



Networking / Dissemination Activity Scientific Report Form

a) Summary

The Passau workshop has been the second and last joint workshop of the two CRPs (BOLDCATS and SolarFuelTandem) of the EuroSolarFuels EUROCORES programme, which ended in May 2014. The programme had been structured in the following way: Talks by the PIs or their representatives of the two CRPs focusing on the results and implications of their research activities structured into four themes: Light-Harvesting processes, Charge separation processes, Catalysts/Devices, and Theory. These talks from the EuroSolarFuels PIs were complemented by talks from several invited experts outside the present EuroSolarFuels programme whom we considered to be important for implementing future networking activities at the European level, or who have important roles in parallel activities like e.g. the AMPEA EERA initiative. The meeting was started by a keynote lecture by Prof. G Centi from the University of Messina who talked about the present state of solar fuels conversion from CO₂. Overall we had 25 talks, and additional work was presented in 10 posters. The talks were interrupted by a poster viewing session and three discussion sessions (one of them running in three parallel sub-groups) focusing on the achieved aims within the EUROSOLARFUELS programme. The three separate sub-group discussions focused on the discussion and preparation of three new networking activities at the European level which should build on the results achieved within the EUROSOLARFUELS EUROCORES programme.

b) Final programme of the event

Second Joint EUROSOLARFUELS WORKSHOP

Hotel Weisser Hase, Passau, Germany, April 12-15, 2014

| Date/Time | | |
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| April 12 | | |
| 12:00-18:00 | Registration | |
| 18:30 | Dinner | |
| 20:00 | Prof. A.R. Holzwarth | Opening |
| 20:10 | Prof. G. Centi University of Messina, Italy | Invited Keynote Lecture: Challenges in solar fuels from CO₂: an opportunity to enable a sustainable use of renewable energy |
| April 13 | | |
| | | Light-Harvesting Processes |
| | | Chair: Prof. S. Mackowski |
| 9:00-9:30 | Dr. P. Lambrev Biological Research Center, Hungary | Energy transfer in plant light-harvesting complex II revealed by room-temperature 2D electronic spectroscopy |
| 9:30-10:00 | Dr. K. Pawlak MPI CEC, Germany | Non-photochemical quenching in the major light-harvesting complex of photosystem II by PsbS in artificial membranes |
| 10:00-10:30 | Dr. A. Pandit Leiden University, The Netherlands | A close view on LHCII: a molecular antenna switch |
| 10:30-11:00 | Coffee Break | |
| | | Chair: Prof. D. Gryko |
| 11:00-11:30 | Prof. T.S. Balaban Marseille University, France | Supramolecular Chirality with Porphyrins |
| 11:30-12:00 | Dr. J. Psencik Prague University, Czech Republic | Biomimetic bacteriochlorophyll aggregates with additional functional molecules |
| 12:30-14:00 | Lunch | |
| | | Chair: Prof. G. Garab |
| 14:00-14:30 | Dr. J. Nielsen Aarhus University, Denmark | In situ atomic-resolution structure of the baseplate antenna complex in <i>Chlorobaculum tepidum</i> obtained combining solid-state NMR spectroscopy and cryo electron microscopy |

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| 14:30-15:00 | Prof. S. Mackowski Torun University, Poland | Enhancing Absorption of Photosynthetic Complexes |
| 15:00-15:30 | Prof. D. Gryko Polish Academy of Sciences, Poland | Diketopyrrolopyrroles revisited – through π -expansion toward new type of dyes for light harvesting |
| 15:30-16:00 | Coffee Break | |
| | | Chair: Dr. A. Barbieri |
| 16:00-16:30 | Prof. H. Paulsen University of Mainz, Germany | The major light-harvesting complex LHCII as a light-harvester in hybrid complexes |
| | | Charge separation processes |
| 16:30-17:00 | Prof. J. Kargul University of Warsaw, Poland | Application of highly robust photosystem I from extremophilic red microalgae in artificial photosynthesis nanodevices |
| 17:00-17:30 | Dr. H. Lokstein University of Glasgow, United Kingdom | Exploiting cyanobacterial Photosystem I and other pigment-protein complexes for nano-photobiotechnology |
| 17:30-18:00 | Dr. K. Ocakoglu Mersin University, Turkey | Strategies for Responsive Matrix Design: Biomolecule Immobilization on Electrode Surfaces |
| 18:30-20:00 | Dinner | |
| | | Chair: Prof. H. Paulsen |
| 20:00-20:30 | Prof. R. van Grondelle VU Amsterdam, The Netherlands | Energy transfer and photoprotection in the major light-harvesting complex LHC II of plants |
| 20:30-21:00 | Prof. L. Hammarström Uppsala University, Sweden | The potential of 2 nd and 3 rd coordination sphere effects on solar fuels catalysis> Lessons from model systems. |
| 21:00-22:00 | Discussion session Prof. H. de Groot | Summary of results of EUROSOLARFUELS Networks: Where do we stand? |
| | Poster Viewing | |
| April 14 | | |
| | | Chair: Dr. K. Ocakoglu |
| 9:00-9:30 | Dr. D. Hetterscheid Leiden University, The Netherlands | Molecular Water Oxidation Catalysts for Solar Fuel Production |

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| 9:30-10:00 | Prof. A. Holzwarth MPI CEC, Germany | Role of charge transfer states in light-harvesting, quenching, and charge separation |
| 10:00-10:30 | Dr. Y. Miloslavina Leiden University, The Netherlands | From natural to semi-artificial chlorine structures and back: A common structural denominator for the chemical design of a responsive matrix for solar fuels |
| 10:30-11:00 | Coffee Break | |
| 11:00-12:30 | Discussion Session | New Projects/Networks at European level (three separate discussion groups discussing new European initiatives); Discussion leaders: Dr. A. Pandit, Prof. H. de Groot, Prof. I. Kargul, |
| 12:30-14:00 | Lunch | |
| 14:00-15:30 | Discussion contd. | New Projects/Networks at European level (continuation, three separate discussion groups) |
| | Poster viewing | |
| 15:30-16:00 | Coffee Break | |
| | | Catalytic processes/Devices |
| | | Chair: Prof. I. Kargul |
| 16:00-16:30 | Dr. N. Cox MPI CEC, Germany | The structure of nature's water splitting catalyst immediately prior to O-O bond formation |
| 16:30-17:00 | Dr. A. Barbieri ISOF-CNR, Italy | Photophysical Investigation of PSI Immobilized on Hematite Surfaces |
| 17:00-17:30 | M. Gullo ISOF-CNR, Italy | Characterization of Oxidized Intermediates of the Synthetic Ru Catalyst for Water Splitting |
| 18:00-19:30 | Organ concert | Passau Dome |
| 20:00 | Conference Dinner | |
| | Poster Viewing | |
| April 15 | | Chair: Dr. F. Buda |
| 8:30-9:00 | Dr. K. Joya Leiden University, The Netherlands | Interfacing water splitting electrocatalysts with photo-responsive materials for solar fuels |
| 9:00-9:30 | Dr. T. Krupnik University of Warsaw, Poland | Characterization and modification of highly stable and robust photosystem I from <i>Cyanidioschyon merolae</i> , suitable for implementation into a Solar-to-Fuel nano-device |

