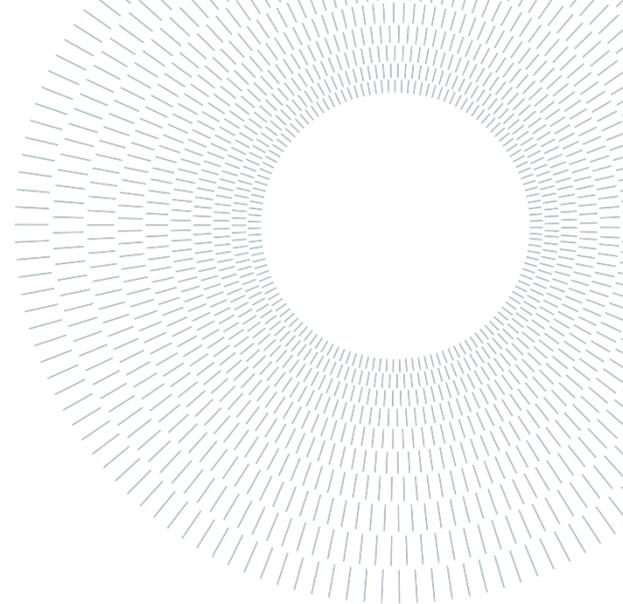




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EXECUTIVE SUMMARY OF THE THESIS

Polarons in P3HT: unravelling vibrational fingerprints of ordered and disordered doped phases in solids and solutions. IR and Raman study of the polymers and oligomers.

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

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1. Introduction

Most polymers are typically insulators, except for conjugated polymers, that can exhibit semiconducting or even metallic properties if suitably doped, thanks to the alternating single and multiple bonds in the polymer backbone that results in π -conjugation. [1] The possibility to tune their electronic structure, either by changing the structure or by doping, allows the development of low cost and flexible organic electronic devices. [2], [3] OSC (organic semiconductor) technology can offer prospects for the overcome of energy issues with their applications in light-emitting diodes (OLEDs), organic solar cells, and organic field-effect transistors (OFETs). [4]

Therefore, a complete understanding of the doping process is an important step for the development of the field of organic electronics.

The polymer of interest of this work is poly(3-hexylthiophene-2,5-diyl), or P3HT. The poly-alkyl-thiophenes family is one of the most widely

studied between many conjugated polymers. The doping of P3HT by both iodine (I_2) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) is studied adopting two different processes, namely doping in solution and by exposure to dopant vapors (in the I_2 case only). This last method has been the subject of many recent reports and it allows to obtain film with a high conductivity; however, the control of the amount of dopant species interacting with the polymer, is still an issue. [5] A more controlled process has been adopted in this work, doping the P3HT directly in solution and exploring different polymer/dopant ratios. Solid samples were obtained from casting of the doped solution in thin films.

In order to better clarify the doping mechanism of P3HT, samples prepared with regiorandom P3HT, dodecyl-substituted (P3DT) and 8T, 13T and 21T oligothiophenes were studied to investigate the role of i) the conformational order of the polymer backbone, ii) the role of the alkyl side chains, and iii) the polymer length. The results of these

experiments are not presented in this executive summary, which mainly focuses on P3HT.

2. Doping of conjugated polymers: ICT and CTC

Chemical doping of π -conjugated materials consists in redox reactions between the host and the dopant. Stable doping of OSCs is obtained by adding strong molecular donors (n-doping) or acceptors (p-doping) species to conjugated polymers. For the p-doping of P3HT there are two different models commonly used to describe the donor-acceptor interaction. The first one is the integer charge transfer model (ICT), where a hole is injected in the polymer chain, resulting in a charged defect. [6],[7] When an electron is removed from the pristine P3HT, the positive charge which remains on the polymer chain delocalizes on several thiophene units. In this region, of about five polymer units, the thiophene rings change their structure from the aromatic one towards a more quinoidal geometry. The unpaired electron that remains on the polymer chain and the perturbed segment of the backbone form a polaron. [8],[9]

Experimental and theoretical studies during the past years have shown that in some cases the interaction of host and dopant can result in the formation of a charge-transfer complex (CTC) as a consequence of a partial charge transfer.

