Sunrise

Solar Energy for a Circular Economy

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SUNRISE FINLAND Stakeholder Workshop, Turku University

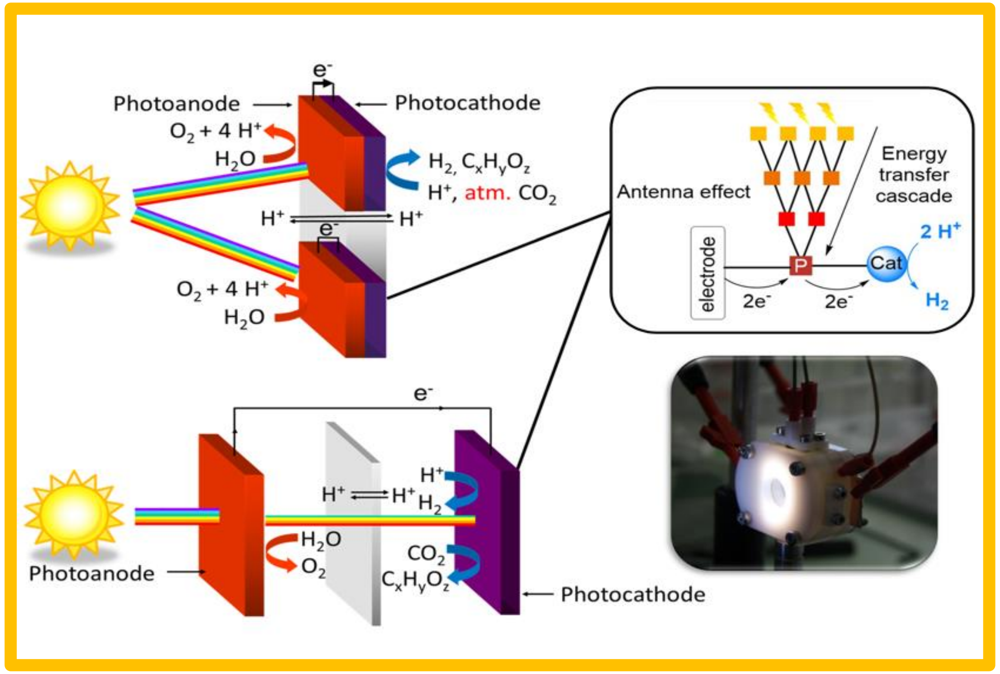
9 December 2019

www.sunriseaction.eu

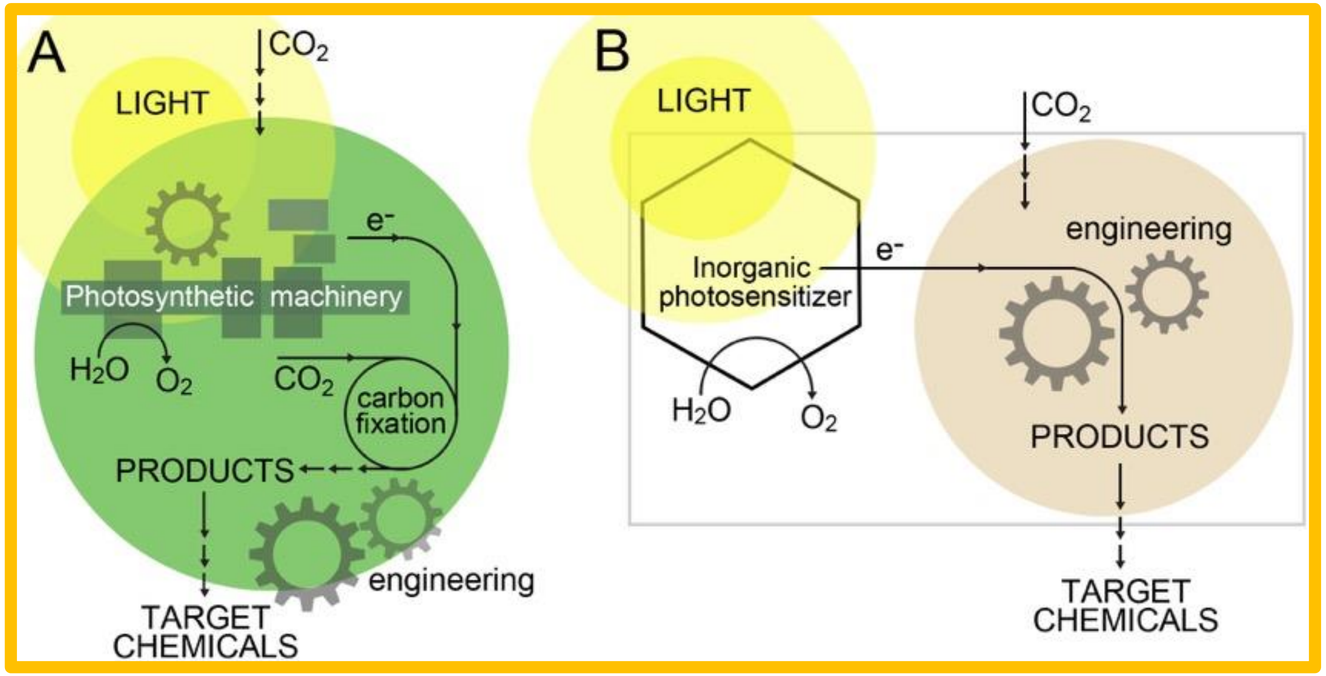
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 816336

SUNRISE: APPROACH 2 and 3

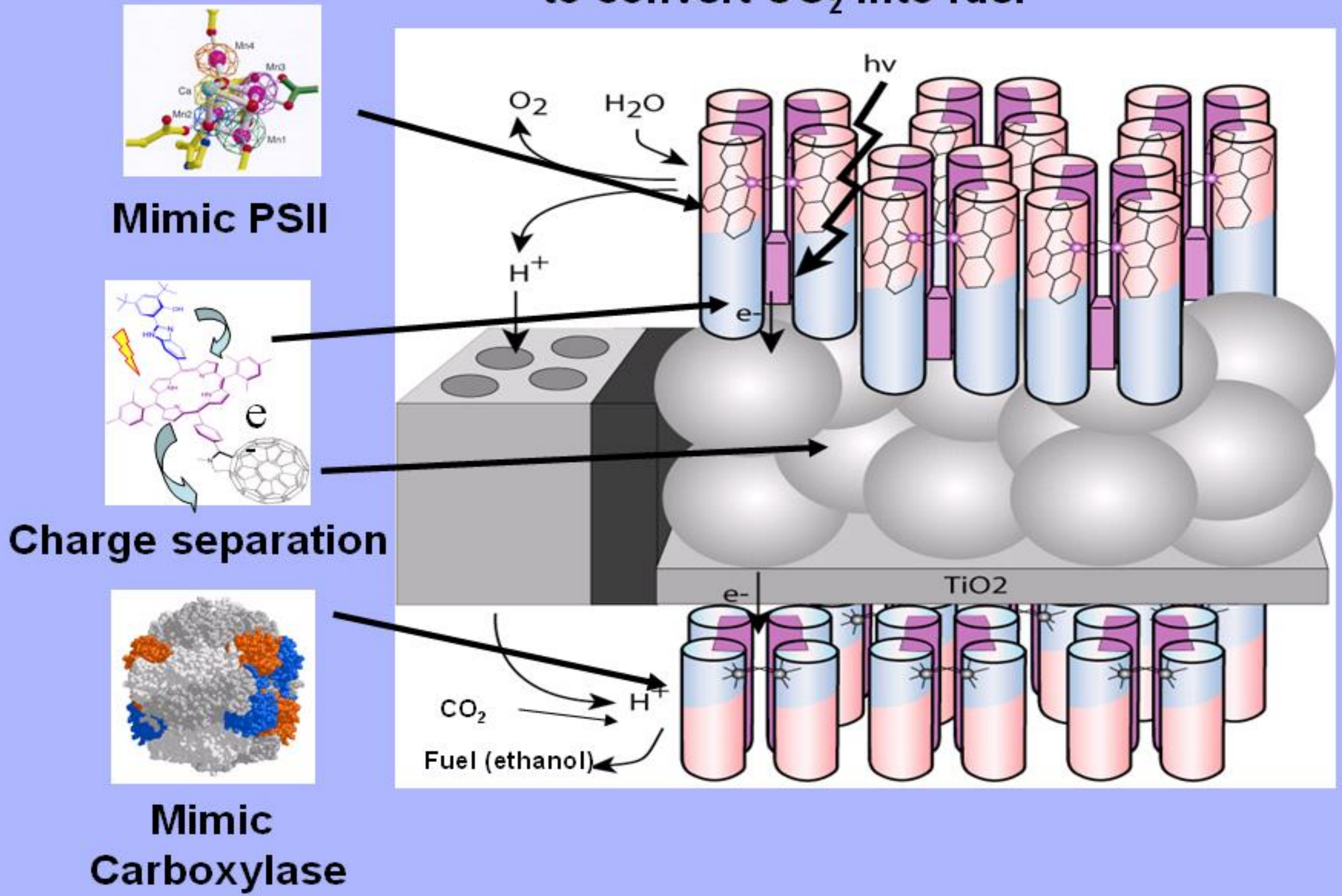
2- Direct conversion *via* integrated artificial and biomolecular photosynthetic systems



3- Direct conversion *via* biological and biohybrid systems



Design of an "Artificial Leaf" using solar energy to spilt water into Oxygen and use the Hydrogen to convert CO_2 into fuel

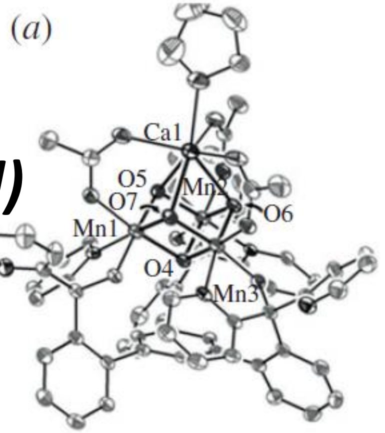


Key issues:

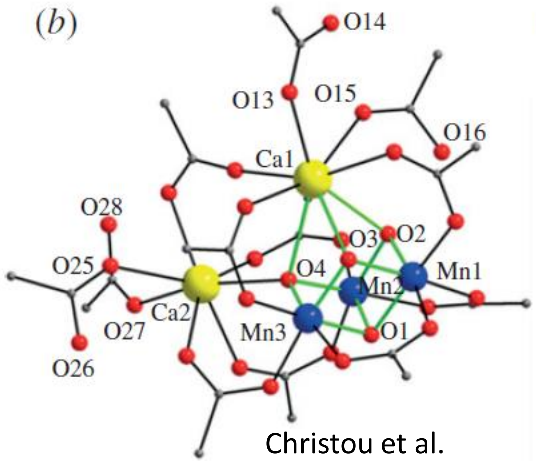
- Efficiency in the lab of ≥10%.
- Cheap materials stable in water
- Properly interfaced catalysts on each electrode
- Nanoscale construction of efficient DET
- Macroscaling

Challenge: Integration of catalysts with high TON and TOF and interfacing modules

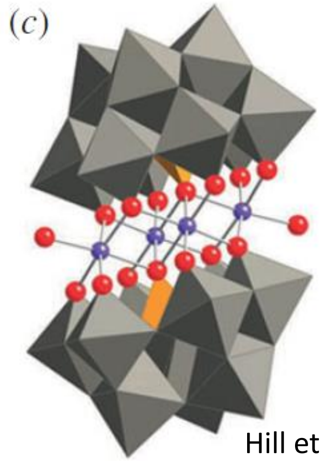
WOCs (a-d)



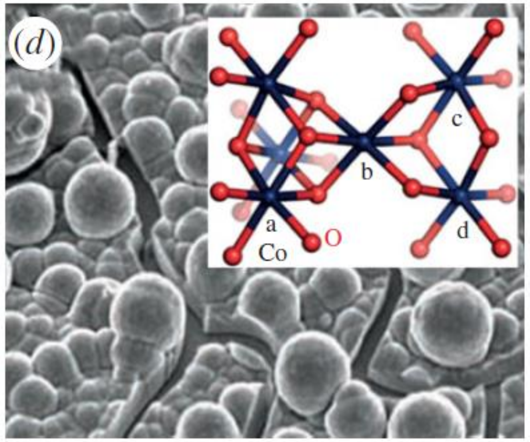
Agapie et al.



Christou et al.



Hill et al.

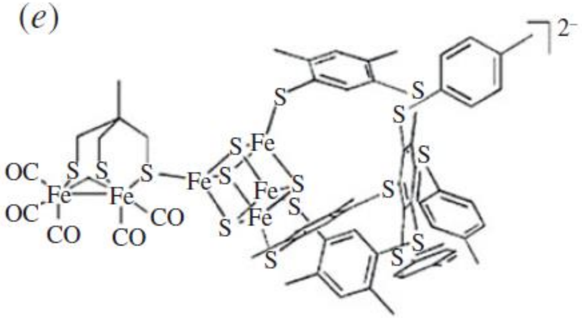


Nocera CoPi

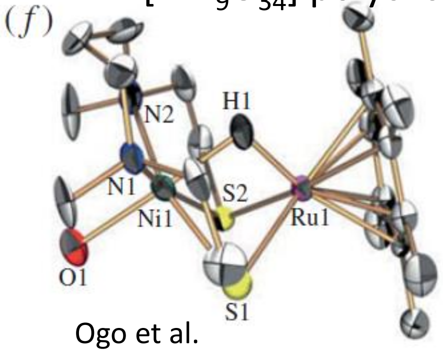
$[Mn_3CaO_4]$-clusters

Co_4O_{16} with
$[PW_9O_{34}]$ polyoxometallate ligands

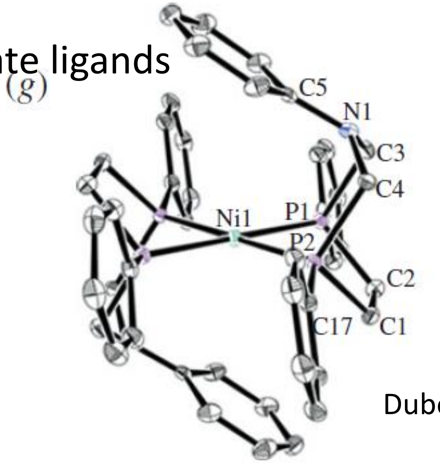
PRCs (e-g)



Pickett et al.



