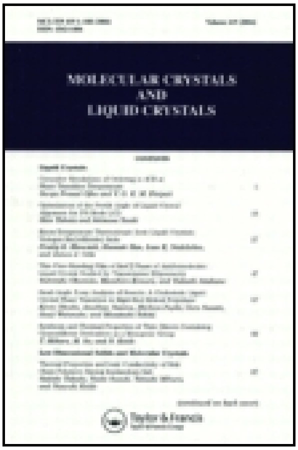

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Effective Exciton Confinement in a Light Emissive Polymer

J. K. Kim [a], J. W. Yu [a], H. N. Cho [a], D. Y. Kim [a] & C. Y. Kim [a]

[a] Polymer Materials Laboratory, KIST, P.O. Box 131, Cheongryang, Seoul, 130-650, Korea

To cite this article: J. K. Kim, J. W. Yu, H. N. Cho, D. Y. Kim & C. Y. Kim (1999): Effective Exciton Confinement in a Light Emissive Polymer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 165-170

To link to this article: http://dx.doi.org/10.1080/10587259908026805

Mol. Cryst. Liq. Cryst., 1999, Vol. 327, pp. 165-170
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Effective Exciton Confinement in a Light Emissive Polymer

J.K. KIM, J.W. YU, H.N. CHO, D.Y. KIM and C.Y. KIM

Polymer Materials Laboratory, KIST P.O. Box 131, Cheongryang, Seoul 130–650, Korea

(Received June 30, 1998; In final form July 15, 1998)

Poly(9,9'-di-n-hexyl-2,7-fluorenylenevinylene) (PDHFV) was synthesized with dibromodihexylfluorene and divinyldihexylfluorene by employing a Heck reaction with a palladium catalyst. The UV-visible absorption maximum at 400 nm from the polymer solution in chloroform has redshifted by 40 nm for the polymer film. The photoluminescence (PL) spectrum of the film showed the emission maximum at 470 nm with a strong excimer emission at 535 nm. The ratio of the excimer emission intensity to that of the singlet decay was constant regardless of the excitation energy. However, the indirect excitation of the fluorophore for the PL emission of a polymer blend at 470 nm was greatly enhanced at the expense of the excimer emission intensity.

Keywords: light-emissive polymer; exciton; excimer; energy transfer; polymer blend

INTRODUCTION

Light-emitting diodes (LEDs) fabricated with a polymer as the light emissive layer has attracted tremendous attention since polymers have advantages over inorganic and organic light emissive materials in terms of processibility, molecular varieties and mechanical properties.[1] Prototypes of polymer LEDs for colors of green, yellow, orange and red have been demonstrated to anticipate practical uses of the new version of display systems in the near future.[2]

It has been possible to synthesize light emissive polymers with high quantum efficiency and good stability except blue emission.[3] Blue-emissive polymers[4,5] were also introduced.

The present work tries to evaluate emission performance of a polymer with monomer units of fluorene and ethylene. The polymer was blended with another polymer to evaluate dilution effect on light emission.

EXPERIMENTAL

Fluorene, palladium (II) acetate, tin-o-tolylphosphine, polymethylmethacrylate (PMMA) and polyvinylcarbazole (PVK) were supplied by Aldrich and used as received. The rest of chemicals used were a reagent grade. Synthesis of 2,7-dibromo-9,9'-di-n-hexylfluorene(I) was introduced previously.[6] 2,7-divinyl-9,9'-di-n-hexylfluorene was prepared by the reaction of 2,7-dibromo-9,9'-di-n-hexylfluorene and ethylene according to the literature procedure.[7] Poly(9,9'-di-n-hexyl-2,7-fluorenylenevinylene) (PDHFV) was synthesized as following: To a 100 mL Schlenk flask equipped with a stirring bar and containing 1.97 g (4 mmol) of 2,7-dibromo-9,9'-di-n-hexylfluorene, 1.54 g (4 mmol) of 2,7-divinyl-9,9'-di-n-hexylfluorene, 36.4 mg of palladium (II) acetate, and 248 mg of tri-o-tolylphosphine was added 40 mL of DMF via a syringe. After a homogeneous solution was obtained, 3.0 mL of tri-n-butylamine was added to the reaction solution. The reaction mixture was stirred vigorously at 100 °C for 24h and then poured slowly into an excess amount of methanol (500 mL). The precipitated material was recovered by filtration. It was redissolved in chloroform and micro-filtered followed by precipitated again into methanol. Filtration and drying under vacuum at 40 °C for 24h afforded 2.58 g of polymer as a yellow solid (Mn=3,300, PD=1.87). ^{1}H-

