

Implementation of functionalized Fullerene-C70 for connecting Photosystem I with electrodes



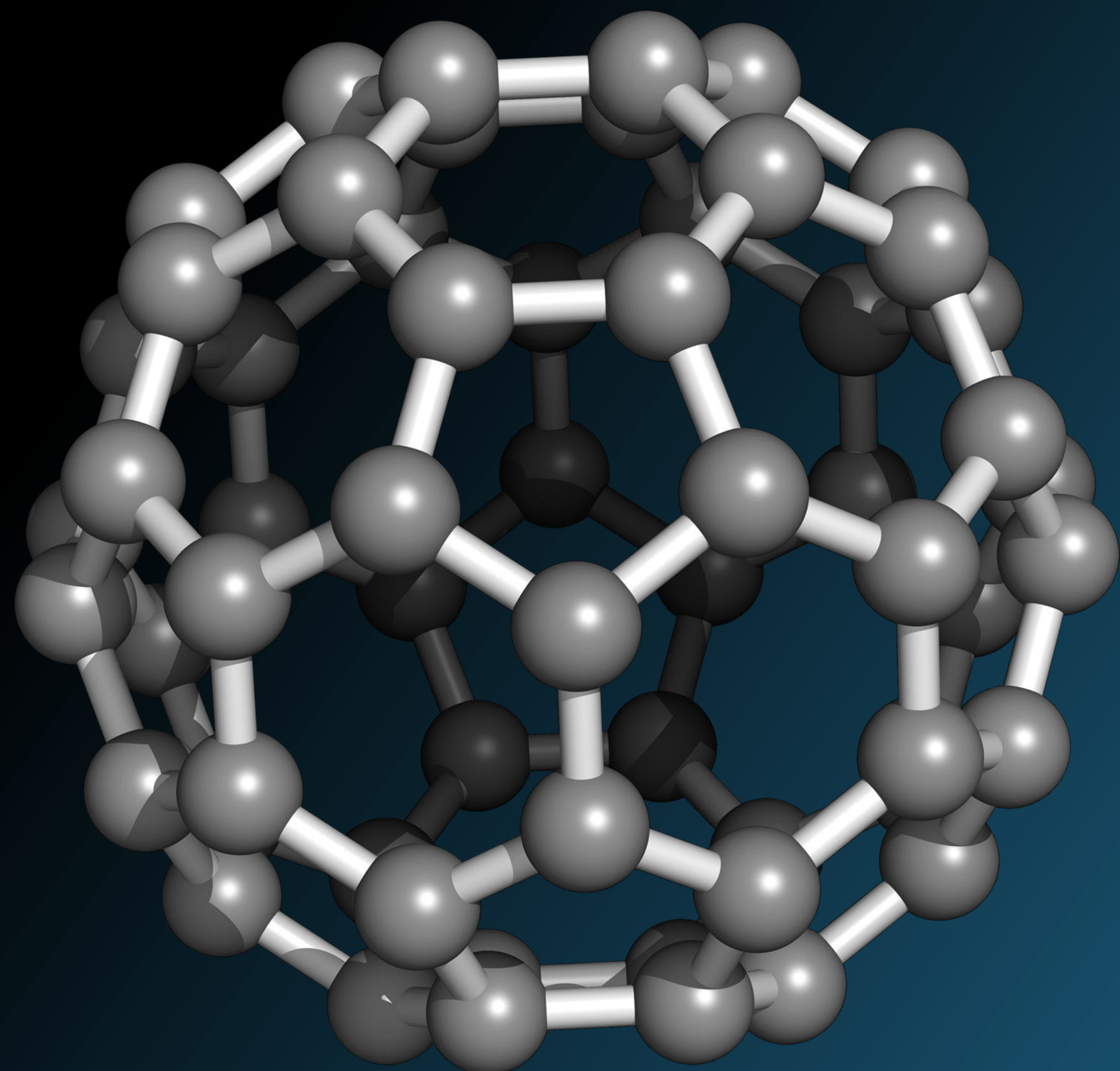
Dmitri Ciornii^{1*}, Marc Riedel¹, Kai Stieger¹, Sven C. Feifel¹, Mahdi Hejazi², Athina Zouni², Fred Lisdat^{1*}

¹ Biosystems Technology, Institute of Applied Life Sciences, Technical University of Applied Sciences Wildau, Hochschulring 1, 15475 Wildau, Deutschland

