ADIOS - Ru

PROJECT FINAL REPORT

Grant Agreement number: 315131

Project acronym: ADIOS-RU

Project title: Advanced Design and Industrialisation of Sensitizers without Ruthenium for DSSC

Funding Scheme: Research for SMEs

Date of latest version of Annex I against which the assessment will be made:

23/08/2012

Periodic report: 1st

Period covered: from 01/11/2012 to 01/04/2014

Name, title and organisation of the scientific representative of the project's coordinator:

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Declaration by the scientific representative of the project coordinator

I, as scientific representative of the coordinator of this project and in line with the obligations as stated in Article II.2.3 of the Grant Agreement declare that:

- The attached periodic report represents an accurate description of the work carried out in this project for this reporting period;
- The project (tick as appropriate) [1]:

  X has fully achieved its objectives and technical goals for the period;

  ☐ has achieved most of its objectives and technical goals for the period with relatively minor deviations.

  ☐ has failed to achieve critical objectives and/or is not at all on schedule.

- The public website, if applicable

  ☐ is up to date

  ☐ is not up to date

- To my best knowledge, the financial statements which are being submitted as part of this report are in line with the actual work carried out and are consistent with the report on the resources used for the project (section 3.4) and if applicable with the certificate on financial statement.
- All beneficiaries, in particular non-profit public bodies, secondary and higher education establishments, research organisations and SMEs, have declared to have verified their legal status. Any changes have been reported under section 3.2.3 (Project Management) in accordance with Article II.3.f of the Grant Agreement.

Name of scientific representative of the Coordinator: Frédéric Oswald..

Date: .2707/2016

For most of the projects, the signature of this declaration could be done directly via the IT reporting tool through an adapted IT mechanism and in that case, no signed paper form needs to be sent

[1] If either of these boxes below is ticked, the report should reflect these and any remedial actions taken.

3.1 Publishable summary

Dye-sensitized solar cells (DSSC) are a promising new generation of photovoltaic which have demonstrated relatively high performance compared to silicon-based solar cells in many non-ideal light environments such as dim, diffuse and indoor light. They are on the verge of wide-scale commercialization but still face challenging issues to solve on long-term stability, materials cost and ability to recycle. Many of these issues are rooted in the liquid phase of the cell, the dye / electrolyte pairing. In particular, the reliance on the rare earth Ruthenium as the active constituent of the dye has strong implications on the raw material cost and could potentially be difficult to source in the long term.

The ADIOS-Ru project aimed to develop a suite of materials for highly stable, low cost DSSC with immediate commercialisation potential. Organic dyes that have reached an advanced stage in laboratory development and the selection, modification, analysis and stability improvement tasks the project have provided the SME partners with a low cost alternative to the universally used Ruthenium dye. An ionic liquid electrolyte with tailored properties to support the dye performance have been selected and developed. The SME partners have used the materials for validation, accelerated stability testing and lab to industrial scaling of production. In cooperation with RTD, they have designed and validated a DSSC device tuned specifically for the dye/electrolyte combination.

As major achievements in this project the partners have identified synthetic routes appropriate for developing new organic dyes without rare elements. In parallel ionic liquid based electrolytes have been developed and improved for a stable cell.
The new dyes show power conversion efficiencies over 10% with liquid electrolytes and over 7% when ionic liquid based electrolytes. The solar cells fabricated with ionic liquids are highly stable over 9000h under accelerated ageing conditions with a loss of only 25% of the initial performances.
The new materials have been implemented in solar modules that show high efficiency and stability.
One dye has been pushed toward commercialization and it has been employed for the fabrication of commercial modules for building integrated photovoltaics.

3.2 Core of the report for the period: Project objectives, work progress and achievements, project management

3.2.1 Project objectives for the period

The major objective for the ADIOS-Ru project, as stated in Annex 1 to the Grant Agreement, are subdivided into RTD objectives and associated exploitation objectives for the SME partners.

