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High Contrast Ratio and Rapid Switching Organic Polymeric Electrochromic Thin Films Based on Triarylamine Derivatives from Layer-by-Layer Assembly

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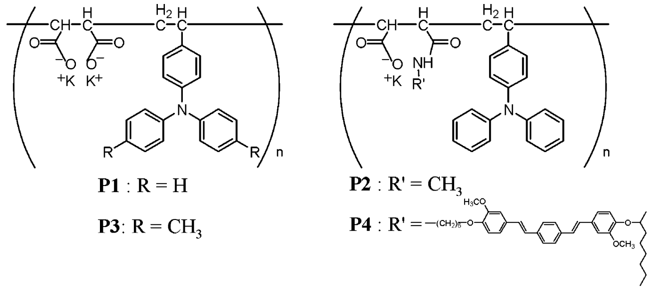
Organic semiconductors and conjugated polymers are currently of wide interest for applications in electronic and optoelectronic devices including light-emitting diodes,[1] thin film transistors,[2] and photovoltaic cells.[3] However, these systems often require expensive and specifically designed organic or polymeric systems to achieve good performance and stability. The desire for cheap and simple displays with reasonable contrast in multiple colors has led to the investigation of an electrochromic device, which can provide reasonable contrast without angle dependence, backlights, or extensive synthetic efforts.[4] More recently thin conducting polymer films have also received attention, and conducting polymers have several advantages such as outstanding coloration efficiency (CE), long lifetime, faster switching time,[5] multiple colors with the same material while switching between their different redox states,[6] and fine-tuning of the band gap (and the color) through chemical structure modification.[7]

Concerning the synthesis of electrochromic films, mostly conventional electropolymerization or spin-casting of soluble derivatives have been used. An interesting alternative is the layer-by-layer (LBL) method developed by Decher and coworkers.[8] It is an effective and convenient method for ultrathin film assembly based on alternatively electrostatic adsorption of oppositely charged species from dilute solutions (solution-dipping variant). The process is simple and inexpensive and allows the incorporation of many different functional materials within a single film without the phase separation. Moreover, typical LBL films consist of highly interpenetrated polymer layers that are regarded as homogeneous composite films, and this technique can create high-quality electrochromic thin films. For the fabrication of thin electrchromic films, the spin-coating variant of the LBL method looks even more promising as it works faster and the films are smoother.[9] So far, electrochromism has been explored on thin films of classical conductive redox-active polymers, like PEDOT:SPS/PXV, polyaniline/Prussian blue nanocomposite, PEDOT-S/PAH and polyoxometalate cluster prepared via the solution-dipping variant of the LBL technique.[10] However, a fast switching time well below 1 s in combination with a high contrast ratio (>50%) has been difficult to achieve, and the typical switching time for electrochromic polymer films is 1−2 s.[10,11] The use of electroactive multilayers with high carrier mobility like triarylamines and their dimers[12] in nanoscale thin film geometry may be a concept to improve switching time.

Scheme 1. Electrochromic Polyanions P1-P4



In this paper, we present electroactive organic polymeric thin films prepared by the LBL method, in which the polyanion species are incorporated in triarylamine polymers. The electroactive triarylamine polymers, **P1**−**P4** (Scheme 1), are newly synthesized, and they are anodically coloring electrochromic species within the LBL film. Anodically colored thin films are chemically and mechanically stable because of the dimer formation of triarylamine. In addition, it is possible to achieve high contrast ratio and a fast switching time. A series of electroactive polymer thin films are used as simple electrochromic cells; their multilayer buildup, electrochemical, and electrochromic characteristics are investigated by UV/vis spectroscopy and cyclic voltam-

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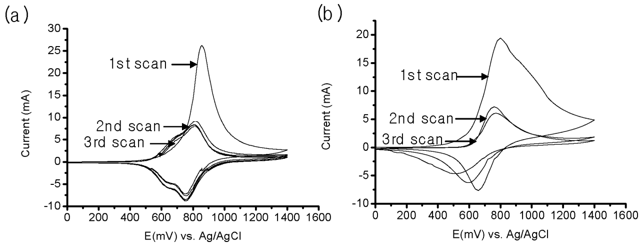

