

## Electrically Generated Intramolecular Proton Transfer: Electroluminescence and Stimulated Emission from Polymers

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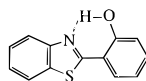
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Received April 23, 1996

Revised Manuscript Received June 5, 1996

The combination of electrochemically generated radical cations (positive polarons) and radical anions (negative polarons) in solution to generate light is known as electrochemiluminescence,<sup>2</sup> a process known for more than 30 years.<sup>3</sup> Exploration of similar processes in organic solids, using small molecules<sup>4</sup> or polymers such as poly(*p*-phenylenevinylene)<sup>5</sup> as the active media, has resulted in the development of organic light-emitting diodes (LEDs). Among the challenges facing development of organic polymers as LED materials are those of stability, processibility, efficiency, questions of mechanism, and the drive to develop organic polymers for electrically driven diode lasers.<sup>6,7</sup> Herein we report an electroluminescent single-component copolymer which is soluble and processible from organic solvents and in which the emissive component is photostabilizing and displays stimulated emission. The mechanism of electroluminescence is *electrically generated intramolecular proton transfer* (EGIPT), a chemical reaction which has not previously been reported.

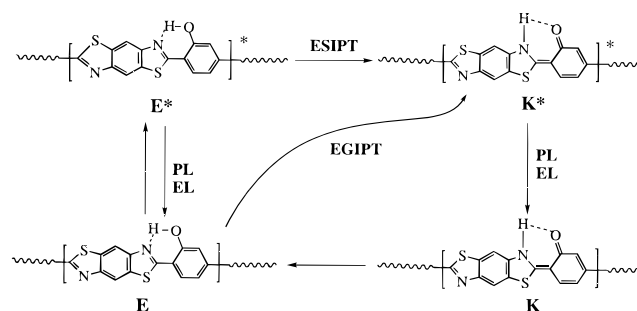
Materials which exhibit excited state intramolecular proton transfer<sup>8,9</sup> (ESIPT, Scheme 1) have been extensively studied as photostabilizing materials and as laser dyes.<sup>10</sup> Intramolecularly hydrogen-bonded heterocyclic molecules such as 2-(2'-hydroxyphenyl)benzothiazole (**1**), exist exclusively in the enol form (E) in the ground state. Upon photoexcitation, tautomerization occurs in the sub-picosecond time regime to generate the excited keto form (K\*<sup>\*</sup>).<sup>11,12</sup> Emission from K\*<sup>\*</sup> occurs with a large Stokes shift. Moreover, a population inversion occurs facilitating stimulated emission.<sup>9,10</sup>



HBT, **1**

It occurred to us that polymers which incorporate intramolecularly hydrogen-bonded moieties such as **1** in the main chain

### Scheme 1

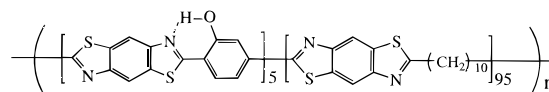


might lead to electroluminescent materials which have photochemical stability, resistance to thermal degradation, and low self-absorption, if they both exhibit ESIPT and fluoresce. Such materials might address issues of photochemical stability needed for development of polymer light sources.

Copolymers which incorporate intramolecularly hydrogen-bonded moieties as side chains have previously been reported. Vogl and co-workers<sup>13</sup> and Scott and co-workers<sup>14</sup> have investigated the photostabilizing effects of 2-(2'-hydroxyphenyl)benzotriazole derivatives covalently attached to various polymers. Acuna and co-workers<sup>15</sup> reported that copolymers of poly(methyl methacrylate) which incorporated 2-(2'-hydroxyphenyl)benzimidazole derivatives could be fabricated into optically pumped solid state proton transfer laser materials.

