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Supporting Information to

Electrochromic Properties of Self–Organized Multifunctional V_2O_5–Polymer Hybrid Films

U. Tritschler[a], F. Beck[a], H. Schlaad[b,c] and H. Cölfen*[a]*

[a] University of Konstanz, Physical Chemistry, Universitätsstraße 10, D-78457 Konstanz, Germany.

[b] Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, D-14424 Potsdam, Germany.

[c] University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Straße 24-25, D-14476 Potsdam, Germany.

Section S1. Experimental Details

S1.1 Chemicals and Materials

Chemicals and solvents were purchased from several suppliers and used as received. Aldrich: 2-chloroethylamine hydrochloride (99%), N-hydroxysuccinimide (98%), 3-mercaptopropionic acid, methyl triflate (99%), thiocholesterol, 4-pentenoic acid, ammonium metavanadate (≥99.5%), bis(trifluoromethane)sulfonimide lithium salt (99.95%), triethylsulfonium bis(trifluoromethylsulfonyl)imide (≥99.0%), propylene carbonate (anhydrous, 99.7%), indium tin oxide (ITO) coated glass slides (70-100 Ω/sq). Iris-Biotech: 1-(3-dimethylpropyl)-3-ethylcarbodiimide hydrochloride (EDAC, 99.4%). 2-(3-Butenyl)-2-oxazoline was synthesized starting from 4-pentenoic acid as described earlier.[1] Synthesis of poly[2-(3-butenyl)-2-oxazoline] and subsequent simultaneous addition of Thiocholesterol and 3-mercaptopropionic acid via thiol-ene chemistry was carried out as described previously,[2] leading to the statistical LC 'gluing' copolymer**.**

S1.2 Analytical Instrumentation and Methods

^{1}H NMR measurements were carried out at room temperature using a Bruker Avance III 400 operating at 400 MHz. $CDCl_3$ (purchased from Deutero GmbH, Germany) was used as solvent, and signals were referenced to $\delta = 7.26$ ppm. Size exclusion chromatography (SEC) with simultaneous UV (270 nm) and RI detection was performed in NMP (+ 0.5 wt % LiBr) at 70 °C, flow rate: 0.8 mL min^{-1}, using a column set of two 300 × 8 mm^2 PSS-GRAM columns (particle size: 7 µm, porosity: 10^2 and 10^3 Å). Calibration was done with polystyrene standards (PSS, Mainz, Germany). MALDI-ToF MS measurement was performed on a Bruker Microflex MALDI-TOF by using 10 µl of polymer precursor solution (2 mg ml^{-1} in THF), 10 µl solution of

DCTB (10 mg ml^{-1} in THF) and 1 µl of sodium trifluoroacetate (0.1 mg ml^{-1} in acetone). Light micrographs were taken in transmission mode with a Zeiss Axio Imager.M2m microscope and a birefringence microscope (Abrio, Cambridge Research&Instrumentation, Inc. CRi, MA, USA). Scanning electron microscopy (SEM) measurements were were performed on a Zeiss CrossBeam 1540XB microscope at an acceleration voltage of 3 kV. The samples were fixed onto standard aluminum stubs by means of double-sided adhesive carbon tape and were sputtered with gold prior to imaging. Contour plots of hybrid films were measured by means of a profilometer (Ambios XP2). The electrochromic behavior of V_2O_5–LC polymer hybrid films was investigated by cyclic voltammetry and simultaneous time-resolved UV-visible spectroscopy. Electrochemical measurements were performed with an Epsilon potentiostat (BASi) und UV-visible measurements with a TIDAS MCS UV/NIR spectrometer (J&M Analytik AG).

