

# $^{57}\text{Fe}$ Mössbauer probe of spin crossover thin films on a bio-membrane

Anil D. Naik · Yann Garcia

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**Abstract** An illustrious complex  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  (ptz = 1-propyl-tetrazole) (**1**) which was produced in the form of submicron crystals and thin film on *Allium cepa* membrane was probed by  $^{57}\text{Fe}$  Mossbauer spectroscopy in order to follow its intrinsic spin crossover. In addition to a weak signal that corresponds to neat SCO compound significant amount of other iron compounds are found that could have morphed from **1** due to specific host-guest interaction on the lipid-bilayer of bio-membrane. Further complimentary information about biogenic role of membrane, was obtained from variable temperature Mossbauer spectroscopy on a  $\sim 5\%$  enriched  $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$  salt on this membrane.

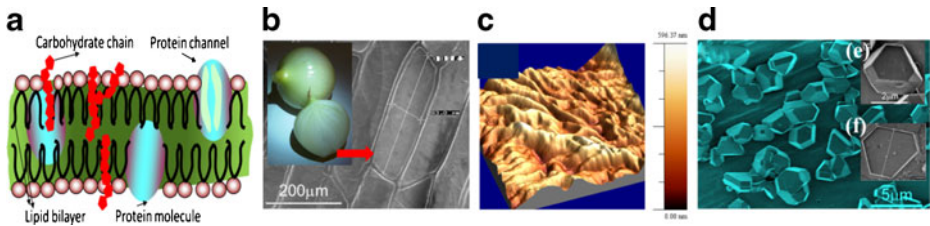
**Keywords** Spin crossover · 1-propyl-tetrazole · Thin films · Nanoparticles · Bio-membrane · Onion

## 1 Introduction

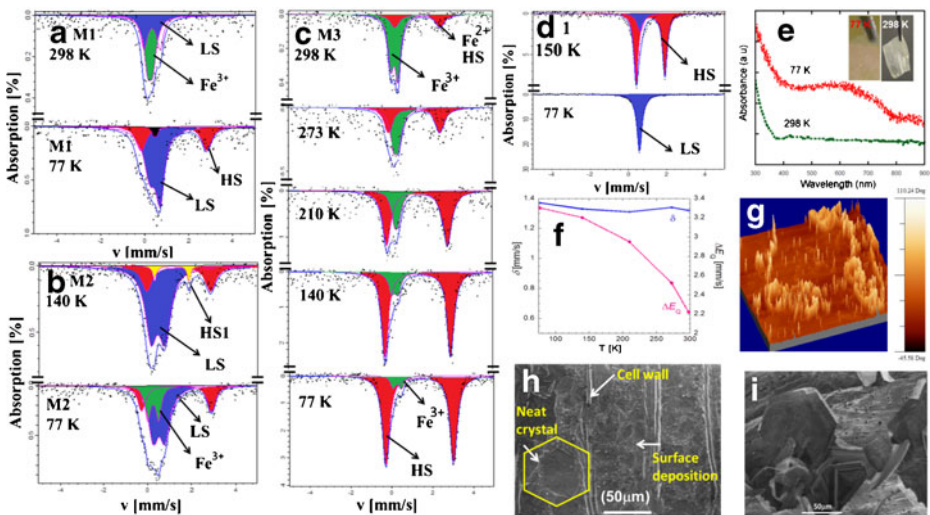
Currently there is an intensive research towards developing novel rational techniques for thin film deposition and nanoparticles synthesis of  $\text{Fe}^{\text{II}}$  spin crossover (SCO) materials that have foreseeable prospects in molecular electronics [1]. In an unique approach under green technology, we recently introduced an inner epidermis of onion bulb (*Allium cepa*) (Fig. 1a–c) as a novel support to grow single crystals (Fig. 1d) of desired size and for thin film processing of a SCO material [2]. This radical approach differs from the classical one using conventional supports like glass, quartz, Si-wafer etc. This hybrid functional material was also used as natural stencil in soft lithography, for the first time, to print nanodots (30–55 nm) on Si wafer [2]. As a proof of concept, we selected a thermochromic  $\text{Fe}^{\text{II}}$  complex,