Our studies on main-chain polymers containing 2-(2'-hydroxyphenyl)benzoxazole (HBO) and related moieties in the main chain showed that ESIPT in polymers is complicated by the effects of concentration quenching, extended conjugation, and competition with excimer formation.<sup>16</sup> Excimers and exciplexes have previously been observed in conjugated polymers such as poly(*p*-phenylene)benzodithiazole, a phenomenon which substantially decreases the photoluminescence quantum yield.<sup>17</sup> On the other hand, a detailed study of rod-coil copolymers showed that the detrimental effects of excimer formation on emission yields could be regulated by introducing flexible segments into the main chain, which prevented the rigid segments from aggregating, favorably changing the supramolecular assembly of the fluorophores in the solid state.<sup>18</sup>

The structure of the random copolymer poly((benzodithiazole)-(1,4-(2-hydroxy)phenylene))-*co*-poly(benzodithiazole-decamethylene), HPBT-*co*-PBTC10 (5% HPBT/95% PBTC10), used in this study is given by **2**. A copolymer with 5% active



HPBT-*co*-PBTC10 (5/95), **2**

component was chosen for investigation since the copolymer is soluble in formic acid, the average conjugation length is sufficiently short that ESIPT is not inhibited,<sup>16</sup> as for the HBO homopolymer, and excimer formation is inhibited by the supramolecular structure of the copolymer.<sup>18</sup> The copolymer **2** was prepared from DABDT (TCI or Daychem), hydroxy-

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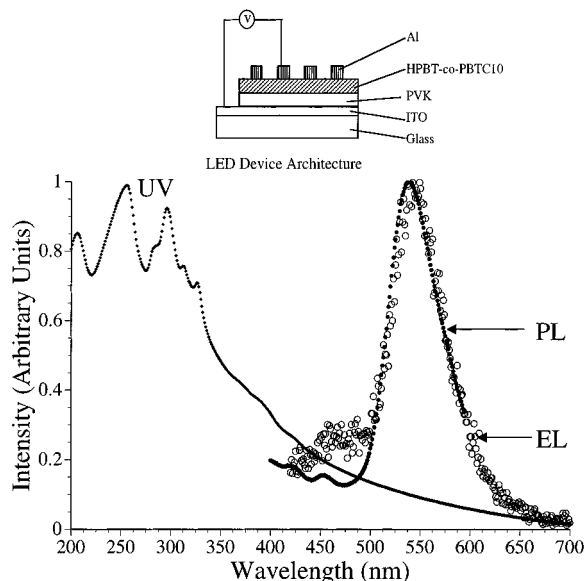
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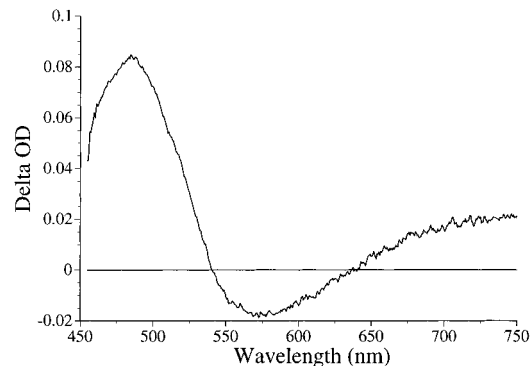


**Figure 1.** Normalized UV ( $\blacklozenge$ ), electroluminescence ( $\circ$ , 12 V), and photoluminescence ( $\bullet$ ,  $\lambda_{\text{ex}} = 396 \text{ nm}$ ) spectra of a thin solid film of HPBT-co-PBTC10 (5% HPBT/95% PBTC10, **2**).

terephthalic acid,<sup>19</sup> and 1,10-decanedicarboxylic acid by condensation reaction in polyphosphoric acid as previously described.<sup>18</sup> Films were prepared by spin coating a 1% w/w solution of the polymer in formic acid onto the appropriate optical window.

To prepare the LED device, a layer about 500 Å of poly(vinylcarbazole) (PVK) was deposited by spin coating from a chloroform solution onto an ITO (indium tin oxide) coated glass substrate. The PVK layer functions as the hole transporting layer and electron blocking barrier to confine electrons to the emissive layer. A 500 Å emissive layer of **2** was spin coated from a formic acid solution and dried at 80 °C in a vacuum oven. An electron-injecting aluminum electrode of ca. 500 Å was thermally evaporated at a vacuum of  $4 \times 10^{-6}$  Torr. The structure of the LED device is shown in Figure 1 (inset). Measurements were performed under ambient conditions. Optical absorption measurements were done using a Perkin-Elmer Lambda-9 UV/vis/near-IR spectrophotometer. Photoluminescence and electroluminescence spectra were measured using a Spex Fluorolog-2 spectrofluorimeter. The transient absorption spectrum was recorded using a pump wavelength of 355 nm and a 50 ps delay.<sup>20</sup> Correction for ambient lighting was made by subtracting the spectrum obtained when neither a pump pulse nor a probe pulse passed through the sample, whereas sample fluorescence was corrected for by subtracting the spectrum obtained by passing a pump pulse (with no probe pulse) through the sample.

