

- [2] a) A. Diedrich, M. Lösche, *Adv. Biophys.* **1997**, *34*, 205. b) J. T. Groves, N. Ulman, S. G. Boxer, *Science* **1997**, *275*, 651. c) W. Knoll, *Annu. Rev. Phys. Chem.* **1998**, *49*, 569.
- [3] *Crystallization of Nucleic Acids and Proteins: A Practical Approach* (Eds: A. Ducruix, R. Giege), Oxford University Press, Oxford **1992**.
- [4] S. D. Durbin, G. Feher, *Annu. Rev. Phys. Chem.* **1996**, *47*, 171.
- [5] O. D. Velev, E. W. Kaler, A. M. Lenhoff, unpublished.
- [6] See for example: a) D. E. Koppel, in *Fast Methods in Physical Biochemistry and Cell Biology* (Eds: R. I. Sha'afi, S. M. Fernandez), Elsevier, New York **1983**, pp. 339–367. b) M. Edidin, in *Mobility and Proximity in Biological Membranes* (Eds: S. Damjanovich, J. Szöllosi, L. Tron, M. Edidin), CRC Press, Boca Raton, FL **1994**, pp. 109–135.
- [7] a) C. V. Kumar, A. Buranaprapuk, G. J. Opitck, M. B. Moyer, S. Jockusch, N. J. Turro, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 10361. b) C. V. Kumar, A. Buranaprapuk, *J. Am. Chem. Soc.* **1999**, *121*, 4262.
- [8] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York **1983**, pp. 341–381.
- [9] I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York **1971**, pp. 383–385.
- [10] See for example: a) A. Ashkin, J. M. Dziedzic, J. E. Bjorkholm, S. Chu, *Opt. Lett.* **1986**, *11*, 288. b) S. Chu, *Science* **1991**, *253*, 861. c) D. G. Grier, *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 264. d) A. Ashkin, *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 4853.
- [11] a) M. Ishikawa, H. Misawa, N. Kitamura, H. Masuhara, *Chem. Lett.* **1993**, 481. b) J. Hotta, K. Sasaki, H. Masuhara, Y. Morishima, *J. Phys. Chem. B* **1998**, *102*, 7687. c) T. A. Smith, J. Hotta, K. Sasaki, H. Masuhara, Y. Itoh, *J. Phys. Chem. B* **1999**, *103*, 1660.

Narrow Bandwidth Luminescence from Blends with Energy Transfer from Semiconducting Conjugated Polymers to Europium Complexes**

By Michael D. McGehee, Troy Bergstedt, Chi Zhang, Andrew P. Saab, Marie B. O'Regan, Guillermo C. Bazan,* Vojislav I. Srdanov,* and Alan J. Heeger*

Semiconducting (conjugated) polymers have several properties that are advantageous for photonic applications:

they have high fluorescence efficiencies (>60%), emit at wavelengths that span the entire visible spectrum, are mechanically flexible, and can be deposited as uniform thin films by casting from solution. Since the fabrication of the first polymer light-emitting diode (LED) in 1990,^[1] there has been extensive research on polymer LEDs and many improvements have been made.^[2–4] Single-color displays fabricated with arrays of polymer LEDs will soon be commercially available. Full color displays will require pure red, green, and blue emission.

Obtaining pure emission colors from conjugated polymers or small organic molecules is difficult because their emission spectra typically have a full width at half maximum (FWHM) of 50–200 nm. Efficient, pure red-emitting polymer LEDs are particularly hard to make because the human eye is more sensitive to orange emission than red; if the spectrum falls even slightly in the orange, the perceived color is “orangish red”. Red LEDs can be made by filtering out orange emission or by using polymers or dyes whose emission starts in the red and extends into the infrared, but these LEDs are inefficient because only part of their emission is useful. In contrast to organic chromophores, rare earth ions have very sharp emission spectra (FWHM < 4 nm).^[5] In this paper we show that pure red emission can be achieved in polymer LEDs by transferring energy from blue-emitting conjugated polymers to europium complexes. Similar methods have been used to make red LEDs from small organic molecules.^[6–10] We show that blends of Eu complexes in poly[2-(6'-cyano-6'-methyl-heptyloxy)-1,4-phenylene] (CN-PPP) have an emission spectral line-width (FWHM) of only 3.5 nm, a photoluminescence (PL) efficiency of 27%, and an electroluminescence (EL) efficiency of 1.1%. These blends could be useful as a source of pure red light for full color displays or for photonic devices that require monochromatic light.

To incorporate Eu³⁺ into conjugated polymers, we synthesized a family of soluble Eu complexes with β -diketonate ligands, codissolved the complexes and polymers in a solvent, and cast films. We chose β -diketonate ligands because they sensitize Eu³⁺ emission.^[5,11] The sensitization process is as follows: the ligand absorbs energy, undergoes intersystem crossing into a triplet state, and then transfers its energy to the Eu³⁺ ion.^[12,13] Thus, the first design rule for making fluorescent Eu complexes is that the triplet level of the ligand must be higher in energy than the emissive level (⁵D₀) of Eu³⁺. A second design rule is imposed by the need for energy transfer from the polymer to the rare earth complex. In order to transfer energy from a conjugated polymer to the ligands of a Eu complex by dipole coupling (Förster transfer), the emission spectrum of the polymer and the absorption spectrum of the ligand must overlap.^[14,15] Since the ligands whose triplet level lies above the ⁵D₀ level of Eu³⁺ absorb in the ultraviolet or blue region of the spectrum, we chose CN-PPP as the host polymer; CN-PPP is a blue-emitting polymer that has been used to make LEDs that emit at wavelengths as low as 385 nm.^[16] We

