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A Mixed-Ligand Approach for Spin-Crossover Modulation in a Linear Fe^{II} Coordination Polymer

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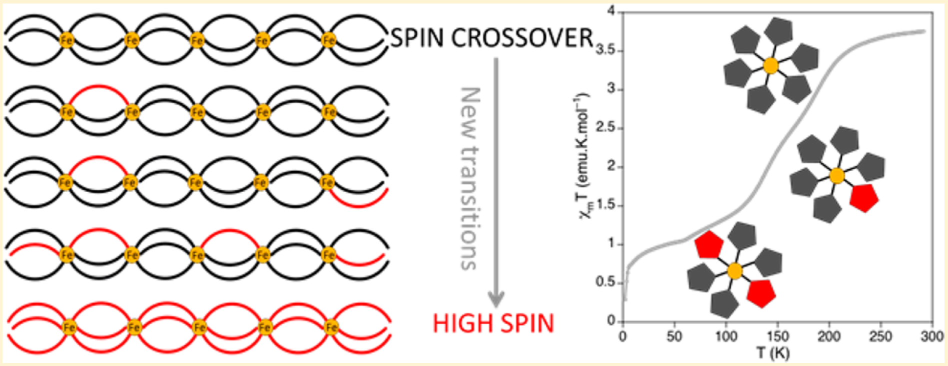
S *Supporting Information*



ABSTRACT: In this work, we present a family of Fe^{II} coordination polymers of general formula $[Fe(btzx)_{3-3x}(btix)_{3x}](ClO_4)_2$ with interesting spin-crossover properties. These coordination polymers have been synthesized using chemical mixtures of two different but closely related ligands, 1,4-bis(tetrazol-1-ylmethyl)benzene (btzx) and 1,4-bis(triazol-1-ylmethyl)benzene (btix), and the effect of a gradual substitution of the ligand in the spin transition temperature has been investigated. Several chemical mixtures have been structurally characterized by X-ray powder diffraction indicating a clear critical amount in the composition of the mixture after which mixed phases rather than a single phase comprising mixed components are observed. Importantly, this approach causes the appearance of a new transition at lower temperatures that is not present in the pure $[Fe(L)_3](ClO_4)_2$ systems.

INTRODUCTION

The preparation of stimuli-responsive materials with potential applications as chemical switches, information storage devices, or molecular sensors is an area that continues to attract considerable interest.[1,2] These materials undergo reversible structural changes in response to an applied stimulus, being exceptionally useful in the preparation of functional materials with tunable or switching physical properties. This is particularly interesting for spin-crossover (SCO) compounds, given their great sensitivity to external changes of distinct nature,[3] which makes them excellent candidates for a number of practical applications within molecule-based materials.[4] However, implementation of SCO compounds into realistic applications remains a challenging issue and requires advanced control of the transition temperatures. Thus, great effort has been made in the modification of the SCO temperature since the detection of this phenomenon in the 1930s.[5] SCO arises from a well-designed ligand with a proper ligand-field strength, but it can also be significantly affected by crystal packing.[6] The tuning of SCO properties has been typically achieved by modifying the ligand,[7] the counterion,[8] the coordination sphere of the SCO centers,[9] or the solvent molecules,[8b,10] although these commonly involve a change in the crystal packing and thus it is difficult to correlate the effects exerted with the modification in the SCO temperature. A different approach consists of the use of metal dilutions, which disrupt the cooperativity between the metal centers and also affect the transition temperature by inducing the so-called negative pressure. This has been investigated in order to understand the thermal spin-crossover and the relaxation behavior, both in monomeric complexes (i.e., formation of true solid solutions)[11] and in polymeric systems (i.e., shortening the length of the polymers).[12] However, the most simple and versatile way to subtly modify the ligand field consists of the use of two (or more) organic building blocks with similar chemical behavior (size and coordination ability) but different ligand-field strength.[13] The use of ligand mixtures to tune physical properties has recently been proven to be extremely successful for the enhancement of gas sorption in metal−organic frameworks (MOFs), which are crystalline coordination polymers that present porous structures.[14] In this sense, the preparation of multivariant MOFs whose pores are decorated by heterogeneous mixtures of functionalities is attracting considerable interest.[15] However, this mixed-ligand approach presents an important challenge since combination of various

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ligands may yield mixed phases rather than a single phase comprising the different components.

In this work, we have studied the effect of a gradual ligand substitution in a SCO coordination polymer by combining two different types of azole organic ligands, which are well studied ligands for the design of SCO coordination polymers.[16] Similar to the monomeric Fe^{II} complexes with 1-*R*-tetrazoles, the Fe^{II} coordination polymers typically undergo spin transition.[8a,17−20] Thus, we have considered two structurally related compounds of formula $[Fe(btzx)_3](ClO_4)_2$ (**1**, a 1-*R*-tetrazole derivative) and $[Fe(btix)_3](ClO_4)_2$ (**2**, a 1-*R*-triazole derivative), one displaying a spin transition centered at 200 K (**1**) and the other remaining in the high-spin state over all temperatures (**2**). We have recently shown that the transition temperature of **1** can be modified by a chemical stimulus such as CO_2 sorption, which produces an increase in the transition temperature of ca. 10 K when 1 bar of CO_2 is physisorbed.[18] Here we have created a series of magnetic frameworks based on partial ligand substitution by using different chemical mixtures of the two organic ligands, yielding a series of isostructural coordination polymers in which not only a shift in the spin transition temperature occurs but also a new SCO transition is achieved.

