

Aqueous Dispersion and Temperature Induced Reversible Fluorescence Properties of 1-Pyrenecarboxaldehyde

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ABSTRACT

The fluorescence intensities for various vibronic fine structures in the 1-pyrenecarboxaldehyde (PyCHO) fluorescence show strong environment dependence. In aqueous solvent, the distribution of dye is highly depended on its concentration labels and varies from excimer to monomeric state. UV-Vis Spectroscopic analysis could not able to detect dye below 10^{-7} M concentration, whereas a new monomeric peak at 342 nm was observed after heating and cooling treatment at above the concentration. At 10^{-8} M concentration, only monomeric distribution of 1-PyCHO reveals a strong temperature (20-50 °C) induced reversible perturbation of the vibronic band intensities. This suggests the operation of some specific solute-solvent dipole-dipole interaction mechanism strongly influenced by heating.

Keywords: Monomeric distribution, 1-pyrenecarboxaldehyde, reversible fluorescence.

1. INTRODUCTION

Investigation of fluorescence probe is becoming an important area in biophysical studies of multimolecular aggregates such as micelles and membranes. Studies with 1-PyCHO as a fluorescence probe have received special consideration, because 1-PyCHO has several interesting photophysical properties which make it suitable for use as an effective probe, notably the long life-time of 1-PyCHO monomers and efficient formation of excimers. 1-PyCHO is one of the derivatives of pyrene structure.

There have been extensive studies on the photophysics of pyrene: its electronic spectrum and state assignments¹, kinetic details of excimer formation², spectral pressure effects³, formation and kinetics of excited state⁴, photoionization⁵, delayed luminescence⁶, and quasilinear spectra⁷, yet there have been few studies directed toward environmental effects on the fluorescence spectrum of pyrene.

The solvent dependence of vibronic band intensities in pyrene monomer fluorescence was first investigated by Nakajima⁸⁻¹¹. The intensities of the various vibronic bands were found to show a strong dependence on the solvent environment.

Recently, pyrene has been using as a labeled probe with polymers to investigate their molecular properties¹²⁻¹⁴. Winnik and his colleagues¹⁴ have reported that aqueous solutions of the pyrene-labeled poly(ethylenimine) (PEI-Py) exhibit typical pyrene monomer and excimer emission, and the excimer - to - monomer ratio (I_E/I_M) decreases with decreasing Py content of the macromolecule. The excimer emission arises from preassociated pyrene aggregates.

Introduction of -CHO with pyrene structure makes it a little polar character, which facilitate to dissolve in aqueous solution.

Mazur and Blanchard¹⁵ have reported that the density of pyrene onto the quartz surface produced monomeric and excimer spectra.

Generally, depending on concentration the free probes reveal monomeric or excimer fluorescence spectra in solution. Excimer formation and their fluorescence intensities are not consistent at all.

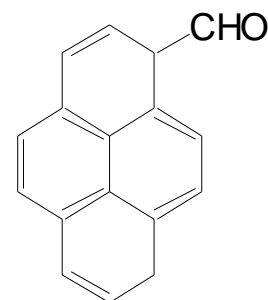
Therefore, the study of 1-PyCHO probe regarding monomeric species is very important to explore unique characteristic in aqueous solution. In this article, we report the temperature induced perturbation of vibronic bands intensities of monomeric 1-PyCHO in aqueous solution.

2. EXPERIMENTAL

2. 1. Materials and method

Fluorescence measurements of 1-pyrenecarboxaldehyde were recorded by using a FP-6500 Spectrofluorometer (serial no. 0041100523, model: FP-6500DS-A) equipped with a heater (Advantec, model: LCH-3000, serial no. 201061, Tokyo Kaisha Ltd, Japan). Microliters of 1-PyCHO stock acetone solutions were first evaporated in vials and diluted with milli-Q water, yielding ca. 1.0-0.01 μ M concentrations of aqueous solution.

