# Supporting information

## Electrogeneration of a free-standing cytochrome *c* – silica matrix at a soft electrified interface

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### Supporting information table of contents

**Experimental set-ups for electrochemistry and spectroelectrochemistry measurements** ..... 2
**Control cyclic voltammetry of Cyt c in the absence of silica hydrogel**..... 4
**Electrochemical stabilisation of Cyt *c*@$SiO_2$ hydrogel after aqueous phase exchange** ..... 5

**Experimental set-ups for electrochemistry and spectroelectrochemistry measurements**

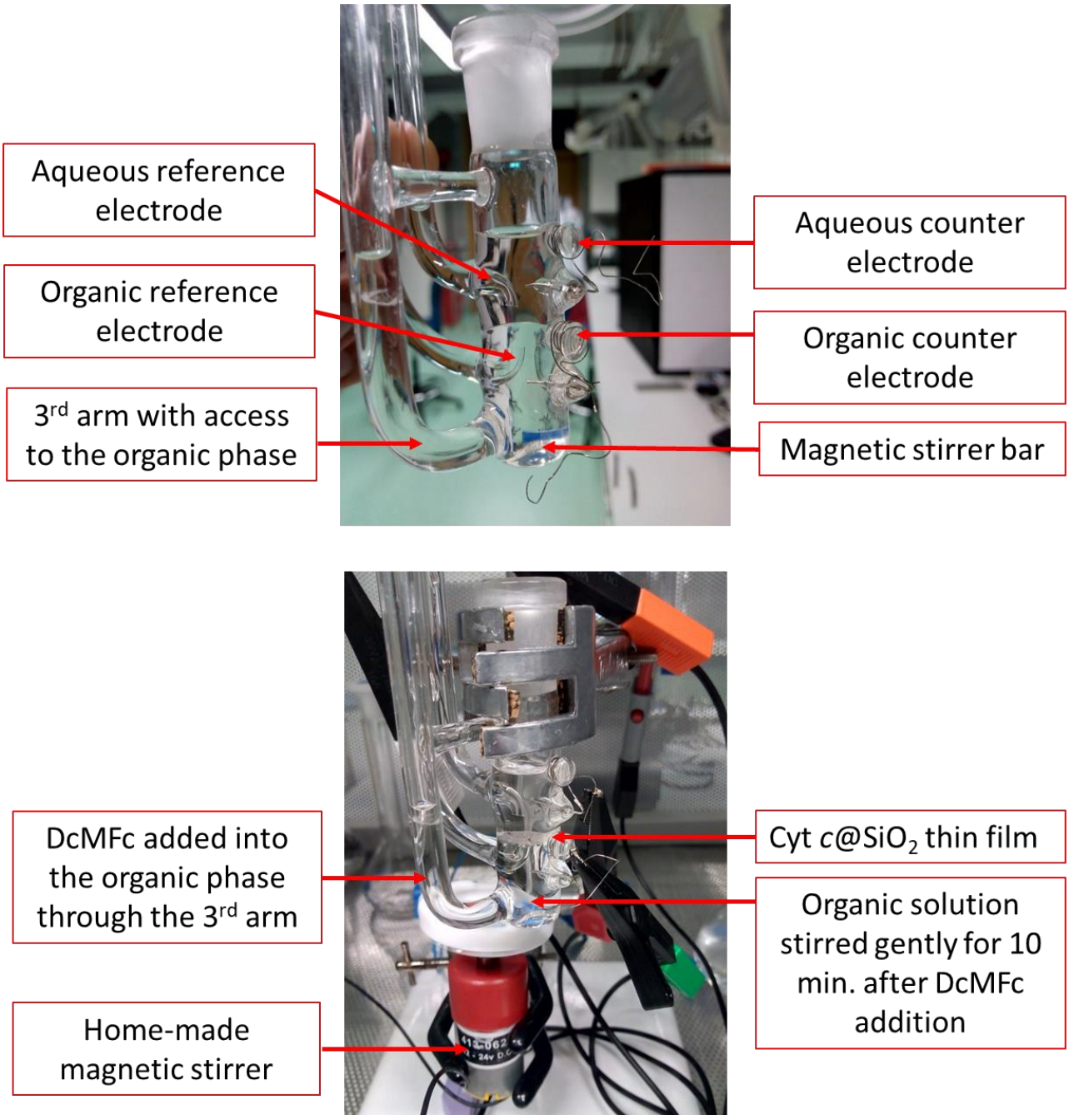


**Figure S1.** Homemade 4-electrode electrochemical cell with a third arm facilitating the addition of hydrophobic electron donors into the organic phase.