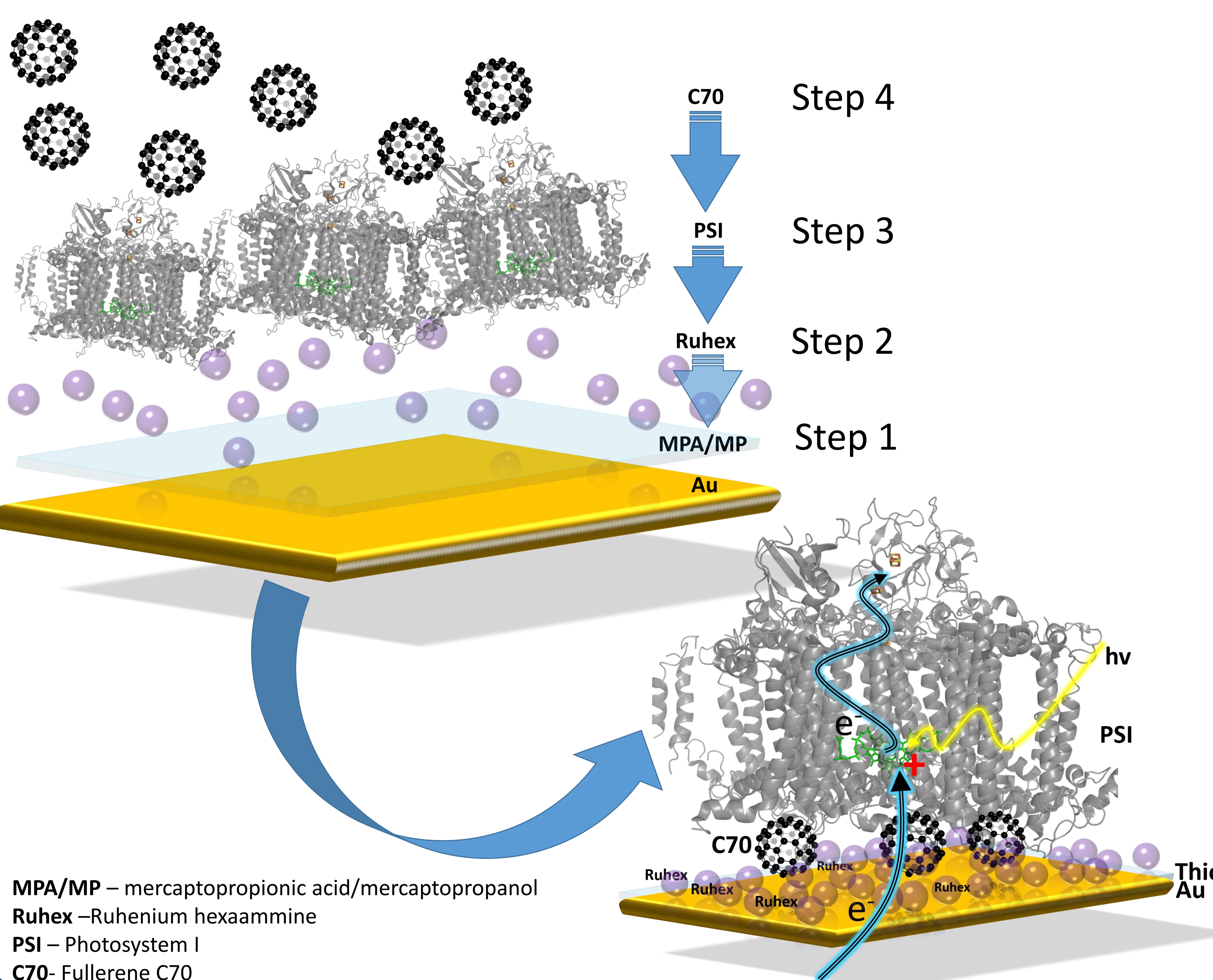
² Institute of Biology, Humboldt-University Berlin, Philippstraße 13, D-10099, Berlin, Germany