S1.3 Hybrid films consisting of V_2O_5 and LC 'gluing' copolymes

The V_2O_5 tactosol was synthesized according to Lagaly et al.[3] The V_2O_5 tactosol was diluted with MilliQ water according to Lausser et al.,[4] finally obtaining an isotropic V_2O_5 dispersion with a concentration of ca. 0.7 wt% (neglecting the amount of coordinated water at V_2O_5 remaining after freeze-drying). The synthesis of V_2O_5–LC polymer hybrid particles was initiated with the isotropic V_2O_5 dispersion and performed as described previously (initial ratio V_2O_5/polymer = 2:1 (w/w), neglecting the amount of coordinated water at V_2O_5 remaining after freeze-drying).[2] Phase-transfer of the hybrid particles (V_2O_5/polymer = ~1.7:1 (w/w),[2] determined by TGA) from aqueous medium to THF was performed by centrifugation, followed by adjusting the final concentration of hybrid particles to ~3 wt. Thin hybrid films on ITO coated glass substrates were prepared by spin-coating the dispersion at 1000 rpm. In case of working with V_2O_5/polymer hybrid films containing the ionic liquid triethylsulfonium bis(trifluoromethylsulfonyl)imide (30-60 wt%), the respective amount of the ionic liquid was added before spin-coating the ~3 wt% hybrid particle dispersion.

S1.4 Assembly of electrochromic device

The electrochromic cells were assembled similar as described by Steiner et al.[5] The devices consisted of two ITO coated glass slides, one acting as working electrode (glass slide coated with the hybrid film) and the other as counter electrode, both separated by means of a thermoplastic gasket (Parafilm). After fusing at ~140°C for few seconds, a platin wire acting as a reference electrode was fixed, and the device was filled with 1 M bis(trifluoromethane)sulfonimide lithium in propylene carbonate and sealed with epoxy glue.

Section S2. Additional Figures

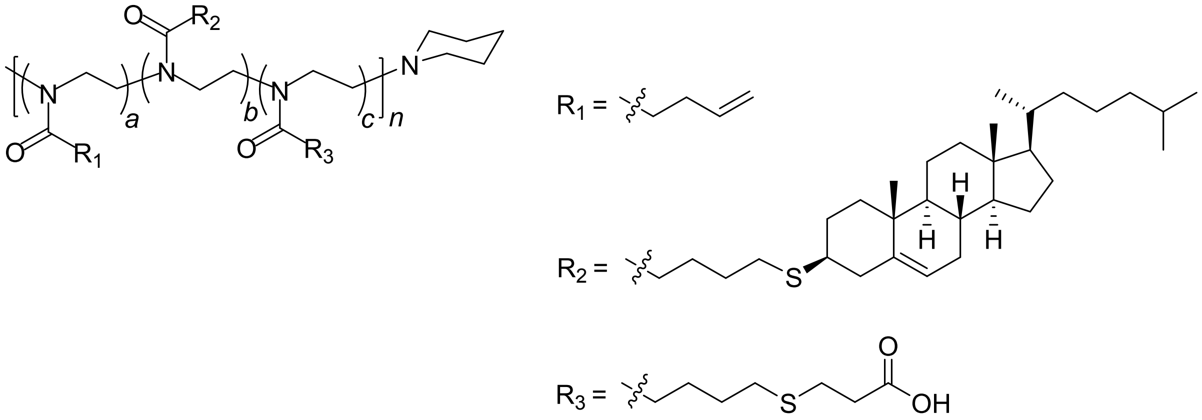

Figure S1. Poly[2-(3-butenyl)-2-oxazoline] (number-average molecular weight, M_n = 9.0 kg mol^{-1}, MALDI-ToF MS, i.e. average number of repeat units n ~ 72), dispersity M_w/M_n = 1.2, GPC) functionalized via simultaneous addition of thiocholesterol (Chol-SH) and 3-mercaptopropionic acid (3-MPA) by thiol-ene photochemistry.[2] The composition was determined to [C=C]/[Chol-SH]/[Boc-Cys] = a/b/c = 0.35/0.23/0.40 by ^{1}H NMR spectroscopy.

