Experimental report

28/05/2019

Proposal: 7-01-464 **Council:** 4/2017

Title: Unravelling the interplay between electronic transport and phonon dynamics in organic thermoelectric materials

Research area: Materials

This proposal is a new proposal

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Samples: PEDOT:PSS
PEDOT:OTf
PEDOT:OTf-Deuterated

Instrument	Requested days	Allocated days	From	To
IN5	4	4	24/05/2018	28/05/2018

Abstract:

Thermoelectric organic or hybrid materials are considered as very promising alternative to inorganic semiconductors for recovering energy from heat sources below 100°C. Among them, the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising. We have recently optimized its electronic conductivity and thermoelectric properties via structure and dopant engineering. We reached the highest electrical conductivities (> 5000 S.cm-1) ever reported for a PEDOT thin film. At this stage of our study, we need to understand the interplay between the phonon modes and the electronic transport, which is basically unknown in such systems. Therefore we propose to investigate the dynamical properties by QENS over the temperature range of interest (150-400K), with the aim of establishing (or not) the relation between composition (hence, nanostructure, in particular crystalline vs amorphous domains), phonons (or, more generally, dynamics) and performance.

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Instrument IN5

Title: Unravelling the interplay between electronic transport and phonon dynamics in organic thermoelectric materials.

Participants: A. Schultheiss, O Bardagot, A. Carella, R. Demadrille, S. Lyonnard, D. Djurado

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The samples were consisting in thick, doped, freestanding films of PEDOT doped with 4 different dopants as shown in the figure 1. The films masses were 125 mg for PEDOT-PSS, 42 mg for PEDOT-OTf, 15 mg for PEDOT-Sulf and 12 mg for PEDOT-SufD.

They were multi-folded and placed into typical IN5 rectangular aluminum sample holders giving a typical thickness of 0.2 mm for the samples.

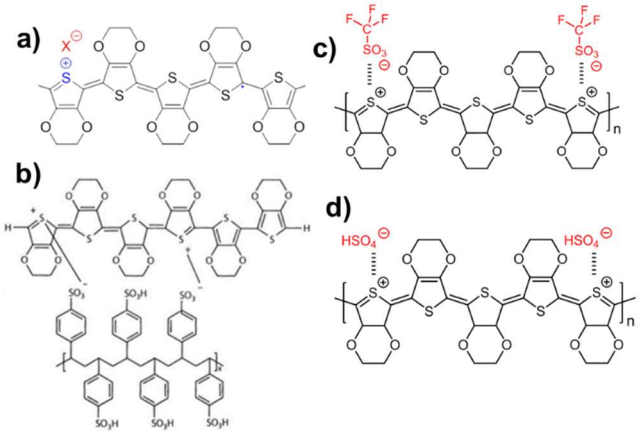

Fig. 1: *a) Generic formula of doped PEDOT, b) PEDOT-PSS, c) PEDOT-OTf, d) PEDOT-Sulf and we also studied the compound with deuterated Sulf dopant that we call PEDOT-SulfD*

The quasi-elastic scattering measurements have been made mainly using the 5Å wavelength for the incoming beam with a Gaussian shaped energy resolution of 86 µeV in FWHM.

In addition all the samples have been measured at 150, 200, 250, 300 and 350K. All the obtained results have been folded according to the recommendations given by the IN5 documentation in order to take into account the absorption, the presence of the sample holder, the instrumental resolution and the calibration of detectors. The quasi-elastic scattering functions have been obtained for 15 different values of scattering angles (or Q values) while all the vibrational density of states have been calculated for all the samples and all the temperatures (see examples in figure 2). Some quasi-elastic broadening is measurable for all samples, but the whole reality of the scattering behavior of all samples is shown in Fig. 2b with a clear existence of an excess of inelastic states very often denominated as a Boson Peak. This excess can also be seen in the low energy part of the vibrational densities of states (Fig.2c).

