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A Novel, Bright Blue Electroluminescent Polymer: A Diphenylanthracene Derivative

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Organic materials have been reported as being applicable to practical electroluminescent (EL) devices due to their high EL efficiency and semiconducting properties.[1−5] One of the most fascinating advantages in using these organic materials is a wide selection of emission colors in EL displays attainable through the molecular design of organic materials. However, small organic molecules present the main disadvantage that they can recrystallize during the device operation, leading to poor device stability. Therefore, conjugated polymers, potentially more durable, have been used in EL devices. In addition, these polymers have advantages over small molecules in the processing of EL devices which can be fabricated simply by casting luminescent polymers from a solution.[6,7]

The most studied polymeric systems for these devices, which are based on poly(*p*-phenylenevinylene) (PPV) and derivatives of PPV, have shown good mechanical properties and some variability in color. But nonderivatized PPV emits basically green light.[8] There are several merits in obtaining highly efficient EL devices, with much recent interest focused on GaN as a light emitting material.[9] Several organic conjugated systems, having larger bandgaps suitable for blue light emission, have been studied such as poly(alkylfluorene)[10] and PPV,[11] but they showed rather poor processibility and mechanical properties. Many studies used PPV derivatives, such as PPV oligomers dispersed in a polymer matrix[12] and partially eliminated PPV.[13]

Recently, it has been reported that the conjugation length of the EL polymer could be effectively tailored by introducing the nonconjugated segment in the backbone. This method gives the polymer uniform conjugation length as well as improved film properties.[14−19]

It has been reported that diphenylanthracene has high photoluminescence quantum yields and stable electrochemical properties.[20] But, the EL device based on the molecular diphenylanthracene that was vapor-deposited showed recrystallization during the device operation, which is a typical problem of an organic molecular EL device. Therefore, a EL device based on a polymer containing diphenylanthracene is expected to have good device properties.

In this Communication, we report on the synthesis and the application in EL devices of a novel efficient blue light emitting material based on a well-defined, alternating copolymer with 9,10-diphenylanthracene, vinylene, phenylene, and alkylene blocks in the main chain.

The method for preparing the polymer is outlined in Scheme 1.[21] The polymer structure shown is consistent with the elemental analysis and the spectroscopic data from ^{1}H NMR, ^{13}C NMR, and IR.[22] In the ^{1}H NMR spectrum, the vinylic protons and aromatic protons show signals between 6.7 and 7.8. The absence of peaks at about 6.5 ppm indicates that no *cis*-vinylene bonds are present. The FT-IR spectrum of the polymer shows drastically decreased intensities at 1692 cm^{-1} which is a characteristic absorption peak of the aldehyde carbonyl in the monomer. In addition, polymers show a peak at 955 cm^{-1} which corresponds to an out-of-plane bending mode of the *trans*-vinylene, whereas no peak

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(21) (a) Spectroscopic data of compound I: ^{1}H NMR (300 MHz, acetone-d_6) δ 2.25 (s, 6 H, $-CH_3$), 5.32 (s, 2 H, $-OH$), 7.03 (d, 4 H, ring protons), 7.11 (m, 4 H, ring protons), 7.3 (m, 4 H, ring protons), 7.45 (d, 4 H, ring protons). (b) Spectroscopic data of compound II: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.5 (s, 6 H, $-CH_3$), 7.3 (m, 4 H, ring protons), 7.4 (d, 4 H, ring protons), 7.7 (m, 8 H, ring protons). (c) Spectroscopic data of compound III: ^{1}H NMR(300 MHz, CD_2Cl_2) δ 4.7 (s, 4 H, $-CH_2Br$), 7.35 (m, 4 H, ring protons), 7.5 (d, 4 H, ring protons), 7.7 (m, 8 H, ring protons). (d) Spectroscopic data of compound IV: ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.4 (d, 4 H, $-CH_2{}^{+}PPh_3Br^{-}$) 7.3 (m, 4 H, ring protons), 7.5 (m, 8 H, ring protons), 7.8−7.9 (m, 30 H, ring protons), 8.0 (m, 4 H, ring protons), Anal. Calcd for $C_{64}H_{50}P_2Br_2$: C 73.8%, H 4.8%. Found: C 73.08%, H: 5.0%. (e) Spectroscopic data of compound V: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58 (m, 4 H, $O-C-C-CH_2-CH_2-$), 1.9 (m, 4 H, $O-C-CH_2-C$), 3.9 (s, 6 H, $-OCH_3$), 4.1 (t, 4 H, $-OCH_2-$), 6.9 (d, 2 H, ring protons), 7.39−7.44 (m, 4 H, ring protons), 9.84 (s, 2 H, $H-C{=}O$). ^{13}C NMR (300 MHz, $CDCl_3$), δ 26, 30, 58, 70, 110, 112, 127, 131, 151, 157, 192. Anal. Calcd for $C_{26}H_{26}O_6$: C 68.4%, H: 6.73%, Found: C 68.25%, H 6.72%.

