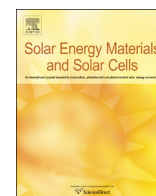




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State-of-the-art electrochromic materials based on metallo-supramolecular polymers

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ABSTRACT

Metal ion induced self-assembly of iron(II)-acetate with the rigid ditopic ligand 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene results in a metallo-supramolecular coordination polyelectrolyte (Fe-MEPE). Fe-MEPE shows a strong absorption band in the visible region around 590 nm, attributed to a metal-to-ligand-charge-transfer (MLCT) transition, which is responsible for the deep blue colour. Large area thin films of high optical quality can be readily fabricated by a dip coating process on transparent conducting electrodes. The Fe-MEPE films have a temperature stability up to 80 °C, measured by optical spectroscopy and XAFS (x-ray absorption fine structure). The cathodically coloured Fe-MEPE shows outstanding electrochromic properties and can be reversibly switched from Fe(II) (blue) to Fe(III) (colourless) by applying a potential of 4.1 V vs. Li/Li⁺. A very high optical contrast ΔT of 71% at a wavelength of 590 nm and a colouration efficiency of around 525 cm² C⁻¹ can be realized. The devices show a long-term stability about 10,000 cycles. Thus, Fe-MEPE is a very promising electrochromic material for future applications of smart windows.

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1. Introduction

Electrochromic materials change their optical properties by application of an external electric potential. Electrochromic or smart windows offer a high potential to enhance the energy-efficiency of buildings. The environmentally significant impact of architectural glazing aims at minimizing climate control and artificial lighting, thus leading to a significant reduction of energy consumption. Metal oxides, such as WO₃, are among the best known materials for electrochromic applications [1]. In the oxidized state, this material is colourless, whereas in the reduced states it is blue. Device fabrication involves costly vacuum deposition and device switching is generally slow. Prussian blue is an attractive electrochromic alternative [2]. Since Prussian blue switches from blue to colourless by reduction, that is complementary to WO₃, it can be used in conjunction with metal oxides to intensify colouration [3]. Polymers such as PEDOT or PANI are also used as electrochromic materials. Like Prussian blue, polymers can be processed from solution and generally exhibit short switching times [4]. Different colours have been realized with these polymers; however, they lack long-term electrochemical reversibility and radiation stability [5]. So far, prohibitive costs, small optical

contrast and low switching speeds have limited commercial applications of electrochromic windows to niche markets. To access the potentially large market for electrochromic glazing new cost-efficient and more variable materials are needed. Here, we present a comprehensive study of an electrochromic metallo-polymer with unparalleled optical properties that is readily processed by wet-chemical means, thus simplifying production and reducing cost. A further advantage compared to traditional electrochromic materials [6,7] is the good scalability.

Electrochromism, first observed by Deb in the metal oxide WO₃, refers to a colour change induced by a redox reaction when an electric potential is applied to the material [8]. The electrochromic active material is applied as a thin film on a transparent conducting substrate, an electrolyte with negligible electronic conductivity, and either an ion-storage or a second electrochromic material on the transparent counter-electrode completes the device. Charging or discharging the device changes the colour in which one species is oxidized while the other one is reduced. Controlling light transmission through an external field remains a challenge in materials science in particular since smart windows are in high demand for prospective applications in climate control, lighting, or privacy as well as displays, data storage, car mirrors and electrochromic inks [9–12]. Among the critical parameters for applications are long-term reversible operations at low switching potential, high optical contrast, low capacities, thermal stability and high-throughput fabrication technologies. Most applications

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require switching from a transparent state to a colour convenient for consumers. While metal oxides belong to the best studied materials to date, the technological implementation of WO_3 in electrochromic windows has been hampered by low colouration efficiencies, low contrast ratios and long switching times [6]. Here, we present an alternative electrochromic material based on a metallo-supramolecular coordination polyelectrolyte (MEPE) [13], which exhibits outstanding properties in performance, variability and fabrication efficiency.

2. Material and methods

2.1. Fe-MEPE synthesis

The 4',4''-(1,4-phenylene)bis(2,2':6',2''-terpyridine) (tpy-ph-tpy) ligand was synthesized and characterized according to the literature procedure [14]. Chemicals were purchased from Aldrich and used without further purification. Fe-MEPE was synthesized with a metal ion to ligand molar ratio of 1:1 [15,16]. 0.78 g (14 mmol) Fe was dissolved in refluxing glacial acetic acid under inert gas to get dispersed $\text{Fe}(\text{OAc})_2$ [17]. After cooling to room temperature the $\text{Fe}(\text{OAc})_2$ solution was added to 7.57 g (14 mmol) of tpy-ph-tpy dissolved in acetic acid (75%) and stirred for 2 h while refluxing. The deep blue solution was dried under vacuum and the obtained solid was dissolved in 100 mL ultrapure water and dried again. 10 g (14 mmol) of a dark blue coloured solid was obtained.

2.2. Dip coating process

Three commercially available types of substrates were used: FTO coated glass (surface resistivity $17 \Omega/\text{sq.}$), ITO coated glass ($15 \Omega/\text{sq.}$) and ITO coated PET (polyethylene terephthalate) foil ($50\text{--}60 \Omega/\text{sq.}$). Before the dip coating process the substrates were washed in ethanol and dried with compressed air. Solid Fe-MEPE was dissolved in EtOH. Concentrations of 14 to 35 mmol L^{-1} and withdrawing speeds ranging from 10 to 100 mm min^{-1} were used. The Fe-MEPE films were dried at 60°C for 24 h. After the dip coating process Fe-MEPE is completely in the reduced state and the films are blue coloured. The reduced state is very stable and do not oxidize in air. A home-built dip coater (Fraunhofer ISC) was used to prepare the films.

