Temperature-dependent recombination in polymer composite light-emitting diodes

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We study the temperature dependence of the current–voltage and radiance–voltage curves in double-carrier injected polymer light-emitting devices comprised of poly(2-methoxy,5-(2′-ethyl-hexoxy)–p-phenylene vinylene) (MEH–PPV) and MEH–PPV/SiO_2 as the active layer. The quantum efficiency increases significantly as the temperature is decreased in agreement with an increase in the recombination efficiency with decreasing temperature. Moreover, the bimolecular recombination efficiency saturates at low temperatures and high currents to a very high value for both the composite and plain MEH–PPV devices with the nanoparticles serving as charge traps only at moderately low current densities. Finally, we find that the order of magnitude improvement in radiance observed in some polymer/nanoparticle composites is due to an increase in the effective electric field across the device. © *1998 American Institute of Physics.* [S0003-6951(98)02952-0]

Since the discovery of polymer light-emitting diodes (PLEDs) early in this decade,[1] the methods and mechanisms leading to high device quantum efficiencies have been pursued and debated. Over the last several years, a general consensus has developed that only singlet states recombine to emit light, that minimal light is reabsorbed by the materials due to a large Stokes shift, and that for nearly Ohmic contacts recombination efficiencies approaching unity can be reached.[2] This yields a formula for the external quantum efficiency η_{ext} of $\eta_{int} = 1/4bC\Phi_{PL}$, where C is the outcoupling efficiency,[3,4] b is the fraction of injected carriers that recombine, and Φ_{PL} is the photoluminescence efficiency. Assuming the validity of Eq. (1), b can be derived from measurements of the external quantum efficiency and Φ_{PL}.[5]

An open question is what are the mechanisms that determine b? Clearly, the relative density of injected electrons and holes, i.e., the carrier balance and its dependence on material parameters, is a critical determining factor for the biomolecular recombination efficiency b.[6–8] The relative carrier mobilities can also affect b since lowering one or more carrier mobilities could increase the probability of two diffusing carriers to recombine.[6,7] The importance of traps has been debated, both in regards to the role of traps induced at the interface[9] and the incorporation of electron traps, via nanoparticles, into the material. The latter has led to significant confusion since polymer/nanoparticle composites have been shown to lead to highly efficient and bright light-emitting diodes (LEDs)[10] and reasonable photovoltaics, which require effective charge quenching (in contrast to LED operation) to operate efficiently.[11]

In this letter, we use temperature-dependent current–voltage and radiance–voltage measurements to address the mechanisms which determine the quantum efficiency in both polymer and polymer/nanoparticle composite light-emitting devices. In contrast with results by Blom *et al.* on a p-phenylene vinylene (PPV) derivative,[8] we show that the quantum efficiency increases with decreasing temperature in poly(2-methoxy,5-(2′-ethyl-hexoxy)–p-phenylene vinylene (MEH–PPV) based devices. We determine that at low temperatures and high currents the recombination rate saturates to a value consistent with effectively all the injected holes and electrons recombining, i.e., $b \sim 1$, using Ca and PAni injecting electrodes. Finally, we conclude that wide-bandgap nanoparticles serve as electron traps only at moderately low current densities, alleviating the discrepancy between LED and photovoltaic performance, and that the role of such nanoparticles is to increase the effective electric field, leading to an order of magnitude increase in radiance at fixed voltages.[10]

The MEH–PPV light-emitting devices were deposited onto glass substrates inside a nitrogen atmosphere with Ca as the cathode and ITO/PAni as the anode, as described previously.[10,12] The composite consisted of 20% by weight SiO_2 nanoparticles 20 nm in diameter.[13] The sample was transferred under inert conditions into a vacuum can attached to the measurement probe, which was then placed inside an Oxford MagLab cryostat. The glass substrate was heat sunk to a copper plate, and the silicon photodetector was mounted directly above the LED on the glass. The photodetector was calibrated against an integrating sphere using the same geometric conditions and with the sample mounted so that only the forward external emitted light entered the integrating sphere. The temperature dependence of the silicon photodetector was determined to be less than 5% over the temperature range studied. Current–voltage and radiance–voltage curves were taken every 5 K from 200 to 340 K. Aging effects were minimal when current densities were limited to below 1000 A/m^2.

