvolution of the different waves obtained in anodic currents in 0.1 M  $\text{Na}_2\text{SO}_4$  at 25 mV/s, respectively. The redox process of  $\text{Co}^{3+/2+}$  is present in all four samples around -1.5 V (see **Table S1**). However, the redox PEDOT process differs from one sample to the other because the deconvolution exhibits different number of peaks, different distribution and different potential values. All this suggests that, besides the anion [COSANE] that is important as doping agent, the cations are active participants in the electropolymerization, giving rise to new materials with different properties.



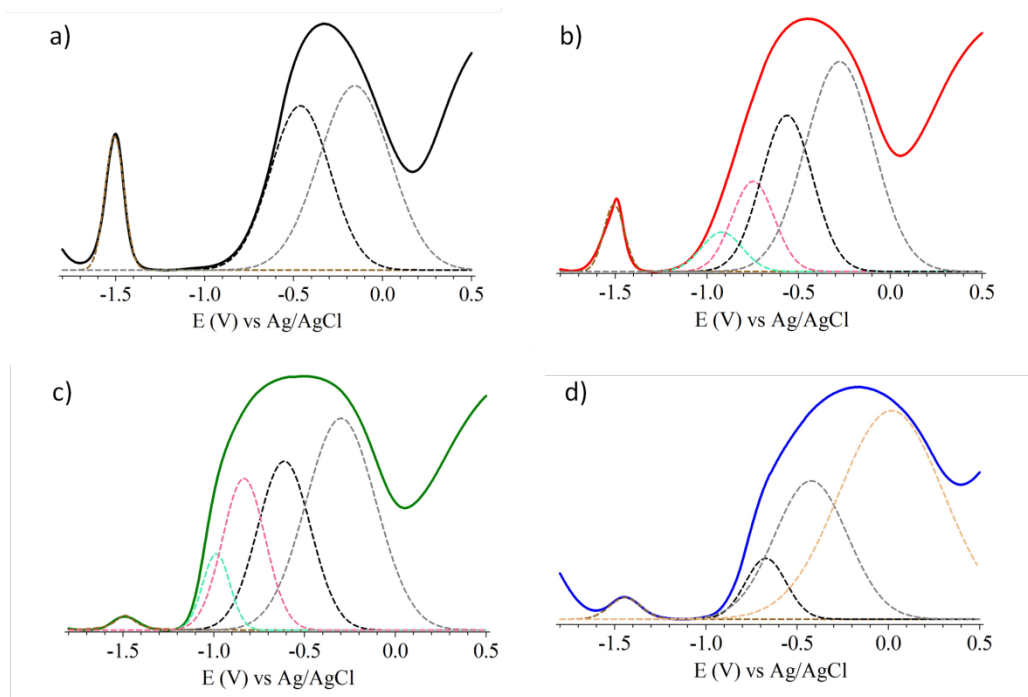
**Fig. 2** Cyclic voltammograms of the electrochemical characterization of a) PEDOT:Cs[COSANE]; b) PEDOT:Na[COSANE]; c) PEDOT:Li[COSANE]; and d) PEDOT:H[COSANE] in 0.1 M  $\text{Na}_2\text{SO}_4$  at 100 mV/s.

**Table 1.** Specific capacitance of PEDOT:M[COSANE] ( $M = \text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ ) with the potential window from -1.3 to 0.5 V ( $\Delta V$  1.8 V) and from -1.8 to 0.5 V ( $\Delta V$  2.3 V).

Sample	$C_s$ (F/g)	$C_s$ (F/g)
	$\Delta V$ 1.8 V	$\Delta V$ 2.3 V
PEDOT:Cs[COSANE]	289	243
PEDOT:Na[COSANE]	228	188
PEDOT:Li[COSANE]	234	191
PEDOT:H[COSANE]	269	216



**Fig. 3** Linear sweep voltammograms of a) PEDOT:Cs[COSANE]; b) PEDOT:Na[COSANE]; c) PEDOT:Li[COSANE]; and d) PEDOT:H[COSANE] in 0.1 M  $\text{Na}_2\text{SO}_4$  at 0.5 mV/s.



**Fig. 4** Square wave voltammograms of the anodic peaks of a) PEDOT:Cs[COSANE]; b) PEDOT:Na[COSANE]; c) PEDOT:Li[COSANE]; and d) PEDOT:H[COSANE] in 0.1 M Na<sub>2</sub>SO<sub>4</sub> at 25 mV/s.

