Spin-transition behaviour in chains of Fe^{II} bridged by 4-substituted 1,2,4-triazoles carrying alkyl tails†‡

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A family of polymeric 1-dimensional chains of iron(II) species showing the spin-crossover phenomenon has been synthesized using 4-*n*-alkyl-1,2,4-triazoles as bridging ligands. The influence of the length of the alkyl tails on the triazole ligands on characteristic features of the spin transition was studied, showing degrading of steepness with increasing length. A set of four counter ions has been used to access a wider range of transition temperatures. Large hysteresis loops are detected with small tails, mainly for the methyl and ethyl substituted products. In most cases longer tails weaken co-operativity and hysteresis gradually decreases to zero. However it is shown that with certain anions hysteresis remains, even with very long tails on the triazoles. Weakening of the co-operativity mainly arises from a diminution of the length of the polymeric chains with increasing alkyl tails on the triazole. This effect is anion dependent. A strong interaction along the polymeric chains is confirmed.

Introduction

Bistable molecular systems have become an increasingly studied and challenging field of research.[1] The spin-crossover phenomenon probably represents the most spectacular example, in particular in iron(II) chemistry, and has indeed thoroughly been investigated since the mid 1970s.[2]

The possible sharp spin transition from low spin (LS) iron(II) $S = 0$ to high spin (HS) $S = 2$ coupled with a thermochromic effect, purple to white, and, in some cases, thermal hysteresis has been at the origin of proposed applications.[3,4] The discovery of the Light Induced Excited Spin-State Trapping (LIESST)[5] and reverse-LIESST[6] effects, showing the possibility of switching from one state to the other with either green or red light, suggested that spin-crossover compounds could be used as optical switches. In mononuclear compounds, which were the first known cases, the sharpness of the transition and the occurrence of thermal hysteresis have been linked to first-order crystallographic phase transitions,[2] or to strong intermolecular interactions, due to an important hydrogen-bonding network,[7] or to π–π interaction.[8] These interactions would spread the molecular distortion due to the HS–LS change over the whole crystal, a lengthening of the Fe–ligand bond of typically 0.15 to 0.2 Å, leading to what is generally called co-operativity. Indeed a model, developed by Spiering and co-workers,[9] based on elastic interactions reproduces well the mechanism of this co-operativity. This model considers each spin-crossover centre as a point defect and has been extended to short-range interactions; the model can therefore be applied to higher nuclearity, as done recently in 1-D linear chains.[10]

One might expect that direct chemical bonding could increase the co-operativity upon the spin transition, by making the contacts between the spin-changing centres stronger. Only very few polymeric iron(II) spin-crossover compounds have been reported so far.[11–14] They involve bridging ligands, such as 4-substituted triazole or N-heterocyclic rings, linked by spacers. Indeed the 2-D compounds $[Fe(btr)_2(NCS)_2]\cdot H_2O$[11] (btr = 4,4′-bis-1,2,4-triazole) and $[Fe((N(entz)_3)_2]$[12] ($N(entz)_3$ = tris[(tetrazol-1-yl)ethyl] amine) display strongly co-operative spin crossovers with thermal hysteresis. However the first catenane $[Fe(tvp)_2(NCS)_2]\cdot CH_3OH$[13] (tvp = 1,2-di(4-pyridyl)ethylene) shows a gradual spin conversion and the 3-D compound $[Fe(btr)_3][A]_2$[14] has a rather sharp transition, but without important hysteresis with $A = ClO_4$ and a gradual, incomplete transition with $A = BF_4$. Eventually most possible industrial applications arise from 1-D linear chain compounds of general formula $[Fe(Rtrz)_3]A_2\cdot xH_2O$, where Rtrz = 4-R-1,2,4-triazole.[15] Direct linkage of the Fe^{II} by triple N^1–N^2 triazole bridges is thought to be the origin of the observed co-operative nature of these substances. Very abrupt spin transitions with stable well shaped large hysteresis loops are rather rare, but have been found in *e.g.* $[Fe(NH_2trz)_3][NO_3]_2$[16] and $[Fe(Htrz)_2(trz)]BF_4$.[17,18] It has recently been considered[10] that very strong short-range interaction along the chains together with overall long-range interaction are necessary to reproduce these features. Possible loss and later reabsorption of water with tosylate type anions gives rise to huge "apparent" hysteresis, leading to at least possible one-shot applications.[19] "Alloys" of differently substituted triazoles permitted the design of spin crossover compounds with large hysteresis centred around RT.[20] However, due to the rapid formation of these polymers, single crystals could not be grown up to now and EXAFS has been a powerful tool to demonstrate the linearity of the chains, with the presence of a peak at about 7 Å characteristic of a Fe–Fe–Fe linear path[21] and Fe–Fe distances of about 3.4 Å; fine tuning appeared possible by comparison with linear trinuclear compounds with triple triazole bridges.[22] Very recently, the first structure of a 1-D spin-crossover chain was solved,[23] but with a much higher Fe–Fe distance (7.2–7.4 Å) due to the larger bridge. $[Fe(btzp)_3][ClO_4]_2$, btzp = 1,2-bis(tetrazol-1-yl)propane,

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† Dedicated to the memory of Olivier Kahn (1942–1999).

