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## Iron(II) Spin-Transition Complexes with Dendritic Ligands, Part II<sup>[‡]</sup>

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

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The dendritic triazole-based complexes [Fe(G1-BOC)<sub>3</sub>](triflate)<sub>2</sub>·xH<sub>2</sub>O (**1**; G1-BOC = tert-butyl {3-[3-(3-tert-butoxycarbonylaminopropyl)-5-([1,2,4]triazol-4-ylcarbamoyl)phenyl]propyl}carbamate, triflate = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), [Fe(G1-BOC)<sub>3</sub>]-(tosylate)<sub>2</sub>·xH<sub>2</sub>O (**2**; tosylate = p-CH<sub>3</sub>PhSO<sub>3</sub><sup>-</sup>), [Fe(G1-DPBE)<sub>3</sub>]-(triflate)<sub>2</sub>·xH<sub>2</sub>O {**3**; G1-DPBE = 3,5-bis(3,5-didodecaoxybenzyloxy)-N-[1,2,4]triazol-4-ylbenzamide}, [Fe(G1-DPBE)<sub>3</sub>]-(tosylate)<sub>2</sub>·xH<sub>2</sub>O (**4**) and [Fe(G1-DPBE)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O (**5**) were designed and synthesized. Magnetic and thermal properties of these novel complexes were characterized by magnetic susceptibility measurements, <sup>57</sup>Fe Mössbauer spectroscopy and thermogravimetric analysis or differential scanning calo-

#### Introduction

Dendritic materials are interesting due to their unique macromolecular monodispersed nature, generation-dependent properties and the possibilities they offer for anchoring various groups for functionalization. These materials have received much attention recently with regards to fundamental research and because of their applications in various fields.<sup>[1-3]</sup> For example, incorporation of metals in a dendritic moiety may provide an opportunity to generate new metallodendrimer materials,<sup>[4–8]</sup> dendritic boxes and other supramolecular dendritic arrangements.<sup>[9–11]</sup> These metallodendrimers can be used as soluble catalysts for various organic reactions. There are a few reports in the literature: aryl–nickel(II) dendrimers have been used as an effective catalyst for the Karasch addition reaction of polyhaloalkanes to olefins,<sup>[12]</sup> P-based polypalladium complexes were

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rimetry, respectively. All dendritic complexes under study show different spin-transition behaviour with respect to the nature of different dendritic ligands and counteranions. Complexes **1** and **2** have pronounced effects of a spin-state change during the first heating process and gradual spintransition properties for further temperature treatments, whereas **3** and **4** exhibited a very sharp spin-state change in the first heating procedures. Complex **5** showed a gradual spin-transition curve. In this paper, we report how the magnetic properties of these complexes are correlated with noncoordinated water molecules and their effects on spin states.

used for the electrochemical reaction of  $CO_2$  to  $CO^{[13,14]}$ and iron dendritic complexes were used as spatially encumbered models of nonheme iron proteins.<sup>[15]</sup> Our motivation also falls in the same line to make metal–dendritic-systembased complexes with various interesting properties dependent on different ligands, metal ions and counteranions.

It is well documented that iron(II)-containing dendritic complexes may exhibit thermal spin-crossover (SCO) behaviour. This particular unique property with an accompanying change of colour and magnetic behaviour is very useful for various applications such as display devices, optical switches and magneto-optical storage systems.<sup>[16,17]</sup> Spin crossover is related to its electronic transition between  $t_{2g}^{6}e_{g}^{0}$  [low spin (LS)] and  $t_{2g}^{4}e_{g}^{2}$  [high spin (HS)]. In some cases, this electronic transition causes a switching of colour of the complexes with respect to its transition state. The electron transition can be triggered by using external perturbations such as change of temperature, pressure, light irradiation and magnetic field.<sup>[16a,18,19]</sup> There are numerous examples of the SCO behaviour of organometallic complexes using various ligands but very few reports about using dendritic ones. Still, it is quite challenging to design and synthesize novel ligands that can show synergic effects in terms of thermal and spin-crossover properties. Among the reported wide range of ligand systems, 4-R-substituted 1,2,4-triazoles were the most studied, in which the functional R group may be any kind of aliphatic or aromatic

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organic moiety. Its combination with iron to provide the  $Fe^{II}N_6$  spin-crossover chromophore is the most attractive one due to its relatively high chemical stability and striking colour change upon spin transition<sup>[20]</sup> that originates either from the dd HS/LS bands or the more intensive metal-to-ligand charge-transfer (MLCT) bands, which in many cases overlap the thermochromic effect associated with the dd HS/LS bands.

Earlier we published the first part of this study using various triazole-based ligand systems combined with iron(II) and its spin transition.<sup>[21]</sup> In this second part, our main focus is the utilization of various triazole-based dendritic ligands (as shown in Figure 1) for making iron(II) complexes with different counteranions to arrive at a structure-property relationship with respect to its spin-crossover behaviour. We have synthesized and characterized various triazole dendritic ligands and their iron(II) complexes, all the while keeping SCO behaviour as the main objective. This study is an extension of our earlier work<sup>[21]</sup> and also a comparative study with that of some of the previously reported dendritic iron(II) complexes by Fujigava et al. (see structure **B** in Figure 1).<sup>[22]</sup> They highlighted a generation number (n) dependency of the abruptness of the spin-state change with temperature and showed that [(G1-trz)Fe] (trz = triazole) was the best-behaved complex in terms of the spin-crossover properties (cooperativity) in terms of eventual applications.<sup>[21]</sup> We have chosen different counteranions such as triflate (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) and tosylate (*p*-CH<sub>3</sub>PhSO<sub>3</sub><sup>-</sup>) because of their interesting influences on spin-crossover behaviour.<sup>[23–25]</sup> The G1-PBE [PBE = poly(benzyl ether)] dendritic triazole-based complexes (see structure A in Figure 1) are already covered in our earlier publication. In this paper, we are mainly focussing on two dendritic triazole ligands (structures **B** and **C** in Figure 1) with different dendritic branches attached to triazole and their iron(II) complexes. Structural differences of dendritic ligands play a crucial role in "tuning" the thermal and magnetic properties of iron(II)



Figure 1. Perspective molecular structures of different dendritic triazoles: G1-PBE  $(\mathbf{A})$ ,<sup>[21]</sup> G1-DPBE  $(\mathbf{B})$  and G1-BOC  $(\mathbf{C})$ .

complexes because of differences in the connection between the triazole ring and the dendron (NH–C=O and CH<sub>2</sub> spacing). Some important rules for the design and the synthesis of the dendritic ligands and their iron(II) complexes with magnetic thermal properties are discussed in this paper.

