

# Relationship between Exciton Lifetime and Energy Transfer in Light Emitting Polymers

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## Abstract

The energy transfer from photoexcited polyvinylcarbazole (PVK) chromophores with a bandgap of 3.7 eV as a donor to fluorophores of poly(dihexylfluorenevinylene) (PDHFV) or poly(dihexylfluorenedihexoxyphenylenevinylene) (PDHFHPV) as an acceptor in bilayered specimens should be carried out since the spectral overlap pairs fulfill the requirement for the Förster-type condition. However, the energy transfer rate from the chromophores with a wider bandgap to the fluorophores with a narrower bandgap is proved to be strongly dependent on the lifetime ratio between the excitons.

## Introduction

Organic and polymer light emitting diodes (LEDs) attracted a great deal of interests for a display system since their introduction in 1987 [1] and 1990 [2], respectively. The device is easy to fabricate, made thin and light, and needs a bias potential less than 10V to operate it. The development progress is fast to achieve the quantum efficiency of light emission of 10%[3]. The electroluminescence (EL) emission spectrum of an LED is generally the same as the photoluminescence (PL) emission spectrum of the light emitting materials of the diode to reveal that the emission center is the same with each other[4]. It is generally accepted that a light emitting material with high PL efficiency gives high EL efficiency of an LED.

The PL efficiency is improved by indirect photoexcitation of a fluorophore with a narrower bandgap in a mixture of chromophores[5]. The energy transfer from excited chromophores to unexcited fluorophores is supposed to be carried out by a Förster mechanism with functions of the energy transfer distance and the superposition between the electronic absorption spectrum of the acceptor and the PL emission spectrum of the donor[6].

The present study observed that the PL intensity of an acceptor was dependent greatly on the ratio of lifetime between the donor and the acceptor compared to the degree of the superposition of the spectra referred to the Förster-type mechanism.

## Experimental

The chemical structures of the polymers used are shown in Fig. 1. Polyvinylcarbazole (PVK) purchased from Aldrich was purified by a precipitation method. Poly(dihexylfluorenevinylene) (PDHFV) and poly(dihexylfluorenedihexoxyphenylenevinylene) (PDHFHPV) were synthesized as described in literature[7].

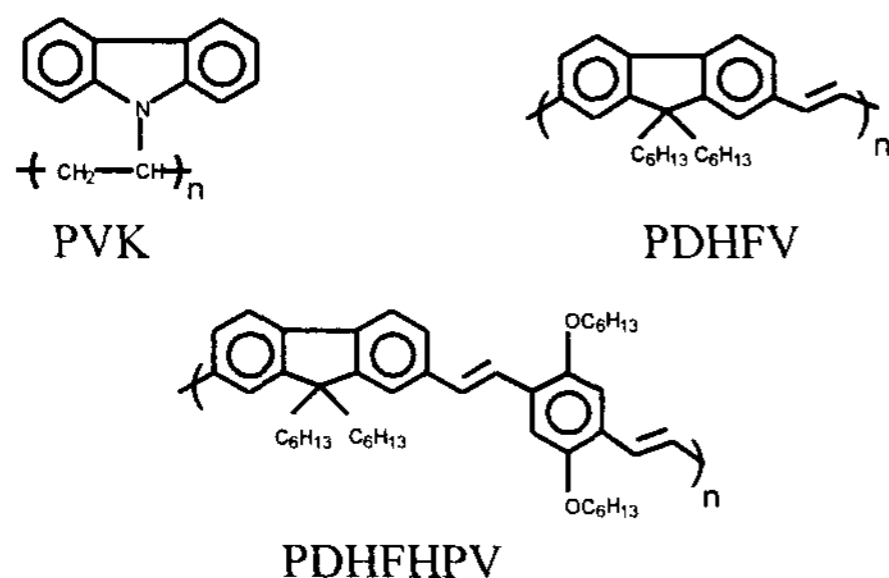


Fig.1. Structures of light emitting polymers

These polymers were soluble in THF. Trichloroethylene was a poor solvent for PVK but a good solvent for PDHFV or PDHFHPV and bilayered specimens were made by spin-casting the acceptor solutions in trichloroethylene on PVK films.

