Synthesis of a Polyphenylene-*co*-furan and Polyphenylene-*co*-thiophene and Comparison of Their Electroluminescent Properties

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ABSTRACT: A new polyphenylene-*co*-furan (PPF) and a polyhenylene-*co*-thiophene (PPT) have been synthesized utilizing the Stille coupling reaction and their luminescence properties characterized. The UV−vis, electroluminescence (EL), photoluminescence (PL), and current−field (I−F) characteristics, as well as the stability of the emission of light, were studied in detail for both polymer LED devices. Comparisons of the EL and PL characteristics between PPT and PPF suggest that the quantum efficiency of PPF is higher than that of PPT. However, it was also found that PPF is photochemically unstable and its electroluminescent intensity decays faster than that of PPT.

Light emitting diodes (LEDs) exhibiting highly efficient and stable emission in the visible wavelength region are of great interest in optical applications such as color flat panel displays.[1−5] Organic conjugated polymers are promising material candidates.[6,7] A large number of conjugated polymers have demonstrated light emission when an electric field is applied to a thin polymer film sandwiched between two appropriate electrodes. Internal quantum efficiencies of up to 4% for the light emitting process were obtained from the use of CN−poly(phenylene)vinylene (CN−PPV) by Greenham *et al.* and with other soluble PPV's by Heeger *et al.*[6,7] These large values and other interesting observations gave the necessary motivation for further work toward the understanding of the mechanism involved in the polymer LED process and for the creation of new electroluminescent polymeric devices. However, organic light emitting diodes have not achieved commercial application, mainly because their quantum efficiencies (no. of photons emitted/no. of electrons injected) are still not high enough and the life-times of polymeric LEDs are not long enough. Different research groups have designed various approaches to solve these problems.[8−10] Work by Heeger *et al.*[11] showed efficient blue light emission from an electrochemical cell working at low voltages when poly(ethylene oxide) and a small amount of lithium trifluoromethanesulfonate salt were blended into a conventional light emitting polymer such as substituted poly(*p*-phenylene) (PPP).[11] A number of research groups devoted great efforts toward enhancing the performance of the LEDs, such as their quantum efficiency and their lifetimes. Adding transport layers to the device assembly assists in the prevention of exciton migration to the electrodes, as demonstrated by Brown *et al.*[12] and also by Adachi *et al.*[13] A great deal of synthetic effort was also devoted toward creating new polymers or modifying the structure of existing polymers.

Our group recently studied the electroluminescent properties of several well-defined oligophenylene vinylenes.[14] These LEDs emit green light with reasonably high quantum efficiency. When our attention turned to other polymers synthesized by our lab, such as polyphenylene-*co*-thiophene (PPT, polymer **2**), it was found that these materials exhibit low quantum efficiency for light emission. To gain insight into the structure/property relationship, we decided to synthesize poly(phenylene-*co*-furan) which is an analog of PPT where the sulfur atoms are replaced with oxygen atoms. It has been demonstrated that intersystem crossing (ISC) can be an efficient route for quenching fluorescence and ultimately reducing the quantum efficiency of the electroluminescence.[15] Heavy atoms favor ISC due to spin−orbital coupling. We expected that the replacement of the S atom with an O atom could enhance the quantum yield of our LED devices. In this paper, we provide the first synthesis and luminescence characterization of a poly(phenylene)furan (PPF) polymer. Comparisons of the EL and PL characteristics between PPT and PPF suggest that the quantum efficiency of PPF is indeed higher than that of PPT. However, it was also found that the PPF is photochemically unstable and its electroluminescent decays faster than that of PPT.

Experimental Section

THF was purified by distillation over sodium chips and benzophenone. Hexane was purified by distillation over sodium chips. All other chemicals were purchased from the Aldrich Chemical Co. and were used as received, unless otherwise stated. The synthesis of monomers and the PPF polymer is shown in Scheme 1. 1,4-Diiodo-2,5-dipentylbenzene (**2**) was synthesized following a procedure reported in the literature.[16] The synthesis of poly(phenylene)thiophene (polymer 2) was reported by our laboratory (Scheme 2).[17]

