

“Novel Nanomaterials as Temperature Sensors in Food Packaging Industry: Fe(II) Coordination Complexes Exhibiting Spin Crossover Phenomenon (SCO) in Food Packaging Polymers”

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ABSTRACT

The food quality, in terms of the consumers' safety, constitutes nowadays a vital issue of great concern. To that end, “smart” food packaging materials exhibiting sensor-type properties, play a key role. Spin-Crossover (SCO) is a well-known phenomenon of a number of coordination complexes.^[1-2] One of the main characteristics of SCO complexes, is that they exhibit temperature-dependent drastic colour changes accompanied by spin state conversion. The main focus of our research is the development and the in-depth study of low nuclearity Fe(II) SCO coordination complexes for potential use as sensors in refrigerated food packaging materials.^[3]

The coordination complexes developed were characterized using various techniques (Raman, ATR, p-XRD, UV/Vis and SEM), which revealed their morphological, optical and structural properties. Temperature-dependent and low-frequency Raman experiments played a significant role for the meticulous examination of the SCO phenomenon. For practical reasons a second step of our efforts was the incorporation of the same materials in conventional food packaging polymer matrices (PLA, PS) and the verification of their functionality in the composites. Finally, migration release studies of the sensors from the polymer matrix in food simulants were performed in order to examine the suitability of these materials according to EU regulations on “plastic materials and articles intended to come into contact with food”.^[4]

INTRODUCTION

The design, isolation and characterization of bistable molecules for use in devices are an important goal in modern science. Spin-crossover (SCO) coordination complexes^[5-6] can exhibit molecular bistability and are ideal candidates as the active components in several devices, for example, in sensors, memory storage units, displays or actuators. The molecular bistability results from the fact that they can undergo switching between two electronic states that differ in the number of unpaired electrons -high spin (HS) and low spin (LS)- by external stimuli such as changes in temperature or pressure, light irradiation or presence/absence of guest molecules, in a detectable and reversible way. Octahedral Fe(II) complexes, usually with six N donor atoms, are the most studied SCO systems, because they present the largest possible change in magnetic response, from a paramagnetic HS state with 4 unpaired electrons per metal site to a diamagnetic LS state. Since ligand vibrational modes can be affected by the spin state of the metal ion, variable-temperature Raman spectroscopy is an important tool for monitoring the SCO event.^[3,7] The vibrational modes most affected by the change in spin state are the stretching and bending vibrations associated with the metal-ligand bonds.

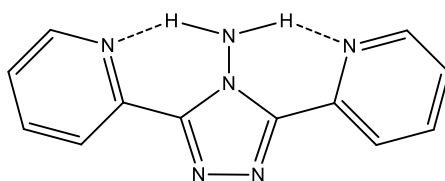
The main goal of this work is to emphasize the utility of Raman spectroscopy in the investigation of SCO complexes, since Raman scattered light can be collected upon *in situ* dynamic measurements, e.g. light-, temperature-, pressure-, magnetism-induced, revealing the probed structure at molecular level. Apart from the typical structural characterization of the materials and despite the lack of associated results in the literature, Raman spectroscopy may also provide indirect information related to the HS species population as a function of relevant external stimuli. Moreover, Raman instrumentation is more widespread than magnetic measuring devices and may allow focus on single monocrystals of these systems that could provide specific and valuable related

vibrational information. In this context, phase transitions in solid samples can be revealed by the Raman effect due to the different vibrational modes accounted for pertinent crystals symmetry; Raman spectra have already served for the construction of phase transition diagrams of materials.^[8] The exploitation of the advantages deriving from Raman scattering for a broad class of materials and applications, has led our group to develop appropriate setups for the Raman study of samples at high and low temperatures.^[8-10]

The bibliographically known complexes $[\text{Fe}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{abpt})_2]$ and $[\text{Fe}^{\text{II}}(\text{SCN})_2(\text{abpt})_2]$, where abpt is 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (Scheme 1) were extensively examined through Raman spectroscopy, while other characterization techniques acted also cooperatively. The structural characteristics and the bibliographically known magnetic properties of the complexes^[11-14] will be briefly mentioned in the “Results and Discussion” section below.

