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Slow magnetization dynamics in a six-coordinate Fe(II)-radical complex[†]

Carolyn A. Michalowicz,^a Michelle B. Mills,^a Ellen Song,^a Dmitriy V. Soldatov,^a Paul D. Boyle,^b Mathieu Rouzières, c,d Rodolphe Clérac, c,d and Kathryn E. Preuss*a

A new paramagnetic ligand, betaDTDA, and its coordination complex with Fe(hfac)₂ are reported (betaDTDA = 4-(benzothiazol-2'-yl)-1,2,3,5-dithiadiazolyl; hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-). The neutral radical betaDTDA is the first dithiadiazolyl ligand designed to include an electropositive sulphur moiety outside the thiazyl heterocycle, increasing the capacity for supramolecular, structure-directing electrostatic contacts and enabling new pathways for magnetic exchange. The Fe(hfac);(betaDTDA) complex is comprised of a hs-Fe(II) center with the three bidentate ligands arranged about the ion in a distorted octahedral 6-coordinate environment. The magnetic properties of crystalline Fe(hfac)₂(betaDTDA) are consistent with strong antiferromagnetic (AF) coupling between the metal and ligand moments, giving rise to a well-defined S_{total} = 3/2 ground state that is the only thermally populated state below 40 K. Below 4 K, this complex exhibits slow relaxation of the magnetization detected by ac susceptibility measurements consistent with a singlemolecule magnet (SMM) behaviour.

Introduction

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The design of molecule-based materials with technologically relevant properties, especially magnetic properties, has attracted a great deal of interest in recent decades. The potential for novel functionalities or novel combinations of functionalities, accessible using well-established synthetic protocols, make molecule-based designs particularly appealing. The flexibility of design in molecule-based materials also allows for incorporation of other attractive qualities, such as solubility in organic media and volatility at low temperature.

An important class of molecule-based magnetic material that is currently receiving significant attention is the singlemolecule magnet (SMM). SMMs exhibit slow dynamics of their magnetization induced by different types of relaxation mechanisms such as quantum tunnelling (QTM), Orbach-type (thermally activated), Raman or direct processes. This property makes them potential candidates for applications in quantum computing and spintronic devices.¹ The first materials identified as SMMs were polynuclear complexes of transition metal ions.² Current work more focussed on mononuclear SMMs of felements is yielding some of the most exciting advancements for example with Orbach-like processes with extremely large energy barriers.³ Now, with a more fully developed understand-

^{a.} Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1,



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Figure 1. Line drawing and ORTEP representation of an excerpt of the crystal structure

depicting Fe(hfac), (betaDTDA); thermal ellipsoids at 50%; colour code: H, white sphere and C, black; N, blue; S, orange; O, red; F, green; Fe, brown ellipsoids.

ding of SMM structure/property relationships, mononuclear 3d transition metal complexes are also being targeted and have shown to exhibit SMM behaviour.⁴ However, been mononuclear transition metal SMMs are significantly less widely reported than other systems.

In general, the design of molecule-based materials requires rational manipulation of the molecular structure to optimize material properties (e.g., magnetic, electric, or mechanical properties). One approach to the design of new materials with interesting magnetic properties is to develop paramagnetic ligands for coordination to metal centres. Coordinating radical ligands to metal ions can result in strong magnetic exchange between the metal- and the ligand-based moments,⁵ potentially increasing the net magnetic moment, providing an effective pathway for coupling between multiple coordinated metal centres, or engendering controllable intramolecular redox processes. In 3d transition metal complexes, exchange coupling with coordinated radical ligands tends to be strong and

Canada. Email: kpreuss@uoguelph.ca

^{b.} Department of Chemistry, Western University, London, Ontario N6A 3K7, Canada. ^{c.} CNRS, CRPP, UMR 5031, F-33600 Pessac, France.

^{d.} Univ. Bordeaux, CRPP, UMR 5031, F-33600 Pessac, France.

