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Photoluminescence Dynamics in Conducting Polymers of Luminescent Disubstituted Polyacetylene and in its Blend with Poorly Luminescent Monosubstituted Polyacetylene

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Luminescence properties of conducting polymers have been much studied in poly(p-phenylenevinylene) (PPV), polythiophene (PT), their derivatives and other conducting polymers with a nondegenerate ground state. On the other hand, luminescence studies of conducting polymers with a degenerate ground state, that is, $trans$-polyacetylene (t-PA) and its derivatives, have rarely been reported. $Trans$-PA have been concluded to be a nonluminescent conducting polymer because of fast relaxation of the photoexcited state into soliton pairs due to strong electron-phonon interactions.[1,2] However, even weak, photoluminescence (PL) in t-PA has been observed in the infrared region and can be explained alternatively in terms of the relative energy level (E) of the lowest excited states: the odd-parity 1^1Bu excited state and the even-parity 2^1Ag excited state.[3,4] Some experimental results such as photoexcitation studies of t-PA and a monosubstituted polyacetylene, poly(1-o-trimethylsilylphenylacetylene) (PPA-oSiMe$_3$), showed that $E(2^1Ag) < E(1^1Bu)$.[5,6] In general, strong PL can be expected when $E(1^1Bu) < E(2^1Ag)$, even in conducting polymers with a degenerate ground state. Several theoretical studies on the electronic structure of linear π-conjugated polyene concluded that the lowest excited state is 2^1Ag because of strong electron correlation.[7,8] On the contrary, if linear π-conjugated chain is assumed to have intermediate electron correlation strength and appropriate large bond alternation, $E(1^1Bu) < E(2^1Ag)$.[9]
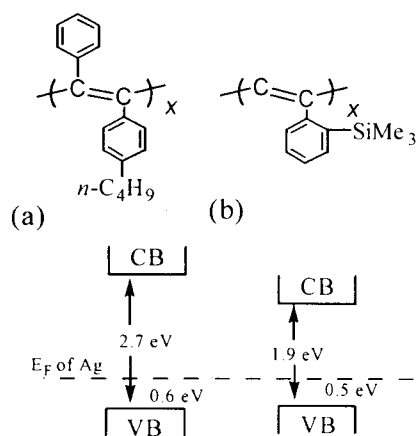

Fig. 1. The molecular structures and electronic band diagrams of PDPA-nBu (a) and PPA-oSiMe$_3$ (b).

It is an important discovery that disubstituted t-PA, that is poly(diphenylacetylene) (PDPA) derivatives and poly(alkylphenylacetylene) (PAPA) exhibit intense PL and can be applied for electroluminescence (EL) device.[10,11,12] In this paper, we report the PL dynamics obtained by performing the time-resolved PL spectroscopy for studying the exciton dynamics in these disubstituted polyacetylenes. The measurements were carried out using a femtosecond laser system consisting of a Ti:Saphire mode-locked laser (Tsunami, Spectra Physics) pumped by a cw-diode laser (Millenia, Spectra Physics), a second harmonic generator unit (Spectra

Physics) and a streak scope camera (Streak Scope C4334, Hamamatsu). The laser beam wavelength is 400 nm. As a representative polymer, PDPA-nBu that has a band gap of about 2.7 eV and PL peak at 2.3 eV (green PL) was used. For further study, polymer blends of PDPA-nBu and poorly luminescent PPA-oSiMe$_3$ was also studied because the steady-state PL of PDPA-nBu is significantly quenched when mixed with even a small amount of PPA-oSiMe$_3$. Figures 1.(a) and 1.(b) show the molecular structures and electronic band diagrams of PDPA-nBu (a) and PPA- oSiMe$_3$ (b).

