

Electroluminescent Properties of Self-Assembled Polymer Thin Films**

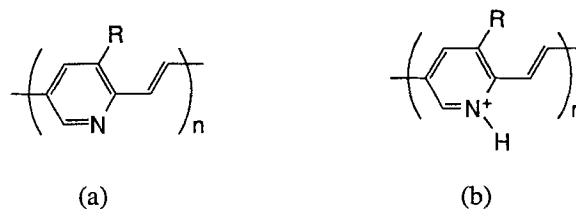
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Organic electroluminescent devices (OLEDs) have attracted a great deal of attention. These devices can be operated at relatively low voltages with good quantum efficiencies. Both polymeric and molecular organic materials have been used in OLEDs, with their optical output covering the entire visible spectrum. The low cost of the organic materials and relative ease with which the devices can be fabricated make OLEDs attractive as candidates for emissive components of flat panel displays.

A number of different factors influence the performance of OLEDs. Some of these factors are inherent to the materials themselves, such as the fluorescence quantum efficiency, charge carrier mobilities, and the stability and processability of the materials. Other factors involve the type of device and the precision with which the device is prepared. In particular it has been shown that the most efficient OLEDs involve heterostructures, which contain separate carrier injection/transport and emissive layers.^[1] Good control of both the uniformity and thickness of these layers is critical in obtaining efficient devices. Vapor deposition of molecular materials allows good structural control of thin films (<300 Å), but the methods used for polymer deposition (spin coating) typically give poor quality films at this thickness.

Here we report the photoluminescent and electroluminescent properties of a new class of polymers for the fabrication of OLEDs. The polymer thin films for OLEDs were prepared by both spin coating and a novel self assembly technique. These new polymers consist of poly(*p*-pyridyl vinylene) (Fig. 1a, R = H), poly(*p*-pyridinium vinylene), (Fig. 1b, R = H) and their butyl-substituted derivatives (Fig. 1a,b, R = C₄H₉). Both the neutral and protonated forms of the poly(*p*-pyridyl vinylene) have good fluorescence quantum yields ($\varphi > 0.8$). The butyl substituted derivatives are soluble in conventional organic solvents.

These polymers are well suited for a novel type of film growth,^[2, 3] which utilizes electrostatic interactions between



PPyV: R = H
Bu-PPyV: R = *n*-C₄H₉

PHPyV: R = H
Bu-PHPyV: R = *n*-C₄H₉

Fig. 1. Neutral (a) and protonated (b) forms of poly(*p*-pyridyl vinylene)s used in this study.

charged polymers to assemble highly uniform films, providing excellent control of film thickness, on a variety of planar and non-planar substrates. Luminescent thin films (100–1000 Å) of poly(*p*-phenylenevinylene) (PPV) have been prepared by first making thin films from the cationic PPV precursor, and then annealing the films at 180 °C for several hours.^[3d, 3e] Uniform thin films made from the poly(*p*-pyridinium vinylene) polymers are highly luminescent and can be prepared without the high temperature annealing step required for PPV thin films.

The electronic absorption spectrum of a thin film of Bu-PHPyV on a glass substrate shows a maximum absorbance at 440 nm (Fig. 2a). The butyl group of Bu-PPyV increases

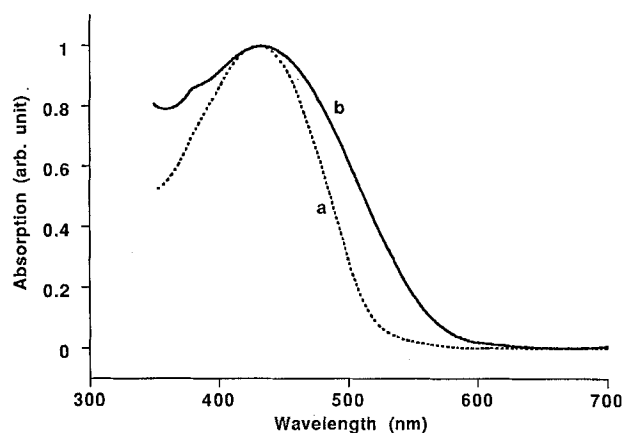


Fig. 2. Electronic absorption spectra of films of Bu-PHPyV (a) and Bu-PHPyV/PSS multilayers (b) on glass.