#### **Results and Discussion**

#### Synthesis of the Dendritic Triazole Ligands

The first-generation dendritic triazole G1-BOC (C), was synthesized by heating to reflux the corresponding tertbutoxycarbonyl (BOC)-protected dendron D<sup>[26]</sup> with 4amino-1,2,4-triazole (atrz) in the presence of diphenyl (2,3dihydro-2-thioxo-3-benzooxazolyl) phosphonate (DBOP) as a catalyst in a mixture of triethylamine and dry THF under nitrogen (Scheme 1). The reaction was worked up by using standard extraction techniques and the compound was isolated from the organic phase. The crude product was purified by column chromatography and the final compound was obtained in 72% yield. The ligands A and B were synthesized according to previously reported publications of Sonar et al.<sup>[21]</sup> and Fujigaya et al.,<sup>[22]</sup> respectively. The dendritic triazoles in Figure 1 were prepared on the gram scale as analytically pure compounds. The purity of the materials was confirmed by elemental analysis, MALDI-TOF spectrometry and NMR spectroscopy.



Scheme 1.

#### Synthesis of the Iron(II) Complexes with Dendritic Triazoles

All the iron(II) complexes with dendritic triazoles,  $[Fe(G1-BOC)_3](triflate)_2 \cdot xH_2O$  (1),  $[Fe(G1-BOC)_3](tosyl$ ate)<sub>2</sub>·xH<sub>2</sub>O (2), [Fe(G1-DPBE)<sub>3</sub>](triflate)<sub>2</sub>·xH<sub>2</sub>O {3; G1-DPBE = 3,5-bis(3,5-didodecaoxybenzyloxy)-N-[1,2,4]triazol-4-ylbenzamide}, [Fe(G1-DPBE)<sub>3</sub>](tosylate)<sub>2</sub>· $xH_2O$  (4) and  $[Fe(G1-DPBE)_3](BF_4)_2 \cdot xH_2O$  (5), were synthesized in high yield. Ascorbic acid was used as antioxidant during the synthesis of all complexes to avoid the oxidation of iron(II) ions. The reactions were carried out using methanol and THF solvent mixtures (1:5) at room temperature. After completion of the reaction, we did not observe any precipitate formation in the solvent mixture, which may be due to similar solubility behaviour of dendritic triazole and its complexes at room temperature. Due to this reason, we could not purify the final iron(II) complexes, as it was difficult to separate the products by precipitation from the reaction solution. After modifying the synthesis procedure, we

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were able to separate the pure dendritic triazole iron(II) complexes at very low temperature. Specifically for the G1-BOC-based iron(II) complexes, when the solvent of the reaction mixture was partially removed, the remaining reaction solution segregated easily into two layers. After cooling in liquid nitrogen to around -100 °C, the pink solid G1-BOC-based iron(II) complex was recovered as a product at the bottom of the flask. The same procedure was carried out several times to get higher yields. For other dendritic triazole-based iron(II) complexes, we used the same procedure as mentioned above and it was much easier to obtain pure complexes in higher yields.

#### Powder X-ray Diffraction Experiments of the Dendritic Triazole Iron(II) Complexes

The powder X-ray diffraction experiments were carried out at various temperatures (first at 300 K, then at 250, 300, 350 and again at 300 K, respectively) using fresh samples of  $[Fe(G1-BOC)_3](tosylate)_2 \cdot xH_2O$  (2) and  $[Fe(G1-DPBE)_3]$ - $(tosylate)_2 \cdot xH_2O$  (4) to compare the effect of different dendritic triazoles. The X-ray powder diffraction pattern shows in each case a single strong diffraction peak beside some small diffraction peaks. The broad halo peak appeared at about  $2\theta$ -20° and originated from the voluminous dendritic branches attached to triazole. It was not possible to determine the crystal structures because only eight diffraction peaks of the poorly structured complexes under study could be recorded.

Figure 2 shows the X-ray powder diffraction pattern measured in the  $2\theta$  range between 2 and 20° at various temperatures for [Fe(G1-BOC)<sub>3</sub>](tosylate)<sub>2</sub>·xH<sub>2</sub>O (**2**). As shown in Figure 2 (a), the diffraction pattern at 300 K shows the strong peak at  $2\theta = 3.440^\circ$ , whereas some other small peaks appear at the positions of  $2\theta = 5.975$ , 6.912, 12.546 and 13.874°. After cooling the samples to 250 K, the strong diffraction signal changes its position from  $2\theta = 3.440^\circ$  to  $2\theta$ 

 $= 3.281^{\circ}$ . This temperature effect was also noticed for other small diffraction peaks at the positions 5.812, 6.729, 12.386 and 13.715° (Figure 2, b). When the sample is heated again to the original temperature at 300 K, the position of the strong signal changes only a little (to  $2\theta = 3.243^{\circ}$ ). Other small peaks appear at 5.788, 6,738, 12.334 and 13.718° (Figure 2, c), respectively. All these signals can be indexed as (1,0), (1,1), (2,0), (3, 1) and (4,0) and belong to a two-dimensional hexagonal lattice with lattice parameters a equal to 29.71, 31.15 and 31.51 Å for 300, 250 and 300 K, respectively. After heating the iron(II) complexes again to 350 K, the complex shows a strong diffraction peak at  $2\theta = 3.247^{\circ}$ and only two small peaks appear at positions at 5.805 and 6.743° (Figure 2, d). During the heating and cooling cycles, we observed the irreversibility of the appearances of the peak. This is due to the loss of water after heating to 350 K [see the thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements below]. By cooling again to 300 K, the strong peak was observed at position  $2\theta = 3.306^{\circ}$  and two small peaks remained at positions 5.906 and 6.845° (Figure 2, e). These peaks can be indexed as (1, 0), (1, 1) and (2, 0) and belong to a twodimensional hexagonal lattice with lattice parameters a equal to 31.47 and 30.91 A for 350 and 300 K, respectively.