The thermo-responsive behavior of 1-PyCHO was investigated by means of a UV-Vis Spectrophotometer (JASCO V-650 Spectrophotometer, serial no. A004061150, Japan).



1-Pyrenecarboxaldehyde

3. RESULTS AND DISCUSSION

At the very beginning, we started to investigate the monomeric level of concentration of 1-PyCHO in aqueous solution and the influence of sonication and temperature on UV-Vis spectrophotometric absorption and fluorometric excitation and emission spectra of the dye.

In UV-Vis spectrophotometric absorption, it was revealed that 1.0 μ M aqueous dye solution persisted aggregation along with dimer or multimer peaks at λ_{\max} 365.5 nm, as shown in Fig. 1. The spectrum recorded after 5 minutes sonication showed an additional peak at λ_{\max} 342 nm, indicates disintegration of dye in the solution.

When the same solution was heated at 50 °C and then subsequently cooled to room temperature (25 °C), the peak at λ_{\max} 365.5 nm was almost diminished although the new peak

at λ_{\max} 342 nm with a shoulder at λ_{\max} 325 nm became prominent which also verify the reduction of dye into smaller fragment.

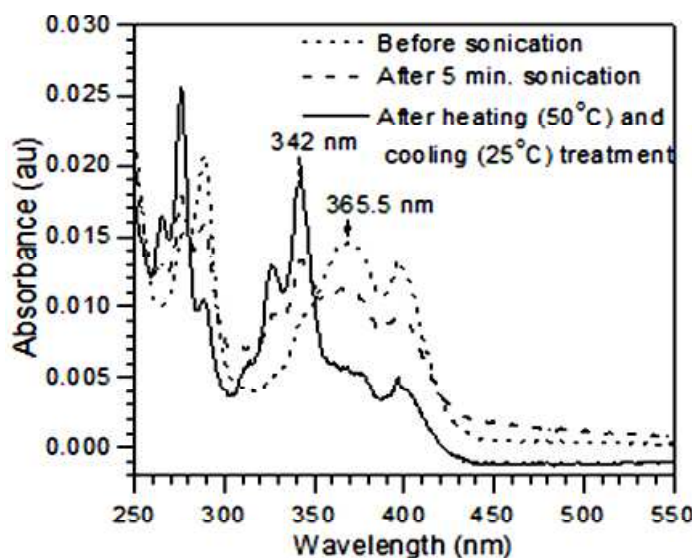


Fig. 1. UV-vis spectra of 1×10^{-6} M 1-PyCHO aqueous solutions

However, when similar experiments were performed using $0.1 \mu\text{M}$ and $0.01 \mu\text{M}$ aqueous solutions shown in Fig. 2 (a, b), an experimental problem was arisen to measure $0.01 \mu\text{M}$ solution because of very low concentration of dye. Besides, $0.1 \mu\text{M}$ solution showed only two peaks at λ_{\max} 342 nm and at λ_{\max} 325 nm representing monomeric species of the dye. On the other hand, more precise investigation with fluorometric spectra was conducted. The original molecular states (monomeric and aggregation) of the dye in aqueous solution was observed as it was excited from two different wavelengths at λ_{\max} 342 nm & 365.5 nm and recorded emission spectra.

When $1 \mu\text{M}$ aqueous solution of 1-PyCHO dye after 5 minutes sonication was excited at λ_{\max} 365.5 nm an excimer emission spectrum was obtained at λ_{\max} 472 nm without any evidence of monomeric peak at λ_{\max} 382 nm, besides two emission peaks were found at λ_{\max} 382 nm and 472 nm as excited the same solution at λ_{\max} 342 nm indicates along with the excimer some monomeric species were formed is shown in Fig. 3 (a, b).