In Fig. 1, we show temperature-dependent current–voltage (left) and radiance–voltage curves (right) for MEH–PPV (open symbols) and MEH–PPV/SiO_2 composite (closed

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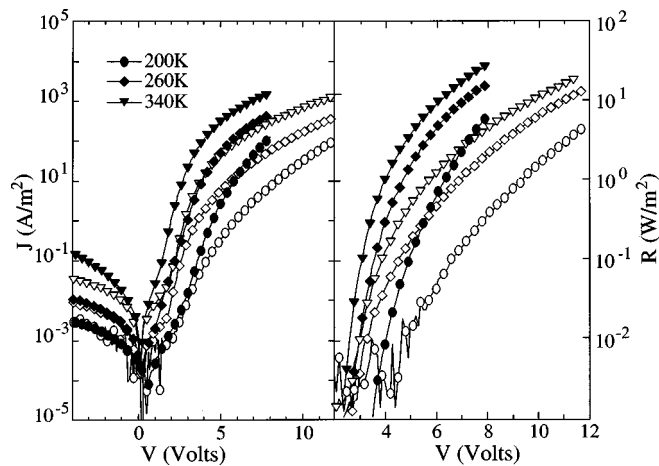a)Corresponding author. Electronic mail: sacarter@cats.ucsc.edu

FIG. 1. Current–voltage (left) and radiance–voltage (right) for MEH–PPV (open) and MEH–PPV/SiO$_2$ composite (closed) at three representative temperatures, 200 K (circles), 260 K (diamonds), and 340 K (triangles). The MEH–PPV film is 140 nm thick. The anode and cathode are ITO/PAni and Ca, respectively. Increases in radiance and current densities up to an order of magnitude are observed for the composite devices over the entire temperature range.
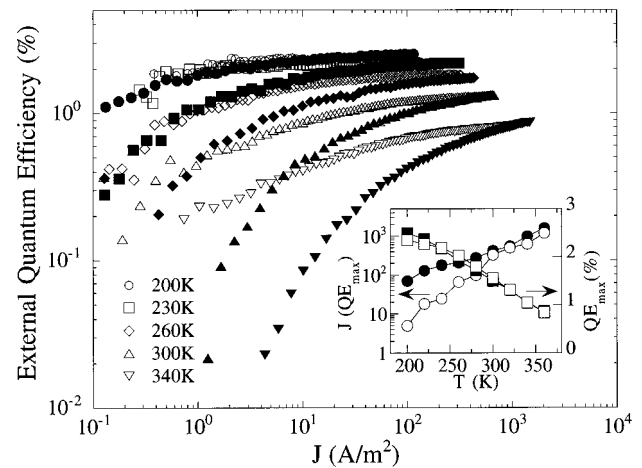

FIG. 2. Log–log plot of external quantum efficiency QE vs current density J for MEH–PPV (open) and MEH–PPV/SiO$_2$ composite (closed) as a function of temperature. The maximum external quantum efficiency (QE$_{max}$) and current at which this efficiency is reached [J(QE$_{max}$)] is shown in the inset.

symbols) at three temperatures, 200 K (circles), 260 K (diamonds), and 340 K (triangles), for clarity. The nanoparticles increase the current density up to an order of magnitude, similar to previous results.[10] The current and radiance decrease by one to two orders of magnitude over this temperature range with the change being largest at lower voltages, consistent with thermionic injection having a greater effect in this regime. The temperature dependence of the current–voltage curves is qualitatively similar to results on PPV-based materials;[8,9] however, the magnitude of the change is considerably less over the same temperature range.

Despite the lack of dramatic change in current, we observe a significant increase in the quantum efficiency with decreasing temperature, shown in Fig. 2 as a log–log plot of external quantum efficiency versus current for both MEH–PPV (open symbols) and MEH–PPV/SiO$_2$ (closed symbols). The inset provides the temperature dependence of the maximum quantum efficiency QE$_{max}$ and the minimum current needed to obtain this quantum efficiency, J(QE$_{max}$). Several remarkable conclusions can be drawn from Fig. 2. Taking the photoluminescence efficiency to be independent of applied voltage, changes in the recombination efficiency b with current are directly proportional to changes in the external quantum efficiency according to Eq. (1). The data, therefore, indicate that the fraction of charged carriers recombining saturates at high current densities and low temperatures. At 200 K, the external quantum efficiency reaches 2.5% at which b obtains its maximum value of 1 for a photoluminescence efficiency Φ_{PL} of 0.23 ± 0.03 with an outcoupling efficiency C of 0.40 ± 0.05.[3] This Φ_{PL} is marginally higher than estimates given for MEH–PPV solid films at room temperature (295 K) of 10%–15%.[5] We note that quantum efficiencies of over 2% have been achieved in MEH–PPV devices at room temperature,[14] implying a minimum photoluminescence efficiency of 18% at room temperature.

Is the temperature dependence due to a change in b or in Φ_{PL}? Fixing Φ_{PL} at 23%, we find that b decreases to 0.65 at 280 K and 0.35 at 340 K; all three values are relatively high,

suggesting nearly Ohmic contacts.[7] A decrease in b with increasing temperature could be attributed to an increased barrier-to-charge injection at either interface, an increase or relative change in the charge mobilities, or an increase in charge imbalance. The former can be discounted since thermionic effects in the presence of small barrier heights should cause an effective decrease in barrier height with increasing temperature. The mobility, though, clearly increases with increasing temperature, providing a possible explanation;[6] however, Blom *et al.* have argued against mobility playing a role for diffusion-controlled recombination processes if the hole and electron mobilities are equal.[8] Last we consider a temperature-dependent change in the relative density of electron and holes in the device. In the absence of deep traps, the charge densities must balance at high saturation voltages independent of the temperature.[7] As such, we would only expect such a deviation from charge balance if deep traps were opened up with temperature due to reversible changes in the interfaces or polymer structure/chemistry.