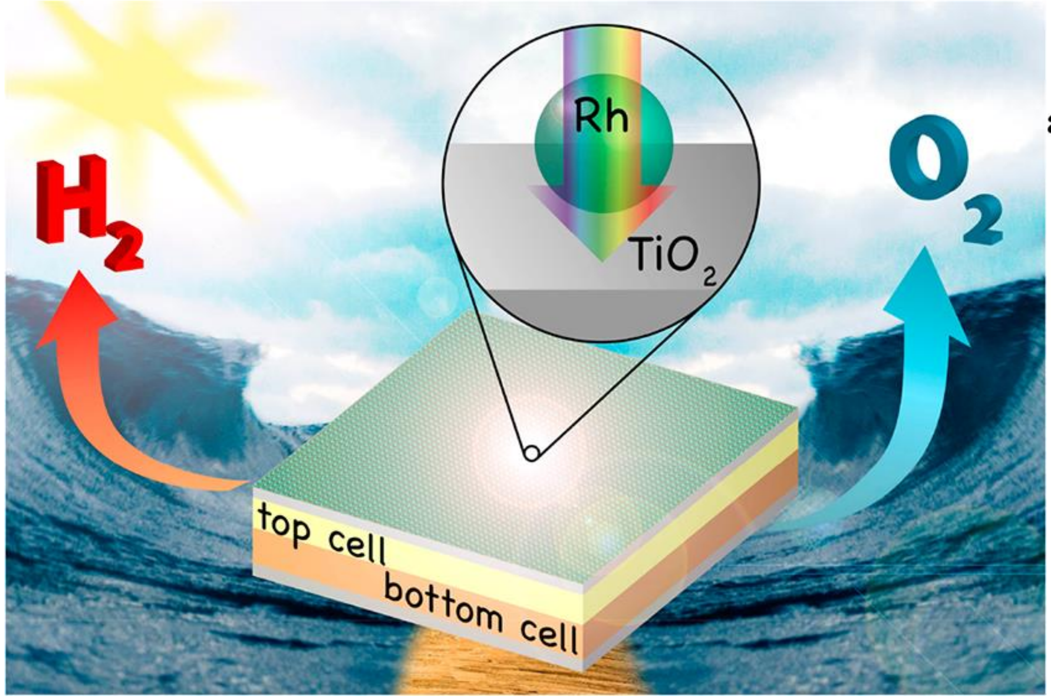
Ogo et al.

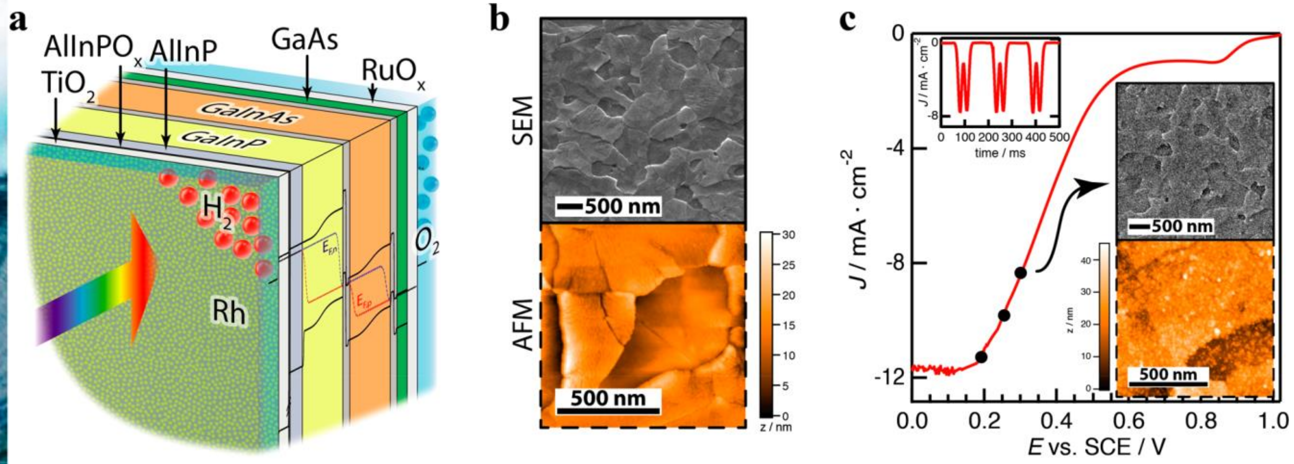


Dubois et al.

Barber and Tran (2013) Interface, 10, 20120984

SUNRISE: State of the art





STATE OF THE ART: monolithic PEC tandem heterojunction device with 19% STH efficiency, ACS Energy Lett. **2018**, *3*, 1795-1800

Sunrise

CHALLENGE:

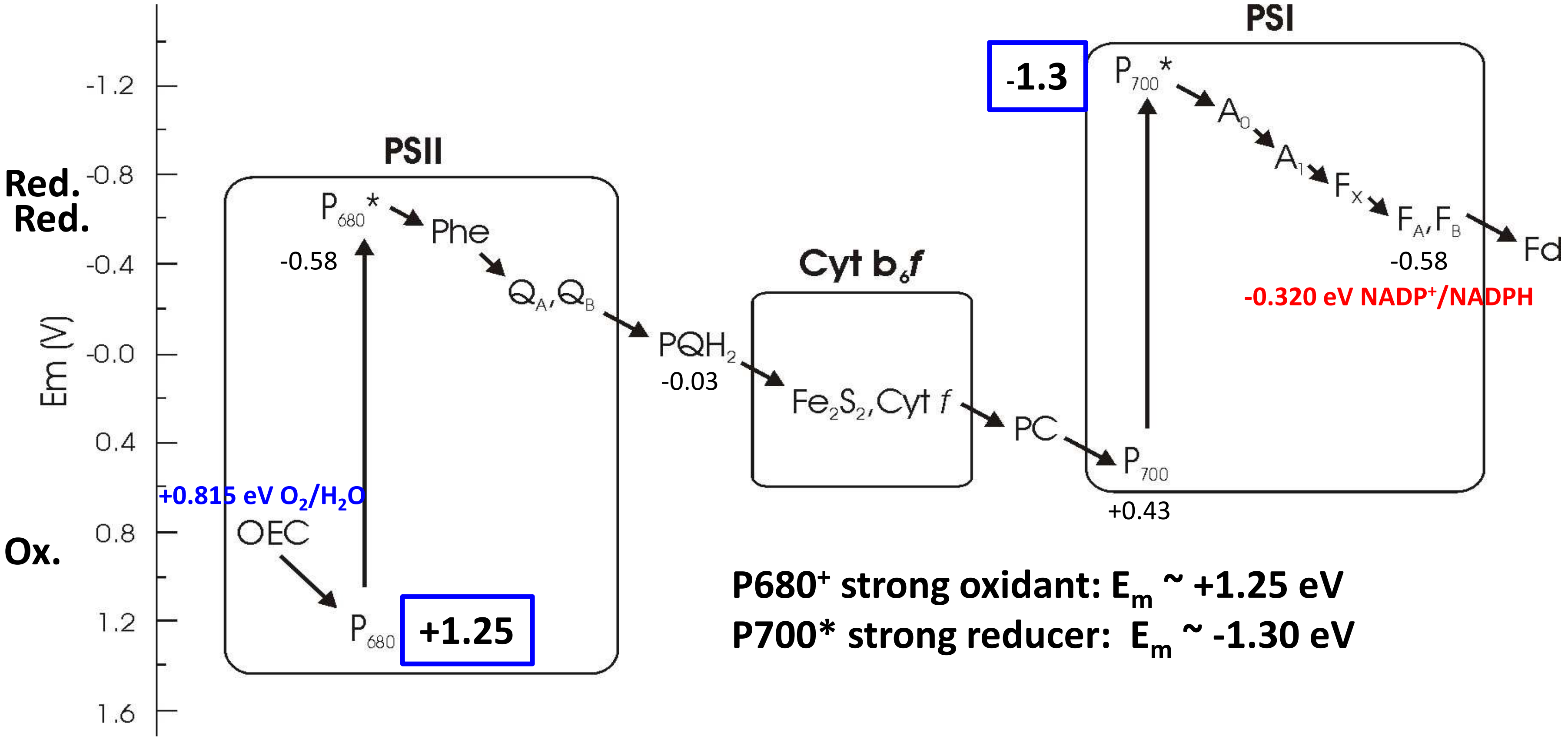
How to construct biomolecular solar-to-fuel devices to efficiently harness, convert and store solar energy?

Biomolecular Artificial Systems

Photosystem-other enzyme (H_2ase)-based solar-to-fuel and solar cell nanodevices:

- Optimised for energy and charge transfer (IQE ~ 100%)
- Self-assembling & self-renewing catalysts for WOR and HER/CRR
- Cheap to obtain
- Non-toxic

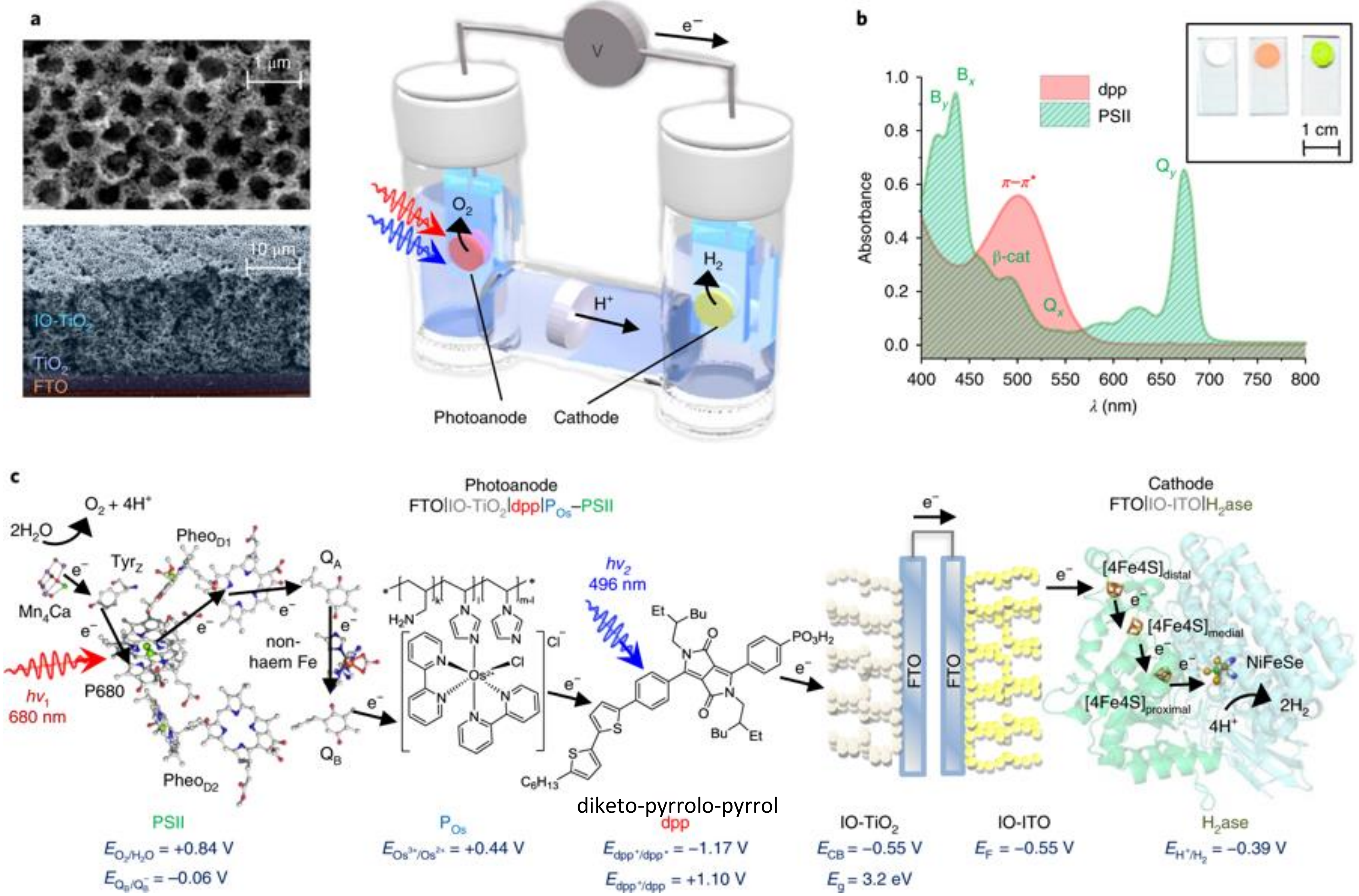
PSII and PSI as a Blueprint for APS



$P680^+$ strong oxidant: E_m ~ +1.25 eV
P700* strong reducer: E_m ~ -1.30 eV

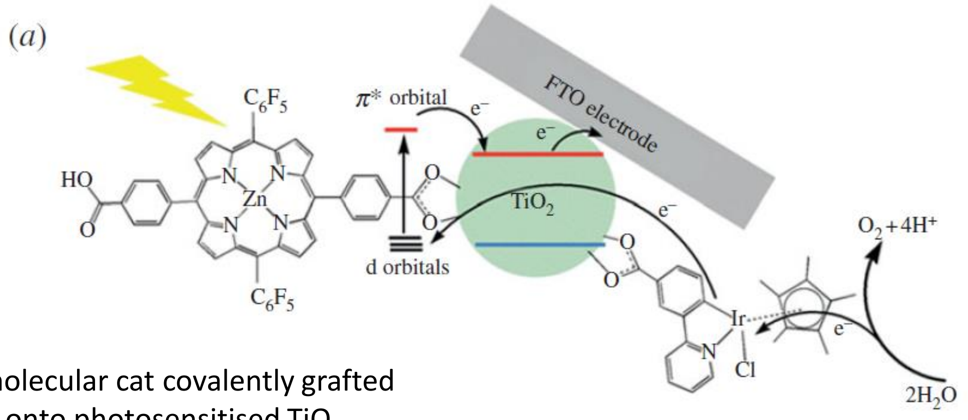
Quantum yield: PSI = 1, PSII = 0.90 (like no man-made system)

Biomolecular *Z*-scheme with PSII and hydrogenase producing H_2 with no overpotential

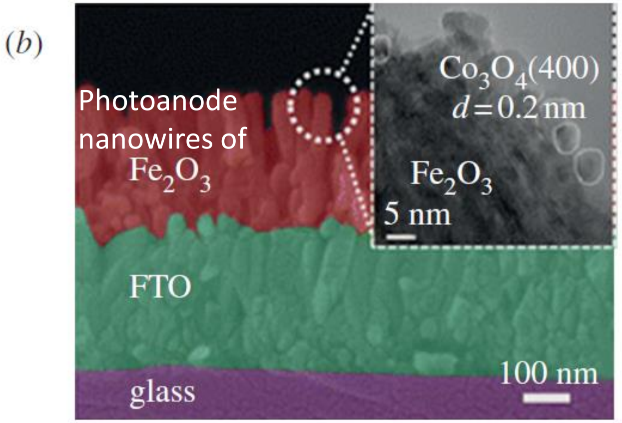


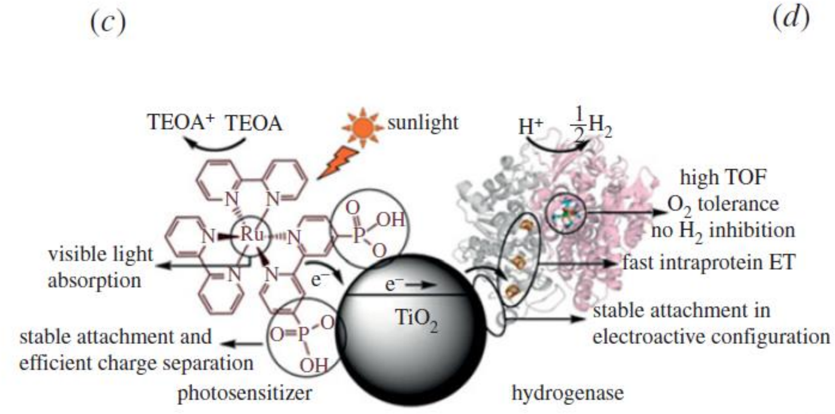
Sokol et al (2018) Nature Energy, https://doi.org/10.1038/s41560-018-0232-y

