Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A Water Soluble Tin(IV) Porphyrin as Bioinspired Photosensitiser for light-driven proton-reduction

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Additional figures and tables

Figure S1a) ^{1}H-NMR-spectra of the TPPC ligand (left) und **1** (right) in DMSO-d$_6$.

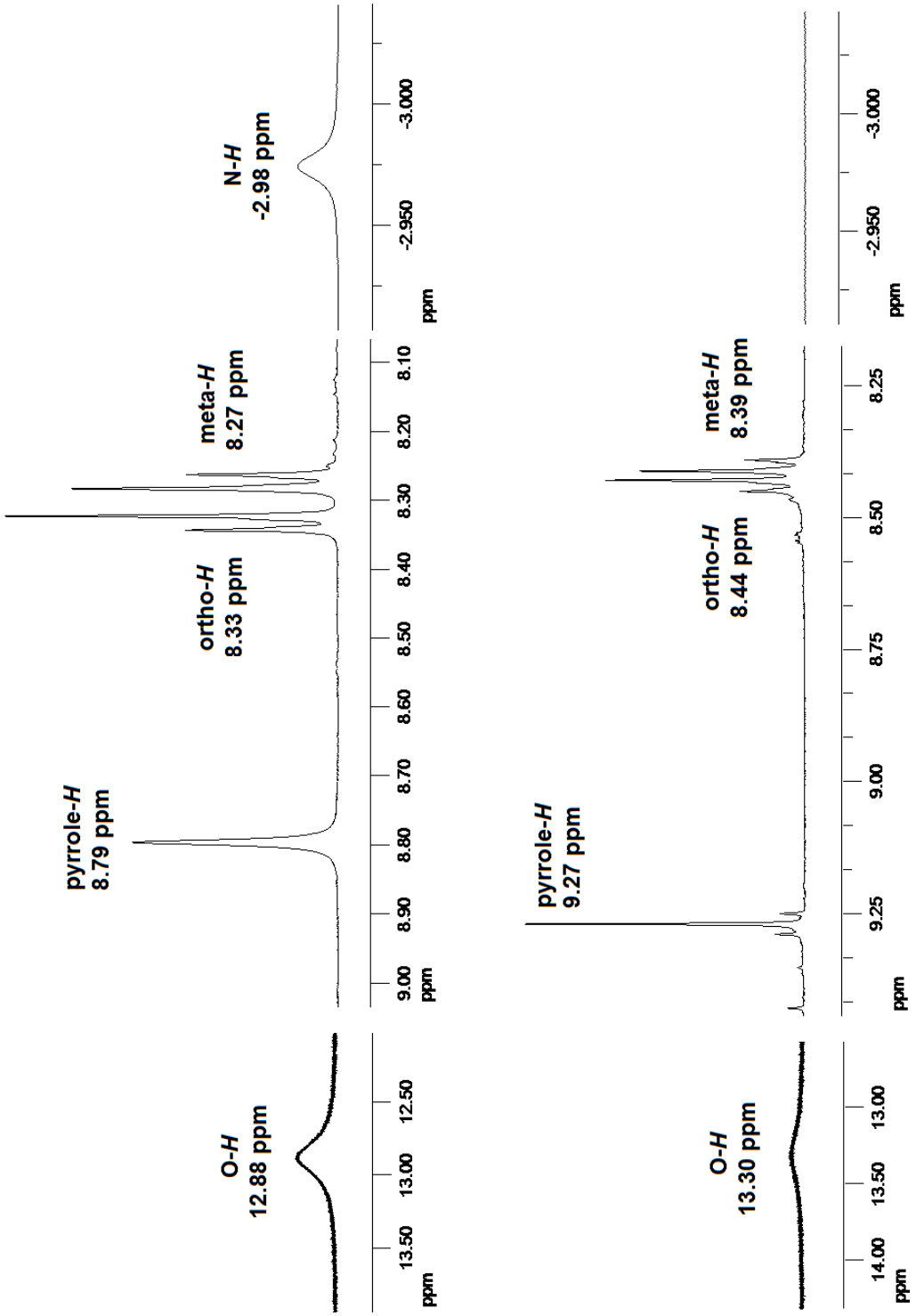

Figure S1b) ^{13}C-NMR-spectra of the TPPC ligand (top) und **1** (below) in DMSO-d$_6$. The signals for the quarternary *C*=N and pyrrole-*C* carbon atoms could not be observed in the ^{13}C-NMR spectrum of TPPC. The slashed signals in the ^{13}C-NMR spectrum of **1** belong to pyridine impurities.

