



## LASERLAB-EUROPE

### The Integrated Initiative of European Laser Research Infrastructures III

Grant Agreement number: 284464

Work package 5 – Human Resources Development

Deliverable D5.3

Final report on Short-term User Training for BIOPTICAL

Lead Beneficiary: 14 FVB

Due date: M42

Date of delivery: M42

Project webpage: [www.laserlab-europe.eu](http://www.laserlab-europe.eu)

<i>Deliverable Nature</i>	
R = Report, P = Prototype, D = Demonstrator, O = Other	R
<i>Dissemination Level</i>	
PU = Public PP = Restricted to other programme participants (incl. the Commission Services) RE = Restricted to a group specified by the consortium (incl. the Commission Services) CO = Confidential, only for members of the consortium (incl. the Commission Services)	PU

## 1 Introduction and objectives of WP5

This workpackage deals with the coordination of Human Resources (HR) Development for Laserlab-Europe. It includes a wide spectrum of activities, focused to enhance the efficient use of the facilities in the Transnational Access programme by attracting and educating new users, to develop the user community, and to reach new scientific sub-communities. The target groups of these activities are namely i) younger scientists at the doctoral or post-doctoral level, and ii) new research groups, e.g. from new members states within the EU or groups from scientific disciplines such as biology and medicine where the use of laser research infrastructures is not yet common practice.

The main Laserlab training objectives are:

- Developing and training of new user communities with no or little past experience in laser research, addressed by Task 1;
- Attracting and training of new users from new scientific communities (e.g. life sciences) in a multi-disciplinary perspective, addressed predominantly in Task 2;
- Coordinating externally funded activities, particularly education activities, for the development of human resources in close collaboration with other organisations, addressed by Tasks 3 and 4.

## 2 Short summary

- Within Task 1, three training schools have been organised: the User Training Workshop on Biophotonics, Kosice, Slovakia, 17-30 June 2013, the User Training Workshop on Laser Applications in Spectroscopy, Industry and Medicine, Riga, Latvia, 9-12 April 2014, and the User Training Workshop on Light-Based Technologies, Trnava, Slovakia, 2-4 September 2015.
- Under the scheme of Task 2: User Training in Lasers and Photonics for Biology and Health, 11 short-term training visits took place.
- In Task 3 Cooperation with existing training programmes, calls for proposals were issued and four external training programmes were selected and supported by Laserlab-Europe.
- Laserlab partners participate in the FP7 outreach projects "GoPhoton! - Photonics for everyone", "LIGHT2015" and "Photonics4all", which promote the importance of photonics and optical technologies to young people, entrepreneurs and the general public in all Member States of the EU during the International Year of Light and Light-based Technologies 2015 (IYL 2015). Within the framework of MoU's, Laserlab-Europe, FELs of Europe and the ESFRI project ELI – Extreme Light Infrastructure, jointly advertise the training events of each other within their own networks and have started to discuss joint organisation of training events.

## 3 Task 2: User Training in Lasers and Photonics for Biology and Health (BIOPTICHAL)

Task 2 is organised through subcontracting to Coimbra Laser Lab (CLL), Portugal. Task leader: 14 FVB

Specific short-term training visits are designed to increase the experience of potential European users and to provide special experimental skills and competencies in the scientific area related to the JRA BIOPTICHAL. Support for short-term training visits is granted on the basis of proposals for research projects, which are evaluated by an external committee of experts.

### ***Selection procedure***

For the implementation of this training activity, two calls for proposals for short-term training visits were opened during the first and second reporting period. The calls were published on the Laserlab-Europe and the Coimbra Laser Lab web pages:

<http://www.laserlab-europe.eu/networking/user-community-training/user-training-cll>

<http://www.uc.pt/en/uid/laserlab/projects/call>

Submission and evaluation of the user training proposals are made through the Laserlab-Europe online proposal management tool for the Coimbra Laser Lab activities, relying on a pool of 20 international reviewers. The selection procedure is an independent process, led by Professor Wolfgang Demtroeder (University of Kaiserslautern, Germany) as chairman of the selection panel. Each proposal is evaluated by two expert reviewers, taking into account the training needs of the applicants, and selection is made on the basis of the scores and comments provided by the referees. The online Laserlab-Europe proposal management system provides close monitoring of administrative processes of the selection procedure leading to a very satisfactory time for evaluation and selection.