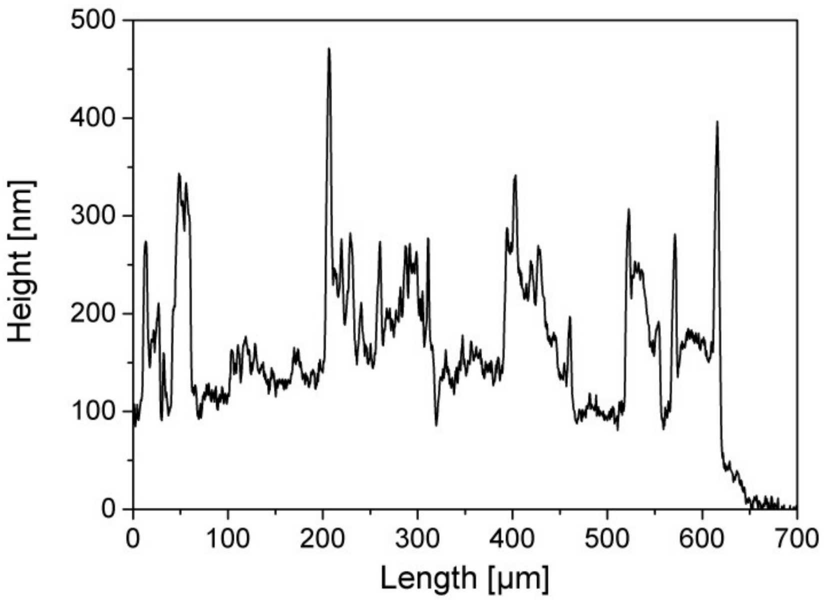

Figure S2. Contour plot of a section of a spin-coated V_2O_5–LC polymer hybrid film, revealing height differences in the range of ca. 100-300 nm. The absorbance for a film shown in this graph is ca. 0.23.

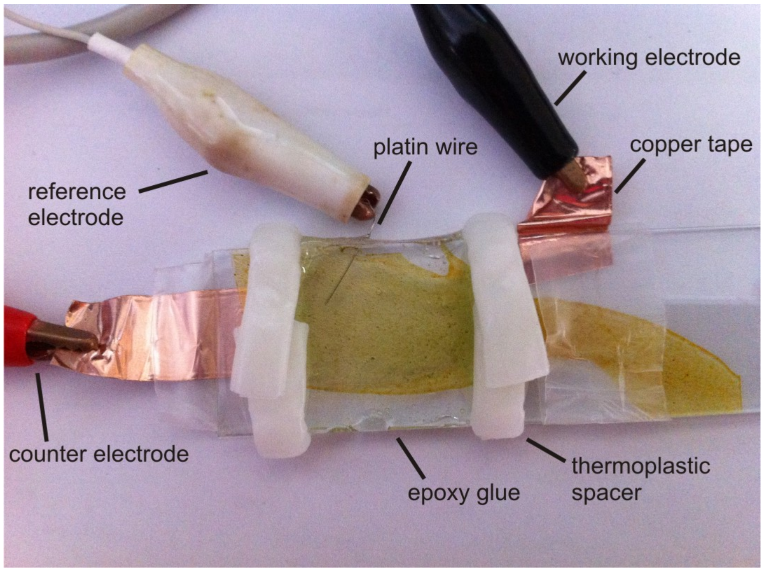

Figure S3. Electrochromic device used for studying the electrochromic performance of V_2O_5–LC polymer hybrid films.