[*] Prof. G. C. Bazan, Dr. T. Bergstedt
Department of Chemistry
University of California at Santa Barbara
Santa Barbara, CA 93106 (USA)
M. D. McGehee, Prof. A. J. Heeger
Institute for Polymers and Organic Solids and Materials Department
University of California at Santa Barbara
Santa Barbara, CA 93106 (USA)
Dr. C. Zhang, Dr. M. B. O'Regan
Uniax Corporation
6780 Cortona Drive, Santa Barbara, CA 93117 (USA)
Dr. A. P. Saab, Dr. V. I. Srdanov
Department of Chemistry and Institute for Polymers and Organic Solids
University of California at Santa Barbara
Santa Barbara, CA 93106 (USA)

[**] The authors thank Dr. Jian Pei and Dr. Wanglin Yu for synthesizing CN-PPP, Joon Young Park for building the integrating sphere apparatus, and Cuiying Yang for performing transmission electron microscopy measurements. This work was primarily supported by the Air Force Office of Scientific Research (AFOSR) under contract # F49620-98-C-0068 and in part by the MRL Program of the National Science Foundation under Award No. DMR96-32716. A.P.S. and V.I.S. also acknowledge partial support from the National Science Foundation Award No. DMR95-20970. M.D.M. is grateful to the Corning Foundation for a fellowship. T.B. was supported by the NSF Science and Technology Center under grant CHE-9120001.

synthesized four Eu complexes: $\text{Eu}(\text{acac})_3\text{phen}$, $\text{Eu}(\text{mppd})_3\text{phen}$, $\text{Eu}(\text{dbm})_3\text{phen}$, and $\text{Eu}(\text{dnm})_3\text{phen}$. The chemical structures of these complexes are shown in Figure 1a and the full chemical names are given in the experimental section. The different Eu ligand substituents were chosen to systematically adjust the ligand energy levels.^[17,18] Figure 1b shows the absorption spectrum of each complex and the emission spectrum of CN-PPP. One can see that as the conjugation length of the ligand is increased, there is better spectral overlap with the polymer.

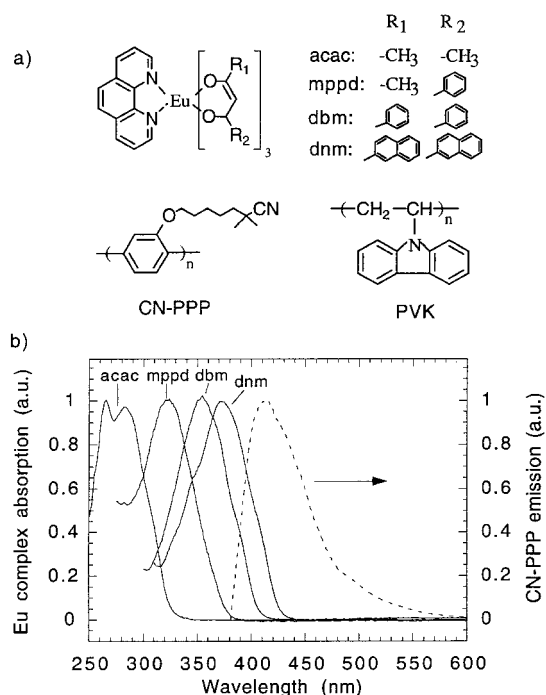


Fig. 1. a) The chemical structure of the Eu complexes, CN-PPP, and PVK. b) The normalized absorption spectra of Eu complexes and the emission spectrum of CN-PPP.

Before beginning careful quantitative measurements of the fluorescence efficiencies of Eu complex/polymer blends, we used an empirical combinatorial approach to quickly determine which Eu complexes could accept energy from several polymers. CN-PPP was pipetted into an array of 5×6 glass vials. Varying amounts of each complex were then pipetted across each row of the array. After the solutions had dried, the vials were illuminated with a UV lamp and the emission was photographed. The photograph in Figure 2 shows the expected trend: energy transfer from the CN-PPP to the Eu complexes is best when the Eu complex has good spectral overlap with the polymer. We also blended the rare earth complexes with other polymers such as poly(*N*-vinylcarbazole) (PVK) and poly(2-butyl-5-(2'-ethyl-hexyl)-1,4-phenylenevinylene) (BuEH-PPV). PVK has an emission spectrum^[19] that is slightly blue-shifted relative to CN-PPP while BuEH-PPV emits in the green.^[20] We found that energy transfer is slightly better for PVK (Fig. 2), but still chose to use CN-PPP for further experiments because it has a conjugated backbone and

