

## Spin-crossover 3D architectures of Fe (II) complex bearing triazole ligand

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### Abstract

A new assembled iron (II) complex with triazole derivative,  $[\text{Fe}(\text{pbtrz})_6](\text{ClO}_4)_2$ : (pbtrz = 4, 4' - (1, 4 - phenylene)bis - 1, 2, 4 - triazole) was synthesized and well characterized. The ligand showed 3D architectures bridging with iron (II) metal through the N-1 and N-2. The investigation of its magnetic properties has revealed a spin-crossover (SCO) between the low-spin (LS) and the high-spin (HS) states ( $T_{1/2} = 242 \text{ K}$ ) without a thermal hysteresis loop. The spin-crossover regime was also followed by Mössbauer spectroscopy. Furthermore, a photo-induced spin transition otherwise known as light-induced excited spin-state trapping (LIESST- effect) was observed when the complex was illuminated at 5 K.

**Keywords:** triazole, iron (II), spin-crossover, Mössbauer spectroscopy

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### Introduction

The diverse applications of cooperative intermolecular SCO phenomenon,  $d^n$  ( $n = 4-7$ ) both in devices [1] and in molecular biology [2] are of keen interest to material scientists. Interestingly, iron(II) complexes have been identified as a d-block metal component with low-spin ( $S = 0$ ) and high-spin ( $S = 2$ ) exhibiting the magnetic response

under external stimuli (e.g temperature, pressure, light, magnetic field) and these have been intensively investigated in the development of SCO research due to this unique mechanism of the spin transition [3]. The 1,2,4-triazole system has been found to be particularly suited towards generating SCO behavior in  $\text{Fe}(\text{II})\text{N}_6$  derivatives[4]. The SCO behavior through N-1, N-2 bridging

coordination mode and N-4 bridging coordination bidentate or tridentate or monodentate 1,2,4-triazole mode respectively for mononuclear and polynuclear systems have been reported [5]. Moreover, only linear trinuclear and linear polynuclear materials of 1,2,4-triazole molecules especially 4-R-substituted triazole form  $\text{FeN}_6$  SCO chromospheres with remarkable properties particularly in new field as intelligent contrast agents for magnetic resonance imaging have been reported[6]. The discovery of light-induced excited spin state trapping (LIESST) suggests that the spin-crossover compounds could be used as optical switches [7]. Nevertheless, among all Fe(II) SCO compounds known to date, the extensively studied polymeric  $[\text{Fe}(4\text{-R-}1,2,4\text{-triazole})_3] (\text{anion})_2$  systems (R= amino, alkyl, hydroxyl alkyl) appear to have the greatest potential for technological applications, for example in molecular electronics or as temperature sensors[8]. Vreugdenhil *et al.* [9] reported the spin transition system of trans-bis-(thiocyanato)-bis (4,4'-bis-1,2,4-triazole) iron(II) with complete and abrupt transition. König *et al.*[10] have used high-resolution X-ray powder diffraction as a function of temperature and the analysis of the resulting peak profiles to study the spin transition in several iron (II) compounds

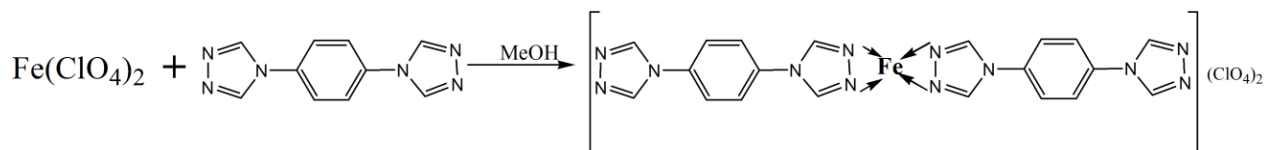
while some of them exhibit a gradual, and some an abrupt transition.

