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Implementation of spin crossover compounds into electrospun nanofibers

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Abstract We synthesised a series of Iron(II)-triazole compounds and used the electrospinning procedure to incorporate spin crossover compounds (SCO) into polylactic acid polymer fibers. Composite fiber/SCO compounds of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ as well as $[Fe(Htrz)_2(trz)]BF_4$ were investigated via Mössbauer spectroscopy at 293 K and 77 K. The Mössbauer studies show that the spin crossover behavior is maintained in the polymer matrix.

Keywords Triazole · SCO · Iron complexes · Electrospinning · Mössbauer

1 Introduction

Miniaturization of electronic components has become increasingly important in recent years. Therefore it is a demanding task to develop electronic components from individual molecules and spin crossover compounds are becoming more and more interesting as potential materials for various nanoscopic applications [1].

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Spin crossover compounds are discussed as valuable sensor materials [2] or in data storage [3]. However, the individual addressing of these molecules is usually a problem for common technologies [4]. For this reason, spin crossover compounds were incorporated into various polymer fibers using the electrospinning technique, thus producing composite materials. The polymer fibers are intended to act as optical fiber and enable a simpler addressing of the spin crossover compounds. Furthermore the influence of the particle size of the compounds were investigated. Various spin crossover iron(II)-triazole compounds as well as iron(II)-triazole nanoparticles have been used. The spin crossover-polymer fiber composite materials were investigated, using Mössbauer spectroscopy. Our studies show that the spin crossover behavior of the molecules is maintained in the polymer fibers.

2 Experimental

We followed a synthetic route described in the literature [5]. Synthesis of the nanoparticles has been adapted from [6].

2.1 $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles

$Fe(BF_4)\cdot 6H_2O$ (1.012 mg, 3 mmol) was dissolved in 2.25 ml H_2O and added to a solution of Triton X-100 (15 ml), 1-pentanol (15 ml) and cyclohexane (60 ml). After 5 minutes a solution of NH_2-trz (756.8 mg, 9 mmol) in water was added. The reaction was stirred for 24 hours in inert atmosphere. To break the micro emulsion 75 ml of acetone was added to the reaction. The solution was centrifuged and the nanoparticles washed three times in ethanol.

Elemental analysis CHN (% calc.): C: 15.50 (14.96); H: 2.78 (2.51); N: 33.81 (34.89)

2.2 $[Fe(NH_2\text{-}trz)_3](BF_4)_2$

$Fe(BF_4)\cdot 6H_2O$ (337.39 mg, 1 mmol) was dissolved in 5 ml methanol and ascorbic acid (5 mg) was added. Afterwards a solution of NH_2-trz (252.2 mg, 3 mmol) in methanol (5 ml) was added. The solution was stirred for 24 hours. Afterwards the complex was filtrated and washed with methanol.

Elemental analysis CHN (% calc. for $[Fe(NH_2\text{-}trz)_3](BF_4)_2\cdot H_2O$): C: 14.51 (14.42); H: 2.82 (2.51); N: 33.17 (33.64)

2.3 $[Fe(Htrz)_2(trz)]BF_4$

$Fe(BF_4)\cdot 6H_2O$ (337.39 mg, 1 mmol) was dissolved in 5 ml methanol and ascorbic acid (5 mg) was added. Afterwards a solution of Htrz (207.21 mg, 3 mmol) in methanol (5 ml) was added. The solution was stirred for 24 hours. Afterwards the complex was filtrated and washed with methanol.

Elemental analysis CHN (% calc. for $[Fe(Htrz)_2(trz)]BF_4\cdot H_2O$): C: 19.84 (19.64); H: 2.23 (2.75); N: 34.74 (34.36)

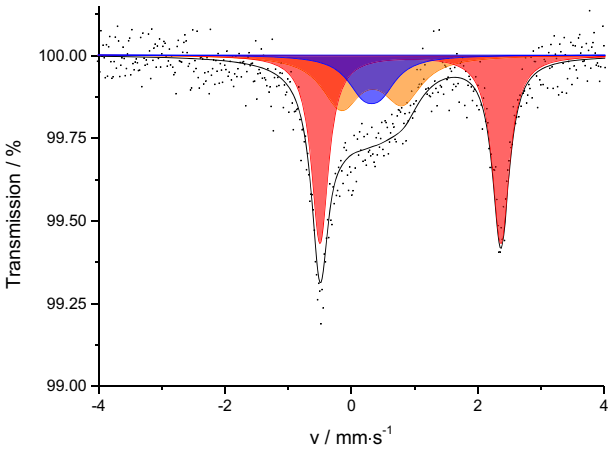

Fig. 1 Mössbauer spectrum of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles in PLA fibers at 293 K