Figure 1. Cyclic voltammograms of triarylamine polymers measured on a Pt working electrode (with 0.1 M TBABF$_4$) at 20 mV/s. (a) Unsubstituted triarylamine polymer, **P1**, and (b) *p*-substituted triarylamine polymer, **P3**.

metry (CV). The chemical structures of these four electrochromic polymers are shown below. (The polymers were synthesized using the route illustrated in Supporting Information.)

As an electrochromic functional moiety, triarylamine has unique properties. Two basic properties of the triarylamine unit are the easy oxidizability of the nitrogen center and its ability to transport positive charges via the radical cation species. Under the influence of an electric field, positive charge is transported by a hopping mechanism, and drift mobility of holes is up to 10^{-3} cm^2/(V·s).[12] Unsubstituted triarylamine undergoes dimerization to tetraarylbenzidine, generally called triaryldiamine, after the formation of the primary monocation radical and the dimer is more easily oxidized than triarylamine. In addition, this dimer forms a more stable radical cation or dication and shows further increased charge carrier mobility.[12] A proof for the formation of the dimer can be observed clearly through the additional oxidation peak of the **P1** or **P2** monolayer films, as seen in Figure 1a. The **P1** monolayer films were simply deposited on a Pt working electrode. Cyclic voltammograms show a clear peak of the monomer at about 855 mV, while the dimer formed during the first oxidation cycle undergoes reversible oxidation at a lower potential of about 685 mV. However, bulky triarylamines, *p*-substituted derivatives of triarylamine, and its higher homologues do not exhibit this dimerization.[12] Therefore, monolayer films from the *p*-substituted polymer, **P3**, or polymer, **P4**, with bulky amine substituents do not show the additional oxidation peak originated from the formation of the dimer, as seen in Figure 1b. In addition, monolayers of **P3** and **P4** are unstable under the applied potential and start to dissolve from the electrode.

The multilayer buildup from the anionic **P1**−**P4** polymers solution and cationic poly(choline methacrylate) (PCM) solution was done by the solution-dipping and the spin-coating methods.[13] The spin-coating method proved, however, to be advantageous, as it can be done faster (multilayer film with 12 bilayers in 24 min). In addition, it needs a fewer number of bilayers to achieve the desired film thickness, as the thickness per bilayer is increased.[9] The multilayer buildup was investigated by UV/vis spectroscopy as shown for the **P1**/PCM film in Figure 2a using quartz as a substrate. It shows the increase of the maximum of the $\pi-\pi^*$ absorbance at 308 nm of the spin-coated conjugated triarylamine film. The deposition process is linear, indicating that the amount of material deposited per bilayer is completely reproducible from layer to layer. A film of five bilayers has thereby usually a thickness between 100 and 130 nm (10 mg/mL concentration), which is not typical for spin-coated LBL layers from less polar polyanions.[13] Alternatively, the multilayer buildup was also performed on an indium tin oxide (ITO)-coated glass substrate with the polyanion and polycation solutions. Monitoring the redox reaction of the **P1**/PCM film by CV as a function of film thickness for up to 10 bilayers reveals the electroactivity of **P1**, as seen in Figure 2b. The films exhibited a redox response despite the insulating nature of the interstitial PCM layer. This supports models suggesting the presence of an interpenetrating polymer network as opposed to discrete bilayers within the film.