■ EXPERIMENTAL SECTION

All reagents and solvents were commercially available and used without further purification. The ligands 1,4-bis(tetrazol-1-ylmethyl)-benzene (btzx) and 1,4-bis(triazol-1-ylmethyl)-benzene (btix) were prepared according to literature methods.[21] ^1H NMR spectra was recorded on a Bruker DPX300 (300 MHz) spectrometer. Proton (^1H) chemical shifts are reported in parts per million (δ) and referenced internally with respect to the protic solvent impurity. Elemental analyses were carried out at the Atomic Spectroscopic Section of the Central Services (SCSIE) of the University of Valencia, using an analyzer EA1110 CHNS from CE Instruments.

Caution! *Perchlorate and azide salts are explosive (especially if they are dry) and should be handled in small quantities with caution. NaN_3 with strong acids forms hydrazoic acid, which is extremely toxic. Therefore, the solution should be prepared inside a laboratory chemical hood. Explosions may occur from concentrating azide salts during evaporation to dryness.*

Synthesis of $[Fe(btzx)_3](ClO_4)_2$ (1).[18] A solution of $Fe(ClO_4)_2\cdot xH_2O$ (112 mg) in 5 mL of MeCN was added into a suspension of btzx (152 mg, 0.8 mmol) in 40 mL of MeCN containing ascorbic acid (ca. 10 mg). The resulting milky suspension was refluxed and stirred for 4 h under Ar atmosphere. A white crystalline precipitate appeared during the reaction. After cooling to room temperature, the white powder was filtered and washed with MeCN. Phase purity was established by X-ray powder diffraction (*vide infra*). Yield = 52 %.

Synthesis of $[Fe(btix)_3](ClO_4)_2$ (2).[22] A solution of $Fe(ClO_4)_2\cdot xH_2O$ (63.7 mg) in 2.5 mL of EtOH was added slowly into an ethanolic solution of btix (120.0 mg, 0.5 mmol) without stirring. The mixture was left at RT for crystallization. After several days, colorless blocked-shaped crystals were filtered off and washed with EtOH. Phase purity was established by X-ray powder diffraction. Yield = 47%.

Synthesis of $[Fe(btzx)_{3-3x}(btix)_{3x}](ClO_4)_2$ (x = 0.05 (3); x = 0.10 (4); x = 0.15 (5); x = 0.20 (6); x = 0.30 (7); x = 0.40 (8); x = 0.50 (9)). The chemical mixtures **3**−**9** were synthesized in a procedure analogous to that of **1** with the appropriate mixtures of the ligands 1,4-bis(tetrazol-1-ylmethyl)benzene (btzx) and 1,4-bis(triazol-1-ylmethyl)-benzene (btix). Phase purity was established by X-ray powder diffraction. The C/N ratio from elemental analyses was used to estimate the ligand composition of the final compounds, which were in good agreement with the starting values: x = 0.06 (**3**); x = 0.04 (**4**); x = 0.12 (**5**); x = 0.22 (**6**). Compound **7** crystallizes with some unreacted tetrazole, as determined by powder diffraction, and thus its C/N ratio is unreliable. Typical yields are about 50% except for compounds **8** and **9**, which were obtained only as a few milligrams. Repetition of the synthesis in these two cases provided always the same results.

Synthesis of $[Fe(btzx)_3](ClO_4)_2$ and $[Fe(btix)_3](ClO_4)_2$ Physical Mixture (10). A physical mixture was obtained by simply grinding **1** and **2** in a ratio 80:20 (**10**). Mixture of two phases was established by X-ray powder diffraction.

X-ray Powder Diffraction Measurements. Polycrystalline samples of **1**−**10** were lightly ground in an agate mortar and pestle and filled into 0.5 mm borosilicate capillaries prior to being mounted and aligned on a Empyrean PANalytical powder diffractometer, using Cu Kα radiation (λ = 1.54056 Å). For each sample, two repeated measurements were collected at room temperature (2θ = 2−60°) and merged in a single diffractogram. Pawley refinements[23] were performed using the TOPAS computer program[24] and revealed an excellent fit to a one-phase model for compounds **3** (R_{wp} = 0.0220; GOF = 1.301), **4** (R_{wp} = 0.0236; GOF = 1.283), **5** (R_{wp} = 0.0240; GOF = 1.274), and **6** (R_{wp} = 0.0229; GOF = 1.383), indicating the absence of any other detectable crystalline phases. Unreacted btzx was also observed in the fit of compounds **7** (R_{wp} = 0.0210; GOF = 1.080), **8** (R_{wp} = 0.0214; GOF = 1.096), and **9** (R_{wp} = 0.0224; GOF = 1.174). In the latter, compound **2** was also detected. Pawley refinement on the physical mixture **10** revealed an excellent fit to a two-phase model of compounds **1** and **2** (R_{wp} = 0.0225; GOF = 1.331). Table S1, Supporting Information, contains the refined structural parameters.

