Modification of Metal Surfaces by Optically Active [7]Helicene Derivatives for Molecular Sensing.

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Modification of Metal Surfaces by Optically Active [7]Helicene Derivatives for Molecular Sensing

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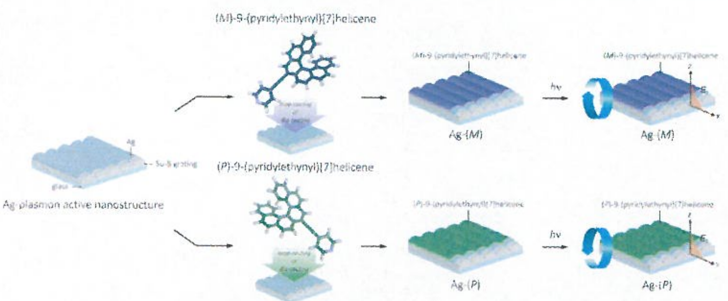
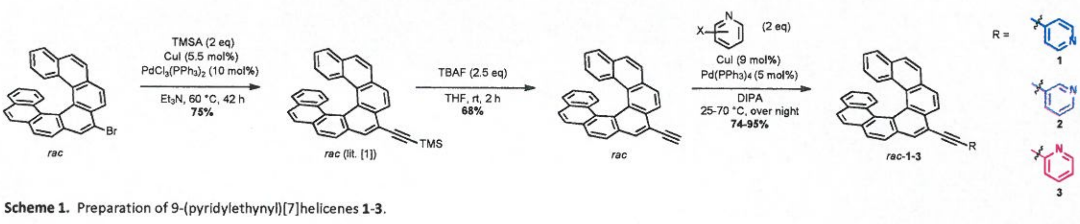


Fig. 1. Preparation of helicene based SPP silver nanogratings for molecular sensing.

Introduction. Helicenes and their functional layers have a great application potential in many fields of research due to their unique electronic and chiroptical properties. Although they were successfully applied in molecular recognition and sensing, their use in surface plasmon polariton-based detection is exceptional indeed. With regard to above mentioned fact, new derivatives of 9-(pyridylethynyl)[7]helicenes were firstly prepared and fully characterized in this study. Consequently, they were successfully separated to their (*P*)- and (*M*)-enantiomers using preparative HPLC with a chiral stationary phase. These optical antipodes were advantageously used for modification of silver plasmon active nanogratings suitable for a SERS-based detection of biomolecules (Fig. 1). Properties of such nanostructures were studied using different spectro- and microscopic techniques. As proved by UV-Vis spectrometry, a change of plasmon resonance wavelength position and intensity was observed and indicated the appearance of chiral surface plasmon polarization.

Synthesis, Separation of Enantiomers and Grating Preparation.



Scheme 1. Preparation of 9-(pyridylethynyl)[7]helicenes **1-3**.

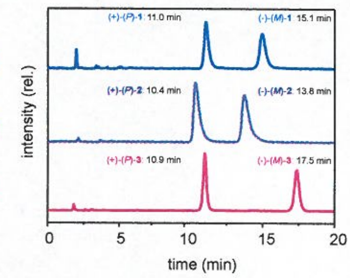
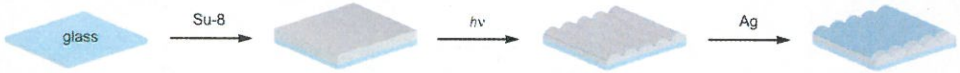


Figure 2. Chiral HPLC chromatograms of *rac*-**1** (blue), *rac*-**2** (violet) and *rac*-**3** (magenta). Diacel® Chiralpak IA (250 x 4.6 mm, 5 μm), n-heptane/2-propanol (97.5 : 2.5 for *rac*-**1** and *rac*-**2**, 95 : 5 for *rac*-**3**), flow-rate: 2 mL min^{-1}.



Scheme 2. Preparation of Ag-grating structure.

SPP Hybrid Nanostructures.

