

# Supporting Information for: Photosystem I Complexes form Remarkably Stable Self-assembled Tunneling Junctions

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## Contents

S1 UV-vis spectra of PSI-LHCI complexes	S-3
S2 Comparison of stability over room temperature between two different PSI complexes in solid-state junctions	S-4
S3 Statistics of EGaIn junctions	S-5
S4 Comparison of rectification between two different PSI complexes in solid-state junctions	S-5
S5 Comparison of current density over time between two different PSI com-	

plexes in solid-state junctions

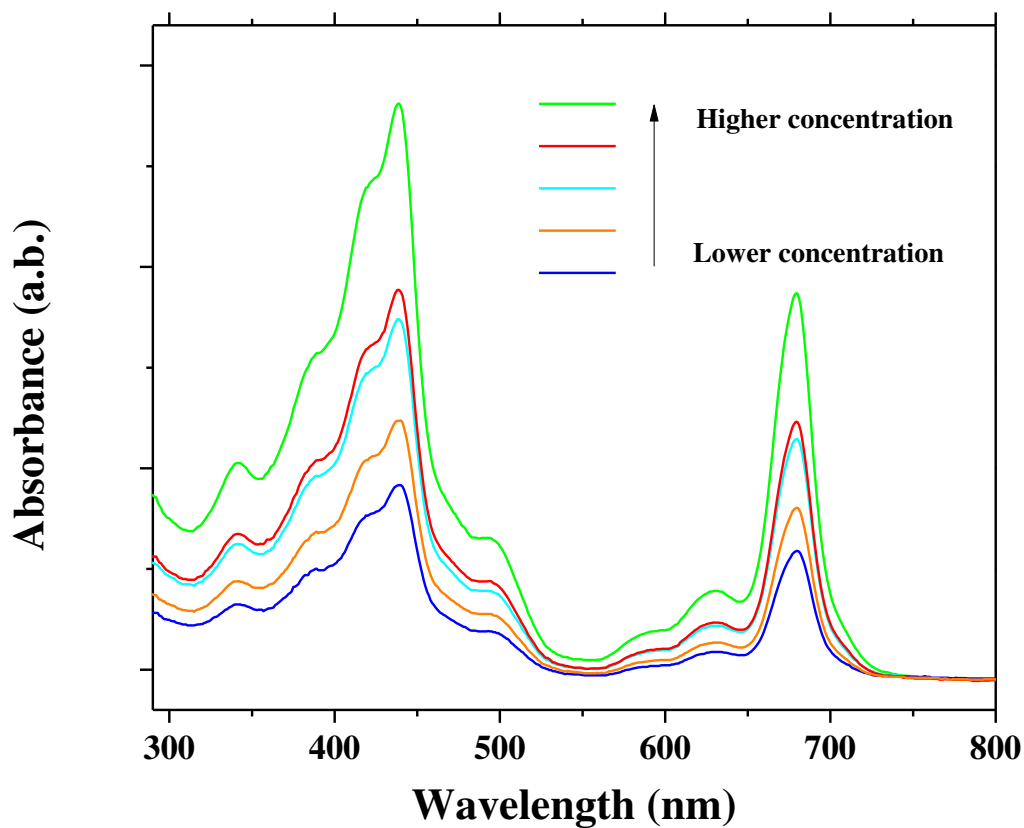
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S6 EGaIn wetting of PSI