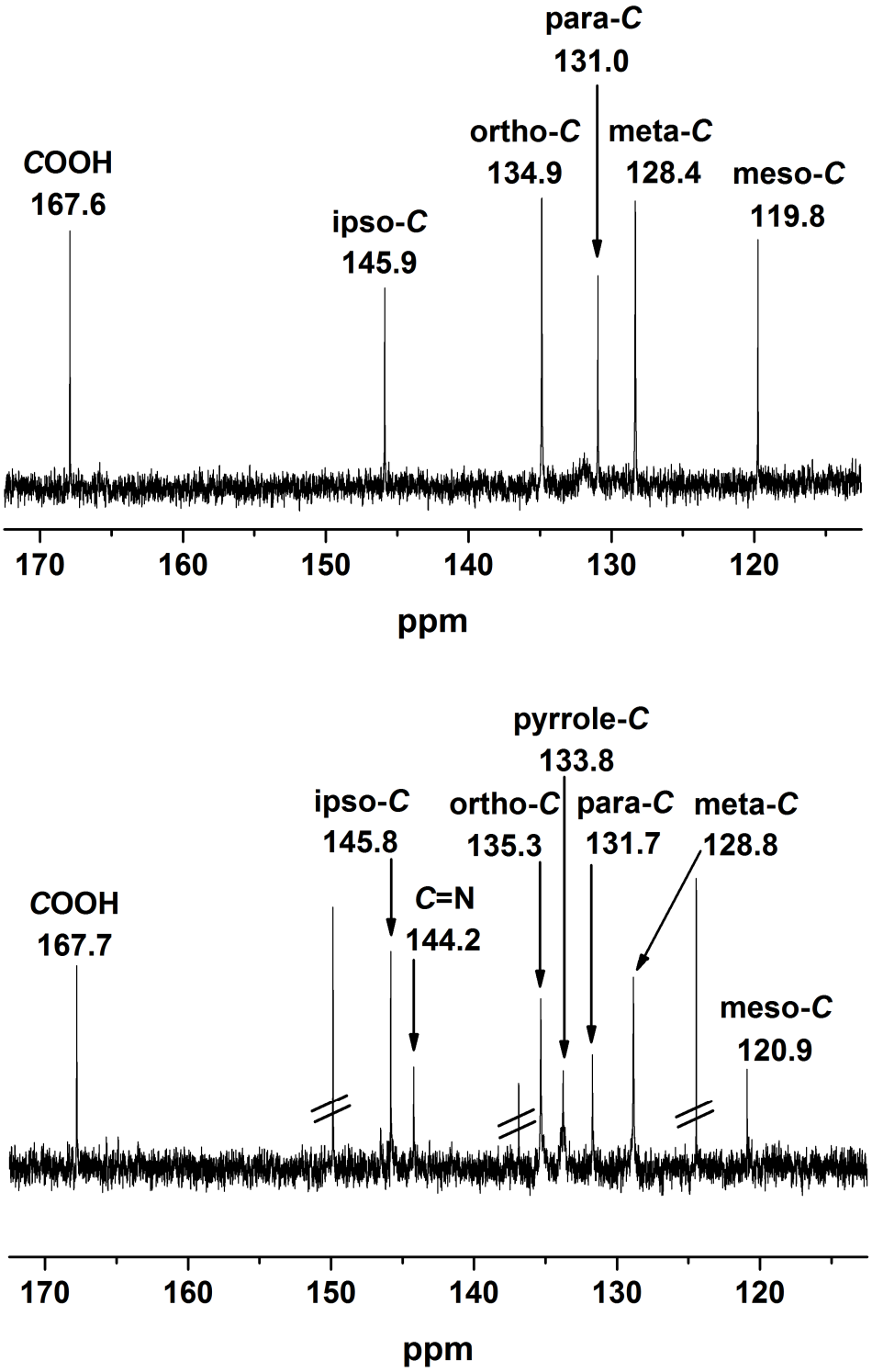

Figure S2. Normalised absorption (black) und emission (red) spectra for aqueous solutions of **1**. The blue line shows the Gaussian fit for the 0-1-absorbtion transition used to determine E_{00} by the "intercept-method".