The G1-DPBE-based iron(II) complex [Fe(G1-DPBE)<sub>3</sub>]-(tosylate)<sub>2</sub>·xH<sub>2</sub>O (**4**) was also analyzed by X-ray powder diffraction under similar conditions to the first sample measurement. (Figure 3). The X-ray diffraction pattern was first analyzed at 300 K using a fresh sample of **4**. The peak appeared at  $2\theta = 4^{\circ}$ ; other small peaks were also observed at various positions at 6.199, 6,988, 8.405 and 12.382°. These can be indexed in two-dimensional hexagonal lattice as (2, 1), (3, 0), (3, 1) and (4, 2), respectively (Figure 3, a). On cooling this sample to 250 K, the small peaks appeared at positions 4.674, 6,209, 7.032, 8.422 and 12.425°, which can be indexed as (2,0), (2,1), (3,0), (3,1) and (4,2), respectively (Figure 3, b). After heating the sample again to 300 K, the



Figure 2. X-ray powder diffraction pattern of a fresh sample of **2** measured at (a) 300, (b) 250 and (c) 300 K after cooling and (d) 350 and (e) at 300 K after heat treatment. The vertical line shows the changes in the  $2\theta$  position of diffraction peak (1).





Figure 3. X-ray powder diffraction pattern of a fresh sample of 4 measured at (a) 300, (b) 250 and (c) 300 K after cooling and (d) 350 and (e) at 300 K after heat treatment. The vertical line shows the changes in the  $2\theta$  position of the diffraction peak.

small peaks appeared at positions 4.131, 4.767, 6.338, 7.171 and 8.543° and this is indexed as (1,1), (2,0), (2,1), (3,0) and (3,1), respectively (Figure 3, c). During the next heating cycle from 300 to 350 K, the complex showed a strong peak at  $2\theta = 2.476^\circ$ . Small peaks at this temperature were observed at positions 4.262, 4.909, 6.516, 7.376 and 8.695°, which can be indexed as (1,0), (1,1), (2,0), (2,1), (3,0) and (3,1), respectively (Figure 3, d). After cooling the sample from 350 to 300 K, the first strong peak appeared at position  $2\theta = 2.458^\circ$  and the small peaks appeared at position  $2\theta = 2.458^\circ$  and the small peaks appeared at positions 4.228, 4.926, 6.485, 7.341 and 8.793°. The smaller peaks can be indexed as (1,0), (1,1), (2,0), (2,1), (3,0) and (3,1), respectively (Figure 3, e).

All visible peaks can be indexed in a two-dimensional hexagonal lattice with lattice parameters *a* equal to 43.64, 43.56, 42.68, 41.14 and 41.50 Å for 300, 250, 300, 350 and again 300 K, respectively. Similar results were obtained for the liquid-crystalline dendritic triazole iron(II) complexes reported by Fujigaya<sup>[22]</sup> and Seredyuk.<sup>[27]</sup> Our earlier paper on this work also reported some common observations.<sup>[21]</sup>

#### Magnetic Measurements of the Dendritic Triazole Iron(II) Complexes

The magnetic properties of 1 were investigated with a superconducting quantum interference device (SQUID) magnetometer at variable temperatures following the sequence  $150 \rightarrow 350 \rightarrow 1.7 \rightarrow 350$  K. The results are plotted as  $\chi_M T$  versus T in Figure 4 (a). For a first heating process from 150 to 250 K, the  $\chi_M T$  curve shows a gradual increase in the  $\chi_M T$  values. After heating above 250 K, the curve ends in a plateau with an  $\chi_M T$  value around 2.8 cm<sup>3</sup> K mol<sup>-1</sup>, which is about 20% below that expected for the spin-only value of iron(II) in the high-spin state. On cooling, the  $\chi_M T$  values match perfectly those of the heating branch in the temperature between 350 and 250 K. When the temperature is lowered from 250 K down to 1.7 K, the

 $\chi_{\rm M}T$  value initially remains constant and then, at about 210 K, starts to lower more gradually compared to the first heating process. It finally reaches a value of 0.28 cm<sup>3</sup> K mol<sup>-1</sup> at 1.7 K. The spin-transition temperature  $T_{\rm SC}$  (at which 50% of all complex molecules actively involved in the thermal spin transition have changed the spin states from high spin to low spin on cooling) of complex 1 is about 30 K. After the first heating process, the  $\chi_{\rm M}T$ curves in both cooling and heating directions are completely reversible and no hysteresis was observed. The shape of the  $\chi_M T$  curves in this case, and somewhat similar also in the cases of Figure 4 (b and d), resemble very much the curves for thermal variation of the high-spin fraction in SCO systems with low-spin transition temperatures (i.e., with small energy gaps between HS and LS states). It has been proposed that in such cases the SCO characteristics, or rather the magnetic response functions  $\chi_M T$ , may be essentially determined by the molecular vibrations due to the closeness of the effective vibrational gap to the electronic gap.<sup>[28]</sup>

The magnetic properties of **2** were studied following the temperature sequence of  $200 \rightarrow 350 \rightarrow 6 \rightarrow 350$  K. The  $\chi_M T$  versus *T* values are shown in Figure 4b. In the first heating process from 200 to 350 K, the  $\chi_M T$  values increase from 1.7 (at 200 K) to 2.45 cm<sup>3</sup> K mol<sup>-1</sup> (at 305 K). In the temperature range 280–305 K, the  $\chi_M T$  values change sharply and merge into a plateau with a  $\chi_M T$  value of 2.8 cm<sup>3</sup> K mol<sup>-1</sup>. After this first heating process, the  $\chi_M T$  versus *T* curve shows a gradual spin transition upon cooling from 350 to 6 K, at which point the  $\chi_M T$  value reaches 0.5 cm<sup>3</sup> K mol<sup>-1</sup>. The second heating curve from 6 to 350 K matches well with the cooling curve but cannot reproduce the same sharp transition that was observed during the first heating process.

