Above room temperature spin transition in a metallo-supramolecular coordination oligomer/polymer†

Chandrasekar Rajadurai, Olaf Fuhr, Robert Kruk, Mohammed Ghafari, Horst Hahn and Mario Ruben*

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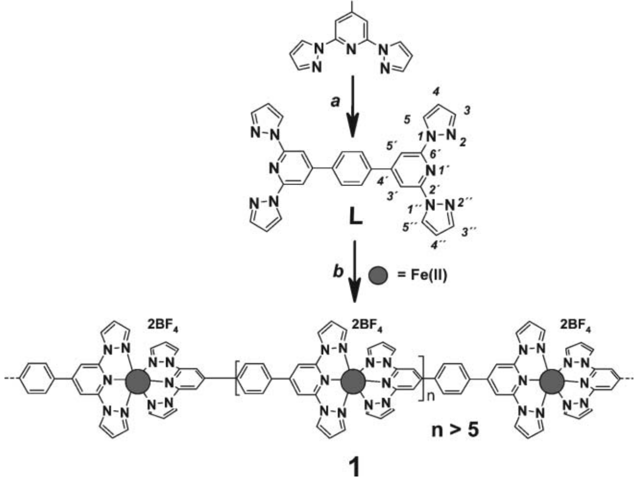
By use of a metallo-supramolecular concept, a linear iron(II) coordination chain $[Fe^{II}(L)]_n(BF_4)_{2n}$ (L = 1,4-bis(1,2′:6′,1″-bispyrazolylpyridin-4′-yl)benzene) was rationally designed and synthesized. The molecular chain shows a reversible spin transition at 323 K with a *ca.* 10 K wide hysteresis loop.

The search for spin transition (ST) materials with a transition temperature ($T_{1/2}$) around room temperature displaying a wide hysteresis loop has continued since the first demonstration of a "ST based display device" by Kahn.[1] Although recent years have witnessed great research activity in ST complexes, compounds with $T_{1/2}$ in the range of room temperature and above are still scarce.[1,2] In contrast to isolated or low-dimensional ST coordination complexes, metallo-supramolecular architectures (linear, Hofmann-like or interpenetrated framework) can increase the molecular cooperativity.[3] Due to the enhanced rigidity in higher dimensional ST architectures, $T_{1/2}$ might be shifted to the room temperature region, with a simultaneously widened hysteresis loop.

Previously, Holland *et al.* have reported the zero dimensional ST complex Fe^{II}[2,6-di(pyrazol-1-yl)pyridine]$_2(BF_4)_2$ exhibiting $T_{1/2}$ at 259 K together with a 3 K wide hysteresis loop.[4a] Following the metallo-supramolecular approach,[5] we have rationally designed an extended iron(II) based linear rigid coordination chain using a taylor-made back-to-back 1,4-phenylene-coupled 2,6-di(pyrazol-1-yl)pyridine ligand L (Scheme 1). Conceptually, the introduction of metallo-supramolecular interactions is expected to increase $T_{1/2}$ and to widen the hysteresis loop in comparison with the monomeric entity.[5] Herein, we report the first synthesis of a linear building block ligand 1,4-bis(1,2′:6′,1″-bispyrazolylpyridin-4′-yl)benzene L, which is subsequently converted into a linear 1-D iron(II) coordination oligomer/polymer $\{[Fe^{II}(L)]_n(BF_4)_{2n}\}$ (**1**). The metallo-supramolecular coordination chain **1** exhibits ST above room temperature with a wide hysteresis loop, as proven by magnetic and Mössbauer studies (Fig. 2 and 3).

The ligand L was synthesized *via* Suzuki cross-coupling reaction of 4-iodo-2,6-di-pyrazol-1-ylpyridine[2e] with 1,4-phenyldiboronic acid (Scheme 1).‡ The structure of L was determined by single crystal X-ray diffraction study,§ which shows linearly arranged 2,6-di(pyrazol-1-yl)pyridine units (N3···N8 distance = 1.14 nm) (Fig. 1). The pyrazolyl rings are orientated in an all-transoid conformation around the C–N single bonds. The 2,6-di(pyrazol-1-yl)pyridine units are almost planar to the 1,4-phenyl bridge with a torsion angle (θ) of *ca.* 34°. Compound L can be considered as a structural alternative ligand in coordination chemistry to the widely used terpyridyl-based back-to-back ligand systems.[6–8] The supramolecular coordination complex **1** was synthesized by stirring a mixture of one equivalent of a dichloromethane solution of L and two equivalents of methanolic $Fe(BF_4)_2{\cdot}6H_2O$ solution at room temperature for 3 days under N_2 atmosphere to afford an orange precipitate of **1**.¶ Repeated attempts to crystallize the complex using different techniques resulted only in precipitation of



