

Effects of polymer sidebranching in double- and single-layer polyfluorene light-emitting diodes

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We study how changes in sidebranching in electroluminescent polymers affect the performance of polyfluorene-based light-emitting diodes with and without additional hole transport materials. We observe that light emission and device efficiency are determined more by the position of the exciton recombination zone than by changes in the polymer morphology induced by sidebranching. Consequently, we find that sidebranching mainly controls the relative emission between vibrational energy levels and has a minimal effect on polymer charge transport properties. Light outputs of 10 000 cd/m² and device efficiencies of 0.85 and 1.8 cd/A are obtained for single- and double-layer devices, respectively. © 2002 American Institute of Physics. [DOI: 10.1063/1.1473692]

Sidebranching off the conducting backbone of semiconducting polymer materials was introduced as a method to improve solubility of electroluminescent polymers;^{1,2} however, it is now known that sidebranching can have more substantial effects on semiconducting polymers. In particular, the underlying polymer morphology, the optical emission, and charge transport properties are subject to those variations. While sidebranching has long been thought to be particularly important in the performance of polyfluorene-based light-emitting diodes,^{3–5} very few systematic studies addressing sidebranching effects have been undertaken.⁶ This omission is partially due to difficulties that arise in deconvoluting the effects of changes in sidebranching with respect to those involving changes in the materials molecular weight, solubility, and end capping, as well as changes in the device structure, preparation, and testing conditions. In this letter, we attempt to overcome some of these difficulties through systematic studies of four different types of sidebranching in polyfluorene-based materials with and without end capping for both single- and double-layer device structures. Our results indicate that while changes in sidebranching can substantially change the optical emission of electroluminescent polymers, these changes do not significantly affect the charge transport properties and underlying device efficiency when emission occurs away from the polymer/anode interface.

In Fig. 1, we show the chemical structures of the electroluminescent polymers discussed in the letter. The derivatives of poly[2,7-(9,9-bis(R)fluorene)-2,7-bis(4-methylphenyl)]phenyl-amine consisted of different sidebranchings, with R1 = 2-ethylhexyl, R2 = 3,5,5-trimethylhexyl, R3 = 2,4,4-trimethylpentyl, and a spiral which contains 0.2% (molar) substitution of R1 with tetrabromospiro[fluorene-9,9-fluorene]. These polyfluorene (PF) derivatives contained between 2% and 9% end capping with triphenylamine (TPA),

a known hole transporter. We also compared the poly[9,9-bis(R1)fluorene] without an end capper. Double-layer devices were prepared with a cross-linkable poly[(4-*n*-hexyltriphenyl)amine] (*x*HPTA) hole transport layer (HTL).⁷ We observe no systematic dependence of the device properties on either the molecular weight or solubility of the materials.

The derivatives of PF were dissolved in toluene and spin casted onto a semitransparent indium–tin–oxide–patterned glass substrates with 3,4-polyethylenedioxythiophene–polystyrenesulfonate (PEDOT:PSS) and calcium serving as the anode and cathode, respectively.⁸ The overall spectral features were not significantly affected by changes in the device thickness within the range of 80–140 nm.⁹ For double-layer devices, a 70-nm-thick layer of *x*HPTA was spin casted onto the PEDOT layers and thermally treated to initiate cross linking prior to the deposition of PF. The absorption and photoluminescence spectra (not shown) were measured under ambient conditions on PF films deposited onto quartz substrates. The current–voltage–luminance and electroluminescence (EL) spectra were measured in a dry-nitrogen glovebox.

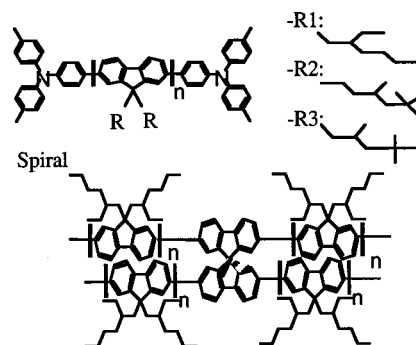


FIG. 1. Derivatives of poly[2,7-(9,9-bis(R)fluorene)-2,7-bis(4-methylphenyl)]phenylamine with different sidebranchings: R1 = 2-ethylhexyl; R2 = 3,5,5-trimethylhexyl; R3 = 2,4,4-trimethylpentyl; and spiral tetrabromospiro[fluorene-9,9-fluorene] branching.