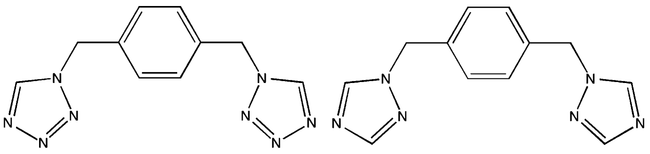
Thermogravimetric Analysis. Thermogravimetric analysis of **1**−**7** and **10** were carried out with a Mettler Toledo TGA/SDTA 851 apparatus in the 25−800 °C temperature range under a 10 $°C\cdot min^{-1}$ scan rate and an air flow of 30 $mL\cdot min^{-1}$. Due to the low amount of sample, TGA analysis on compounds **8** and **9** were not possible.

Magnetic Measurements. Magnetic susceptibility measurements were performed with a Quantum Design SQUID magnetometer with an applied field of 1000 G. The susceptibility data were corrected from the diamagnetic contributions as deduced by using Pascal's constant tables.

■ RESULTS AND DISCUSSION

Structural Characterization. With the aim of modulating the transition temperature of a SCO coordination polymer, we have employed a mixture of two closely related organic ligands, 1,4-bis(tetrazol-1-ylmethyl)benzene (hereafter btzx) and 1,4-bis(triazol-1-ylmethyl)benzene (hereafter btix), which only differ in a nitrogen atom in the five-membered ring (Scheme 1). Separately these ligands yield two structurally related coordination polymers, $[Fe(btzx)_3](ClO_4)_2$ (**1**)[18] and $[Fe(btix)_3](ClO_4)_2$ (**2**),[22] which are formed by 1D chains with three ligands serving as bridges between each pair of metal centers, as depicted in their crystal structures shown in Figure 1. The minor difference between these two ligands causes important changes in the magnetic behavior of the coordination polymer, as will be described below. The two ligands can adopt two different conformations, *syn* and *anti*, due to the presence of methylene groups between the tetrazole or triazole rings and the benzene ring, which can lead to different coordination frameworks.[25]

Scheme 1. Chemical Structures of btzx and btix Ligands



bis(tetrazol-yl)-p-xylene
(btzx)

bis(triazol-yl)-p-xylene
(btix)

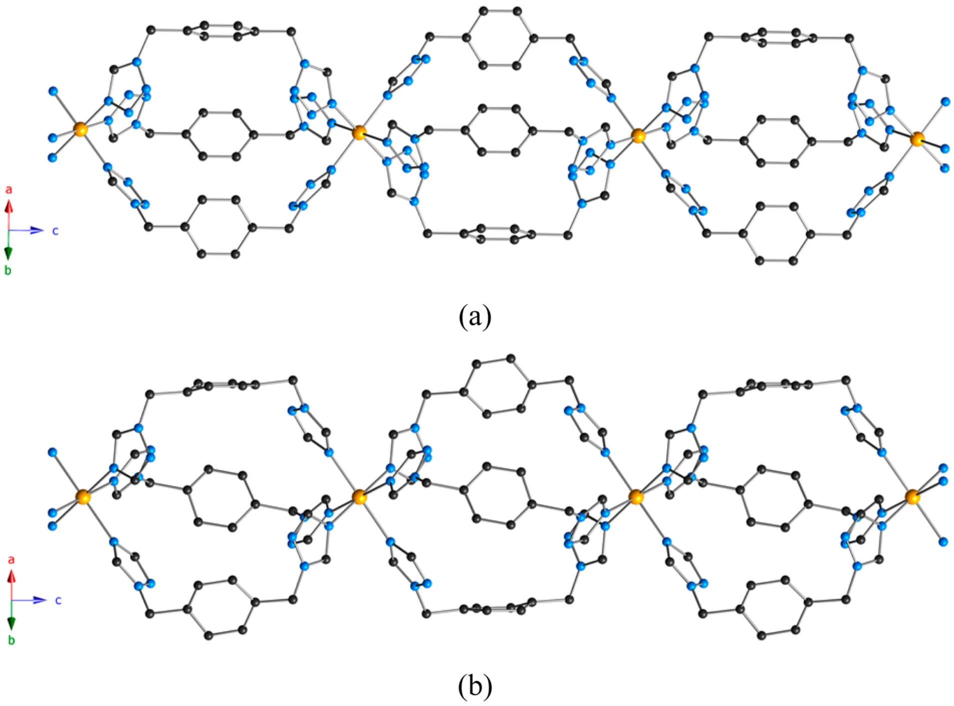
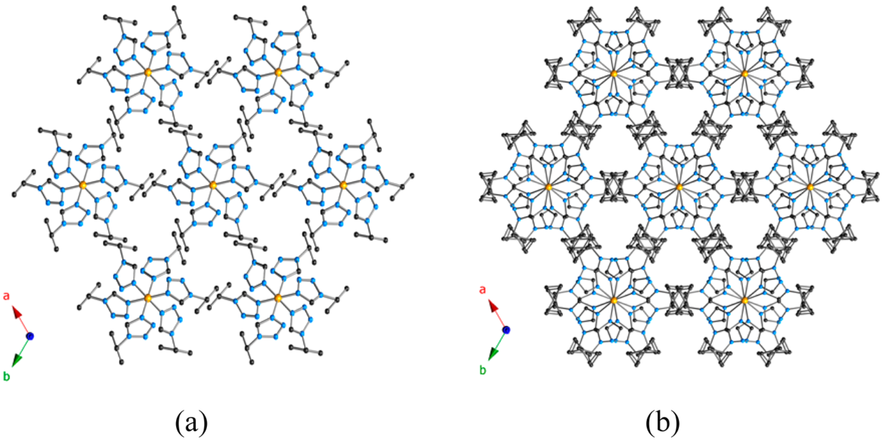