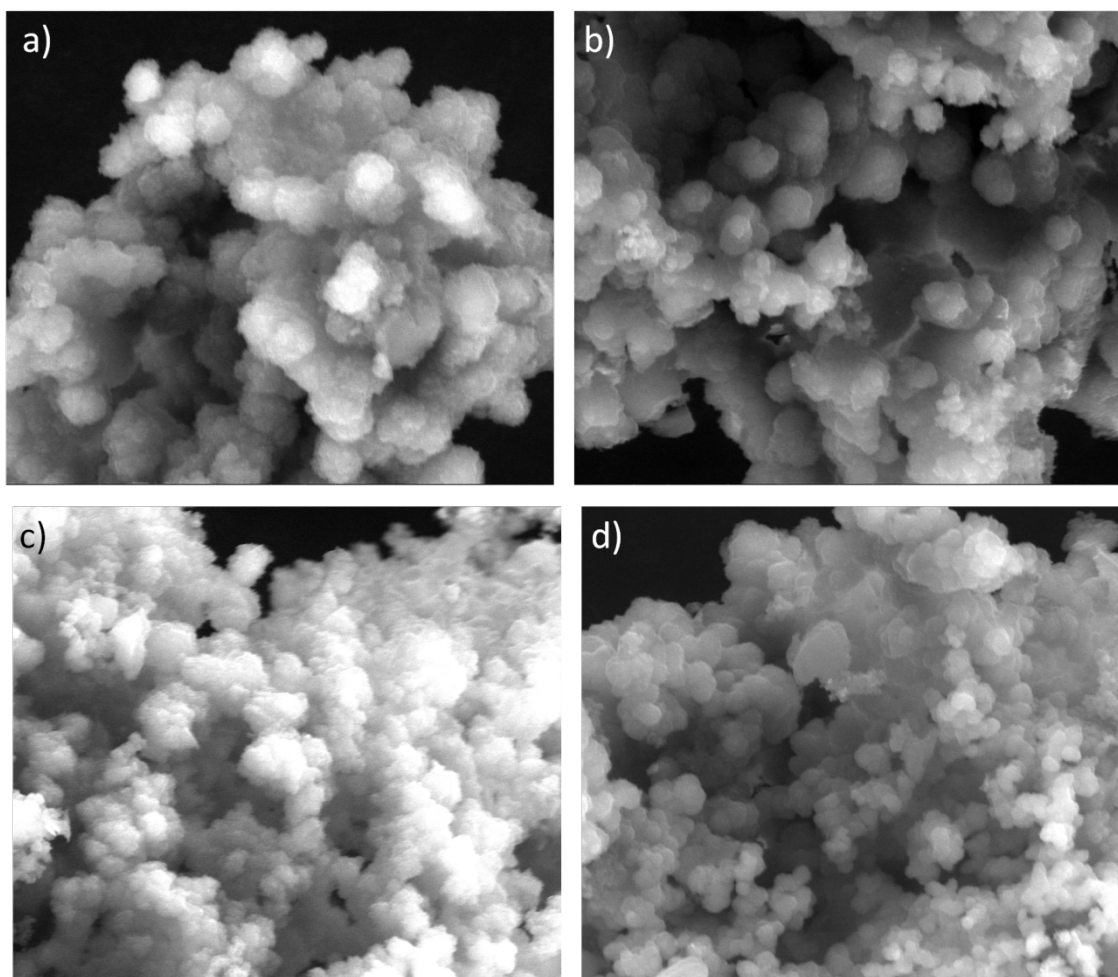
The deconvolution studies along with the relative intensity of the [COSANE] vs. the PEDOT redox wave establishes that increasing amounts of [COSANE] perform electrochemically in synergy with the so called PEDOT wave. To say the redox process of one component influences the redox behavior of the second. This is consistent with the number of Gaussians needed to fit the “PEDOT” curve. For PEDOT:Cs[COSANE] only two, 2, Gaussians are needed to fit its slender PEDOT wave; additionally this polymer has the redox signal due to [COSANE], totaling then 3 Gaussians. The number of Gaussians remains 3 in PEDOT:H[COSANE] and rises to 4 in PEDOT:M[COSANE] (M= Na and Li). The drift from 2 to 4 gaussians in the PEDOT wave of the redox polymers suggests that the independent redox [COSANE] wave in PEDOT:Cs[COSANE] synergizes with the PEDOT wave in PEDOT:M[COSANE] (M= H, Na and Li). This is also supported by the areas ratio of the PEDOT/ [COSANE] assigned Gaussians: in PEDOT:Cs[COSANE] 9.08, in PEDOT:Na[COSANE] 8.69, in PEDOT:Li[COSANE] 9.52 and in PEDOT:H[COSANE] 9.80. All these values are very similar and are consistent with the synergy between the two redox processes being interrelated.

### **Morphology and elemental composition. Interpretation of the key role of the accompanying cations in the composition EDOT/Doping anion.**

The morphology of the four samples has been studied by SEM (see **Fig 5**). All of them have the same morphology: small spheres with dimensions 2.5, 2.0, 1.0 and 1.0  $\mu\text{m}$  for the cations  $\text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ , respectively. Only the PEDOT:Li[COSANE] produces aggregates; further, in this polymer the spheres are not well defined.