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A. D. Naik · Y. Garcia (✉)  
Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L.  
Pasteur 1, 1348 Louvain-la-Neuve, Belgium  
e-mail: yann.garcia@uclouvain.be



**Fig. 1** **a** Model of membrane lipid-bilayer. **b** SEM image on onion membrane. **c** AFM image revealing surface inhomogeneity [2]. **d** SEM image showing dense crystal growth on **M1**. **e** SEM image on single metamorphosed crystal. **f** Neat hexagonal crystal grown on ITO support shown for comparison [6]



**Fig. 2** **a–d** Selected  $^{57}\text{Fe}$  Mossbauer spectra of **M1**, **M2**, **M3** and **1**. **e** Thermal SCO detected by Uv-vis [2], the inset showing thermochromism of the membrane. **f** Temperature variation of  $\delta$  and  $\Delta E_0$  for **M3**. **g** AFM image of **M1**. Elevated bright areas indicate presence of crystals [2]. **h** SEM image on dip coated **M2**. **i** SEM image of **M3**

$[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  (**1**) (ptz = 1-propyl-tetrazole), whose thermally and light-induced spin transition has been very well documented [3–5]. Thin films ( $\sim 25$  nm thickness) and nanoparticles/crystals ( $< 40$  nm– $3$   $\mu\text{m}$ ) of **1** were successfully produced on the membrane and the SCO was confirmed by Uv-visible spectroscopy and visual thermochromism (Fig. 2e) [2]. Scanning electron micrographs (SEM) of membrane with deposited crystals (**M1**) shows drastic morphogenesis to truncated hexagonal bipyramid (Fig. 1e) as opposed to neat hexagonal crystals grown on glass/ITO plates (Fig. 1f) [6] whereas membrane with thin film (**M2**) leads to neat hexagonal crystals along with thin film deposition (Fig. 2h). In continuation of this work, and for the first time  $^{57}\text{Fe}$  Mossbauer spectroscopy was explored not only to study intrinsic SCO on *Allium cepa* membrane but also to probe any possible metamorphosed iron complex entrapped in/over lipid-bilayer of the membrane (Fig. 1a) that could have escaped routine spectroscopic radar. The perspective of the present study not only assures

tremendous prospects in green chemistry under nanotechnology umbrella but is also expected to shed light on diverse important topics like transport mechanism across bio-membrane, bio-membranes in heavy metal retention from industrial effluents, iron uptake and trafficking in biological systems etc.

## 2 Experimental

**1** was synthesized according to the reported procedure [3]. Details about *Allium cepa* membrane (Fig. 1b) processing, loading and characterization of **1** on membrane, SCO operation were earlier described [2]. Membrane (**M1**) with sub-micron sized crystals of **1** and membrane with thin film (**M2**) were selected for the present study [2]. A significant deposition has occurred on **M2** surface with large neat hexagonal crystals being evidenced (Fig. 2h). A 5% enriched sample of  $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$  (**2**) was dip coated on the membrane to produce **M3**. Several pieces of **M1/M2** were stacked together for Mössbauer measurements in order to improve signal to noise ratio.

