Supporting Information

Combining broadband absorbing electrochromic materials for hybrid greyto-colourless flexible devices

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1. General remarks

1.1. Instrumentation

Nuclear magnetic resonance (NMR) characterizations were performed in a Bruker Fourier 300 MHz spectrometer equipped with a dual (¹H, ¹³C) probe. ¹H spectra were acquired at 300 MHz and ¹³C NMR spectra at 75 MHz. All spectra were obtained at room temperature. Carbon spectra were acquired with a complete decoupling for the proton. Proton and carbon chemical shifts are reported in parts per million (ppm, δ scale) according to tetramethylsilane ($\delta_{H} = \delta_{C} = 0$ ppm) using the solvent residual signal as an internal reference (CDCl₃: $\delta_{H} = 7.26$ ppm, $\delta_{C} = 77.16$ ppm). Coupling constants (*J*) are given in Hz. Resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *dq* (doublet of quartets), *o* (octet), or *m* (multiplet).

Gel-Permeation Chromatography (GPC) was measured on an Agilent Technologies instrument equipped with a UV detector and two SDV columns (porosity 1000 Å; Polymer Standard Services) with THF as the eluent (Concentration;1 mg/mL, Flow rate; 1 mg/min, Temperature; 25 °C).

High-resolution mass spectrometry (HRMS) analyses were performed at Mass Spectrometry Centre of the University of Vienna. ESI mass spectra were obtained on a Bruker timsTOF Flex mass spectrometer in positive ion mode.

Optical, spectroelectrochemical and electrochemical characterization of the Red1/Red1 ECD.

UV-vis absorbance and transmittance was recorded on a Cary 5000 UV-vis-NIR Spectrophotometer (Agilent Technologies, US) running in double beam mode with a solid sampler holder in place. All absorption measurements were performed at 21 °C.

For spectroelectrochemical measurements, the ECDs were connected to an AutoLab PGSTAT 100N potentiostat (Metrohm, CH) and a fixed cell voltage was applied (at selected values) for 60 s, after which the absorbance spectra were recorded.

For switching time measurements, a pretreatment of 15 cycles (-1.5 / 1.5 V, 10 s period) was applied, followed by three cycles with a 120 s period, while monitoring the %T change at a fixed wavelength. The charge consumed by the ECD during a cycle was calculated from the current developed during the experiment through integration of the chronoamperometric signal.

Optical, spectroelectrochemical and electrochemical characterization of **Red1** and **PB** electrodes, and the **Red1/PB** ECD.

UV-vis absorbance was recorded on an Avantes AvaSpec-2048 standard fibre-optic spectrometer equipped with a balanced deuterium-halogen light source. *In situ* spectroelectrochemical measurements of **Red1** and **PB** electrodes were carried out under an argon atmosphere (glovebox) at room temperature in a quartz cell with 1 M LiTFSI/PC as electrolyte and Li as counter and reference electrodes, respectively.

A Solartron Multistat 1470E multi-channel potentiostat was used for electrochemical characterization (cyclic voltammetry and charging/discharging measurements) of the EC electrodes. For the measurements of the EC electrode materials, a three-electrode set-up with **Red1** or **PB** on ITO-coated PET as working electrodes (active area: 1 x 1 cm²), Li as counter and reference electrodes, and 1 M LiTFSI/PC as electrolyte under an argon atmosphere (glovebox) at room temperature was used.

The spectroelectrochemical measurements of the ECDs (incl. UV-Vis and L*a*b* colour coordinates according to CIELAB colour space of the dark and bleached state) were performed *in situ* during device operation. The optimal cell voltages for colouration/bleaching of the ECDs were determined by stepwise increasing/decreasing the cell voltage until no further transmittance changes were observed. The τ_v values were calculated according to DIN EN410. The electrochemical characterization (potentiostatic cycling) of the ECDs was performed with a Solartron Multistat 1470E potentiostat.