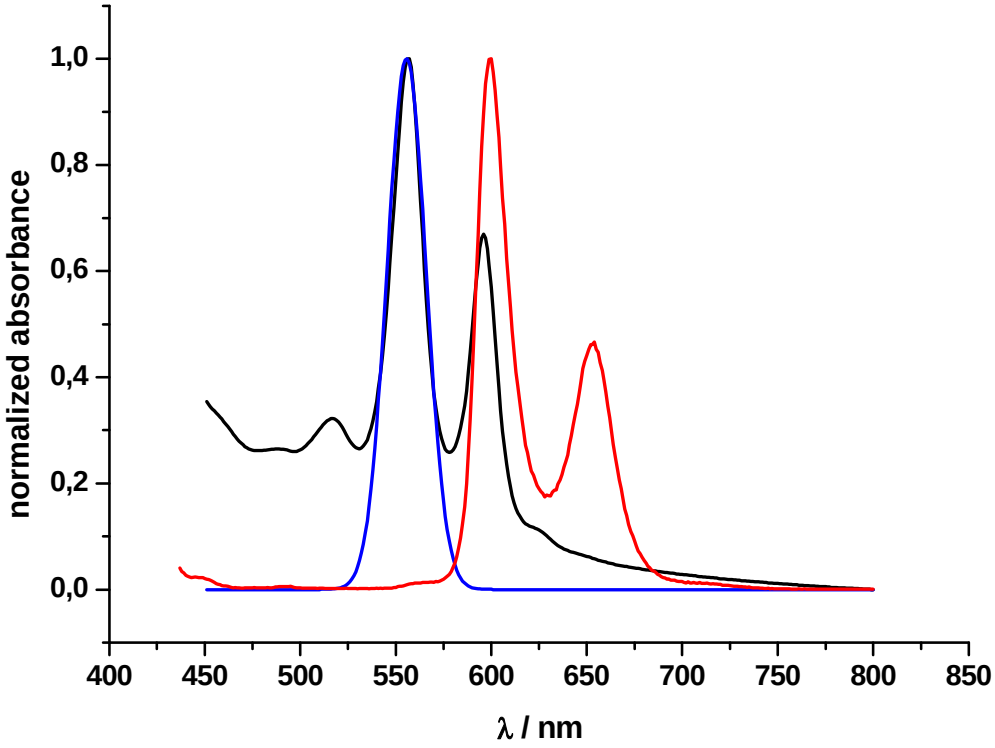

Table S1. Values obtained for E_{00} of **1** by using either the medium wavelength between corresponding absorbance and fluorescence peaks (method A) or the "intercept-method" (B).

method	transition	E_{00} / eV
A	$Q_{0\text{-}1}$	2.14
	$Q_{0\text{-}0}$	1.98
B	$Q_{0\text{-}1}$	2.13
	$Q_{0\text{-}0}$	2.00

Figure S3. Aggregation studies of compound **1**: Absorbance at 557 nm in absorption spectra of different concentrations of **1** (10^{-6} -10^{-3} M). All solutions were prepared in phosphate buffer (0.1 M, pH 7).

