



Vibrational Spectroscopy and Molecular Simulation of Thiophene Polymerization

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Introduction

- Conjugated polymers have been of recent interest in biomedical devices due to their ability to conduct both electronically and ionically; which makes them ideal for interfacing soft ionically conducting tissues with electron conducting metals.
- Poly(3,4-ethylene dioxithiophene) or PEDOT has received particular interest due to its chemical and mechanical stability. There has been considerable focus on the design, synthesis and characterization of functionalized PEDOT conjugates.
- A major limiting in this effort has been the insolubility of PEDOT in most known solvents; this makes molecular weight measurements by conventional techniques like Column Chromatography, Gel Permeation Chromatography essentially impossible.
- Here, we examine the use of vibrational spectroscopy techniques to obtain insights about the electrochemical polymerization of PEDOT.



Fig.1: Illustration of a bionic hand

Electrochemical Polymerization

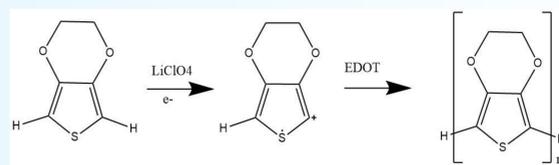


Fig. 2: PEDOT electropolymerization mechanism

- PEDOT was electrochemically polymerized in water on a 0.5 cm x 0.5 cm Indium Tin Oxide working electrode passing a constant current of 75 μ A for 600 seconds. Water was used as a solvent with LiClO_4 as a counterion.
- A dark blue film of PEDOT develops on the electrode.

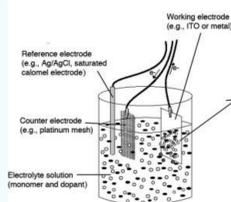


Fig. 3: Schematic of Electrochemical Polymerization of PEDOT (Courtesy of Nathalie Guimard and Dr. Christine Schmidt, The University of Texas at Austin)

In-Situ TEM imaging of electrochemical deposition of PEDOT

- Low dose (0.1-1 mC/cm^2), in-situ transmission electron microscopy (TEM) was used to image the early stage nucleation processes and the liquid to solid transitions involved in the polymerization process.

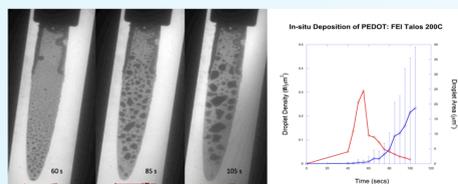


Fig. 4: (Left) Bright field images of oligomeric clusters of PEDOT depositing on a glassy carbon electrode (scale bar -20 nm) using a constant current of 150nA imaged at 200 kV on Talos F200C (Right) Nucleation density plot of the in-situ polymerization of PEDOT

- Transitions between liquid and solid interfaces were observed and quantitative estimates of the change in droplet intensity with total charge are being tracked.

Experimental Results

- The patterns of EDOT and PEDOT were compared and peak assignments were made. Additionally EDOT and EDOTacid Raman spectra was measured.

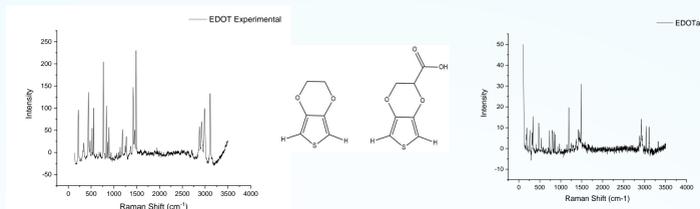


Fig.5. (From left to right) EDOT Raman spectrum; molecular structures of EDOT and EDOTacid; EDOTacid Raman spectrum

- A comparison of the Raman spectra for EDOT, PEDOT and EDOTacid was done and the peaks were tabulated.
- A peak is seen at 1510 cm^{-1} which has been associated with the quinoidal C=C stretch.

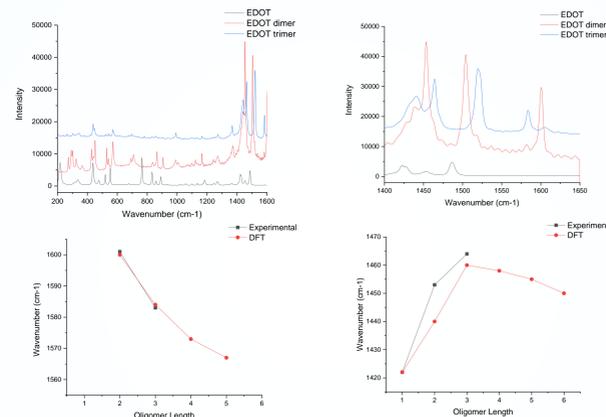


Fig. 6: (From top left clockwise) EDOT monomer, dimer and trimer experimental spectrum; closeup of the 1400-1650 cm^{-1} region; Comparison of DFT and experimental results for 1601 cm^{-1} dimer stretch; Comparison of DFT and experimental results for 1422 cm^{-1} stretch

