Part 1 - General Information

Project Title: Noval Fluorescent Receptors With Amino & Aromatic Residues: Design, Synthesis & Applications

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Part 2 - Exchange Participant(s) Details

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Part 3 - Scientific & Technical Information

Objectives of Visit:

The scientific visit under the Indo Swiss Joint Utilisation of Advance Facility Programme provided a very good opportunity to establish a good relationship between Prof. Reinhard Neier’s research group and myself. It is quite useful to create a platform between the scientists in the two countries, sharing of their best practices, sharing of information, exchange of ideas and utilization of advance instruments and facilities. It also offered an international exposure through scientific exchange programs. Moreover, it will help promote long term research collaborations between scientists from India and Switzerland.

Short Description of Work Carried Out During the Visit:

**Novel Fluorescent Receptors with Amino and Aromatic Residues: Design, Synthesis and Applications**

Development of chemosensors for heavy and transition metal ions (HTM) are currently a task of prime importance for medical, environmental and biological applications. Chemosensor or Molecular sensor is a molecule that interacts with an analyte to produce a detectable change. Among them, fluorescent chemosensors offer distinct advantages in terms of sensitivity, selectivity and response time. Thus the design and synthesis of new fluorescent receptors for chemosensors selective for ions is of considerable interest in recent years.

The above objective has been realized via design and synthesis of a series of luminescent receptors containing the structural motif, -N=C-CH=N-NH-C=N-, obtained via condensation of various hydrazines and aldehydes as shown below.
During this period a series of ligands and some of their metal complexes were characterized by ESI-MS, $^1$H NMR, $^{13}$C NMR provided by SAF (Faculty of Science, Analytical Services). A total of 20 ESI-MS and 32 NMR spectra were recorded with the help of Dr. Armelle Vattat and Cristelle Schenk, Institute of Chemistry, Neuchâtel. We have carried out single-crystal X-ray diffraction studies for 20 crystals of different ligands and complexes in collaboration with Prof. Helen Stoeckli-Evans, out of them 15 crystals refined well. We have also performed DSC and TG studies of 4 samples with the help of Anais Pitto-Barry, member of the group of Professor Robert Deschenaux of the Institute of Chemistry, Neuchâtel. The powder diffraction studies of a few more samples are in progress.

We also have found some new interesting findings:

**New Chromogenic and Fluorescent Chemosensors for Copper(II)**

The recognition of ions and molecules is an essential part of supramolecular chemistry. Considerable interest has been placed to the creation of new chemosensors for heavy and transition metal (HTM) ions which allows naked eye real time and space detection of the change of color upon metal ion binding without the use of any spectroscopic instruments. But it is still a challenge to design a chemosensor, which can be used for detecting different metal ions by both selective coloration and the change in the absorption and/or emission spectra.

Herein, we have investigated Pyridine-2-carboxaldehyde 2-imidazoline hydrazone, HL as a new chromogenic agent for selective detection of Cu$^{2+}$ in aqueous medium. The ligand 1, undergoes
1:1 complexation with $\text{Cu}^{2+}$ to form a green water soluble complex $[\text{Cu}^{\text{II}}(\text{HL})]\text{Cl}_2$. Molecular structures of both the ligand and the complex were determined by single crystal X-ray diffraction studies. The bands appearing in the UV region (200 nm – 340 nm) are characteristics of the ligand, HL, 1. In the complex $[\text{Cu}^{\text{II}}(\text{HL})]\text{Cl}_2$ these ligand centered bands are accompanied by multiple bands extending into the visible region (350 nm – 800 nm) with characteristic absorption peaks at 410 nm and 680 nm. The association constant ($K_{\text{ass}}$, UV-Vis) was found to be $(5.95\pm0.004) \times 10^4$ for $[\text{Cu}^{\text{II}}(\text{HL})]\text{Cl}_2$ at 298 K determined by the UV–Vis spectroscopy. We have carried out the ratiometric analysis where the absorbance ratiometric responses ($A_{410}/A_{287}$) gives the highest value for $\text{Cu}^{2+}$. Moreover, a rapid color change from yellow to bright green was observed upon addition of copper(II) that can easily be detected from other metal complexes by the naked eye also. No
obvious interference was observed in presence of other metal ions (Ca\(^{2+}\), Mg\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Ag\(^{+}\), Sn\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\), Co\(^{2+}\), Cr\(^{3+}\), Cd\(^{2+}\)). Thus the ligand Pyridine-2-carboxaldehyde 2-imidazoline hydrazone, HL might be useful as a chromogenic chemosensor for copper(II).

