# **Electronic Supplementary Information**

# Slow Spin Relaxation in a Low-Spin S=1/2 Fe<sup>III</sup> Carborane Complex

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# **INDEX.-**

I.	- Experimental section	5
	Synthesis and characterization of [NMe <sub>4</sub> ][3,3'-Fe(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> ) <sub>2</sub> ]:	
	FTIR, Cyclic Voltammetry, UV-Vis, <sup>1</sup> H-NMR; <sup>1</sup> H{ <sup>11</sup> B}-NMR, <sup>11</sup> B-NMR;	
	<sup>11</sup> B{ <sup>1</sup> H}-NMR; <sup>13</sup> C{ <sup>1</sup> H}-NMR; MALDI-TOF-MS	
	Experimental X-ray diffraction.	11
	Comparison between $[NMe_4][2,2]{-Fe}(1,7-C_2B_{10}H_{11})_2]$ and	
	$[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2].$	12
	Figure S1. The asymmetric unit of [NMe <sub>4</sub> ][3,3'-Fe(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> ) <sub>2</sub> ],	
	showing the atoms numbering scheme.	13
	Figure S2. View of the 2D layer structure in the crystal of	
	$[NMe_4][2,2'-Fe(1,7-C_2B_{10}H_{11})_2].$	14
	Figure S3. 3D structure in the crystal of $[NMe_4][2,2'-Fe(1,7-C2B_{10}H_{11})_2]$ .	
	Hydrogen atoms omitted for clarity.	15
	Figure S4. Zig-zag chain view though a axis in	
	the crystal of $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ .	16
	Figure S5. 3D structure in the crystal of $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ .	
	Hydrogen atoms omitted for clarity.	17
	<b>Table S1.</b> Crystal data and structure refinement for [NMe4][3,3'-Fe(1,2-C2B9H11)2].	18
	Table S2. Selected interatomic distances (Å) between Fe-C and	
	Fe-B obtained in ferrabis (dicarbollide) anions.	19
	Figure S6. Static susceptibility and magnetization measured	
	for a powder and THF solution samples of the [NMe4][3,3'-Fe(1,2-C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> ) <sub>2</sub> ] compound (	black
	color) and the same calculated magnitudes at the NEVPT2+spin orbit level.	21

page

Figure S7. Real and Imaginary susceptibility measured at different	
frequencies (above) dependence with temperature with an external field of 0.05 T	
and (below) dependence with the external field for a saturated	
THF solution of the $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ .	22
Figure S8. EPR (X-band 9.3 GHz) powder sample and THF solution	
of the $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ complex.	23
Figure S9. Static susceptibility and magnetization measured	
for a powder and THF solution samples of the $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$	
compound and the same calculated magnitudes at the NEVPT2+spin orbit level for	
the three isomers of this molecule.	27

## II.- Computational details

Table S3. Calculated relative energies (in kcal/mol) between the three	
isomers for the isolated molecules or in a CPCM model using THF as solvent.	24
Table S4. Calculated NEVPT2 state energies (in cm <sup>-1</sup> ) including	
spin-orbit effects using the three active spaces using the experimental X-ray structure.	25
<b>Table S5.</b> Calculated energy splitting of the 5 d orbitals using the NEVPT2(5,5)	
method using the experimental X-ray structure.	25
Table S6. Calculated g components using NEVPT2 method including	
spin-orbit effects using the three active spaces using the experimental X-ray structure.	25
Table S7. Calculated g components and excited states	
(D doublet or Q quartet states, in cm <sup>-1</sup> ) for the three DFT optimized	
isomers using B3LYP calculations and CPCM model to simulate the THF solvent.	26
<b>Table S8.</b> Calculated energy splitting of the 5 d orbitals using the NEVPT2(5,5)	
method using the DFT optimized $c$ isomer using B3LYP calculations (CPCM-THF).	26

<b>Table S9.</b> Spin relaxation values $(\tau)$ extracted from the Cole-Cole diagram	
for different temperatures using the CC-fit code for a saturated THF solution	
of the $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ compound with an external field of 0.05 T.	28
<b>Table S10.</b> Spin relaxation values $(\tau)$ extracted from the dependence with the	
external field for a saturated THF solution of the	
$[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ compound at 3 K.	29