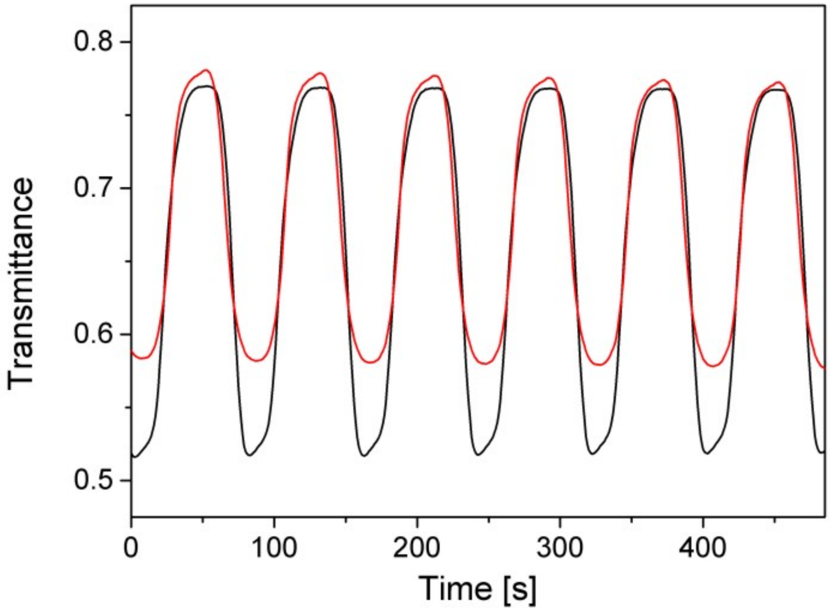

Figure S4. Long-term stability of the V_2O_5–LC polymer hybrid film, which is described in Figure 1 and Figure 2. After over 100 switching cycles (black curve: switching cycles 91-96), the electrochromic device was stored for more than 1 month. Applying alternating potentials (-0.5V–1.5 V; sweep rate of 50 mV s^{-1}) after storing reveals a similar cycling behaviour (red curve). The decrease in transmittance change of ~20 % is mainly attributable to the higher initial transmittance at 450 nm of the film in the oxidized state.

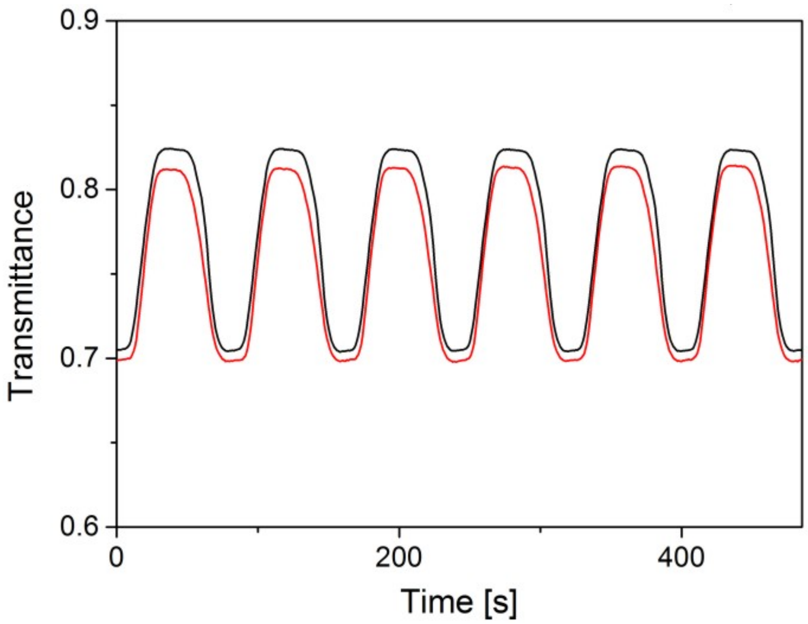

Figure S5. Long-term stability of the V_2O_5–LC polymer hybrid film with a minimum transmittance of ca. 0.7. After over 100 switching cycles between -0.5V and 1.5 V with a sweep rate of 50 mV s^{-1} (black curve: switching cycles 91-96), the electrochromic device was stored for more than 1 month. Application of alternating potentials (-0.5V–1.5 V; sweep rate of 50 mV s^{-1}) after storing reveals a similar cycling behaviour showing only a negligible decrease in transmittance change (red curve). Transmittance values were taken at 450 nm.