## 3 <sup>57</sup>Fe Mossbauer spectroscopy

Hyperfine parameters for **M1-3**, **1** and **2** are summarized in Table 1 and selected spectra are shown in Fig. 2a–d. At 77 K, the Mössbauer spectrum of **M1** shows three resonance signals with different quadrupole splitting: (i) a major signal (68 %) with  $\delta = 0.47(1)$  mm/s and  $\Delta E_Q = 0.47(1)$  mm/s which stems from low-spin (LS) **1** species, with a distorted octahedron, after adhesion on the membrane support. This observation confirms the SCO occurrence that was precluded from the color change to pink on cooling (Fig. 2e). (ii) Another quadrupole doublet with  $\delta^{\text{HS}} = 1.34(2)$  mm/s and  $\Delta E_Q^{\text{HS}} = 2.97(1)$  mm/s (28 %), which corresponds to the co-deposited iron salt **2** with a smaller quadrupole splitting compared to the powder sample (Table 1) indicative of a more distorted octahedron, as expected on the biomembrane support. (iii) a minor doublet (4%) with  $\delta = 0.48(3)$  mm/s and  $\Delta E_Q = 0.16(1)$  mm/s which point out to LS octahedra of **1** that are less distorted compared to the major species (Fig. 2a). At 298 K, the HS signal is no longer detected as a major fraction of  $\text{Fe}^{\text{III}}$  and LS  $\text{Fe}^{\text{II}}$  species dominate the spectrum. This result is consistent with the ones obtained on **M3** at r. t. for which **2** is hardly observed whereas a major ferric fraction is detected (Fig. 2c) due to the overestimation of these species at r.t. [7]. The situation is slightly different for **M2** at 77 K with detection of  $\text{Fe}^{\text{III}}$  species as observed for **M3** (Fig. 2c), which was prepared under similar conditions, along with signals of LS **1** and of HS **2**. A 140 K, co-deposited complex **2** is still observed along with LS **1**, whereas a weak doublet with  $\delta = 1.07$  mm/s and  $\Delta E_Q = 1.57$  mm/s, is now detected. It corresponds to HS **1** [3], which expectedly disappear at 77 K where the HS to LS crossover is complete.

In both deposition methods (leading to **M1** and **M2**), the remote possibility of fractional internalization of sensor, which might not be seen in its original form through the semi-permeable membrane, for instance as  $\text{Fe}^{\text{III}}$  species, cannot be excluded [8]. The membrane permeability might also be subjected to any kind of adverse effect under the working acid pH of 3–4 [2] and may facilitate iron ions to

**Table 1**  $^{57}\text{Fe}$  Mossbauer parameters of **M1**, **M2**, **M3**, **1** and **2**

Code T(K)	Parameters			
	$\delta$ mm/s	$\Delta E_Q$ mm/s	$\Gamma/2$ mm/s	Rel. area, Spin, oxi. state
<b>M1</b> 298	0.30(1)	0.73(3)	0.18(1)	41, LS-Fe <sup>II</sup>
	0.22(3)	0.24(1)	0.2(5)	59, Fe <sup>III</sup>
<b>M1</b> 77	0.47(1)	0.47(1)	0.24(1)	68, LS <b>1</b>
	1.34(2)	2.97(1)	0.27(1)	28, <b>2</b>
	0.48(3)	0.16(1)	0.12(1)	4, LS <b>1</b>
<b>M2</b> 140	0.43(3)	0.63(1)	0.32(5)	71, LS-Fe <sup>II</sup>
	1.39(1)	2.91(1)	0.29(1)	24, <b>2</b>
	1.07(1)	1.57(1)	0.11(1)	5, HS, <b>1</b>
<b>M2</b> 77	0.53(1)	0.54(5)	0.28(1)	56, LS <b>1</b>
	1.32(1)	3.19(3)	0.23(1)	23, <b>2</b>
	0.25(1)	0.49(1)	0.16(2)	21, Fe <sup>III</sup>
<b>1</b>				
298 [3]	0.91	1.05	–	100, HS-Fe <sup>II</sup>
150 <sup>a</sup>	1.13(3)	1.49(1)	0.14(5)	83, HS-Fe <sup>II</sup>
	0.59(2)	0	0.2 <sup>b</sup>	17, LS-Fe <sup>II</sup>
77 <sup>a</sup>	0.56(2)	0	0.16(2)	100, LS-Fe <sup>II</sup>
77 [3]	0.44	0	–	100, LS-Fe <sup>II</sup>
<b>2</b> <sup>c</sup> 298	1.26(3)	1.30(1)	0.14(5)	100 HS-Fe <sup>II</sup>
<b>2</b> <sup>c</sup> 77	1.38(4)	3.46(3)	0.18(6)	100 HS-Fe <sup>II</sup>
<b>M3</b> 298	1.32(5)	2.22(1)	0.26(1)	28, HS-Fe <sup>II</sup>
	0.18(1)	0.34(2)	0.16(1)	72, Fe <sup>III</sup>
<b>M3</b> 273	1.14(1)	2.52(2)	0.26(1)	49, HS-Fe <sup>II</sup>
	0.25(1)	0.26(1)	0.21(1)	51, Fe <sup>III</sup>
<b>M3</b> 210	1.31(4)	2.95(8)	0.25(6)	75, HS-Fe <sup>II</sup>
	0.30(7)	0.18(2)	0.2(1)	25, Fe <sup>III</sup>
<b>M3</b> 140	1.33(1)	3.2(3)	0.20(2)	83, HS-Fe <sup>II</sup>
	0.22(1)	0.32(1)	0.2(1)	17, Fe <sup>III</sup>
<b>M3</b> 77	1.37(8)	3.30(1)	0.21(1)	91, HS-Fe <sup>II</sup>
	0.26(6)	0.40(1)	0.16(7)	9, Fe <sup>III</sup>

