



EUROPEAN COMMISSION  
RESEARCH DIRECTORATE-GENERAL

Marie Curie Actions – Fellowships

EIF-OIF-IIF-IRG-ERG Final Activity  
and Management Report

**Project n°: 219856**  
**Project Acronym: FENASY**  
**Project Full Name:**  
**Space and Time Resolved Ultrafast Dynamics of Few Porphyrin Derivatives in**  
**Nanosystems**

**Marie Curie Actions**

## **EIF-OIF-IIF-Final Activity and Management Report**

**Period covered: from** 02.06.2008 **to** 30.11.2009

**Period number:** 2

**Start date of project:** 02.06.2008

**Project coordinator name:** Abderrazzak Douhal

**Project coordinator organisation name:** Universidad de Castilla-La Mancha.

**Date of preparation:** 9 of February 2010.

**Date of submission (SESAM):** February 9, 2010

**Duration:** 18 months

**Version:**

## 1. FINAL PUBLISHABLE SUMMARY REPORT

*This section normally should not exceed 2 pages.*

*This is a comprehensive summary overview of results, conclusions and the socio-economic impacts of the project. The publishable report shall be formatted to be printed as a stand alone paper document. This report should address a wide audience, including the general public.*

*Please ensure that it:*

- *Is of suitable quality to enable direct publication by the Commission.*
- *Is comprehensive, and describes the work carried out to achieve the project's objectives; the main results, conclusions and their potential impact and use and any socio-economic impact of the project. Please mention any target groups such as policy makers or civil society for whom the research could be relevant.*
- *Includes where appropriate, diagrams or photographs and the project logo, illustrating and promoting the work of the project.*
- *Provides the address of the project Website (if applicable) as well as relevant contact details.*

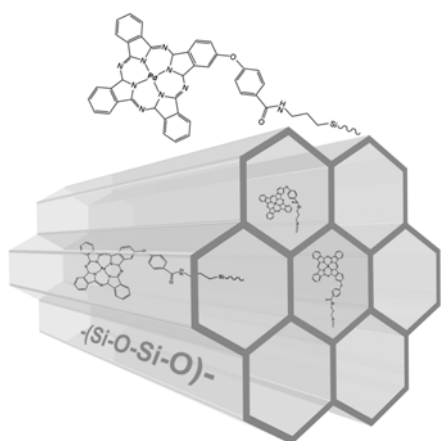
The goals set forth in the original project (FENASY) were focused on obtaining comprehensive information and in-depth knowledge about the interaction of selected potential candidates for use in nanoscience, nanotechnology and nanomedicine with chemical and biological nanocavities, such as cyclodextrins, human serum albumin protein and mesoporous silicate nanomaterials. During the period of the contract we carried out extensive studies using picoseconds and femtosecond spectroscopic techniques to investigate the excited state behavior of palladium phthalocyanine interacting with MCM-41 mesoporous material and 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin (p-THPP) confined by the Human Serum Albumin protein.

Following is an outline of the main results stemming from these studies.

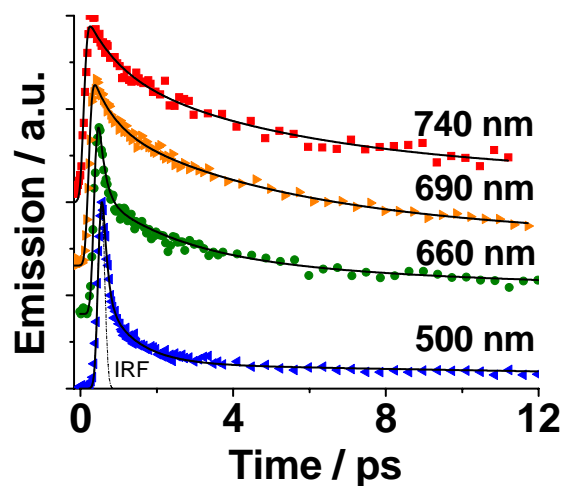
1. **Fast to Ultrafast Dynamics of Palladium Phthalocyanine Covalently Bonded to MCM-41 Mesoporous Material.** In this work, we have shown that the steady-state absorption and emission spectra of a suspension (in dichloromethane) of palladium phthalocyanine (MO-PdPc) covalently bonded to the internal framework of MCM-41 (Figure 1) are different from the nonbonded one prepared by physical sorption (PdPc\_MCM41). The presence of a new absorption band in MO-PdPc at 708 nm suggests a large distortion of the PdPc molecular frame inside the nanochannels. Moreover, the emission