the solubility of the polymer relative to PPyV. PPyV is only soluble in strong acids and *m*-cresol, while Bu-PPyV is soluble in many organic solvents, including toluene, tetrahydrofuran and chloroform. The photoluminescent quantum yields of the butyl-substituted polymers were measured as THF solutions. The quantum yield of Bu-PPyV is greater than 0.9, and the quantum yield of Bu-PHPyV is *ca* 0.8. The absorption spectrum of Bu-PHPyV is very similar to that observed for films of PHPyV ($\lambda_{\text{max}} = 440$ nm), consistent with the butyl substitution having little effect on the electronic structure of the polymer.

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[**] This work was supported by the New Jersey Commission of Science and Technology through the Advanced Technology Center for Photonic and Optoelectronic Materials (ATC/POEM), as well as the Princeton Materials Institute (PMI), the National Science Foundation MRL Program (DMR-91-20668, TMS and MJM).

The cationic nature of Bu-PHPyV and PHPyV makes them ideally suited for a film growth technique which uses electrostatic interactions between charged polymers to sequentially grow multilayer films.^[2, 3] The first step involves derivatizing the substrate to give it a charged surface; this charged substrate is then dipped into a solution containing the oppositely charged polymer. For example, a positively charged substrate would be dipped into a solution of a negatively charged polymer. The polymer adheres strongly to the surface. The substrate is removed from the solution and washed thoroughly to remove any excess polymer. The sample is then treated with a solution of a cationic polymer, which adheres strongly to the now anionic surface. The sample is removed and washed thoroughly and is now ready for a second treatment with the anionic polymer.

We have successfully prepared a number of multilayer films using this electrostatic self-assembly technique. The multilayer polymer thin films (*i.e.* Bu-PHPyV/PSS, Bu-PHPyV/SPANI) have essentially the same electronic absorption spectrum (Fig. 2b) as that of Bu-PHPyV bulk film. Growth of the polymer films was followed by monitoring the absorbance at 440 nm as a function of the number of layers. As illustrated in Figure 3, the absorbance of multilayer Bu-PHPyV/PSS and Bu-PHPyV/SPANI films increases linearly with the number of bilayers (each bilayer consists of one cationic and one anionic polymer layer). The thin film in this case was assembled on ITO-covered glass, which was initiated with polyaniline to give it a positive surface charge.

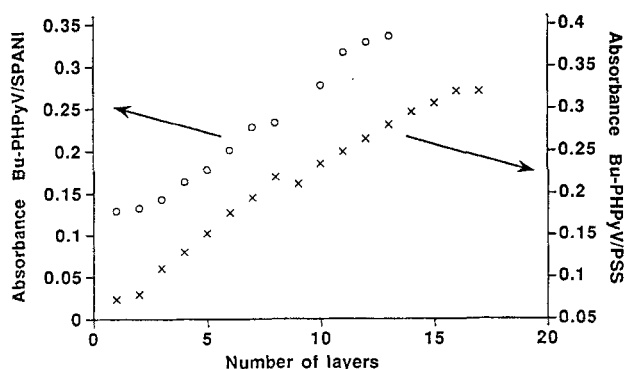


Fig. 3. Plot of absorption versus number of bilayers for Bu-PHPyV/PSS (indicated by x) and Bu-PHPyV/SPANI (indicated by o) on a polyaniline-initiated surface.

