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**Infrared Spectroscopic investigation on films of substituted polythiophenes
for photovoltaic systems
Final Report**

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This is a final report on the research activity performed at ISMAC - CNR institute in Milan, hosted by Dr Silvia Luzzati, in the period December 9, 2007 - December 21, 2007.

The experimental work has consisted of infrared and Raman spectroscopic investigation of substituted polythiophenes both in solid state and in solution and of the monomer PEDST (the selenium equivalent of PEDOT) electropolymerized on Pt foil covered Germanium electrode in nitrogen atmosphere.

The goals were:

- to learn about Raman and Infrared spectroscopy measurements technique and to acquire new skills useful to solar energy conversion research activity;
- to collect Raman spectra in the visible and Near Infrared range of POPT, PEOPT, POMeOPT and electropolymerized PEDST;
- to collect Photoinduced Infrared Absorption Spectra of POPT, PEOPT, POMeOPT and electropolymerized PEDST;
- to analyze experimental results and compare with previously *in situ* FTIR spectroelectrochemistry experiments results on the same materials.

My stay in ISMAC-CNR has been very fruitful and leading to publishable data. Moreover I had the opportunity to gain new skills and competences that I could use in my future scientific activity. The team in Milan provide me a great and enjoying working atmosphere, supporting me during my experiments. It has already been planned a future collaboration and contact between my institute LIOS and ISMAC-CNR in order to continue and complete presented work.

I would like to thanks ESF for the accepted grant and the detailed report about the experimental results will be presented as follows; the discussion part will be mainly improved during writing future manuscript for possible publication.

Best Regards,

Sandro Lattante

January 10, 2008

I. INTRODUCTION

Organic photovoltaic systems promise efficient low-cost and large area solar cell devices. Photovoltaic devices based on electron acceptor-donor system have been extensively studied and have reached power conversion efficiencies around 5% under AM 1.5 [1]. However improvements in efficiency are needed for practical applications. In order to overcome the disadvantages of small molecule photovoltaic systems (i.e. insufficient absorption in the visible range and unbalanced transport properties of both types of charge carriers), heterostructures can be realized using polymers as donor and acceptor materials.

Substituted polythiophenes are very interesting materials as they can be modified by proper design of side groups and have been tested successfully in organic solar cells [2].

In order to deeply understand the properties of devices based on such materials, spectroscopic investigations on the individual components as well as the mixture are necessary. The formation and transfer of charge carriers is the fundamental process in photovoltaic devices: more details about the overall process can be obtained by combining electrochemistry (oxidation and reduction processes) and spectroscopic methods (UV-VIS-NIR, Raman and Photoinduced Infrared Absorption) in order to gain information on the kinetics of electron transfer and on the stability of the charged states of donors and acceptors as well as the identification of charge carriers.

II. EXPERIMENT

The molecular structures of the studied materials are reported in Fig. 1.

Previously ATR-FTIR (Attenuated Total Reflection FTIR) *in situ* spectroelectrochemistry experiments were done in LIOS by Prof. Teketel Yohannes of Chemistry Department of Addis Ababa University during oxidation and reduction of the materials, showing that among electroactive conjugated polymers POPT, PEOPT and POMeOPT can be both oxidized and reduced reversibly (paper in progress), while in case of PEDST the reduction seems to be irreversible.

In order to complete those experiments, photoinduced absorption measurements and Raman measurements (in the visible and infrared range) have been performed in ISMAC-CNR in Milan, as due to the strong electron-phonon coupling in conjugated polymers Raman and infrared spectroscopy technique are very useful for the investigation of charge induced lattice relaxations.

Solid samples of POPT, PEOPT and POMeOPT have been realized by drop casting from chlo-

roform solution (6 mg/ml) on glass substrates at room temperature and in air for Raman experiments, while a KBr substrate has been used for photoinduced infrared absorption experiments. PEDST has been used as obtained from Prof. Yohannes (electropolymerized from the EDST monomer at positive bias on Germanium electrode coated with a thin layer of Platinum, and then carefully dedoped). EDST monomer was synthesized by Prof. Peter J. Skabara at Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow.

For Photoinduced Absorption FTIR (PIA-FTIR) the samples have been mounted on the cold finger of a liquid nitrogen cooled cryostat equipped with ZnSe windows and illuminated at 45° exciting with the 488 nm line of an Argon laser with intensity of 30 mW cm^{-2} . The spectra have been obtained collecting first 10 single spectra with pumping laser on and then 10 single spectra with pumping laser off. In order to obtain a good signal-to-noise ratio 100 to 400 repetitions of this sequence have been accumulated.

Raman experiments have been performed in air at room temperature. In the near infrared range samples have been excited with a Nd-YAG diode laser (1064 nm) and spectra have been recorded using a Bruker IFS66+ FRA 106 FT spectrometer. In the visible range excitation has been supplied by 457, 488 and 514 nm lines from an Argon laser and 633 nm from an He-Ne laser, and the spectra have been collected with a Jasco TRS 300 monochromator coupled with a OMA 1420 cooled diode array.

Resolution was 4 cm^{-1} .

Absorption spectra have been collected both with an UV-Vis-NIR Perkin Elmer Lambda 900 spectrophotometer and a Cary Varian 3G UV-Vis Spectrophotometer.

III. RESULTS AND BRIEF DISCUSSION

Absorption spectra of POPT, PEOPT and POMeOPT solutions and cast films are reported in Fig. 2 and in Fig. 3 respectively. As expected a general red shift of the solid samples spectra is seen; a wide broadening of the lineshape in the case of solid samples is evident to respect the solution spectra. While no clear vibronic features could be seen in the case of film absorption spectrum of POPT and PEOPT, the spectrum of POMeOPT shows a clear vibronic structure and a less pronounced lineshape broadening. Photoluminescence spectra of POPT, PEOPT and POMeOPT solutions and cast films are reported in Fig. 4 and in Fig. 5 respectively. No substantial differences are present in the PL spectra from solutions, while in the case of solid samples PL spectra

from POPT and POMeOPT are clearly redshifted to respect solid POMeOPT PL spectrum and extremely weaker in intensity. These features could be explained with the formation of broad absorbing and low emitting species in POPT and PEOPT cast films. The different substituting groups led to aggregates and morphology packing that substantially modify the optoelectronic properties of the samples. It has been not possible to perform absorption and photoluminescence experiments on PEDST on Pt foil.