decay also shows a new component with a lifetime of 1.4 ns. The results of the femtosecond studies (Figure 2) showed two times in the ultrafast dynamics. The shortest one changes from 170 to 500 fs, depending on the interrogated region and was assigned to intramolecular vibrational-energy redistribution,  $S_2$ - $S_1$  internal conversion and probably to a photoinduced Pd ion loosing. The other one has a time constant of 1.5 - 4.4 ps, which reflects vibrational relaxation/solvent cooling at the  $S_1$  manifold. At a longer time scale, the presence of Pd ion in the PdPc sample induces a 20 ps decay in addition to the nanosecond one (5.4 ns), observed in the free-base emission as a single exponential decay (6.1 ns). The results show that bonding PdPc to the framework of MCM-41 alters its chemical physics properties, spectroscopy, and longer-time relaxation.

*The obtained results from this study suggest the possibility to tune and modify the excited state properties of Palladium Phthalocyanine, upon interaction with MCM-41 mesoporous material with potential applications in various important scientific areas, such as nanophotonics, photodynamic therapy and photovoltaic and solar cell design by encapsulation and by changing the mode of preparation of the selected complexes.*



**Figure 1.** Molecular structures of Palladium Phthalocyanine covalently bonded to MCM-41 (MO-PdPc).

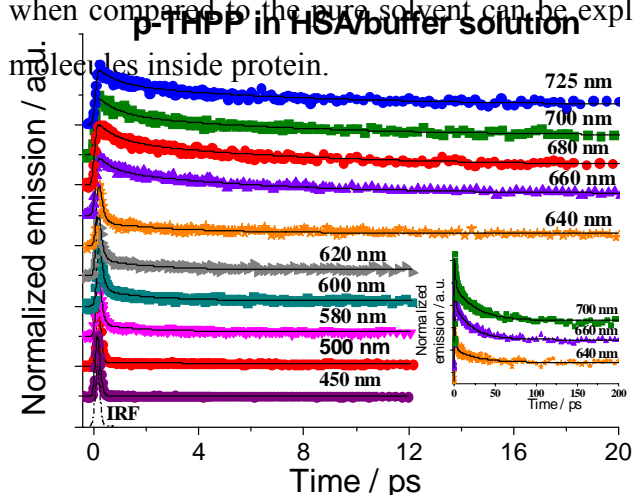


**Figure 2.** Magic-angle fs-emission transients of (A) MO-PdPc in DCM at different wavelengths of observation after excitation at 415 nm,

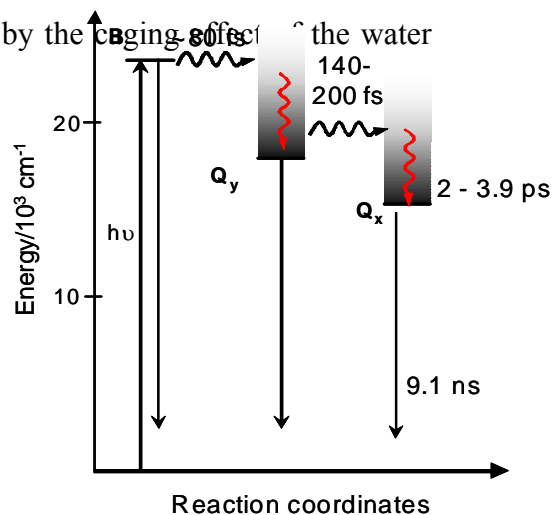
This work, of which Dr. Anna Synak was the leading author, was published in the **Journal of Physical Chemistry C**, 2009, *113*, 19199-19207 and was a direct result of the collaborative work within Prof. Douhal's group and the collaboration with Prof. Felix Sanchez from Instituto de Quimica Organica, CSIC in Madrid.