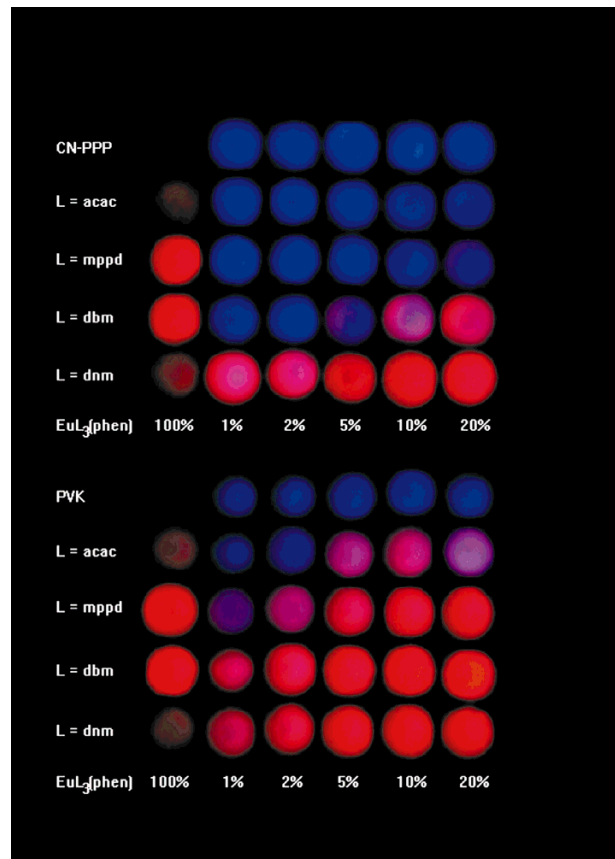


Fig. 2. A photograph that captures the emission from a series of Eu complex/polymer blends. The top array uses the polymer CN-PPP and the bottom array uses PVK. The Eu ligand is indicated to the left of each row. The first row of each array consists of pure polymer. The concentration of the Eu complex is indicated at the bottom of each column. The excitation wavelength was 365 nm. The color of the polymer emission was slightly distorted by the camera. The actual color was a "whitish blue".

should therefore be better for making LEDs with balanced carrier transport. We found that energy transfer does not occur from BuEH-PPV to any of the Eu complexes. This result is expected because there is no spectral overlap between any of the complexes and BuEH-PPV.

To quantitatively determine the effectiveness of the Eu complexes at accepting energy from CN-PPP, a series of thin films was cast with each complex blended into the polymer at a concentration of 5 wt.-% and their PL spectra were measured. Transmission electron microscopy (TEM) showed that the films were homogenous. A pump wavelength of 351 nm was used for the PL measurements because CN-PPP absorbs strongly at this wavelength. The absorption spectra of the blends are virtually identical to the absorption spectrum of CN-PPP; hence, when the films are photopumped at 351 nm, most of the excitations form on polymer chains. The emission spectra of the films are shown in Figure 3. The broad band below 500 nm arises from CN-PPP emission; the sharp lines between 550 and 650 nm arise from the transitions between the $^5\text{D}_0$ state and the ^7F levels of Eu^{3+} . The effectiveness of energy transfer from CN-PPP to the Eu complexes can be determined

by looking at the degree to which the Eu complexes eliminate CN-PPP fluorescence. As expected, energy transfer is much better for complexes whose ligands have longer conjugation lengths. Eu(acac)₃phen, which has almost no spectral overlap with CN-PPP, does not reduce the polymer fluorescence at all, but Eu(dnm)₃phen, which has good spectral overlap with CN-PPP, eliminates almost all of the polymer emission. Since the radiative and non-radiative lifetimes of excited states of CN-PPP are on the order of 1 ns, we conclude that the energy transfer from CN-PPP to Eu(dnm)₃phen is fast and efficient.

To determine the optimal amount of Eu(dnm)₃phen to use for accepting energy from CN-PPP, the concentration of the complex was varied from 0.1 wt.-% to 100 wt.-%. The quantum efficiency for Eu fluorescence is highest when the Eu(dnm)₃phen concentration is approximately 5–10 wt.-%.

At lower concentrations, the energy transfer from CN-PPP to the Eu(dnm)₃phen is incomplete because the average distance from a photoexcited polymer chain to the nearest Eu complex is too large. At higher concentrations, all of the energy is transferred to Eu(dnm)₃phen, but the fluorescence efficiency is reduced by concentration quenching. When the concentration of Eu(dnm)₃phen in CN-PPP is 5 wt.-%, the number density of Eu complexes is 2×10^{19} Eu ions/cm³. Assuming that the Eu complexes do not aggregate, the average distance between the centers of neighboring complexes is calculated to be 4 nm; hence, the distance over which energy transfer is effective is approximately 4 nm.

To study the fluorescence efficiency of the Eu complexes, the absolute PL quantum efficiency (η_{PL}) and PL lifetime (τ_{PL}) of each complex was measured at a concentration of 5 wt.-% in CN-PPP and polystyrene. To examine the effects of concentration quenching, films of pure Eu complex were also studied. The results are shown in Table 1. All of the complexes had a PL efficiency of at least 17% and a PL lifetime of at least 490 μs when blended in CN-PPP or polystyrene. The extremely long PL lifetimes arise because the f-shell transitions are parity forbidden.^[5] The high quantum efficiencies and long PL lifetimes indicate that the Eu³⁺ ion is protected from most quenching mechanisms.