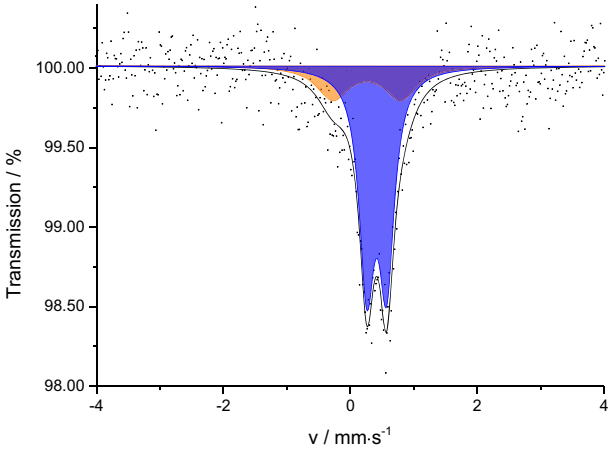

Fig. 2 Mössbauer spectrum of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles in PLA fibers at 77 K

2.4 Integration of SCO into polymer fibers

To implement the SCO compounds into polymer fibers the electrospinning procedure was used. The SCO compounds were added to a solution of polylactic acid (PLA) in 2,2,2-Trifluoroethanol (TFE). A SCO/polymer ratio of 5 w% was used. In a typical electrospinning setup with a continuous solvent flow rate of 1 ml/h a voltage of 23 kV was applied to the solution with a fixed collector to needle distance of 20 cm. The electrospinning procedure was performed in air atmosphere.

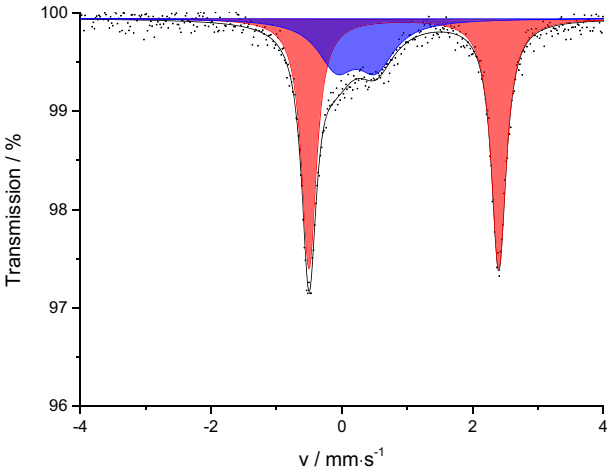

Fig. 3 Mössbauer spectrum of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles at 293 K

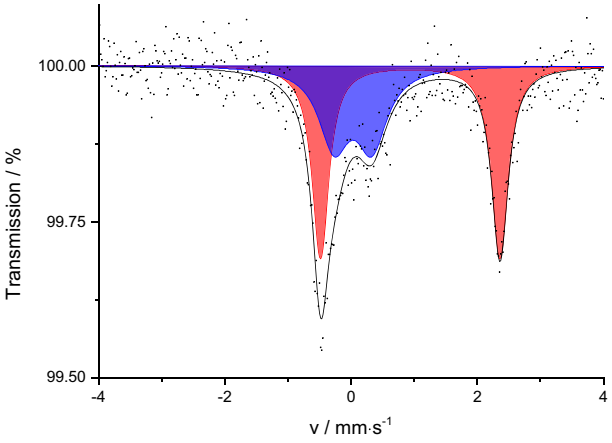

Fig. 4 Mössbauer spectrum of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ in PLA Fibers at 293 K

3 Results and Discussion

Figures 1–8 show the collected Mössbauer spectra relative to the ^{57}Co/Rh source. The corresponding parameters of all compounds are listed in Table 1 and are related to $\alpha-$iron.

