Ultrathin Conjugated Polymer Network Films of Carbazole Functionalized Poly(p-Phenylenes) via Electropolymerization

Renu Ravindranath,[†] Parayil Kumaran Ajikumar,[†] Sheeja Bahulayan,[†] Nurmawati Bte Muhammad Hanafiah,[†] Akira Baba,[‡] Rigoberto C. Advincula,[‡] Wolfgang Knoll,[§] and Suresh Valiyaveettil*,[†]

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Department of Chemistry, University of Houston, Houston, Texas 77204, and Institute of Materials Research and Engineering, 3 Research Link, Singapore 117543

Received: January 7, 2007; In Final Form: March 23, 2007

Ultrathin films of a cross-linked and chemically distinct conjugated poly(p-phenylene) network via electropolymerization are described. The amphiphilic network precursor was synthesized by incorporating the alkoxy carbazole group ($-O(CH_2)_5Cb$) to a poly(p-phenylene) (C_6PPPOH) backbone. In order to investigate the combined thin film electrochemical and photophysical properties of poly(p-phenylene)s and polycarbazole conjugated polymers, C_6PPPC_5Cb was deposited on substrates using the Langmuir Blodgett Kuhn (LBK) method. The monolayer isotherm of the polymer, C_6PPPC_5Cb, showed a liquid expanded region slightly different from the parent polymer C_6PPPOH. Multilayers (up to 30 layers) were transferred to different substrates such as quartz, gold coated LaSFN9 and ITO substrates for analysis. For conversion to a conjugated polymer network (CPN) film, the electroactive carbazole group was electropolymerized using cyclic voltammetry (CV) resulting in polycarbazole linking units. The differences in the film properties and corresponding changes in the electrochemical behavior indicate the importance of film thickness and electron/ion transport process in cross linked network films. From the electrochemical studies, the scan rate was found to have a considerable effect on electropolymerization with higher oxidation and reduction peak values found for the rigid network polymer compared to the uncrosslinked polymers.

Introduction

Ultrathin films of conjugated polymers have received tremendous interest during the past few decades owing to their diverse applications and interesting physicochemical properties.[1–4] The intrinsic film forming abilities of polymers cast from solution using conventional solution coating techniques are an attractive advantage for practical applications.[5] Polymers with a variety of tailored physicochemical properties can be fabricated as ultrathin films with many different methods such as spin coating, Langmuir–Blodgett technique, layer-by-layer self-assembly, and surface-initiated polymerization.[6–7] Thin films of conjugated polymers are expected to have a wide range of applications in thin film devices including organic light-emitting diodes (OLED), field-effect transistors (FET), and bio- and chemosensors which were fabricated by spin coating or through physisorption of polymers on the substrate. Generally, the properties of conjugated polymers are interesting domains for chemists, who can incorporate functional groups with specific electroactive properties to fine-tune structure–property relationships.[8,9] It is well-known that a balanced and efficient charge injection/transport for both carrier types (electron and hole) is essential for high device efficiency.[10] Polymers, however, are rarely good conductors for both electrons and holes. In most

cases, they transport holes better than electrons. In order to facilitate the charge injection/transport, an additional electron injection/transport layer between the emitter and cathode or/and a hole-transporting layer on the anode side is introduced. Polymer blends which contain a polymer matrix doped with the necessary components, usually small molecules, can provide electron/hole transporting properties.[11] In addition, a more robust approach which minimizes the conventional problems involves the design of new polymers containing both electron and hole transporting segments as well as emissive units.[10a,12] A hole transporting group such as oxadiazole or carbazole can be incorporated either on the main chain or on the side chains to improve the hole transporting ability of the polymer. Even when these structural modifications are incorporated, it is necessary to optimize the quality of the emitting layer by an appropriate deposition technique, to control the film morphology, carrier mobility, and emission yield for achieving high efficiency from devices.[13] In this respect, the Langmuir–Blodgett Kuhn (LBK) technique has been most useful as a technique to get self-organized thin films with good molecular order and alignment.[14–15] The present study summarizes the preparation of two chemically distinct π-conjugated moieties, a poly(p-phenylene) backbone and a hole transporting polycarbazole as the side chain. Moreover, the development of highly crosslinked functional conjugated thin films is delineated.

Poly(p-phenylene)s or PPPs are an interesting class of polymers which have quantitative emission properties, rigid-rod structure with interesting LC phases (anisotropic properties), and enhanced ordering at interfaces.[16,17] Our group has focused on the design and development of homologous series of

* To whom correspondence should be addressed. Tel: +65 68744327. Fax: +65 67791691. E-mail: chmsv@nus.edu.sg.
† National University of Singapore.
‡ University of Houston.
§ Institute of Materials Research and Engineering. Permanent Address: Max-Planck Institute for Polymer Research, Ackermannweg 10, Mainz, Germany.

Carbazole Functionalized Poly(*p*-Phenylenes)

J. Phys. Chem. B, Vol. 111, No. 23, 2007 **6337**
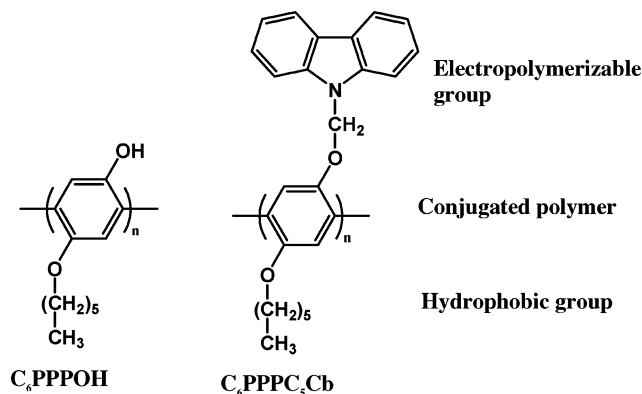
Figure 1. Chemical structure of the polymers, C_6PPPOH and C_6PPPC_5-Cb.

conjugated polymers and micro-/nano-architectures[18−19] toward different film deposition techniques which lead to interesting morphologies and improved properties. Among the various polymers, a six carbon alkoxy chain and hydroxylated poly(*p*-phenylene) (C_6PPPOH) backbone provided the desired amphiphilicity (Figure 1). It displayed a three-phase region with interesting structural contrast along the polymer backbone directly observable in a Langmuir film.[19]

The study of carbazole-based conjugated polymers have gained tremendous interest for preparing functional materials, such as photorefractive materials,[20] photoconductors,[21] nonlinear optical materials,[22] light-emitting,[23] and hole-transporting materials.[24] This is due to their inherent electron-donating nature, excellent photoconductivity and unique nonlinear optical properties. Among the various carbazole incorporated polymers, poly-(N-vinylcarbazole), poly(3,6-N-vinylcarbazole) and polycarbazole have been extensively studied toward electrochemical device applications.[25−26] Among these, poly(N-vinylcarbazole) exhibit interesting electro-optical properties and has been used as light emitting diode materials[27] and photovoltaic materials.[28] Applications in various electrochromic devices and amperometric chemical sensors make carbazole based polymers attractive thin film forming materials.[29,30] The surface grafting of carbazole-functionalized polyfluorenes on indium tin oxide (ITO) surfaces has been demonstrated to form network films.[31] Recently, electropolymerization of a substituted polyacetylene such as poly(*N*-alkoxy-(*p*-ethynylphenyl)carbazole), with electropolymerizable carbazole resulted in the formation of conjugated polymer network (CPN) films.[30a] Here we report the synthesis of an alkoxy carbazole group ($-O(CH_2)_5Cb$) incorporated on poly(*p*-phenylene) (C_6PPPC_5Cb) (Figure 1). The thin films of the polymer were prepared using the LBK and spin coating techniques and subsequently electropolymerized for the preparation of mixed π-conjugated polymer network films.