Figure 1. Crystal structures of compounds **1** (a) and **2** (b). The ClO_4^- anions and hydrogen atoms have been removed for clarity. Key: Fe, orange; C, gray; N, blue.

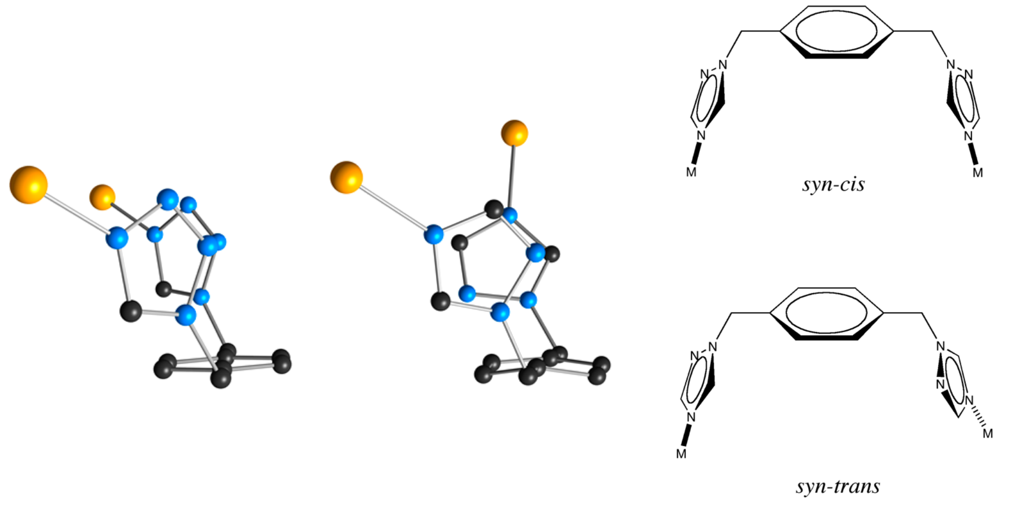


(a) (b)

Figure 2. Hexagonal packing of **1** (a) and **2** (b) viewed along the *c*-axis. Color code as in Figure 1. The ClO_4^- anions and hydrogen atoms have been removed for clarity.

We have recently reported the controlled reaction of $Fe(ClO_4)_2{\cdot}xH_2O$ and btzx in a refluxing solution of MeCN resulting in the formation of a crystalline powder of $[Fe(btzx)_3](ClO_4)_2$ (**1**) after several hours.[18] Crystallographic analysis of **1**, which crystallizes in the space group $P6_3/m$, shows that it is composed of $[Fe(btzx)_3]^{2+}$ units that form one-dimensional chains that run parallel to the crystallographic *c*-axis with Fe···Fe distances of 11.7881(12) Å at 240 K (Figure 1). The Fe^{II} centers are triply bridged by the organic ligands, as has been seen previously in other Fe^{II} linear chain compounds with extended tetrazole ligands.[8a,17a−c,18] The ClO_4^- counter-ions separate the different chains, which are packed affording a framework with no permanent channels. However, internal cavities of 132 Å^3 (as estimated using PLATON) are present in the structure, which have been shown to be able to accommodate each one molecule of CO_2 at 1 bar and 273 K.[18] Each Fe^{II} center, which lies on the 3-fold axis, is octahedrally coordinated by six tetrazole nitrogen atoms from six *syn*-btzx ligands, with Fe−N distances of 2.160(6) Å.

The reaction of $Fe(ClO_4)_2{\cdot}xH_2O$ and btix in EtOH at room temperature results in the formation of block-shaped crystals of formula $[Fe(btix)_3](ClO_4)_2$ (**2**).[26] Similarly to **1**, compound **2** is composed of $[Fe(btix)_3]^{2+}$ units that form one-dimensional chains that run parallel to the crystallographic *c*-axis (Figure 1), although **2** crystallizes in the $P\bar{3}c1$ space group. Each Fe^{II} is also located on the 3-fold axis and is octahedrally coordinated by six triazole nitrogen atoms derived from six *syn*-btix ligands, with Fe−N distances of 2.188(7) Å. These chains are also close packed in a hexagonal array, separated by ClO_4^- counterions (Figure 2), presenting a similar framework with no permanent channels but with internal voids (discrete voids of 145 Å^3). The *syn*-btix ligands act as bridges between adjacent metal centers leading to Fe···Fe distances of 11.029(2) Å, which are considerably shorter than those in **1**. This results in the main



(a) (b) (c)

Figure 3. Representation of the *syn-cis* conformation of the btzx ligand (a) and *syn-trans* conformation of the btix ligand (b) adopted in compounds **1** and **2**, respectively. (c) Scheme of the two possible conformations for the btix ligand.

