Electronic Supporting Information

RYB Tri-Colour Electrochromism based on a Molecular Cobaloxime

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Low-tech patterning of mesoporous ITO films

The here presented fabrication route to macroscopically patterned ITO electrodes is schematically illustrated in Fig. 2. Fluorine-doped tin oxide coated glass substrates (FTO; 15 Ω/□, 2.2 mm, Solaronix) were cut into 15 cm long stripes and pre-scratched at the back with a diamond scribe. These were then cleaned with piranha solution, specifically 3 parts sulphuric acid to 1 part hydrogen peroxide, at 90 °C for 10 min. This solution reacts violently with most solvents, and extreme caution should be exercised when carrying out this cleaning step. After piranha cleaning, the substrates were rinsed and then sonicated for 10 min in de-ionised water before being blown dry with nitrogen. This treatment removes all organic contaminants from the FTO surface, but also leaves it with a high surface energy and a water contact angle of 0 °.

Next, ITO films were blade-coated with a K Print Applicator (RK Print Coat Instruments) and a Model 360 Blade (Erichsen) using a mixture of 35%$_{\text{wt}}$ ITO nanopowder (particle size < 40 nm; 90% In_2O_3 and 10% SnO_2; Aldrich) and acetic acid (5 M) in EtOH (Fig. S1 Step1). After solvent evaporation the coated stripes were broken into smaller pieces and the ITO thickness was measured with a Dektak Profilometer (Veeco) to be about 7 and 14 μm for a substrate/blade gap of 60 and 120 μm, respectively. The negative photoresist SU8 2000.5 (MicroChem) was sequentially spin-cast first using a diluted (50%$_{\text{vol}}$ in propylene glycol monomethyl ether acetate) and then an undiluted solution at a spin speed of 6000 rpm. Thereafter, the samples were soft-baked, UV-exposed for 15 s using a MJB4 mask aligner (SussMicroTec; $\lambda > 365$ nm; $60-80\,\text{mJ}\,\text{cm}^{-2}$) and a chrome mask (JD PhotoTools), post-baked, and developed for 30 s with propylene glycol monomethyl ether acetate (Fig. S1 Step4). The applied soft- and post-bake procedure was as follows: 3 min at 65 °C, 3 min at 100 °C, and 3 min at 65 °C.

In order to liftoff the cross-linked SU8|ITO areas the samples were immersed in a *tert*-butanol/acetonitrile mixture (*t*-BuOH/ACN:1/1) for 12 h and finally annealed in air at 450-550 °C for 20 min (Fig. S1 Step4). During the thermal sintering the patterned areas initially turned black and gradually got brighter again indicating the oxidation of remaining polymer trapped inside the mesoporous ITO. Although a mask aligner was used in this study, a standard UV-lamp can be facilitated for the pattern exposure, making it an affordable and low-tech technique.

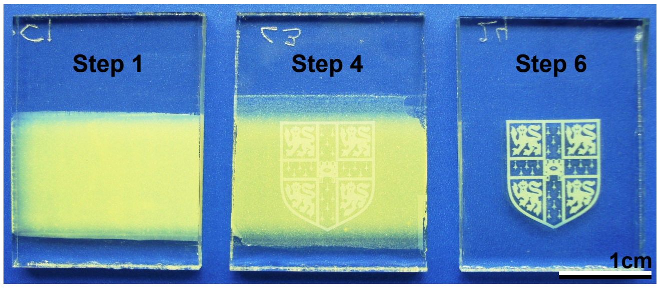

Fig. S1 Photograph showing the different stages during the patterning process of samples with a 14 μm thick ITO layer: as-deposited film (Step1), developed sample with dark SU8|ITO composite areas surrounding the bright ITO pattern (Step4), and the final pattern showing the crest of the University of Cambridge (Step6).

[Co] immobilisation and device assembly

The [**Co**] complex shown in Fig. 1b was synthesised as reported elsewhere[1] and immobilised on the patterned ITO by soaking for 24 h in an anhydrous dimethylformamide solution containing 6 mM of [**Co**]. Layered electrochromic cells were assembled by the following steps (Fig. S2 and S3): capping with a FTO counter electrode using a precut thermoplastic gasket (Parafilm) as spacer and fusing at 150 °C for 30 s, infiltration of the electrolyte consisting of tetrabutylam-

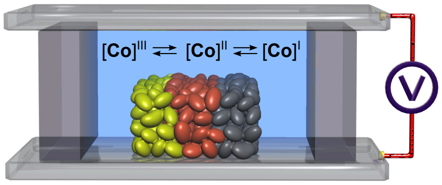

Fig. S2 Schematic illustration of the transparent electrochromic cell design based on two FTO-coated glass electrodes. The electron-transfer between the ITO and the [**Co**]-complex cause the oxidation/reduction of the latter.

