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Organized polyvinyl alcohol assemblies: Eligible luminescent centers for species dependent metal sensing

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ABSTRACT

Solutions of polyvinyl alcohol have been found to show fluorescence emission upon excitation ($\lambda_{ex} = 300$ nm, $\lambda_{em} = 420$ nm). The site of luminescence generation has been attributed to its tendency to form organized micelles in solution which result in an electron dense region in the hydrophilic zone. The expected micellar size was evaluated using dynamic light scattering and the cmc was predicted from the conductance measurements. The spectral changes of the PVA solution were spectacular in the presence of different oxidation states of the metal ions Cr(III)/(VI), Mn(II)/(VII) and Fe(II)/(III). The spectral studies indicated a weak ground state complexation of PVA micelles with the lower oxidation state metal ions. However for the higher oxidation state species both ground and excited state fluorescence quenching were observed. The present system offers a simple and cost effective method of species dependent metal ion sensing.

1. Introduction

Fluorescent polymers based on conjugated molecular systems are used to detect a variety of analytes. Conjugated polymers contain a chromophore requiring low energy for excitation of an electron. Because it is highly delocalized, the excited electron (exiton) can travel along the polymer until fluorescence (or quenching) occurs [1]. Each chemical sensor carries a receptor that binds to the analyte causing a change in the fluorescence. A conjugated polymer-based chemical sensor has one receptor site for every repeat unit, and since the exiton can travel across the polymer, it encounters many receptor sites causing it to be more sensitive than a non-polymeric system. Recently we have reported the fluorescence activity in an unusual class of polymers (polyethylene glycols) originating from their vesicular organization which offer electron dense regions at the center of the vesicle [2]. By monitoring fluorescence intensity of such amphiphiles and change in their fluorescence property upon treatment with a foreign entity, it is possible to determine the nature of its immediate surroundings. Thus fluorescence spectroscopy serves as an important and reliable tool for investigating the environment prevailing within organized assemblies over a nano-dimensional length scale. Metal ions with high positive charge density get accumulated in this electron dense region and exhibit fluorescence turnoff. This observation boosts up the possibility of functional applications of polymeric amphiphiles towards the formation of chemosensory devices.

Polyvinyl alcohols (PVAs) are nontoxic amphiphilic water soluble polymers having multitude chemical applications [3,4]. PVA is mainly used as a protective colloid in emulsion polymerization in polymer industry [5]. It also has medical applications for example as a lubricant in eye drops and hard contact lens solution [6]. When doped with iodine, PVA can be used to polarize light [7]. PVAs having wide applications in material designing are also potential compounds to be used as a medium for sample analysis [8]. In addition, due to its biocompatibility, high water solubility, and chemical resistance PVA is an eco-friendly system to be used in detection studies.

Elemental behavior strongly depends on its oxidation state. For example, the toxicity of chromium compounds depends on its oxidation state and solubility. Cr(VI) compounds are powerful oxidizing agents and thus tend to be irritating and corrosive. Cr(III) compounds on the other hand are much less toxic and are required in trace amounts for metabolic activities. This variation in toxicity may be related to the ease with which Cr(VI) can pass through cell membranes and its subsequent intracellular reduction to reactive intermediates [9]. Depending on their oxidation state, manganese ions have various colors and are used industrially as pigments. The permanganates are powerful oxidizers. Biologically, Mn(II) ions function as cofactors for a large variety of enzymes with many functions [10]. Manganese containing enzymes are particularly essential in the detoxification of superoxide free radicals in organisms that deal with elemental oxygen. Manganese also functions in the oxygen-evolving complex of photosynthetic plants. Mn(VII) however exhibits a higher toxicity than the Mn(II) compounds. The strong oxidative effect leads to the necrosis of the mucous membrane. Various iron(II)-complexes of biological, clinical and chemical interest are known to reduce molecular oxygen to reactive oxy-radicals which are detrimental to living cells after a certain concentration [11]. In humans, the host protein transferrin (Tf) sequesters extracellular iron(III) with extremely high affinity. This chelation prevents it from

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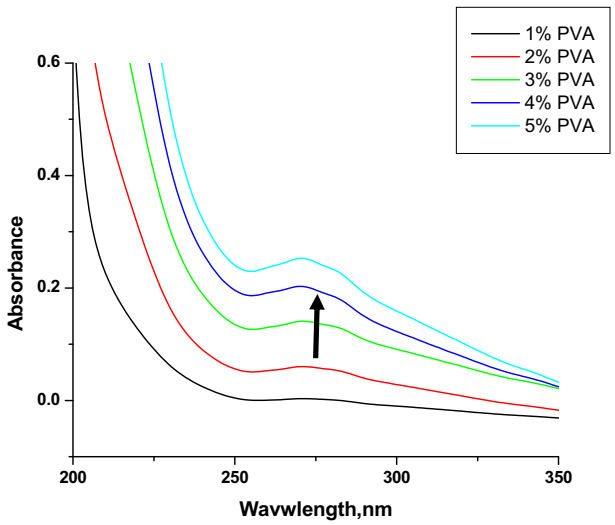

Fig. 1. Room temperature absorbance spectra of PVA solution with increasing concentrations.

precipitation and also has a bacteriostatic effect by keeping iron as an essential nutrient from being available to bacterial pathogens. Iron is stored in ferritin as Fe(III). To release iron when the body needs it, the iron must be changed from the Fe(III) to the Fe(II) oxidation state [12].