Alternatively, a temperature-dependent photoluminescence efficiency could explain the results. If all the injected carriers are recombining when the quantum efficiency saturates (i.e., $b=1$), the photoluminescence efficiency would be 15% at 295 K and 8% at 340 K according to Eq. (1). We have measured the relative change in photoluminescence efficiency between 285 and 340 K and find very weak temperature dependence (less than 25%), similar to results obtained on other PPV-based materials.[15] Such weak dependence cannot account for the changes in the quantum efficiency that we observe.

Having discussed the temperature dependence, we now address the dependence of the external quantum efficiencies on current as shown in Fig. 2. At all temperatures, the efficiencies start out low before saturating; therefore, the charge injection is initially unbalanced due to either the presence of one (or more) tunneling contacts or charge traps. As the electric field is increased, the charge densities become more balanced and the traps become filled. The current required to reach such charge balance decreases rapidly (inset) as the temperature is lowered, consistent with diffusion-mediated recombination (i.e., fewer charges are needed because the
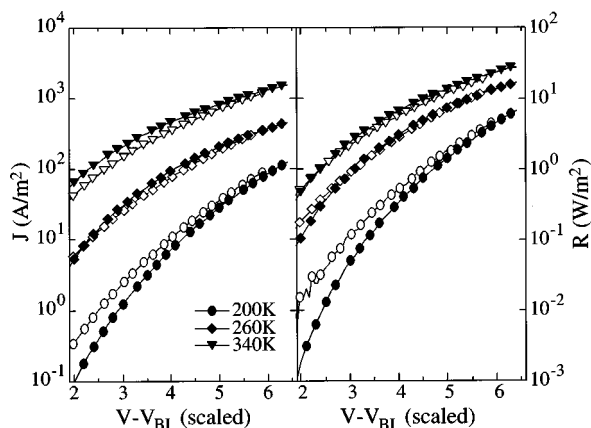
FIG. 3. Scaling plots of current–voltage and radiance–voltage. A built-in voltage of 1.6 V is subtracted, and the voltage scale for the MEH–PPV device is multiplied by 7/12 to scale it onto the MEH–PPV/SiO$_2$ composite data. The incorporation of nanoparticles serve to effectively enhance the electric field, leading to higher radiances and currents. Deviations at low currents are due to charge trapping by the nanoparticles.

lower mobility allows each charge to diffuse longer in the active region).

For the nanoparticle-based devices, we observe clear evidence of charge trapping in the external quantum efficiency at low current densities. Each isolated nanoparticle, whether TiO$_2$ or SiO$_2$, is an electron acceptor and will grab electrons from the MEH–PPV until it reaches its optimum surface charge density. At that point, the Coulomb force repels any additional charges and the quantum efficiency can increase rapidly with increasing current. At high enough currents, the number of electrons trapped on the surfaces of the isolated dielectric particles is negligible compared to the total charge such that no reduction in quantum efficiency is observed. A networked lattice allows the charge to leave the nanoparticle through an interface with a metal electrode, thus allowing for efficient photodiodes and light-emitting diodes in the same material system with adjustments to morphology.[11]

The similar temperature dependence and magnitude of QE$_{max}$ for the composite and noncomposite devices indicate that scattering effects cannot be causing the increase in radiance (or current density). We graph in Fig. 3 the composite (closed symbols) and noncomposite (open symbols) current and radiance where the estimated built-in potential of 1.6 V has been subtracted and the voltage scale for the MEH–PPV-based devices have been multiplied by a fitting-determined factor of 0.58 representing an effective change in the electric field. The data sets are remarkably similar except at low current densities where the currents are lowered for the nanoparticle device due to quenching effects. These results indicate that the nanoparticles cause a factor of nearly 2 increase in the effective electric field, resulting in the order of magnitude improvement in performance.

In conclusion, we have shown that temperature-dependent recombination efficiencies close to unity can be achieved in MEH–PPV films resulting in large external quantum efficiencies and radiances despite low photoluminescence efficiencies. Assuming the validity of Eq. (1), these low photoluminescence efficiencies will limit the internal quantum efficiency of MEH–PPV-based devices to below 6% making it an unlikely candidate for electrically pumped stimulated emission. Nonetheless, the incorporation of nanoparticles into MEH–PPV can significantly decrease the voltages needed for driving super-radiant devices by dramatically increasing the effective electric fields. Finally, we have provided detailed temperature-dependent current and radiance curves for MEH–PPV. The additional information gained from the temperature-dependent radiance should prove valuable for more rigorous testing of charge injection, transport, and recombination models in polymer LEDs.

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