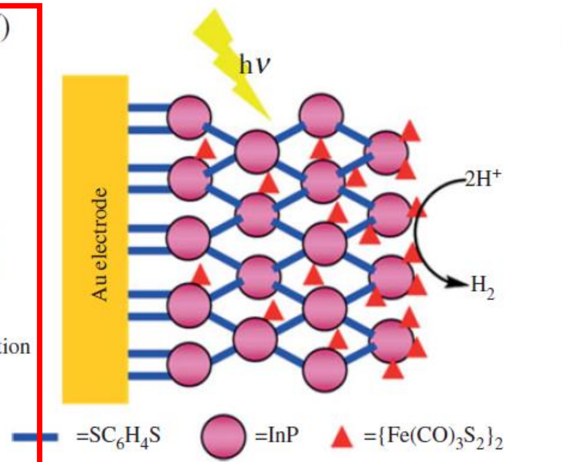
Grafting catalysts onto semiconductor substrates



Ir molecular cat covalently grafted onto photosensitised TiO_2

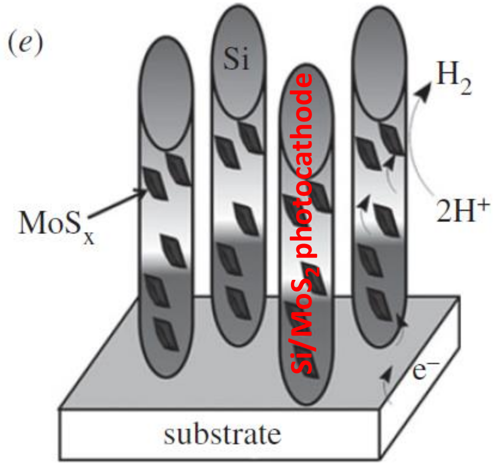






Mesoporous InP electrode

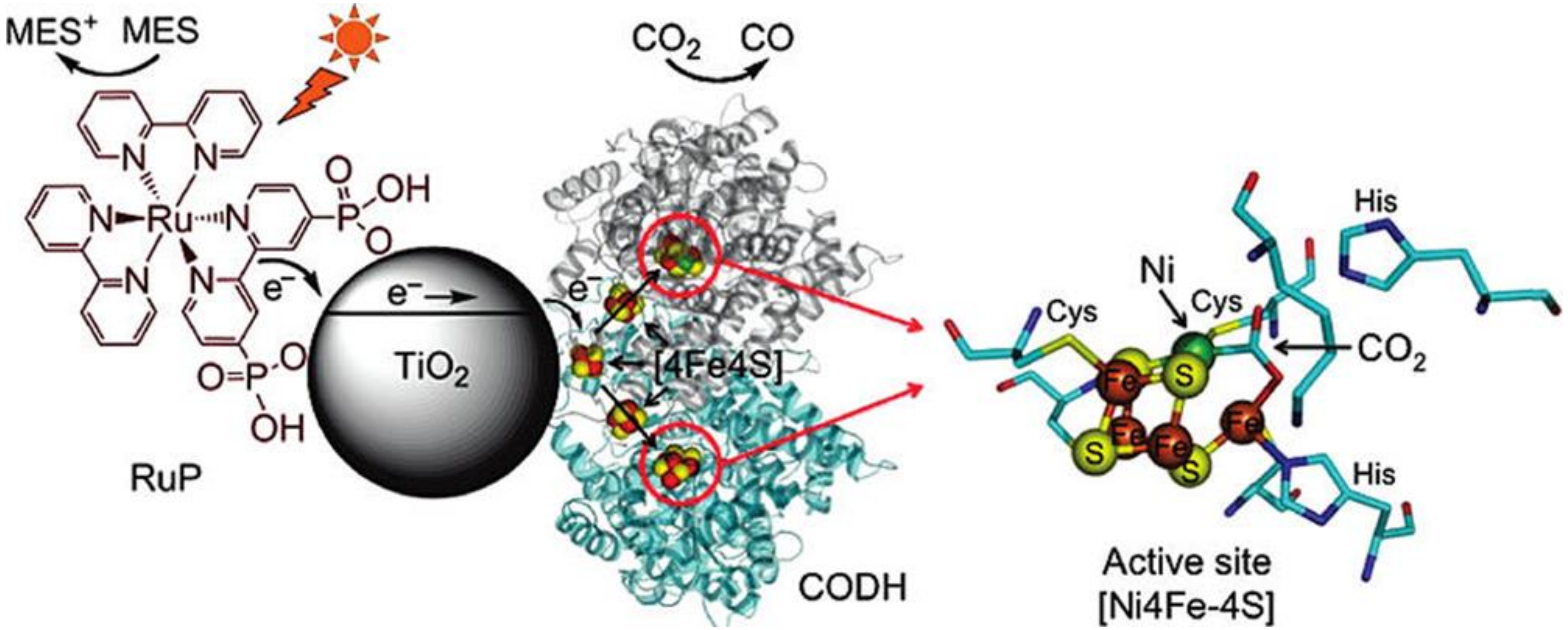
HEC Fe-Fe molecular catalyst



Functionalisation of TiO_2 with hydrogenase for H_2 production

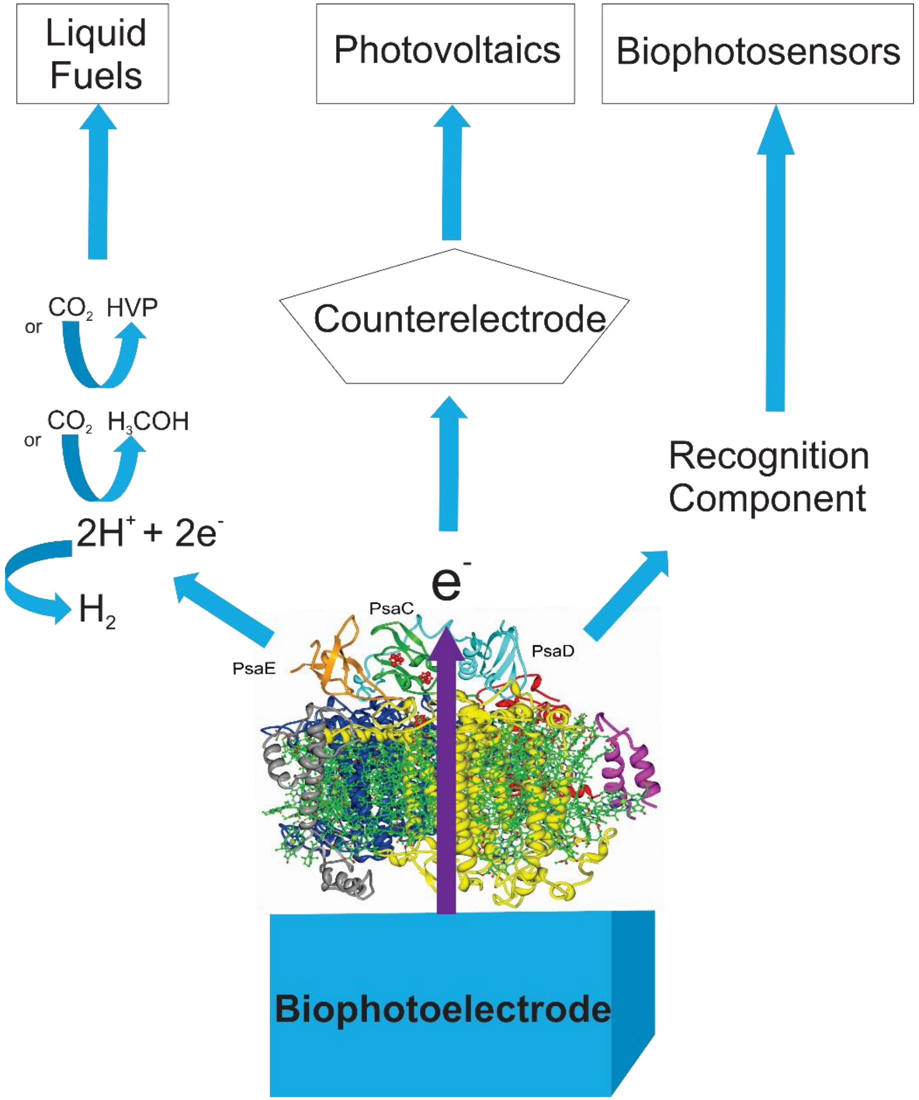
Barber i Tran (2013) Interface, 10, 20120984

Photosensitised TiO_2/CO dehydrogenase reduces CO_2 into CO in VIS



Woolerton et al (2010) Efficient and Clean Photoreduction of CO_2 to CO by Enzyme-Modified TiO_2 Nanoparticles Using Visible Light. J. Am. Chem. Soc., 132, 2132–2133.

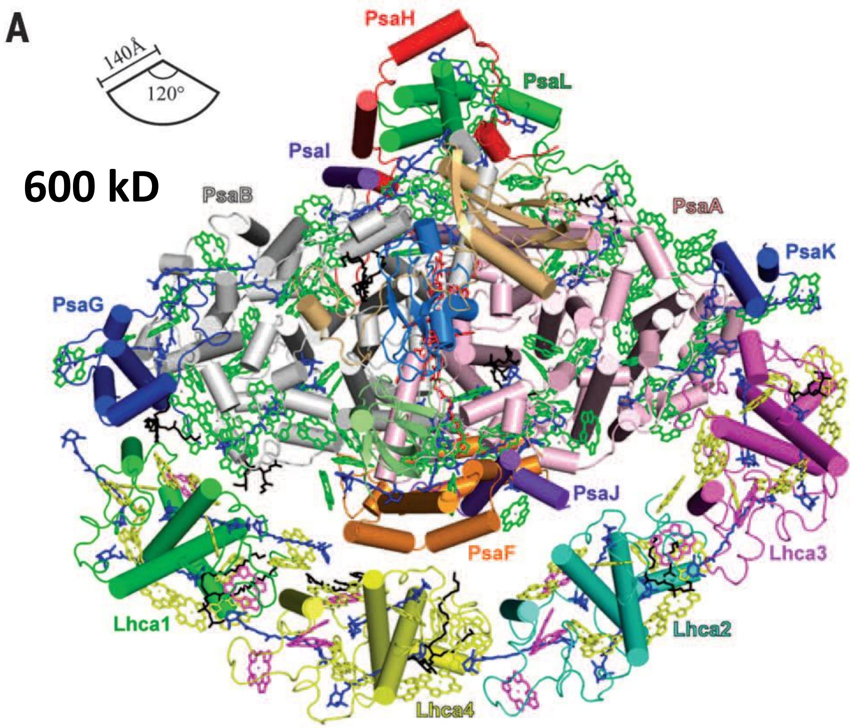
PSI-based Devices



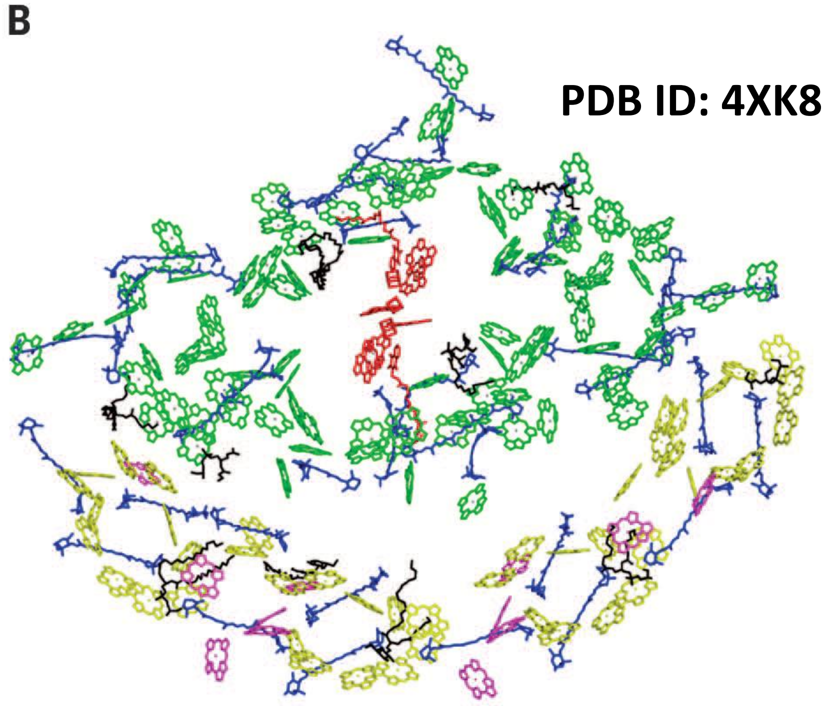
Janna Olmos and Kargul (2015) Int. J. Biochem. Cell Biol., 66, 37-44

X-ray Structure of PSI-LHCI at 2.8 Å

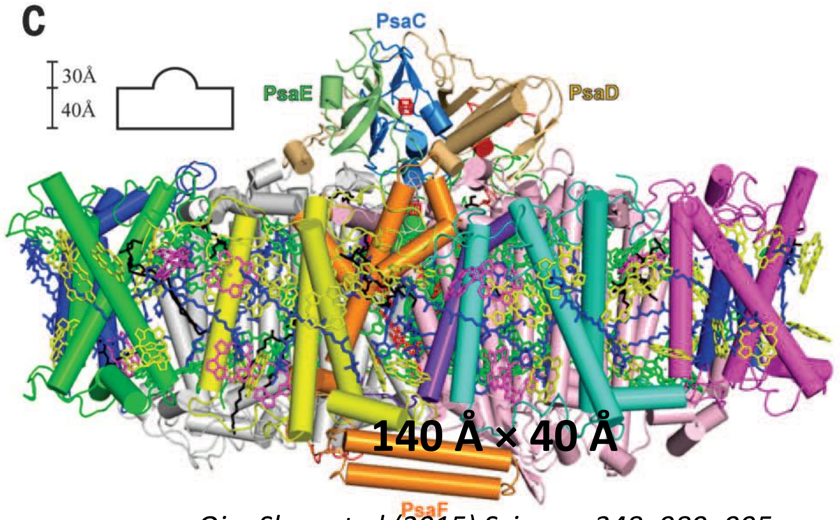
600 kD



PDB ID: 4XK8

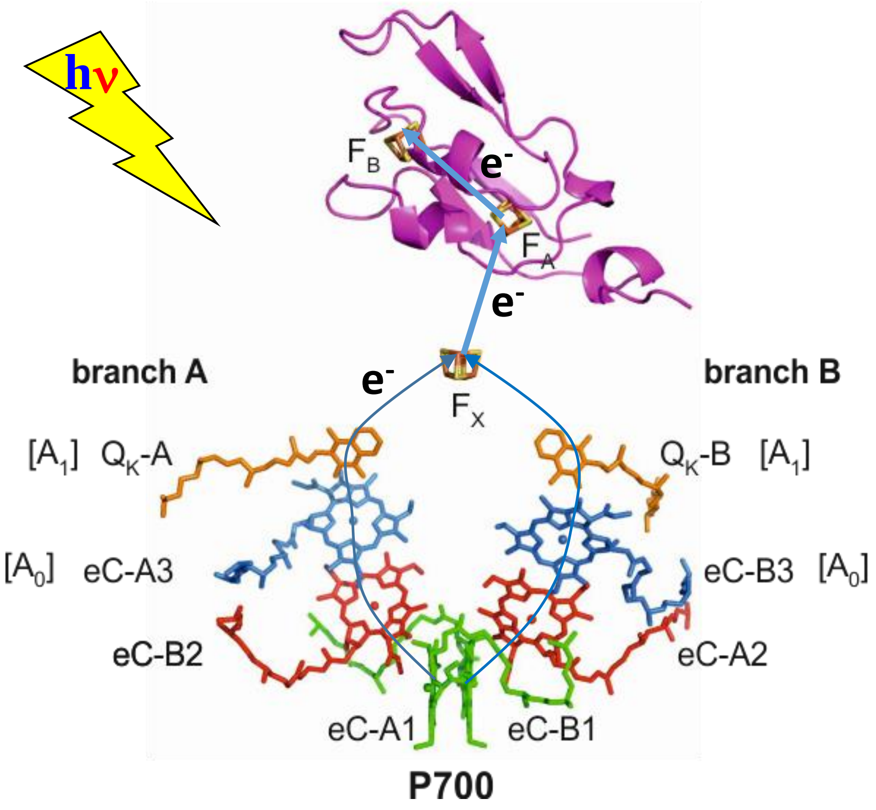


- **16 protein subunits:** 12 core subunits and 4 Lhcas (PsaO and PsaN absent in xtls)
- **205 cofactors:** 155 Chls (143 Chlas and 12 Chlbs), 35 Cars (26 BCRs, 5 Luts, 4 Viols), 2 phylloquinones, 3 Fe_4S_4 clusters, and 10 lipids (6 PGs, 3 MGDGs, and 1 DGDG)

