ANNEX A

PUBLIC SELECTION BASED ON QUALIFICATIONS AND INTERVIEW FOR THE AWARDING OF NO. 1 EXPERIENCED GRANT LASTING 17 MONTHS FOR CONDUCTING RESEARCH PURSUANT TO ART. 22 OF LAW NO. 240/2010 AT THE DEPARTMENT OF ENGINEERING AND APPLIED SCIENCES A.R.F. 03/B2 - PRINCIPLES OF CHEMISTRY FOR APPLIED TECHNOLOGIES - A.D. CHIM/07 - PRINCIPLES OF CHEMISTRY FOR APPLIED TECHNOLOGIES (CUP: F52F16001350001) TYPE A WITHIN THE FRAMEWORK OF THE 2017/2018 STARS PROGRAMME – I PART 2018

announced with decree of the Chancellor Rep. no. 792/2019 of 09.12.2019 and posted on the official registry of the University on 09.12.2019

RESEARCH PROJECT

Chiral Materials for Novel Applications

Research structure: Department of Engineering and applied sciences

Duration of the grant: 17 months

Scientific Area: 03 - Chemistry

Academic recruitment field: 03/B2 - Principles of chemistry for applied technologies

Academic discipline: CHIM/07 - Principles of chemistry for applied technologies

Scientific Director: Prof. Francesca Fontana

The project is based on the preparation and characterization of organic molecules (azahelicenes) endowed with an extended aromatic conjugation, which absorb light in the range of the visible-near UV radiation and show marked fluorescence and phosphorescence properties, as well as intrinsic chirality due to their helical shape. The aim is to enhance the study towards applications of these molecules in the fields, already object of some preliminary work, of sensors and of spectroscopic analysis. It is also desired to apply optically stable azahelicenes also in the field of chirality induction in ionic liquids for electrochemical applications.
The work performed to date was mostly limited to the class of aza[5]helicenes, which are not optically stable. Due to the extremely marked optical activity of this class of compounds, it would be desirable to widen investigations to more extended and optically stable systems (aza[6]helicenes), whose utilization may open application fields of paramount interest. It will be therefore necessary to develop effective synthetic strategies for new mono- and diaza[6]helicenes, to be then separated into their enantiomers and subsequently modified for specific applications. They can be endowed with hydrocarbon chains bearing appropriate functional groups, in order to bind them to carbon nanotubes or to nanostructured noble metal surfaces, to obtain highly enantioselective materials. They can also be quaternarized onto the nitrogen atom, with the purpose of obtaining ionic compounds utilizable in electrochemistry for chiral catalysis.
The project is structured in the following phases:
1)preparation and characterization of aza[6]helicenes, either known or as yet undescribed, and separation of the pure enantiomers by means of chiral chromatographic techniques;
2)modification of the molecules prepared in phase 1) by a) addition of hydrocarbon chains bearing appropriate functional groups or b) quaternarization of the nitrogen atom;
3)modification of carbon nanotubes or nanostructured noble metal surfaces, by using the molecules prepared in phase 2) through the development of methods for the formation of stable bonds between the reactive functional groups and the surfaces to be modified; modification of the properties of ionic liquids by means of the chiral molecules obtained in phase 2b);
4)characterization of the materials obtained in phase 3) by different techniques, such as spectroscopic or electrochemical analysis, in order to assess the effectiveness and reproducibility of the preparative methods, so as to optimize the procedures, and also to evaluate the stability of these materials;
5)verification of the effectiveness of the realized materials for the specific applications which represent the object of the research, namely:
a.nanostructured gold surfaces modified with optically stable chiral azahelicenes for applications in Raman-SERS and SEF (Surface-Enhanced Fluorescence) spectroscopies;

b.carbon nanotubes functionalized with azahelicenes for applications in electrochemical sensors;
c.ionic liquids modified by addition of chiral quaternary salts for applications in electrochemical stereoselective processes.
A sufficient quantity of 5-aza[6]helicene will be preliminarly produced, by already known methods, in order to separate its enantiomers and/or modify its structure for the various applications. Subsequently the phase of preparation and characterization of nanostructured surfaces and of modified ionic liquids should take place, and the optimal reaction conditions for their preparation defined. At the same time, the materials obtained as described would be tested to assess their effectiveness and durability in the specific application. Based on the observed results, it will be possible to devise structural modification of the helicene itself or of the added side chain in order to modulate the performance of the material.
The diverse synthetic methods to be perfectioned should converge towards the preparation of a wide range of molecular materials, viable for the obtainment of different specific goals, some of which already preliminarly explored and others not yet essayed. The approach is synergistic, in that it optimizes the efforts by developing general synthetic procedures utilizable, with appropriate variations, in different fields.
The practical objectives that are pursued are, among others:
•realization of sensors for biomolecules based on the modification of carbon nanotubes; a study was already performed to prepare a selective epinephrine sensor for biological fluids, and the results encourage the prosecution of the investigation, trying to clarify the structural requirements for the molecules to modulate their properties on the basis of the desired applications;
•realization of nanostructured noble metal surfaces modified by optically active azahelicenes for applications in Raman-SERS spectroscopy, particularly to the aim of realizing a portable biomolecule sensor for the continuous monitoring of ematic levels of antiepileptic drugs;
•realization of nanostructured noble metal surfaces modified by optically active azahelicenes for applications in SEF spectroscopy, to exploit the intense fluorescence of azahelicenes for analytic purposes;
•preparation of modified ionic liquids as catalyzers for the realization of enantioselective electrochemical reactions by the electrodic surface.