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Electrochromic Materials and Devices



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Figure 5.33 PEDOT/PABTS composite polymer repeat unit structures, along with three colour states made possible by utilisation of three electrochromes. Adapted from Ref. [163].

<u>Figure 5.34 Typical cyclic voltammetry</u> polymerisation/deposition of polypyrrole in 0.1 M TBAPF₆/acetonitrile (+1% water) at a scan rate of 100 mV s⁻¹ and at 298 K. Reproduced from Ref. [164]. Figure 5.35 Scanning electron microscope images for a series of PEDOT polymer films on ITO/glass electropolymerized using cyclic voltammetry (a, b, e, f, i, j, m, n) and using potentiostatic polymerization (c, d, g, h, k, l, o, p) in acetonitrile (left image in each pair) and PC (right imagine in each pair). The supporting electrolytes are LiBF_4 (a-d), TBABF_4 (i-l), and TBAClO_4 (m-p). Magnification ~1000, scale bar 10 µm, working distance is 3 mm. Reproduced from Ref. [166].

Figure 5.36 Electrochromic devices fabricated by first dissolving the monomer of the ECP in a precursor electrolyte and sandwiching between two substrates (1) and (2), followed by curing the electrolyte (3) and (4), and applying a potential to polymerise the monomer and achieve the ECP in its fully oxidised (5) and fully neutralised state (6). Reproduced from Ref. [175].

<u>Figure 5.37 Repeat unit structures for several</u> <u>ProDOTs functionalised with various solubilising</u> <u>groups, and photographs of spray-cast films of</u> <u>PProDOT-(CH₂OEtHx)₂ (left) and PProDOT-(C18)₂</u> (right). Reproduced from Ref. [73].

Figure 5.38 Photographs (left), optical microscope images (centre) and AFM images (two far right) illustrating the differences in the film morphology between PProDOTs with linear (top) and branched (bottom) chains [73]. The top images are for dihexylsubstituted PProDOT and the bottom images are for the branched, methylbutyl-substituted PProDOT spray-cast films. Reproduced from Ref. [184].

Figure 5.39 Synthesis and structure of PEDOT:PSS.

<u>Figure 5.40 Addressable pixels (896) in a PEDOT:PSS</u> passive display. Reproduced from Ref. [194].

<u>Figure 5.41 Repeat unit, for example, water-soluble</u> <u>ECPs achieved through electropolymerisation.</u>

<u>Figure 5.42 Repeat unit structures, for example,</u> <u>water-soluble ECPs achieved through chemical</u> <u>polymerisation.</u>

Figure 5.43 (a) Repeat unit structure and steps used to convert an organic-soluble PProDOT into a waterprocessable version, followed by conversion to a film insoluble in aqueous and non-aqueous solvents (top). Solution spectra of the organic-soluble and aqueoussoluble versions (left) and chronoabsorptometry experiment demonstrating the rapid switching possible for the polymer film when switched in an aqueous electrolyte. Reproduced from Ref. [222]. (b) Chemical defunctionalisation of an organic-soluble alkyl-ester PProDOT-BTD to an insoluble polyanion and photographs of the films on submersion in chloroform. Reproduced from Ref. [83].

<u>Figure 5.44 Reaction scheme for chemically amplified</u> <u>photolithography route to pattern polythiophene film.</u>

Figure 5.45 Direct photo-patterning of methacrylatesubstituted ECP-Magenta. (a) Polymer-coated ITO/glass. (b) Application of photomask followed by irradiation. (c,f) Patterned film in neutral state. (d,e) Patterned film on oxidised state. Bottom left shows measured colorimetry of the polymer film before and after cross-linking. Reproduced from Ref. [234].

Chapter 6: Electrochromism within Transition-Metal Coordination Complexes and Polymers

<u>Figure 6.1 (a) Schematic molecular orbital diagram</u> <u>and electronic transitions for an octahedral</u> <u>monometallic complex. (b) Potential energy surfaces</u> <u>of mixed-valence compounds with MMCT transitions.</u> <u>Dashed curves are diabatic states; solid curves are</u> <u>adiabatic states.</u>

<u>Figure 6.2 Polypyridyl ligands for reductive</u> <u>electropolymerisation</u>. Tol is the *p*-tolyl group.