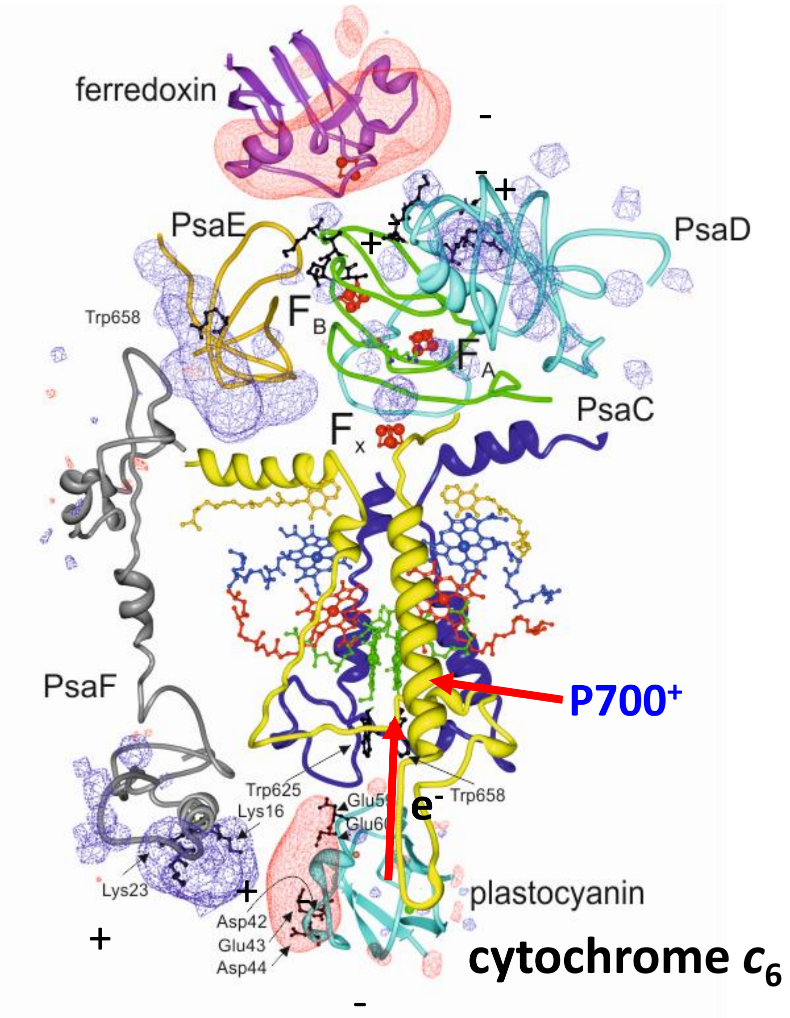


Qin, Shen et al (2015) Science, 348, 989–995

Charge Separation and e$^-$ Transfer in PSI

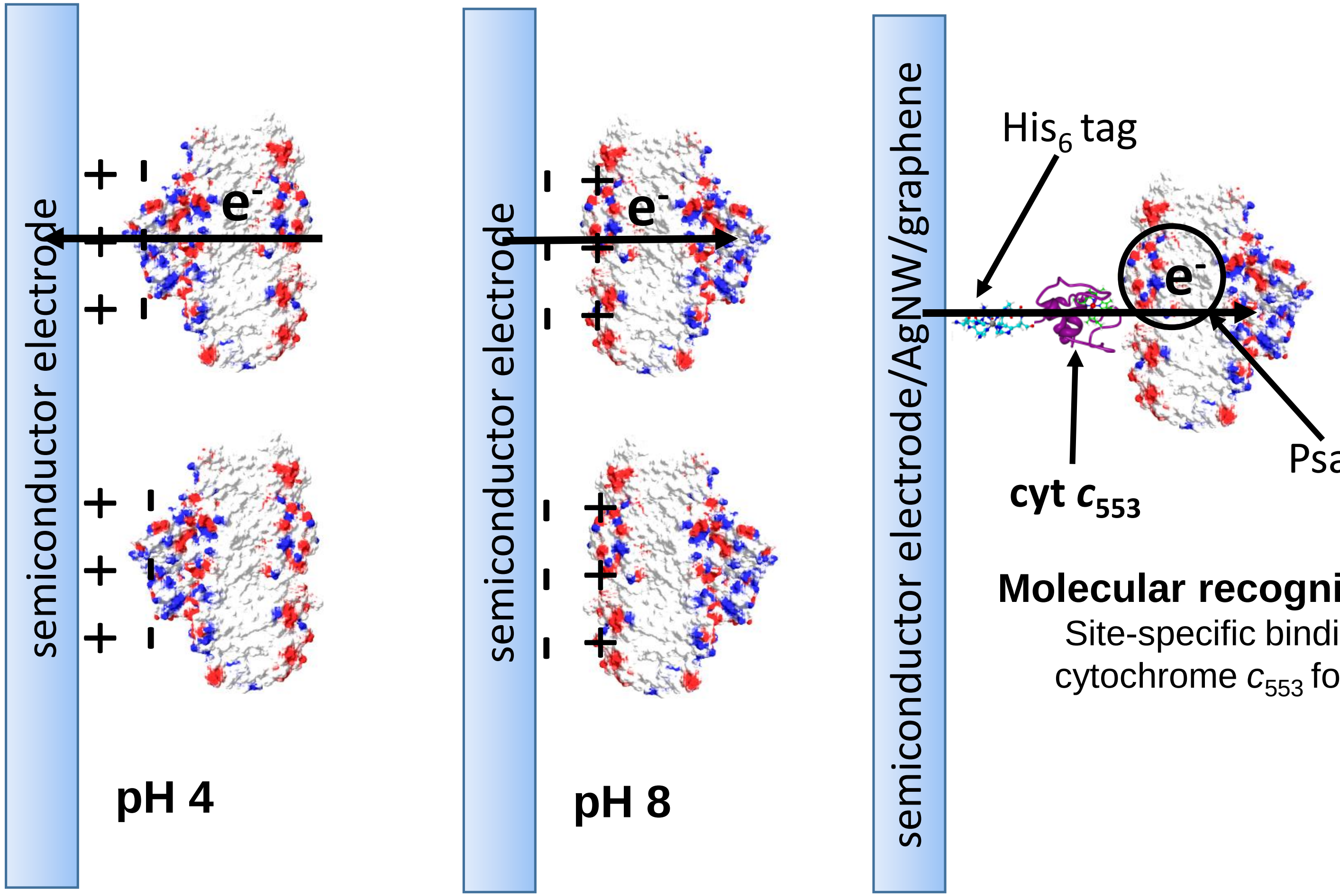


Jordan et al (2001) Nature, 411, 909



Kargul et al (2012) J. Plant Physiol., 169, 1639

Critical Path: Developing strategies for oriented (bio)conjugation of PSI with the electrode surface

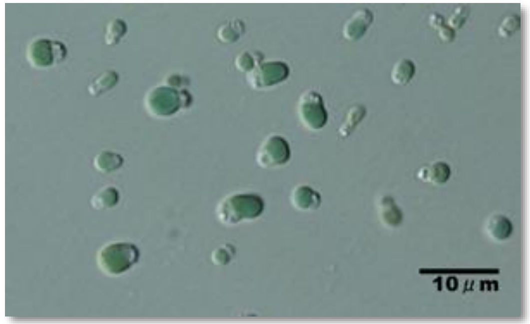


Molecular recognition approach:
Site-specific binding of PSI with cytochrome c_{553} for µs e^- transfer

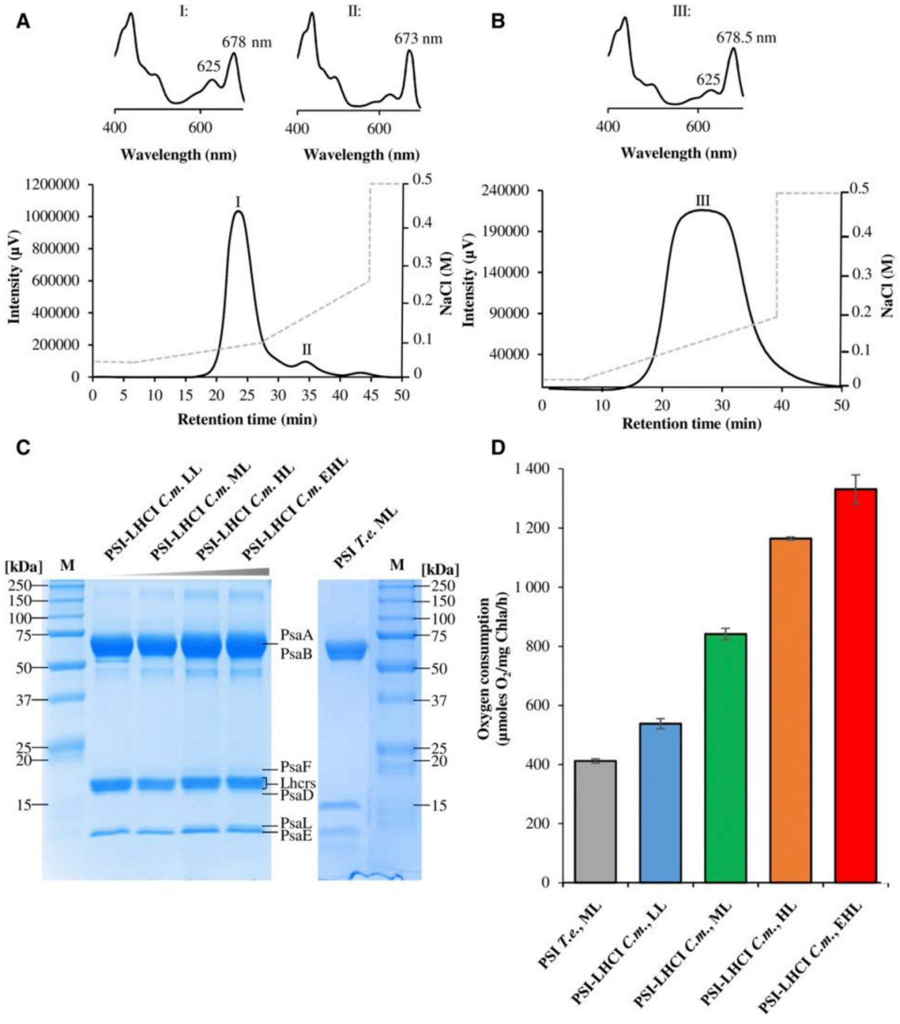
anodic photocurrent *cathodic photocurrent* *cathodic photocurrent*

Manipulation of electrostatic interactions approach:
Inherent asymmetric charge distrubution in PSI

Highly robust PSI from a volcanic extremophilic red microalga *Cyanidioschyzon merolae*

