Light Emitting Properties of Linear π-Conjugated Poly(arylene)s

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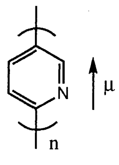
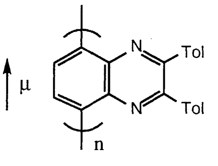
Dichroism of photoluminescence PL of linear poly(2,3-di-*p*-tolylquinoxaline-5,8-diyl) indicates that the PL has a transition moment along the direction of the polymer main chain and an energy transfer takes place in the polymer. Poly(phenanthroline-3,8-diyl) and poly(pyridine-2,5-diyl) give analogous results and show a strong tendency to give excimer-type emission in both PL and electroluminescence.

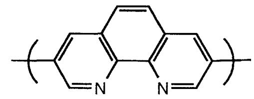
Optical properties of π-conjugated poly(arylene)s are the subject of recent many papers.[1] The π-conjugated poly(arylene)s are considered to have π-π^* absorption and photoluminescence PL bands with their transition moments along the linear main chain. The lowest energy π-π^* absorption bands of poly(pyridine-2,5-diyl) PPy[2] and poly(2,3-di-*p*-tolylquinoxaline-5,8-diyl)PQx-(diTol)[3] actually have the transition moment μ along the polymer chain as revealed by their dichroism in a stretched poly(vinyl alcohol) PVA film.[2,3] However, the direction of the transition moment of PL has received much less attention.



PPy



PQx(diTol)



PPhen

Excimer-type PL caused by a strong interaction of the photo-excited linear polymer molecule with neighboring polymer molecule(s) is the subject of another recent interest.[2,4] This paper reports determination of the transition moment of PL of three polymers shown above, energy transfer occurred in the PL process, and excimer-type emission from the polymers.

It has previously been reported that a PVA-PQx(diTol) film shows two π-π^* absorption bands Band A and Band B, at 380 and 420 nm, respectively (Figure 1).[3] Dichroism of the two bands observed with a stretched PVA-PQx(diTol) film indicates that Band B has its transition moment μ along the polymer main chain, whereas Band A is associated with π-π^* transition occurred in the recurring single di-*p*-tolylquinoxaline monomer unit.[3]

Irradiation of the PVA-PQx(diTol) film with light at 420 nm gives PL with a peak position at 492 nm, which agrees the onset position of Band B (curve b in Figure 1), indicating that this PL takes place by electron transfer between electronic states concerned with Band B. Irradiation with light at 380 nm gives essentially the same PL spectrum centered at 492 nm, suggesting that the photoenergy captured by the monomer unit is transferred to the π-conjugation system along the polymer chain. Band A is considered to have a transition moment perpendicular to the polymer chain based on AM-1 Hamiltonian calculation,[5] and the energy absorbed at Band A seems to be transferred to the main chain π-conjugation system.

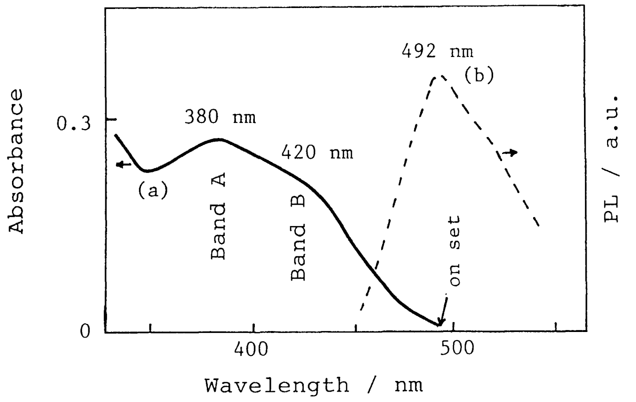
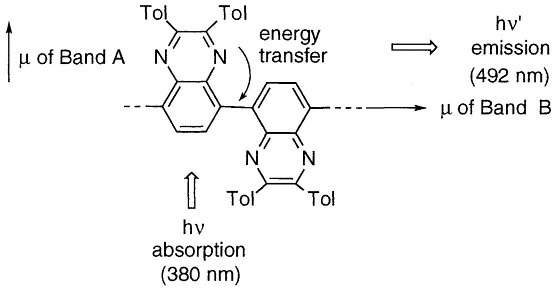


Figure 1. (a) UV-visible (–) and (b) PL (---) spectra of PVA-PQx(diTol) film



The following dichroic data of PL, (i) and (ii), obtained with the stretched PVA-PQx(diTol) film confirm this situation and the assignment.