(22) ^{1}H NMR (300 MHz, CD_2Cl_2), δ 1.5 (br, 4 H, $-O-C-C-CH_2$-CH_2-), 1.8 (br, 4 H, $-O-C-CH_2-$), 3.7 (br, 3 H, $-OCH_3$), 3.9 (br, 3 H, $-OCH_3$), 4.1 (br, 4 H, $-OCH_2-$), 6.7−7.8 (br, 26 H, ring protons, vinyl protons). ^{13}C NMR (300 MHz, $CDCl_3$) δ 26.3, 29.5, 56.4, 69.3, 109.8, 113.3, 120.4, 122.6, 125.4, 126, 127.4, 129.5, 130.3, 131.1, 132.1, 137.3, 138.4, 149.1, 150. IR (KBr); 3030(w), 3021(w), 2932(m), 1597(m), 1513(s), 1463(m), 1390(m), 1267(s), 1135(s), 1028(m), 955(m), 769(m). Anal. Calcd. for $C_{50}H_{44}O_4$ (repeating unit): C 84.74%, H 6.2%, Found: C 80.65%, H 6.3%.

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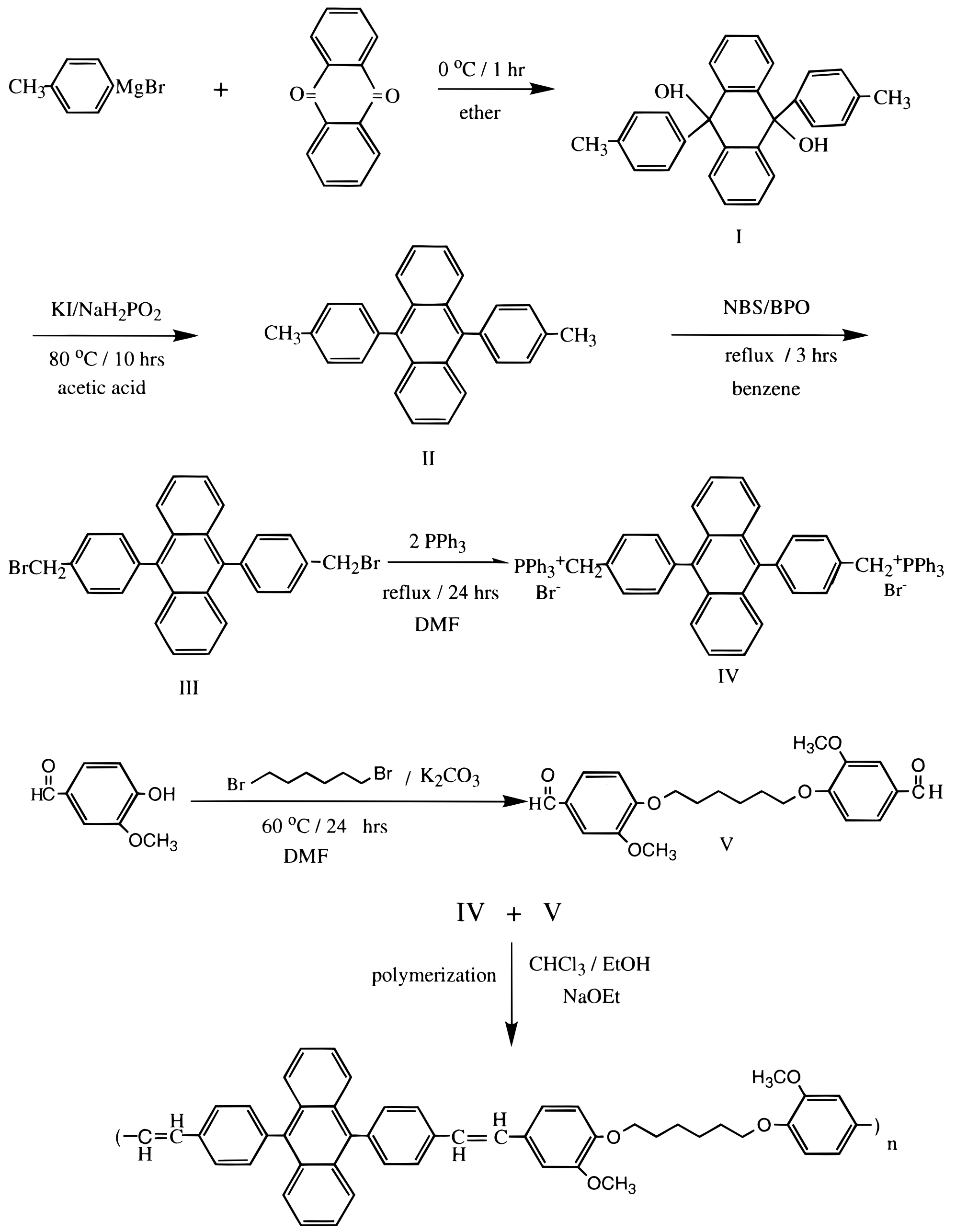
Scheme 1. Preparation of Electroluminescent Polymer Containing Diphenylanthracene



corresponding to the stretching of *cis*-vinylene bonds can be seen in the 890−900 cm^{-1}. The IR data also suggest that the generated double bonds are mainly in the trans configuration. Gas permeation chromatography (GPC) measurement of the polymer with polystyrene as the calibration standard shows that the number average molecular weight (M_n) is ~6000 with a polydispersity of 1.5. The thermal gravimetric analysis (TGA) thermogram of the polymer shows that the polymer has good thermal stability up to 260 °C. The synthesized polymer is soluble in $CHCl_3$ and CH_2Cl_2. A uniform and pinhole-free thin film can be obtained by spin-casting from either $CHCl_3$ or CH_2Cl_2 solution.