2,5-Bis(tributylstannyl)furan (1). To a refluxing solution of furan (2.55 g, 37.5 mmol) and tetramethylethylenediamine (8.7 g, 75 mmol) in dried hexane (40 mL) was added a 2.5 M hexane solution of butyllithium (31 mL, 75 mmol). The resulting mixture was refluxed for 1 h and then treated with tributyltin chloride (26 g, 80 mmol) dropwise. After an additional 2 h of refluxing, the resulting mixture was quenched with water. The organic layer was separated and the aqueous layer was extracted with hexane (2 × 25 mL). The organic layers were combined, washed with water and then dried over $MgSO_4$. Evaporation of the solvent gave a brown oil which was distilled under vacuum, yielding a colorless oil (9.8 g, 40%, bp 222−224 °C at 0.6 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 0.88 (t, $J = 7.1$ Hz, 18H), 0.98 (m, 12H), 1.05 (m, 12H), 1.35 (m, 12H), 6.54 (s, 2H). Anal. Calcd for $C_{28}H_{56}OSn_2$: C, 52.05; H, 8.73. Found: C, 51.49; H, 8.70.

Synthesis of Poly(phenylene)furan (PPF). To a solution of 1,4-diiodo-2,5-dipentylbenzene (**2**) (0.42 g, 0.89 mmol)

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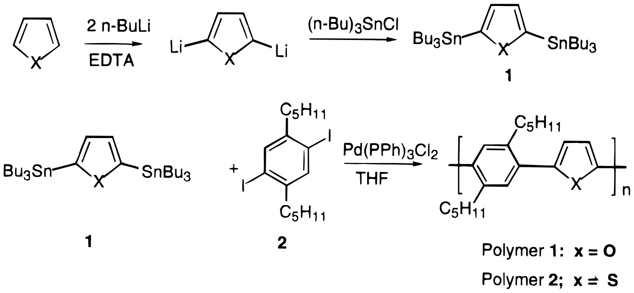
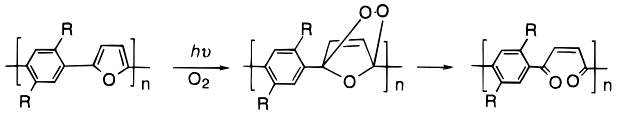
Scheme 1. Synthesis of Polymers



Scheme 2. Mechanism of Photooxidation of Poly(phenylenefuran)



and 2,5-bis(tributylstannyl)furan (**1**) (0.58, 0.90 mmol) in THF (10 mL) was added $PdCl_2(PPh)_3$ (12.5 mg, 0.018 mmol, 2 mol % equiv). The resultant mixture was refluxed under nitrogen until the black metallic palladium precipitated (ca. 4 days). The mixture was filtered and concentrated to approximately 7 mL and then precipitated into methanol. The precipitate was collected by filtration and was further purified by redissolving in THF and precipitating into methanol. The polymer was collected and extracted with methanol for 24 h and then dried under vacuum (0.23 g, 91%). ^{1}H NMR ($CDCl_3$, ppm): δ 0.90−1.85 (broad peaks, $-(CH_2)_3CH_3$, 18 H), 2.95 (broad, Ar−CH_2−, 4H), 6.65 (s, furanyl protons, 2H), 7.60 (s, phenyl protons, 2H). Anal. Calcd for $C_{20}H_{26}O$: C, 85.05; H, 9.28. Found: C, 83.49; H, 9.06.

Characterization. The ^{1}H NMR spectra were collected on a Varian 500-MHz FT NMR spectrometer. FTIR spectra were recorded on a Nicolet 20 SXB FTIR spectrometer. UV−visible spectra were recorded using a Shimadzu UV-240IPC spectrophotometer. Thermal analyses were performed using the DSC-10 and TGA-50 systems from TA instruments under nitrogen atmosphere. The GPC measurements were performed on a Waters RI system equipped with a UV detector and an Ultrastyragel linear column at 35 °C using THF (HPLC grade; Aldrich) as an eluent. Elemental analysis was performed by Atlantic Microlab, Inc.

Device Fabrication. Single-layer devices were prepared by spin coating the active polymer from a solution of dichloroethane on an indium−tin−oxide (ITO) (Delta Technologies, Limited) conducting substrate, and then depositing the top calcium electrode on top of the polymer layer. The Ca metal was evaporated in a bell jar under vacuum (4×10^{-6} Torr). The deposition rate was 1 A/s, and the area of the deposited Ca was approximately 0.5 cm^2. The Ca electrode was very sensitive to air and therefore was protected by a layer of silver. Film thickness measurements were performed with an ellipsometer. The EL spectra were obtained from a SPEX monochromator equipped with a photo multiplier tube for detection in the visible wavelength region. The I−F characteristics were obtained from a Keithley 236 SMU interfaced to a PC.