## UV-vis spectroelectrochemistry setup

The spectrometer used was a USB 2000 Fiber Optic Spectrometer (Ocean Optics). The light source was a DH-2000-BAL deuterium–halogen (Ocean Optics) was guided through the optical fibre of 600 μm of diameter (Ocean Optics, USA). The light beam was collimated using optical lenses (Thor-lab, focal length: 2 cm) before and after the transmission of the beam through the electrochemical cell. The light beam passed through the electrochemical cell slightly above the water|TFT interface, i.e., through the aqueous phase. The interfacial Galvani potential difference ($\Delta_o^w\phi$) was controlled using an Autolab PGSTAT204 potentiostat (Metrohm, Switzerland). An image of this setup is shown in Figure S2.

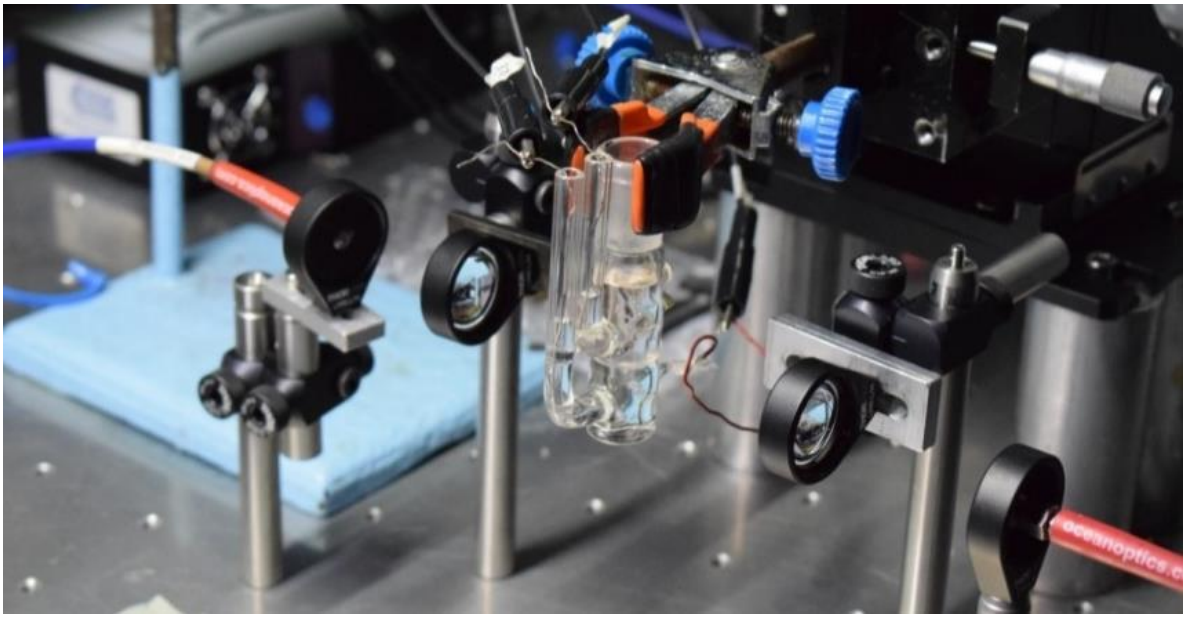

**Figure S2.** Optical setup for in situ parallel beam UV-vis absorbance measurements using a four-electrode electrochemical cell.

## Control cyclic voltammetry of Cyt *c* in the absence of silica hydrogel

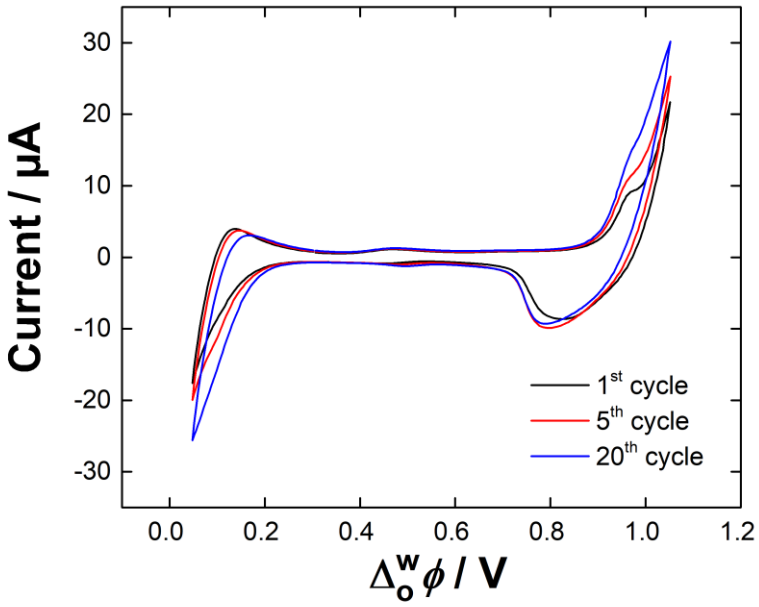


**Figure S3.** CV of 10 µM of Cyt *c* (pH 9) at a liquid-liquid interface in the absence of TEOS in the aqueous phase or $CTA^+$ in the organic phase. ν = 20 mV $s^{-1}$.