The long-term goal of this project is to introduce SCO complexes with suitable features (convenient $T_{1/2}$ value, abrupt spin transition) as temperature sensors for refrigerated food packaging materials, an application possibility which is still at its infancy. Food packaging industries are already focused on the development of new technologies for hybrid food packaging materials with “intelligent” characteristics (sensing ability, oxygen scavenging, etc.), very useful for the accreditation of the food quality. The exploitation of SCO complexes for sensing applications is currently a challenging target.^[15] To that end, the incorporation of SCO systems in polymeric food packaging materials (PLA, PS) was performed. The preservation of the SCO transition after the incorporation in the polymer matrix as well as the possibility of migration into food simulants was also studied.

Scheme 1. Structural Formula of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole, abbreviated as abpt



EXPERIMENTAL

Complex $[\text{Fe}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{abpt})_2]$ (complex **1**) was prepared in three different (nano)particle sizes (~300 nm, ~80 nm, ~20 nm) by a modified procedure of a method already reported.^[11-12] With analogous alterations on the literature synthesis^[13-14] of complex $[\text{Fe}^{\text{II}}(\text{SCN})_2(\text{abpt})_2]$ (complex **2**), nanowires (Diameter: 50-120 nm, length: >1 μm) of the material were isolated.

Raman Studies. Raman backscattering spectra were collected using the T-64000 model of Jobin Yvon (Horiba group) excited with a He-Ne laser (Optronics Technologies S.A. model HLA-20P, 20 mW) operating at 632.8 nm. The intensity of the laser excitation on the samples was kept low at around 0.4 to 0.8 mW in order to avoid any influence on spin distribution due to local heating. Dispersion and detection of the Raman scattered photons were performed by either a 600-groove/mm or an 1800-groove/mm (high resolution spectra, <2 cm⁻¹ for the wavelength of 632.8 nm) grating and a symphony II 2D CCD detector (liquid nitrogen-cooled at 140 K), respectively. Instrument calibration was initially carried out by using the standard 520.5 cm⁻¹ Raman peak position of Si and additionally by regularly collecting the Ne lamp spectrum at the spectral windows of interest. Temperature-dependent Raman spectra, employed for the study of the SCO behavior of the samples, were collected using a temperature-controlled stage, THMS600/720, adapted to the Raman instrumentation. The temperature range which can be reached by this setup is -196 to 600 °C; a cooling LNP95 pump was used. The cooling rate of the samples was 10 K/min. The temperature controller of the THMS600/720 stage maintained the temperature fixed during each measurement, with a stability better than 0.1 °C.

RESULTS AND DISCUSSION

In the following “Results and Discussion” part, the analysis of the Raman experiments results are elaborated for the two complexes.

Raman Studies of Complex 1 (in the form of nanoparticles of ~300 nm)

Figure 1a shows the low frequency Raman spectra of complex 1 at four different temperatures (room temperature, 223 K, 123 K and 83 K). Remarkable spectral changes were noticed, attributed to structural modifications that are caused by the SCO behavior of the sample (spin transition from the HS-HS to the LS-HS state). Two different Fe sites are present on the crystal structure of the complex, Fe1 and Fe2. Two new peaks at 162 and 457 cm^{-1} appear at low temperatures, whose intensity increases upon decrease of the temperature. These modes are characteristic of the LS $\{\text{Fe}^{\text{II}}\text{N}_6\}$ coordination sphere and are associated mainly with the bending vibration of the NFeN group involving the axial coordination $\text{Fe}^{\text{II}}\text{-N}_{\text{dicyanamido}}$ bonds (at 168 cm^{-1}) and a stretching vibration of the equatorial Fe-N bonds (at 463 cm^{-1}).