The optical properties of this novel polymer are of primary interest for our purpose. The UV−visible absorption spectrum of the polymer in $CHCl_3$ has maxima at 332, 378, and 399 nm. Upon UV excitation, solutions of the polymer exhibit the very intense fluorescence with a maximum at 450 nm. The lack of a mirror image relationship between the absorption and emission spectra is related to vibronic coupling. The fact that the emission band is much narrower than the absorption bands and shows well-resolved vibronic bands are consistent with emission from localized exited states, most likely after a migration of the excitons along the polymer main chains to segments that represent low energy states.[23] The photoluminescence quantum yield was measured to be $\phi = 0.88 \pm 10\%$ upon excitation at 365 nm.[24]

The solid-state optical properties of the new polymer were also investigated. Figure 1 shows the UV−visible absorption and photoluminescent spectra of a thin polymer film. The maximum for the solid-state photoluminescence of the polymer is at 470 nm. The red shift from that of the solution can be attributed either to the difference in the energy transfer processes between the film and the solution due to the presence of rotational

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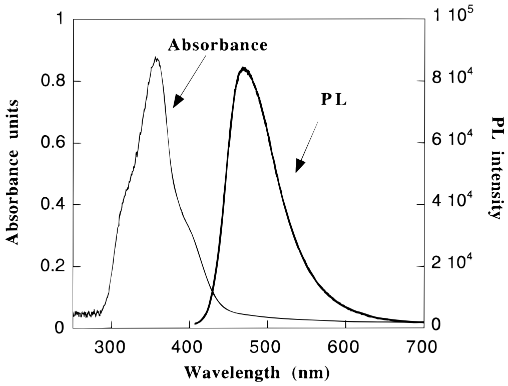

Figure 1. Absorption and photoluminescent spectra of the polymer film.

conformers in the solution reducing the π conjugation of the chromophore, or to the effect of packing and local geometry of the polymers. Because the thin film of the polymer shows high solid quantum yield ($\phi = 0.32 \pm 10\%$)[25] and self-absorption of the emission is negligible as indicated by the small overlap of its absorption and emission spectra, the polymer is a good candidate for EL devices.

A polymer film, 120–150 nm thick, was prepared by spin casting on a glass substrate covered with an indium–tin oxide (ITO) conducting layer (anode). The Al electrode (cathode) was then evaporated onto it in vacuo. Figure 2 shows that this single-layered device had a turn-on voltage of ~18 V and that the emission intensity exhibited an approximately linear increase with injection current. This linear dependence of the EL intensity on the current is attributed to linear response of the recombination of the charge carriers injected from the electrodes into the bulk of the polymer film. The light intensity of the devices was in the range of 45–80 cd/m^2 at a voltage of 32 V and it is quite reversible even at this high voltage. The external quantum efficiency for number of photons per electron passed of best device is around 0.01%. The emitted light is bluish white with an EL spectrum almost identical with the photoluminescent (PL) spectrum of the polymer in Figure 3. Considering that we have used an Al cathode and only a pure organic single layer film, the blue light intensity is remarkably high. We are now pursuing the study of devices with multilayer organic structures, including additional charge injection and transport layers, which we expect to be more efficient devices with lower turn on voltage.[26]

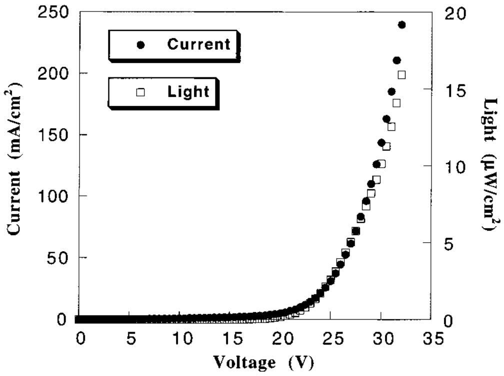

Figure 2. Light–voltage and current–voltage plots of ITO/polymer/Al device.

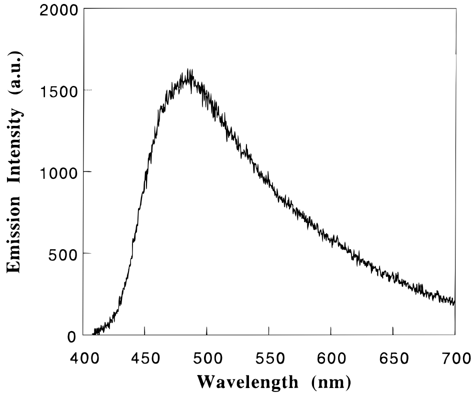

Figure 3. Electroluminescent spectrum.

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