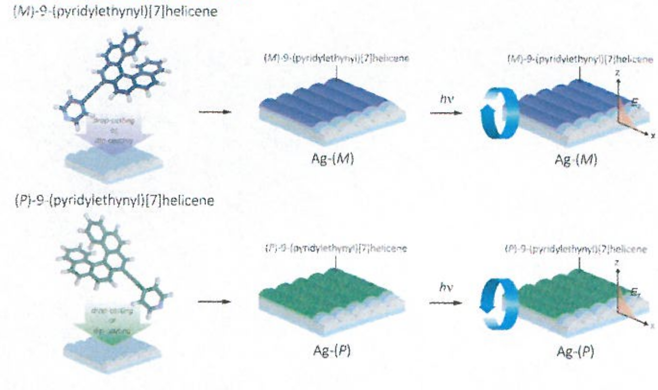


Fig. 3. Preparation of hybrid SPP nanostructures (e.g. **1**).

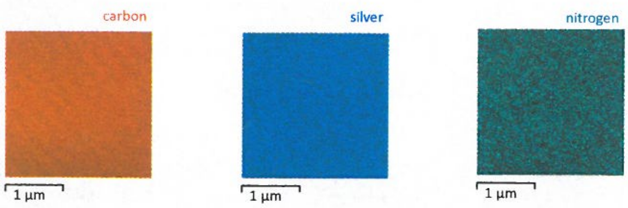


Fig. 6. SEM-EDX images of Ag-(*P*)-**3** for carbon, nitrogen and silver.

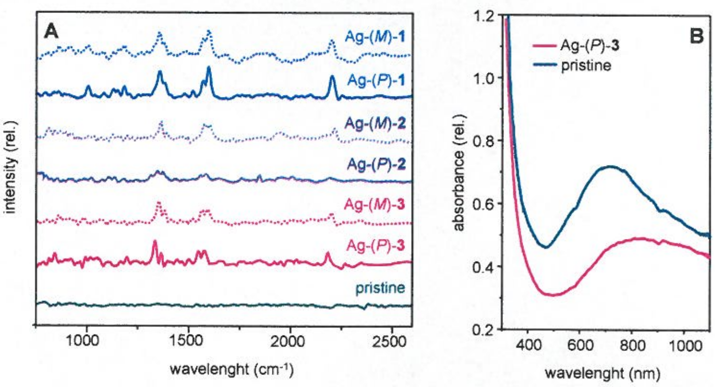


Fig. 5. SERS spectra (**A**) of nanogratings Ag-(*P*)-**1-3** (solid) and Ag-(*M*)-**1-3** (dotted) prepared by dip-coating; UV-Vis spectrum of Ag-nanograting (**B**) before (deep blue) and after (magenta) modification by (+)-(*P*)-**3**.

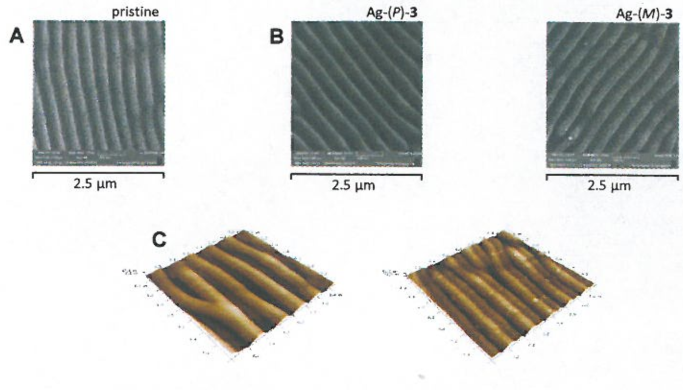


Fig. 4. SEM image of pristine silver nanograting before (**A**) and after (**B**) modification by (*P*)-/(*M*)-**3** and AFM images (**C**) of Ag-(*P*)-/Ag-(*M*)-**3**.

Conclusion. Helicene-based hybrid SPP nanostructures were prepared and characterized by various spectro- and microscopic techniques in this study. Chiral plasmon response was observed by UV spectroscopy and its further study is recently under a progress in our lab. Based on previous results [2], such nanostructures are very promising in a recognition of chiral molecules as one of the most encouraging topics in a photonics research.

VŠCHT PRAHA

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[1] Žádný, J.; Velíšek, P.; Jakubec, M.; Sýkora, J.; Církva, V.; Storch, J. *Tetrahedron* **2013**, *69*, 6213
[2] Kalachyova, Yevgeniya; Guselnikova, Olga; Elashnikov, Roman; Panov, Illia; Žádný, Jaroslav; Církva, Vladimír; Storch, Jan; Sýkora, Jan; Švorčík, Václav; Lyutakov, Oleksiy, *unpublished results*

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