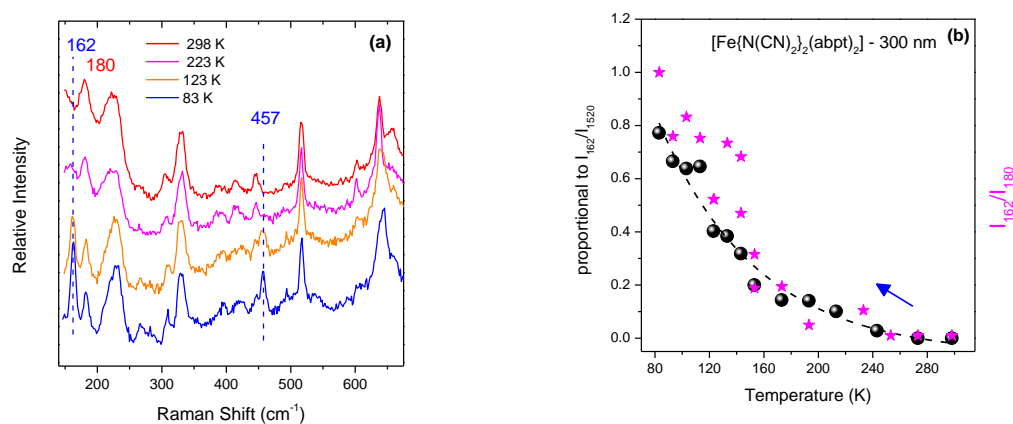


Figure 1. (a) Low-frequency Raman spectra of complex 1 (from top to the bottom) at room temperature (red line), 223 K (pink line), 123 K (orange line) and 83 K (blue line); the excitation wavelength is $\lambda_0 = 632.8$ nm. (b) Temperature dependence of the intensity ratios between the 162 and 1520 cm^{-1} peaks (circles), and between the 162 and 180 cm^{-1} peaks (stars). The arrow indicates the direction of the temperature variation.

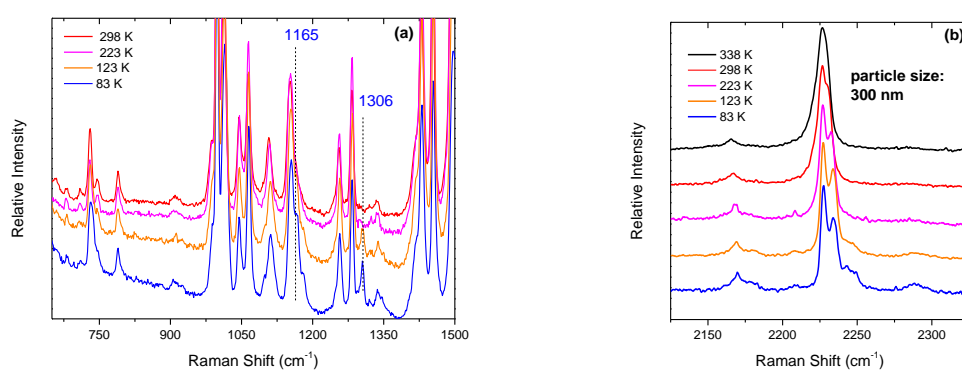


Figure 2. (a) Mid-Raman spectra of complex 1 (from top to the bottom) at room temperature (red line), 223 K (pink line), 123 K (orange line) and 83 K (blue line); the excitation wavelength is $\lambda_0 = 632.8$ nm. (b) From the top: Raman spectra of complex 1 in the wavenumber region 2125-2325 cm^{-1} at 338 K (black line), 298 K (red line), 223 K (pink line), 123 K (orange line) and 83 K (blue line); the excitation wavelength is $\lambda_0 = 632.8$ nm.

These two new peaks reflect the gradual formation of the LS form of the Fe1-containing molecules as the temperature decreases. Figure 1b depicts the temperature dependence of the intensity ratio between the 162 cm^{-1} peak and the 1520 cm^{-1} peak; the latter corresponds to an internal mode of

coordinated abpt (assigned to $\nu(\text{C}\equiv\text{C})/\nu(\text{C}\equiv\text{N})$ vibrations) which is independent upon temperature alterations. The intensity ratio is zero at 298 K and progressively increases as the temperature is lowered. The values of the intensity ratio at various temperatures are considered to be proportional to the population of the LS Fe1 sites. The temperature variation does not only critically affect the metal-donor atom bonds in SCO complexes; it also influences other bonds in the molecule, including those within the ligands. The Raman peaks associated with such bonds may also be used as markers of the spin transition. The impact of this secondary effect is imprinted for complex **1** in the spectral range dominated by the coordinated abpt vibrational modes, but more intensely on the stretching vibration of the $\text{C}\equiv\text{N}$ bond of the terminal dicyanamido ligands (Figure 2).

