

Neutral and anionic duality of 1,2,4-triazole α -amino acid scaffold in 1D coordination polymers

Anil D. Naik · Marinela M. Dîrtu · Yann Garcia

© Springer Science+Business Media B.V. 2011

Abstract A tiny supramolecular synthon, 4H-1,2,4-triazol-4-yl acetic acid (HGlytrz) which is bifunctional by design having an electronic asymmetry and conformational flexibility has been introduced to synthesize iron(II) complexes. Having 1,2,4-triazole or carboxylic extremities on the same framework HGlytrz could display dual functionality by acting as a neutral as well as anionic ligand based on the possibility of deprotonation of carboxylic group. Four new iron(II) HGlytrz complexes with ClO_4^- (**1**), NO_3^- (**2**), BF_4^- (**3**) and CF_3SO_3^- (**4**) anions were prepared. Formulation of their composition which is complicated due to ligand deprotonation is discussed. Unlike its ester protected counterpart ethyl-4H-1,2,4-triazol-4-yl-acetate (α Glytrz) which show hysteretic room temperature spin crossover, **1–4** remain in the high-spin state as revealed by ^{57}Fe Mössbauer spectroscopy. Prospects of such 1D coordination polymers with dangling unbounded carboxylic entities in the realm of self-assembled monolayer (SAM) are discussed.

Keywords ^{57}Fe Mossbauer spectroscopy · Coordination polymers · Spin-transition · 1,2,4-triazole

1 Introduction

Tailor made bifunctional molecular fragments are greatly sought in the fabrication of wide range of functional materials. We recently synthesized several supramolecular 1,2,4-triazole synthons that were introduced in thermochromic spin crossover (SCO) materials [1, 2], inhibitors for antibiotics [3], modular approach in the design of metal-organic frameworks (MOFs) [4, 5] and logistics for non-linear optics [5]. Among them ethyl-4H-1,2,4-triazol-4-yl-acetate (α Glytrz) has emerged as a prospective

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

scaffold for the design of SCO materials with $[\text{Fe}(\alpha\text{Glytrz})_3](\text{ClO}_4)_2$ showing abrupt, complete hysteretic SCO operating around room temperature [1]. In continuation of this work we now investigate the iron(II) coordination chemistry of the hydrolyzed derivative of αGlytrz , 4H-1,2,4-triazol-4-yl acetic acid (HGlytrz). This latter molecule has an interesting topology wherein the two extremities are occupied by potentially coordinating groups of 1,2,4-triazole and carboxylic group [4]. We have shown earlier by X-ray crystallography of a series of 3d complexes how this ligand could act either as anionic or neutral ligand depending upon reaction conditions [3, 4]. In the present work four new iron(II) HGlytrz complexes were prepared with ClO_4^- (**1**), NO_3^- (**2**), BF_4^- (**3**) and CF_3SO_3^- (**4**) counteranions. FTIR and ^{57}Fe Mössbauer spectroscopies provide complimentary information about ligand's ability to act either as neutral (HGlytrz) or anionic form (Glytrz). Complexes **1,3,4** are 1D coordination polymers (CP) with bridging $N1, N2$ -1,2,4-triazole with ligand acting as neutral with concurrent formation of a small amount of 1D CP with dual status of ligand. Interestingly, **2** is exclusively formed of a 1D CP with HGlytrz which opens up a new strategy to induce the formation of a linear chains with non-coordinated potentially anchoring carboxylic groups that could be expected to find broad scope in self-assembled monolayers (SAM) in thin film fabrications.

2 Experimental

Iron(II) complexes were isolated by reaction of the corresponding Fe^{II} salts, $[\text{Fe}(\text{H}_2\text{O})_6](\text{Anion})_2$ (anion = BF_4^- , ClO_4^- , CF_3SO_3^-) and $[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (prepared *in situ* [6]) with HGlytrz (1:3 stoichiometry) dissolved in methanol in a $\text{N}_2(\text{g})$ atmosphere. The off-white powders thus obtained are highly sensitive to air and moisture and therefore stored under N_2 atmosphere/desiccator.