‡ Electronic supplementary information (ESI) available: elemental analyses. See http://www.rsc.org/suppdata/nj/b0/b007094g/

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indeed shows a gradual spin transition probably related to the higher flexibility of the chain due to the presence of a spacer.

Linear [Fe(Rtrz)$_3$] chains seem to remain the best candidates for possible applications, especially because of the richness of possibility of substituents, and the large range of spin-transition features accessible, due to the strong influence of the anion used and the substituent. A direct relationship between the diameter of the spherical anions and the transition temperature has indeed been found in the series [Fe(NH$_2$trz)$_3$]A$_2$[16,24] and [Fe(hyetrz)$_3$]A$_2$[14](hyetrz = 4-hydroxyethyl-1,2,4-triazole): the bigger the anion the lower is the temperature transition. Also the change in the triazole substituent and doping with other metals was found to drive spin transition features by affecting the 10*Dq* values of the LS state.[25] In this work attention is focussed on four different types of anions that give access to a wide range of temperature transitions and the influence of the length of *n*-alkyl substituents on the spin-transition features is reported here for the first time in detail.

Experimental

Physical measurements

Magnetic susceptibility of powder samples was measured using either a Quantum Design MPMS-5S SQUID magnetometer operating at 0.5 or 1 T, a MANICS DSM8 susceptometer operating at 1.3 T equipped with a TBT continuous flow cryostat or a Quantum Design PPMS model 600 operating at 1 T. Calibration was achieved with samples of palladium and [HgCo(NCS)$_4$]. Independence of the susceptibility value with regard to the applied field was checked at 300 K on one sample. The measured values were corrected for diamagnetism of the sample as estimated from Pascal tables and for the magnetic contribution of the sample holders. For LIESST effect experiments a Y-shaped optical fiber was used as the SQUID sample holder, together with a xenon arc lamp and a blue-green filter (300–600 nm). Elemental analyses (C, H, N, S) were performed on a Perkin-Elmer 2400 series II analyser. UV-visible-NIR spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. A home-made set-up was used to obtain low temperature spectra. The temperature of the sample was estimated to be 90–100 K using known samples with transitions close to this value.[26] FTIR spectra were obtained on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}, resolution 4 cm^{-1}). Heat capacity measurement was performed by use of the specific heat option of a Quantum Design PPMS model 600 instrument. The sample was a piece (3 mg) of a pellet obtained by pressing 50 mg of the compound under 5 tons.

Syntheses

4-*n*-Alkyl-1,2,4-triazoles. Those were obtained from hydrazine monohydrate, ethyl formate, triethyl orthoformate and primary *n*-alkylamines following the Bayer synthesis.[27] Freshly prepared monoformylhydrazine was refluxed for 3 to 5 hours with a 20% excess of triethyl orthoformate in water free methanol. After cooling to 40 °C, the *n*-primary amine was added, and the reaction mixture refluxed for 5 to 20 hours more. The *n*-alkylamines used were n = 1–10, 12, 13, 16 or 18. For $n > 9$, white crystalline solids were precipitated from the concentrated mother liquor by adding a small amount of water. Lower values of *n* gave yellowish oils, in some cases after distillation under reduced pressure. Purity of the 4-substituted triazoles was checked by ^{1}H NMR, IR spectroscopy and elemental analysis. The signal of the triazole protons was not affected by the length of the alkyl tail and was found at δ 8 to 8.1 (in CDCl$_3$). The triplet of the first CH$_2$ of the alkyl substituents was observed at δ 4 to 4.1. Aliphatic $\nu_{\text{C–H}}$ stretchings of the alkyl substituents were found in the range 2850 to 2965 cm^{-1} and aromatic $\nu_{\text{C–H}}$ of the triazole ring between 3055 and 3125 cm^{-1}.

