

## A Thin-Film Electrochromic Device Based on a Polyoxometalate Cluster\*\*

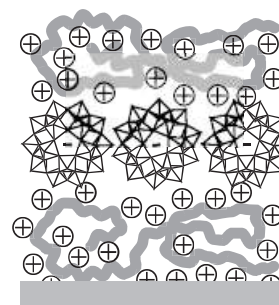
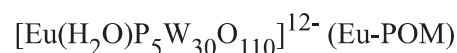
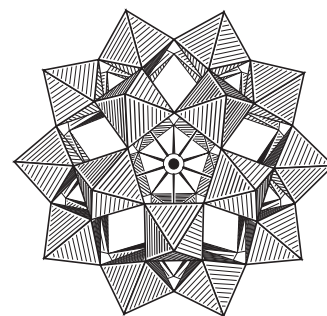
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The realization of molecular-based switching and display devices faces two entirely different challenges that require a scientific remedy. First, components possessing addressable states with distinct physical properties have to be identified and synthesized. The components must operate reversibly with long-term stability and suitable response times. The stimulus threshold and the power consumption for switching between states ought to be low. Second, one or several active components have to be positioned in a predefined way into the actual device's structure. An efficient and rational approach towards this goal is to use strategies from supramolecular chemistry. The future fabrication of such materials may, therefore, rely on principles of molecular self-organization.<sup>[1]</sup> Most likely, thin-film technologies will play a major role in future applications.<sup>[2]</sup>

In terms of possible components for electrochromic devices, polyoxometalates (POMs) are promising candidates due to their ability to act as an electron reservoir, thereby giving rise to colored mixed-valence state species while retaining their structural integrity.<sup>[3-7]</sup> In contrast to many semiconductor nanoparticles and quantum dots, POMs are discrete, molecularly defined metal-oxide clusters with an extensive range of structures and properties. For the realization of such devices it will, therefore, be necessary to identify existing and to synthesize novel POMs with sizeable electrochromic response and stable redox states.<sup>[8]</sup> Despite the potential of POMs, their implementation in advanced materials has remained elusive, mainly due to the fact that they are obtained as crystalline solids, which are difficult to process.<sup>[9]</sup>

Traditionally, thin films of POMs are made by spin coating, the Langmuir-Blodgett technique, electrodeposition, or simply by compressing POM solids against an indium tin oxide (ITO)-coated glass slide.<sup>[10]</sup> More recent approaches involve the use of surfactant-encapsulated POM clusters.<sup>[11]</sup> A simple and versatile technique to prepare thin films of defined thickness and composition has been introduced by Decher, generally referred to as the layer-by-layer (LbL) self-assembly method.<sup>[12]</sup> The consecutive adsorption of oppositely charged polyelectrolytes has since been used in many laboratories and

it was also shown that charged particles could be incorporated into these films in defined ways.<sup>[13,14]</sup> The LbL deposition of POMs with oppositely charged polyelectrolytes has also been demonstrated recently.<sup>[15]</sup> Insertion of functional inorganic components into a polyelectrolyte matrix permits preparation of flexible films of arbitrary shape and diverse properties. The feasibility of preparing POM-containing LbL films with electrochromic properties has been demonstrated by Moriguchi and Fendler.<sup>[15b]</sup> This work presents the structure, the electrochemistry, and response of the films but falls short of realizing sufficient optical contrast and adequate response time. To move towards realistic technological implementations of POM devices, we elaborated on this approach by diligently selecting appropriate POM clusters and taking care of stringent structural control that shall be discussed further in a dedicated publication. In this work, we employed the europium(III) derivative of the Preyssler-type<sup>[16]</sup> heteropolytungstate  $[\text{Eu}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$  (Eu-POM, Scheme 1) as an active component because it exhibits reversible electrochemical behavior accompanied by a large electrochromic response.<sup>[17]</sup>



Scheme 1. Top: Structure of the Eu-POM. Bottom: Schematic representation of the LbL film.

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[\*\*] D.G.K. and D.V. thank the BMBF (MaTech 03N8618B) for financial support. S.L. thanks the Alexander von Humboldt Foundation for a fellowship.