3 Results and discussion

SEM (scanning electron microscopy) images (Fig. 1b) reveals texture of the powders at the microscopic level. The texture is indefinable in **2** and **4** which is also evident from poor X-ray powder diffraction pattern (XRPD) (Fig. 2a). Comparatively **1** and **3** have distinct XRPD pattern which is apparent from SEM images on the bulk sample. In fact **3** show elongated needles of 60–80 nm thickness. Contrary to its ester analogue [1], **1–4** were not precipitated instantly during their syntheses thus increasing precipitation probability of more than one species in the bulk sample.

The strong $\nu(\text{C}=\text{O})$ band in FTIR of ligand around 1730 cm^{-1} is still found as a strong band in **1–4** with shift in band position (up to 1744 cm^{-1}) except in **1** where the intensity is reduced comparatively. FTIR also supports the presence of anions with characteristic bands [$\nu(\text{ClO}_4^-) \sim 1050\text{ cm}^{-1}$ (**1**); $\nu(\text{NO}_3^-) \sim 1382\text{ cm}^{-1}$ (**2**); $\nu(\text{BF}_4^-) \sim 1060\text{ cm}^{-1}$ (**3**); $\nu(-\text{SO}_3^-) \sim 1259\text{ cm}^{-1}$ (**4**)]. This situation suggests that these complexes form 1D CPs with dangling carboxylic group which is still protonated thus acting as neutral ligand and coordinating iron ions through $N1, N2$ of 1,2,4-triazole units. In addition, except for **2**, there is a medium to strong band around 1630 cm^{-1} (1660 cm^{-1} in **1**) which is assigned to asymmetric stretching of $\nu(\text{COO}^-)$ and a medium band around 1250 cm^{-1} indicative of symmetric $\nu(\text{COO}^-)$

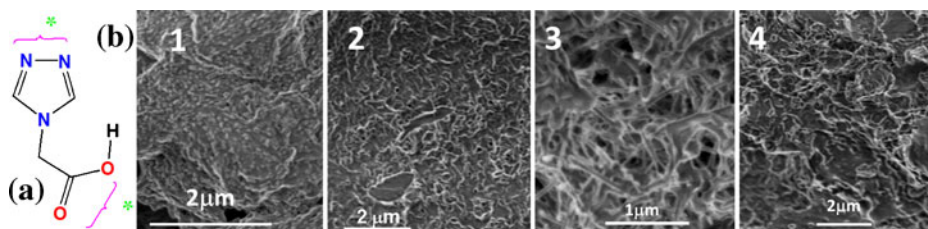


Fig. 1 **a** Molecular structure of HGlytrz with *indicating possible bifunctionality; **b** SEM images on **1–4**

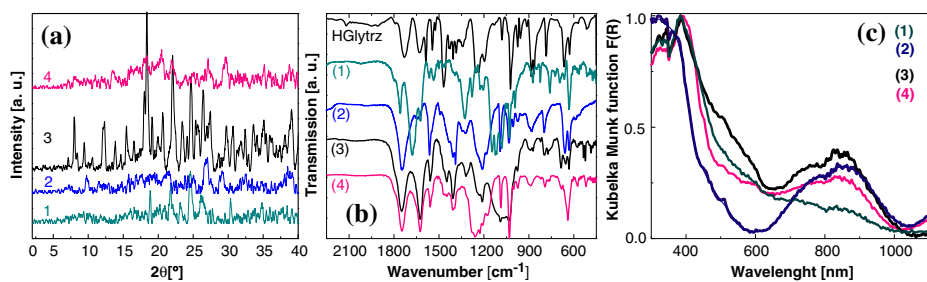


Fig. 2 **a** XRPD pattern for **1–4** at r.t. **b** FTIR for **1–4** expanded between $2200\text{--}500\text{ cm}^{-1}$ at r.t. **c** Diffuse reflectance spectra of **1–4** at r.t.

