Optical Properties of M(II) Schiff-base Complexes Dispersed in Ethylene based Polymers

Massimiliano Boccia,[1] *Vincenzo Liuzzo,*[1] *Andrea Pucci,**[1] *Piero Narducci,*[2] *Giacomo Ruggeri*[1,3]

Summary: Several salicylaldiminate M(II) complexes of Nickel, Copper and Cobalt have been prepared and mixed with ethylene based polymers in order to prepare new composite materials with interesting morphological and optical properties by profiting of the presence of alkyl chains and push-pull substituents connected to the ligand structure. The phase dispersion behaviour of the binary films has been studied by scanning electron microscopy (SEM) and x-ray microanalysis, whereas the optical properties of the composite samples have been evaluated by UV-vis and fluorescence spectroscopy. The results in absorption have been analysed in terms of the anisotropy induced by the mechanical orientation of the polymer matrix and by the role of the metal centre according to the different strength of the complexes transition dipole moment. The luminescence behaviour have been discussed in terms of potential developments aimed at preparing polymeric supported Schiff base ligands for metal ions sensor applications.

Keywords: Bis(salicylaldiminate) M(II) complexes; composite films; ethylene based polymers; optical properties

Introduction

Polymer film with field responsive optical properties can be produced by dispersing into oriented polymers, light absorbing low molecular weight species such as highly conjugated organic molecules (organic metals) or metal clusters and complexes.[1–3]

The modulation of the chromophore structure by introducing linear or branched alkyl chains and the use of polyethylene matrices with different molecular weight and density, with the possibility to take advantages from different preparation routes, allowed to reduce or even eliminate the phase separation between the components.[4–6] Actually, the formation of chromophore aggregates as a consequence of their separated crystallization from the polymer matrix strongly limits their alignment along the macromolecular chains providing oriented films with poor dichroism.[5,7,8]

The efficient strategy based on coupling the optical and tailored structural properties of the organic moiety and the metal properties of the inorganic core with extremely high dispersion in polymer matrices suggested the preparation of different metal complexes from ligands bearing alkyl chains with various length, in order to provide the metal with a hydrophobic shell that allows a preferred dispersion into polyethylene matrix.

In this work, this approach and concepts are used to develop materials combining the excellent thermomechanical properties of polymers from 1-alkenes with the electro-optical properties of bis(salicylaldiminate) metal(II) complexes. Owing to the relatively simple preparation procedures of

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[1] Department of Chemistry and Industrial Chemistry, Via Risorgimento 35, 56126 Pisa, Italy
Tel: +39 050 2219270, Fax: +39 050 2219320
E-mail: apucci@dcci.unipi.it

[2] Department of Chemical Engineering Industrial Chemistry and Materials Science, Via Diotisalvi 2,- 56126 Pisa, Italy

[3] INSTM, Pisa Research Unit, Via Risorgimento 35, 56126 Pisa, Italy

bis(salicylaldimines) as Schiff bases, it is possible to obtain ligands of different design and characteristics by selecting appropriate reactants. The ligands most often applied are Schiff bases of o-hydroxyaromatic aldehydes with aliphatic and/or aromatic mono- and diamines.

Nickel, Copper and Cobalt with ligands providing the molecule with a permanent dipole moment are prepared and then dispersed by different preparation routes in polymer matrices thanks to the substantially hydrophobic shell around the metal atom(s) provided by the ligands selected geometry.

The results are discussed in terms of the effect of the molecular structure of the metal complexes on their dispersion into the polymer and on their modulated optical response both in absorption and emission induced by polymer orientation and the ligand conjugation.

Experimental

Materials

Diaminomaleonitrile and 4-(diethylamino)-salicylaldehyde (Aldrich) were used as received. 2,3-bis[[(2-hydroxy-4-(diethylamino)phenyl)(methylidene)]amino] 2-butenenitrile (*H_2L*), *NiL* and *CuL* has been synthesized as reported in literature.[9]

Ethylene-Vinyl Acetate copolymer (EVAc, Greenflex FF35), supplied by Polimeri Europa (Italy) and characterized by 9 wt.-% of vinyl acetate and melt flow index = 1.6 g/10 min (190 °C/2.16 kg, ISO 1133) were used as polymer matrices.