In total, 14 proposals for training visits were received and reviewed by the selection panel, out of which 11 were approved and performed.

### ***User training activity***

During the project, eleven visits were performed. From the 12 visiting scientists nine were young researchers (4 post-graduate and 5 post-doctoral students) and three were experienced researchers. Nine of the visitors were female researchers. The scientist came from Turkey, Germany, Poland, Slovakia, Romania, The Netherlands, Finland and Spain.

The projects were carried out using all three laser facilities at CLL, the Transient Absorption and Photoacoustic Lab, the Lifetimes Lab and the Low Temperature Molecular Spectroscopy Lab. The average total duration of the training visits was about 18 days. The table below gives details about the duration of each visit.

Visit number	Duration	Laser days
1	29	15
2	20	11
3	15	7
4	18	8
5	16	8
6	20	11
7	13	7
8	24	14
9	20	11
10	20	11
11	10	6

For all visits the laser facilities use was intense. On average 80% of the usable week days during the visit were laser experiment time. The remaining 20% of visit time was spent in experimental sample preparation (wet lab), experimental design and results discussion. During these visits we performed 109 full experimental laser days (thus, nine days more than the 100 days foreseen for the total contract time).

Number of visits	Week days present in the lab	Full laser days
11	140	109

**Scientific output of the users at the facilities**

All visiting researchers judged the results as publishable and expressed the intention to publish. Several manuscripts are under preparation or have been submitted for publication. The following publications have appeared in peer-reviewed journals so far:

*Unusual photophysical properties of conjugated, alternating indigo–fluorene copolymers*

Pina, J., J. Seixas de Melo, A. Eckert, U. Scherf  
J. Mater. Chem. A 3, 6373-6382 (2014)  
<http://dx.doi.org/10.1039/C4TA06272H>

*Structure and Photochemistry of N-Salicylidene-p-carboxyaniline Isolated in Solid Argon*

Avadanei, M., V. Cozan, N. Kus, R. Fausto  
J. Phys. Chem. A 119, 9121 (2015)  
<http://dx.doi.org/10.1021/acs.jpca.5b06516>

*Infrared Spectrum and UV-Induced Photochemistry of Matrix-Isolated 5-Hydroxyquinoline*

Kus, N., S. Sadginc, R. Fausto  
J. Phys. Chem. A 119, 6296 (2015)  
<http://dx.doi.org/10.1021/acs.jpca.5b03942>

*Near-Infrared Laser-Induced Generation of Three Rare Conformers of Glycolic Acid*

Halasa, A., L. Lapinski, I. Reva, H. Rostkowska, R. Fausto, M. J. Nowak  
J. Phys. Chem. A 118, 5626-5635 (2014)  
<http://dx.doi.org/10.1021/jp5051589>

*Three Conformers of 2-Furoic Acid: Structure Changes Induced with Near-IR Laser Light*

Halasa, A., L. Lapinski, I. Reva, H. Rostkowska, R. Fausto, M.J. Nowak  
J. Phys. Chem. A 119, 1037-1047 (2015)  
<http://dx.doi.org/10.1021/jp512302s>

*Polycarbazoles and Polytriphenylamines Showing Aggregation-Induced Emission (AIE) and Intramolecular Charge Transfer (ICT) Behavior for the Optical Detection of Nitroaromatic Compounds*

Dong, W., J. Pina, Y. Pan, E. Preis, J.S. Seixas de Melo, U. Scherf  
Polymer 76, 173-181 (2015)  
<http://dx.doi.org/10.1016/j.polymer.2015.08.064>

*Multifaceted Regioregular Oligo(thieno[3,4?b]thiophene)s Enabledby Tunable Quinoidization and Reduced Energy Band Gap*

Liu, F., G.L. Espejo, S. Qiu, M. Moreno Oliva, J. Pina, J. S. Seixas de Melo, J. Casado, X. Zhu  
J. Am. Chem. Soc. 137, 10357-10366 (2015)  
<http://dx.doi.org/10.1021/jacs.5b05940>

*Acetic Acid Dimers in a Nitrogen Matrix: Observation of Structures Containing the Higher-Energy Conformer*