More informations can be obtained from Raman and infrared spectroscopy. Raman, Infrared absorption and Photoinduced Infrared Absorption spectra are reported in Figg. 6, 7 and 8 for POPT, PEOPT and POMeOPT respectively (x axis is wavenumber).

The lack of relevant Raman lines around 1100 cm^{-1} and the presence of intense line around 1350 cm^{-1} (that are generally absent in polythiophenes) could be the sign of an increased density of quinoid form of the ground state with increasing in the inter-ring electronic delocalization.

As can be seen in Figg. 9 and 10 a clear shift of the Raman peak at 1470 cm^{-1} as a function of the excitation wavelength appears, while in the case of POMeOPT (see Fig. 11) no such shift can be clearly noticed. The shift of the frequency with excitation wavelength has been demonstrated in the case of Poly(dithiophenes) [3]. These figures will be improved including the PIA bands and the *in situ* infrared bands after the correct band assignment will be made.

From the comparison of these Raman spectra and *in situ* IR spectra and from the comparison of the *in situ* obtained IRAV band and the reported Photoinduced absorption spectra it will be possible to gain knowledge about the charge species and the photodoping processes in this class of materials. This analysis and the correct assignment of Raman bands are in progress.

In the case of PEDST it has been possible to record only Raman spectra in the visible range as can be seen in Fig. 12. Despite many attempt, no infrared spectra were recorded due to the few quantity of material on Pt and the consequent impossibility to realize a solid blend with KBr in order to be able of performing Photoinduced Infrared Absorption measurements. Also in this case a Raman peak (1467 cm^{-1}) shift with the excitation wavelength can be seen (see Fig. 13).

IV. CONCLUSIONS AND FUTURE PLANS - FUTURE COLLABORATION WITH ISMAC-CNR

Interesting set of data has been reported and a general introductive discussion has been performed about Raman and Infrared experiments on reversible reduction-oxidation capable polymers to be used in novel organic solar cells. A detailed analysis, discussion and comparison with data

from Prof. Yohannes is at present in progress. New infrared experiments on PEDST are in planning as there is the necessity to electropolymerize more quantity of material from the monomer EDST in order to perform such measurements. This will be performed again in collaboration with ISMAC-CNR in the next future.

V. PROJECTED PUBLICATIONS

A paper to be submitted to an international scientific Review is in progress: all the data of present experiments are being fully analysed focusing on the comparison between the presented results and *in situ* results of Prof. Teketel Yohannes. Moreover new electropolymerized PEDST infrared experiments are going to be performed at ISMAC-CNR.

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 - [3] A. Cravino, H. Neugebauer, S. Luzzati, M. Catellani, N. S. Sariciftci, *J. Phys. Chem. B* **105**, 46 (2001)

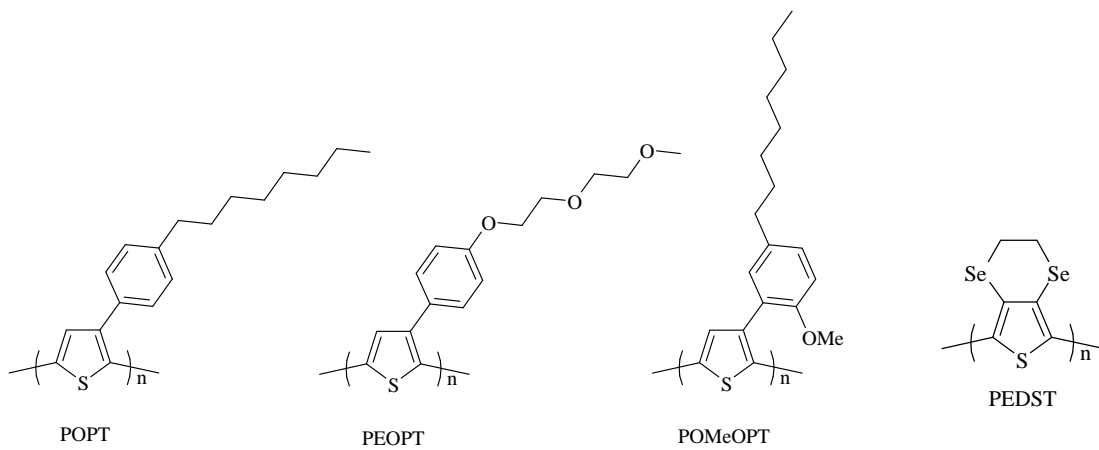


FIG. 1: Molecular structure of POPT, PEOPT, POMeOPT and PEDST.