⁺ Electronic Supplementary Information (ESI) available: synthetic details for the preparation of 2-cyanobenzothiazole; crystallographic details and tables; additional figures and magnetic measurement details. See DOI: 10.1039/x0xx00000x

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the nature of the exchange coupling is readily predicted using a simple orbital overlap approach. $^{\rm 6}$

Paramagnetic ligands have been developed from a variety of heterocyclic organic radicals.^{7,8} We find the 1,2,3,5dithiadiazolyl (DTDA) radical particularly appealing because paramagnetic DTDA-based ligands are able to participate in numerous intermolecular interactions as a result of their molecular and electronic structure. DTDAs often participate in pancake bonding9 through overlap of their singly occupied molecular orbitals (SOMOs). Manipulation of pancake bonding as a supramolecular synthon has led to interesting SMM behaviour¹⁰ and magnetic switchability¹¹ in solid state metal complexes of DTDA ligands. Design of DTDA ligands with Rgroups that can participate in other types of intermolecular interactions has led to supramolecular pairs with a high spin ground state,¹² magnetic ordering,^{13,14} and isomerization in the solid state.¹⁵ Directional electrostatic interactions, such as sigma hole bonds,¹⁶ enable crystal engineering that influences the magnetic properties of metal-radical complexes by creating new intermolecular exchange pathways.^{12,13} We have developed a number of thiazyl radical ligands with electronegative substituents on the R-group, but have not until recently pursued the effect of incorporating regions of partial positive charge density into the DTDA R-group.

Herein, we report a new DTDA radical ligand, 4-(benzothiazol-2'-yl)-1,2,3,5-dithiadiazolyl (**betaDTDA**), and its coordination complex with the Fe(hfac)₂ fragment (Figure 1). Magnetic measurements of Fe(hfac)₂(**betaDTDA**) indicate strong antiferromagnetic (AF) coupling between the metal- and the ligand-based magnetic moments. This complex also exhibits slow relaxation of magnetization below 4 K in agreement with SMM properties.

Results and Discussion

Synthesis

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BetaDTDA is prepared from the corresponding 2benzothiazolecarbonitrile, betaCN, following a modification of well-established general procedures,^{17,18} and is isolated by sublimation, yielding X-ray quality crystalline material. BetaCN is not commercially available, but is readily prepared from 2aminothiophenol using standard organic synthetic protocols (Scheme S1).† In the first step, ethyl 2benzothiazolecarboxylate is produced by refluxing 2aminothiophenol with diethyl oxalate.¹⁹ The corresponding amide is afforded by reaction of the ethyl carboxylate with aqueous ammonia.²⁰ Conversion of the amide to **betaCN** is then achieved by dehydration using POCl₃.²¹ Isolation of white, crystalline betaCN in high yield is achieved by sublimation of the crude product (10⁻² Torr, 60 °C).

Fe(hfac)₂(betaDTDA) is prepared by stoichiometric reaction of betaDTDA with Fe(hfac)₂(THF)₂.²² Sublimation of the crude product under vacuum (10⁻⁵ Torr, 120 °C) yields pure, crystalline material, suitable for bulk analysis (magnetometry, elemental



Figure 2. Excerpts from the crystal structure of **Fe(hfac)₂(betaDTDA)** illustrating the π -stacking of the betaDTDA ligands and supramolecular S \odot O contacts, viewed from two different positions; for clarity, only O atoms of hfac ligands are shown; colour code: H, white; C, grey; N, blue; S, yellow; O, red; F, green; Fe, dark red.

analysis). Slow re-sublimation of the isolated product under static vacuum (10^{-1} Torr, 115 °C) yields crystals suitable for analysis by single crystal X-ray diffraction.

Crystal Structures

A dark brown prismatic crystal of betaDTDA, grown by sublimation under static vacuum (10⁻¹ Torr, 120 °C), was selected for single crystal X-ray analysis. Diffraction data were collected at 150 K. BetaDTDA crystallizes in $P2_1/c$ with two molecules in the asymmetric unit (Figure S1; Table S1).⁺ The two molecules form a pancake-bonded (betaDTDA)₂ dimer, with a cis-cofacial arrangement of the thiazyl rings, which is common for DTDA radicals in the solid state.²³ Bond lengths and angles of the thiazyl rings, and distances between the pancakebonded pair (Table S2), + are comparable to those observed for other pancake-bonded DTDA radicals. Close $S^{\delta+} \cdots N^{\delta-}$ contacts between thiazyl S and N atoms of the pancake-bonded (betaDTDA)₂ pairs define arrays of molecules along [001] (Figure S1; Table S2).[†] Further S^{δ+}…N^{δ−}, S…S, and S…C contacts, involving the thiazyl and benzothiazole sulphur atoms, are present in multiple directions. The incorporation of a benzothiazole sulphur atom clearly contributes to the formation of a dense 3-dimensional network of contacts.