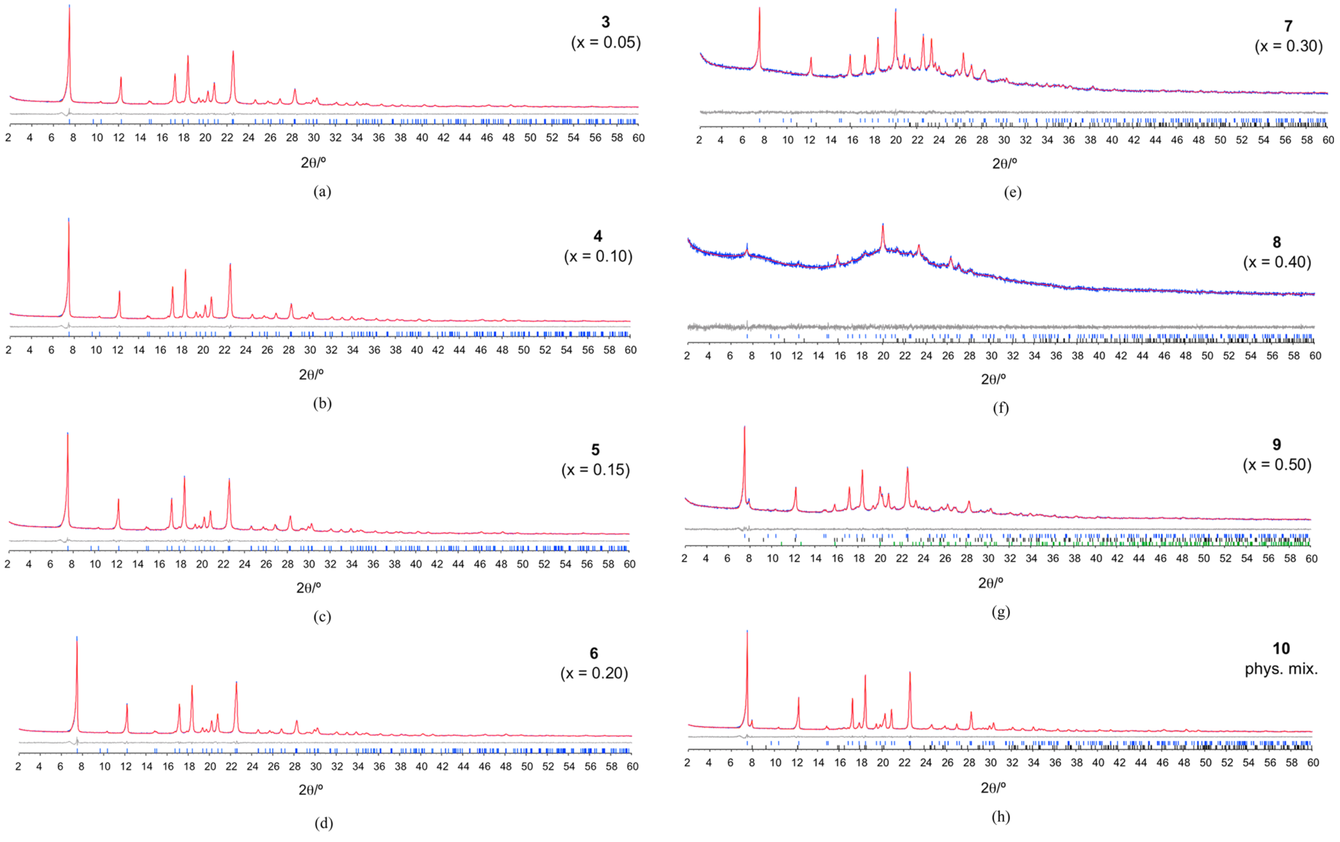


Figure 4. Observed (blue) and calculated (red) profiles and difference plot $[(I_{\mathrm{obs}} - I_{\mathrm{calcd}})]$ (gray) of the Pawley refinements for compounds **3**−**10** (2θ range 2.0−60.0°; maximum resolution 1.54 Å).

difference that can be observed between **1** and **2**, which is at the origin of their different space group: whereas in **1** the ligand btzx presents a *syn-cis* conformation, the btix ligand in **2** presents a *syn-trans* conformation, thus causing a twist in the ligand, which shortens the intermetallic distances (see Figure 3 and also compare Figure 1, parts a and b).