UV-Visible absorption (AB) spectra were recorded with a HP8452A Diode Array Spectrophotometer. The samples were photoexcited by a xenon lamp and PL spectra were recorded with an ISS PL-1 Fluorometer. A time-correlated single-photon counting system (TCSPC) was employed to draw time-correlated decay profiles of the PL emission intensity.

## Results and Discussion

The AB spectra of both PDHFV and PDHFHPV were overlapped substantially with the PL spectrum of PVK as shown in Fig. 2. PVK shows the PL emission maximum at 410 nm on photoexcitation at 340 nm. The AB maxima of PDHFV and PDHFHPV were 420 and 430 nm, respectively. The spectral overlap was perfect for PDHFV and also substantial for PDHFHPV predicting a good Förster-type energy transfer.

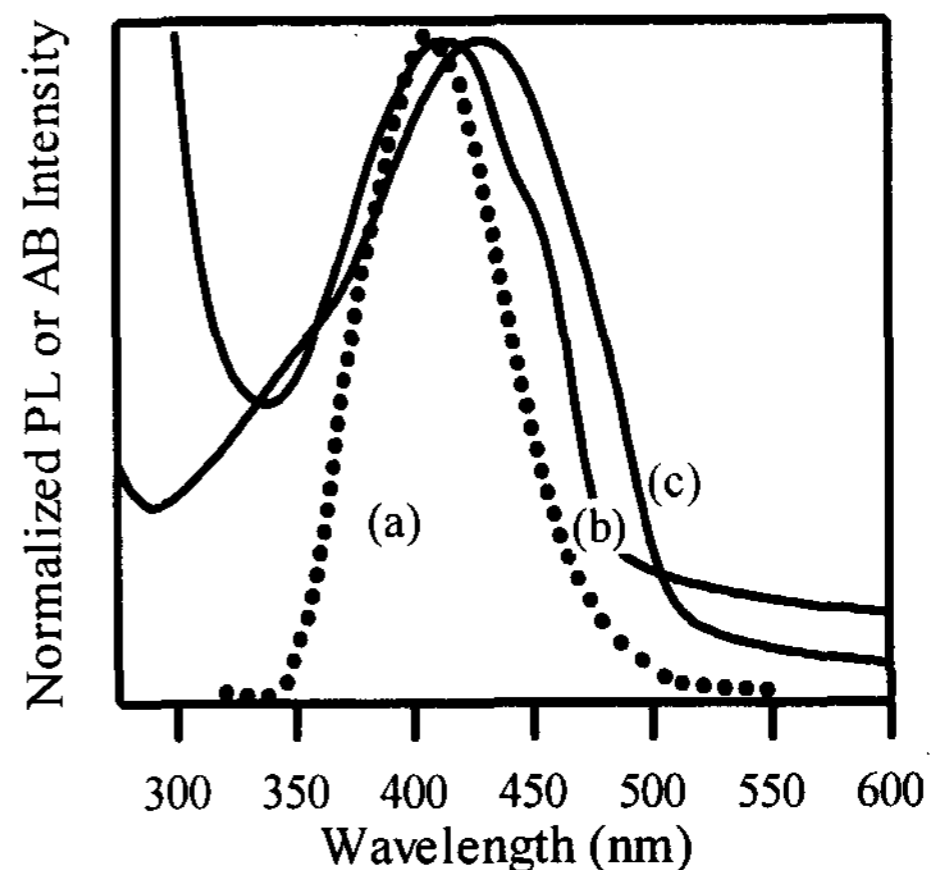


Fig.2. PL emission spectrum of PVK(a), UV-Vis absorption spectrum of PDHFV(b) and PDHFHPV(c)