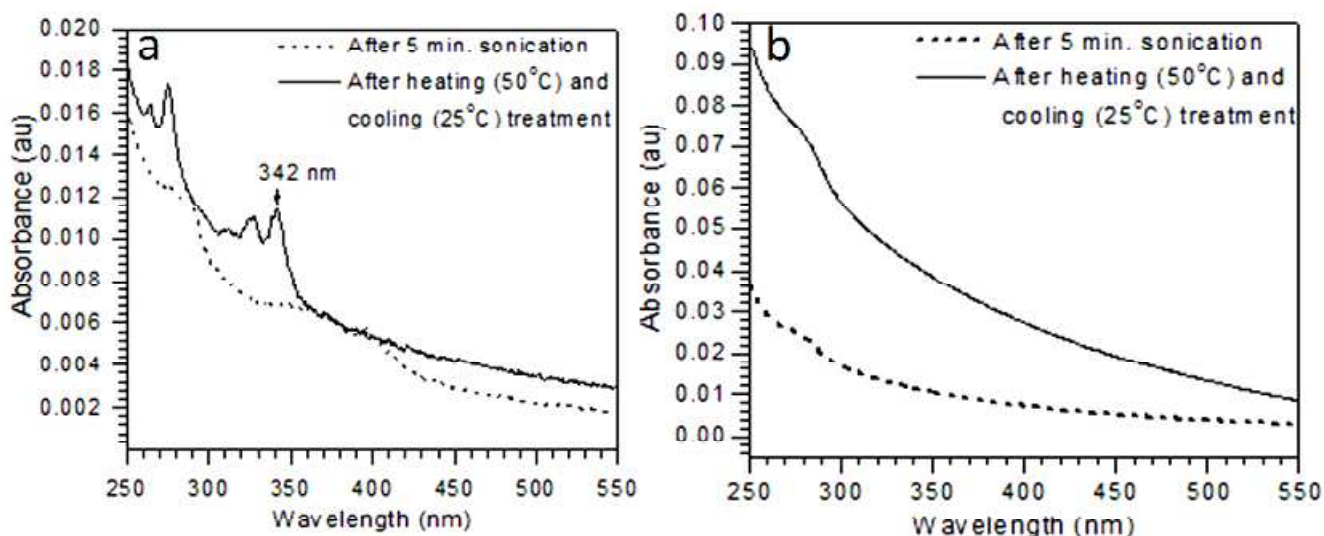


Fig. 2. UV-vis spectra of 1×10^{-6} M (A) and 1×10^{-7} M (B) 1-PyCHO aqueous solutions

Solution of $0.1\mu\text{M}$ 1-PyCHO showed excitation and emission spectra with resemblance of $1\mu\text{M}$ PyCHO solution only giving very low peak intensity at λ_{max} 382 nm and a quenched excimer peak at λ_{max} 472 nm when excited at λ_{max} 365.5 nm and 342 nm respectively as shown in Fig. 3 (c, d). In Fig 3 (e, f), the more diluted solution $0.01\mu\text{M}$ 1-PyCHO was unable to detect peak by UV-Vis spectrophotometer, gave an excellent emission spectra by fluorometry at λ_{max} 382 nm with a mirror image of excited spectra at λ_{max} 342 nm having a shoulder at λ_{max} 400 nm indicates the monomeric form of dye in aqueous solution.