For Eu(dbm)₃phen and Eu(mppd)₃phen, the PL efficiency

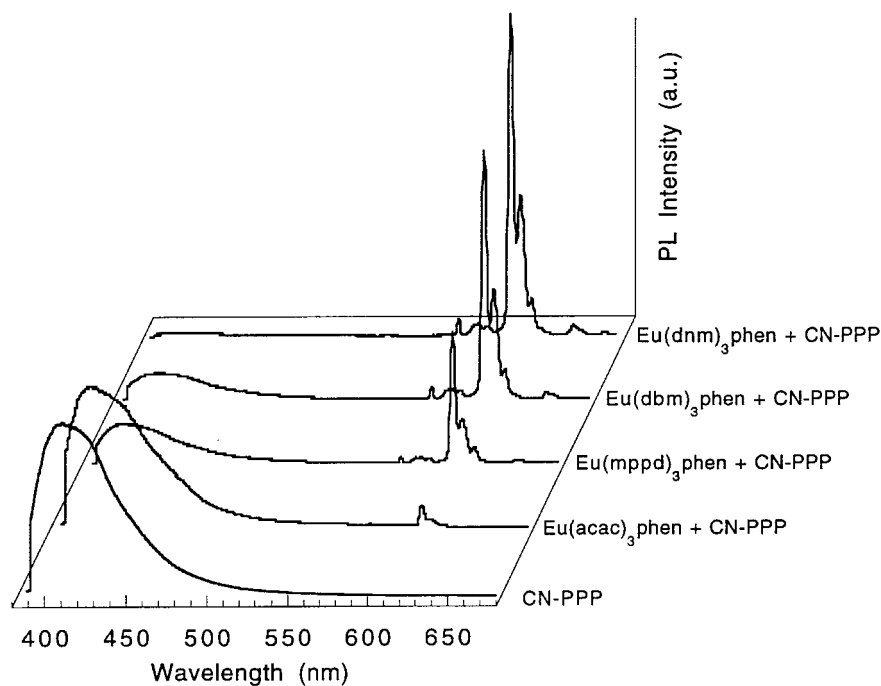


Fig. 3. The PL spectra from CN-PPP and CN-PPP doped with 5 wt.-% of the indicated Eu complexes. All of the films had the same thickness and absorbed approximately the same amount of light, so the emission spectra can be compared to each other to determine relative quantum yields.

and PL lifetime are almost as high in neat films as in the films where the complex is diluted in a polymer. Evidently the β -diketonate and phenanthroline ligands prevent concentration quenching by sterically shielding neighboring Eu³⁺ ions from each other. For reasons that are not yet apparent, concentration quenching was severe for Eu(dnm)₃phen (Fig. 2); η_{PL} was only 2% and τ_{PL} was 22 μs for a neat film.

To make LEDs with the Eu complex/CN-PPP blends, we used the device design that was previously used by Yang et al.^[16] to make CN-PPP LEDs. Indium tin oxide (ITO) was used as the anode, 30 nm of PVK was used as a hole transporting layer, 110 nm of Eu complex/CN-PPP was used as the emitting layer, and a low work function metal was used as the cathode. Figure 4 shows the EL spectra of LEDs made with 2 wt.-% of each complex in CN-PPP and an LED made with pure CN-PPP. The striking feature of these spectra is that there is no CN-PPP emission from any of the LEDs that contain Eu complexes. The PL spectra of the same blends show substantial amounts of CN-PPP emis-

Table 1. PL quantum efficiencies and lifetimes of solid films of europium complex/polymer blends and europium complexes [a].

Complex	5 wt.-% complex blended in CN-PPP [b]		5 wt.-% complex blended in polystyrene		undiluted Eu complex	
	η_{PL}	τ_{PL} [μs]	η_{PL}	τ_{PL} [μs]	η_{PL}	τ_{PL} [μs]
Eu(dnm) ₃ phen	0.27	570	0.22	490	0.02	22
Eu(dbm) ₃ phen	0.26	740	0.29	650	0.23	540
Eu(mppd) ₃ phen	0.17	840	0.18	690	0.18	750

[a] $\lambda_{\text{ex}} = 351$ nm for η_{PL} measurements and 355 nm for τ_{PL} measurements. [b] A 520 nm high pass filter was used so that only the Eu emission was measured for samples that had blue emission from CN-PPP.

sion. LEDs with varying concentrations of $\text{Eu}(\text{dnm})_3\text{phen}$ in CN-PPP were made and it was found that the CN-PPP emission was fully replaced by Eu emission at concentrations as low as 0.5 wt.-%. Recall that 5 wt.-% was needed to quench the CN-PPP emission when the blend was photo-excited.

The reason for the substantial difference between the PL and EL spectra probably arises from the different ways that neutral excitations are formed. When the blends are excited by absorption of light, electron-hole pairs are created on polymer chains and must transfer to the Eu complex. In contrast, when the blends are excited by injecting electrons from one side of the film and holes from the other side of the film, the electrons and holes are probably trapped by the Eu ligands, which have energy levels in the bandgap of CN-PPP. Under these circumstances, neutral excitations are formed directly on the Eu complexes.

The current-voltage curves of LEDs made with 2 wt.-% of each complex and of pure CN-PPP are shown in Figure 5. The operating voltage of the LEDs increases from approximately 12 V to 20 V when the Eu complexes are incorporated. This effect probably arises from the Eu ligands acting as traps that reduce conductivity. Further experiments are needed to investigate the transport properties of conjugated polymer films containing Eu complexes.