The reaction of $Fe(ClO_4)_2 \cdot xH_2O$ and appropriate mixtures of the two ligands btzx and btix in refluxing MeCN affords the different coordination polymers with partial ligand substitutions **3**−**9** as crystalline powders (see Table S1, Supporting Information). This family of coordination polymers responds to the general formula $[Fe(btzx)_{3-3x}(btix)_{3x}](ClO_4)_2$ with $0.05 \leq x \leq 0.5$. Pawley refinements on crystalline powder samples of each material with partial ligand substitution (Figure 4) reveal a decrease of the *c*-axis (−5.7% in the direction of the polymeric chain) upon increasing the amount of btix (Figure 5), which

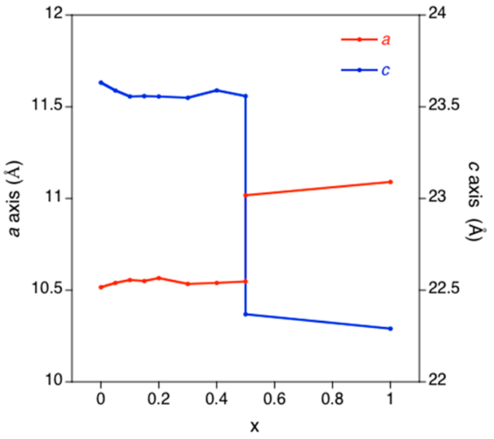


Figure 5. Variation of the *a* and *c* axes with *x* in compounds **1**−**9**. The family of coordination polymers **1**−**9** responds to the general formula $[Fe(btzx)_{3-3x}(btix)_{3x}](ClO_4)_2$ with $0 \leq x \leq 1$.

can be ascribed to the insertion of btix ligands in the chains due to the different conformation of the triazole derivative ligand. This decrease of the intrachain distance is also accompanied by an increase of the interchain distance (*a*-axis), which is 5.5%. Thus, when btix ligand is present in a small proportion ($x < 0.3$), the ligand is inserted into the chains. An alternative situation with different regions of chains of single components is discarded because this would result in the observation of two phases with powder diffraction. Interestingly, for $x = 0.3$ (compound **7**), the crystallinity of the sample is decreased, as observed by the lower intensity of the diffraction peaks (see Figure 4e), which is even more evident for $x = 0.4$ (see Figure 4f). In addition, some unreacted tetrazole is found in the crystalline solid of these two samples. Upon further increase of btix composition ($x = 0.5$), the crystallinity of the sample is recovered, although the system becomes a mixed phase in which the pure compound **2** is present in the mixture. This amorphization of the sample when $0.3 \leq x \leq 0.5$ (samples **7**−**9**) is attributed to a competition between different conformations of the ligands, which causes loss of structural coherence as *x* increases. In fact, amorphous materials based on the related ligand 1,4-bis(imidazol-1-ylmethyl)benzene have been reported.[27]

Magnetic Properties. As previously reported, the tetrazole derivative **1** is a coordination polymer that presents a cooperative SCO transition centered at 200 K,[18] whereas the triazole compound **2** remains in the high spin state in the whole temperature region (Figure 6). The use of two related ligands with different ligand-field strengths (a tetrazole derivative vs a triazole derivative) permits the chemical modification of the system inducing subtle changes in the ligand field around the Fe^{II} centers through a gradual ligand substitution while maintaining the linear polymeric structure.

The gradual substitution of the tetrazole derivative btzx by the triazole derivative btix causes the appearance of a new transition at lower temperatures as can be clearly deduced by the presence of a shoulder in the $\chi_M T$ plots at ca. 140 K (Figure 7). Furthermore, the residual fraction of high spin Fe^{II} increases with the amount of btix ligand. The new transition is more evident by inspection of the derivative of the $\chi_M T$ product (insets in Figure 7), which shows the gradual disappearance of the transition at 200 K and the emergence of a new transition at ca. 140 K. In addition, a small displacement of the high temperature transition to lower temperatures (ca. 190 K) is also observed. Such a displacement can be related to a chemical pressure effect exerted by the inclusion of the btix ligands in the chains, which induces a shortening of the length of the chains. In fact, with slight btix insertion the transition at ca. 190 K appears only as a minor shoulder in the derivative curve since only a minor chemical pressure is introduced, and thus the main transition at 200 K is maintained. The confirmation that the new transition is due to a new coordination environment is proven by the magnetic measurement of a physical mixture of **1** and **2**, which shows only a single transition centered at 200 K (Figure 7h). Upon further incorporation of btix ligand the transition at 200 K disappears, and it is only evident that at 190 K. The second transition at 140 K, which increases in intensity upon btix incorporation (see derivative curves in Figure 7a−d and Figure S1, Supporting Information), is distinct in origin, because it occurs as a consequence of the change of the metal environment. Thus, in contrast to the six tetrazole rings that give rise to the transition centered at 200 K, the incorporation of btix ligands causes some Fe^{II} centers to be coordinated by five tetrazole rings and one triazole ring, thus modifying the ligand field and consequently the transition temperature (see