Analyses of S and Co by means of EDX has made possible to know about the stoichiometries of these polymers along with doping percentage. For the latter it was also needed the ratio of the company cation, that in our case has been studied for  $\text{Cs}^+$  and  $\text{Na}^+$ . **Table 2** displays the ratio S/Co and Co/M ( $M = \text{Cs}^+$  and  $\text{Na}^+$ ). The S/Co ratio tells on the ratio of EDOT units to metallacarborane whereas the Co/M tells us on the ratio of metallacarborane to company cations. Remarkable are the distinct stoichiometries found, rounded off to the nearest integer figures, as a function of the company cation EDOT:[COSANE] 2:1 for  $\text{Cs}^+$  and  $\text{H}^+$ , and EDOT:[COSANE] 3:1 for  $\text{Na}^+$  and  $\text{Li}^+$ . Remarkable is also that the lower the ratio of EDOT to doping agent the higher is the ratio of company cations, whereas the opposite is also true, the higher the ratio of EDOT to doping agent the lower is the ratio of company cations. This makes sense if it is assumed that each EDOT is oxidized up to 0.3+. This is consistent with the commonly encountered 3:1 EDOT to doping agent ratio with PSS and other conventional anions, for which the presence of company cations is not reported. The higher ratio of the company cation suggests a higher interaction between COSANE and the company cations. Even though carborane cluster anions can be considered as weakly coordinating anions, it has been demonstrated that they can interact with many cations<sup>34</sup>,<sup>35</sup> and as it has been demonstrated experimentally and theoretically the solvation shell has an important role as well.<sup>36</sup> During the formation of the PEDOT polymer, COSANE anions move from the bulk solution towards the surface of the new polymer layer. In the case of a strong interaction between the COSANE anion and the company cations they will move together and tend to stay together. The strength of this interaction depends on the solvation of the cations, a better solvation prevent the formation of strong ion pairs. Analyzing the literature data the first solvation sphere contains four acetonitrile molecules in case of  $\text{Li}^+$  and six in case of  $\text{Na}^+$  and  $\text{Cs}^+$ .<sup>37-39</sup> In case of the proton it is accepted that the so called Zundel cation ( $\text{H}_5\text{O}_2^+$ ) is the main form even in case of extreme low water concentration.<sup>40</sup> Since H[COSANE] was prepared by

liquid/liquid extraction, it always contains minimum amount of water. Despite alkali ions have higher affinity to be solvated by water than by acetonitrile, molecular dynamic calculations demonstrated that in case of acetonitrile/water 9:1 mixture the coordination of the acetonitrile is more dominant,<sup>41</sup> thus in low water concentration the first coordination sphere of alkali cations presumably contains only acetonitrile molecules in the first coordination shell. Keeping these considerations in mind DFT calculations were carried out (more details in the SI). The above mentioned cations with the first solvation shell  $[\text{H}_5\text{O}_2(\text{ACN})_4]^+$ ,  $[\text{Li}(\text{ACN})_4]^+$ ,  $[\text{Na}(\text{ACN})_6]^+$   $[\text{Cs}(\text{ACN})_6]^+$  were optimized in the presence of COSANE anion (**Fig S1** in the SI). DFT calculations verified that in case of  $[\text{Li}(\text{ACN})_4]^+$ ,  $[\text{Na}(\text{ACN})_6]^+$  the solvation shell somewhat distorts, but solvent molecules are between COSANE and the cation (see the optimized structures in **Fig S1** in the SI), which suggests weaker interaction between them. On the other hand in case of  $[\text{Cs}(\text{ACN})_6]^+$  the distortion of the solvation shell is more significant and the  $\text{Cs}^+$  ion can directly interact with the anion. This is in good agreement with the solvation energies following the trend  $\text{Cs}^+ < \text{Na}^+ < \text{Li}^+$ .<sup>42</sup> In case of  $[\text{H}_5\text{O}_2(\text{ACN})_4]^+$  the center of the cation was not shielded by solvent molecules,<sup>43</sup> therefore it can easily interact with COSANE. Despite gas phase calculations (even with solvent models) do not necessarily account accurately for cation-anion interactions within the bulk of the liquid, we shall indicate that the simple model system described above, containing the solvated cation and the COSANE anion provide an explanation on the impact of accompanying cations on the PEDOT/doping anion stoichiometry that is consistent with the experimental observation.



**Fig. 5** SEM images of a) PEDOT:Cs[COSANE]; b) PEDOT:Na[COSANE]; c) PEDOT:Li[COSANE] and d) PEDOT:H[COSANE] at 5000x.

**Table 2.** Ratio S/Co %Atomic (S from EDOT and Co from metallacarborane), ratio Co/Cs and Co/Na (%At) of the samples PEDOT:M[COSANE] by EDX analysis. Li can not be safely measured with EDX

Sample	S/Co (%At)	Co/Cs (%At)	Co/Na (%At)
PEDOT:Cs[COSANE]	$1.87 \pm 0.13$	3.00	-
PEDOT:Na[COSANE]	$2.80 \pm 0.24$	-	4.80
PEDOT:Li[COSANE]	$2.73 \pm 0.42$	-	-