The cyclic voltammogram (CV) of Eu-POM, shown in Figure 1A, consists of three peaks at potentials of  $-0.414$  (C1),  $-0.481$  (C2), and  $-0.530$  V (C3) during the cathodic sweep and three peaks at potentials of  $-0.363$  (A1),  $-0.448$  (A2), and  $-0.498$  V (A3) during the anodic sweep; A1, A2, and A3 are the anodic counterparts of C1, C2, and C3. The three pairs of peaks, C1/A1, C2/A2, and C3/A3, correspond to three  $2e^-/2H^+$  redox processes. The values reported here are

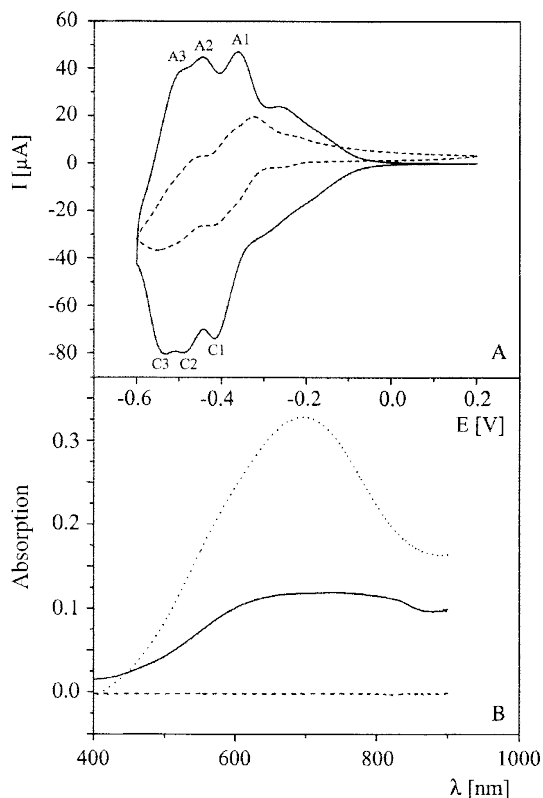


Fig. 1. A) Cyclic voltammograms (versus Ag/AgCl) of Eu-POM in solution (dashed line, ITO electrode, 0.25 mM, ordinate magnified five-fold) and a (PSS/PAH/Eu-POM/PAH)<sub>20</sub> multilayer (solid line, ITO electrode). B) UV-vis spectra of oxidized (dashed line) and reduced (dotted line, -0.65 V versus Ag/AgCl) Eu-POM in solution and a reduced (PSS/PAH/Eu-POM/PAH)<sub>20</sub> multilayer (solid line).

somewhat different to those reported in the literature<sup>[2,3]</sup> because the authors used 1 M H<sub>2</sub>SO<sub>4</sub> and HCl solutions. The peak potentials of Preyssler-type heteropolytungstates are known to exhibit a strong pH dependence, which may be attributed to the deprotonation of the reduced species with concomitant splitting of the reduction steps.<sup>[18]</sup>

As can be seen in Figure 1B, the oxidized form of Eu-POM is completely transparent in the visible region, while the reduced Eu-POM exhibits a broad adsorption band at approximately 700 nm. Each individual redox step is accompanied by an increasing coloration of the solution. The molar extinction coefficient of the six-electron reduced form of Eu-POM is approximately  $2.63 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

The electrochromic device is fabricated by LbL deposition of Eu-POM, poly(allylamine hydrochloride) (PAH), and poly(styrenesulfonate) (PSS) on ITO-coated glass slides. The CV of the (PSS/PAH/Eu-POM/PAH)<sub>20</sub>-modified ITO electrode recorded in Eu-POM-free buffer solution (pH 3.0) is shown in Figure 1A. We observe three peaks at potentials of -0.384 (C1), -0.466 (C2), and -0.522 V (C3) during the cathodic sweep and three peaks at -0.371 (A1), -0.453 (A2), and -0.508 V (A3) during anodic sweep. The multilayer CV demonstrates that the electrochemical property of Eu-POM is fully maintained in the LbL film. For poly(ethylenimine) (PEI)/(PSS/PAH/Eu-POM/PAH)<sub>m</sub> multilayers ( $m \leq 20$ ), the

peak currents increase linearly with the number of layers, confirming that equal amounts of Eu-POM anions are adsorbed in each deposition cycle (not shown). At the same time, the cathodic peak potentials shift slightly negative and the anodic peak potentials shift slightly to positive potential. Moreover, the three pairs of peaks C1/A1, C2/A2, and C3/A3 show the characteristics of reversible surface redox electrochemistry. A plot of the cathodic ( $i_{pc}$ ) and anodic ( $i_{pa}$ ) peak currents as a function of the scan rate  $\nu$  is linear up to  $300 \text{ mV s}^{-1}$  with zero intercept, and the ratio  $i_{pc}/i_{pa}$  is unity at all scan rates, which demonstrates that the redox processes of the surface-confined Eu-POM anions are fast and not diffusion limited.<sup>[19]</sup> Therefore, the surface coverage  $\Gamma$  of Eu-POM anions in the films can be calculated by

