

Abstract of the PhD thesis

**Single molecule surface-enhanced Raman spectroscopy  
of porphycene and its derivatives**

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This thesis is focused on single molecule studies of porphycene and its derivatives by means of surface-enhanced Raman spectroscopy (SERS). Although the extraordinary sensitivity of the SERS technique was reported over two decades ago, only about 40 different chromophores have been detected on a single molecule level so far. We managed to extend this list by a few more species: porphycene and some of its derivatives. In this research, we investigated the spectroscopic features of these chromophores as well as the phenomena related to the SERS technique.

The single molecule studies were preceded by the detailed characteristics of porphycene using Raman spectroscopy and the SERS technique using different excitation wavelengths. Reaching a single molecule level was confirmed by numerous observations: the results of bi-analyte approach performed for mixture of porphycene and its perdeuterated isotopologue, and characteristic time evolution of the SERS signal exhibiting intensity fluctuations, blinking, and one-step bleaching. The in-depth analysis of the enhancement factor was performed, including determination of the contributions from both resonance Raman and electromagnetic effects. While the resonance effect provides the enhancement of Raman signal up to  $10^3$ , the maximum value of the enhancement due to the presence of plasmonic nanostructures was estimated as  $10^{11}$ .

Two methods of the analysis of correlations between Raman peaks were presented: from a single time trace and from a collection of single spectra recorded at different hot spots. Such analysis revealed that a molecule immobilized in a hot spot cannot move freely. Indeed, the patterns of correlations changed over time. Moreover, it was shown that from the measured SERS spectrum the approximate orientation of a molecule can be extracted. This can be done, however, only with support of predictions of shapes of Raman tensors.

Furthermore, the detectability of different chromophores by the SERS technique was compared. It turned out that it is highly influenced not only by the electronic structure of a molecule, but also by its spatial structure. This was demonstrated on a family of *tert*-butyl substituted porphycenes. The more of these bulky groups were introduced into molecular structure, the lower was the number of detected single molecules. The decreased detectability was in this case accompanied by the increase in the fluorescence background observed in the

SERS spectra. These findings show the limitations of the SERS technique in both qualitative and quantitative analysis.

Finally, the effect of lowering the temperature on photostability and spectral features was explored. It was demonstrated that by decreasing the temperature the higher sensitivity could be achieved.

The theoretical and experimental results presented in this thesis extend our knowledge regarding the investigated chromophores and contribute to a better understanding of the phenomena related to detection of single molecules by the SERS technique. Moreover, the findings demonstrates that using single molecule studies we can acquire knowledge that cannot be gained from bulk measurements. For instance, the observation of exotic species and behaviours, such as a *trans-cis-trans* tautomerization reaction.