

## Supporting Information

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### **Photoelectron Generation by Photosystem II Core Complexes Tethered to Gold Surfaces**

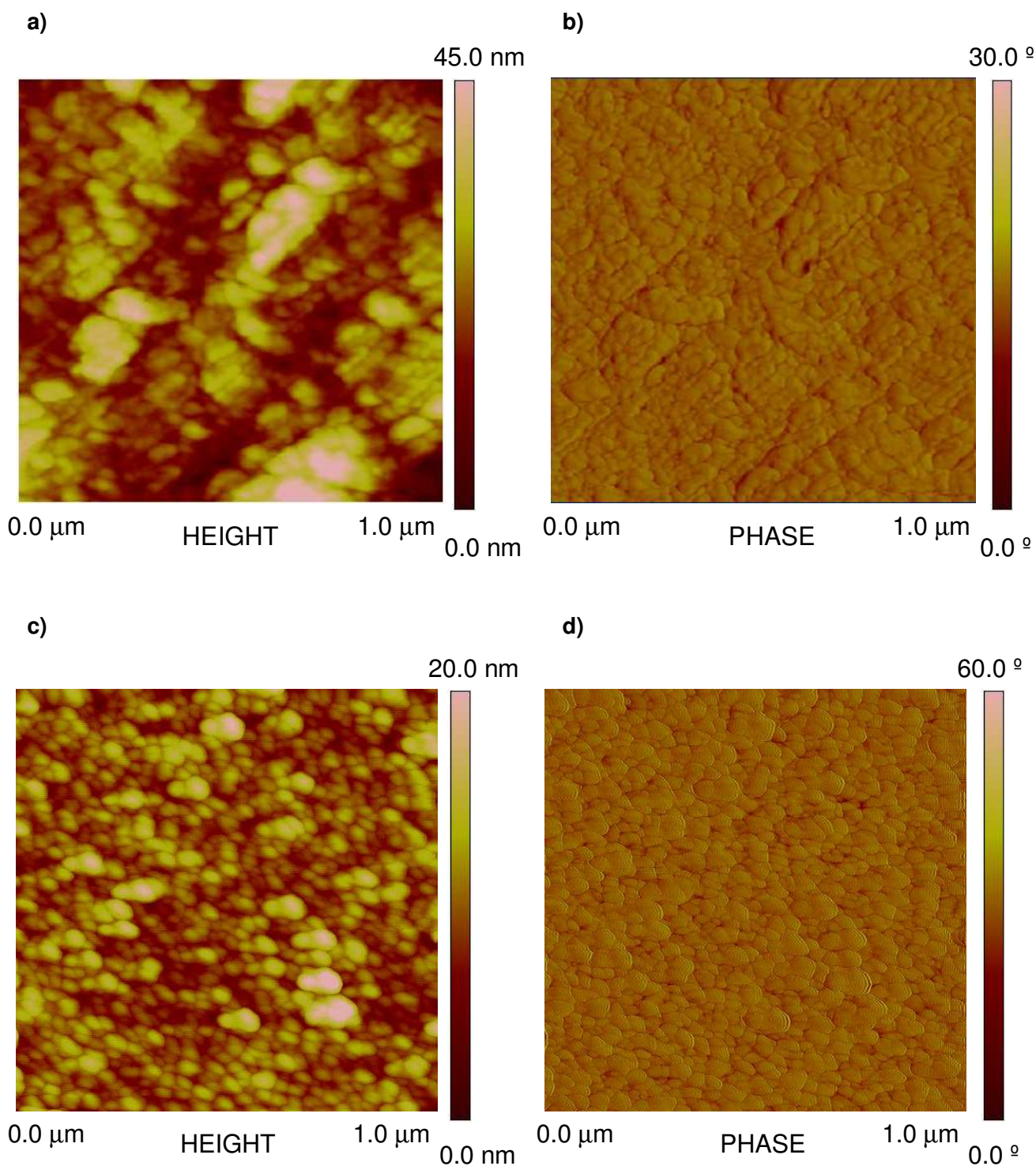
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## Supplementary Information

