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# Solvent effect in the spin-state of an Fe(II)-triazole trimer

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**Abstract:** We report a triazole-based trinuclear Fe(II) compound with bridging 4-(p-methylphenyl)-1,2,4-triazole ligands with solvatochromic spin crossover (SC) behavior. The magnetic properties of this trimer depend on crystallization solvent molecules. Pink crystals (color suggesting low spin state), showing a triclinic structure can be obtained by slow diffusion of diethyl ether in acetonitrile solution. As in other SC materials, immersion of these crystals in different solvents promote color change. In this case, we have been able to define the microscopic effect of the solvent substitution following the single crystal to single crystal transformation by UV-vis absorption spectroscopy and X-Ray diffraction. In this case, the solvent-induced switching can be explained by weak intermolecular interactions provoking a variation in the relative orientations of the two aromatic rings in the ligands, which, in turn, determines the ligand field on the central Fe(II), and its SCO behavior. This study brings important details to the origin of solvatochromism in SCO materials, offering alternatives for better control of this switching and, potentially, for their application as colorimetric sensors.

## Introduction

Spin crossover <sup>[1]</sup> (SC) is a reversible process commonly observed in metal centers of coordination compounds of electronic configuration  $3d^4-d^7$ . This transformation involves a transition between the low spin ground state (LS, in which the occupation of electrons in the  $e_g$  and  $t_{2g}$  orbitals follows the Aufbau principle), and the high spin excited state (HS, whose electron configuration follows Hund's rule of maximum multiplicity). The process is entropy-driven and can be triggered by diverse external stimuli such as temperature, pressure, magnetic or electric fields, or light irradiation. These external stimulus-responsive properties make SC materials useful candidates for molecular sensing. <sup>[2]</sup> At the macroscopic level, SC is also affected by structural factors like intermolecular interactions, <sup>[3]</sup> counterions <sup>[4]</sup> or solvation. <sup>[5]</sup> The latter can induce small structural changes, very often in the crystal packing, that may significantly alter the spin transition. <sup>[5c-f]</sup>

On the other hand, Fe(II) – 1,2,4-triazole (trz) compounds stand out as one of the most widely studied amongst spin-crossover materials. <sup>[6]</sup> These compounds are linear species, comprising Fe(II) centres bridged by the triazole ligands. Polynuclear compounds of the formula  $[\text{Fe}(\text{trz})_3]_n\text{X}_{2n}$ , where X is an anion, display large hysteresis in their spin transitions, and this bistability has posed them as candidates for data storage applications. <sup>[7]</sup> Analogous molecular linear species, mostly trimers, can be obtained with certain 4-substituted triazole ligands. The first

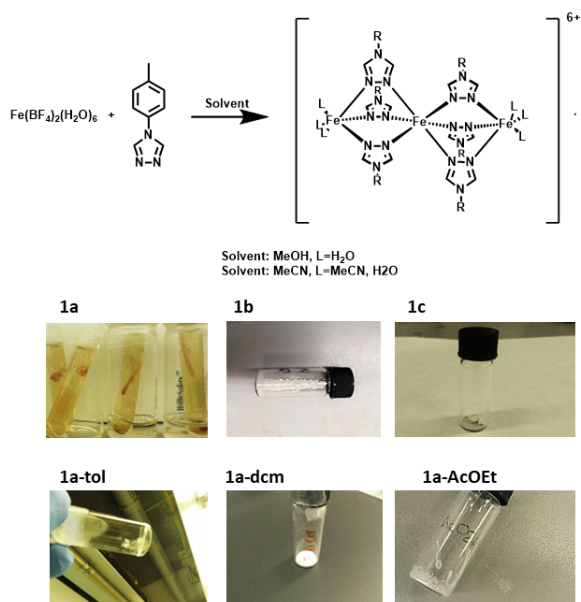
example of this family was reported by Reedijk et al, <sup>[8]</sup> with 4-Ethyl-1,2,4-triazole as ligand and triflate as anion. In these trimers, the central Fe(II) is doubly bridged by triazole ligands, whereas the terminal ones complete their octahedral environment with water molecules. In these trimers, only the central Fe(II) undergoes spin transition, while the external ones remain in HS given the weak ligand field imposed by solvent molecules; although recently, an exception to this trend was reported. <sup>[9]</sup>