Raman Studies of Complex 2 (in the form of nanowires ~100 nm in diameter)

An analogous study was also performed for complex **2**. The $T_{1/2}$ value of the complex (180 K) allowed the fully monitoring of the transition (HS and LS species could be detected) *via* Raman spectroscopy. In Fig. 3, relevant magnetic susceptibility measurements covering the HS \leftrightarrow LS transition, already reported,^[13] are correlated with the corresponding derived in this work from temperature dependent Raman spectra. The pairs of bands selected for the calculation of the HS population were the 165/1330 cm^{-1} , the 1525/1505 cm^{-1} and the 2080/2125 cm^{-1} . The bands at 165 and 1525 cm^{-1} are due to LS species, while the bands at 1330 and 1505 cm^{-1} are independent upon temperature change (their intensity remains constant in the whole temperature range).

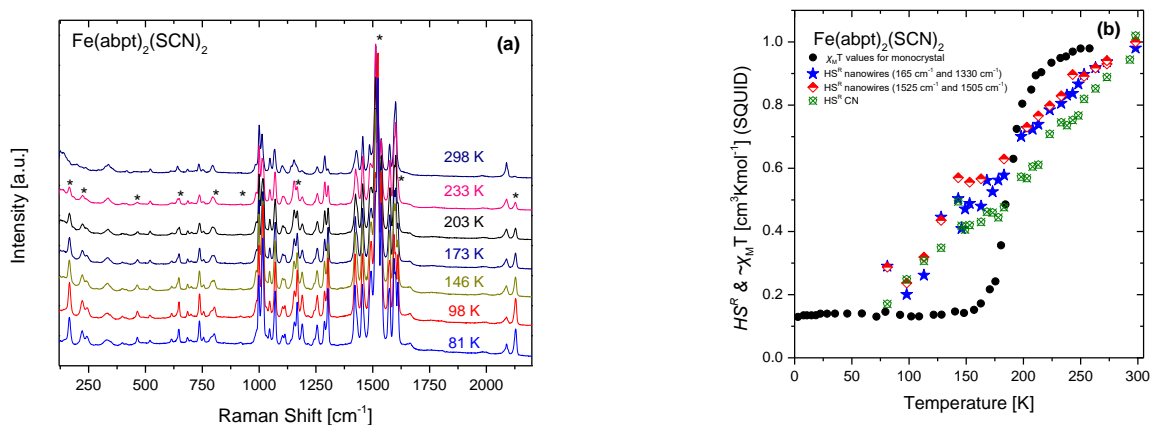


Figure 3. (a) Raman spectra of sample **2** at the various temperatures (298 K and 81 K are the higher and the lower temperature, respectively; from top to the bottom). Star symbols indicate the LS Raman peaks. The excitation wavelength is $\lambda_0 = 632.8$ nm. (b) (black circles) χ_{MT} values as a function of temperature deriving from magnetic susceptibility measurements for complex **2**, which were previously determined. In this work, the HS population, for the same complex, has derived from the ratio of the Raman integrated intensities (i) $I_{135}/I_{1330} \text{ cm}^{-1}$ (blue stars), (ii) $I_{1525}/I_{1505} \text{ cm}^{-1}$ (red rhombus) and (iii) $I_{2080}/I_{2125} \text{ cm}^{-1}$ (green squares) as a function of temperature. ($\lambda_0 = 632.8$ nm).