Red crystals of Fe(hfac)₂(betaDTDA) were grown by slow sublimation under static vacuum (10⁻¹ Torr, 115 °C). The metal complex crystallizes in $P2_1/c$ with one molecule in the asymmetric unit (Figure 1; Table S1).⁺ The slightly distorted octahedral coordination geometry is consistent with a typical 6coordinate hs-Fe(II) centre (Table S3).⁺ Coordinated betaDTDA ligands are not involved in pancake bonding, however multiple other non-covalent contacts are present. Contacts between electropositive benzothiazole sulphur atoms and electronegative hfac oxygen atoms support arrays wherein the nearly planar radical ligands form slipped π -stacks in [001], with a distance of ca. 3.5 Å between ligand planes (Figure 2). Noncovalent S…O contacts have been identified as an important factor in the stability of a wide range of solid state structures,²⁴ and are likely to be a significant structure-directing interaction in Fe(hfac)₂(betaDTDA) as well. Additional close contacts within the slipped π -stacks include those between hfac fluorine atoms and thiazyl sulphur atoms, and between hfac fluorine atoms and



Figure 3. Temperature dependence of the χT product for **Fe(hfac)**₂(**betaDTDA**) (χ is defined as *M*/*H* per mole of complex) at 0.1 T; open circles indicate measured data points; red and green lines represent best fits as described in text. Inset: magnetization as a function of applied field between 1.85 and 8 K. The solid lines correspond to the complete model discussed in the text.

aromatic H atoms. Multiple contacts between π -stacks contribute to a dense 3-dimensional network. Of particular note is a contact between a fluorine atom and both sulphur atoms of a neighbouring thiazyl ring (Figure S2),[†] the geometry of which is similar to that commonly observed between sulphur atoms and electronegative moieties in DTDAs²⁵ and in metal complexes of DTDA radical ligands.²⁶ The geometry of this contact can be rationalized using calculated electrostatic potential surfaces which indicate significant partial positive charge between the two S atoms, in the plane of the σ system.²⁵

Magnetic Properties

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Magnetic susceptibility data collected on a crystalline sample of **betaDTDA** confirm that it is diamagnetic over the measured temperature range (1.85 K – 350 K; Figure S3),[†] consistent with pancake bonding observed in the crystal structure (150 K).

The magnetic susceptibility of a polycrystalline sample of Fe(hfac)₂(betaDTDA) was measured at an applied field of 0.1 T, between 1.85 and 300 K (Figure 3). The χT product at room temperature is 3.22 cm³ K mol⁻¹, close to the expected value for an ideal Curie system comprised of one $S_{rad} = 1/2$ betaDTDA ligand and one $S_{Fe} = 2 hs$ -Fe(II) ion ($C = 3.375 \text{ cm}^3 \text{ K mol}^{-1}$ for g_{iso} = 2), and consistent with the absence of pancake bonding in the Fe(hfac)₂(betaDTDA) crystal structure. Upon cooling, the χT product decreases, indicating dominant antiferromagnetic (AF) coupling interactions between the spins of the hs-Fe(II) metal centre and the radical ligand. The χT product reaches a value of 2.3 cm³ K mol⁻¹ at ~45 K and remains relatively constant upon further cooling, until ~25 K. Below 25 K, the value of χT decreases, reaching a minimum of 1.42 cm³ K mol⁻¹ at 1.85 K. The decrease in χT below 25 K can be attributed to either weak AF interactions between complexes or the hs-Fe(II) magnetic anisotropy or both effects. The field dependence of the magnetization measured at various temperatures between 1.85 and 8 K is shown in Figure 3 (inset). At the highest applied field (7 T), the magnetization is still well below that expected for an $S_{\text{total}} = 3/2$ unit (3 μ_{B}), consistent with significant magnetic aniso-



Figure 4. Temperature (left) and frequency (right) dependence of the real (χ' , top) and imaginary (χ'' , bottom) parts of the ac susceptibility between 10 and 10000 Hz and between 1.85 and 6 K, respectively, for **Fe(hfac)₂(betaDTDA)** in zero dc field. Solid lines are visual guides for the eye.

tropy, which is not uncommon for hs-Fe(II).