Another interesting feature of these Fe(II) trimers arises when the ligand is a 4-phenyl-substituted triazole, as reported by Varret et al. <sup>[10]</sup> In this case, the non-coordinated counterion can dictate the degree of conjugation between the triazole and the 4-methoxyphenyl substituent, and this, in turn, drastically changes the magnetic properties. With tetrafluoroborate, the phenyl rings are perpendicular to the triazole, and the Fe(II) trimers remain in HS state across the whole range of temperatures. When the anion is tosylate, the phenyl rings become closer to co-planar to the triazoles (dihedral angles of 29-36°), and can donate electronic density to the latter, thus increasing the ligand field on the central Fe(II) center. This stabilizes the HS-LS-HS phase, and the trimer presents a gradual transition to HS with  $T_{1/2} = 245$  K. In this work, we present a further exploration of the versatility of these ligand types, with the introduction of 4-(p-methylphenyl)-1,2,4-triazole yielding the trimer  $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_n(\text{MeCN})_{6-n}][\text{BF}_4]_6$ . The spin state and magnetic properties of this molecule can be modulated in the solid state by solvent. The structural reasons behind this phenomenon have been elucidated by a study of the solvent-induced single-crystal to single-crystal transformations. This could potentially open interesting sensing capabilities of this molecule in the solid state.

## Results and Discussion

Reaction of the ligand 4-(p-methylphenyl)-1,2,4-triazole (L) with Fe(II) in a 2:1 ratio in acetonitrile or methanol yield a yellow solution. The product can be isolated as pink single crystals of  $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_n(\text{MeCN})_{6-n}][\text{BF}_4]_6$  (**1a**, Figure 1), by slow vapour diffusion of diethyl ether into the acetonitrile mixture, or as a white powder upon fast precipitation by addition of diethyl ether to an acetonitrile (**1b**) or methanol (**1c**) solution. The single crystals rapidly turn colourless upon air exposure, while retaining good crystallinity for about 30-40 minutes. XRD of the single crystals showed that the trinuclear cationic compound,  $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_n(\text{MeCN})_{6-n}]^{6+}$ , is formed by a linear chain of octahedral

Fe (II) ions (Fe1–Fe2–Fe1) connected by two triple  $\mu$ -triazole bridges (Figure 1 and S6). The terminal irons complete their coordination with disordered solvent molecules, acetonitrile or water, in an approximate ratio of 70:30 H<sub>2</sub>O:MeCN occupancy. The triclinic unit cell (Figure S6 and Table S2) contains two crystallographically independent trimers (A, on the unit cell b axis, and B, on the center). The trimers are linked by  $\pi$ - $\pi$  stacking interactions between phenyl rings of the ligands. The phenyl ligands are face to face with an angle of  $\approx 10^\circ$ . This  $\pi$ - $\pi$  stacking extends along the  $[\bar{1}0\bar{1}]$  (A-B stacking, Figure S7a) and  $[010]$  (A-A stacking, Figure S7b) directions, with C $\cdots$ C distances in the 3.6–3.9 Å, and 4.1–4.2 Å range, respectively. The dihedral angles in each ligand between phenyl and triazole rings are 34–36° (Table S3), except for those involved in  $\pi$ - $\pi$  stacking: narrower in B trimers (13–16°), and wider in A trimers (48°). The metal-to-ligand distances at 100 K (Table S3), indicate an all HS-HS-HS configuration, with average Fe–N  $\geq 2.1$  Å.

