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Excimer Emission and Wavelength Control from Light-Emitting Diodes Based on Side-Chain Polymers

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Several years ago, Tang et al. reported observing electroluminescence in diodes in which the emissive layer comprised an organic fluorophore.[1] These diodes were composed of at least three layers: (1) a transparent ITO electrode which serves as the anode; (2) an electroactive material, i.e., a fluorophore, that is either dissolved in a polymeric binder and coated from solvent or vacuum evaporated directly onto the anode; (3) a low work function metal cathode such as calcium, magnesium, or aluminum. The utility of additional organic layers for charge injection and confinement was also demonstrated and reported in these patents. In 1989, interest in organic light-emitting diodes intensified when a group of researchers at Cambridge University reported observing electroluminescence from diodes containing poly(phenylenevinylene) (PPV) and its homologues.[2] The high level of interest is due to the potential utility of this technology in a wide variety of applications including flat-panel displays.

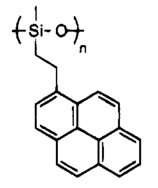
Recent advances for both nonpolymer, i.e., "molecular devices", and polymeric LED's indicate the great potential of organic-based diodes. For molecular devices special chemical treatment of the junctions between the electrodes and the organic electroluminescent layer reportedly improved both brightness and operating lifetime.[3] The original problem of heat-induced diffusion and crystallization of the small molecular species which resulted in degradation of the diode seems to have been solved. In the polymer area, the Cambridge University group recently reported 4% internal efficiency for a double layer structure comprising PPV which in this example was used as the hole injector and an electroluminescent layer (cyano-substituted PPV) with an Al cathode.[4] The key to this significant improvement is the correct balance of ionization potentials which prevents hole/electron recombination at or very near the surface of the cathode.

These main-chain, conjugated polymers have the disadvantages that they are somewhat difficult to synthesize, they exhibit poor solubility which makes them difficult to process into optical quality thin films, and they inevitably contain randomly distributed defects, i.e., nonconjugated segments, which lead to a statistical distribution of lumophore lengths. A potential solution of this problem was discovered recently by several groups simultaneously which demonstrated electroluminescence in rigid−flexible main-chain polymers. In these materials the electroluminescent group, or its precursor, was first synthesized as a comonomer.[5−7] The rigid, conjugated comonomer was condensed with a second comonomer containing a saturated, flexible segment which prevents extended conjugation and aids solubility. The resulting strictly alternating rigid−flexible copolymers exhibit electroluminescence which closely coincides with the fluorescence of the monomer. The major drawback of these materials is the multistep synthesis required for difunctionalization and the stringent process requirements of condensation polymerization.

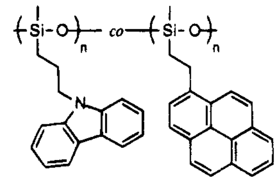
It seemed desirable therefore to find simpler, shorter synthetic routes to processable polymers with predictable emission wavelengths. In addition, since electroluminescence had been observed in molecular devices, it seemed reasonable to us that a wide variety of organic fluorophores should exhibit some level of electroluminescence. With this in mind, we concluded that attachment of the fluorophore to the pendant group of a random-coil polymer should present several advantages: (1) the synthetic route would be simpler than that used for main-chain polymers; (2) the solubility would be dominated by the nature of the backbone; (3) the emission wavelength would be predetermined; (4) diffusion of the lumiphore with concomitant degradation of the diode would be prevented. In addition, an electroluminescent group could be placed on every repeat unit, or nearly every one, depending on whether it was added to an already-formed polymer or polymerized separately, thereby maintaining a high concentration of the active species.

In this paper we outline the syntheses and general characteristics of two side-chain electroluminescent polymers and briefly mention our observations regarding copolymers. A large number of side-chain polymers have been made and characterized,[8] and a full report is being prepared.

Two types of polymers, siloxanes, and methacrylates, were synthesized. For the former, lumophores such as pyrene or carbazole functionalized with olefins were attached to the siloxane backbone via a hydrosilation reaction. For example, when vinyl- or allyl-functionalized pyrene or carbazole, respectively, was reacted with a Pt catalyst and poly(methylhydrosiloxane) in toluene at ~70 °C, the olefinic group was efficiently inserted into the Si−H bond generating the polymers **I**, poly[2-(1′-pyrenyl)ethylmethylsiloxane], and **II**, poly[2-(1′-pyrenyl)ethylmethylsiloxane-*co*-3-(*N*-carbazolyl)propylmethylsiloxane] (shown below along with their electroluminescent wavelengths). The degree of substitution for both polymers is greater than 80% as estimated by NMR. The molecular weights of these polymers, as determined by size-exclusion chromatography using polystyrene standards, are $M_w = 1.48 \times 10^4$, $M_n = 6.22 \times 10^3$ and $M_w = 3.09 \times 10^4$, $M_n = 9.40 \times 10^3$, respectively. Both are readily soluble in toluene, THF, and chlorinated solvents. Films were spin-coated from 1−2% toluene solutions.