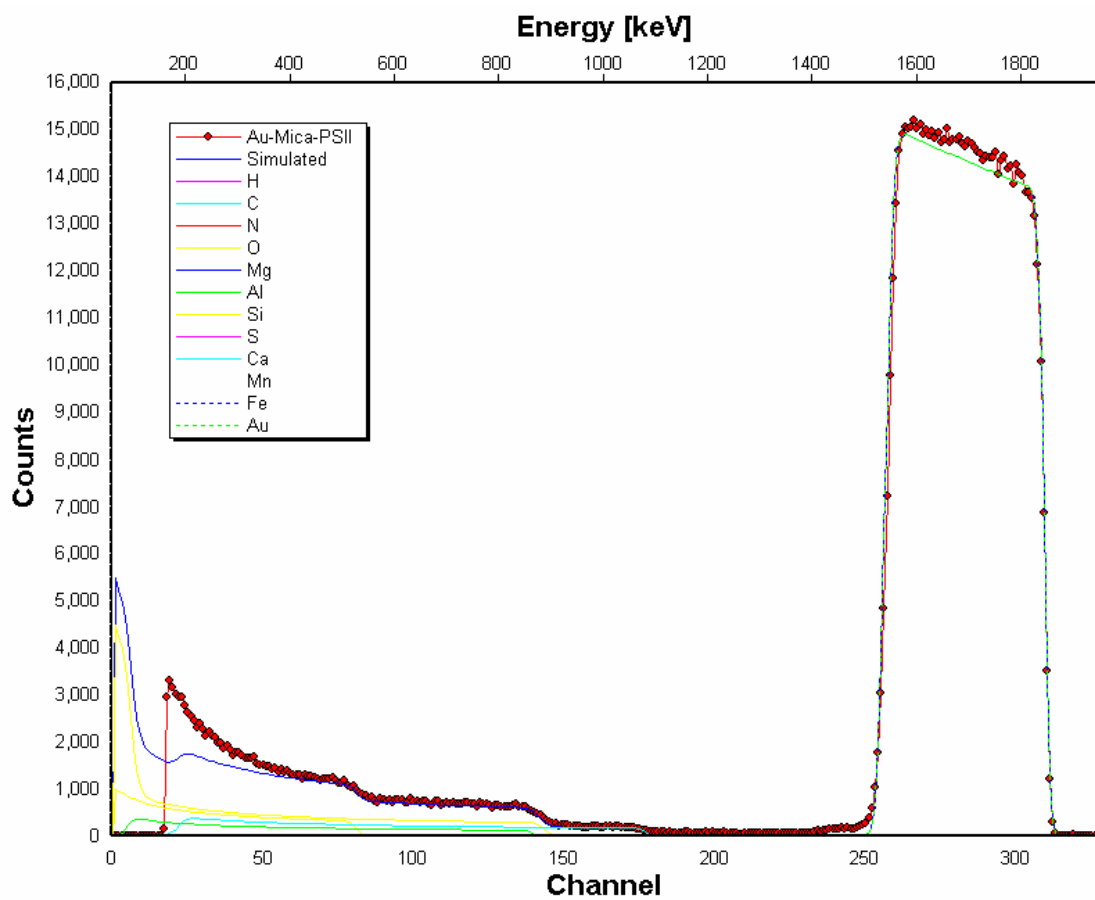
**Comparison with Photovoltaic Devices.** The potential of gold or gold-coated electrodes with oriented PSII core complexes in solid state devices can be evaluated by comparing the expected current density with that of photovoltaic cells (PV). The current density of a PV cell is measured under standard test conditions at  $1000 \text{ W/m}^2$  which include the entire solar spectrum (UV-visible and infrared). A device based on PSII core complexes tethered to gold would be capable of capturing only the visible portion of the solar spectrum with an irradiance of about  $2000 \mu\text{mol quanta}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  ( $500 \text{ W/m}^2$  ca.). Although this irradiance is high in the case PSII core complexes were to be exposed directly to it, if we hypothesize that suitable protection mechanisms could be put in place as in photosynthetic organisms, we can still calculate the maximum achievable current density. For this purpose, we can determine the average cross section of a monomer in the visible region knowing that the cross section at  $470 \text{ nm}$  ( $30 \text{ nm}$  bandwidth) is  $30.9 \text{ \AA}^2$  by considering the intensity variation in the optical spectrum of isolated PSII core complexes. Since the surface density of PSII dimers comprising an ideal monolayer is  $0.74 \text{ pmol/cm}^2$  and the average cross section of a monomer is about  $24.9 \text{ \AA}^2/\text{q}$  in the visible region, we would obtain a current density of  $43 \mu\text{A/cm}^2$  under white light conditions. This current density is three times higher than that electrochemically measured on PSII core complexes tethered to gold<sup>[1]</sup> and approximately two orders of magnitude smaller than the best experimental short circuit current density of an organic PV cell under white light conditions ( $9.39\text{-}16.2 \text{ mA/cm}^2$ ).<sup>[2, 3]</sup> The turnover time per PSII core complex would have to be at least  $3.3 \text{ ms}$ , comparable to the turnover time of  $\sim 4 \text{ ms}$  obtained on the basis of electrochemical data.<sup>[1]</sup> Higher current density levels might be achievable by promoting electron transfer from multilayers of PSII core complexes to the electrode surface, by increasing the cross section, or by modifying the tethering chemistry to enhance charge transfer and separation.

