**NIR Emitting Molecules: Toward Low Threshold Amplified Spontaneous Emission**

1. **Scientific and technological aims**
2. **Background/State of art**

Light-emissive organic solids are key materials toward a large panel of technologies including chemical sensing, bioimaging, information displays and processing, and telecommunications[Shimizu *et al.* *Chem. Asian J.* **2010,** *5*, 1516]. It is usually believed that strong -stacking of -conjugated molecules limits fluorescence emission as a result of aggregation induced quenching. A notable exception is provided by J-aggregates that are highly packed assemblies with enhanced emission properties in the solid[Würthner *et al.* *Angew. Chem. Int. Ed.* **2011,** *50*, 337] contrary to H-aggregates. More recently, it has been demonstrated that even H-aggregates can emit in single crystals [Gierschner *et al.* *J. Phys. Chem. Lett.* **2013,** *4*, 2686]. The seminal work of Hanack and Oelkrug[Oelkrug *et al.* *Synth. Met.* **1996,** *83*, 231], evidenced the enhancement of photoluminescence in (solid state) phenylene vinylene films. It triggered the continuous growth of the efforts made to design such emitting -stacking supramolecular assemblies and highlighted the key role of aggregation induced (enhanced) emission[Hong *et al.* *Chem. Soc. Rev.* **2011,** *40*, 5361; *Gierschner et al.* *J. Mater. Chem. C* **2013,** *1*, 5818]. These efforts led to the tremendous development of libraries of luminescent dyes in the condensed phase. However, there is still no definitive theoretical model for the emission of such molecular assemblies mainly because of the difficulty to describe the complex interplay of intra- and intermolecular contributions. While, lately, emission in the NIR becomes more **common in solution**, an even trickier case concerns far red to near infrared (NIR) emission **in solid state**, which represents a spectral region of interest for bioimaging, sensing (two applications that require a minimum of interferences from the medium such as autofluorescence and measurements in depth), night vision devices or optical communication for instance. While numerous visible emitters (wavelengths below 600 nm) have been reported, exhibiting quantum efficiencies up to unity, it appears much more challenging to reach such an efficiency for solids emitting in the far red to NIR range[Qian *et al.* *Chem. Asian J.* **2010,** *5*, 1006].

For those reasons, organic solid-state semiconductor lasers (OSSLs) and organic light emitting diodes (OLEDs) with emission in the NIR are particularly difficult to obtain. Such systems require displaying amplified spontaneous emission (ASE) at low excitation threshold. Within OSSLs, two types of stimuli can be used: i) optically pumped OSSLs within which pulsed and continuous wave (CW) laser can be found and ii) the Holy Grail: electrically pumped OSSLs. To date, only a few families of NIR emitting organic molecules have been developed that fill the requirements for ASE: high fluorescence quantum yield, stability against oxidation and moisture, limited triplet formation. However, it is commonly accepted that - interactions have to be limited to avoid “concentration quenching”. It is not the case in this proposal where such interactions are beneficial for obtaining efficient NIR emission.