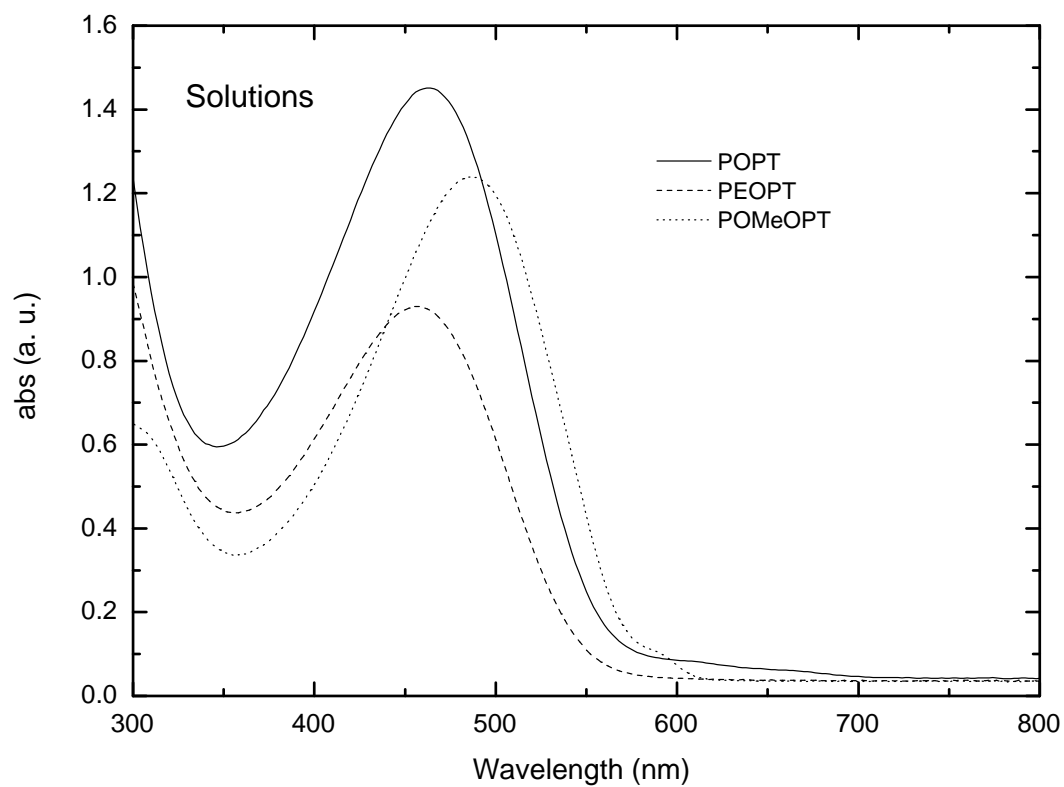


FIG. 2: Absorption spectra of POPT, PEOPT, POMeOPT solutions

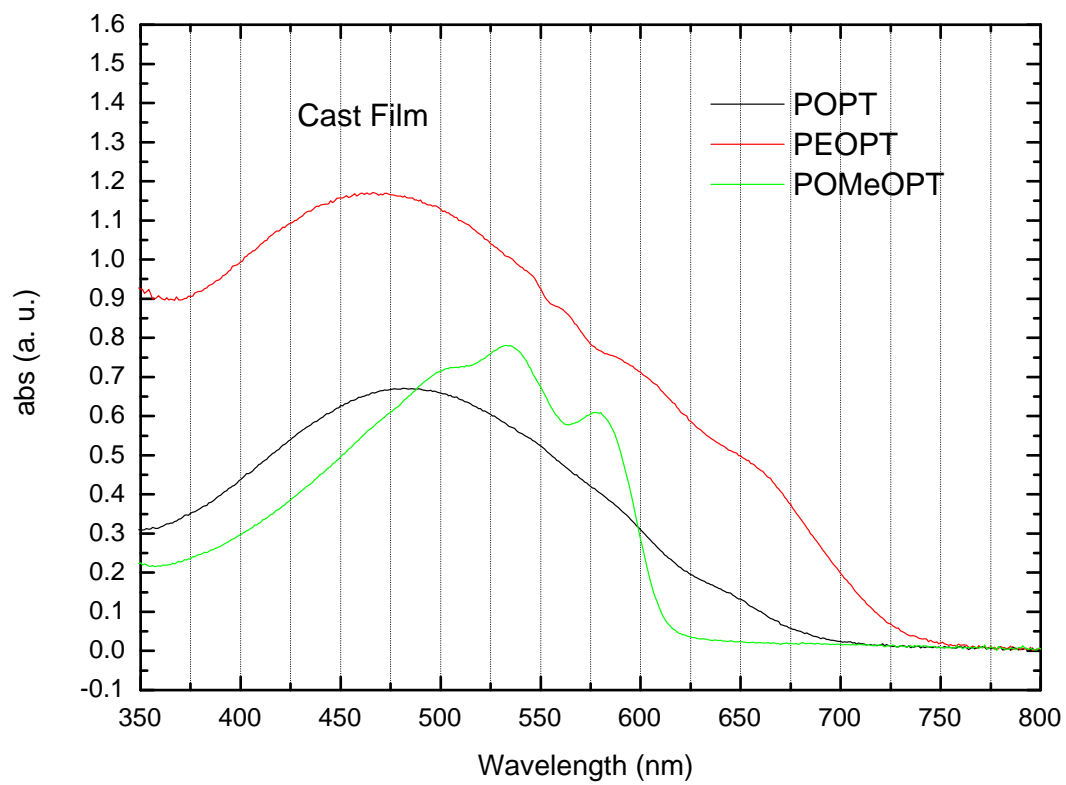


FIG. 3: Absorption spectra of POPT, PEOPT, POMeOPT cast films

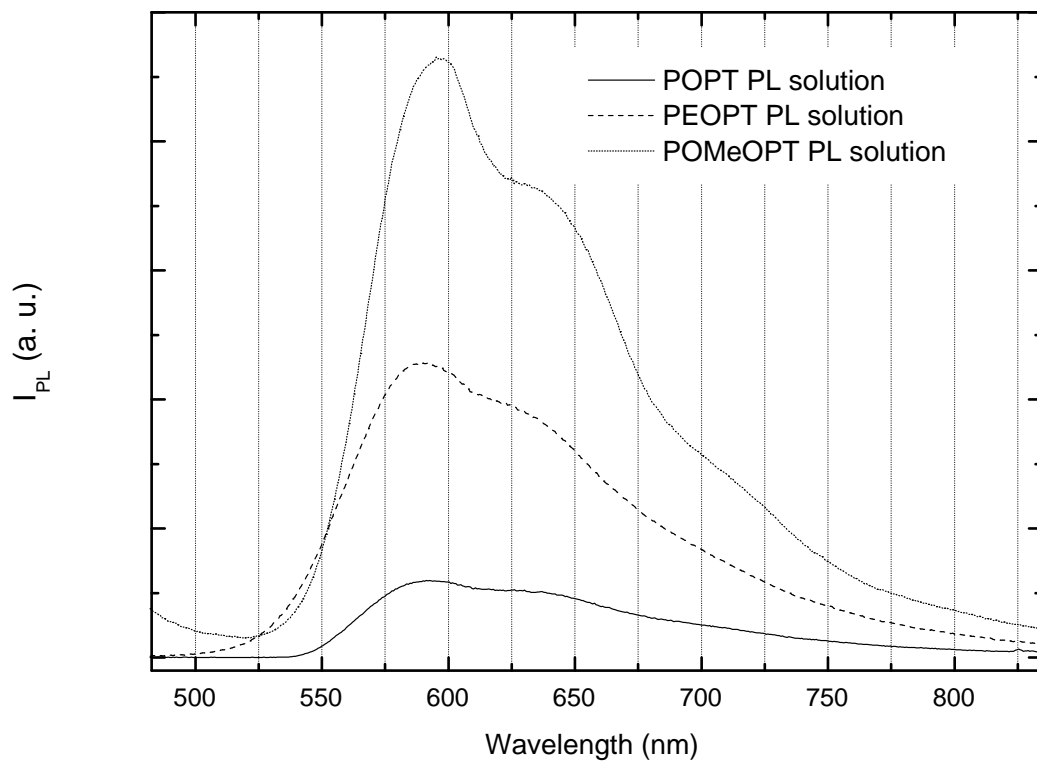


