ION AND MOLECULE SENSORS USING MOLECULAR RECOGNITION IN LUMINESCENT, CONDUCTIVE POLYMERS

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INTRODUCTION

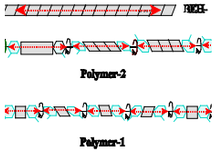
Purpose

The purpose of this project is to use molecular recognition strategies to develop sensor technology based on luminescent, conductive polymers of the poly(phenylenevinylene) type (PPV) that contain sites for binding specific molecules or ions in the presence of related molecules or ions. Selective binding of a particular molecule or ion of interest to these polymers will result in a large change in their luminescence and/or conductivity, which can be used to both qualitatively and quantitatively sense the presence of the bound molecules or ions.

Target Problem

Research problems that are being addressed by this project include:

1) designing molecular recognition sites that are highly selective for the ions and/or molecules of interest in the presence of a large background of other chemical species,
2) finding ways to incorporate many different selective groups into a single polymer,
3) fabricating polymer films, strips, sheets, and coatings that can be applied to other materials, such as fiber optics and surfaces,
4) developing interfaces between the polymers and substrates that can be used to produce prototype arrays of many sensor elements for rapid multi-contaminant detection and quantitation,



Basic Concept

PPV based polymers are very important materials for photonic device applications because they absorb and emit light strongly in the visible region of the spectrum. There spectral properties are very sensitive to the structure of the polymer. Incorporation of a ligand, such as 2,2'-bipyridyl (bpy), into the PPV backbone, polymers **-1** and **-2 (Figure 1)**, breaks the π electronic conjugation of the polymer backbone **(Figure 2)**, blue-shifting both the optical absorption and emission spectra of the polymer compared to those of PPV itself as a result of limited π electronic conjugation. Binding of metals to the bpy ligands increases the π electron conjugation within the polymer due to partial recovery of the coplanar conformation of the polymer chain. This results in strong optical shifts that are sensitive to the

Synthesis of Metal Ion Sensing Polymers

Figure 3 shows the synthetic route to the bpy-containing sensor polymers. This synthesis is based on Pd catalyzed coupling reactions. We have developed novel routes to the required bpy derivatives that make the polymer synthesis efficient. The bpy ligands are useful for sensing transition metals as well as lanthanides.

Figures 4a and **4b** show the synthetic route leading to a conjugated polymer that is selective for Pu(IV) binding. The polymer backbone was designed and prepared in the Wasielewski lab, while the Pu(IV) binding ligand was prepared in the Raymond lab.

FIGURE 3

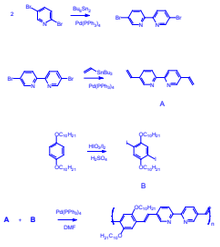


FIGURE 4A

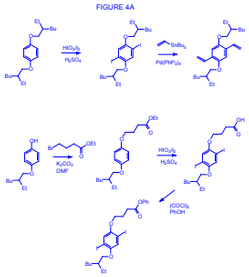


FIGURE 4B

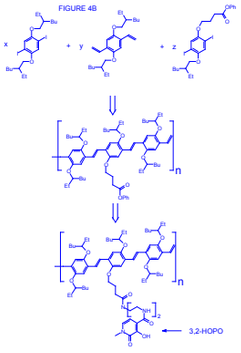
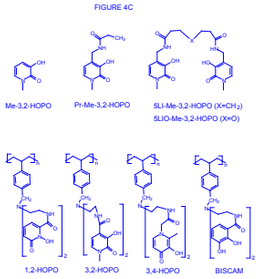


FIGURE 4C



Correlating Optical Sensing of Metal Binding with Polymer Structure

Parallel measurements using both X-ray absorption spectroscopy (XAS) and optical spectroscopy have been carried out on polymers- **1** and - **2** with and without metal ions bound to them. These results were compared directly with those obtained for the parent PPV polymer. These results establish the scope of these polymeric systems for sensing metal ions.