However, to the best of our knowledge, ligating properties of 1,2,4-triazole derivatives as well as the effect of counter ions and solvents have not been studied for their spin- crossover behaviour with attention on heterocyclic moieties e.g pyridyl , phenanthroline as bridger[11-13]. To explore more potential useful applications of spin-cross over molecules which depend on the nature of intermolecular interactions (e.g hydrogen bond,  $\pi$ - $\pi$  stacking etc), as indices for cooperativity, our group synthesized new polynuclear 3D-iron (II) 1,2,4-triazole complexes with benzene bridging between the bidentate triazole chelate system with good spin transition.

## Materials and Methods

**$[\text{Fe}(\text{pbtrz})_6](\text{ClO}_4)_2$ .** The ligand was synthesized as previously described with little modification [14]. The complex was prepared by reacting methanol (MeOH) solution of  $\text{Fe}(\text{ClO}_4)_2$  with the 4, 4' - (1, 4 - phenylene)bis - 1, 2, 4 - triazole ligand in (1:1 metal-to-ligand molar ratio).

$[\text{Fe}(\text{pbtrz})_6](\text{ClO}_4)_2$ , Anal. Calcd. for  $\text{C}_{60}\text{H}_{48}\text{O}_8\text{N}_{36}\text{Cl}_2\text{Fe}_1$ : C, 47.16; H, 3.17; N, 33.00. Found: C, 47.26; H, 3.18; N, 30.05.



**Scheme 1:** Synthesis of  $[\text{Fe}(\text{pbtrz})_6](\text{ClO}_4)_2$

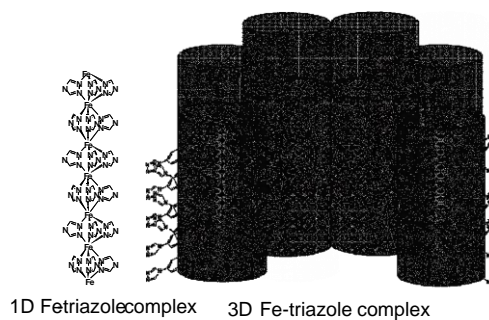
**Magnetic Susceptibility.** Temperature-dependant magnetic susceptibility ( $\chi_m T$ ) for the complex was measured between 5 and 350 K with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) in an external field of 1 T. Magnetic behaviour after light irradiation was also investigated to confirm photo magnetic property at 5K.

**Mössbauer Spectra.** The Mössbauer spectra (isomer shift versus metallic iron at room temperature) were measured with a Wissel MVT-1000 Mossbauer spectrophotometer with a  $^{57}\text{Co}/\text{Rh}$  source in the transmission mode. All isomer shifts are given relative to  $\alpha\text{-Fe}$  at room temperature. Measurements at low temperatures were performed with a closed-cycle helium refrigerator cryostat (Iwatani Co. Ltd). In order to enhance the Mössbauer spectra, the sample was enriched with  $^{57}\text{Fe}$ .

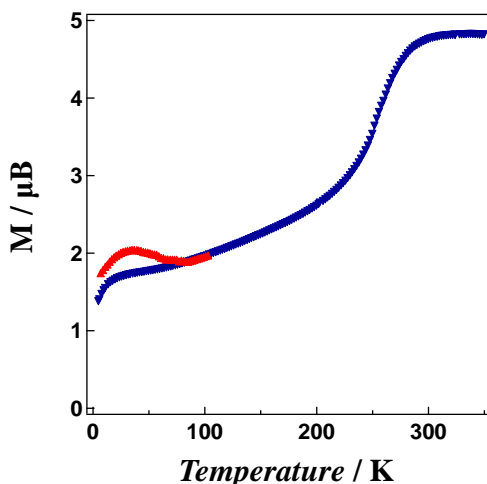
## Results and Discussion

One dimensional Fe(II) polymeric complex structures have been investigated by many

researchers in the context of cooperative effects associated with the spin transitions[15-16]. Interestingly, by introduction of phenyl group, 1D triazole derivative, Fe(II) complex changed its structure to three dimension (3D) architecture, where the ligand bridged iron(II) center. Additionally, the structure became like a honeycomb. Moreover, pbtrz contains N donor atoms for metal population, which is expected for coordination polymer like metal-organic framework (MOF) [17].