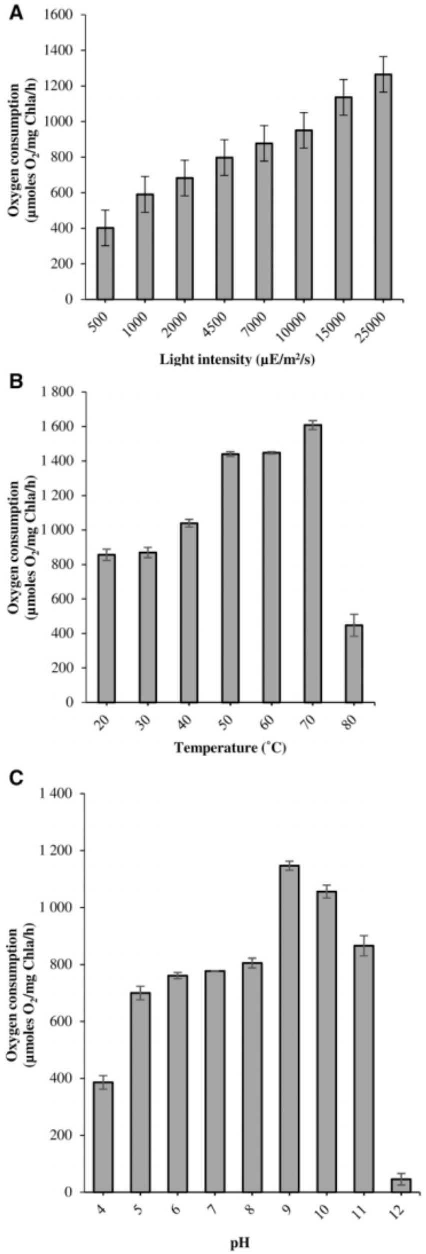


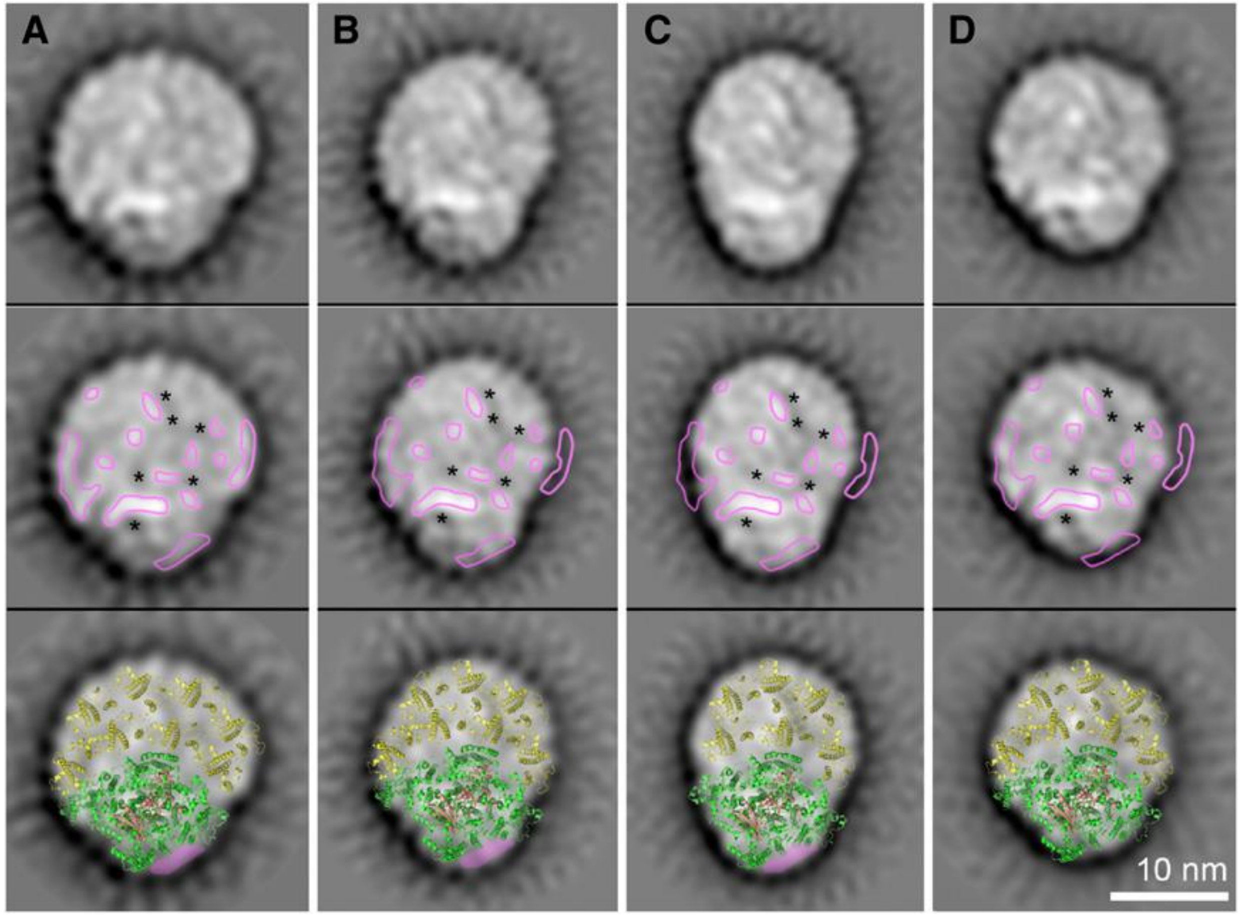
pH 2.5, 42 °C, 90 μE/m²/s



Haniewicz et al. (2018) Plant Physiol., 176, 1433–1451

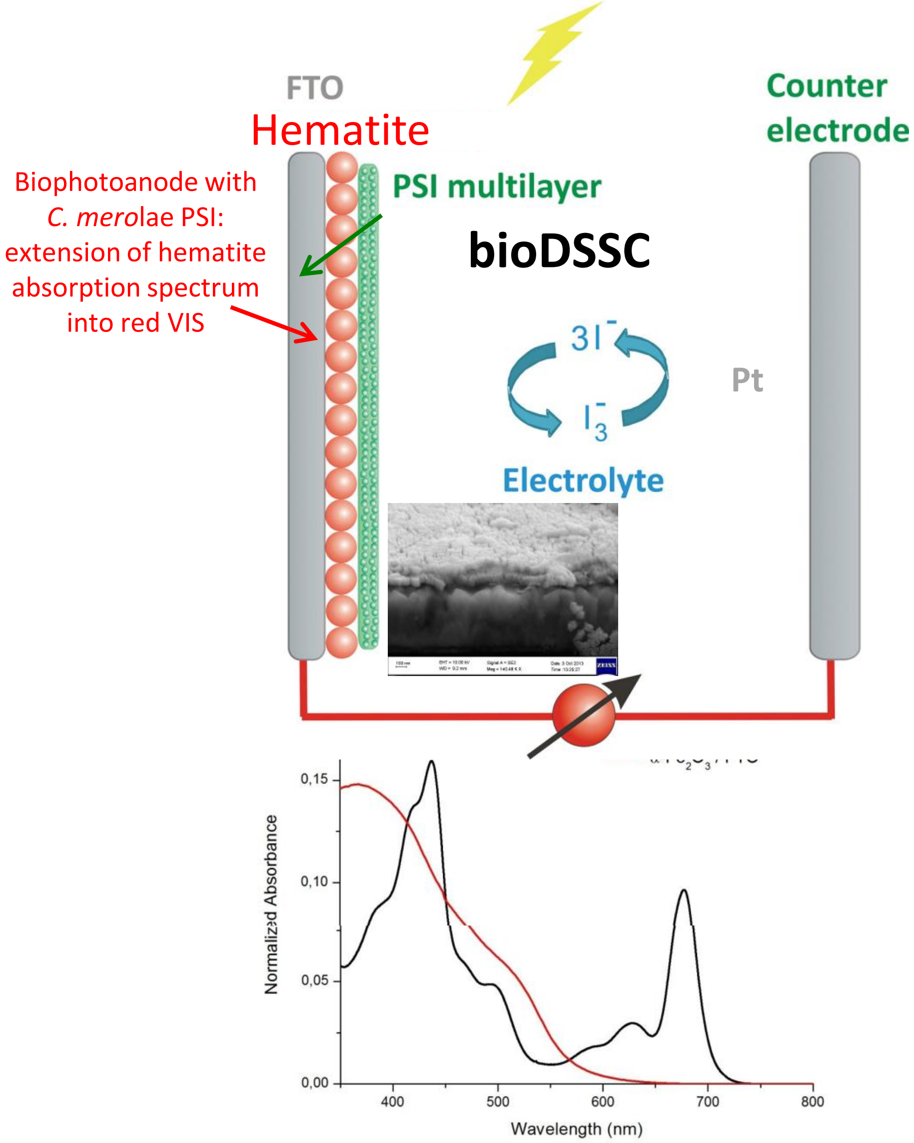
Robust PSI-LHCI from *C. merolae* operates in a broad range of conditions.



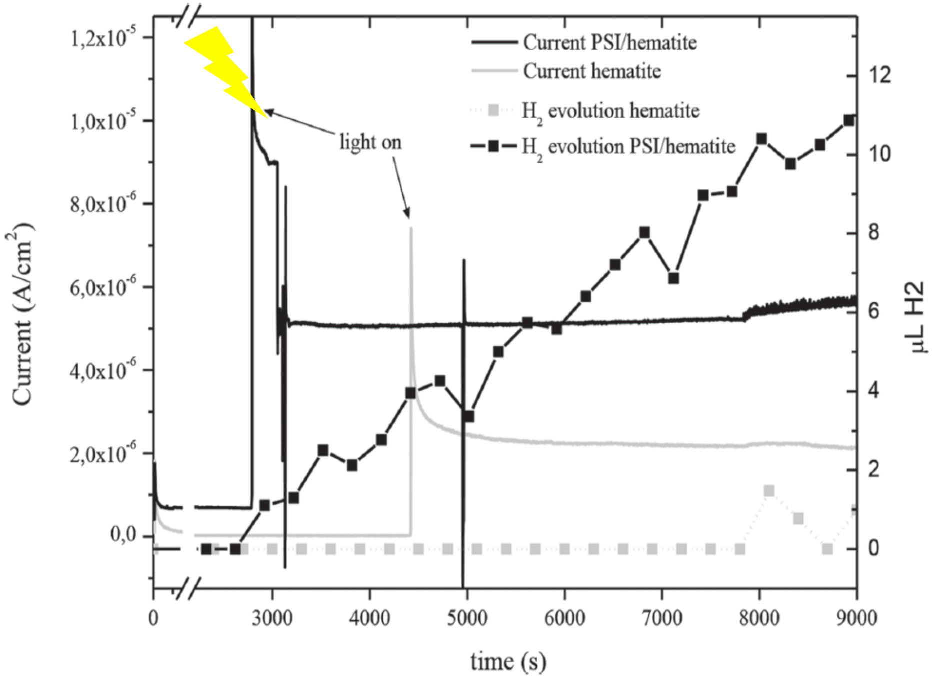


Haniewicz et al. (2018) Plant Physiol., 176, 1433–1451

PSI-based Dye-Sensitised Solar Cell and PEC



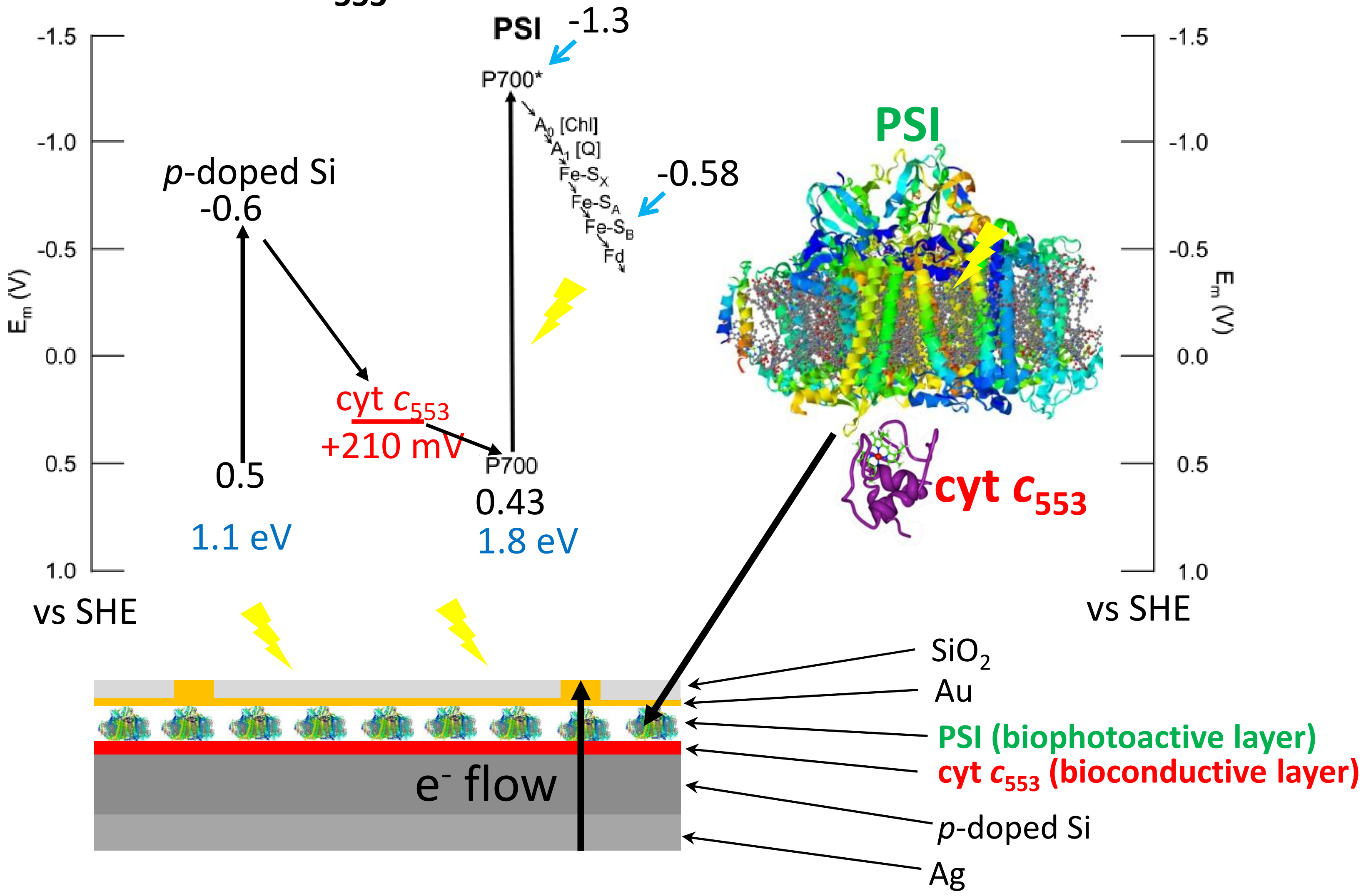
bioPEC in aqueous buffer



H_2 evolution rate: 744 µmoles H_2 mg Chl^{-1} h^{-1}

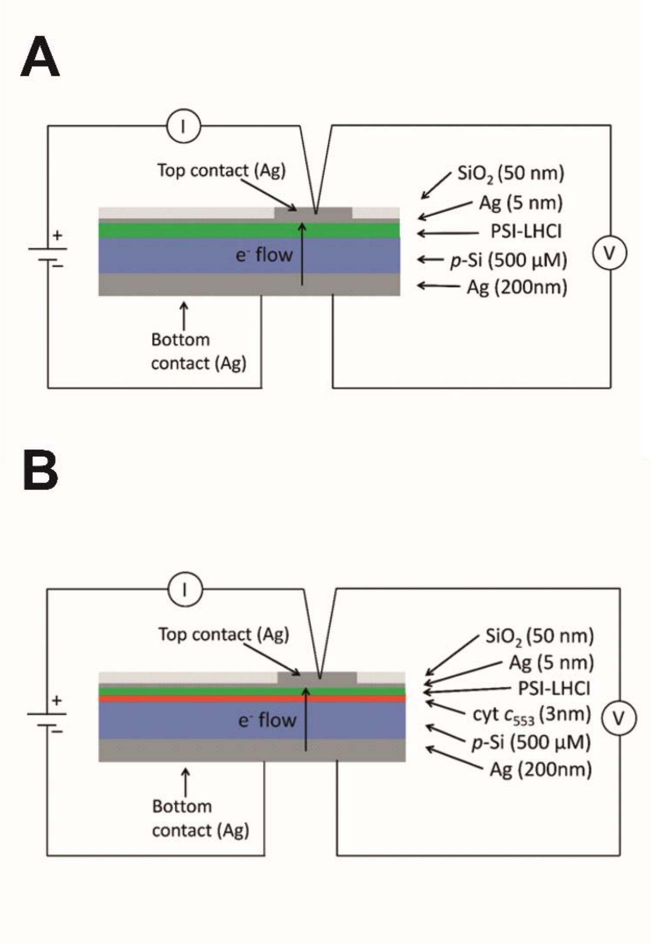
Ocakoglu, Kargul et al (2014) Adv. Funct. Mat., 24, 7467–7477

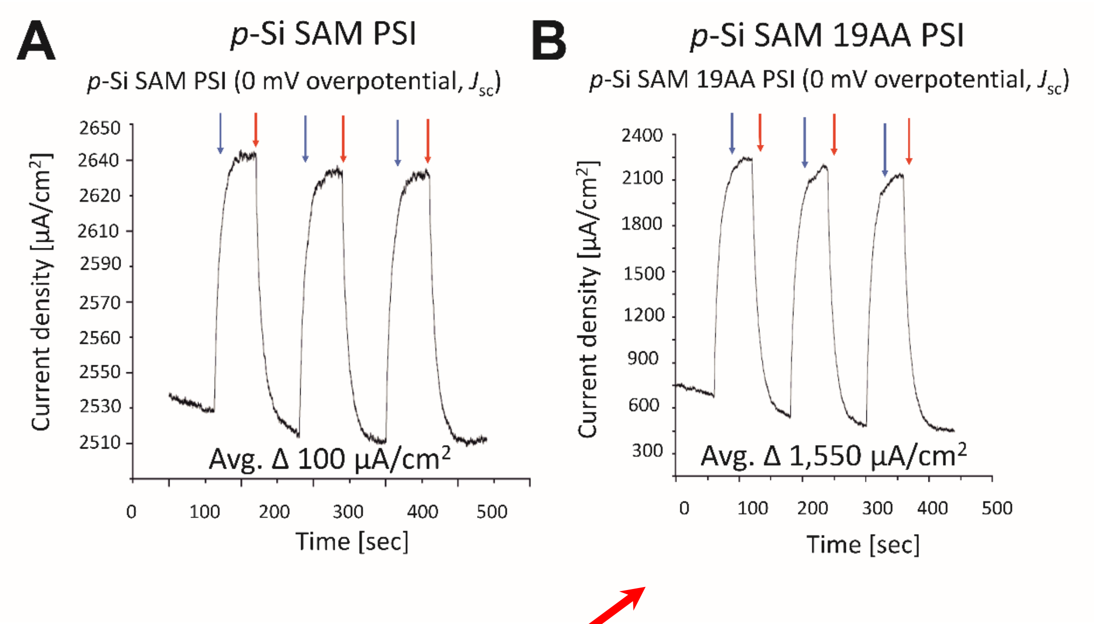
All-Solid State *p*-doped Si-PSI Biophotoelectrode with Cytochrome c_{553} as the Conductive Interface