NMR: δ 0.5-1.2(br, m, $-CH_2$ and $-CH_3$), 1.8-2.0(br, s, $\alpha-CH_2$), 7.0-7.7(m, vinyl and aromatic). The polymer synthesis was illustrated in Figure 1.

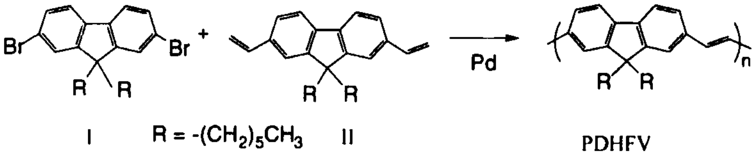

FIGURE 1 Synthetic route to PDHFV polymer..

Ultra violet-visible (AB) spectra were recorded with a HP 8452 Diode Array Spectrophotometer. Photoluminescence (PL) spectra were recorded for the films or the polymer solution with the concentration of 10-5 mol/L with an ISS K-2 Fluorometer. Fabrication of LEDs was described elsewhere.[5] Electroluminescence (EL) spectra of the LEDs were reproduced by employing the fluorometer used in the PL measurement

RESULTS AND DISCUSSION

AB and PL spectra of PDHFV were shown in Figure 2. The absorption maximum at 400 nm red-shifted by almost 40 nm from that of polyfluorene[6] indicating a completely new electronic state different from that of polyfluorene. The PL spectrum of the film shows the emission maximum at 470 nm and a vibronic shoulder at 490 nm, and a broad peak at 535 nm. The PL spectrum blue-shifted on dilution in chloroform by 15 nm at the peak-to-peak position. The broad peak at 535 nm shrank significantly while the vibronic peak at 500 nm changed less and a new shoulder appeared at 410 nm.

It is generally known that the emission maximum blue-shifts on dilution in a solvent.[8] The shrinkage at 535 nm should be attributed to the disrupt of the dimeric moieties in the solution. But a fluorophore with more than one monomeric unit seems to reside in the chain in the solution state to show not complete disappearance but the diminished shoulder at 535 nm. It is interesting to observe the new shoulder at 410 nm, which might be the singlet decay of the fluorene unit freed from the vinylene unit in the solution.

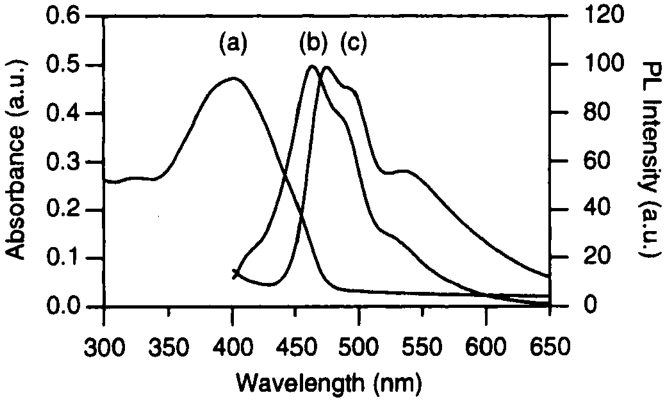

FIGURE 2 AB (a) and PL spectra of PDHFV in solution (10^{-5} M)(b) and solid film (c).

It has been attempted to eliminate the broad peak at 535 nm in the PL spectrum by blending PDHFV with PMMA or PVK to give the dilution effect. The PL spectra of the blend with PMMA showed a decrease of the emission intensity with a decrease of the PDHFV concentration without a change in the PL spectrum shape on excitation at 410 nm where the AB spectra had the absorption maximum. It is clear that the effect of PMMA on PL of PDHFV is negligible except lowering the PDHF emission.