For the pure CN-PPP LED the quantum efficiency was 0.3 %. When $\text{Eu}(\text{dnm})_3\text{phen}$ is blended into the CN-PPP, the efficiency is increased to 1.1 %. The enhancement of the efficiency is particularly interesting considering that the PL efficiency of the CN-PPP is approximately 80 %, which is much higher than the PL efficiency of $\text{Eu}(\text{dnm})_3\text{phen}$. One possible explanation for the increase in the EL efficiency is that $\text{Eu}(\text{dnm})_3\text{phen}$ traps charge carriers and thereby enhances the probability of radiative recombination. Another possibility is that $\text{Eu}(\text{dnm})_3\text{phen}$ enhances the efficiency because singlets and triplets that form on the dnm ligand can be transferred to the Eu^{3+} ion to generate light; in CN-PPP only the singlets are radiative, so triplet excitations are wasted. Baldo et al.^[21] and Cleave et al.^[22] have recently observed similar behavior by incorporating the phosphorescent dopant platinum octaethylporphyrin into organic LEDs. The EL efficiencies of devices with $\text{Eu}(\text{dbm})_3\text{phen}$, $\text{Eu}(\text{mppd})_3\text{phen}$, and $\text{Eu}(\text{acac})_3\text{phen}$ are 0.7 %, 0.1 %, and 0.03 %, respectively. One can see that the EL efficiency decreases as the π - π^* gap of the ligand

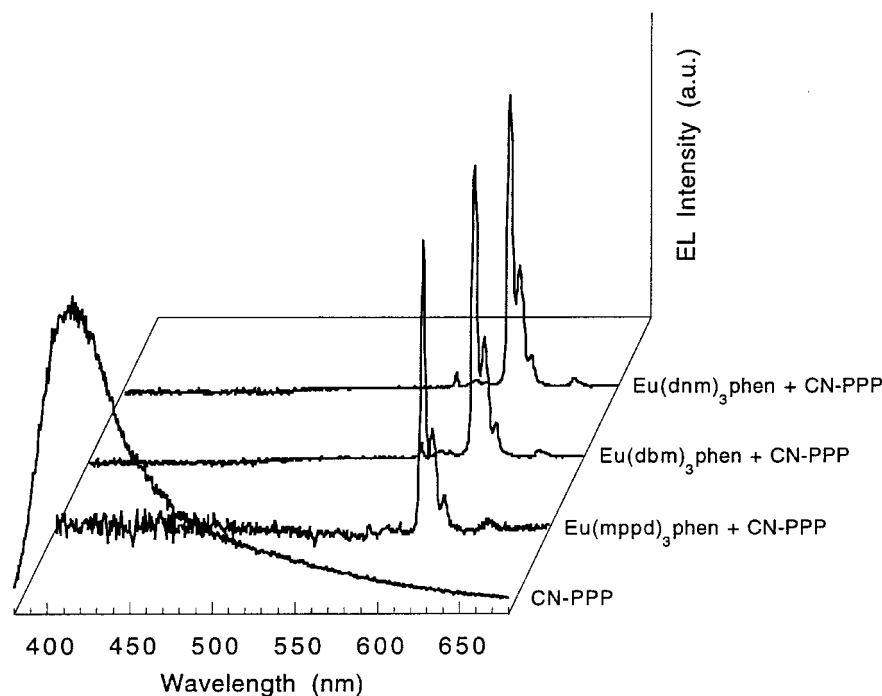


Fig. 3. The PL spectra from CN-PPP and CN-PPP doped with 5 wt.-% of the indicated Eu complexes. All of the films had the same thickness and absorbed approximately the same amount of light, so the emission spectra can be compared to each other to determine relative quantum yields.

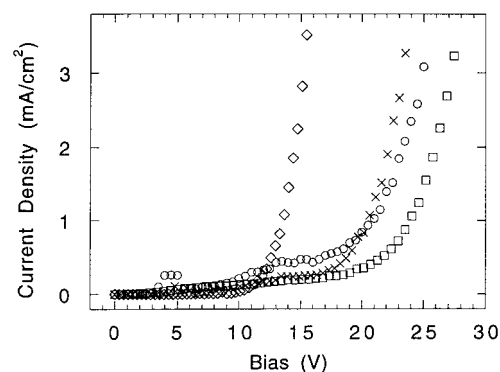


Fig. 5. Current-voltage curves of the LEDs described in the text. The EL layer consisted of CN-PPP (\diamond), 2 wt.-% $\text{Eu}(\text{dnm})_3\text{phen}$ in CN-PPP (\times), 2 wt.-% $\text{Eu}(\text{mppd})_3\text{phen}$ in CN-PPP (\circ), and 2 wt.-% $\text{Eu}(\text{dbm})_3\text{phen}$ in CN-PPP (\square).

increases. We suspect that $\text{Eu}(\text{dnm})_3\text{phen}$ yields the highest EL efficiency because the π and π^* energy levels of the dnm ligand fall in the energy gap of CN-PPP. Hence, both electrons and holes can be transferred to $\text{Eu}(\text{dnm})_3\text{phen}$. We suspect that $\text{Eu}(\text{acac})_3\text{phen}$ quenches electroluminescence because it acts as a trap for one carrier type (either electrons or holes), but not for the other. If one carrier type resides only on the CN-PPP and the other carrier type is trapped efficiently on a Eu ligand, then radiative recombination is hindered and neither species is emissive. Thus, it is crucial to optimize not only the energy gap of the Eu ligands, but also their location relative to the conduction and valence band of the host polymer.