Polymeric [Fe(R$_n$trz)$_3$][A]$_2$·*x*H$_2$O. The synthesis of the polymeric compounds was achieved following as strictly as possible the same procedure. A hot ethanolic solution (3.5 mmol, 10 ml) of the triazole was added slowly to a hot aqueous solution of an iron(II) salt (1 mmol, 10 ml). Iron(II) tetrafluoroborate and perchlorate hexahydrate were purchased from Aldrich and Ventron, respectively, and used without further purification. Iron(II) trifluoromethanesulfonate (triflate) and *p*-toluenesulfonate (*p*-tol) were obtained by warming iron powder (ACROS) and the corresponding acid (Aldrich) in water. Ascorbic acid was used to prevent oxidation of iron(II) to iron(III) during complexation. For $n > 13$ a white precipitate formed almost immediately on addition. For n = 9, 10 or 12 no solid could be obtained whatever procedure was used with these solvents. For lower *n* values a white solid formed in a relatively short time, *i.e.* after a few minutes to a few hours. In all cases the precipitate was left ageing for half an hour to an hour before filtration and washed with absolute ethanol and diethyl ether. Upon drying the compounds with p-tol anions turned purple, indicating the presence of iron(II) low spin species. The linear structure of the polymers obtained is depicted in Fig. 1, as known from the literature.[21] Infrared spectroscopy gives a first confirmation of this structure. First the triazoles are clearly bonded to the iron(II) since the aromatic $\nu_{\text{C–H}}$ is shifted to lower energies, and one observes ring vibrations in the region 1400 cm^{-1} dependent on the spin state of the iron(II).[28] Moreover the infrared spectra point to bridging triazoles, since there is no indication of loss of the C_{2v} symmetry.[17] NIR-visible spectroscopy enables one to verify the thermochroism and to measure the energies corresponding to the $^1A_1 \rightarrow {}^1T_1$ LS transition and $^5T_2 \rightarrow {}^5E$ (giving directly 10Dq^{HS}) HS transition of all samples (*cf.* Fig. 2). It also allows one to evaluate the amount of HS species at low temperature. Elemental analyses are in all cases consistent, within a minimal error usually observed for this type of samples,[29] with the formulae [Fe(Rtrz)$_3$][A]$_2$·*x*H$_2$O (R = alkyl, x = 0 to 3). The amount of water was found to vary little among all

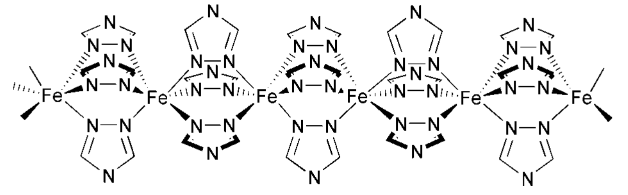

Fig. 1 Schematic representation of the linear structure of compounds of general formula [Fe(4-Rtrz)$_3$][A]$_2$·*x*H$_2$O, deduced from EXAFS, magnetic, optical and Mössbauer measurements.

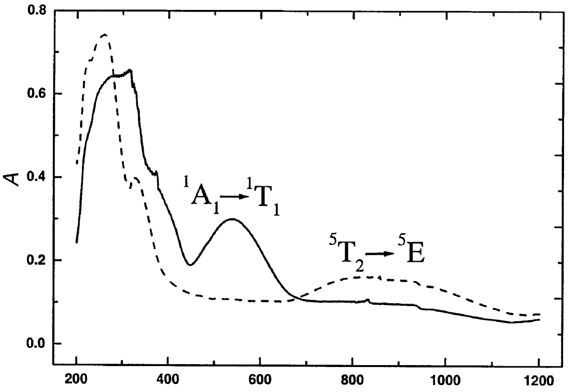

Fig. 2 Ligand field spectra of [Fe(4-octyl-trz)$_3$][CF$_3$SO$_3$]$_2$·2H$_2$O at room temperature (dashed line) and approximately 90 K (full line).

compounds. Altogether these results, summed up in Table 1, confirm the 1-D polymeric chain-like type of the compounds synthesised. Table 1 also includes the amount of HS species present at low temperatures (90–100 K) as estimated from magnetic susceptibility and NIR-visible measurements. The size of the chains can be estimated from the amount of HS species at low temperatures, considering that they correspond to chain extremities with water co-ordinated and therefore showing no spin-transition behaviour. Such species are assumed to be similar to trinuclear compounds in which only the central atom shows a spin-crossover behaviour.[22] It is verified that $10Dq^{HS}$ is hardly affected by a change in the triazole.[25b] However since the $^1A_1 \rightarrow {}^1T_2$ absorption could not be determined accurately, $10Dq^{LS}$ cannot be calculated. Repeated synthesis of identical compounds showed reproducible magnetic behaviour.

Results and discussion

General magnetic properties

All compounds showed typical dependence of $\chi_m T$ *vs.* T for a HS ($S = 2$) ↔ LS ($S = 0$) crossover of the iron(II) ions. Values of 3 to 3.6 cm^3 K mol^{-1} are found at high temperature in the HS state, and 0.2 to 1 cm^3 K mol^{-1} at low temperature in the 'LS' state, indicating in some cases the presence of a residual HS fraction, which is also detected and even quantified in NIR-visible. When hysteresis was detected a second thermal cycle was measured. Indeed, in most cases, samples were first cycled several times so that the measured curves are stable ones. Some compounds, *i.e.* those with p-tol (butyl-, hexyl-, octyl-, hexadecyl-triazole polymers), showed a first LS → HS transition at 360 K and then a stable hysteresis at lower temperatures. As previously discussed on the basis of TGA data,[14,19,20] this behaviour can be attributed to loss of water upon the first warming inducing a spin change of the sample. However in the present case the samples do not show again the transition at 360 K when left in the ambient atmosphere, meaning that they do not reabsorb water. Indeed water remained present in the samples. As proposed previously,[19] this type of behaviour can be used as a one-shot application that indicates a certain temperature has been passed, but the samples of this study have rather high transition temperatures after the loss of water.