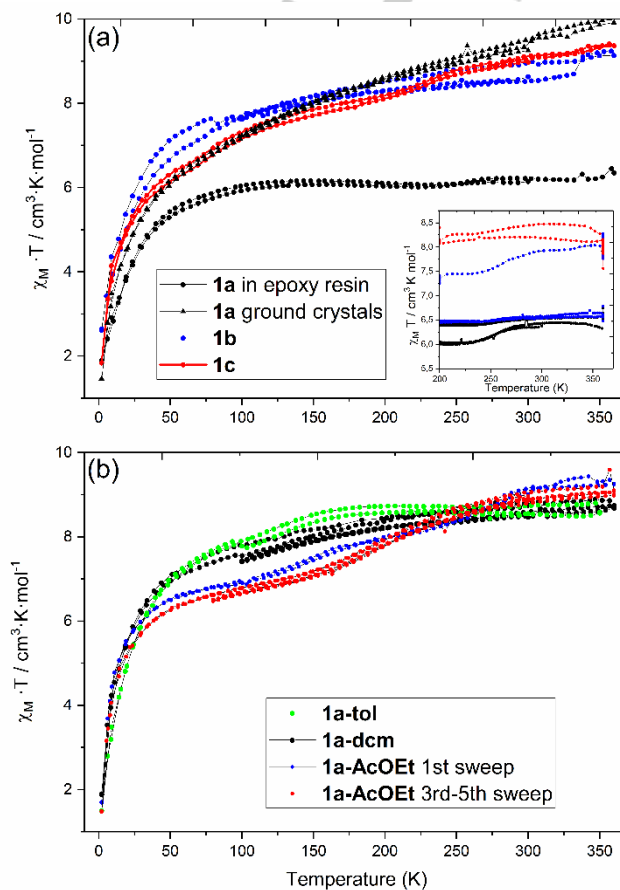


**Figure 1.** Scheme of the synthesis of cationic trimer **1** and pictures of the different samples studied.

The initial single crystal colour change, probably associated to a different spin state, between pink crystals in solution becoming rapidly colorless upon dessolvation in air prompted us to investigate the effect of other solvents on these crystals. The crystals turn colourless when immersed into non-polar solvents, such as toluene (**1a-tol**) or hexane (Figure S10a), retaining the crystallinity. The pink color of the single crystals is recovered when immersed in the original, polar mother liquor (acetonitrile). Other solvents like ethyl acetate (**1a-AcOEt**), dichloromethane (**1a-dcm**), chloroform, diethyl ether disrupt the crystal structure and make them collapse into amorphous powder (Figure S10b). The crystals are soluble in polar solvents, such as water, acetone or alcohols, and become white powder, analogous to **1b** and **1c** when dessolvated in air or dried under vacuum.

FTIR spectra of all the samples show bands at 600–800  $\text{cm}^{-1}$  that correspond to vibrations of the Fe–N bonds. This region is nearly identical for all samples (Fig S4), as well as the bands from

aromatic groups (1000–1300  $\text{cm}^{-1}$ ). **1a** shows three weak bands around 2200  $\text{cm}^{-1}$ , which were assigned to the C–N stretching of the acetonitrile molecules coordinated to terminal Fe. For all the other compounds, these bands are not observed, and therefore it was assumed that terminal Fe positions are exclusively occupied by water molecules.



**Figure 2.** a)  $\chi_M T$  vs  $T$  plot measured at 5K/min of trimer as-obtained directly from the different synthetic methods, compounds **1a-c**; Inset shows successive scans of compound **1a** inside epoxy resin, measured first at 2K/min and at 5K/min in the later sweeps; b)  $\chi_M T$  vs  $T$  plot of solvent-induced modifications of **1a** measured at 5K/min.

Magnetic susceptibility measurements were performed for samples **1a-c**, dried *in situ* (2–360 K, Figure 2). At room temperature (300 K),  $\chi_M T$  has a value close to 9  $\text{cm}^3 \text{K mol}^{-1}$ , which corresponds to three HS iron centers in the trimers. Samples **1a-b** show nearly identical behavior. As temperature is lowered,  $\chi_M T$  decreases down to 2.6  $\text{cm}^3 \text{K mol}^{-1}$  at 2 K. This behavior suggests dominant antiferromagnetic interactions between the three HS Fe centers in the trimers, with no sign of spin transition phenomenon. These magnetic data can be modeled with the Hamiltonian for a linear trimer of  $S_1=S_2=S_3=2$  centers with a  $j$  superexchange parameter, and introducing a single ion anisotropy term ( $D$ ):

$$H = -2j(S_1 S_2 + S_2 S_3) + D[(S_1^z)^2 + (S_2^z)^2 + (S_3^z)^2]$$

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The experimental data can be satisfactorily reproduced with  $g = 2.0$ ,  $j = -2.7$  K; and  $D = +1.5$  K (Figure S12).