RTD Objectives:

a) Identify synthetic routes appropriate for developing new organic dyes without rare elements
b) Determine and improve the electro-optical and stability properties of the new organic dye matched with a TiO_2 photo-electrode
c) Match the new organic dyes with ionic liquid based electrolytes and improve the key electrolyte properties for a stable cell
d) Determine the optimum dye-uptake procedure for a given photo-electrode, and develop characterisation tools to analyse the process

e) Optimize of the thickness of the TiO_2 photoelectrode, pore size and porosity factors to suit the dye
f) Improve expertise and leadership in the area of organic materials for hybrid photovoltaic technologies

Strategic SME objectives:

a) Gain access to high performance, low cost and stable organic dyes
b) Resolve compatibility and integration issues within DSSC for ionic liquid electrolytes
c) Address the issues of stability and lifetime for materials in DSSC, and the completed cell
d) Use characterisation tools for dye-uptake to progress from optimized laboratory processes (hours) to industrial dying processes (minutes)
e) Reduce the time to market for integration of new dyes and electrolytes into DSSC through greater knowledge and understanding of their development
f) Enable scaled manufacturing of both DSSC component materials and complete DSSC
g) Develop and contribute to transferrable standards for performance and stability testing for DSSC materials and products
h) Remove uncertainty in issues of toxicity from DSSC products
i) Build EU expertise, competitiveness and leadership in the area of printable DSSC technology

The major technical tasks and deliverables reaching conclusion in this reporting period relate to selection, optimisation and release of a novel set of organic dyes to the delivery to the project consortium to allow sample preparation. Another task relates to the optimization of the synthetic routes and the preparation of selected dyes at the industrial level.
Secondary tasks relate to selection, optimisation and analysis of ionic liquids electrolytes tailored to the dyes, and to assembly of complete DSSC devices as test vehicles leading towards prototype commercial products.

3.2.2 Work progress and achievements during the period

Overview of the progress of the work in line with the structure of Annex I to the Grant Agreement.

Reminder of the work plan.

The methodology followed during the project was a close collaboration between the SME partners and the RTD performers, in order to effectively develop organic dyes with associated ionic liquid electrolytes that have the required performance, stability and scalability to be integrated into a commercially attractive DSSC module.
The RTD activities are split in five work packages (WPs), each with its particular objectives and activities:

WP1 Preparation and Characterisation of new dyes (led by CEA)
WP2 Dyes assessment and draft design of DSSC modules (SPR)
WP3 Development of ionic liquid based electrolytes (ICIQ)
WP4 Study of manufacturing processes to scale-up dye production (KK)
WP5 Final design of DSSC modules (SPR)

Two additional work packages for management of Exploitation, IPR and the overall project by the SME partners are included; WP6 Dissemination and Exploitation (SPR) and WP7 Project Management (SPR).

WP1 Preparation and Characterisation of new dyes

The first objective of the WP1 was to design and synthesize organic dyes capable to absorb over a wide range of wavelengths in the visible and showing high molar extinction coefficients for a good sensitization of the nanostructured electrodes even at low thicknesses.
The key objectives of the WP1 are:
i) To prepare highly efficient organic dyes for high performance DSSC
ii) To characterize the optoelectronic properties of the dyes, i.e. to evaluate the positions of the energy levels of their frontier orbitals, to determine the absorption coefficients and the absorption domains of the dyes
iii) To evaluate the photochemical and thermal stability of the dyes when they are grafted on the surface of TiO_2
iv) To study and optimize the grafting conditions and to evaluate the attachment stability of the monolayer

Summary of Progress

During the period, CEA has designed and synthesized purely organic dyes capable to absorb photons over a wide range of wavelengths (from UV to visible). The dyes were designed to demonstrate high molar extinction coefficients in order to allow a good sensitization of the nanostructured electrodes even at low thicknesses. Dyes showing at least two times higher molar extinction coefficients compared to N719 ruthenium dye (reference) were targeted.

For their design, we have selected triarylamine moiety as electron donor group and cyano-acrylic acid as electro withdrawing anchoring group. These two synthons were bridged together by means of various pi-conjugated linkers in order to tune the range of absorption of the dyes toward the visible. Two families of dyes have been investigated, the first one comprising symmetric linkers and the second one comprising non symmetric linkers. In order to obtain cost effective dyes, low-cost building blocks were selected for their preparation (thiophene, benzothiadiazole or triarylamine).

Density Functional Theory (DFT) calculations were performed on the different chemical structures to identify the electron density distribution of the frontiers orbitals.

To facilitate the photo-physical processes, i. e. charge injection and dye regeneration, that are responsible for the generation of current, the dyes were designed to possess Highest Occupied Molecular Orbital (HOMO) preferentially localized on the donor part of the molecule (triphenylamine) and the Lowest Unoccupied Molecular Orbital (LUMO) localized close to the anchoring function (cyanoacrylic acid) to favour the charge injection from the excited state of the dye into the metal oxide electrode and to prevent charge recombination processes.