The magnetic properties of the freshly synthesized iron(II) complex 3 were characterized by following the temperature sequence of  $80 \rightarrow 350 \rightarrow 5.5 \rightarrow 350$  K; the results



Figure 4. Thermal dependence of  $\chi_M T$  of complexes (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5.

are shown in Figure 4 (c). The  $\chi_M T$  values increase mildly with increasing temperature in the region 80 to 350 K, starting from an  $\chi_{\rm M}T$  value of 0.85 cm<sup>3</sup> K mol<sup>-1</sup> at 80 K. Apparently, the thermal spin transition is very gradual due to weak cooperativity between the complex molecules in this material. After crossing the temperature from 300 K onward, the spin state changes very sharply and merges into a plateau with an  $\chi_{\rm M}T$  value of 2.8 cm<sup>3</sup>K mol<sup>-1</sup> at 320 K. Upon cooling from 350 to 5.5 K, the  $\chi_M T$  value remains nearly constant between the 350 and 300 K zone but on further cooling down to 280 K,  $\chi_M T$  decreased rather gradually from 2.7 to 2.2 cm<sup>3</sup> K mol<sup>-1</sup>. At 50 K an  $\chi_{M}T$  value of  $1.0 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$  was recorded. Below 50 K the  $\chi_M T$  value dropped down to 0.35 cm<sup>3</sup> K mol<sup>-1</sup> at 5.5 K most likely due to the well-known zero-field-splitting effect. In the second heating process from 5.5 to 350 K, the transition curve matches very well that of the cooling mode. The  $\chi_M T$  values start rising sharply between 5.5 and 50 K. Further heating leads to much more gradual spin transition until the sample is heated up to 300 K. During this cycle the  $\chi_M T$  values change from 1.0 to 2.3 cm<sup>3</sup> K mol<sup>-1</sup>. Another sharp transition appeared between 300 and 317 K, at which the  $\chi_M T$ values change from 2.3 to 2.8 cm<sup>3</sup> K mol<sup>-1</sup>. A hysteresis loop of around 15 K width has been observed in the temperature region between 270 and 300 K.

The magnetic characteristics of 4 were measured in the temperature sequence of  $200 \rightarrow 350 \rightarrow 6 \rightarrow 350$  K, as shown in Figure 4 (d). During the first heating step from 200 to 350 K, this iron(II) complex shows an extremely sharp spin-state change from the low-spin to the high-spin state. The  $\chi_M T$  values change from 0.15 to 2.9 cm<sup>3</sup> K mol<sup>-1</sup> within a relatively narrow temperature range of 290 to 350 K. Dur-

ing the subsequent cooling and heating processes, the  $\chi_M T$  versus T curve is much more gradual relative to the first heating process. As the temperature is lowered from 350 to 300 K,  $\chi_M T$  first remains constant and then decreases more strongly between 330 and 300 K; the  $\chi_M T$  values decrease from 2.4 to 1.7 cm<sup>3</sup> K mol<sup>-1</sup>. With a further decrease in temperature down to 6 K, the  $\chi_M T$  values decrease to 0.84 cm<sup>3</sup> K mol<sup>-1</sup>, thereby revealing an incomplete HS  $\rightarrow$  LS conversion. The drop of  $\chi_M T$  at temperatures below 50 K is again most likely due to the occurrence of zero-field splitting of the remaining HS iron(II) ions. There was no obvious difference in the  $\chi_M T$  values between the cooling and heating curves and hysteresis was not observed.

Figure 4 (e) shows the thermal dependence of the  $\chi_M T$  values of the iron(II) complex 5. The magnetic properties were measured in the temperature regime between 400 and 4 K following the sequence of  $330 \rightarrow 4 \rightarrow 400$  K. At room temperature, the  $\chi_M T$  value is  $2.5 \text{ cm}^3 \text{ K mol}^{-1}$ , which points to the presence of a small fraction of low-spin molecules. Cooling the sample leads to a gradual  $\chi_M T$  curve with values of  $1.5 \text{ cm}^3 \text{ K mol}^{-1}$  at 50 K and 0.44 cm<sup>3</sup> K mol<sup>-1</sup> at 4 K. The  $\chi_M T$  versus *T* response is completely reversible. During these measurements we did not find any plateau despite heating the sample up to 400 K. The  $\chi_M T$  value at 400 K was around 2.7 cm<sup>3</sup> K mol<sup>-1</sup>.

From all these measurements of the dendritic triazole complexes under study, it is quite clear that the magnetic behaviour depends on various factors such as the nature of the counteranions, the structure of the dendrons attached to the triazoles and the type of the spacer between the triazole nitrogen and the dendron (NH–C=O and  $CH_2$  spacing).

# <sup>57</sup>Fe Mössbauer Spectroscopy Study of the Dendritic Triazole Iron(II) Complexes

The measured Mössbauer spectra of all dendritic triazole iron(II) complexes under study are shown in Figure 5. The corresponding hyperfine parameters obtained from leastsquares fitting to Lorentzians are collected in Table 1.

A representative Mössbauer spectrum of complex 1 recorded at 80 K is shown in Figure 5 (a). The spectrum shows two quadruple doublets. The best fits could be obtained with isomer shift  $\delta = 0.55 \text{ mm s}^{-1}$  and quadrupole splitting  $\Delta E_{\rm O} = 0.28$  mm s<sup>-1</sup> for the inner doublet, which is typical for iron(II) in the low-spin state, whereas the parameter values  $\delta = 1.17 \text{ mm s}^{-1}$  and  $\Delta E_{\rm Q} = 3.35 \text{ mm s}^{-1}$  for the doublet that consists of the outer two lines that are assigned to the high-spin state of the iron(II) site. The large quadrupole splitting mainly arises from a noncubic valence electron contribution to the electric field gradient and calls for a compressed octahedral coordination sphere around iron(II) sites. The area ratio  $A_{\rm HS}/A_{\rm HS+LS}$  ( $A_{\rm HS}$  = area of the HS doublet;  $A_{\text{HS+LS}}$  = total area of the HS and LS doublets) shows that still 70% of HS exists in the sample at 80 K. The estimation is based on the assumption that the Lamb-Mössbauer factors for HS and LS states are similar.