## 2. Femtosecond Studies of a Confined Porphyrin Derivative by Human Serum Albumin Protein.

Through a combination of steady-state, and femtosecond and picosecond-resolved fluorescence spectroscopy we studied the excited state relaxation dynamics of p-THPP and p-THPP–Human Serum Albumin protein complex (Figure 3). The dynamics of p-THPP in pure solvent can be described by four consecutive processes: a fast internal conversion from the B state to the  $Q_y$  state taking place within 80 fs, internal conversion from the  $Q_y$  to the  $Q_x$  state in 140 - 200 fs (120 - 130 fs in MeOH), vibrational relaxation in the  $Q_x$  state in 2 - 3.9 ps, and the intersystem crossing from  $Q_x$  to the triplet state with a lifetime of 9.1 ns (8.3 ns) (Figure 4). When p-THPP was encapsulated within the HSA, the  $B \rightarrow Q_y$  and  $Q_x \rightarrow Q_y$  internal conversion are slightly faster and occur within  $\sim 50$  fs and 100 fs, respectively, while the lifetime of the relaxed  $Q_x$  state is slightly longer, 9.9 ns. The most prominent changes are observed in the dynamics of the hot  $Q_x$  state that are accompanied by energy transfer to the protein with the time constant of about 1 ps that decreases the final population of the relaxed  $Q_x$  state when compared to the pure solvent. Further vibrational relaxation dynamics in the hot  $Q_x$  state that takes place in even longer 17 - 32 ps time scale and its slowing down when compared to the pure solvent can be explained by the



**Figure 3.** Fs-ps emission transients of p-THPP in HSA/aqueous buffer solution at different wavelengths of observation after excitation at 415nm, (Inset: Examples fs-emission transients of p-THPP in HSA/buffer in longer time scale).



**Figure 4.** Schematic diagram of energy levels and involved times in the photodynamics of (A) p-THPP in Tetrahydrofuran.

The results of this study have a wide impact since the Metal Phtalocyanines find broad applications in enzymatic catalysis, photonics and photodynamic therapy (PDT). For PDT p-THPP may be used as a potential drug for anticancer treatment. The porphyrins are usually introduced in the blood as relatively concentrated solutions, which may diminish its action or even cause adverse effects. Interactions with the Human Serum Albumin protein may control their efficacy and biodistribution. Thus, our study of the interaction of those molecules with HSA might provide the basis for further investigations to help formulate safe drug and effective dosages.

The manuscript corresponding to these results will be submitted soon for publication.

## USE AND DISSEMINATION OF FOREGROUND

### Section A (public) – DISSEMINATION MEASURES

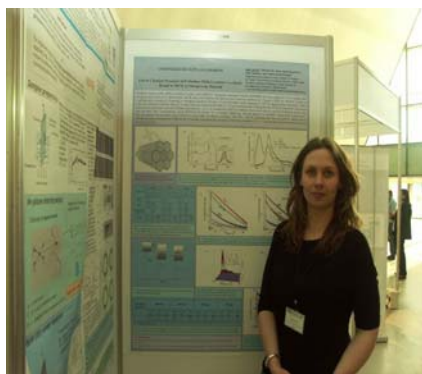
*This section should describe the dissemination measures, including any scientific publications relating to foreground and specify any applications for patents etc. Its content will be made available in the public domain thus demonstrating the added-value and positive impact of the project on the European Community.*

#### Dissemination activities Dissemination activities

As a result of the research conducted in this project, one article has been published in the Journal of Physical Chemistry C, at the moment. The impact factor of this journal in was 3.396. A second article is almost ready to be submitted.

