Luminescence characteristics and room temperature phosphorescence of naphthoic acids in polymers

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ABSTRACT

In the present work we have investigated the luminescence properties of 1-naphthoic acid (1NA) and 2-naphthoic acid (2NA) in three polymeric systems viz. poly methyl methacrylate (PMMA), poly vinyl alcohol (PVA) and cellulose acetate (CA). In case of PVA, strong room temperature phosphorescence (RTP) besides fluorescence is also noticed whereas in PMMA, weak phosphorescence is observed only after nitrogen purging and in CA it is practically not observed. Moreover, oxygen quenches the RTP in PVA significantly. Study reveals that in case of 1 NA in PVA, two types of species – strongly hydrogen bonded as well as weakly hydrogen bonded should exist. However, in PMMA and CA only weakly hydrogen bonded species appear to be present. On the other hand in case of 2NA we could not find such type of behaviour. The difference in the behaviour of these two probes is discussed.

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1. Introduction

Fluorescence spectroscopy is a powerful tool to investigate the structure, dynamics and micro-environment of organized assemblies of complex molecular systems viz. polymers and biopolymers [1]. Polymers are complex systems with large structural heterogeneities on microscopic level. The heterogeneities arise from distributions of molecular weights of the polymers and from complex chain conformations and entanglements. Optical absorption, scattering and luminescence methods provide many convenient tools for polymer characterization [2].

Polymers are important as the base materials for organic light emitting devices. In organic light emitting diodes (OLEDs), light is generated from the decay of molecular excited states, also known as excitons [3]. Hence understanding the properties and the interactions of excitons is crucial in the design of efficient organic devices. The excitons can be created either from the singlet state or from the triplet state. Because of the random nature of spin production in electroluminescent devices, simple statistics predicts that only 25% of the injected charges result in fluorescence (from singlet states) whereas 75% give phosphorescence (from triplet states) in suitable device architectures. Thus, uncorrelated

electrons and holes form triplet states have a threefold higher probability than singlet states [4].

In general, the energy in triplet excitons is wasted because of non radiative decay. However, if there is perturbation in symmetry, triplets may decay radiatively and produce phosphorescence [5]. Although it is often inefficient at higher temperatures, room temperature phosphorescence (RTP) may be enhanced by the presence of a heavy atom (present in matrix/solvent or added externally) [6]

Further, the nature of the chemical structure of a molecule in terms of flexibility and rigidity is of major influence on the fluorescence and phosphorescence signal. Molecules with more rigid structures have lower probability of rotations/collisions and thus have more phosphorescence potential. However, those molecules with higher degree of flexibility will tend to decrease phosphorescence due to higher rotational/collisional probability.

Besides heavy atom effect and structural rigidity of the fluorophore, increase in the phosphorescence also depends on some other physical parameters e.g. effect of matrix [7], pH [8,9], dissolved oxygen [10–13] and temperature [14] etc.

Although RTP was observed in some organic systems in fibrous materials [15], recently there had been renewed interest in trapping RTP because of its importance in OLEDs [16]. RTP has been reported in miceller systems [17], halogen bonded mixed crystals [18], graphene, quantum dots [19] and nanocomposites [20].

Phosphorescence is not observed under the conditions when the triplet state is in general efficiently deactivated by collisions with solvent molecules (or oxygen and impurities) because their

lifetime is long. These effects can be reduced and may disappear when the molecules are in a frozen solvent, in a rigid matrix (e.g. polymer) at room temperature [21] or linked with hydrogen bond [15].

In view of the above, choice of the host matrix as well as probe molecule is important for the development of any device related to luminescent phenomenon for OLEDs. Hence, in this paper we studied the fluorescence and phosphorescence properties of two simple probes viz 1-naphthoic acid (1NA) and 2- naphthoic acid (2NA) in three different polymers of varying nature and interestingly found that RTP is quite strong for 1NA in PVA matrix whereas in PMMA and CA it is not significant. In case of 2NA, phosphorescence is practically very small in all these three polymers. We discuss the luminescence of these two systems and explore the possible explanation of the observed results.