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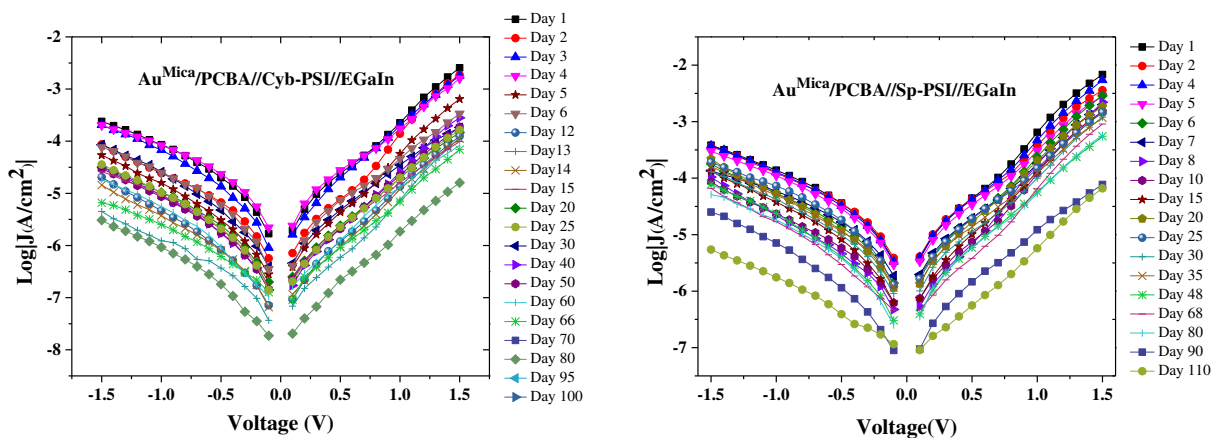
## S1 UV-vis spectra of PSI-LHCI complexes

In this work, during ion exchange chromatography, various solutions were extracted from the column. Absorbance spectra were obtained for the solutions collected at different times. The solutions had different concentrations, and we selected the solution with the highest concentration for device fabrication.



**Figure S1:** UV-vis spectra of PSI-LHCI complexes were gathered from the chromatography column at different times. Throughout the experiment, the concentration of the solution increased, as indicated by the progression from the blue line to the green line.

## S2 Comparison of stability over room temperature between two different PSI complexes in solid-state junctions



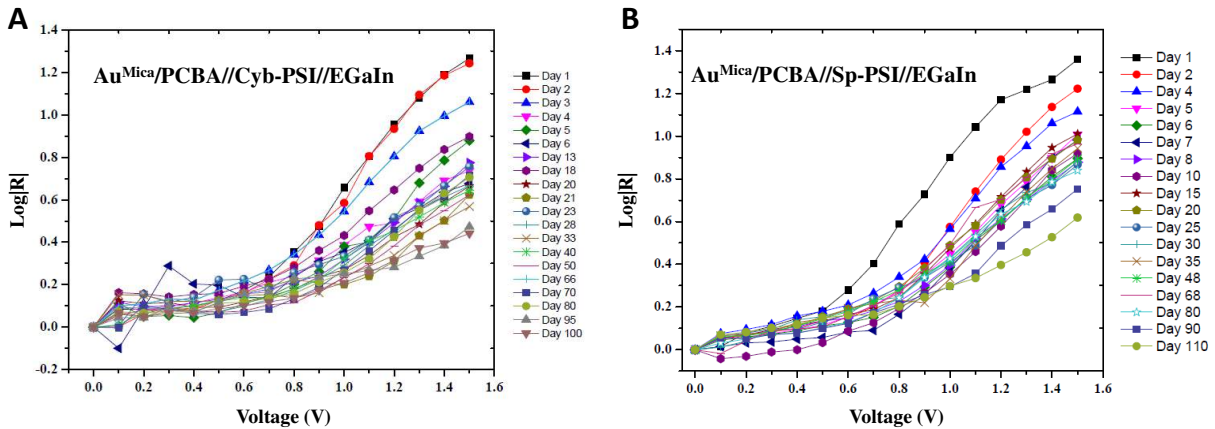
**Figure S2:** Room-temperature current density-voltage characteristics of A)  $\text{Au}^{\text{Mica}}/\text{PCBA}/\text{Cyb-PSI}/\text{EGaIn}$  junctions and B)  $\text{Au}^{\text{Mica}}/\text{PCBA}/\text{Sp-PSI}/\text{EGaIn}$  junctions during 100 d and 110 d respectively. The conductance of devices fabricated of  $\text{Au}^{\text{Mica}}/\text{PCBA}/\text{Cyb-PSI}/\text{EGaIn}$  and  $\text{Au}^{\text{Mica}}/\text{PCBA}/\text{Sp-PSI}/\text{EGaIn}$  junctions decreased after 100 d and 110 d respectively.