1.2. Materials and methods

Commercially available PET-ITO films from Eastman Chemical Company (Flexvue OC50, sheet resistance: approx. 50 $\Omega \Box^{-1}$) were used as transparent conductive substrates. All reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise noted.

Fabrication of the Red1/Red1 ECD

Preliminary investigation of the EC properties of **Red1** was performed in 1 x 1 cm² vertical stack ECDs following the cell configuration [PET-ITO/**Red1**/electrolyte/**Red1**/ITO-PET]. The **Red1** electrodes were prepared by spray coating on PET-ITO substrates. **Red1** was dissolved in CHCl₃ (1 mg/mL, total of 10 mL) by sonication (30 min), and the solution loaded in an aerograph. To assure the homogeneity of the depositions, the aerograph was used at a continuous applied pressure of 1 bar with a 0.3 mm opening and kept at a constant distance from the substrate (5 cm) so that only the aerosol part of the sprayed mixture would deposit onto the plastic substrate. Additionally, the spraying rate was kept constant for each layer and the substrate was placed on top of a heating plate kept at 60 °C, to promote fast evaporation of the solvent and avoid coffeestain effects in the films. The sprayed layers were then assembled into solid-state ECDs with a vertical stack architecture by depositing a UV curable Li⁺-based gel electrolyte layer¹ (thickness: 220 µm) between the previously sprayed ITO substrates and laminate them with a double-sided pressure sensitive adhesive tape (Nitto Denko, JP).

Fabrication of Prussian Blue electrodes

The manufacturing of PB thin films on PET-ITO is described elsewhere.^{2, 3}

Fabrication of the Red1/PB ECD

The ECDs with the cell configuration [PET-ITO/**Red1**/electrolyte/**PB**/ITO-PET] were fabricated with an active (switchable) area of 5 x 5 cm². The ECDs were assembled with a proprietary LiTFSI-containing gel electrolyte under an argon atmosphere in a glove box. A solid polymer electrolyte (HQ674) with LiTFSI as salt, was used as electrolyte and separator in the devices.⁴ The electrolyte was doctor blade coated onto the active area (wet film thickness: 90 μ m) of **Red1**. The **PB**

electrode was then aligned to match the electrolyte-coated electrode and laminated on top. Adhesive Cu tape was used as bus bars.

2. Synthetic procedures

Synthesis of 3,4-di(2-methylbutyloxy)thiophene 1



A solution of 3,4-dimethoxythiophene (502 mg, 3.5 mmol), 2-methylbutan-1-ol (1284.8 mg, 14.6 mmol) and *p*-toluenesulfonic acid (79.7 mg, 0.4 mmol) was stirred in dry toluene (50 mL) for 24 h at 110 °C. During the stirring, the methanol formed during the reaction was regularly removed from the flask through a needle. After cooling at room temperature, water (40 mL), the organic phase separated and again washed with H₂O (2 x 20 mL), dried over NaSO₄, filtered and the solvent removed under reduced pressure. The crude was purified by silica gel column chromatography (PE/DCM: 80/20 to 50/50) to yield **1** as an oil in 28% yield.

¹**H NMR** (400 MHz, CDCl₃) δ: 6.17 (s, 2H), 3.80 (*dq*, *J* = 28.6, 5.2 Hz, 4H), 1.92 (*o*, *J* = 6.6 Hz, 2H), 1.65 – 1.47 (m, 2H), 1.35 – 1.18 (m, 2H), 1.01 (*d*, *J* = 6.7 Hz, 6H), 0.95 (*t*, *J* = 7.5 Hz, 6H); ¹³**C NMR** (75 MHz, CDCl₃) δ 148.0, 97.2, 75.5, 34.7, 26.3, 16.6, 11.4. **HRMS** (timsTOF) *m/z*: calcd for $C_{14}H_{24}O_2SNa$: 279.1389 [M+Na]⁺, found: 279.1389.

