

Concentration Dependence of the Photoluminescence Energy and Anisotropy from Dye Molecules and Dye Molecule - Zeolite Composites

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We analyzed the photoluminescence (PL) peak shift and the anisotropy of dye molecules and dye molecule - zeolite composites as function of the concentration of pyronine B (PyB) molecules. We used PyB dye molecules and zeolite *L*. The PL of PyB molecules was red-shifted with increasing concentration of PyB molecules. However the PL of PyB incorporated zeolite composite was independent of the concentration. The PL intensity anisotropy value also increased with increasing concentration in these composites. The anisotropy of zeolite - dye composites was about 2.8 at high concentration; which is close to the theoretical anisotropy value of 3. Since the host zeolite protects dye molecules from aggregation, these results are different from the case of dye molecules in a solvent. In addition, we observed the confinement effect of dye molecule - zeolite composites from the blue shift of the PL spectrum.

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I. INTRODUCTION

Nanoporous materials have been studied by many researchers due to their interesting properties and various applications in electrical transport, micro lasers, non-linear optics, optical switches, *etc.* [1-7] Zeolite is a 3-dimensional nanoporous material that has been used as a catalyst, a ion exchanger, and even detergent. Today, zeolite is synthesized in the laboratory with various structures, and organic or inorganic molecules can be inserted into the pores [3,8,9].

Energy transfer is a well - known property and has been studied by many research groups for applications of luminescent materials, solar energy transfer, *etc.* [1,9, 10]. Dye molecules tend to aggregate at high concentrations. Due to this aggregation, energy transfer between dye molecules leads to changes in the electronic structure of the dye molecules, which in turn causes changes in the optical properties [11,12].

In this paper, we report our effort to control the energy transfer using zeolite, and we observe the changes in the optical properties as a function of the concentration. The anisotropy change of dye molecules in solvents has not been reported whereas there have been some reports on the change of fluorescence properties [13-16]. Aggre-

gation can be prevented by locking the dye molecules inside the pores of a zeolite crystal [11]. We focused on pyronine B (PyB) molecules and zeolite *L* as guest and host materials, respectively. A zeolite *L* crystal has a cylindrical shape and contains long channels with a pore opening of 7.1 Å, which is a large enough size to insert PyB molecules. Figure 1 shows a simple illustration and SEM image of PyB incorporated in zeolite *L*. The average length of the zeolite *L* crystal is about 2.5 μm, and the diameter is about 1 μm.

II. EXPERIMENT

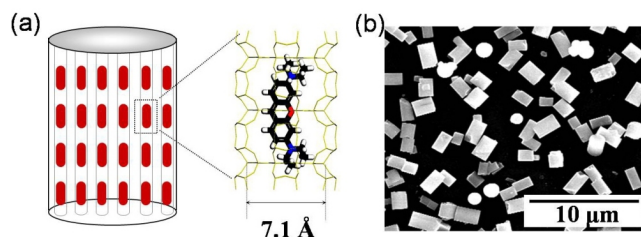


Fig. 1. (a) PyB incorporated in a zeolite *L* crystal. (b) SEM image of zeolite *L*. The average length is 2.5 μm and the diameter is about 1 μm.

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Pyronine B ions were inserted into the channels of zeolite *L* crystals by using ion exchange of the K^+ ions of the zeolite with PyB^+ ions in water. These incorporated PyB^+ ions are lined up along the direction of the zeolite channel with a tilt angle of less than 20° [1]. The surfaces of the dye molecule - zeolite composites were treated with (3-aminopropyl) trimethoxysilane (AP-TMS) to tether 3-aminopropyl (AP) groups onto their surfaces and to prevent the egress of the incorporated PyB^+ ions from the channels into the solution during the measurements [9,17]. The dye molecules and the crystals were randomly dispersed in glycerol. Since glycerol is index-matched to zeolite, scattering from the surfaces of the crystals could be eliminated. Because of the high viscosity of glycerol, dye molecules or dye molecules incorporated in zeolite *L* crystals do not move or rotate as freely as they do in other low-viscosity solvents.