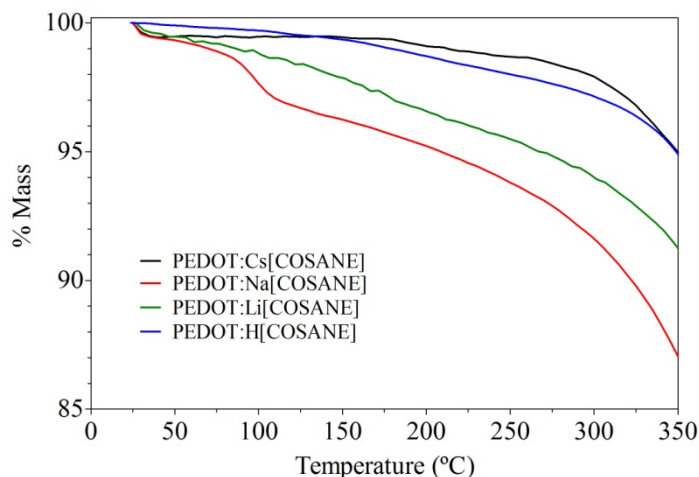


### Infrared spectroscopy analysis, FTIR-ATR.

**Fig S2** shows the infrared spectra of the different samples. The stretching frequency of B-H of [COSANE]<sup>-</sup> is a strong and sharp band that appears around 2500 cm<sup>-1</sup>. The infrared spectra of the polymers PEDOT:M[COSANE] don't show strong and sharp B-H bands, if not a small and broad band. Previous studies demonstrate that the metallacarborane with conducting polymers don't show strong and sharp B-H band, but after the overoxidation of the polymer a strong and sharp B-H band appear.<sup>12</sup> Therefore, the small B-H band is characteristic from metallacarborane as doping agent of conducting polymers.

### Thermogravimetric analysis.

The thermal stability of the different polymers was studied by TGA. **Fig 6** shows the thermogravimetric curves of the different PEDOT:M[COSANE]. Up to 350 °C the polymers show a stability following the trend PEDOT:Cs[COSANE] > PEDOT:H[COSANE] > PEDOT:Li[COSANE] > PEDOT:Na[COSANE]. It seems that these polymers with the lower ratio of EDOT to doping agent display the highest stability and viceversa. The behavior of the curves from 350 to 900 °C (**Fig S3**), particularly for Cs<sup>+</sup> and Li<sup>+</sup> is erratic despite they have been done several times and from different syntheses, indicating that they may have a physical origin but that we are not able to interpret.



**Fig. 6** Thermogravimetric analysis of PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>) in N<sub>2</sub>.

### Electrical conductivity by four probe method.

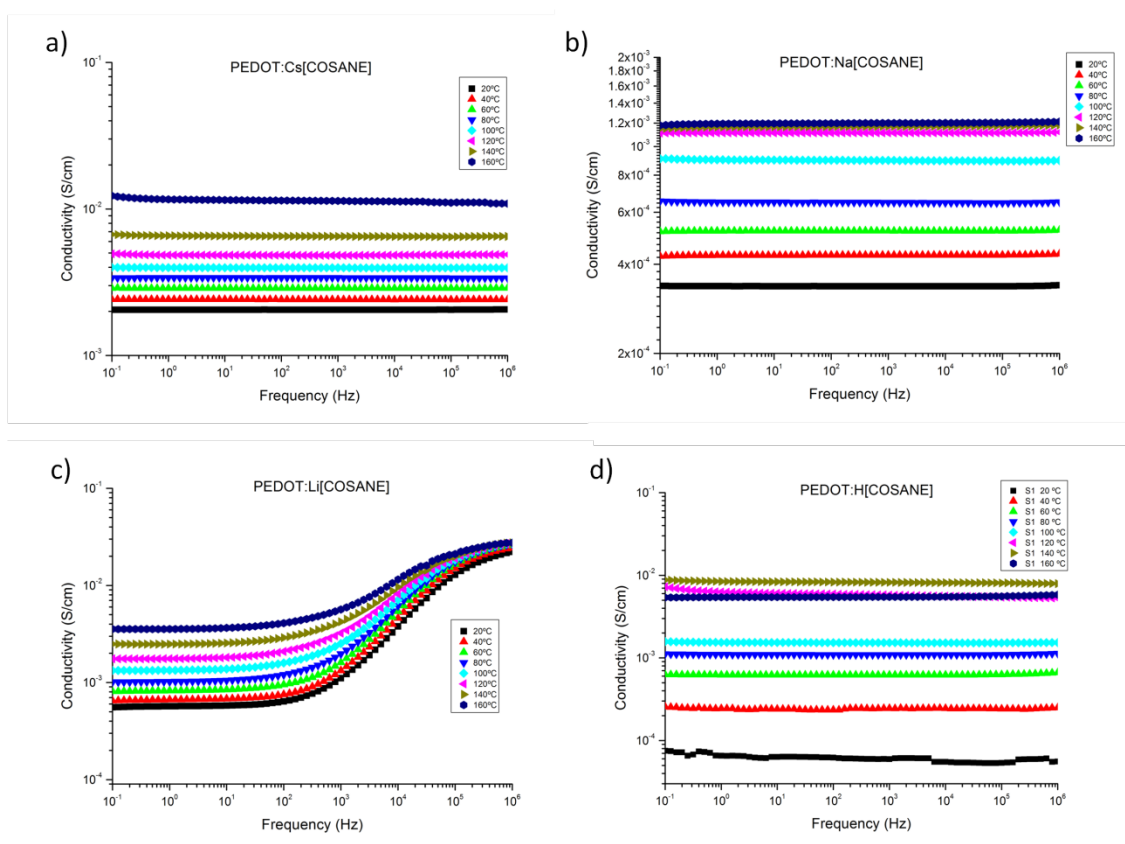
The electrical in-plane conductivity of the different samples are between 188 and 275 S/cm (see **Table 3**). Depending on the cation used to produce PEDOT:M[COSANE], the electrical conductivity changes, being higher for PEDOT:Cs[COSANE] > PEDOT:H[COSANE] > PEDOT:Li[COSANE] > PEDOT:Na[COSANE]. The different values of conductivity confirm that the counter cations play an important role during the electropolymerization of the polymer. This sequence agrees again with the sequence for the capacitance and both follow the trend lower ratio of EDOT to [COSANE] first then higher ratio of EDOT to [COSANE]. Comparing these PEDOT:M[COSANE] electrical conductivity values (see **Table 3**) with pristine PEDOT:PSS (0.8 S/cm),<sup>44</sup> PEDOT:PSS treated with organic solvents as DMSO (80 S/cm),<sup>44</sup> PEDOT:PSS with ionic liquids (136 S/cm),<sup>45</sup> PEDOT:PSS with HNO<sub>3</sub> (197 S/cm)<sup>46</sup> and PEDOT:PSS treated with tannic acid and temperature (453 S/cm),<sup>47</sup> these PEDOT:M[COSANE] data show very attractive values of electrical conductivities without requiring a post-treatment with solvents, reagents or temperature.

