Weak cooperativity in selected iron(II) 1D coordination polymers

Marinela M. Dîrțu · Damien Gillard · Anil D. Naik · Aurelian Rotaru · Yann Garcia

Abstract The spin crossover behaviour of a new class of Fe\textsuperscript{II} coordination polymers [Fe(phtptrz)\textsubscript{3}]I\textsubscript{2} (1), [Fe(phtptrz)\textsubscript{3}](ReO\textsubscript{4})\textsubscript{2}•CH\textsubscript{3}OH (2) and [Fe(phtptrz)\textsubscript{3}]TaF\textsubscript{7}•6H\textsubscript{2}O (3) based on a novel ligand 4-(3\textsuperscript{′}-N-phtalimido-propyl)-1,2,4-triazole (phtptrz), were investigated by temperature dependent \textsuperscript{57}Fe Mössbauer spectroscopy and magnetic susceptibility measurements. The adverse effect of bulky substituent on 1,2,4-triazole, favorable supramolecular interactions and influence of increasing anion size on spin crossover profile is discussed. 1 and 2 show thermally induced spin conversions of gradual and incomplete nature with associated thermochromism, and transition temperatures T_{1/2} ∼ 163 K and 137 K, respectively. A spin state crossover is also identified for 3.

Keywords \textsuperscript{57}Fe Mössbauer spectroscopy · Coordination polymers · Spin-transition · 1,2,4-triazole

1 Introduction

Cooperativity factors which determine the importance in iron(II) spin crossover (SCO) materials performances have long been the subject matter of intensive research with targeted fascinating applications in sensor and memory devices [1, 2]. Abruptness, completeness and hysteresis width/shape of magnetic profiles are key elements to probe strength of cooperative interactions in SCO complexes which can be influenced by ligand design, anion geometry and charge, crystal defects, solvent...
occupancy etc. [3]. Self-assembled coordination polymers (CPs) represent a family of compounds where precisely organised molecular building blocks generate a long range cooperative phenomenon that has effective means of propagation through rigid covalent bonding and flexible supramolecular interactions [4]. Although this situation is usually set for small ligand modules, larger molecular fragments such as dendrimers [5] or extended alkyl chains [6] often show promising SCO profiles without cooperativity loss thus reviewing the selection criteria of ligand topology. We introduce in this context a new module for CPs: 4-(3′-N-phtalimido-propyl)-1,2,4-triazole (phtptrz) (Fig. 1a) where a bulky substituent is attached to N4 of 1,2,4-triazole via a multiple carbon spacer. This aromatic group, although bulkier, is a potential promoter of supramolecular interactions due to π–π stacking and H-bonding interactions involving carbonyl groups. Further, influence of modifying anions geometry (spherical I−, tetrahedral ReO4−, monocapped trigonal prism TaF27−) and charge (monovalent and bivalent) is evidenced in the series of [Fe(phtptrz)3]I2 (1), [Fe(phtptrz)3](ReO4)2•CH3OH (2) and [Fe(phtptrz)3]TaF7•6H2O (3) whose spin switching properties are discussed herein.

2 Experimental

The phtptrz molecule was prepared according to ref [7]. Complexes were prepared as white powders by reacting phtptrz to [Fe(H2O)6]2+ including a suitable anion (I−, ReO4−, TaF27−, Fig. 1b) in a 1:3 ratio in MeOH/H2O following ref [8]. Spectroscopic, microanalysis and thermal analyses lead to the formulation of the new 1D coordination polymers 1–3. Magnetic measurements were recorded on a SQUID device.

3 Results and discussion

Preliminary indications of SCO occurrence were obtained by a clear thermochromic response on quench cooling of the materials to N2(0). Indeed, white powders of 1 and 2...
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Table 1  Comparison of $^{57}$Fe Mössbauer parameters for 1–3

<table>
<thead>
<tr>
<th>Compound</th>
<th>T[K]</th>
<th>$\delta$[mm/s]</th>
<th>$\Delta E_Q$[mm/s]</th>
<th>$\Gamma/2$[mm/s]</th>
<th>$A_{HS}/A_{tot}$</th>
<th>Spin state</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>300</td>
<td>1.13(1)</td>
<td>2.78(1)</td>
<td>0.18(1)</td>
<td>100</td>
<td>HS</td>
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<tr>
<td></td>
<td>77</td>
<td>1.17(1)</td>
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<td>0.19(1)</td>
<td>35</td>
<td>HS</td>
</tr>
<tr>
<td></td>
<td>0.55(1)</td>
<td>0.29(1)</td>
<td>0.16(1)</td>
<td>65</td>
<td></td>
<td>LS</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>1.09(1)</td>
<td>2.84(1)</td>
<td>0.22(1)</td>
<td>100</td>
<td>HS</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>1.18(1)</td>
<td>3.21(1)</td>
<td>0.18(1)</td>
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<td>HS</td>
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<tr>
<td></td>
<td>0.51(1)</td>
<td>0.10(1)</td>
<td>0.19(1)</td>
<td>25</td>
<td></td>
<td>LS</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>1.09(1)</td>
<td>2.84(2)</td>
<td>0.18(1)</td>
<td>100</td>
<td>HS</td>
</tr>
<tr>
<td></td>
<td>77</td>
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<td>3.36(1)</td>
<td>0.17(1)</td>
<td>75</td>
<td>HS</td>
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<td>0.65(1)</td>
<td>0.23(1)</td>
<td>25</td>
<td></td>
<td>LS</td>
</tr>
</tbody>
</table>

