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Poly(salphenyleneethynylene)s: A New Class of Soluble, Conjugated, Metal-Containing Polymers

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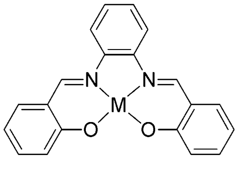
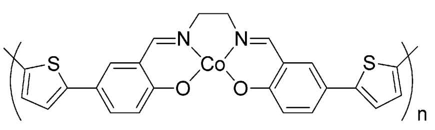
Polymers containing transition metals in the backbone have been the subject of extensive research as these polymers offer properties distinct from their individual organic and inorganic components.[1,2] Recent investigations show that metal-containing polymers may be useful as catalysts, sensors, and convenient ceramic precursors.[3−5] Incorporation of metals into conjugated polymers is anticipated to generate new materials with semiconducting properties that may be tuned via coordination of ligands to the metal center.[6,7] Moreover, rigid metal-containing components allow facile assembly of the metallopolymers into supramolecular structures.[8] Unfortunately, the synthesis of high molecular weight conjugated polymers containing transition metals has been hampered by synthetic difficulties and solubility problems.



1 (salphen)
M = metal



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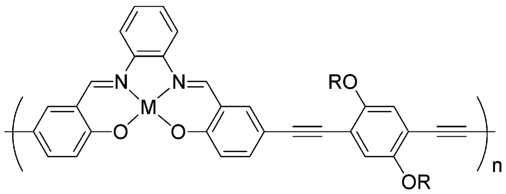
We identified Schiff base complexes (e.g., salphen **1**) as building blocks of new conjugated polymers and supramolecular structures. These molecules have attracted enormous attention as they are known to catalyze oxidation and epoxidation reactions and have recently been used as highly luminescent molecules for LED applications.[9,10] A few conjugated polymers/oligomers incorporating **1** have been prepared, but most are of low molecular weight or insoluble.[11,12] Others have prepared conjugated Schiff base polymers by electropolymerization (e.g., **2**), and these polymers have interesting redox behaviors.[13] Despite the attractive properties of poly(phenyleneethynylene)s (PPEs),[14] relatively few studies of metal-containing PPEs have been undertaken.[15] Recently, Lavastre et al. reported a large library of new fluorescent conjugated polymers from a combinatorial synthesis and screening method.[16] Among these polymers, the postulated structures **3** incorporating Schiff base Zn^{2+} and Ni^{2+} complexes were found to be highly luminescent and may be excellent candidates for applications in LEDs. We now report on our preliminary investigations of this new class of polymers.



3a (M = Zn, R = OC$_8$H$_{17}$) **4a** (M=Zn, R = OC$_{16}$H$_{33}$)
3b (M = Ni, R = OC$_8$H$_{17}$) **4b** (M=Ni, R = OC$_{16}$H$_{33}$)

We were very surprised that polymers **3** would be soluble in THF as our work in this area has shown that rigid, metal-containing polymers are difficult to dissolve. The synthesis of polymers **3** was repeated according to the method in the literature via Pd(0)-catalyzed Sonogashira cross-coupling of bromo- or iodosalphen complexes with 1,4-dialkoxy-2,5-diethynylbenzene.[16] In our hands, the polymers were insoluble in THF. In fact, when the substituents were changed from octyl in **3** to hexadecyl in **4**, the polymers obtained were still nearly insoluble in THF. It is quite likely that the luminescence measured in the literature was due to oligomers or remaining dibromosalphen complex, which is luminescent and soluble in THF.[17]

To synthesize soluble poly(salphenyleneethynylene)s (PSPEs), we prepared a new salphen ligand **7** possessing two dodecyloxy substituents and two iodo groups (Scheme 1). Compound **7** was prepared in 81% yield and isolated as a bright orange solid. Subsequent reaction of ligand **7** with Zn(OAc)$_2$, Ni(OAc)$_2$, and VO(acac)$_2$ yielded metal-containing monomers **8a**−**c**, respectively, in 87−96% yield. These were recrystallized 2−3 times to afford pure compounds; ^{1}H and ^{13}C NMR data, IR spectra, UV−vis spectra, mass spectra, and elemental analyses confirmed the composition and purity of these compounds. IR spectra of the monomers show an intense C═N stretching mode at 1603−1612 cm^{-1}. The V═O stretching mode of monomer **8c** (978 cm^{-1}) indicates that it is monomeric in the solid state.[18] UV−vis spectra of **8a**−**c** all show multiple bands between 200 and ~550 nm, the compounds appearing yellow, red, and orange, respectively, in the solid state. Unlike the fluorescent bromo analogues employed in the synthesis of **3**, monomers **8a**−**c** are nonemissive in solution or as solids.