The results have been presented in 3 national and international conferences. One of these conferences (XXIV International Conference on Photochemistry) was organized by the hosting research group in July 2009 and it was attended by more than 450 participants from over 30 countries. Below there is the list of the attended conferences:

1. *Authors:* A. Synak, M. Gil, J. A. Organero, F. Sanchez and A. Douhal  
*Title:* Fast to Ultrafast Dynamics of Palladium Phthalocyanine Covalently Bound to MCM-41 Mesoporous Material.  
*Type of presentation:* **poster**  
*Conference:* Nanospain, Zaragoza, Spain, 2009
2. *Authors:* A. Synak, M. Gil, J. A. Organero and A. Douhal  
*Title:* Femtosecond Dynamics of Porphyrin Derivative within Human Serum Albumin Protein  
*Type of presentation:* **poster**  
*Conference:* XXIV International Conference on Photochemistry, Toledo, Spain, 2009
3. *Authors:* A. Synak, M. Gil, J. A. Organero and A. Douhal  
*Title:* Femtosecond Studies of a Confined Porphyrin Derivative by Human Serum Albumin Protein  
*Type of presentation:* **oral presentation**  
*Conference:* IX Conference on Photochemistry, Bilbao, Spain, 2009



Dr. A.Synak explaining her contribution at the NanoSpain Conference (March 2009)



Dr. A.Synak giving a talk at the IX Conference on Photochemistry (September 2009)

▪ **Publications**

The list of scientific publications (see article II.12 of the grant agreement) starting with the most important ones, should specify:

- publication name,
- date and page in order to be able to identify it (see proposed template).

LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES								
NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages
1	<i>Fast to Ultrafast Dynamics of Palladium Phthalocyanine Covalently Bonded to MCM-41 Mesoporous Material</i>	<i>Anna Synak</i>	<i>Journal of Physical Chemistry C</i>	113, 2009	<i>American Chemical Society</i>	USA	2009	<i>pp. 19199-19207</i>
2	<i>Femtosecond Studies of a Confined Porphyrin Derivative by Human Serum Albumin Protein</i>	<i>Anna Synak</i>	To be submitted for publication					

**Section B (confidential) - EXPLOITABLE FOREGROUND AND PLANS FOR EXPLOITATION**

*This section should specify the exploitable foreground and provide the plans for exploitation. It will be kept confidential and will be treated as such by the Commission.*

The results are on fundamental science, and we do not expect any patent.

**The applications for patents, trademarks, registered designs, etc. shall be listed according to the template provided hereafter.**

*The list should, specify at least one unique identifier e.g. European Patent application reference. If applicable, contributions to standards should be specified.*

TABLE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.			
Type of IP Rights: Patents, Trademarks, Registered designs, Utility models, etc.	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant(s) (as on the application)

*Please complete the table hereafter:*

TABLE B2: OVERVIEW TABLE WITH EXPLOITABLE FOREGROUND					
Exploitable Foreground (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable, commercial use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved

*In addition to the table, please provide a text to explain the exploitable foreground  
[One text box per row in table B2]*

*Open space (2 pages maximum) composed as following:*

- *Its purpose*
- *How the foreground might be exploited, when and by whom*
- *IPR exploitable measures taken or intended*
- *Further research necessary, if any*
- *Potential/expected impact (quantify where possible)*

### 3. SCIENTIST IN CHARGE QUESTIONNAIRE

#### RESEARCH TRAINING ASSESSMENT:

What is the size of the hosting research group?	1 Full Professor 1 Associate Professor 1 Associate Researcher 2 Postdoctoral Researchers 2 PhD. Students
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How many researchers have you supervised, within the past 10 years? Of which funded by:	
EC/Marie Curie actions	2
EC Other Funding	0
University fellowships	6
National public bodies	8
Industry	0
Other	1 (NATO fellowship)
Other, please specify:	NATO fellowship to Dr. Alexander Roshal (Kharkov university Ukraine)