Lopes, S., A. Domanskaya, M. Räsänen, L. Khriachtchev, R. Fausto  
J. Chem. Phys. 14, 3104307 (2015)  
<http://dx.doi.org/10.1063/1.4929575>

Publications resulting from the CLL training projects are listed and regularly updated at <https://laserlab.mbi-berlin.de/access/publish/listCLLPublications.jsf>

## **List of Projects and Users**

### *Project 1*

Title: FTIR Spectroscopic and Theoretical Study of Matrix-Isolated Ionic Liquids

Visiting researcher: Nihal Kuş, nationality: Turkey, status: young researcher (post-doctoral researcher)

Home institution: Anadolu University, Eskişehir, Turkey

Objectives:

Ionic liquids (ILs) have been attracting much attention during the last decade and started to receive industrial use. It is nowadays well-known that the initial belief that ionic liquids exert no measurable vapor pressure was wrong, since many ionic liquids could already been distilled at low pressure without deterioration. Though there are now strong indications that when aprotic ionic liquids vaporize under reduced-pressure distillation the gas phase is composed of discrete anion-cation pairs, whereas protic ionic liquids seem to exist as separated neutral molecules in the gas phase, the nature of the species that are present in the gaseous phase are still controversial. To investigate this problem, we propose here to use matrix-isolation spectroscopy together with quantum chemical calculations and in situ laser-photochemistry as an alternative methodology to the general approaches previously used, which have been mostly focused on variants of mass spectrometry.

Achievements:

In this mission, the molecular structures and vibrational signatures of isolated 1-ethyl-3-methyl and 1,3-dimethylimidazolium cations and of this species in the presence of Cl<sup>-</sup> and methylsulfate anions were investigated using quantum chemistry theoretical methods and FTIR spectroscopy. The studied ionic liquids were found to exhibit local environments in both the liquid and crystalline phases which are very similar. In both environments, the dominant forces were found as being of Coulomb type, between the ions. This is reflected in the fact that the IR spectra obtained for the compounds in the liquid and crystalline phases as a function of temperature practically do not change in the whole temperature range studied (room temperature up to 150 °C). Nevertheless, in agreement with the non-negligible contribution to the intermolecular interactions in the studied systems of the hydrogen bond like interactions between the C(2)-H moiety of the imidazolium ring and the anion, some spectral changes could be observed upon changing temperature in the spectral features associated with this fragment (in particular in the  $\nu$ C(2)-H stretching band). For the isolated species, the observed spectra were in consonance with the presence in the cryogenic matrices of the isolated ions, with bands of the anions dominating the spectra. Assignment of the spectra and normal coordinate analyses to characterize the vibrations in both DMIM-MS and EMIM-Cl were undertaken. The calculations also indicated that the imidazolium cation possesses a modest degree of  $\pi$ -resonance, measured in terms of the aromaticity index HOMA (Harmonic Oscillator Measure of Aromaticity, defined by Kruszewski and Krygowski), similar to those found for the  $\alpha$ -pyrone ring of coumarin. UV-irradiation of the matrices proof that, under the used experimental conditions, the isolated species are photostable within the 230-370 nm range.

### *Project 2*

Title: Excited state dynamics of indigo-fluorene-copolymers

Visiting researcher: Anika Eckert, nationality: Germany, status: young researcher (post-graduate researcher)

Home institution: Wuppertal University, Wuppertal, Germany

Objectives:

Characterization of the excited states in indigo-fluorene-copolymers in solution and thin films at different temperatures.

**Achievements:**

During my stay in the Coimbra Laser Lab a comprehensive investigation of the excited state characteristics of four indigo-fluorene-copolymers with different chain length (degrees of polymerization, DP: 3, 5, 8 and 11) and a didodecylfluorene-dibromindigo model compound together with the dibromo-didodecylfluorene and dibromindigo counterparts was undertaken in solution at room temperature and as a function of temperature. The study comprised absorption, fluorescence and phosphorescence emission and triplet-singlet difference spectra, together with quantitative measurements of fluorescence, phosphorescence and triplet decay times.

*Project 3*

Title: Study of physicochemical properties of NADH and its binding dynamics to enzymes.