Synthesis of CoL

0.20 g of $Co(OAc)_2.4H_2O$ (0.80 mmol) was dissolved in 100 mL of degassed ethanol. A hot solution of H_2L (0.40 g, 0.87 mmol) and Et_3N (0.3 mL) in 20 mL of chloroform was slowly added under nitrogen atmosphere and the mixture refluxed for 20 min. The black precipitate was filtered off, dried and crystallized from chloroform/ethanol (0.37 g, 0.71 mmol, yield 88%). FT-IR (KBr): 1613 cm^{-1} ($\nu_{C=N}$), 2211 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calc. $C_{26}H_{28}N_6O_2Co$: C, 60.58 %; H, 5.48%; N, 16.30%. Found: C, 60.25%; H, 5.38%; N, 16.56%.

Film Preparation

Blend films containing 0.02–0.5 wt.% of H_2L or ML complexes in EVAc were prepared by dissolving in a vial the appropriate amount of the additive in about 2 mL of dichloromethane in the presence of polymer pellets. After slow solvent evaporation, the decorated pellets were melt-pressed in a press (Campana PM20/200) at 180 °C for 5 min. After removal from the press, the films were allowed to reach slowly room temperature ($\sim$5 °C min^{-1}). The films (thickness about 80–100 μm) were generally analysed after 2–3 days. Solid-state drawings of the host-guest films were performed on a thermostatically controlled hot stage at 100 °C. The drawing ratio (Dr), defined as the ratio between the final and the initial length of the samples, was determined by measuring the displacement of ink-marks printed onto the films before stretching.

Physico-Chemical Characterization

FT-IR spectra were recorded by a Perkin-Elmer Spectrum One spectrophotometer on dispersions in KBr. ^1H-NMR spectra were recorded with the help of a Varian-Gemini 200 on 5–10% $CDCl_3$ (Aldrich, 100.0 atom % D) solutions. NMR spectra were registered at 20 °C and the chemical shifts were assigned in ppm using the solvent signal as reference. The melting points were accomplished by a Reichert Polyvar optical microscope with crossed polarizers, equipped with a programmable Mettler FP 52 hot stage. Elementary analyses were made by microanalysis laboratory at the Faculty of Pharmacy, University of Pisa. The Scanning Electron Microscopy (SEM) analysis was performed with a Jeol 5600-LV microscope, equipped with Oxford X-rays EDS microprobe, instrument at the Chemical Engineering Department of Pisa University. Optical absorption studies were carried out in dilute ($5 \cdot 10^{-6}$ M) solutions with a

Perkin-Elmer Lambda 650, or on polymer films in linearly polarized light by mounting motor-driven Glan-Taylor linear polarizers.

Fluorescence spectra were recorded under isotropic excitation with the help of a Perkin-Elmer Luminescence spectrometer LS50B equipped with motor-driven linear polarizer on the detection side. The position of the sample was adjusted in the direction of the excitation beam in such a way that the optical axis of excitation and emission crossed in the film plane.

The films roughness was diminished, using ultrapure silicon oil (Poly(methylphenylsiloxane), 710 ® fluid, Aldrich) to reduce surface scattering between the polymeric films and the quartz slides used to keep them planar. In the analysis of the absorption and emission data, the scattering contribution was corrected by the use of appropriate baselines. The fitting procedure was performed by using Origin 7.5, software by Microcal Origin®.

Results and Discussion

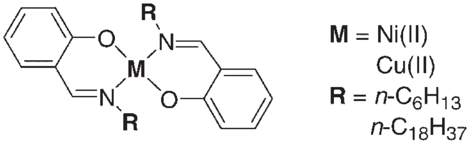
Metal complexes such as Bis(salicylaldiminate)metal(II) complexes have been widely investigated since the second half of the last century, due to the easy preparation and modulation of their structural and electronic characteristics by changing the nature of the substituents on the imino and aromatic moieties, respectively.[10] Bis(salicylaldiminate) metal(II) complexes with long alkyl chains and Salophen complexes were prepared by the incorporation of metals(II) on substituted salicylaldehydes with *o*-phenylenediamine according to literature procedures[11–14] (Figure 1).