FIG. 4: Photoluminescence spectra of POPT, PEOPT, POMeOPT solutions

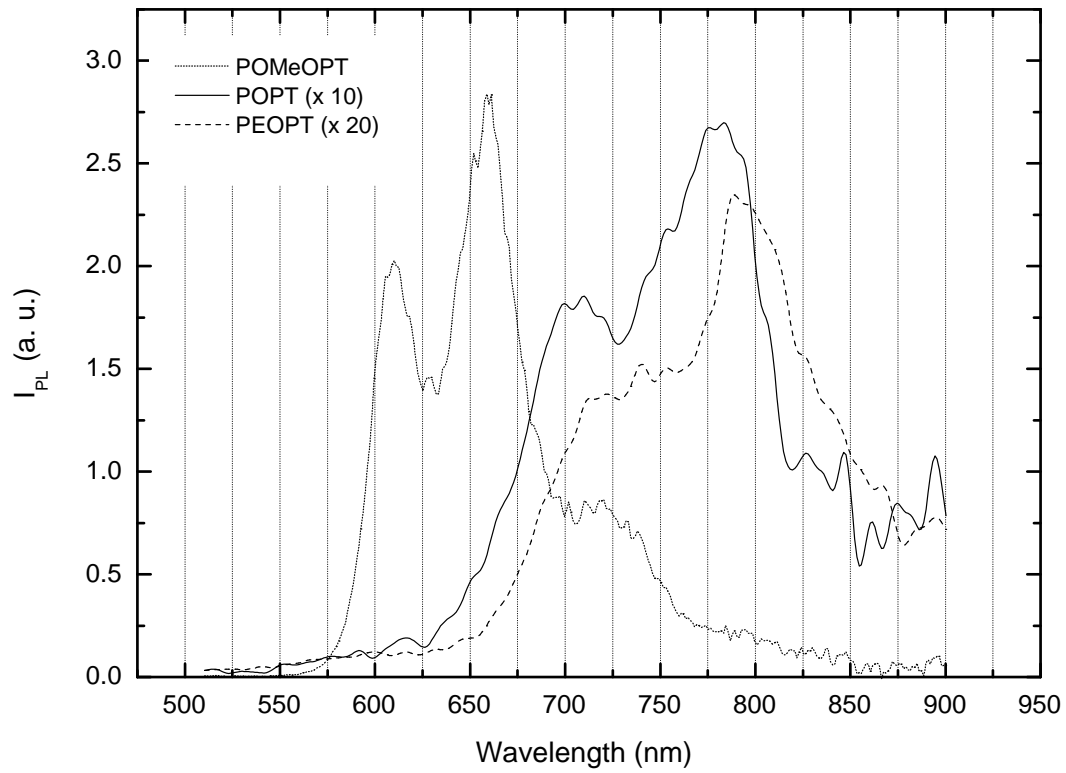


FIG. 5: Photoluminescence spectra of POPT, PEOPT, POMeOPT films. POPT and PEOPT spectra are multiplied by 10 and 20 respectively and smoothed by FFT filter for clarity.