Experimental Section

Preparation of the Substrates for LBK and SPR. ITO substrates for cyclic voltammetric experiments were cleaned using 2% Hellmanex solution using ultrasonication followed by washing with copious amount of water and then dried under a stream of nitrogen. The quartz substrates for UV and PL measurements were cleaned using a hot solution of $H_2O/H_2O_2/NH_3$ (15.1 g/26.6 g/8.57 g) and finally rinsed with copious amounts of distilled water. The gold-coated LaSFN9 glass substrates for SPR and ESPR measurements were prepared using thermal evaporation. The glass substrate was precleaned using ultrasonication in 2% Hellmanex solution, water, and ethanol, and then dried under a stream of nitrogen. A 2 nm Cr underlayer

was deposited immediately before 50 nm of Au was thermally evaporated at a rate of 0.1 nm/s in a vacuum chamber (Biemtron Co. Inc.) operating at 1×10^{-5} Torr.

Preparation and Characterization of LBK Films of C_6PPPC_5Cb. The polymer C_6PPPOH was synthesized using Suzuki polycondensation as reported previously.[18a, 19a] C_6PPPC_5Cb was synthesized from the precursor polymer by grafting 9-(5-bromopentyl)-9H-carbazole onto the C_6PPPOH side chain. (Supporting Information). The first experiment used to study the interfacial properties of these films at the air−water interface was the isotherm. The experiments for monolayer spreading were performed on a KSV-2000 Langmuir−Blodgett trough (KSV Instruments, Helsinki, Finland) equipped with computer controls. Monolayers were obtained by spreading a 150 μL chloroform solution of C_6PPPC_5Cb (0.5 mg/mL) onto pure Milli-Q water at a neutral pH. After 15 min of solvent evaporation, the monolayer was compressed, e.g., between 0.02 and 5.0 nm^2/repeat unit·min (typically = 0.3 nm^2/repeat unit·min unless otherwise specified). Isotherms of surface pressure vs mean molecular area/repeating unit were measured at 22 $\pm$ 0.2 °C. Isobaric creep measurements and compression expansion cycles were also performed.

The UV measurements were performed on a Shimadzu SPD-10A spectrophotometer. Different layers were transferred to hydrophilic quartz substrate through Z-type deposition and the dependence of film absorption of the number of transferred layers was investigated. Angular scan SPR measurements were performed to investigate the uniform transfer of the different layers on gold substrates. Films transferred onto bare gold were used for electrochemical SPS experiments. SPR set up was based on the configuration introduced by Kretschmann. Details of the set up were described elsewhere.[32a] In short, a 90° high refractive index glass (LaSFN9, $n = 1.845$ @ $\lambda = 633$ nm) prism was used as the plasmon coupler. The light of a p-polarized HeNe laser ($\lambda = 632.8$ nm) mechanically chopped for lock-in detection was reflected off the metal-coated base of the prism. The intensity of the beam reflected at the gold surface was monitored by a photodiode detector and recorded as a function of the incident angle for 'angular scan' measurements.

Electrochemical surface plasmon resonance spectroscopy (EC-SPS) measurements were performed using a surface plasmon resonance (SPR) setup combined with a three-electrode electrochemical cell in a Kretschmann configuration for the excitation of surface plasmons. The details of this setup were described elsewhere.[32] Kinetic measurements were performed to monitor the formation of the film and the oxidation/reduction and doping/de-doping properties of thin film via reflectivity changes as a function of time. Angular measurements were also performed by scanning an incident angle range while the potential was held constant. The cyclic voltammetry (CV) experiments were carried out on a Princeton Applied Research Parstat 2263. The electrode surface area was 0.785 cm^2.

Electropolymerization of the Precursor Polymer on Solid Substrates. The electropolymerization of the thin films of polymer was carried out in a computer controlled μ-Autolab type II potentiostat/galvanostat controlled by the Autolab GPES software version 4.7. The precursor polymers were transferred on to ITO and bare gold substrates. Up to 20 layers were transferred in Z-type deposition to both substrates. The substrates were dried under vacuum and were used as working electrodes for the electrochemistry experiments. The cyclic voltammetry was performed in a three-electrode cell containing 0.1 M tetrabutylbutyammonium perchlorate in acetonitrile solution. The electropolymerization was performed in each case by sweeping
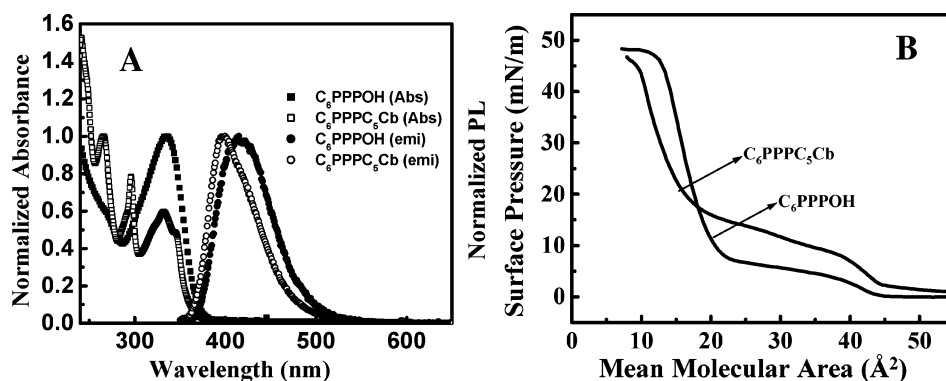
Figure 2. Absorbance and emission spectra of C_6PPPOH and C_6PPPCb in chloroform solution (A) and surface pressure−area ($\pi-A$) isotherms of C_6PPPOH and C_6PPPCb (B).
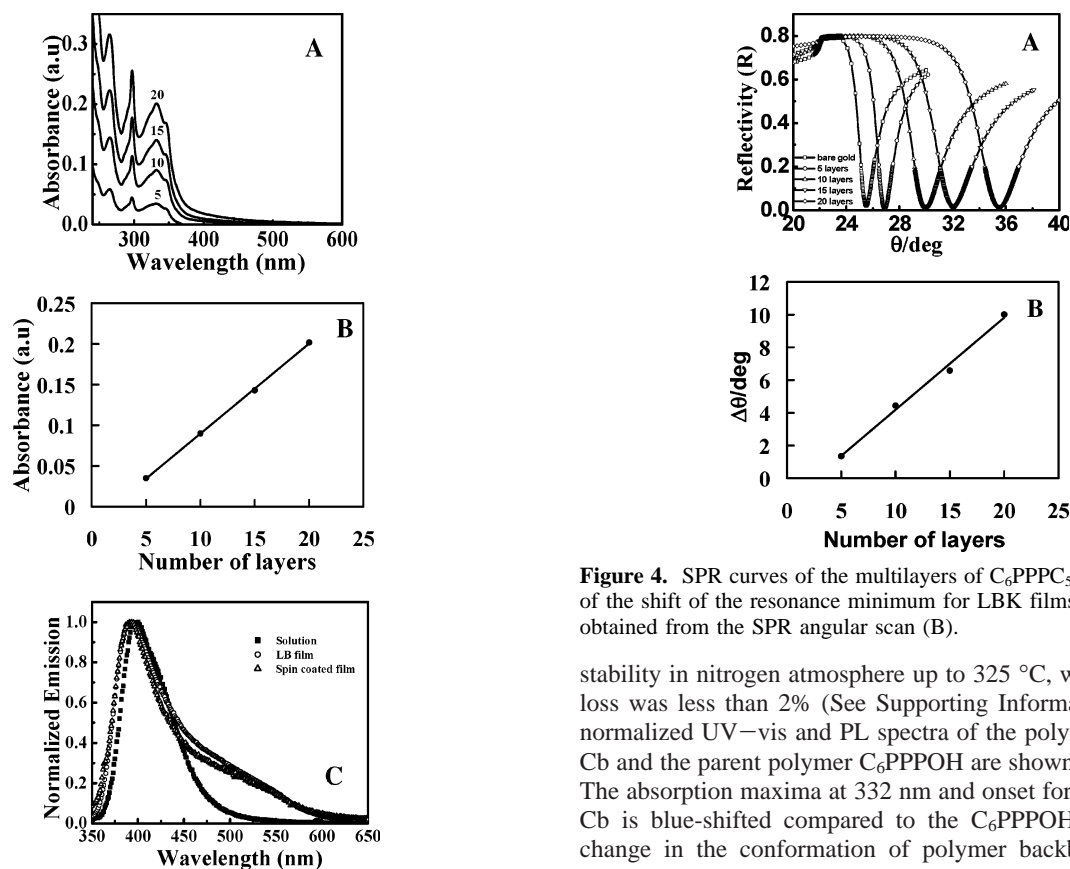