The solubility of the dyes in organic solvents is of crucial importance for the preparation of stable dyeing baths even at high concentrations. A good solubility is also mandatory to achieve good surface coverage of the electrodes during the dyeing process. To prevent aggregation phenomenon in solution, the dyes were decorated by alkyl chains. Different solubilizing groups were investigated. All the dyes are soluble in chlorinated solvents such as dichloromethane and chloroform and some of them show good solubility in methanol or ethanol which is of particular interest regarding to the industrial applications.

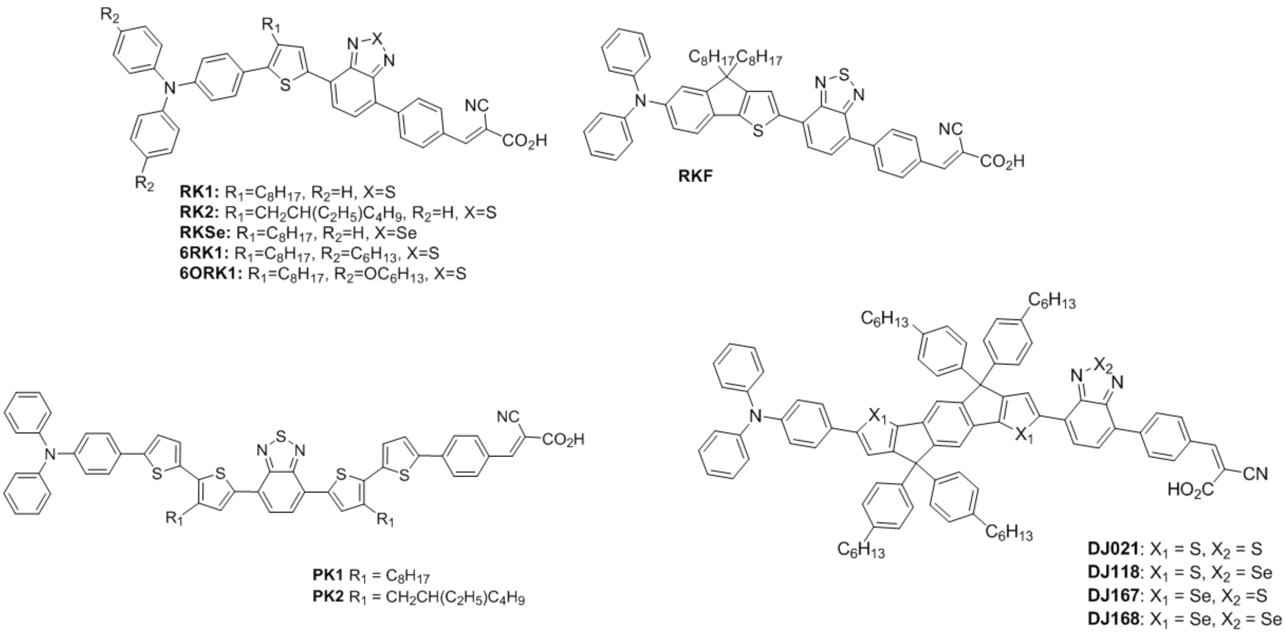

Figure 1: Chemical structures of the dyes synthesized in WP1

Significant results:

During the period twelve dyes were synthesized and characterized. All the dyes were provided to different members of the consortium for evaluation of their performances and advanced characterizations.
Several design rules can be drawn.

- The combination of an electro withdrawing unit such as benzothiadiazole with electron-rich thiophene units in the core of the dyes allows for the extension of the absorption spectrum across the visible thanks to the occurrence of an internal charge transfer absorption band. The range of absorption has been extended to 700nm for some of the dyes.

- High molar extinction coefficient (3 times higher than the ruthenium reference compound N719) can be achieved using extended pi-conjugated segments as donating groups (bithiophene or indaceno dithiophene). As a consequence the TiO_2 thickness can be significantly reduced in devices.

- When planar pi-conjugated cores are employed (such as bithiophene segments) the dyes show a strong tendency to self-aggregation and reveal lower solubility limits in organic solvents. However we have found that branched alkyl chains such as ethyl-hexyl groups can help improving the solubility of the dyes better than linear alkyl chains. The use of bulky building blocks with a spiro geometry helps also reducing aggregation of the dyes in solution.
The dyeing baths are then found stable for long storage periods.

As a general statement, it appears that the syntheses of dissymmetric compounds are easier to perform. Convergent approaches can be developed to access to dissymmetric compounds and the purification steps are usually easier to carry out. The scale up is therefore facilitated.