INTRODUCTION

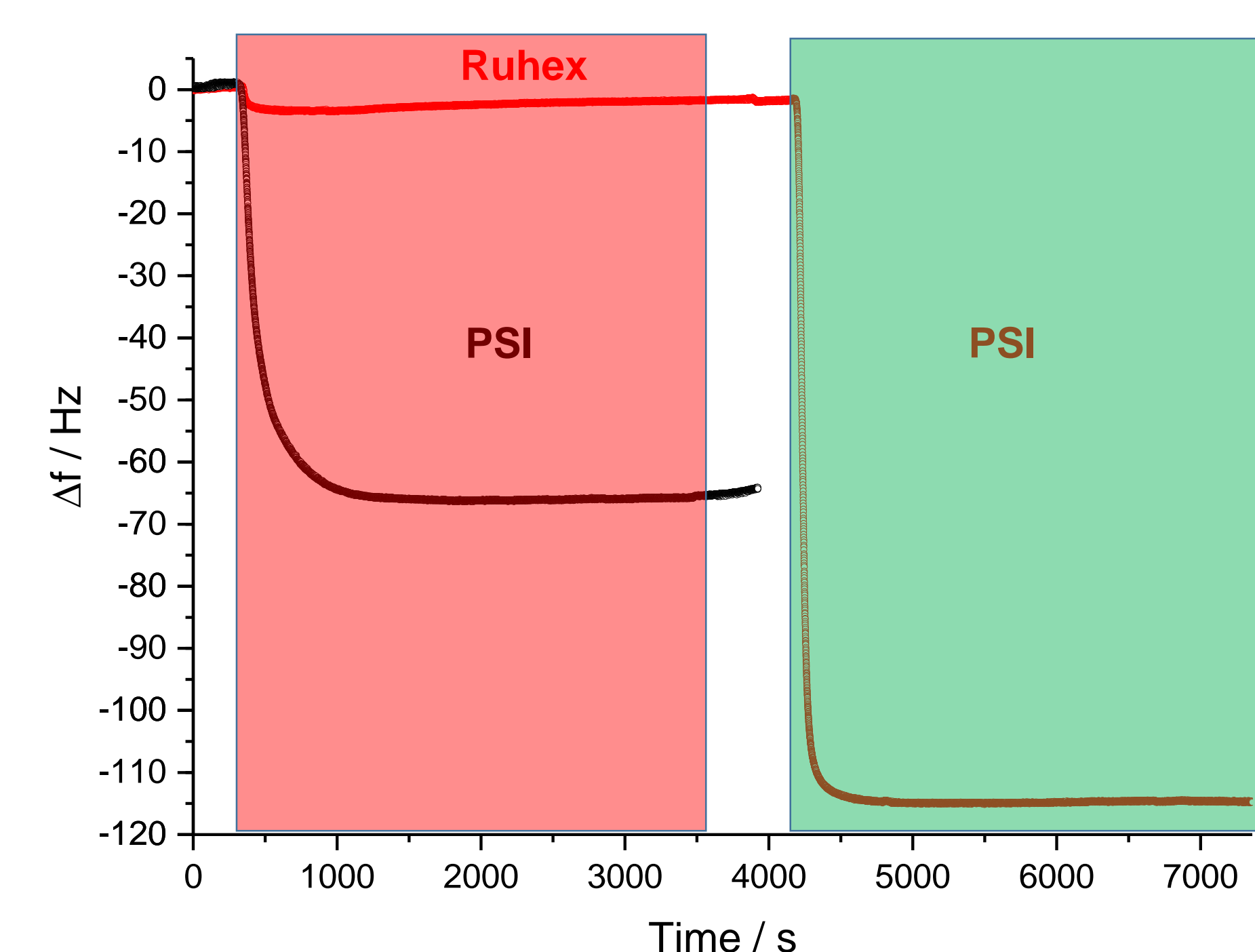
The goal of this study was to construct a photosystem I (PSI)-based photobioelectrode with preferred orientation of PSI molecules for improved performance. We combined a thiol layer approach with a positively charged metal complex (Ruthenium hexaammine - Ruhex) for directed assembly of PSI. We applied a kind of carbon nanoparticles – fullerenes – for enabling good electrical communication between PSI and electrode. Here COOH-modified fullerenes have been used. We can show that such a combination results in a well performing photobioelectrode.



Electrode design



1) Adsorption of components on the mixed thiol layer Quartz crystal microbalance (QCM)