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| | | Theory |
| | | Chair: Prof. R. van Grondelle |
| 9:30-10:00 | Dr. F. Buda Leiden University, The Netherlands | Computational study of the thermodynamics and reaction path of mono-nuclear water oxidation catalysts. |
| 10:00-10:30 | Prof. M. Plenio Ulm University, Germany | Vibrations, Noise and Electronic Motion in Biological Systems |
| | | |
| 10:30-11:00 | Coffee Break | |
| | | |
| 11:00-12:00 | Final Discussion | Future directions; General wrapup Discussion leader: Prof. A. R. Holzwarth |
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| 12:00-13:00 | Lunch | |
| | | |
| 13:00- | Departure | |

c) Description of the scientific content of the event (abstracts can be provided)

Abstracts / Talks

Challenges in solar **fuels from CO₂**: an opportunity to enable a sustainable use of renewable energy

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To realize a sustainable, resource-efficient and low-carbon economy is a major current challenge for society. While from one side it is not questioned the need to progressively introduce higher shares in renewable energy, there are main issues to couple actual renewable energy sources with energy infrastructure, even considering smart grids. All renewable energy sources, except biomass but for which major concerns exist about the effective positive environmental impact, produce electrical energy, still suffering of major problems to be stored (due to discontinuous production)/transported at long distance (for geographical mismatch between potential production and use zones), as well as integrated in the industrial production chain. CO₂ conversion to (liquid) fuels using renewable energy sources appears as the preferable and more sustainable solution to store/transport renewable energy in a way that easily integrate into the actual energy infrastructure, avoiding thus the need of very large additional investments. The chemical (re)use of CO₂ using renewable energy thus become a key aspect towards the more general goal of resource and energy efficiency, because combines the reuse of a waste and of a relevant carbon sources to the reduction of fossil fuel use as well as GHG and pollutants emissions.

After introducing this strategic scenario, the lecture will discuss more specifically on the advantage/ issues of the different routes to convert CO₂ to fuels, with focus on the conversion of carbon dioxide to methanol. The relevance of availability, cost and environmental footprint of H₂ production routes using renewable energies is also addressed. The final part discusses the roadmap towards a CO₂ economy, and recent developments to go in the direction towards artificial leaves.

References

- 1) Quadrelli EA, Centi G, Duplan JL, Perathoner S. Carbon dioxide recycling: Emerging large-scale technologies with industrial potential. *ChemSusChem* 2011, 4: 1194-1215.
- 2) Centi G, Quadrelli EA, Perathoner S, Catalysis for CO₂ conversion to introduce renewable energy in the value chain of chemical industries, *Energy & Env. Science* 2013, 6: 1711-1731.
- 3) Centi, G. Perathoner S., *Green Carbon Dioxide: Advances in CO₂ Utilization*, John Wiley & Sons (2014).
- 4) Bensaid S, Centi G, Garrone E, Perathoner S, Saracco G, Towards Artificial Leaves for Solar Hydrogen and Fuels from CO₂, *ChemSusChem*, 2012, 5: 500-521.
- 5) Lanzafame P, Centi G, Perathoner S, Catalysis for biomass and CO₂ use through solar energy: opening new scenarios for a sustainable and low-carbon chemical production. *Chem. Soc. Rev.* 2014, DOI: 10.1039/C3CS60396B.
- 6) Genovese C, Ampelli C, Perathoner S, Centi G, Electrocatalytic conversion of CO₂ on carbon nanotube-based electrodes for producing solar fuels, *J. Catal.* 2013, 308: 237-249

Energy Transfer in Plant Light-Harvesting Complex II Revealed by Room-Temperature 2D Electronic Spectroscopy

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Two-dimensional electronic spectroscopy (2DES), like the pump-probe absorption spectroscopy, is a valuable tool to monitor the excited state dynamics in systems of coupled chromophores. While both methods can identify molecular excited states based on their spectral properties and population dynamics, only 2DES provides separate spectral information about the donor and acceptor molecules involved in energy transfer. This makes it especially powerful in disentangling the energy transfer network in multichromophore systems such as light-harvesting complexes.

Pump-geometry 2DES utilizing phase cycling was performed at room temperature on isolated trimeric plant light-harvesting complex II (LHCII). The time-dependent 2D spectra reveal cross peaks representing energy transfer from Chl *b* to Chl *a* and within the Chl *a* exciton manifold, occurring on time scales from <300 fs to >10 ps. Global analysis of the 2DES with three lifetime components produced 2D decay-associated spectra (2D DAS) whereby separate Chl *b* pools coupled to the bulk Chl *a* exciton states can be distinguished. These energy transfer components occur with lifetimes in the range of 0.3-3 ps. Rapid (0.3 ps) energy transfer from high-energy (15400-15500 cm⁻¹) Chl *b* exciton states to the lowest-energy (14600 cm⁻¹) Chl *a* exciton states is observed. An indirect energy transfer pathway via an intermediate Chl *a/b* exciton state is also clearly resolved in the 2D DAS. This intermediate state (1500 cm⁻¹) is rapidly populated from low-energy Chl *b* states and has a long (several ps) lifetime due to weak coupling to the low-energy Chl *a* excitons. The 2D DAS also reveal that Chl *a* – Chl *a* equilibration on a time scale of few ps. A more detailed kinetic scheme was obtained with the help of spectro-temporal model. The experimentally resolved kinetics scheme generally agrees with and adds further details to published structure-based excitonic models and spectroscopic results.

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Non-photochemical quenching in the major light-harvesting complex of photosystem II by PsbS in artificial membranes

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Non-photochemical quenching (NPQ) is one of the most important photo-protective mechanisms in intact higher plants and algae, which allows these organisms to survive under quickly variable light intensities. NPQ is responsible for dissipating of excess excitation energy to heat [1] and acts mostly in the major light-harvesting antenna complex (LHCII) of Photosystem (PS) II. NPQ depends on several factors: a pH gradient across the membrane [2], protonation of PsbS – a small membrane protein [3], and production of zeaxanthin (Zx) from violaxanthin (Vx) under high light (HL) conditions. The fastest and major part of NPQ is the so-called qE-mechanism which can develop and relax in less than a minute. The qE quenching is related to the activation of the PsbS protein by the pH gradient across the membrane but does not necessarily require conversion of Vx to Zx [4].

In the present study we showed the results of time-resolved fluorescence measurements of LHCII and PsbS reconstituted into proteoliposomes under various conditions. This model system is most similar to the *in vivo* qE-quenching situation. The experimental results were used to develop a detailed structure-based molecular quenching model. The experimental data were complemented with quantum mechanical calculations for testing the proposed model.