The small drop in the curves at 9 layers corresponds to the point where the film was left out for ten hours between treatments. The film in this case was stored in air. Ellipsometric measurements made on identical films grown on silicon substrates give a thickness of $17 \pm 3 \text{ \AA}$ for the Bu-PHPyV/PSS bilayer. The final thickness of a 17 bilayer film is roughly 290 \AA . Atomic force microscopy (AFM) showed that these films are highly uniform. AFM images of films grown on silicon substrates are featureless with similar RMS roughness to the initial substrate (RMS roughness = 4 nm).

The photoluminescent yields for Bu-PHPyV/SPANI films were much lower than for analogous Bu-PHPyV/PSS films. The energy band gaps of Bu-PHPyV and SPANI are close (PPyV, $\lambda_{\text{max}} = 440 \text{ nm}$; SPANI, 320, 435, 1400 nm); as a consequence, an exciton generated in Bu-PHPyV may migrate to the SPANI chain. Because of the large number of trap sites on the SPANI chain, the exciton will decay non-radiatively, reducing the fluorescence quantum yield.^[4] This process in the Bu-PHPyV/PSS thin film is eliminated because of the much wider band gap in the PSS relative to that in Bu-PHPyV. The excitons thus remain localized on Bu-PHPyV.

Aluminum electrodes were vapor deposited onto spin-coated films of Bu-PPyV and Bu-PHPyV as well as a 17-bilayer film of Bu-PHPyV/PSS. The current–voltage profile of the Bu-PHPyV/PSS device is shown in Figure 4 (forward bias, *i.e.* ITO positive and Al negative). The device has a turn-on

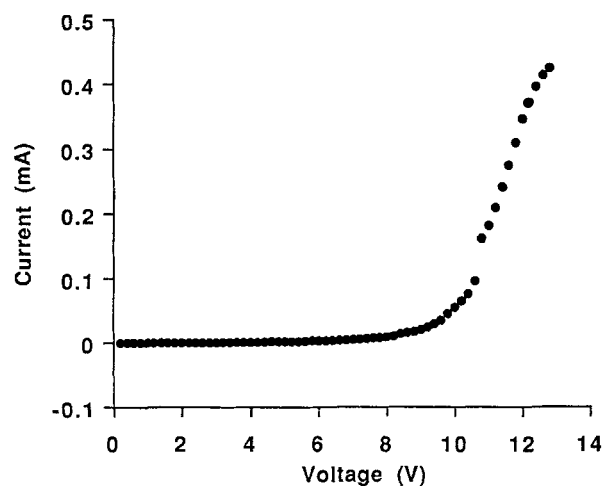


Fig. 4. Current–voltage profile of the Bu-PHPyV/PSS (17 bilayers on polyaniline-initiated ITO).

voltage of about 10 V. No significant leakage current was observed as the device is operated, indicating there is no significant counterion migration in the polymeric thin film. Interestingly, the reverse bias turn-on voltage is comparable to the forward bias turn-on voltage for the Bu-PHPyV/PSS device, although the device fails within a few seconds under reverse bias. The relatively low reverse turn-on voltage in this device may make it possible to operate these OLEDs efficiently with an AC current. Further detailed study is in progress in our laboratory.

Figures 5a, b show the photoluminescence (PL) and electroluminescence (EL) spectra, respectively, of the Bu-PHPyV/PSS film. Visually the PL and EL output appear very similar, but the spectra are clearly different. Vibronic fine structure is observed in the EL spectrum (the vibronic energy separation is roughly 1500 cm^{-1}), which is not present in the PL spectrum. Similar fine structure is observed in the EL spectra of PPV LEDs.^[5] The EL spectra for devices prepared with Bu-PPyV and Bu-PHPyV films are also shown in Figure 5 (c and d, respectively). The EL spectra of both the