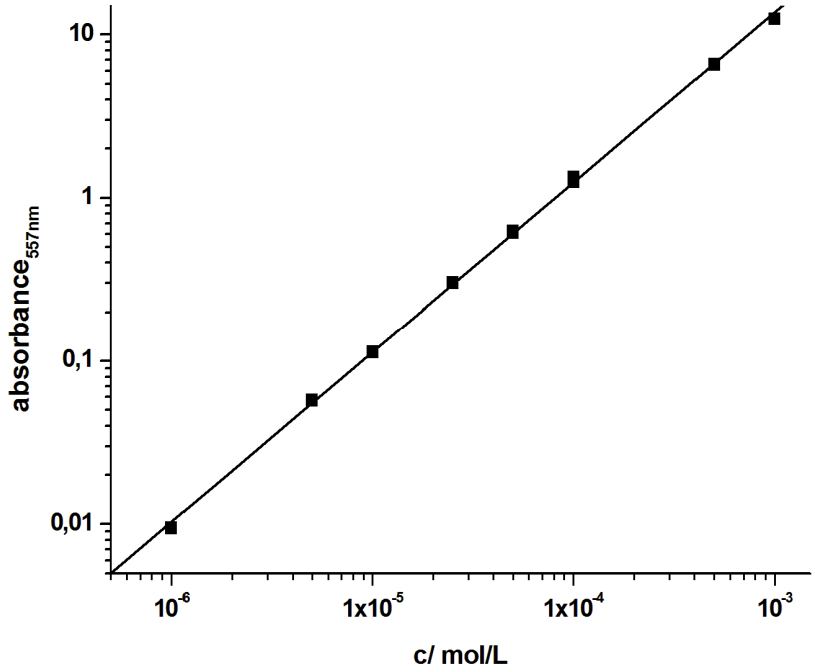

Figure S4. Differential pulse voltammogramm (DPV) of **1** (straight line) measured with a mercury electrode (hanging mode) from 0 V to -1.2 V in neutral phosphate buffer ([**1**]=0.5 mM). The dashed line shows the electrolyte background (phosphate buffer, 0.5 M, pH7).

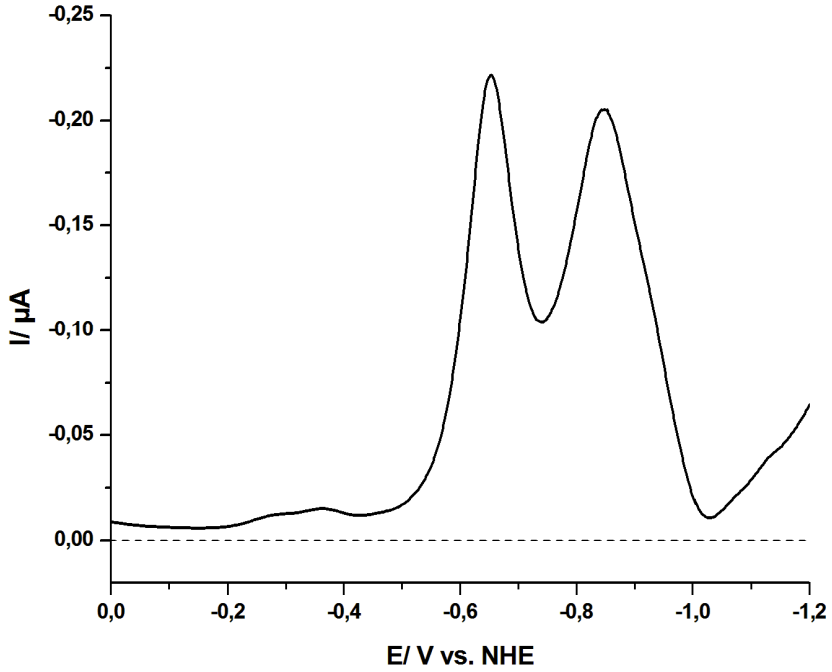

Figure S5. Reductive cyclic voltammogramm (CV) of **1** in aqueous phosphate buffer ([**1**]=0.5 mM) measured with a mercury electrode as working electrode. It shows a re-oxidation wave at -0.42 V vs. NHE, most likely caused by tin amalgam formation during the measurement. The dashed line shows the electrolyte background (phosphate buffer, 0.5 M, pH 7).