Based on the crystal structure, the complex can be viewed magnetically as a hetero-spin pair composed of an $S_{Fe} = 2$ Fe(II) and an $S_{rad} = \frac{1}{2}$ betaDTDA radical. The *intra*molecular exchange interaction can thus be modelled on the basis of an isotropic spin Heisenberg Hamiltonian:

$$\hat{H} = -2J(\vec{S}_{Fe} \cdot \vec{S}_{rad}) + g_{av}\mu_B(\vec{S}_{Fe} + \vec{S}_{rad}) \cdot \vec{H}$$
{Fatila, 2016 #2014

where J is the Fe(II) – radical coupling constant and \vec{S}_i are the spin operators (with $S_{Fe} = 2$ and $S_{rad} = \frac{1}{2}$). The theoretical expression of the magnetic susceptibility can be estimated by applying the van Vleck equation²⁷ in the weak field approximation:

$$\chi_{\rm Fe-rad} = \frac{Ng_{av}^2\mu_B^2 10 + 35e^{\frac{5j}{k_BT}}}{4k_BT} \frac{5j}{2 + 3e^{\frac{5j}{k_BT}}}$$

with the parameters having the usual meanings. In order to fit the data for the χT product below 25 K, inter-complex interaction have been introduced in the frame of the mean-field theory. The following definition of mean-field susceptibility, $\chi_{\rm MF}$, has been used:

$$\chi_{\rm MF} = \frac{\chi_{\rm Fe-rad}}{1 - \frac{2zJ'}{Ng_{av}^2 \mu_B^2} \chi_{\rm Fe-rad}}$$

where $\chi_{\text{Fe-rad}}$ is the susceptibility of the non-interacting complex, *z* is the number of nearest neighbours, and *J'* is the magnetic interaction between two neighbouring complexes.²⁸ A very good fit of the data collected at 0.1 T down to 1.85 K has been achieved, with the following parameters: $g_{av} = 2.2(1)$, J/k_B = -62(2) K and $zJ'/k_B = -0.62(5)$ K. The remarkably large intramolecular interactions stabilize the $S_{\text{total}} = 3/2$ ground state which is separated from the first $S_{\text{total}} = 5/2$ excited state by 315 K, explaining the observed plateau of the χT product between 25 and 45 K. The zJ' term, which is introduced in the

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above model as mean-field intermolecular interactions, is also phenomenologically taking into account the effects of *hs*-Fe(II) magnetic anisotropy. In order to evaluate the role of the magnetic anisotropy on the low temperature magnetic data, the χT vs *T* and *M* vs. *H* data below 45 K have been fitted to a $S_{\text{total}} = 3/2$ macrospin model considering the following Hamiltonian:

 $\hat{H} = DS_{total,z}^2 + g_{av} \mu_B \vec{S}_{total} \cdot \vec{H} \{ \text{Fatila, 2016 #2014} \}$

The χT product and magnetization data are simultaneously well-reproduced²⁹ (solid green line for the χT vs. *T* data) by this approach, leading to $g_{av} = 2.22(5)$ and $D/k_B = +8.9(4)$ K. Even if the value of the *D* parameter needs to be taken with caution as the presence of intermolecular interactions cannot be ruled out, this analysis shows that the magnetic anisotropy of the *hs*-Fe(II) centre is relevant to describe the magnetic ground state of the **Fe(hfac)₂(betaDTDA)** complex. With these preliminary analyses in hand, a more general approach to model the magnetic properties of this complex was considered using the following Hamiltonian:

$$\hat{H} = -2J(\vec{S}_{Fe} \cdot \vec{S}_{rad}) + D_{Fe}S_{Fe,z}^2 + \mu_B(g_{Fe}\vec{S}_{Fe} + g_{rad}\vec{S}_{rad}) \cdot \vec{H}$$
{Fatila, 2016 #2014}

A converging numerical fit of the experimental data is only achieved (solid red line for the χT vs. *T* data and solid lines for the *M* vs. *H* data) when using as initial values the ones obtained in the above simplified models and fixing $g_{rad} = 2.0.^{29}$ The following set of parameters are found, $g_{Fe} = 2.17(5)$, $J/k_B = -$ 61.1(6) K and $D_{Fe}/k_B = +6.3(2)$ K, confirming the values found with the simplified approaches. It is worth mentioning that adding a transverse anisotropy term ($E_{Fe}(S_{Fe,x}^2 - S_{Fe,y}^2)$) in the above Hamiltonian or intermolecular magnetic interactions (zJ') does not improve the experimental-theory agreement. A relatively large D_{Fe} value is indeed expected (typically up to 30 K) for a non-Kramer *hs* ions like an S = 2 Fe(II) centre.³⁰