Visiting researcher: Júlia Horilová, nationality: Slovakia, status: young researcher (post-graduate researcher)

Home institution: Pavol Jozef Šafárik University, Košice, Slovakia and International Laser Centre Bratislava, Slovakia

**Objectives:**

Endogenous fluorescence of NADH is a useful tool in monitoring mitochondrial metabolic oxidative state in living cells and tissues. Time-resolved approach provides additional information about this molecule; however precise physicochemical properties of NADH and mechanisms of its binding to dehydrogenases are still largely unknown.

**Achievements:**

Time-resolved data of NADH fluorescence in vitro were obtained for the first time with picosecond time resolution. Higher time-resolution of data gathered with ps TCSPC set-up revealed ultrafast NADH fluorescence decay component. Moreover, valuable information was obtained on management of the instrument response function. In addition, binding of NADH to its dehydrogenase was tested: treatment with specific inhibitor rotenone prior to addition of NADH modestly decreased the fluorescence lifetimes of NADH indicating possible alteration of pre-inhibited enzyme affinity to NADH. However, experiments mimicking changes in molecular environment showed that fluorescence lifetimes are more likely to be caused by the environment than by its chemical binding. Gathered results also pointed to the possibility that the NAD(P)H fluorescence is predominantly caused by the adenine moiety of this fluorophore.

*Project 4*

Title: Early events in the interaction between photosensitizers and small molecules

Visiting researcher: Janusz M. Dabrowski, nationality: Poland, status: young researcher (post-doctoral researcher)

Home institution: Jagiellonian University, Krakow, Poland

**Objectives:**

Electron and/or energy transfer between small molecules and porphyrin-based compounds are among the most important types of reactions occurring in biological systems. They are key stages of many biochemical processes, take responsibility for activation or deactivation of biologically relevant compounds. They also play a considerable role in the photocatalysis and photodynamic therapy. Despite the broad-scale studies and a number of reports on the

courses of these reactions, many of them still await in-depth mechanistic explanation. It particularly concerns the reactions that may take place in the excitation of ground-state complexes that occur in the femto and picosecond timescales.

The nature of the reactive oxygen species generated by photosensitizers, namely singlet oxygen, superoxide ion and hydroxyl radical may depend on the extent of the charge transfer interactions in the encounter complex between the photosensitizer and the small molecules such as O<sub>2</sub> and probably also NO. A good understanding of the mechanisms of energy and electron transfer taking place in the ultrafast regime may contribute to improve the success of the photosensitizers in photodynamic therapy and photocatalysis.

The charge transfer interactions in complexes between the photosensitizers and the small molecules, the tendency of these sensitizers to associate with serum albumin and the ability of such formed complexes sensitizer-albumin to induce ROS/RNS will be investigated using the picosecond time-correlated single photon counting and femtosecond transient absorption spectroscopy.

#### Achievements:

The “early events in the interaction between photosensitizers and small molecules” were studied in Coimbra LaserLab with picosecond time-correlated single photon counting and femtosecond transient absorption spectroscopy, using 5,10,15,20-tetrakis(2,6-difluorophenyl-3-N-methylsulfamoylphenyl)bacteriochlorin as prototype photosensitizer. In particular this bacteriochlorin was investigated with excitation at 370 nm (S3 band), 750 nm (S1 band) and 1480 nm (2-photon absorption). In the latter case, a first analysis of the data did not support the relevance of 2-photon absorption for this specific bacteriochlorin. On the other hand, the excitation at 370 nm revealed the existence of a 770 fs intermediate in the decay to a 3.3 ns intermediate, that was identified using fluorescence techniques as the S1 state. The data collected on this and other systems will be further analyzed and will hopefully lead to a better understanding of the early events taking place in bacteriochlorins used for the photodynamic therapy of cancer.