Janna Olmos, Kargul et al (2017) RSC Advances, 7, 47854–47866

p-doped Si-PSI All-Solid-State Device

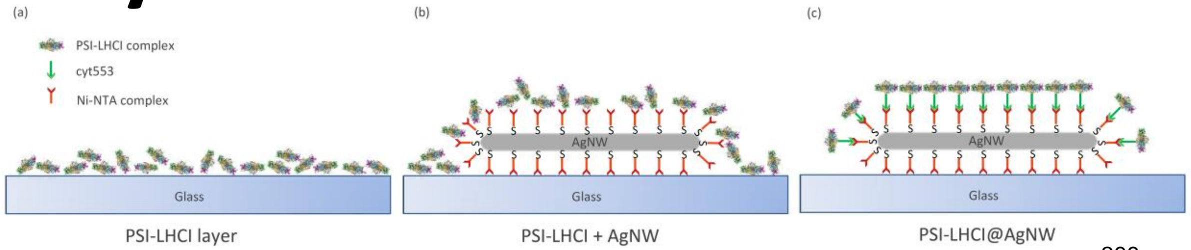


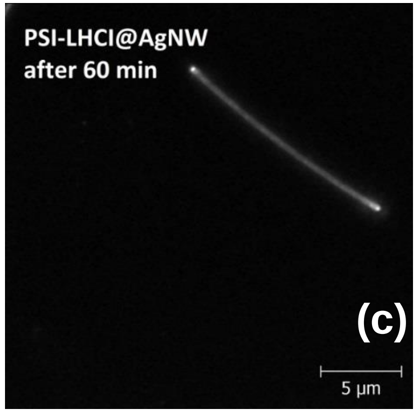


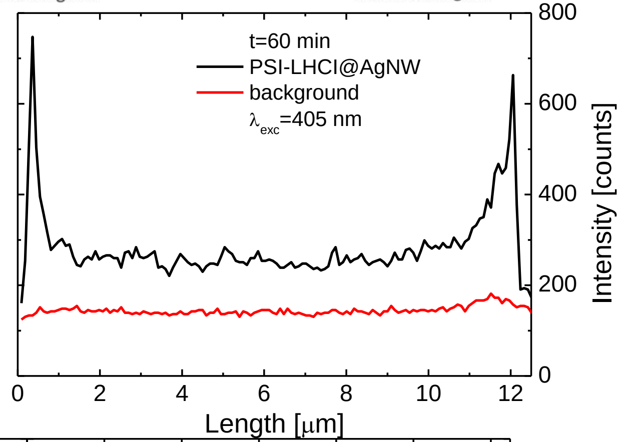
16x higher photocurrent in the presence of cyt and PSI – cyt biopassivation works!

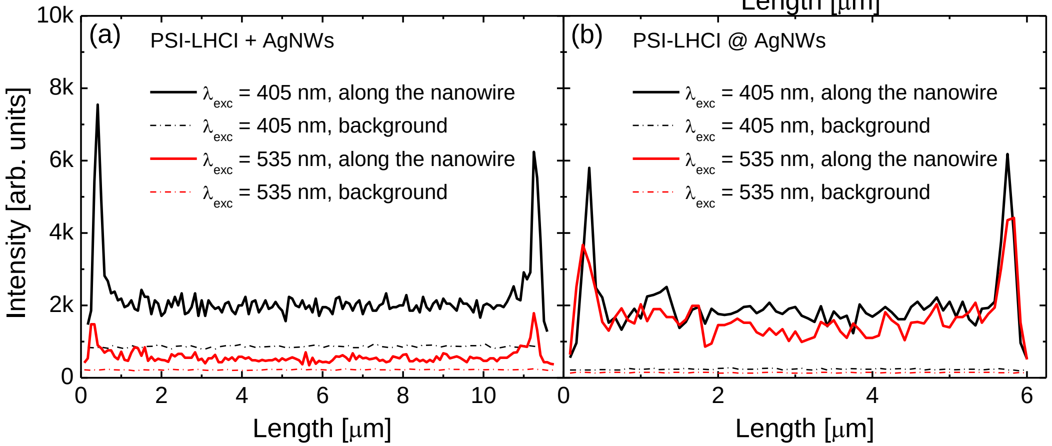
Janna Olmos, Kargul et al (2017) RSC Advances, 7, 47854–47866

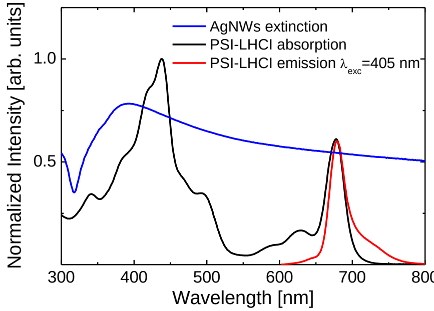
Improving Nature: Enhanced Functionality of PSI-LHCI by Plasmonic Interactions with AgNWs





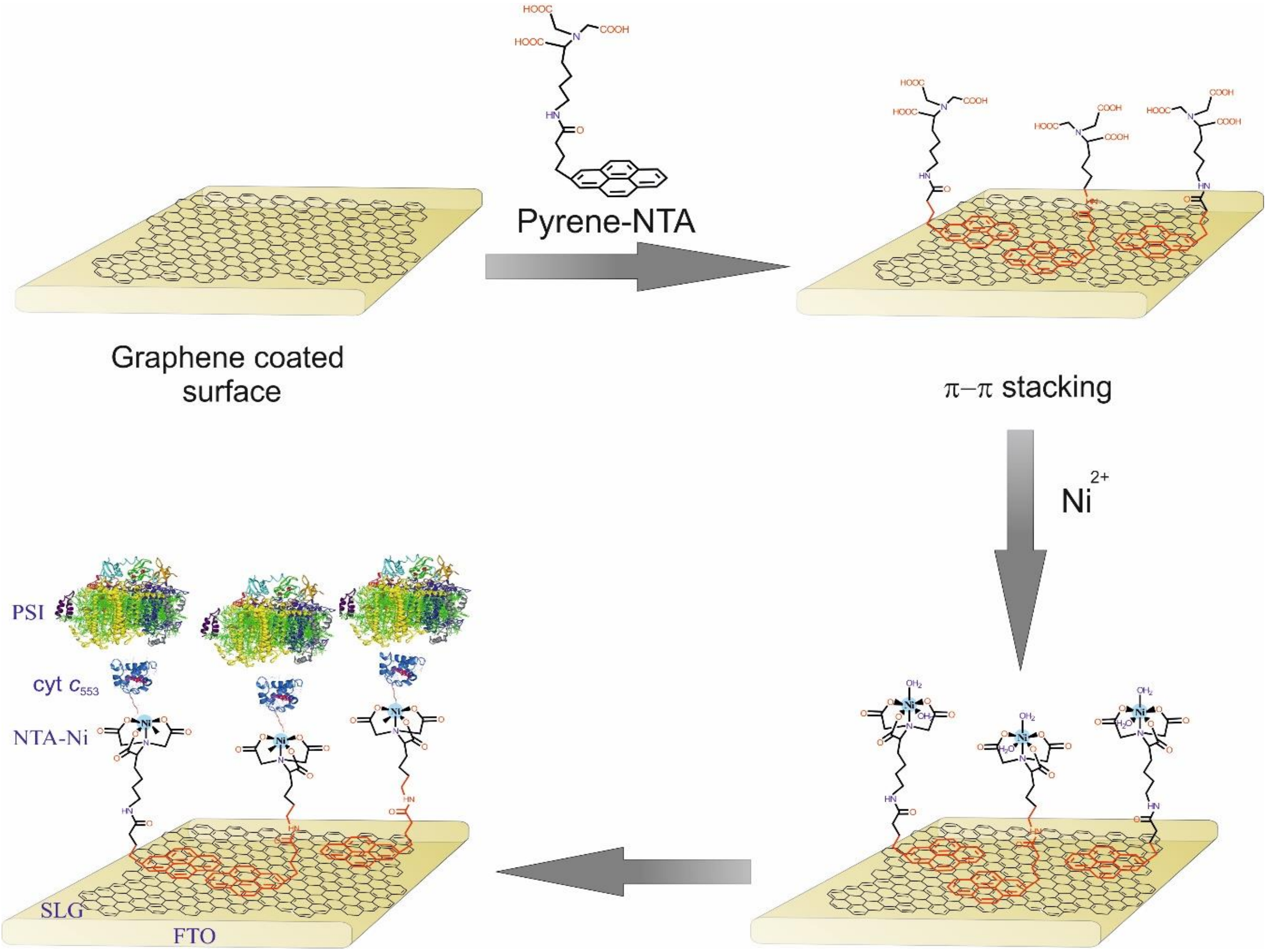






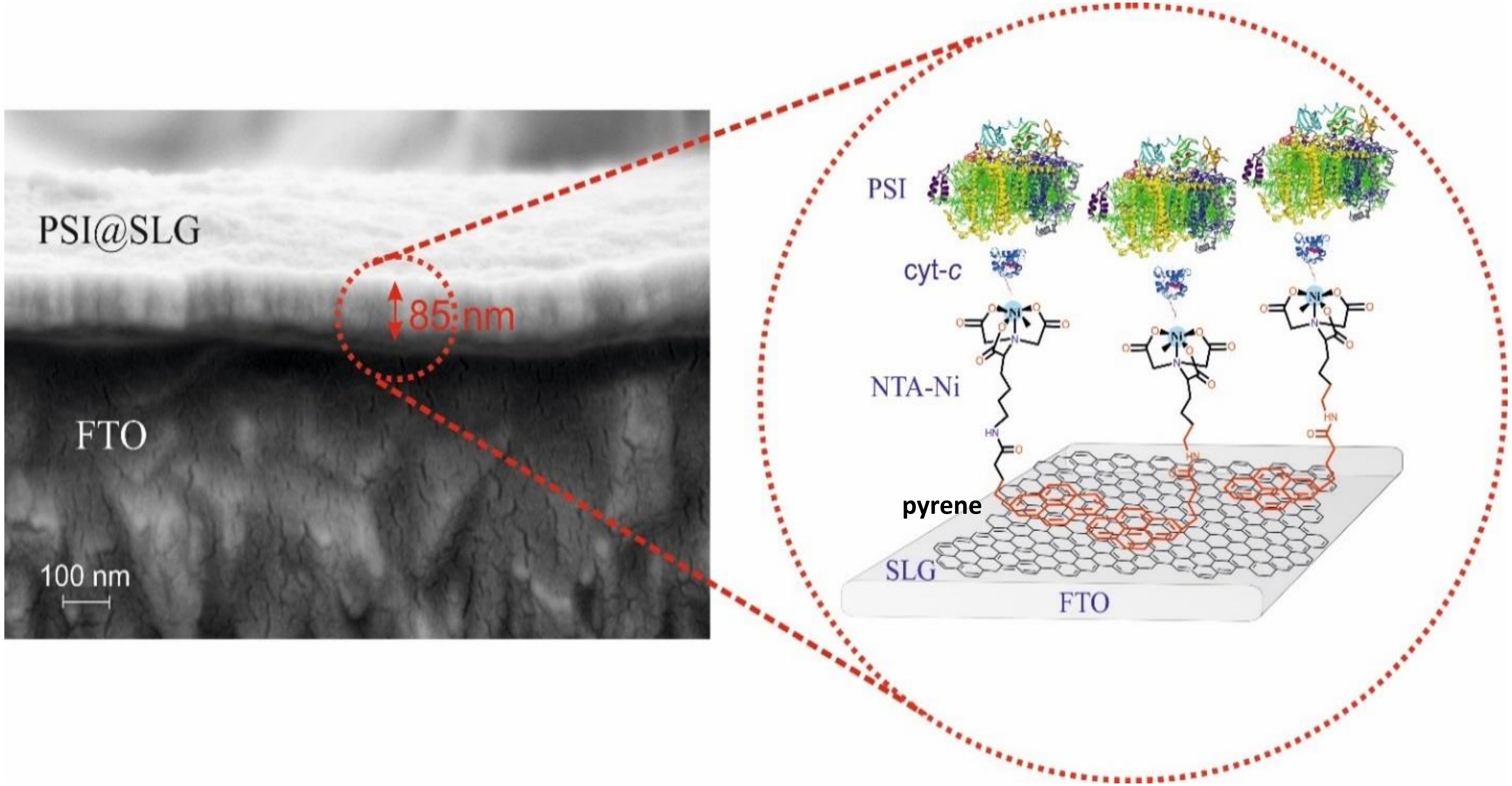
Szalkowski, Janna Olmos, Kargul, Kowalska, Maćkowski et al (2017) Nanoscale, 9, 10475

Nanostructuring of Bio-organic Interface by Molecular Recognition: pyrene-NiNTA/cytochrome c_{553}



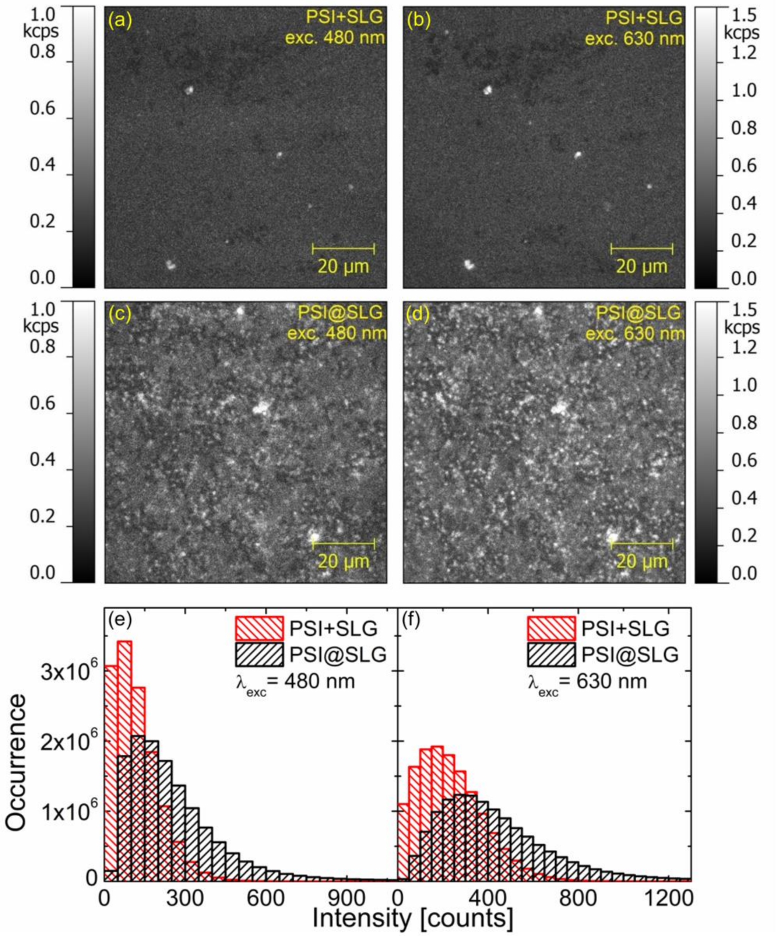
Kiliszek et al (2018) J. Mater. Chem. A, 6, 18615