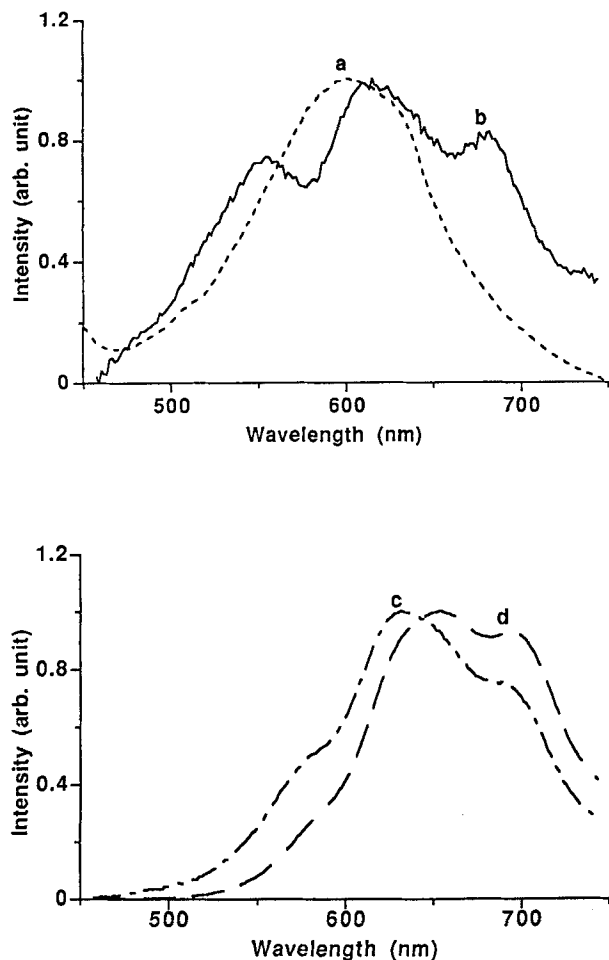


Fig. 5. a) Photoluminescence spectrum of a film of Bu-PHPyV/PSS; b) electroluminescence spectrum of Bu-PHPyV/PSS; c) electroluminescence spectrum of a spin coated Bu-PPyV film; d) electroluminescence spectrum of a spin coated Bu-PHPyV film.

Bu-PHPyV and Bu-PPyV devices are red-shifted relative to the Bu-PHPyV/PSS device. Similar red-shifts were also observed in PL spectra of these films. One explanation for this red shift is that the relatively thicker films formed by spin coating absorb more of the short wavelength light than the self-assembled films. This filtering of the shorter wavelength light would lead to an apparent red shift of spun coated films as observed.

We have found the OLEDs made from these pyridyl-vinylene polymers to have short lifetimes. At an applied bias of < 25 V (for a 1000 \AA film) the devices will run for a fairly long time (≈ 1 hour), but if the voltage is raised above this level the devices fail in < 10 minutes. The quantum efficiency of the device is typically 10^{-4} photons/electron or less. The electrochemical properties of this class of polymers suggest that they may be stable to reduction (electron injection), but not oxidation (hole injection).^[6a, 6b] In order to determine if hole injection from ITO leads to device failure we prepared a single heterostructure device with a hole injecting layer between the poly(*p*-pyridyl vinylene) films and the ITO anode. This device had a 500 \AA film of PPV between the ITO

and the Bu-PPyV film, and was capped with an Al cathode. PPV is known to be an excellent hole conductor.^[7]

The heterostructured device operates with a good quantum efficiency (5×10^{-4} photons/electron) and will run for several hours on the benchtop under a bias that would cause a simple device (non-heterostructured) to fail within a few minutes. The EL output is identical to that of a Bu-PPyV device without the PPV hole injection layer, suggesting that the EL comes exclusively from the poly(*p*-pyridyl vinylene) layer. Presumably holes and electrons accumulate at the PPV/Bu-PPyV interface, leading to exciton formation in Bu-PPyV and not oxidation. We are currently working on growing a film of Bu-PHPyV/PSS on a PPV film to see if device heterostructure can lead to improvements in the efficiencies and lifetimes of OLEDs prepared from these self-assembled films as well.