Fig. 3(a) depicts the case of amyltriazole polymers ($n = 5$). The transitions are complete for BF_4, triflate and *p*-tol, but a residual fraction of HS at low temperature is detected for ClO_4. The triflate, BF_4 and *p*-tol show rather steep transitions with small hysteresis whereas the transition of the perchlorate polymer is gradual. Fig. 3(b) shows some selected transition curves of polymers with triflate as anion (see legend), showing the different behaviour observed in this family of compounds, from the steep transition with hysteresis (hexyltriazole polymer) to the more gradual transition (tridecyltriazole polymer). From this type of curves typical variables describing the characteristics of the spin transition are extracted for all compounds studied. T_c (up and down when hysteresis is

Table 1 Analytic, spectroscopic and electronic data for the series $[Fe(4\text{-}n\text{-alkyl-trz})_3][A]_2 \cdot xH_2O$. Spectroscopic features were obtained from diffuse reflectance Vis-NIR. The residual value of HS was estimated from magnetic and Vis-NIR data

n	Anion	*x*	RT state	$10Dq^{HS}/cm^{-1}$	$\tilde{v}(^1A_1 \rightarrow {}^1T_1)/cm^{-1}$	Residual HS (%)
1	BF_4	0.5	HS	11 695	18 115	<2
	ClO_4	0.5	HS	12 121	18 518	<2
2	BF_4	3	HS	11 904	18 018	<2
	ClO_4	2	HS	11 764	18 654	<2
3	BF_4	3	HS	11 904	18 412	6
	Triflate	2	HS	12 121	18 456	2
4	BF_4	1	HS	12 121	18 018	2
	ClO_4	1	HS	11 904	18 348	3
	Triflate	2	HS	11 695	18 348	6
	p-tol	2	L/HS	11 985	18 456	<2
5	BF_4	2	HS	11 904	18 518	4
	ClO_4	2	HS	11 695	18 018	20
	Triflate	2	HS	11 904	18 691	<2
	p-tol	2	LS	11 840[a]	18 585	<2
6	BF_4	2	HS	11 764	18 456	4
	ClO_4	3	HS	11 625	18 018	15
	Triflate	2	HS	11 764	18 518	2
	p-tol	2	LS	11 764[a]	18 566	<2
7	BF_4	2	HS	11 625	18 518	8
	ClO_4	2	HS	11 625	18 450	20
	Triflate	2	HS	11 428	18 181	8
	p-tol	2	LS	11 625[a]	18 518	<2
8	BF_4	2	HS	11 904	18 115	3
	ClO_4	3	HS	11 985	18 566	17
	Triflate	2	HS	11 834	18 518	5
	p-tol	2	L/HS	11 985	18 518	<2
13	BF_4	2	HS	11 625	18 450	11
	ClO_4	2	HS	11 560	18 115	18
	Triflate	2	HS	11 904	18 518	2
	p-tol	2	L/HS	11 904	18 518	2
16	BF_4	2	HS	11 764	18 248	15
	ClO_4	2	HS	11 904	18 581	15
	Triflate	2	HS	11 764	18 181	10
	p-tol	2	LS	11 714[a]	18 581	<2
18	BF_4	2	HS	11 625	18 181	20
	ClO_4	3	HS	11 625	18 348	25
	Triflate	2	HS	11 695	18 181	10
	p-tol	2	LS	11 690[a]	18 518	2

[a] $10Dq^{HS}$ of p-tol polymers are approximate due to the very low amount of HS at RT.

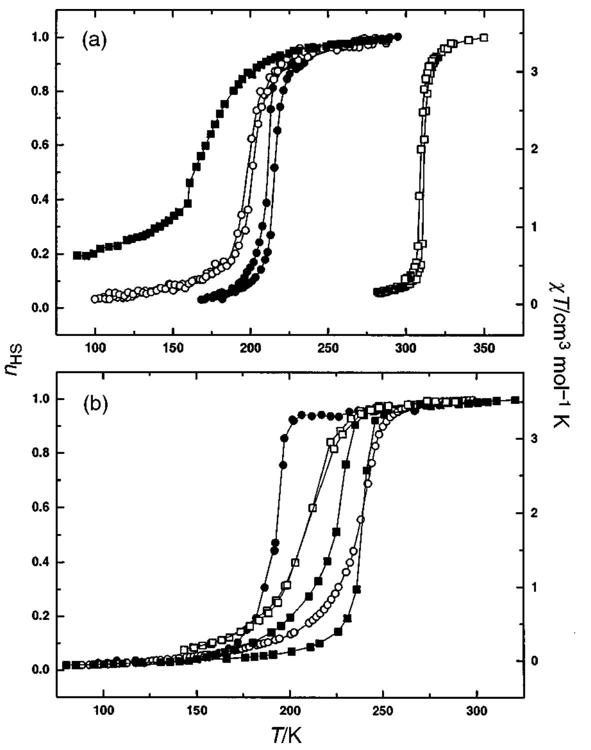

Fig. 3 Spin transition curves as obtained from magnetic measurements (a) of $[Fe(4\text{-amyl-trz})_3][A_2]$ A = ClO_4 (■), BF_4 (○), triflate (●) or *p*-tol (□), (b) of $[Fe(4\text{-}R_n trz)_3][CF_3SO_3]_2 \cdot xH_2O$, $n = 3$ (●), 6 (■), 7 (□) or 13 (○).

present) corresponds to the temperature for which half of the "transiting" iron(II) have changed spin, and ΔT_{80} is the smallest temperature range that covers 80% of the spin transition. The latter characterises the steepness of the transition, and was found identical on each branch of the eventual hysteresis loops. Fig. 4 recapitulates these results for each counter ion with increasing *n*-alkyl tail.