The Mössbauer spectrum of complex **2** recorded at 80 K is displayed in Figure 5 (b). The fitted parameters are  $\delta = 0.54 \text{ mm s}^{-1}$  and  $\Delta E_Q = 0.31 \text{ mm s}^{-1}$  with reference to the low-spin state and  $\delta = 1.16 \text{ mm s}^{-1}$  and  $\Delta E_Q = 3.42 \text{ mm s}^{-1}$  for the high-spin state of the iron(II) sites. These parameter values are typical for LS and HS iron(II) sites in Fe<sup>II</sup>N<sub>6</sub> core complexes. The area fraction of about 35% of HS in the sample of **2** at 80 K is much lower than that of **1** at the same temperature. This can be explained by the hydrogenbonding interaction being more dominant in compound **2** than in **1**, which plays a crucial role in stabilizing the LS state.<sup>[29]</sup> A structural proof was given by single-crystal X-ray diffraction on a trinuclear triazole iron(II) SCO compound.<sup>[30]</sup>

The Mössbauer spectra of **3** (fresh sample) were recorded at 80 and 4 K, respectively, and the fitted spectra are shown in Figure 5 (c). The parameters obtained from the fitting procedure of the 80 K spectrum are  $\delta = 0.49 \text{ mm s}^{-1}$  and  $\Delta E_Q = 0.21 \text{ mm s}^{-1}$  for the LS state and  $\delta = 1.19 \text{ mm s}^{-1}$  and  $\Delta E_Q = 3.30 \text{ mm s}^{-1}$  for the HS state of iron(II). The area fraction  $A_{\text{HS}}/A_{\text{HS+LS}}$  comes out to be  $\gamma = 0.36$  at 80 K and only slightly lower with  $\gamma = 0.29$  at 4 K.

The Mössbauer spectra of 4 (fresh sample) were also recorded at 80 and 4 K, as shown in Figure 5 (d). At 80 K the spectrum shows a major doublet (with area fraction of 94%) with an isomer shift of 0.47 mm s<sup>-1</sup> and a quadrupole splitting of 0.21 mm s<sup>-1</sup>, which is assigned to the iron(II) LS sites. The minor contribution of 6% with isomer shift of 1.16 mm s<sup>-1</sup> and a large quadrupole splitting of 3.50 mm s<sup>-1</sup> refers to high-spin iron(II) sites. Corresponding to the SQUID data, the value of  $0.15 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$  (at 200 K) of a fresh sample at low temperature probably arises from a small fraction of HS sites located at hydrated chain-end positions.<sup>[22,31]</sup> Therefore, the average degree of polymerization  $(D_{\rm p})$  can be estimated to be about 37 using the equation  $D_{\rm p}$ =  $2\chi T_{\rm HS}/\chi T_{\rm LS}$ .<sup>[27]</sup> However, with Mössbauer spectroscopy data it is possible to calculate  $D_{\rm p}$  at very low temperatures, at which the zero-field splitting prevails in many instances and vitiates the determination of the magnetic susceptibilities that originate from the spin transition. It turned out that the 6% of iron(II) in the HS state determined by Mössbauer spectroscopy at 80 K had converted totally (to less than two percent, which is approximately the detection limit of Mössbauer spectroscopy) into low spin upon further cooling; the spectrum recorded at 4 K contains no more resonances of Fe<sup>II</sup> in the HS state. By taking an error limit of maximum 2% in the high-spin signal into account, we can estimate that the average chain length would contain about one hundred iron(II) centres.

An estimate of  $D_p$  was possible only for complex 4, because it was the only one among the five compounds under study that showed an extended plateau in the  $\chi_M T$  versus Tplot of the low-spin phase. For the other complexes, it cannot be decided whether the residual high-spin species in the low-temperature region arise mainly from iron(II) complexes at the end of the iron-triazole chains or whether other influences are operative such as various kinds of defects in the crystal lattice that are responsible for the incomplete spin transition.



Figure 5.  $5^{7}$ Fe Mössbauer spectra of the iron(II) dendritic complexes (a) 1, (b) 2, (c) 3, (d) 4 and (d) 5 at the temperatures indicated in the figures.

Table 1. <sup>57</sup>Fe Mössbauer spectrum parameters for all the iron(II) complexes under study.

Complexes		Low-spin state			High-spin state			
-	Т [K]	$\delta$ [mm s <sup>-1</sup> ]	$\Delta E_{ m Q}^{ m LS}$ [mm s <sup>-1</sup> ]	$\Gamma/2$ [mm s <sup>-1</sup> ]	$\delta$ [mm/s]	$\Delta E_{ m Q}^{ m HS}$ [mm s <sup>-1</sup> ]	$\Gamma/2$ [mm s <sup>-1</sup> ]	$A_{\mathrm{HS}}/A_{\mathrm{HS+LS}}$ [%]
$[Fe(G1-BOC)_3](triflate)_2 \cdot xH_2O(1)$	80	0.55	0.28	0.14	1.17	3.35	0.18	70
$[Fe(G1-BOC)_3](tosylate)_2 \cdot xH_2O(2)$	80	0.54	0.31	0.14	1.16	3.42	0.17	35
$[Fe(G1-DPBE)_3](triflate)_2 \cdot xH_2O(3)$	80	0.49	0.21	0.15	1.19	3.30	0.21	36
$[Fe(G1-DPBE)_3](triflate)_2 \cdot xH_2O(3)$	4	0.49	0.21	0.17	1.17	3.26	0.24	29
$[Fe(G1-DPBE)_3](tosylate)_2 \cdot xH_2O(4)$	80	0.47	0.21	0.13	1.16	3.50	0.16	6
$[Fe(G1-DPBE)_3](tosylate)_2 \cdot xH_2O(4)$	4	0.48	0.21	0.15	_	_	_	0
$[Fe(G1-DPBE)_3](BF_4)_2 \cdot xH_2O$ (5)	80	0.53	0.31	0.15	1.19	3.35	0.19	49

A sample of complex 5 showed nearly half of low-spin and high-spin states at 80 K as can be distinguished from Figure 5 (e). The parameters for the complex molecules in the LS state are  $\delta = 0.53 \text{ mm s}^{-1}$  and  $\Delta E_Q = 0.31 \text{ mm s}^{-1}$ , whereas for those in the HS state these values are  $\delta =$  1.19 mm s<sup>-1</sup> and  $\Delta E_Q = 3.35$  mm s<sup>-1</sup>. It is worth noting that the relatively large quadrupole splitting of 3.35 mm s<sup>-1</sup> for HS-Fe<sup>II</sup> sites, which seems to arise mainly from a noncubic distribution of valence electrons around the iron(II) centres, points to a relatively high symmetry (close to  $O_h$ ) of the



 $\text{FeN}_6$  chromophore despite the bulkiness of the dendritic ligands. There appears to be little perturbation of the  $\text{FeN}_6$  cores that leads to a rather small lattice contribution to the electric field gradient, which usually opposes the valence electron contribution.