**1c**, however, only remained fully in HS at temperatures above 250 K. It showed a gradual and incomplete spin transition centered at  $T_{1/2} = 217$  K, involving  $\approx 40\%$  of the trimers. This percentage was estimated from the average  $\chi_{MT}$  value in the range of temperature where it was stable, approximately between 145 and 160 K. The low temperature range is also dominated by antiferromagnetic interactions and/or zero-field splitting (ZFS), as in the case of **1a** and **1b**.

The original pink color of **1a**, suggests the trimers should be in the LS state at room temperature before dissolution. In order to protect the crystals from this process, the as-prepared crystals were isolated inside an inert polymer matrix (see Supporting Information for details about preparation of samples in epoxy resin).

Once immobilized in epoxy-resin, **1a** shows a  $\chi_{MT}$  value of  $6.45 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K, which corresponds to a majority HS-LS-HS state ( $> 85\%$ ), which fully converts to the HS-LS-HS state when cooling, with  $T_{1/2} = 257$  K. This transition is initially reversible, but disappears after several temperature cycles when HS-HS-HS becomes the ground state (Figure 2a, inset). We associate this event to solvent loss, not sufficiently prevented by the resin coverage, especially at high temperatures. In fact, when the sample is heated up to 360 K and maintained at such temperature, a progressive increase in its  $\chi_{MT}$  value is observed (Figure S13).

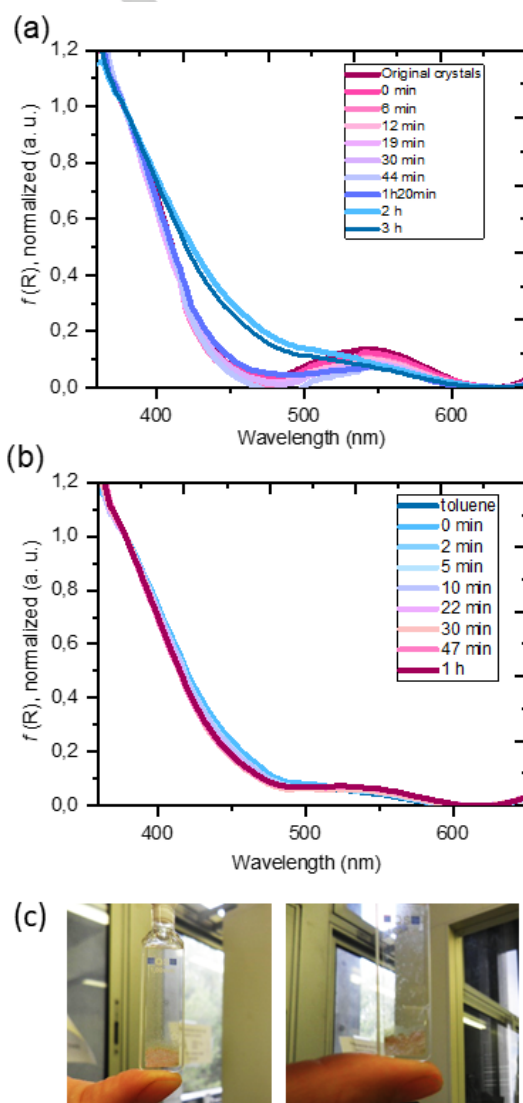
Next, we studied the samples resulting from solvent-induced transformations of **1a** (Figure 2b). Colourless **1a-tol**, like dissolved **1a**, exhibited a room temperature  $\chi_{MT}$  value close to  $9 \text{ cm}^3 \text{ K mol}^{-1}$ , indicating that the trimers are all in HS configuration. The behavior of **1a-dcm** and **1a-AcOEt**, are analogous to that of **1b** and **1c**, respectively. **1a-AcOEt** showed an incomplete and gradual spin transition that was cycle dependent, changing transition temperature after successive heating-cooling cycles, and becoming stable and repeatable at  $T_{1/2} = 202$  K.

In order to have a deeper insight into the effect of solvent exchange on the stabilization of the magnetic state in these salts, with the corresponding spectroscopic effects, we studied the single crystal to single crystal solvent-induced transformations. Thus, we analysed the **1a** to **1a-tol** reversible transformation by UV-vis absorption spectroscopy and single crystal XRD.