## References

#### **Experimental section:**

#### Instrumentation.

Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra (v, cm<sup>-1</sup>; ATR) were recorded on a JASCO FT/IR 4700 spectrophotometer. *NMR spectroscopy*: The <sup>1</sup>H-NMR, <sup>1</sup>H{<sup>11</sup>B}-NMR (400 MHz), <sup>11</sup>B-NMR and <sup>11</sup>B{<sup>1</sup>H}-NMR (128.38 MHz), and <sup>13</sup>C{<sup>1</sup>H}-NMR (100 MHz) spectra were recorded with a Bruker Advance III (400MHz) instrument equipped with the appropriate decoupling accessories. Chemical shift values for <sup>11</sup>B-NMR and  ${}^{11}B{}^{1}H{}$ -NMR spectra were referenced to external BF<sub>3</sub>·OEt<sub>2</sub>, and those for  ${}^{1}H{}$ -,  ${}^{1}H{}^{11}B{}$ - and  ${}^{13}C{}^{1}H{}$ -NMR spectra were referenced to Si(CH<sub>3</sub>)<sub>4</sub>. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz. EPR. Bruker ELEXYS E500 X band EPR spectrometer equipped with a variable temperature unit, a field frequency (F/F) lock accessory and built in NMR Gauss meter. Mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N2 laser;  $\lambda$ exc 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. Cyclic Voltammetry was obtained with an Autolab PGSTAT302N at a scan rate of 100 mV/s. A three-electrode set up was used, being a glassy carbon the working electrode; an Ag as pseudoreference electrode and Pt wire as counter electrode. All measurements were done in dry and pure acetonitrile with TBA[PF<sub>6</sub>] 0.1 M as the inert electrolyte and referenced to internal Fc<sup>+</sup>/Fc. The concentrations of all the measured samples were always 1 mM. All solvents and electrolytes used for the electrochemical measurements were purchased from Sigma-Aldrich. Reagent grade acetonitrile was pre-dried over CaCO<sub>3</sub>, and then distilled over P<sub>2</sub>O<sub>5</sub>. Prior to use, acetonitrile was degassed by the standard freeze-pump-thaw technique in order to remove the dissolved oxygen, and stored over 0.4 nm molecular sieves. TBA[PF<sub>6</sub>] was dried overnight at 50° under vacuum to remove possible traces of water. UV-Vis spectrum was recorded on Shimadzu UV-1700 Pharmaspec spectrophotometer, using 1 cm cuvette. Different concentrations of the compounds were used to calculate the molar extinction coefficient: 15.86 mmol·L<sup>-1</sup>.

### Synthesis of [NMe<sub>4</sub>][3,3'-Fe(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]

The complex was synthesized using the reported procedure.<sup>1</sup>

Characterization of [NMe<sub>4</sub>][3,3'-Fe(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]: <sup>1</sup>H{<sup>11</sup>B} NMR (300MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ : 69.65 (s, B-H), 46.04 (2H, s, B(10)-H), 40.2 (s, B-H). <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ : 103.5 (2B, s, B(6,6')), 21.02 (4B, B(5,5',11,11')), -0.70 (4B, B(9,9',12,12')), -32.47 (2B, B(10,10')), -407.20 (4B, B(4,4',7,7')), -457.35 (2B, B(8,8')). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$ : -440.2 (4C, C<sub>c</sub>).<sup>2</sup> FTIR (v in cm<sup>-1</sup>): 3039.26 (w, v (C<sub>c</sub>-H)), 2548.47 and 2519.54 (s, v (B-H)), 1478.17 (m, v (C<sub>sp</sub><sup>3</sup>-N)). Elemental analysis. Found: C, 24.49; H, 8.70; N, 3.62. Calc. for [N(CH<sub>3</sub>)<sub>4</sub>][Fe(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]: C, 24.34; H, 8.68; N, 3.55%). MALDI-TOF-MS: Teor: 321.285 m/z Found: 321.1467 m/z.