## SUPPLEMENTARY FIGURES AND LEGENDS



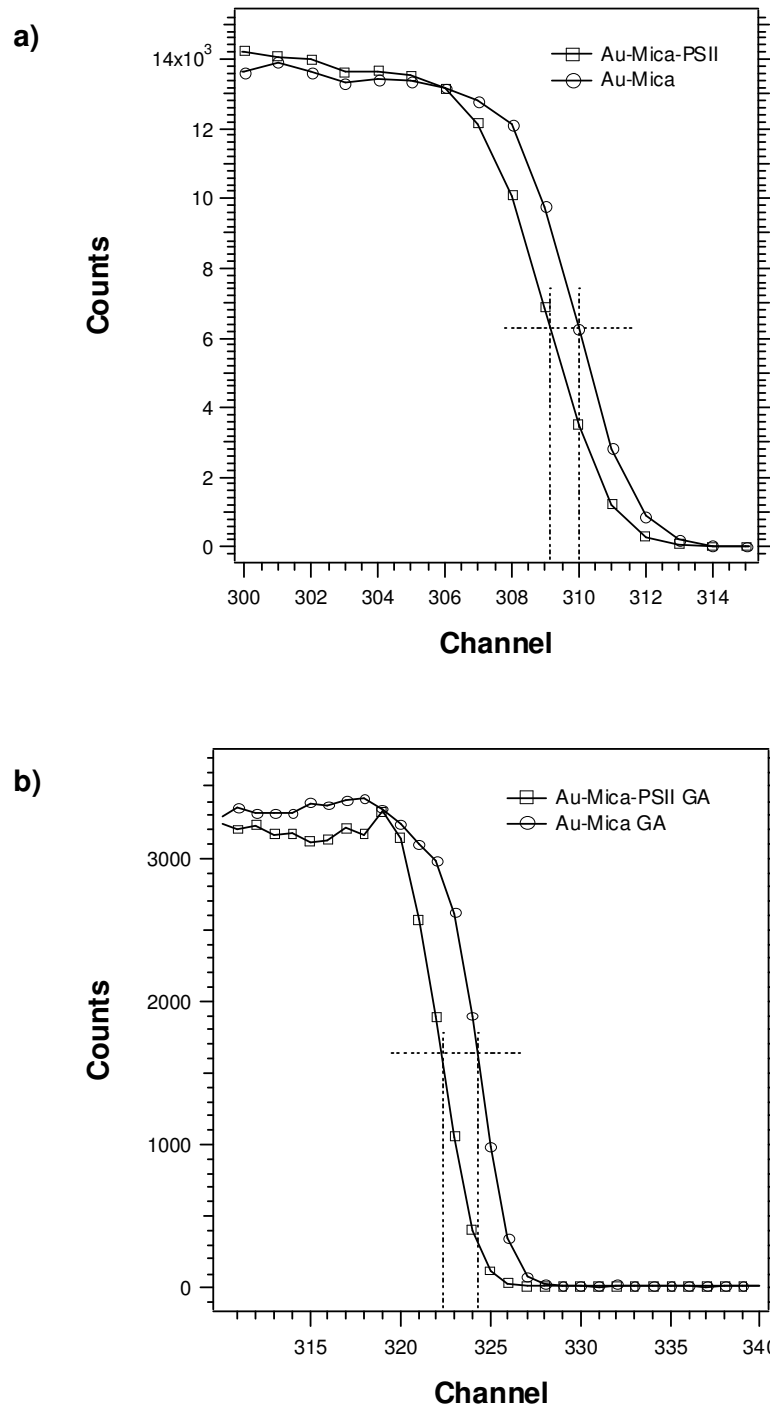
**Fig. 1s**

AFM images of PSII reaction centers complexes on gold surfaces: a) height and b) phase images of PSII core complexes on Au-mica obtained from a PSII suspension having 0.92 mg Chl / mL concentration; c) height and c) phase images of PSII core