References

- [1] Demmig-Adams, B. & Adams, W.W. (1992) Photoprotection and other responses of plants to high light stress. *Ann. Rev. Plant Physiol. Plant Mol. Biol.* **43**, 599-626.
- [2] Wraight, C.A. & Crofts, A.R. (1970) Energy-dependent quenching of chlorophyll a fluorescence in isolated chloroplasts. *Eur. J. Biochem.* **17**, 319-327.
- [3] Niyogi, K.K., Li, X.-P., Rosenberg, V., & Jung, H.-S. (2005) Is PsbS the site of non-photochemical quenching in photosynthesis? *J. Exp. Bot.* **56**, 375-382.
- [4] Holzwarth, A.R., Miloslavina, Y., Nilkens, M., & Jahns, P. (2009) Identification of two quenching sites active in the regulation of photosynthetic light-harvesting studied by time-resolved fluorescence. *Chem. Phys. Lett.* **483**, 262-267.

Biomimetic bacteriochlorophyll aggregates with additional functional molecules

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Chlorosomes are main light-harvesting complexes of green photosynthetic bacteria. They contain self-assembling aggregates of bacteriochlorophyll (BChl) *c*, *d* or *e* molecules. Aggregates with similar properties can also be prepared *in vitro*, either in non-polar or polar environments. Thanks to self-assembly and stability, the BChl aggregates and their synthetic analogs are promising materials for artificial light-harvesting systems.

In polar environments, e. g. aqueous solutions, the aggregation is driven by hydrophobic interactions. Addition of a suitable non-polar component is necessary to induce the aggregation. The additional component may be chosen to affect the properties of the formed assemblies in a defined way. For instance, it may absorb at the wavelengths where pure aggregates absorb poorly and thus extend spectral coverage of the final assembly. We have tested representatives of several groups of molecules, including quinones [1], carotenes [2] and xanthophylls [3], each of which interacts with BChl molecules in a specific way, and thus provides also important information about self-assembly principles of BChl aggregates. Properties of BChl *c* assemblies with selected functional molecules will be overviewed.

[1] Alster, J.; Zupcanova, A.; Vacha, F.; Psencik, J. *Photosynth. Res.* **2008**, 95, 183

[2] Alster, J.; Polivka, T.; Arellano, J. B.; Chabera, P.; Vacha, F.; Psencik, J. *Chem. Phys.* **2010**, 373, 90

[3] Alster, J.; Polivka, T.; Arellano, J. B.; Hribek, P.; Vacha, F.; Hala, J.; Psencik, J. *Photosynth. Res.* **2012**, 111, 193

In situ atomic-resolution structure of the baseplate antenna complex in *Chlorobaculum tepidum* obtained combining solid-state NMR spectroscopy and cryo electron microscopy

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Abstract: Photosynthetic antenna systems enable organisms to sense and harvest light and transfer the energy to the photosynthetic reaction centre, where the conversion to chemical energy takes place[1]. One of the most complex antenna systems, the organelle, found in the photosynthetic green sulfur bacteria *Chlorobaculum tepidum* contains a baseplate, which is a scaffolding super-structure, formed by the protein CsmA and bacteriochlorophylls[2]. Here we extend our initial studies of resonance assignments and secondary analysis[3] by presenting the first atomic-resolution structure of the CsmA baseplate using preparations of intact fully functional, light-harvesting organelles [2], by combining three complementary methods: solid-state NMR spectroscopy, cryo electron microscopy, and circular dichroism spectroscopy. We show that the baseplate is composed by rods of repeated dimers of the strongly amphipathic CsmA with pigments sandwiched within the dimer at the hydrophobic side of the helix.

1. D. A. Bryant, N. U. Frigaard, *Trends Microbiol.* **2006**, 14, 488-496.
2. N.-U. Frigaard et al., *Photosynth. Res.* **2006**, 86, 101-111.
3. N. V. Kulminskaya et al., *Angew. Chem. Int. Ed. Engl.* **2012**, 51, 6891.

Enhancing Absorption of Photosynthetic Complexes

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The focus of the presentation will be an overview of research carried out during the last three years within the BOLDCATS project and aimed at developing ways of enhancing absorption of photosynthetic complexes by using plasmon excitations in metallic nanostructures. The influence of plasmon excitations upon the optical properties of Photosystem I, Reaction Center from the Green Sulphur Bacteria, and the FMO complex, was investigated using various means of fluorescence microscopy and spectroscopy. We find that in contrast to simple light-harvesting complexes, such as peridinin-chlorophyll-protein, these multichromophoric systems feature huge enhancement factors. The enhancement strongly depend on the excitation wavelength, although we find no clear correlation between values of enhancement factors and extinction of metallic nanostructure. This indicates that by applying metallic nanostructures with defined geometry we can artificially enhance absorption in a certain spectral region, as well as even reverse the actual absorption efficiency of photosynthetic complexes.

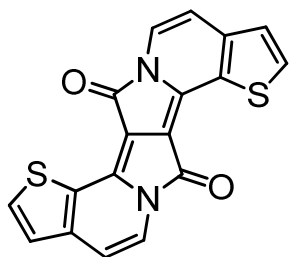
This research has been carried out in collaboration with the Group of Richard J. Cogdell (University of Glasgow).

Diketopyrrolopyrroles revisited – through π -expansion toward new type of dyes for light harvesting

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The core function of photosynthesis is a cascade of photoinduced energy and electron transfers between donors and acceptors in the antenna complexes and the reaction center. Although many diverse model systems have been synthesized and studied and significant progress has been achieved, numerous problems still remain. Among various systems porphyrins and other porphyrinoids are of particular importance as building blocks for the construction of models [1]. Diketopyrrolopyrroles (pigments developed by Ciba-Geigy in 80-ties) strongly absorb green light. We designed π -expanded diketopyrrolopyrroles with superb optical properties including large two-photon absorption cross-section [2]. Two-photon absorption (2PA) is a non-linear optical phenomenon with broad scope of applications. It has already been applied, or is under intensive investigation, in fields such as: optical limiting, multiphoton pumped frequency-upconversion lasing, polymerization-microfabrication, 3D-data storage, photodynamic therapy, two-photon excited fluorescence etc. All these applications originate from two special features of 2PA. For certain applications, the two-photon-property requirement has basically been met with current dyes, but, for two-photon technology to realize its full potential, the development of more two-photon-active chromophores, together with important secondary properties such as processability, biocompatibility, photostability and durability is vital. Therefore, when designing the next generation of two-photon materials, one should not only consider their two-photon absorptivity but also tailor their secondary properties to meet their specific applications. The synthesis, linear and non-linear optical properties of new diketopyrrolopyrrole-based organic functional dyes with large two-photon absorption cross-section will be presented and discussed.