I

[blue-green, λ_{em} = 500 nm]


II

[blue-green, λ_{em} = 500 nm]

In order to synthesize acrylic polymers (**III** and **IV**), the fluorophores were first functionalized with either alcohol or amine groups; the nitrogen of carbazole is reactive enough to be used directly. This was followed by their conversion into urethane/acrylate or urea/acrylate monomers by reaction with the isocyanate group of 2-isocyanatoethyl methacrylate. Free-radical

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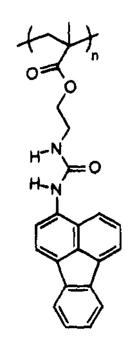
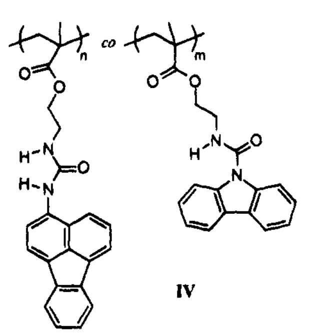
initiation generated high molecular weight, soluble polymers containing pendent lumophores an example of which is polymer **III**, poly[2-(3-fluoranthenylureido)ethyl methacrylate]. Copolymers comprising equimolar amounts of two monomers were also synthesized via the latter procedure (polymer **IV**, poly[2-(3-fluoranthenylureido)ethyl methacrylate-*co*-2-(*N*-carbazolylcarbonylamino)ethyl methacrylate]. Monomer and polymer structures were confirmed by spectral characterization. The weight- and number-average molecular weights of polymers **III** and **IV** are $M_w = 1.33 \times 10^6$, $M_n = 3.42 \times 10^5$ and $M_w = 3.56 \times 10^3$, $M_n = 1.77 \times 10^3$, respectively. These polymers are soluble in THF, DMF, and cyclopentanone.



III

[yellow-green, λ_{em} = 521, 535(sh) nm]



IV

[yellow-green, λ_{em} = 521, 535(sh) nm]

For diode fabrication a continuous film of ITO (100 Ω/cm^2) on a 5 × 5 cm glass plate was etched to form an array of electrically isolated, 1 × 2 mm, rectangular ITO pads. A polymer solution was then spin coated onto the glass substrate containing the ITO pads. The resulting 800–1000-Å-thick polymer film was then heated to ~70 °C for 1–3 h in a nitrogen-purged oven to facilitate solvent removal. Diode fabrication was completed by vacuum deposition of 2-mm-wide Al stripes onto the test polymer film. The Al stripes were aligned so that each stripe could serve as the cathode for an entire row of ITO pads. Each ITO pad with its associated Al stripe formed a single, 0.5 × 1.25 mm, isolated diode that could be individually tested. Electrical contact with individual diodes was made with appropriately placed probe needles. Diode characteristics were measured with a photodetector (UDT Sensors, Model PIN 10 9245-1); approximately 60% of the emission from the LED's is lost to internal reflections at the polymer/ITO interface.[9]

The performance of an ITO/polymer **III**/Al diode is presented in Figure 1. Figure 1a is plot of the current passing through the light-emitting diode vs the applied voltage. The turn-on voltage is approximately 17–18 V which is lower than many polymeric "single layer" diodes particularly using Al as the cathode. The current density of this material at an applied voltage ≈3 × 10^6 V/cm is 1800 mA/cm^2—a surprisingly high value. With the exception of polythiophene, the latter far exceeds that of many of the main-chain polymers at comparable voltages.[4,10] Figure 1b shows that light emission begins at 17 V and starts to level off at ~19 V before increasing rapidly at voltages above 23 V. We do not have an explanation for this behavior at the present time, but it is not unique to this polymer. The brightness level for polymer **III** is ~57 Cd/m^2 as indicated in Figure 1c. The ratio of the detector current to the LED current is proportional to the diode's external efficiency. Typical efficiencies for single layer devices of these side-chain polymers with an Al cathode are ~10^{-2}% (corrected).