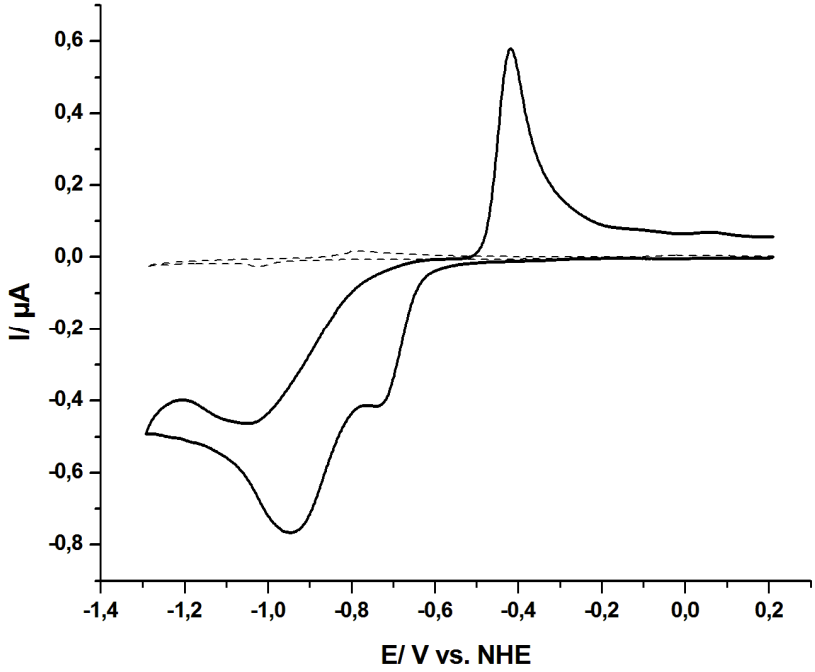

Figure S6. DPV of **1** (straight line) and tin(II) chloride $SnCl_2$ (dashed line) measured with a mercury electrode (hanging mode) ([**1**], [$SnCl_2$]=0.5 mM). The DPV was measured from -1.4 V to 0 V, with an equilibration time of 5 seconds at -1.4V and a scan rate of 20 mV/s. The black line shows the electrolyte background (phosphate buffer, 0.5 M, pH7).

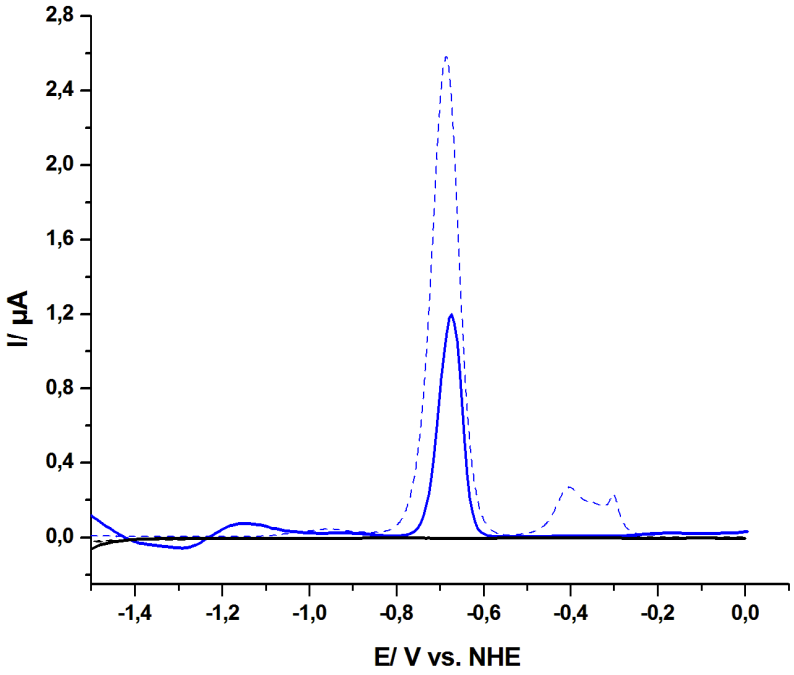

Figure S7. CV of **1** in aqueous phosphate buffer ([**1**]=0.5 mM) measured with a *glassy carbon electrode* as working electrode. The dashed line shows the electrolyte background (phosphate buffer, 0.5 M, pH7).