After studying the scalability of the compounds, Kaironkem has developed a synthetic strategy to produce RK1 derivative in large scale (tens of grams) starting from low cost precursors.
These batches have been provided to Solaronix for the fabrication of solar panels applicable in buildings.

WP2 Dye assessment and preliminary design of DSSC modules

The major evaluation of any dye for use in DSSC is how it performs when applied in a test cell. Therefore this work package was mainly focus on the use of the dye in assembled DSSC. Performance, photoelectric properties and reliability were be determined, using industrial standards and practices.
Since the optical and electrochemical properties of purely organic dyes are tuned with high precision through suitable molecular design in WP1, their molar extinction coefficients of absorption should be significantly higher than the ones of ruthenium dyes. It is possible therefore to adjust the thickness of the semiconducting oxide layers (and as a consequence potentially reduce the amount of material and number of processing steps necessary to fabricate them) without damaging the light-harvesting efficiency and the performances of the solar cells. In this work package we hawe also perform the preliminary design of the layer structure of the TiO2 metal oxide layer on the working electrode to take advantage of the organic dye extinction coefficient.

Summary of Progress

SolarPrint has assembled test cells from three of the ADIOS-Ru project first generation organic dyes, RK1 and DJ021, comparing with the standard Ruthenium dye N719. The two dyes were selected on the basis of their opto-electronic properties determined in WP1.

Test cells manufactured by SolarPrint are configured for optimised power output under low light (specifically, 200lux illumination from fluorescent white bulb, a broadly accepted 'indoor' standard).
These "low light" test cells were prepared on SolarPrint's pilot production line. The procedure is outlined in Appendix 1. Since the D2.1 report, SolarPrint has improved the test cell design. The larger Mark II test cell has a 12.3 cm2 active area, compared to 1cm2 in the first version test device, and also utilises a screen-printable UV-curable sealant (as opposed to a thermoplastic gasket).
This improvement means the testing results and materials are now directly transferrable to commercial production devices, both in terms of size and manufacturing processes employed.
As before, these test cells were used to rapidly infer the performance and stability of the novel dye/electrolyte pairings from the project. The test cells are compared to 'classic' DSSC made by an identical method but using standard N719 dye.

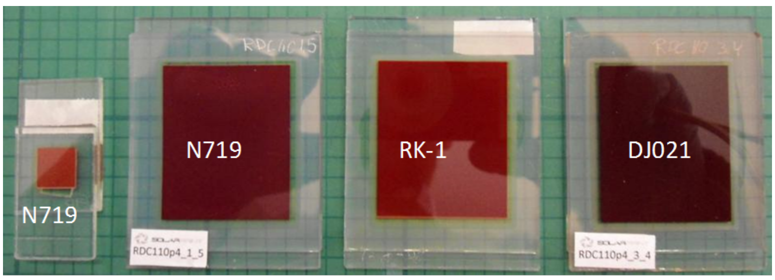

Figure 2: Test cells manufactured by SolarPrint for indoor applications

Solaronix and ICIQ have assembled test cells with the twelve different dyes developed in WP1. The thickness of the TiO_2 layer has been optimized regarding to the molar absorption coefficient of the dyes

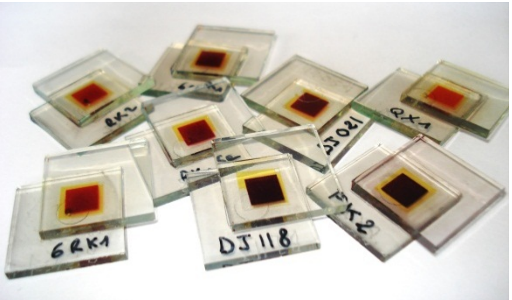

Figure 3: Test cells manufactured by SolarPrint

Significant results:

Several dyes that appear suitable for indoor applications have been investigated at Solarprint.

The optimum thickness of the titania absorption layer for each dye was determined by experiments, and it was found that with a 2µm layer DJ021 outperforms N719 by ~18% under indoor light levels (200Lux white fluorescent source).
This relatively thin titania structure also appears to increase device stability under elevated temperatures, and reduces overall material cost per cell. DJ021 appears most promising for low light generation and will be tested further.
On the basis of the performance and stability results, it has been determined that DJ021 dye significantly outperformed the standard dye, N719, and exhibits greater potential for use in commercial devices than RK1 for indoor applications.
The thinner optimised titania thickness required also means less dye and titania material are required, reducing the overall cell cost.

All the dyes were investigated for outdoor applications at Solaronix and ICIQ.
Four dyes have demonstrated power conversion efficiencies over 9% in testing devices based on liquid electrolytes, and two dyes have passed the 10% efficiency barrier.

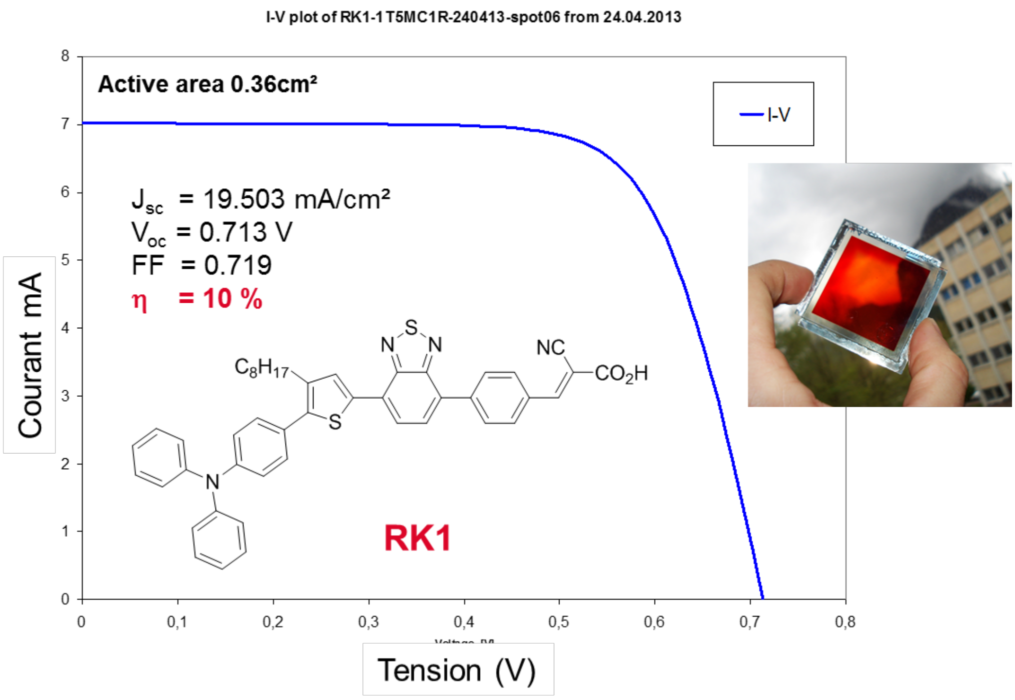

Figure 4: IV curve of RK1 testing device showing 10% of power conversion efficiency

These results rank among the best in the field.

WP3 Development of ionic liquid based electrolytes

Of specific interest to this project, in which novel organic dyes will be used, the following parameters are critical: viscosity, wetting, stability, effect on dye, effect on Electron Injection Rate (ie. photovoltaic operation)

The ultimate objective of this WP is to develop and characterize a simple electrolyte where the roles of all typical additives are provided by the two-component, structured ionic liquid. The decreased complexity will increase the chance of achieving high stability, especially with regard to water. Also, the acid base qualities of different ionic liquids can have an effect on the band edge position of the TiO_2.
Solaronix and ICIQ have therefore selected or synthesised, developed and characterised ionic liquids specifically for indoor or outdoor applications. They have ddetermined the optimum viscosity, and thus iodide diffusion coefficient, of the ionic liquids and the corresponding regeneration of the dye.

Significant results:

Solaronix has provided specific ionic liquid formulations. All the dyes were tested with ionic liquid mixture developed at Solaronix.
When liquid electrolytes are replaced by ionic liquid based electrolytes two dyes have demonstrated power conversion efficiencies over 7% and up to 7.9%.
The life time of the devices have been assessed using the ISOS-L2 ageing test. The best devices retain 70% of their initial performances after 9000h at 65°C under continuous irradiation at 1000W/m².
This corresponds to 9 years in real conditions. This stability is the highest ever achieved with organic dyes.

WP4 Study of manufacturing processes to scale-up dye production

Objectives

In this work package Kaironkem had to define and validated the process for the volume production of the most promising dye(s) (as selected in WP2), and produce a sufficient sample of dye for the production of DSSC modules in WP5.

Summary of Progress

KK has performed a bibliographic study of the different synthetic routes and methods to be used for the production of dye. When chemical steps involving toxic intermediates or chlorinated solvents are employed, alternative synthetic strategies have been envisioned and developed.
Comparative evaluation of the different processes, options and selection of the most economical, scalable and environmental friendly route have been made to produce the most promising dye identified in WP1. KK and CEA have exchanged their knowledge and information to select the best synthetic route.

Significant results: KK have developed and optimised a production process to produce RK1. The dye RK1 has been prepared in 10 gram scale and commercialized by Kaironkem and Solaronix
http://shop.solaronix.com/sensitizing-dyes/organic-dyes/sensidizer-rk1.html

WP5 have not been initiated due to the termination of the project on April 2014.

WP6: dissemination activities

Papers related to the project published in peer-reviewed journals:

-D.Joly, L.Pelleja, S.Narbey, F.Oswald, J.Chiron, J.N. Clifford, E.Palomares*, R.Demadrille* "A Robust Organic Dye for Dye Sensitized Solar Cells Based on Iodine/Iodide Electrolytes Combining High Efficiency and Outstanding Stability", *Sci. Rep.* (Nature Publishing Group), **2014**, 4, 4033.

-D.Joly, L.Pelleja, S.Narbey, F.Oswald, T. Meyer, Y. Kervella, P. Maldivi, J.N. Clifford, E.Palomares*, R.Demadrille* "Metal-free organic sensitizers with narrow absorption in the visible for solar cells exceeding 10% efficiency" *Energy Environ. Sci.*, **2015**, 8, 2010-2018.

- J. Idigoras*, M. Godfroy, D.Joly, A. Todinova, P. Maldivi, G. Oskam, R. Demadrille, J. A. Anta. "Organic dyes for the sensitization of nanostructured ZnO photoanodes: effect of the anchoring functions". *RSC Adv.*, **2015**, 5, 68929-68938.

Lectures related to the project published in conferences:

[1] "***Novel Materials for Organic Photovoltaic and Dye-Sensitized Solar Cells***". R. Demadrille

Workshop on “organic and hybrid photovoltaic cells: from molecular design to performance characterization by scanning probe microscopy”, Invited seminar de Université de Mons, Worshop on OPV, Belgique, 5-6 Mars 2013

[2] "***Preparation and characterization of high band gap pi-conjugated Polymers and organic dyes for applications in photovoltaic devices***”. R. Demadrille, Invited seminar de l’Université de Bordeaux 28 Novembre 2013.

[3] "***Design and Synthesis of Organic Semiconductors for Solar Cells Applications : from Materials to Devices***" R. Demadrille, N. Delbosc, Z. Yahya, F. Lincker, S. Berson, R. DeBettignies, B. Grévin, JP. Travers. Invited seminar dans le cadre du workshop EPFL-LANEF, 9 juillet 2013 Lausanne Suisse

[4] "***New high efficiency dyes for DSSC using various photoanodes and various electrolytes***" D. Joly, Y. Kervella, S.Narbey, F. Oswald, I.-D. Kim, J. Bouclé, R. Demadrille. MNPC 2013, Annecy, 6-10 Octobre 2013. Oral communication

[5] - “***Materials for organic solar cells and dye-sensitized solar cells***” Caffy F, Delbosc N, Godfroy M, Joly D, Demadrille R, **Invited lecture (30min)**: 4èmes Journées Nationales sur la Récupération et le Stockage d'Energie JNRSE2014 (Annecy, France, April 7-8, 2014)

[6]- “***Molecular Engineering of Organic Sensitizers for High Performance Dye-sensitized Solar Cells***” Joly D, Pellejà L, Narbey S, Kervella Y, Oswald F, Godfroy M, Maldivi P, Clifford JN, Palomares E, Demadrille R. **Poster**: 6th International Conference on Hybrid and Organic Photovoltaics HOPV14 (Lausanne, Switzerland, May 11-14, 2014) **Best poster award.**

[7]- “***Molecular design organic dyes for robust and efficient Dye Sensitized Solar Cells: from synthesis to solar panels***” Joly D, Pellejà L, Narbey S, Oswald F, Chiron J, Clifford JN, Palomares E, Demadrille R**. Oral communication**: 6th International Conference on Hybrid and Organic Photovoltaics HOPV14 (Lausanne, Switzerland, May 11-14, 2014)

[8]- “***Design of semiconducting polymers and organic dyes for applications in photovoltaic devices***.” F. Caffy, M. Godfroy, D. Joly, Y. Kervella, N. Lemaitre, R. Demadrille. **Invited lecture (30min)** Indo-French Workshop on Organic Photovoltaics for Solar Energy Conversion, October 15-17, 2014.