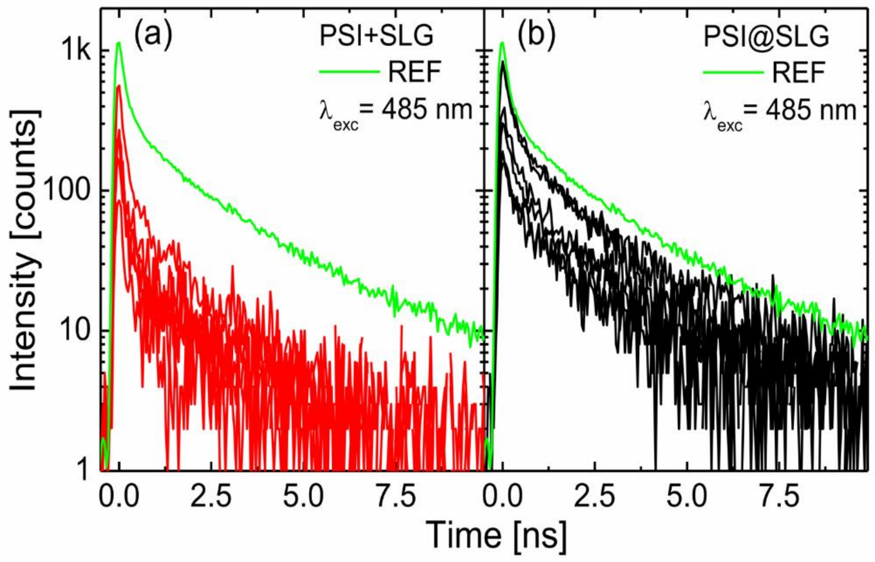
Highly Ordered PSI/cyt c_{553}/SLG Device



Kiliszek et al (2018) J. Mater. Chem. A, 6, 18615

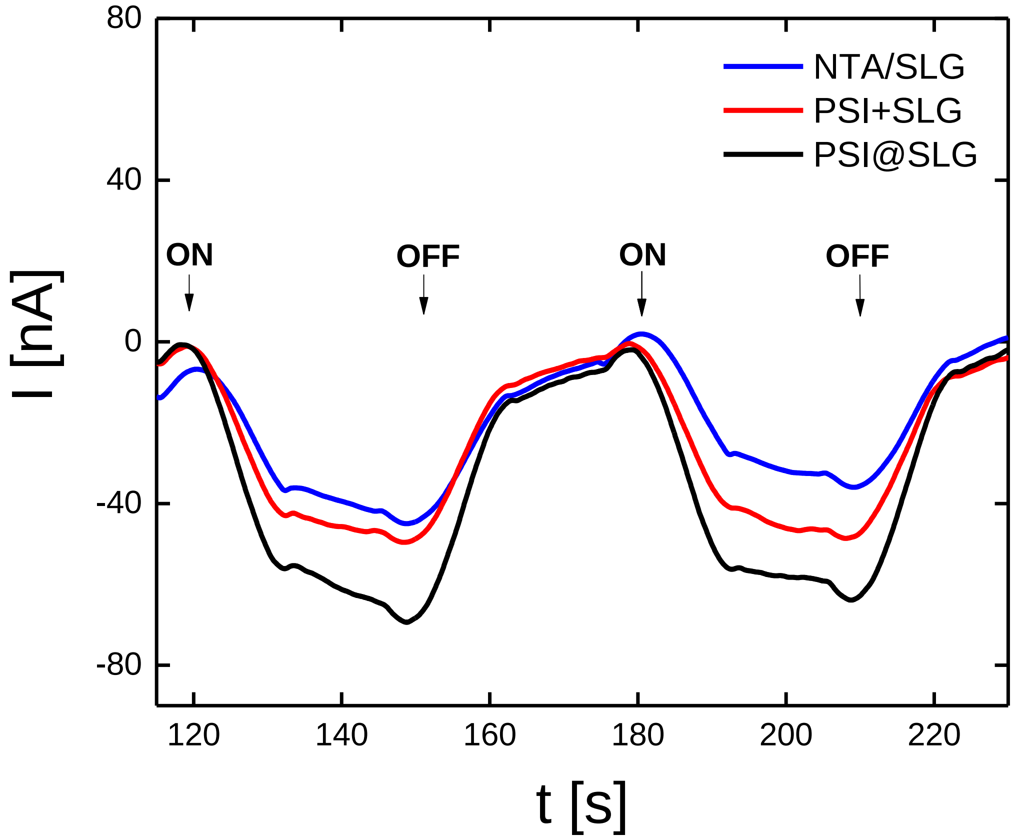
Fluoresce Intensity Mapping: uniform electrode coverage for PSI@SLG devices

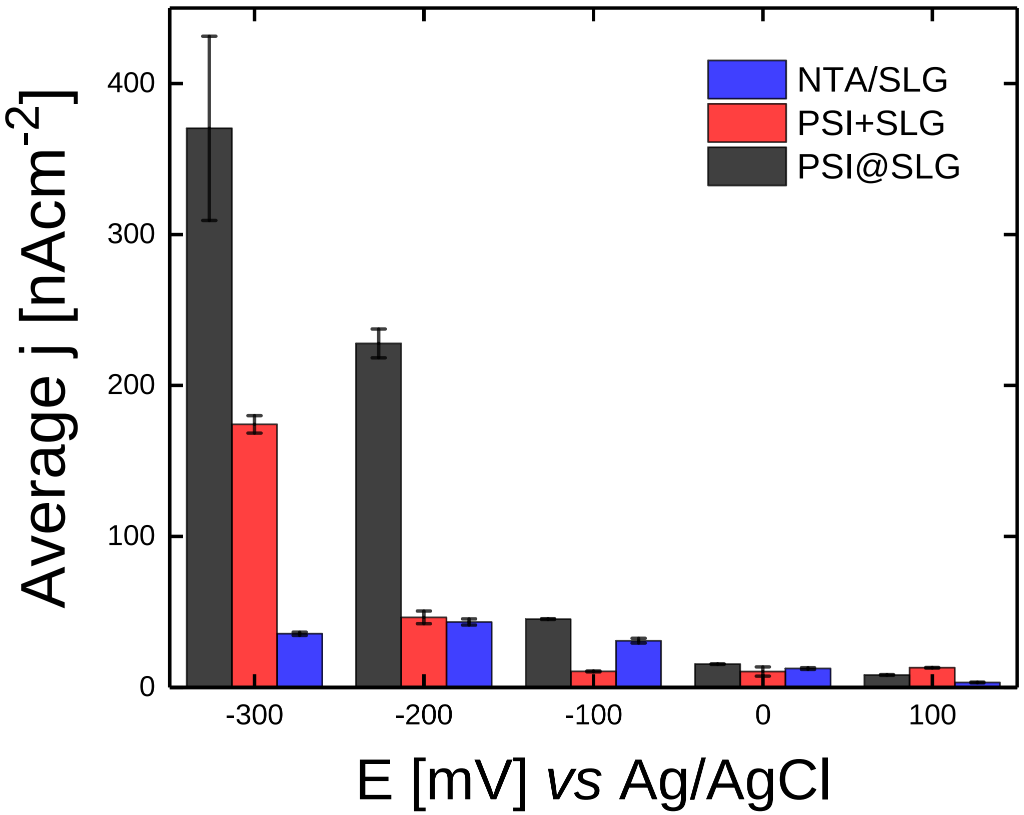




Kiliszek et al (2018) J. Mater. Chem. A, 6, 18615

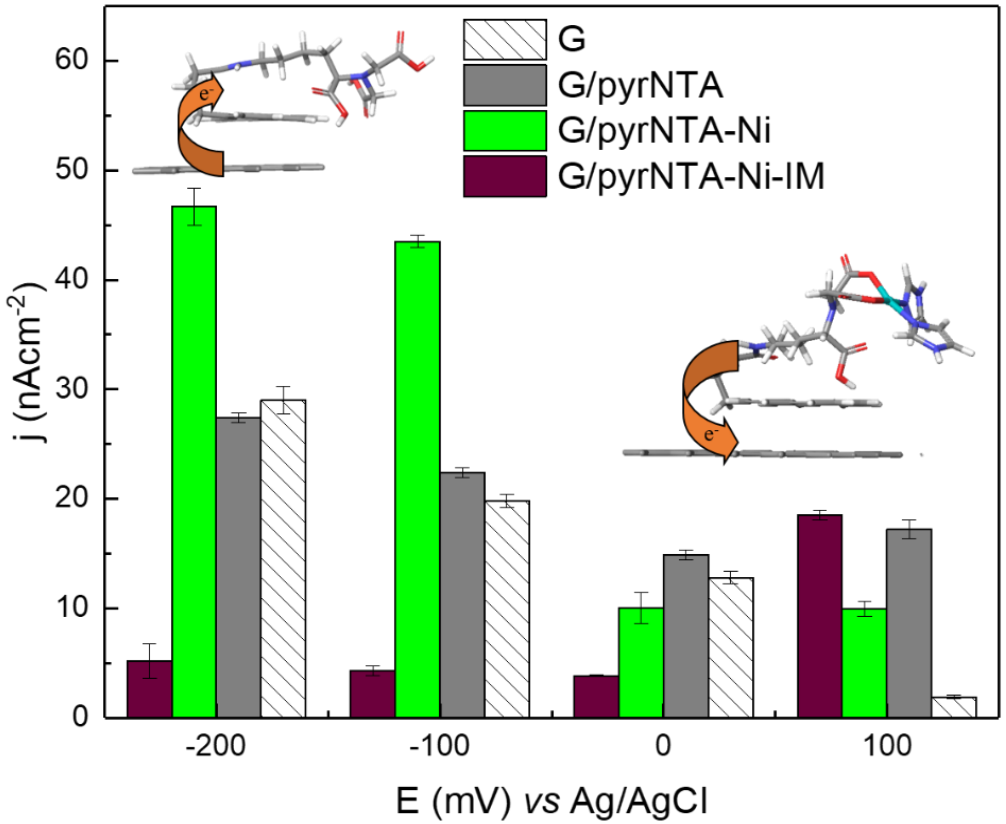
Photocurrent Output from PSI-based SLG Electrodes





Kiliszek et al (2018) J. Mater. Chem. A, 6, 18615

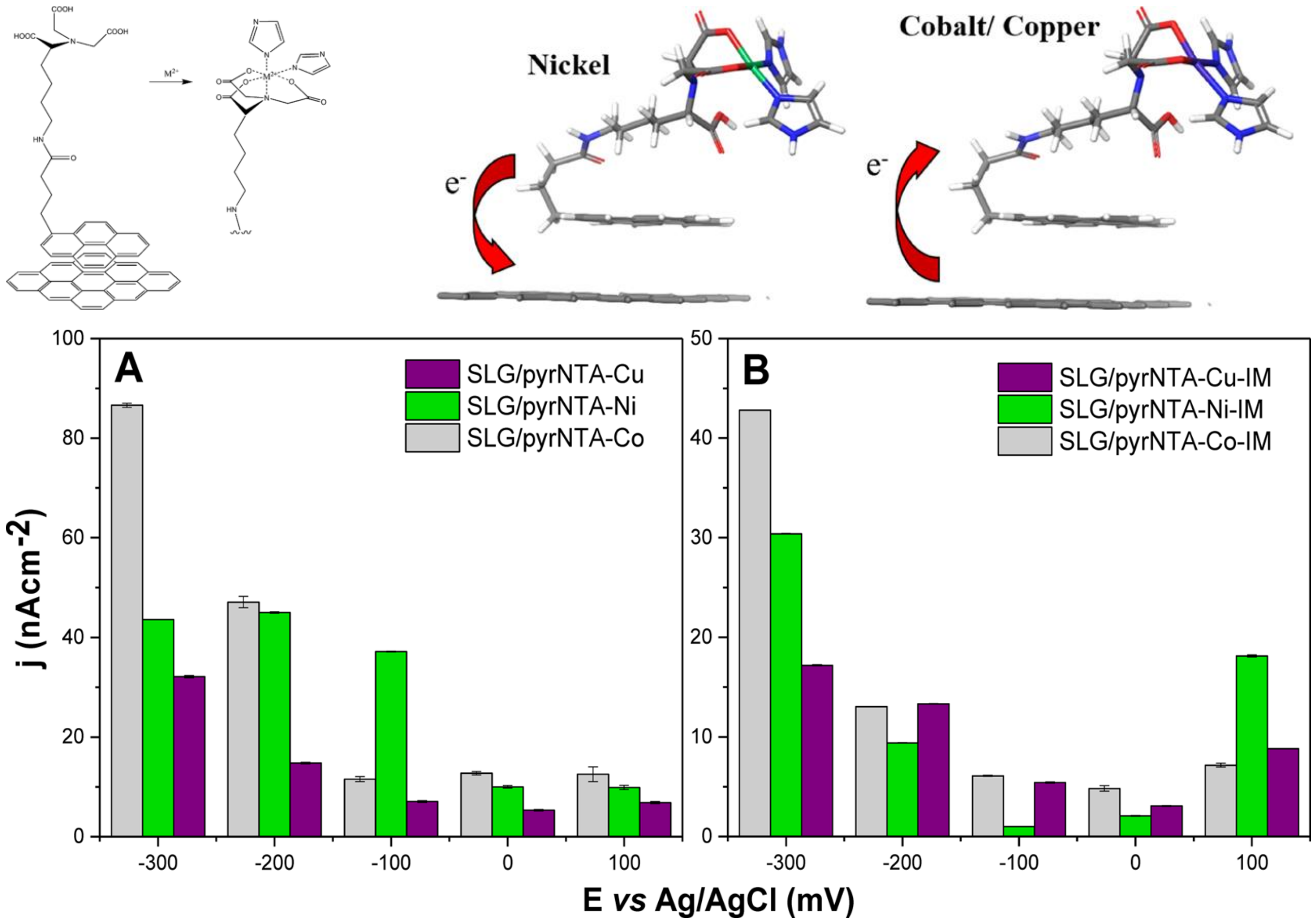
Optimisation of DET:
Role of Metal Redox Centres at the Bio-organic Interface



(1) Pyrene-nitrilotriacetic acid SAM enforces a direct electron transfer from graphene to SAM, (2) Addition of Ni^{2+} cation and imidazole reverses the charge transfer direction.

