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Multicolor Emission in Poly(4-vinyl-pyridine) Gel

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The photoluminescence (PL) of organic polymers was shown recently to be morphology-dependent.[1−5] The PL of pyridine-containing polymers, poly(*p*-pyridine) and poly(*p*-pyridil-vinylene), was redshifted in thin film compared to that in solution.[3] The most likely explanation of the dependence of optical properties on the morphology is an interchain interaction.[6] An interchain interaction leads to the formation of extended photoexcited species that are delocalized over more than one polymeric chain. The energy band gap decreases with changes in the optical properties.[1] Interest in a better understanding of polymer photophysics was particularly stimulated by the discovery of organic light-emitting devices with multicolor PL from the same device.[1,3] Novel light-emitting devices have been fabricated based on bipyridine-containing poly(*p*-phenylene-vinylene) derivatives where emission tunability was achieved by controlling interchain interaction by exposure to acid/base vapor.[5] Reversible and tunable optical properties of thin films of that material were found to depend on protonation−deprotonation processes.

The PL tunability of side-chain polymers has been less extensively studied than those of conjugated polymers.[7] Control over the emission color in light-emitting devices containing side-chain polymers was demonstrated by the induction of excimer emission.[7]

We report here the observation of PL tunability in the gel: poly(4-vinyl-pyridine)/pyridine. The initial solution of poly(4-vinyl-pyridine) (P4VPy) in pyridine (Py) has a single band emission at 440 nm. When kept for 3 weeks in the dark, the solution spontaneously turns into a gel. The gel has different PL properties than those of the solution. Blue (at 470 nm), green (at 527 nm), and red (at 598 nm) emissions radiate by excitation of the appropriate wavelengths from the same sample. An FTIR study indicates that hydrogen bonds are responsible for the gel formation. At least two kinds of hydrogen bonds maintain the gel structure. Different kinds of interchain interactions lead to the formation of different emitting centers. The inherent properties of the nonconductive saturated polymer backbone manifest themselves as restricted energy-transfers between emitting centers; thus blue, green, and red PL are observed independently.

Only a deep blue emission (the experimental details are given below)[8] with a maximum at 440 nm is observed for the initial solution of P4VPy in Py. The excitation spectrum has mirror symmetry to the emission spectrum with a peak at 377 nm. Stokes losses for the PL of the solution have been found to be 0.47 eV, and the characteristic emission bands have full widths at half-maxima (fwhm) of 0.43 eV. After spontaneous gelation, three different color PLs appeared in the gel by irradiation of the appropriate excitation wavelength (Figure 1). Excitation by a wavelength of 385 nm produces a blue PL with maximal intensity at 470 nm. Under an excitation wavelength of 464 nm, green PL appears at 527 nm. Excitation with 557 nm produces red PL with a peak at 598 nm. The emission quantum yields were determined to be 0.11, 0.06, and 0.08 for blue, green, and red PL, respectively. Stokes losses are 0.58, 0.32, and 0.16 eV, and the fwhm values are 0.54, 0.49, and 0.40 eV for blue, green, and red emissions, respectively.

The excitation spectrum of blue PL consists of a single band ($\lambda = 385$ nm). The excitation spectra of green and red emissions have a resolved band structure (see Figure 1). It is important to note that although the excitation spectra of blue PL has a single band probability distribution form, its fwhm is larger than that of similar values for green and red PL. This means that in the gel a set of blue emitting centers exist with a ground state energy level distribution wider than that of the green and particularly the red ones. Stokes losses for blue PL (0.58 eV) indicate that the nonradiative decay of the blue emitting center requires more energy than those of the green and the red ones.

This is also reflected in lifetime measurements where blue, green, and red PLs have a multiexponential decay. The emission lifetimes of the main components (with higher population) were 10, 4, and 2 ns for blue, green, and red PLs, respectively. On comparing the lifetime data with the excitation spectra, we can conclude that the green and red emitting centers also participate in the blue PL (Figure 1) with a different probability. Blue emitting centers are partially involved in green PL and

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(8) For the gel preparation, dried P4VPy (Polyscience) of low molecular weight (50.000) was dissolved in anhydrous pyridine in a 1:1 molar ratio. Emission and excitation spectra were recorded on a Shimadzu RF-5301PC spectrofluorimeter. The data were collected at right angles to the excitation beam. Absorption spectra were taken from the same samples on a Shimadzu UV-3101PC scanning spectrophotometer. The emission lifetime was obtained by phase-modulation measurements carried out with an ISS K-2 unit. The PL quantum yield was evaluated by comparing the total emitted light to a total emitted light of standard quinine-sulfate solution: Velapoldi, R. A.; Mielenz, K. D. *Standard Reference Materials: A Fluorescence Standard Reference Material: Quinine Sulfate Dihydrate*; U.S. Department of Commerce, National Bureau of Standards, 1980. FTIR spectra were recorded in the CaF_2 cell (0.01 mm) by means of a Bruker IFS-113v spectrometer. The polymer film for FTIR measurement was prepared by heating the powder at 250 °C between CaF_2 plates.