While in ICT ionic species are formed, the CTCs should be considered a tightly bounded polymer/dopant pair, electrically neutral. [10] In this work we will study both the ICT and CTC phases in doped P3HT.

3. Experimental section

3.1. Materials preparation and characterization

The experiments have been performed on regioregular poly(3-hexylthiophene-2,5-diyl), or P3HT, ($M_w=50000-65000$ g/mol, polydispersity index < 6.0 , $RR \geq 90\%$). Iodine and F_4TCNQ have been used to dope the P3HT in solution of $CHCl_3$ by gradually increasing the level of doping. All samples were purchased by Sigma Aldrich.

Three different levels of doping were analyzed: the less doped case is the 25:1 meaning that there is one molecule of the dopant for every 25 hexyl thiophene units, the medium doping regime 5:1,

with one dopant molecule for every five thiophene units, and, finally, the highly doped one, the 1:1, with one molecule of dopant for each monomer unit.

The final solutions were obtained by mixing a fixed concentration of P3HT in chloroform solution, with a suitable solution of the dopant in order to obtain the final desired molar ratio.

All the samples were analysed by vibrational IR and Raman spectroscopies.

In crystalline π -electron conjugated polymers, as for example poly-acetylene, normal modes characterized by the collective bond length alternation (BLA) oscillation are strongly Raman-active but no or weakly IR-active. These vibrations are described as simultaneous stretching of the C=C and shrinking of the C-C, usually coupled with CH wagging. They are called Effective Conjugation Coordinate (ECC) modes and are sensitive to the electronic structure, and in particular to the conjugation length. The ECC Raman-active modes could become also strongly active in the IR if the π -electrons system is polarized. This happens when electric charges are injected into the polymer backbone, as in the case of chemical doping. The resulting strong features observed in the spectra of doped conjugated polymers are called IR activated vibrations, IRAV.[11][12] This phenomenon makes the use of IR spectroscopy as a powerful and widely employed technique to investigate the doping process in organic semiconducting materials. [11] In this work, IR and Raman spectroscopy are used to investigate and monitor the doping process of P3HT from the doped solution to its deposition in thin films.

3.2. IR spectroscopy of P3HT solutions

In Figure 1 are reported the spectra of P3HT doped with iodine and F_4TCNQ in $CHCl_3$ solution at three doping ratios compared to the case of the pristine polymer. In the doped samples we can easily recognize the very strong IRAV bands in the region $1450-500$ cm^{-1} . It can be noticed that, in the region α , between 1450 cm^{-1} - 1250 cm^{-1} , highlighted in Figure 1, different IR patterns are observed depending on the level of doping.

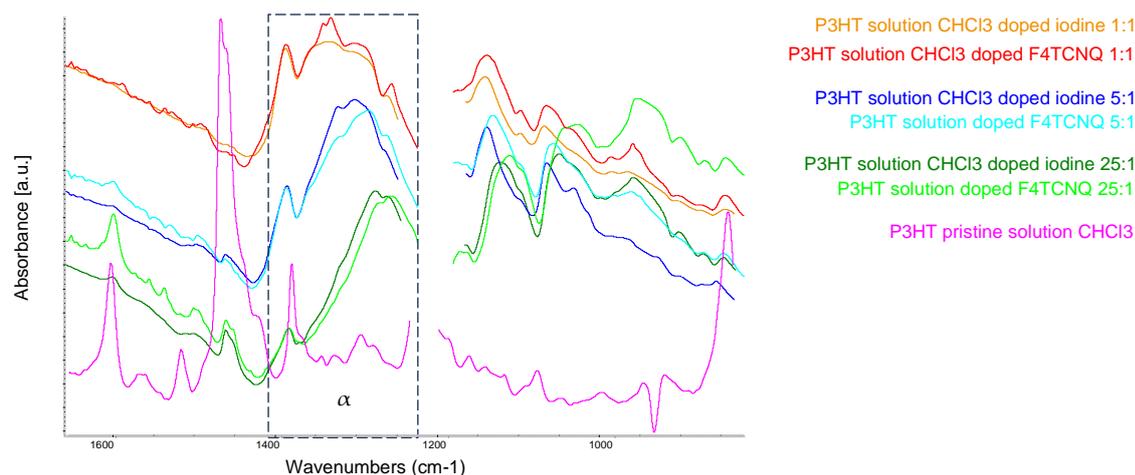


Figure 1: IR spectra of P3HT solution in CHCl_3 doped iodine 25:1 (dark green line), 5:1 (blue line), 1:1 (brown line) and F_4TCNQ 25:1 (light green line), 5:1 (light blue line), 1:1 (red line). The dotted area identifies the region α .

The IR patterns are the same for both dopants at the same doping ratios and suggest that different P3HT / dopant species are present as a function of the quantity of dopant added to the solution. We identified these components as: an incipient polymer/dopant species (I) observed for the low doping case (25:1); a pre-ordered polaronic structure (P) for the medium doping case (5:1) and a third component (C) at the highest (1:1) doping level.

3.3. IR spectroscopy of doped P3HT films

The IR spectra of solid samples obtained by casting the solutions, show a common pattern, regardless of the doping species and the doping level, as it is clearly shown in Figure 3. In particular in the α region they show an IR pattern with the same band P_s at around 1295 cm^{-1} . This may suggest that when the solutions are deposited, P3HT and dopant molecules can rearrange during the solvent evaporation and can reach the most stable form of the complex. The resulting IR spectrum could be assumed as the vibrational signature of the stable doped state of P3HT and the P_s IRAV at 1295 cm^{-1} could be taken as the vibrational marker of the polaron in a solid and ordered state. We named this ordered doped phase as “polaron_OA”, meaning that it occurs in domains where P3HT and dopant molecules develop a crystal-like ordered architecture.

If we compare the spectra of doped P3HT in solution and in film at the same doping ratio we can notice that with both dopants at the doping level 5:1 the two patterns obtained are very similar (see Figure 2). On the contrary, in the other two cases (the high and the low doping level) some differences going from liquid to solid samples are observed. This suggests that already in solution, the doping ratio 5:1 allows the formation of pre-ordered polaronic structures by clustering of doped chains. These stable and ordered structures does not change significantly going from solution to the solid phase.

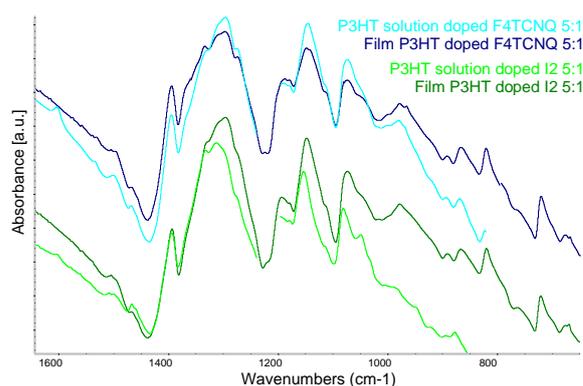


Figure 2: IR spectra of P3HT doped 5:1 iodine (solution: light green line, film: dark green line) and F_4TCNQ (solution: light blue line, film: blue line)