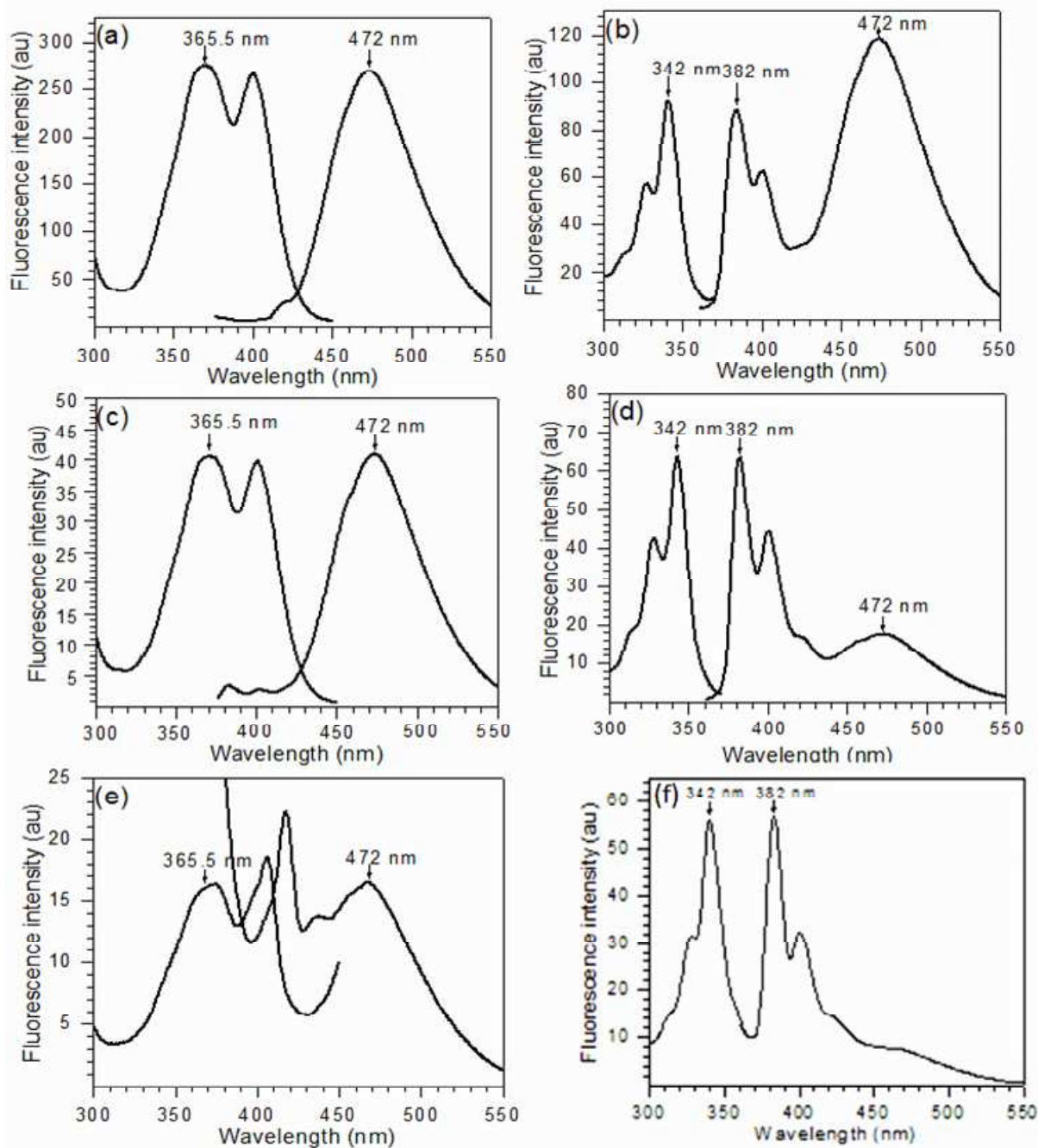


Fig. 3. Spectrofluorometric analysis of 1-pyrenecarboxaldehyde at different concentrations (a, b) 1.0×10^{-6} M, (c, d) 1.0×10^{-7} M and (e, f) 1.0×10^{-8} M where excitation and emission spectra were recorded at 365.5 nm and 472 nm for excimer (a, c, e) and 342 nm and 382 nm for monomer (b, d, f) respectively

Aqueous dispersion of 1-PyCHO depending on concentration is schematically presented in Fig. 4 and the summary of instrumental responses is given in Table 1.

