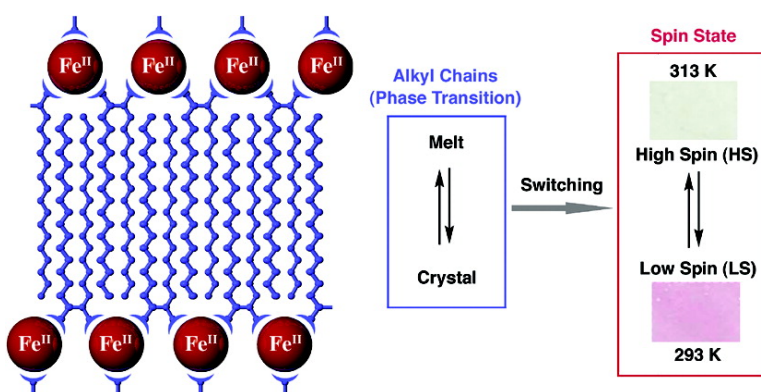


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*J. Am. Chem. Soc.*, **2003**, 125 (48), 14690-14691 • DOI: 10.1021/ja038088e • Publication Date (Web): 08 November 2003

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## Switching of Spin States Triggered by a Phase Transition: Spin-Crossover Properties of Self-Assembled Iron(II) Complexes with Alkyl-Tethered Triazole Ligands

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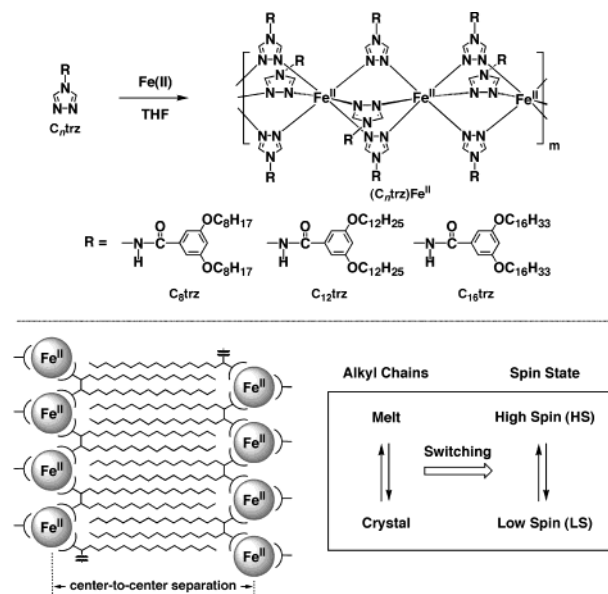
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Metal complexes with  $d^4-d^7$  electron configurations can adopt two different magnetic states, that is, high-spin (HS) and low-spin (LS) states, which can cross over thermally or by electronic excitation.<sup>1</sup> Spin-crossover phenomena have attracted attention in relation to their potential applications in molecular electronics.<sup>2</sup> An important challenge is to fabricate spin-crossover materials that can respond to external stimuli such as light and electric/magnetic fields. Gütllich and co-workers have reported liquid-crystalline (LC) ligands for the preparation of iron(II) complexes,<sup>3</sup> where one may expect the LC-phase transitions could trigger the spin-state transition. However, the phase transitions in that example occur at much higher temperatures than for the spin crossover, so that these two transition events are not synchronous.

Here, we report the first successful example of “phase transition”-triggered spin crossover by use of self-assembled iron(II) complexes having triazole ligands with two long alkyl chains ( $C_n\text{trz}$ )Fe<sup>II</sup> (Chart 1). The newly designed triazole derivatives ( $C_n\text{trz}$ ) serve as bidentate ligands that covalently bridge the iron(II) centers to form rigid coordination polymers. In the self-assembled state, the polynuclear species thus formed are fastened by the interdigitation of the long alkyl chains, resulting in a cooperative magnetic response among the iron(II) sites.  $C_n\text{trz}$  ligands ( $n$  [number of carbon atoms in each alkyl chain] = 8, 12, and 16) were synthesized by coupling of the corresponding 3,5-dialkoxybenzoic acids with 4-amino-1,2,4-triazole and unambiguously characterized by <sup>1</sup>H/<sup>13</sup>C NMR and FT-IR spectroscopies as well as MALDI-TOF-MS spectrometry. Iron(II) complexes ( $C_n\text{trz}$ )Fe<sup>II</sup> were prepared by refluxing  $C_n\text{trz}$  with Fe(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O in THF.<sup>4</sup>