#### *Project 5*

Title: Solid state photochemistry of two salicylidene anilines studied by time resolved spectroscopy

Visiting researcher: Mihaela Avadanei, nationality: Romania, status: experienced researcher

Home institution: “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

#### Objectives:

1. Learning the Laser Flash Photolysis method
2. Learning the Time Resolved Fluorescence method
3. Determining the short – lived transient species (presumably cis-keto\*) for the two structurally related salicylidene anilines by flash photolysis studies
4. Monitoring the possible emission decay of the excited states/ cis-keto\* form to the “cold” cisketo by time resolved fluorescence for the two compounds. Assessing the excited species lifetime

#### Achievements:

The main objective of this short term visit was getting insight into the time – resolved spectral methods as Laser Flash photolysis and Time Resolved Fluorescence. The compounds under study were two anils, named N-salicylidene-*p*-cyanoaniline (SA-CN, code 513) and N-salicylidene-*p*-carboxyaniline (SA-COOH, code 514). According to their photoreactivity determined from stationary measurements, SA-CN is non-photochromic in solid state and fluorescent both in solution and powder, while SA-COOH is both fluorescent and

photochromic in powder form. The starting form is an anti-enol type. The final photochromic form is a *trans*-keto species. The photophysics is given by a proton transfer in excited state that would be followed by isomerisation in certain conditions. The experiments were performed in solid state, as microcrystalline powders. The summary of the measurements:

#### 1. Laser Flash photolysis

*Excitation wavelength:* 355 nm

*Mode:* diffuse reflectance

*Laser energy:* 40 mJ and 15 mJ

*Results:* The experiment were done at two levels of laser energy, i.e. high ( $\approx 40$  mJ) and low ( $\approx 15$  mJ), in order to see if its influence on the photochemistry of the two compounds. SA-CN and SA-COOH show dissimilar transient absorption spectra. At the temporal scale of micro- and milliseconds, the positive main band is connected to the absorption of the final photochromic form, which is the *trans*-keto form. The existence of this species in the case of SA-CN is yet to be clarified. The negative band related to the enol ground state depopulation is also observed. From here, it can be concluded that the photoreactivity of SA-CN is mainly related not to the proton transfer to give a keto product, but to a twisting process of the excited enol. This fact would explain the absence of the photochromism. The existence of the transient *cis*-keto species would be speculated to be correlated to a tautomerisation in a lower yield. The decay of the main transient absorption band was found bi-exponential for both compounds. Apparently, there is no direct influence of the laser energy on the photochemical reactions.

#### 2. Time Resolved Fluorescence

*Excitation wavelength:* 350 nm

*Emission wavelength:* 550 nm

The monitorization was made at the emission wavelength of the excited *cis*-keto form. The fluorescence decays are bi-exponential for both SA-CN and SA-COOH. In the case of SA-CN, the faster component has a contribution of more than 98%. The distribution of the short and long decay components are more equally distributed in the case of SA-COOH. The radiative rate constants are of the same order of magnitude for both compounds. In contrast, there are differences in the non-radiative rate constants. The  $k_{nr}$  value of solid SA-CN is by 2.5 – fold larger than that of solid SA-COOH, which points out the less fluorescent character of SA-CN. This fact is in complete agreement with the lower quantum yield of SA-CN, but also is in contrast with the absence of its photochromism.

The results obtained in solid state by this short term visit are corroborated with those made in several solutions of different polarity, at two emission wavelengths, which were also made by laser flash photolysis and time resolved fluorescence. The comparative studies, beneficial of the Laserlab-funded project (grant agreement n° 284464), are the subject of two manuscripts.

#### Project 6

Title: Photophysics and photochemistry in molecular switches: the mechanism of laser-induced proton migration in compounds with aldehyde group

Visiting researcher: Anna Halasa, nationality: Poland, status: young researcher (post-graduate researcher)

Home institution: Institute of Physics; Polish Academy of Sciences, Warsaw, Poland

Objectives:

The scientific goal of the visit is the study of photochemistry of monomeric 2-pyridinecarboxaldehyde isolated in solid Ar at 10 K. The study is directed at the investigation



of the possibility of photochemical shift of hydrogen atom from the aldehyde group. The finding of such photochemical process will provide some indications against proposed previously mechanism of a long distance hydrogen transfer *via* a “molecular crane” [1]. The next (and probable even more important) aim of the visit is a training of a young researcher, at the beginning of her carrier, in the experimental techniques applied in the Chemistry Laser Lab Coimbra.

#### Achievements:

Since no expected UV-induced intramolecular hydrogen-atom transfer was observed for 2-pyridinecarboxaldehyde (upon UV irradiation only the carbonyl group of this compound rotates), this case could not be a basis for proposition of an alternative mechanism of the photochemical transformation observed for 7-hydroxyquinoline-8-carbaldehyde [1].