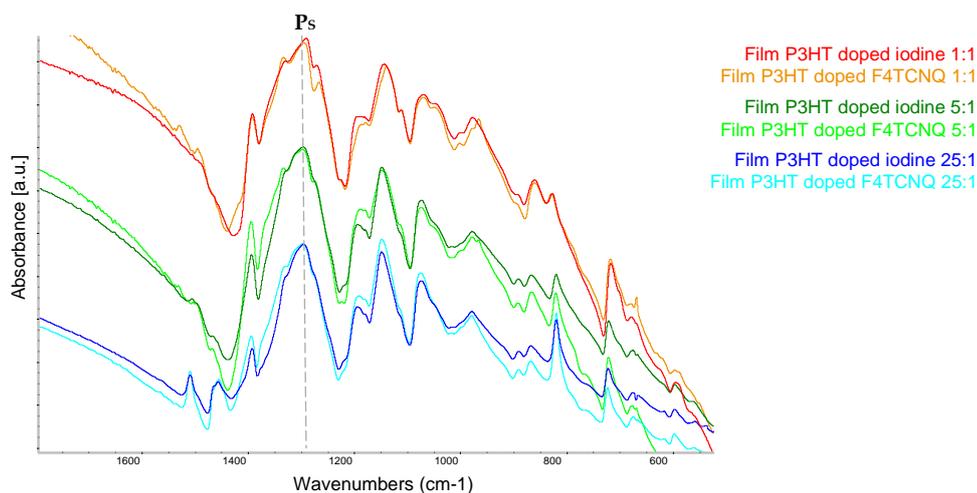


Figure 3: IR spectra of P3HT solutions in CHCl_3 doped iodine 25:1 dark green line), 5:1 (blue line), 1:1 (brown line) and F_4TCNQ 25:1 (light green line), 5:1 (light blue line), 1:1 (red line). The dotted line identifies the band Ps.

3.4. Raman spectroscopy of doped P3HT films

As it can be seen the FT-Raman spectra of solid doped P3HT, reported in Figure 4 (left panel), is dominated by a strong Raman band, associated to the ECC vibration. The ECC band is broader and shifted towards lower frequency of about 10 cm^{-1} with respect to the ECC band of the pristine sample occurring at 1445 cm^{-1} . Recalling what happens in the case of doped polyacetylene, we can hypothesize that the strong band in the Raman spectra of doped P3HT is preferentially due to vibrational transitions mostly localized on the neutral segments of the polymer chain. These segments consist of sequences of CC bonds adjacent to the polarons, characterized by CC stretching modes with a stronger Raman intensity in respect with vibrations localized in the charged polaron regions. However, this does not imply that Raman spectroscopy does not see the effect of doping: indeed the doped samples, both in solution and in film, show a distinguishable Raman pattern compared to the pristine case. The fact that the Raman spectra of doped samples are different from the pristine ones suggests that even if the polaron is confined over a few thiophene units it can induce some effects on the neutral segments of the polymer chain. In particular, for the solid samples we observe a lowering of the frequency of the ECC band (see Figure 4, left panel). This shift could be attributed to the fact that

the neutral rings close to the polaron have geometry and force constants slightly modified due to the presence of the defect. A possible description of the different features observed in the Raman spectra of doped P3HT is schematically represented in Figure 4, right panel. In the lower doping case, the situation can be described by rather diluted polarons (blue rectangles), which have a size of around five P3HT monomer units, far from each other (Figure 4, case i). Portions of the chain next to the defect (blue dotted rectangles) perturbed by the presence of the polaron and extended neutral unperturbed segments are present. Figure 4, case ii shows a higher polaron density, where polarons are separated by short neutral and slightly perturbed domains. We called these neutral regions perturbed by the defects as PIBs (Polaron Influenced Backbone segment section). When the dopant concentration is very high (Figure 4, case iii) there are almost all polarons close one to each other, without unperturbed thiophene units in between. Assuming that polarons show no or very low Raman features and assigning the Raman band observed at 1430 cm^{-1} to neutral but perturbed regions (PIBs), we can explain the Raman spectra of the doped samples.