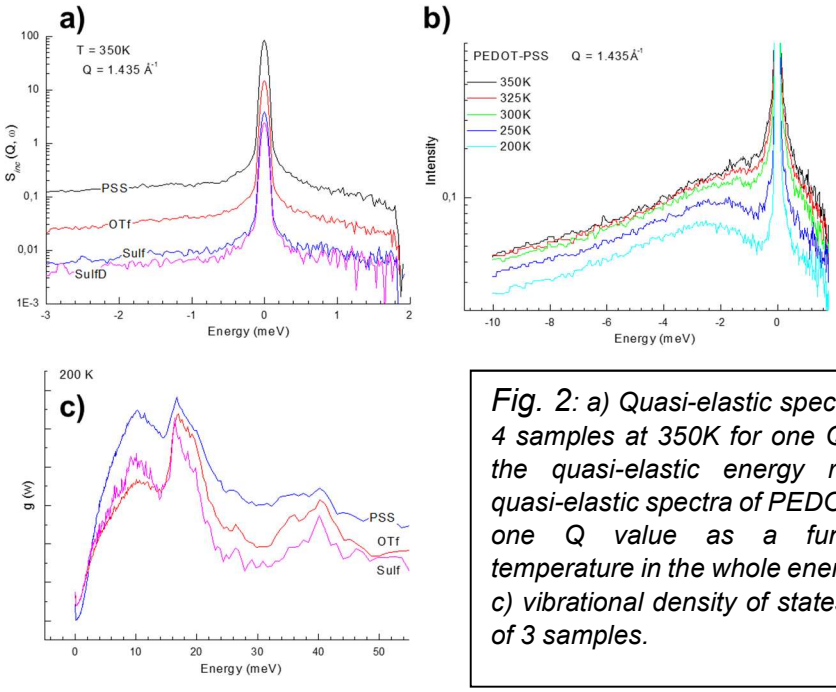

Fig. 2: a) Quasi-elastic spectra for the 4 samples at 350K for one Q value in the quasi-elastic energy range, b) quasi-elastic spectra of PEDOT-PSS at one Q value as a function of temperature in the whole energy range, c) vibrational density of states at 200K of 3 samples.

At this moment the analysis of all these results is far from being finished. We have first considered only the quasi-elastic energy range and considered we were measuring here the local diffusion of incoherent scatterers. By doing so we could extract some activation energies as seen in figure 3. The behaviors obtained with the samples Sulf and SulfD suggest that the main origin of these incoherent quasi-elastic components would mainly come from the counter-ions and not from the chains for which the quasi broadening would be too small or too large to be seen with this energy resolution.

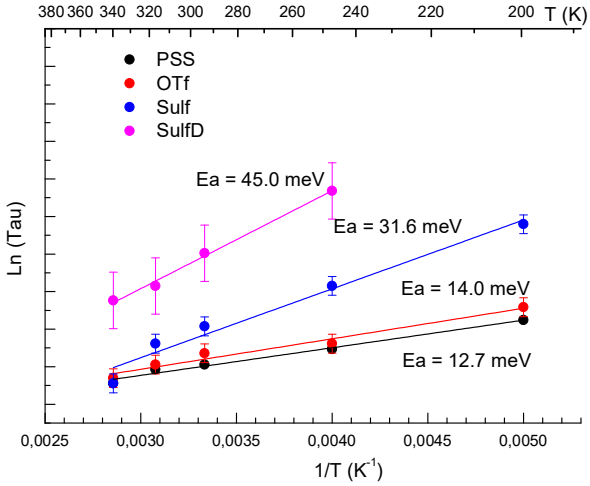

Fig. 3: *Activation energies obtained for all the samples after exclusive treatment of the quasi-elastic energy domain without considering the excess of inelastic states (Boson Peak)*

We are working on the complete treatment taking into account all the components contained in the whole energy range of scattering functions. Comparing these analysis with structure analysis performed by XRD and with molecular dynamics calculations should help us to offer some interpretation about the local and possibly one-phonon mode present in these systems.