All the prepared non-centrosymmetric complexes are known to be planar[15] and thermally stable and are widely studied as materials for nonlinear optical applications and more generally as precursors for the fabrication of conjugated materials to be employed as opto-electronic devices.[16–18] The ligand functionalization with long and linear alkyl chains was introduced to ensure the complexes good phase dispersion into polyethylene matrix.[3] The Bis(salicylaldiminate) metal complexes were successively mixed (2–3 wt.-%) with Ultra High Molecular Weight PolyEthylene (UHMWPE) by solution-casting and the phase dispersion behaviour of the binary films investigated by scanning electron microscopy (SEM).[3,19] SEM micrographs taken for 3 wt.% M(II) bis(salicylaldiminate) and M(II) Salophen complexes dispersed into polyethylene films revealed good dispersion behaviour of the metal complexes into the polymer matrix since no molecular aggregates are detectable at the polymer film surface. SEM investigations coupled with X-ray microanalysis were also performed on the section of the same films. In all cases, a preferential distribution of the metal complex close to the surface exposed to air, in the first 10 μm thick layer approximately, was observed as similarly reported for terthiophene chromophores dispersed in polyethylene films and attributed to a mass effect during solvent evaporation.[2,4,6]

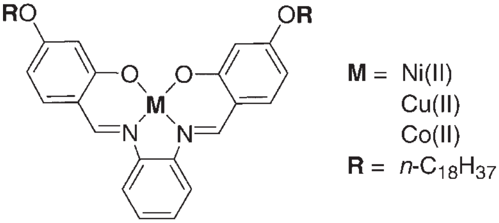
For M(II) bis(salicylaldiminate) complexes dispersed into PE films, additional investigations based on Differential Scanning Calorimetry (DSC) evidenced the fundamental role of the octadecyl alkyl chains (n-$C_{18}H_{37}$) linked to the ligand structure on conferring the metal complex high compatibility with the polymer matrix even at high concentration (≈12 wt.%).[3]

The binary films were successively oriented by thermo-mechanical stretching up to 30 times the original length of each tape at a temperature close to, but below, the melting temperature of the polymer (130 °C).

The opto-electronic properties of the metal complexes were studied in terms of their sensitivity to polymer matrix orientation. UV-vis spectra were recorded by irradiating oriented UHMWPE films containing the 3 wt.% of M(II) complexes with a linearly polarized light respectively parallel (0°) and perpendicular (90°) to the drawing direction. The UHMWPE films containing the M(II) bis(salicylaldiminate)



M(II) Bis(salicyldiminate)



M(II) Salophen

Figure 1.
Bis(salicylaldiminate) Metal (II) complexes: chemical structure.

complexes showed absorption spectra with maxima in the visible wavelength range connected to the π-π∗ and n-π∗ electronic transition. As expected, concerning the non linear structure of such complexes, very poor dichroic behaviour was observed.[3] The poor influence of the angle between the polarization direction of the exciting radiation and the drawing axis on the absorption could be probably attributed to the low directionality of the complexes transition dipole moment and to the almost centrosymmetric structure of bis(salicylaldiminate) derivatives that confer them very low orientations also at high drawing ratio. Analogously, the dichroic performances were also investigated for oriented PE films containing the M(II) Salophen complexes, characterized by a similar structure of the bis(salicylaldiminate) derivatives, but increased conjugation of the ligand moiety. The polarized UV-vis spectra of the PE films containing the 3 wt.% of the M(II) Salophen complexes were characterized by a particular dichroic behaviour of the absorption band located in the range from 400 to 500 nm. This absorption is attributed to the charge-transfer (CT) transitions from the excited filled d orbital electrons of the metal to the empty π∗ orbitals of the imine chromophore of the ligand[20] and is demonstrated to be responsible for the non-linear optical response of the metal complexes.[21] The particular anisotropy of the d-π∗ transition band reflects the preferential orientation of some M(II) Salophen chromophores along the drawing direction of the film. The insertion of the aromatic nuclei on passing from bis(salicylaldiminate) to Salophen ligand did not change the phase behaviour of the derived M(II) complexes into polyethylene but strongly contribute to the special dichroic behaviour of the oriented PE films.