The results of the temperature dependent Raman study shown in Fig. 3 are in accordance with those of magnetic measurements concerning the transition temperature. As we can observe in this figure, the nanowired form of complex **2** resulted in the smoothness of the transition. This trend (especially for systems' alteration from micro- to nanoscale) has been widely reported in the past.^[16]

Incorporation of complex 1 in polymeric matrices (PLA, PS): Examination of the SCO behaviour ability of the sensor after its incorporation in food packaging & migration release studies

Two different polymer matrices were used during this study, polylactic acid (PLA), which is a biodegradable polymer used recently more and more for food packaging applications and the more “traditional” polymer widely used in food packaging, polystyrene (PS). The preparation of the films was based on the “non-destructive” film casting technique. The SCO behaviour of the sensor after its incorporation in the polymer was also examined *via* Raman spectroscopy, revealing analogous results with the bulk material. Since the potential use of these materials concerns the food packaging industry, the migration release study was necessary and extremely important. Two approaches for the migration release study were applied, *via* a migration cell and *via* a vial. The releasing medium was a solution of 50% v/v EtOH, which is considered as food simulant according to EU regulations. By comparing the two polymer matrices used, the migration release in the food simulant in the case of PS was found significantly lower compared to PLA for the same migration procedure followed. It is worth mentioned that in all cases the amount of the sensor released into the food simulant was much lower when the migration cell was utilized. This observation is attributed to the difference in the sink conditions that apply, which is related to the differentiation of the contact between the film and the food simulant.. The different results deriving from the two migration release study approaches revealed the necessity of using, whenever possible, the accredited migration cells. In Figure 4 representative release studies for a 2% w/w sensor/PLA film in a migration cell and by “vial method” (by dipping a piece of the polymeric film with specified dimensions in the food simulant solution) are presented.

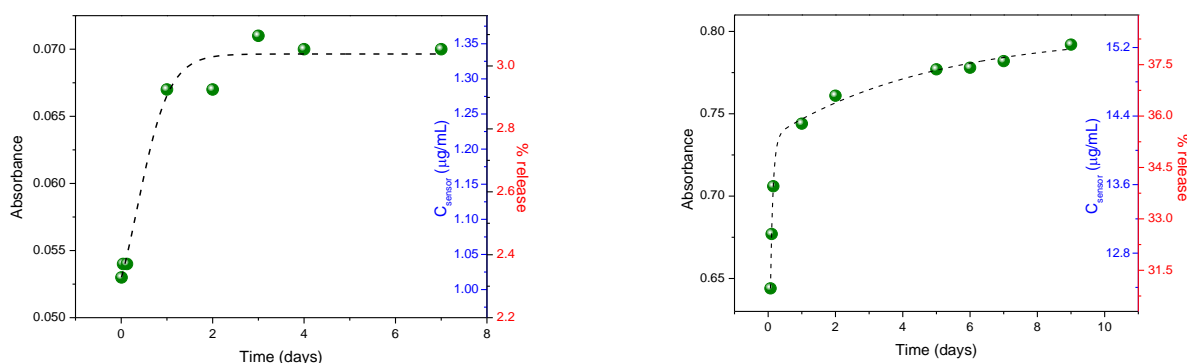


Figure 4. The absorbance and the corresponding concentration and percentage of the sensor released in the food simulant as a function of time (a) by using a migration cell for a 2% w/w sensor/PLA film and (b) in the case of a “dipping method” for the same film.

CONCLUSIONS

The main goal of the present work was the investigation of the SCO behaviour of Fe(II) mononuclear complexes which could potentially act as temperature sensors in refrigerated food packaging materials. The sensing ability would be based on the colour variation though the HS-LS transition of the complex. The SCO behaviour of the complexes $[\text{Fe}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{abpt})_2]$ and $[\text{Fe}^{\text{II}}(\text{SCN})_2(\text{abpt})_2]$ was examined in detail *via* Low-temperature Raman spectroscopy. Raman spectroscopy could provide numerous benefits in an accurate SCO behaviour monitoring, despite the fact it is/was considered to be a non-conventional technique for such an application. The incorporation of complex $[\text{Fe}^{\text{II}}\{\text{N}(\text{CN})_2\}_2(\text{abpt})_2]$ in conventional food packaging polymer matrices (PLA, PS) and the verification of their SCO behaviour in the composites were also investigated. Moreover, migration release studies of the sensor in selected food simulants (according to EU regulations) were also studied in order to examine the suitability of these materials.

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