**Table 3.** Electrical conductivity values (S/cm) of the samples PEDOT:M[COSANE] (M = Cs<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> and H<sup>+</sup>) by four probe method.

Sample	Electrical Conductivity (S/cm)
PEDOT:Cs[COSANE]	275.2
PEDOT:Na[COSANE]	188.3
PEDOT:Li[COSANE]	220.8
PEDOT:H[COSANE]	238.0

## Ionic conductivity by electrochemical impedance spectroscopy of PEDOT:M[COSANE] ( $M = \text{Cs}^+$ , $\text{Na}^+$ , $\text{Li}^+$ and $\text{H}^+$ ) membranes.

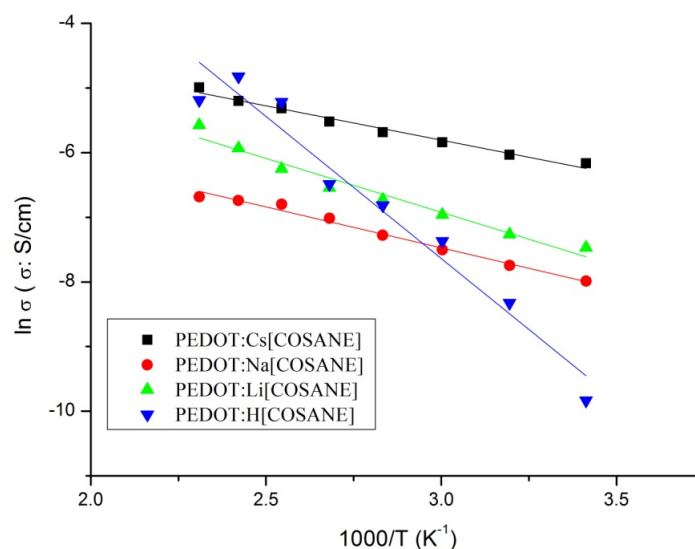
The ionic conductivity of the synthesized PEDOT:M[COSANE] ( $M = \text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ ) membranes at different temperatures (from 293 to 433 K) was determined by electrochemical impedance spectroscopy (EIS). The data of real part of the conductivity were analyzed following the Bode diagram such is shown in **Fig 7**. These results show that the conductivity of the samples depends on the accompanying cations. It is there seen that the conductivity increases as the temperature increases and it has higher values at higher temperature in dry conditions.



**Fig. 7** Bode diagrams for the compounds: a) PEDOT:Cs[COSANE], b) PEDOT:Na[COSANE], c) PEDOT:Li[COSANE] and d) PEDOT:H[COSANE] at different temperatures (from 293 to 433 K).