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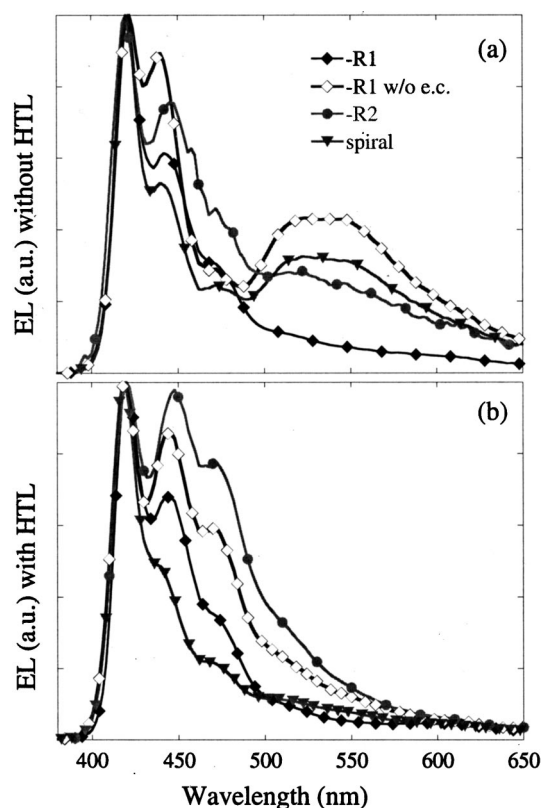


FIG. 2. EL spectra with various sidebranchings of (a) single-layer devices and (b) double-layer devices with the HTL as indicated.

The absorption spectra for all the PF materials are relatively broad and featureless, peaking at 384 nm with an initial onset of 423 nm. In Fig. 2, we show the EL spectra for single-layer [Fig. 2(a)] and double-layer devices [Fig. 2(b)] to compare the effects of the sidebranching and HTL. The EL spectra show peaks of varying strength at 421 ± 2 , 443 ± 2 , and 470 ± 5 nm. The photoluminescence spectra also show peaks at 422 ± 2 and 445 ± 2 nm with a weak shoulder at 470 ± 5 nm; we attribute these peaks to arising from vibrational structure with a corresponding 150 ± 10 meV separation between the energy levels. In addition, a broad peak between 510 and 550 nm is observed for all sidebranching, except R1. This peak is typically assigned to emission from an aggregated species, excimer, or exciplex.^{10,11} We note that the absorption spectra are broader for R1 branching than for other branchings, with full width at half maxima of 85, 70, 60, and 63 nm for R1, spiral, R2, and R3 branching, respectively. These results imply that the R1 branching leads to greater interchain interactions; nonetheless, the lack of correlation between the ground- and excited-state properties suggests that the origin of the broad peak is due to an excimer-like emission.

We contrast these results for double-layer devices [Fig. 2(b)] where the HTL has been added. The emission peaks occur in the same position as for single-layer devices, indicating that the emission is still occurring in the PF layer rather than the HTL. The addition of the HTL suppresses the emission from aggregates. A similar effect can be achieved by introducing end capping,¹² as observed for R1 branching with and without end capping [Fig. 2(a)].

These results can be understood by considering the po-

sition of the recombination zone in single- versus double-layer devices. PF devices are known to have a relatively low highest occupied molecular orbital (HOMO) of around 5.8 eV,¹³ making hole injection from PEDOT with a work function near 5.2 eV difficult.¹⁴ Conversely, electron injection from calcium (work function ~ 2.9 eV) into the lowest unoccupied molecular orbital of PF (~ 3.0 eV) is considered to be relatively easier.¹³ Consequently, electron-hole recombination is expected to occur close to the anode. The xHTPA has a HOMO of 5.4 eV,⁷ providing improved hole injection over PEDOT, thereby shifting the recombination zone further into the bulk of the material. Our result in which excimer-like emission is reduced when the HTL is added implies then that the PF structure is more aggregated close to the anode than in the bulk. This effect can be caused by the spinning deposition process, which can force liquid-crystalline-like PF molecules to stack at the interface but lose their order deeper in the bulk.¹⁵ The interpretation that the PF molecules only have strong interchain interactions near the anode interface and not in the bulk is further supported by the observation that the photoluminescence spectra, which measures the bulk emission, does not contain any aggregation peak for all types of sidebranching and end capping. We find that devices that have significant emission from aggregate species tend to increase their aggregation with aging while those with minimal aggregation maintain spectral stability (data not shown). These results are consistent with previous results that suggest emission from excimer states promotes further stacking into the bulk of PF.¹⁶

