

Supplementary information

Preparation of template stripped gold and sputtered gold electrodes

Pre-cleaning of glass surface and preparation of gold surfaces

Immediately prior to sputtering, the glass was cleaned in a solution of acidified potassium permanganate for 2 h to oxidise any organics; rinsed with acidified hydrogen peroxide solution; rinsed with ultrapure water six times; dried under a stream of nitrogen and finally dried upright at 110 °C for 5 min.

Template stripped gold surfaces were prepared by sputtering a 100 nm layer of gold (Emitech K575X sputterer with Emitech TK8859 gold targets) onto 2 cm × 7.5 cm VWR International Super Premium glass microscope slides. The gold surface was then bonded to glass rectangles (approximately 1 cm × 2 cm) using Buehler Epo-Thin Low Viscosity Epoxy Resin. Following curing of the epoxy for at least 24 h at room temperature, the glass rectangles were pulled off the microscope slide when needed. Surface morphologies were characterised with an Agilent Technologies 5500 AFM using PointProbe Plus Non-Contact / Tapping Mode - High Resonance Frequency probes (Nanosensors, Switzerland). Image processing involved tilt removal and was performed using Agilent PicoView version 1.8 software.

Sputtered gold surfaces were prepared by sputtering 100 nm of gold onto glass (cleaned as described above) with a 20 nm titanium interlayer (Emitech TK8879 titanium target). Gold surfaces were rinsed with ultrapure water (Millipore Milli-Q, 18.2 MΩ cm) prior to use.

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Electrowetting response for 2-chloro propanol

Due to the mild acidity of 3-chloro-1-propanol, there is a background low Faradaic current due to H⁺ reduction at potentials below -500 mV versus Ag/AgCl. The addition of NaOH delays the

onset of this reductive process by 800 mV suggesting that the reaction is indeed H^+ reduction rather than reduction of the 3-chloro-1-propanol (supplementary information, figure S4).

It is feasible that the Faradaic process reduces hysteresis of the electrowetting response, although the authors believe that several pieces of evidence suggest otherwise. Firstly, the background Faradaic reaction is present at all LiCl concentrations; however, it is only at 0.16 mol dm^{-3} LiCl, and not at other concentrations, that there is no hysteresis. Secondly, the addition of HCl to acidify an electrowetting system with DCE to the same pH as the 3-chloro-1-propanol system only serves to increase the hysteresis. Finally, (as discussed in the paper), although pinned, the 3-chloro-1-propanol system shows an electrowetting response positive of the PZC (in a region where no Faradaic processes occur). This was not seen with any other solvents, suggesting that 3-chloro-1-propanol is particularly conducive to electrowetting.

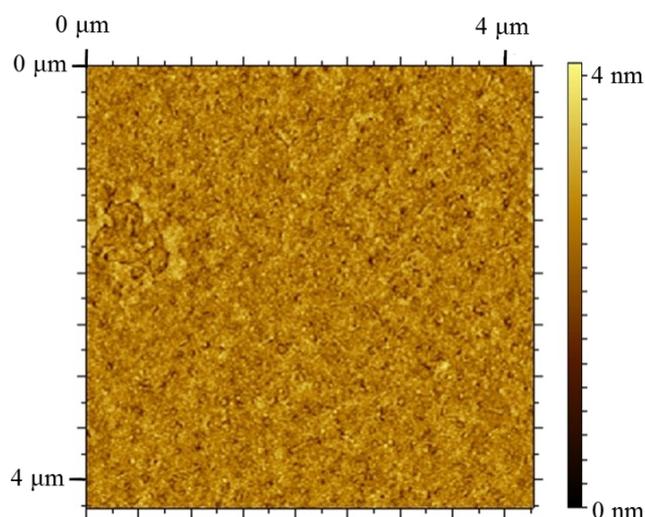


Figure S1. AFM image of template stripped gold. This surface has an RMS roughness of 3.9 \AA over $4.3 \times 4.3 \text{ \mu m}^2$ with a peak height of 28 nm. Over 80 \mu m^2 the RMS roughness was 4.5 \AA with a peak height of 184 nm.