In summary, we have reported a novel class of fluorescent polymers and their application in the design and fabrication of organic light emitting devices. The success in fabrication of OLEDs by a simple electrostatic deposition technique suggests that this technique may be useful for the preparation of uniform thin films for large area displays. Heterostructured devices, utilizing a PPV as a hole injector, were shown to have good efficiencies and reliabilities. We are currently investigating other methods for the fabrication of heterostructured devices, including depositing self-assembled multilayer films onto PPV and other hole-injecting substrates, as well as the use of electrostatic deposition to lay down both the carrier transport layers and the emissive layer.

Experimental

Poly(*p*-pyridyl vinylene) (PPyV) and poly(3-*n*-butyl-*p*-pyridyl vinylene) (Bu-PPyV) were prepared by cross-coupling the corresponding 2,5-dibromopyridine and *E*-1,2-bis(tributylstannylethylene) in the presence of a palladium catalyst.^[6] Gel permeation chromatography of Bu-PPyV gives a molecular weight of roughly 7000 g/mol. Poly(*p*-pyridinium vinylene)s (PHPyV and Bu-PHPyV) were prepared by treating the neutral polymer solutions with dodecylbenzene sulfonic acid (DBSA) or methane sulfonic acid (MSA). 2,5-dibromopyridine (98%), 3-*n*-butylpyridine (98%), MSA (99%), triphenylphosphine (99%) and palladium chloride (99%) were purchased from Aldrich Chemical Company and used as received. DBSA (BIO-SOFT S-100, 96%) was kindly provided by Stepan Company. Sulfonated polyaniline was synthesized according to literature procedures.^[8]

The solution of Bu-PHPyV used for the layer growth was prepared by first dissolving Bu-PPyV in tetrahydrofuran followed by dilution with acetone to a final composition of 70/30 v/v THF/acetone. This solution was then acidified with MSA to a measured pH of 0.0 (Corning model 220 pH meter). The final solution concentration was roughly 1 mM based on the polymer repeat unit. The PHPyV solution was prepared by dissolving poly(*p*-pyridylvinylene) in *m*-cresol solution followed by addition of acetonitrile to a final solution composition of 40/60 v/v *m*-cresol/acetonitrile. To this solution, an excess amount of DBSA was added to a measured pH of ~ 0.0 . At this stage, the solution color changed from orange-yellow to orange-red. The solution concentrations were in the range of 1 mM to 5 mM based on the monomer unit.

Poly(sodium 4-styrene sulfonate) was prepared in a way similar to the literature method^[3a]. The polymer was dissolved in 0.1 M aqueous NaOH followed by addition of MSA to a pH of 2.5. Acetone was then added give a final solution composition of 70/30 v/v water/acetone. The solution concentration was also 1 mM (polymer repeat unit). Sulfonated polyaniline was first dissolved in *N,N*-dimethylformamide (DMF), then diluted with acetonitrile to 40/60 v/v DMF/acetonitrile. The acidity of the solution was then adjusted with DBSA to give a measured pH of 4.5. Any precipitate was removed by filtration through a $1.0 \mu\text{m}$ filter prior to use.

Simple polymer films were prepared by spin-coating solutions of either PPyV or Bu-PPyV onto a glass or indium/tin oxide (ITO) coated glass substrates. The

self-assembled thin films were fabricated by an electrostatic deposition technique similar to that described by Decher[2], Rubner[3], and others[9]. The polymer films consist of alternating layers of a cationic poly(*p*-pyridinium vinylene) (PPhyV or Bu-PPhyV) and anionic sulfonated polyaniline (SPANI) or poly(4-styrene sulfonate) (PSS). Films are grown by first initiating ITO-coated glass substrates with positive charges. This initiation is carried out by treating the ITO-coated glass with (3-aminopropyl)triethoxysilane[7] or by depositing a thin film of polypyrrole or polyaniline directly on the substrate[3b]. In the latter case, the thickness of the conducting polymer film was limited to keep the total optical density of the resulting substrate below 0.1 in the visible part of the spectrum. The assembly of the multilayer polymer film on the cationic substrate was carried out by sequentially dipping the substrate into each polymer solution (alternating between anionic and cationic). Dipping time in each solution was 30 minutes. After each dip, the film was rinsed with water (for PSS or SPANI) or THF-acetone (for Bu-PPhyV) or *m*-cresol-acetonitrile (for PPhyV) and dried under nitrogen flow before the next deposition.