### S3 Statistics of EGaIn junctions

**Table S1:** Statistics of EGaIn junctions comprising the samples studied in the stability measurements of this work over around four months.

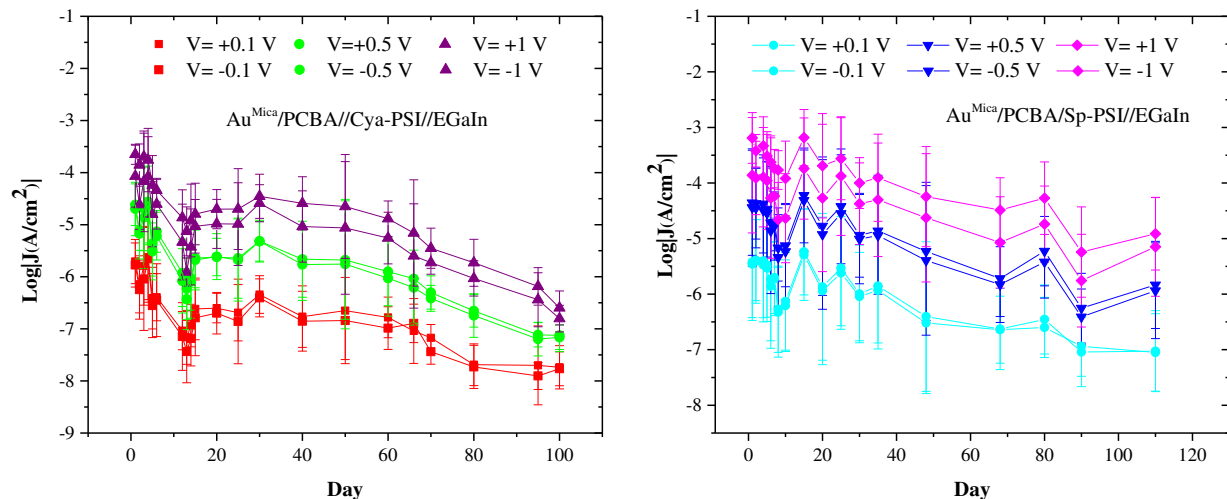
		Junctions	Shorts	Traces	Yield (%)
$\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Cyb-PSI}//\text{EGaIn}$	Day1	60	0	600	100
$\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Sp-PSI}//\text{EGaIn}$	Day1	60	0	600	100
$\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Cyb-PSI}//\text{EGaIn}$	Day100	60	30	600	95
$\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Sp-PSI}//\text{EGaIn}$	Day110	60	18	600	97

### S4 Comparison of rectification between two different PSI complexes in solid-state junctions



**Figure S3:** Plots of  $\log |R|$  versus voltage of A)  $\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Cyb-PSI}//\text{EGaIn}$  junctions and B)  $\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Sp-PSI}//\text{EGaIn}$  junctions during during 100 d and 110 d respectively. The rectification ratio decreases for both  $\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Cyb-PSI}//\text{EGaIn}$  and  $\text{Au}^{\text{Mica}}/\text{PCBA}//\text{Sp-PSI}//\text{EGaIn}$  junctions over time.

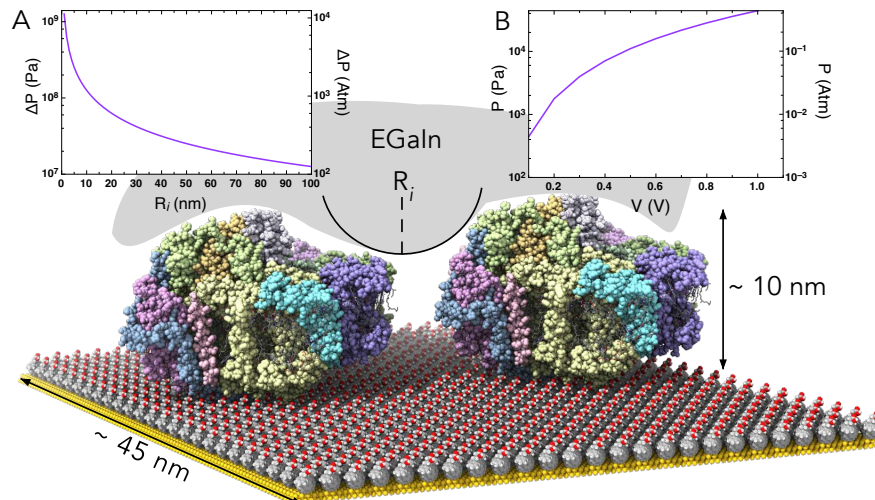
## S5 Comparison of current density over time between two different PSI complexes in solid-state junctions



