Electronic Supplementary Information

for

<u>*B*-Fe₂O₃ nanomaterials from an iron(II) diketonate-diamine complex: a study</u> from molecular precursor to growth process

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NMR analysis of Fe(hfa)₂•TMEDA

NMR spectra were recorded at 25 °C on acetone- d_6 or CDCl₃ solutions using a Bruker DMX-400 spectrometer (9.4 T magnet) equipped with a quadrinuclear QNP-400 5 mm probe operating at 400.13 MHz on ¹H and at 100.61 MHz on ¹³C, as well as on a Bruker DMX-200 spectrometer (4.7 T magnet) equipped with a quadrinuclear QNP-200 5 mm probe operating at 200.13 MHz on ¹H and 188.31 MHz on ¹⁹F. Chemical shift values (δ) are referenced to Me₄Si for ¹H and ¹³C nuclei, and to CFCl₃ for ¹⁹F.

NMR (CDCl₃): ¹H, δ 121.1 and 47.8 (6H each, TMEDA CH₃ protons), 80.2 and 47.7 (2H each, TMEDA CH₂ protons), -5.9 (2H, hfa CH protons); ¹⁹F, δ -56.2 and -79.1 ($\Delta v_{\frac{1}{2}} \approx 800$ Hz); ¹³C, δ 1480, 611, 115 and -835.

The monomer nature of Fe(hfa)₂•TMEDA in solution is confirmed by the paramagnetic characteristics of its ¹H, ¹³C and ¹⁹F NMR spectra (Figs. S1-S4). In fact, the interaction between the nuclear and electronic spin moments induces a dramatic line broadening, as well as an extreme chemical shift value spreading with respect to that usually observed for diamagnetic systems. In agreement with the X-ray structural determination, two moderately broad resonances were observed in CDCl₃ for the ¹⁹F nuclei at δ -56.2 ($\Delta v_{\frac{1}{2}} \approx 800$ Hz) and δ -74.5 ($\Delta v_{\frac{1}{2}} \approx 800$ Hz) (Figure S1).

Similarly, in the ¹H spectrum recorded in acetone- d_6 (see Fig. S3) well distinct broad resonances were located at δ 79.6 ($\Delta v_{\frac{1}{2}} \approx 1300 \text{ Hz}$) and δ 32.6 ($\Delta v_{\frac{1}{2}} \approx 1600 \text{ Hz}$) for the methylene protons and at δ 120.8 ($\Delta v_{\frac{1}{2}} \approx 1600 \text{ Hz}$) and δ 47.8 ($\Delta v_{\frac{1}{2}} \approx 1400 \text{ Hz}$) for the methyl protons of TMEDA. In contrast, the CH protons belonging to the two hfa moieties resonated isochronously at δ -5.93 and exhibited a much lower line broadening ($\Delta v_{\frac{1}{2}} \approx 120 \text{ Hz}$). The isochronicity could be due to the position of these nuclei in a very internal part of the molecular structure where an increased local higher symmetry is possible, and the reduced effect of the paramagnetism on the line width could be ascribable to the higher distance of these protons from the metal center. Very similar ¹H chemical shift values and line broadening were observed in CDCl₃ (Fig. S4).

The paramagnetic effects on the ¹³C NMR properties were even more prominent, and the observed resonances spread over a 3000 ppm range. The spectrometer hardware enabled to record spectra with a maximum sweep width of \approx 75 kHz, so that spectra were acquired as contiguous and slightly overlapping ends 740 ppm windows. Very broad signals at δ 1480 ($\Delta v_{\frac{1}{2}} \approx$ 24 kHz), 611 ($\Delta v_{\frac{1}{2}} \approx$ 33 kHz), 115 ($\Delta v_{\frac{1}{2}} \approx$ 2.4 kHz) and -835 ($\Delta v_{\frac{1}{2}} \approx$ 27 kHz) were obtained. A computer reconstruction of the whole spectrum is provided in Fig. S2. The resonance at δ 115

could be reasonably attributed to the hfa CH carbons on the basis of its reduced broadening, similarly to the corresponding ¹H signal (see above).



Figure S1. ¹⁹F NMR (a) and ¹H NMR (b) spectrum of Fe(hfa)₂•TMEDA in CDCl₃ (25 °C).



Figure S2. ¹³C-NMR spectrum of Fe(hfa)₂•TMEDA in CDCl₃ (100.6 MHz, 25 °C). The variuos acquisition windows are indicated by different colors. The signal intensity in the -500 \div -1240 range is magnified by a 20× factor for sake of clarity. The signal at δ 77.0 is that of ¹³CDCl₃.



Figure S3. ¹H-NMR spectrum of Fe(hfa)₂•TMEDA in acetone-*d*₆, with integrals (25 °C).



Figure S4. ¹H-NMR spectrum of Fe(hfa)₂•TMEDA in CDCl₃, with integrals (25 °C).