complexes on Au-Si substrate obtained from a PSII suspension having 0.10 mg Chl / mL concentration.



**Fig. 2s**

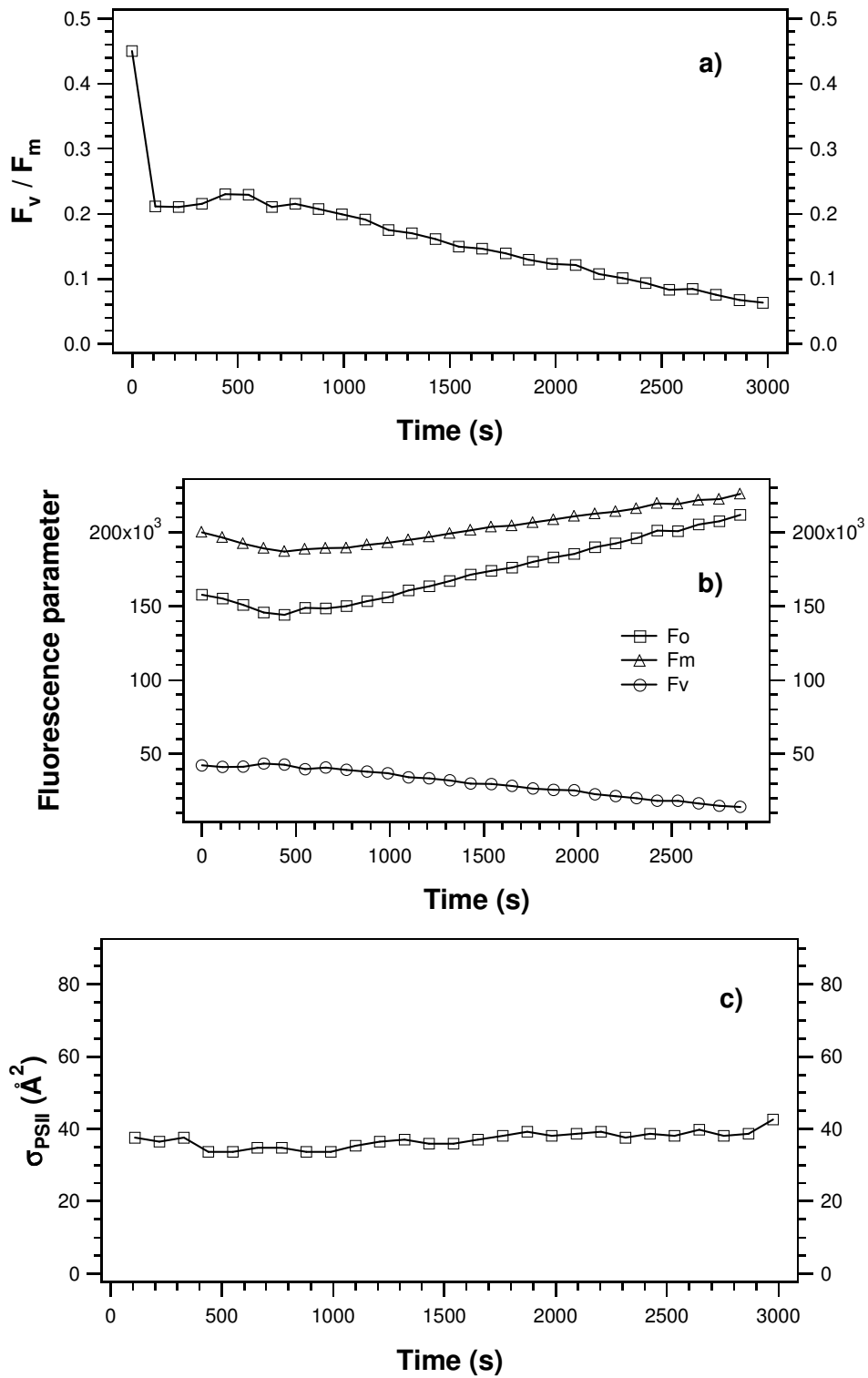
RBS measurements of PSII core complexes on gold-coated mica. The experimental signal intensity profiles vs channel number is simulated on the basis of the protein atomic composition.