Comparing the different PEDOT:M[COSANE] ( $M = \text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ ) pellets, it is seen that their conductivities were  $2.0 \times 10^{-3}$ ,  $4.3 \times 10^{-4}$ ,  $7.7 \times 10^{-4}$  and  $2.4 \times 10^{-4}$  S/cm, respectively, at 313 K. As with previous experiments, the PEDOT:Cs[COSANE] has been the one giving the best results, but usually it was accompanied by the  $\text{H}^+$  polymer. This is not the case at 313 K, but it does happen at 393 K where the values are  $4.9 \times 10^{-4}$

<sup>3</sup>,  $1.1 \times 10^{-3}$ ,  $2.2 \times 10^{-3}$  and  $5.4 \times 10^{-3}$  S/cm, respectively. The dependence of the conductivity with the temperature is represented in **Fig 8**. An overview of these data shows an increase, at least one order of magnitude in the conductivity, when we compare  $\text{Cs}^+$  versus  $\text{H}^+$ ,  $\text{Li}^+$  and  $\text{Na}^+$ , respectively. The conductivity activation energy  $E_a$  is calculated from the slope of the line fitted to the experimental values in figure 8, and follow the trend  $E_{a(\text{H}^+)} = 36.4 > E_{a(\text{Li}^+)} = 16.8 > E_{a(\text{Na}^+)} = 13.5 > E_{a(\text{Cs}^+)} = 11.7$  kJ/mol.



**Fig. 8** Temperature dependence of the conductivity of (■) PEDOT:Cs[COSANE], (●) PEDOT:Na[COSANE], (▲) PEDOT:Li[COSANE] and (▼) PEDOT:H[COSANE].

Except for PEDOT:H[COSANE], all other compounds have values of the activation energy similar or slightly larger than Nafion membranes (10.5 kJ/mol)<sup>48</sup> and significantly smaller than previous values reported for polycrystalline salts of  $\text{CsH}_2\text{PO}_4$  and of  $\text{CsH}_2\text{PO}_4/\text{silica}$  composite, which values are around 38.6 and 48.2 kJ/mol in the same range of temperatures.<sup>49</sup> Similar results are found when we compare PEDOT:M[COSANE] with different ortho-phosphates, based on the partial substitution of  $\text{Cs}^+$  by  $\text{Rb}^+$  and  $\text{Ba}^{2+}$ , to give  $\text{Cs}_{1-x}\text{Rb}_x\text{H}_2\text{PO}_4$  and  $\text{Cs}_{1-x}\text{Ba}_{0.5x}\text{H}_2\text{PO}_4$ . On the other hand, the calculated activation energies are higher than powders of Na[COSANE], Li[COSANE] and H[COSANE] which values are respectively 7.8, 7.9 and 5.6 kJ/mol.<sup>33</sup>

#### Aqueous asymmetric supercapacitor.

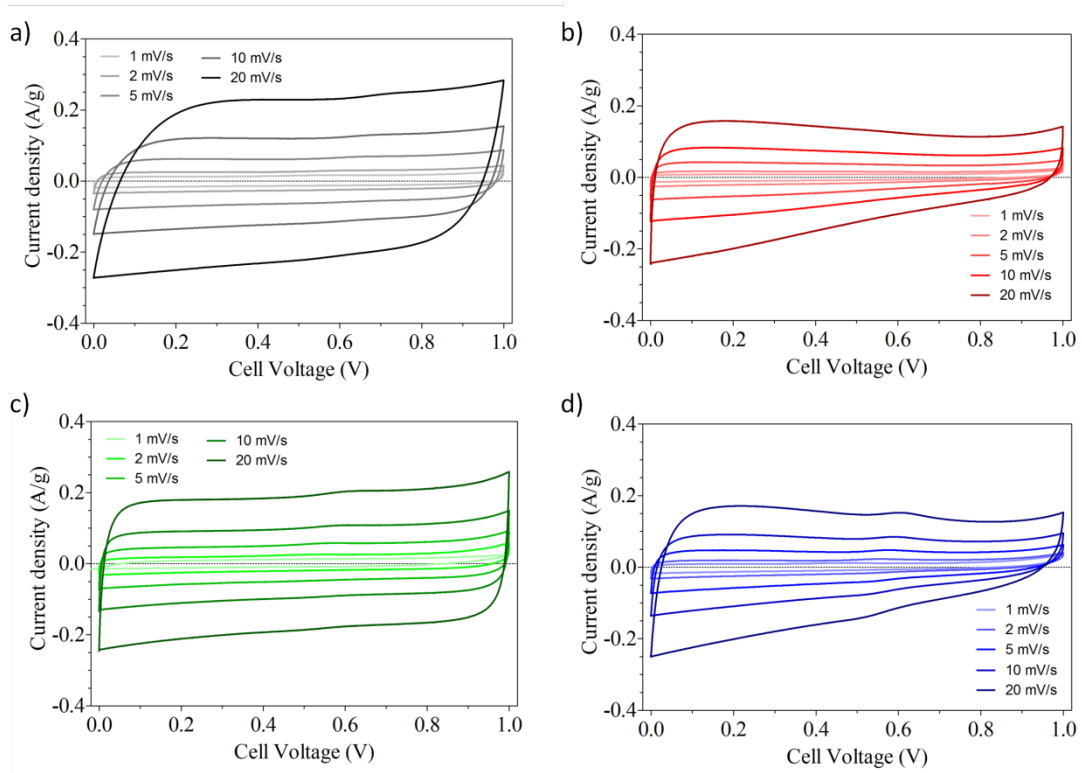
**Fig 9** shows the voltammograms at different scan rates for the different capacitors prepared using the PEDOT:M[COSANE] as positive electrode and a commercial