(i) Irradiation of the film with non-polarized light at 380 nm (Band A) causes emission of light polarized along the direction of the stretching of the film. A dichroic ratio Rd[6] for the 492 nm PL is 4.2 at a stretching ratio Rs[2,3] of 7.3. When 420 nm (Band B) light polarized along the direction of the stretching is irradiated at a // mode,[7] // polarized 492 nm light (Rd = 9.5 at Rs = 7.3) is emitted.

(ii) Irradiation of polarized light at a ⊥ mode[7] and monitoring the PL at the // mode give excitation spectra depicted in Figure 2.

The results shown in Figure 2 indicate that when the stretching ratio Rs is large (Rs = 7.3; curve b) light absorbed at Band A mainly contributes to the // mode PL and Band B gives negligible contribution to the PL. Figure 3 shows this situation, and thus the stretched PVA-PQx(diTol) film serves as a unique polarizer which causes rotation of the electric field of light by 90 °. Monitoring the PL light at other various modes give data consistent with the above results.

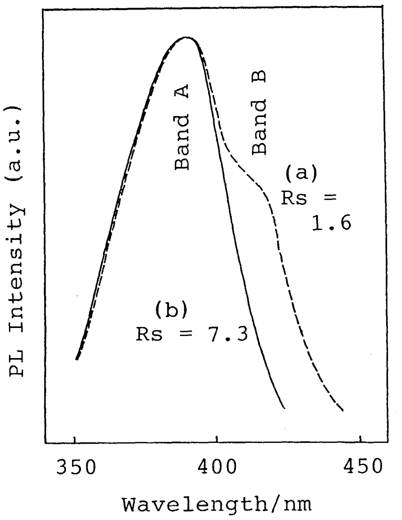


Figure 2. Excitation spectra of the PVA-PQx(diTol) film at (a) Rs = 1.6 (---) and (b) Rs = 7.3 (–)

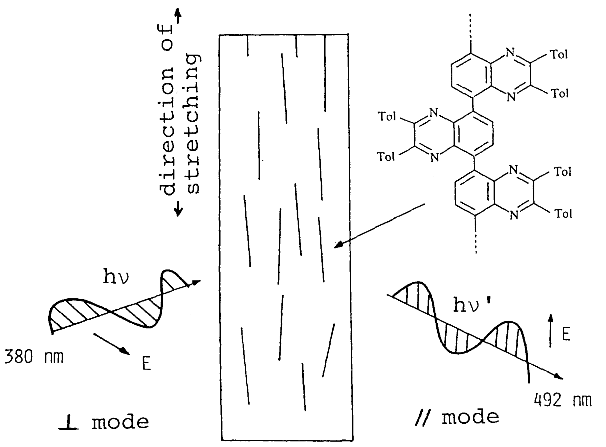


Figure 3. PVA-PQx(diTol) film to rotate the 380 nm ⊥ mode light to the 492 nm // mode light.

Use of a stretched PVA-PPhen film gives analogous results. However, in this case, PPhen gives excimer-type emission (λmax = ca. 500 nm), which was observed in neat film of PPhen,[8] even in the PVA film containing PPhen not in a high concentration. A linear and simpler structure of PPhen makes the formation of the excimer-type adduct possible. PL data of the stretched PVA-PPhen film reveal that the excimer-type emission also has transition moment along the polymer chain.

PPhen has π-π^* absorption bands at about 290 nm (Band A') and 385 nm (Band B'), and both the 290 nm light and 385 nm light cause the excimer-type emission at about 500 nm. PL data indicate that the π-π^* absorptions at Band A' and Band B' have transition moments perpendicular and parallel to the polymer main chain, respectively, and the energy absorbed at Band A' is transferred to Band B' to give the excimer-type emission.

A PVA-PPy film also shows excimer-type emission at about 520 nm,[2] and irradiation of non-polarized light to the film give a polarized excimer-type PL with a Rd value of 4.3 at Rs of 9.3, indicating that the excimer-type PL of PPy also has the transition moment along the direction of the polymer chain.

The stronger tendency of PPhen and PPy to form the excimer-type adduct than that of P(5,8-Qx(diTol)), due to their simpler structure, is also observed in electroluminescence EL. An ITO/PPy (30 nm)/Mg(Ag) junction[9] (ITO = indium-tin-oxide glass) and an analogous junction using PPhen[9], at about 10 V, give EL spectra which show peaks at 510 nm and 540 nm, respectively, corresponding to the excimer-type emission. On the other hand, a similar junction using PQx derivatives gives an EL spectrum corresponding to unimolecular emission.[10] These results indicate that PPy and PPhen with the linear and simple structure form the excimer-type adduct even when excited electrically.

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References and Notes

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6 Rd: (intensity of PL light at // mode[7])/(that at ⊥ mode[7]).
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