The minimum energy structure of the complex

To determine the spin state of the complex, three geometry optimizations have been performed with the PBE0 functional and the D95+* basis set on Fe(hfa)₂•TMEDA with Fe in the quintet, triplet and singlet state. The quintet was predicted to be the most stable spin state for the complex, with the quintet-triplet and quintet-singlet energy differences amounting to 25.6 and 23.6 kcal×mol⁻¹, respectively. On the basis of this result, further calculations on Fe(hfa)₂•TMEDA were carried out by considering the quintet spin state. The minimum energy structure of the complex was calculated by using different hybrid density functional approximations (Table S1). In all cases, the resulting geometrical parameters were very close to the corresponding experimental values (see also Table 2).

	PBE0	HSE	M06
Fe(1)-O(21)	2.064	2.058	2.041
Fe(1)-O(25)	2.091	2.093	2.091
Fe(1)-O(11)	2.091	2.093	2.091
Fe(1)-O(15)	2.064	2.058	2.041
Fe(1)-N(31)	2.271	2.269	2.230
Fe(1)-N(34)	2.271	2.269	2.230
N(31)-C(32)	1.472	1.473	1.474
N(34)-C(33)	1.472	1.473	1.474
O(21)-C(22)	1.261	1.262	1.260
O(25)-C(24)	1.251	1.252	1.251
O(11)-C(12)	1.251	1.252	1.251
O(15)-C(14)	1.261	1.262	1.260
O(21)-Fe(1)-O(25)	84.6	85.0	86.0
O(11)-Fe(1)-O(15)	84.6	85.0	86.0
N(31)-Fe(1)-N(34)	81.7	81.4	82.4
O(21)-Fe(1)-O(15)	177.6	175.4	175.3
O(25)-Fe(1)-N(34)	171.2	175.0	177.8
O(11)-Fe(1)-N(31)	171.2	175.0	177.8
Fe(1)-O(21)-C(22)	128.4	127.6	126.0
Fe(1)-O(25)-C(24)	128.4	127.5	125.0
Fe(1)-O(11)-C(12)	128.4	127.5	125.0
Fe(1)-O(15)-C(14)	128.4	127.6	126.0
Fe(1)-N(31)-C(32)	104.1	104.6	104.7
Fe(1)-N(34)-C(33)	104.1	104.6	104.7

Table S1 Selected bond lenghts (Å) and bond angles (°) for Fe(hfa)₂•TMEDA from optimized geometries calculated with the PBE0, HSE and M06 hybrid density functional approximations and the D95+* basis set.