**Fig 1.** Chemical structure of  $[\text{Fe}(\text{triazole})_6](\text{ClO}_4)_2$  in 1D and  $[\text{Fe}(\text{pbtrz})_6](\text{ClO}_4)_2$  in 3D

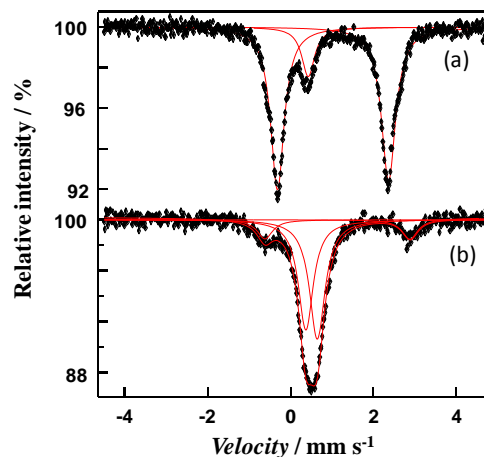


**Fig 2.**  $\chi_m T$  vs T plots for  $[\text{Fe}(\text{pbtrz})_6](\text{ClO}_4)_2$  were cooled from 350 to 5 K without irradiation, settle mode ( $\blacktriangle$ ).

LIESST experiment for the sample was carried out and  $\chi_m T$  vs T plots were recorded in the warming mode after irradiation (800 nm) at 5 K ( $\blacktriangle$ ).

The temperature dependences of the magnetic susceptibilities for the complex were measured in the form of the  $\chi_m T$  vs T curve, where  $\chi_m$  is the molar magnetic susceptibility and T is the temperature (**Fig 2**). The complex exhibited gradual SCO behaviour in the temperature range of 5 - 350 K. The  $\chi_m T$  value for the complex gradually increases from  $1.38 \text{ cm}^3 \text{ K mol}^{-1}$  at 5 K to  $4.82 \text{ cm}^3 \text{ K mol}^{-1}$  at 350 K (behavior of mixture of iron(II) complex and iron(III) complex) which corresponds to what is expected due to the possibility of  $\text{Fe}^{2+}$  being oxidized to  $\text{Fe}^{3+}$  [15]. After irradiation at 5 K,

the increase of the  $\chi_m T$  value was observed, maximum value is  $2.04 \text{ cm}^3 \text{ K mol}^{-1}$  at 37 K. Thus, it is expected that this increment attribute to iron(II) complex.



**Fig 3.**  $^{57}\text{Fe}$  Mössbauer spectra for  $[\text{Fe}(\text{pbtrz})_6](\text{ClO}_4)_2$  at 300 K (a) and 80 K (b).

The spin transition was also investigated by Mössbauer spectroscopy in the temperature range of 300 and 80K which support the existence of iron(II) valence in the HS and LS states and the occurrence of SCO behavior (Fig 3). At 300K, the spectrum consists of a unique quadrupole splitting doublet ( $\Delta E_Q$ ) with an isomer shift ( $\delta$ ) are  $0.4 \text{ mms}^{-1}$  and  $2.4 \text{ mms}^{-1}$ . These two parameters are typical of high-spin (HS)  $\text{Fe}^{2+}$ . As the temperature is lowered, the intensity of the low-spin (LS) doublet increases at the expense of that of HS. Below 80K only this LS doublet is detectable in agreement with

the results of the magnetic measurements [18].

### Conclusion

A new assembled 3D Fe(II) complex was synthesized. The complex also showed SCO phenomenon and LIESST effect. Although there are is no hysteresis loop or abruptness in the 3D architectural complex magnetic behaviour but with hexagonal shape, there is a hole in each pbtrz ligand representing metallo-organic porous networks with potential applications to gas adsorption, bio sensor, catalysis.

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