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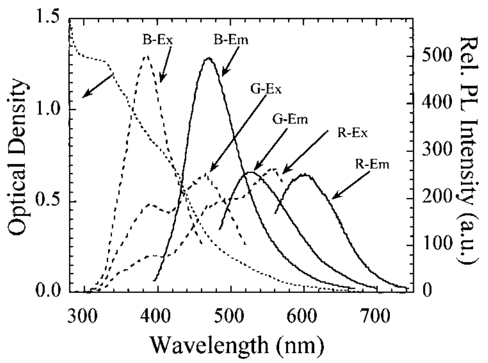

Figure 1. Gel spectra: edge absorption and blue (B), green (G), and red (R) PL excitation (Ex) and emission (Em). The gel is produced by spontaneous self-organization of poly(4-vinyl-pyridine) dissolved in pyridine in molar ratio 1:1.

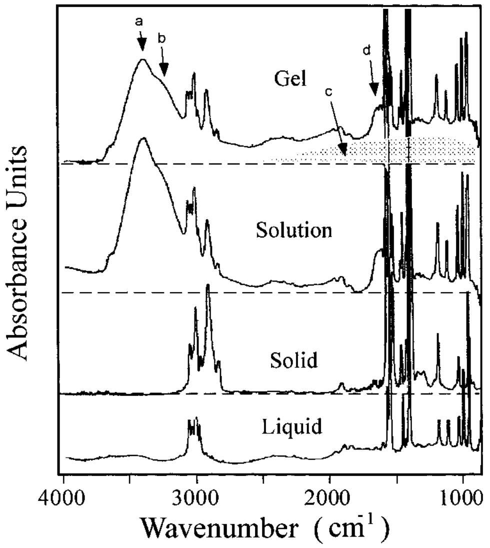

Figure 2. FTIR spectra of liquid pyridine (liquid), thin film of poly(4-vinylpyridine) (solid), 50 wt % solution of P4VPy in pyridine (solution), and gel (gel).

practically not at all in red PL. The range of the lifetime, 10−2 ns, suggests a direct transition from the singlet excited state, with no triplet state or excimer formation. The absorption spectrum of the gel (Figure 1, right graph) shows a prolonged tail into the visible range up to 600 nm. Taking into account all of the spectroscopic data, we can conclude that three kinds of emitting centers coexist in the gel.

The gel structure was investigated by FTIR. The FTIR spectra of liquid pyridine, solid P4VPy film, a solution of P4VPy/Py, and the gel are represented in Figure 2. A wide absorption band appears at 3400 cm^{-1} (trace a in Figure 2) in the P4VPy solution spectrum, but no such band was observed in liquid Py and solid P4VPy. During the process of gelation, this band intensity apparently decreases and simultaneously a very wide absorption appears centered around 1700 cm^{-1} (c in Figure 2). The band at 3400 cm^{-1} may be assigned to the proton stretching vibration of the N^+−H bond of pyridinium ion (Py^+H) in solution and the gel (the band of a neutral NH group H-bonded to Py is positioned at 3150 cm^{-1}).[9]

The low-frequency shoulder at 3300 cm^{-1} (b in Figure 2) can presumably be accounted for by the overtone of the N^+−H deformational mode at 1670 cm^{-1} (d in Figure 2) intensified by Fermi resonance interaction with the stretching mode. The weak wide absorbance at 1670 cm^{-1} includes pyridinium skeletal bands[10] at 1640 cm^{-1}. A new band of unknown assignment with a width of 5.8 cm^{-1} appears at 1587.8 cm^{-1}, which definitely does not belong to liquid Py or P4VPy. The band intensity at 3400 cm^{-1} increased with an increase in the polymer concentration in solution. This indicates that protonation takes place at pyridinic side groups of the polymer. The source of protons is supposedly the polymer's methyne groups: they are the most acidic protons in the system due to π-conjugation of the C to the pyridinic electron-withdrawing nitrogen atom. Such a self-protonation process is initiated by the formation of an H bond with a liquid pyridine molecule. Proton shuttling from the methyne unit to the P4VPy pyridinic nitrogen can be either assisted by the pyridine molecule or is simultaneous within two side chains. It should be noted that this band at 3400 cm^{-1} is present in the spectrum of a dried gel.

Evidence for the formation of free H^+ ions under 385 nm irradiation is found from the photoinduced pH change measurements. Under steady state photoexcitation at 385 nm, the gel basicity decreased from a pH of 9.1 to 8.4. Turning the light source off leads to the restoration of the initial value of 9.1. This process is fully reversible and can be repeated for many cycles.

The self-protonation of P4VPy is followed by the formation of a complex hydrogen-bonded network structure. The wide absorbance below 1700 cm^{-1} (c in Figure 2) can be modeled by the formation of quasisymmetrical H bonds (Py···H···Py) that are quite strong (~50 kJ/mol), as is well-known for pyridine.[9] Association of two pyridinium ions (P4VPy or Py) may lead to the liberation of free H^+ ions, which can then be accepted by free pyridine molecules. The strong symmetrical H bonds (head-to-head) and their head-to-tail associates might be responsible for the formation of the polymeric network during the gelation process. The formation of these new assemblies in the gel is probably related to the edge absorption in the visible range (Figure 1).

A detailed study of the emitting center nature will be given in a forthcoming publication. Here, we will make a tentative suggestion as to the mechanism behind the described process. Pierola et al.[11] have reported that the fluorescence of poly(2-vinyl-pyridine) is pH-dependent. Apparently, in the gel, different kinds of hydrogen bonds, which are responsible for gel formation, have resulted in an arrangement of new emitting centers. Most probably, the blue emitting centers are the protonated form of pyridine side-chain units, whereas green emitting centers reflect interchain interaction through the quasisymmetrical hydrogen bonds, and the red emitting centers reflect interchain interaction through the protonated pyridinium ion.

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