Effect of the alkyl tail length

The transition temperatures do not remain stable when only the alkyl tail size is changed, although it should not affect strongly the donor strength of the triazoles. Alkyl substituents are weakly donating groups, and therefore only a slight difference in electronic effect can be expected between a methyl and a CH_2R group. The only effect of a growing alkyl chain would be to increase the distance between the anion and the cationic chains, and therefore to lower electrostatic cation–anion interactions and by consequence lower the ligand field and T_c. However, only with tetrafluoroborate as anion one can observe a real correlation with *n*, with a downward shift of T_c with increasing *n* (*cf.* Fig. 4c). In the other cases no such correlation is seen. In the three mononuclear compounds $[Fe(Rtrz)_6][BF_4]_2$ with long alkyl chains ($n = 8$, 12 or 18) also T_c was found not to be constant, but no real difference in steepness was found.[30]

Hysteresis disappears with high *n* values for spherical anions and for triflate. The spherical anions indeed give rather large hysteresis width at low *n* values, that gradually lowers to zero with increasing *n*. This is consistent with a recent theoretical study[10] that shows the importance of the existence of a long-range interaction together with a strong intrachain interaction for large hysteresis. Considering that the chain itself is not changing much, the long-range interaction appears to be related to interchain contacts, that are lowered when enlarging the alkyl tails on the triazoles. Extremely gradual transitions are found with the spherical anions when $n = 16$ or 18, but up to $n = 13$ for BF_4 and 6 for triflate the transitions remain rather steep. The increase of *n* then mainly results, apart from the disappearance of hysteresis, in a smoothing or rounding of the extremities of the transitions. The *p*-tol compounds show hysteresis up to $n = 18$, and the widths remain in the 5–10 K range. A study of octadecyltriazole polymers as precursors for Langmuir–Blodgett films[28] showed similar results and led the authors to the conclusion that in tosylate compounds the co-operativity process is mainly intramolecular, *i.e.* between iron(II) centres of the same polymer chain. The case of ClO_4 is different. From $n = 5$, increasing the length of the alkyl tail results in more and more gradual transitions with the presence of a rather high HS residual fraction at LT. A simple calculation gives an average chain size of 10 iron(II) ions for a residual fraction of 20%.

In theoretical considerations on 1-D spin crossover chains[10] the size of the chains was considered high, fixed and homogeneous. However due to the fast formation of the present compounds there is no reason for only one size. Indeed the perchlorate polymers with long tails on the triazoles are examples of rather short chains, as confirmed by the high amount of HS species at low temperatures. It has been proven that the existence of domains containing only like-spin iron(II) species, LS or HS, within a chain upon the transition and their interaction with each other was of importance.[31] The size of these domains indeed has been proposed to control the co-operativity[31] in Cu-doped $[Fe(Htrz)_2(trz)][BF_4]_2$. Calculations showed that a minimum number of iron(II) species having the same spin state within a domain was necessary for the occurrence of hysteresis and for sharp transitions.[31] When the size of the chain is lowered the size of these domains is likely to decrease. Considering the non-co-operative transitions observed in the perchlorate polymers, and also with $n = 16$ or 18 with tetrafluoroborate and triflate, which all show high amounts of HS at low temperatures, the results of this study are in agreement with these theoretical calculations. One also has to consider the homogeneity of the samples. When the size of a chain is calculated using the residual amount of HS at low temperatures it is an average value. If the chains are long enough, the behaviours of all the chains remain comparable and the transition is steep, whatever the long-range interaction is. However, if the distribution is not homogeneous with the presence of very short chains, that may have different transition temperatures, then different behaviours coexist in the sample, and the macroscopic result is a more gradual transition, a summation of the different transitions present. This appears to be the case here with ClO_4 from $n = 5$, for BF_4 from $n = 13$ and triflate from $n = 7$, but for the last with lower HS residual values. The amount of HS species at low temperature is then up to 25%, which corresponds to an average size of 8 irons. Therefore the main effect of an increase of the *n*-alkyl tails on the triazoles is to prevent the formation of long polymeric chains, except apparently with *p*-tol as anion. This would suggest that the ageing of the precipitate is of importance. Indeed when the precipitates formed are filtered off immediately after formation extremely gradual transitions are obtained, indicative of a wide range of chain size. However, when ageing was allowed for at least 10 minutes, no further difference in the transition curves were observed. Therefore, after the first minutes of ageing in contact with the mother liquor, the chain length is no longer dependent on the ageing time.

Finally it has to be kept in mind that a long alkyl tail can be packed in many different ways, which would generate another source of randomness in the interchain contacts and in the anion–cation interactions.