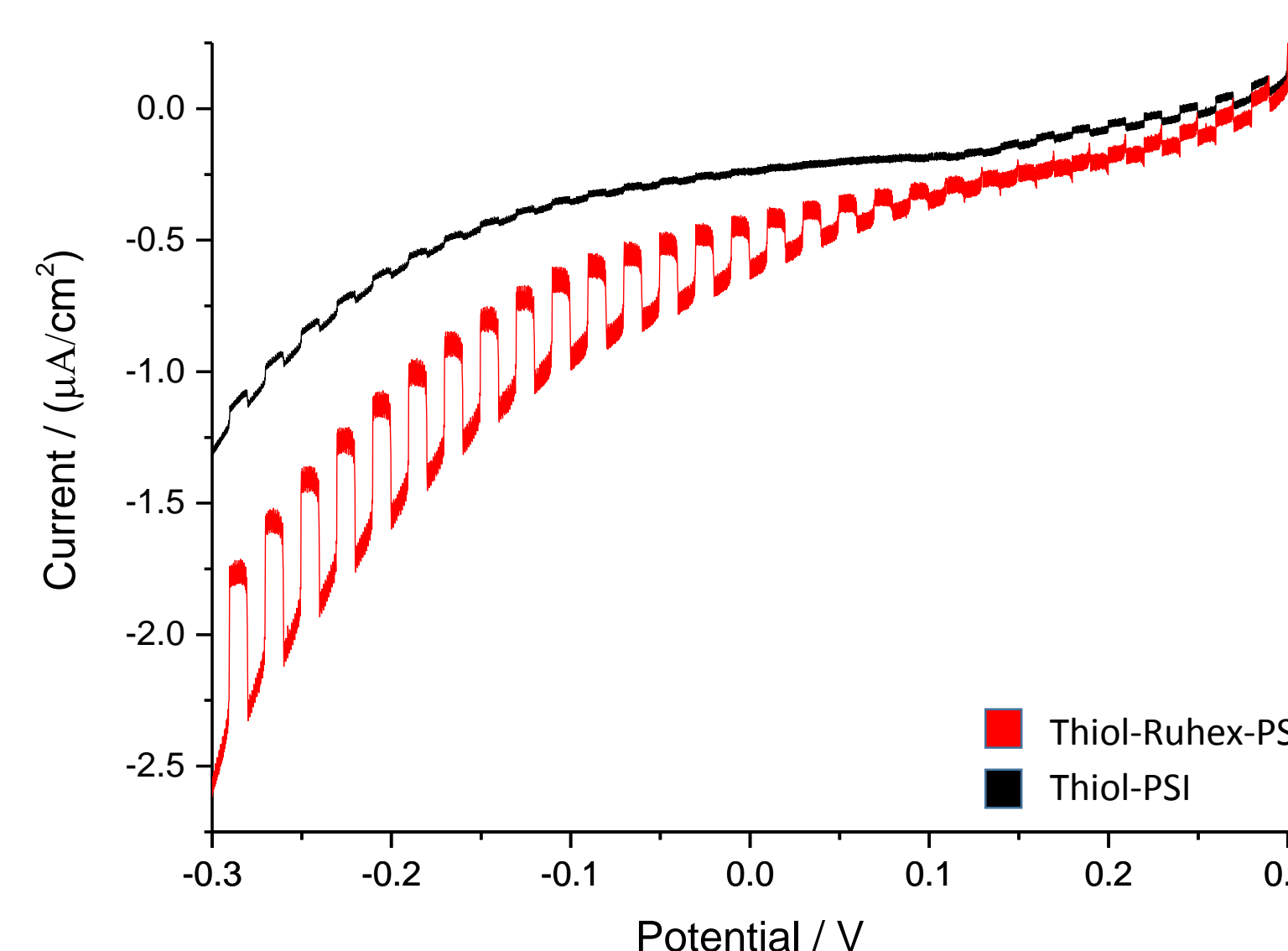


- PSI molecules have been successfully assembled on (MPA/MP) surface (black line)
- Positively charged Ruhex has bound to MPA/MP
- On the thiol-Ruhex surface PSI deposition has been further improved (red line)

Experimental conditions:
 - Flow rate 50 µl/min
 - Washing with ddH₂O (before Ruhex assembly) and KPP8 (before PSI assembly)
 - Assembly for 1h