The pure red emission from Eu complexes and the blue emission from CN-PPP provides two of the colors that are needed for full color displays. To achieve green emission, we made LEDs in which the CN-PPP was doped with coumarin 6, a commercially available green-emitting laser dye. It is possible to make a full color display with an array of CN-PPP LEDs in which the blue pixels are undoped, the green pixels are doped with a green dye, and the red pixels are doped with a Eu complex. We have found that the dopants can be incorporated into a polymer film by placing drops of the dopant solutions on top of the film. If the right solvents are used, the dopants diffuse into the polymer. Thus, an attractive method for making full color displays is to spin-cast a high-quality blue-emitting polymer film and then use screen printing,^[23,24] microcontact printing,^[25] or hybrid inkjet printing^[26] to deposit green dye and Eu complex on the desired locations. In addition to being easy to fabricate, these displays could be fully transparent if transparent electrodes were used.^[27]

In summary, we have shown that spectrally sharp, long lifetime emission can be obtained from polymer films by transferring energy from conjugated polymers to rare earth complexes. Optimizing the energy levels of the rare earth ligands is the key to obtaining effective energy transfer and efficient electroluminescence. Pure red-emitting LEDs with a quantum efficiency of 1.1 % were made by doping CN-PPP with Eu(dnm)₃phen. Blue- and green-emitting LEDs were also made using CN-PPP and CN-PPP doped with coumarin 6, respectively. Although the operating voltage of the LEDs was high, we expect that improved performance will be achieved by optimizing the energy levels of the electrodes, polymers, and dopants. The research described in this paper could lead to the fabrication of high-quality full color displays. Furthermore, rare earth/polymer blends could be quite useful as a source of monochromatic emission in photonic crystals.^[28,29] Photonic crystal-based devices work best with monochromatic light because they only function optimally over a small range of wavelengths.

Experimental

The following chemicals were used to synthesize Eu complexes: benzoylacetone, dibenzoylmethane, 2,4-pentanedione, 1,10-phenanthroline, europium(III) chloride hexahydrate, 2'-acetophenone, and 2-naphthoic acid. They were obtained from Aldrich Chemical, Lancaster Synthesis, or Acros Organics and used as received without further purification.

Dinaphthoymethane (dnm) was prepared by modification of a literature procedure [30]. A solution of 2-naphthoic acid (10.0 g, 58 mmol) and 2 mL concentrated sulfuric acid in 125 mL absolute ethanol was heated for 2 h with continuous azeotropic removal of water. Purification by flash chromatography on silica afforded 10.1 g (87 %) of the desired ester, ethyl 2-naphthoate. To a stirred solution of 5.0 g of this ester (25 mmol) and 4.25 g 2'-acetophenone (25 mmol) in 100 mL dimethoxyethane was added 1.2 g (50 mmol) sodium hydride in small portions. Upon final addition of base, the mixture was heated to reflux for 3 h, followed by room temperature stirring overnight. A small amount of water (ca. 5 mL) was added carefully to the solution, followed by acidification with portions of 0.1 M HCl. The crude product was extracted with ether and purified by multiple recrystallizations from petroleum ether to afford 1.27 g (16 %) of the diketone.

The synthesis of tris(acetylacetonato)(monophenanthroline)europium(III) [Eu(acac)₃phen] is illustrative of a typical europium complex synthesis:

a solution of acetylacetone 0.601 g, 6 mmol), 1,10-phenanthroline (0.360 g, 2 mmol), and sodium hydroxide (6 mmol) in 20 mL ethanol was warmed with stirring. Europium chloride hexahydrate (0.733 g, 2 mmol) was dissolved in 2 mL of water and added dropwise to the stirred ligand solution, inducing precipitation of the complex. The crude product was recrystallized from ethanol/water, yielding 0.545 g (44 %) of a white solid (recovered as the monohydrate). Anal. calcd. (found) for C₂₇H₃₁EuN₂O₇: C 50.08 % (49.92), H 4.82 % (4.84), N 4.32 % (4.35).

Tris(benzoylacetato)(monophenanthroline)europium(III) [Eu(mppd)₃phen] was prepared as above, substituting acetylacetone by benzoylacetone. The product was purified by multiple precipitations by dropwise addition of a concentrated benzene solution into stirred hexanes. Anal. calcd. (found) for C₄₂H₃₅EuN₂O₆: C 61.84 % (61.66), H 4.32 % (4.50), N 3.43 % (3.35).

Tris(dibenzoylmethane)(monophenanthroline)europium(III) [Eu(dbm)₃phen] was prepared as above using dibenzoylmethane. Recrystallization was from 5 % ethanol/hexanes. Anal. calcd. (found) for C₅₇H₄₁EuN₂O₆: C 68.3 % (68.6), H 4.12 % (4.00), N 2.80 % (2.87).

Tris(dinaphthoymethane)(monophenanthroline)europium(III) [Eu(dnm)₃phen] was prepared as above, employing dinaphthoymethane from the synthesis previously described. The recovered solid was washed with 5 % ethanol/hexanes to remove unreacted ligand. Anal. calcd. (found) for C₈₁H₅₃EuN₂O₆: C 74.71 % (74.4), H 4.10 % (4.02), N 2.15 % (2.25).