Considering the presence of a significant magnetic anisotropy in this complex, the ac susceptibility was also measured in zero dc-field as a function of ac frequency at various temperatures (1.83 - 5.5 K) and as a function of temperature at various ac frequencies (10 - 10000 Hz). As shown in Figure 4, plots of the temperature and frequencydependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility in zero dc field reveal the slow dynamics of the magnetization below 4 K. Unfortunately, the relaxation time cannot be estimated from these measurements as there is no clear maximum in the out-of-phase ac susceptibility at the lowest temperature we are capable of measuring and as the relaxation process is not of Debye nature (Figure S4).⁺ The application of a dc-field up to 1 T does not slow the relaxation process and therefore even under dc-field it is not possible to evaluate the relaxation time of this system with our instruments. Nevertheless, Fe(hfac)2(betaDTDA) is one of comparatively few mononuclear transition metal - radical complexes³¹ and a rare example of a 6-coordinate Fe(II) complex^{8,32} that exhibits observable slow dynamics of the magnetization consistent with a SMM behaviour.

Conclusions

View Article Online DOI: 10.1039/C9DT00558G 4-(benzothiazol-2´-yl)-1,2,3,5-

Neutral radical ligand dithiadiazolyl (betaDTDA) has been designed to possess an electropositive sulphur atom (external to the thiazyl ring) that can participate in electrostatic interactions. The solid state structure of the Fe(hfac)₂(betaDTDA) complex is dominated by π -stacking of coordinated **betaDTDA** ligands, supported by electrostatic contacts between benzothiazole sulphur atoms and neighbouring hfac oxygen atoms. Short contacts between thiazyl sulphur atoms and hfac fluorine atoms, in a geometry typical for DTDAs, also contribute to the dense, threedimensional network of contacts. Magnetic measurements of Fe(hfac)₂(betaDTDA) indicate strong antiferromagnetic (AF) coupling between the radical and Fe(II) ion moments, which stabilizes a well-defined $S_{total} = 3/2$ ground state. At low temperature (<4 K), Fe(hfac)₂(betaDTDA) exhibits slow dynamics of the magnetization consistent with SMM behaviour.

Experimental

General Considerations. All reactions and manipulations were performed under inert atmosphere and using anhydrous solvents, unless stated otherwise. Anhydrous solvents were dispensed from refillable solvent kegs, filled by Caledon Labs, from an LC-SPS solvent purification system equipped with drypacked columns of 3 Å molecular sieves. Reagents were purchased from Strem, Sigma-Aldrich, and Alfa Aesar and used without further purification unless otherwise noted. LiN(TMS)₂·Et₂O was prepared from LiN(TMS)₂ in large quantities following a literature procedure.¹⁷ SbPh₃ from Sigma was recrystallized from hot acetonitrile prior to use. 2-Cyanobenzothiazole (betaCN) was prepared following slight modifications of literature procedures, as described in the Supplementary Information.[†] NMR spectra were collected at the University of Guelph using Bruker instruments (frequency as indicated). Infrared spectra (KBr pressed pellet or KBr plate) were recorded on a Nicolet 4700 FTIR spectrometer at 4 cm⁻¹ resolution and ambient temperature. Elemental analyses were performed by MHW Laboratories in Phoenix, AZ, USA.

4-(Benzothiazol-2´-yl)-N,N,N'-tris(trimethylsilyl)amidine. 2-Cyanobenzothiazole (1.49 g, 9.31 mmol) was added to a clear, colourless solution of LiN(SiMe₃)₂·Et₂O (2.30 g, 9.53 mmol) in anhydrous diethyl ether (100 mL). After 3 hours of stirring the resulting dark purple solution, trimethylsilylchloride (1.4 mL, 11 mmol) was added. The reaction mixture was left to stir for 12 hours at room temperature before it was filtered in situ to remove LiCl byproduct. The solvent was removed in vacuo from the red filtrate to obtain a dark red waxy solid which was used immediately, without purification, in the next step; crude yield 3.2 g (87%). FTIR (KBr, cm⁻¹): 3279 (w), 3066 (w), 2955 (s), 2898 (m), 1942 (w), 1786 (w), 1641 (s), 1603 (m), 1561 (m), 1498 (m), 1456 (w), 1410 (m), 1348 (w), 1314 (s), 1282 (w), 1251 (s), 1205 (s), 1154 (w), 1124 (m), 1096 (m), 1055 (s), 965 (s), 932 (m), 888 (w), 840 (s), 758 (s), 729 (m), 711 (m), 687 (m), 659 (w), 638 (w), 619 (w), 582 (w), 434 (s).