2) Photoelectrochemical characterization of PSI electrodes

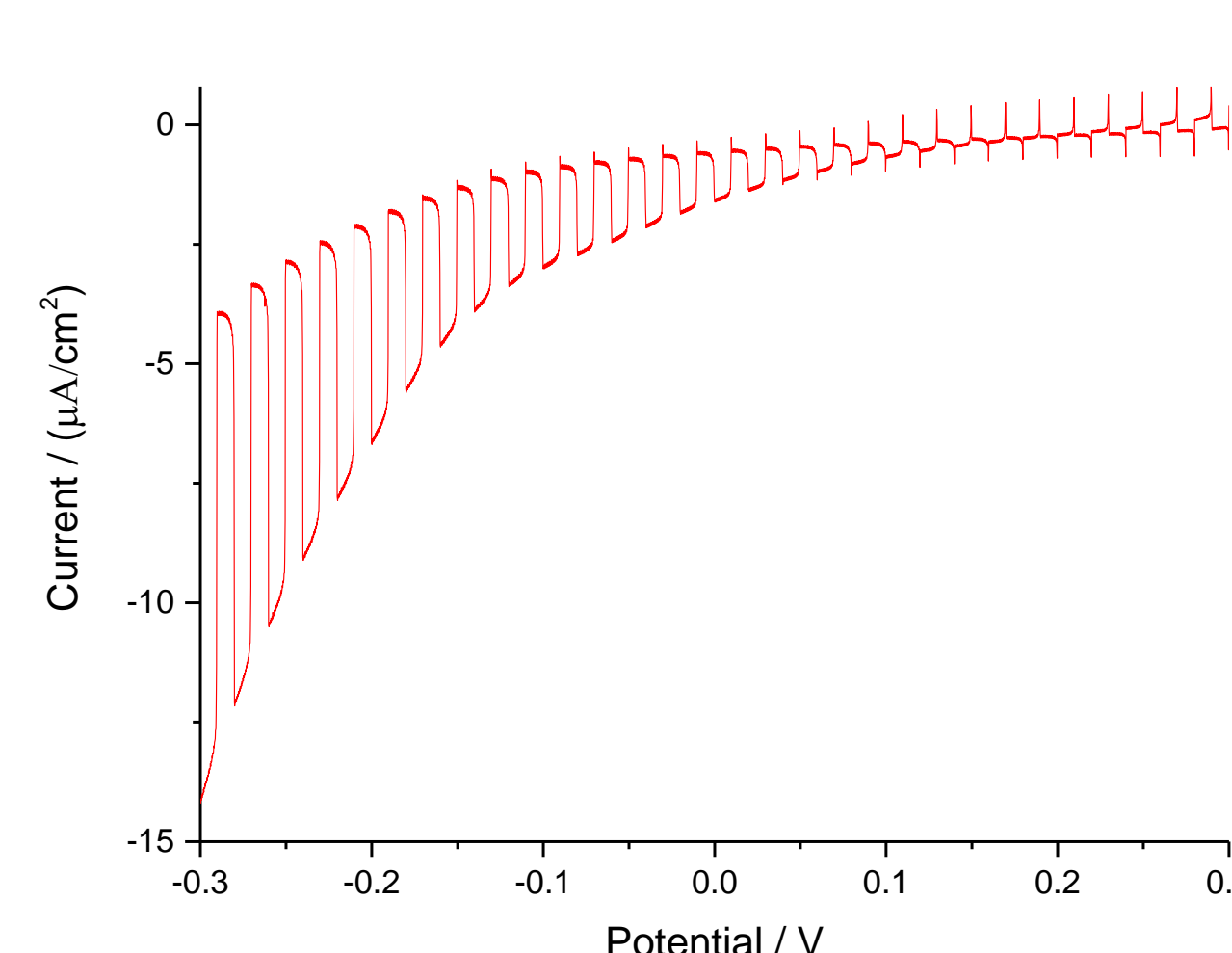
Chopped light voltammetry



- Larger photocurrents magnitude on thiol-Ruhex surface
- The onset potential of cathodic photocurrent has been shifted to a more positive potential as compared to thiol only
- PSI molecules assemble in an oriented way on MPA/MP-Ruhex surface

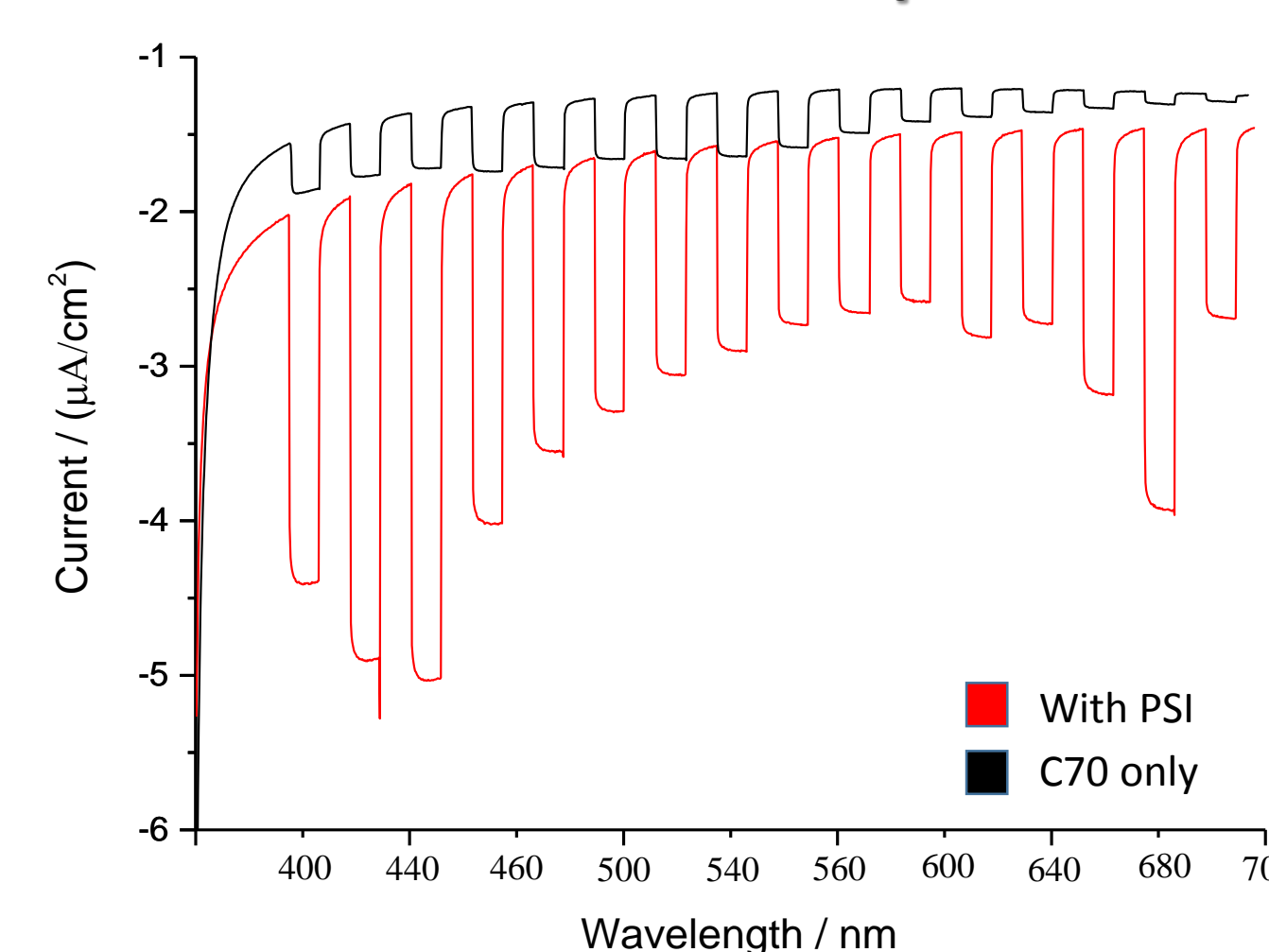
3) Photoelectrochemical characterization of PSI-Fullerene-C70 electrodes