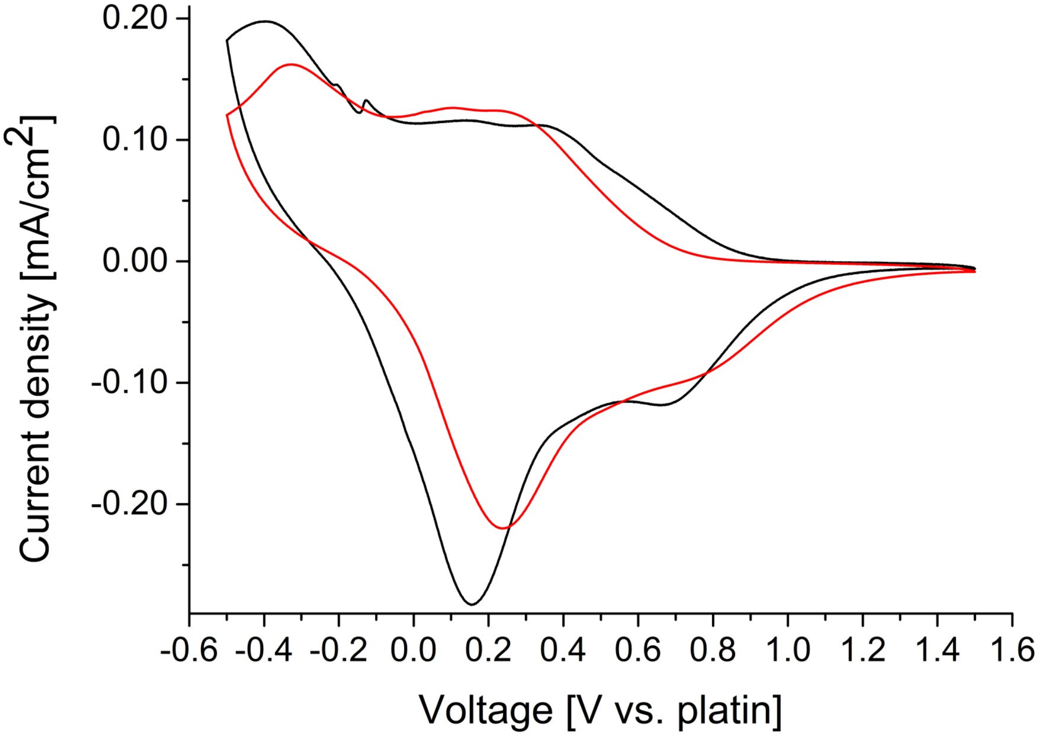

Figure S6. Example cyclic voltammograms of V_2O_5–LC polymer hybrid films, which was recorded in 1 M Lithium bis(trifluoromethylsulfonyl) imide in propylene carbonate with a sweep rate of 50 mV s^{-1} before and after equilibration of the system (cycle number 3 (black) and 17 (red), respectively).

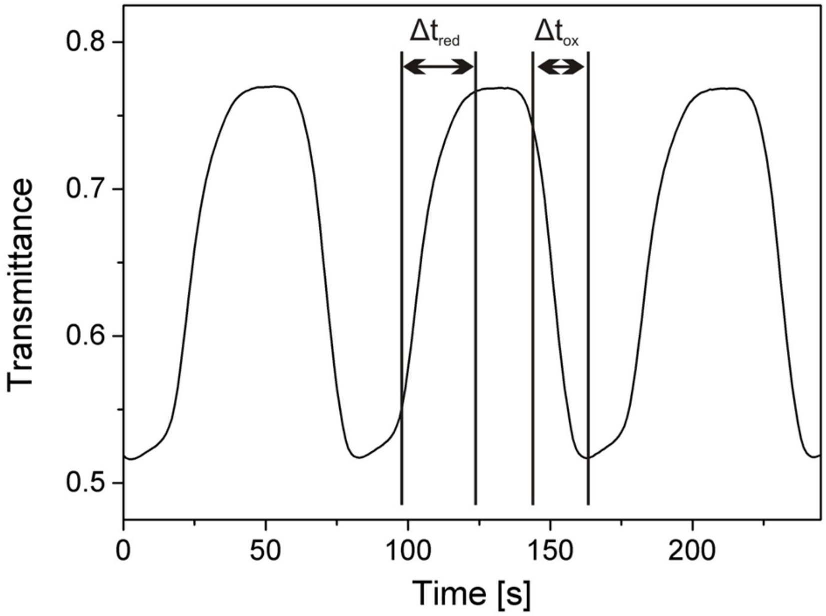

Figure S7. Determination of the response time of oxidation and reduction step of the V_2O_5–LC polymer hybrid species upon applying alternating potentials from -0.5 V and 1.5 V with a sweep rate of 50 mV s^{-1}.

1. A. Gress, A. Völkel and H. Schlaad, *Macromolecules*, 2007, **40**, 7928-7933.
2. U. Tritschler, I. Zlotnikov, P. Zaslansky, P. Fratzl, H. Schlaad and H. Cölfen, *ACS Nano*, 2014, **8**, 5089-5104.
3. G. Lagaly, O. Schulz and R. Zimehl, *Dispersionen Und Emulsionen*, Steinkopff, Darmstadt, Germany, 1997.
4. C. Lausser, H. Cölfen and M. Antonietti, *ACS Nano*, 2011, **5**, 107-114.
5. M. R. J. Scherer, L. Li, P. M. S. Cunha, O. A. Scherman and U. Steiner, *Adv. Mater.*, 2012, **24**, 1217-1221.