The structure of **8b** was verified by single-crystal X-ray diffraction (Figure 1).[19] Crystals of **8b** suitable for X-ray diffraction studies were obtained by slow diffusion of Et$_2$O into a solution containing **8b** in CHCl$_3$. The structure shows the Ni^{2+} ion is in a square-planar geometry (mean deviation of 0.007(1) Å from the plane). The alkoxy substituents are extended and project from the plane of the didodecyloxybenzene ring at an angle of ca. 25°.

Sonogashira Pd-catalyzed cross-coupling of **8a**−**c** with **9** in THF/HN^{i}Pr$_2$ afforded the new polymers **10a**−**c** (Scheme 2) in high yields (77−86%) after precipitation.[20] These polymers, though very soluble in THF, were still insoluble in other solvents such as chloroform and toluene despite the additional alkoxy substituents. The

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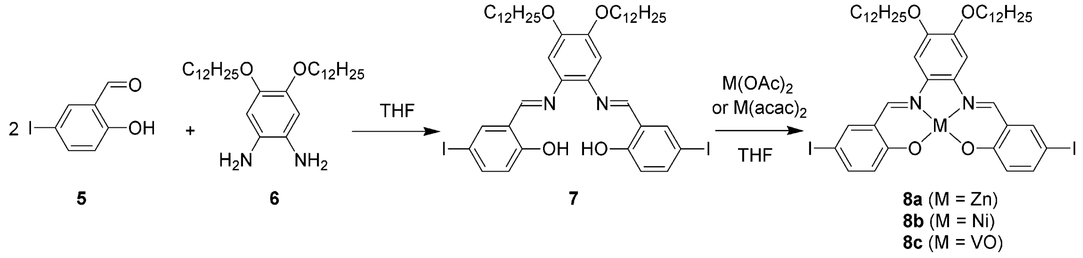
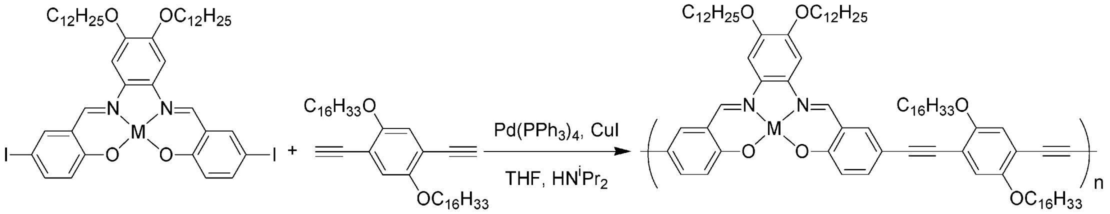
Scheme 1. Synthesis of Monomers 8a−c



8a (M = Zn)
8b (M = Ni)
8c (M = VO)

Scheme 2. Synthesis of the PSPEs 10a−c



8a (M = Zn)
8b (M = Ni)
8c (M = VO)

9

10a (M = Zn)
10b (M = Ni)
10c (M = VO)