At 296 K, solid ( $C_{16}\text{trz}$ )Fe<sup>II</sup> was colored pink, characteristic of  $d-d$  electronic transitions of low-spin iron(II) species. Discoloration occurred upon heating to give a virtually white solid at 313 K. On cooling below the phase transition, the white solid returned to its original color.<sup>4</sup> This thermochromism reflects the spin-state transition between LS and HS states. The magnetic susceptibility profile of ( $C_{16}\text{trz}$ )Fe<sup>II</sup> (Figure 1C) showed that the  $\chi T$  value, on heating from 70 K,<sup>5</sup> gradually increased from 0.8 cm<sup>3</sup> K mol<sup>-1</sup> and then displayed a jump from 2.0 to 2.9 cm<sup>3</sup> K mol<sup>-1</sup> at 298–328 K (inflection temperature [ $T_c$ ] = 310 K), characteristic of the LS-to-HS transition.<sup>6</sup> On the other hand, when the resulting sample in the HS state was cooled from 350 to 70 K, the  $\chi T$  value decreased from 2.9 cm<sup>3</sup> K mol<sup>-1</sup> through a drop at 318–298 K with a hysteresis loop width of 5 K. ( $C_{12}\text{trz}$ )Fe<sup>II</sup> with shorter alkyl chains (Figure 1B) exhibited a spin-crossover profile similar to that of ( $C_{16}\text{trz}$ )Fe<sup>II</sup>, but spin transition occurred at a lower temperature  $T_c$  = 276 K. On the other hand, ( $C_8\text{trz}$ )Fe<sup>II</sup> hardly showed a clear

Chart 1



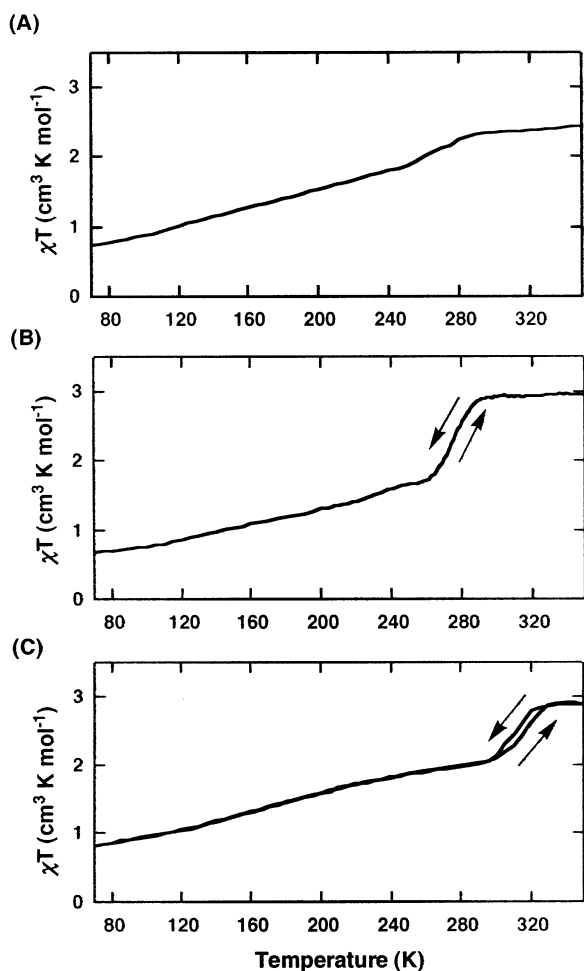
spin-state transition (Figure 1A). Thus, the spin-crossover profiles of ( $C_n\text{trz}$ )Fe<sup>II</sup> are strongly affected by the length of the alkyl chains.

EXAFS analysis<sup>4</sup> of solid ( $C_{16}\text{trz}$ )Fe<sup>II</sup> at 296 K displayed peaks at 1.7, 3.5, and 7 Å, assignable to Fe–N, neighboring Fe–Fe, and linear Fe–Fe–Fe scatterings, respectively, indicating the presence of iron(II) polynuclear chains.<sup>7</sup> The X-ray diffraction (XRD) pattern<sup>4</sup> of ( $C_{16}\text{trz}$ )Fe<sup>II</sup> at 296 K showed a sharp peak in the small angle region with a  $d$  spacing of 36.5 Å. This value most likely suggests an interdigitation of the long alkyl groups to give parallel-aligned polynuclear iron(II) chains, whose center-to-center separation is estimated to be 36 Å (Chart 1). A similar XRD pattern with a smaller  $d$  spacing (30.2 Å) was observed for ( $C_{12}\text{trz}$ )Fe<sup>II</sup>. Therefore, the iron(II) centers are fastened with one another not only by ligation with the triazole ligands but also through interdigitation with the long alkyl chains.