$$\Gamma = i_p RT [4 - 2\gamma\Gamma] / n^2 F^2 \nu A \cong 4i_p RT / n^2 F^2 \nu A \quad (1)$$

where  $i_p$  is the peak current,  $\gamma$  is the interaction term,  $n$  is the number of electrons transferred per electroactive species,  $\nu$  is the scan rate,  $A$  is the geometric area of the electrode, and all other terms have their usual meaning; the approximation holds because  $4 \gg 2\gamma\Gamma$ . The surface coverage of Eu-POM anions deposited on the electrode can be directly calculated from the peak current  $i_p$  because the polyelectrolytes constituting the multilayer matrix are not electroactive. The average surface coverage of Eu-POM anions per layer amounts to  $1.47 \times 10^{-10} \text{ mol cm}^{-2}$  or  $1.13 \text{ nm}^2$  per POM. From the single-crystal X-ray structure analysis, the lateral dimensions of the cluster are  $1.7 \times 1.1 \times 1.7 \text{ nm}^3$  or, on average, 1.5 nm mean spherical diameter.<sup>[20]</sup> Assuming an isotropic distribution, the surface area of the POM is estimated to be  $2.3 \text{ nm}^2$ , that is, the electrochemically determined surface coverage corresponds to approximately two Eu-POM monolayers.

A visually noticeable optical contrast (transparent to blue) during potential scanning between 0.2 and -0.6 V manifests that the film is electrochromic. The UV/vis spectrum of the (PSS/PAH/Eu-POM/PAH)<sub>20</sub>-modified ITO electrode shown in Figure 1B was recorded during cyclic voltammetry. The absorbance at 700 nm,  $A_{700}$ , increases to 0.12 at -1.75 V. For a (PSS/PAH/Eu-POM/PAH)<sub>100</sub>-modified ITO electrode,  $A_{700}$  becomes as large as 0.7 at -1.85 V. A single PSS/PAH/Eu-POM/PAH layer generates an optical density of 0.006 in the reduced state. A film less than 1  $\mu\text{m}$  thick would create an optical density of approximately 1, which is sufficient for practical device applications.

To evaluate the response time of the Eu-POM/polyelectrolyte multilayer, a double-potential step chronoamperometric experiment was done by simultaneously recording the absorbance of the film. Figure 2 shows the applied potential, the current, as well as the absorbance of the layer at 700 nm for a (PSS/PAH/Eu-POM/PAH)<sub>20</sub> multilayer. We observe a charging current, which decays rapidly to zero (during bleaching) or to a residual leakage current (during coloration). The residual leakage current may result from reduction of the buffer solution. Both current and absorbance respond within seconds during coloration and bleaching. The stability and reversibility

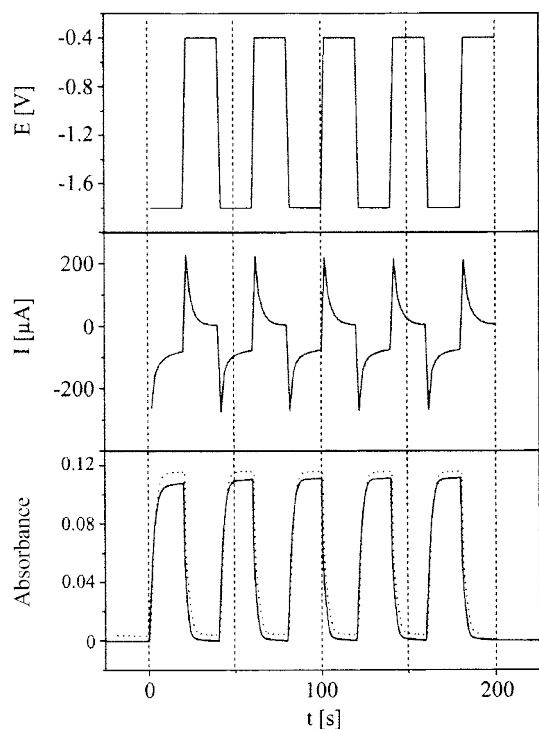


Fig. 2. Potential (Pt electrode), current, and absorbance at 700 nm of the (PSS/PAH/Eu-POM/PAH)<sub>20</sub>-coated ITO electrode during subsequent double-potential steps between  $-0.4$  and  $-1.8$  V. Bottom: 1st (solid line) and 500th (dashed line) cycle; traces are offset for clarity. The response time for coloration and bleaching is 4.2 and 4.4 s, respectively.