References:

[1] Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40-48.

[2] Grzybowski, M.; Głodkowska-Mrówka, E.; Stokłosa, T.; Gryko, D. T. *Org. Lett.* **2012**, *14*, 2670-2673.

The major light-harvesting complex LHCII as a light-harvester in hybrid complexes

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The major light-harvesting chlorophyll *a/b* complex (LHCII) of the photosynthetic apparatus in green plants absorbs light energy and conducts the excitation energy towards the photosynthetic reaction centers where light-driven charge separation takes place. In an attempt to make use of this light-harvesting function in artificial environments, recombinant LHCII was immobilized on a gold surface. The immobilized LHCII retained its light-harvesting function and exhibited efficient inter-complex energy transfer [1]. Recombinant LHCII was also immobilized on the surface of semiconductor nanocrystals referred to as quantum dots (QDs) of type II that are capable of undergoing charge separation between core and shell in their excited state. LHCII served as an efficient light-harvester to these particles, significantly enlarging their absorption cross section [2,3]. A limiting factor for all potential applications of LHCII is its stability towards thermal dissociation and protein denaturation which is relatively high in comparison to many other biological (chlorophyll) protein complexes but quite low in technical terms. Co-precipitating LHCII with silica significantly increased its stability towards thermal disintegration, the extent of stabilization being strongly dependent on the size of silica particles formed during precipitation. This makes the enclosure of the complex in a silica shell by directed biomineralization a promising approach to stabilizing LHCII.

- [1] Lauterbach, R.; Liu, J.; Knoll, W., and Paulsen, H. (2010) Energy transfer between surface-immobilized light-harvesting chlorophyll *a/b* complex (LHCII) studied by surface plasmon field-enhanced fluorescence spectroscopy. *Langmuir* 26, 17315-17321.
- [2] Werwie, M.; Xu, X.; Haase, M.; Basché, T., and Paulsen, H. (2012) Bio serves nano: biological light-harvesting complex as energy donor for semiconductor quantum dots. *Langmuir* 28, 5810-5818.
- [3] Werwie, M.; Fehr, N.; Xu, X.; Basché, T., und Paulsen H. (2014) Comparison of quantum dot-binding protein tags: affinity determination by ultracentrifugation and FRET. *Biochim. Biophys. Acta - Gen. Subjects* in press (<http://dx.doi.org/10.1016/j.bbagen.2013.11.025>)

Application of highly robust photosystem I from extremophilic red microalgae in artificial photosynthesis nanodevices

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The eukaryotic red alga *Cyanidioschyzon merolae* is an extremophile which thrives at low pH (approximately 0.2 to 4) and high temperature (40-56°C) environments. This unicellular alga provides an excellent model system to study the components of the photosynthetic electron transfer chain for production of carbon-free fuels (such as hydrogen) from water in artificial systems due to the high stability and activity of its photosynthetic complexes. In natural photosynthesis, the primary charge separation in the reactions centre of photosystem II (PSII) and photosystem I (PSI) upon absorption of two quanta of light triggers vectorial electron flow from PSII to PSI via the cyt *b₆f* complex, with the concomitant release of protons and molecular oxygen. PSI, via the second photoact, uses reducing equivalents (in the form of water-derived protons and electrons) derived from PSII to reduce the final acceptor ferredoxin. This feature has been utilised in the artificial photosynthesis research aimed at mimicking the function of PSI as a powerful and stable oxidoreductase for the production of molecular hydrogen. Here we report development of a stable self-organised catalyst based on immobilised *C. merolae* PSI particles for production of molecular hydrogen using water as an electron/H⁺ source. We will present a novel application of the highly stable complexes of red algal PSI and associated light harvesting antenna as a robust natural component working in tandem with the hematite photoanode to generate reducing equivalents of sufficient energy, ultimately leading to production of water-derived molecular hydrogen. We will also show the characteristics of the sustained photovoltaic activity of the biohybrid *C. merolae* PSI-Au photocathode in the presence of cytochrome *c₅₅₃* used as the specific electron donor to the photooxidised reaction centre of PSI.

Exploiting cyanobacterial Photosystem I and other pigment-protein complexes for nano-photobiotechnology

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Abstract: Photosystem I (PSI) isolated from the thermophilic cyanobacterium *Thermosynechococcus elongatus* is exceptionally stable and retains a high rate of light-induced electron transfer under a wide range of conditions (pH, temperature, etc.) for extended times. PSI or its subunits can be readily (chemically/genetically) modified, e.g. by reconstitution and/or attachment of polyHis/Cys-tags. This renders PSI highly suitable for biotechnological applications such as in bio-hybrid (nano-)devices.

PSI was spin-coated on different nano-structured particles, e.g. silver nanowires, silver island films (SIFs) and stability as well as the resultant optical properties were studied. A hitherto unreported fluorescence enhancement of more than 200-fold was observed when PSI was coupled to SIF plasmons [1]. Other (photosynthetic) pigment-protein complexes from a variety of organisms, such as light-harvesting complex II (LHC II), water-soluble chlorophyll protein (WSCP) have been explored for their suitability for photobiotechnological purposes as well.

PSI can be effectively coupled via cytochrome *c* to different electrode materials. The light-induced electron transport properties of such hybrid assemblies were studied and photocurrent generation was optimized [2].

Acknowledgements: Financial support by the BBSRC/EuroCores and the BMBF of Germany (Biotechnologie 2020+) is gratefully acknowledged.

References:

[1] Czechowski, N., Lokstein, H., Kowalska, D., Ashraf, K., Cogdell, R.J., Mackowski, S., Appl. Phys. Lett., submitted

[2] Stieger, K.R., Feifel, S.C., Lokstein, H., Lisdat, F., PhysChemChemPhys, submitted

Strategies for Responsive Matrix Design: Biomolecule Immobilization on Electrode Surfaces*

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The studies focused on immobilization strategies of biological materials onto matrix surfaces have been continuously growing [1-4]. A variety of interactions can be seen between biomolecule and surface such as covalent bonding, electrostatic interactions, hydrogen bonding, self-assembly, physisorption on the surface via Van der Waals interactions, and physical entrapment. It should be considered that an immobilized biomolecule is a system more complex than its free counterpart, thus the reliability and repeatability of the experiments and interpretation of theoretical data are more complicated [2]. However, nanosized materials and their use as a carrier matrix for biomaterials show optimistic expectations. In some cases, they are more feasible materials for conformational investigations and modifications. The detailed knowledge of the size and shape at the nanoscale level can provide useful information about the nature of interactions established between biomolecule and the surface. Here, we will give a brief discussion the new strategies and examples for responsive matrix design in light of recent findings obtained with the use of nanomaterials.