The LEDs were finished by vacuum depositing an aluminum electrode on top of the organic film. The base pressure of the chamber was 10^{-6} mbar and the evaporating pressure was 10^{-5} mbar. The thickness of the electrode was ca. 1000 Å and the area of the electrode was 1 mm². The *I*-*V* characteristics of the devices were measured on an HP 414BB analyzer and the electroluminescent spectra were collected using an EG & G monochromator and Electrim 1000 TE CCD camera. The light intensity was detected by a calibrated broad-area silicon photodiode, whose photocurrent was measured by HP picoampere meters.

The electronic absorption spectra were measured on an AVIV Spectrophotometer model 14DS (modified Cary-14) and the photoluminescence spectra were taken with a Perkin-Elmer LS-50 Luminescence Spectrometer. The excitation wavelengths used were the maximum absorption wavelengths in the electronic absorption spectra. PSS is transparent at both the excitation and emission wavelengths, while polypyrrole, polyaniline and SPANI have very low optical densities at these wavelengths in the samples prepared here. Photoluminescence quantum yields of Bu-PPyV and Bu-PPhyV were measured in degassed THF solutions, typically 10^{-6} M (based on the monomer repeat unit). The Bu-PPhyV was made by adding stoichiometric amount methane sulfonic acid to the Bu-PPyV solution. Rhodamine B in ethanol was used as a reference ($\phi = 1$)[11]. The excitation wavelengths for the polymer solutions and Rhodamine B were 420 nm and 530 nm, respectively. The photoluminescent quantum yield of Bu-PPyV is greater than 0.9, and the quantum yield of Bu-PPhyV is ca. 0.8.

Received: November 4, 1994
Final version: January 2, 1995

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Room-Temperature Electrosynthesis of Carbonaceous Fibers**

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Carbon fibers are useful for a wide range of structural, electronic, and catalytic applications.^[1, 2] The typical synthesis involves pyrolysis of either gaseous or polymeric precursors, and must be carried out at high temperatures (above ca. 350 °C).^[2] The local structure of carbon fibers can be either highly ordered, as observed in graphitic nanotubes ("bucky-tubes") derived from a carbon arc,^[3-7] or highly disordered, as seen in materials grown from metal catalyst particles via gas-phase pyrolysis.^[8-14]

Fibrous morphologies have also been prepared via electrochemical synthesis. For example, fibers of the amorphous conductive polymers polyaniline and polypyrrole can be electrochemically synthesized in either porous template membranes or at electrode surface defects.^[15-19] The electrochemical route has the advantage of providing good control over the materials' composition and growth rate. In this work, we report the room-temperature electrochemical synthesis of amorphous carbonaceous fibers that are structurally and morphologically similar to those produced in high-temperature pyrolysis reactions. The fibers form spontaneously at an electrode surface, without the aid of a template, during cathodic decomposition of carbon tetrachloride in non-aqueous electrolytes.

The electrochemical reduction of halogenated organic compounds has been intensively studied because of its utility in organic synthesis, and the mechanism of reduction has been investigated in some detail.^[20-23] The commonly proposed motif involves one-electron reduction of the organic compound, followed by elimination of halide to generate a carbon-based radical (Eqs. 1, 2).^[20, 24]



Subsequent radical chemistry (e.g., coupling, nucleophilic attack, etc.) can then proceed. A number of workers have

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[**] This work was supported by the Office of Naval Research and the NSF Young Investigator Program through grant # DMR 9357415. The authors wish to thank Victor Gruol for assistance with the XPS measurements, and Andrew Gewirth (University of Illinois) for generous donation of the HOPG substrate.