Results and Discussion

In our previous work, we synthesized polymer **2** by utilizing the Stille coupling reaction.[17] This reaction can be further extended to synthesize polymer **1**. Scheme 1 shows the synthesis of monomers and polymer **1**. Furan was reacted with butyllithium to generate dilithiofuran, which then treated with tributyltin chloride to yield compound **1**. Polymerization was carried out in THF in the presence of a catalytic amount (2 mol %) of $PdCl_2(PPh)_2$ under nitrogen atmosphere. After the reaction was completed, the polymer was precipitated into MeOH. The polymer was soluble in common organic solvents, such as THF, $CHCl_3$, and CH_2Cl_2. Optical-quality films were cast from the polymer solution for further studies.

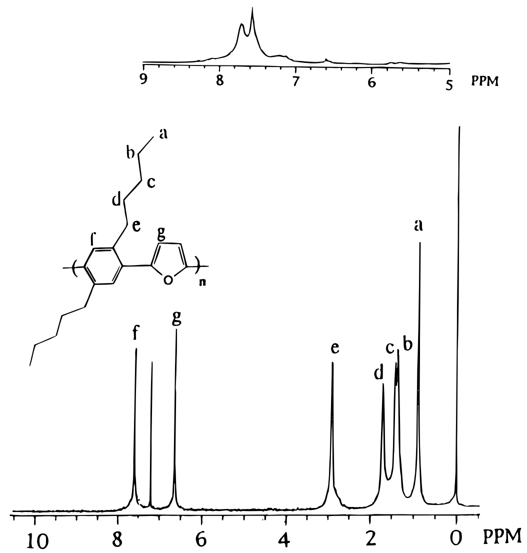


Figure 1. NMR spectrum of the PPF polymer. The inset shows the NMR of the photooxidation product.

The structure of polymer **1** was characterized by spectroscopic methods. The ^{1}H NMR spectrum of polymer **1** is shown in Figure 1. The spectral assignments clearly support the proposed structure. For example, the chemical shifts of furanyl protons and phenyl protons appear at 6.65 and 7.60 ppm, respectively. The remaining peaks in the range of 0.90−2.95 ppm correspond to the C_5H_{11} alkyl side chain. Thermogravimetric (TGA) analyses showed that this polymer remains stable up to 430 °C under nitrogen. The DSC thermogram indicated a glass transition temperature at around 54 °C. The side chain melting transition occurs at approximately 84 °C. GPC measurements of polymer **1** indicated a number average molecular weight of ca. 12 kDa (with a polydispersity of 2.1) against polystyrene standards, corresponding to about 42 repeating units.

Poly(phenylene)thiophene (polymer **2**) exhibited a number-average molecular weight, determined by GPC, of 9.5 kDa with a polydispersity of 2.81. The glass transition temperature of the polymer was determined by DSC to be 34 °C. The melting point temperature was 58 °C.

The UV−vis, PL, and EL spectra for the PPF and PPT polymeric films are shown in Figure 2. The UV−vis absorption maximum is at 420 nm for the PPF and 335 nm for the PPT film. The PL spectra shows a maximum at 455 nm for the PPT film and 490 nm for the PPF film. The Stoke shift in the two systems can clearly be seen by comparison of the maximum for the UV−Vis and PL spectra. The EL spectra for the PPT and PPF systems “follow” closely the PL spectra, suggesting that a similar mechanism may be responsible for both radiative processes. In the case of the PPF system, there is a small shoulder in the PL spectrum that is also present in the EL spectrum.

Figure 3 shows the field−EL intensity characteristics and the current−field (*I*−*E*) characteristics of the PPF and PPT LED devices. In the inset are the current-field (*I*−*E*) characteristics for the devices. Significant differences can be noted in the turn-on fields for the two systems. The PPT device has a turn-on voltage of 10 V, corresponding to a turn-on field of 1.35×10^5 V/cm. The turn-on voltage for the PPF device is 17 V, corre-