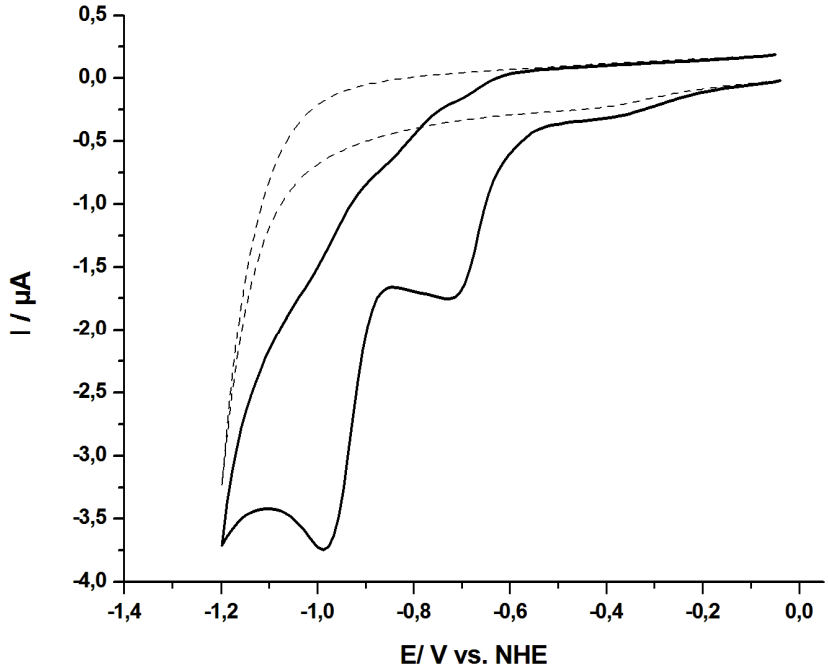

Figure S8. CVs (straight lines) and DPVs (dashed lines) of the quenchers methyl viologen (blue), triethanolamine (red) and ethylendiamine-tetraacetic acid (green) in aqueous phosphate buffer ([Quencher]=1 mM) measured with a glassy carbon electrode as working electrode. The dotted black line shows the electrolyte background (phosphate buffer, 0.5 M, pH7).

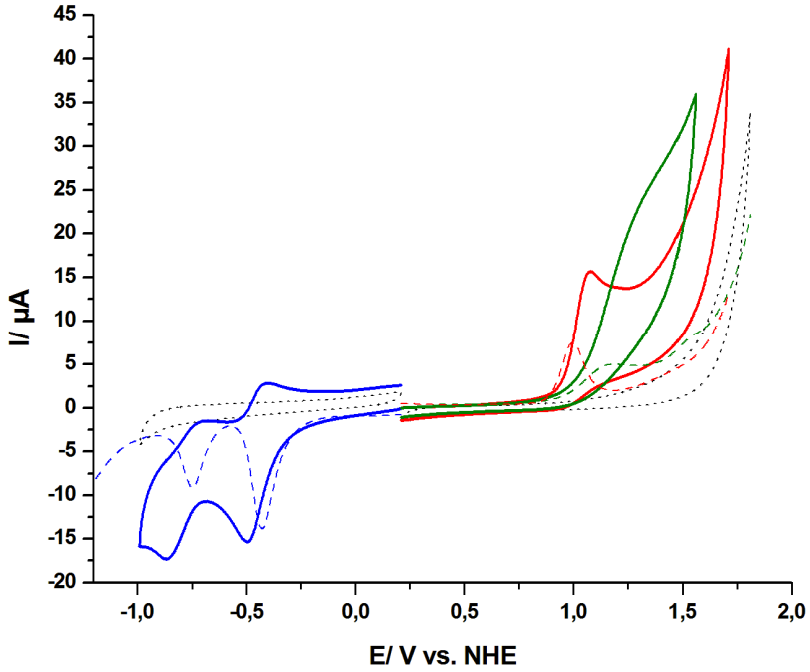

Figure S9. Aggregation studies of compound **1** in a higher concentration range (1- 6 mM): Absorbance at 557 nm in absorption spectra of different concentrations of **1**. All solutions were prepared in phosphate buffer (0.1 M, pH 7).