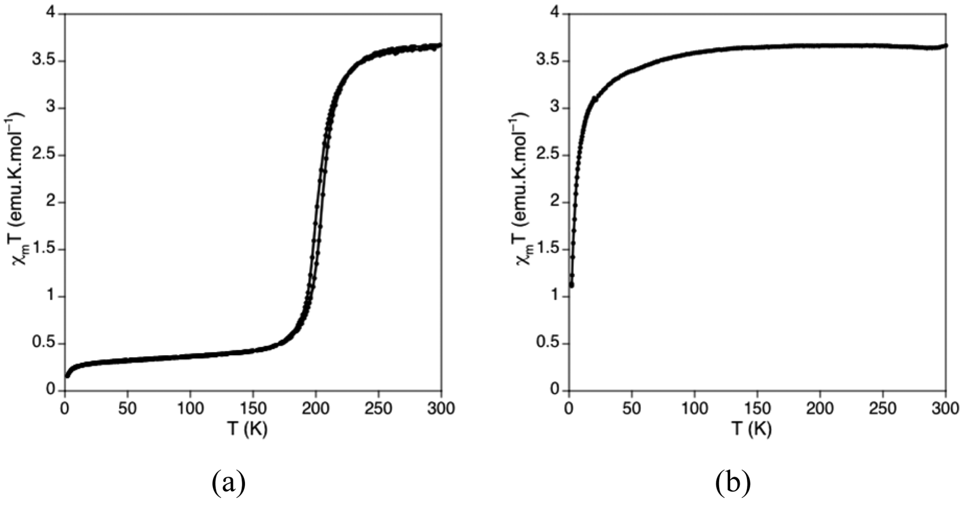
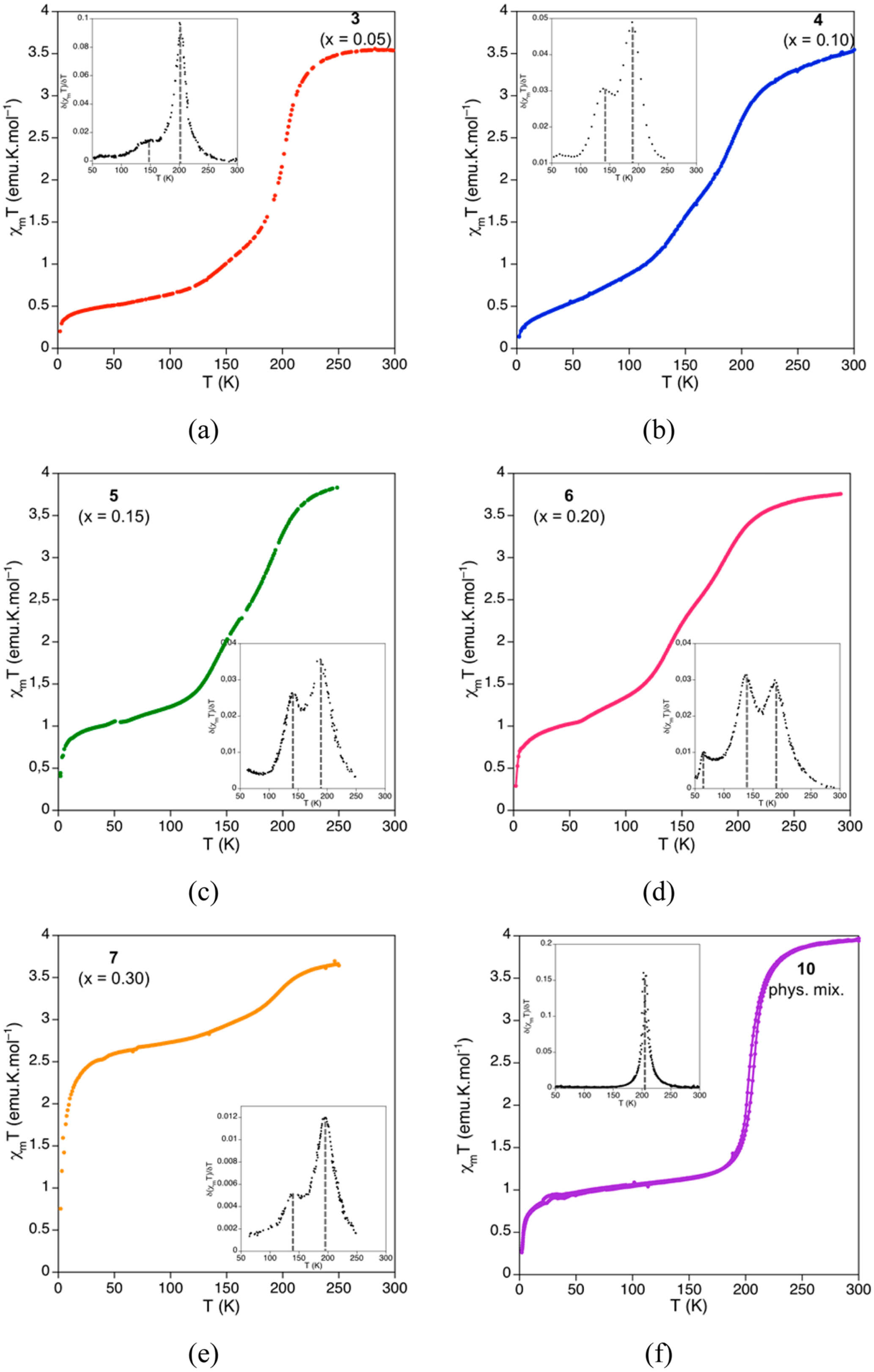


Figure 6. Temperature dependence of $\chi_M T$ for **1** (a) and **2** (b).



