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Conjugated Metallopolymers

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Summary: Conjugated polymers incorporating transition metals have enormous potential for chemically-tuneable conducting and semiconducting polymers. Unfortunately, progress in this field has been limited by the challenge of preparing suitable metal-containing monomers, the difficulty of polymerizing them in a controlled manner, and the limited solubility of the resulting polymers. We are developing new, soluble conjugated metal-containing polymers that contain transition metals in a conjugated organic backbone.

Keywords: conjugated polymers; fluorescent; metal-containing polymers; porphyrins

Introduction

Recently, there has been a great deal of interest in the development of specialty functional polymers for applications as diverse as catalysts, chemical sensors, and biomedical implants. Conducting polymers containing a conjugated organic backbone are fascinating materials that combine properties associated with both organic and inorganic elements. Although they can be processed like other organic polymers (e.g., polyesters, polyethylene), these polymers may have semiconducting or metallic properties as a virtue of their conjugated backbones. It is for this unusual combination of properties that conjugated polymer researchers received the 2000 Nobel Prize in Chemistry.[1]

Although conducting polymers have been investigated for many years, it is much more recently that researchers have begun to investigate the incorporation of inorganic elements into conjugated polymer backbones.[2,3] The addition of metals to conjugated organic polymers is anticipated to deliver new properties to the material. For example, the polymers may exhibit enhanced thermal stability necessary for increasing lifetimes in polymeric LEDs. Alternatively, the interaction of the metal's d-orbitals may modify the electronic properties of the conjugated polymers. Three key areas that conjugated metallopolymers appear promising are for the development of new catalysts, sensors, and electroluminescent materials.

Unfortunately, the preparation of conjugated metallopolymers has been hampered by the

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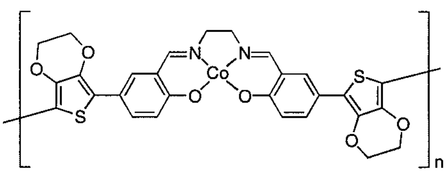
difficulty of preparing suitable monomers, of finding suitable polymerization methods, and of making the resulting polymer soluble. Solubility is often the most difficult problem to overcome as rigid metallopolymers are generally very insoluble. For this reason, most conjugated polymers have been synthesized on an electrode via electropolymerization.

In this paper, some prominent recent investigations of conjugated metallopolymers are described.

Catalysis

One clear application of conjugated metallopolymers is in new catalytic materials. Planar, conjugated molecules (e.g., porphyrins) that are known catalysts may be incorporated into conjugated polymers to modify their characteristics, or to combine the favourable electronic and optical properties of the polymer with the catalyst. Cobalt-containing polymers have excellent electrocatalytic properties and good stability. Electropolymerizable cobalt porphyrin and salen derivatives have been polymerized on an electrode (e.g., polymer **1**) and demonstrated to undergo highly efficient 4 electron reduction of oxygen to water without significant formation of H_2O_2.[4,5] Polymer **2**, formed by Ni(0) catalyzed coupling of 5,5'-dibromo-2,2'-bipyridine, is an active catalyst for the photoevolution of H_2 from water.[6] These reactions are relevant to energy conversion and storage.



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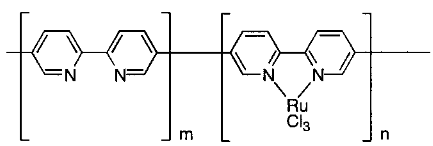

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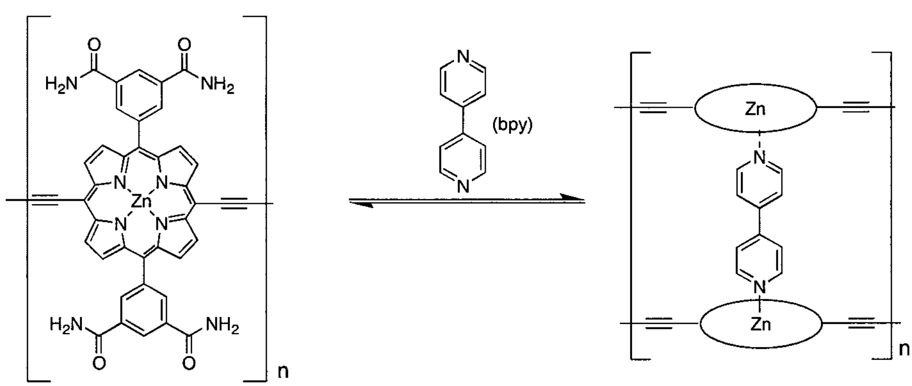
Sensing

In addition to catalysis, the availability of empty coordination sites on a conjugated metallopolymer offers the opportunity to affect the polymers' properties by coordination of a ligand to the metal site. In this way, a response may be measured and the polymer may serve as a sensor for Lewis bases. Polymer **1**, formed by electropolymerization of a cobalt salen with 3,4-ethylenedioxythiophene groups, behaves as a sensor for Lewis bases.[7] When exposed to pyridine or 2,6-lutidine, this polymer showed a significant reduction in conductivity, attributed to coordination of the Lewis base to the metal sites.