The PL spectra were measured with all the samples placed in a quartz cuvette. The details of the experimental setup for polarized PL measurements have been described elsewhere [9]. The excitation source was the 514.5-nm line of an Ar ion laser. A half - lambda waveplate and a compensator were used for changing the polarization. Polarizers were used for cleaning-up the polarization direction of the excitation beam in the excitation part and for selecting the polarization of the PL signal as an analyzer in the detection part. Since the grating of the spectrometer is optimized for the horizontal polarization direction, an achromatic half - lambda waveplate was used to rotate the polarization of the PL signal coming from the analyzer to the horizontal direction. Lastly, the signal was filtered with an edge filter to block the laser line and dispersed by using a TRIAX 550 (Jobin Yvon) spectrometer. A liquid-nitrogen-cooled charge-coupled-device (CCD) array was used for detection. The isotropy of the measurement system was checked by using a PL ratio analysis of randomly dispersed PyB molecules in glycerol with a circularly polarized excitation laser beam. The obtained PL ratio was almost 1, which showed that the measurement system was isotropic.

III. RESULT AND DISCUSSION

The symbols *H*, *V* and *R* in the figures indicate a horizontal, a vertical, and a circular polarization of the incident polarization direction, respectively. We obtained the anisotropy from the ratio of the PL intensities. When the polarization of incident light is horizontal (vertical), parallel (perpendicular) to the optical table, the anisotropy is obtained by dividing the PL intensity at 0° (90°) degrees of the analyzer by the PL intensity at 90° (0°) degree of the analyzer.

In Figures 2 and 3, the anisotropy is almost 1 for circularly (*R*) polarized incident light at any concentration. These results show that dye molecules and the dye

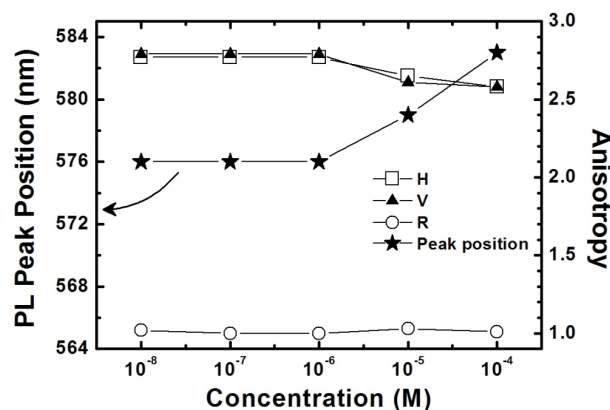


Fig. 2. PL peak position and anisotropy vs. concentration of PyB molecules in glycerol.

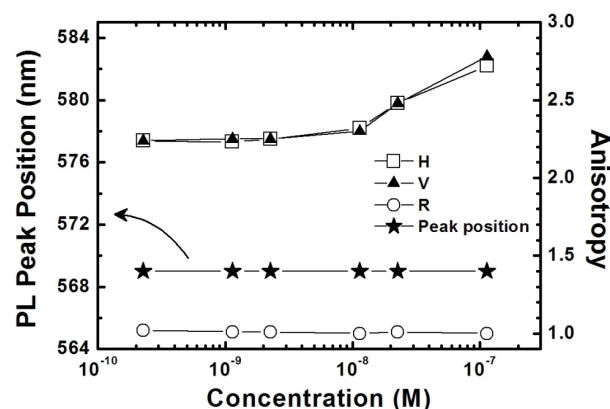


Fig. 3. PL peak position and anisotropy vs. concentration of PyB molecules incorporated in zeolite *L* crystals in glycerol.

molecule - zeolite composites are dispersed randomly in the solvent and that our system is, indeed, isotropic. In Figure 2, the PL of PyB molecules is red-shifted from 576 nm to 583 nm as the concentration in glycerol increases. From this, we can infer that energy transfer between molecules occurs at high concentrations. As the average molecule-to-molecule distance is reduced by increasing concentration, dye molecules are partly aggregated and move together. A molecule absorbs the light if its dipole moment is in the same direction as the polarization direction of the incident light. It then emits luminescence in the same polarization direction if this molecule is isolated from other molecules. However, if the molecules aggregate, the molecule can transfer its energy to another molecule, which absorbs this energy and luminesces. In this process, some energy is lost [1, 9, 18], which results in a red-shift of the PL peak energy for higher dye molecule concentrations. We can also infer this aggregation and energy transfer effect from anisotropy measurements. The anisotropy decreased as the concentration increased, as shown in Figure 2. Even though the decreasing value is small (~ 0.2), one can no-