<u>Figure 6.3 Electrochromism of (a) poly-</u> [(dvtpy)Ru(dpb)]²⁺ and (b) poly-[(dvtpy)Ru(Mebip)]²⁺.

Figure 6.4 Polymers for spatial electrochromism.

<u>Figure 6.5 (a) Polymerisation of $[Ru_2(vtpy)_2(tpb)]^{2+}$.</u> (b,c) Absorption spectral changes of the film upon stepwise applying potential from (b) +0.01 to +0.4 V and (c) +0.4 to +1.0 V versus Ag/AgCl, respectively.

Figure 6.6 (a) Poly- $[(dvtpy)Ru(dpba)]^{\pm}$. (b) Logic circuit for a Set/Reset flip-flop. In1 = +0.55 V; In2 = +1.05 V; Out1 = 700 nm; Out2 = 1070 nm. (c-f) Electrochromism at two wavelengths.

<u>Figure 6.7 $[M(NH_2-ttpy)_2]^{2+}$ and $[Fe(bis-anilbpy)_3]^{2+}$ </u> for oxidative electropolymerisation.

Figure 6.8 (a) Electropolymerisation of $[Ru(bis-NPh_3-phen)(Phen)_2]^{2+}$. (b) CV recorded during electropolymerisation. (c) Absorption spectra of the film at (A) 0, (B) +0.9 and (C) +1.3 V versus Ag/AgCl.

Figure 6.9 (a) Poly- $[(Nptpy)_2Ru_2(tppyr)]^{2+}$, (b) CV of poly- $[(Nptpy)_2Ru_2(tppyr)]^{2+}$ and (c) absorption spectra of the film at five different redox stages as shown in (b).

<u>Figure 6.10 (a) [(CN-pbp)Pt(CCPh)] and (b)</u> <u>Absorption spectral changes of poly-[(CN-</u> <u>pbp)Pt(CCPh)] film upon stepwise oxidation versus</u> <u>SCE.</u>

<u>Figure 6.11 Complexes with bithiophene groups for</u> <u>oxidative electropolymerisation.</u>

Figure 6.12 (a) Schematic diagram of layer-by-layer assembly. (b) Molecular structures of polyiminoarylenes with terpyridine substituent groups. (c,d) Different electrochemical oxidation states and colours of complex films with P1 and different metal ions.

<u>Figure 6.13 $[Os(pybpy)_3]^{2+}$ and H_2NDI-X for multilayer assembly.</u>

<u>Figure 6.14 Binuclear complexes with carboxylic or</u> <u>phosphonic acid groups.</u>

Figure 6.15 Ruthenium dioxolene with carboxylic acid groups.

<u>Figure 6.16 Multinuclear ruthenium dioxolene</u> <u>complexes.</u>

<u>Figure 6.17 Ditopic ligands for preparations of</u> <u>coordination polymers.</u>

<u>Figure 6.18 Acrylate-containing [Ru(bpy)₃]-type</u> <u>complexes.</u>

Figure 6.19 Cross-linked polymer film formation.

Chapter 7: Organic Near-Infrared Electrochromic Materials

Figure 7.1 Chemical structures of quinone derivatives **1-7**.

<u>Figure 7.1 Absorption spectra for 1= (-) and 2= (--) in</u> <u>*N*-dimethylformamide (DMF).</u> Figure 7.2 Chemical structures of **14-16** and vis-NIR spectra of **15**⁼ (-) and **16**⁼ (--) in DMF.

<u>Figure Scheme 7.1 Corresponding polymers **17a-d**</u> <u>based on pentacenediquinone.</u>

Figure 7.3 UV/vis/NIR spectra of polymer **17c** in DMF containing tetrabutylammonium perchlorate (TBAP) in its neutral, anionic and dianionic states. The inset showed the NIR absorptions in solution and in the solid state.

Figure 7.2 Chemical structures of NDIs, PDIs, AQIs, **18** and **19**.