(a) (b)

(c) (d)

(e) (f)

Figure 7. Temperature dependence of $\chi_M T$ for the partial ligand substitutions **3**−**7** (a−e) and the physical mixture **10**. Insets show the derivative curves, indicating the position of the maxima with dashed lines.

also Figure 8). Interestingly, further incorporation of btix ligands results in the appearance of another transition at 60 K (see inset of Figure 7d), which might be attributed to the presence of a coordination environment with four tetrazole rings and two triazole rings. Such an unusually low transition temperature value has been also observed for some monomeric Fe^{II} complexes with 1-*R*-tetrazoles, which have been shown to have $T_{1/2} < 80$ K.[28]

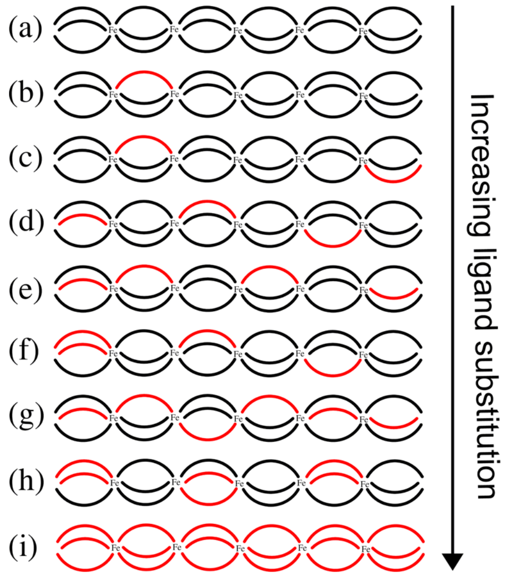


Figure 8. Schematic representation of the variation of the Fe^{II} coordination environment upon ligand substitution, with the bis-tetrazole ligands represented as black lines and the bis-triazole ligands represented by red lines. Note that only some possibilities are shown in this figure. (a) The pure bis-tetrazole coordination polymer shows all Fe centers with coordination environment of six tetrazoles. (b) The inclusion of some bis-triazole ligands causes some environments to be five tetrazoles and one triazole, although the major proportion of Fe centers has coordination of six tetrazoles. (c) Further inclusion of bis-tetrazole produces an increase of the number of centers with five tetrazoles and one triazole. (d) A regular distribution with 1/6 of the bis-tetrazole ligands substituted by bis-triazole would yield a coordination environment of five tetrazoles and one triazole in all centers (although statistically this is not likely to happen). (e,f) Further increase of the bis-triazole ligand causes the mandatory appearance of Fe centers with a coordination environment of four tetrazoles and two triazoles (although they can also be present with a lower proportion of bis-triazole). (g,h) A regular distribution with 1/3 of the bis-tetrazole ligands substituted by bis-triazole would yield a coordination environment of four tetrazoles and two triazoles in all centers (although statistically this is not likely to happen). (i) The pure bis-triazole coordination polymer, which shows all Fe centers with coordination environment of six triazoles, appears with 50% substitution, indicating that further inclusion of triazole is not possible.

The incorporation of btix ligands is likely to occur as a statistical distribution along the chains. Thus, coordination environments of four tetrazoles and two triazoles might be formed even with low values of x, as is actually inferred by close inspection of the derivative curves, which show a small signal at 60 K. This coordination environment of four tetrazoles and two triazole rings might result from two possibilities: (i) two btix ligands are located in consecutive bridges between Fe centers, or (ii) two btix ligands serve as bridges of two Fe centers (theoretical chains with these possibilities are shown in Figure 8). The latter is expected to cause larger loss of structural coherence, and it might be the origin of the amorphization observed with X-ray powder diffraction.

The further increase of btix content causes only an increase of the residual high spin fraction with no other transition observed at lower temperatures, which corresponds to the presence of a coordination environment with three tetrazoles and three triazoles. This could be due either to the lack of formation of such a compound or to the lack of SCO transition in such an environment.

■ CONCLUSIONS

In this work, we have used a mixed ligand approach to subtly modify the chemical environment in a family of Fe^{II} coordination polymers, $[Fe(btzx)_{3-3x}(btix)_{3x}](ClO_4)_2$, without changing the crystal packing. The gradual substitution of the tetrazole derivative ligand btzx by the triazole analogue btix causes the appearance of new spin-crossover transitions at different temperatures, which can be explained as a result of different chemical environments. Thus, a coordination environment of six tetrazoles is related to the transition at $T_{1/2}$ = 200 K, whereas a coordination of five tetrazoles and one triazole is associated with $T_{1/2}$ = 140 K and that of four tetrazoles and two triazoles with $T_{1/2}$ = 60 K. Control of the transition temperature is an important aspect for the possible application of spin-crossover materials into functional devices. Here we have presented a simple methodology to tune the transition that could be widely applied in many other systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Structural parameters from Pawley refinements, additional figures, and TGA analyis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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