**Figure 1.**

1. **Scientific objectives**

Anthony D’Aléo has recently discovered that borondifluoride complexes of 2’-hydroxy-chalcones and of curcuminoids containing boron complex present broad electronic absorption and display far red to NIR light emission in the solid-state [D’Aléo *et al.* *Chem. Eur. J.* **2012,** *18*, 12764; Felouat *et al.* *J. Org. Chem.* **2013,** *78*, 4446; D’Aléo *et al.* *J. Mater. Chem. C* **2014**, *2*, 5208]. It has been demonstrated that this property originates from the peculiar packing of the dye within the crystal lattice. This opened the path to borondifluoride-containing NIR emitters with rather high fluorescence quantum yields. Initially, the work at CINaM focused on their borondifluoride complexes. Recently, we started the investigation of the free curcuminoid ligands (lacking the BF2 moiety) and we discovered that they are emitting both in solution and in the solid state. With those curcuminoids, while 1H NMR spectroscopy shows that the enol form is present in solution, one can not rule out the occurrence of the diketo form (transiently formed through keto-enolic tautomerism) in interconverting photoexcited states which could be detrimental for obtaining good ASE properties in solution. However, in the case of the solid state, the X-Ray crystal structures reveals that the enol form is the only one present in the solid (see Figure 1 for illustration). Remarkably, compounds functionalized with properly selected substituent display NIR emission with high fluorescence quantum yields. In the meantime, two papers were published showing the case of two 2’-hydroxychalcone derivatives (such as the one presented in Figure 1) that were particularly attractive for ASE[Wang *et al. J. Am. Chem. Soc.* **2015**, *137*, 9289; Chang *et al. Angew. Chem. Int. Ed.* **2015**, *54*, 8369]. Since the structure of the chalcone with its phenol associated to the acetyl group retains the enol form, these data encouraged us to test ASE properties of curcuminoid derivatives. Indeed, we found that two curcuminoids (including that shown in Figure 1) exhibit ASE in dichloromethane solution.

1. **Work package**

In this project, we specifically target new organic -conjugated molecules (curcuminoids) as dyes or organic semiconductors (OSCs) according to the classification by Forget [Chénais *et al. Polym. Int.*, **2012**, *61*, 390] for NIR OSSLs. In particular, this project is intended to i) unravel structure-ASE relationship within curcuminoid’s family of conjugated compounds, and ii) propose guidelines to synthesize new molecular systems with improved NIR ASE in the solid state. In a first step, we will study the steady-state and time-resolved spectroscopic properties (*vide infra*) of already existing curcuminoids in both solution and films in order to assess the photophysical requirements for ASE. Both doped film in polymer matrix and neat films are planned to be tested. Then in a second step, following the experimental data and the theoretical feed-back, new dyes with enhanced properties will be prepared and studied.

This project joints **experimental and theoretical approach.** It is an **interdisciplinary fundamental** project that aims to study new functional materials which could be used in the fabrication of OSSLs.

 *WP1*- *Preparation of curcuminoid dye with emitting solid state properties*

We will focus on curcuminoid derivatives. While borondifluoride complexes of those ligands will also be evaluated, the main focus will be made on the free molecules since they have higher solubility allowing them to be easily processed. Classical theoretical calculations will be made on the already existing molecules with attempt to predict the best candidates (by C. Attaccalite). Those new ligands will be prepared using a modular approach developed by A. D’Aléo and E. Zaborova, which will allow the generation of compounds with tailored electronic properties and stacking ability. Particularly the effect of the *meso* group (see Figure 1) that affects both features will be inspected both on the emission in solid state and on the ASE properties. Currently we have in hands dyes with emission ranging from the visible (with 100% fluorescence quantum yield) to the NIR region of the spectrum (emission with maxima at 685nm and 760nm and fluorescence quantum yield of 40% and 25%, respectively) which represent very promising candidates.

It is to be noted that theoretical calculations will be performed on the dyes of interest with the aim to modelize the absorption of the film and its fluorescence properties (C. Attaccalite).

*WP2*- *Engineering of the photophysical properties (radiative fluorescence decay rate of the dyes/ fluorescence quantum yield / triplet formation and T1-Tn position)*

The dyes will therefore be characterized using spectroscopic methods (steady state and nanosecond time-resolved techniques present in CINaM) with the expertise of A. D’Aléo. One of the key issues in the design of low threshold ASE active dyes with high optical gain is to obtain very high fluorescence quantum yield (**f) and very fast decay time (**f) yielding therefore a radiative constant decay rate (*kf*) as large as possible (fluorescence radiative constant decay rate is defined as *kf* = **f / **f). As such, free curcuminoid derivatives are of interest since we found that those ligands could reach almost 100% quantum yield in their condensed phase. In addition, the naturally-occuring curcumin has been found to have lifetimes of 347 ps in acetonitrile solution and close to 990 ps in film.