- An antisymmetric benzoidal C=C stretch develops at 1601 cm^{-1} and then shows a redshift for the trimer. Correlating strongly with DFT calculations, this trend continues for higher oligomers as shown with the calculations
- Conversely we see a blueshift for the symmetric C=C stretch going from 1424 cm^{-1} to 1463 cm^{-1} experimentally
- These oligomer peaks are visible even in the experimental Polymer spectra

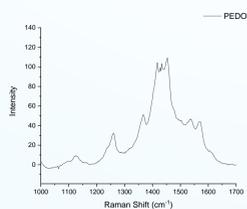


Fig.7: PEDOT Raman spectrum

Oligomer	Cm^{-1}	Measure
Monomer	Absent	Experimental
Dimer	1601	Experimental
Trimer	1582	Experimental
Quartamer	1573	Gaussian
Pentamer	1566	Gaussian
Hexamer	1558	Gaussian
Septamer	1559	Gaussian

Table.1: Evolution of C=C antisymmetric benzoidal stretch as a function of oligomer length; experimental and DFT projection

Gaussian Simulations

- Geometry Optimization and Frequency calculations were performed on EDOT and its oligomers to identify critical peaks which could give us an indication about polymerization.
- DFT calculations were performed with the 6311G(2d,p++) basis set with a tight convergence criterion.
- Using the spectral data of EDOT, EDOT oligomers and EDOTacid we were able to assign peaks corresponding to the various vibrational modes as shown by the Gaussian calculations with confidence

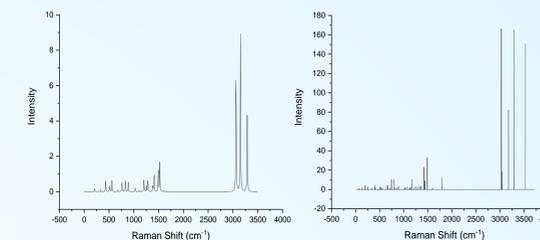


Fig.6. Calculated Raman spectra of EDOT and EDOTacid

- The C-H stretching region (2800-3200 cm^{-1}) is of special interest to us, since the thiophene proton is the reactive proton in our reaction. We are carefully examining modes that could indicate the progress of the polymerization reaction.

Relative Intensity Model

- There is strong correlation between experimental and simulation data to suggest that the mode at 3110 cm^{-1} corresponds to the thiophene C-H stretch. We expect this mode's intensity to stay relatively constant; with minor changes due to coupling effects.
- Additionally, the peak seen at 1422 cm^{-1} has been identified in the literature as the C=C stretching vibration which is also consistent with our experimental data. We expect this mode to show a drastic change in intensity due to the formation of extended conjugation due to polymerization.
- We plotted the theoretically predicted ratio of the relative intensity of these peaks as a function of oligomer length to give us a model for analyzing our PEDOT data

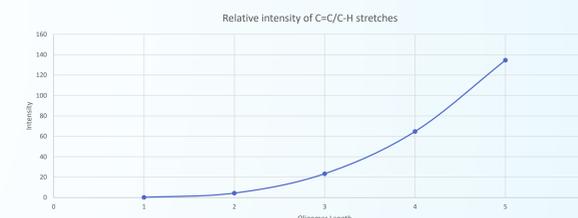


Fig.7. Relative intensities of C=C stretch/ thiophene C-H stretch as a function of oligomer length

- Then, we determined these ratios for our experimental measurements to get an estimate for average PEDOT oligomer length. This was done using Indium Tin Oxide (ITO), gold interdigitated (GID), and platinum interdigitated (PID) as working electrodes. The model fit for ITO,GID and PID working electrodes gives us oligomer lengths of 7.8, 4.7 and 3.9 respectively.
- Thus, according to the model fit ITO gave longer oligomers than GIDs or PIDs for the given conditions.

Conclusions and Future Work

- We have developed a model for molecular weight estimation of PEDOT oligomers using experimental and simulated Raman spectra.
- We demonstrated its potential utility in differentiating oligomer lengths and reaction optimization
- Correlations of Raman spectroscopy data with in-situ TEM experiments should give us valuable insights into the physical transformations correlated with chemical changes.
- A higher degree of correlation between experimental and simulated results can be obtained through geometrical optimization forcefield calculations combined with experimental data.

- Thus, we can track polymerization in insoluble hard to characterize polymers.

Acknowledgements

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