Figure 3. Absorption spectra of LB films of C_6PPPC_5Cb with different number of layers (A) and the dependence of the film absorption on the number of transferred layers (B). Comparison of the emission spectrum of polymer in $CHCl_3$ solution, 20 layers transferred to quartz at a surface pressure 10 mN/m and spin-coated film (C).

the voltage at a scan rate of 100 and 20 mV/s from 0 to 1.1 V against Ag/AgCl as a reference electrode and Pt as a counter electrode.

Results and Discussion

Preparation and Characterization of C_6PPPC_5Cb Polymer Films. The polymer C_6PPPOH was synthesized using Suzuki polycondensation from their respective monomers.[18a,19a] The 9-(5-bromopentyl)-9H-carbazole was grafted on to the phenolic groups of the parent polymer C_6PPPOH to prepare C_6PPPC_5-Cb and characterized using, spectroscopic techniques (NMR, FT-IR, UV−vis), gel permeation chromatography (GPC), and thermogravimetric analyses (Supporting Information). The thermogravimetric analyses of the polymer showed good thermal
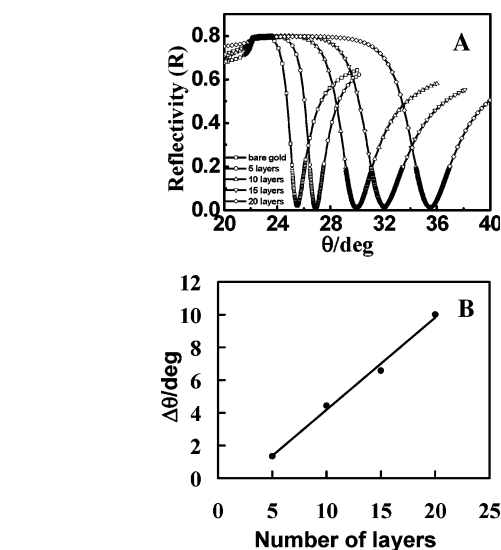
Figure 4. SPR curves of the multilayers of C_6PPPC_5Cb (A) and plot of the shift of the resonance minimum for LBK films of C_6PPPC_5Cb obtained from the SPR angular scan (B).

stability in nitrogen atmosphere up to 325 °C, where the mass loss was less than 2% (See Supporting Information S1). The normalized UV−vis and PL spectra of the polymer C_6PPPC_5-Cb and the parent polymer C_6PPPOH are shown in Figure 2A. The absorption maxima at 332 nm and onset for the C_6PPPC_5-Cb is blue-shifted compared to the C_6PPPOH, indicating a change in the conformation of polymer backbone after the incorporation of the carbazole group. The additional shoulder peaks below 300 nm correspond to the $\pi-\pi^*$, and $n-\pi^*$ transitions of the carbazole peak and were absent in the case of C_6PPPOH. The calculated electro-optical band gap of the polymer C_6PPPC_5Cb is 3.4 eV, which is slightly higher compared to C_6PPPOH (3.19 eV). The emission maximum (λ_{emis} = 400 nm) of C_6PPPC_5Cb was blue-shifted by 15 nm compared to the parent polymer C_6PPPOH. This may be due to a reduction in the persistence conjugation length of the PPP backbone due to the grafting of the bulky carbazole moiety.

In order to study the film deposition of the newly synthesized polymer, LBK technique was used, which could provide self-organized thin films with high molecular order and alignment. Our previous studies on Langmuir−Schaefer (LS) monolayer and LBK multilayer film of a newly designed amphiphilic hydroxylated poly(p-phenylenes) (C_nPPPOH) showed that the polymer with a short alkoxy group (C_6PPPOH) forms a more uniform monolayer at the air−water interface and can be transferred to form multilayered films as compared to a long-alkoxy chain derivative. The isotherm of the polymer C_6PPPOH

Carbazole Functionalized Poly(*p*-Phenylenes)

J. Phys. Chem. B, Vol. 111, No. 23, 2007 **6339**
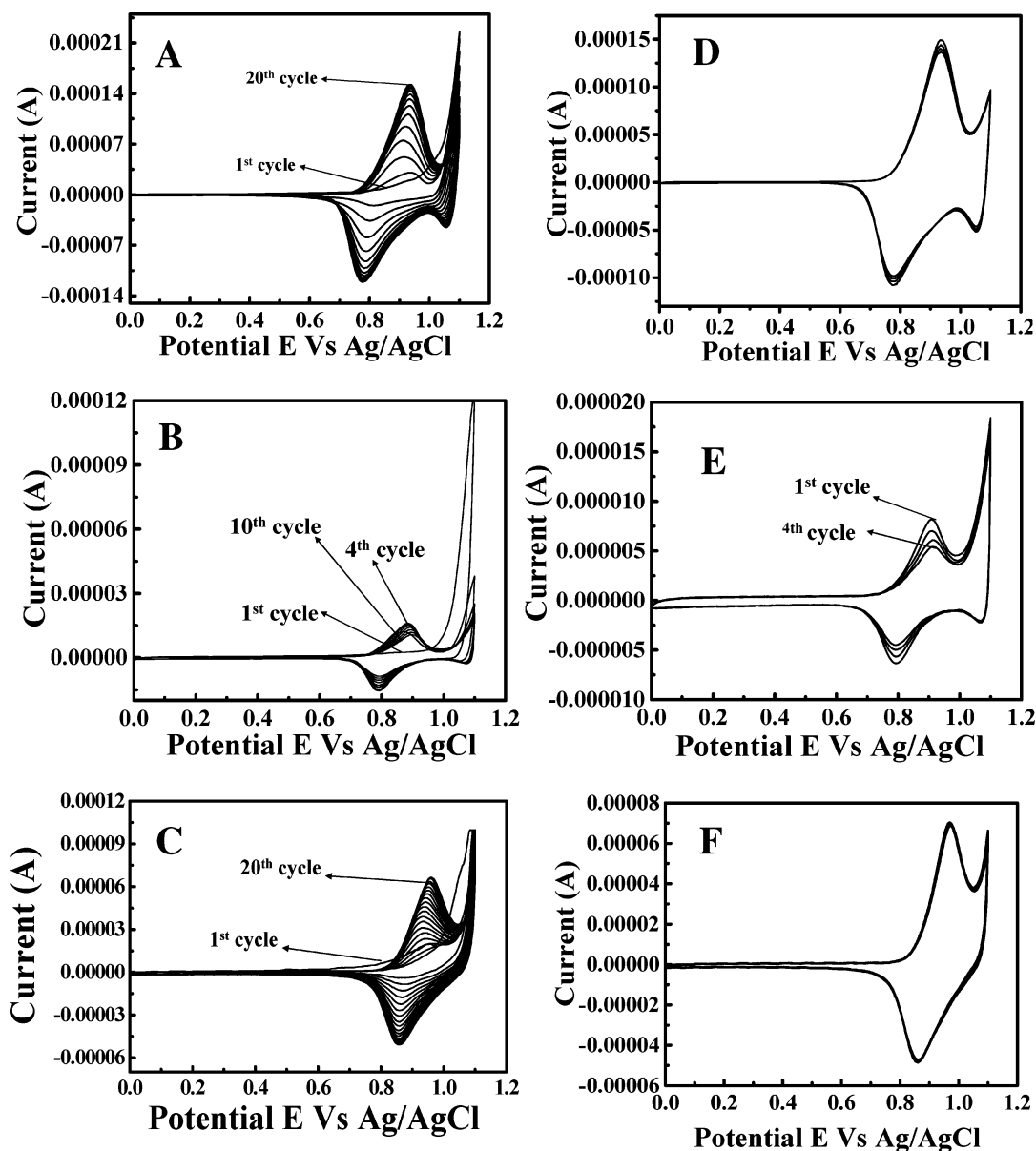
Figure 5. CV for electrochemical cross-linking of 20 layers (A) and 5 layers (B) of LB film and spin-coated (C) of C_6PPPC_5Cb at scan rate of 100 mv/s. (D–F) Corresponding precursor polymer free scan.