Fig.3 shows the PL emission spectra of PVK and a bilayered specimen of PVK/PDHFV with the thickness ratio of 1300 nm / 80 nm on photoexcitation at 340 nm, and the PL emission spectra of PDHFV on photoexcitation at 340 and 420 nm. The emission maximum at 410 nm was assigned as the radiative excimer emission of PVK. The PL emission intensity of PDHFV on

photoexcitation either at 340 or 420 nm was weak compared to that of PVK. However, the PL emission spectrum of the bilayered specimen on photoexcitation at 340 nm was identical to that of PDHFV on photoexcitation either at 340 or 420 nm except an intensity enhancement of almost one order. It is apparent that there should be energy transfer from the PVK excitations to the PDHFV fluorophores and the energy transfer was very efficient for the indirect PL emission.

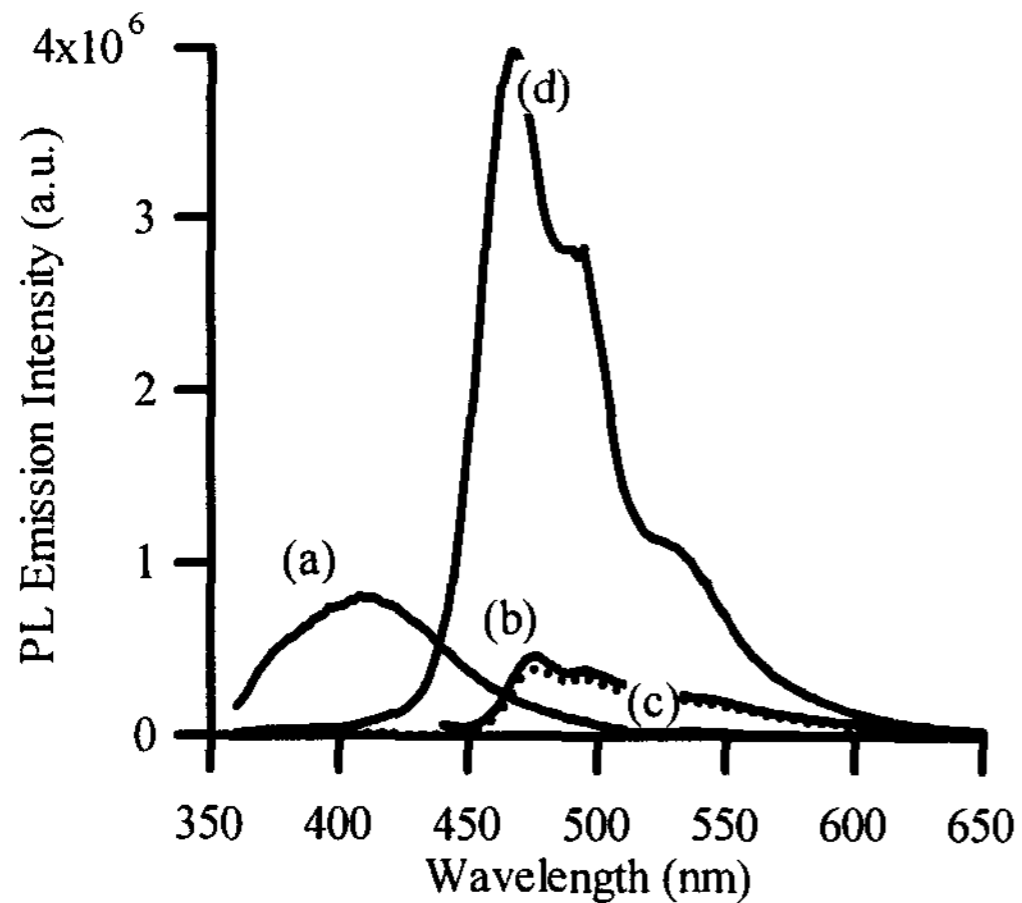


Fig.3. PL emission spectra of PVK(a), PDHFV(b), PDHFV at 420 nm(c), and PVK/PDHFV(d) photoexcited at 340 nm except (c)