Instead a study on near-IR induced conformational transformations in glycolic acid has been carried out. This was one of the most thorough studies ever made for a conformational transformation induced by excitations with narrowband tunable near-IR laser light. For glycolic acid isolated in Ar matrices, two conformers were photogenerated. The sequential mechanism of photogeneration of these forms was experimentally proven. We have demonstrated that near-IR excitation of the most stable form of this compound leads to photogeneration of only one of the new forms. We have also shown that the other photoproduct conformer emerges upon excitation of the primary photoproduct with another near-IR photon. For glycolic acid isolated in N<sub>2</sub> matrices, a fourth conformeric structure was produced upon near-IR excitation. The latter conformer was never observed till that date. Moreover, spontaneous conformational transformations, governed by hydrogen-atom tunneling, were also experimentally studied for matrix-isolated glycolic acid. This study has been published in the Journal of Physical Chemistry A [2], where it received very good reviewer's comments.

[1] L. Lapinski, M.J. Nowak, J. Nowacki, M.F. Rode, A.L. Sobolewski “A bistable molecular switch driven by photoinduced hydrogen-atom transfer” *ChemPhysChem* **2009**, *10*, 2290-2295.

[2] A. Halasa, L. Lapinski, I. Reva, H. Rostkowska, R. Fausto, M.J. Nowak, M. “Near-Infrared Laser-Induced Generation of Three Rare Conformers of Glycolic Acid”. *J. Phys. Chem. A* **2014**, *118*, 5626-5635.

#### Project 7

Title: Role of doping profile on the charge carrier dynamics of metal oxide photoelectrodes for solar fuel applications

Visiting researcher: Mónica Barroso, nationality: Portugal, status: experienced researcher

Home institution: Utrecht University, Utrecht, The Netherlands

#### Objectives:

Our goal is to investigate the role of different doping patterns on the charge carrier dynamics in metal oxide photoelectrodes for water oxidation. In recent years it has been shown that low mobility of charge carriers and related fast electron-hole recombination is one of the main limitations of otherwise promising photoanode materials, such as Fe<sub>2</sub>O<sub>3</sub>, BiVO<sub>4</sub> and WO<sub>3</sub>. One of the strategies usually followed to tackle this problem is, specifically in the case of oxygen evolution photoelectrodes, doping with one or more electron donor species.

In this work we will employ ultrafast transient absorption spectroscopy to monitor the effect of different doping strategies (homogeneous vs gradient-doping) on the rates of charge recombination and transport. Following on our previous work, we will use hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) as a model system, aiming to establish a correlation between the profile of Ti-doping and the rates of electron-hole recombination, as well as the implication of the changes in carrier dynamics to the overall photoelectrochemical performance. With this work we expect to obtain a better understanding of the role of dopants in determining the decay pathways in

bulk photoelectrodes and, with this knowledge, devise material design strategies to reduce the impact of electron-hole recombination in photoelectrochemical devices.

**Achievements:**

Transient absorption of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) based materials with distinct doping (Ti) deposition patterns was done with excitation at 400 nm and collecting the transmitted light from 400 nm to 900 nm. We observed a doping effect on the mobility of charges, which could be related with the defects introduced on the materials. The signals were also collected under an external potential.

*Project 8*

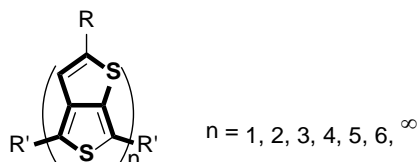
Title: Singlet fission in quinoidal enriched oligothiophenes featuring the cyanine limit

Visiting researcher: Maria Moreno Oliva, nationality: Spanish, status: young researcher (post-doctoral researcher)

Home institution: University of Málaga, Faculty of Science, Spain

**Objectives:**

The main objective of the project is the characterization of a series of oligothiophenes in the limit of quinoidal/aromatic conjugation by means of spectroscopic and theoretical studies. This series of compounds has potential to present the phenomenon of singlet exciton fission (SEF). In this way, the analysis of the triplet excited states, especially by femtosecond transient absorption spectroscopy, will be the essential key. Owing to the importance of these molecules for a variety of applications in organic electronic, the establishment of structure-property relationships is strongly pursued.



Scheme 1. Chemical structures of the compounds object of study.