Potential behavior



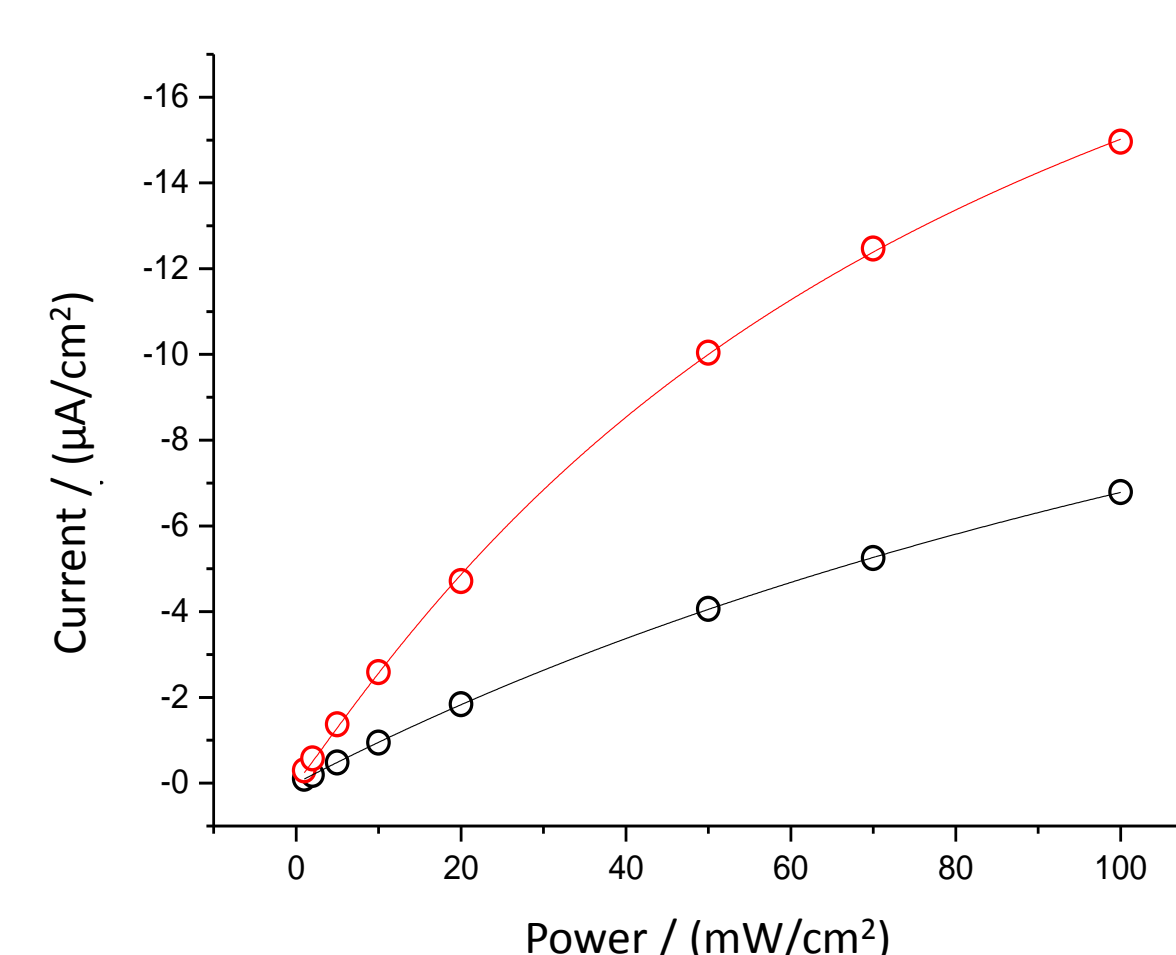
- Improved photocurrent production and even more positive onset