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References

1. M. Nagata, M. Amano, T. Joke, K. Fujii, A. Okuda, M. Kondo, S. Ishigure, T. Dewa, K. Iida, F. Secundo, Y. Amao, H. Hashimoto, M. Nango, *ACS Macro Lett.* **2012**, 1, 296–299.
2. F. Secundo, *Chem. Soc. Rev.* **2013**, 42, 6250
3. P. N. Ciesielski, F. M. Hijazi, A. M. Scott, C. J. Faulkner, L. Beard, K. Emmett, S. J. Rosenthal, D. Cliffl, G. K. Jennings, *Bioresource Technology* **2010**, 101, 3047–3053.
4. P. N. Ciesielski, A. M. Scott, C. J. Faulkner, B. J. Berron, D. E. Cliffl, G. K. Jennings, *ACS Nano* **2008**, 2 2465–2472

Energy transfer and photoprotection in the major light- harvesting complex LHC2 of plants

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In my talk I will review the energy transfer transfer in LHC2 and its modeling based on the disordered exciton-Redfield model. Using single molecule spectroscopy we have studied the fluorescence properties of single LHC2 trimers which are interpreted in terms of its disordered energy landscape and the control exerted by the environment. Finally I will show some results on the A2-mutant of LHC2, that misses 2 of the 3 chlorophylls that make up the lowest excitonic state, and which explains the chlorophyll organization and energetics as observed in native LHC2

The role(s) of a "smart matrix": 2nd and 3rd coordination sphere effects on solar fuels catalysis

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The discovery of the different ways that a protein matrix controls biological electron transfer and catalysis is an important challenge of fundamental interest as well as of practical importance for the development of molecular solar fuels systems. There are obvious and general effects of the protein matrix that we understand to a large extent. For example, the low dielectric constant of protein interiors allows for electron transfer reactions with low reorganization energy. However, this also means that charged intermediates are destabilized so that strategies to reduce electrostatic self-repulsion has been developed, such as delocalizing the charge: redox equivalents are delocalized over metal clusters and excess protons are delocalizing over a hydrogen-bonding network. Another important strategy is charge-compensatory proton-coupled electron transfer (PCET). Other clear effects of the protein matrix include stabilization by restricting access of unwanted and reactive bulk species, and the key-and-lock principle of enzyme-substrate recognition.

There are also effects of the protein matrix that are not fully understood and that are sometimes controversial, which remain to be elucidated. One example is dynamic effects of protein reactions, which could occur on many different levels and time-scales. They range from slow and large scale subunit motions that gate reactions, to very specific vibrations that are speculated to control e.g. PCET reactions or the quantum coherence of excited states.

We will present and discuss some recent results and ideas on 2nd and 3rd coordination sphere effects relevant to solar fuels catalysis, as a basis for a general discussion on future research needs in this area.

Molecular Water Oxidation Catalysts for Solar Fuel Production

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Abstract: In my group catalytic water oxidation is studied predominantly by electrochemical techniques rather than using the stoichiometric oxidants in ill defined reaction media.[1,2,3] Using on line electrochemical mass spectroscopy (OLEMS) the formation of dioxygen is studied as a function of applied potential, while tracking formation of e.g. CO₂ and NO₂ illustrates at which potentials degradation of the organic ligands occurs (see Figure 1). Complementary to these experiments, the deposition of material on the electrode is studied by electrochemical quartz crystal microbalance (EQCM) techniques and after the catalytic reaction with surface analysis techniques such as extended X-ray absorption fine structure (EXAFS) and X-ray photoelectron spectroscopy (XPS). Using these techniques we have been able to pinpoint the catalytic activity to a molecular species in case **Ir**(OH)₂ was used as the anticipated catalyst, while in case of several other catalytic systems we found that formation of CO₂ takes place prior to evolution of dioxygen and thus that catalysis is most likely mediated by degradation products of the original molecular system (**Ir** = Ir(Cp*)(Me₂-NHC), where Cp* = pentamethylcyclopentadienyl and Me₂-NHC = N-dimethylimidazolin-2-ylidene).[4,5] In situ spectro-electrochemical techniques (e.g. Raman, IR, UVvis) are used to further unravel the reaction mechanisms in combination with DFT calculations.[6] At present we are investigating the effect of a responsive matrix near the active site to control proton transfer during water oxidation catalysis in order to achieve superior catalytic rates.

References:

- [1] D. G. H. Hetterscheid, J. I. van der Vlugt, B. de Bruin, J. N. H. Reek, *Angew. Chem. Int. Ed.* 2009, 48, 8178
- [2] D. G. H. Hetterscheid, J. N. H. Reek, *Angew. Chem. Int. Ed.* 2012, 51, 9740.
- [3] D. G. H. Hetterscheid, J. N. H. Reek, *Eur. J. Inorg.* 2014, ejic.201300249.
- [4] C. J. M. Van der Ham, D. G. H. Hetterscheid, unpublished results
- [5] D. G. H. Hetterscheid, J. N. H. Reek, *Chem. Commun.* 2011, 47, 2712
- [6] A. Venturini, A. Barbieri, J. N. H. Reek, D. G. H. Hetterscheid. *Chem. Eur. J.* 2014, chem.201303796

Light-Harvesting, antenna quenching, and ultrafast charge separation in reaction centers. A unifying view.

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Comparing pigment arrangements in the many available structures of photosynthetic antenna complexes with those appearing in reaction centers, one notices that very similar arrangements of the same pigments have been chosen to function either as efficient light harvesters or as centers of ultrafast charge separation. It thus becomes obvious that the detailed pigment arrangement is not the main factor controlling excited state processes. Rather it is the surrounding protein that actually decides about the specific functioning in a particular case, i.e. whether a pigment cluster functions as an antenna or as a reaction center. Thus the protein – or more generally the “environment” - takes the role of a “smart responsive matrix”. At present we do not understand well the governing factors at a molecular level. However the design of efficient artificial antenna and charge separation units – with or without proteins – requires a deeper understanding and control of these environmental effects, i.e. the properties of the “responsive matrix”.

Recent studies on non-photochemical quenching (NPQ) in antenna complexes have turned out to provide fundamental insights into these environmental effects controlling the fate of the excited state energy. A common denominator of most NPQ quenching processes is the ultrafast formation of a chlorophyll-chlorophyll charge transfer state, by a mechanism that in many details operates in the same way as the “normal” processes of ultrafast photosynthetic charge separation occurring in reaction centers. Astounding and unexpected parallels between those - at first glance unrelated - processes of NPQ and of reaction center function have been found.

The talk will discuss the general common principles governing the role of the surrounding protein in switching excitonically coupled pigment arrangements between light-harvesting, non-photochemical quenching, and energy-storing ultrafast charge separation in reaction centers.

From natural to semi-artificial chlorine structures and back. A common structural denominator for the chemical design of a responsive matrix for solar fuel.