#### Thermal Properties of the Dendritic Triazole Iron(II) Complexes

The TGA and DSC curves of the iron(II) complexes 1 to 5 are presented in Figures 6 and 7, respectively. The TGA

curves of 1 and 2 show similar weight-loss profiles (see Figure 6, a and b). Both complex compounds started to show weight loss at around 50 °C and had weight loss of about 5 and 6% when the temperature reached around 100 °C. The weight can be attributed to the loss of about five and six molecules of water from the iron(II) complexes 1 and 2. In each complex there are two regions of sharp weight loss above 150 °C, which can be attributed to the decomposition of the alkyl chain of the complexes. During water release, the DSC curves show strong endothermic peaks around 70 °C. Both signals



Figure 6. TGA data of the iron(II) dendritic complexes (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5.



Figure 7. DSC data of the iron(II) dendritic complexes (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5.

are of rather complicated shape, which points to the occurrence of a combination of water release and structural rearrangement. The latter peak around 150 °C might be due to decomposition of the compound. After the first heating process, there were no endothermic or exothermic peaks detected in the range between 50 and 250 °C. Only a small change in the slope of the curve can be recognized around 150° for compound **1** and at about 170 °C for compound **2**, which probably indicates small structural changes due to alkyl-chain-length reduction. The calculation of the enthalpy and entropy of the heating and cooling processes was not possible due to the overlap of the signals in the calorimetric data.

The results obtained from the thermal analysis are in agreement with the interpretation of the magnetic properties. Water loss detected by TGA indicates a drastic change of spin state in the magnetic response function  $\chi_M T$  versus T, which is irreversible due to the loss of noncoordinated water. The complex signals around 70 °C observed by DSC further confirm the irreversible nature due to structural rearrangement of the fresh sample into a thermodynamically more stable configuration. Therefore, the thermally induced release of noncoordinated water molecules alters markedly the magnetic behaviour of these complex compounds.

In the first heating branch of complex 3, there were two sharp endothermic peaks in the DSC curve observed at 40 and 50 °C (Figure 7, c). These changes are in accordance with the sharp increases in the  $\chi_{M}T$  versus T curve in the same temperature region. After the first warming, the  $\chi_{\rm M}T$ versus T curve is irreversible because of loss of crystal water. This complex shows about 1.3% loss of weight before decomposition of the sample starts above 250 °C, as seen in the TGA curve (Figure 6, c). The declining mass of the iron(II) complex assigns a loss of about 2.7 molecules of water. During the second cycle of DSC, the calorimetric feature showed much weaker endothermic and exothermic peaks. The different temperature peak maxima in the second cycle of DSC can be attributed to the observed small hysteresis in the  $\chi_{\rm M}T$  curves. In this case, it seems that the change of spin state is a direct consequence of the release of water and would probably not occur without it. Therefore, the increasing  $\chi_{\rm M}T$  values are not an indication of thermal spin transition, but moreover an irreversible change of spin state.

In the case of 4, the effect of loss of water on the spin state is even more pronounced relative to the other complexes. The TGA data (Figure 6, d) signal the loss of water around 60 °C, which amounts to 1.6 molecules of water per formula unit. As an immediate consequence, this complex shows abrupt and irreversible change of spin state from low spin to high spin at about 60 °C. The DSC data did not show any noticeable change, which is most likely due to the fact that an extra dried sample was used particularly for this DSC analysis. After the synthesis of this complex, the sample was dried under high vacuum for a long time. The TGA curve of 5 is shown in Figure 6 (e). The gradual weight loss of the complex is due to evaporation of the solvent from the complex. The weight loss between 200 and 250 °C is related to the decomposition of the compound. The water content of the fresh complex is less than 1%, which corresponds to the loss of less than one molecule of water per formula unit. A rapid loss in weight due to decomposition of the complex was observed in the temperature range of 250-380 °C. The DSC curve of 5 showed moderate and broad ( $\Delta T$  of around 50 °C) exothermic and endothermic peaks at about -30 °C during heating and cooling cycles. These peaks not only arise from a  $HS \rightarrow LS$ transition but also presumably from structural rearrangements.[32]

From all these observations it is clear that in each series of complexes, the abruptness of spin-state changes is more pronounced in the freshly prepared tosylate-based iron(II) complexes than in the triflate compounds. The only exception is 5, which showed a gradual change of spin state. This is most likely due to the absence or little content of noncoordinated water in this complex. Kahn et al. previously reported this kind of gradual change of spin state as a function of temperature, which they suggested to arise from a combination of thermal spin-state change and dehydration process.<sup>[23]</sup> The dehydrated complex is stable under normal conditions, and the sharp spin-state change is not reversible after the heating process. The influence of noncoordinated water on the spin state is much more pronounced in the G1-DPBE derivatives in which the difference in the magnetic behaviour between a fresh sample and a heated one is more evident than in the others. For example, the freshly prepared sample of 4 was diamagnetic at the beginning and became paramagnetic after heating. Thus the observed spin-state change that occurred above room temperature was driven by the release of the noncoordinated water molecules upon heating, and this procedure is not reversible. The dehydrated forms of the iron(II) complexes do no show abrupt spin-state changes around room temperature but rather a gradual and reversible thermal spin crossover below room temperature. This can be understood as a consequence of changes of lattice parameters due to loss of water. In this compound the loss of water is particularly small, whereas the changes of the two-dimensional hexagonal lattice parameters a are remarkably strong, which supports the aforementioned explanation. It is conceivable that the structure of a thermally cycled sample has a different hydrogenbonding network than a sample before thermal treatment. For the complex 4, the lattice parameter a is bigger for the LS state, which is consistent with similar compounds reported in the literature.<sup>[33]</sup> Complex 5 shows a significant loss of water below 350 K; it is therefore difficult to correlate the lattice parameter a with the spin-state change.

According to the results of the TGA measurements, the content of noncoordinated water molecules per formula unit is different in all the complex compounds under study and amounts to x = 5 in 1, x = 6 in 2, x = 2.7 in 3, x = 1.6 in 4 and x = 1 in 5. As these numbers are only approximate estimates, which most likely vary from one preparation to another of one and the same compound, we have preferred not to articulate the water content in the chemical formulae of the five systems under study. The common feature in all cases, however, is the more or les dramatic change of spin state on losing water by warming the substance.