CN-PPP was prepared using the methods described by Yang et al. [16]. Polystyrene and PVK were obtained from Aldrich and used without purification. All of the polymer films that were used in photoluminescence experiments were prepared by spin-casting chloroform solutions of the polymer and Eu complex onto glass substrates. Phase separation in the films was not observed by TEM when the Eu complex concentration was 5 wt.-%, but was observed when the concentration was 25 wt.-%.

Absorption spectra were measured with a Shimadzu UV-2401 PC UV-vis recording spectrophotometer. For the photoluminescence spectrum measurements, the 351 nm line from an argon ion laser was used as the excitation source; neutral density filters were used to set the pump intensity to 0.1 mW/cm². The emission was spectrally dispersed by a 50 cm focal length monochromator with a 150 lines/mm grating and detected by a charge coupled device (CCD) camera. The response of the spectrometer was calibrated by measuring the blackbody spectrum from a tungsten halogen lamp (Ocean Optics LS-1). All measurements were performed in air, but samples were stored in vacuum. The total time of exposure to air was always kept to less than five minutes to avoid photo-oxidation.

Quantum efficiency measurements were made using the 351 nm line from the argon laser, an integrating sphere, a high pass filter that blocks the laser line, and a silicon diode. The laser intensity was 2.5 mW/cm². The technique was similar to those reported on previously by de Mello et al. [31] and Greenham et al. [32].

The PL lifetime measurements were made using 10 ns pulses from a Nd:YAG laser as the excitation source ($\lambda = 355$ nm). The PL was dispersed by the monochromator described above and detected by a Hamamatsu R928 photomultiplier tube. The signal from the photomultiplier tube was detected by a digital oscilloscope. The fluorescence decays were fit to the equation $I = I_0 \exp(-t/\tau)$, where τ is the PL lifetime.

The procedure for making LEDs was as follows: A 30 nm thick film of PVK was deposited onto an ITO-coated glass substrate by spin-casting a solution of 10 mg PVK per mL 1,1,2,2-tetrachloroethane at 3000 rpm. A 110 nm thick film of Eu complex/CN-PPP was deposited on top of the PVK by spin-casting a solution of 30 mg Eu complex/CN-PPP per mL toluene at 3000 rpm. The low work function electrodes were thermally evaporated through a shadow mask at a pressure of 1×10^{-6} torr. Film thicknesses were measured by a Tencor profilometer. Current-voltage and light-voltage curves were measured using a Keithley 236 source-measure unit and a calibrated silicon diode. EL spectra were measured using an Oriel Multispec monochromator with a CCD camera.

Received: May 12, 1999
Final version: August 11, 1999

- [1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539.
- [2] Y. Cao, I. D. Parker, G. Yu, C. Zhang, A. J. Heeger, *Nature* **1998**, *397*, 414.
- [3] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.
- [4] A. Dodabalapur, *Solid State Commun.* **1997**, *102*, 259.
- [5] A. P. B. Sinha, in *Spectroscopy in Inorganic Systems*, Vol. 2 (Eds: C. N. R. Rao, J. R. Ferraro), Academic, New York **1971**.

- [6] J. Kido, H. Hayase, K. Hongawa, K. Nagai, K. Okuyama, *Appl. Phys. Lett.* **1994**, *65*, 2124.
- [7] J. Kido, W. Ikeda, M. Kimura, K. Nagai, *Jpn. J. Appl. Phys.* **1996**, *35*, L394.
- [8] T. Sano, M. Fujita, T. Fujii, Y. Hamada, K. Shibata, K. Kuroki, *Jpn. J. Appl. Phys.* **1995**, *34*, 1883.
- [9] L. Liu, W. Li, Z. Hong, J. Peng, X. Liu, C. Liang, Z. Liu, J. Yu, D. Zhao, *Synth. Met.* **1997**, *91*, 267.
- [10] N. Takada, T. Tsutsui, S. Saito, *Jpn. J. Appl. Phys.* **1994**, *33*, L863.
- [11] W. R. Dawson, J. L. Kropp, M. W. Windsor, *J. Chem. Phys.* **1966**, *45*, 2410.
- [12] G. A. Crosby, R. E. Whan, R. M. Alire, *J. Chem. Phys.* **1961**, *34*, 743.
- [13] G. A. Crosby, *Mol. Cryst.* **1966**, *1*, 37.
- [14] T. Forster, *Discuss. Faraday Soc.* **1959**, *27*, 7.
- [15] A. Dogariu, R. Gupta, A. J. Heeger, H. Wang, *Synth. Met.* **1999**, *100*, 95.
- [16] Y. Yang, Q. Pei, A. J. Heeger, *J. Appl. Phys.* **1996**, *79*, 934.
- [17] M. Uekawa, Y. Miyamoto, H. Ikeda, K. Kaifu, T. Nakaya, *Synth. Met.* **1997**, *91*, 259.
- [18] M. Uekawa, Y. Miyamoto, H. Ikeda, K. Kaifu, T. Nakaya, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2253.
- [19] C. Wu, J. C. Sturm, R. A. Register, J. Tian, E. P. Dana, M. E. Thompson, *IEEE Trans. Electron Devices* **1997**, *44*, 1269.
- [20] M. R. Andersson, G. Yu, A. J. Heeger, *Synth. Met.* **1997**, *85*, 1275.
- [21] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151.
- [22] V. Cleave, G. Yahioglu, P. Le Barny, R. H. Friend, N. Tessler, *Adv. Mater.* **1999**, *11*, 285.
- [23] Z. Bao, Y. Feng, A. Dodabalapur, V. R. Raju, A. J. Lovinger, *Chem. Mater.* **1997**, *9*, 1299.
- [24] F. Pschenitzka, J. C. Sturm, *Appl. Phys. Lett.* **1999**, *74*, 1913.
- [25] J. A. Rogers, Z. Bao, V. R. Raju, *Appl. Phys. Lett.* **1998**, *72*, 2716.
- [26] S. Chang, J. Bharathan, Y. Yang, R. Helgeson, F. Wudl, M. B. Ramey, J. R. Reynolds, *Appl. Phys. Lett.* **1998**, *73*, 2561.
- [27] G. Parthasarathy, P. E. Burrows, V. Khalfin, V. G. Kozlov, S. R. Forrest, *Appl. Phys. Lett.* **1998**, *72*, 2138.
- [28] J. D. Joannopoulos, P. R. Villeneuve, S. Fan, *Nature* **1997**, *386*, 143.
- [29] A. Dodabalapur, E. A. Chandross, M. Berggren, R. E. Slusher, *Science* **1997**, *277*, 1787.
- [30] K. Ohta, A. Ishii, H. Muroki, I. Yamamoto, K. Matsuzaki, *Mol. Cryst. Liq. Cryst.* **1985**, *116*, 299.
- [31] J. C. de Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230.
- [32] N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, R. H. Friend, *Chem. Phys. Lett.* **1995**, *241*, 89.