Effect of the counter ion

The first and most important effect of the counter ion used is on the transition temperature. Tetrafluoroborate and perchlorate, which are among the biggest of commonly used

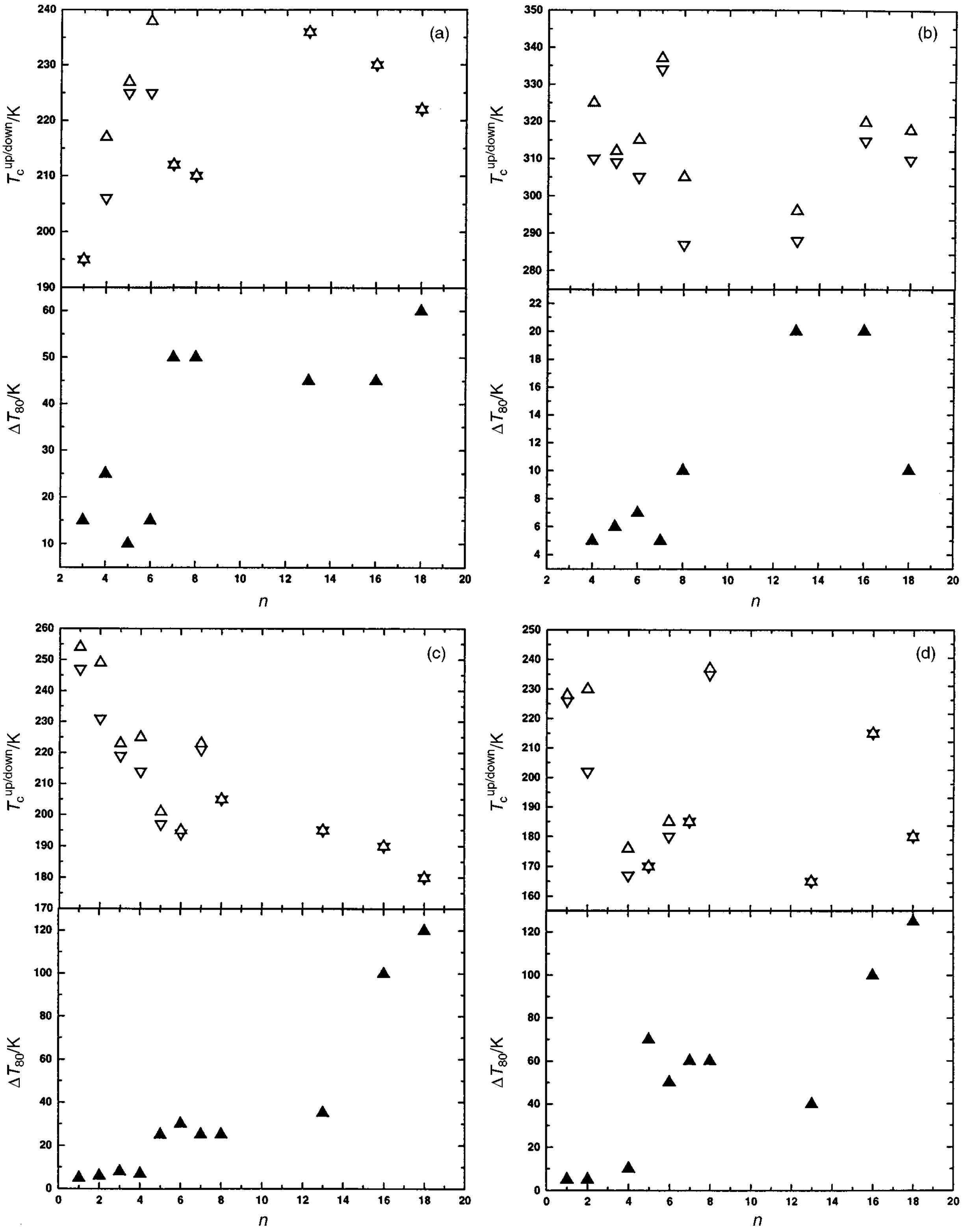

Fig. 4 Plots of $T_{c\,\mathrm{up/down}}$ and ΔT_{80} (see text) as a function of the size *n* of the *n*-alkyl tail on the triazole for (a) triflate, (b) *p*-tol, (c) BF_4 and (d) ClO_4 polymers.