3.1 $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles

The $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles show a spin crossover in the polymer fibers. At room temperature a mixture between the HS and the LS state can be observed. At 77 K

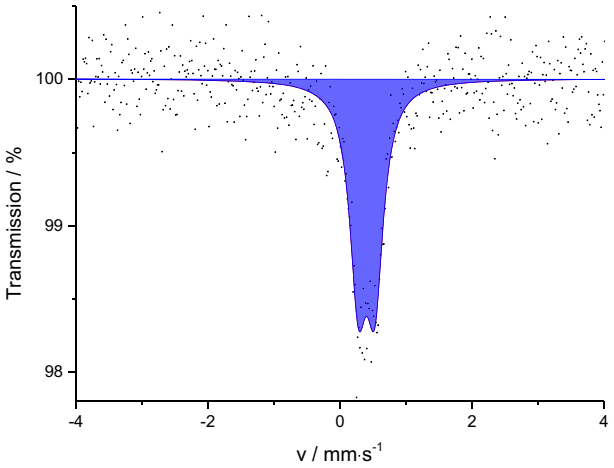

Fig. 5 Mössbauer spectrum of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ in PLA Fibers at 77 K

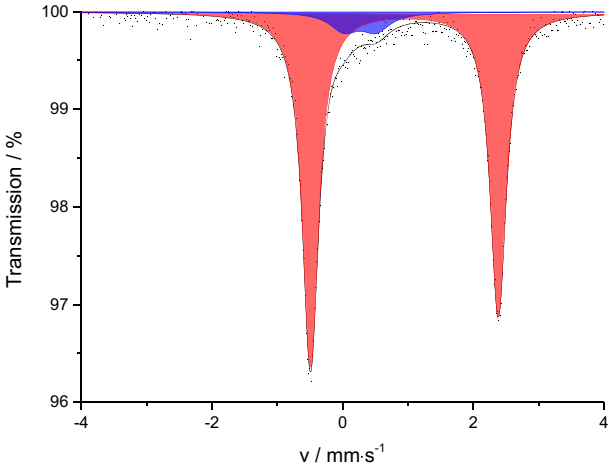

Fig. 6 Mössbauer spectrum of $[Fe(NH_2\text{-}trz)_3](BF_4)_2 \cdot H_2O$ at 293 K

only an Iron(II)-LS can be observed. In addition an Iron(III)-HS can be noticed at both temperatures. We explain this observation with the harsh conditions during the electrospinning procedure. Due to the high voltage up to 23 kV the nanoparticles might be partly oxidized. The Mössbauer spectra show no presence of Fe(III) before the spinning procedure (Fig. 3).

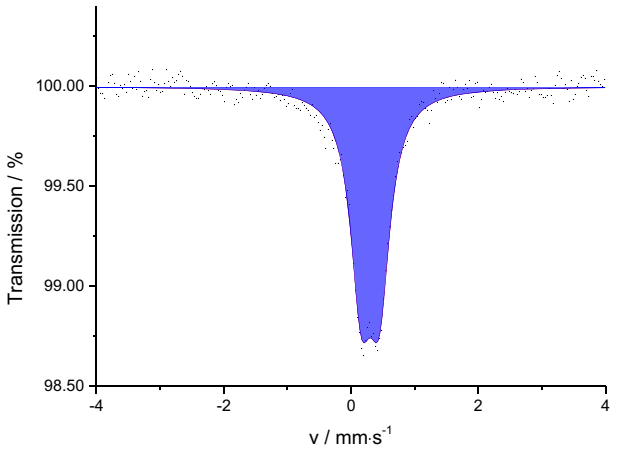

Fig. 7 Mössbauer spectrum of $[Fe(Htrz)_2(trz)](BF_4)$ in PLA fibers at 293 K

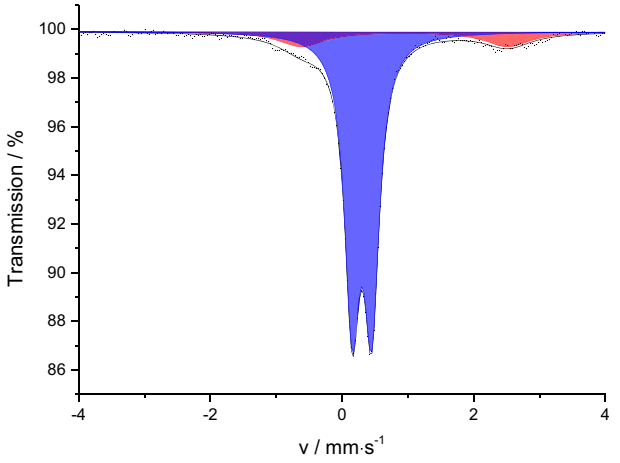

Fig. 8 Mössbauer spectrum of $[Fe(Htrz)_2(trz)](BF_4)\cdot H_2O$ at 293 K

3.2 $[Fe(NH_2\text{-}trz)_3](BF_4)_2$

The compound $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ was also integrated into the PLA polymer fibers. As well as the nanoparticles they show a spin crossover between 77 K and 293 K. (Figs. 4 and 5)