Optical Absorption and Emission Spectra

Optical absorption spectra of polymer-**2** in the presence of several metal ions is shown in **Figure 5**. Note

Optical absorption spectra of polymer-**2** in toluene titrated with four different metal ions are shown in **Figure 7**. All the ions cause significant red-shifts in the absorption maximum. The isobestic points in all four sets of spectra indicate that metal ion binding to polymer-**2** involves two species. As the metal ion concentration increases, the proportion of the polymer chain with two or more consecutive bpy sites occupied by the metal ions becomes larger, not only expanding the π-conjugation, but also introducing new metal-to-ligand charge transfer states with absorption at longer wavelengths compared to that of PPV. Based on the results, the binding efficiency is Fe^{2+}>Ni^{2+}>Cu^{2+}>Zn^{2+}>Pd^{2+}, where Fe^{2+} has possible second bpy ligation. These complexes can be further investigated by the examining the structures of metal binding sites.

Metal Ion Binding Site Structures in Polymers

Metal binding site structures in polymers-**1** and -**2** and in metal-bpy complexes have been examined with steady-state XAS measurements. **Figure 8** displays the Fourier transform EXAFS spectra and **Figure 9**, the XANES spectra for different metal ions in the polymers along with those for their corresponding bpy complexes. The FT-EXAFS spectra of Ni^{2+} ion binding sites in the polymers resemble that of $Ni(II)(bpy)_3$ with reduced amplitudes for the second and the third shells. The nearest neighbors of Ni atoms (1st peak) in both polymers can be best described by two Ni-N bonds with 2.15Å and four Ni-O bonds with 2.04 Å. The former are 0.06 Å longer than that in $Ni(II)(bpy)_3$. Cu^{2+} ion binding sites shows the similar trend of structural

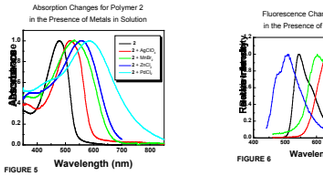


FIGURE 5

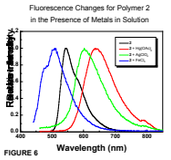


FIGURE 6

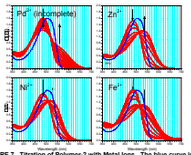


FIGURE 7. Titration of Polymer-2 with Metal Ions. The blue curve in each frame is the PPV spectrum.

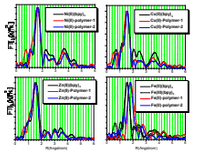


FIGURE 8. Fourier transform EXAFS spectra for different metal ion binding sites and metal-bpy complexes (not phase corrected).

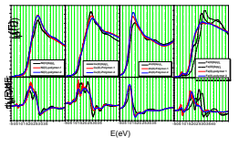


FIGURE 9. XANES and the first derivative spectra of different metal binding sites in polymers and in metal-bpy complexes.

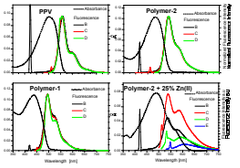


Figure 10. Excitation dependent steady-state photoluminescence of polymers in toluene.

Photophysics of the Polymers

The optical absorption bands of these polymers in toluene solution at room temperature are very broad **(see Figure 7)**, which may be due to the distribution of the conjugation length in the polymers in the solution. In order to verify this, the excitation wavelength dependent steady-state emission and transient absorption spectra of the polymers have been measured. **Figure 10** shows the steady-state emission spectra with different excitation wavelengths for the polymers. The normalized emission spectra of all neat polymer solutions show little excitation wavelength dependence and relatively narrow 0-0 bands compared to their absorptions. When the excitation wavelength is longer that of the 0-0 band, the fluorescence disappears as one expects. This suggests that the wavelength is longer than the 0-0 band, the sharp features of the 0-0 disappear and only a significantly red-shifted emission band remains, revealing a emission due to a new species from the charge transfer between the Zn-bpy and the polymer-**2**.

