Supporting Information:

Molecular Interfaces for Plasmonic Hot Electron

Photovoltaics

F. Pelayo García de Arquer, Agustín Mihi[†], Gerasimos Konstantatos*

F. P. García de Arquer, Prof. G. Konstantatos: ICFO - Institut de Ciències Fotòniques, Mediterranean Technology Park 08860 Castelldefels, Barcelona, Spain

† present Address: Department of Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, 43007 Tarragona, Spain

Contents:

S1. Surface passivation and Voc-workfunction shift correlation

S2. Binding of alkanoic acid molecules to TiO₂ and SAM properties

S3. Performance statistics of the aliphatic carboxylic acids

S4. Gold versus silver electrodes for VA

S5. Voc – contact potential difference for HOOC-C₆H₄-X molecules

S6. Performance statistics of the conjugated carboxylic acids

S7. Summary of Au devices performance

References

S1. Surface passivation and Voc-workfunction shift correlation



Figure S1. Correlation of the open-circuit voltage and workfunction shift as measured with contact potential differentiometry (CPD). The shift is calculated with respect to a bare TiO_2 sample. The Fermi level shift arises as a consequence of passivation of surface states, due to the adsorption of the SAM.

S2. Binding of alkanoic acid molecules to TiO₂ and SAM properties



Figure S2. CH_x and C-H stretching frequencies of studied carboxylic acid aliphatic chains after incubation of TiO₂ substrates. The FTIR CH₂ symmetric stretching provides information about the conformational order of the molecule tails. The shift of the v_{as}(CH₂) frequency, around 50 cm⁻¹ (from 2918 cm⁻¹ to 2937 cm⁻¹), may be indicative of different SAM packing and/or orientation [2], [3]. A different density of the SAM would explain the observed trend in V_{oc} and indeed the observed shift correlates well with the obtained open-circuit voltages for the molecules under study. Also, the different in the relative amplitude of the v_{as}(CH₂) and v_s(CH₂) resonances has been attributed in previous works to a change in the tilt angle of the grafted molecules [4]. The angle with respect to the normal was found to depend on the v_s(CH₂)/v_{as}(CH₂) ratio, the smaller the closer to 0°. This would also account for the observed differences in V_{oc}, although we must note the low signal to noise specially for the small molecules does not allow for a quantitative comparison in this case

| | Stearic acid | Oleic acid | Caprylic acid | Valeric acid |
|----------------------------|--------------|-------------|---------------|--------------|
| $\int_{sc} (mA \ cm^{-2})$ | 0.257±0.01 | 0.264±0.03 | 0.391±0.04 | 0.440±0.03 |
| V _{oc} (V) | 0.28±0.02 | 0.34±0.02 | 0.33±0.03 | 0.41±0.03 |
| FF | 0.53±0.02 | 0.54±0.04 | 0.44±0.01 | 0.47±0.02 |
| PCE (%) | 0.042±0.004 | 0.050±0.006 | 0.056±0.005 | 0.083±0.005 |

S3. Performance statistics of the aliphatic carboxylic acids

Table S3. Average photovoltaic figures of merit for aliphatic carboxylic acids. Errors represent standard deviations. The maximum PCE is 0.10% for valeric acid.



Figure S3. Statistics for the relevant photovoltaic figures of merit of the different aliphatic carboxylic acid SAMs. Error bars represent standard deviations and rhombs correspond to champion values. For the 18C the black-colored point represents oleic acid.

S4. Gold versus silver electrodes for VA



Figure S4. IPCE for silver and gold devices over a valeric acid SAM-TiO₂ substrate. The IPCE of gold has been rescaled for clarity.

S5. Voc – contact potential difference for HOOC-C₆H₄-X molecules



Figure S5. Correlation of the open-circuit voltage and workfunction shift as measured with contact potential differentiometry (CPD). The shift is calculated with respect to a bare TiO_2 sample.

S6. Performance statistics of the conjugated carboxylic acids

| | BA | MBA | ABA | HBA |
|---------------------------------------|-------------|-------------|-------------|-------------|
| | 0.268+0.020 | 0.220+0.020 | 0.440+0.040 | 0.494+0.025 |
| $V_{oc}(V)$ | 0.268±0.020 | 0.320±0.020 | 0.440±0.040 | 0.484±0.035 |
| $J_{\rm sc} ({\rm mA} {\rm cm}^{-2})$ | 0.273±0.040 | 0.249±0.020 | 0.253±0.020 | 0.357±0.030 |
| FF | 0.46±0.06 | 0.27±0.03 | 0.42±0.03 | 0.53±0.03 |
| PCE (%) | 0.035±0.008 | 0.023±0.004 | 0.043±0.008 | 0.091±0.010 |

Table S6. Average photovoltaic figures of merit for conjugated carboxylic acids: 4mercaptobenzoic acid (MBA), 4-aminobenzoic acid (ABA), benzoic acid (BA), and 4hydroxybenzoic acid (HBA). Errors represent standard deviations. The maximum PCE is 0.11% for HBA.



Figure S6. Statistics for the relevant photovoltaic figures of merit of the different aliphatic carboxylic acid SAMs. Error bars represent standard deviations and rhombs correspond to champion values.

S7. Summary of Au devices performance



Figure S8. Statistics for the relevant photovoltaic figures of merit of a set of molecules with Au electrodes. The trends discussed in the main text (i.e. change of J_{sc} and V_{oc} with molecule parameters) are conserved in the case of gold, although the overall performance is lower due to the lower J_{sc} associated with the molecule barrier.[4]

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