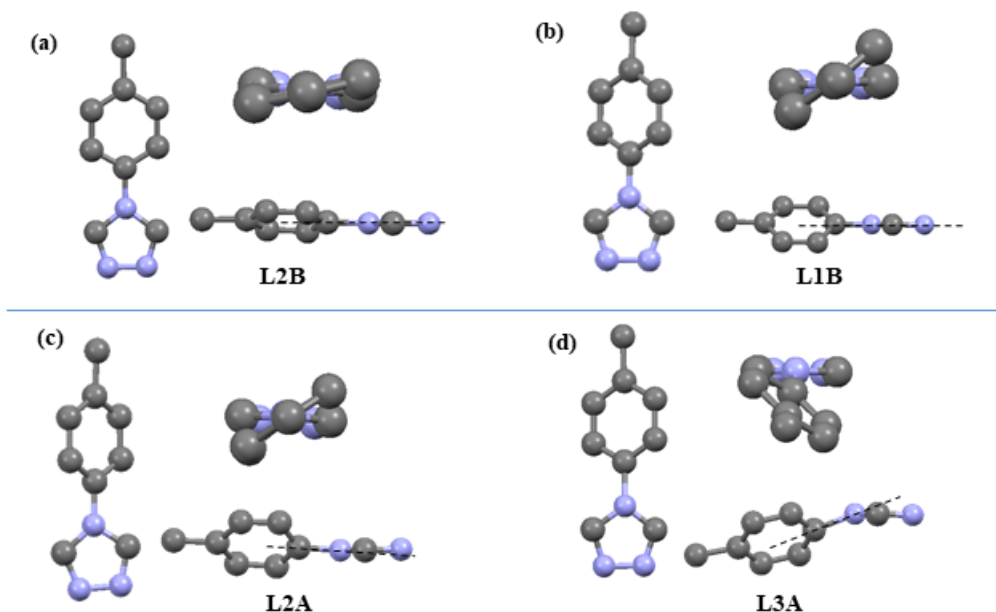
Firstly, we measured the diffuse reflectance of both crystals when immersed in different solvents to monitor their colour change. Measurement of reflected light has been previously used to monitor spin transitions in Fe(II) compounds.<sup>[6b]</sup> In our case, a 1 mm wide cuvette was filled with crystals inside their mother solution, until a "layer" of crystals of approximately  $1 \text{ cm} \times 1 \text{ cm}$  was formed. Then, solvent was exchanged without removing the crystals. Reflectance spectra were recorded at different times. To ease the analysis of the data, reflectance data was transformed with the Kubelka-Munk equation and normalized at 378 nm. Figure 3 shows the resulting spectra of the crystals in the original solution – i.e. the MeCN:Et<sub>2</sub>O where they were formed – (purple line) and its changes with time when they were immersed in

toluene. The crystals in their mother solution show an absorption band in the visible region with maximum at 542 nm that is responsible for the pink colour and that corresponds to  $^1A_1$  to  $^1T_1$  transition.<sup>[1b]</sup> Upon solvent exchange, this band decreased progressively, disappearing after 3h of toluene exposure. During this process, an increase in absorption was also observed in the 400-500 nm region. Then, we exchanged again toluene by the mother solution and recorded the changes in the absorption spectrum. This caused a red shift and an increase in the absorption in the region around 542 nm, although the intensity of the original band could not be completely recovered, suggesting that this process is only partially reversible in the solid state.

The good quality of the single crystals after toluene immersion (24 h) allowed collection of single-crystal XRD data. The unit cell is analogous to **1a** in its main features (Figure S8 and S9). Most of the ligands show dihedral angles of  $41\text{--}50^\circ$  between the phenyl



**Figure 3.** a) Evolution of the spectrum of crystals **1a** after immersion in toluene; b) Evolution of the UV-vis absorption spectrum of crystals **1a-tol** after immersion in MeCN:Et<sub>2</sub>O; c) Photo of the cuvette with crystals of **1a** (left), and photo of a cuvette where some drops of toluene were carefully injected at the bottom with a syringe: both **1a** and **1a-tol** can be observed together to better illustrate the colour change (right)..