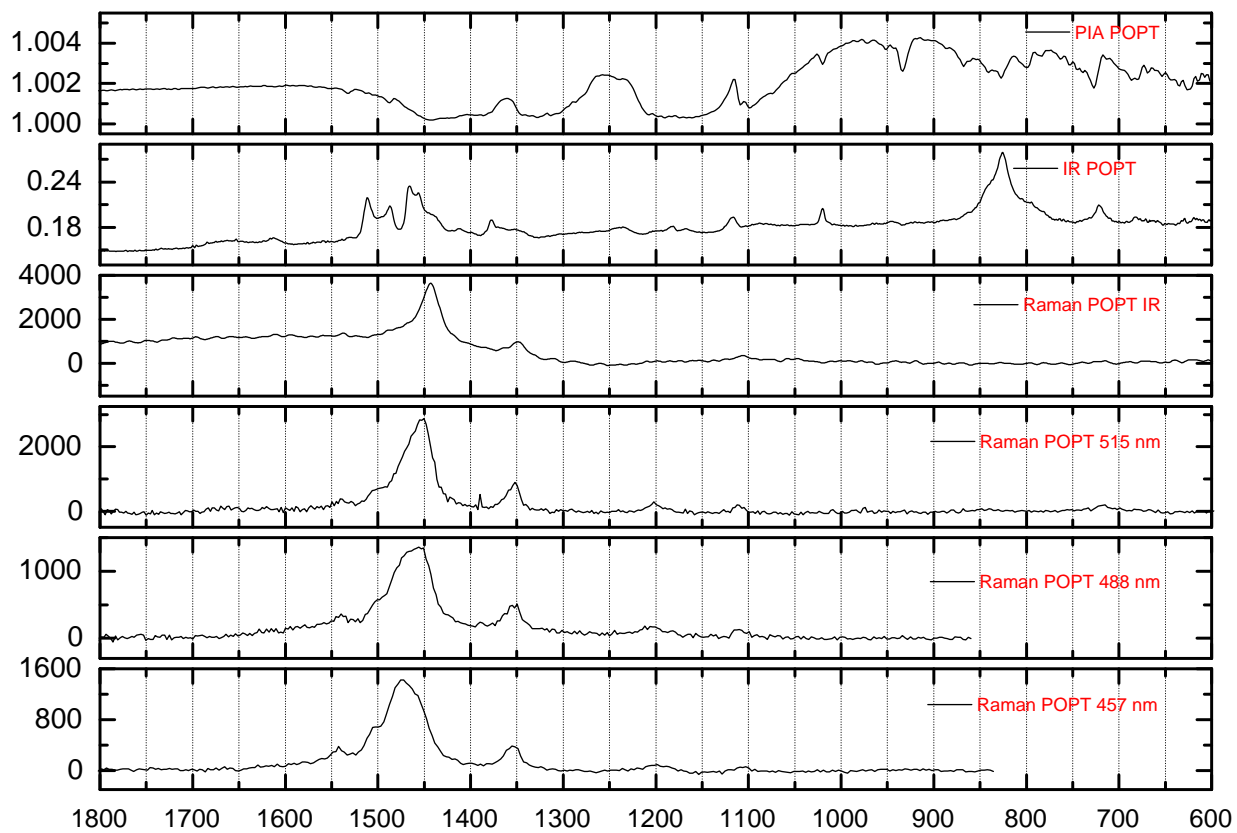


FIG. 6: POPT spectra: from bottom to top 457, 488, 514 and 1064 nm Raman, Infrared absorption and Photoinduced Infrared Absorption. x axis in wavenumber.

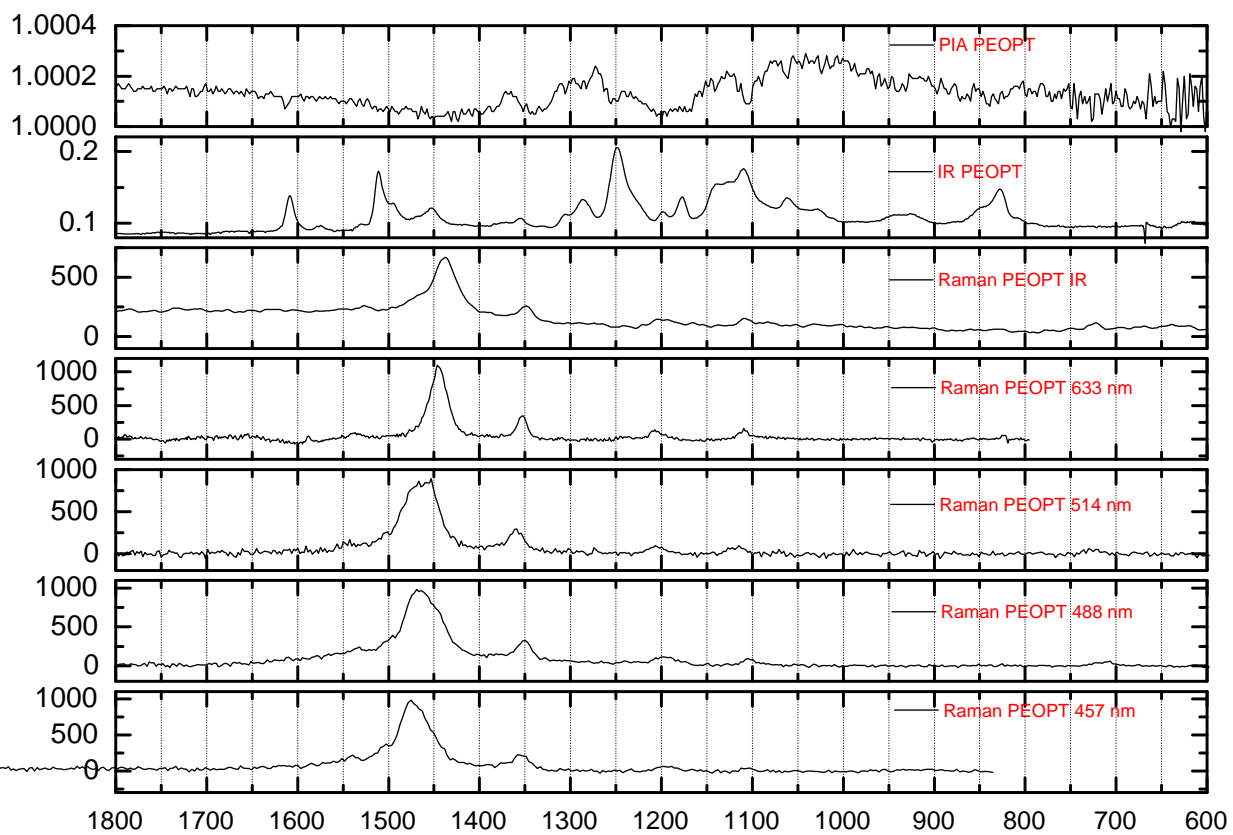


FIG. 7: PEOPT spectra: from bottom to top 457, 488, 514, 633 and 1064 nm Raman, Infrared absorption and Photoinduced Infrared Absorption. x axis in wavenumber.