$\delta$ : isomer shift (with respect to  $\alpha$ -Fe at 298 K);  $\Delta E_Q$ : quadrupole splitting;  $\Gamma/2$ : half width at half maximum

<sup>a</sup>**1** recrystallized from MeOH

<sup>b</sup>Fixed data

<sup>c</sup>Powder sample [10]

traverse the membrane. In this context, it is interesting to note the presence of K<sup>+</sup> ions in metamorphosed nanocrystals on **M1** [2].

This intriguing possibility prompted us to investigate the possible biogenic role of *Allium cepa* membrane on **2**, proposed here as a reference material, by recording a series of Mössbauer spectra at selected temperatures (Table 1, Fig. 2c), which indeed reveals interesting features. Spectrum of **M3** at 77 K is dominated by a quadrupole doublet with  $\delta = 1.37$  mm/s and  $\Delta E_Q = 3.30$  mm/s that matches very well with powder sample of **2** (Table 1). There is also a small amount of Fe<sup>III</sup> species which is due to iron oxidation. Indeed, the iron percentage in onion is too low (0.2 mg/100g of onion, 2%) to yield any inherent signal [9]. Subsequent spectra recorded upon warming up to 298 K indicate a decrease of

$\delta^{\text{HS}}$  and  $\Delta E_{\text{O}}^{\text{HS}}$  as expected (Fig. 2f). It has to be noted that even for the neat sample **2**,  $\Delta E_{\text{O}}$  (3.46 mm/s) at 77 K was drastically reduced to 1.30 mm/s at 298 K which is in agreement with a phase transition due to temperature dependent anion disorder [10]. The area fraction of  $\text{Fe}^{\text{III}}$  species in **M3** grew upon warming and dominates the r.t. spectrum which can be rationalized on the basis of the Debye temperature ( $\theta_{\text{D}}$ ) differences between ferrous and ferric ions [11] as HS ferric species tend to have a higher  $\theta_{\text{D}}$  than HS ferrous species [7]. Having confirmed by Mössbauer spectroscopy that no disproportion of **1** occurs, as already shown by X-ray powder diffraction and Raman data [2], we were interested to learn if the crystal field of **1** could have been affected by the deposition. This hypothesis is confirmed, by comparing the spin state properties of **M1/M2** with the one of the powder sample of **1** which has a transition temperature  $T_{1/2} \sim 135$  K, on warming from 77 K [4]. Thus, a LS state stabilization is observed as the SCO only starts at 140 K for **M2**. This situation may result from possible interactions with membrane organics, which may affect the immediate surrounding of the complex, thus modifying the crystal field, as much as non coordinated anions can do in a crystal lattice [1].

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