**Fig. 3s**

RBS measurements of PSII core complexes on gold-coated mica. The gold edge shift in the signal intensity profiles vs channel number observed by using a) backscattering and b) glancing angle detection.

**Fig. 3s**



**Fig. 4s**

Variation of the fluorescence parameters *versus* time to assess the stability *in vitro* (quartz cuvette) of isolated PSII core complexes from *Thermosynechococcus elongatus* cells: a)  $F_v/F_m$  vs. time; b)  $F_o$ ,  $F_m$ ,  $F_v$  vs. time (initial point of curve 5 is not included); c)  $\sigma_{PSII}$  vs. time. Measurements of each point were conducted by using the following sequence  $(\delta-t_a)_{50-t_b}$ -STF(300 $\mu$ s) with  $\delta = 300\mu$ s,  $t_a = 2$ s;  $t_b = 30$ s with the exception of the initial point in Fig. 5 a, which was obtained by a STF(300 $\mu$ s)- $\tau$ .

## SUPPLEMENTARY TABLE

**Table 1s. RBS analysis of PSII core complexes from *T. elongatus* cells onto gold surfaces.**

Sample	Original solution	Substrate	Assumed molecular mass	Average Number of Ideal Monolayers and calculated average density of PSII dimers	
1	0.92 mg Chl / mL	Au-Mica	680 kDa	BA: 2.5±0.8 1.82 pmol/cm <sup>2</sup>	GA: 1.6±0.4 1.19 pmol/cm <sup>2</sup>
2	0.92 mg Chl / mL	Au-Mica	500 kDa	BA: 3.9±0.8 2.84 pmol/cm <sup>2</sup>	GA: 2.5±0.4 1.84 pmol/cm <sup>2</sup>
3	0.10 mg Chl / mL	Au-Si	680 kDa	BA: 1.4±0.8 1.04 pmol/cm <sup>2</sup>	GA: 1.3±0.4 0.93 pmol/cm <sup>2</sup>
4	0.10 mg Chl / mL	Au-Si	500 kDa	BA: 2.2±0.8 1.61 pmol/cm <sup>2</sup>	GA: 2.0±0.4 1.45 pmol/cm <sup>2</sup>

BA: Backscattering Angle; GA: Glancing Angle. An ideal monolayer has a density of 0.74 pmol/cm<sup>2</sup>. See text for more details.

## REFERENCES

- [1] A. Badura, B. Esper, K. Ataka, C. Grunwald, C. Wöll, J. Kuhlmann, J. Heberle, M. Rögner, *Photochemistry and Photobiology* **2006**, *82*, 1385-1390.
- [2] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, *Progress in Photovoltaics* **2009**, *17*, 85-94.
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