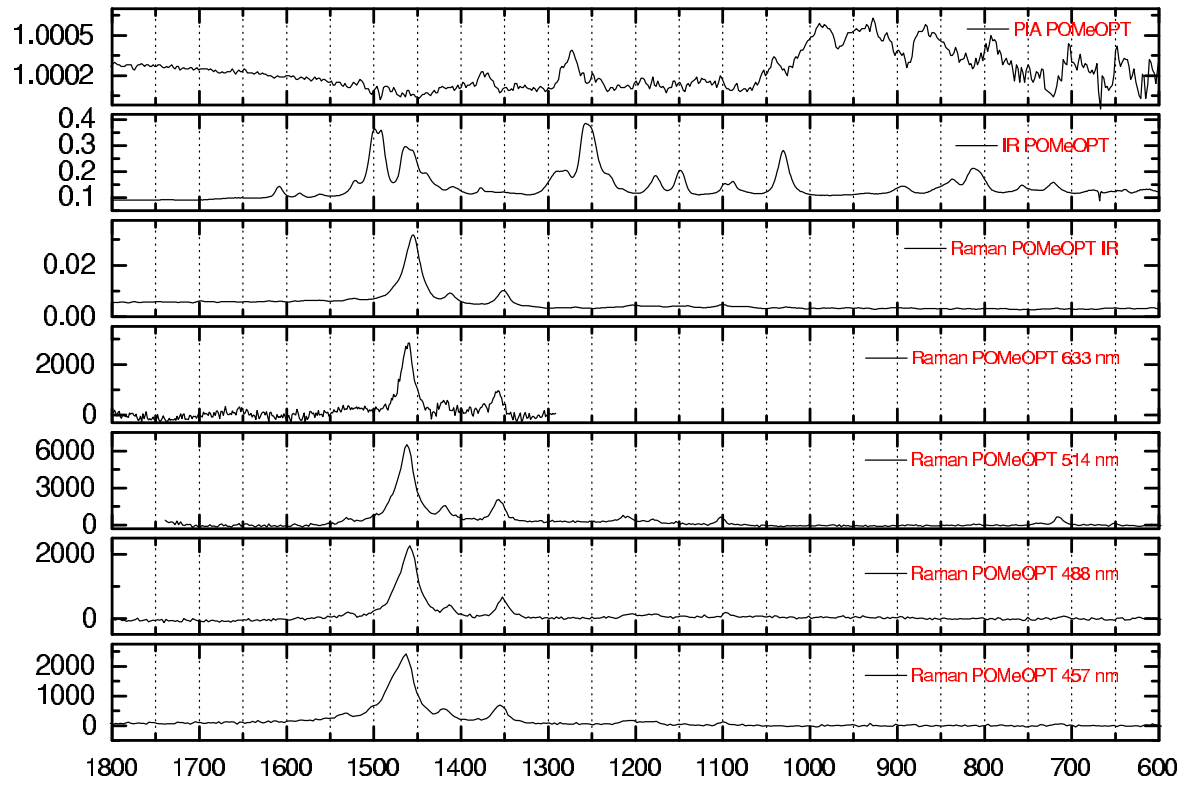


FIG. 8: POMeOPT spectra: from bottom to top 457, 488, 514, 633 and 1064 nm Raman, Infrared absorption and Photoinduced Infrared Absorption. x axis in wavenumber.

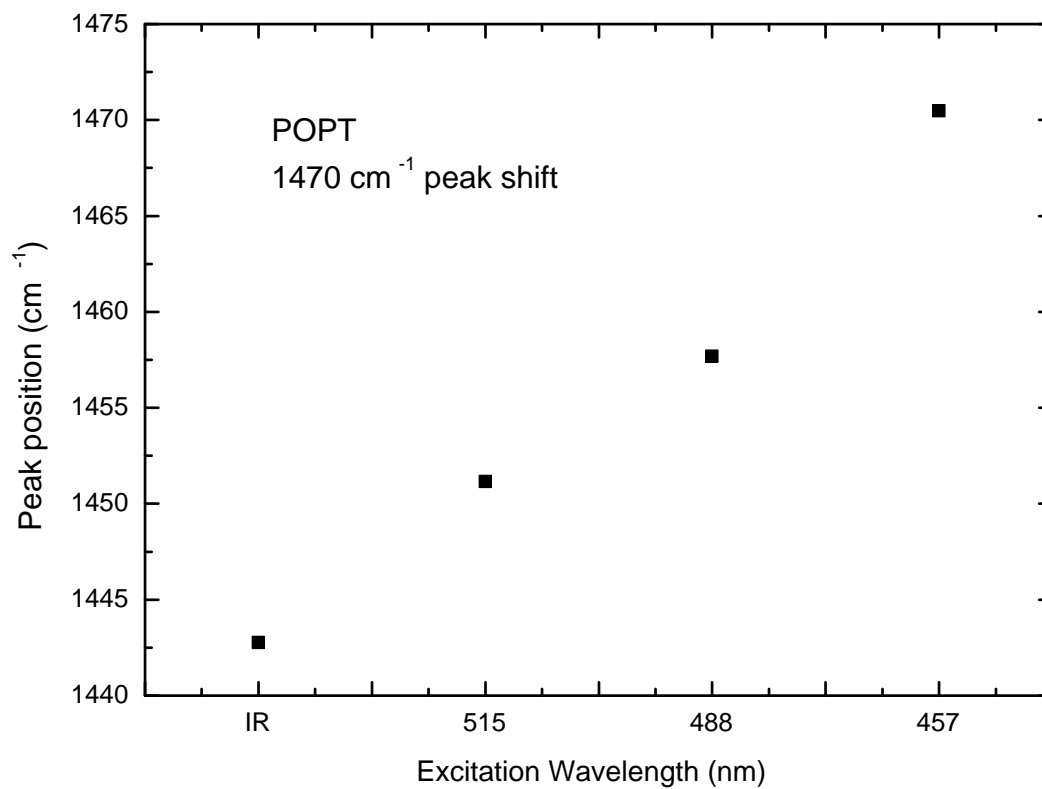


FIG. 9: POPT 1470 cm⁻¹ shift as a function of excitation wavelength. IR = 1064 nm.