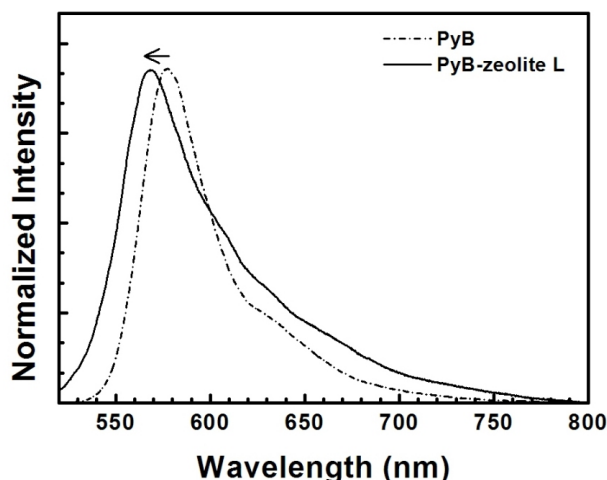


Fig. 4. Comparison of the PL spectra of PyB molecules at 10^{-6} M and PyB molecules incorporated in zeolite *L* at any concentration.

tice that the decreasing anisotropy coincides with an increase in the PL peak energy. At high concentrations, the polarization of the luminescence is less dependent on the original polarization direction of the excitation light because the dye molecule that is excited by the incident light transfers its energy to another molecule, the direction of which does not correlate with the direction of the excitation polarization. At the concentrations, less than 10^{-6} M, the PL peak energy and the anisotropy are independent of the concentration.

Figure 3 shows the dependences of the peak energy and the anisotropy of the PL for PyB incorporated in zeolite *L* (PyB - zeolite *L*) in glycerol. The concentration scale is much lower than that in Figure 2 because a small amount of PyB molecules was incorporated into the zeolite pores. The PL of the PyB - zeolite *L* composite does not change at any concentration (569 nm). This result indicates that energy transfer does not occur in the PyB - zeolite *L* system. One can also observe the blue-shift of the PL relative to that of dye molecules in glycerol due to the confinement effect (Figure 4) as mentioned in a previous report [8]. As Figure 1(a) shows, because the pore opening of zeolite *L* is almost the same size as a PyB molecule, the dye molecules do not aggregate inside the channels of the zeolite *L* crystal. Thus, zeolite *L* prevents aggregation of dye molecules. The anisotropy of PL from PyB - zeolite *L* increased as the concentration increased. The value becomes close to 3 at high concentrations. At low concentrations, the anisotropy value is less than 3, mainly due to the rotation of the zeolite *L* crystals between absorption and emission of light. This rotation was clearly visible under optical microscope. As the PyB concentration increases, the number of PyB - zeolite *L* per unit volume increased; at the highest concentration, the average distance between PyB - zeolite *L* crystals is about 20 μm . The close proximity of zeolite *L* crystals effectively increases the viscosity of the

solution because the mechanical coupling between the crystals through the solvent hinders relative motion or rotation of the crystals. As a result, the direction of the PyB molecule when the light is emitted is close to that when the light is absorbed, which in turn increases the anisotropy. In other words, a high concentration system is close to an ideal system where all dye molecules have random fixed directions [19].

IV. SUMMARY

The PL of PyB molecules in glycerol red-shifts as the concentration is increased due to the aggregation effect and the energy transfer from one molecule to another. This concentration dependence disappears when PyB molecules are incorporated into zeolite *L* crystal pores. The anisotropy of PyB molecules decreased, but that of PyB - zeolite *L* increased as the concentration was increased. The decrease in the anisotropy for PL from PyB molecules is explained in terms of the aggregation-induced energy transfer whereas zeolite act as a barrier, preventing the energy transfer when dye molecules are embedded in the pores of zeolite crystals. In conclusion, we demonstrated that the energy transfer could be controlled using zeolite.

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