Fujigaya et al. published<sup>[22]</sup> a report on (Gn-trz)Fe-based (n = 0-2) dendritic triazole complexes that showed spintransition dependence on the generation number (n) of the dendritic unit. They observed a similar behaviour for their (G1-trz)Fe complexes with a most abrupt spin transition. We also selected the same triazole dendritic ligands for making iron(II) complexes with different counteranions and tried to correlate the influence of various anions on the spin-transition behaviour. From the behaviour of the  $\chi_{\rm M}T$ versus T function, it is clear that noncoordinated water molecules play a crucial role. Attention should be drawn to the possibility that the ligand influences strongly depend on how the noncoordinated water interacts with the ligands through hydrogen bonding. It is known that if water is hydrogen-bonded to the ligand through N-H···OH<sub>2</sub> interaction close to the coordinating triazole ring of the ligand, the complex tends to stabilize in the LS state; if the hydrogen bonding occurs in the mode N···H<sub>2</sub>O, the HS state is favoured.<sup>[29]</sup> Comparing the magnetic properties of [Fe(G1-DPBE)<sub>3</sub>](A)<sub>2</sub>·xH<sub>2</sub>O (A = triflate and tosylate) and the complexes  $[Fe(G1-BOC)_3](A)_2 \cdot xH_2O$  (A = triflate and tosylate), the NH groups indeed exist in both structures (G1-BOC and G1-DPBE complexes), whereas the earlier studied G1-PBE derivatives do not have such NH groups. The influence of water in both derivatives  $\{[Fe(G1-DPBE)_3](A)_2 \cdot xH_2O\}$ (A = triflate and tosylate) and  $[Fe(G1-BOC)_3](A)_2 \cdot xH_2O$  (A = triflate and tosylate)} seems to be much more predominant than in the earlier studied G1-PBE derivatives because of the formation of N-H···OH<sub>2</sub> hydrogen-bonding interaction that involves the noncoordinated water molecules. Furthermore, G1-BOC-based dendritic triazole has three -NH groups in the structure, among which only one is connected to the triazole ring. In this case, the -NH group connected to the triazole ring in G1-BOC-based iron(II) complexes is less suited to the formation of N-H···OH<sub>2</sub> hydrogen bonding than the -NH group in G1-DPBE. As a result, G1-DPBE derivatives show much more abrupt spin transition in the first warming procedure. On the contrary, the magnetic properties of G1-PBE derivatives show almost no difference between the fresh sample and the heated one.

### Conclusion

We have synthesized first-generation dendritic triazolebased ligands and their iron(II) complexes with different counteranions. Their thermal, magnetic and spin-transition properties were studied in detail using various characterization techniques. All complexes showed spin-transition behaviour that is dependent on the coordinated water molecules present in the iron(II) complex. Spin-state conversion was triggered by thermally induced water release and a gradual spin transition took place after a first heat treatment to 350 K. The  $[Fe(G1-DPBE)_3](BF_4)_2 \cdot xH_2O$  (5) iron(II) complex shows exceptional behaviour due to lack or little content of crystal water in the initial sample. Therefore, this particular iron(II) complex did not show any change in the spin-state change behaviour between initial and first heating cycle, whereas complexes 1 to 4 clearly show noticeable changes in magnetic behaviour upon heating. The influence of noncoordinated water is more predominant in iron(II) complexes with tosylate than with triflate anions. Similar effects are also observed for G1-DPBE-based iron(II) complexes than G1-BOC-based derivatives. The nature of the counteranions and the type of dendritic ligands play an important role for the magnetic behaviour as reflected by the  $\chi_M T$  versus T curve and by variable-temperature Mössbauer spectroscopy.

## **Experimental Section**

Materials and Characterization: Commercially available chemicals were reagent grade and used without further purification. The synthesis of dendritic ligands were published by Fujigaya et al.<sup>[22]</sup> and Sonar et al.<sup>[21]</sup> <sup>1</sup>H (300 MHz) and <sup>13</sup>C (62.5 MHz) NMR spectroscopy was carried out on a Bruker spectrometer at room temperature. Elemental analysis (C, H, N and S Analyzer) and mass spectrometry (Ionspec Ultrima spectrometer) techniques were utilized for the confirmation and purity of the samples. 1H-1,2,4-triazole-1-propanenitrile was synthesized from 1H-1,2,4-triazole and acrylonitrile as described in the literature.<sup>[31]</sup> Infrared spectra were recorded by using a Brooker Tensor 27 with samples prepared as pellets in KBr. DSC measurements were performed on Perkin-Elmer, Norwalk, Connecticut, whereas TGA analyses were carried out on TA Instruments, New Castle, Delaware. The elemental analyses of all complexes were performed on a Vario EL (Elemental) for C, H, N and S determination. For structural investigations powder X-ray diffraction were recorded at 300, 250 K and then again at 300, 350 and 300 K, with Cu- $K_{\alpha}$  radiation using a PANalytical X'Pert PRO diffractometer equipped with the Paar HTK 1200. The temperature-dependent magnetic susceptibilities were measured on a MPMS SQUID device of Quantum Design. The magnetic data were corrected for magnetization of the sample holder and diamagnetic contributions. 57Fe Mössbauer spectroscopy was carried out at 80 K using a constant-acceleration conventional spectrometer with a nitrogen cryostat. The source used was <sup>57</sup>Co in a Rh matrix with an activity of about 10 mCi kept at room temperature. For measurements at 4 K the samples were immersed in helium gas in a helium cryostat. In this case the used source was <sup>57</sup>Co in a Rh matrix with an activity of about 5 mCi kept at 4 K. It was impossible to record Mössbauer spectra at room temperature within acceptable measuring time because of the softness of the material with too low Debye temperatures. The isomer shift values are given with reference to  $\alpha$ -iron.