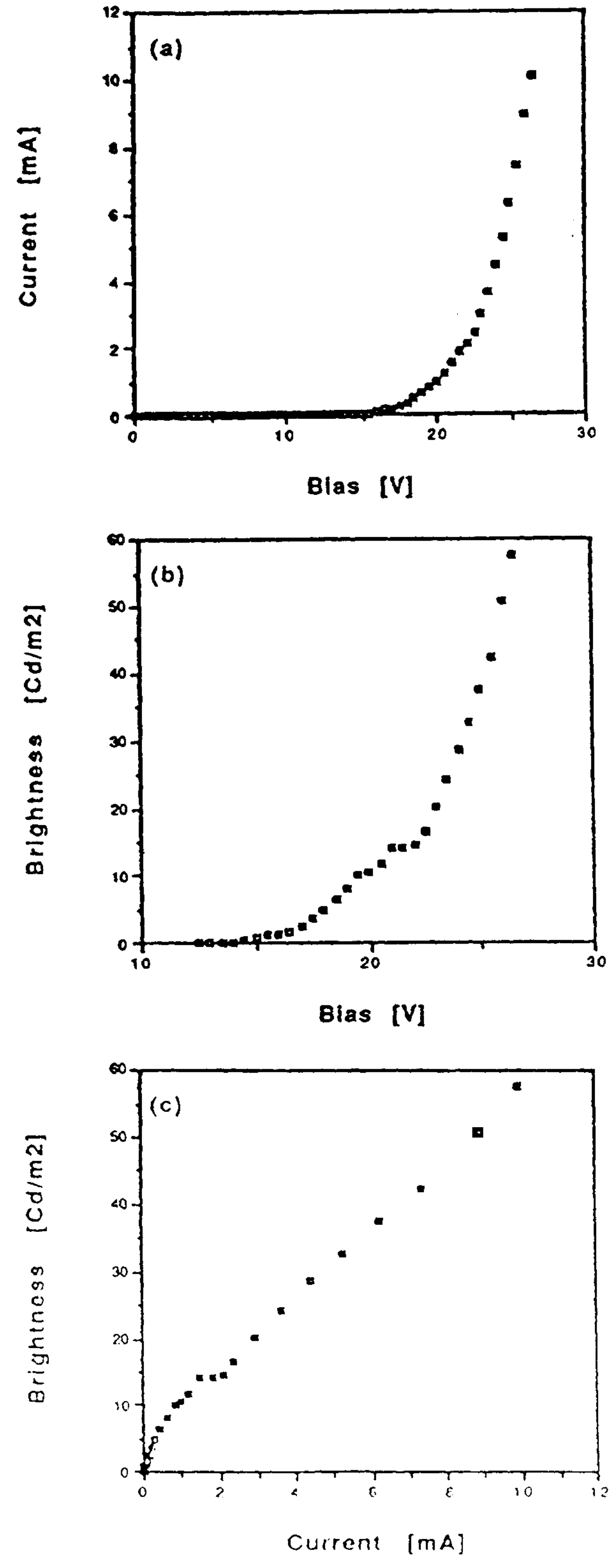


Figure 1. Characteristics exhibited by a diode comprising ITO (anode), polymer **III**, and Al (cathode); (a) current/voltage curve; (b) brightness/voltage curve; (c) brightness/current curve.

Incorporation of a thin electron injection layer composed of 2-*p*-biphenyl-5-(*p*-*tert*-butylphenyl)oxadiazole in poly(methyl methacrylate) between the cathode and the electroluminescent layer results in a 5× increase in efficiency and brightness of 173 Cd/m^2. At the present time none of these diodes have been optimized with respect to the work function of the cathode or anode, and only a few experiments have been performed in regard to charge confinement layers with the appropri-

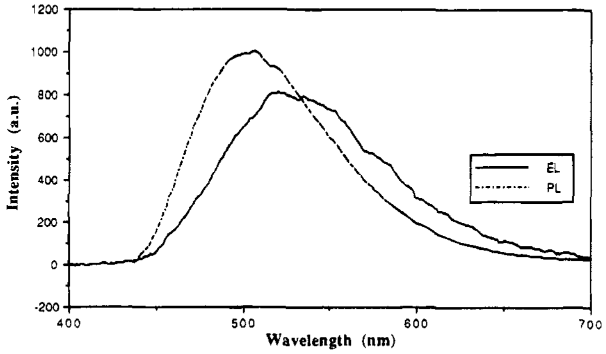


Figure 2. Photoluminescence (PL) and electroluminescence (EL) spectra of a fluoranthene-containing side-chain polymer **III**.

ate redox potentials. The fact that the current densities are so high suggests that with an improvement in efficiency these polymers should make useful LED's.

In regard to stability, it should be noted that whether a polymer film was spin coated in an inert atmosphere or not had very little effect on the lifetime of these diodes. In fact the diodes could be stored in ambient conditions for several weeks without significant reduction in efficiency or operating lifetime when Al was used as the cathode. This result suggests that exposure to atmospheric moisture and oxygen prior to cathode deposition is inconsequential in these polymer systems.

The emission color and electroluminescent wavelength of each of the lumiphores is given below each structure. As expected, the shape and position of the photoluminescent and electroluminescent emission bands are similar but not identical (see Figure 2) in analogy to the emission characteristics of molecular and main-chain polymeric diodes. Small bathochromic shifts in electroluminescent emission relative that of fluorescence are common in both acrylate and siloxane polymers and may be attributable to thermal effects.