Various tools for speciation analysis of different oxidation states of metal ions have been reported during recent years [13–15]. However, fluorescence active materials may also contribute significantly towards speciation of different metal ions. The effect of different oxidation states of the same metal ion may influence the luminescence property of the fluorescent material in different ways as the fluorophor would face different microenvironments upon interaction with different charged species of the metal center. In the present study the fluorescence activity of the PVA solution is reported for the first time which originates due the self assembly of the polymer in solution. The detected fluorescence has been applied to differentiate between the lower and higher oxidation sates of the same metal ion which may open the possibility of speciation of these metal ions in solution.

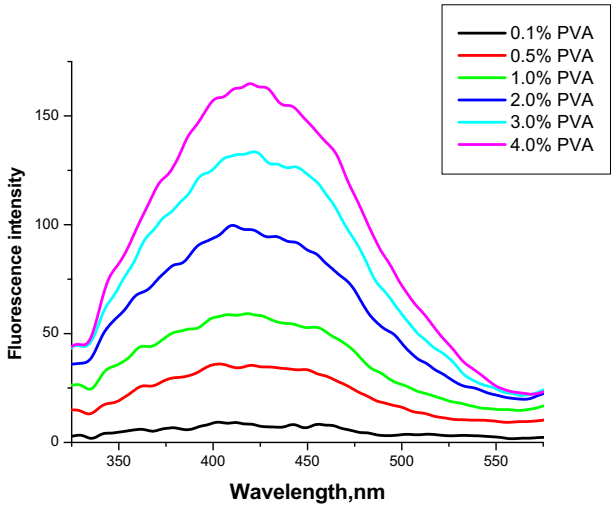

Fig. 2. Room temperature fluorescence emission spectra of PVA solution with increasing concentrations ($\lambda_{ex} = 300$ nm).

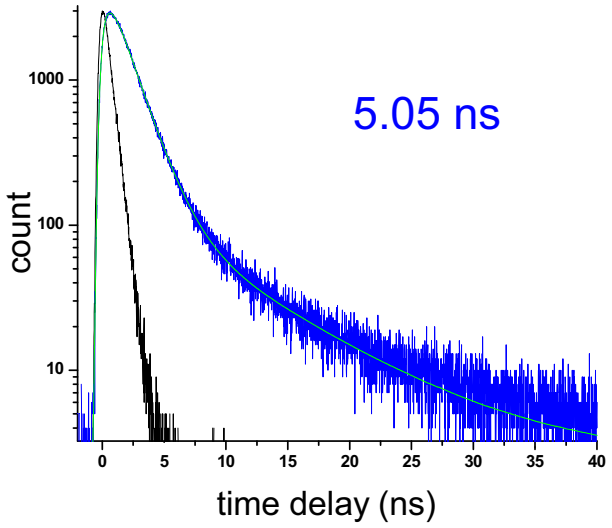

Fig. 3. Fluorescence decay of 5% PVA solution ($\lambda_{ex} = 291$ nm).

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA# 89,000–98,000; 99 + % hydrolyzed) (Sigma Aldrich), potassium dichromate, chromium(III) chloride, potassium permanganate, manganous chloride, sodium iodide, potassium iodide, zinc sulfate, nickel sulfate, aluminium sulfate, gallium nitrate (Merck) and all other chemicals were of analytical grade and used as received.

2.2. Apparatus

The absorbance spectra were obtained using an Agilent 8453 diode array spectrophotometer. Luminescence spectrometer LS-55B (Perkin -Elmer, U.S.A.) was used for fluorescence intensity measurement. Horiba Jobin Yvon Fluorocube 01-NL and 291 nm Horiba nanoLED, IBH *DAS-6* decay analysis software was used for Time Correlated Single Photon Counting (TCSPC) Lifetime Spectroscopy. Conductivity meter (JENWAY-4520) was used to measure the conductances. Dynamic light scattering studies were performed using Malvern Instrument zetasizer nano.

3. Methods

3.1. Spectral studies

Different concentrations of PVA solutions were prepared in warm water (60°–70 °C), cooled and subjected to UV–visible as well as

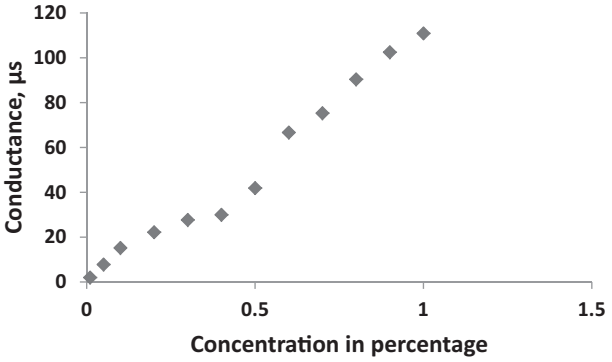

Fig. 4. Conductance of different concentrations of PVA solutions.