exhibited a liquid expanded region. A similar characteristic was observed for the C_6PPPC_5Cb. The isotherm was shifted more toward the condensed solid-state phase (Figure 2B). The addition of the carbazole group seems to increase the viscoelastic component of the film while retaining amphiphilicity to form a good monolayer at the air–water interfaces. Both polymers C_6PPPOH and C_6PPPC_5Cb have a collapse pressure of ~43 mN/m. The extrapolation of the solid region in the surface pressure–area isotherm to zero pressure resulted in the area per repeat unit of ca. 0.20 nm^2, which is close to the cross sectional area of the alkyl chain. This confirms that the carbazole incorporated polymer, C_6PPPC_5Cb, forms a stable monolayer at the air–water interface with close packed alkyl chains.

In order to study the deposition of multilayers of C_6PPPC_5-Cb polymer, the monolayers were transferred to different hydrophilic substrates by Z-type deposition at a surface pressure of 10 mN/m. Increase in absorbance in UV–vis studies and change in peak shifts ($\Delta\theta$) from SPR data of LBK films of C_6PPPC_5Cb transferred to quartz and Au/LaSFN9 substrates were linear to the number of layers deposited (Figure 3A,B and Figure 4A,B). The peak-shifts ($\Delta\theta$) of angular scans of the

plasmon curves of LBK multilayer assemblies on the Au surface relative to the bare gold increases linearly with the number of layers (Figure 4A,B). A similar result was found for C_6PPPOH polymer too.[19a] The thickness was calculated from SPR data using a refractive index value of $n = 1.6$ for the polymer C_6PPPC_5Cb. For different layers the observed thickness was 8.2 ± 0.1, 18.5 ± 0.1, 24.5 ± 0.1, and 32.4 ± 0.1 nm for 5, 10, 15, and 20 layers respectively. Multilayers (20 layers) were deposited with a uniform transfer ratio and used for electropolymerization of the carbazole group for preparing a cross-linked conducting polymer network film. The comparison of the solution and film state UV and PL spectra indicated that the emission maxima were blue-shifted for the film with clear peak broadening at the higher wavelength region along with the appearance of a shoulder peak around 530 nm (Figure 3C).

Electropolymerization of C_6PPPC_5Cb Thin Films. Recent studies about the electrochemical polymerization and cross-linking of poly(vinyl-*N*-carbazole) (PVK), poly[9-[2-(4-vinylphenoxy)ethyl]-9*H*-carbazole] (PHC), and poly(*N*-alkoxy-(*p*-ethynylphenyl)carbazole) (PAA-Cz-C6) through the carbazole units demonstrated the ability to form thin films with unique

optical, electrochemical and morphological properties.[30c,33] The cross-linked structures were formed through a three-electron-transfer process with dimerization of pendant carbazole ring occurring via the 3,6-position leading to intermolecular cross-linking. The intermediate is believed to be based on a carbazolylium radical cation which rapidly reacts via coupling-deprotonation to form the dimer.[34] Subsequent cycles lead to higher oligomeric species and further cross-linking, as evidenced by a lowering of the oxidation potential and increase in charge density with each succeeding cycle. Similarly, multilayer thin films of carbazole incorporated polymer C_6PPPC_5Cb on ITO were prepared using Langmuir−Blodgett technique and spin coating and used for the electropolymerization to prepare the crosslinked film. CV measurements were carried out using an electrolyte solution of 0.1 M tetrabutylammoniumpercholorate (Bu_4NClO_4) dissolved in acetonitrile, in which the precursor polymer was not soluble. An undivided three electrode configuration cell was used with the thin films of the polymer on ITO or gold coated LaSFN9 as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. Different scan rates such as 100 and 20 mV/s were used to study the influence of scan rates on the stability of the cross-linked polymers. The polymerization with slow scan rate (20 mV/s) showed a reduction in the intensity of the oxidation and reduction peaks after two cycles which may be due to degradation of the crosslinked film after one cycle. Thus, all further experiments were solely performed at a scan rate of 100 mV/s. This was further investigated using a combined SPR-cyclic voltammetry set up. The oxidation and reduction potentials of C_6PPPOH were not in the range of the applied potentials for electropolymerization; therefore, oxidation of only carbazole groups was expected within this potential range. Cross-linking of the carbazole monomer units occurs during the electropolymerization without affecting the PPP conjugated polymer backbone.

Cyclic voltammogram of the cross-linking of the LB multilayer and spin-coated films of C_6PPPC_5Cb deposited on ITO substrates with a scan rate of 100 mV/s is shown in Figure 5. The oxidation onset for 20 layers of LB multilayers is 0.93 V and the corresponding reduction peak is 0.78 V(vs Ag/AgCl) (Figure 5A) This oxidation peak was absent in the first cycle with an appearance of another peak at 1V, which indicated that first cycle is different from the second cycle with the possibility of cross-linking of carbazole units at about 1.0 V. Peaks due to doping and dedoping are found in the second to the subsequent cycles with doping at 0.93 and 0.80 V for dedoping. The peaks due to dedoping were slightly shifted to 0.78 V in the subsequent cycles. The observed peak value for doping and dedoping is slightly higher than previously reported carbazole incorporated films. The current increased with the number of cycles. For carbazole-grafted poly(phenylacetylene) polymer, the oxidative doping were observed at about 0.7−0.8 V and followed by another current increase at about 1.0 V during the anodic scan of the cycle,[29a] whereas in the case of the PVK, the first cycle always showed an oxidation onset at 0.9 V and the appearance of the oxidation doping peak in the 0.6−0.7 V range with subsequent cycles.[26] The slightly higher value in the doping and dedoping for new polymer C_6PPPC_5Cb can be accounted for the rigid rod structure of the polymer backbone with very good chain-to-chain polymer packing in the film. This generates a very dense structure of the carbazole moiety compared to the previously reported flexible polymers such as the copolymers of carbazole and thiophene, PVK or poly(*N*-alkoxy-(*p*-ethynylphenyl)carbazole), but at the same time slows down the
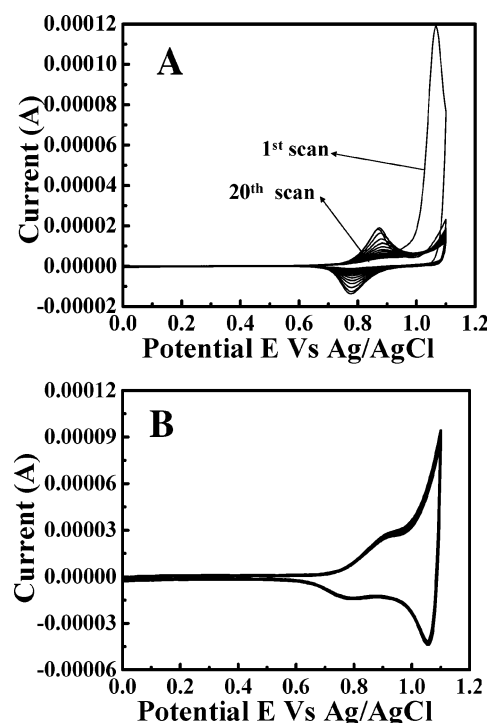

Figure 6. (A) CV for electrochemical cross-linking of 20 layers LB film of C_6PPPC_5Cb at scan rate of 20 mv/s. (B) Corresponding precursor polymer free scan.

counterion transport properties due to a less porous structure.[29] The oxidation onset for 5 layers of LB multilayers is at 0.93 V, and the corresponding reduction peak is at 0.8 V. However, there is a decrease in the peak area after four cycles which could indicate a slight degradation of the film. In the case of the spin-coated film the electrochemical behavior is almost the same as the 20 layers LB film. The difference in behavior with the film thickness could be due to the availability of more carbazole groups in the film which is crucial for the formation of a stable cross linked network of C_6PPPC_5Cb.