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Abstract:

In chlorosomes, bacteriochlorophylls (BChls) self-assemble to form concentric helical nanotubes. An alternating parallel syn-anti stacking of the BChls with bistability in the intermolecular interactions is considered an essential structural motif. It allows to mix charge transfer character into the excited state to promote delocalization of excitons and possibly charge separation across an interface in an artificial photosynthetic system.

The structural model for the chlorosomes was derived from mutants of green sulfur bacteria *Chlorobaculum tepidum*. Here we study the wild type based on new improved solid state nuclear magnetic resonance (NMR) data. The ¹³C-¹H heteronuclear correlation and CHHC proton driven spin diffusion experiments reveal well resolved cross peaks (interstacks between C3¹/C12¹ and C3¹/C18 (can be also C13²) and intrastacks between C5/C17^{1&2} and C5/C12^{1&2}) that point to a structure where monomer building blocks are rotated with respect to their location in the chlorosomes from the mutants species determined earlier. In addition, we present the first results obtained from unlabeled chlorosomes from *Chlorobaculum limnaeum*, containing BChl *e* (wild type) and BChl *f* (bchU mutant, without the C-20 methyl group). The combination of NMR and EM point to a syn-anti parallel stacking for the BChl *e* and a parallel stacking for the BChl *f* mutant. Apparently for the natural systems parallel stacking is ubiquitous, which we attribute to the presence of the long tails that promote phase separation between electron rich aromatic regions for the rings and regions with interdigitating saturated aliphatic tails. Hence to promote parallel stacking with artificial systems, moderately long tails were attached. Two of the artificial systems, AT29 and OV1 artificially prepared Zn-chlorines exhibit a parallel structure, resembling natural BChl *d* but having dodecyl or methyl tails instead of farnesyl, respectively. Finally we report ¹H-NMR spectroscopy data that can provide more rapid assays of the aggregates precipitated from solution [1].

Reference: [1] Miloslavina, Y.; Sai Sankar Gupta, K. B.; Tank, M.; Bryant, D.A.; de Groot, H. J. M. *Israel Journal of Chemistry* **2014**, 54, 147.

The structure of nature's water splitting catalyst immediately prior to O-O bond formation

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Abstract: Multi-frequency pulse EPR spectra are reported for the final metastable intermediate (S_3 state) of nature's water splitting catalyst [1, 2]. Simulations of the entire EPR data using the spin Hamiltonian formalism require the S_3 state to have an electronic ground state $S = 3$ and a small fine structure splitting ($|D| < 0.2 \text{ cm}^{-1}$), consistent with an all Mn^{IV} cofactor. Concomitant double resonance measurements (^{55}Mn -EDNMR) support this assignment. These measurements allow the site properties of the four Mn ions that constitute the water splitting catalyst to be examined. It is observed that only two types of Mn ions are observed with both types representing octahedral Mn^{IV} ions of similar local ligand field. These results require:

1. the binding of a water molecule, possibly the second substrate water to the manganese cofactor during the S_2 to S_3 transition [3, 4]; and
2. assign its binding position to the open coordination site of Mn_1 .

These results provide a pathway for the biological water splitting reaction. O-O bond formation likely occurs between two manganese bound oxygen atoms in the transition state, an oxo-bridge and an oxyl radical. It is demonstrated that structural flexibility is important for second substrate inclusion [5] and the coupling reaction is facilitated by the spin topology of the cofactor.

References:

- [1] Cox, N., Pantazis, D.A., Neese, F., Lubitz, W. *Acc. Chem. Res.*, 2013 46, 1588.
- [2] Umena, Y., Kawakami, K., Shen, J.-R., Kamiya, K. *Nature* 2011 473, 55
- [3] Cox, N.; Messinger, J. *Biochim. Biophys. Acta* 2013, 1827, 1020
- [4] Rapatskiy, L., Cox, N., Savitsky, A., Ames, W.M., Sander, J., Nowaczyk, M., Rögner, M., Boussac, A., Neese, F., Messinger, J., Lubitz, W. *J. Am. Chem. Soc.* 2012 134, 16619.
- [5] Pérez Navarro, M., Ames, W.M., Nilsson, H., Lohmiller, T., Pantazis, D.A., Rapatskiy, L., Nowaczyk, M.M., Neese, F., Boussac, A., Messinger, J., Lubitz, W., Cox, N. *Proc. Natl. Acad. Sci. U.S.A* 2013 110, 15561
- [6] Pantazis, D. A.; Ames, W.; Cox, N.; Lubitz, W.; Neese, F. *Angew. Chem. Int. Ed.* **2012** 51, 9935

Photophysical Investigation of PSI Immobilized on Hematite Surfaces

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Nowadays, the need to develop renewable energy sources stimulates the scientific research towards cheap, efficient and robust photovoltaic devices. Integration of the photosystem I (PSI) with its associated light harvesting antenna (LHCI) into low-cost, earth-abundant semiconductor surfaces offers an attractive approach to achieve these goals [1]. Recently, the PSI-LHCI extracted from the extremophilic red microalga *C. merolae* was linked to the surface of the *n*-type semiconductor α -Fe₂O₃ (hematite) and used for the fabrication of a bio-hybrid dye-sensitized solar cell (DSSC) by the groups led by Kargul and Ocakoglu [2].

Here, we report on the photophysical investigation of the bio-hybrid PSI-LHCI-functionalised hematite system. Steady state and time resolved fluorescence spectra of the PSI-LHCI supercomplex in PBS 7.4 solution as model and immobilized on the semiconductor surface were recorded at room temperature (rt). The fluorescence decay were convoluted with the measured instrumental response function (fwhm \approx 230 ps) and fitted to a sum of exponentials by the global fitting analysis. The wavelength dependences of the amplitudes of the individual kinetic components were then plotted as fluorescence decay associated spectra (FDAS).

The experiments have shown that when the complex is immobilized on the hematite surface the fluorescence decay is characterized by a sum of three-four exponential components with lifetimes of 36-38 ps, 200-240 ps, 620-640 ps and 1.47-1.63 ns. The dominating short time fluorescence phase is associated to photochemical trapping processes in the PSI core and the relevant FDAS have different shape in the three samples. The phase of the fluorescence decay with lifetime around 200 ps is likely to be ascribed to the peripheral antenna systems in the LHCI, energetically coupled to the PSI core. The observed component with lifetimes around 500-600 ps seems to indicate the presence of slowed energy transfer processes between the peripheral antennas in the LHCI and the PSI core. This might come from a distortion of the protein structure upon immobilization on the hematite surface than can increase the distance between the pigments without affecting the overall functionality of PSI. Less than 5% of the fluorescence decay is related to processes with ns lifetimes that might come from uncoupled or free chlorophylls.

References

[1] (a) Wen, F.; Li, C. *Acc. Chem. Res.* 2013, 46, 2355. (b) Tachibana, Y.; Vayssieres, L.; Durrant, J. R. *Nature Photonics* 2012, 6, 511. (c) Concepcion, J. J.; House, R. L.; Papanikolas, J. M.; Meyer, T. J. *Proc. Natl. Acad. Sci. USA* 2012, 109, 15560.