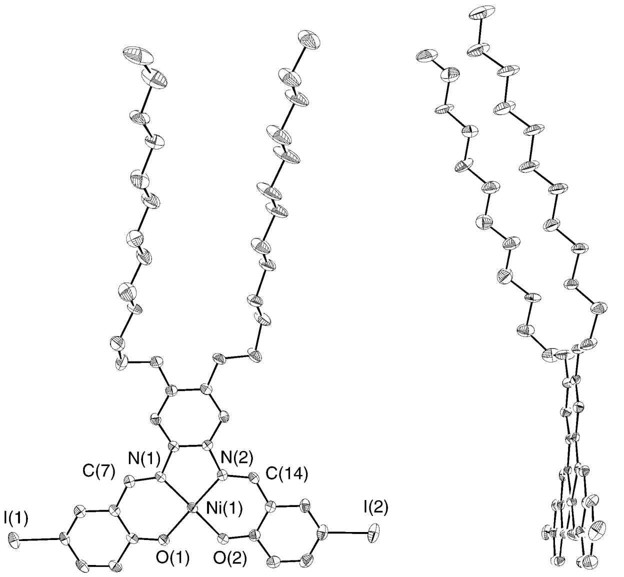


Figure 1. Single-crystal X-ray diffraction structure of **8b** perpendicular (left) and parallel (right) to the plane of the salphen ligand. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths for **8b**: Ni(1)−O(1) = 1.841(2) Å, Ni(1)−O(2) = 1.845(3) Å, Ni(1)−N(1) = 1.864(3) Å, Ni(1)−N(2) = 1.861(3) Å.

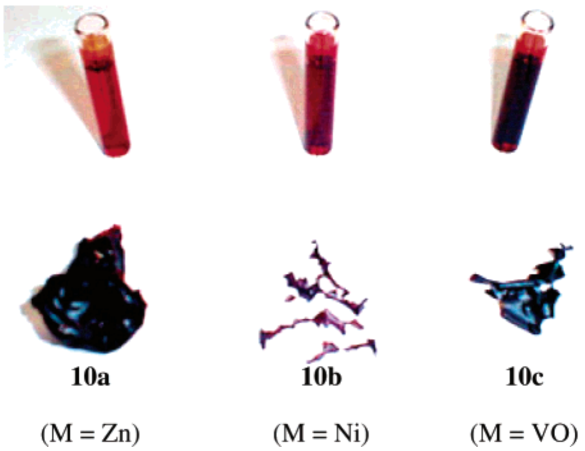


Figure 2. Photograph of thin films of polymers **10a−c**. In THF, the polymers form intensely colored solutions (ca. 10 mg mL^{-1}).

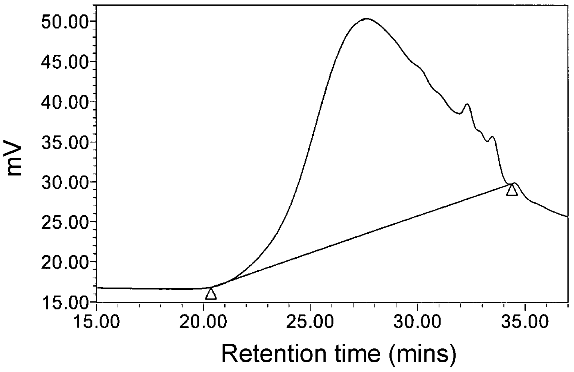


Figure 3. Gel permeation chromatogram for polymer **10c**.

polymers were purified by multiple precipitations from THF into methanol and acetone. The resulting red, film-forming polymers (Figure 2) were characterized by GPC and UV−vis, IR, and NMR spectroscopies.

The new PSPEs readily form free-standing films, indicating that their molecular weights are high enough to ensure substantial interchain entanglement. GPC of the PSPEs indicated that the polymers are essentially monomodal (molecular weights (M_w) of 37 000 for **10a**, 17 000 for **10b**, and 84 000 for **10c**, PDIs of 2−4) with shoulders visible corresponding to oligomeric components (Figure 3). The synthetic procedure for preparation of these polymers required optimization of temperature and solvent as bimodal distributions were characteristic of many samples prepared. In particular, the THF:HN^iPr_2 ratio had a strong effect on the molecular weights obtained. Wide-angle X-ray scattering (WAXS) analysis of polymer **10b** showed that this polymer is amorphous, exhibiting only an amorphous halo centered at 20° 2θ.

^{1}H NMR spectroscopy of polymers **10a,b** showed broad peaks corresponding to the alkoxy substituents on the polymers. The aromatic peaks could not be resolved as they are severely broadened. This broadening is probably due to slow tumbling of the rigid

