SYNTHESIS AND CHARACTERIZATION OF SERS-ACTIVE HETEROAROMATIC MOLECULES

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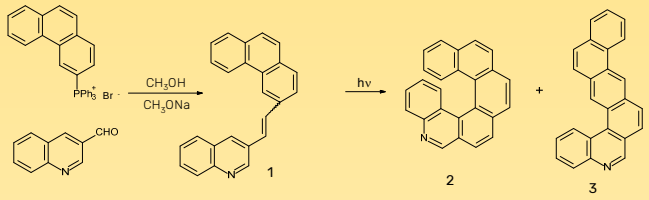
Abstract

Azahelicenes are extensively conjugated, intrinsically chiral molecules with interesting optical and optoelectronic properties. They show interesting SERS activity as well as fluorescence. While synthesizing 5-aza[6]helicene (**2**) we observed concurrent formation of derivative (**3**). Since it was formed in non-negligible amount, we decided to characterize it as well respect to its spectroscopic and emission properties. We recorded UV-Vis absorption and concentration-dependent fluorescence spectra of (**3**) excited at 314 nm. We observed an excellent linear dependence of the emission maximum (429 nm) vs. concentration in diluted MeOH solutions ($5x10^{-5}$ - $3x10^{-4}$ mM). We also carried out density functional theory calculations, aiming at the interpretation of the observed SERS features of the molecule once adsorbed on gold substrates produced by PLD with a plasmon resonance close to 785 nm. We concluded that this molecule, too, shows promising features for applications in the manufacturing of SERS-active surfaces.

Synthesis

The synthesis follows the Scheme below:

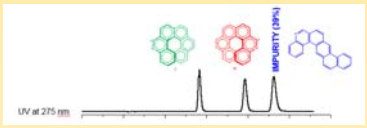


During the last step of the synthesis of 5-aza[6]helicene (**2**), namely photolysis of precursor (**1**), we noticed the formation of byproduct (**3**), phenanthreno[2,3-k]phenanthridine. Overall, about 18% of the products are constituted by (**3**) when the photolysis is performed in ethyl acetate with visible light, after 7 h, when no more starting material (**1**) is present. When the photolysis is performed in acetonitrile, after 7 h the solution contains 30% of the starting material, 46% of product (**3**) and 7% of (**2**). We noticed that the formation of (**3**) increases in time, so that, to minimize it, the process is interrupted at a relatively early stage, product (**2**) separated and the remaining precursor further photolysed. Performing the photolysis under cooling did not avoid the formation of (**3**), which becomes observable after 3 h of photolysis.

Synthesis and characterization of 5-aza[6]helicene described in : Abbate, S. et al. *J. Phys. Chem. C*, **2014**, *118* (3), 1682-1695

Separation

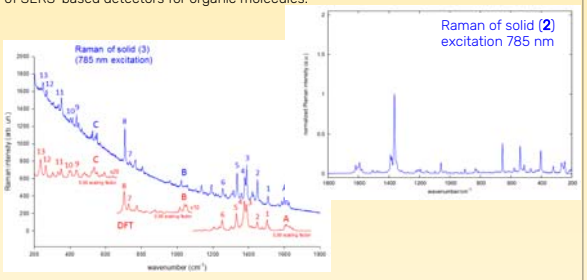
The separation can be performed on alumina by eluting with hexane/ethyl ether 1:1.
HPLC separation … The product mixture resulting from several batches was separated on a chiral semipreparative IA 250 mm x 4.6 mm column, with the purpose of separating the two enantiomers of azahelicene (**2**), with mobile phase *n*-hexane-IPA-ethyl acetate-DEA 100/5/5/0.2. In the procedure, achiral product (**3**) was separated.



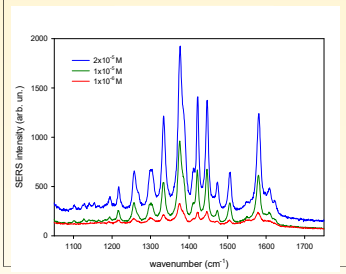
we thank prof. Cirilli – University of Rome for the HPLC separation

Azahelicenes and their SERS activity

Since azahelicenes proved to be remarkably SERS-active molecules, we tried to examine the SERS response of product (**3**), to verify the possibility of using it in the design of SERS-based detectors for organic molecules.



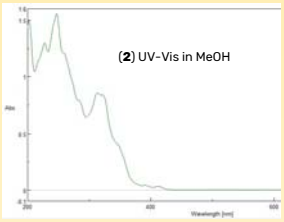
After studying the Raman spectra of products (**2**) and (**3**), also comparing them with DFT calculations, we produced SERS-active surfaces by immersing nanostructured gold surfaces into solutions of (**2**) and (**3**), in order to highlights their features and differences.

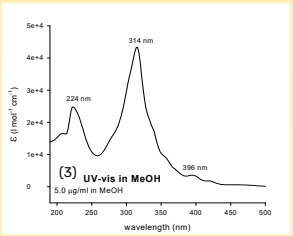


SERS on Au of (**3**) in MeOH
excitation 785 nm

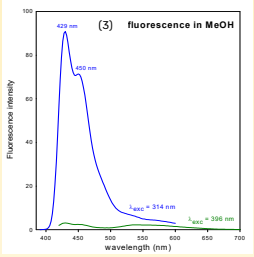
Spectroscopic features

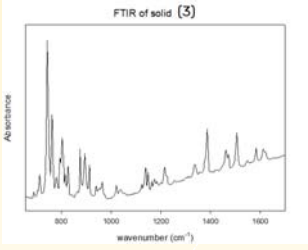
Given the considerable amount in which we obtained product (**3**), we considered the possibility that it, too, could show interesting optical properties; therefore we analysed its IR, UV and fluorescence spectra comparing them to those of product (**2**).





(**2**) fluorescenza (da fare)





Commenti sulle differenze negli spettri: il composto (3) dà veramente una maggior fluorescenza rispetto a (2)?

Conclusions

- Nanostructured gold surfaces, fabricated by PLD and previously optimized for SERS activity, were functionalized with organic moieties endowed with both SERS activity and fluorescence.
- The surfaces were characterized for their structure, activity and robustness to verify the viability of the method for the preparation of chiral sensors, with very promising results
- Future work will concern the preparation of similar surfaces functionalised with enantiomerically stable aza[6]helicenes for the sensing of biomolecules, both by SERS and fluorescence spectroscopy

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