

# EXTENDED METAL ATOM CHAINS (EMACS) AS MAGNETIC NANOSTRUCTURES: SYNTHESIS AND MAGNETIC BEHAVIOR

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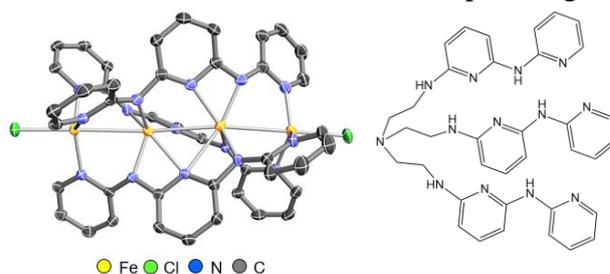
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## ABSTRACT

**Extended Metal Atom Chains (EMACs)** consist in arrays of metal ions, wrapped together by oligo- $\alpha$ -pyridylamido, or related ligands.<sup>[1-3]</sup> The arrangement of the donor atoms often promotes the formation of metal-metal bonds.<sup>[1]</sup> EMACs have attracted renewed interest since the pentachromium(II) complex  $[\text{Cr}_5(\text{tpda})_4\text{Cl}_2]$  ( $\text{H}_2\text{tpda} = N^2, N^6$ -di(pyridin-2-yl)pyridine-2,6-diamine) was shown to exhibit a directionally-bistable magnetic moment at low temperature ( $S = 2$  ground state).<sup>[4]</sup> Here, by refluxing  $[\text{Fe}_2(\text{Mes})_4]$  ( $\text{HMes} = \text{mesitylene}$ ),  $\text{Fe}_4\text{Cl}_8 \cdot 6\text{THF}$  and  $\text{H}_2\text{tpda}$  in toluene and in **strictly anaerobic and anhydrous conditions**, we isolated crystals of the first homometallic iron(II)-based EMAC supported by oligo- $\alpha$ -pyridylamido ligands: the tetrairon(II) complex  $[\text{Fe}_4(\text{tpda})_3\text{Cl}_2]$  (**1**) (Fig. 1).<sup>[5]</sup> In similar conditions, also  $[\text{Fe}_4(\text{tpda})_3\text{Br}_2]$  (**2**) was isolated. The spectroscopic and electronic properties of **1** and **2** were investigated in  $\text{CH}_2\text{Cl}_2$  by UV-Vis-NIR absorption spectroscopy,  $^1\text{H-NMR}$  spectroscopy and cyclic voltammetry.  $^1\text{H-NMR}$  showed that **1** and **2** possess  $D_3$  symmetry in  $\text{CH}_2\text{Cl}_2$  solution. In both cases, the electrochemical measurements showed four fully resolved, quasi-reversible one-electron redox processes, implying that both **1** and **2** can adopt five oxidation states in a potential window of only 0.8 V. Direct current magnetic measurements on **1** indicate dominant ferromagnetic coupling at room temperature, although the ground state is only weakly magnetic.<sup>[5]</sup> Based on Density Functional Theory and Angular Overlap Model calculations, this magnetic behavior was explained as being due to two pairs of ferromagnetically-coupled iron(II) ions ( $J = -21 \text{ cm}^{-1}$  using  $J\hat{S}_i \cdot \hat{S}_j$  convention) weakly antiferromagnetically coupled with each other.<sup>[5]</sup> Alternating-current susceptibility data revealed the onset of slow magnetic relaxation below 2.8 K (estimated  $U_{\text{eff}}/k_B = 10.1(1.3) \text{ K}$ ).<sup>[5]</sup> To attempt activating the electronic interaction mechanism known as double-exchange, which provides an effective source of ferromagnetic coupling in **mixed valent compounds**, the one-electron chemical oxidation of **1** was carried out using ferrocenium hexafluorophosphate (1 equiv) in  $\text{CH}_2\text{Cl}_2$ . The isolated product is indeed a mixed-valence species showing an intervalence electronic absorption band around 700-750 nm, but containing one metal center less:  $[\text{Fe}^{\text{II}}_2\text{Fe}^{\text{III}}(\text{tpda})_3]\text{PF}_6$  (**3**). In order to better stabilize these chain like structures, a new tripodal ligand (**4**) based on three covalently linked oligo- $\alpha$ -pyridylamido units was designed and synthesized (Fig. 1). Preliminary results in the investigation of its coordinating properties will be presented.

## REFERENCES

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**Figure 1.** Molecular structure of **1**, viewed approximately normal to the metal ion chain (left). Structure of **4** (right).