The fact that end-capped R1 has no significant aggregation peak is in agreement with the results of Miteva *et al.* in which TPA end capping results in suppression of the aggregation peak.¹² R1 has 9% end capping as opposed to 2% and 4% for R2 and R3 sidebranching, respectively, implying that 9% end capping is sufficient to improve hole injection and shift the recombination zone away from the polymer/anode interface. Finally, we note that the voltage-dependent emission observed by Miteva *et al.* for end-capped R1 sidebranching can be explained within our model as a shift of the recombination zone further into the bulk due to greater hole penetration at higher voltages.

The bulk effects of the sidebranching can, therefore, most clearly be seen in the double-layered devices [Fig. 2(b)]. The more flexible R1 branching leads to more emission at 420 nm than the bulkier R2 branching, resulting in moderate color shifts. With the substitution of 0.2% spiral branching for R1, we observe strong broad emission from aggregate species for single-layer devices yet for double-layer devices we observe the greatest spectral purity (defined by the highest percentage of emission occurring at 420 nm) with no broad aggregate emission. This implies that spiral branching may significantly reduce interchain interactions in the bulk of the PF material, promoting emission from isolated polymer chains, but not at the anode interface.

To evaluate the effect of sidebranching on charge transport properties, we compare the current (solid line) and luminance (dashed line) for all types of sidebranching in Fig. 3. For single-layer devices [Fig. 3(a)], we observe substantially higher currents, luminance, and quantum efficiency for R1 versus other branching. We observe higher currents and

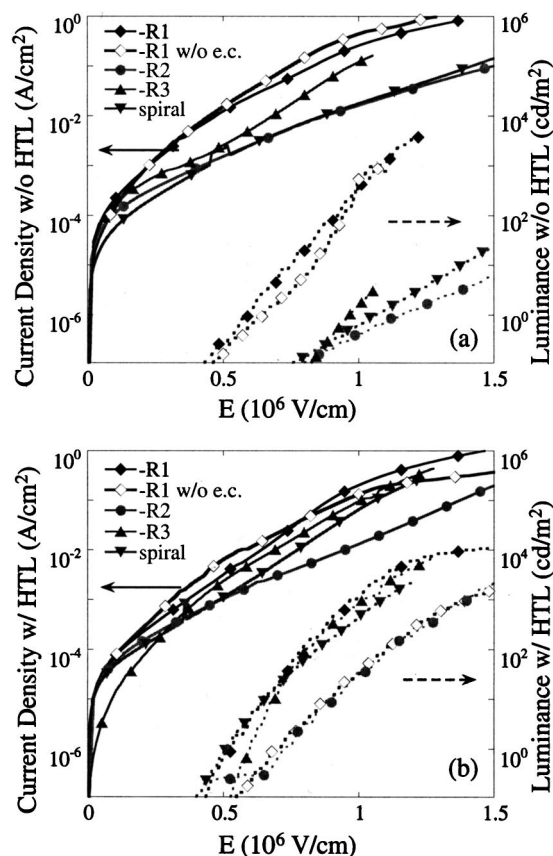


FIG. 3. Current (solid)–luminance (dashed)–electric-field characteristics of (a) single-layer devices and (b) double-layer devices with various sidebranchings and end cappings as indicated.

luminances for R1 with and without end capping, suggesting that the R1 sidebranching itself, and not just the end capping, may improve hole injection, perhaps via improved π -orbital overlap. A rapidly increasing, nonsaturating quantum efficiency occurs for all single-layer devices, indicating that these devices are operating far from charge balance and are dominated by a single charge, presumably electrons.¹⁷

For double-layer devices [Fig. 3(b)], substantial improvements in current density, turn-on voltage, luminance, and device efficiency are observed for R2, R3, and spiral branching, as expected since χ HTPA can improve hole injection as well as block electrons. We observe only modest improvements for R1 branching. Consequently, the HTL neutralizes the effect of branching on the electrical properties of the material. Changes in the optical properties observed for double-layer devices [Fig. 2(b)] are, therefore, mainly due to changes in the polymer folding, which modify the relative weights of the emission from the vibrational state. For double-layer devices, we achieve a typical brightness of 100 cd/m² at 0.8 MV/cm, maximum luminances of 10 000 cd/m² at 1.5 MV/cm, and device efficiencies between 1.3 and 1.8 cd/A for R1, spiral, and R3 branching. The device efficiency for the double layers also increases rapidly with increasing electric field, suggesting that these results can be improved by using thinner polymer layers.¹⁸