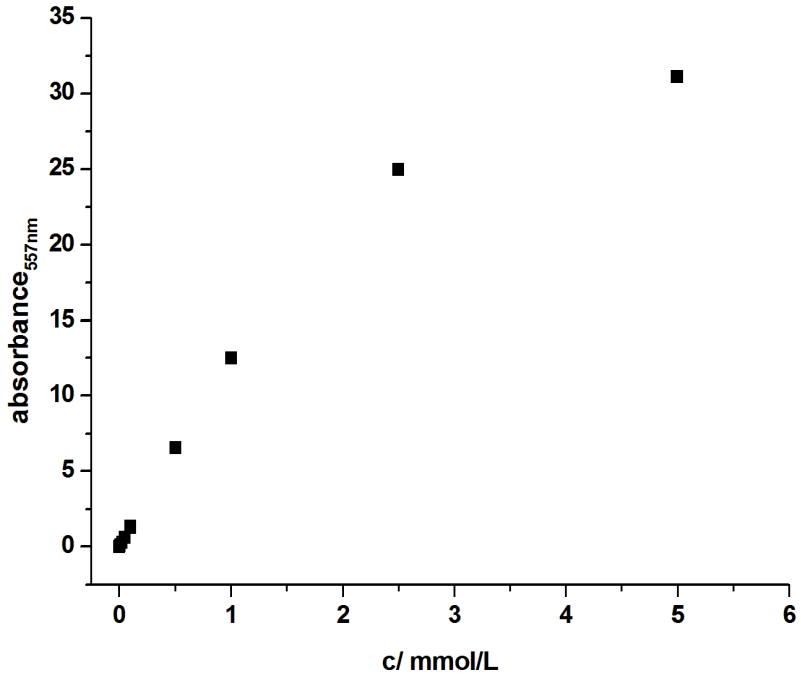

Figure S10. Absorption spectra of 10 µM SnTPPC (Q-bands 100 µM) after irradiation of a "quencher-only system" (0.5 mM SnTPPC and 50 mM TEOA in 0.1M neutral phosphate buffer) for 0, 30, 90, 150, 180 min..

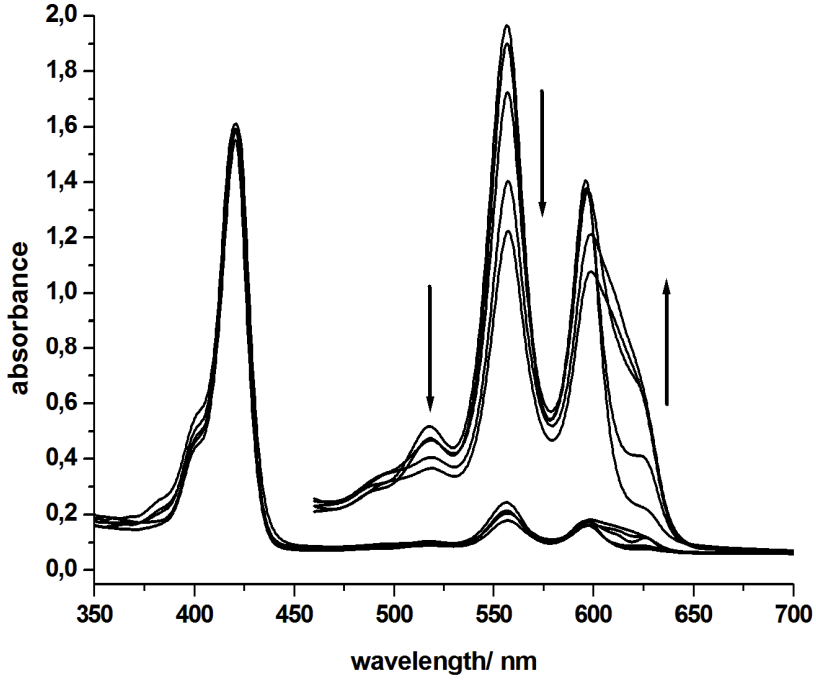

Figure S11. Cyclic voltammograms of **1** in aqueous phosphate buffer at different pH values ([**1**]=0.5 mM, total phosphate concentration 0.5M): pH 5 (black), pH 6 (blue), pH 7 (red) and pH 8 (green).