### FTIR



## Cyclic Voltammetry



### UV-Vis

Absorption spectra of compound  $[N(CH_3)_4][Fe(C_2B_9H_{11})_2]$ .





Plot of absorbance vs. concentration of [N(CH<sub>3</sub>)<sub>4</sub>][Fe(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] in acetonitrile.

<sup>1</sup>H-NMR



<sup>1</sup>H{<sup>11</sup>B}-NMR





<sup>11</sup>B{<sup>1</sup>H}-NMR







### Crystallography

### **Experimental X-ray diffraction**

Measured crystal was prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. A suitable crystal was mounted on MiTeGen Micromounts<sup>TM</sup>, and this sample was used for data collection. Crystallographic data was collected at 100K at XALOC beamline at ALBA synchrotron ( $\lambda = 0.82654$  Å). Data were indexed, integrated and scaled using with APEX3 program<sup>3</sup> and corrected for absorption using SADABS.<sup>4a</sup> The structure was solved by direct methods and subsequently refined by correction of F<sup>2</sup> against all reflections.<sup>4b</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F<sup>2</sup>. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameter 1.2 (C-H, B-H) or 1.5 (-CH<sub>3</sub>) times those of the respective atom. A summary of crystal data is reported in Table S1.

Comparison between  $[NMe_4][2,2'-Fe(1,7-C_2B_{10}H_{11})_2]$  and  $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ . The crystal structure of the monoanionic *meta*-ferrabis(dicarbollide) complex was recently reported by Bennour et al.<sup>5</sup> A structural comparison with the new monoanionic *ortho*-

ferrabis(dicarbollide) reported in this paper was carried out in order to evaluate the effect of the position of the carbon atoms. Both monoanionic ferrabis(dicarbollide) isomers crystallize in the monoclinic crystal system, but unlike the meta isomer, the *ortho*-ferrabis(dicarbollide) complex belong to a lower symmetry space group (Cc) and exhibits an ordered tetramethylammonium cation and two dicarbollide units sandwiched around an iron ion adopting a *cisoid* conformation with the C<sub>2</sub>B<sub>3</sub> faces of the two ligands which are nearly parallel (Fig. S1). The distance between the iron atom and the two pentagonal planes is the same in the meta isomer (1.519 Å) meanwhile in the *ortho* isomer that distance is slightly different (1.525 and 1.527 Å) but higher than in the case of *meta* isomer, showing an increased volume of this space as observed from the Fe–C and Fe–B bond distances (Table S2).

**Figure S1.** The asymmetric unit of  $[NMe_4][3,3]$ –Fe(1,2–C $_2B_9H_{11})_2$ ], showing the atoms numbering scheme.



Figure S2. View of the 2D layer structure in the crystal of [NMe<sub>4</sub>][2,2'-Fe(1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub>].



In the crystal of the *meta*-isomer, each monoanionic ferrabis(dicarbollide) is connected with four additional adjacent anions through dihydrogen bonds involving (C7–H7···H3–B3, 2.317 Å and C1–H1···H8–B8, 2.233 Å) generating a 2D layer structure running parallel to the *bc* plane (Fig. S2). Tetramethylammonium cations connect these structures to finally build up the supramolecular 3D architecture (Fig. S3).

**Figure S3.** 3D structure in the crystal of  $[NMe_4][2,2'-Fe(1,7-C2B_{10}H_{11})_2]$ . Hydrogen atoms omitted for clarity.



Figure S4. Zig-zag chain view though a axis in the crystal of [NMe<sub>4</sub>][3,3'-Fe(1,2–C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>].



In the crystal of the reported  $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ , dihydrogen bonds (C13-H13····H7-B7, 2.036 Å) connect monoanionic ferrabis(dicarbollide) units to generate a zig-zag chain (Fig. S4). Additional dihydrogen interactions involving tetramethylammonium cations connect these structures to build up the supramolecular 3D architecture (Fig. S5).