Scheme 1 Synthesis of iron(II) coordination chain (**1**). *Reagents and conditions*: (*a*) 1,4-phenyldiboronicacid, $Pd(PPh_3)_4$, dioxane, 2 M Na_2CO_3, 95 °C; (*b*) $Fe^{II}(BF_4)_2{\cdot}6H_2O$, CH_2Cl_2, MeOH, 3 days, RT, N_2 atmosphere.

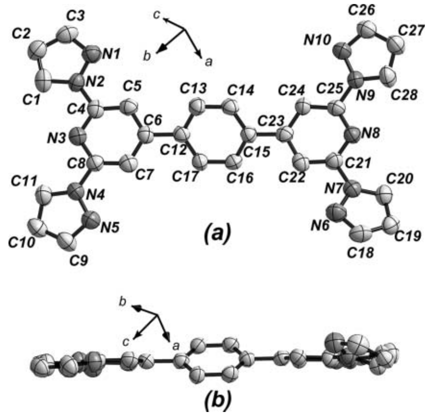


Fig. 1 ORTEP plot (50% probability) of ligand L: (a) front view, (b) side view, showing the linear arrangements of the two 2,6-di(pyrazol-1-yl)pyridine units.

Institute of Nanotechnology, Research Centre, Karlsruhe, PB-3640, D-76021, Germany. E-mail: Mario.Ruben@int.fzk.de; Fax: :(+49) 724-782-6781; Tel: (+49) 724-782-6434

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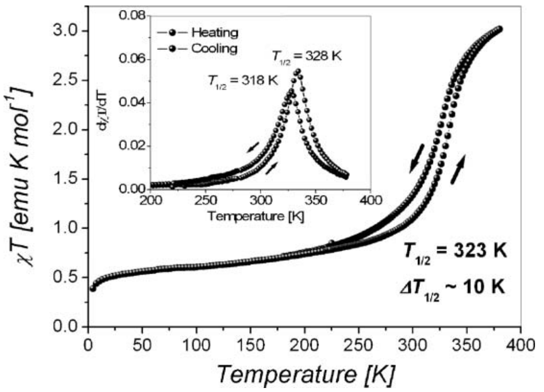

Fig. 2 The χT *vs.* T plot for complex **1** from 4.5 to 380 K (↓ cooling mode and ↑ heating mode) measured with a 1000 Oe applied DC magnetic field. The sample was cooled from 300 to 4.5 K and χT was first measured upon warming from 4.5 to 380 K, followed by the cooling mode. Inset shows the dχT/dT curve.

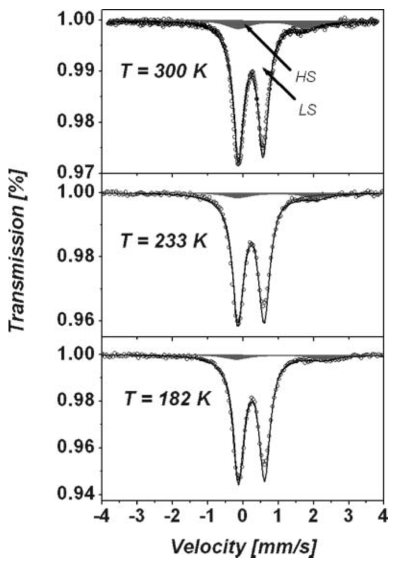

Fig. 3 Zero-field ^{57}Fe Mössbauer spectra of complex **1** recorded at different temperatures; the solid lines represent the best fit curves with the parameters given in Table 1.

complex **1**. Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis of a methanol–DMF–acetonitrile solution of complex **1** provides evidence for the presence of a pentanuclear oligomeric unit $[Fe_5L_5–8BF_4\cdot(OH^-)_6]^{2+}$ at m/z = 1518.5 (calcd m/z = 1518.81) together with fragmented smaller nuclear entities (see ESI,† S4). Since the bulk of compound **1** is not soluble in the same solution, complex **1** is supposed to represent the higher chain homologue with more than five repeating units. FTIR spectroscopy (1800–900 cm^{-1} region) of the precipitate of **1** shows a clear major shift of the ligand bands and new vibrational modes for the metal complex **1** (see ESI,† SI 1). In addition, it was shown that the reaction of an analogous, linear ligand 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene ligand with metal(II) ions leads to linear coordination polymers.[6–8] The formation of cyclic oligomers can be excluded because of the rod-like shape of L. Hence, it is reasonable to assume that complex **1** possesses a linear polynuclear structure.