[2] Ocakoglu, K.; Krupnik, T.; van den Bosch, B.; Harputlu, E.; Gullo, M. P.; Olmos, J. D. J.; Yildirimcan, S.; Gupta, R. K.; Yakuphanoglu, F.; Barbieri, A.; Reek, J. N.; Kargul J. "Photosystem I-based biophotovoltaics on nanostructured hematite", submitted to *Energy Environ. Sci.*

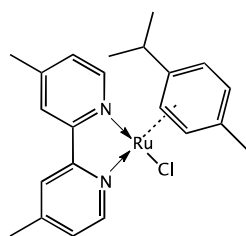
Characterization of Oxidized Intermediates of the Synthetic Ru Catalyst for Water Splitting

Maria Pia Gullo, Mila D'Angelantonio and Andrea Barbieri

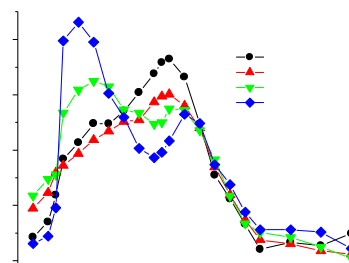
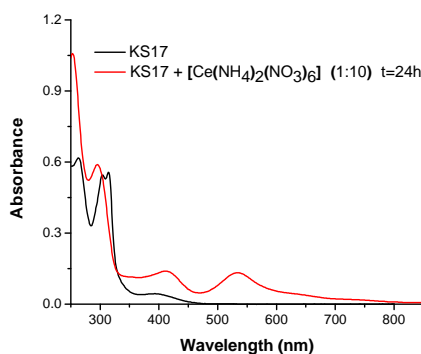
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The catalysis of water oxidation process by transition-metal complexes has received considerable attention during the last years, thanks to the accessible synthesis, strong stability, robustness and efficiency of such systems. Recently, a new class of mono metal water splitting catalysts based on Ru(II) and able to form dioxygen in homogeneous conditions through a four steps proton coupled electron transfer cycle has been prepared [1]. In these single ruthenium complexes [(cy)Ru^{II}L-Cl]Cl the metal centre is coordinated to a bipyridyl ligand (L) and stabilized by a cyclic conjugated hydrocarbon (cy = p-cymene). Such systems can be considered suitable models for the design of more efficient water-oxidation catalysts and, for this purpose, it is important to understand the pathways that lead to O₂ evolution from water and the nature of the involved intermediate species.

A detailed characterization of one- and two-electron oxidized intermediates of these mononuclear Ru complexes has been carried out using different techniques: for the long lived species, UV-vis spectroscopy supported by stopped flow apparatus, and for the transients with short lifetimes, pulse radiolysis. In the first case, [Ce(NH₄)₂(NO₃)₆] has been used as sacrificial oxidant, activating the metal complex towards oxidation process. Upon addition of 10 eq. of Ce(IV) to [(cy)Ru^{II}L-H₂O]Cl in acidic solution, gradual formation of a new species is achieved, whose absorption features are ascribable to the Ru(IV) species involved in the cycle [2]. In the second case, sulphate radical anion $\text{SO}_4^{\cdot-}$ has been chosen as sacrificial one-electron oxidant. The reaction between $\text{SO}_4^{\cdot-}$ and [(cy)Ru^{II}L-H₂O]Cl at pH 1.4 in HClO₄ diluted solution yielded the one-electron-oxidized species, revealed by two distinct peaks in the absorption spectrum, that could agree with the spectrum of the elusive Ru(III) species.



KS17



Schematic structure of the complex **KS17**, [(cy)Ru^{II}dmbpy-Cl]Cl (left). UV/Vis absorption spectra at rt of **KS17** 5×10^{-5} M in H₂SO₄ 1 N, before and after addition of [Ce(NH₄)₂(NO₃)₆] (10 eq.) (centre). Transient absorption spectra of the oxidized species of **KS17** upon reaction with $\text{SO}_4^{\cdot-}$, at different times after the pulse (dose 37.7 Gy); [**KS17**] = 1×10^{-5} M (right).

References

- [1] (a) Zong, R.; Thummel, R. P. *J. Am. Chem. Soc.* 2005, 127, 12802. (b) Joya, K. S.; Vallés-Pardo, J. L.; Joya, Y. F.; Eisenmayer, T.; Thomas, B.; Buda, F.; de Groot, H. J. M. *ChemPlusChem* 2013, 78, 35.
- [2] Polyansky, D. E.; Muckerman, J. T.; Rochford, J.; Zong, R.; Thummel, R. P.; Fujita, E. *J. Am. Chem. Soc.* 2011, 133, 14649.

Interfacing Water Splitting Electrocatalysts with Photo-Responsive Materials for and Solar Fuels

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Abstract:

An “Artificial Leaf” is a stand-alone Solar to Fuel conversion system, where the catalytic materials are mounted on top of light-harvesting (LH) semiconductor photo-responsive materials. Recently, thin film photoanodic materials like Hematite, WO₃, Ta₃N₅, BiVO₄ on transparent conducting surfaces have been studied for light-assisted water oxidation catalysis. The charge transfer kinetics can be improved by nano-structuring the semiconductor materials and for a better catalytic performance, synergetic interfacing of the photo-responsive materials with benchmark water oxidation co-catalysts is crucial step [2]. Here we present immobilization and deposition of highly efficient electrocatalytic materials on top of nano-structured photo-active materials for light-driven water oxidation [3]. Our method enhances the light harvesting properties of the inorganic semiconductor materials and improves catalytic performance of the solar water oxidation assembly.

References:

[4] Joya, K. S.; Subbaiyan, N. K.; D'Souza, F.; de Groot, H. J. M. *Angew. Chem. Int. Ed.* **2012**, 51, 9601.

[5] Joya, K. S.; de Groot, H. J. M. *ChemSusChem* **2014**, 7, 73.

[4] Joya, K. S.; Joya, Y. F.; de Groot, H. J. M. *Adv. Energy Mater.* **2014**, 4, DOI:10.1002/aenm.201301929.

Characterization and modification of highly stable and robust photosystem I from *Cyanidioschyon merolae*, suitable for implementation into a Solar-to-Fuel nano-device.