of the Eu-POM/polyelectrolyte multilayer was evaluated by performing repetitive double-potential steps. The CVs, the response times for coloration and bleaching, and the absorbance of the electrochromic window do not change noticeably even after 500 cycles.

The optical memory effect of a (PSS/PAH/Eu-POM/PAH)<sub>20</sub>-coated ITO electrode was studied as follows: Initially, the film is colored by applying a potential of  $-1.8$  V versus a Pt electrode and its absorbance at 700 nm is recorded. Then the potential is removed, and  $A_{700}$  is measured under open circuit conditions. Under ambient conditions, bleaching, as observed by a decrease in  $A_{700}$  from 0.1 to 0.01, occurs within 7 min. Under exclusion of oxygen,  $A_{700}$  decays in 20 min and for thicker films the optical memory effect is even better. For example, the blue color of a (PSS/PAH/Eu-POM/PAH)<sub>100</sub>-modified ITO electrode persists for 30 min under ambient conditions. Therefore, it is possible to display information with this device without power consumption.

In conclusion, we have identified the Preyssler ion as a technically attractive component for electrochromic devices. Device fabrication rests on principles of molecular self-organization involving sequential adsorption of the POM and an oppositely charged polyelectrolyte on the conductive substrate from an aqueous solution. The method is readily extended to patterned substrates, so films can be prepared on predefined areas. Moreover, the devices can be prepared at ambient conditions by a robot. The device operates reversibly with suitable response times, which may be reduced further

by optimizing the polyelectrolyte matrix. The low operation voltage and low power consumption are additional advantages of this device. Power is required only for switching and leakage currents can be minimized by operating the device under open circuit conditions. Finally, sufficiently high optical contrast can be achieved even for very thin films. First experiments confirm a stable function, although long-term stability of the device under adverse conditions remains to be tested. Compared to previous studies, we have improved the response time by one to two orders of magnitude and the optical contrast by at least one order of magnitude, thus opening an avenue towards realistic technological targets.

## Experimental

**Synthesis:**  $(\text{NH}_4)_{11.5}\text{K}_{0.5}[\text{Eu}(\text{OH})_2\text{P}_5\text{W}_{30}\text{O}_{110}]\cdot 24\text{H}_2\text{O}$  was prepared as described by Pope et al. [20].

**Layer-by-Layer Assembly:** ITO-coated glass (on one side, about  $6\ \Omega\ \text{m}$ ,  $7 \times 50\ \text{mm}^2$ ) substrates were cleaned according to a literature procedure [21]. Before assembly, the cleaned ITO-coated glass electrodes were functionalized with 3-aminopropyltrimethoxysilane [22]. Layer-by-layer deposition was performed according to published procedures [15c,d]. The following concentrations and adsorption times were used: PEI ( $M_w$  50 000, Aldrich)  $10^{-2}\ \text{mol L}^{-1}$  20 min; PSS ( $M_w$  70 000, Aldrich) and PAH ( $M_w$  8 000–11 000, Aldrich)  $10^{-3}\ \text{mol L}^{-1}$  aqueous solutions containing  $1\ \text{mol L}^{-1}$  NaCl (pH 2.5), 10 min; Eu-POM anions,  $5 \times 10^{-4}\ \text{mol L}^{-1}$  (pH 2.5), 10 min.

**Instrumentation:** Cyclic voltammetry measurements were carried out in a three-electrode glass cell with Eu-POM/polyelectrolyte multilayer coated ITO electrodes ( $1.05\ \text{cm}^2$ ) as working electrode, platinum foil as counter electrode, and Ag/AgCl/KCl ( $3\ \text{mol L}^{-1}$ ) as reference electrode in pH 3.0 buffer solutions. Spectroelectrochemical experiments were performed by measuring adsorption spectra and monitoring the absorbance at 700 nm as a function of time during chronoamperometric measurements with potential steps between  $-0.4$  and  $-1.8$  V versus Pt electrode.