**Figure S5.** 3D structure in the crystal of  $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$ . Hydrogen atoms omitted for clarity.



|--|

Empirical formula	C <sub>8</sub> H <sub>34</sub> B <sub>18</sub> FeN	
Formula weight	394.79	
Temperature	100.0 K	
Wavelength	0.82654 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 6.8764(3)  Å	α= 90°.
	b = 28.8263(15) Å	β= 91.2940(10)°.
	c = 10.7581(5)  Å	$\gamma = 90^{\circ}$ .
Volume	2131.94(18) Å <sup>3</sup>	
Ζ	4	
Density (calculated)	1.230 Mg/m <sup>3</sup>	
Absorption coefficient	1.056 mm <sup>-1</sup>	
F(000)	820	
Crystal size	0.10 x 0.10 x 0.08 mm <sup>3</sup>	
Reflections collected	12144	
Independent reflections	3506 [R(int) = 0.0925]	
Data / restraints / parameters	3506 / 2 / 257	
Goodness-of-fit on F <sup>2</sup>	1.057	
Final R index [I>2sigma(I)]	R1 = 0.0610, wR2 =	
	0.1461	
R index (all data)	R1 = 0.0618, wR2 =	
	0.1470	
Absolute structure parameter	0.051(10)	

$[NMe_4][2,2'-Fe(1,7-C_2B_{10}H_{11})_2]$	$[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$
Fe(2,2)—C(1) 2.083 (2)	Fe(1)–C(1) 2.088(5)
$Fe(2,2)-C(1^{\#1}) 2.083 (2)$	Fe(1)–C(2) 2.083(6)
Fe(2,2)—C(7) 2.111 (2)	Fe(1)-C(12) 2.078(6)
Fe(2,2)-C(7 <sup>#1</sup> ) 2.111 (2)	Fe(1)-C(13) 2.074(9)
Fe(2,2)—B(6) 2.111 (2)	Fe(1)–B(3) 2.128(6)
Fe(2,2)—B(6 <sup>#1</sup> ) 2.111 (2)	Fe(1)–B(4) 2.145(10)
Fe(2,2) –B(3) 2.100 (2)	Fe(1)–B(5) 2.135(7)
Fe(2,2)—B(3 <sup>#1</sup> ) 2.100 (2)	Fe(1)–B(14) 2.129(6)
Fe(2,2)-B(11) 2.131 (2)	Fe(1)–B(15) 2.156(6)
$Fe(2,2)-B(11^{\#1}) 2.131 (2)$	Fe(1)–B(16) 2.136(6)

**Table S2.** Selected interatomic distances (Å) between Fe–C and Fe–B obtained in ferrabis (dicarbollide) anions.

Symmetry code: #1: 1/2-x, 1/2-y, 1-z

**Magnetic Measurements.** Susceptibility measurements (Direct (DC) and alternating (AC) current) were carried out with a Quantum Design SQUID MPMS device. An oscillating ac field of 4 Oe was used in the AC measurements and frequencies ranging from 1 to 1500 Hz and a 0.05 T external DC field. Polycrystalline sample was mounted in a capillary tube made of polyimide. The 20 mg powder sample was unfixed within the sample tube and then it aligned along the magnetic field direction. Solution sample (55.7 mM) was prepared by first dissolving 11 mg of solid sample in 0.5 ml THF in an Eppendorf; afterwards, it was transferred to one side sealed tube of polyimide and immediately after introduced in liquid nitrogen; then the second side of the tube was sealed.

The ac susceptibility data were analyzed within the extended Debye model using the CC-fit  $code^{6a}$  in which a maximum in the out-of-phase component  $\chi_M''$  of the complex susceptibility is observed when the relaxation time  $\tau$  equals  $(2\pi v)^{-1}.^{6b-c}$  The Cole-Cole expression is introduced to describe distorted Argand plots,

$$\chi_{ac}(w) = \chi_{S} + \frac{(\chi_{T} - \chi_{S})}{1 + (i\omega\tau)^{1-\alpha}}$$

where  $\omega = 2\pi v$ ,  $\chi_T$  and  $\chi_S$  are the isothermal and adiabatic susceptibilities *i.e.*, the susceptibilities observed in the two limiting cases  $v \to 0$  and  $\infty$ , respectively. The  $\alpha$  parameter (between 0 and 1) describes the distribution of relaxation times, wider distribution larger  $\alpha$ . If  $\alpha$  is equal to 0 only one single  $\tau$  value. The frequency dependence<sup>6d</sup> of  $\chi_M$ ' and  $\chi_M$ " can be split into:

$$\chi_{M}'(\omega) = \chi_{S} + \frac{(\chi_{T} - \chi_{S})[1 + (\omega\tau)^{1-\alpha}\sin(\pi\alpha/2)]}{1 + 2(\omega\tau)^{1-\alpha}\sin(\pi\alpha/2) + (\omega\tau)^{2-2\alpha}}$$

$$\chi_{M}''(\omega) = \frac{(\chi_{T} - \chi_{S})[(\omega\tau)^{1-\alpha}\cos(\pi\alpha/2)]}{1 + 2(\omega\tau)^{1-\alpha}\sin(\pi\alpha/2) + (\omega\tau)^{2-2\alpha}}$$

**Figure S6.** Static susceptibility and magnetization (at 2 K) measured for a powder sample of the [NMe<sub>4</sub>][3,3'-Fe(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] compound (black color) and in THF solution (blue color, magnetization at 4 K) and the same calculated magnitudes at the NEVPT2+spin orbit level (red, green and blue colors for different active spaces). The calculated curves at 2 K and 4 K are practically identical. The increase at low temperature of the  $\chi$ T value for the powder sample should be due to intermolecular interactions that are not present in the solution measures.



**Figure S7.** Real and Imaginary susceptibility measured at different frequencies (above) dependence with temperature with an external field of 0.05 T and (below) dependence with the external field for a saturated THF solution of the  $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$  at 4 K. The last representation is for comparison the dependence of the powder sample.



**Figure S8.** (a) EPR (X-band) powder sample (9.31635 GHz) and (b) THF solution (9.302873 GHz) of the  $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$  complex. Simulated EPR spectra were done with PHI program<sup>6e</sup> obtaining the g components, 1.60, 1.60 and 3.60 for the powder and 2.05, 2.05, 4.20 for the THF solution.



#### **Computational details**

Relative stabilities of the isomers (see Fig. 1 Top right) was checked by performing geometry optimizations (corroborating the energy minima with frequency calculations) by using B3LYP functional with Gaussian09 code and a  $6-31G^*$  for light elements and pseudopotential (LANL2DZ) for the iron atoms.<sup>7</sup> The results (see Table S3) show that the most stable isomer is the *c* one while in the X-ray structure was the *a* isomer.

**Table S3.** Calculated relative energies (in kcal/mol) between the three isomers for the isolated molecules or in a CPCM model using THF as solvent.

_	isomer	isolated	THF
	а	4.0	0.6
	b	1.3	0.3
_	С	0	0

Electronic structure calculations were performed to estimate the magnetic properties using the ORCA 4.0 software package<sup>7</sup> following the CASSCF methodology employing the def2-TZVP basis set.<sup>8</sup> The non-relativistic states and energies of the system were obtained with using three active spaces (electrons, orbitals) (5,5), (9,7) and (5,10); afterwards the spin-orbit effects were included using quasi-degenerate perturbation theory (QDPT). Dynamical correlation was introduced by the N-electron valence perturbation theory (NEVPT2)<sup>9</sup> by calculating 75, 24 and 1 doublet, quadruplet and sextet states. The inclusion of the dynamic correlation is required to obtain a doublet ground state at CASSCF level a sextet state is found. Finally, the energies for the d orbitals were obtained from the ab initio Ligand Field theory (AILFT) approach in this case such option must be done with only the 5d orbitals in the active space.<sup>10</sup> However, the three active spaces (including two ligand bonding orbitals (9,7) or empty d orbitals (5,10)) show very similar results (see results for the X-ray structure in Tables S4 and S6), especially, for the ground and first excited state that play the main role for the magnetic anisotropy. Thus, the

results of energies and g components in the main text are those corresponding to the (5,5) active space to have all the information (AILFT only can be obtained with such active space) despite that lowest energy at CASSCF level was calculated with the (5,10) active space. Differentiation of the QDPT Hamiltonian with respect to the magnetic field allowed the calculation of magnetization and magnetic susceptibility curves.