In connection with those findings, we tried to confer the organic moiety the highest conjugation degree by introducing in its structure push and pull substituents as diethylamino and cyano groups respectively, in order to exploit the optical properties of the ligand (H_2L, Figure 2) both in absorption and in emission.

Due to the high conjugation degree and the absence of a hydrophobic shell around the ligand, H_2L and cobalt, nickel and copper ML complexes showed very low compatibility in PE films prepared by solution-casting. Very well homogeneous films were on the contrary prepared by processing in the melt polymeric pellets

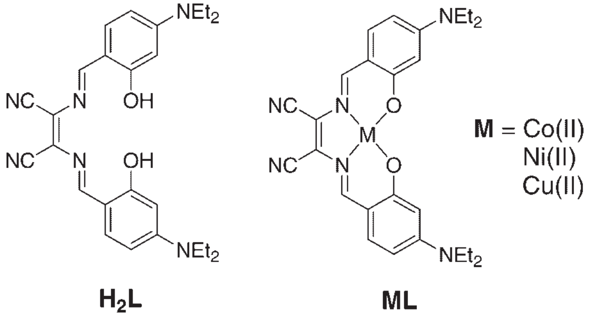


Figure 2.
New salicylaldiminate derivatives: chemical structure.

based on Ethylene-Vinyl Acetate copolymer ($EVAc_9$, containing 9% by mol of vinyl acetate groups) covered by H_2L and ML complexes. The presence of vinyl acetate units in the macromolecular backbone should help the formation of dipole-dipole interaction between the components' mixture thus improving the phase dispersion behaviour of M(II) complexes in the continuous matrix.

SEM micrographs taken for 3 wt.% H_2L and 3 wt.% ML (in Figure 3, top, we

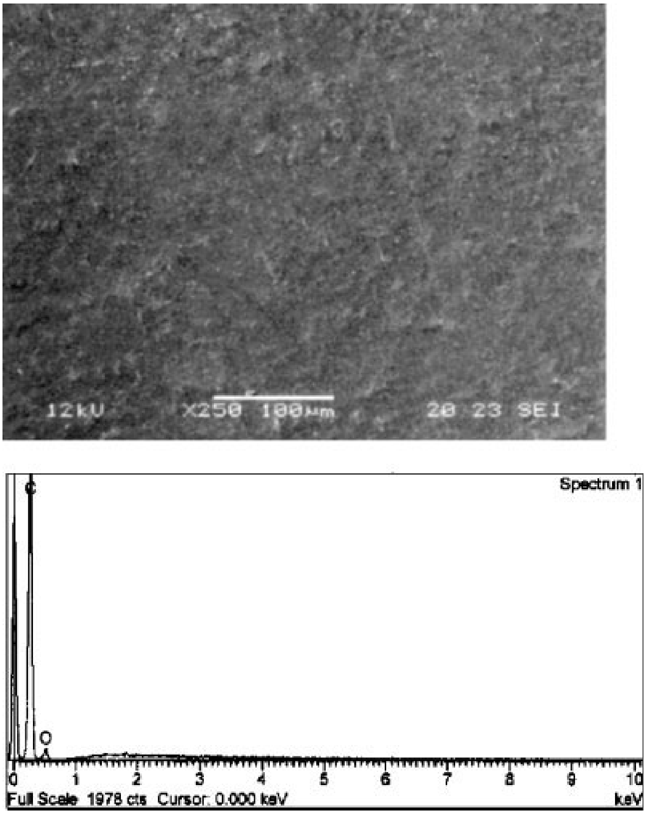


Figure 3.
SEM micrograph of 3 wt.% CuL/ $EVAc_9$ film (top) and energy dispersive (EDS) spectrum of the film polymer surface (bottom).

reported the results obtained for CuL) polyethylene films revealed a good dispersion behaviour of the metal complexes into the polymer matrix. No molecular aggregates are actually detectable at the polymer film surface. The x-ray energy dispersive spectra (EDS)[22] obtained in analyzing the film surface of the film containing the CuL complex did not display at 0.93 and 8.05 keV (Figure 3, bottom) the typical L_α and K_α lines of Copper indicating the dispersion of the complex down to the instrument resolution. All the composite films displayed similar phase behaviour between the ML complexes and the polymeric continuous matrix.