**Achievements:**

The working plan performed in Coimbra Laser Lab (CLL) was focused on the analysis of the electronic structure of the excited states, specially measuring the transient absorption spectra in femtosecond and nanosecond time scales. I learnt a lot about these techniques, and about the setup.

As a result of this research in CLL, we have just been accepted to publish an article in *J. Am. Chem. Soc.*: Multifaceted Regioregular Oligo(thieno[3,4-*b*]thiophene)s Enabled by Tunable Quinoidization and Reduced Energy Band Gap, Feng Liu, Guzmán L. Espejo, Shuhai Qiu, María Moreno Oliva, João Pina, J. Sérgio Seixas de Melo, Juan Casado, and Xiaozhang Zhu.

In the abstract: "Thiophene-based materials have occupied a crucial position in the development of organic electronics. However, the energy band gaps of oligo- and polythiophenes are difficult to modulate without resorting to push-pull electronic effects. We describe herein a new series of monodisperse oligo(thieno[3,4-*b*]thiophene) derivatives with well-defined regioregular structures synthesized efficiently by direct C-H arylation. These compounds show a unique palette of colors and amphoteric redox properties with widely tunable energy band gaps. The capacity to stabilize both cations and anions results in both anodic and cathodic electrochromism. Under excitation, these compounds can produce

photoionized states able to interconvert into neutral triplet or form these through singlet exciton fission or intersystem crossing. These features arise from a progressive increase in quinoidization on a fully planar platform making the largest effective conjugation length among hetero-oligomers. Oligo(thieno[3,4-*b*]thiophene)s might represent the more distinctive family of oligothiophenes of this decade.”

We are working on another manuscript, also with this family of molecules, extending the discussion with all the performed measurements.

### *Project 9*

Title: Characterization of the excited state kinetics of AIE-active polymers in different solvent mixtures and as thin films, also in the presence of trinitrobenzene (TNB) as photoluminescence quencher

Visiting researcher: Wenyue Dong, nationality: Chinese, status: young researcher (post-graduate researcher)

Home institution: Bergische Universität Wuppertal, Germany

Objectives: Within the project the excited state kinetics of AIE-active polymers will be investigated, both in different solvents and solvent mixtures causing different degrees of aggregation as well as in thin films. We will, especially, study how ongoing aggregation of these polymers into nanoaggregates affects the photoluminescence (PL) decay dynamics in order to extract a more conclusive picture of the AIE phenomenon. Further, a model compound for nitroaromatic explosives, trinitrobenzene (TNB), will be added as analyte. Analyzing the changes of the PL decay will help to understand the PL quenching mechanism in AIE-active polymers for PL sensing.

Achievements: During the three weeks training visit in University of Coimbra, a series of experiments for photophysical characterization of polythiophenes, polycarbazole and polytriphenylamine was carried out. All the polymers possess aggregation-induced emission (AIE)-active tetraphenylethylene side chains or crystallization-induced emission (CIE)-active 2,3,3-triphenylacrylonitrile side chains.

#### 1. Polythiophenes:

Relevant PLQYs in toluene solution and films were determined:

- In toluene:  $\phi_{\text{homoPT}} = 12\%$ ;  $\phi_{\text{coPT}} = 19\%$ .
- In film:  $\phi_{\text{homoPT}} = 8\%$ ;  $\phi_{\text{coPT}} = 8\%$ .
- Singlet oxygen formation yields (in toluene):
- $\Phi_{\text{P3HT}} = 27\%$ ;  $\phi_{\text{homoPT}} = 5.2\%$ ;  $\phi_{\text{coPT}} = 10.2\%$

Time-resolved transient absorption data in visible and NIR region and associated decay kinetics for homoPT, coPT and P3HT (for comparison), both in solution and films, were obtained.

Room temperature fluorescence emission decays homoPT, coPT and P3HT (for comparison), both in solution and films were obtained.

#### 2. Polycarbazole and polytriphenylamine:

PLQYs in films:  $\phi_{\text{PCzTPAN}} = 10\%$ ;  $\phi_{\text{PTPATPAN}} = 19\%$ .

Singlet oxygen formation yields:

No signal was observed that could be attributed to the phosphorescence emission of singlet oxygen at 1270 nm.