A precursor polymer free scan was performed and showed a characteristic oxidation peak at 0.93 V (vs Ag/AgCl (0.01 M)) and corresponding reduction peak at 0.78 V (Figure 5D−F). The CV gives clear evidence of the electropolymerization of the carbazole units. However at a lower scan rate 20 mV/s, the peak area is reduced with each successive cycles indicating that it utilizes the species that were left unpolymerized or crosslinked in the first few cycles. (Figure 6A,B) This can be correlated with the carbazole groups tendency to dimerize first followed by higher orders of reaction and the formation of higher orders of oligomers with possible 2,7 connectivity.[35] Interestingly the aforementioned behaviors are consistent with different LB films thicknesses as well as the spin casted film.

The morphologies of the polymer films after electropolymerization were studied using atomic force microscopy (AFM). Figure 7 shows the morphologies of 5 (A) and 20 layers (B) of LB film and spin-coated film (C) after the electropolymerization and extensive washing with acetonitrile. Roughness (rms) of the films increased with the number of layers, 2.6 and 6.8 nm for 5 and 20 layers, respectively. For spin coated film, the rms roughness was 0.6 nm. The smooth surface morphology highlighted the possibility of formation of homogenously cross linked polymeric network film using both LB and spin-coating techniques. The film properties can also be affected by the molecular structure of the polymeric systems. The present study showed that our previously optimized amphiphilic PPPs can be

Carbazole Functionalized Poly(*p*-Phenylenes)

J. Phys. Chem. B, Vol. 111, No. 23, 2007 **6341**
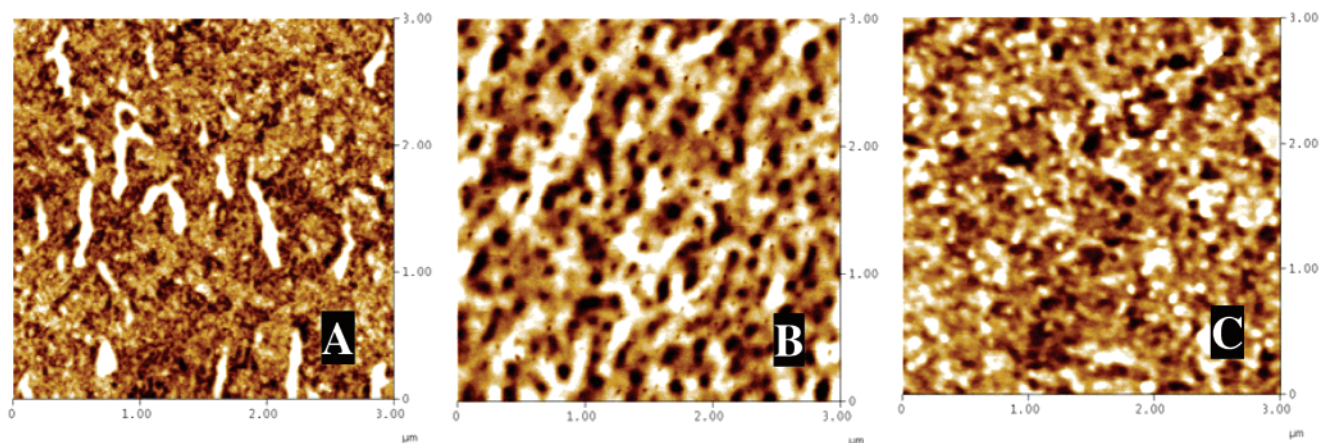
Figure 7. Morphology of the films after electropolymerization at scan rate of 100 mV/s. (A) Five layers, (B) 20 layers, and (C) spin-coated films of C$_6$PPPC$_5$Cb.
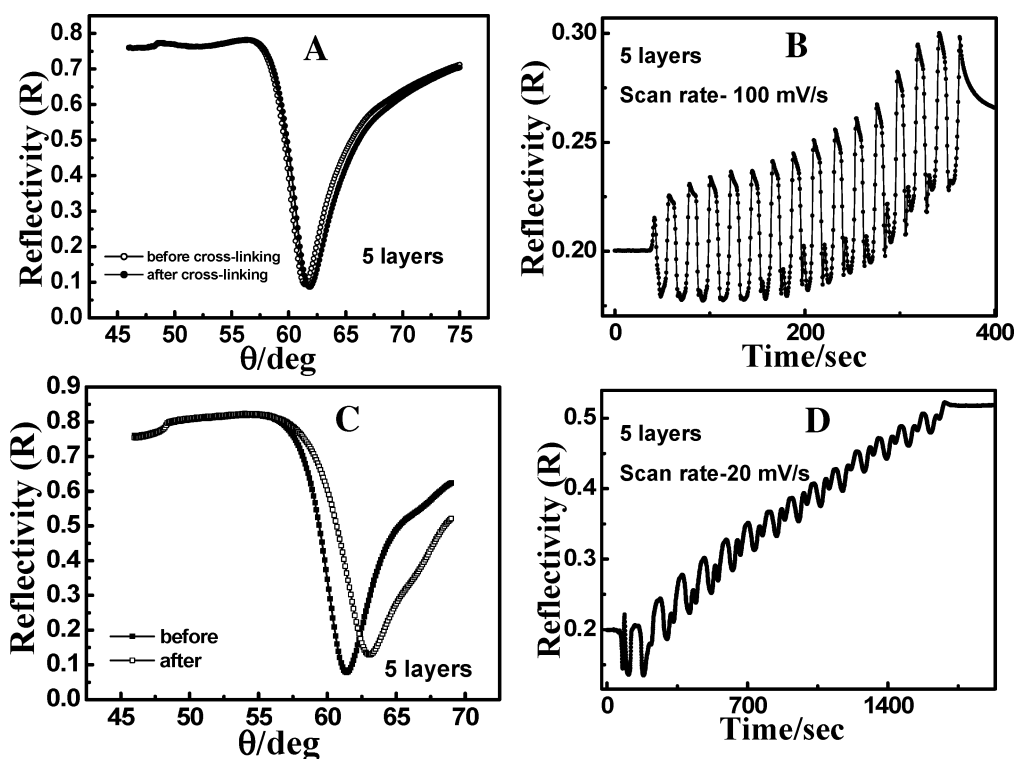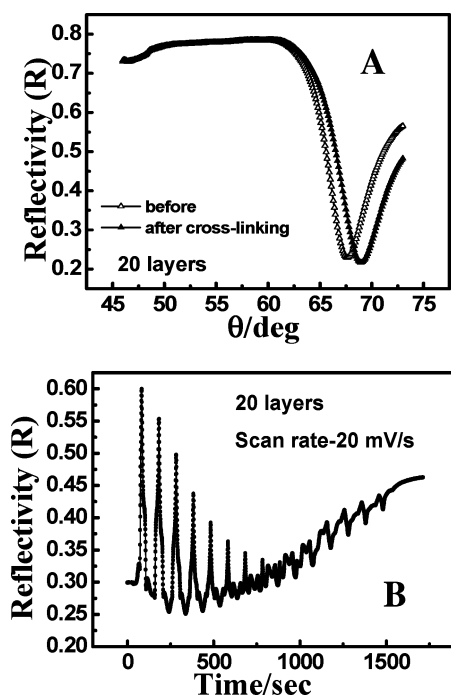

Figure 8. ESPS curves of 5 layers LB film measured before and after electropolymerization at a scan rate of 100 mV/s (A) and 20 mV/s (C) respectively. Difference in reflectivity with time at a scan rate of 100 (B) and 20 mV/s (D).

used even after grafting functional groups for homogeneous film preparation and subsequent electropolymerization.