The time-resolved PL spectra of a pure PDPA-nBu film observed at different time between 0 ns and 3 ns after photoexcitation are shown in Fig. 2.(a). A dynamic Stokes shift can be seen in these spectra, that is, the spectra are largely redshifted by about 20 nm (or about 0.1 eV in photon energy) in less than 1 ns after photoexcitation, but the Stokes shift becomes much smaller at longer than 1 ns. Figure 2.(b) shows the PL decay observed at three different PL wavelengths of 475, 550 and 625 nm within a time window of 5 ns. The duration of the excitation laser pulse of about 100 fs is considerably short compared to the time window of observation, therefore, the observed decay curve can be identified as PL decay without convolution of the laser pulse. The PL decay at 625 nm can be well approximated by a single exponential decay function : $I(t) \propto exp(-t/\tau)$, where $I(t)$ is the PL intensity at time t, and τ is the lifetime constant which is evaluated to be about 2.7 ns. In contrast, the PL decay at shorter wavelengths is fast following a suppressed exponential decay function. PL decay at 475 and 550 nm shows fast decay within 0.5 ns after photoexcitation but relatively slower decay at longer time. In the case of PL decay at 550 nm, PL decay as slow as that at 625 nm ($\tau \approx 2.7$ ns) at time longer than 0.5 ns. However, τ of slow PL decay at 475 nm is shorter (about 1.2 ns).

These PL dynamics of PDPA-nBu can be explained in terms of exciton migration from short conjugation segment to the longer one, resulting in a fast suppressed-exponential PL decay at short wavelengths, but a slow single-exponential decay at longer wavelengths because the excitons in a long conjugation segments cannot be transferred further. That is, fast decay of excitons in the short segments should be determined by competing process between radiative
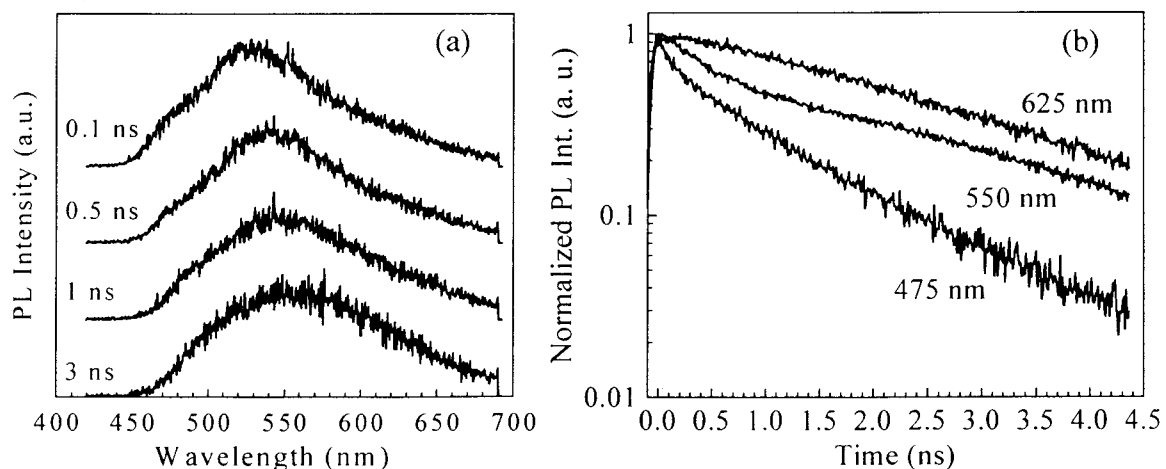

Fig. 2　The time-resolved PL spectra of a PDPA-nBu film observed at different time, that is, 0.1, 0.5, 1 and 3 ns after photoexcitation. (a) The PL decay observed at different PL wavelengths of 475, 550 and 625 nm. (b)

recombination and exciton migration to long conjugation segments. In general, the exciton migration may occur by exciton hopping from one segment to another segment, or through non-excitonic processes such as long range dipole-dipole interactions (Förster type of excitation energy transfer) or electron exchange interactions (Dexter mechanism).

A small bump at short wavelengths (around 475 nm) in the PL spectrum observed within 0.5 ns after photoexcitation may be attributed to PL originated in the short conjugation segments that exist due to an inhomogeneous distribution of polymer chains with different conjugation lengths. This PL decays faster than PL at longer wavelengths because at short time after photoexcitation the excitons have not to diffuse as far to reach recombination centers.[13] However, at longer time, the survival excitons in the short segments may also relax to lower energy through migration to longer conjugation segments.