<u>Figure 7.4 CD spectra of films of gels of **19** in its neutral, radical anionic and dianionic states.</u>

<u>Figure 7.3 NIR electrochromic polymers **20-22** based on NDI and PDI.</u>

<u>Figure Scheme 7.2 A novel synthetic route of</u> <u>substituted AQIs.</u>

<u>Figure 7.5 UV/vis/NIR spectra of **23b** (a) and **24** (b) in different states in CH₂Cl₂ solution.</u>

<u>Figure 7.6 Selected frontier molecular orbitals of</u> <u>unsubstituted and six-substituted AQIs in their</u> <u>neutral and radical anionic states obtained at the</u> <u>UB3LYP/6-31G+(d, p) level.</u>

<u>Figure 7.7 CD spectra of **25a** film at 0.0, -0.6 and</u> -1.0 V with stepping potentials between -2 and 0 V.

Figure 7.8 Optical attenuation of 26a film at 810 nm.

<u>Figure 7.9 (a) Reaction sequence shows redox</u> <u>transitions between LB, emeraldine salt (ES) and PB</u> (pernigraniline base) states, where A⁼ represents the counter ion. (b) DCA-treated PANI-PAAMPSA films on <u>bisphosphonic-acid-modified indium tin oxide (ITO) to</u> <u>series of switching potentials.</u>

<u>Figure Scheme 7.3 Examples of poly(triarylamine)s</u> <u>by means of Suzuki coupling, Yamamoto coupling and</u> <u>oxidative coupling.</u>

Figure 7.4 Chemical structures of polymers 31-33.

Figure 7.11 (a) Electrochromic behaviour of polyimide **31a** thin film at a (0.00 V), b (0.65 V), c (0.70 V), d (0.75 V), e (0.79 V), f (0.83 V), g (0.88 V), h (0.92 V) and i (0.98 V). (b) Potential step absorptiometry of polyimide **31a** by applying a potential step between 0.00 and 0.98 V.

<u>Figure Scheme 7.4 Schematic diagram of the</u> <u>dimerisation of radical cations of TPAs.</u>

<u>Figure 7.5 Examples of poly(triarylamine)s with</u> <u>different functional groups.</u>

<u>Figure 7.6 Examples of poly(triarylamine)s with</u> <u>starburst triarylamine.</u>

Figure 7.12 Molecular design and electrochromic switching between 0.00 and 0.55 V of **38a** thin film on ITO-coated glass substrate.

<u>Figure Scheme 7.5 Examples of polymers from TPAbased diacids and TPA-based diamines.</u>

<u>Figure 7.7 Copolymer of poly(triarylamine)s from TPB</u> <u>and TPPA.</u>

<u>Figure 7.8 Chemical structures of the electrochromic</u> <u>thermosetting epoxies.</u>

Figure 7.13 Spectroelectrochemistry of a PEDOT thin film in different oxidation states with inset pictures of variation in the blue colour at different oxidation levels. <u>Figure 7.9 Modifications of the side chains of</u> <u>polythiophene and polypyrrole.</u>

Figure 7.14 (a) Percentage transmittance for a 500 nm thick film of PProDOT- $(CH_2OEtHx)_2$ on ITO|glass as a function of applied potential at 1.55 µm (**■**) and 550 nm (•). (b) Percentage total reflectance for a 500nm-thick PProDOT- $(CH_2OEtHx)_2$ reflective electrochromic device (ECD) as a function of applied potential at 1.55 µm (**■**) and 550 nm (•).

<u>Figure 7.10 Examples of copolymers of different</u> <u>electron-donating monomers.</u>

<u>Figure 7.11 Common acceptor units in D-A type</u> <u>electrochromic conjugated polymers.</u>

<u>Figure 7.12 Structures of both p- and n-dopable D-A</u> polymers **58-61**.

Figure 7.15 (a) p- and n-dopable **58** film in monomerfree electrolyte solution. (b) Spectroelectrochemistry of **58** film in three different states: neutral, n-dopable and p-dopable.

