Supporting Information:
Molecular Interfaces for Plasmonic Hot Electron Photovoltaics

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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 TiO$_2$ and SAM properties

Figure S2. CH$_x$ and C-H stretching frequencies of studied carboxylic acid aliphatic chains after incubation of TiO$_2$ substrates. The FTIR CH$_2$ symmetric stretching provides information about the conformational order of the molecule tails. The shift of the $v_{\text{as}}$(CH$_2$) 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 $V_{\text{oc}}$ 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 $v_{\text{as}}$(CH$_2$) and $v_s$(CH$_2$) 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 $v_s$(CH$_2$)/$v_{\text{as}}$(CH$_2$) ratio, the smaller the closer to 0º. This would also account for the observed differences in $V_{\text{oc}}$, although we must note the low signal to noise specially for the small molecules does not allow for a quantitative comparison in this case.
S3. Performance statistics of the aliphatic carboxylic acids

<table>
<thead>
<tr>
<th></th>
<th>Stearic acid</th>
<th>Oleic acid</th>
<th>Caprylic acid</th>
<th>Valeric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{sc}$ (mA cm$^{-2}$)</td>
<td>0.257±0.01</td>
<td>0.264±0.03</td>
<td>0.391±0.04</td>
<td>0.440±0.03</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.28±0.02</td>
<td>0.34±0.02</td>
<td>0.33±0.03</td>
<td>0.41±0.03</td>
</tr>
<tr>
<td>FF</td>
<td>0.53±0.02</td>
<td>0.54±0.04</td>
<td>0.44±0.01</td>
<td>0.47±0.02</td>
</tr>
<tr>
<td>PCE (%)</td>
<td>0.042±0.004</td>
<td>0.050±0.006</td>
<td>0.056±0.005</td>
<td>0.083±0.005</td>
</tr>
</tbody>
</table>

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-TiO$_2$ 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 TiO₂ sample.
S6. Performance statistics of the conjugated carboxylic acids

<table>
<thead>
<tr>
<th></th>
<th>BA</th>
<th>MBA</th>
<th>ABA</th>
<th>HBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.268±0.020</td>
<td>0.320±0.020</td>
<td>0.440±0.040</td>
<td>0.484±0.035</td>
</tr>
<tr>
<td>$J_{sc}$ (mA cm$^{-2}$)</td>
<td>0.273±0.040</td>
<td>0.249±0.020</td>
<td>0.253±0.020</td>
<td>0.357±0.030</td>
</tr>
<tr>
<td>FF</td>
<td>0.46±0.06</td>
<td>0.27±0.03</td>
<td>0.42±0.03</td>
<td>0.53±0.03</td>
</tr>
<tr>
<td>PCE (%)</td>
<td>0.035±0.008</td>
<td>0.023±0.004</td>
<td>0.043±0.008</td>
<td>0.091±0.010</td>
</tr>
</tbody>
</table>

Table S6. Average photovoltaic figures of merit for conjugated carboxylic acids: 4-mercaptobenzoic acid (MBA), 4-aminobenzoic acid (ABA), benzoic acid (BA), and 4-hydroxybenzoic 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]
References