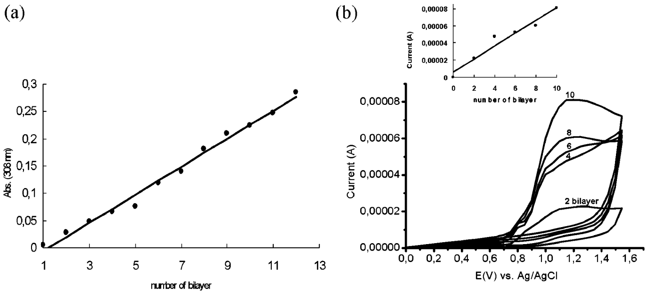

Figure 2. Multilayer buildup from a **P1**/PCM film. (a) The growth of the multilayer films assembled by the spin-coating method at 308 nm. (b) Cyclic voltammograms of sequential bilayer deposition, from 2 to 10 bilayers, at a scan rate of 20 mV/s, between 0 V and +1.6 V (inset: the peak current vs the number of bilayers deposited on ITO-coated glass).

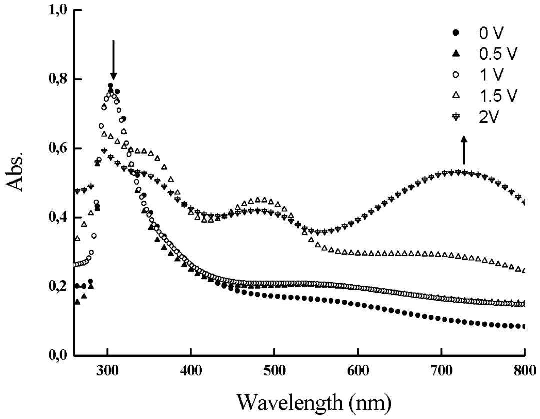

Figure 3. Spectroelectrochemistry of the **P2**/PCM film on the ITO-coated glass substrate at applied potential levels: at neutral (0 V) and oxidized (+2.0 V) states.

Following the electrochemical tests, the optical properties of the electrochromic films were evaluated by using spectroelectrochemistry. For these investigations, five bilayer **P1**−**P4**/PCM films were assembled on an ITO-coated glass substrate, as described earlier.[13] The result of the **P2**/PCM film is presented in Figure 3 as a series of UV/vis absorbance curves correlated to film potentials. Upon oxidation of the **P2**/PCM film, a second band appears at 350 nm besides a band at 303 nm, which is characteristic for triarylamine. We attribute this band to the dimerization of triarylamine, after the formation of an unstable monocation radical. As the potentials became more positive, the absorption bands of the triarylamine and triaryldiamine decreased gradually, with the formation of two new bands at 480 and 710 nm. The lower energy intra-band transitions are assigned to charged species

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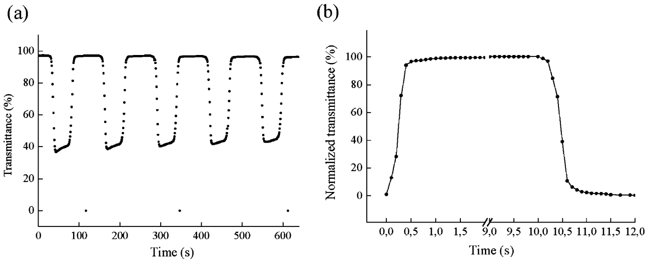

Figure 4. (a) In situ transmittance curves during the continuous cycling test of applied potential of **P2**/PCM film. (b) Normalized transmittance curve during the first pulse potential cycling.

such as cation and dication radicals, which exhibit strong absorption in the near-infrared region.[14] Consequently, the spectroelectrochemical studies confirm the findings using CV regarding the dimer formation and prove the formation of highly colored radical cations and dications.