In the case i, representative of the low level of doping, the polarons are far from each other, and the neighboring regions coexist with long sequences of neutral thiophenes. These two different domains are supposed to give origin to a structured band peaking at 1435 cm^{-1} , which

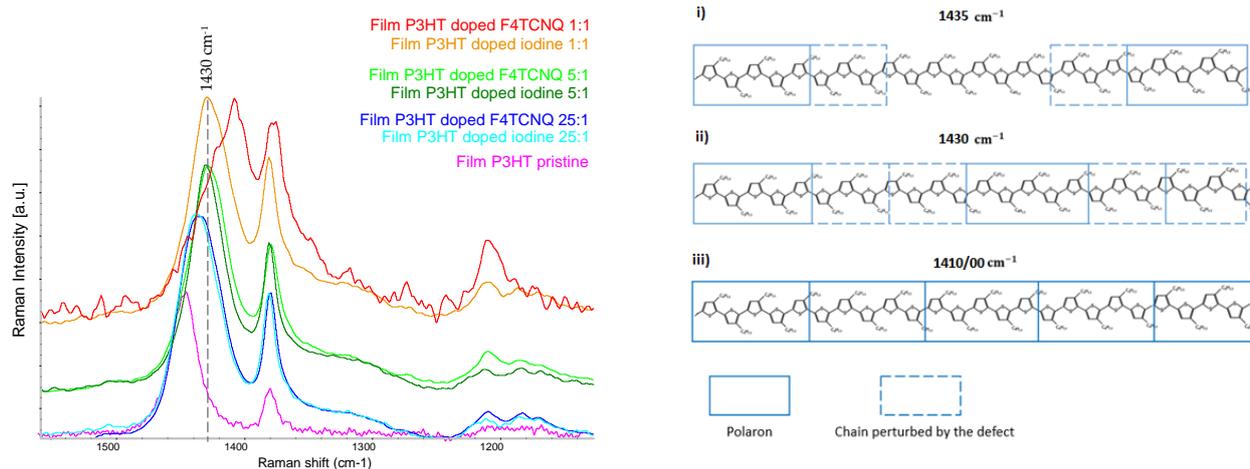


Figure 4: left panel: FT-Raman spectra of P3HT films doped iodine 25:1 (light blue line), 5:1 (dark green line), 1:1 (brown line) and F₄TCNQ 25:1 (blue line), 5:1 (light green line), 1:1 (red line); right panel: schematic representation of the three different components observed in the FT-Raman spectra at i) $1435 = 1445 + 1430 \text{ cm}^{-1}$, ii) 1430 cm^{-1} and iii) $1410\text{-}1400 \text{ cm}^{-1}$.

originates from the ECC mode vibration at 1445 cm^{-1} (as for the pristine polymer in Figure 4) and from a ECC mode shifted at lower frequency (1430 cm^{-1}).

For the case ii) representative of the medium level of doping only the band at 1430 cm^{-1} is observed because only the polarons and the neighboring perturbed domains (PIBs) coexist. When the dopant concentration is very high case iii) there are almost all polarons close one to each other, without unperturbed thiophene units in between, and so a band tentatively ascribed to the ring at the polarons interface appear at 1410 cm^{-1} , as observed for the polymer doped with F₄TCNQ: in Figure 4.

3.5. Raman spectroscopy of doped P3HT solutions

In Figure 5 are reported the spectra of P3HT solutions, doped with both I₂ and F₄TCNQ. It can be noticed that, as for the IR spectra in solution, there is a dependence on the doping ratio. Three main components seem to be present: the low intensity band ν_1 at 1445 cm^{-1} (solid pristine polymer), the 1430 cm^{-1} , and the last one at 1410 cm^{-1} .

Looking at the iodine doped solutions it can be observed that in the lowest doping level, 25:1, the band is centred at 1430 cm^{-1} ; the component observed at 1445 cm^{-1} in the solid sample is missing because in solution the long neutral sequences of thiophenes are no more co-planar but disordered.