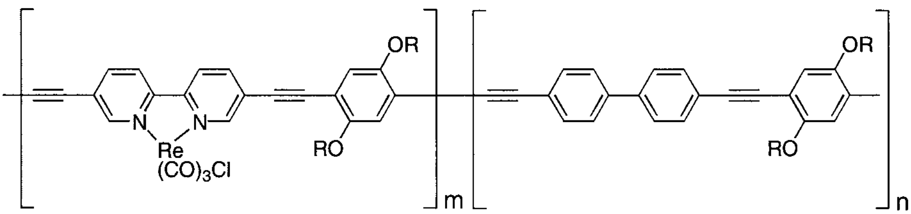
Another recent example that highlights the ability of conjugated metallopolymers to function as sensors, as well as supramolecular building blocks, can be found in the conjugated butadiyne-linked porphyrin polymers recently reported by Screen *et al.*[8] Polymer **3**, which is soluble in chloroform, undergoes changes in its optical spectrum when a Lewis base, such as 1,4-diazabicyclo[2.2.2]octane (DABCO), binds to the zinc atoms. Anderson and coworkers explored the use of rigid bidentate ligands (e.g., 4,4'-bipyridine) to link the linear polymers **3** into ladder polymers **4**. When the ratio of Zn:bpy is 1:0.5, the polymer forms a double stranded ladder structure which shows a considerable redshift (75 nm) relative to the coordinated linear polymer, indicating enhanced conjugation. The enhanced conjugation present in the ladder polymer, presumably due to restricted rotation of the porphyrins along the polymer chains, results in a 7-fold increase in the third-order nonlinear optical properties ($\chi^{(3)}$, measured by degenerate four-wave mixing, DFWM). With the addition of more 4,4'-bipyridine, the polymers may link theoretically into a 2-D grid. Such grids may show size- and shape-selective adsorption of analytes, making them useful for chemical sensors.



3 **4**

Electroluminescence

Conjugated polymers have received enormous attention for application in organic LED technology, and are now the basis of numerous start-up companies producing flexible displays. It is surprising that metal-containing conjugated polymers have received very little attention for their electroluminescent properties, particularly with growing attention to phosphorescent LED materials.[9] Such polymers may offer the ability to engineer the bandgap of the polymer on the basis of the metal choice and ligand variation. Schanze and coworkers have been investigating poly(phenyleneethynylene)s incorporating Re and Ru complexes on the backbone (e.g., **5**).[10] These polymers exhibit fluorescence from the conjugated polymer, as well as phosphorescence from the metal-to-ligand charge transfer (MLCT) band of the complex. The efficiency of energy transfer from the polymer to the metal complex depends on the concentration of metal centres along the polymer backbone. In this case, incorporation of transition metals into the conjugated polymer backbone dramatically affects the photophysical properties of the polymer.



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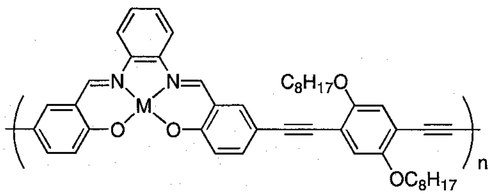
Lavastre *et al.* recently synthesized a large number of poly(phenyleneethynylene) polymers using a combinatorial approach.[11] Their results indicated that conjugated poly(phenyleneethynylene)s **6** incorporating Ni(salphen) or Zn(salphen) complexes, are highly luminescent and may be excellent candidates for metal-organic LED materials. These polymers are worthy of further study.



6 (M = Zn, Ni)

Our Research

It is clear that conjugated metallopolymers have interesting properties as a virtue of their conjugated organic backbone and transition metals. These materials may be important for developing new catalysts, nonlinear optical (NLO) devices, electroluminescent displays, or supramolecular architectures. We are investigating new soluble conjugated polymers that can be prepared on a bulk scale. Figure 1 shows a photograph of a new conjugated metallopolymer we have recently synthesized. This red polymer, which has a fully conjugated organic backbone with metals interspersed, is soluble in THF and readily forms free-standing films. We are investigating its electroluminescence.

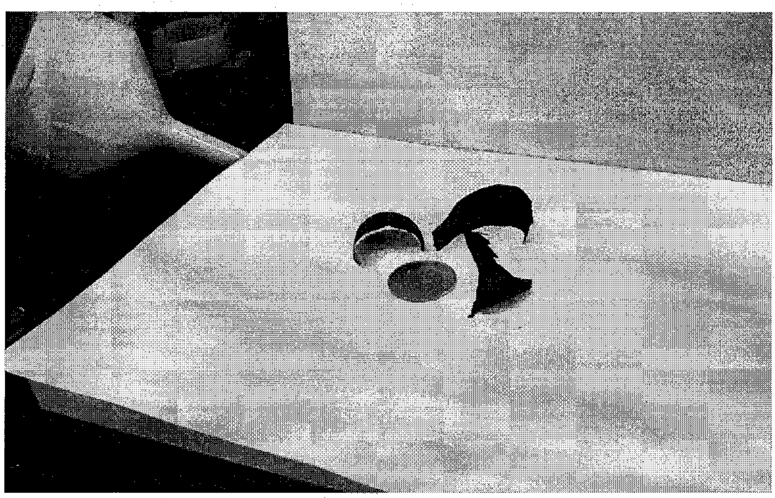


Figure 1. Photograph of thin films of a conjugated metallopolymer prepared in our laboratory. The coin is provided as a size reference.

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