Excimer-like Emission from Linear π-Conjugated Poly(pyridine-2,5-diyl)

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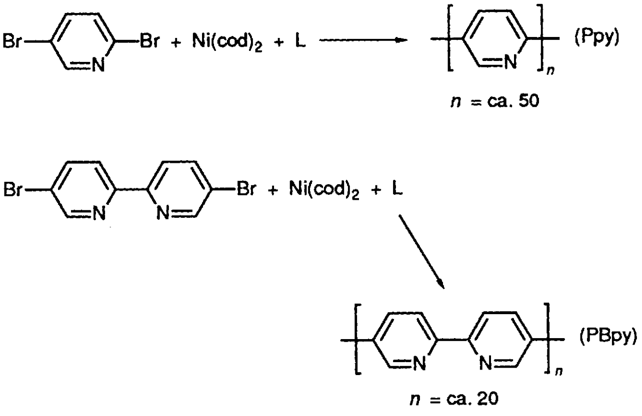
π-Conjugated poly(pyridine-2,5-diyl) and poly(2,2′-bipyridine-5,5′-diyl) give rise to fluorescence in formic acid solutions, in the solid state (film), and in an adduct with poly(vinyl alcohol); the fluorescence in the solid state, in the adduct with poly(vinyl alcohol), and in the formic acid solution with relatively high concentration of the polymer is interpreted by assuming excimer formation.

C–C coupling of 2,5-dibromopyridine and 5,5′-dibromo-2,2′-bipyridine with zerovalent nickel complexes, typically a mixture of bis(cyclo-octa-1,5-diene)nickel[$Ni(cod)_2$] and a neutral ligand L, affords the corresponding electrically conducting π-conjugated polymers, poly(pyridine-2,5-diyl) (Ppy) and poly(2,2′-bipyridine-5,5′-diyl)(PBpy) (Scheme 1).[1–3]

The polymers are soluble in formic acid and adopt a rod-like rigid linear structure both in formic acid solution[1,3] and in the surface region of a poly(vinyl alcohol) (PVA) film,[4] as judged from their large degree of depolarization in formic acid and the applicability of the stretched poly(vinyl alcohol)–Ppy adduct film as an excellent polarizer. Owing to their rod-like linear π-conjugated structure, Ppy and PBpy would be expected to form an excimer when irradiated with light. Although electrically conducting properties of π-conjugated poly(arylene)s have attracted much attention, and the excimer emission from non-conjugated aromatic polymers such as poly(2-vinylpyridine) has been reported,[5] the fluorescence properties of π-conjugated poly(arylene)s have attracted much less attention.



Scheme 1

We now report fluorescence from Ppy and PBpy, which shows the π–π* absorption bands listed in Table 1. Powdery Ppy and PBpy showed a strong green fluorescence when irradiated by UV light (365 and 253.7 nm). Figure 1 shows the fluorescence spectra of Ppy in dilute (2.0×10^{-6} mol of monomer unit dm^{-3}) formic acid solution, in a higher concentration (0.5 mol of monomer unit dm^{-3}) of formic acid solution, and as a film on a quartz plate, prepared by spreading a formic acid solution of Ppy on the quartz plate and removal of formic acid *in vacuo*. Steady-state (Figure 1) and time-resolved fluorescence measurements on Ppy showed the following characteristics of the fluorescence. A picosecond time-correlated single-photon counting system was used for the time-resolved measurements, details of which have already been reported.[6]

Table 1. π–π* Absorption band ($\lambda_{max.}$/nm) of Ppy and PBpy.

Polymer	In HCO_2H	In PVA film	Film on quartz plate
Ppy	373	390	390
PBpy	373	380	350

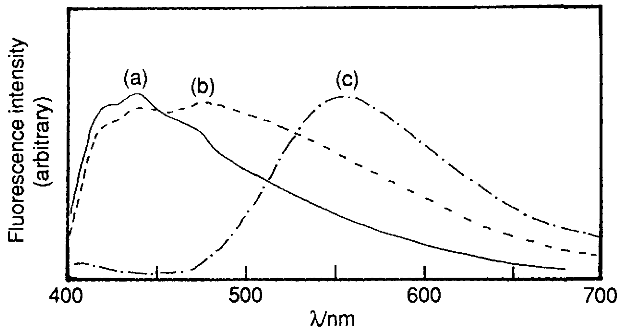


Figure 1. Steady-state fluorescence spectra of Ppy; (a) in HCO_2H (2.0 × 10^{-6} mol of monomer unit dm^{-3}), (b) in HCO_2H (0.5 mol of monomer unit dm^{-3}), (c) film on quartz plate. Excited at 380 nm.

The dilute solution (2 × 10^{-6} mol dm^{-3}) gives rise to a fluorescence with a maximum at 440 nm [(a) in Figure 1]. The energy difference between the absorption and fluorescence is 2900 cm^{-1}. When the concentration is increased to 0.5 mol dm^{-3} [(b) in Figure 1], the fluorescence spectrum shows a contribution from fluorescence at longer wavelength (presumably centred at 550 nm). Further increase in the concentration of Ppy was not possible owing to its relatively low solubility. The fluorescence lifetime measurement reveals that the fluorescence decay of the dilute Ppy solution (2 × 10^{-6} mol dm^{-3}) is composed mainly of two components with lifetimes of 60 and 250 ps when monitored at 440 nm. At the higher concentration (0.5 mol dm^{-3}), the fluorescence decay was triplet-exponential with lifetimes of <10, 90, and 300 ps when monitored at 440 nm. Furthermore, the fluorescence decay observed at longer wavelength (570 nm) gives a rise component with a lifetime of <10 ps as well as decay components with lifetimes of 90 and 350 ps. Agreement in the lifetimes between the fast-decaying component at 440 nm and the rise component at 570 nm and between the slow components at both wavelengths strongly suggests the formation of an excimer. In the film, we observed no rise component in the longer wavelength region, suggesting that the excimer is directly formed from a pair-like configuration of the ground-state chromophores. When Ppy forms a film, it gives rise to the fluorescence at longer wavelength with a peak at 550 nm [(c) in Figure 1]. PBpy film also shows a similar fluorescence with a peak at 535 nm. Ppy in the surface region of a PVA film affords a fluorescence spectrum similar to (c) in Figure 1 with a peak at 530 nm.

These data (especially the appearance of fluorescence in the longer wavelength region at higher concentrations of Ppy, observation of the rise component in the fluorescence lifetime measurements at higher concentrations of Ppy, and entirely different fluorescence spectra for the dilute solution and film) suggest the formation of an excimer at the higher concentration and in the film, and imply formation of an ordered and aggregate structure in the film and in the surface region of PVA. If the fluorescence at 550 nm (film) and 540 nm (in the PVA film) is assigned to an excimer emission, the energy difference between the monomer and excimer emission is about 4500 cm^{-1}, which is comparable to the value (4000—6000^{-1}) reported for monomer and dimer emission of poly(2-vinylpyridine).[5]

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