Electrochemical Surface Plasmon Spectroscopy (ESPS) of LB Films. In order to further observe the electropolymerization of carbazole on the PPP backbone, the LB film was deposited on gold coated LaSFN9 substrate and simultaneous electrochemical surface plasmon spectroscopy (ESPS) measurements were carried out. This technique allows the in situ characterization of the changing dielectric constant and thickness of a film during the electropolymerization process. Surface plasmon spectroscopy (SPS) was used to investigate the electrochromic properties of C$_6$PPPC$_5$Cb upon doping and dedoping and the effect on reflectivity was studied. The use of electrochemical SPS for in situ characterization of the electropolymerization of conjugated polymers has recently been described.[35] The change of SPS curves when the polymer film was switched to different electrochromic states upon doping and dedoping reveals im-

portant changes in dielectric constants and electrochromic behavior of the film.

For ESPS measurement, the polymer was transferred to gold substrates with two different film thicknesses (5 layers and 20 layers). Figure 8 shows the SPS curves, which were measured with in situ electropolymerization of the C$_6$PPPC$_5$Cb in acetonitrile solution before and after the electropolymerization. As shown in Figure 8A, the minimum angle is shifted to higher angles due to cross-linking, indicating an increase of dielectric constant or thickness of the film. In the case of the scan rate at 100 mV/s, the amplitude of the vibration increased as the number of cycling increased, which implies that the film becomes more electroactive due to the higher degree of cross-linking (Figure 8B). On the other hand, in the case of the scan rate at 20 mV/sec., the reflectivity largely changed only in first scan, and then the amplitude of the vibration decreased (Figure 8D). This may be due to the fact that cross-linking was mostly

Figure 9. ESPS curves of 20 layers films measured before and after electropolymerization at a scan rate of 20 mV/s. (A) Difference in reflectivity with time at a scan rate of 20 mV/s (B).

completed in first scan followed by some degradation with subsequent cycling. These ESPR data confirmed the results from the previous CV experiment. Similar trend was also observed in the case of film with 20 layers shown in Figure 9. The nature of the cross-linking behavior is thus correlated with the film thickness of the LBK films and the scan rate dependence is a reflection of the tighter chain-to-chain packing in higher order films.

Conclusion

Detailed electrochemical cross-linking studies have been reported toward the CPN film formation for an alkoxy carbazole group $(-O(CH_2)_5-Cb)$ functionalized poly(*p*-phenylene) (C_6PPPC_3-Cb) LB film. This work delineates the formation of CPN films using a precursor polymer where the carbazole moiety is separated by an alkyl spacer from the polymer backbone. The precursor polymer thin film was first deposited using the LBK technique. The rigid-rod structured poly(*p*-phenylene) backbone facilitated the formation of a highly uniform and well packed thin film. This enabled the efficient secondary polymerization of the carbazole side group to form a "mixed conjugated" polymeric network. Furthermore, the electropolymerization was facilitated without decomposing the PPP backbone. The electrochemical data indicated carbazole cross-linking. ESPR data showed interesting film thickness dependence on scan-rate, highlighting a possible structural parameter control for CPN film formation. Thus, a network film of conjugated PPP with polycarbazole links has been prepared. It is possible that other types of polymer structure combinations of PPP with other electropolymerizable monomers, e.g., pyrrole, fluorene, thiophene, etc., or another amphiphilic conjugated polymer backbone be utilized as LB films. Possible anisotropic alignment and polarized emission studies of these materials are underway.

Supporting Information Available: Synthesis procedure, workup results, and characterization of the monomer and polymer. Figures showing thermogravimetric analysis and electrochemical (CV) studies of five layer and spin-casted LB film. Scan. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kline, R. J.; Mcgehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 222. (b) Bartic, C.; Borghs, G. *Anal. Bioanal. Chem.* **2006**, *384*, 354. (c) Tanese, M. C.; Farinola, G. M.; Pignataro, B.; Valli, L.; Giotta, L.; Conoci, S.; Lang, P.; Colangiuli, D.; Babudri, F.; Naso, F.; Sabbatini, L.; Zambonin, P.; Torsi, L. *Chem. Mater.* **2006**, *18*, 778. (d) Yoshimura, T.; Terasawa, N.; Kazama, H.; Naito, Y.; Suzuki, Y.; Asama, K. *Thin Solid Films* **2006**, *497*, 182. (e) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**; *100*, 2537. (f) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430. (g) Kertesz, M.; Choi, C. H.; Yang, S. *Chem. Rev.* **2005**, *105*, 3448.

(2) (a) Talham, D. R. *Chem. Rev.* **2004**, *104*, 5479. (b) Ding, H.; Bertoncello, P.; Ram, M. K.; Nicolini, C. *Electrochem. Commun.* **2002**, *4*, 503. (c) Ram, M. K.; Carrara, S.; Paddeu, S.; Nicolini, C. *Langmuir* **1997**, *13*, 2760. (d) Bertoncello, P.; Notargiacomo, A.; Ram, M. K.; Riley, D. J.; Nicolini, C. *Electrochem. Commun.* **2003**, *5*, 787. (e) Ram, M. K.; Bertoncello, P.; Nicolini, C. *Electroanalysis* **2001**, *13*, 574. (f) Ram, M. K.; Adami, M.; Faraci, P.; Nicolini, C. *Polymer* **2000**, *41*, 7499. (g) Bertoncelloa, P.; Notargiacomob, A.; Nicolini, C. *Polymer* **2004**, *45*, 1659.

(3) (a) Bilewicz, R.; Majda, M. *J. Am. Chem. Soc.* **1991**, *113*, 5464. (b) Lindholm-Sethson, B. *Langmuir* **1996**, *12*, 3305. (c) Royappa, A.; Saunders, R.; Rubner, M.; Cohen, R. *Langmuir* **1998**, *14*, 6207. (d) Ferreira, M.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7107.

(4) (a) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934. (b) Yu, G.; Pakbaz, K.; Heeger, A. J. *J. Electron. Mater.* **1994**, *23*, 925. (c) Yang, H. C.; Shin, T. J.; Yang, L.; Cho, K.; Ryu, C. Y.; Bao, Z. N. *Adv. Funct. Mater.* **2005**, *15*, 671. (d) Rost, C.; Karg, S.; Riess, W.; Loi, M. A.; Murgia, M.; Muccini, M. *Appl. Phys. Lett.* **2004**, *85*, 1613. (e) Murphy, J. M.; Frechet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc.* **2004**, *126*, 1175.

(5) (a) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477. (b) Yam, P. *Sci. Am.* **1995** (July), 82. (c) Yu, G.; Pakbaz, K.; Heeger, A. J. *J. Electron. Mater.* **1994**, *23*, 925. (d) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* **1996**, *382*, 695.

(6) (a) Ding, L.; Lu, Z. E.; Daniel, A. M.; Karasz, F. E. *Macromolecules* **2004**, *37*, 10031. (b) Bjørnholm, T.; Hassenkam, T.; Reitzel, N. *J. Mater. Chem.* **1999**, *9*, 1975. (c) Futterer, T.; Hellweg, T.; Findenegg, G. H.; Frahn, J.; Schluter, A. D.; Bottcher, C. *Langmuir* **2003**, *19*, 6537. (d) Baigent, D. R.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1996**, *80*, 119.