In summary, we observe that the optical properties of polyfluorene materials are strongly affected by increased ag-

gregation of the PF molecules near the anode interface, with sidebranching serving mainly to modify the emission between vibrational states. This effect results in substantial changes in the spectral purity and, subsequently, the CIE x , y coordinates, ranging from (0.172, 0.103) to (0.262, 0.290) for the least and most aggregated structures, respectively. For single-layer devices, we observe that flexible sidebranching, such as 2-ethylhexyl, leads to greater emission to lower-energy vibrational states and improvements in the electrical properties in comparison to bulkier sidebranching, such as 3,5,5-trimethylhexyl. The recombination zone can be shifted from the polymer/anode interface into the bulk of the electroluminescent polymer by improving hole injection through the incorporation of triphenylamine groups, either as layers or end cappers, and thereby greatly reducing emission from aggregate species.¹⁹ For devices with hole transport layers, we observe that the electrical performance of polyfluorene devices is not significantly affected by changes in the optical properties induced by different sidebranchings. Our results suggest that high efficiency and pure blue emission can be achieved in single- (and clearly double-) layer polyfluorene light-emitting devices with careful selection of sidebranching and hole transporting species.

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- ¹J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).
- ²D. Braun and A. J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991).
- ³Q. Pei and Y. Yang, *J. Am. Chem. Soc.* **118**, 7416 (1996).
- ⁴A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Wu, *Appl. Phys. Lett.* **73**, 629 (1998).
- ⁵J. Teetsov and M. A. Fox, *J. Mater. Chem.* **9**, 2117 (1999).
- ⁶W.-L. Yu, J. Pei, W. Huang, and A. J. Heeger, *Adv. Mater.* **12**, 828 (2000).
- ⁷J. P. Chen, G. Klaerner, J.-I. Lee, D. Markiewicz, V. Y. Lee, R. D. Miller, and J. C. Scott, *Synth. Met.* **107**, 129 (1999).
- ⁸S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock, and J. C. Scott, *Appl. Phys. Lett.* **70**, 2067 (1997).
- ⁹J. M. Leger (private communication).
- ¹⁰E. M. Conwell, *Synth. Met.* **85**, 995 (1997); S. A. Jenekhe and J. A. Osaheni, *Science* **265**, 765 (1994).
- ¹¹M. Yan, L. J. Rothberg, E. W. Kwock, and T. M. Milles, *Phys. Rev. Lett.* **75**, 1992 (1995); L. M. Herz and R. T. Phillips, *Phys. Rev. B* **61**, 13691 (2000), and references therein.
- ¹²T. Miteva, A. Meisel, W. Knoll, H.-G. Nothofer, U. Scherf, D. C. Müller, K. Meerholz, A. Yasuda, and D. Neher, *Adv. Mater.* **13**, 565 (2001).
- ¹³S. Janietz, D. D. C. Bradley, M. Grell, C. Giebeler, M. Inbasekaran, and E. P. Woo, *Appl. Phys. Lett.* **73**, 2453 (1998).
- ¹⁴T. M. Brown, J. S. Kim, R. H. Friend, F. Cacialli, R. Daik, and W. J. Feast, *Synth. Met.* **111–112**, 285 (2000).
- ¹⁵M. Grell, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, *Adv. Mater.* **9**, 798 (1997); M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H. G. Nothofer, U. Scherf, and H. Yasuda, *ibid.* **11**, 671 (1999).
- ¹⁶V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klärner, R. D. Miller, and D. C. Miller, *Macromolecules* **32**, 361 (1999).
- ¹⁷An electron mobility of $\mu_0 \sim 2 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\gamma \sim 0.005 \text{ cm}^{1/2} \text{ V}^{-1/2}$ was obtained using space-charge-limited current analysis.
- ¹⁸Our results focused on thicker layers to obtain an improvement in device stability and reproducibility. We did not observe as much light emission for R2 branching; however, the device efficiency was similar.
- ¹⁹M. Redecker, D. D. C. Bradley, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Adv. Mater.* **11**, 241 (1999).