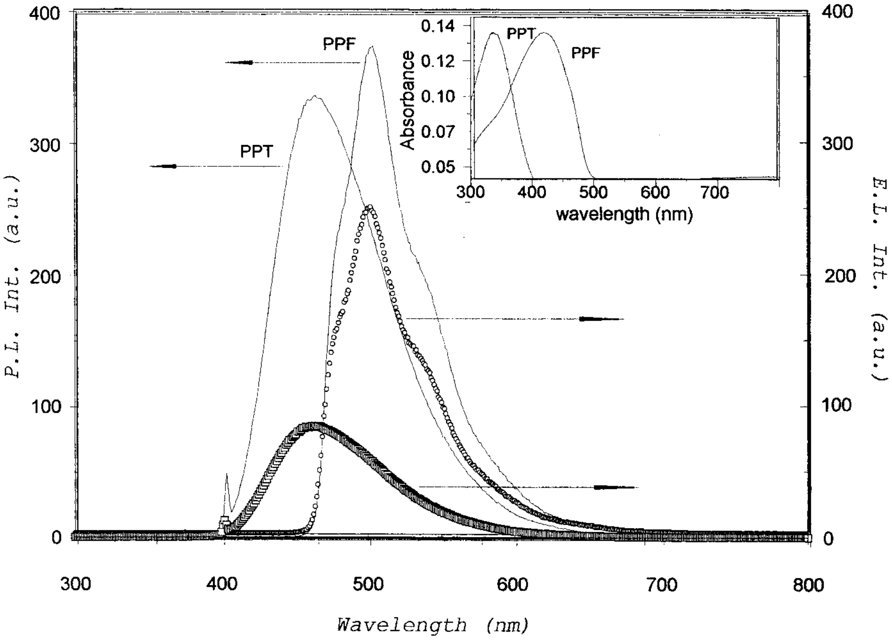


Figure 2. Photoluminescence (PL) and electroluminescence (EL) spectra of the PPF and PPT polymers. The inset shows the UV–vis spectra of the two polymers.

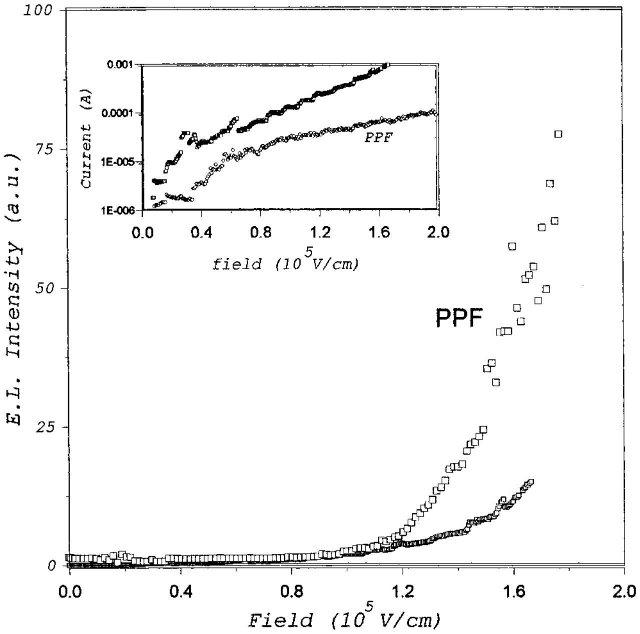


Figure 3. Electroluminescence intensity–field characteristics of the PPF and PPT polymeric devices. The inset shows the current–field characteristics of the two devices.

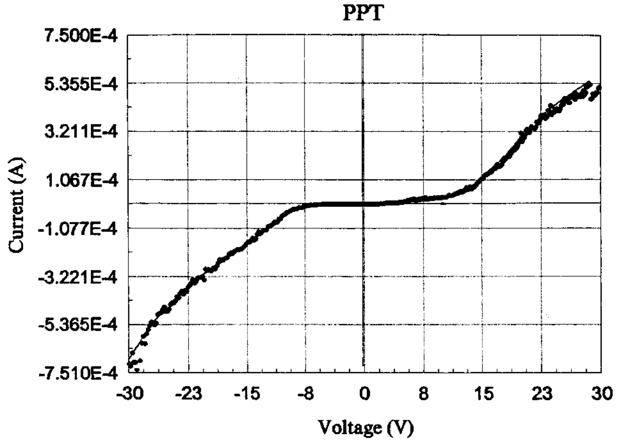


Figure 4. Current–voltage characteristics of forward and negative bias operation of the Ca–PPT–ITO device.

sponding to a turn-on field of 1.1 × 10^5 V/cm. The difference between the two polymers is also reflected in their external EL quantum efficiencies: 0.1% for the PPF polymer and 0.03% for the PPT device.