(7) (a) Tian, S. J.; Baba, A.; Liu, J. Y.; Wang, Z. H.; Knoll, W.; Park, M. K.; Advincula, R. C. *Adv. Funct. Mater.* **2003**, *13*, 473. (b) Inaoka, S.; Advincula, R. C. *Macromolecules* **2002**, *35*, 2426. (c) Prucker, O.; Ruhe, J. *Langmuir* **1998**, *14*, 6893. (d) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424. (e) Zhao, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 342–348. (f). Jordan, R.; Kang, J. F.; Ulman, A. *J. Am. Chem. Soc.* **1999**, *121*, 1016. (g) Jordan, R.; Ulman, A. *J. Am. Chem. Soc.* **1998**, *120*, 243.

(8) (a) Wang, Y.; Hou, L. T.; Yang, K. X.; Chen, J. W.; Wang, F.; Cao, Y. *Macromol. Chem. Phys.* **2005**, *206*, 2190. (b) Zheng, J. Y.; Feng, X. M.; Bai, W. B.; Qin, J. G.; Zhan, C. M. *Eur. Polym. J.* **2005**, *41*, 2770. (c) Zhu, Y.; Babel, A.; Jenekhe, S. A. *Macromolecules* **2005**, *38*, 7983. (d) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281. (e) Morin, J. F.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4619. (f) Nakazawa, Y. K.; Carter, S. A.; Nothofer, H.-G.; Scherf, U.; Lee, V. Y.; Miller, R. D.; Scott, J. C. *Appl. Phys Lett.* **2002**, *80*, 3832. (g) Chu, Q.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecule* **2003**, *36*, 3848. (h) Egbe, D. A. M.; Bader, C.; Klemm, E.; Ding, L.; Karasz, F. E.;

Grummt, U.-W.; Birckner, E. *Macromolecules* **2003**, *36*, 9303. (i) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141. (j) Vaidyanathan, S.; Dong, H.; Galvin, M. E. *Synth. Met.* **2004**, *142*, 1. (k) Zheng, L.; Urian, R. C.; Liu, Y.; Jen, A. K.-Y.; Pu, L. *Chem. Mater.* **2000**, *12*, 13.

(9) (a) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47. (b) Gettinger, C. L.; Heeger, A. J.; Drake, J. M.; Pine, D. J. *J. Chem. Phys.* **1994**, *101*, 1673. (c) Brandon, K. L.; Bentley, P. G.; Bradley, D. D. C.; Dunmur, D. A. *Synth. Met.* **1997**, *91*, 305. (d) Stenger-Smith, J. D.; Zarras, P.; Merwin, L. H.; Shaheen, S. E.; Kippelen, B.; Peyghambarian, N. *Macromolecules* **1998**, *31*, 13. (e) Huang, W.; Yu, W.-L.; Meng, H.; Pei, J.; Li, S. F. Y. *Chem. Mater.* **1998**, *10*, 3340. (f) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776.

(10) (a) Peng, Z.; Bao, Z.; Mary, G. E. *Chem. Mater.* **1998**, *10*, 2086. (b) Peng, Z.; Zhang, J. *Chem. Mater.* **1999**, *11*, 1138.

(11) (a) Zhang, C.; Seggern, H. V.; Kraabel, B.; Schmidt, H. W.; Heeger, A. J. *Synth. Met.* **1995**, *72*, 185. (b) Johnson, G. E.; Mcgrane, K. M.; Stolka, M. *Pure Appl. Chem.* **1995**, *67*, 175. (c) Wu, C. C.; Sturm, J. C.; Register, R. A.; Tian, J.; Dana, E. P.; Thompson, M. E. *IEEE Trans. Electron Devices* **1997**, *44*, 1269.

(12) (a) Li, H.; Zhang, Y.; Hu, Y.; Ma, D.; Wang, L.; Jing, X.; Wang, F. *Macromol. Chem. Phys.* **2004**, *205*, 247.

(13) (a) Bilewicz, R.; Majda, M. *J. Am. Chem. Soc.* **1991**, *113*, 5464. (b). Lindholm-Sethson, B. *Langmuir* **1996**, *12*, 3305. (c) Bjørnholm, T.; Hassenkam, T.; Reitzel, N. *J. Mater. Chem.* **1999**, *9*, 1975. (d). Futterer, T.; Hellweg, T.; Findenegg, G. H.; Frahn, J.; Schluter, A. D.; Bottcher, C. *Langmuir* **2003**, *19*, 6537.

(14) (a) McQuade, D. T.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 5885. (b) Montali, A.; Bastiaansen, C.; Smith, P.; Weder, C. *Nature* **1998**, *392*, 161. (c) Wan, W. M. V.; Greenham, N. C.; Friend, R. H. *Synth. Met.* **1999**, *102*, 1055. (d) Dyreklev, P.; Berggren, M.; Inganas, O.; Andersson, M. R.; Wennerstrom, O.; Hjertberg, T. *Adv. Mater.* **1995**, *7*, 43. (e) Fou, A. C.; Onitsuka, O.; Ferreira, M.; Rubner, M.; Hsieh, B. R. *J. Appl. Phys.* **1998**, *79*, 7501.

(15) (a) Ferreira, M.; Constantino, C. J. L.; Olivati, C. A.; Balogh, D. T.; Aroca, R. F.; Faria, R. M.; Oliveira, O. N. *Polymer* **2005**, *46*, 5140. (b) Ferreira, M.; Constantino, C. J. L.; Olivati, C. A.; Vega, M. L.; Balogh, D. T.; Aroca, R. F.; Faria, R. M.; Oliveira, O. N. *Langmuir* **2003**, *19*, 8835. (c) Wu, Z.; Wu, S.; Liang, Y. *Langmuir* **2001**, *17*, 7267.

(16) (a) Bockstaller, M.; Köhler, W.; Wegner, G.; Fytas, G. *Macromolecules* **2001**, *34*, 6353. (b) Bo, Z.; Zhang, C. H.; Severin, N.; Rabe, J. P.; Schluter, A. D. *Macromolecules* **2000**, *33*, 2688. (c) Bo, Z.; Rabe, J. P.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2370. (d) Moliton, A.; Hiorn, R. C. *Polym. Int.* **2004**, *53*, 1397. (e) Schluter, A. D. *J. Polym. Sci., Part A. Polym. Chem.* **2001**, *39*, 1533. (f) Kim, J. *Pure Appl. Chem.* **2002**, *74*, 2031. (g) Berresheim, A. J.; Muller, M.; Mullen, K. *Chem. Rev.* **1999**, *99*, 1747. (h) Fiesel, R.; Neher, D.; Scherf, U. *Synth. Met.* **1999**, *102*, 1457.

(17) (a) Grem, G.; Leising, G. *Synth. Met.* **1993**, *55−57*, 4105. (b) Scherf, U.; Mullen, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 489. (c) Scherf, U.; Mullen, K. *Synthesis* **1992**, 23. (d) Savvateev, V. N.; Yakimov, A.; Davidov, D. *Adv. Mater.* **1999**, *11*, 519. (e) Gruner, J. F.; Hamer, P.; Friend, R. H.; Scherf, U.; Huber, J.; Holmes, A. B. *Adv. Mater.* **1994**, *6*, 161. (f) Jing, W. X.; Kraft, A.; Moratti, S. C.; Grfiner, J.; Cacialli, F.; Hamer, P. J.; Holmes, A. B.; Friend, R. H. *Synth. Met.* **1994**, *67*, 161.

(18) (a) Baskar, C.; Lai, Y. H.; Valiyaveettil, S. *Macromolecules* **2001**, *34*, 6255. (b) Vetrichelven, M.; Valiyaveettil, S. *Chem. Eur. J.* **2005**, *11*, 5889. (c) Vetrichelven, M.; Hairong, L.; Ravindranath, R.; Valiyaveettil, S. *J. Polym. Sci., Part A: Poly. Chem.* **2006**, *44*, 3763. (d) Valiyaveettil, S.; Baskar, C.; Wenmiao, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42*, 432.