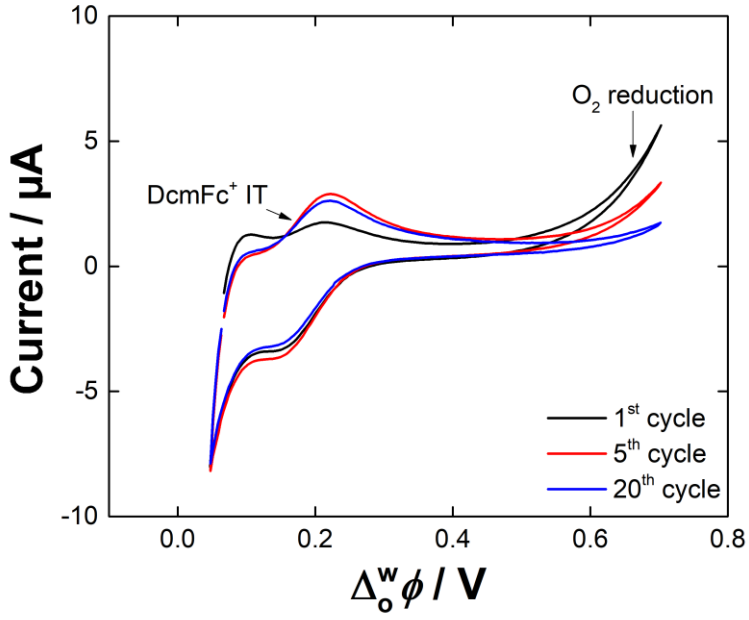


**Figure S4.** CV of 10 µM of Cyt c (aqueous phase) || 500 µM DcMFc (organic phase). ν = 20 mV $s^{-1}$.

## Electrochemical stabilisation of Cyt *c*@$SiO_2$ hydrogel after aqueous phase exchange

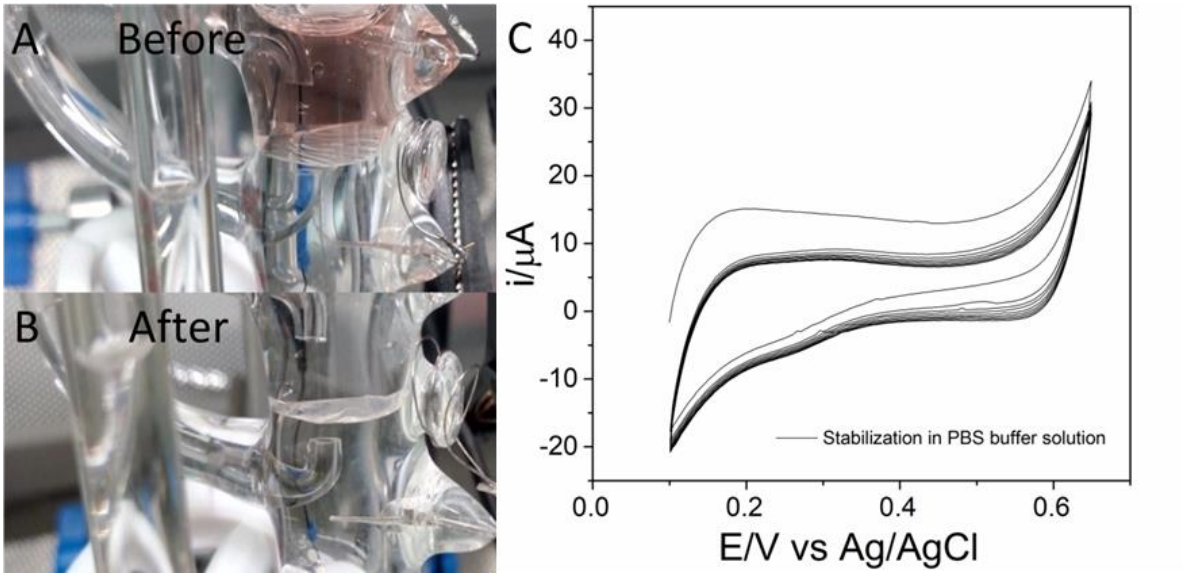


**Figure S5**. Image of the 4-electrode cell after (A) Cyt *c*@ $SiO_2$ electrogeneration and (B) after replacing the aqueous phase with 10 mM PBS solution. (C) Electrochemical stabilisation of Cyt *c*@$SiO_2$ by repetitive voltammetric scans at liquid-liquid interface (Electrochemical cell 3).