2.3. Electrochemical measurements

The electrochemical testing was performed in a half-cell. For the half-cell measurement with lithium as the counter- and reference electrodes, the coated glass with an area of $1 \times 1 \text{ cm}^2$ was masked with tape and immersed in propylene carbonate with 1 M LiClO_4 as electrolyte. Copper tape was attached on the TCO to maintain a good electrical contact. The electrochemical characterization was performed with a Solartron Multistat 1470E potentiostat/galvanostat. The UV/vis spectra were recorded with an Avantes AvaSpec-2048 standard fibre optic spectrometer combined with a balanced deuterium-halogen light source. All measurements were done at a controlled temperature of 21°C . The spectro-electrochemical measurements were carried out in a two electrode half-cell with platinum as a counter-electrode and 3 M KCl in water as electrolyte.

2.4. X-ray absorption spectroscopy

The x-ray absorption fine structure (XAFS) experiment was carried out at the BAMline at BESSY II synchrotron light source in Berlin, Germany. The XAFS spectra at the *K*-edge of iron (7112 eV)

were recorded using a Si(111) double crystal monochromator with a relative energy resolution of 10^{-4} . The XAFS scans in the near edge region (XANES) were carried out in the range from 7032 eV (80 eV below the edge) to 7182 eV (70 eV above the edge) with a step of 1 eV. The extended x-ray absorption fine structure region (EXAFS) was scanned up to $k_{\text{max}}=15 \text{ \AA}^{-1}$ above the absorption edge ($E_{\text{max}}=7968 \text{ eV}$) with a constant step in the momentum space of 0.05 \AA^{-1} . The incident beam intensity has been monitored using an air filled ionisation chamber (Oxford Danfysik IC Plus 50).

The XAFS spectra of the annealed thin film Fe-MEPE samples on quartz glass were measured at room temperature in a fluorescence mode. The fluorescence signal was detected by a silicon drift detector (XFlash 5030 by Bruker Nano) perpendicular to the incident x-ray beam, and the samples were mounted in the standard 45° geometry.

The in-situ XAFS measurements of the annealed solid Fe-MEPE sample were carried out in a transmission mode. The absorption signal was detected using an ionisation chamber of the same type as above filled with Ar gas at ambient pressure. The sample was placed in the beam path in a quartz glass capillary mounted in a PID controlled oven. At each temperature point four XAFS spectra were recorded, so that the last scan followed after 2 h of annealing at the respective temperature.

3. Results and discussion

3.1. Optical properties

Metal ion induced self-assembly of iron(II)-acetate with the rigid ditopic ligand 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene (tpy-ph-tpy) in environment friendly aqueous solutions at room temperature results in spontaneous formation of a rigid-rod type metallo-supramolecular coordination polyelectrolyte (Fe-MEPE) [18]. Fe-MEPE shows a strong absorption band in the visible region around 590 nm, attributed to the metal-to-ligand-charge-transfer (MLCT) transition of the central Fe^{2+} -metal ion in the quasi-octahedral coordination geometry constituted by the terpyridine ligands. This transition is responsible for the deep blue colour of Fe-MEPE [19]. The molar absorptivity ϵ of Fe-MEPE at the MLCT band is $46,890 \text{ M}^{-1} \text{ cm}^{-1}$ in MeOH, $36,980 \text{ M}^{-1} \text{ cm}^{-1}$ in water, and $29,720 \text{ M}^{-1} \text{ cm}^{-1}$ in EtOH. The molar absorptivity of Fe-MEPE films amounts to $27,830 \text{ M}^{-1} \text{ cm}^{-1}$ (see Fig. S1, Supplementary data).

MEPEs are readily processed by conventional polymer processing technologies due to the macromolecular nature of the assemblies. Large area thin films of high optical quality are readily fabricated by layer-by-layer deposition [20] or dip coating. Using a standard laboratory equipment, we routinely fabricate electrochromic Fe-MEPE layers up to a size of $20 \times 30 \text{ cm}^2$ (see Fig. S2, Supplementary data) and larger. The resulting Fe-MEPE films on FTO (fluorine tin oxide) or ITO (indium tin oxide) coated glass as well as on flexible ITO coated PET foil exhibit a total haze value below 1%. The electron microscopy image in Fig. 1c shows a smooth homogeneous surface of fibres or bundles, which are presumably made of individual MEPE rods. The cross-section images (Fig. 1d and e) show very smooth interfaces towards the ambient as well as at the substrate indicating salient wetting and adhesion of the positively charged MEPE to the underlying substrate.

To the eye the films are defect free and perfectly transparent with a pleasant deep blue tint (see Table 1 for $L^*a^*b^*$ values). The film thickness is controlled by the concentration of the dipping solution and/or the withdrawing speed according to the Landau-Levich equation [21]. Changing the film thickness from 32 to 381 nm results in a transmittance of 60% to 3% at 590 nm (see Fig. S1, Supplementary data). According to DIN EN410 a visible light

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