For CW (or laser with long pulse) optically pumped laser, another requirement for the dyes is to avoid the triplet formation which can be achieved by having fluorescence quantum yield as high as possible. In case the triplet excited state is formed, the T1-Tn absorptions have to not overlap with the emission of the dyes because, upon emission, this could result in excitation to the Tn excited state that would enhance non radiative deactivation pathways. The position of the T1-Tn absorption will therefore be assessed by using transient absorption spectroscopy at IPCMS (L. Mager).

 *WP3*- *Surface assembly engineering*

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) properties of the dyes will be assessed in order to obtain information on the degradation temperature and temperature that could be used for annealing (temperature for evaporation and melting process) and the filmogenic properties will be observed. Film on fused silica will be prepared to observe the fluorescence properties of the dyes. To this end, spin coating and evaporation processes will be used. In addition, films obtained by melting process will be realized. All this part will take benefit from the expertise of F. Mathevet in thin film and crystal growth and characterization. X-Ray diffraction will allow the comparison of the organizations in monocrystals powder, and thin films. It can be noted that already ten X-ray crystal structures of curcuminoids (with interesting fluorescence quantum yield at various wavelengths) have been obtained and that the powder X-Ray patterns show that the same arrangement is present in the powder that the one observed in the monocrystals. This part will benefit of the theoretical support that will analyze the changes induced by the different arrangements on the electronic structure and the optical properties of the different dyes (C. Attaccalite).

Finally, we plan to use plasmonic nanostructured substrates to improve the optical properties of the films. For instance, it is known that for curcumin film, a fluorescence lifetime of 990 ps was measured on fused silica, and a much faster decay of 29 ps with increase of fluorescence quantum yield was observed in plasmonic platforms[Mukerjee *et al. Curr. Pharma. Biotech.* **2010**, *11*, 223]. In the same trend, deposition of the fluorophore on silver nanoparticle–dielectric–metal substrate will be test since such approach led to a 400-fold increase of the fluorescence quantum yield of a cyanine dye[Ray *et al. Chem. Commun.* **2015**, *51*, 15023]. Such approach will be highly interesting in this project since it will allow to **avoid processes competing with fluorescence**. The preparation of those plasmonic surfaces will be realized at PLANETE, the micro-nanofabrication facility of CINaM hosting a 250 m2 clean room.

 *WP4*- *Measurements and optimization of the ASE properties*

ASE properties of the dyes fulfilling the photophysical requirements will therefore be tested in solution (IPCMS), and mainly in polymer films and in neat films. Here, it can be highlighted that, before the end of this project, we aim at setting up such experiment in CINaM.

In order to evaluate the ability of the dyes to be used for lasing, we plan to estimate the quantity of singlet-singlet annihilation by measuring fluorescence spectra as a function of the excitation density. In addition, singlet-triplet annihilation will also be inspected because those two latter phenomena are representing limiting process in OSSLs[Forget *et al.* in Organic Solid-State Lasers (**2013**)Springer series in optical science, vol. 175].

It is to be noted that the first results of this project are currently obtained and the first ASE test in solution show that those curcuminoid dyes are promising compounds for ASE project. The test of the lasing properties on thin film is ongoing.

Finally, charge mobility on the pure films will be measured to assess whether such molecules behave as semiconductours and could thus be used in electrically pumped laser. This will be done by making organic field effect transistors (OFETs) with curcuminoid dyes as active layer. Here, it can be highlighted that we recently demonstrated that some borondifluoride complexes of curcuminoids have been found to transport charges in thin films (patent being filled).

The properties that will be found in the photophysical study as in the ASE study will permit to target the type of laser that will be tested (CW or pulsed ones). Except the pre-test, this latter part will be done in OPERA (Japan) because of the greater facilities and their expertise.

Ultimately,microcavities will be tested using organic particles or patterned thin films to provide first test beds toward applications of OSSLs.