$\delta$: isomer shift (with respect to $\alpha$-Fe at 300 K); $\Delta E_Q$: quadrupole splitting; $\Gamma/2$: half width at half maximum; $A_{HS}$: Area of HS doublet; $A_{tot}$: total area

show reversible colour change to pink, contrary to 3. Variable temperature magnetic susceptibility measurements for 1–3 were recorded over the temperature range 300–4 K (Fig. 1c). These SQUID measurements reveal a very smooth incomplete spin conversion for 1 and 2 with transition temperatures $T_{1/2} \sim 163$ K and 137 K, respectively. For 1 the room temperature $\chi_M T$ value of 3.18 cm$^3$ mol$^{-1}$ K corresponds to high-spin (HS) Fe$^{II}$ species. When cooled, this value gradually decreases to 1.1 cm$^3$ mol$^{-1}$ K around 72 K after which the inflection becomes more gradual until 27 K, revealing an incomplete spin conversion. The subsequent drop of $\chi_M T$ at lower temperatures is attributed to zero-field splitting (ZFS) of remaining HS Fe$^{II}$ species. This type of spin conversion is commonly observed for Fe$^{II}$ complexes having a voluminous substituent on the N4 position of the triazole ring [9]. Complex 2 with ReO$_4^-$ as counter anion has a similar magnetic profile; however, the decrease in $\chi_M T$ begins at a higher value, 3.42 cm$^3$ mol$^{-1}$ K at 300 K, which is consistent with the HS state. It is followed by a slow decrease to 1.8 cm$^3$ mol$^{-1}$ K at 40 K, after which ZFS causes a decrease in $\chi_M T$ product. In contrast, the magnetic curve of 3 does not apparently reflect any SCO process. As the temperature is lowered, the $\chi_M T$ value smoothly decreases until 50 K and drops rapidly below this temperature reaching a minimum at 4 K. Such a magnetic curve indicates very weak antiferromagnetic (AF) interactions between HS Fe$^{II}$ ions. The best fit of the magnetic data with a Curie-Weiss law afforded a Weiss temperature $\theta = -55$ K, $g = 2.30(5)$ and by considering the number of nearest neighbours atoms ($z = 2$) [10], $J/k_B = -13(1)$ K was derived. The absence of maximum in the $\chi_M$ vs. $T$ plot confirms the weak AF coupling nature in 3.

$^{57}$Fe Mössbauer spectroscopy further reveals variation of temperature dependent population of spin states in 1–3. Selected Mossbauer spectra are shown in Fig. 1e and parameters are summarized in Table 1. In 1, a quadrupole doublet (100% population) with isomer shift $\delta = 1.13(1)$ mm.s$^{-1}$ and quadrupole splitting $\Delta E_Q = 2.78(1)$ mm.s$^{-1}$ is identified at 300 K which is clearly indicative of HS Fe$^{II}$ species. A slight asymmetry of the lines is observed which is attributed to a texture effect. On cooling, a spin conversion to the low-spin (LS) state is identified with appearance of a new signal depicted in blue at 203 K and 143 K. Indeed, at 77 K, another quadrupole doublet with $\delta_{LS} = 0.55(1)$ mm.s$^{-1}$ and $\Delta E_Q^{LS} = 0.29(1)$ mm.s$^{-1}$ is found, thus confirming the incomplete nature of the SCO process. For 2, only 25% of HS
ions have switched to the LS state at 77 K whereas 65% have switched for 1, in full agreement with SQUID data (Fig. 1c). Interestingly, δ^{HS}(77 K) for 1 and 2 are identical (Table 1) indicating absence of any appreciable change in the electronic distribution around each individual iron atoms. The absence of SCO is not confirmed for 3 as HS ions are detected at 300 K, whereas a mixture of LS/HS ions is probed at 77 K. Most interestingly, ΔE^{LS}_Q(77 K) is higher for 3 compared to 1–2 which indicate an important strained situation at the iron centers.

The trend in loss of SCO properties from 1 to 3 can be explained based on certain structural aspects. Although bulky substituent on the triazole ring with multiple carbon spacer of the ligand scaffold is not expected to give a favorable situation for cooperative SCO, as trinuclear species formation could have been expected [11], the affinity of π − π stacking of aromatic groups and supramolecular interaction through carbonyl groups on the framework overcomes this barrier thus promoting the observed weakly cooperative SCO in 1 and 2. This behaviour, which is also depicted in terms of variation of HS molar fraction derived by integration of the Mössbauer signals (Fig. 1d), indicates a cooperativity weakening which can be attributed too to a decrease of intermolecular contacts between chains. A clear influence of increasing anion size is consistent with a chain spacing [8]. The doubly charged voluminous anion in 3 considerably weakens cooperativity of the SCO system compared to singly charged anions [8], thereby leading to an almost HS material. Further incompleteness of SCO at lower temperature can also be attributed to steric factors that delay further growth of LS population. The progressive network shrinking during HS to LS conversion, on cooling, is thus halted due to network instability to further shrink that encounter steric clashes in the molecular packing with bulkier substitution, compared to 1D chains of the [Fe(4-amino-1,2,4-triazole)_3](anion)_2 series [4, 8].

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References