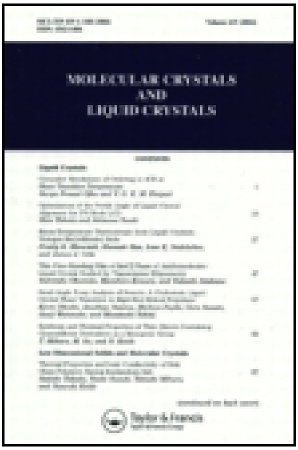

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Investigation of the Charge Complex Formation of Novel Silicon-Based Copolymers Containing Carbazole Unit by Time-Resoved Laser Spectroscopic Technique in the Electronic Excited State

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Abstract SiPhPVK has unusual photophysical characterisitcs that are attributed to the formation of charge transfer complex in the excited state. The photoluminescence (PL) and excitation spectra for SiPhPVK at emission wavelengths of 440 and 520 nm were compared with those for SiHMPVK. Two excitation spectra of SiPhPVK monitored at two probes were observed different obviously. However, the excitation spectra of SiHMPVK obtained at two different probes showed the same spectral feature. In addition, upon photoexcitation with 300 nm, the PL life time of SiPhPVK became longer with increasing the probe wavelength. Expeimental data suggest that the electron transfer can occur from carbarzole to SiPh unit of SiPhPVK to generate the stabilized excited state. However, the PL decay profiles of SiHMPVK exhibited almost same at all probes with photoexcitation of 325 nm. Therefore, the PL emission of SiHMPVK at 325 mainly results from carbazole segments.

Keywords SiPhPVK; time-resoved PL spectra; life time; charge transfer

INTRODUCTION

In recent years, π-conjugated polymers have been extensively studied in science and technology area as light-emitting materials for their variety application to electroluminescence (EL) devices. A large number of light-emitting polymers have been developed in the past few decades. Polymers with aromatic and heterocyclic units absorb light with wavelength in the UV region and emit the energy radiatively as well as nonradiatively returning to the ground state. Light-emission in EL device based π-conjugated polymeric thin layers may arise from singlet excitons resulting from the electron-hole combination within the polymer. The quantum efficiency and lifetime are the important parameters for determining the performance of EL organic materials. There have been many efforts to improve the performance of polymeric light-emitting devices. The spectroscopic tools, such as photoluminescence (PL) spectrometer and time-resolved PL instrument, has been used to investigate the light-emitting behavior of EL polymer. Recently, our group reported the new synthetic method of processable silicon-based copolymers containing carbarzole unit by the Witting and the Heck reactions for blue light-emitting diodes[1]. SiPhPVK has the unusual spectroscopic characteristic which may be attributed to the formation of charge transfer complex in the excited state. The proposed structure in the excited state is shown in Figure 1.

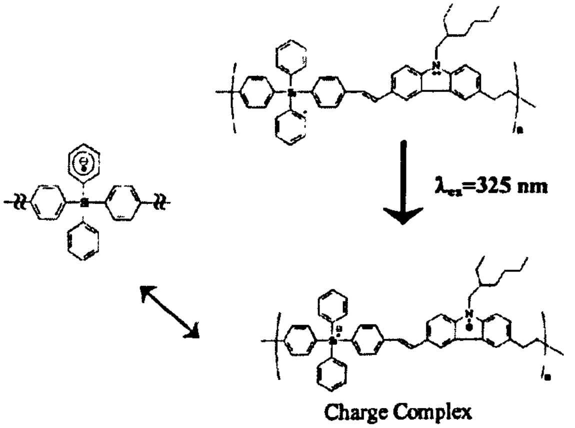


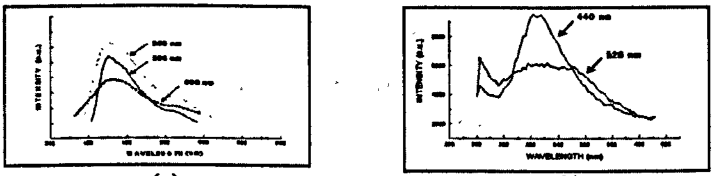
Figure 1. The Proposed Structure of Charge Complex in the Excited State.

We compared the photoluminescence (PL) spectra and life time profiles for SiPhPVK with those for SiHMPVK. We prove that the electron transfer can occur from carbarzole to SiPh unit of SiPhPVK to generate the stabilized excited state.