When increasing the doping to 5:1 the band moves to 1425 cm^{-1} probably due to the convolution of the component at 1430 cm^{-1} with those at 1410 cm^{-1} . Finally, in the highest doping level there is a significant shift of the band down to 1410 cm^{-1} with a shoulder at around 1430 cm^{-1} due to the presence of many disordered polarons. The origin of the 1410 cm^{-1} vibration is still unclear and needs further studies.

Considering the F₄TCNQ doped solutions it can be seen that the spectra of samples 25:1 and 5:1 are very similar to the iodine doped ones, but some differences can be spotted out when looking at the 1:1 solution. In this case the band is much broader for the F₄TCNQ doped sample and is composed by different peaks: 1400 cm^{-1} , 1410 cm^{-1} and 1430 cm^{-1} . This complex and structured band could be due to the fact that, being the Raman intensity lower for charged segments, we are able to see components that in other cases we weren't able to observe because the strong Raman intensity of the neutral species dominate the spectra.

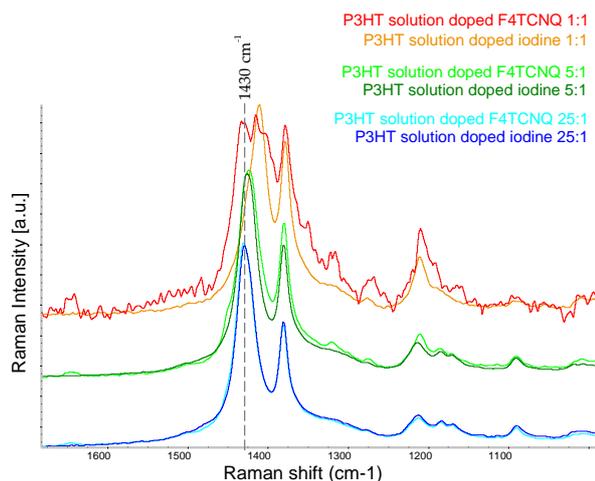


Figure 5: FT-Raman spectra of P3HT solutions in CHCl_3 doped iodine 25:1 (blue line), 5:1 (dark green line), 1:1 (brown line) and F4TCNQ 25:1 (light blue line), 5:1 (light green line), 1:1 (red line).

4. Conclusions

The mechanism of the chemical doping of P3HT with I_2 and F4TCNQ and the characterization of the different charged defects have been studied by means of IR and Raman spectroscopies by monitoring the doping process both in CHCl_3 solution and in solid state. This led to the identification of several spectroscopic markers associated to specific features of the doping process, so far not reported in the literature. We found that:

- In solution the doped samples show distinct spectroscopic features in function of the polymer/dopant ratio, thus highlighting the presence of three different types of polarons.
- The spectra of all the solid samples deposited from the solutions at different molar ratios, evolved towards a common pattern assigned to the polaron_OA phase which can be assumed to be the stable doped state of P3HT.
- A stable doping condition in CHCl_3 solution was achieved with the 5:1 polymer/dopant ratio, which allows to obtain the ordered polaron_OA phase already solution and then in the solid state.
- Finally, this study confirmed that Raman spectroscopy shows preferentially vibrational transitions of the neutral segments of the polymer chain.

Additional experiments, not reported in this executive summary, were conducted on P3HT

oligomers, regiorandom P3HT and P3DT, which allowed to validate the previous finding and to further characterize the three different kinds of charged defects observed in doped P3HT in solution. They are:

- i) the ordered polaron phase (polaron_OA) that is a kind of ICT present where the structure of the doped polymer chains can adopt an ordered crystal like architecture;
- ii) the disordered polaron phase, another kind of ICT, observed at high doping ratios;
- iii) charge-transfer complexes (CTC) that, differently from ICT, implies a partial charge transfer between polymer and dopant.

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