The temperature dependent magnetic measurements of **1** in the range of 4.5–380 K are shown in Fig. 2. The measurements were performed during both heating (↑) and cooling (↓) cycles, which revealed a reversible ST behaviour with a wide hysteresis loop. At 380 K the value of χT is 3.02 emu K mol^{-1}, which is lower than the expected value for a high-spin (HS) iron(II) ion in the S = 2 state. This shows that the thermally saturated HS state is situated above 380 K, which was the upper limit of the experimental set up. The ST temperatures for the heating ($T_{1/2}\uparrow$ = 328 K) and cooling ($T_{1/2}\downarrow$ = 318 K) modes revealed the occurrence of a *ca.* 10 K wide thermal hysteresis. Importantly, the observed $T_{1/2}$ value of **1** is above room temperature. Below 225 K, the χT value was almost constant and reached a minimum value of 0.38 emu K mol^{-1} at 4.5 K. The residual magnetic moment most likely arises from the high spin state of the water end-capped iron(II) or iron(III) coordination sites at the linear chain ends. Indeed, the presence of water molecules in **1** is supported by FTIR spectroscopy ($\nu_{O–H}$ at 3440 cm^{-1}, broad) and FT-ICR mass analysis (ESI,† Fig. S1).

The zero-field ^{57}Fe Mössbauer spectra and the hyperfine parameters of complex **1** measured at 300, 233 and 182 K are shown in Fig. 3 and Table 1, respectively. Least squares analysis of the spectra revealed the presence of a mixture of LS and HS states. At all temperatures, the values of the main doublet parameters are typical for LS state iron(II) and the minor doublet parameters correspond to the HS state iron(II). Significantly at 300 K the relative area of distribution of the LS fraction is *ca.* 86%, which further confirms the ST property associated with complex **1**. Upon decreasing the temperature from 300 to 182 K the LS fraction has increased further from 86% to 91% at the expense of the HS fraction. At 182 K, the presence of 91% LS fraction (δ_{iso} = 0.390(1) mm s^{-1}; ΔE_Q = 0.738(2) mm s^{-1}; Γ = 0.35(1) mm s^{-1} and AR = 91%) indicates the near completion of the ST event in complex **1**. Overall, the relative areas of distribution of the HS and LS components are in good agreement with the magnetic susceptibility data. Detailed high temperature Mössbauer spectroscopic investigations are currently in progress.

In conclusion, a distinctive iron(II) coordination chain was synthesized by exploiting for the first time a new back-to-back ligand with 2,6-di(pyrazol-1-yl)pyridine as terminal binding sites. The complex undergoes a reversible ST at 323 K with a *ca.* 10 K wide hysteresis loop. This approach provides the general concept for achieving technologically appealing high $T_{1/2}$ systems by supramolecular interlinking of the ST-iron(II) centers.[5] Both the high temperature shift of $T_{1/2}$ and the widening of the hysteresis can be attributed to the increased cooperativity in the rigid metallo-supramolecular ST system in comparison to the 0-D, non-interlinked systems.[4] Further investigations of the structural and

Table 1 Mössbauer data for complex **1** at different temperatures[a]

T/K	Component	δ_{iso}/mm s^{-1}	ΔE_Q/mm s^{-1}	Γ/mm s^{-1}	AR (%)
300	LS	0.364(2)	0.702(2)	0.36(1)	86
	HS	0.96(3)	1.91(4)	0.86	14(1)
233	LS	0.390(2)	0.740(3)	0.37(1)	92
	HS	1.10(6)	2.2(1)	0.86	8(2)
182	LS	0.390(1)	0.738(2)	0.35(1)	91
	HS	1.2(1)	2.6(1)	0.86	9(2)

[a] δ_{iso}: isomer shift relative to α-Fe, ΔE_Q: quadrupole splitting, Γ: width of the line, AR: area ratio of the components A_{HS}/A_{tot}. Statistical standard deviations are in parentheses.

above room temperature ST characteristics of **1** at the single molecule level are in progress.[9]