For the electrochromic studies, the potential of multilayer films on ITO-coated glass was cycled between the neutral (0 V) and the oxidized (+1.6 V) states. While the films were switched, the percentage transmittance (at 633 nm) was simultaneously monitored. Figure 4a shows the in situ transmittance of the **P2**/PCM film during a continuous cycling test of applied potential. **P1**/PCM and **P2**/PCM films showed stable pulse potential cycling performances and similar high transmittance differences ($\Delta T\%$) of 45.83% and 50.01% at 633 nm. In contrast, the **P4**/PCM film showed poor pulse potential cycling performance ($\Delta T\% = 26.12\%$), whereas the polymer film of the **P3**/PCM film did immediately disintegrate after switching under the applied potential. The result for the **P3**/PCM film can be explained by the fact that it consists of p-substituted triarylamine polymers. As a result of the lack of dimerization, it does not form stable thin films after oxidation (the positive charges of the radical cation compensate the negative charges of the carboxylate groups). As a result, the formation of the dimer via the radical cation species could be the key factor to achieve stable and high contrast ratio electrochromic films, both with respect to mechanical stability (no dissolution due to the cross-linking) and chemical stability (more stable radical cations of the dimer). For the **P4**/PCM film, dimerization is also limited (it was not observed in the CV measurements), but generally is possible. Here the bulky bisstilbene side group may hinder the hopping process of the charge carriers because they have a larger band gap than the triarylamine monomers. The most important figure of merit for electrochromic materials is the contrast between oxidation and reduction. **P1**/PCM and **P2**/PCM films showed that the high (>50%) electrochromic contrast ($\Delta T\%$) values are attainable using five bilayers with thin polymer films in nanoscale. Therefore, these results demonstrate that dimerizable **P1** and **P2** are the proper candidates as electrochromic materials to make efficient electrochromic devices. Although these contrast values are already quite high, it is clear that an even greater maximum contrast might be achievable in a film of 10 or 15 bilayers. In addition, the switching time of electrochromic films may limit their applications. For the switching time between all samples, the normalized transmittance was introduced as measured previously.[15] Figure 4b shows the normalized transmittance during the coloring/bleaching processes of the **P2**/PCM film. **P1**/PCM and **P2**/PCM films showed very rapid switching times on the order of 0.30−0.55 s, which is faster than the typical switching time of 1−2 s for electrochromic polymer films.[10] This is a result of both the high charge carrier mobility[12] and the thin nanoscale film structure.

To quantitatively determine the electrochromic properties of **P1**/PCM and **P2**/PCM films, the transmittance difference ($\Delta T\%$) during the coloring/bleaching processes, CE, and response time were calculated as shown in Supporting Information. CE values were calculated for the **P1**/PCM and **P2**/PCM films and the average CE value of the two samples showed approximately 63 cm^2/C. This value is already good enough for electrochromic films; however, the performance would increase further if a solid electrolyte is used as in commercial electrochromic devices. The stability of the electrochromic films was tested by performing continuously 500 cycle numbers in the same experimental setup under the same conditions as described above. After 500 potential cycles, the **P1**/PCM film had degraded slightly whereas the **P2**/PCM film did not change (it is able to retain approximately 93% of its optical response after 500 cycles; see Supporting Information). This gives an indication of the relatively high environmental and redox stability of the **P2**/PCM film compared to the **P1**/PCM film. It can be explained by the fact that the **P1**/PCM film showed 24% of conversion from triarylamine monomer to dimer based on the quatitative analysis of the UV/vis spectra. Interestingly, the **P2**/PCM film showed 63% of conversion, suggesting that a relatively high amount of dimer can be the origin of the stablity.

In summary, we have presented thin organic electrochromic films from newly synthesized anionic triarylamine polymers. The thin polymer films were fabricated using LBL assembly, which is the ideal processing technique to prepare electroactive polymer thin film composites with fine control over morphology and composition. As a result of the dimerization of the triaylamine in multilayers of **P1** and **P2**, fabricated thin films were electrochemically and mechanically stable. Electrochemical and electrochromic characterizations of assembled films revealed that the newly synthesized polymers give rise to high contrast ratio and fast switching electrochromic films. This is a result of the thin nanoscale film formed by the spin-coating variant of the LBL technique in combination with the high charge carrier mobility of triarylamine dimers.

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Supporting Information Available: Synthetic procedures of **P1**−**P4**, multilayer buildup, and optical, electrochemical, and electrochromic analysis and stability test for the assembled films (RTF). This material is available free of charge via the Internet at http://pubs.acs.org.

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