RESULTS AND DISCUSSION

The PL spectra of SiPhPVK with two photoexcitation wavelength at 300 and 400 nm are shown in Figure 2(a). The excitation wavelengths at 300 nm and

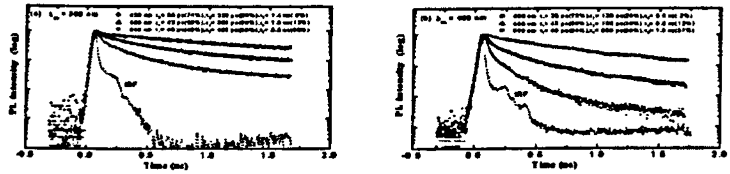
400 nm correspond to selective photoexcitation of carbazole and SiPh units in SiPhPVK, respectively. The PL spectra of SiPhPVK have the two emission bands around 440 nm and 520. The intensity ratio between these two bands at 300 nm is different from that obtained with excitation wavelength at 400 nm. This may be because the origin of these two emission band is different. Figure 2 (b) shows the excitation spectra in the wavelength range from 280 to 420 nm at two probes of 440 and 520 nm. The observed band around 310 nm monitored at 440 nm is almost same as the absorption band at 315. In addition, Two excitation spectral feature of SiPhPVK monitored at two probes was observed different obviously. The emission band (see Figure 2 (a)) around 440 results from the carbazole unit. Because the carbazole unit of SiPhPVK has a bulk and branched alkyl chain which might prevent the excimer formation between carbarzole segments due to the steric hindrance, the emission band around 520 nm is mainly attributed to photoexcitation of a SiPh unit.



(a) (b)

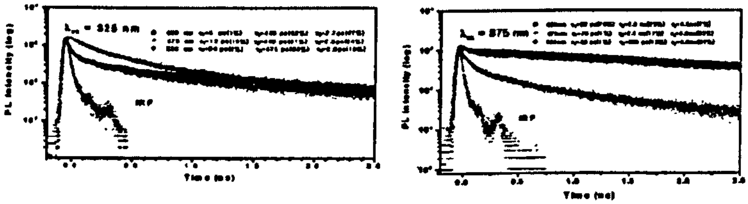
Figure 2. (a) PL spectra of SiPhPVK with three photoexcitation wavelength at 300, 320 and 400 nm; (b)PL excitation spectra of SiPhPVK at two probe of 440 and 520 nm.

However, the PL spectra of SiHMPVK show the same emission maximum band around 430 nm, which is attributed to photoexcitation of carbarzole unit, at three excitation wavelengths. Also the excitation spectra of SiHMPVK obtained at two different probes, unlike SiPhPVK, showed the same spectral feature. The SiPh unit of SiPhPVK has phenyl side chain which can generate the stable resonance sutrure in the excited state (see Figure1).[2,3] Figure 3 shows the PL decay profiles of SiPhPVK with photoexcitation of 300 and 400 nm monitered at three probes of 430, 480,and 550 nm. The PL life time became longer with increasing the probe wavelength. The PL decay time at the probe of 550 nm is relatively long [4] compared with that at the other probes. These results suggest that the unusual long emission lifetime of SiPhPVK at the probe of 550 nm is attributed to the occurrence of the charge transfer from carbarzole to SiPh unit in the excited state. Upon photoexcitation wavelength at 300 nm, the PL decay time of SiPhPVK is longer than that obtained at 400 nm. We propose that the electron transfer process is easy upon photoexcitation of carbazole of SiPhPVK as compared with the photoexcitation of SiPh unit. Figure 4 shows the PL decay profiles of SiHMPVK with photoexcitation at 325 and 375 nm monitored at 430, 470, 520nm. The PL decay profiles showed almost same at all probes with photoexcitation of 325 nm. Experimental data indicate that SiHMPVK can not form the stabilized structure in the excited state because a silicon atom has an alkyl side chain. Upon photoexcitation with high energy (325nm), the PL decay of SiHMPVK is faster than that with lower energy (375 nm) due to the defect site in polymer.[5]



(a) (b)

Figure 3. Transient PL decay profiles for SiPhPVK monitored at 430, 480, and 550 nm with two photoexcitation wavelengths of (a) 300 (b) 400nm



(a) (b)

Figure 4. Transient PL decay profiles for SiHMPVK monitored at 430, 475, and 520 nm with two photoexcitation wavelengths of (a) 325(b) 375 nm.

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