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Notes and references

‡ 4′,4′′′′-(1,4-Phenylene)bis(1,2′:6′,1″-bispyrazolylpyridine) (L): A solution of 1,4-dioxane (50 ml) containing 2 M Na_2CO_3 (5 ml) was taken in a clean 250 mL flask and N_2 gas was bubbled into the solution for 10 min. To this solution 4-iodo-2,6-di-pyrazol-1-ylpyridine (0.674 g, 2 mmol), 1,4-phenyldiboronic acid (0.166 g, 1 mmol) and $Pd(PPh_3)_4$ (0.200 g, 0.173 mmol) were added and heated in the dark at 70 °C for 3 days. The solvent was evaporated and the crude solid was extracted with a water–CH_2Cl_2 mixture several times. The collected organic layers were combined and the concentrated solution was filtered through a silica column using CH_2Cl_2 at first to remove coloured impurities and then with ethyl acetate to collect a colourless solution, which upon evaporation yielded analytically pure white powder of L. Yield *ca.* 210 mg; 22%. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.63 (dd, 4H, $^3J_{H,H}$ = 2.64 Hz, pyrazole), 8.12 (s, 4H), 7.98 (s, 4H), 7.81 (dd, 4H, $^3J_{H,H}$ = 1.7 Hz, pyrazole), 6.54 (m, 4H, $^3J_{H,H}$ = 4.14 Hz; $^4J_{H,H}$ = 1.7 Hz, pyrazole) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 153.1, 150.7, 142.5, 138.7, 127.9, 127.3, 108.0, 107.2 ppm. FTIR (KBr, ν/cm^{-1}) : 916, 939, 956, 999, 1016, 1036, 1070, 1095, 1124, 1159, 1194, 1206, 1252, 1285, 1311, 1395, 1435, 1461, 1520, 1542, 1561, 1578, 1608, 1738. MALDI-TOF: *m*/*z* (relative intensity of isotopic distribution in %) experiment: 496.63 (100%), 497.63 (35%), 498.63 (15%); simulation: 496.19 (100%), 497.19 (35%), 498.19 (5%).

§ *Crystal data* for L: $C_{28}H_{20}N_{10}$; $M = 496.54$; orthorhombic; space group $Pca2_1$; $a = 9.3026(19)$, $b = 9.4892(19)$, $c = 26.467(5)$ Å; $\alpha, \beta, \gamma = 90°$; $V = 2336.4(8)$ Å^3; crystal size = 0.6 × 0.1 × 0.03 mm; index ranges = $-9 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 10$, $-32 \leqslant l \leqslant 21$; theta range for data collection = 2.15–25.68°; $Z = 4$; $D_{obsd} = 1.412$ g cm^{-3}; $F(000) = 1032$; $\mu = 0.091$ mm^{-1}; 5658 reflections measured, 1308 unique ($R_{int} = 0.0611$), $R(F_o) = 0.0527$; $R_w(F) = 0.1095$; GOF on $F^2 = 0.926$; $T = 200$ K. CCDC 632648. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702468a

¶ Coordination complex (**1**): 60 mg (0.12 mmol) of ligand L was dissolved in a deaerated dichloromethane (75 ml). To this a deaerated methanolic solution containing 81 mg (0.24 mmol) of $Fe(BF_4)\cdot 6H_2O$ was added and stirred for 3 days under N_2 atmosphere. The solvents were evaporated from the turbid solution and the formed orange precipitate was collected and washed with dichloromethane–methanol and finally air dried. Yield 82 mg; 94%. FTIR (KBr, ν/cm^{-1}): 913, 939, 954, 969, 1065 (b), 1084, 1224, 1174, 1212, 1261, 1288, 1339, 1408, 1465, 1497, 1526, 1550, 1566, 1623, 3136, 3440 (broad, O–H stretch). FT-ICR MS (in MeOH–CH_3CN–DMF) : $[Fe_5L_5{-}8BF_4\cdot(OH^-)_6]^{2+}$ at m/z = 1518.5 (exptl), 1518.81 (calcd); $[Fe_5L_4{-}8BF_4\cdot(OH^-)_6]^{2+}$ at m/z = 1270.5 (exptl), 1270.73 (calcd); $[Fe_4L_3{-}5BF_4\cdot(OH^-)_3\cdot H_2O]^{2+}$ at m/z = 1021.75 (exptl), 1021.17 (calcd). Elemental analysis (%) calcd for $C_{28}H_{20}B_2F_8FeN_{10}\cdot H_2O$: C 45.16, H 2.96, N, 18.82; Found C 45.58, H 3.47, N, 18.41.

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