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Abstract:

Cyanidioschyon merolae is an extremophilic red alga that thrives in hot (40 – 52 °C) and very acidic (pH 1.5 – 2.5) conditions. One of its evolutionary adaptation to those conditions was developing very stable and highly active photosynthetic apparatus [1]. We here present a newly developed set of methods allowing for purification of homogenous photosystem I (PSI) and separation of antennae (LHCI). To investigate the stability and resilience to solar irradiation of this molecule, *C. merolae* was grown in 3 different light intensity conditions. Collected data allows to propose three mechanisms of light protection: Zeaxanthin dependent, LHCI dependent and red-chlorophylls dependent. The inherent stability of this complex allows it to be implemented into a solar-to-fuel nano device on both: anodic and/or cathodic side. When PSI was immobilized on hematite anode in a head-to-tail multilayer a photocurrent was generated upon illumination with simultaneous production of hydrogen on platinum cathode. Similarly, PSI with chemically attached hydrogen reducing catalyst to specific cysteine in the PsaC subunit will be overlaid on photocathode to maximize production of hydrogen. The ability to specifically label a cysteine, located on the electron path can prove beneficial in chemical linking of hydrogenase or other synthetic catalyst capable of proton reduction. Additionally we are developing a system of transient and stable genetic transformation, that could allow to introduce changes in the very structure of PSI helping to anchor the molecule on electrode surface on either donor or acceptor side as well as making the electron path more accessible for functionalization with a catalyst.

References:

[1] Krupnik T, Kotabová E, van Bezouwen LS, Mazur R, Garstka M, Nixon PJ, Barber J, Kaňa R, Boekema EJ, Kargul J. *J Biol Chem*. 2013, 288: 23529-4

COMPUTATIONAL STUDY OF THERMODYNAMICS AND REACTION PATH OF MONO-NUCLEAR WATER OXIDATION CATALYSTS

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The search for efficient and stable water oxidation catalysts is a crucial step in the development of artificial photosynthesis devices. Here density functional theory (DFT) and ab initio molecular dynamics are used to investigate reaction mechanisms [1] and to predict the free-energy profile [2] for the catalytic water oxidation cycle in different mononuclear catalysts of the type [(bpy)M(Ar)(OH₂)]ⁿ⁺, where Ar is an aromatic ligand attached to the metallic center M in a π – cation interaction and bpy is a bipyridine ligand.

It is shown that an explicit inclusion of the solvent environment is essential for a realistic description of the reaction path. Clear evidence is presented for a concerted reaction in which the O-O bond formation is quickly followed by a proton transfer leading to a Ru-OOH intermediate and a hydronium ion. An alternative path in which the approaching water first coordinates to the metal centre is found to induce a structural instability of the catalyst.

From the thermodynamic analysis [(bpy)Ru(cymene)(OH₂)]²⁺ turns out to be a very promising catalyst with the smallest overpotential. Time-Dependent DFT calculations of the optical properties also provide direct evidence of specific intermediates in the catalytic cycle. Overall our free-energy results follow quite closely the same scaling relationship found in metal oxide surfaces, suggesting similar fundamental limitations in the optimization of the catalyst.

REFERENCES

- [1] (a) J.L. Vallés-Pardo, M.C. Guijt, M. Iannuzzi, K.S. Joya, H.J.M. de Groot, F. Buda, *ChemPhysChem* **2012**, *13*, 140-146; (b) J.L. Vallés-Pardo, H.J.M. de Groot, F. Buda, *Phys. Chem. Chem. Phys.*, **2012**, *14*, 15502–15508; (c) K.S. Joya, J.L. Vallés-Pardo, Y.F. Joya, T. Eisenmayer, B. Thomas, F. Buda, and H.J.M. de Groot, *ChemPlusChem*, **2013**, *78*, 35–47.
- [5] J.L. Vallés-Pardo, H.J.M. de Groot and F. Buda, *to be submitted*

Vibrations, Noise and Electronic Motion in Biological Systems

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Abstract: Both electronic transport and vibrational motion are recognized as being of considerable importance in biology. In this lecture I will discuss how the two processes may cooperate to produce optimal function [1, 2] and that nature may have adapted structures for an optimal interplay between electronic and vibrational motion [3]. I will discuss the role of the dynamical interaction of long-lived vibrational motion with electronic motion to generate long-lived oscillatory signals in optical 2D spectroscopy [4, 5, 6]. This work and the underlying fundamental principles are laid out in a recent review [7].

References:

- [1] Plenio, M.B.; Huelga, S.F. *New J. Phys.* 2008, 10, 113019.
- [2] Caruso, F.; Chin, A.W. ; Datta, A.; Huelga, S.F.; Plenio, M.B. *J. Chem. Phys.* 2009, 131, 105106.
- [3] del Rey, M; Chin, A.W.; Huelga, S.F.; Plenio, M.B. *J. Phys. Chem. Lett.* 2013, 4, 903.
- [4] Caycedo-Soler, F.; Chin, A.W.; Almeida, J.; Huelga, S.F.; Plenio, M.B. *J. Chem. Phys.* 2012, 136, 155102.
- [5] Chin, A.W.; Prior, J.; Rosenbach, R.; Caycedo-Soler, F.; Huelga, S.F.; Plenio, M.B. *Nature Physics* 2013, 9, 113.
- [6] Plenio, M.B.; Almeida, J.; Huelga, S.F. *J. Chem. Phys.* 2013, 139, 235102.
- [7] Huelga, S.F.; Plenio, M.B. *Contemp. Phys.* 2013, 54, 181.

a) Assessment of the results and impact of the event on the EUROCORES programme.

We had three main aims for the workshop: i) Discussing and critically assessing the results of the research activities in this EUROCORES programme on the international scene in the solar fuels research area, ii) to discuss the implications of these results for future research activities in the field, and iii) to discuss and prepare new networking activities at the European level, in particular with respect to EU programs within HORIZON 2020, in this rapidly developing field. These three activities are: i) Preparation of a FET application (within HORIZON 2020) focusing on “Extremophilic photosynthesis as a blueprint for efficient direct solar conversion” with the participation of several PIs of the two CRPs and additional outside partners. The application is coordinated by Ioanna Kargul, Warsaw, a PI of SolarFuelTandem. ii) Preparation of a FET application (within HORIZON 2020) focusing on the “Design of an artificial solar fuels conversion device based on the smart matrix concept” (coordinated by Huub de Groot, Leiden, coordinator of the SolarFuelTandem network). The important implications of the “smart matrix” concept, based on results of work within the EUROSOLARFUELS CRPs had been addressed in several talks at the workshop. This activity has been extended recently into the formation of a parallel discussion group (headed by Huub de Groot, Leiden) evaluating the aims and prospects of a possible European FLAGSHIP programme activity on this subject. This group will meet for a special one-day meeting end of June in Brussels. iii) Preparation of a network activity application on “Reengineering Light-Harvesting-Complex II as an artificial antenna/reaction center unit” (coordinated by Anjali Pandit, Leiden, and Alfred Holzwarth, Mülheim; participation of several EUROSOLARFUELS PIs and several groups from outside). While the scientific content and aims are clear, the prospects of applying within a FET programme was discussed but finally dismissed, since the project would probably not find the necessary industry application because it was at an early stage of development. We are presently discussing a different possible funding scheme to support that application, among them an ITN network.

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