Figure 1 shows the UV spectrum of a thin film of **2** together with the photoluminescence (PL) and electroluminescence (EL) spectra. Both the PL and EL spectra have a strong emission band at 543 nm, with very weak bands at shorter wavelengths. The PL quantum yield for emission is 6–12% for copolymers with 5–10 mol % of HPBT. The origin of the minor bands is not from the PVK layer which emits at 430 nm,<sup>21</sup> but is probably normal enol emission from the E\* state (Scheme 1).<sup>22</sup> It has previously been demonstrated that extended conjugation inhibits ESIPT and leads to enol emission due to an increase in the



**Figure 2.** Transient absorption spectrum of a thin solid film of HPBT-co-PBTC10 (5% HPBT/95% PBTC10, **2**). Delay = 50 ps and  $\lambda_{\text{ex}} = 355 \text{ nm}$ .

energy barrier on the excited state potential energy surface.<sup>16</sup> The conjugation length of the shortest fluorophore in **2** which is capable of existing in the keto form is 10 double bonds, twice as long as **1** for which there is no such barrier. It is possible that there is a small potential energy barrier to proton transfer on the excited state potential energy surface of **2**, leading to incomplete proton transfer and emission from both E\* and K\* (Scheme 1).

The PL and EL peak at 543 nm clearly arises from emission of the excited keto tautomer (K\* in Scheme 1). Evidence for this assignment is as follows: (1) The large Stokes shift between the emission band and the absorption band is typical of ESIPT processes leading to the keto state, a process very well-known to occur for intramolecularly hydrogen-bonded molecules structurally similar to the HPBT component of **2**.<sup>8,9</sup> In contrast, the corresponding 5% copolymer without hydroxy side groups, which is not capable of ESIPT, has a much smaller Stokes shift, with the emission  $\lambda_{\text{max}}$  occurring at 486 nm.<sup>18</sup> (2) The transient absorption spectrum of **2** shown in Figure 2 has a region of optical gain (stimulated emission) between 540 and 640 nm. The keto form K does not initially exist in the ground state, so formation of K\* after excitation leads to a population inversion, facilitating the observed stimulated emission. This phenomenon has been well-documented in the case of molecules structurally similar to the HPBT component of **2**.<sup>8–10</sup>

The mechanism of formation of K\* by photoexcitation is well-documented<sup>8–10</sup> to occur by a rapid proton transfer in the E\* form. For EGIPT, injection of electrons and holes will lead to immediate formation of enol radical anions and enol radical cations. These radicals might undergo electron transfer to form E\*, which would lead to the observed results. However, more experimental evidence is needed before other plausible mechanisms can be definitively ruled out.

EGIPT and related proton transfer electroluminescence, which are demonstrated here, have implications for understanding proton transfer reactions and organic light-emitting devices. For example, theoretical predictions of the effects of an electric field on tunneling in proton transfer reactions<sup>23</sup> might now be tested with EGIPT. The device architecture and proton transfer copolymer of the LED discussed here represent unoptimized initial results. Current- and luminance-voltage measurements indicate a turn-on voltage of 12 V and a luminance of ca. 1 cd/m<sup>2</sup> at a current density of 12 mA/cm<sup>2</sup>. Optimization of device parameters should significantly increase the performance of EGIPT-based LEDs.

**Acknowledgment.** This research was supported by the Office of Naval Research and in part by the National Science Foundation (CTS 9311741, CHE-9120001). We thank E. Gaillard for technical assistance with the picosecond transient absorption spectroscopy measurements.

JA9613365

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