spherical anions, give transitions at rather low temperature, in the range 160 to 250 K. Polymers with these two anions in fact have almost identical transition temperatures, which can be related to the comparable size of these anions. The direct correlation between T_c and the diameter of a spherical anion in this type of materials[14,16,24] is therefore confirmed here. However, when non-spherical anions are involved, other parameters will be involved. Triflate polymers give slightly higher transition temperatures for high *n*, and as observed in many systems with tosylate type anions[14,19,20] all *p*-tol polymers have much higher transition temperatures, in the 290–340 K range. Since size is obviously not the main parameter in this case, interaction between anionic species and cationic chains has to be considered. In fact, it has been shown for spherical anions that the Fe–N distance in the LS state decreases when the diameter of the spherical anion decreases.[32] Anion–cation interactions can give rise to an electrostatic pressure that grows with the interaction and gives higher ligand fields and therefore higher T_c.[32,33] This effect is related to the application of an external pressure, which also displaces the transitions to higher temperatures.[34] For the same reason the amount of water is of importance and for direct comparison has to be identical. How the anion, whatever its form, can 'fit' in between the alkyl chains therefore can affect strongly T_c, by increasing the internal electrostatic pressure. If the case of [Fe(Htrz)$_2$(trz)][BF$_4$] is remarkable it is because of the delocalised charge carried by the bridges [(Htrz)$_2$(trz)], give rise to very strong electrostatic interaction. The transition temperature in [Fe(Htrz)$_3$][BF$_4$]$_2$ in which no negative charge is present on the chain is indeed lower. In the series [Fe(trim)$_2$]X$_2$ with X = halide (trim = 4-(4-imidazolylmethyl)-2-(2-imidazolylmethyl)imidazole) the opposite effect of the size of the halogen was observed.[35] However, this was ascribed to a weakening of the Fe–N bonds due to the transmission of the inductive effect of the electronegative anions to the co-ordinated nitrogen through hydrogen bonds, the higher electronegativity resulting in weaker Fe–N bonds and lower T_c. The higher transition temperatures of all tosylate polymers probably originates from a larger electrostatic pressure created by this type of anion. One can imagine stacking of the aromatic ring with the triazole that would keep the anion very close to the chains, although no real reason was found for it. Provided that the tail on the triazole is rather small, spherical anions BF$_4$ and ClO$_4$ favour large hysteresis, more than the triflate anion. Probably hydrogen bonding between the chains has to be considered, since it can still be an efficient pathway for interchain interaction. The case of *p*-tol is unusual, since it does not seem to have any influence on the size of the hysteresis. All the polymers with this anion have the same abrupt transitions occurring within a few K. This hysteresis phenomenon is maintained with *n* up to 18. In this case either the anion does not play any role in the co-operativity mechanism, or its effect is the same whatever the value of *n*. Armand *et al.*[28] pointed at the first explanation, but the anion can also take part in intrachain interaction. It is, however, evident that in these samples the hysteresis arises mainly from intrachain co-operativity.

As seen previously with long tails on the triazole, the size of the polymeric chains formed is dependent on the anion, ClO$_4$, triflate and to a lesser extent BF$_4$ giving the smallest chains and therefore the most gradual transition curves.

Although it was not the goal of this study, outer sphere anions proved to be the most influential on the spin transition features, especially in regard to the temperature, provided that the chains are long. The main origin of this effect is the electrostatic anion–cation interaction that affects the ligand-field strength of the central iron(II) ion.

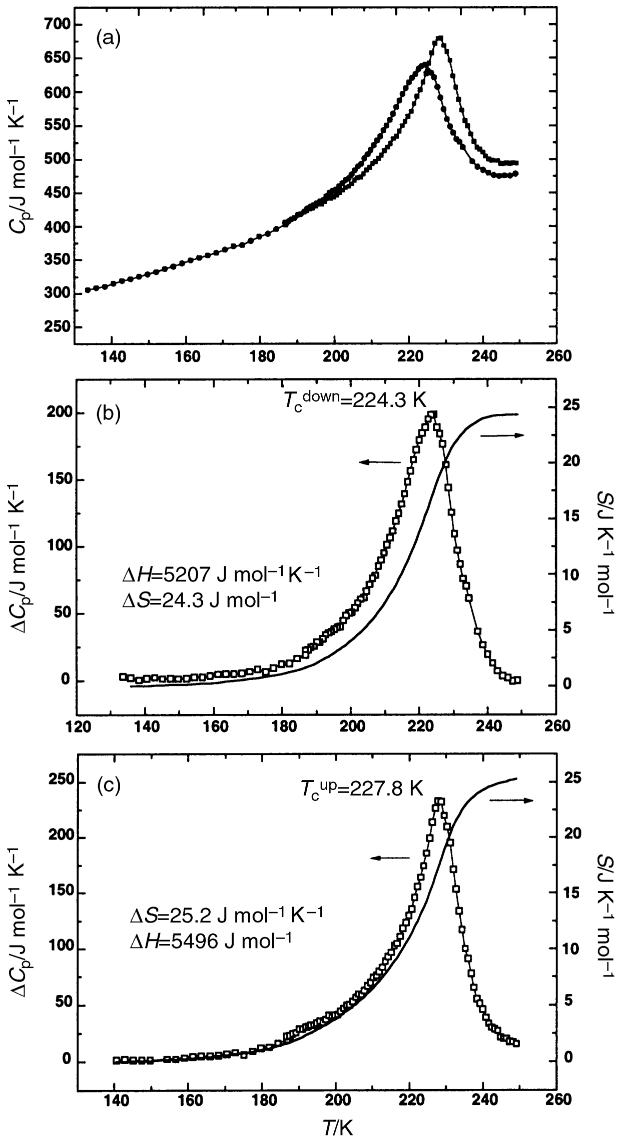

Fig. 5 Temperature dependence of (a) the heat capacity $C_p$of [Fe(4-amyl-trz)$_3$][CF$_3$SO$_3$]$_2$ · 2H$_2$O in both cooling and warming modes, with plots of ΔC_p showing the derived thermodynamic parameters of the transition (see text) in the cooling (b) and warming (c) modes.

