The work presented by Mr Przemyslaw Data deals with the spectroscopic, electrochemical and spectrochemical study of a wide series of PP and PPV analogues prepared with α-thieno, furano, seleno and telluro side heterocycles.

The manuscript begins with a very well written and documented presentation of the state of art in oligomers, both of PPV and analogues and poly(heterocycles). Interestingly, stress is put on the bibliography amount analysis, which reflects both the interest of the community in these compounds and related ones, and also the difficulty of the syntheses. The introduction also features the description of the advancement of research in organic photovoltaics, which is the avowed goal of this study.

The description of the work is then divided into two logical parts, namely the electrochemical analysis on one hand, and the spectroscopic and spectroelectrochemical on the other hand. The electrochemical study is cautiously made, using DPV for a precise measure of the redox potentials since almost all the oligomers exhibit a reversible behavior both in oxidation and reduction, at least for the first couple.

Then is described the spectroscopic study, presenting not only the absorption but also the fluorescence behavior of the compounds. The spectroelectrochemistry comes after, and allows to precise the spectra of the cation-radicals. Comparison is presented between the electrochemical gap and the optical gap, and it is quite interesting to notice than an excellent agreement is reached between the two set of measurements. Accordingly, the fluorescence emission wavelength is increased when the heteroatom changes to a less electronegative one. Mr Data has also calculated the HOMO and LUMO energies (despite I could not find the method employed) and the results correlate nicely with both the results of the electrochemical and optical investigations. However, it should be remarked that the correlation is better with the monomers than with the polymers, as it could be expected.

To complete the presentation of the work arrives then a discussion stressing out the main teachings of this study.

Many interesting points can be extracted out of this important work. First, all monomers prepared are fluorescent, which was not obvious, especially with tellurium because of the “heavy atom effect”, which could move the excited state of the molecules into the triplet state and quench the fluorescence. This is one of the key points of the work, since this
is also the first demonstration of fluorescence with tellurophene based organic oligomers. The redox potentials of all monomers have been examined in relation with the nature of the heteroatom present. It comes out that, besides the expected relationship between the potential lowering and the electronegativity of the heteroatom of the heterocycle, a special situation arises with the tellurophene based compounds which have sometimes an interesting, and lower than expected band gap. Therefore it is expectable to bring on noticeable improvements on the efficiency of solar cells based on such oligomers. The P3 (selenophene based) oligomers of the phenylene-vinylene type also features very promising properties in this direction.

The vinylene type monomers happen to be more conjugated than the purely aromatic ones, as it could be expected. It would have been interesting to study a couple of monomers with a rigid vinyl linker, in order to check if even lower band gaps could be obtained. The candidate also discusses the coloration of the polymers in relation to the redox states. It happens that again the selenophene based polymer P3 display a much better coloration efficiency than other polymers.

Finally, the candidate has also examined a last point of interest, which is often neglected in concurrent works, the influence of the alkyl chains on both the monomer and the polymer behaviours within a same aromatic core. He shows that, as expected, the growing length of the alkyl chains induces a bathochromic effect to the absorption, whose maximum is shifted towards longer wavelengths. This is understandable since longer alkyl chains separate the monomers and probably eliminate the aggregation of the aromatic cores and induce a better planarity in the conformation of the molecules.

A pleasant feature of the manuscript is the inclusion of all the publication into the document. It should be noticed that Mr Data has already a solid file of publications, which confirms the quality of the overall work.

Altogether, this manuscript describes a very complete and huge work on the physicochemical characteristics of completely new organic oligomers with promising characteristics in the ultra-fast growing of organic electronics, and I definitely recommend the public defense of this excellent work.