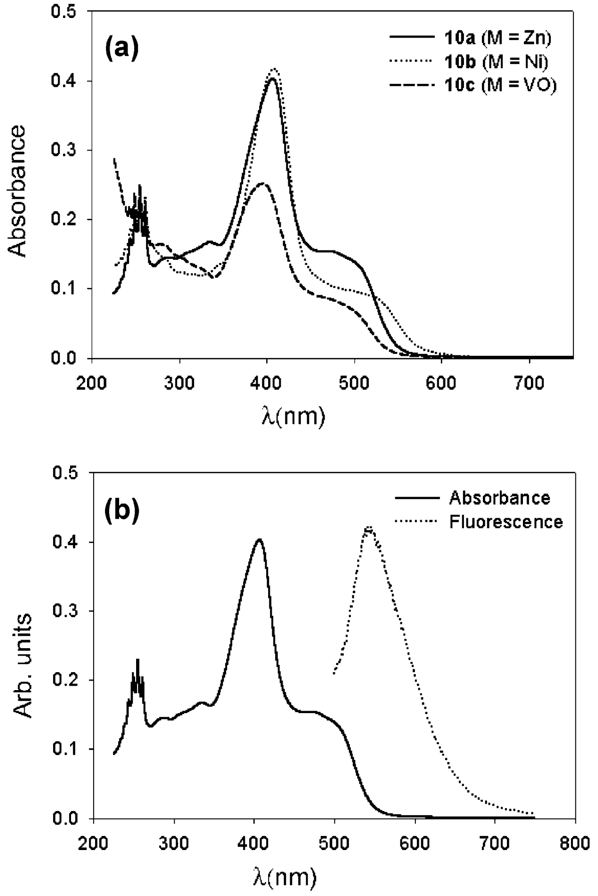


Figure 4. (a) UV–vis spectra for polymers **10a**–**c** in THF. (b) Emission spectrum of polymer **10a** in THF ($\lambda_{exc} = 406$ nm).

polymers in the very viscous solution.[21] However, the absence of sharp peaks indicates that there are no monomers or small molecules present in the samples. IR spectroscopy of the polymers indicated the starting material was absent, and the salphen moieties were still intact ($\nu_{C=N} \sim 1609-1612$ cm^{-1}). Moreover, the spectra of the polymers were more complicated than the starting monomers and consistent with an alternating copolymer made up of **8a**–**c** and **9**. A new peak at 2200 cm^{-1} was observed in each polymer; this is assigned to the C≡C stretching mode. In the case of polymer **10c**, the $\nu_{V=O}$ mode was observed at 998 cm^{-1}.

UV–vis spectra of the polymers (Figure 4a) show peaks that are broader than for the monomers. Notably, the spectra of **10a**–**c** show an enhancement of the peak near 400 nm relative to the monomers; this is probably due to the π–π* transitions associated with the conjugated backbone. In addition, they show a tail at ca. 450–600 nm that appears to be associated with the metal complexes since the tails are observed in the monomers.

We anticipated that PSPE polymers **10a** and **10b** would be highly luminescent in solution. Unfortunately, when illuminated with a UV source, polymer **10a** was only weakly luminescent (Figure 4b) and **10b** showed virtually no emission at all (**10c** was also nonemissive as expected for a paramagnetic polymer).[22] The luminescence spectrum of **10a** in THF shows a maximum at 546 nm; an excitation spectrum of **10a** is similar to the UV–vis spectrum, indicating that the luminescence arises from the polymer rather than an impurity. We postulate that energy transfer from the polymer absorption into localized states of the metal complexes is responsible for the poor emission properties of these materials.

In summary, we have prepared and characterized the first examples of soluble poly(salphenyleneethynylene)s. Preliminary studies of these polymers indicate that they are not good candidates for LED applications, but they may be suitable for new chemical sensors or assembling into nanogrids and other supramolecular structures. We are continuing to investigate the photophysical properties of these polymers.

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Supporting Information Available: Complete experimental details, representative spectra, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Crystal data for **8b**: red needle, $a = 21.247(2)$ Å, $b = 8.9428(4)$ Å, $c = 25.480(2)$ Å, $b = 111.589(3)°$, $V = 4501.8(5)$ Å^3, space group $P2_1/a$ (monoclinic), $Z = 4$, mol wt = 1025.52 for **8b**·MeOH $C_{45}H_{64}N_2O_5NiI_2$, $T = -100(1)$ °C, μ(Mo Kα) = 18.48 cm^{-1}, 9575 observed reflections, 611 variables, $R1 = 0.075$, $wR2 = 0.081$, GOF = 0.88.

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(21) Solutions containing as little as 1 wt % of polymer form highly viscous solutions. It was necessary to analyze very dilute solutions by NMR.

(22) The quantum efficiency of polymer **10a** was <0.1% in THF, using a solution of anthracene in EtOH ($\Phi = 0.30$) as a reference standard.

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