Supplementary Figures



Supplementary Figure 1

Supplementary Figure 1. Calculation of the Gibbs free energy for randomly generated peptide linkers. Top half in (A): Energy values of the randomly generated 5AA linkers, maximum values are displayed in orange, minimum values in dark red. Lower half: Length values of the randomly generated 5AA linkers, maximum values are displayed in light green, minimum values in blue. The last linker to the right GSGLE, is the experimental 5AA peptide linker. All the maximum and minimum values were calculated while applying a set of random movers to the linkers, after they were generated. To reduce the number of linkers displayed and filter the very high energy values, only the values E < (E(series)max)/20appear here. Rosetta energies are on an arbitrary scale, referred to as REU (for "Rosetta Energy Unit"). Length units are in Angstrom [Å].



Top half in (**B**): Energy values of the randomly generated 7AA linkers, maximum values are displayed in orange, minimum values in dark red. Lower half: Length values of the randomly generated 7AA linkers, maximum values are displayed in light green, minimum values in blue. There was no experimental linker of 7AA length. All the maximum and minimum values were calculated while applying a set of random movers to the linkers, after they were generated. To reduce the number of linkers displayed and filter the very high energy values, only the values E < (E(series)max)/20 appear here. Rosetta energies are on an arbitrary scale, referred to as REU (for "Rosetta Energy Unit"). Length units are in Angstrom [Å].



Top half in **(C)**: Energy values of the randomly generated 10AA linkers, maximum values are displayed in orange, minimum values in dark red. Lower half: Length values of the randomly generated 10AA linkers, maximum values are displayed in light green, minimum values in blue. The last linker to the right GSGSGSGSLE, is the experimental 10AA peptide linker. All the maximum and minimum values were calculated while applying a set of random movers to the linkers, after they were generated. To reduce the number of linkers displayed and filter the very high energy values, only the values E < (E(series)max)/20 appear here. Rosetta energies are on an arbitrary scale, referred to as REU (for "Rosetta Energy Unit"). Length units are in Angstrom [Å].



Top half in **(D)**: Energy values of the randomly generated 12AA linkers, maximum values are displayed in orange, minimum values in dark red. Lower half: Length values of the randomly generated 12AA linkers, maximum values are displayed in light green, minimum values in blue. The last linker to the right GSSVDKLAAALE, is the experimental 12AA peptide linker. All the maximum and minimum values were calculated while applying a set of random movers to the linkers, after they were generated. To reduce the number of linkers displayed and filter the very high energy values, only the values E < (E(series)max)/20 appear here. Rosetta energies are on an arbitrary scale, referred to as REU (for "Rosetta Energy Unit"). Length units are in Angstrom [Å].



Top half in (E): Energy values of the randomly generated 19AA linkers, maximum values are displayed in orange, minimum values in dark red. Lower half: Length values of the randomly generated 19AA linkers, maximum values are displayed in light green, minimum values in blue. The last linker to the right AEAAAKEAAAKEAAAKALE, is the experimental 19AA semi- α -helical peptide linker. All the maximum and minimum values were calculated while applying a set of random movers to the linkers, after they were generated. To reduce the number of linkers displayed and filter the very high energy values, only the values E < (E(series)max)/20 appear here. Rosetta energies are on an arbitrary scale, referred to as REU (for "Rosetta Energy Unit"). Length units are in Angstrom [Å].

Supplementary Figure 2



Supplementary Figure 2. Redox difference absorbance spectra of the other four cyt c_{553} linker peptide variants (excluding the 10AA linker peptide variant which is displayed in Fig. 5C). Presence of α , β and γ peaks and their full redox reversibility indicate that all the cyt c_{553} proteins are active in electron transfer. Each variant, indicated in the panels, displayed the identical redox characteristics (including the 10AA variant). The reversibility of the red-ox spectra indicates the appropriate haem group maturation and incorporation into the holoprotein. Spectra of fully reduced species were truncated below 370 nm as the sodium dithionite spectrum overshadows the cyt c_{553} -specific peaks.

Supplementary Figure 3



Supplementary Figure 3. Workflow for the synthesis of nickel-nitrilo acetic acid self-assembled monolayer. Protocol was essentially reproduced from⁵⁸ using steps *A-D*. First, a gas-phase aminosinilation was performed on the SiO₂ surface. Subsequently, 1,4-phenylene diisothiocyanate (DITC) was reacted with the aminosilane functionalised Si for 2 hours at 40° C in ethanol (*A*). Wafers were then rinsed thoroughly with water and ethanol and dried under a N₂ stream. N,N-

bis(carboxymethyl)-L-lysine was reacted by immersion in an aqueous solution for 30 min. (B). Samples were subsequently rinsed thoroughly with water and dried under a N₂ stream. Ni²⁺ was chelated to the tricarboxylic acid functionality by immersion in a 1 mM aqueous NiCl₂ solution for 20 min. (C). The functionalised Si wafers were employed immediately for cyt c_{553} biofunctionalisation (D).



Supplementary Figure 4

Supplementary Figure 4. Dark *J-V* characterisation of cytochrome c_{553} /Si bioelectrodes. Dark current density *J* (mA/cm²) was measured for all the cyt c_{553} variant/Si electrodes, as shown in Fig. 7. Semi-logarithmic representation of the measured *J-V* values allows for estimation of the J_0 recombination parameter which corresponds to the *y*-intercept and is calculated according to Eq. 1.

Supplementary Figure 5



Supplementary Figure 5. Flow-chart depicting preparation of all-solid-state cyt c_{553}/p -doped Si and PSI/cyt c_{553}/p -doped Si biophotovoltaic devices. For a detailed protocol of Ni-NTA synthesis on Si refer to Suppl. Fig. 3. Roman numbers correspond to the consecutive generations of the biophotovoltaic devices prepared in this study.