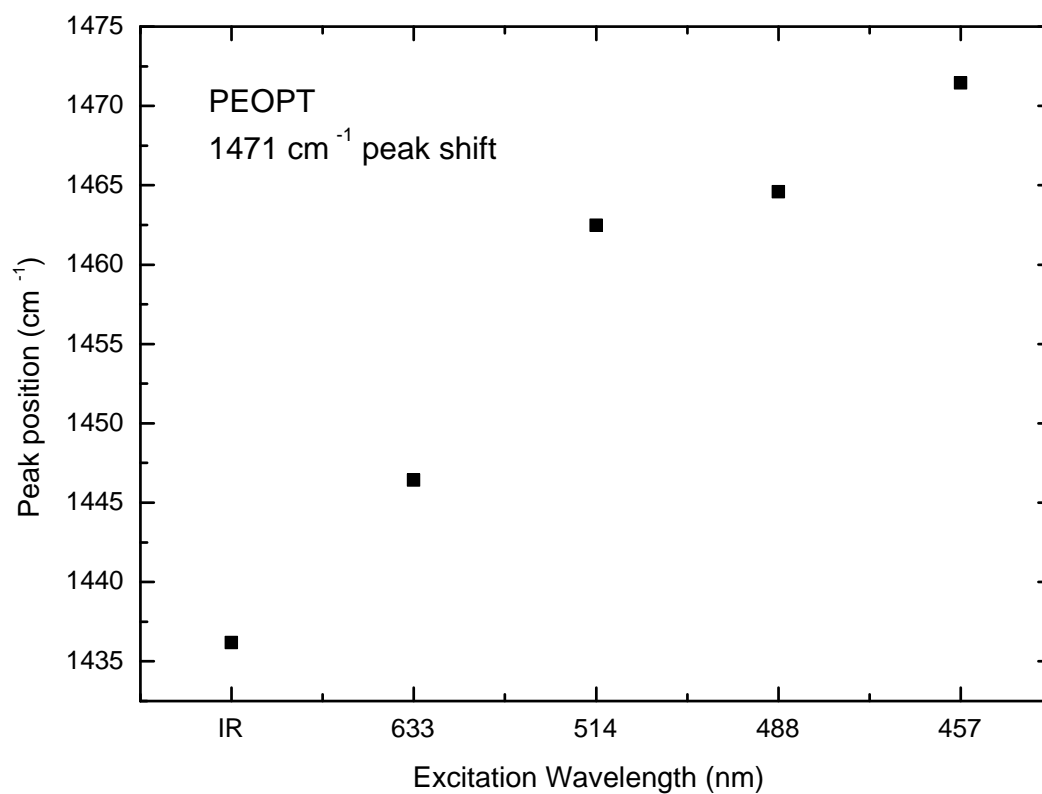


FIG. 10: PEOPT 1471 cm⁻¹ shift as a function of excitation wavelength. IR = 1064 nm

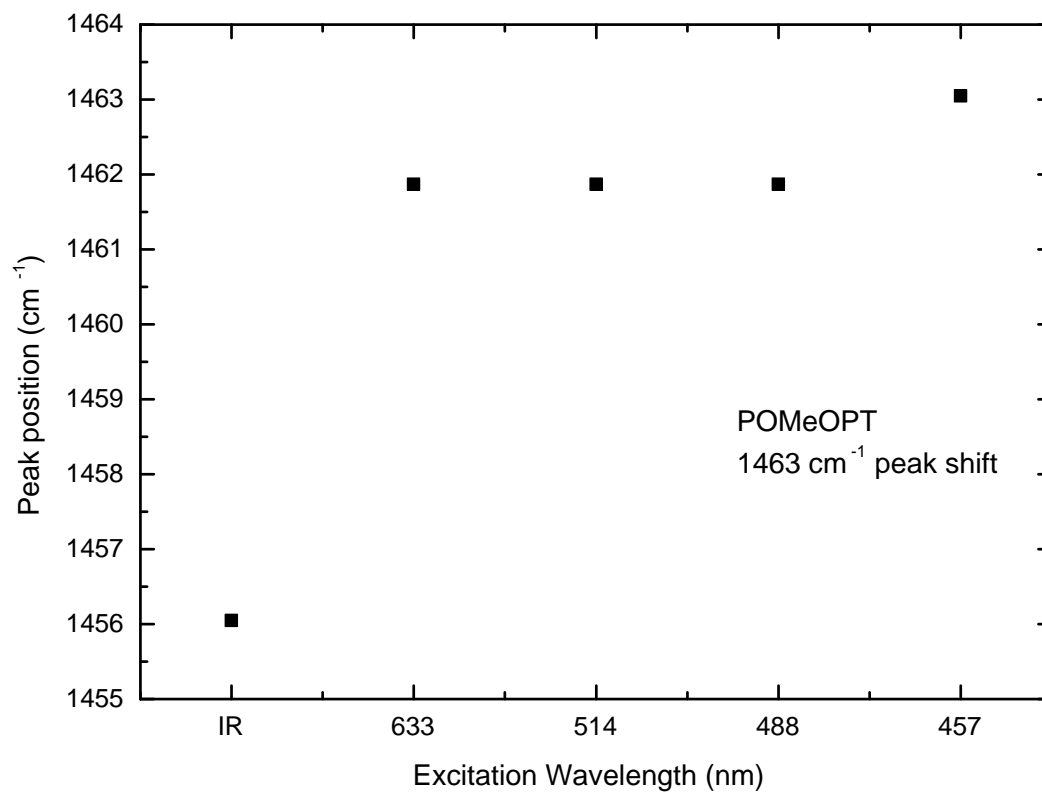


FIG. 11: POME OPT 1463 cm^{-1} shift as a function of excitation wavelength. IR = 1064 nm