activated carbon as negative electrode. The voltammograms between 0 and 1 V exhibit quasi-rectangular shape, indicating that the main contribution to the capacitance is the charge and discharge of the electrical double layer. However, the PEDOT:Na[COSANE] and PEDOT:H[COSANE] deviate from this rectangular form mainly at high voltages. Moreover, the PEDOT:H[COSANE] capacitor shows a peak at 0.6 V that could be related with the redox processes in the polymer that are well-defined in the voltammograms (**Fig 2**). The capacitance values obtained at 1 mV/s are 14, 9.5, 12.2 and 11.2 F/g, respectively for the capacitors PEDOT:Cs[COSANE], PEDOT:Na[COSANE], PEDOT:Li[COSANE] and PEDOT:H[COSANE]. The capacitance values for PEDOT:Cs[COSANE] and PEDOT:Li[COSANE] are higher than those obtained for the other polymers. The retention of capacitance with the scan rate is presented in **Fig 10**. It can be observed that there are differences among the polymers, having the lowest performance PEDOT:H[COSANE] and PEDOT:Cs[COSANE] and the highest retention of capacitance the sample PEDOT:Li[COSANE], which maintains more than 70% of the capacitance at 1 mV/s.

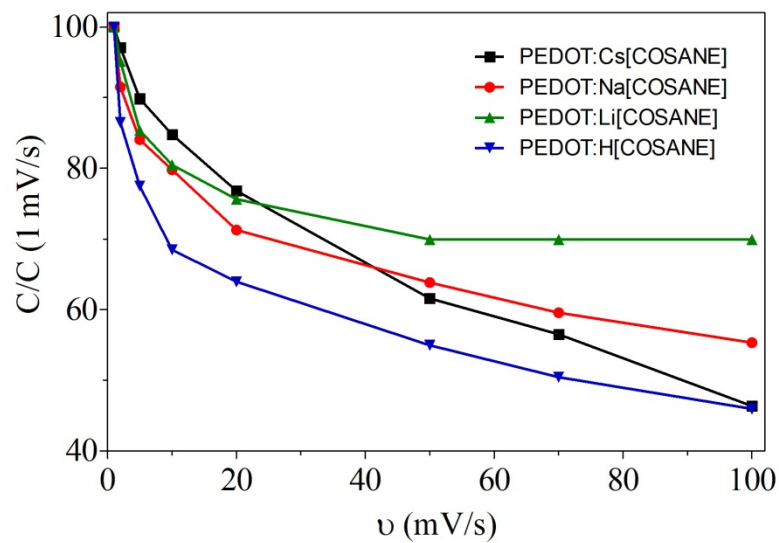
**Fig 11** shows the chronopotentiograms at  $50 \text{ mA g}^{-1}$  and  $250 \text{ mA g}^{-1}$  for the different capacitors in a potential window of 1 V. The chronopotentiograms of all capacitors showed a quasi-triangular shape, indicating the absence of faradic processes. The capacitance of PEDOT:Cs[COSANE] at low current density is higher than the obtained for the other capacitors (**Fig 12**). However, when the current density increases, an important ohmic drop and a decrease in capacitance are observed for this capacitor. Interestingly, the PEDOT:Li[COSANE] capacitor shows the highest retention of capacitance from these measurements, being the capacitance very stable with the current density (**Fig 12**).

The lowest performance observed for PEDOT:H[COSANE] and PEDOT:Cs[COSANE] samples can be related to the differences in transport properties, especially in ionic conductivity (**Fig 8**). In the case of PEDOT:H[COSANE], the activation energy for ion hopping is the highest, what can explain the important decrease in capacitance with increasing the rate of charge and discharge. In the case of PEDOT:Cs[COSANE] the ionic conductivity is the highest and the activation energy is the lowest among the materials studied. This means that the exchange among  $\text{Cs}^+$  and  $\text{Na}^+$  cations, which are present in the electrolyte at high concentration, will be the easiest, making that the

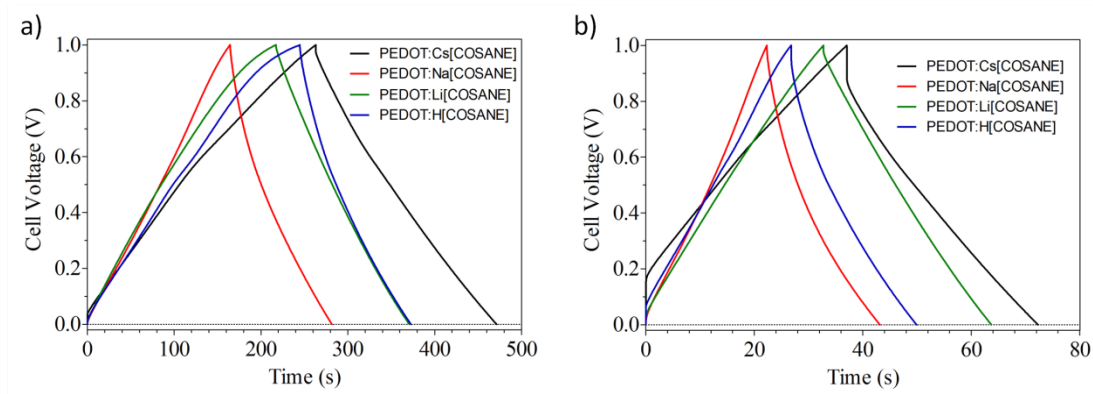
capacitance values decrease and that may reach the values for PEDOT:Na[COSANE] sample as observed in Fig 10.