1. **Project organisation and Efforts**

This project relies on strong expertise in organic synthesis, steady state and time resolved spectroscopy of the coordinator (Anthony D’Aléo, CINaM) where all photophysical study represent new research theme brought to CINaM since the recruitment of A. D’ALÉO. The CINaM team composed of Anthony D’Aléo, Elena Zaborova and Claudio Attaccalite will be strongly involved in this project. The organic synthesis and the steady state spectroscopy will be realized in CINaM (Marseille), where A. D’Aléo, and E. Zaborova will actively participate to the project. The theoretical part will be performed by C. Attaccalite.

The CINaM team will be complemented by the expertise of Loïc Mager (IPCMS) and Fabrice Mathevet (UPMC). Loïc Mager, physicist in CNRS, will be in charge of the ultrafast spectroscopy part and of the first ASE test using the facilities of IPCMS. In addition, it is planed that L. Mager come and visit CINaM to help setting the ASE in Marseille using the already “in house” femtoseconde MaiTai laser. Fabrice Mathevet (UPMC) will be implicated with the TGA and DSC measurements. Further, his expertise in surface structuration will be a keystone in this project since it will help in having well-structured thin layer on fused silica and plasmonic platforms.

Finally, Jean-Charles Ribierre (Kyushu University, OPERA) will be involved as external partner bringing his great expertise in organic laser physics. The presence of the external partner is essential since it involves one of the best laboratory in organic electronic. J.-C. Ribierre, associate professor in Prof. C. Adachi’s lab (inventor of the 3rd OLED generation) will be crucial due to his long standing expertise in organic electronics with a strong knowledge in organic lasers (work started in I. Samuel’s group and continued as a group leader in Adachi’s lab). As such, all the facilities of the Center for Organic Photonics and Electronics Research (OPERA) could be used for characterizing and developing materials for laser.

This consortium is active since March 2014 working on various projects that resulted in the submission of two papers all together. As a JCJC ANR program, this project aims at developing a **new** **topic of research** and a **new team** in CINaM working on ASE of nanomaterials for organic lasers. Such topic is **not yet developed** in the lab but perfectly fit the **priority axis** of CINaM.

**Anthony D’ALÉO** CR, CNRS (38years old, thesis defended in January 2006)

**52 publications, 3 book chapters, 1 patent, 26 oral presentations** in conferences (H-factor 17, scifinder)

[1]: A. D’Aléo, A. Bourdolle, S. Brustlein, T. Fauquier, A. Grichine, A. Duperray, P. L. Baldeck, C. Andraud, S. Brasselet, O. Maury *Angew. Chem. Int. Ed.* **2012**, *51*, 6622.

[2]: A. D’Aléo, E. G. Moore, G. Szigethy, J. Xu, K. N. Raymond; *Inorg Chem.* **2009**, *48*, 9316

[3]: A. D’Aléo, R. M. Williams, F. Osswald, P. Edamana, U. Hahn, J. van Heyst, F. D. Tichelaar, F. Vögtle, L. De Cola; *Adv. Funct. Mater.* **2004**, *14*, 1167

The coordinator of this ANR JCJC has good experience in organic synthesis, steady state photophysical study and in ultra-fast photophysical measurements. He also has a good knowledge in managing project since, during his PhD thesis (group Prof L. De Cola, Amsterdam), he worked on a training mobility and research European program (SUSANA: Supramolecular Self-Assembly of Interfacial Nanostructures). This project was at the interface between chemistry, physical chemistry and surface science that permitted to the coordinator to develop knowledge in these fields. Furthermore, in this project, A. D’Aléo was in charge of few collaborations receiving and training other workers from the project in Amsterdam. This European project was also an opportunity to have training in various groups dealing with different aspect of chemistry (plasmonic nanoparticles in Prof. D. Schiffrin group, organic synthesis in Prof. F. Vögtle and Prof. P. Belser groups, non-linear optics in Prof. Zyss group). It is especially interesting to note that the experience acquired by A. D’Aléo in photophysics and in solid state spectroscopy will be instrumental in the design of dyes that emits in the NIR with ASE properties. A. D’Aléo entered in CNRS 6 years ago and the defense of his habilitation is planned in 2016.