A Simple and Complete Purification of Single-Walled Carbon Nanotube Materials**

By Anne C. Dillon, Thomas Gennett, Kim M. Jones, Jeffrey L. Alleman, Philip A. Parilla, and Michael J. Heben*

Carbon single-walled nanotubes (SWNTs) must be thoroughly purified if they are to be used in a variety of projected applications and basic studies. Here we describe a

non-destructive, scaleable, three-step purification process that produces materials with >98 wt.-% purity. A dilute nitric acid reflux digests, functionalizes, and redistributes the non-nanotube carbon fractions to form a uniform and reactive coating on the SWNTs. This coating is selectively removed by oxidation in air. Raman spectroscopy, inductively coupled plasma spectroscopy (ICPS), and thermogravimetric analysis (TGA) are used to evaluate the purity of the material at each step of the process, and illustrate that very few tubes are consumed. Such a purification technique is not currently available,^[1-4] and the use of TGA and ICPS defines a technique by which the components in raw and processed materials may be accurately determined on a weight percent basis.

SWNT materials were synthesized by a laser vaporization method similar to that of Thess et al.^[5] but a single Nd:YAG laser was used (~450 ns pulses at 1064 nm and 10 Hz, average power of 20–30 W/cm²). Material was produced at rates of 75–150 mg/h. The power density was selected to operate in a vaporization regime^[6] during synthesis so that graphite particles were not ejected from the target and incorporated into the vaporized soot. Graphite particles introduced by such “sputtering” are not removed effectively with the purification process described here. Targets were made by pressing powdered graphite (~1 μm particle size) doped with 0.6 at.-% each of Co and Ni in a 1 inch × 1/8 inch dye (1 inch = 2.54 cm) at 10000 psi (1 psi ≈ 6.89 kN m⁻²). Crude soot was produced at 1200 °C with 500 torr Ar flowing at 100 sccm. The transmission electron microscopy (TEM) image in Figure 1a reveals the components of the laser-generated material. Bundles of SWNTs span between large agglomerations of amorphous and nanocrystalline carbon and metal nanoparticles. Raw materials were estimated to contain ~20–30 wt.-% SWNTs by a detailed analysis of numerous different TEM images.^[6] ICPS was performed after complete air-oxidation of the carbon and thorough digestion of the residue in concentrated HNO₃. The same metal content was found in both the laser-generated crude material and the initial target (6 wt.-%).

Approximately 80 mg of crude material produced at ~20 W/cm² was refluxed in 60 mL 3 M HNO₃ for 16 h at 120 °C. The solids were collected on a 0.2 μm polytetrafluoroethylene-coated polypropylene filter in the form of a mat and rinsed with deionized water. After drying, an 82 wt.-% yield was obtained. The weight lost is consistent with the digestion of the metal and an additional ~12 wt.-% of the crude material. TEM showed that SWNTs were encased within the mat by a relatively thick and uniform carbonaceous matrix (Fig. 1b). The carbon matrix was completely removed by oxidation in stagnant air at 550 °C for 30 min, leaving behind pure SWNTs having a weight of ~20 % of the initial crude material (Fig. 1c). TGA in flowing air (100 sccm) showed the purified tubes to be quite stable (Fig. 2a). The decomposition temperature (*T_d*) at 735 °C, defined here as the inflection point during oxida-

[*] Dr. M. J. Heben, Dr. A. C. Dillon, Dr. T. Gennett,^[†] K. M. Jones, J. L. Alleman, Dr. P. A. Parilla
National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, CO 80401-3393 (USA)

[†] On sabbatical from: Chemistry Department, Rochester Institute of Technology, 85 Lomb Memorial Drive, Rochester, NY 14623-5604, USA.

[**] This work was funded by the US Department of Energy Hydrogen Program.