Figure 3.(a) shows the significant quenching of steady-state PL intensity of the PDPA-nBu/PPA-oSiMe$_3$ blend films with increasing of molar ratios of PPA-oSiMe$_3$. Figure 3.(b) shows PL decay of the blend films with various molar ratios of PPA-oSiMe$_3$ observed at PL wavelengths of 625 nm. These blend films also show the dependence of PL decay on wavelength as observed in pure-PDPA-nBu. Moreover, their PL spectra (not shown) resemble with that of PDPA-nBu, indicating that PL only originates from PDPA-nBu without any contribution from PPA-oSiMe$_3$. For all molar ratios of these polymer blends, the PL decay at the wavelength of 625 nm can be approximated by a single-exponential decay function. The PL decay indicates that the PL lifetime is drastically shortened by mixing PPA-oSiMe$_3$ into PDPA-nBu. These results suggest exciton migration from PDPA-nBu with a large band gap to PPA-oSiMe$_3$ with a small band gap (Fig. 1.(b)), which may occur through Förster excitation energy transfer. The spectral overlap between PL spectrum of a donor molecule (PDPA-nBu) and absorption spectrum of an acceptor (PPA-oSiMe$_3$) molecule required for Förster energy transfer is fulfilled. This process may lead PPA-oSiMe$_3$ into either 1^1Bu excited state through dipole-dipole resonance or 2^1Ag excited state though dipole-quadrapole resonance. In both
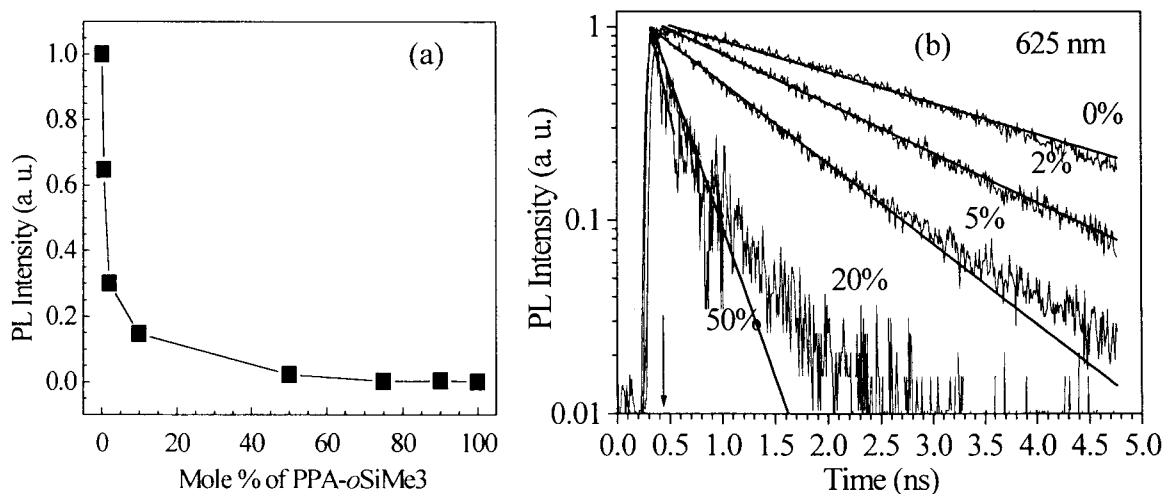

Fig. 3 The normalized peak intensity of steady-state PL of PDPA-nBu/PPA-oSiMe$_3$ blend as function of molar ratio of PPA-oSiMe$_3$. (a) The dependence of PL decay of the polymer blend on the molar ratio of PPA-oSiMe$_3$ observed at wavelength of 625 nm. (b)

cases, the excited PPA-oSiMe$_3$ may relax nonradiatively to the ground state because its 2^1Ag excited state lies below the 1^1Bu excited state in energy. It is also possible that the 2^1Ag excited state relaxes into soliton pairs accompanying by phonon emission in a very short time of a few picoseconds.[14]

In conclusions, PL dynamics related to the dynamics of exciton in disubstituted t-PA, PDPA-nBu, have been observed by the time resolved PL spectroscopy. Excitons in short conjugation segments decay non-single exponentially with shorter PL lifetime than those in long conjugation segments because of competing process between radiative recombination and excitons migration to longer conjugation segments. PL decay at long wavelengths, which is originated from excitons in long conjugation segments, decay exponentially with long lifetime larger than 2 ns. This shows efficient radiative recombination of excitons in this polymer. However, the significant quenching of PL intensity and decreasing of PL lifetime of PDPA-nBu upon mixing of PDPA-nBu with PPA-oSiMe$_3$ show that the excitons in PDPA-nBu easily migrate to other polymer chain with a smaller bandgap (PPA-oSiMe$_3$) surrounding them, which may occurs through Förster mechanism or charge transfers mechanism.

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