2. Experimental section

2.1. Materials and polymer film preparation

1NA and 2NA (obtained from Aldrich) of 99% purity were tested for its fluorescence purity and used as such. The molecular structural formulae of 1NA and 2NA are shown in Scheme 1. All the polymers were purchased from Sigma-Aldrich, India. All the solvents used were either of spectroscopic grades or were checked for their fluorescence purity. NA doped PVA films were prepared by mixing PVA (average molecular weight 1,25,000) grains with desired amount of NA in water. This mass was spread in polypropylene dish and was dried in an incubator. NA doped CA films were prepared by dissolving CA (average molecular weight 30,000 and degree of acetylation 38.6%) powder in acetone and mixing it with the desired concentration of NA in acetone. The resultant mass was spread in polypropylene dish to obtain the film. NA doped PMMA films were prepared by dissolving PMMA (average molecular weight 2,00,000) grains in chloroform and mixing it with desired concentration of NA in chloroform. The films were again obtained by drying the mass in polypropylene dish. All the films were prepared for different concentrations between 0.02 wt% and 0.4 wt%. The film thickness was ∼40–50 μm.
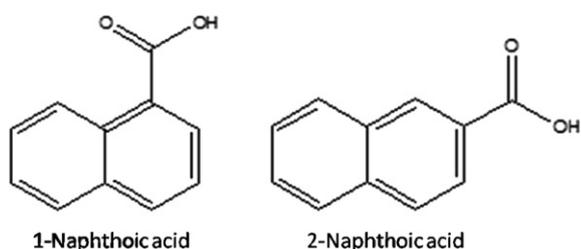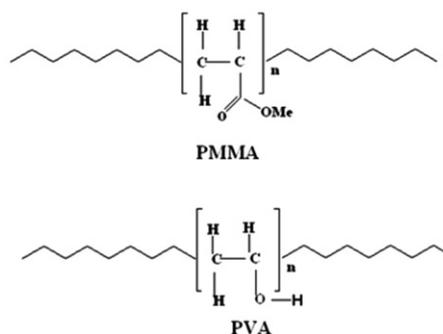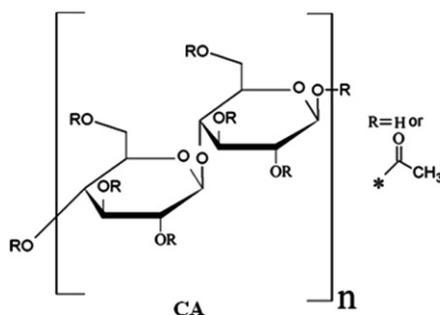
Scheme 1

The molecular structural formulae of different polymer matrices viz PVA, PMMA and CA are shown below as Scheme 2.

2.2. Instrumentation

Steady state absorption spectra were recorded by dual beam JASCO V-550 spectrophotometer. The excitation and emission spectra were recorded by using JASCO FP – 777 spectrofluoremeter and data were analysed by related software. The spectra are corrected for spectral response of the system. Fluorescence decay curves of 1NA were obtained by using a time-correlated, single-photon counting (TCSPC) setup, coupled to a micro-channel plate photo-multiplier (model R2809u; Hamamatsu Corp.). The excitation source was a femtosecond Ti-sapphire laser (Tsunami model 3960). The half-width of the instrument response function was 40 ps, and the time per channel was 80 ps. The samples were excited at 295 nm and 310 nm and the fluorescence decay emission was collected by a monochromator at different emission wavelengths. Fluorescence decay times of 2NA were recorded with the help of Edinburgh-199 time domain spectrometer and analysed by TCC-900 and FAST software. The excitation source was a thyratron-gated hydrogen filled nanosecond flash lamp. The pulse width of ns flash lamp was about ∼1.0 ns with repetition rate of 30 kHz. Lamp profile was measured at the excitation wavelength using Ludox scatterer. The number of counts in the peak channel was at least 10,000. Time-resolved fluorescence decay curves were analysed by deconvoluting the observed decay with the instrument response function (IRF) to obtain the intensity decay function represented as a sum of discrete exponentials;

$$I(\tau,t) = \sum_i \alpha_i e^{-t/\tau} \qquad (1)$$

where $I(t)$ is the fluorescence intensity at time t and α_i is the amplitude of the ith life time such that $\sum_i \alpha_i = 1$. Average decay time (τ_{av}) was estimated after weighing with pre exponential factors given by

$$\tau_{av} = \Sigma \alpha_i \tau_i / \Sigma \alpha_i. \qquad (2)$$

Phosphorescence decay measurement was carried out with steady state fluorometer (Spex Fluorolog).

3. Results and discussion

3.1. 1NA

Steady state parameters of 1NA in these three different polymers at different solute concentrations are summarized in Table 1. Absorption spectra of 1NA (0.1 wt%) in PVA (polymer), PMMA/CA (polymers) are depicted in Fig. 1(i). The absorption maximum of 1NA in PVA polymer is observed at ∼287 nm and at ∼297 nm in PMMA and CA polymers, respectively.

Scheme 2