The blends with PVK also showed the same trend on excitation at 410 nm. However, a completely new set of the PL spectra were observed for the blend with PVK when it was excited at 340 nm where PVK showed the AB maximum as shown in Figure 3. There was no trace of the PL spectrum of PVK and no change in the PL emission peak position of PDHFV was observed by the blending. The inset in Figure 3 revealed that the highest emission intensity at 470 nm was observed from the blend with only 10% of PDHFV. The intensity at the peak maximum decreased with an increase of the PDHFV concentration.

The results of the polymer blends with PVK revealed that singlet excitons formed in PVK on excitation at 340 nm became donors to release the energy to the fluorophore of a lower band gap in PDHFV before a singlet decay. The efficiency of the energy transfer was higher with a lower density of the acceptors. It is speculated that the new excitons formed in PDHFV by the energy transfer from those of PVK tend to roam in PDHFV and have a good chance to meet each other and to result in the concentration quenching. The excitons confined in the molecular chain of PDHFV diluted highly in the blend showed a high quantum yield of PL. It has been proved by a time-resolved fluorescence spectroscopy that the intramolecular energy transfer was less effective than that of the intermolecular energy transfer.[9] The excitons confined in the blend with a low concentration of PDHFV performed the singlet decay efficiently before loosing the energy for a non-radiative decay.

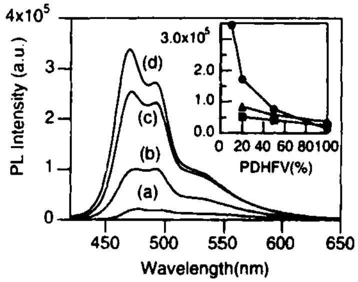

FIGURE 3 PL spectra of PDHFV/PVK blends excited at 340 nm; (a) 100/0, (b) 50/50, (c) 20/80 and (d) 10/90. Inset shows the PL intensity at 475 nm with different excitation wavelength: 340 (●), 365 (■) and 420 nm (▲).

The normalized LED spectra of the polymer and the blends were shown in Figure 4. The forward bias potential was 10~20 V to emit blue color with the emission maximum at 470 nm. The broad peak at 535 nm diminished as the PVK concentration increased in the blends. The EL spectra were almost identical to the PL spectra.

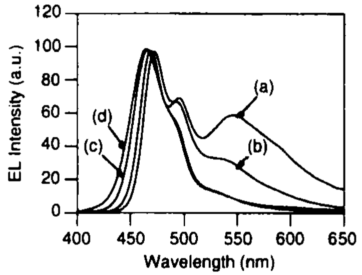

FIGURE 4 Normalized EL spectra of PDHV/PVK blends; (a) 100/0, (b) 50/50, (c) 20/80 and (d) 10/90.

References

[1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, and A.B. Holmes, *Nature,* **Vol. 347,**539 (1990).

[2] M. Berggren, O. Inganäs, G. Gustafsson, M.R. Anderson, T. Hjertberg. and O. Wennerström, *Synth. Met.,* **Vol. 71,** 2185 (1995).

[3] A. Kraft, A.C. Grimsdale, and A.B. Holmes, *Angev. Chem.,* **Vol. 37,** 402 (1998).

[4] G. Grem, G. Leditzky, B. Ulrich, and G. Leising, *Adv. Mater.,* **Vol. 4,** 36 (1992).

[5] H.N. Cho, D.Y. Kim, Y.C. Kim, J.Y. Lee, and C.Y. Kim, *Adv. Mater.,* **Vol. 9,** 326 (1997).

[6] M. Fukuda, K. Sawada, and K. Yoshino, *J. Polym. Sci.: Part A. Polym. Chem.* **Vol. 31,** 2465 (1993).

[7] H.P. Weitzel. A. Bohnem, amd K. Müller, *Macromol. Chem.,* **Vol. 191,** 2815 (1990).

[8] S.A. Jenekhe and J.A. Osaheni, *Science,* **Vol. 265,** 765 (1994).

[9] H.N. Cho, D.Y. Kim, and C.Y Kim, *Macromolecules,* to be submitted.