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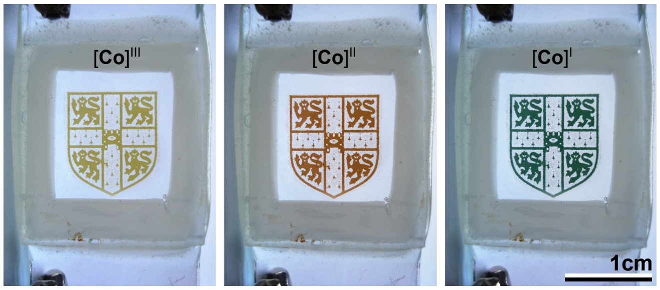

Fig. S3 Photographs of an electrochromic display based on a 14 μm thick ITO|[**Co**] electrode showing the vivid colours of the three oxidation states of [**Co**].

monium tetrafluoroborate (0.1 M) or lithium perchlorate (1 M) dissolved in anhydrous propylene carbonate, and finally sealing the cell with Double Bubble epoxy glue (Henkel). The [**Co**] immobilisation and device assembly were performed in a nitrogen-filled glove box with a water and oxygen content below 2 ppm.

Optical spectra

The optical spectra of the three oxidation states for a thin (7 μm) and thick (14 μm) ITO|[**Co**] electrode are presented in Fig. S4. The spectra were recorded with a QE65000 spectrometer (Ocean Optics; 50 ms integration time) attached to a BX51 microscope (Olympus) which was equipped with a condenser and a long working distance 20× objective. The optical focus was adjusted to coincide with the ITO/FTO interface. The bright-field transmittance measurements were normalised with respect to the fully transparent area of the devices. A white scatter underneath a FTO substrate was used as reference for the dark-field reflectance measurements.

As expected, the thin film exhibits a higher overall transmissivity compared to its thicker counterpart, however, the maximal optical transmission contrasts at $\lambda = 650$ nm are comparable ($\Delta T_{\text{thin}} = 32.3\,\%$ and $\Delta T_{\text{thick}} = 28.3\,\%$). In contrast, increasing the ITO|[**Co**] layer thickness dramatically enhances the colouration contrast measured in reflection ($\Delta R_{\text{thin}} = 5.0\,\%$ and $\Delta R_{\text{thick}} = 14.7\,\%$). These findings are consistent with the optical appearance to the human eye, the thin sample looks pale whereas the thicker one presents a vivid colouration.

For many electrochromic applications a colourless or highly transmissive state is desirable. The high absorbance of the mesoporous ITO electrode (Fig. S1) is mainly responsible for the low transmittance of the 14 μm thick ITO|[**Co**] device (Fig. S4). Increasing the transmittance of the fully oxidised state [**Co**]^{III} without compromising the colouration contrast is conceptually possible by applying a more transparent electrode material than ITO.

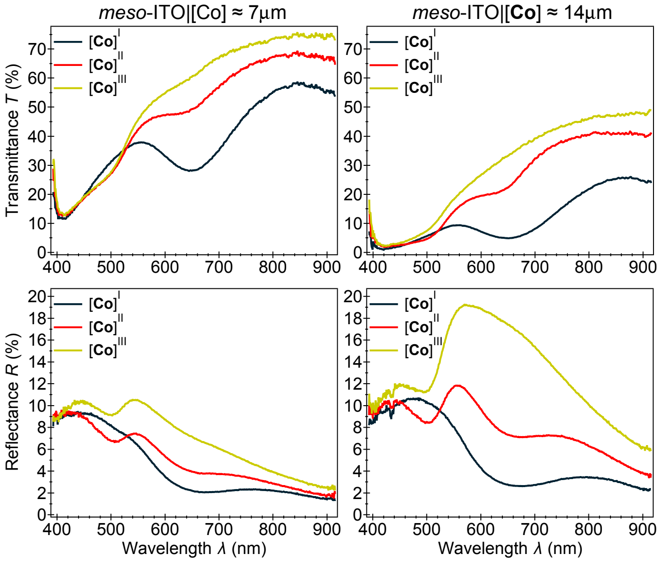

Fig. S4 Optical bright-field transmittance (top row) and dark-field reflectance (bottom row) spectra of the three [**Co**] oxidation states for a 7 μm (left column) and 14 μm (right column) thick ITO|[**Co**] electrode.

Redox potentials of [Co]

Fig. S5 shows the cyclic voltammogram of [**Co**] in solution. Two one-electron reduction were assigned to $[\mathbf{Co}]^{III}/[\mathbf{Co}]^{II}$ and $[\mathbf{Co}]^{II}/[\mathbf{Co}]^{I}$ processes at ${}^{III/II}E_p = 0.01$ V and ${}^{II/I}E_{1/2} = -0.37$ V vs. NHE.

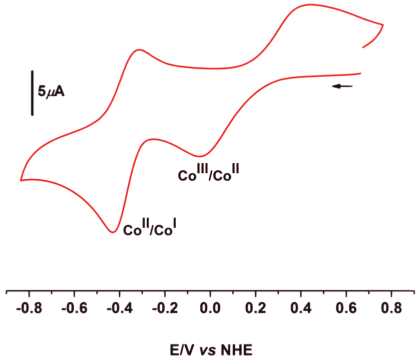

Fig. S5 Cyclic voltammogram of [**Co**] (0.8 mM) dissolved in DMF with Bu_4NBF_4 (0.1 M) measured at a scan rate of 0.1 V s^{-1} as reported by Muresan *et al.*.[1] A glassy carbon working, $Ag/AgNO_3$ reference and platinum wire counter electrode were employed.

References

1 N. M. Muresan, J. Willkomm, D. Mersch, Y. Vaynzof and E. Reisner, *Angew. Chem. Int. Ed.*, 2012, **51**, 12749–12753.