Table 1. Aqueous dispersion of 1-pyrenecarboxaldehyde fluorescence dye at different concentrations with instrumental responses

Dispersion	Monomeric dispersion	Excimer/Monomeric dispersion	Aggregated dispersion	Precipitation
Concentration	1.0×10^{-8} M	1.0×10^{-7} M	1.0×10^{-6} M	$>1.0 \times 10^{-6}$ M
UV-Vis spectroscopy	×	0	0	×
Spectrofluorometry	0	0	0	×

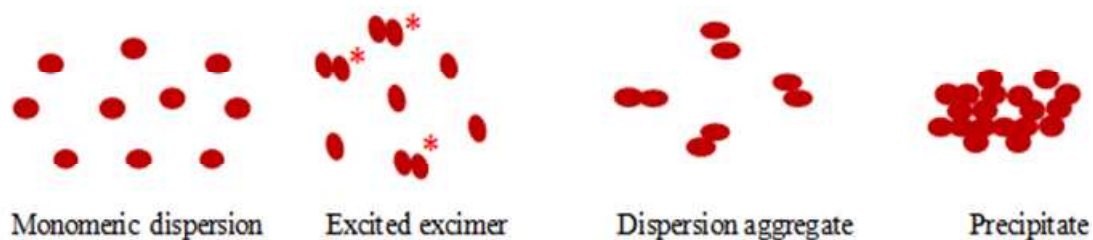


Fig. 4. Schematic presentation of aqueous dispersion of 1-pyrenecarboxaldehyde fluorescence dye

The solvent-dependent fluorescence behavior of aromatic aldehydes, including PyCHO has been reported by Brederick et al¹⁶. In nonpolar solvents such as *n*-heptane, the fluorescence spectrum of PyCHO is structured with peaks around 400-420 nm, and the quantum yield ($\phi_F < 0.001$) is small.

This particular fluorescence is due to an $n-\pi^*$ transition, however, on increasing the polarity of the solvent media, the $\pi-\pi^*$ level by solvent relaxation during the lifetime of the excited state.

Thus in polar solvents the $\pi-\pi^*$ state becomes the fluorescence emitting state. Presumably a solvent environment with dielectric constant ca. 10 is required to equalize the $n-\pi^*$ and $\pi-\pi^*$ levels. The monomeric fluorescence of PyCHO shows a strong dependence on solvent polarity has also been reported by Kalyanasundaram et al¹⁷.

The fluorescence in nonpolar solvents such as *n*-hexane is very weak (quantum yield < 0.001), but becomes quite intense in polar solvents (ϕ_F in methanol = 0.15).

Water as a polar solvent, $\pi-\pi^*$ state would be the fluorescence emitting state where, water molecules essentially surrounded the PyCHO molecules with hydrogen bonds. It is noteworthy to mention that at low temperature, the entropy of water molecules is lower than the entropy in boiling water.