A PL work was also carried out for the bilayered specimen of PVK/PDHFHPV as shown in Fig.4. It is observed that the PL emission of PDHFHPV was weak while that of PVK on photoexcitation at 340 nm substantial. It seems that the energy transfer was ineffective compared to that in the PVK/PDHFV specimen, which suggested that the rate constant equation of energy transfer based on the Förster-type mechanism was not ideally applicable to this system.

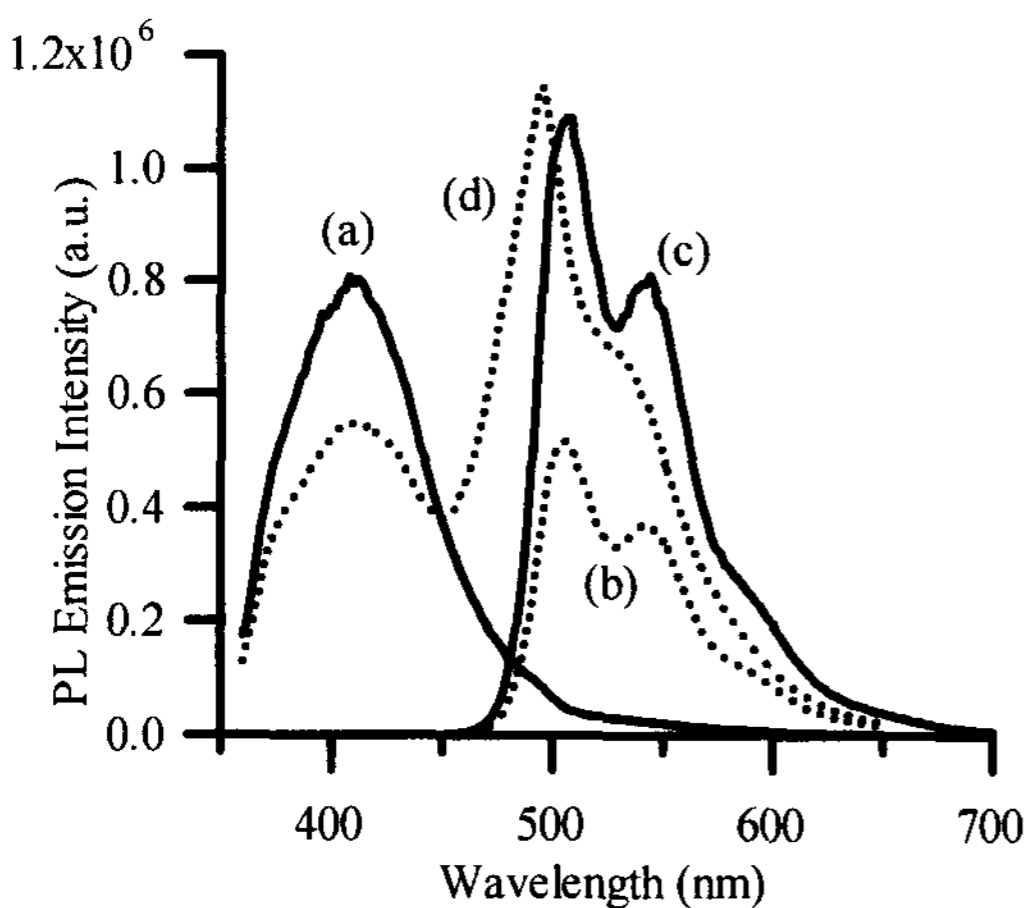


Fig.4. PL emission spectra of PVK(a), PDHFHPV(b), PDHFHPV at 430 nm(c), PVK/PDHFV(d), and PVK-PDHFHPV photoexcited at 340 nm except (c)