The steady-state emission spectra with excitation at isobestic points of a set of polymer solutions **(see Figure 11)** indicated that the fluorescence quantum yields of polymers- **1** and - **2** are about four and two times larger, respectively, than that of PPV. The excited state decay kinetics measured in 700-800 nm region of the three polymers are displayed in **Figure 12**. The lifetimes of the excited states are inversely correlated to the minimum conjugation length in the polymers. The inset in **Figure 12** shows an initial rise of the excited state for polymer- **1** due to the energy diffusion process that is too fast

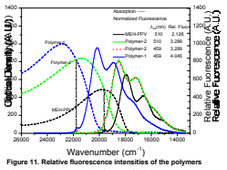


Figure 11. Relative fluorescence intensities of the polymers when normalized at equal optical densities.

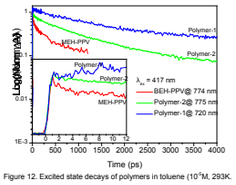


Figure 12. Excited state decays of polymers in toluene (10^{-5}M, 293K.

Figure 13 shows how the PL spectra of polymer-**2** with 20% Zn doping can be reconstructed with the spectra of the neat and 100% Zn doped polymer-**2** excited by different wavelengths. The reasonably good agreements between the measured and the reconstructed spectra strongly suggest that the metal bound sections of the polymer do not interact much with the unbound sections. The emission from both type of the sections can coexist and the relative intensities can be scaled with their respective absorption spectra. Although metal binding changes the π-conjugation, a significant contributor to the red-shifts of the absorption may be from new species due to the existence of the metal-bpy complexes.

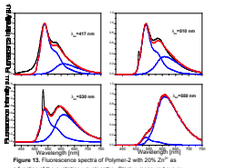


Figure 13. Fluorescence spectra of Polymer-2 with 20% Zn^{2+} as a function of the excitation wavelengths. Black = measured curve. blue= Zn = 0% and Zn = 100%; red = fit curve.

Development of Fiber Optic Sensors Based on Metal Ion Recognition by Conjugated Polymers

Metal ion sensors have been prepared using metal binding polymer **2**. **Figure 14** shows the basic principle of operation for a fiber-optic metal ion sensor. Polymer **2** was entrapped in a polymer host layer immobilized on the distal end of a single core optical fiber. PS802, a siloxan-based polymer served as the polymer host in our experiments. The excitation and emission spectra for this sensor were recorded using a double monochromator system. The sensor was tested by placing it in a solution of an individual metal ion in an organic solvent, and the spectra were recorded again.

The observed spectral effects due to this treatment were similar to those obtained in bulk solutions and films of polymer **2**. That is, for instance, there was a dramatic shift of the emission maximum from 542 nm to 590 nm upon exposure to Zn^{2+}. The emission spectra obtained without and with Zn^{2+} are presented on **Figure 15** (excitation: 470 nm). Current efforts are focusing on testing polymer 1 with a host polymer made from the hydrophilic acrylate host polymer, 2-hydroxyethyl methacrylate (HEMA). The latter polymer blend will permit sensing metal ions at the tip of the optical fiber immersed in aqueous environments. Also, regeneration of the sensor layer by competitive metal complexing agents will be demonstrated.

Figure 14

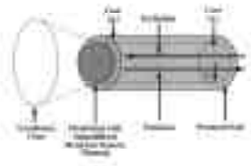
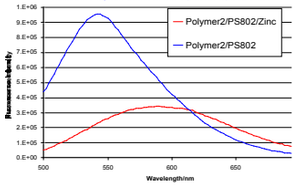



Figure 15. Metal Ion Sensing by a Conjugated Polymer / Siloxane Polymer Blend at the Tip of an Optical Fiber