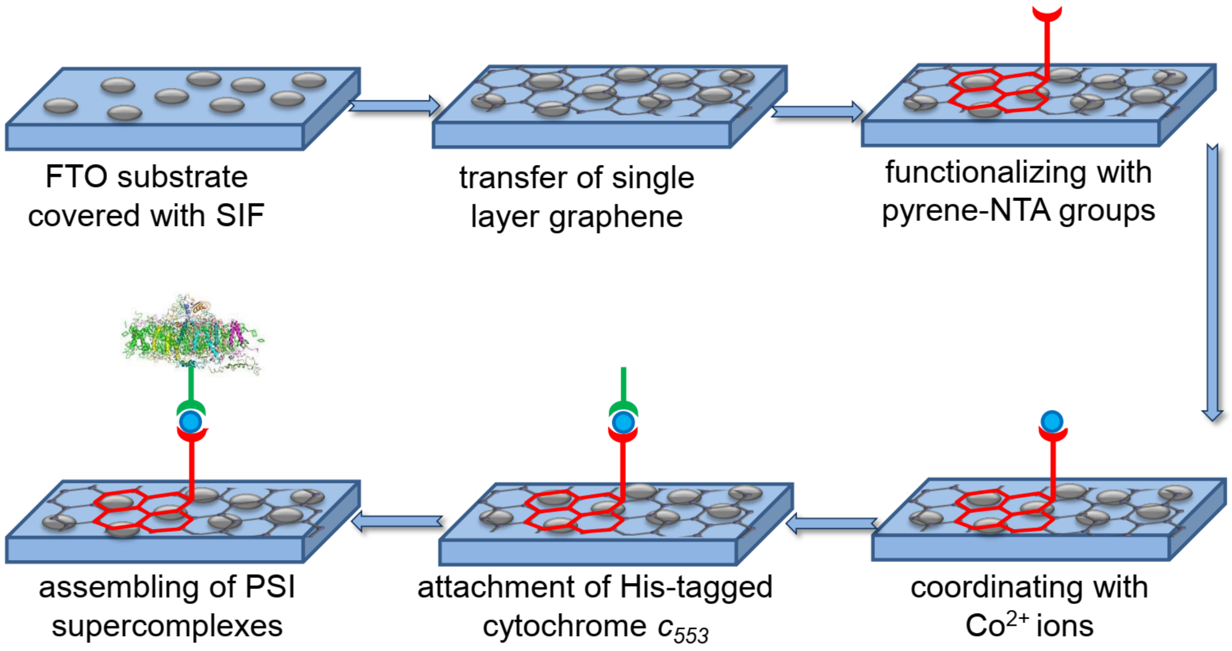
Silvio Osella, Małgorzata Kiliszek, Ersan Harputlu, Cumhur G. Unlu, Kasim Ocakoglu, Joanna Kargul*, Bartosz Trzaskowski (2018)*
J. Mater. Chem. C, 6, 5046-5054

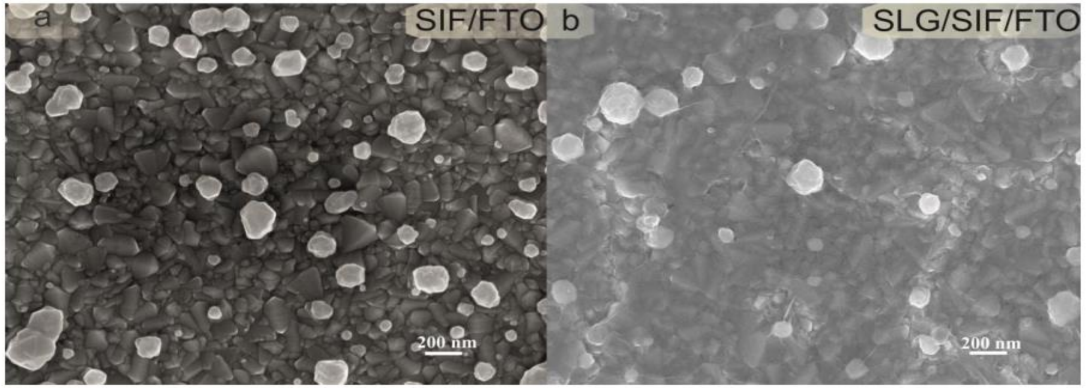
Modification of Fermi Energy Levels of Conductive Pyrene-NTA-Me^{2+} SAM

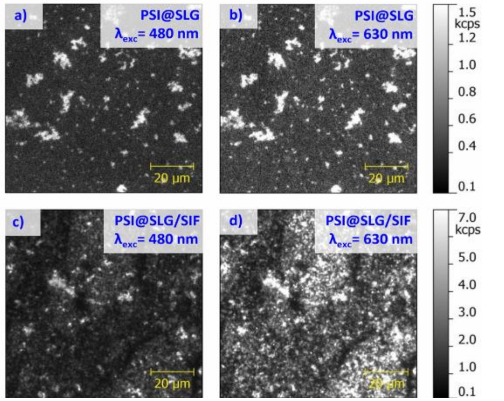


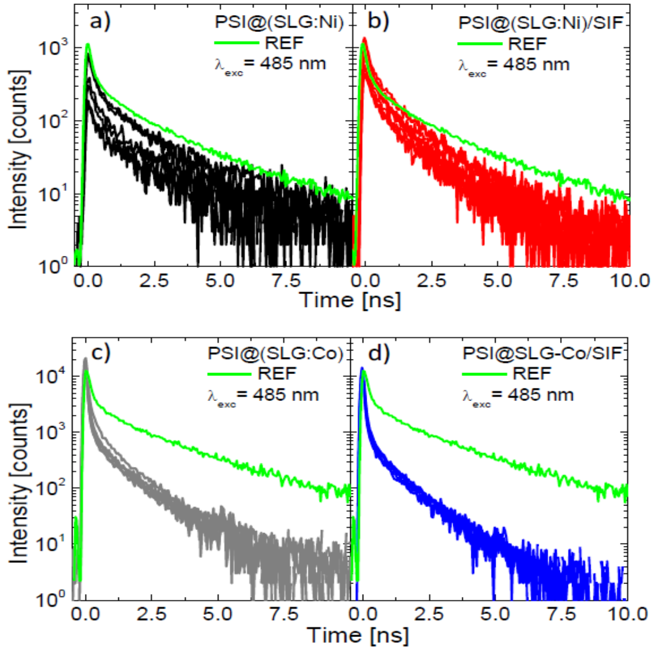
Silvio Osella, Małgorzata Kiliszek, Ersan Harputlu, Cumhur G. Unlu, Kasim Ocakoglu, Bartosz Trzaskowski, Joanna Kargul* (2019)*
J. Phys. Chem. C, 123, 8623−8632

Improved Energy Transfer by Plasmonic Enhancement of Absorption and Application of Metal Centres at the Bio-organic Interface



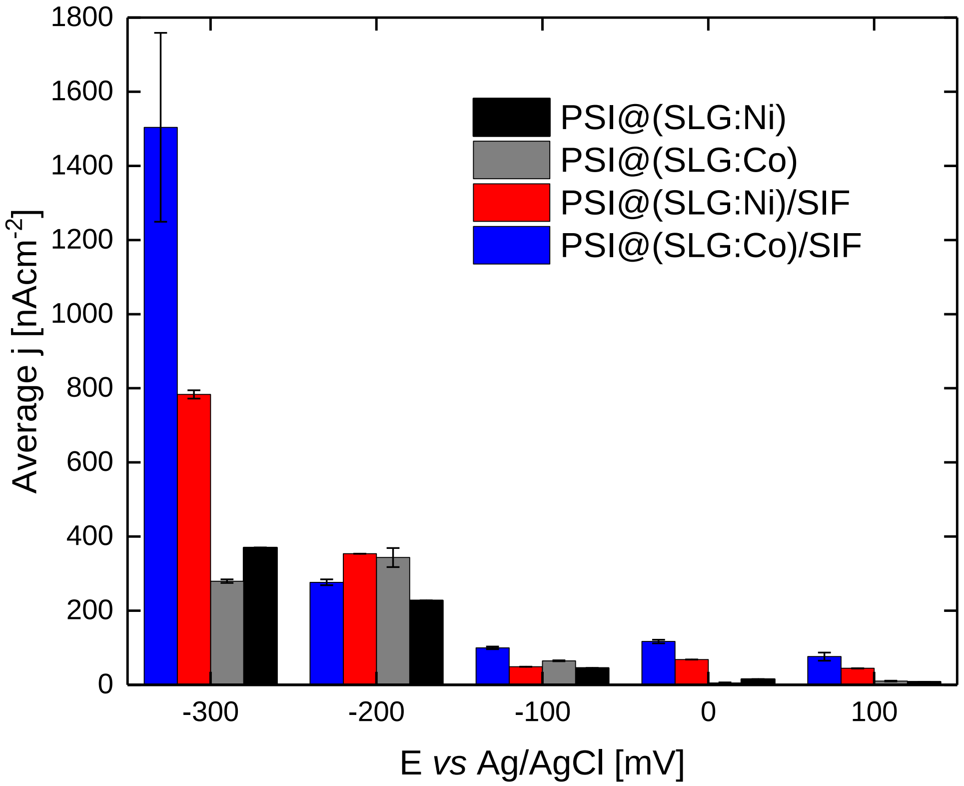


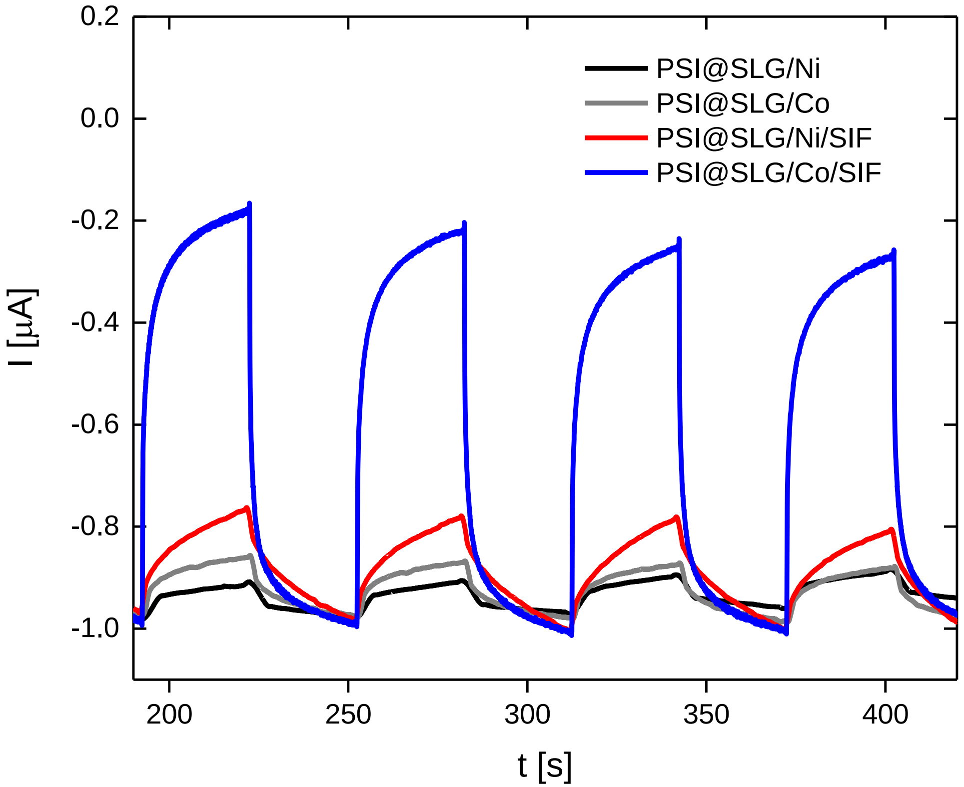




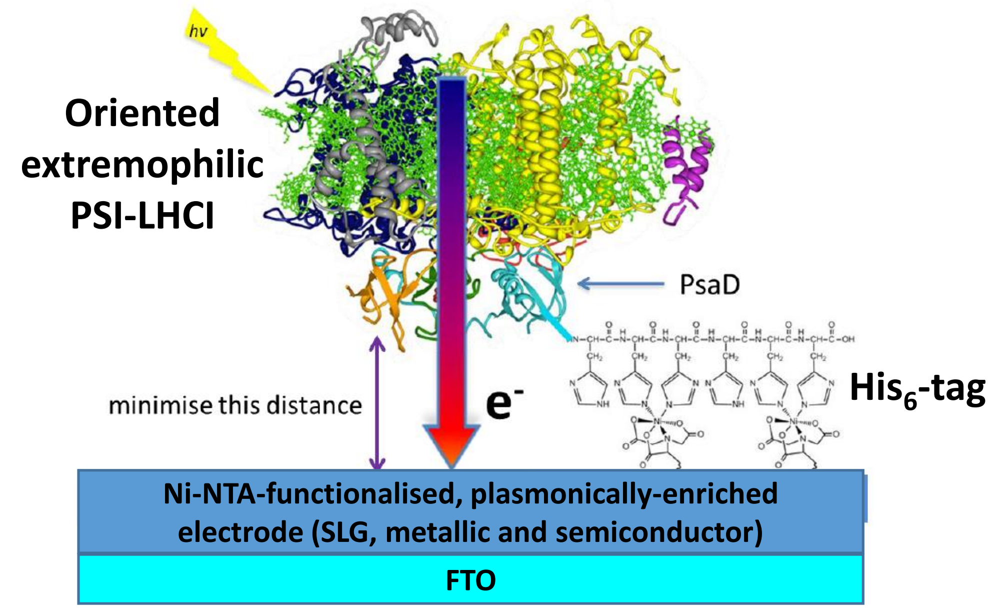
Kiliszek et al submitted

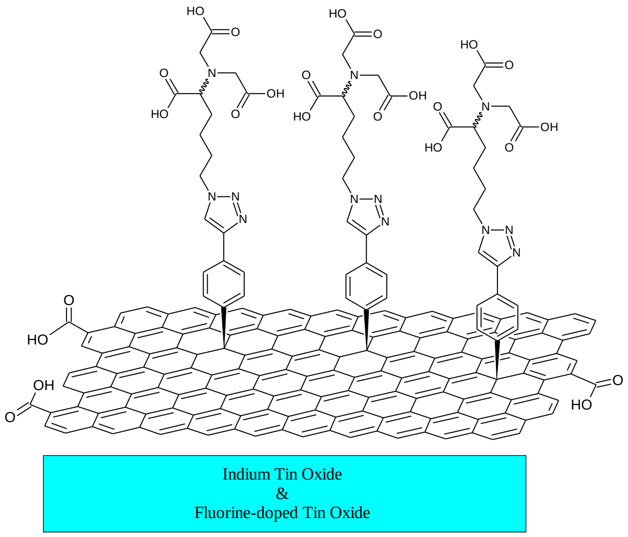
Improved Photocurrent Output by Application of Specific Redox Metal Centres and Plasmonic Nanostructures at the Bio-organic Interface





Kiliszek et al submitted





Summary:

A rational approach for construction of **novel biohybrid architectures**:

- **Attachment** ultrastable extremophilic PSI in an **oriented** manner to the functionalized graphene, metallic and semiconductor electrodes.
- Obtained **homogenous coverage** of the electrode, as well as better control of orientation of the light harvesting proteins.
- Improved performance of the biohybrid device by **plasmonic interactions** with metal nanoparticles in order to selectively enhance absorption of the light-harvesting complexes.
- Exploring the role of specific **redox metal centres in bio-organic interface** for power output improvement.

Acknowledgements

Warsaw (PL):
Małgorzata Kiliszek (SFL)
Patrycja Haniewicz (SFL)
Mateusz Abram (SFL)
Julian Janna Olmos
Bartosz Trzaskowski (LSSCB)
Silvio Osella (LSSCB)
Phillippe Becquet (TEMPUS)
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SUNRISE – SUN-ERGY Consortia

H2020 CSA no. 816336, NCN OPUS14, NCBiR GraphESol/POLTUR, ESF/MNiSW (EuroSolarFuels)

Thank you!