**Figure S4:** Variation of current density with time at different applied voltages for A)  $\text{Au}^{\text{Mica}}/\text{PCBA}/\text{Cya-PSI}/\text{EGaIn}$  junctions and B)  $\text{Au}^{\text{Mica}}/\text{PCBA}/\text{Sp-PSI}/\text{EGaIn}$  junctions during 100 d and 110 d respectively.

## S6 EGaIn wetting of PSI

To explain why PSI does not need to pack as densely as small-molecules to prevent shorting, two Sp-PSI complexes on a SAM of PCBA are depicted in Fig. S5 along with plots of the relevant pressures at that length-scale. The Laplace pressure at the EGaIn interface between PSI complexes (Sp-PSI or Cya-PSI) can be estimated using Eq. (S1) using the surface tension  $\gamma = 630 \text{ mN m}^{-1}$  from Ref. 1. In this context  $P_o$  is atmospheric pressure and  $P_i$  is the internal pressure of EGaIn at the radius of curvature  $R_i$ . Due to the large value of  $\gamma$ , EGaIn will



**Figure S5:** An illustration of two Sp-PSI complexes on a SAM of PCBA depicting the radius of curvature that would have to occur for EGaIn to penetrate between the complexes. The insets plot of the pressure required to achieve radii between 1 to 100 nm using a surface tension value of  $630 \text{ mN m}^{-1}$  taken from Ref. 1 (A) and the electrostatic pressure created when a bias is applied (B).

not even spontaneously flow through posts placed  $10 \mu\text{m}$  apart at  $\Delta P \leq 1 \text{ Atm}$ .<sup>2</sup> The plot in Fig. S5A shows that PSI complexes spaced to produce  $R_i = 1$  to  $100 \text{ nm}$  would require  $\Delta P = 1 \times 10^2$  to  $1 \times 10^4 \text{ Atm}$  to form. These values far exceed the pressure drops generated from gravity,<sup>3</sup> meaning EGaIn will not spontaneously flow.<sup>1</sup>

$$\Delta P = P_i - P_o = \gamma \left( \frac{1}{R_i} + \frac{1}{R_o} \right) = \gamma \frac{2}{R_i} \quad (\text{S1})$$

The analysis above explains how EGaIn can wet monolayers of PSI without penetrating the space between the complexes and shorting to the underlying SAM of PCBA, but are seemingly belied by the common observation that pinholes in SAMs of small molecules readily precipitate shorts in EGaIn junctions. Equation (S2) is the additional pressure created by the

voltage drop across a junction, where  $E$  is the electric field. For SAMs of small molecules of  $\sim 1$  nm in thickness,  $P \approx 4 \times 10^4$  to  $4 \times 10^6$  Pa at the typical range of applied bias of  $V = 0.1$  to  $1$  V. While, due to the thickness of the PSI complexes,  $P \approx 4 \times 10^2$  to  $4 \times 10^4$  Pa as shown in Fig. S5B. This simple analysis does not take into account the migration of Au atoms and other nano-scale phenomena that occur in molecular junctions, but it is consistent with the observation that monolayers of PSI lead to extraordinarily high yields of non-shortening junctions; that those yields remain high even as PSI degrades (and stop rectifying current); and that shorts are observed at bias.

$$P = \frac{\varepsilon_0}{2} E^2 \tag{S2}$$



## References

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