Infrared spectroscopy of ( $C_{16}\text{trz}$ )Fe<sup>II</sup> at 296 K displayed CH<sub>2</sub> stretching vibrations at 2850 ( $\nu_{\text{sym}}$ ) and 2920 cm<sup>-1</sup> ( $\nu_{\text{anti}}$ ), which were blue-shifted to 2853 and 2923 cm<sup>-1</sup>, respectively, at 313 K on heating. Thus, the alkyl chains of low-spin ( $C_{16}\text{trz}$ )Fe<sup>II</sup> are crystallized and adopt a stretched conformation, while those of the high-spin complex adopt a shrunken conformation. Furthermore, these spectral changes were thermally reversible. We also investigated the variable-temperature XRD pattern of ( $C_{16}\text{trz}$ )Fe<sup>II</sup>, where the  $d$  spacing of 36.5 Å, observed at 296 K, was decreased to 35.0 Å at 313 K on heating, and then reverted to the original value when cooled to 296 K.<sup>4</sup> In relation to these observations, differential

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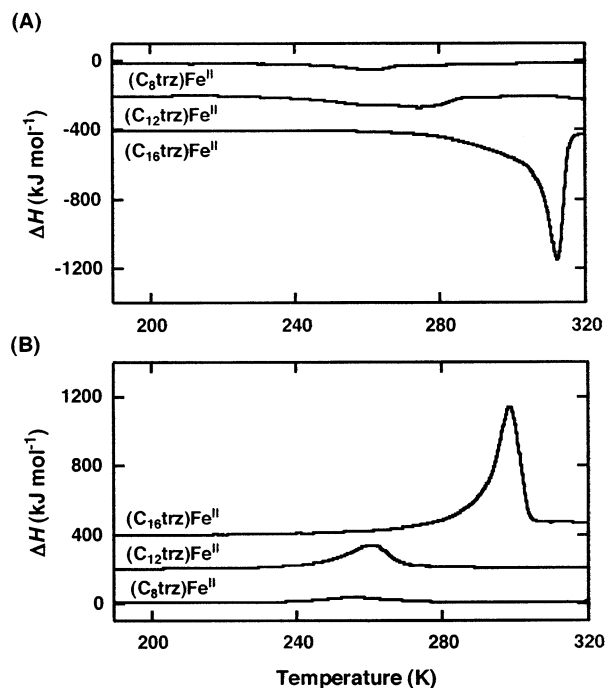
<sup>‡</sup> ERATO Aida Nanospace Project, JST.



**Figure 1.** Magnetic susceptibility profiles of (A)  $(C_n\text{trz})\text{Fe}^{\text{II}}$ , (B)  $(C_{12}\text{trz})\text{Fe}^{\text{II}}$ , and (C)  $(C_{16}\text{trz})\text{Fe}^{\text{II}}$ .

scanning calorimetry (DSC) of both  $(C_{16}\text{trz})\text{Fe}^{\text{II}}$  and  $(C_{12}\text{trz})\text{Fe}^{\text{II}}$  displayed single endothermic and exothermic peaks, respectively (Figure 2A and B).<sup>4,8</sup> However,  $(C_{16}\text{trz})\text{Fe}^{\text{II}}$  showed higher transition temperatures and larger  $|\Delta H|$  values than those of  $(C_{12}\text{trz})\text{Fe}^{\text{II}}$ . More importantly, the transition temperatures in DSC on heating were in good agreement with their spin-transition temperatures,  $T_c$ . In sharp contrast,  $(C_8\text{trz})\text{Fe}^{\text{II}}$  exhibited very broad DSC peaks with small  $|\Delta H|$  values. All of the above results clearly demonstrate that the spin crossover of  $(C_n\text{trz})\text{Fe}^{\text{II}}$  ( $n = 12$  and  $16$ ) is triggered by the phase transition. At low temperatures, the crystalline alkyl chains of  $(C_n\text{trz})\text{Fe}^{\text{II}}$ , upon interdigitation, most likely lock the Fe–N bond distance of the low-spin iron(II) complex. On heating, the above lock can be released by melting of the alkyl chains, thereby permitting elongation of the Fe–N bond, necessary for transition to the HS state.<sup>2b</sup> By virtue of the thermoreversibility of the phase transition, the spin crossover can be repeated without deterioration.

In summary, we have succeeded in the first demonstration of synchronous spin crossover and phase transition, by use of self-assembling triazole ligands with long alkyl chains for the polynucleation of iron(II) species. This approach allowed mesoscopic cooperativity among the magnetic species through interdigitation of the alkyl chains and enabled a “lock-and-release” feature of the



**Figure 2.** DSC profiles of  $(C_n\text{trz})\text{Fe}^{\text{II}}$  ( $n = 8, 12,$  and  $16$ ) on (A) second heating and (B) second cooling at a rate of  $5 \text{ K min}^{-1}$ .

spin state. The successful synchronization of spin crossover with phase transition would provide an opportunity to switch the spin state by external stimuli. Elaboration of self-assembling triazole ligands and development of, for example, photoresponsive dopants are the subjects worthy of further investigation.

**Acknowledgment.** We thank JASCO for VT-IR spectroscopy, and Dr. T. Sasagawa and Prof. H. Takagi of the University of Tokyo for magnetic susceptibility measurements.

**Supporting Information Available:** Details of the synthesis and spectral data for  $C_n\text{trz}$  and  $(C_n\text{trz})\text{Fe}^{\text{II}}$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA038088E