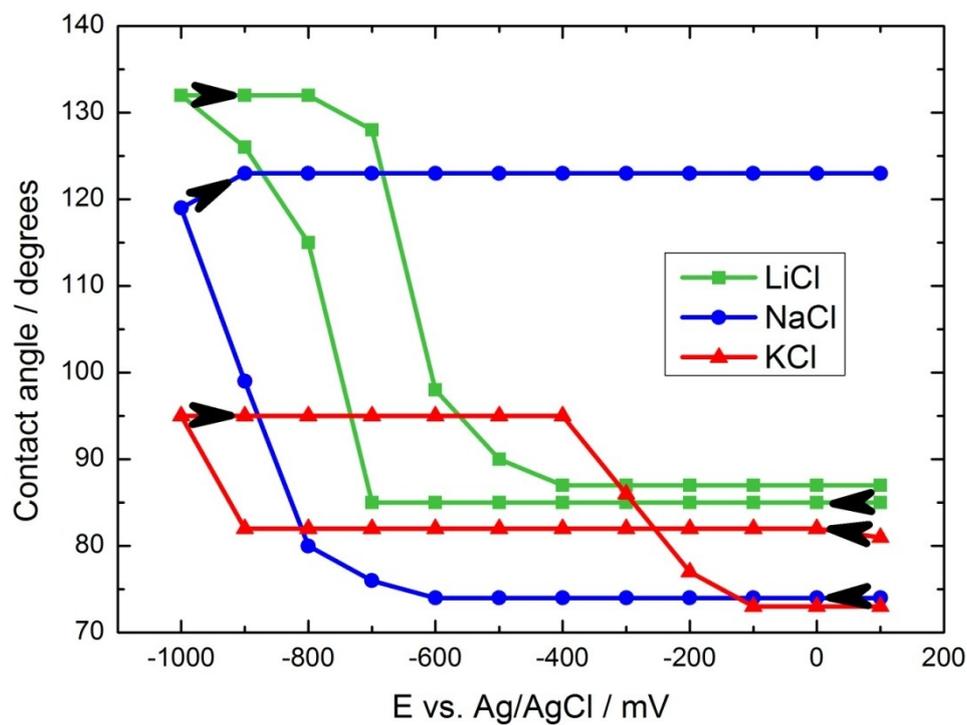


Figure S2. Electrowetting response of a ~ 1 mm diameter pure DCE droplet on a template stripped gold electrode surrounded by an aqueous electrolyte composed of 0.10 mol dm^{-3} LiCl, NaCl or KCl. Contact angles were measured 10 s after polarization at each potential at a temperature of 22 ± 2 °C.

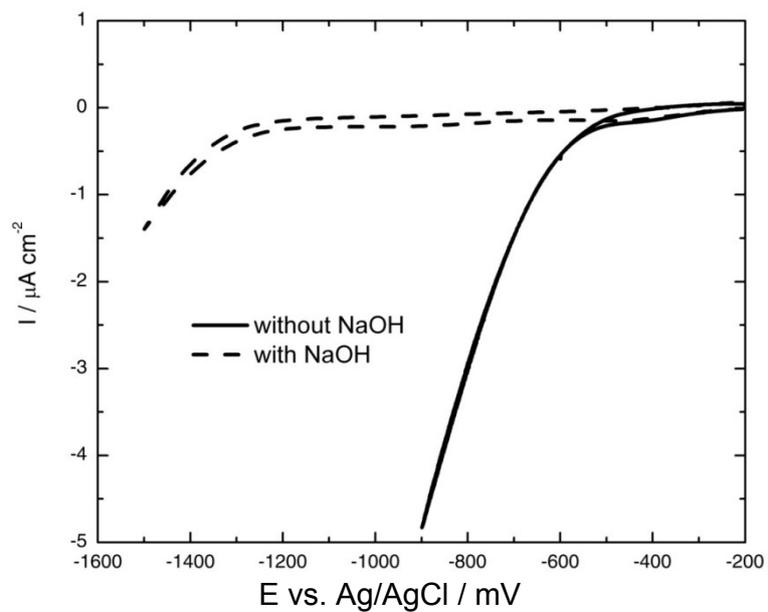


Figure S3. Cyclic voltammetry of 0.10 mol dm^{-3} LiCl solution saturated with 3-chloro-1-propanol. The addition of 0.05 mol dm^{-3} NaOH reduces the acidity of the solution and shifts the reductive process to a more negative potential. This suggests that the current is due to H^+ reduction rather than reduction of 3-chloro-1-propanol.