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4-(Benzothiazol-2´-yl)-1,2,3,5-dithiadiazolium chloride. Excess sulphur monochloride (4 mL, 50 mmol) was added to a solution of crude 4-(benzothiazol-2'-yl)-N,N,N'red tris(trimethylsilyl)amidine (3.2 g, 8.1 mmol) in CH₂Cl₂ (20 mL), forming a bright orange precipitate. The orange slurry was stirred for 16 hours at room temperature, and the bright orange solid product was collected by filtration. The crude product was used without further purification; crude yield 2.3 g (>100% due to S₈ byproduct). FTIR (KBr, cm⁻¹): 3060 (w), 1685 (w), 1550 (w), 1507 (s), 1384 (s), 1316 (m), 1131 (s), 878 (s), 847 (m), 840 (m), 778 (s), 705 (m), 541 (w).

4-(Benzothiazol-2'-yl)-1,2,3,5-dithiadiazolyl. Triphenylantimony (1.02 g, 2.01 mmol) was added to an orange slurry of crude 4-(benzothiazol-2´-yl)-1,2,3,5-dithiadiazolium chloride (1.41 g, 5.15 mmol) in acetonitrile (35 mL). The resulting dark purple slurry was stirred for 30 minutes at room temperature. The slurry was then filtered in vacuo to afford a dark purple powder. The product was purified by dynamic vacuum sublimation (10⁻² Torr; 120 °C) using a temperature gradient tube furnace. Sublimation under static vacuum (10⁻¹ Torr; 120 °C) was then used to grow crystals suitable for X-ray crystallography. Sublimed yield 0.66 g (54% from nitrile). FTIR (KBr, cm⁻¹): 1552 (w), 1508 (m), 1451 (w), 1355 (m), 1301 (m), 1115 (s), 1059 (m), 902 (s), 833 (s), 813 (s), 797 (s), 765 (s), 754 (s), 724 (m), 687 (w), 498 (s), 425 (w). Anal. Calcd. for C₈H₄N₃S₃: C, 40.31; H, 1.69; N, 17.63%. Found: C, 40.48; H, 2.00; N, 17.38%. EPR (toluene, 25 °C) five-line pattern consistent with exchange between coupling to two equivalent ¹⁴N nuclei; a_N = 5.026 G, g = 2.010.

Fe(hfac)₂(betaDTDA). Black, crystalline betaDTDA (165 mg, 0.692 mmol) and dark purple Fe(hfac)₂(THF)₂ (350 mg, 0.692 mmol) were combined and dissolved in anhydrous dichloromethane (30 mL) to form a dark red solution. The solution was stirred at room temperature for 2 hours, then the solvent was removed in vacuo to yield a dark red solid (445 mg). The solid residue was purified by sublimation under dynamic vacuum (10⁻⁵ Torr; at 120 °C) to yield red microcrystalline material; yield 133 mg (27%). Small red crystals suitable for X-ray crystallography were obtain by re-sublimation under static vacuum (10⁻¹ Torr; 115 °C) during 3 weeks. FTIR (KBr, cm⁻¹): 3139 (w), 2924 (w), 2852 (w), 1635 (s), 1556 (m), 1528 (m), 1496 (w), 1479 (m), 1450 (w), 1391 (m), 1340 (m), 1266 (s), 1213 (m), 1194 (m), 1140 (s), 1104 (w), 950 (w), 923 (w), 875 (w), 807 (m), 795 (m), 762 (s), 742 (m), 730 (m), 703 (w), 666 (s), 585 (m), 528 (w), 516 (m), 432 (m). Anal. Calcd. for C₁₈H₆F₁₂FeN₃O₄S₃: C, 30.52; H, 0.85; N, 5.93. Found: C, 30.66; H, 1.05; N, 5.93.

Magnetic measurements. Magnetic susceptibility measurements were carried out with the use of a MPMS-XL Quantum Design SQUID magnetometer and a PPMS-9 Quantum Design susceptometer. These instruments function between 1.8 and 400 K for dc applied fields ranging from -7 to +7 T (MPMS-XL) and -9 to 9 T (PPMS-9). Measurements were performed on polycrystalline samples of betaDTDA and Fe(hfac)₂(betaDTDA) (8.7 and 9.8 mg, respectively) enclosed in sealed polyethylene bags (typical sizes and mass: $3 \times 0.5 \times 0.02$ cm; 15-25 mg) under nitrogen. Prior to experiments, the fielddependent magnetization was measured at 100 K field of the confirm the absence of any bulk ferromagnetic impurities. The magnetic data were corrected for the diamagnetic contributions from the sample (Fe(hfac)₂(betaDTDA) only) and sample holder.

Conflicts of interest

The authors declare no conflicts of interest.

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