We have investigated the current characteristics in detail under forward and reverse bias conditions (+ or − voltage). Shown in Figure 4 are the forward and reverse bias operations of the PPT device. This result shows that the current level in the forward direction is larger than that in the reverse direction. The curve (including both + and − voltage) can be fit to a well-known exponential relationship which is commonly used in describing Schottky-like contacts at metal interfaces. This expression is given by[18]

$$I = I_o e^{((Vq/NK_BT)-1)} \tag{1a}$$

where the prefactor I_0 is given by,

$$I_o = A'T^2 e^{(q\beta/K_BT)} \tag{1b}$$

Here β is the injection barrier at the metal–polymer interface, A is Richardson's constant (assumed to be 120 A/cm^{2}K^2 here), and n is the ideality factor. According to this analysis, a Schottky barrier height of 0.6 is obtained. The ideality factors are determined by the slope of the I–F curve at low forward biases varying from 5 to 7. Normally, these high values are associated with Fermi-level pinning at the interface, or with a relatively large voltage drop in an interface region that has interacted chemically with the metal electrode.[19] This may suggest that the voltage (or E-field) across the top calcium electrode is not homogeneous. These small defects in voltage (or areas of low E-field) could result in an imbalance of injected electrons and holes, limiting the possibility of efficient recombination.

The stability of the LED devices with PPF and PPT have been investigated as a function of driving voltage. Initially, long-term stability of the emission of light from these devices was tested. Shown in Figure 5 are the time-dependent EL intensity measurements for the two

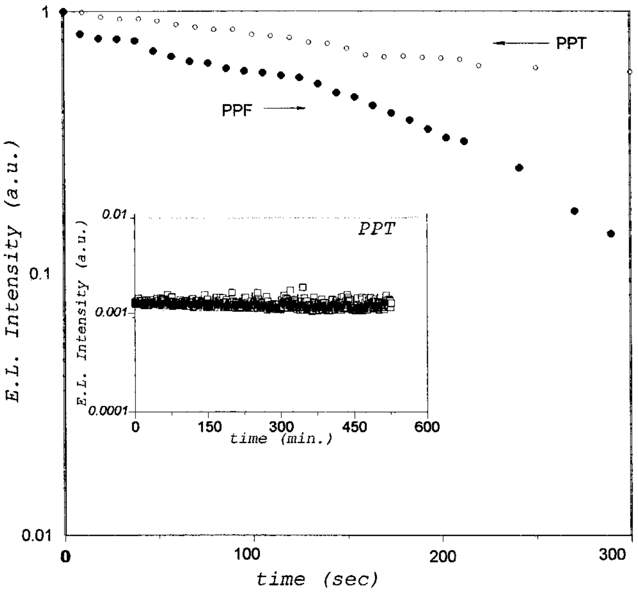


Figure 5. Stability measurements for the PPF and PPT devices operating at moderate voltages relative to their turn-on voltage. The insert show the long-term stability measurement of the PPT device.

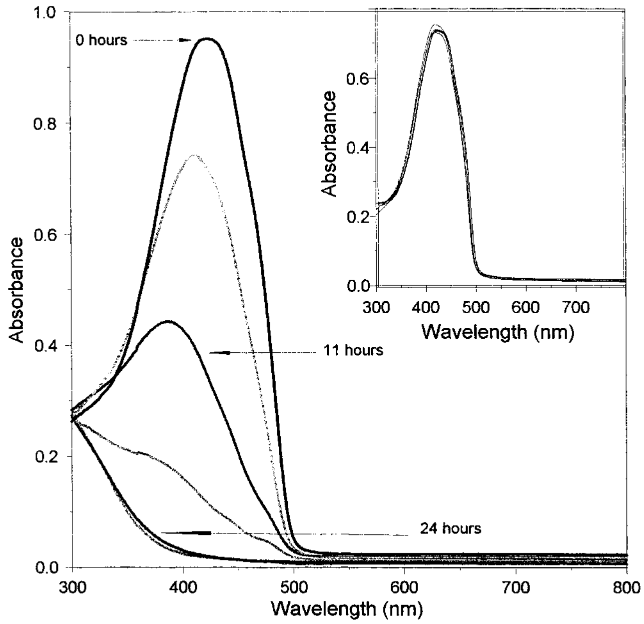


Figure 6. UV–vis stability measurement of a PPF device operating in normal room light under nitrogen. The inset shows a similar device operating under nitrogen but in a dark environment.

devices. In each case, the turn-on field (or approximation of that value) was used to drive the device. The inset in Figure 5 shows that the PPT system possesses relatively good stability over an 8 h time scale. The curve shows an initial drop in intensity followed by a very stable emission. At higher voltages, the decay of the emission from the PPT device is much faster. This is possibly due to breakdown at the metal electrodes and the lack of efficient injection into the interface of the polymer–metal. The stability measurements, as shown in Figure 5, were reproducible, and several films under similar conditions afforded the result of good long-term stability of the system.