**Table S4.** Calculated NEVPT2 state energies (in cm<sup>-1</sup>) including spin-orbit effects using the three active spaces using the experimental X-ray structure.

(5,5)		(9,7)		(5,10)	
0	Doublet	0	Doublet	0	Doublet
1122	Doublet	922	Doublet	973	Doublet
21170	Quadruplet	7693	Doublet	12123	Quadruplet
21210		8952	Quadruplet	12226	
22529	Quadruplet	9093		12490	Doublet
22554		9634	Quadruplet	13187	Quadruplet

**Table S5.** Calculated energy splitting of the 5 d orbitals using the NEVPT2(5,5) method using the experimental X-ray structure.

$E(cm^{-1})$	
d <sub>xy</sub>	0
$d_{x^2-y^2}$	412
$d_{z^2}$	1590
$d_{xz}$	29446
d <sub>yz</sub>	30951

**Table S6.** Calculated *g* components using NEVPT2 method including spin-orbit effects using the three active spaces using the experimental X-ray structure.

	$g_{xx}$	$g_{yy}$	$g_{zz}$
(5,5)	1.35	1.36	4.79
(9,7)	1.06	1.06	5.32
(10,5)	1.22	1.22	4.98

**Table S7.** Calculated NEVPT2 *g* components and excited states (D doublet or Q quartet states, in cm<sup>-1</sup>) for the three DFT optimized isomers using B3LYP calculations and CPCM model to simulate the THF solvent.

isomer	$g_{xx}$	$g_{yy}$	$g_{zz}$	energies
а	0.68	0.69	5.60	0 (D), 877 (D), 19857 (Q)
b	1.71	1.72	3.91	0 (D), 1660 (D), 19417 (D,Q)
С	1.74	1.75	3.80	0 (D), 1757 (D), 18784 (Q)

**Table S8.** Calculated energy splitting of the 5 d orbitals using the NEVPT2(5,5) method using the DFT optimized *c* isomer using B3LYP calculations (CPCM-THF).

	$E(cm^{-1})$
d <sub>xy</sub>	0
dx2-y2	1138
d <sub>z</sub> 2	2512
$d_{xz}$	28271
d <sub>yz</sub>	28533

**Figure S9.** Static susceptibility and magnetization (at 2 K) measured for a powder sample of the  $[NMe_4][3,3'-Fe(1,2-C_2B_9H_{11})_2]$  compound (black color) and in THF solution (blue color, magnetization at 4 K) and the same calculated magnitudes at the NEVPT2+spin orbit level using the B3LYP optimized geometries with CPCM model to simulate the THF solvent, red, green and blue colors for the three isomers a (cis 1), b (cis2) and c (trans). The calculated curves at 2 K and 4 K are practically identical.



**Table S9.** Spin relaxation values ( $\tau^{-1}$  in s<sup>-1</sup>) extracted from the Cole-Cole diagram (Fig. 2) for different temperatures using the CC-fit code for a saturated THF solution of the [NMe<sub>4</sub>][3,3'-Fe(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] compound with an external field of 0.05 T (see dependence in Fig. 3).

T (K)	$ au^{-1}$
1.8	502.51
1.9	571.43
2.0	653.59
2.1	735.29
2.3	900.90
2.5	1091.7
2.7	1314.1
3.0	1672.2
3.3	2070.4
3.6	2544.5
4.0	3289.5
4.5	4608.3
5.0	6172.8
5.5	8620.7
6.0	11806
7.0	28409

**Table S10.** Spin relaxation values  $(\tau^{-1} \text{ in s}^{-1})$  extracted from the dependence with the external field (Fig. S2 below) for a saturated THF solution of the [NMe<sub>4</sub>][3,3'-Fe(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] compound at 4 K.

H (T)	$\tau^{-1}$
0.025	7246.4
0.050	4405.3
0.10	2673.8
0.20	1727.1
0.30	1569.9
0.50	1883.2
0.70	2358.5
0.90	2673.8
1.0	3773.6

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