Co-operativeness?

For discussion of the strength of interaction, co-operativity and comparison with known compounds, thermodynamic parameters of the spin transition have to be known. Therefore specific heat measurements were performed on [Fe(amyl-trz)$_3$][CF$_3$SO$_3$]$_2$ · 2H$_2$O. This compound does not have residual HS at low temperature and is typical of the series under investigation. Results are shown in Fig. 5. The spin transition is found at 224.3 K on cooling and 227.8 K on warming, which is in good agreement with the magnetic measurements. The enthalpy variation, Δ*H*, accompanying the HS ↔ LS transition is found to be equal to about 5.3 kJ mol^{-1}. The entropy associated is estimated as 24.7 J K^{-1} mol^{-1}. For comparison, an extremely large Δ*H* of 27 kJ mol^{-1} was found for the transition of the polymeric [Fe(Htrz)$_2$(trz)][BF$_4$].[18] However, this compound seems to be peculiar due to its charged bridge. The value found here is of the same order, although smaller, as in the strongly co-operative 2-D [Fe(btr)$_2$(NCS)$_2$] · H$_2$O;[36] *i.e.* 10 kJ mol^{-1}, and comparable to that of the prototype spin transition compound [Fe(phen)$_2$(NCS)$_2$],[37] *i.e.* 8.6 kJ mol^{-1}. The entropy change is here about half that in other spin-transition compounds, about 40–50 J K^{-1} mol^{-1}, and much smaller than those of very co-operative materials such as the two mentioned above, 75–80 J K^{-1} mol^{-1}. One could imagine that the system under study is not really co-operative, even though the transition occurs within 10 K, with a small hysteresis.

Since the positions of the $^1A_1 \rightarrow {}^1T_1$ bands of the present samples lie in the same area as for [Fe(ptz)$_6$][BF$_4$]$_2$(ptz = 1-propyltetrazole), the LIESST effect was studied on two selected samples, *i.e.* [Fe(amyl-trz)$_3$][BF$_4$]$_2$ · 2H$_2$Oand [Fe(heptyl-trz)$_3$][CF$_3$SO$_3$]$_2$ · 2H$_2$O at 10 K. No change in magnetism was observed under the conditions used, whatsoever the power of the lamp, although, due to practical reasons, the actual power at the sample was probably not higher than a few mW cm^{-2}. Light-excited HS species were detected only recently[38] in [Fe(NH$_2$trz)$_3$][A$_2$], A = NO$_3$ or SiF$_6$, by EXAFS at 4.2 K. The conversion appeared to be only 50% and the relaxation was fast even at very low temperature. In [Fe(btr)$_2$(NCS)$_2$] · H$_2$O the LIESST effect has not been possible yet, due to the high power needed.[39] In both cases very strong co-operativity due to a strong chemical bond is invoked to explain the difference in the light-induced processes for molecular complexes with weak bonding. The absence of any detectable excitation here is indeed a confirmation of the high co-operativity present, at least along the chains in [Fe(*n*-alkyl-trz)$_3$][A]$_2$. The rather large values of

ΔT_{80} do not indicate the absence of such an intrachain co-operativity, only an overall lower co-operativity, that may be due to a lower long-range interaction. Very high co-operativity is only achieved in a few particular cases, when strong contacts between iron(II) centres are present, such as in $[Fe(Htrz)_2(trz)][BF_4]$, $[Fe(btr)_2(NCS)_2]\cdot H_2O$, or in this study with only a methyl or ethyl group on the triazole. Strong interaction within the chain is not enough; an additional long-range interaction has to be present. The importance of such an interaction is the subject of theoretical studies.[10]

Conclusion

The expected lowering of co-operativity with increasing size of the *n*-alkyl substituent on the triazole of chain-like spin-transition compounds $[Fe(4\text{-}R_n trz)_3][A_2]\cdot xH_2O$ has been observed and analysed for the first time. Also a correlation was found between T_c and the value of n in $[Fe(4\text{-}R_n trz)_3][BF_4]_2$, which has been ascribed to the lowering of anion–cation electrostatic interaction by increasing the distance between the ionic species. Nevertheless the main effect of increasing the size of the alkyl substituent is to prevent the formation of long polymeric chains. However, when using A = *p*-tol, the only effect observed is a smoothening of the extremities of the transition curves. The electrostatic anion/cationic chain interaction is also at the origin of the differences between the anions used, mediated through the electrostatic pressure it creates on the spin transition chains. The high intrachain interaction has been confirmed here by the impossibility of trapping HS species by light excitation. The importance of the existence of a long range interaction for large hysteresis has finally been confirmed, although this interaction can not simply be considered as the interchain contacts. It has to be emphasised that the size of the polymeric chains is the first and most important parameter to check.

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