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Concentration-dependent Fluorescence Properties of a Water-soluble Perylene Ammonium Derivative in Solutions and Polymer Matrices

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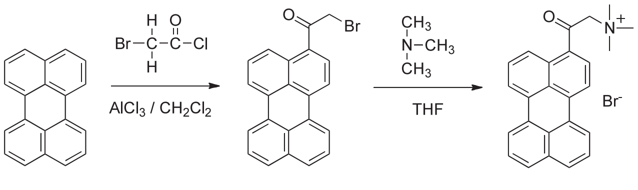
A water-soluble perylene ammonium derivative was synthesized and its fluorescence spectra in solution and in polymer matrices were measured as a function of concentration. The concentration-dependent fluorescence spectral change in polymer films is useful for probing the initial processes of crystal nuclei growth by matrix isolation and/or freezing.

Recently, optical properties of size-controlled materials have been widely studied in the field of nanotechnology. For example, the emission properties of quantum dots were found to be affected by particle size.[1] In organic crystals formed by molecular interactions such as van der Waals interactions, size-dependent optical properties have also been observed.[2–9]

We have reported the fluorescence properties of pyrene ammonium derivative (PyAm) aggregates formed in a poly(vinyl alcohol) (PVA) matrix by phase separation.[10] The size of PyAm aggregates in the PVA thin films increased with increasing dye concentration. The fluorescence spectra of PyAm in the PVA film at a lower concentration showed only monomer emission. The fluorescence peak shifted to the red with increasing dye concentration, which was assigned to a dimer or excimer-like emission. Changes in the fluorescence spectra were related to the formation of nanocrystals and/or aggregates in the films by phase separation, which was presumed to show a hierarchal change (like a consecutive reaction) of the fluorescence property depending on the domain size. We have proposed that the concentration-dependent fluorescence spectral change is due to matrix isolation and/or freezing of crystal nuclei growth by the polymer chain. In this letter, we report our investigations of the fluorescence properties of π-extended dye aggregates formed in a polymer matrix. We synthesized different polycyclic aromatic ammonium derivatives to demonstrate our general idea for the molecular assembly process in a polymer matrix.

The perylene ammonium derivative (trimethyl-[2-oxo-2-(perylen-3-yl)ethyl]ammonium bromide; PeryAm) was synthesized according to Scheme 1. Bromoacetylperylene was prepared by the Friedel–Crafts reaction of perylene with 2-bromoacetyl chloride in CH_2Cl_2 at room temperature (298 K) for 2 days.[11] An excess amount of trimethylamine gas was introduced to 3-(bromoacetyl)perylene in dry tetrahydrofuran (THF) at room temperature (298 K).[12] This solution was then stirred for 1 day. The produced precipitate was separated and then dried in vacuo to give PeryAm as an orange solid. PeryAm was characterized by ^{1}H NMR spectroscopy and elemental analysis.[13] The PeryAm-doped PVA thin films were prepared by drop-casting onto quartz plates. The PVA concentration in ion-exchanged and distilled water was fixed to 0.113 mol dm^{-3} (0.5 wt %). To change the PeryAm molecular fraction in the films, concentrations of PeryAm in aqueous PVA solutions were 0.001, 0.002, 0.01, 0.02, 0.06, 0.1, 0.2, 0.3, and 0.4 mol % for monomer units. The coated films were dried under vacuum for 24 h at 298 K. UV–vis absorption spectra were measured with a Shimadzu UV-2450 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5300PC fluorescence spectrophotometer. All experiments were carried out at room temperature (298 K).



Scheme 1. Synthetic route of PeryAm.

Figure 1a shows the absorption spectra of PeryAm in aqueous solution. Absorption peaks were observed at 450 nm. Concentration dependence was not observed in the spectral shape. The molar absorption coefficient of this band was estimated to be 17000 M^{-1} cm^{-1}. Figure 1b shows the fluorescence spectra of PeryAm in aqueous solution excited at 400 nm as a function of concentration. In the case of 1×10^{-6} mol dm^{-3}, the fluorescence peak was observed only around 460 nm. Upon increasing concentration, the intensity of this band decreased and a broad fluorescence band around 610 nm was observed. The fluorescence excitation spectra monitored at 480 nm indicate a vibrational structure at 390, 415, and 440 nm, which can be seen in the mirror image of the fluorescence band at shorter wavelengths. On the other hand, the broad band observed around 470 nm was monitored at 610 nm. The fluorescence bands observed in the shorter wavelength region are assigned to emissions from the monomer state. The fluorescence bands observed at shorter and longer wavelengths can be assigned to the emission of the monomer and excimer or aggregates, respectively.

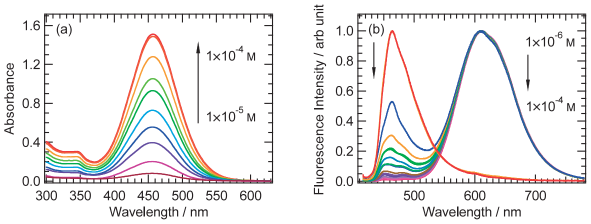


Figure 1. Absorption (a) and fluorescence (b) spectra of PeryAm in aqueous solution as a function of concentration. The excitation wavelength was $\lambda = 400$ nm. The fluorescence spectra were normalized at the maximum intensity.