Photo-action spectra



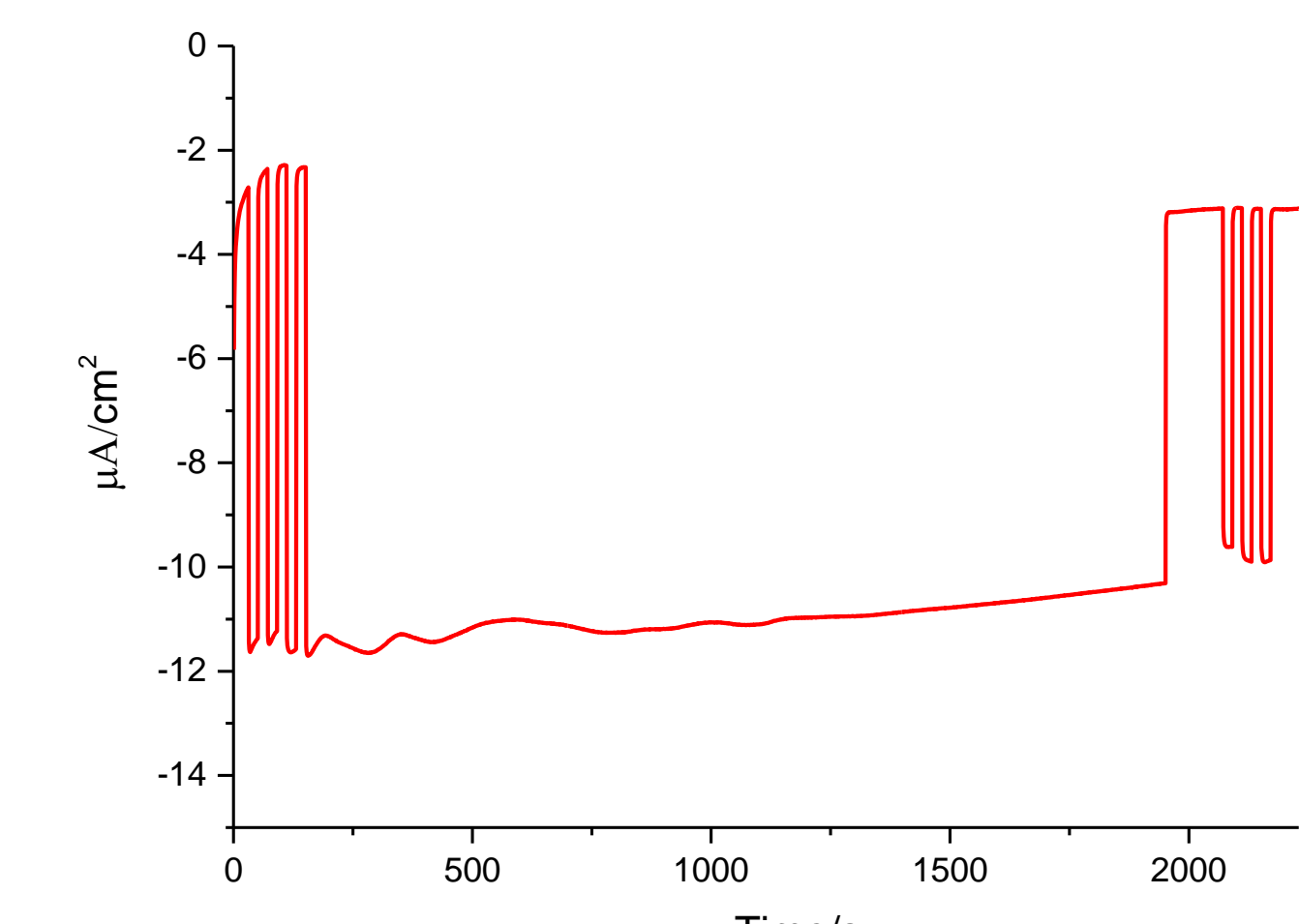
- Variation of wavelength of incident light demonstrates that photocurrents can be assigned to PSI activity, since the photo-action spectra follow UV-Vis spectrum of PSI