**Figure 4.** Three views (obtained from XRD single crystal data) of the ligands in  $[\text{Fe}_3(\mu\text{-L})_6(\text{H}_2\text{O})_n(\text{MeCN})_{6-n}]^{6+}$  cation in **1a** (top) and **1a-tol** (bottom). a) Ligand in trimer B of **1a** with a dihedral angle of 18°; b) Ligand in trimer B of **1a** with a dihedral angle of 33°; c) Ligand in trimer B of **1a-tol** with a dihedral angle of 45°; d) Ligand in trimer A of **1a-tol**, where the nitrogen of the triazole ring is pyramidal.

and the triazole rings, slightly higher than in the case of **1a**. Nevertheless, we cannot observe any ligand with quasi-coplanar rings as it happens in the crystal structure of **1a** (vide supra).

In turn, looking closely at the ligands of **1a-tol**, especially when observed along the N-C bond that joins the two aromatic rings, (Figure 4c and d), it is observed that the nitrogen of the triazole tends to be slightly pyramidal rather than completely planar. The clearest example of this is found in two of the ligands of A trimers. In those (Figure 4d), the angle on the triazole nitrogen is of ca. 150°. The planes of the two aromatic rings form an angle of ca. 45°. This means that, particularly in these two ligands,  $\pi$ -conjugation between the triazole and the phenyl rings will be further hindered.

Therefore, the main difference between the two structures concerns the conformation of the ligands: the  $\pi$ -conjugation of the phenyl and triazole rings of the ligands is significantly stronger in sample **1a** than in sample **1a-tol**. A higher degree of conjugation may result in electron donation from the phenyl towards the triazole ring. This electronic effect may cause an increase in the ligand field exerted by the coordinating nitrogens on the central Fe(II) ion, thus stabilizing the low spin state. As we mentioned before, a similar effect has been previously reported,<sup>[10]</sup> but dictated by the shape of the anions, rather than the solvent.

Our hypothesis to explain the relative orientations of the two aromatic rings of the ligands, is that polar solvents like acetonitrile, methanol or ethyl acetate will be capable of stabilizing the dipole moment created in the electron density shift that may arise from a more planar conformation of the ligands. Thus, when the trimer is synthesized in methanol or acetonitrile, a spin transition may appear, since polar solvents favour ligand conformations that stabilize the LS state.

On the other hand, non-polar solvents like toluene, diethyl ether or dichloromethane have the opposite effect, and the ligands adopt a conformation where the conjugation between the triazole and the phenyl ring is not present. A similar effect could be taking place when the crystals of **1a** dry up, since its magnetic properties are analogous. In all these cases, the magnetic properties of the trimer are dominated by antiferromagnetic interactions.

Interestingly, although solvents, in our case, and anions, in the case reported by Varret et al,<sup>[10]</sup> seem to induce analogous modifications in the magnetic properties of the trimers, there are also some differences that are worth highlighting. Firstly, the structural variations in the dihedral angles of the ligands; when the anion tetrafluoroborate is replaced by tosylate, the dihedral angles change from 33° to 71°. In our case, the variation observed in the single crystal to single crystal transformation is in general less drastic, most dihedral angles shift from 30-34° to 45-50°; except for the two ligands that have almost co-planar rings **1a** (dihedral angles of 14-18°). Moreover, it must be noted that the few cases in which we observe a spin transition, it is either partial



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or it occurs gradually, across a wide range of temperature. Achieving a sharp and complete spin transition would increase the applicability of our approach. Anion exchange, in contrast, allows the trimers to display a complete spin transition.<sup>[10]</sup> This might be due to the methoxy donor substituent on the phenyl rings, that also cooperates in increasing the ligand field on the Fe(II), provided the dihedral angle of the ligands is appropriate. In general, the advantage that the solvent effect offers is that at least it is partially reversible, and more studies, for example, with solvent mixtures, could reveal a way of better control of this transformation