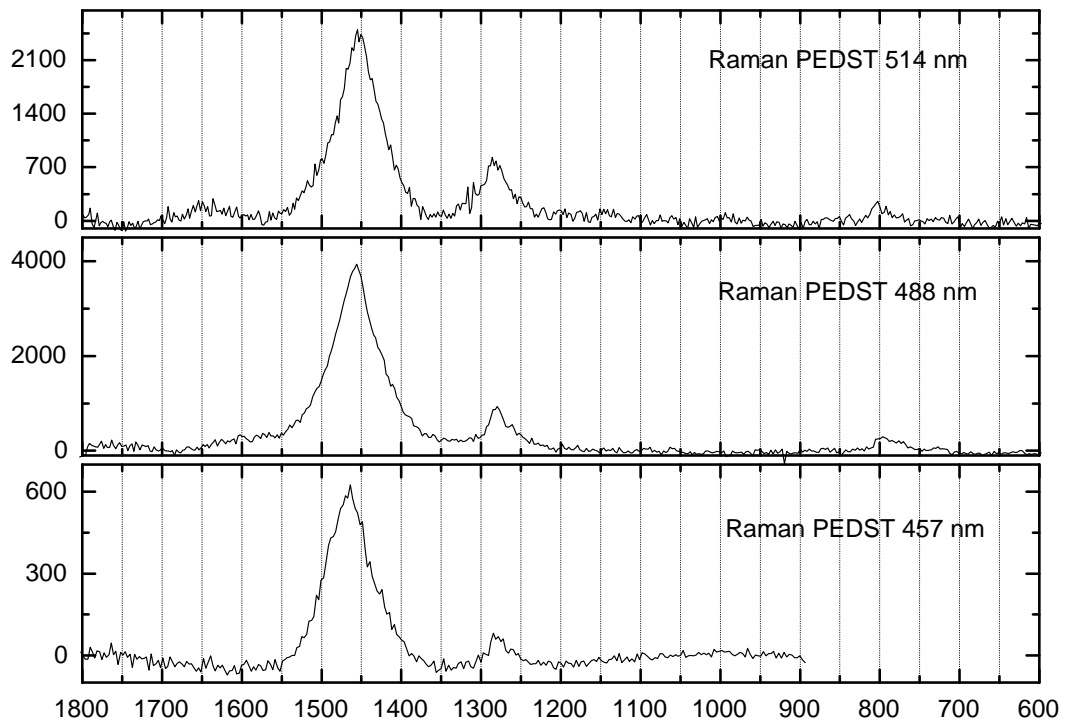


FIG. 12: PEDST spectra: from bottom to top 457, 488, 514 nm Raman.

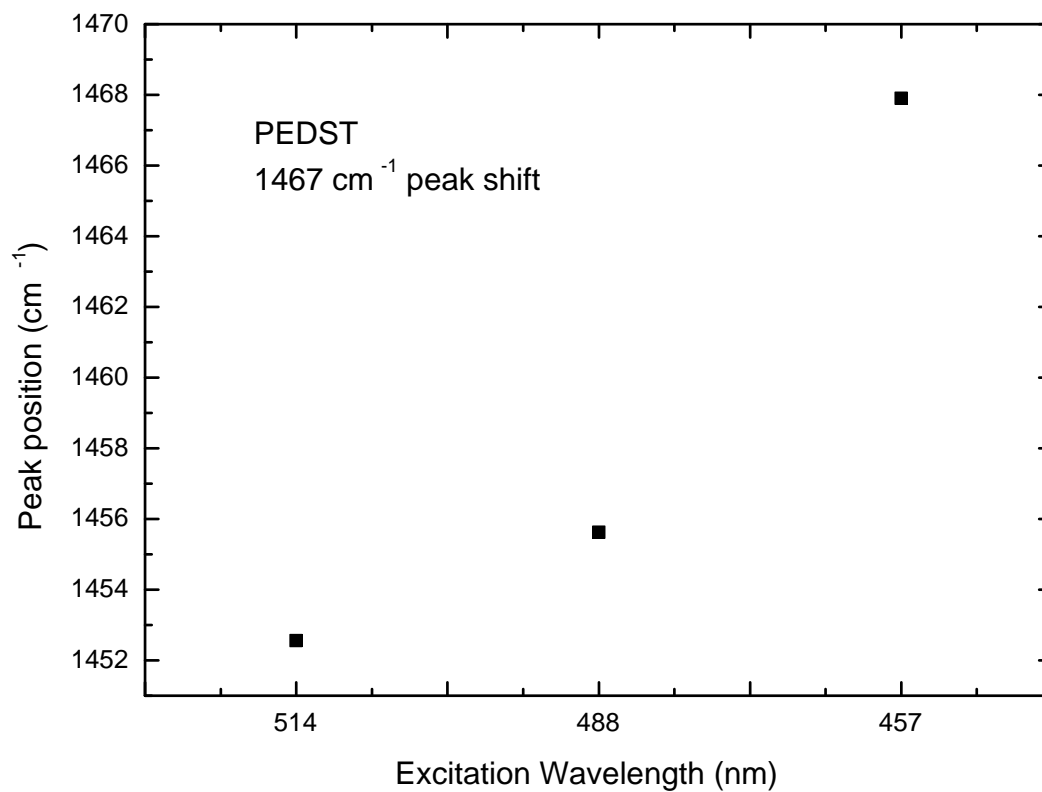


FIG. 13: PEDST 1467 cm⁻¹ shift as a function of excitation wavelength.