Figure 7.13 Chemical structures of D-A conjugated polymers **62-65**.

Figure 7.16 (a) Optical transmittance changes of **62** monitored at 1310 nm while switching the potentials between its oxidised and reduced states. (b) Electrochromic switching, optical absorbance change monitored of at 1550 nm for **63** between oxidised and neutral states.

<u>Figure 7.14 Examples of polymers based on</u> <u>selenophene derivatives.</u>

<u>Figure 7.15 Structures of LuPc₂(**70**) and azulenebased compounds **71** and **72**.</u> <u>Figure Scheme 7.6 Redox-system of azulene-</u> <u>substituted enediynes **71**</u>.

Chapter 8: Metal Hydrides for Smart-Window Applications

<u>Figure 8.1 Basic structure (a) and cross-sectional</u> <u>TEM image of switchable-mirror thin film (b).</u>

<u>Figure 8.2 Transmittance change of Mg–Ni alloy</u> <u>switchable mirrors with different compositions</u> <u>following gasochromic switching.</u>

<u>Figure 8.3 Mirror and transparent states of</u> <u>switchable mirror and its transmittance and</u> <u>reflection spectra.</u>

<u>Figure 8.4 Switching durability of Mg–Ni switchable</u> <u>mirror (a) and Mg–Y switchable mirror (b).</u>

<u>Figure 8.5 Transmittance spectra of Pd/Mg-Ni,</u> <u>Pd/Mg-Ti and Pd/Ta/Mg-Y thin films.</u>

<u>Figure 8.6 Structure of all-solid-state switchable-</u> <u>mirror device and its mirror and transparent states.</u>

<u>Figure 8.7 Structure of switchable-mirror window of</u> <u>practical size and its mirror and transparent states.</u>

Chapter 9: Nanostructures in Electrochromic Materials

<u>Figure 9.1 Operation principle of a typical</u> <u>complementary electrochromic device.</u>

Figure 9.2 Schematic illustration of (a) EDL at the interface between TMO and electrolyte [36]. IHP and OHP are Helmholtz planes (see Section 9.2). (b) The proposed model of EDL [37]. Adopted from Refs [36, 37].

<u>Figure 9.3 (a) Low-magnification TEM image, (b)</u> <u>higher-magnification TEM image showing the coarse</u> <u>surface of WO₃ nanorods and (c) High resolution</u> <u>transmission electron microscopy (HRTEM) images of</u> <u>the as-synthesised WO₃ nanorods. The inset shows</u> <u>the selected area electron diffraction pattern (SAED)</u> <u>takes from the single nanorods. Reproduced from</u> <u>Ref. [30] by Ma, J. with permission from American</u> <u>Chemical Society.</u>

Figure 9.4 Field emission scanning electron microscope (FESEM) images of the WO₃ nanorod film at (a) low magnification and (b) higher magnification. The inset shows a high-magnification FESEM image of the highly oriented compact assembly of WO₃ nanorods. Reproduced from Ref. [30] by Ma, J. with permission from American Chemical Society.

Figure 9.5 Colour changes of the WO_3 nanorod film at different voltages with 1.0 M lithium perchlorate (LiClO₄) in propylene carbonate (PC) as the electrolyte: (a) the as-prepared film, (b) coloured at -1.0 V, (c) coloured at -2.0 V, (d) coloured at -3.0 V, (e) bleached at 3.0 V, (f) corresponding UV-vis spectra and (g) switching time characteristics between the coloured and bleached states for the WO_3 nanorod film measured at ± 3.0 V with an absorbance wavelength of 632.8 nm. Reproduced from Ref. [30] by Ma, J. with permission from American Chemical Society.

<u>Figure 9.6 Cyclic voltammograms of the macroporous</u> and non-porous WO_3 film at 100 mV s⁻¹ scan rate. (Electrolyte: 1 M LiClO₄/PC)

<u>Figure 9.7 (a) Schematic diagram of the synthesis of</u> <u>PEDOT nanotubes in porous alumina structures on an</u> <u>ITO/glass substrate. (b) Electrochromic device with</u>