The SEM investigations were also performed on the section of the same films (Figure 4).

In all cases, the SEM micrographs performed on the films sections did not show the presence of any chromophore aggregates indicating the efficiency of the preparation method on providing highly compatible composite films.

The binary films were successively analyzed in terms of their opto-electronic properties by UV-vis and luminescent spectroscopy. UV-vis spectra of H_2L or ML complexes dispersed into $EVAc_9$ films (Figure 5) were found to be rather similar and dominated by the broad molecular π-$\pi*$ transition of the organic moiety centred at about 550 nm.

In fact, also in the case of ML/$EVAc_9$ composites this absorption is still predominant and characterized by a wider structure. Nevertheless, an additional absorption band is observed at lower wavelengths probably to be attributed to the metal-ligand charge-transfer (CT) d-$\pi*$ transition band.[9]

On the contrary, a completely different optical behaviour were registered in emission between H_2L/$EVAc_9$ and ML/$EVAc_9$ films (Figure 6). $EVAc_9$ film containing the 0.5 wt.% of H_2L showed a very brilliant homogeneous emission all over the surface with emission maximum pointed at about 580 nm, confirming the high level of compatibility between the components mixture as well.

In the case of ML/$Evac_9$ composites, the luminescent properties showed by the organic chromophore dispersed in the continuous polymer matrix resulted completely suppressed probably due to the effective quenching operated by the metal.

Fluorescence quenching by metals represents today an important feature for the development of fluorogenic and chromogenic chemosensors for the detection of heavy metal ions in many environments.[23] Generally, a typical fluorescence lifetime

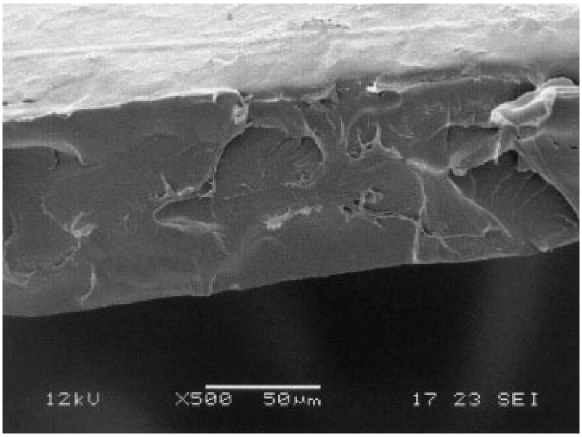


Figure 4.
SEM micrograph of the section of a 3 wt.% CuL/ $EVAc_9$ film.