## Conclusion

An iron-triazole trimer with single-crystal solvatochromic properties has been synthesized, characterized and studied. Intriguing changes in its magnetic properties caused by solvents were observed, where polar solvents favour a spin transition in the material, whereas non-polar solvents seem to stabilize the HS-HS-HS state. A single-crystal to single-crystal transformation could be identified, and XRD studies allowed us to determine the structural origin of the distinct magnetic behaviours observed. We concluded that these differences arise from the conformation of the bi-aromatic ligands, which determines if charge donation can take place from the phenyl to the triazole ring. In a polar solvent like acetonitrile, where this charge donation is favoured, the ligand field exerted on the metal centers is stronger and the central Fe(II) of the trimer is in low spin. In a non-polar solvent like toluene, where the ligands are non-conjugated and the intra-ligand charge transfer is not present or weaker, in contrast, the central Fe(II) is in high spin. The solvent-induced "tuning" of magnetic properties open an easy strategy for the use of one single compound in different applications. Nevertheless, before this can be achieved, further efforts need to be done to overcome the limitations detected in this study. For example, the lack of reversibility in the single crystal to single crystal transformation, and the fact that the visual changes are not sufficiently prominent, since 1a is the only case where the compound is not white. Extending the study of the single crystals to more solvents, or even to solvent mixtures, and synthetic modifications of the ligands may help progressing towards application of these compounds.

## Experimental Section

### Synthetic procedures

**4-(p-methylphenyl)-1,2,4-triazole** <sup>[11]</sup>: 4-methylaniline (200mg, 1.86 mmol) was placed in a round-bottomed flask with p-toluene sulphonic acid monohydrate (530 mg, 2.80 mmol). Toluene (5mL) and Methanol (1mL) were added and the reaction was heated up with stirring to 111°C. The azine (284 mg, 2mmol), dissolved in 1mL of toluene, was added dropwise over 1-2h. The reaction was refluxed for 24-36h (the reaction can be checked by TLC on silica gel, with dichloromethane as eluent). Toluene was evaporated, the crude was redissolved in dichloromethane and extracted with a 10% solution of NaHCO<sub>3</sub> (2x10mL), water (3x10mL) and brine (2x10mL). The organic layer was then dried over MgSO<sub>4</sub> and concentrated under vacuum. Hexane was added and the ligand was obtained as white or beige crystals, 327 mg, 82%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 8.46 (s, 2H, H1), 7.35 (AA'BB', 2H, J<sub>6</sub>=7.9 Hz, H3), 7.28 (AA'BB', 2H, J<sub>6</sub>=7.9 Hz, H4), 2.43 (s, 3H, H6). <sup>13</sup>C-NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 141.3

(C1), 139.1 (C2), 131.1 (C5), 130.7 (C3), 121.9 (C4), 20.98 (C6). Mass (ESI, MeOH): 160 [M+H]<sup>+</sup>, 319 [2M+H]<sup>+</sup>.

**Synthesis of trimer 1:** 4-(p-tolyl)-4H-1,2,4-triazole (20mg, 0.126 mmol) and Fe(H<sub>2</sub>O)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub> (28.4 mg, 0.084 mmol) were dissolved in 2 mL of MeCN. The mixture was stirred at 50°C for 20 min. The product crashes out as white powder upon addition of diethyl ether, 91%. Alternatively, slow vapour diffusion of Et<sub>2</sub>O into the MeCN solution afforded pink crystals of the product. FTIR,  $\nu$  (cm<sup>-1</sup>) = 3478 (br), 3120 (m), 2308-2246 (w, only in 1a), 1365 (w), 1530 (m), 1242 (m), 1033 (s), 806 (m), 649-605 (w), 518 (m). Elemental Analysis, Calc: C 37.03 H 3.80 B 3.70 F 26.03 Fe 9.56 N 14.39 O 5.49; Found: C 36.90 H 4.16 B 3.45 F 24.18 Fe 8.88 N 14.84 O 7.59.

Crystallographic data available in the Cambridge Database: CCDC-1999780 (1a) and CCDC-1999781 (1a-tol) contain the supplementary crystallographic data for this paper

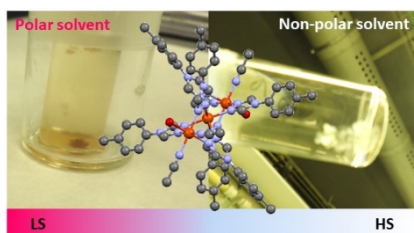
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**Keywords:** spin crossover • solvatochromism • Fe trimers • solvent polarity •  $\pi$ -conjugation

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**Entry for the Table of Contents**

An iron triazole-bridged trimer capable of changing colour and magnetic properties with solvent was synthesized and characterized. A study of its single crystals in different solvents provides evidence of the structural reasons behind this intriguing behaviour.

**Key topic:** solvatochromism, spin crossover.

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