The lifetime of a radiative excimer or exciton was deduced by a study with TCSPC as shown in Fig.5. PVK showed the lifetime

of over 11 ns while those of PDHFV and PDHFHPV were 50 and 175 ps, respectively. The energy transfer might be correlated with the lifetime ratio between a donor and an acceptor. The excitations of PVK with a long lifetime transfer effectively the energy to an acceptor with a short lifetime but the transfer is less effective to an acceptor with a long lifetime. The excitations in the lifetime become radiative excimers when the energy is not transferred to acceptors.

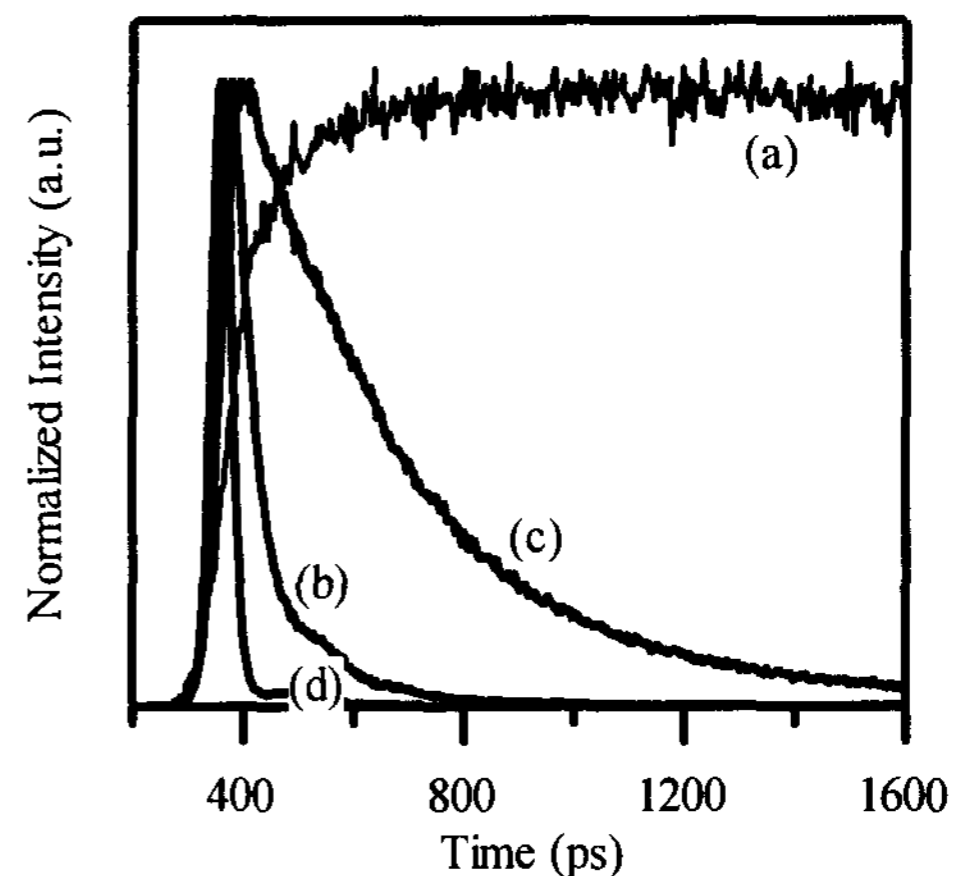


Fig.5. Time-resolved PL emission intensity profiles of PVK at 420 nm (a), PDHFV at 475 nm (b), PDHFHPV at 505 nm (c) and IRF (d)

In summary, efficiency of energy transfer from the excitations in PVK on photoexcitation at 340 nm to an acceptor was dependent less on the spectral overlap between the donor PL emission and the acceptor absorption but more on the lifetime ratio between the donor and the acceptor.

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