#### Synthesis of Ligands and Complexes

Synthesis of G1-BOC (A): Triethylamine (1 mL, 6.88 mmol), 4amino-1,2,4-triazole (0.89 g, 10.6 mmol) and diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate (DBOP) (2.63 g, 6.87 mmol) were added to a solution of A' (3.00 g, 6.88 mmol) in 150 mL of THF at room temperature. The mixture was heated at reflux overnight and allowed to cool to room temperature. The organic solvent was evaporated and the crude compound purified by column chromatography using hexane/ethyl acetate mixture as eluent (gradient from 100:0 to 90:10). The fraction was collected and the solvents evaporated to dryness to give compound 5 as white powder (yield: 72%, 2.50 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.56 (s, 2 H, Trz), 7.61 (s, 2 H, Ph), 7.33 (s, 1 H, Ph), 4.70 (s, 3 H, NH), 3.09 (t, 4 H, 2CH<sub>2</sub>), 2.73 (t, 4 H, 2CH<sub>2</sub>), 1.86 (t, 2 H, 2CH), 1.32 (s, 18 H,  $6CH_3$ ) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 168.14, 157.92, 143.65, 134.45,$ 131.31, 126.14, 79.72, 48.90, 40.35, 33.35, 31.96, 30.82, 28.69, 24.07 ppm. MALDI-TOF calcd. for  $C_{25}H_{38}N_6O_5$ : [M + H]<sup>+</sup> 502.62; found 502. C25H38N6O5 (502.61): calcd. C 59.74, H 7.62, N 16.72; found C 59.14, H 7.09, N 16.28.

Synthesis of [Fe(G1-BOC)<sub>3</sub>](triflate)<sub>2</sub>·xH<sub>2</sub>O (1): A solution of Fe(triflate)<sub>2</sub>·6H<sub>2</sub>O (0.13 mmol, 0.062 g) and ascorbic acid [0.014 g; to prevent iron(II) from oxidation] in methanol (1 mL) were added dropwise to a solution of G1-BOC (0.4 mmol, 0.2012 g) in methanol (2 mL) at 60 °C while stirring. The reaction mixture was stirred for one hour at 60 °C and then was cooled down to room temperature. The solvent was removed under reduced pressure, and the colourless colloidal substance precipitated on cooling with liquid nitrogen. The product was fast-washed with cold MeOH and THF and dried in vacuo; yield 93%. C<sub>77</sub>H<sub>114</sub>F<sub>6</sub>FeN<sub>18</sub>O<sub>21</sub>S<sub>2</sub> (1861.81): calcd. C 49.63, H 6.12, N 13.53, S 3.44; found C 47.15, H 5.93, N 12.10, S 4.14. IR (KBr pellets):  $\tilde{v} = 2978.6$  (m, CH<sub>3</sub>), 2936.0 (–CH<sub>2</sub>–), 758.8, 715.2, 640.1 (m, substituted Ar), 3365.8, 1690.2 (s, –CONH–), 1029.8 (s, CF<sub>3</sub>), 1277.9, 1251.5 (m, R–SO<sub>3</sub><sup>-</sup>), 1524.5, 1455.1, 1394.2, 1367.4, 1168.8 (triazole) cm<sup>-1</sup>.

**Synthesis of [Fe(G1-BOC)<sub>3</sub>](tosylate)<sub>2</sub>·xH\_2O (2): A similar procedure as described above was employed to obtain the complex 2**, except for the quantity of the Fe(tosylate)<sub>2</sub>· $6H_2O$  salt (0.068 g, 0.13 mmol); yield 96%. C<sub>89</sub>H<sub>128</sub>FeN<sub>18</sub>O<sub>21</sub>S<sub>2</sub> (1906.07): calcd. C 56.03, H 6.72, N 13.22, S 3.36; found C 54.66, H 6.96, N 11.31, S 3.33. IR (KBr pellets):  $\tilde{v} = 2977.4$  (m, CH<sub>3</sub>) 2932.6 (-CH<sub>2</sub>) 684.0, 625.1 (m, substituted Ar) 3358.0, 1692.5 (s, -CONH-) 1275.1, 1251.5 (m, R-SO<sub>3</sub><sup>-</sup>), 1523.7, 1453.6, 1392.7, 1366.2, 1170.7 (triazole) cm<sup>-1</sup>.

Synthesis of [Fe(G1-DPBE)<sub>3</sub>](triflate)<sub>2</sub>·xH<sub>2</sub>O (3): A methanol solution of Fe(triflate)<sub>2</sub>·6H<sub>2</sub>O (0.0310 g, 0.067 mmol) that contained a small amount of ascorbic acid was added dropwise to a solution of G1-DPBE (0.227 g, 0.2 mmol) in 20 mL of THF at 70 °C. The reaction mixture was stirred at this temperature for about 30 min, then cooled down to room temperature. The solvent was partially removed under reduced pressure until the solution was separated into two layers. The pink gelatine-form product was cooled with liquid nitrogen, washed with cold methanol and was dried under vacuum; yield 89%. C<sub>215</sub>H<sub>348</sub>F<sub>6</sub>FeN<sub>12</sub>O<sub>27</sub>S<sub>2</sub> (3767.13): calcd. C 68.49, H 9.24, N 4.46, S 1.70; found C 69.13, H 10.27, N 4.40, S 2.39. IR (KBr pellets):  $\tilde{v} = 1606.2$ , 1594.8 (s, Ar), 2921.3, 2853.6 (-CH<sub>2</sub>-), 813.4, 720.8, 681.3, 639.9 (m, substituted Ar), 1074.0 (s,



Synthesis of [Fe(G1-DPBE)<sub>3</sub>](tosylate)<sub>2</sub>·xH<sub>2</sub>O (4): A similar procedure was employed to prepare 4 using Fe(tosylate)<sub>2</sub>·6H<sub>2</sub>O (0.0338 g, 0.067 mmol) and G1-DPBE (0.2271 g, 0.2 mmol); yield 93%. C<sub>227</sub>H<sub>362</sub>FeN<sub>12</sub>O<sub>27</sub>S<sub>2</sub> (3811.39): calcd. C 71.47, H 9.50, N 4.41, S 1.68; found C 71.31, H 9.51, N 4.30, S 1.79. IR (KBr pellets):  $\tilde{v} = 1599.3$  (s, Ar), 2923.5, 2853.3 (-CH<sub>2</sub>-), 683.7 (m, substituted Ar), 1054.6 (m, C–O) 1696.4 (s, -CONH–), 1217.3 (m, R–SO<sub>3</sub><sup>-</sup>), 1466.0, 1378.5, 1348.9, 1326.2, 1164.5 (triazole) cm<sup>-1</sup>.

Synthesis of [Fe(G1-DPBE)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O (5): The same procedure as for 4 was employed to prepare 5 using Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0231 g, 0.067 mmol) and G1-DPBE (0.2252 g, 0.2 mmol), and was dried under vacuum; yield 90%.  $C_{223}H_{348}B_2F_8FeN_{12}O_{21}$  (3762.72): calcd. C 70.23, H 9.62, N 4.61; found C 70.28, H 9.50, N 4.41.

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