(19) (a) Renu, R.; Ajikumar, P. K.; Advincula, R. C.; Knoll, W.; Valiyaveettil, S. *Langmuir* **2006**, *22*, 9002. (b) Fitrilawati, F.; Renu, R.; Baskar, C.; Xu, L. G.; Chan, H. S. O.; Valiyaveettil, S.; Tamada, K.; Knoll, W. *Lamguuir* **2005**, *21*, 12146. (c) Ravindranath, R.; Valiyaveettil, S.; Baskar, C.; Putra, A.; Fitrilawati, F.; Knoll, W. *Mater. Res. Soc. Symp. Proc.* **2003**, *776*, 201. (d) Ji, W.; Elim, H. I.; He, J.; Fitrilawati, F.; Baskar, C.; Valiyaveettil, S.; Knoll, W. *J. Phys. Chem. B* **2003**, *107*, 11043. (e)

Renu, R.; Ajikumar, P. K.; Hanafiah, N. B. M.; Valiyaveettil, S.; Knoll, W. *Chem. Mater.* **2006**, *18*, 1213. (f) Renu, R.; Vijila, C.; Ajikumar, P. K.; Fathima, S. J. H.; Ng, K. L.; Wang, H.; Chua, S. J.; Knoll, W.; Valiyaveettil, S. *J. Phys. Chem. B* **2006**, *110*, 25958.

(20) (a) Zhang, Y.; Cui, Y.; Prasad, P. N. *Phys. Rev. B* **1992**, *46*, 9900. (b) Marcher, B.; Chapoy, L.; Christensen, D. H. *Macromolecules* **1988**, *21*, 677. (c) Manickam, M.; Belloni, M.; Kumar, S.; Varshnoy, S. K.; Rao, D. S. S.; Ashton, P. R.; Preece, J. A.; Spencer, N. *J. Mater. Chem.* **2001**, *11*, 2790.

(21) Scott, J. C.; Pautmeier, L. T.; Moerner, W. E. *J. Opt. Soc. Am. B* **1992**, *9*, 2059.

(22) (a) Zhang, Y.; Wang, L.; Wada, T.; Sasabe, H. *Chem. Commun.* **1996**, 559. (b) Kuo, W.-J.; Hsiue, G.-H.; Jeng, R.-J. *J. Mater. Chem.* **2002**, *12*, 868.

(23) (a) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Ko, C.-W. *J. Am. Chem. Soc.* **2001**, *123*, 9404. (b) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *Chem. Mater.* **2002**, *14*, 3852. (c) Thomas, K. R. J.; Lin, J. T.; Lin, Y.-Y.; Tsai, C.; Sun, S.-S. *Organometallics* **2001**, *20*, 2262.

(24) (a) Ostraskaite, J.; Voska, V.; Antulis, J.; Gaidelis, V.; Jankauskas, V.; Grazulevicius, J. V. *J. Mater. Chem.* **2002**, *12*, 3469. (b) Hu, N.-X.; Xie, S.; Popovic, Z.; Ong, B.; Hor, A.-M.; Wang, S. *J. Am. Chem. Soc.* **1999**, *121*, 5097.

(25) (a) Shirota, Y.; Kakuta, T.; Kanega, H.; Mikawa, H. *J. Chem. Soc. Chem. Commun.* **1985**, 1201. (b) Pearson, J. M.; Stolka, M. *Polymer Monographs*; Gordon and Breach: New York, 1981; Vol. 6.

(26) (a) Skompska, M.; Hillman, A. R. *J. Electroanal. Chem.* **1997**, *433*, 127. (b) Borjas, R.; Buttry, D. A. *J. Electroanal. Chem.* **1990**, *280*, 73. (c) Romero, D.; Nuesch, F.; Benazzi, T.; Ades, D.; Siove, A.; Zuppiroli, L. *Adv. Mater.* **1997**, *9*, 1158. (d) Ambrose, J.; Carpenter, L.; Nelson, R. *J. Electrochem. Soc.* **1975**, *122*, 876.

(27) (a) Burrows, P. E.; Forrest, S. R.; Sibley, S. P.; Thompson, M. E. *Appl. Phys. Lett.* **1996**, *69*, 2959. (b) Mori, T.; Obata, K.; Imaizumi, K.; Mizutani, T. *Appl. Phys. Lett.* **1996**, *69*, 3309. (c) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281.

(28) Michelotti, F.; Borghese, F.; Bertolotti, M.; Cianci, E.; Foglietti, V. *Synth. Met.* **2000**, *111*, 105.

(29) (a) Tamada, M.; Omichi, H.; Okui, N. *Thin Solid Films* **1995**, *268*, 18. (b) Papez, V.; Josowicz, M. *J. Electroanal. Chem.* **1994**, *365*, 139. (c) Kawde, R.; Santhanam, K. *Bioelectrochem. Bioeng.* **1995**, *38*, 405. (d) Laxmeshwar, N.; Kawde, R.; Santhanam, K. *Sens. Actuators* **1995**, *23*, 35.

(30) (a) Fulghum, T.; Karim, S. M. A.; Baba, A.; Taranekar, P.; Nakai, T.; Masuda, T.; Advincula, R. C. *Macromolecules* **2006**, *39*, 1467. (b) Jegadesan, S.; Sindhu, S.; Advincula, R. C.; Valiyaveettil, S. *Langmuir* **2006**, *22*, 780. (c) Baba, A.; Onishi, K.; Knoll, W.; Advincula, R. C. *J. Phy. Chem. B* **2004**, *108*, 18949. (d) Xia, C. J.; Advincula, R. C.; Baba, A.; Knoll, W. *Chem. Mater.* **2004**, *16*, 2852. (e) Xia, C. J.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854.

(31) Xia, C. J.; Advincula, R. C. *Chem. Mater.* **2001**, *13*, 1682.

(32) (a) Knoll, W. *Annu. Rev. Phys. Chem.* **1998**, *49*, 569. (b) Baba, A.; Park, M.-K.; Advincula, R. C.; Knoll, W. *Langmuir* **2002**, *18*, 4648. (c) Baba, A.; Tian, S.; Stefani, F.; Xia, C.; Wang, Z.; Advincula, R. C.; Johannsmann, D.; Knoll, W. *J. Electroanal. Chem.* **2004**, *562*, 95. (d) Baba, A.; Lübben, J.; Tamada, K.; Knoll, W. *Langmuir* **2003**, *19*, 9058. (e) Baba, A.; Advincula, R. C.; Knoll, W. *J. Phys. Chem. B* **2002**, *106*, 1581.

(33) (a) Taranekar, P.; Baba, A.; Fulghum, T. M.; Advincula, R. C. *Macromolecules* **2005**, *38*, 3679. (b) Hilger, V.; Gisselbrecht, J. P.; Tykwinski, R.; Boudon, C.; Schrieber, M.; Martin, R.; Luthi, H.; Gross, M.; Diederich, F. *J. Am. Chem. Soc.* **1997**, *119*, 2069.

(34) (a) Romero, D.; Nuesch, F.; Benazzi, T.; Ades, D.; Siove, A.; Zuppiroli, L. *Adv. Mater.* **1997**, *9*, 1158. (b) Ambrose, J.; Carpenter, L.; Nelson, R. *J. Electrochem. Soc.* **1975**, *122*, 876.

(35) (a) Welzel, H.-P.; Kossmehl, G.; Boettcher, H.; Engelmann, G.; Hunnius, E.-D. *Macromolecules* **1997**, *30*, 7419. (b) Svecjean, W. R.; Frechet, M. J. *Polymer* **1990**, *31*, 165. (c) Sanda, F.; Kawaguchi, T.; Masuda, T.; Kobayashi, N. *Macromolecules* **2003**, *36*, 2224. (d) Sanda, F.; Nakai, T.; Kobayashi, N.; Masuda, T. *Macromolecules* **2004**, *37*, 2703.