Stability measurements with PPF showed different behavior when operating at fields close to the turn-on point. Although the decay of the emission from the PPF illustrated a similar initial drop in the intensity encompassing approximately 10%, the total intensity decreased much faster than PPT: approximately 50% loss in about 2 h. From previous work with LED devices of conjugated polymer films, we suggested that this rapid decrease in intensity was due to the saturation of electrons at the metal electrode leading to breakdown.

From these results, we can see that the replacement of S atoms with O atoms leads to high quantum efficiency of light emitting. However, it was also found that PPF is photochemically unstable. To determine the chemistry and the effects of environment, we performed the following experiments: A spin-coated film was placed in an evacuated chamber (10^{-4} Torr) and was then purged with N_2 and kept in the dark. This film was monitored by taking UV/vis measurements after 24 h, while taking great precautions to keep the film in a dark environment. The results of these measurements show that the initial maximum and amplitude of the absorbance for the film were conserved over the 24 h time scale. Another experiment was carried out with another two films of PPF. The first film was exposed to air and UV light; however, the second one was exposed to air and kept in the dark. The behavior of these two films was monitored periodically by measuring their UV over 24 h as shown in Figure 6. The first film exhibited a dramatic decrease in the amplitude of the maximum absorbance, and after about 24 h, the amplitude of absorbance had vanished. The second film exhibited no change in the amplitude of the absorbance over 24 h (inset of Figure 6). These results support our hypothesis that the decomposition caused in the PPF polymer is due to a photochemical reaction, since those films kept in the dark exhibited no change in the UV/vis absorbance after 24 h. However, a spin-coated film of PPT was exposed to air and UV light for more than 24 h and exhibited no change in the amplitude of maximum absorbance.

To gain more insight into this process, we monitored it by using the FTIR spectrometer. A strong absorption at 1692 cm^{-1}, which corresponds to a C=O conjugated to a benzene ring, appeared in the FTIR spectrum after the film was exposed to the light. An absorption at 1260 cm^{-1}, ascribed to C–CO stretching, was also observed. These results suggest that the furan ring is the core of a photochemical reaction that opens up the ring and eventually breaks the conjugation of the backbone. Crude ^{1}H NMR of the exposed polymer sample (inset of Figure 1) shows the absence of furan protons which should appear at 6.50 ppm. The appearance of a new doublet peak at 7.85 ppm corresponds to vinyl protons in the ring-opening product. The photooxidation mechanism of the furan ring has been subject to much investigation, and a singlet oxygen is thought to be involved.[20,21] In the case of PPF, the photoexcited PPF transfers energy to the triplet oxygen. A singlet oxygen is thus formed, which is a good dienophile in a [$_\pi$ 4s + $_\pi$ 2s] reaction. The photooxidation goes through the formation of an unstable peroxide adduct which breaks down to the corresponding dicarbonyl product (Scheme 2). This process can be observed visually by the gradual change in color from yellow to colorless. The ease of photooxidation of the furan ring, in comparison to the thiophene ring, is due to the difference in the aromaticity of these two rings. According to conjugation energy estimations,[22] the furan ring has a lower delocalization energy of π-electrons compared to the thiophene ring. This makes the furan ring behave more like a diene than the thiophene ring.[23] However, this photooxidation observed with the PPF system seems to be less severe than that seen with the conjugated polymer studied by Scurlock *et al.*[24]

Conclusions

We have synthesized polyphenylene-*co*-furan and polyphenylene-*co*-thiophene utilizing the Stille coupling reaction. The polymer bulk characterization showed that these materials are pure and have moderate molecular weights which aided our device fabrication process. The PL and EL spectra for both polymer systems seem to exhibit similar characteristics. The external quantum efficiency for PPF was 0.1%, much larger than that of PPT (0.03%) in a simple device of Ca/PPF or PPT/ITO. The PPT system possesses relatively good stability over an 8 h time scale. The PPF system showed different behavior when operating at voltages close to turn on. A much faster decay was observed, approximately 50% in about 2 h. The PPF was also found to be photochemically instable because of photooxidation.

Supporting Information Available: Figures showing UV and IR spectra (2 pages). Ordering information is given on any current masthead page.

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