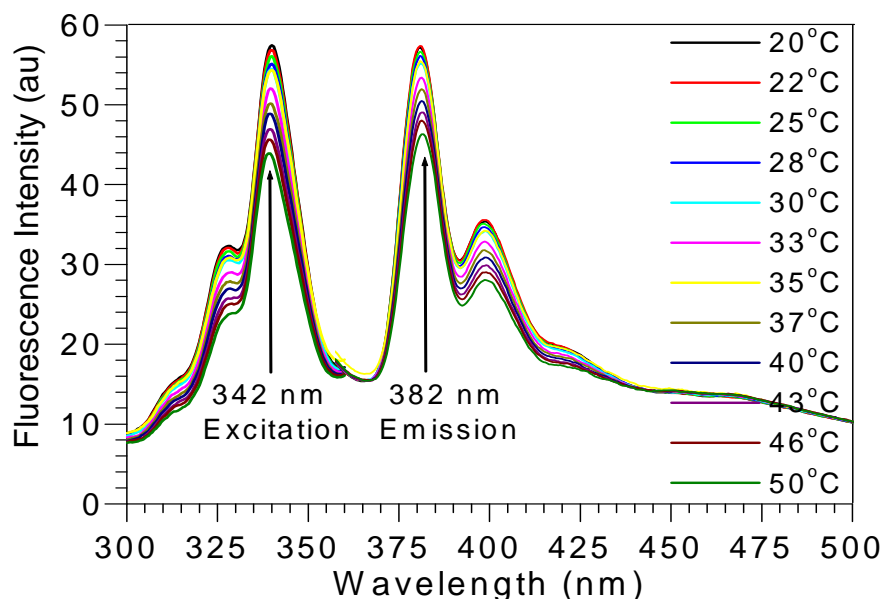


Fig. 5. The spectra for the variation of fluorescence intensities, when temperature was gradually increased from 20°C to 50°C at a heating rate of 1°C/min.

Fig. 5, represents the spectra for the variation of fluorescence intensities, when temperature was gradually increased from 20 °C to 50 °C at a heating rate of 1 °C/min. The solution was excited at 342 nm wavelength, emission spectrum at 382 nm was obtained as we

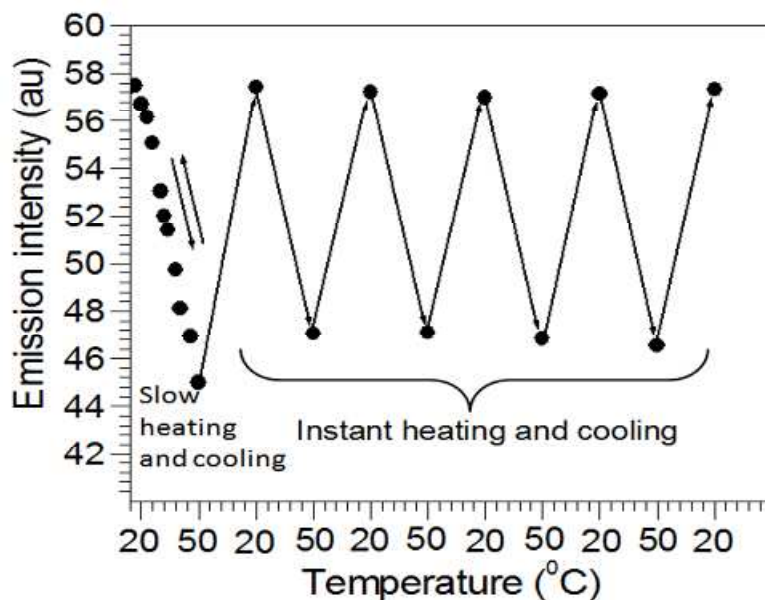


Fig. 6. The influence of temperature on monomeric fluorescence intensities of I-PyCHO in water at 10^{-8} M concentration during slow and rapid heating.

mentioned earlier. The shoulder at 400 nm of the emission spectra were more pronounced than the shoulder at 325 nm of excited spectra. During heating and cooling operation, the maxima at 382 nm of emission spectra were remained unchanged, indicates no excimer was grown in the solution at 10^{-8} M concentration.

Fig. 6 reveals the intensities change for emission spectra. The intensity was varied steadily and reversibly (linear dotted line) between ca.44 au and ca.58 au during slow heating and cooling process.

On the other hand, in rapid heating process, cell solution was dipped into bath water which was preheated at 50 °C and kept for 3 minutes to raise the desired temperature; spectra were then recorded at 50 °C temperature from a preset spectrofluometer. At 20 °C, the intensities were recorded ca. 58 au, but at 50 °C temperature, emission intensities ca 46 are also very close to ca. 44 au, as we obtained from slow heating process. It is expected that the fluorescence intensity is sensitive to the change of temperature because it affects the viscosity of the medium and hence the number of collisions of the molecules of dye with solvent molecules and the strength of hydrogen bonding.

4. CONCLUSION

Investigation of aqueous monomeric distribution of 1-pyrenecarboxaldehyde and its reversible tuning properties with temperature would be crucial for direct surface modification of substrate to use in the fields of medical, electro-chemical as well as industrial applications.

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