In order to study the effect of substituents on the chemical and photophysical properties we have incorporated carboxyl hydrazine in place of imidazoline hydrazine and synthesized the ligand HL\(^1\), as shown below. The molecular structure of this ligand was determined by single crystal X-ray diffraction studies. The bands appearing in the UV region (200 nm – 340 nm) are characteristic of the ligand, HL\(^1\). It undergoes 1:2 binding with copper (II) which was confirmed by Job’s method of continuous variation. In the complex [Cu\(^{II}\)(HL)\(_2\)]Cl\(_2\) these ligand centered bands are accompanied by multiple bands extending into the visible region (350 nm–550 nm). The association constant
(\(K_{\text{ass}}\), UV-Vis) was found to be \((5.06\pm0.01) \times 10^5\) at 298 K determined by the UV–Vis spectroscopy. On excitation at 285 nm, the ligand HL strongly emits at 405 nm due to an intraligand \(1(\pi - \pi^*)\) transition. After addition of copper(II) a strong quenching is observed and the \(F/F_0\) value is found to be 0.036, which indicates almost complete quenching takes place. We have also measured the emission intensity ratios for HL\(^1\) at 405 nm in presence of other metal ions viz. Mn\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Hg\(^{2+}\), Mg\(^{2+}\), Pb\(^{2+}\), Sn\(^{2+}\) and Al\(^{3+}\) etc, where no significant quenching is observed. Therefore the ligand Pyridine-2-carboxaldehyde 2-carboxyl hydrazone, HL\(^1\) might be useful as a fluorescent chemosensor for copper(II) in aqueous medium.
Other Activities during this Period:

During this period I have visited the different laboratories of the University of Neuchatel and the University of Fribourg and gathered information about the facilities available there. Also, I have visited the Benefri Crystallographic Centre and other laboratories at the CSEM and explored the scope of various research activities. So it was a great opportunity for me to interact with the scientists working in different areas.

I have delivered lectures in the Department of Chemistry, at the University of Neuchatel and at the University of Fribourg

**Lecture I:** Investigation of Some New Fluorescent Chelators For Chemosensors: Synthesis and Reactivity

**Lecture II:** Synthesis and Functional Evaluation of New Fluorescent Receptors for Chemosensors

I attended the lecture delivered by the Noble Prize Winner, Prof. Ada Yonath from Weizmann Institute, Israel on *The amazing ribosome, its tiny enemies and hints about its evolution*, on March 21, 2011 organized by the University of Fribourg, Faculty of Science – Chemistry, and a number of lectures in the University of Neuchatel organized by Prof. Reinhard Neier.

I have also gathered hands-on experience in crystallographic analysis followed by the structure determination with the help of Prof. Helen Stoeckli-Evans and handled the 400Hz Bruker NMR.

**Future Collaboration Envisaged with the Host Institution:**

The University of Neuchatel and the CSEM (Swiss Center for Electronics and Microtechnology) have well equipped research laboratories with a number of sophisticated instruments. Hence, future collaboration with the host institution will be highly beneficial
from my point of view and an active continuation of our scientific exchanges and mutual cooperation is planned.

Place: Kalyani, India Neuchâtel

Date: 24.03.2011 24.03 2011

Signature: Soma Mukherjee

Signature: