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in Science and Technology  
- COST -**

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**Secretariat**

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**COST 4120/12**

**MEMORANDUM OF UNDERSTANDING**

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Subject : Memorandum of Understanding for the implementation of a European Concerted Research Action designated as COST Action CM1202: Supramolecular photocatalytic water splitting (PERSPECT-H2O)

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Delegations will find attached the Memorandum of Understanding for COST Action as approved by the COST Committee of Senior Officials (CSO) at its 185th meeting on 6 June 2012.

**MEMORANDUM OF UNDERSTANDING**  
**For the implementation of a European Concerted Research Action designated as**  
**COST Action CM1202**  
**SUPRAMOLECULAR PHOTOCATALYTIC WATER SPLITTING (PERSPECT-H2O)**

The Parties to this Memorandum of Understanding, declaring their common intention to participate in the concerted Action referred to above and described in the technical Annex to the Memorandum, have reached the following understanding:

1. The Action will be carried out in accordance with the provisions of document COST 4154/11 “Rules and Procedures for Implementing COST Actions”, or in any new document amending or replacing it, the contents of which the Parties are fully aware of.
2. The main objective of the Action is to develop a fundamental understanding of the function determining light-induced elementary reactions in supramolecular photocatalytic water splitting and to realize novel supramolecular photocatalysts for water splitting.
3. The economic dimension of the activities carried out under the Action has been estimated, on the basis of information available during the planning of the Action, at EUR 72 million in 2012 prices.
4. The Memorandum of Understanding will take effect on being accepted by at least five Parties.
5. The Memorandum of Understanding will remain in force for a period of 4 years, calculated from the date of the first meeting of the Management Committee, unless the duration of the Action is modified according to the provisions of Chapter V of the document referred to in Point 1 above.

**A. ABSTRACT AND KEYWORDS**

PERSPECT-H<sub>2</sub>O will enable spectroscopy/theory guided design of supramolecular photocatalysts for water splitting, and hence the generation of molecular hydrogen as a renewable fuel. The network will integrate leading European groups and national research centres, focusing on a central theme of contemporary research in homogeneous photocatalysis and integration of supramolecular photocatalysts towards the construction of functional materials. The Action combines synthetic chemistry, photophysics and photochemistry, electrochemistry, and theory aiming at (i) a detailed molecular mechanistic understanding of photoinduced reaction steps in supramolecular photocatalytic water splitting, and (ii) development of functional systems. The envisioned approach identifies relations between molecular and electronic structure, photoinduced structural and electronic dynamics, catalytic efficiency, and the stability of long-lived intermediates and catalytically active species. Finally it yields functional photocatalytic materials based on earth-abundant elements and prototypes of supramolecular photocatalytic water-splitting systems.

**Keywords:** Artificial photosynthesis, solar fuels and water splitting (renewable hydrogen), supramolecular photocatalyst design, time-resolved spectroscopy and spectroelectrochemistry, theoretical chemistry

**B. BACKGROUND****B.1 General background**

The looming energy crisis due to limited stocks of fossil fuels makes the search for environmentally clean and renewable energy and fuel sources indispensable. One approach to address these problems is to use photocatalytic systems, which harvest sunlight and split water, producing molecular oxygen and hydrogen. The latter can be either stored and utilized as a transportable fuel or converted into energy-rich organic molecules, to cope with the intermittent character of the solar radiation. The emerging concept of supramolecular photocatalysts (SPCs) utilizes strategies known from molecular design. An SPC is comprised of a photoactive centre, where ultrafast photoinduced charge generation occurs, an intramolecular electron relay to transport the charge, and photoactivated catalytically active centres for water splitting.

Additional light-harvesting antennas can be integrated into the molecular structure to enhance the absorption cross-section of the photocatalyst and to transfer energy to the photoactive primary electron donor. This design differs from the concept of quasi-homogeneous catalysis (which has been intensively studied over the last two decades), in which a photoactive primary electron donor, a molecular electron relay, and a colloidal catalyst are mixed in solution. Here, the electron-transfer processes, which are initialized by absorption of light, rely on collisions between the individual molecular functional units present in solution. As a consequence, principles of molecular design to improve the function-determining charge transfer processes cannot be applied readily. In SPCs, on the other hand, alterations of the molecular framework directly enable tuning its catalytic activity by (i) controlling the electron transfer from the photoactive electron donor to the catalytically active centre, (ii) prohibiting the back-electron transfer, (iii) controlling the stability of the charge-separated state and (iv) protecting the ligand framework against decomposition pathways under both reductive/oxidative and acid/alkaline conditions.

Optimization of SPCs for water splitting requires characterization of the photoinduced processes by spectroscopic, spectroelectrochemical and theoretical means. Understanding the photoinduced reaction steps proceeding on an exceptionally broad femtosecond-to-minutes time scale and ultimately leading to the catalytically active species, requires interplay between spectroscopy and theory to derive correlations between the photoinduced steps, structural elements, their organization, the molecular environment, and catalytic activity. Design principles for SPCs must be optimized for rapid and efficient energy and electron transfer, based on inspiration both from theoretical simulations and nature: e.g. the high level of organization or the use of coherent energy transfer. To cope with these tasks, PERSPECT-H<sub>2</sub>O addresses the photophysics and photochemistry of SPCs aiming at a spectroscopy/theory-guided design of novel water splitting SPCs. The process towards such an ambitious paradigm presents a truly interdisciplinary task that requires collaboration over both discipline and national boundaries.

## B.2 Current state of knowledge

Preliminary results indicating the feasibility of photoinduced hydrogen production using supramolecular photocatalysts (SPCs) have recently been reported, which also have introduced some of the central concepts of proton reduction. Reports discussed in literature deal with Ruthenium-polypyridine-complexes as photoactive primary electron donors [1-3], Iridium [4] and Rhodium [5] as photoactive primary electron donors. Alternative concepts have been reported and recently summarized [6,7]. Also an organic dye was employed in an SPC, which presents an appealing solution as no (potentially rare) metals are required in designing the photoactive electron donor unit [8]. Generally, the structures of the bridging ligands are designed to mediate intramolecular electron transfer from the photoactive centre to the catalytically active centre. As an exception, a phosphine donor centre was reported for the catalytic unit – however, the resultant SPC has not been employed for photocatalytic hydrogen generation but for alkene isomerization only. The catalytic centres integrated into the ligand environments include rare metals such as

- Palladium [3,9] leading to relatively high turn-over-numbers (TON) of more than 150; however, the metal is relatively instable within the currently reported SPCs and decomposition of the SPC into colloidal nanostructures under catalytic conditions is likely;
- Platinum [6] leading to an increased stability of the SPC as compared to using Pd, however, at the expense of a greatly reduced TON;
- Cobalt [4-6,10,11] often requires the use of additional stabilizing ligands such as glyoximes but yields relatively high TON and – under some circumstances – enables the self-assembly of the photocatalyst in water [12];
- Rhodium [13] leading to low catalytic activity (TON around 30) in SPC;
- artificial hydrogenase reaction centres have been reported, which rely on intermolecular electron transfer from e.g.  $[\text{Ru}(\text{bpy})_3]^{2+}$  [14,15].

SPCs for photoinduced water oxidation have not been reported in literature so far. Nonetheless, from electrochemical catalysis several lead structures based on e.g. IrO<sub>2</sub> or RuO<sub>2</sub> have been identified [16], which will constitute the starting point for the work within PERSPECT-H<sub>2</sub>O. Furthermore, latest results show the use of Ru-catalysts within a photocatalytic cell for water oxidation [17], while electrocatalytic water oxidation by Co(III)-corroles was reported.[18,19] The “Hangman” architecture as well as specific ligand design (introduction of perfluorinated corrole ligands) made the water oxidation feasible.

Having considered the proof-of-concept work on the realization of SPCs for proton reduction and water oxidation, the next logical step towards functional devices will be the immobilization of SPCs. This central conceptual step towards device integration includes immobilization, orientation and organization of SPCs either on (nano-structured) surfaces or in membranes. Today, no fully molecular photocatalytic systems have yet been immobilized on surfaces or in membranes. The only functional heterogeneous systems based on synthetic H<sub>2</sub>-evolving catalysts use semi-conductor materials for light harvesting and charge separation. Coating p-type silicon with conducting polypyrrole covalently functionalized with [1.1]ferrocenophane allowed the design of a H<sub>2</sub>-evolving photocathode: under illumination, the voltage photogenerated within the silicon layer allows the proton reduction to occur [20]. In addition, a [Cp\*Rh(bipy)] catalyst grafted on TiO<sub>2</sub> particles via carboxylate anchors was reported to catalyze H<sub>2</sub> evolution under UV-light in the presence of sacrificial electron donors [21]. Similarly, a H<sub>2</sub>-evolving photoelectrode was realized based on InP nanocrystals, a semiconducting material absorbing a significant part of the visible spectrum, which were connected through 1,4-benzenedithiolate to a gold electrode. [Fe<sub>2</sub>(μ-S)<sub>2</sub>(CO)<sub>6</sub>] was then adsorbed as a H<sub>2</sub>-evolving catalyst on this material, and ≈250 nA·cm<sup>-2</sup> photocurrents associated with H<sub>2</sub> evolution from neutral aqueous solution could be measured under illumination.[22] There are, however, several issues related to this last result: (i) indium is a rare and toxic element and (ii) the chosen grafting procedure (interaction of thiolate on gold or InP surfaces) is quite fragile, especially under reductive conditions. Alternative and stable immobilization methods however exist to graft photosensitizers [23] and catalysts [24-26] on conductive materials.

As it is apparent from the range of structural units, which have been reported so far in the context of supramolecular catalysis for proton reduction and water oxidation, a variety of complementary spectroscopic approaches needs to be combined to (i) describe the functionally relevant photoinduced reaction steps in SPCs and their interplay with structural features, (ii) to identify the nature of catalytically active species and structural intermediates, as well as (iii) to detail the nature of deactivation pathways in SPCs. Recently, e.g., a series of spectroscopic/catalytic work was published that dealt with the impact of structural variations of the hydrogen-evolving photocatalyst  $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{PdCl}_2](\text{PF}_6)_2$  [1,27-29]. Resonance Raman spectroscopy allowed for correlating the initial charge-distribution in the heteroleptic photocatalyst with its photocatalytic efficiency, while time-resolved spectroscopy revealed the interplay between structural modifications, electron-transfer properties, and catalysis. The coherent application of the complementary spectroscopic techniques sensitive both to the electronic and the geometrical structure of the catalysts as well as to electronic and structural dynamics within PERSPECT-H<sub>2</sub>O will result in a comprehensive understanding of the function-determining photoinduced processes in SPC and will guide – in concert with theoretical and (spectro-)electrochemical studies – the design and improvement of novel solutions towards functional SPCs for water splitting.

The theoretical study of SPCs is a challenging task which involves synergy from different fields of theoretical chemistry. A lot of the aspects to be studied within this Action are far from being a standard problem in theoretical chemistry. In the last years, a strong interaction between theoreticians from different background such as quantum chemistry, theoretical spectroscopy, supramolecular materials or biophysics has become required to deal with the primary processes induced by light absorption. Nowadays, a number of theoretical methods exist, which can assist to the prediction of structure and molecular properties of the integrating parts of the SPCs. Methods able to treat the whole molecular framework and simulate the interaction between different species are an emergent field of research. Hybrid quantum mechanical and classical methods are being developed to simulate spectroscopic properties and dynamics of systems in solution or a surrounding supramolecular medium. The impressive development of computers and numerical methods in the last few years will allow theory to study more and more complex systems, thus increasing our ability to make realistic predictions than can guide design of SPCs.

- [1] S. Tschierlei et al., *Angew. Chem. Int. Ed.* 2010, 49, 3981-3984.
- [2] A. Fihri et al., *Angew. Chem. Int. Ed.* 2008, 47, 564-567.
- [3] L. Hammarstrom et al., *J. Am. Chem. Soc.* 2008, 130, 26–27.
- [4] A. Fihri et al., *Dalton Trans.* 2008, 5567-5569.
- [5] B. Probst et al., *Inorg. Chem.* 2010, 49, 6453-6460.
- [6] H. Ozawa, K. Sakai, *Chem. Comm.* 2011, 47, 2227-2242.
- [7] A. Inagaki, M. Akita, *Coord. Chem. Rev.* 2010, 254, 1220-1239.
- [8] T. Lazarides et al., *J. Am. Chem. Soc.* 2009, 131, 9192-9194.
- [9] S. Rau et al., *Angew. Chem. Int. Ed.* 2006, 45, 6215 –6218.
- [10] S. Losse et al., *Coord. Chem. Rev.* 2010, 254, 2492-2504.
- [11] W.R. McNamara et al., *J. Am. Chem. Soc.* 2011, 133, 15368–15371.
- [12] Sk. Jasimuddin et al. *Chem. Comm.* 2010, 46, 8466-8468.
- [13] K.J. Brewer et al., *J. Am. Chem. Soc.* 2007, 129, 10644-10645.
- [14] D. Streich et al., *Chem. Eur. J.* 2010, 16, 60-63.
- [15] V. Loredana et al., *Dalton Transact.* 2010, 39, 3043-3049.
- [16] B. Geiß, C. Lambert, *Chem. Comm.* 2009, 1670-1672.
- [17] L. Li et al., *Chem. Comm.* 2010, 46, 7307-7309.
- [18] D. K. Dogutan et al., *J. Am. Chem. Soc.* 2011, 133, 9178-918.
- [19] D. K. Dgutan et al., *J. Am. Chem. Soc.* 2011, 133, 131-140.
- [20] U. T. Muellerwesterhoff, A. Nazzal, *J. Am. Chem. Soc.* 1984, 106, 5381-5382.
- [21] U. Kölle, M. Grätzel, *Angew. Chem. Int. Ed.* 1987, 26, 567-570.
- [22] T. Nann et al., *Angew. Chem. Int. Ed.* 2010, 1574-1577.
- [23] M. Grätzel, *Nature* 2001, 414, 338-344.
- [24] A. Le Goff et al., *Science* 2009, 326, 1384-1387.
- [25] A. Le Goff et al., *Int. J. Hydrogen Energy* 2010, 35, 10719-10724.
- [26] P. D. Tran et al., *Angew. Chem. Int. Ed.* 2011, 50, 1371-1374.
- [27] S. Tschierlei et al., *Chem. Eur. J.* 2009, 15, 7678-7688.
- [28] M. Karnahl et al. *ChemPhysChem* 2011, 12, 2101-2109.
- [29] J. Guthmuller, L. González, *Phys. Chem. Chem. Phys.* 2010, 12, 14812-14821.

### **B.3 Reasons for the Action**

The development of SPCs for hydrogen production and water splitting presents a new, ambitious and interdisciplinary task, which addresses both fundamental scientific questions and – in the long run – important and imminent societal needs. To provide these benefits of both scientific and technological values, understanding of fundamental aspects and interdisciplinary links are missing. These include (i) theoretically and spectroscopically derived design principles as well as (ii) new efficient components for light-absorption, electron transfer, catalysis, and stable ways for their assembly and (iii) immobilization and organization of the molecular catalysts on surfaces and membranes for device integration. To accelerate these ambitious goals and progress towards functional paradigm molecular materials presents a truly interdisciplinary task, which can be accomplished only by combining efforts of a range of European research groups with diverse but complementary expertise and experimental techniques.

Therefore, this Action combines individual competences of nationally well-funded groups to advance the state-of-the-art and to ensure European leadership in this scientifically and economically utmost important research field. Hence, COST is the ideal scheme nurturing the interaction, communication and joint research between strong research groups and national research programs and centres.

Such Action is particularly important and very timely as the USA has already created several centres focusing on solar fuels, each funded on a 10-120-Mio-US\$ scale. The Action PERSPECT-H<sub>2</sub>O creates a multidisciplinary European solar-fuels research base and interdisciplinary education network, which might be potentially extended, e.g. towards European centres.

## **B.4 Complementarity with other research programmes**

On a European level the research included in this COST Action has not yet been funded, though it is anticipated that several consortia will emerge within the future Framework Programme for Research and Innovation "Horizon 2020", ideally stimulated by the interdisciplinary and transnational networking achieved in this Action. Such interdisciplinary consortia will apply within the framework of energy-research in particular as PERSPECT-H2O will disseminate the (at the moment predominantly academic) research towards industry.

## **C. OBJECTIVES AND BENEFITS**

### **C.1 Aim**

The aim of the Action is to develop a fundamental understanding of the function determining light-induced elementary reactions in supramolecular photocatalytic water-splitting and develop novel spectroscopy- and theory-guided water-splitting supramolecular photocatalysts through understanding the underlying molecular interactions and energy decay mechanisms. The Action will result in innovative functional systems operating in solutions, membranes or at surfaces, as well as in formulation of general design rules.

### **C.2 Objectives**

The main networking objective of the Action is to develop an interdisciplinary European program towards world-class research, education and dissemination in the field of molecular photocatalysis. The Action will strive to place Europe's science at the forefront of this emerging field of high potential for industrial applications aimed to generate molecular hydrogen as a renewable fuel. As a consequence PERSPECT-H2O is anticipated to

- deliver guiding principles and enabling knowledge to develop SPC-based solar-energy conversion,

- generate hitherto unknown functional molecular fragments, e.g., bridging ligands, photoactive primary electron donors, auxiliary light-harvesting chromophores, whose properties can be varied and controlled through synthetic manipulations,
- generate efficient strategies towards the stabilization of catalytic centres in all required redox states within the ligand scaffold provided by the SPC,
- generate protocols for the synthesis and (self)assembly of novel SPCs integrating units for both photooxidation and photoreduction of water and protocols for evaluating of limitations to their function in terms of identifying the dominant deactivation channels,
- provide functional models and prototypes for SPC-based light-to-energy conversion devices, contributing in the long run to the supply of renewable energy,
- establishing an active European community dedicated to a photochemical use of solar energy, including academic-industrial partnerships aimed towards new projects and exploitation of academic research,
- train PhD students and early-stage researchers by, e.g., favoring exchanges of staff between participating groups and publicizing results of such visits,
- developing joint research projects across different disciplines (to be funded by the EU or national agencies),
- generating further support from both national and international agencies to contribute to developing clean energy in Europe,
- disseminating of the work and objectives of the Action to a wide scientific, political and public audiences and improve (establish) the public awareness of photochemical solar energy harvesting in the form of solar fuels (hydrogen).

### **C.3 How networking within the Action will yield the objectives?**

The primary objectives will build on

- synthesis, i.e., generation of SPC building blocks providing a variety of photocenters with related bridging ligands bound to active catalytic centres. Such families of SPCs structure-reactivity correlation will be established as the basis of a detailed understanding within this new field of catalysis. Furthermore, integration of self-healing concepts into SPCs will be investigated;

- spectroscopic characterization, which will combine time- and frequency-resolved spectroscopy and electrochemistry, will be employed to decipher (i) the photoinduced energy-, electron- and proton-coupled electron transfer pathways in SPCs and (ii) the thorough characterization of structural intermediates, catalytically active species and decay products, to guide e.g. the implementation of self-healing concepts;
- theoretical chemistry related to (i) modeling of geometric and electronic structures of long-lived intermediates and catalytically active species, (ii) the development of hybrid methods to predict structural relaxation dynamics and deactivation mechanisms in SPCs and (iii) an ab-initio description of function-determining ultrafast reaction steps in complex SPCs and achieve control of reaction dynamics e.g. proton-coupled electron transfer, coherent multi-chromophore excitation and energy transfer, role of spin-orbit coupling, and electron-transfer theory as a guidance for electron-transfer acceleration;
- device-integration of SPCs, i.e. immobilization and organization of SPCs on surfaces of high-surface area transparent conducting oxides (TOC) electrode materials or in membranes, characterization of the resultant electronic states, electron-transfer pathways and catalytic behaviors; proof-of-concept design of photocatalytic cells based on the principles developed for isolated SPCs.

The challenging and interdisciplinary objectives will be achieved by creating a network of leading European groups and national centres dedicated to performing joint research, structuring the communication, to organizing the research efforts in the most efficient way and to pave the path for young researchers starting in the field. As the Action's objectives present long-term challenges, the Action carefully balances between established scientists and groups headed by early stage researchers, who will significantly benefit from scientific, communicational and generic skills. To ensure the medium- and long-term strengthening of the network, novel research groups working in the field of PERSPECT-H2O are constantly invited to join the Action, bringing their specific knowledge and expertise.

## C.4 Potential impact of the Action

This Action will combine fragmentary European efforts in water splitting photocatalysis with the aim to advance the state-of-the-art and to launch a platform that will ensure that the EU will develop a vibrant research community capable of providing international leadership in this new and exciting field of research. The research and outreach activities will attract and educate young scientists. Moreover, the Action will

- provide the international scientific community with: (i) functional design principles of molecular photocatalysts with respect to improved long term stability and photocatalytic turnover, and (ii) novel theoretical tools to model the efficiency limiting steps in molecular photocatalysis on dynamic scales ranging from few fs to  $\mu$ s and ms;
- form a European forum to identify, characterize and address challenges to be met in this emerging field of science and its applications. It will bring together the leading experts to address these challenges and, thus, to ensure European leadership in this scientifically and economically utmost important research field. Such Action is particularly important as the USA has already created centres focusing on solar fuels funded on a 10-120-Mio-US\$ scale;
- create a multidisciplinary European solar-fuels research base and interdisciplinary education network, which might be potentially extended, e.g., towards European centres;
- establish the basis for a Marie-Curie network or an upcoming form of research network in the Framework Programme for Research and Innovation Horizon 2020;
- link Europe's academic partners with Europe's industrial research in this rapidly developing field, thereby, providing the necessary instruments to assure rapid exploitation of new knowledge in the field to actual products and applications;
- raise public awareness on the emerging concepts in (photo)chemical energetics and provide the public with relevant information and understanding of various ways of solar-energy utilization".

## **C.5 Target groups/end users**

The target groups of the COST Action PERSPECT-H2O are

- the international scientific community, universities and non-profit research laboratories in Europe operating in the fields of supramolecular photocatalytic water splitting, spectroscopic and electrochemical characterization of the underlying (photophysical) processes, as well as simulation and quantum chemical characterization of such systems,
- decision makers and the interested public in the European Union and other COST countries, who will become informed on innovative approaches towards this important contribution to a clean and sustainable energy supply,
- research and development departments of European-based companies committed towards a future commercialization of the PERSPECT-H2O results.

## **D. SCIENTIFIC PROGRAMME**

### **D.1 Scientific focus**

As mentioned above, the Action will combine the diverse European expertise in synthetic chemistry, photocatalysis, spectroscopy, (spectro-)electrochemistry and theoretical chemistry to yield a unified experimental/theoretical approach towards supramolecular photocatalytic water splitting. The Action is structured in four different Working Groups (WGs) devoted to central aspects of the work: (1) synthesis of SPCs, (2) device integration at photoactive electrodes and photochemical cells, (3) photoinduced dynamics within SPCs and (4) identification of structural intermediates and catalytically active species, and their deactivation channels. Apart from WG1, all WGs are laid out to intrinsically combine competences from synthesis, theoretical chemistry and spectroscopy/ electrochemistry. As WG1 is to develop the central molecular building blocks for the SPCs and the integrated photocatalytically active cells, the direct and close interaction between the WGs is indispensable. To achieve the overall scientific goal of PERSPECT-H2O, WG1 will transfer the molecular fragments, SPCs and integrated electrodes and cells to WG2, 3 and 4 for detailed studies of the photophysical processes and the deactivation pathways determining the limits of the functionality in the molecular functional materials.

## D.2 Scientific work plan – methods and means

The scientific focus of WG 1 Synthesis and Photocatalysis will be to generate efficient strategies towards stabilization of the catalytic centres (both for proton reduction and water oxidation) in all required redox states within the ligand scaffold provided by the SPC. This presents a central aspect, since well-stabilized catalytic centres present an indispensable prerequisite for long-term operating catalytic systems. Here, differences for H<sub>2</sub>-evolving SPCs and O<sub>2</sub>-evolving SPCs arise. For proton reduction, very soft metal centres, e.g., Pd(I) or Pd(0), have to be stabilized by comparatively soft bridging ligands. The development of SPCs for photocatalytic water oxidation is a very challenging task for which ligand frameworks will be generated to stabilize the highly oxidized metal centres and which are inert towards being oxidized/reduced by the metal centre during the catalytic turnover. The set of donor functions of the coordinating ligands has to be optimized separately for each catalytic centre as it defines the stabilizing potential and the catalytic potential of the metal centre. Furthermore, the incorporation of light-harvesting functionalities into the framework of the SPCs will be researched. Such additional units will be designed to absorb light with high absorption cross-sections over a wide spectral range, and to subsequently transfer the energy to the photoactive primary electron donor. It will be investigated in collaboration with WG3, if artificial structures can be designed, which are capable of coherent energy transfer – a process recently discovered in natural light-harvesting systems and considered to be (partially) responsible for their high light-collecting efficiency. Moreover, the ligand structures to be developed will need to be designed to be stable under illumination in a wide pH-range and in the presence of the oxidation/reduction products of the sacrificial electron donors/acceptors. The oxidation of water releases protons, which lowers the pH considerably, while the reduction of protons to evolve hydrogen will raise the pH. Strong pH changes might cause decomposition of the ligand-metal-attachment. Working in buffered solution is the first way to compensate the immediate pH changes. But ultimately, the combination of both processes in one SPC is the final goal for efficient overall water splitting.

Furthermore, the bridging ligand needs to be designed in a way that the fast forward electron-transfer to or from the catalytic metal centre occurs (for photoreduction and photooxidation, respectively) and that the back electron transfer is prevented. Thus, strong collaboration with WG 3 and 4 is needed to i) determine structure-reactivity relationships and ii) optimize the ligand framework modifications. A very intriguing aspect for ligand design is the aspect of the second coordination sphere. Especially proton-donor/acceptor functionalities in close proximity to the reaction centre can assist in proton coupled electron transfer events that occur in the first metal coordination sphere, and in doing so can raise the catalytic activity by several decades.

As laid out above, the current state-of-the-art of the field often involves rare (and toxic) metals, which will ultimately limit any subsequent up-scaling and a wide-spread application of SPCs. To cope with this problem, the research in WG1 will be directed to integrating both photoactive organic dyes and abundant metals, e.g., Mn, Fe and Ni into functional SPCs and SPC-based photoelectrodes. As conceptual starting points, recent work by the Action members and e.g. on electrocatalysis using [Fe,Fe]-hydrogenases models, Co(III)-corroles or [Ni(PCy<sub>2</sub>NBn<sub>2</sub>H)<sub>2</sub>]<sup>2+</sup> (PCy<sub>2</sub>NBn<sub>2</sub> =,5-dibenzyl-3,7-dicyclohexyl-1,5-diaza-3,7-diphosphacyclooctane) will be used.

Of central importance in WG1 is the conduction of photocatalytic experiments. The synthesized SPCs will be tested in either the water oxidation or proton reduction catalysis under illumination with visible light. Variation of solvent, solvent mixtures, sacrificial electron donor or electron acceptor, as well as intensity and wavelength of the excitation light will be done to identify the best catalytic conditions. Isolation of decomposition products should help to identify the weak points of the ligand architecture that need to be optimized for long-term stability, and assist the research undertaken in WG4.

WG2 Device integration will immobilize hydrogen- and oxygen-evolving SPCs developed in WG1 on large-surface area transparent conducting oxides and semiconductors as well as in membranes. Thereby, building on the results of WG1, novel concepts for integration of SPCs into functional photocatalytically active electrodes will be developed and characterized both photophysically and photocatalytically and theoretical tools to describe electronic states induced upon binding and their correlation with photoinduced electron transfer and catalytic properties will be developed.

To achieve proof-of-concept demonstration of a functional photocatalytic cell based on immobilized hydrogen- and oxygen-evolving SPCs, specific attachment chemistries will be employed to link SPCs onto transparent conducting oxide (TCO) electrode materials such as indium-tin oxide (ITO), Fluorine-doped tin oxide (FTO) or n and p-type semi-conductors with large band gaps such as TiO<sub>2</sub> or NiO. Several methods for a covalent attachment between the catalyst and surface and SPCS are known in the literature. For example, phosphonate and carboxylate linkages between the metal oxide surface and the catalyst have shown promise as a stable attachment method for materials designed to work in aqueous environments. The anchoring ligands have to be designed such that their impact on the electronic and photophysical properties of the SPCs – optimized for the molecular species in solution – is minor, while stable anchoring on the surface and electron-transfer from the solid electrode to the molecular SPC is optimal. Here again, theoretical chemistry will help in designing systems with the correct energetic match between the positions of the valence/conduction bands of the electrode material and the HOMO/LUMOs levels of the SPC.

Furthermore, it will be researched how concepts known from material healing, e.g., the use of pH-reversibly-switchable connections between different functional subunits can be integrated into the molecular-semiconductor framework of photocatalytically active cells. Such concepts shall enable the controlled exchange of molecular components within the functional device, which might be particularly prone to chemical degradation, and thereby significantly prolong the lifetime of the devices. Finally, research in WG2 will focus on the development of prototypes of photoelectrochemical cells utilizing above mentioned photocatalytic materials. Nanostructured metal oxides will be prepared and used to coat conductive transparent electrodes in order to obtain the highest loading of the photocatalyst on the surface. A high loading of catalyst on the surface is necessary for the highest possible photocatalytic efficiency and successful hydrogen production from sunlight. Improved electrode-fabrication techniques, which bear the potential to subsequently speed and upscale the production of photoactive cells. In particular, low temperature solution processes for the fabrication of TCO materials, simple deposition methods on glass substrate and straightforward grafting processes requiring a minimal number of steps and achievable in water at low temperature will be developed.

The scientific focus of WG3 Photoinduced dynamics will be placed on the synergetic combination of state-of-the-art time-resolved as well as stationary spectroscopic characterization techniques with theoretical chemistry to obtain a full description of photoinitiated reaction steps in SPCs. This challenge presents one of the cores of PERSPECT-H<sub>2</sub>O, since photoinduced energy and electron transfer as well as proton-coupled electron transfer are the central function-determining steps in SPC photocatalysis. In particular, multi-electron electron-transfer will be studied in detail as generally more than one redox-equivalents need to be accumulated for proton reduction and water oxidation to take place. Dealing with this challenge requires coordinated joint research activities aimed towards characterization of both electronic and structural changes on a wide range of time-scales spanning the initial dynamics from the Franck-Condon-point immediately after light absorption to the second-to-minutes changes associated with formation and deactivation of photocatalytically active species. This will be achieved by combining resonance Raman spectroscopy, femtosecond transient absorption and fluorescence upconversion with nano-to-millisecond flash photolysis, coherent control and two-dimensional IR and UV/Vis spectroscopy, transient resonance Raman spectroscopy, transient EPR spectroscopy and time-resolved X-ray absorption, as well as time-resolved X-ray diffraction. To understand the function-determining ultrafast steps in detail and – in particular – to identify the nature of the relevant electronic states and their correlation with molecular (sub)structures, it is essential to support the experimental work with theoretical investigations. Theory, which will be an integral part of PERSPECT-H<sub>2</sub>O, will be focused on the characterization and prediction of electronic excited states of supramolecular photocatalysts also including explicit solvation, but also on the development of tools that allow identifying reaction coordinates for proton-coupled electron transfer, following radiationless dynamics after excitation in such complex systems, and finally modeling coherent control in SPCs.

WG4 will extend the scientific focus of WG3 towards identifying structural intermediates and catalytically active species. Such studies are necessary for understanding and optimizing molecular photocatalysts and guiding the design of novel systems. The central experimental tasks will be to (i) perform spectroscopic experiments under constant illumination not in neat solvents (as most of the work in WG3 will deal with) but to use complex molecular environments, which contain e.g. sacrificial electron donors and acceptors either in solution or imbedded in polymers and membranes to study photochemical half-reactions of proton reduction and water-oxidation, and (ii) combine electrochemical, spectro-electrochemical and spectroscopic studies.

Thereby, intermediates of the photocatalytic cycles can be produced electrochemically and be investigated spectroscopically. This is of utmost scientific importance as only very little is known on the function-determining role of the photoinduced processes in long-lived molecular intermediates, created in catalytic cycles. In particular in SPCs, in which the accumulation of redox-equivalents occurs via the sequential absorption of a number of photons and respective re-reduction/oxidation of the photoactive centre by sacrificial electron donors/acceptors, the spectroscopic features of the singly-reduced/oxidized species are to be investigated in detail.

Spectroscopic studies will be complemented by the development and application of ab initio and density functional theory based methods to describe long-lived intermediates ( $\mu\text{s}$  to min) and their extension towards quantum-classical methods to deal with supramolecular systems in complex environments. The latter aspect is critical in understanding collision-mediated interactions of the SPCs with sacrificial electron donors and acceptors, and the substrates of the photocatalytic water splitting. Aside from the detailed characterization of long-lived intermediates, the second central question to be addressed in this Working Group by interdisciplinary research at the interfaces between synthesis, spectroscopy, electrochemistry and theory concerns the identification of catalytically active species and decay products, together with their deactivation channels. This research is fundamental both for understanding the functional mechanisms within SPCs and for integration of SPCs into functional devices. It forms the basis for developing tailor-made strategies to prevent the SPC deactivation and thereby promoting their applicability in functional devices such as photocatalytic cells.

## **E. ORGANISATION**

### **E.1 Coordination and organisation**

The Action will present a robust yet flexible framework, which will be managed as far as possible relying on electronic communication (webpage, e-voting within the Management Committee (MC), possibly video conferences, etc.) as primary communication and coordination channel. To achieve success, the Action PERSPECT-H2O relies on creative input from leading European scientists in concert with a high-level efficient coordination between the members. In the first stage, the Action's focus and goals will be publicized at relevant conferences, in scientific journals, webpages and mailing lists (to be compiled by the founding members) in order to attract new researchers to PERSPECT-H2O (the Action aims at including approximately 60-70 research groups).

The COST Action will provide the contact, networking, and research coordination among the different disciplines and research groups with complementary expertise, as well as between individual WGs through annual workshops, MC and Core Group meetings. Short-Term Scientific Missions (STSMs) will be coordinated by a STSM Manager. STSMs will be regarded as the principal means to carry out collaborative research. PERSPECT-H2O will organize one major conference, Action meetings (Annual Scientific Conferences) including all WGs and two Training Schools. The Action will work towards organizing a special symposium in association with the 5th EuCheMS Chemistry Congress held in 2014. The Action's Core Group is constituted by one member from each WG (preferably the WG coordinator) together with the Action Chair and the Vice-Chair, the Grant Holder, STSM and Dissemination Managers. The Core Group will recommend missions, reviews, advances and disseminates progress and assists the MC in organizing conferences and discussing the work plan. The dissemination of results is coordinated by the Dissemination Manager and primarily done via publications in high-impact journals, conference contributions, and an Action webpage. Additionally, the Dissemination Manager will take care that the Action offers communication channels with the media and the public domains by presenting itself at science festivals, public scientific events, as well as posting successful stories, interviews or videos in the e-world.

To ensure a fast and effective Action start, soon after its approval:

- a Management Committee will be appointed in accordance with the COST rules and will start working in good agreement with the COST Science Officer and the Domain Committee,
- a Core Group will be established including the Action Chair and Vice-Chair, WG Coordinators, the STSM Manager and the Dissemination Manager,
- The first MC meeting will be followed in 3-4 months by a scientific kick-off meeting including all the WGs and Action participants. Here, the WGs will be established and their particular scientific program and tasks further specified, as well as the basic links for future inter-WG interactions.

In later stages of the Action the coordination will work towards reaching central milestones to turn PERSPECT-H2O into a long-term basis for research, training and public awareness of molecular photocatalysis for renewable energy in Europe. Central milestones that will be reached in this respect include:

- a significant number of high-class collaborative publications in leading scientific journals by PERSPECT-H2O members (starting as soon as possible after the Action start),
- special issues dedicated to the work pursued in PERSPECT-H2O in distinguished international journals (e.g., ChemSusChem, in years 2 and 4 of the Action),
- joint interdisciplinary research-proposals by PERSPECT-H2O members both to the EU and (trans)nationally funded programs (starting in year 2 of the Action),
- a proposal to establish a Marie-Curie-Network or another novel form of research network within the Framework Programme for Research and Innovation Horizon 2020 based on the Action PERSPECT-H2O (year 3 or 4 of the Action).

## E.2 Working Groups

The scientific work program will be carried out by the Working Groups (WG) reflecting core synthetic, physical/chemical, and practical problems of SPCs. No single lab or a local centre alone can address these diverse yet interconnected problems because of the need of a broad range of expertise and unique experimental and theoretical techniques. While the individual competences to address specific aspects of these problems are established within Europe, interconnecting links are missing. PERSPECT-H2O is innovative in offering a unique interdisciplinary approach at the interface between synthesis, physical chemistry and theory focusing on the interplay between supramolecular structure, photoinduced dynamics and functionality of SPCs for water splitting. This is reflected in the interdisciplinary nature of the WG2, 3 and 4, which address specific sets of scientific questions involving members from spectroscopy, electrochemistry, theoretical chemistry and synthesis. On top of that, the Action will ensure interactions between the four WGs, namely an interchange of ideas and a research-task progress from synthetic groups to fundamental physical-chemical studies and, ultimately, to the construction of functional SPCs and photoactive electrodes. This WG setup will help to formulate a common language between the different scientific communities and solve scientific targets to advance Europe's leading role in renewable-energy research. In particular, the WGs will focus on:

### *WG1: Synthesis and photocatalysis*

- Synthesis and characterization of lead structures of SPCs for water oxidation (based on Co, Ru, Ir units) and reduction (based on Pt, Pd and Rh polypyridine units), incorporation of earth abundant metals, e.g., Mn, Fe, Co, Ni and organic dyes
- Design of intramolecular electron relays and testing the catalytic activity of the integrated SPCs
- Synthesis of SPCs optimized for spectrally broad absorption, efficient energy and electron transfer, self-healing capacity and long-term stability

### *WG2: Device integration*

- Interfacing of hydrogen- (oxygen-) evolving SPCs with conductive oxides and other p- or n-semiconductors, and their photocatalytic characterization
- Photophysical studies of interfacial and intramolecular electron-transfer processes within the photoactive electrodes
- Development of theoretical tools to describe electronic states induced upon binding and their correlation with photoinduced electron transfer and catalytic properties
- Assembly of proof-of-concept functional photocatalytic cells

### *WG3: Photoinduced dynamics*

- Joint experimental/theoretical investigations of ultrafast electronic and structural changes of SPCs and their photoactive building blocks upon photoexcitation
- Coherent control of energy and electron transfer processes in SPCs, development of realistic computational tools, including solvation and supramolecular interactions
- Experimental and theoretical study of proton-coupled electron transfer reactions for multi-electron photocatalytic water splitting, acceleration of vectorial electron transfer, and multi-electron transfer (i.e., charge accumulation)

### *WG4: Structural intermediates and catalytically active species*

- Spectroelectrochemical identification of intermediates and catalytically active species
- Time-resolved spectroscopic characterization of long-lived intermediates ( $\mu\text{s}$  to min) within the catalytic cycle of SPCs
- Application of ab initio and TD-DFT methods to describe long-lived intermediates, extension towards quantum-classical methods to deal with supramolecular systems
- Identification of decay products and deactivation channels of the catalytically active species, development of computational methods to predict deactivation mechanisms in SPCs

### **E.3 Liaison and interaction with other research programmes**

The Action PERSPECT-H2O includes research topics, which might be of mutual relevance to on-going activities within the following COST Actions:

- COST Action CM1005 Supramolecular Chemistry in Water
- COST Action TD1102 Photosynthetic proteins for technological applications: biosensors and biochips
- COST Action CM1002 Convergent Distributed Environment for Computational Spectroscopy

Furthermore, the Action will be seeking contacts beyond the COST countries, e.g., with the US Center for Chemical Innovation Solar – Powering the Planet (funded by the NSF) and the JCAP – Joint Center for Artificial Photosynthesis (funded by the DoE). It is anticipated that the interaction between the different initiatives will be of mutual benefit to solve the specific scientific tasks of the individual initiatives. Therefore, PERSPECT-H2O will actively contact the Chairs and Core Groups of the related initiatives to stimulate joint workshops and invite selected researchers (both experienced and early-stage researchers) from these initiatives as guests to the WG meetings and the Annual Scientific Conferences, which will be a principal instrument to review the scientific progress achieved, plan and coordinate new collaborative research, establish new contacts between WGs and possibly also between different research programs.

### **E.4 Gender balance and involvement of early-stage researchers**

This COST Action will respect an appropriate gender balance in all its activities and the Management Committee will place this as a standard item on all its MC agendas. The Action will also be committed to considerably involve early-stage researchers. This item will also be placed as a standard item on all MC agendas.

With respect to gender balance and the involvement of early-stage researchers the Action PERSPECT-H2O will establish a flexible framework to ensure full participation of females and early-stage researchers in the scientific as well as organizational positions and activities of the Action. Participation of early-stage researchers will improve their scientific skills as well as their network. Scientific training and integration of early-stage researchers (master students, PhD students and postdoctoral researchers) into the Action will be promoted in particular by Short-Term Scientific Missions (STSM) – an instrument valid to broaden and deepen the scientific knowledge of the researchers and boost their carrier development. Each member within the Action will actively announce possibilities for (interdisciplinary) STSMs. Subject-specific tutorial lectures specifically addressing early-stage researchers are offered by senior researchers at the annual WG meetings. Furthermore, two Training Schools will be organized by the Action to train early-stage researchers in the disciplines relevant for the emerging field of photocatalytic water splitting and solar fuels. Particularly early-stage researchers will benefit from participation in the Annual Scientific Conferences (see also section F), in which they can establish face-to-face contacts to senior scientists from within the consortium but also to experts from outside the Action, who will be invited to join the conferences.