Synthesis of the red EC polymer (Red1)



To a solution of **1** in EtOAc (384.2 mg, 1.5 mmol; in 10 mL) was added a solution of FeCl₃ in EtOAc (292.0 mg, 1.8 mmol; in 10 mL). The reaction mixture was stirred for 24 h at RT. After stirring, CHCl₃ (40 mL), H₂O (20 mL), and CH₃OH (20 mL) were added, and the organic and aqueous phases separated. The collected aqueous phase was then subjected to additional extractions with CHCl₃ (2 x 20 mL). The organic phases were eventually combined, washed with a 1:1 mixture of H₂O and CH₃OH (20 mL), and evaporated completely. The crude material was washed (2 x 40 mL) of CH₃OH to remove the impurities and unreacted monomer from the product and afford **Red1** as a red solid in 32% yield.

¹H NMR (300 MHz, CDCl₃) δ: 3.89 (*bd*, *J* = 33.9 Hz, 4H), 1.95 (*m*, 2H), 1.55 (*m*, 4H), 1.22 (*m*, 2H),
1.02 (*d*, *J* = 4.8 Hz, 6H), 0.91 (*t*, *J* = 7.3 Hz, 6H). GPC MW: 109403 Da.

3. NMR spectra



Figure S2. ¹³C NMR (75 MHz, CDCl₃) of **1**.



Figure S3. 1 H NMR (300 MHz, CDCl₃) of Red1.

4. Mass spectra



Figure S4. HRMS (ESI) spectra of 1.

5. Gel permeation chromatography



Figure S5. GPC elugram of Red1 (1 mg/ml) obtained in THF (1 mL/min) at 25 °C.

Table S1. GPC results of Red1	(1 mg/ml) obtained in	THF (1 mL/min) at 25 °C.
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Entry	Мр	Mn	Mw	Mz	Mz+1	Mv	PD
Red1	92719	69878	109403	165781	229733	102329	1.56563

6. Spectro and Electrochemical characterization

Table S2. L*a*b* colour coordinates and visible light transmittance (τv) of the **Red1** and **PB** electrodes.

EC electrodes	τ, / %	L*	a*	b*
Red1	64	83.0	17.7	4.8
PB1	71	88.1	-10.3	-8.8
PB2	63	84.5	-12.9	-11.2
PB3	51	77.8	-17.4	-15.4
Red1/PB1	44 ^a	72.1ª	6.3ª	-4.2ª
Red1/PB2	39ª	68.9ª	3.2ª	-4.2 ^a
Red1/PB3	31 ª	62.9ª	-2.1 ^a	-10.9ª

^a Calculated from the combined absorbance spectra.



Figure S6. Spectroelectrochemical characterization of the **Red1/Red1** ECD at cell voltages of - 1.5 V to 1.5 V.



Figure S7. Switching time measurement of the Red1/Red1 ECD $(1 \times 1 \text{ cm}^2)$ at 1.5 V.

Table S3. Overview of the switching time, visible light transmittance, $L^*a^*b^*$ colour coordinates, and contrast (ΔE) of the **Red1/Red1** device, as a function of the cell voltage.

ECD Red1/Red1	Cell voltage / V	t ₉₀ / s	τ, / %	L*	a*	b*	ΔΕα
Coloured	-1.5	1.8	37	65.8	27.9	7.3	24 5
Bleached	1.5	3.8	61	82.4	-2.2	4.6	34.5

^{*a*} Calculated using the equation: $\Delta E = V[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]$, where ΔL^* , Δa^* , and Δb^* are the differences in the CIE L^{*}, a^{*}, and b^{*} values between the two states.



Figure S8. Cyclic voltammetry of a) **Red1** and b) **PB2** with Li as counter and reference electrodes in 1 M LiTFSI/PC (scan rate: 10 mV/s) before and after 1000 charge/discharge cycles.



Figure S9. Galvanostatic characterization of a) Red1 and b) PB2 with Li as counter and reference electrodes in 1 M LiTFSI/PC.



Figure S10. Electrochemical characterization of the **Red1/PB2** ECD. a) Cyclic voltammetry and b) peak current vs scan rate profile.

7. References

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