The absorption spectra of PeryAm in PVA films were similar to that in solution. We measured the fluorescence spectra of PeryAm in PVA films. Figure 2a shows the fluorescence

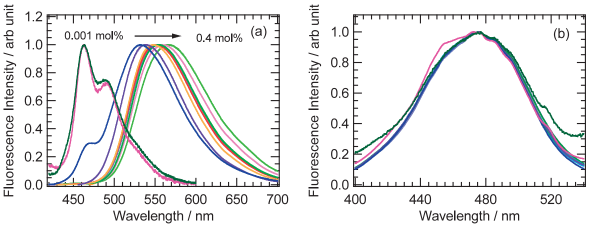


Figure 2. (a) Fluorescence spectra of PeryAm in PVA films excited at $\lambda = 400$ nm and (b) fluorescence excitation spectra monitored at $\lambda = 570$ nm, as a function of concentration. Both spectra were normalized at the maximum intensity.

spectra of PeryAm in PVA thin films excited at 400 nm at concentrations ranging from 0.001 to 0.4 mol %. At 0.001 mol %, the fluorescence peak was observed around 450 nm. This peak decreased with increasing concentration concomitant with a new broad fluorescence peak that appeared around 530 nm at 0.01 mol %. The fluorescence band peaks shifted to the red with increasing concentration. The fluorescence peak reached 565 nm with a shoulder around 680 nm at a concentration of 0.4 mol %. The fluorescence band observed in the shorter wavelength region was assigned to the emission of the monomer state analogous to that in solution. The fluorescence band observed in the longer wavelength region was assigned to dimer and/or excimer-like emission. The shoulder around 680 nm was identical to the fluorescence spectrum of PeryAm powder (Figure S1[15]) indicating that crystallization occurred in the films upon increasing local concentration during solvent evaporation. These findings suggest PeryAm formed nanoparticles or nanocrystals by phase separation depending on the concentration in the PVA films. The excitation spectra of PeryAm in PVA films monitored at 570 nm was the same at all concentrations as shown in Figure 2b, which suggested that all the emissive species originated from the same molecule in the ground state.

The characteristic fluorescence properties of organic nanoparticles have been widely reported. Kasai et al. reported the optical properties of perylene nanoparticles prepared by reprecipitation.[3] The fluorescence spectra of the nanoparticles differ from that of the bulk crystals. They proposed the lattice softening in nanoparticles as a cause of the size-dependent optical properties. Yao et al. reported the size dependence of emission spectra for pyrazoline nanoparticles, which originates from the formation of charge-transfer exciton due to the flexibility and various inter- and intramolecular overlapping structures in the nanoparticles.[5,6] One model of size-dependent optical properties of perylene nanoparticles was proposed by Asahi et al.[9] It is well-known that electronic excitation energy is trapped in a sandwich-like pair of two molecules, i.e., excimer formation, in the crystals.[14] Because the monomer fluorescence peak of the nanocrystal is identical to that of the bulk, half the value of the free exciton bandwidth can be considered to be independent of size. Therefore, the size dependences of the excimer fluorescence peak should be attributed to reduction in lattice relaxation energy (E_{LR}) with decreasing size. The size dependence of E_{LR} is attributable to a change in elastic properties due to excimer formation of the nanocrystal with size. The lattice instability caused by the large surface-to-volume ratio is most likely responsible for lowering the lattice vibration or rigidity with decreasing crystal size, which leads to the up-shift of the excimer energy level. It is proposed that the energy difference between the excimer and ground states increases monotonously with the surface-to-volume ratio. The increase in free energy of the nanocrystal or nanoaggregate most probably results in a contribution of the surface free energy, because the size effect on organic nanoparticles is related to some molecular conformation, packing, and elastic properties of nanoparticles at the surface.

In conclusion, we investigated the fluorescence properties of PeryAm in aqueous solution and PVA matrix. It was found that nanoaggregates were formed in PVA matrix by phase separation. The peaks of dimer and/or excimer-like fluorescence originated from the aggregates shifted to the red with increasing concentration. It is ascribable to the size effect due to stabilization of the surface free energy. We propose that the concentration-dependent fluorescence spectral change in the polymer films is useful as a probe for the initial processes of crystal nuclei growth by matrix isolation or freezing. Detailed studies on the matrix effect for fluorescence spectral change, X-ray and thermal analysis, and time-resolved studies in films are now in progress.

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13 Anal.; Calcd for $C_{25}H_{22}NOBr + H_2O$: C, 66.67; H, 5.37; N, 3.11%. Found: C, 66.69; H, 5.17; N, 2.79%. ^{1}H NMR (300 MHz, CD_3OD, 25 °C, TMS): δ 8.7–7.5 (m, 11H, PeryH), 4.79 (s, 2H, CH_2N^+), 4.58 (s, 9H, $(CH_3)_3N^+$).
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