**Elena Zaborova** MCF, AMU (32years old)

**11 publications, 6 oral presentations** in conferences

[1]: B. Wang, E. Zaborova, S. Guieu, M. Petrillo, M. Guitet, Y. Bleriot, M. Menand, Y.M Zhang, M. Sollogoub *Nature Comm.* **2014**, *5*, 5354.

[2]: P.-O. Schwartz, L. Biniek, E. Zaborova, B. Heinrich, M. Brinkmann, N. Leclerc, S. Méry, 2014, *J. Am. Chem. Soc.* **2014**, *136*, 5981.

[3]: E. Zaborova, P. Chávez, R. Bechara, P. Lévêque, T. Heiser, S. Méry, N. Leclerc, *Chem. Commun.* **2013**, *49*, 9938.

**Claudio ATTACCALITE** CR1, CNRS (38years old)

**41 publications, 1 patent, 11 talks** in conferences, in conferences (H-factor 18, ISI-Web)

[1] C. Attaccalite, M. Grüning, Phys. Rev. B, 88, 235113 (2013)
[2] X. Blase, C. Attaccalite, V. Olevano, Phys. Rev. B **83**, 115103 (2011)
[3] C. Attaccalite and S. Sorella, Phys. Rev. Lett. **100** , 114501 (2008)

Claudio Attaccalite has a good expertise in excited state properties of solids and molecular systems. He also participates in the development of different *ab-initio* codes for the study linear and non-linear optical response of solids and nanostructure. C. Attaccalite entered in CNRS 6 years ago and the defense of his habilitation is planned in 2016.

This fundamental project is projected to last 42months and would require **210k€**.

PhD student (36months) : 100 k€

Operating costs for PhD thesis + A. D’Aléo : 50 k€

NIR detector to implement Fluorolog® with possibility of lifetime measurements : 50 k€

Missions : 10 k€

1. **Impact and benefits of the project**

This project is **interdisciplinary** and **fundamental**, although it aims at addressing challenging issues for applications of organic materials in photonics. The approach is based on a molecular design strategy towards novel π-conjugated systems with solid-state NIR photoluminescence and ASE. A literature survey shows that the range of such structures used to date is still limited and leads to the conclusion that progress in OSSL research requires the development of new classes of dyes and OSCs that emits in the visible and the NIR. Actually, π-conjugated materials are mostly developed for applications in nonlinear optics, photovoltaics and display technology (OLED). In contrast, tailoring dyes for solid-state ASE, as proposed in this project, is not a direction as explored as the previous ones [Ishow *et al.Chem. Mater.* **2008**, *20*, 6597, Rabani-Haghighi *et al. Appl. Phys. Lett.* **2009**, *95*, 03305] and, especially, if NIR emitting organic solids are to be targeted. Given the recent achievements of CINaM team, we believe that this project will bring novel insights in molecular design, crystal engineering, and photophysics of a new family of π-conjugated molecular systems. The participation of high level physicists (C. Attaccalite, L. Mager and J.-C. Ribierre) will be instrumental in achieving breakthroughs in the field. Especially, reaching a diode-pumped OSSL with bright NIR emission represents an exciting objective for bioimaging applications. Of course, the electrically-pumped OSSL, the Holly Grail, would be the ultimate goal of the project, but “the road’s still long” ! We intend anyway to address some of the major bottlenecks for electric pumping.

This project represents a nice opportunity for A. D’Aléo to develop a newly-emerging research topic in CINaM which will be based on a strong interface between chemistry and physics. The results arising from this project will be published in high impact journals and will likely lead to valorization. Moreover, results will also be presented as posters and oral communications in national or international meetings.