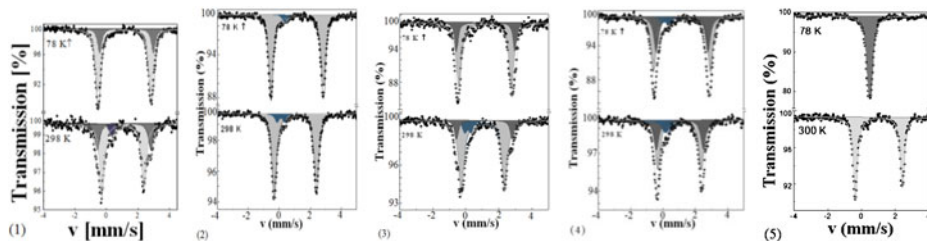


Fig. 3 ^{57}Fe Mössbauer spectra of **1–5** at 78 K and 298 K. Grey, dark grey and blue gray correspond to the HS(1), HS(2) and Fe^{III} impurities doublets, respectively

stretching based on our earlier reports [2–4]. This would indicate the presence of 1D chains with deprotonated ligands. Thus this observation leads to the conclusion that bulk samples of **1**, **3** and **4** have co-precipitation of two types of 1D CP with tentative composition: $[\text{Fe}(\text{HGlytrz})_3](\text{Anion})_2$ and $[\text{Fe}(\text{HGlytrz})_2(\text{Glytrz})]\text{Anion}$. Interestingly **2** which was prepared in aqueous methanol which does not show $\nu_{\text{asym}}(\text{COO}^-)$ exclusively forms 1D chain with neutral ligand of the composition $[\text{Fe}(\text{HGlytrz})_3](\text{NO}_3)_2 \cdot \text{CH}_3\text{OH}$ (**2**). The presence of a non-coordinated solvent molecule was confirmed by thermogravimetric analyses. Selected ^{57}Fe Mössbauer Spectra are shown in Fig. 3 and hyperfine parameters are grouped in Table 1.

As a consequence of these formulations, two types of high-spin (HS) sites would be expected for **1**, **3**, **4** which are indeed observed, hereafter denoted as HS1 and HS2 (Table 1). HS1 with isomer shift, δ^{HS1} , which is in the range of 1.05–1.13 mm/s

Table 1 Selected ^{57}Fe Mössbauer parameters in **1–5**

Compound	T (K)	δ (mm/s)	ΔE_Q (mm/s)	$\Gamma/2$ (mm/s)	%	Species
1	78	1.28(1)	3.41(2)	0.16(1)	25.7	HS1
		1.13(1)	3.36(1)	0.18(1)	74.3	HS2
	298	1.13(1)	3.39(2)	0.18(1)	25.4	HS1
		1.04(1)	2.66(1)	0.17(1)	67.3	HS2
		0.34(1)	–	0.2*	7.3	Fe ^{III}
2	78	1.16(1)	3.38(1)	0.17(1)	97	HS
		0.33(1)	0.29(1)	0.10(1)	3	Fe ^{III}
	298	1.04(1)	2.74(2)	0.18(1)	92	HS
		0.10(3)	0.49(1)	0.15(1)	8	Fe ^{III}
3	78	1.20(1)	3.54(1)	0.12(1)	23.3	HS1
		1.17(1)	3.19(1)	0.18(1)	76.7	HS2
	298	1.12(1)	3.37(3)	0.14(1)	13.6	HS1
		1.04(1)	2.62(1)	0.20(1)	76.6	HS2
		0.13(3)	0.38(1)	0.16(1)	9.8	Fe ^{III}
4	78	1.18(1)	3.20(2)	0.19(1)	38.4	HS1
		1.17(1)	3.51(1)	0.17(1)	54.1	HS2
		0.15(2)	0.43(1)	0.26(1)	7.5	Fe ^{III}
	298	1.05(1)	2.91(1)	0.19(1)	33.6	HS1
1.03(1)		2.69(3)	0.18(1)	54.2	HS2	
		0.18(1)	–	0.32(1)	12.2	Fe ^{III}
5^a	298	1.03(1)	2.78(1)	0.15(1)	100	HS
	78	0.48(1)	0.20	0.16(1)	100	LS