Light intensity behavior



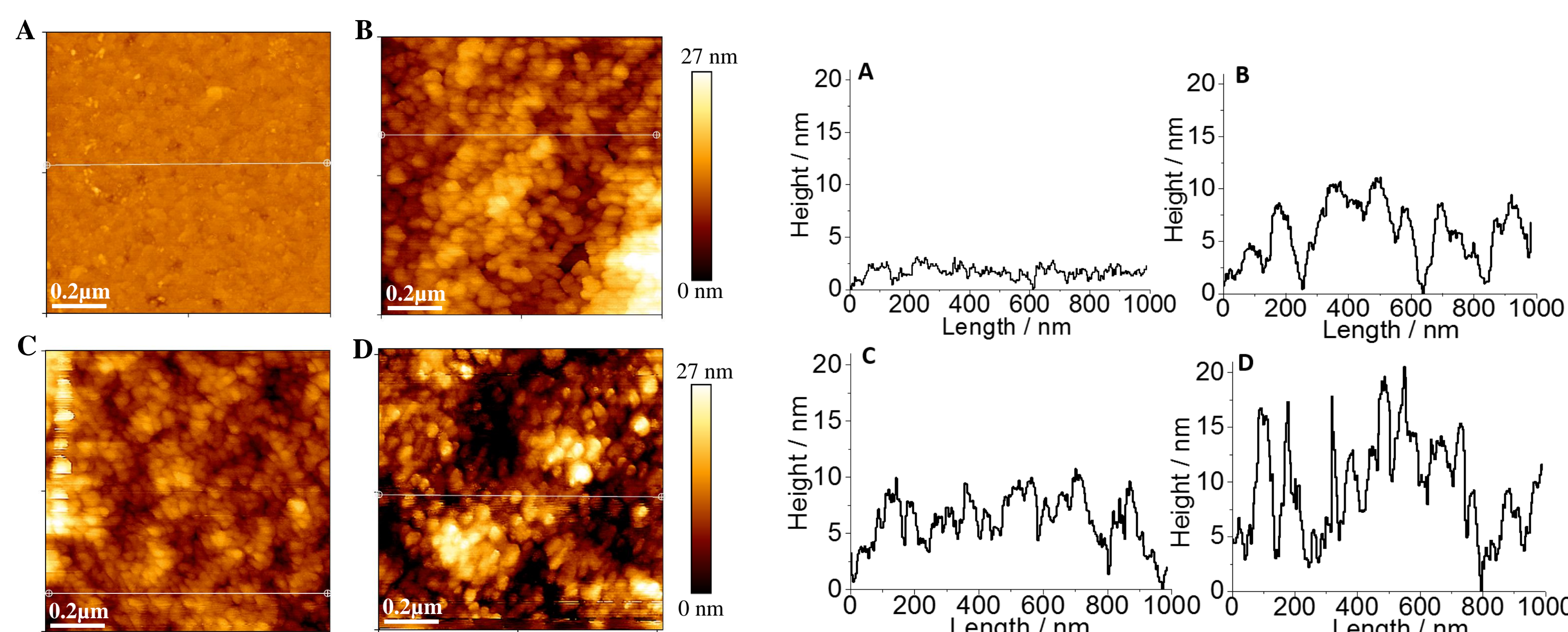
- Photocurrent can be enhanced upon increasing light intensity power
- Additional enhancement upon addition of e-scavenger MV²⁺

Stability experiments



- Rather good stability upon continuous illumination for 30 min

4) Structural investigations Atomic force microscopy (AFM)



- A) Bare gold electrode surface
- B) Deposition of PSI layer on thiol-modified gold
- C) Deposition of PSI on thiol-Ruhex surface
- D) Deposition of C70 layer on thiol-Ruhex-PSI surface

- A) Crosssection of bare gold electrode surface
- B) Crosssection of PSI layer on thiol-modified gold
- C) Crosssection of PSI layer on thiol-Ruhex surface
- D) Crosssection of PSI-C70 layer on thiol-Ruhex surface

CONCLUSIONS

- A functional biohybrid electrode has been constructed and photoelectrochemically characterized
- The orientation of the PSI molecules on the electrode surface has been improved
- Photocathode has been established using oxygen as electron acceptor
- A positive onset potential of the cathodic photocurrents could be obtained

ACKNOWLEDGMENTS

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