3.3 $[Fe(Htrz)_2(trz)](BF_4)$

$[Fe(Htrz)_2(trz)](BF_4)$ could be integrated into the polymer fibers. At 293 K the majority of the compound is present in the HS-state. It is interesting, that a difference can be

Table 1 Mössbauer parameters of the discussed compounds from Figs. 1, 2, 3, 4, 5, 6, 7 and 8 related to α-Fe

Compound	Temperature	δ_{IS}/ mm· s^{-1}	ΔE_Q/ mm· s^{-1}	Spin State	Figure
$[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles in PLA fibers	293 K	1.043	2.863	Fe(II)-HS (53.6 %)	1
		0.427	0.279	Fe(II)-LS (15.9 %)	
		0.430	0.970	Fe(III)-HS (30.5 %)	
	77 K	0.523	0.311	Fe(II)-LS (75.0 %)	2
		0.370	1.071	Fe(III)-HS (25.0 %)	
$[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles	293 K	1.057	2.901	Fe(II)-HS (68.7 %)	3
		0.328	0.601	Fe(II)-LS (31.3 %)	
$[Fe(NH_2\text{-}trz)_3](BF_4)_2$ in PLA fibers	293 K	1.046	2.842	Fe(II)-HS (57.8 %)	4
		0.149	0.599	Fe(II)-LS (42.2 %)	
	77 K	0.511	0.251	Fe(II)-LS (100 %)	5
$[Fe(NH_2\text{-}trz)_3](BF_4)_2 \cdot H_2O$	293 K	1.055	2.874	Fe(II)-HS (91.3 %)	6
		0.382	0.496	Fe(II)-LS (8.7 %)	
$[Fe(Htrz)_2(trz)](BF_4)$ in PLA fibers	293 K	0.411	0.285	Fe(II)-LS (100 %)	7
$[Fe(Htrz)_2(trz)](BF_4) \cdot H_2O$	293 K	0.411	0.296	Fe(II)-LS (85.4 %)	8
		1.059	3.133	Fe(II)-HS (14.6 %)	

noticed between the pure compound and the polymer-composite counterpart. This effect can be noticed also at the aminotriazole substituted compound. In both cases the LS population is increased. The same effect has been also shown by Janiak et al. [7] in MCM-41 structures. The nanostructuration of the 1-D chains stabilizes the LS population inside the SCO-composite material.

4 Conclusion

In conclusion, it could be shown that $[Fe(NH_2\text{-}trz)_3](BF_4)_2$, $[Fe(Htrz)_2(trz)](BF_4)$ as well as nanoparticles of $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ could be successfully integrated into PLA polymer fibers via electrospinning. For the $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ spin crossover compounds as well as their nanoparticles the spin crossover behavior still occurs in the polymer matrix. For the $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ compounds at 77 K only the LS state can be observed, whereas a mixture of HS and LS occurs at 293 K. In both cases for the $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ and the $[Fe(Htrz)_2(trz)](BF_4)$ compound different HS/LS ratios can be found in the polymer fibers compared to the bulk material. In both cases, the LS population of the SCO increases in the composite material.

In case of the $[Fe(NH_2\text{-}trz)_3](BF_4)_2$ nanoparticles also a Fe(III)-HS is present at 77 K and 293 K. This could be because of an oxidation process during the electrospinning process, since there is no Fe(III)-HS observed in the non-spun compound.

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References

1. Molnar, G., Salmon, L., Nicolazzi, W., Terki, F., Bousseksou, A.: J. Mater. Chem. C **2**, 1360–1366 (2014)
2. Linares, J., Codjovi, E., Garcia, Y.: Sensors **12**, 4479–4492 (2012)
3. Hu, L., Duan, Y., Xu, Z., Yuan, J., Dong, Y., Han, T.: J. Mater. Chem. C **4**, 5334–5341 (2016)
4. Bogue, R.: Sens. Rev. **29**, 310–315 (2009)
5. Kröber, J., Audière, J.-P., Claude, R., Codjovi, E., Kahn, O., Haasnoot, J.G., Grolière, F., Jay, C., Bousseksou, A., Linarès, J., Varret, F., Gonthier-Vassal, A.: Chem. Mater. **6**, 1404–1412 (1994)
6. Qiu, D., Ren, D.H., Gu, L., Sun, X.L., Qu, Gu, Z.G., Li, Z.: RSC Adv. **4**, 31323–31327 (2014)
7. Zhao, T., Cuignet, L., Dîrtu, M.M., Wolff, M., Spasojevic, V., Boldog, I., Rotaru, A., Garcia, Y., Janiak, C.: J. Mater. Chem. C **3**, 7802–7812 (2015)