δ : isomer shift (with respect to α -Fe at 298 K); ΔE_Q : quadrupole splitting; $\Gamma/2$: half width at half maximum; *Fixed parameter; ^a[Fe(α Glytrz)₃](ClO₄)₂·MeOH [1]

and quadrupole splitting, ΔE_Q^{HS1} in the range 2.91 to 3.39 mm/s which is found in 15–30% in population. The situation is not very different at 77 K in terms of spin state change but the value of ΔE_Q value increases further. The relatively (compared to HS2, Table 1) higher value of ΔE_Q at 298 K indicates significant distortion at the iron centers which could be possible due to the strain created by supramolecular interactions that is established by the deprotonated ligand in **1**, **3** and **4**. The second HS signal (HS2) dominates the spectra (~54–76%, Table 1). The δ is in the range of 1.03 mm/s and $\Delta E_Q = 2.62$ –2.74 mm/s which is in the range of FeN₆ octahedra reported for the analogous complex **5** (Table 1) [1]. These results are in good agreement with our hypothesis about an admixture of two types of 1D chains in the bulk sample delineated from IR spectra of **1**, **3** and **4**. It has to be noted that in **2**, there is exclusively one type of HS species thus strongly supporting the interpretation from FTIR about the composition and coordination mode. The observed decrease in δ (Table 1) on warming from 77 K to 298 K in **1–4** is due to relativistic second order Doppler shift [6]. Due the fact that these complexes are highly susceptible to aerial oxidation, all complexes shows 8–12% of Fe^{III} species. Further supportive informations, on admixture of CP in **1–4**, were obtained from diffuse reflectance spectra (Fig. 2c). The broad band of $^5T_{2g} \rightarrow ^5E_g$ around 800 nm clearly indicates the presence of more than one HS species. It has to be noted that even though the spectrum for **2** does not show multiple species, the band around 800 nm begin to split hinting the formation of other species when recorded in air atmosphere. The fact that self-assembly of HGlytz occurs in these CPs is highly desirable in the field

of self-assembled monolayers (SAM) where advantage of unbound carboxylic groups could be explored further in binding to a wide variety of substrate while maintaining the functional core intact [7].

Acknowledgements We gratefully acknowledge support from IAP INANOMAT, the FNRS (2.4508.08, 4.4507.10), a ARC grant of the Académie Universitaire Louvain and from the Groupe Francophone de Spectrométrie Mössbauer for supporting A. D. N. to attend GFSM 2011 (Strasbourg) and ICAME 2011 (Kobe).

References

1. Dîrtu, M.M., Naik, A.D., Marchand-Brynaert, J., Garcia, Y.: Room temperature hysteretic spin transition in 1D iron(II) coordination polymers. *J. Phys. Conf. Ser.* **217**, 012085 (2010)
2. Dîrtu, M.M., Schmit, F., Naik, A.D., Rotaru, A., Marchand-Brynaert, J., Garcia, Y.: Spin transition sensors based on β -amino-acid 1,2,4-triazole derivative. *Int. J. Mol. Sci.* **12**, 5339 (2011)
3. Naik, A.D., Beck, J., Dîrtu, M.M., Bebrone, C., Tinant, B., Robeyns, K., Marchand-Brynaert, J., Garcia, Y.: Zinc complexes with 1,2,4-triazole functionalized amino acid derivatives: Synthesis, structure and β lactamase assay. *Inorg. Chim. Acta* **368**, 21 (2011)
4. Naik, A.D., Dîrtu, M.M., Léonard, A., Tinant, B., Marchand-Brynaert, J., Su, B.L., Garcia, Y.: Engineering three-dimensional chains of porous nanoballs from a 1,2,4-triazole-carboxylate supramolecular synthon. *Cryst. Growth Des.* **10**, 1798 (2010)
5. Dîrtu, M.M., Neuhausen, C., Naik, A.D., Léonard, A., Robert, F., Marchand-Brynaert, J., Su, B.L., Garcia, Y.: Superlattice scaffold of 1,2,4-triazole derivative of glycine steering linear chain to a chiral helicate. *Crystal Growth Des.* **11**, 1375 (2011)
6. Dîrtu, M.M., Rotaru, A., Gillard, D., Linares, J., Codjovi, E., Tinant, B., Garcia, Y.: Prediction of the spin transition temperature in Fe^{II} one dimensional coordination polymers: an anion based database. *Inorg. Chem.* **48**, 7838–7852 (2009)
7. Naik, A.D., Stappers, L., Snauwaert, J., Fransaer, J., Garcia, Y.: A biomembrane stencil for crystal growth and soft lithography of a thermochromic molecular sensor. *Small* **6**, 2842 (2010)