Received: September 14, 2001  
Final version: October 30, 2001

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## Hole Conduction along Molecular Wires: $\sigma$ -Bonded Silicon Versus $\pi$ -Bond-Conjugated Carbon\*\*

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According to Moore's Law,<sup>[1]</sup> by the year 2020 the dimensions of integrated circuit components will have been reduced to approximately 10 nm. The interconnecting wires within such circuits will by then have approached the ultimate limit; that of a linear array of single atoms. Potential candidates for such semiconductive "molecular wires" are  $\sigma$ -bonded chains of silicon and  $\pi$ -bond-conjugated chains of carbon. In recent years readily soluble, high molecular weight polymeric chains of both types have been synthesized. This has made it possible to study their optoelectronic properties in isolation, free from the interchain interactions and morphological complexities which dominate their electronic properties in the bulk solid phase. Here we show that mobilities well in excess of 0.1  $\text{cm}^2/\text{Vs}$  are possible for hole transport along isolated chains of both  $\sigma$ -bonded silicon and  $\pi$ -bond-conjugated carbon. In both cases disorder within the backbone plays a deci-

sive role in determining the magnitude of the mobility and we conclude that values in excess of 1  $\text{cm}^2/\text{Vs}$  should be realizable, even at room temperature (RT), if the disorder can be reduced by either chemical or physical means.

The molecular structures of the polymers studied are shown in Figure 1. All had molecular weights in excess of 10 kDa and consisted of chains of approximately 100 or more monomer units. They could be readily dissolved in benzene with no evidence of aggregation for the conditions used (monomer-unit concentration ca. 1 mM at RT). The solutions were saturated with oxygen prior to irradiation with single nanosecond pulses of 3 MeV electrons from a Van de Graaff accelerator.

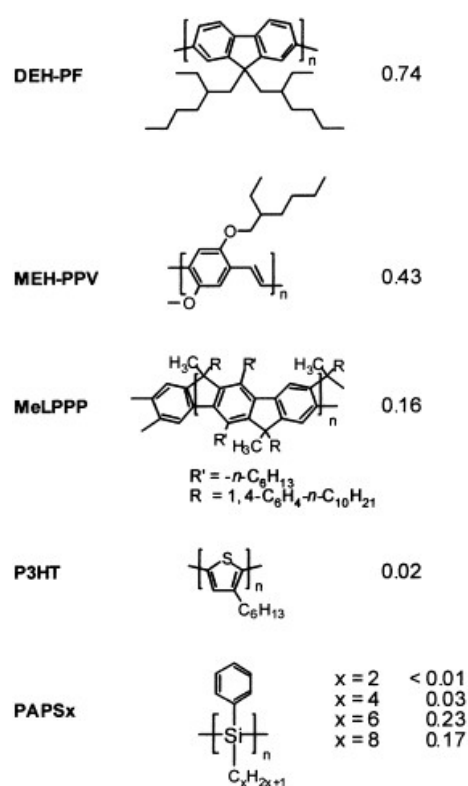
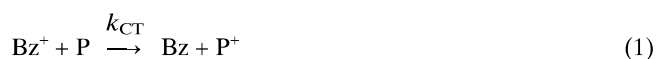


Fig. 1. The molecular structures of the polymers investigated in the present work together with their pseudonyms (left) and one-dimensional, intrachain hole mobilities  $\mu(h_p^+)$  [ $\text{cm}^2/\text{Vs}$ ] (right) determined from the experimental data shown in Figure 2.

Irradiation produces initially a close to uniform concentration of benzene radical cations,  $\text{Bz}^+$ , and excess electrons,  $e^-$ . The latter are highly mobile ( $\mu(e^-) = 0.11 \text{ cm}^2/\text{Vs}$ )<sup>[2]</sup> and react within a nanosecond with the dissolved oxygen to form  $\text{O}_2^-$ . The  $\text{Bz}^+$  ions are unaffected by  $\text{O}_2$  and can diffuse to polymer chains where they undergo charge transfer to the lower ionization potential polymer resulting in the formation of a "radical cation site" or "hole" on the polymer backbone.



If the mobility of the positive charge on the polymer chain is larger than the mobility of  $\text{Bz}^+$  in the solution ( $\mu(\text{Bz}^+) = 0.4$

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\*\* This work was financially supported by The Priority Programme for Materials Research of The Netherlands Organization for Scientific Research (NWO). We thank Dr. T. Kawamori and Dr. Y. Kunimi for assistance in the synthesis of the polysilane derivatives.