Fluorescence decays of PCzTPAN and PTPATPAN in THF/water solution with water content of 0, 50%, 90% for PCzTPAN and 0, 10%, 90% for PTPATPAN, were obtained.

Fluorescence as the function of temperature enabled the detection of the glass transition temperature of polystyrene by doping with PTPATPAN.

#### *Project 10*

Title: Studies of mechanisms of photoisomerization of aromatic azo compounds isolated in cryogenic matrices

Visiting researchers:

- Leonid Khriachtchev, nationality: Russian, status: experienced researcher
- Luis Duarte, nationality: Portuguese, status: young researcher (post-doctoral researcher)

Home institution: Department of Chemistry, University of Helsinki, Finland

Objectives:

- Investigate the UV-vis induced transformations of azobenzene, 2,2'-dihydroxyazobenzene and 2,2'-azotoluene isolated in cryogenic matrices.
- Study the azoenol-ketohydrazone phototautomerism in 2,2'-dihydroxyazobenzene induced by excitation with narrowband UV light.
- Study the conformational transformations within the two azoenol-ketohydrazone forms of 2,2'-dihydroxyazobenzene induced by excitation with narrowband NIR light.

Achievements:

During this visit, we investigated the structure and photoinduced transformations of three matrix-isolated compounds of the azobenzene series: parent azobenzene (AB), 2,2'-dimethylazobenzene (DMAB), and 2,2'-dihydroxyazobenzene (DHAB). The AB molecule may adopt only two distinct isomers (E and Z) regarding the orientation of the two phenyl groups with respect to the central N=N bond. The DMAB and DHAB may additionally adopt several conformational structures due to the presence of the OH and CH<sub>3</sub> substituents breaking the local symmetry of the phenyl groups.

The DHAB and DMAB compounds were isolated in argon and xenon matrices and their conformational structure was characterized by infrared spectroscopy. Irradiation of the monomeric compounds with a narrowband source in the UV-visible range generated additional isomeric forms, which due to their high internal energy were absent in the originally deposited samples. These new forms could be interconverted back to the originally populated isomers, and vice versa, using different irradiation wavelengths (in the 250-600 nm range). In addition, DHAB was also irradiated in the near-IR range, at the position of the first OH stretching overtone but there was no evidence of structural changes resulting from these irradiations.

Azobenzene was isolated in a xenon matrix and its structure was characterized by IR spectroscopy. The temperature effects (in the 16-60 K range) on the UV-visible induced E-Z isomerization were also studied.

The obtained experimental results are currently under analysis and theoretical calculations are being performed in order to provide the spectral assignments and the identification of the different isomeric forms produced for DHAB and DMAB. This is an important step to understand the mechanisms of the photochemical interconversions in azobenzenes, and to prepare subsequent publication(s).

There was also exchange of know-how between the researchers of the two collaborating groups regarding the design and improvement of sampling devices required for preparation of matrix-isolated samples from compounds that range from gases to solids at room temperature.

*Project 11*

Title: Non-radiative Deactivation Pathways in AIEE Active Conjugated Organic Compounds

Visiting researcher: Shi Junqing, nationality: Chinese, status: young researcher (post-doctoral researcher)

Home institution: Madrid Institute for Advanced Studies - IMDEA Nanoscience, Spain

Objectives:

A set of eight AIEE-active compounds with systematically varied substitution pattern is investigated by photoacoustic spectroscopy to quantify the thermal relaxation pathways of the molecules in solution, to complement the spectroscopic characterization by fluorescence and pump-probe measurements and computational studies in the applicant's group. This allows to fully elucidate the AIEE mechanism by revealing all relevant relaxation pathways.

Achievements:

During ten days training visit at Coimbra LaserLab, time-resolved photoacoustic calorimetry (PAC) measurements have been performed for the applicant compounds both in THF and chloroform solutions exactly as planned, and extra Flash Photolysis measurements have been carried out in chloroform solutions. All the data analysis has been done with the assistance of the expert from CLL and targeting results (i.e. yields and rate constants of multi nonradiative pathways of the library of functionalized compounds) have been achieved, which completes the previous research and leads the research to the objective powerfully. The paper is in preparation and the funding from Laserlab-Europe (grant agreement n° 284464, EC's Seventh Framework Programme) will be acknowledged.