Figure 3a shows the *dilute* solution absorption spectrum (dotted line) and photoluminescence spectrum (solid line) of 1-ethylpyrene, and model compound for the expected chromophore of polymer **I**. Several distinct emission bands centered around 400 nm originating from the unassociated compound are clearly evident. The spectrum shown in Figure 3b is that of a coated film of polymer **I**. Although the absorption spectra of the model compound and the polymer are identical, the emission spectrum of the latter can be readily interpreted as that of the pyrene excimer. It is bathochromically shifted, devoid of fine structure, and nearly identical to the excimer spectrum of pyrene found in the literature. Figure 3c shows the electroluminescent spectrum of the same polymer. Although its emission wavelength is slightly longer and broader, it very closely resembles the photoluminescence of the film. We conclude that the species responsible for electroluminescence is the pyrene excimer. Excimer emission is reported to be the exclusive form of radiative decay in the electroluminescence of poly(vinylcarbazole).[10]

In the copolymers, interestingly, electroluminescent emission originates from the singlet exciton of the lower electron species exclusively, and the spectrum closely matches that of the homopolymer of the emitting species. For example, in copolymer **II**, pyrene excimer is the electroluminescent species, and in the case of copolymer **IV**, emission is due to fluoranthene. Not one of the side-chain copolymers studied to date exhibits a hypsochromic shift in its emission band in contradistinction to literature reports regarding blends of poly(vinylcarbazole) with electroluminescent main-chain polymers.[11,12] Hence, at this time, we have no evidence for either solvatochromic shifts, charge transfer, or exciplex formation.

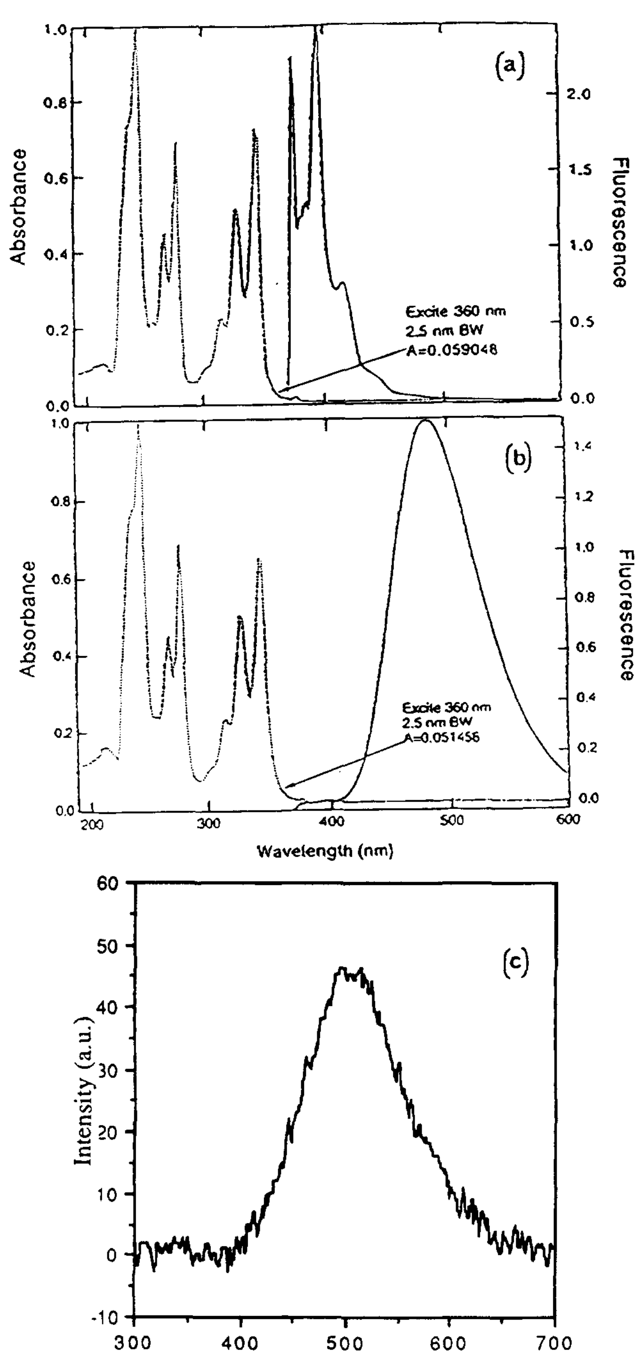


Figure 3. Photoluminescence (PL) and electroluminescence (EL) spectra of a pyrene-containing side-chain polymer **I**: (a) pyrene model compound (PL); (b) pyrene side-chain polymer (PL); (c) pyrene side-chain polymer (EL).

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