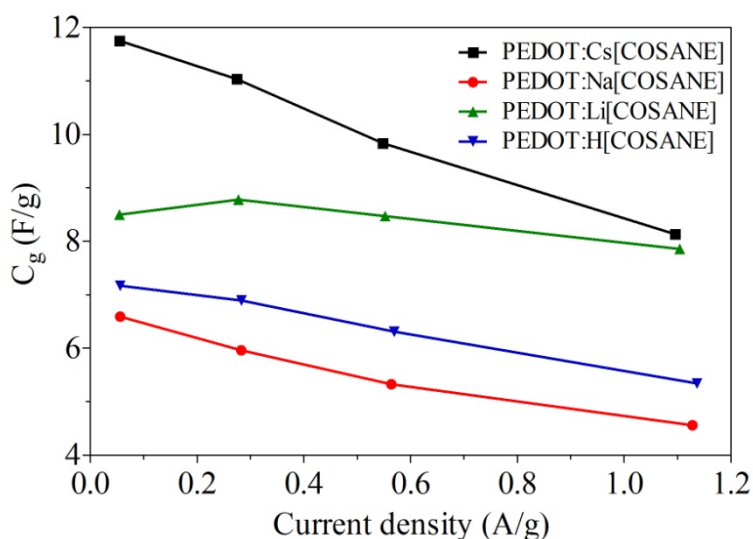
**Fig. 9** Cyclic voltammograms curves at 1, 2, 5, 10 and 20 mV/s of: a) PEDOT:Cs[COSANE], b) PEDOT:Na[COSANE], c) PEDOT:Li[COSANE] and d) PEDOT:H[COSANE].



**Fig. 10** Normalized capacitance values of the capacitors prepared with PEDOT:M[COSANE] as positive electrode at different scan rates.



**Fig. 11** GCDs curves of PEDOT:M[COSANE] at a) 0.05 A/g and b) 0.25 A/g.



**Fig. 12** Specific capacitance calculated from GCDs curves of PEDOT:M[COSANE] at different current densities.

## Conclusions

We have demonstrated that the company cations, these that accompany the doping agent at the moment of synthesizing the COP, are more influential than it was expected. Indeed their relevance in the stoichiometry and physico-chemical properties of the resulting COP had been overlooked. In this work through the use of the

metallacarborane  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  we prove that the stoichiometry then the electrochemical response, electronic conductivity, ionic conductivity, and capacitance of the resulting PEDOT polymers is altered. Remarkably the counter cations influenced stoichiometry is expressed in the properties of the materials. Four have been the counter cations studied:  $\text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  and  $\text{H}^+$ , all having one positive charge, but all having distinct solvation capabilities. It turns out that this may be the explanation, or at least the explanation is consistent with the experimental results. The anion  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  has many B-H units beaming out of each one of the two icosahedral units that make up the anion. These negatively charged units interact with the solvated cations distinctly. If the interaction is strong they form a relatively stable ion pair whereas if it is weak the ions are free to move. These would be the two extremes. The interaction of  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  with the counter ions is between the two extremes, but interestingly  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  is able to group the four counter cations in two sets,  $\text{Cs}^+$  and  $\text{H}^+$  in one and  $\text{Na}^+$  and  $\text{Li}^+$  in the second that have influenced the stoichiometry 2 EDOT: 1  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  for  $\text{Cs}^+/\text{H}^+$  and 3 EDOT: 1  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  for  $\text{Na}^+/\text{Li}^+$ . This grouping is manifested not only in the stoichiometries but in the properties. For instance the  $\text{Cs}^+/\text{H}^+$  show the highest electrical conductivity and the highest ionic conductivities at 393 K. However what is clear is that the PEDOT:Cs[COSANE] polymer is the best in most of the applications, which means that counter cations are influencing in stoichiometry and properties. *They are non-innocent.*

### **Conflicts of interest**

There are no conflicts to declare.

### **Acknowledgements**

We gratefully acknowledge Spanish Ministerio de Economía y Competitividad (MINECO) for financial support by the ENE/2015-69203-R project and CTQ2016-75150-R project, and Generalitat de Catalunya (2014/SGR/149). I. Fuentes is enrolled in the PhD program of the UAB. Z. Kelemen is grateful for the general support of the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement MSCA-IF-2016-751587.



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