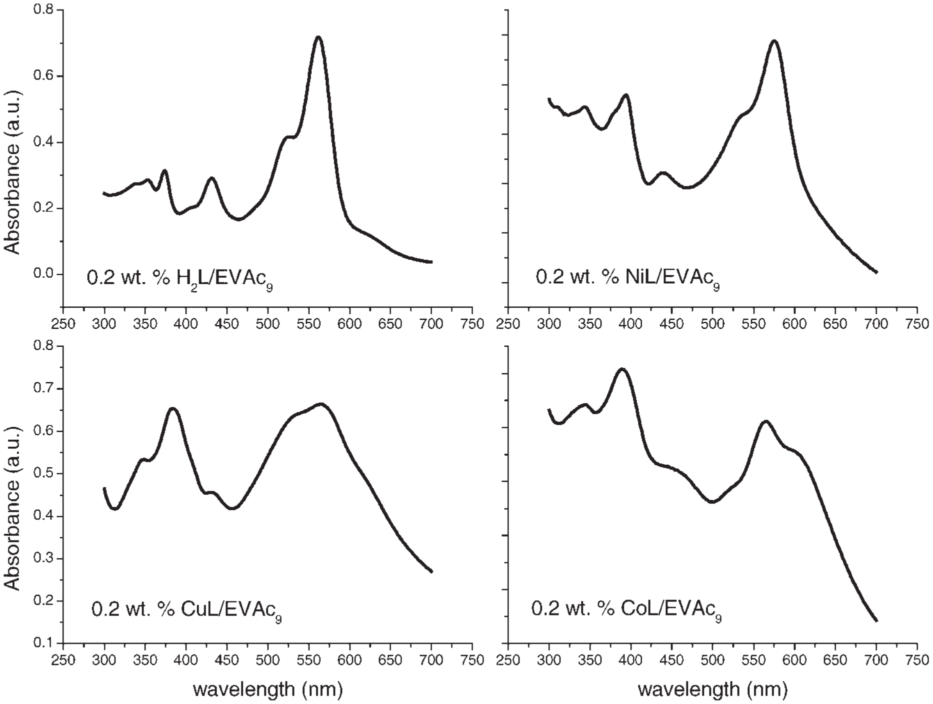


Figure 5.
UV-vis absorption spectra of 0.2 wt.% H_2L/ or ML/$EVAc_9$ composite films.

sensor consists of fluorescent dye molecules (a fluorophore) embedded in a matrix such as a sol-gel glass or porous polymer, but with access to either the analyte or physical variable to be detected. Analogously, in our case the fluorescence of the organic salicylaldiminate nuclei results strongly affected by the presence of Co(II), Ni(II) and Cu(II) (differently from recent luminescent studies regarding Zinc(II) complexes[24]) and suggest attractive and potential developments devoted to the preparation of polymeric supported Schiff base ligands for metal ions sensor applications.

Conclusions

Salicylaldiminate Nickel(II), Copper(II) and Cobalt(II) complexes were prepared by functionalizing the ligand moiety with long and linear alkyl chains able to confer the metal complex a good compatibility with the polyethylene matrix. The strategy based on increasing the optical properties by extending the conjugation path of the molecule was here applied modifying the ligand structure with the introduction of a phenyl ring. The insertion of this aromatic unit did not change the phase behaviour of the complexes in polyethylene with respect to M(II) bis(salicylaldiminate) complexes but, on the other hand, strongly contributed to the increase of the organic moiety conjugation leading to materials characterized by a special anisotropy of the charge-transfer transition band.

The further extension of the conjugation degree of the salicyladiminate ligand by introducing push and pull groups provided scarcely miscible M(II) complexes in polyethylene and forced the modification of both the polymer matrix and the films preparation procedure. Highly compatible $EVAc_9$ composite films were efficiently prepared by blending in the melt 0.2–

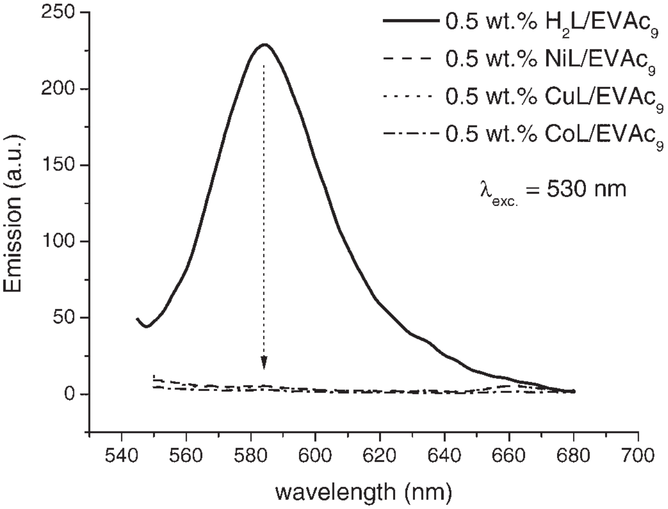


Figure 6.
Emission properties of 0.5 wt.% H_2L/ or M(II)L/$EVAc_9$ composite films.

0.5 wt.% of Nickel(II), Copper(II) and Cobalt(II) complexes. The optical properties of these films are dominated in absorption by the molecular π-π∗ transition of the ligand but resulted strongly different in emission due to the quantitative quenching of the luminescent by the metal.

These results reported here provide an excellent starting basis for the preparation of polyolefin composite films with molecularly dispersed metal complexes where the supramolecular interactions between the dispersed phase and the continuous matrix is confirmed by the optical response both in absorption and in emission.

The presence of these metal species with a controlled morphology can be considered as a way to prepare polymer films showing new optical properties for sensor applications.

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