## **F. TIMETABLE**

### **Year 1**

M1-2	First MC meeting
M3	Website Publication
M3-4	Scientific Kick-Off Meeting, held together with the second MC meeting Action Meeting including all WGs
M3-4	Collaborative research starts in all WGs (following the first MC meeting)
M3-12	First round of STSMs

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**Year 2**

M1-12	Collaborative research in all WGs, establishing inter-WG cooperation
M3-5	3 <sup>rd</sup> MC meeting joint with a Training School
M1-12	STSMs
M8-11	Annual Action scientific conference (includes all WG)

**Year 3**

M1-12	Collaborative research in all WGs
M3-5	4 <sup>th</sup> MC meeting held together with the second Training School This meeting and School will be associated with the 5 <sup>th</sup> EuCheMS Chemistry Congress. The Action will work towards including a symposium dedicated to molecular photocatalysis into the 5 <sup>th</sup> EuCheMS Chemistry Congress.
M1-12	STSMs
M10-12	Annual Action scientific conference (includes all WGs) associated with the 5 <sup>th</sup> MC meeting, preparation of Action final conference and for evaluation

**Year 4**

M1-12	Collaborative research in all WGs, development of functional SPC prototypes
M1-12	STSMs
M8-12	Annual Action scientific conference (includes all WG) embedded in an International Scientific Conference on Solar Fuels, which will be held jointly together with related overseas programs and European national centres.
	Final Conference of the Action and MC meeting to finalize report

## **G. ECONOMIC DIMENSION**

The following COST countries have actively participated in the preparation of the Action or otherwise indicated their interest: AT, BE, CH, CY, CZ, DE, EL, ES, FI, FR, IE, IL, IT, LT, NL, PL, SE, UK. On the basis of national estimates, the economic dimension of the activities to be carried out under the Action has been estimated at 72 Million € for the total duration of the Action. This estimate is valid under the assumption that all the countries mentioned above but no other countries will participate in the Action. Any departure from this will change the total cost accordingly.

## **H. DISSEMINATION PLAN**

### **H.1 Who?**

PERSPECT-H2O will disseminate its results with the aim to establish and promote the European leadership in the field of renewable energy research, solar fuels and molecular photocatalysis. The Action will aim at creating a European platform to ensure Europe's knowledge lead. Universities, non-university research institutes as well as relevant industry laboratories will be informed on the activities and results of the Action to promote research and application of SPCs. Although the Action is driven by academic research, its results – in particular with respect to immobilization of SPCs and device integration – are expected to have significant impact on the industrial sector.

Therefore, the main targets of the Action are:

Target group 1: researchers in university laboratories and non-profit research laboratories in Europe operating in the fields of supramolecular photocatalytic water splitting, spectroscopic and electrochemical characterization of the underlying (photophysical) processes, simulation and quantum chemical characterization of such systems, as well as researchers in industry research labs;

Target group 2: decision makers in the Europe Union and the national states, who will become informed on innovative approaches towards solar fuels contribution to a clean and sustainable energy supply;

Target group 3: undergraduate and graduate students at universities, senior high-school students and postdoctoral researchers advancing their education in the field of utilization solar energy and its conversion in storable energy;

Target group 4: the interested public increasing the general awareness on photocatalytical water splitting and use of sunlight to generate fuels and solar energy.

## **H.2 What?**

The Action will actively disseminate results, concepts and long-term strategies along with the outcome of training schools, annual joint meetings of all WGs and promotion of early-stage researchers and female researchers, who will be actively involved in the Action. Collaborative projects between members will be supported. The dissemination will target the four groups outlined in part H.1 to meet the Action's objectives (see parts C1 and C.2) and in working towards harvesting the benefits outlined in part C.4. The primary means of dissemination are summarized in part H.3.

## **H.3 How?**

Efficient dissemination with minimal bureaucratic effort will be achieved by the following means:

- Creation of a corporate layout by using both the Action's logo (to be created) and the COST logo on the webpage, press releases and on acknowledgement slides in talks and on posters,

- The Action's web page, which will be publicly accessible, will contain dissemination-oriented information on (i) the members within PERSPECT-H2O, (ii) the scientific program of PERSPECT-H2O and a description of the workgroups, (iii) a searchable description of the scientific projects pursued within the Action, (iv) a database of the scientific publications of the Action as well as press releases and figures/photographs for public use and (v) an updated schedule for the Action's meetings and STMSs. Furthermore, the results of the Action's annual Domain Committee evaluation and – if required – refinement of the Action's objectives will be published on the webpage. For internal use, the webpage will additionally include e.g. the following features: (vi) a web-based mailing list and an archived discussion forum and (vii) a data base for the exchange of unpublished data. The mailing list to be compiled within the Action will be open not only to the Action's participants but to any scientist and student interested in the emerging topic of photocatalytic water splitting. Hence, it will be a valuable tool to exchange information about scientific and technical problems and to advertise meetings and openings beyond the range of Action participants,
- Each Action participant will acknowledge the PERSPECT-H2O Action in relevant scientific presentations and – if applicable – mention the focus and goals of the Action,
- International scientists belonging to target the group 1 will be identified and invited to the Action's annual WG meetings,
- Each Action participant will be committed to publish the scientific results to be obtained in high-class international scientific journals – in particular to address target groups 1 and 3,
- The Action is committed to publish two special issues in relevant scientific journals – to address target groups 1 and 3, acknowledging PERSPECT-H2O,
- The Action will proactively promote the publication of results, concepts and long-term strategies of using SPCs to cope with the apparent energy crisis in non-scientific educational journals and – if possible – in radio or TV broadcasts devoted to science to particularly address target groups 2, 3 and 4,
- Press releases of central scientific results, Action meetings, conferences and training schools will be communicated to the public media to particularly address target groups 2, 3 and 4.