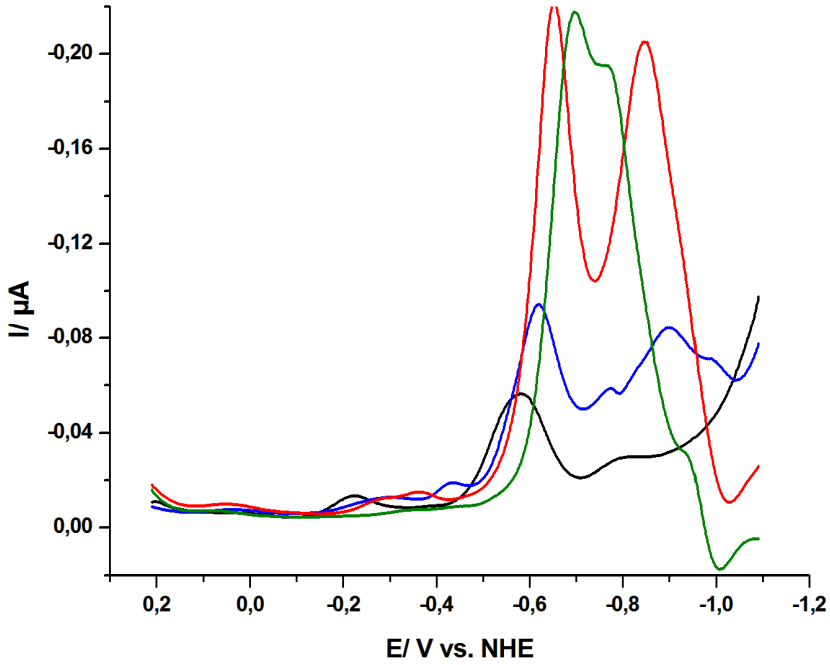

Figure S12. A section of the structure of the multi-domain enzyme Photosystem II, highlighting the position of the central pigment P680, an arrangement of four interacting chlorophylls. The molecules of the electron transfer chain, chlorophylls, pheophytin and quinones (in green and purple), are arranged inside the hydrophobic membrane space with virtually no water molecules nearby. In contrast, the OEC (below left) as catalytic site for water-oxidation is surrounded by water.

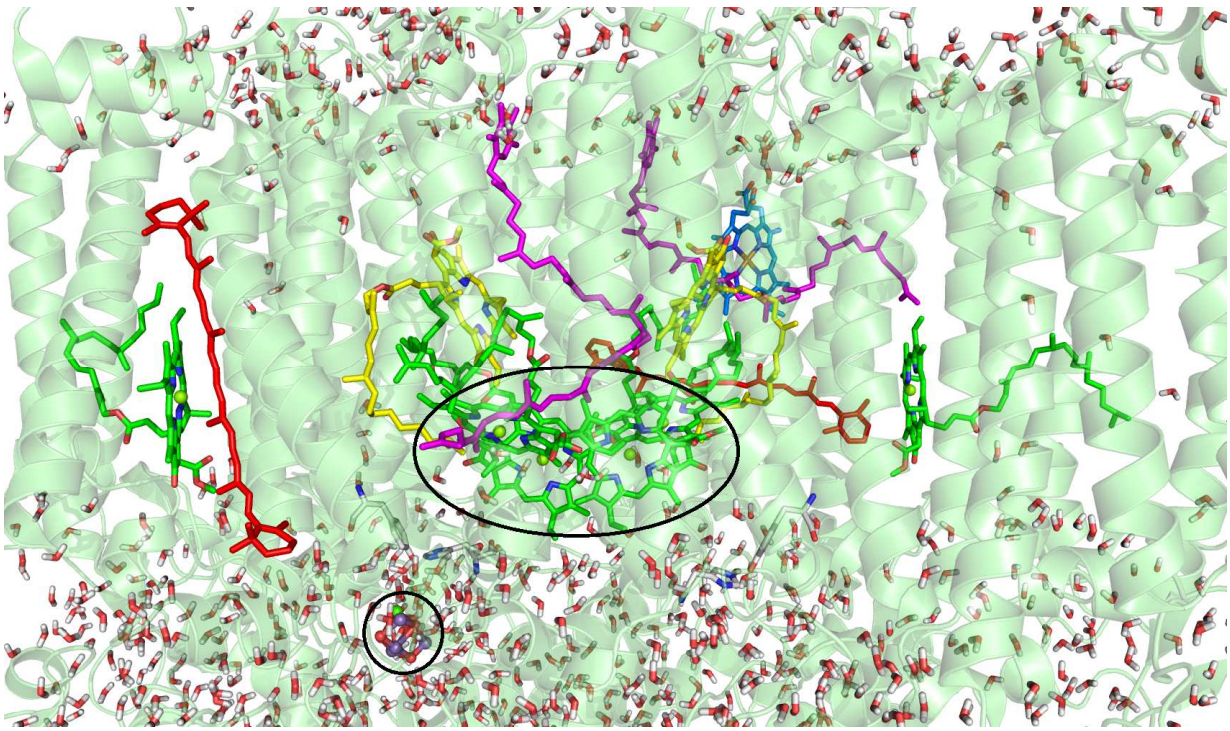

Figure S13. *Top:* MALDI-TOF-MS spectrum for **1** from a Cl-CCA matrix. *Below:* Measured and simulated signal for the peak detected at m/z = 943.