How many researchers have you supervised within this project?	1
Corresponding to how many person months?	1

Number of publications resulting directly from the research project: 2	
Recruited researcher(s) and yourself	2
Recruited researcher(s) alone	0
Recruited researcher(s) with authors other than yourself	0

Participation of the recruited researcher(s) at conferences (number): 4	
Passive	1
Active	3
How do you rate the overall success of the research training?	Very good

General assessment: The size of the group is not very large, but is enough good to allow fruitful interactions between the members. In addition to this, researchers from several labs have made short visit and stays. The researcher interacts with the member to get a good training in ultrafast spectroscopy, and gained a lot in understanding the photophysics within nanohost. He also learned how to handle several programmes to analyse the data. She participated in the 24<sup>th</sup> international conference of photochemistry, held in Toledo, by assisting the organization during that week.

#### RESEARCHERS ASSESSMENT:

Rate the overall level of the recruited researcher(s) integration in the research team and the host organisation with regards to:	
participation in meetings/seminars	Very good
discussions of results and project-related	good

topics	
co-operation with other team members	good
co-operation with other researchers of the host institution	good

Rate the overall performance of the recruited researcher(s) with regard to:	
originality of fellow(s) approach towards research (initiative/independent thinking)	good
capacity to develop new skills and to benefit from training	good
productivity (research results/publications/international conference attendance)	good
communication skills	good
group leader skills (collaboration with other groups/project management)	Very good
training and/or teaching skills	Very good
Please comment: The researcher spent a not expected long time to handle the setup of the femtosecond spectroscopy. At the beginning she had problems with the samples. During the second part of the first year she got results and could handle the fs-setup.	

#### RESEARCH TRAINING OUTCOMES:

Has this project provided additional links with other research groups or institutions?	Yes
If yes, indicate the number of contacts in each case	6
Universities	- Universidad Politecnica de Valencia, Spain. - Adam Mickiewicz University, Poznan, Poland
Research Centres	- Institute of Organic Chemistry (CSIC, Madrid) - Instituto de Tecnologia Quimica, UPV, Valencia (Spain). - Instituto de catálisis, CISIC, Madrid. - Kyusho Institute of Technology, Japan.
Industry/private companies	0
Others	0
If Other, please specify:	

Rate the importance of the following outcomes of the research training:	
results of the research	Very good
number of publications	good
development of research	Very good
establishment of international collaborations	Very good
transfer of knowledge/technology	Very good
Training of researcher	Very good

further academic qualifications (PhD, habilitation etc.) for fellows	Very good
Please comment: The research was fundamental and we could not make a transfer of knowledge to an industrial part. But, the obtained results have opened to us news windows and collaborations with other labs in the world.	



**YOUR OPINION ABOUT THE MARIE CURIE ACTIONS:**

Do you have any other comments or suggestions of how to improve the concerned Marie Curie actions? In my opinion, a substantial amount of financial support should be given to the host lab in order to cover the cost of the stay, and specifically when the lab is an experimental one involving high technology with a lot of cost of maintenance, in addition to the cost consumable. The current amount is not enough to cover the cost of the experimental labs. Part of the fellowship (for example the carrier exploratory allowance) should be directed to cover the cost of attending the conferences and meetings.
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Did you have previous knowledge of the Marie Curie actions?	Yes
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If yes, what sort of image do you think that the Marie Curie actions have among the scientific community in your research area?	Very good
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<b>Attachments:</b>	The `published work in 2009
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<b>Date: February 9<sup>th</sup>, 2010</b> <b>Signature Scientist in Charge:</b> Abderrazzak Douhal 	<b>Date: February, 9<sup>th</sup>, 2010.</b> <b>Signature Researcher: Anna M. Synak</b> 
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