E (nm) (<i>exp</i>)	E (nm) <i>(calc)</i>	f	Composition	Nature of the transition and assignment
530 (m)	496	0.0205	β HOMO $\rightarrow \beta$ LUMO	$\mathbf{M}(\mathbf{d_x^{2}}_{-\mathbf{y}}^{2}) \rightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})}$
	494	0.0050	β HOMO $\rightarrow \beta$ LUMO+1	$\mathbf{M}(\mathbf{d_x^{2}}_{-\mathbf{y}}^2) \rightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})}$
480 (w)	457	0.0084	β HOMO-2 → $β$ LUMO β HOMO-1 → $β$ LUMO+1 β HOMO → $β$ LUMO α HOMO-2 → $α$ LUMO+1 α HOMO-2 → $α$ LUMO+1	$\begin{array}{l} \mathbf{L}_{(\mathrm{hfa\ homo})} \longrightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \\ \mathbf{L}_{(\mathrm{hfa\ homo})} \longrightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \\ \mathbf{M}(\mathbf{d}_{\mathrm{x}}^{2} \cdot \mathbf{y}^{2}) \longrightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \\ \mathbf{L}_{(\mathrm{hfa\ homo})} \longrightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \end{array}$
	457	0.0023	β HOMO-1 $\rightarrow \beta$ LUMO+1 β HOMO-1 $\rightarrow \beta$ LUMO β HOMO-2 $\rightarrow \beta$ LUMO+1 α HOMO-3 $\rightarrow \alpha$ LUMO+1 α HOMO-2 $\rightarrow \alpha$ LUMO	$\begin{split} \mathbf{L}_{(\mathrm{hfa}\;\mathrm{homo})} &\to \mathbf{L}_{(\mathrm{hfa}\;\mathrm{lumo})} \\ \mathbf{M}(\mathbf{d}_{\mathrm{X}}^{2} \cdot \mathbf{y}) &\to \mathbf{L}_{(\mathrm{hfa}\;\mathrm{lumo})} \\ \mathbf{L}_{(\mathrm{hfa}\;\mathrm{homo})} &\to \mathbf{L}_{(\mathrm{hfa}\;\mathrm{lumo})} \\ \mathbf{L}_{(\mathrm{hfa}\;\mathrm{homo})} &\to \mathbf{L}_{(\mathrm{hfa}\;\mathrm{lumo})} \\ \mathbf{L}_{(\mathrm{hfa}\;\mathrm{homo})} &\to \mathbf{L}_{(\mathrm{hfa}\;\mathrm{lumo})} \\ \mathbf{L}_{(\mathrm{hfa}\;\mathrm{homo})} &\to \mathbf{L}_{(\mathrm{hfa}\;\mathrm{lumo})} \\ \end{split}$
425 (w)	386	0.0010	α HOMO $\rightarrow \alpha$ LUMO	$\mathbf{M}(\mathbf{d}_{xy}) \rightarrow \mathbf{L}_{(hfa \ lumo)}$
	386	0.0008	α HOMO-1 $\rightarrow \alpha$ LUMO+1 α HOMO $\rightarrow \alpha$ LUMO+1 α HOMO-1 $\rightarrow \alpha$ LUMO	$ \begin{split} \mathbf{M}(\mathbf{d_z}^{-}) &\rightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \\ \mathbf{M}(\mathbf{d_{xy}}) &\rightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \\ \mathbf{M}(\mathbf{d_z}^{-2}) &\rightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \end{split} $
350 (w)	311	0.0004	β HOMO-4 → $β$ LUMO β HOMO-5 → $β$ LUMO+1	$\begin{array}{l} L_{(hfa\ homo-1)} \rightarrow L_{(hfa\ lumo)} \\ L_{(hfa\ homo-1)} \rightarrow L_{(hfa\ lumo)} \end{array}$
316 (vs)	293	0.0075	α HOMO-2 $\rightarrow \alpha$ LUMO	$L_{(\rm hfa\ homo)} \rightarrow L_{(\rm hfa\ lumo)}$
	290	0.0054	β HOMO-1 → $β$ LUMO α HOMO-3 → $α$ LUMO+1 β HOMO-1 → $β$ LUMO	$\begin{array}{l} L_{(hfa \ homo)} \rightarrow L_{(hfa \ lumo)} \\ L_{(hfa \ homo)} \rightarrow L_{(hfa \ lumo)} \\ L_{(hfa \ homo)} \rightarrow L_{(hfa \ lumo)} \end{array}$
301 (vs)	272	0.2069	β HOMO-1 $\rightarrow \beta$ LUMO+1 β HOMO-2 $\rightarrow \beta$ LUMO α HOMO-3 $\rightarrow \alpha$ LUMO α HOMO-2 $\rightarrow \alpha$ LUMO+1	$\begin{array}{l} L_{(\mathrm{hfa\ homo})} \longrightarrow L_{(\mathrm{hfa\ lumo})} \\ L_{(\mathrm{hfa\ homo})} \longrightarrow L_{(\mathrm{hfa\ lumo})} \\ L_{(\mathrm{hfa\ homo})} \longrightarrow L_{(\mathrm{hfa\ lumo})} \\ L_{(\mathrm{hfa\ homo})} \longrightarrow L_{(\mathrm{hfa\ lumo})} \end{array}$
	271	0.0786	β HOMO-2 → $β$ LUMO+1 α HOMO-3 → $α$ LUMO+1 α HOMO-2 → $α$ LUMO	$\begin{array}{l} \mathbf{L}_{(\mathrm{hfa\ homo})} \longrightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \\ \mathbf{L}_{(\mathrm{hfa\ homo})} \longrightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \\ \mathbf{L}_{(\mathrm{hfa\ homo})} \longrightarrow \mathbf{L}_{(\mathrm{hfa\ lumo})} \end{array}$

^{*a*} Only calculated transitions with oscillator strengths f > 0.01 are reported unless related to a feature in the experimental spectrum. The reported assignments are approximate, and the dominant character of each excitation is evidenced in bold. Capital and lower case characters refer to MOs in Fe(hfa)₂•TMEDA and in the ligands, respectively. Contributions to the transitions with weights < 20% are not listed. L = ligands; f = calculated oscillator strength; M = metal; w = weak intensity; m = medium intensity; vs = very strong intensity.

Table S2. UV-Vis spectral data, TD-DFT calculated electronic excitations, oscillator strenghts and relative assignments for Fe(hfa)₂•TMEDA.



Figure S5. $Fe(hfa)_2 \cdot TMEDA \beta$ -spin frontier molecular orbitals. Left panel: 140 β (HOMO); right panel: 141 β (LUMO). Atom color codes: Fe: violet; O: red; F: green; C: grey; N: blue; H: white.



Figure S6. Fe(hfa)₂•TMEDA α -spin frontier molecular orbitals. Left panel: 144 α (HOMO); right panel: 145 α (LUMO). Atom color codes as in Figure S5.



Figure S7. Left panel: Fe(hfa)₂•TMEDA α -spin HOMO-1 orbital. Right panel: Fe(hfa)₂•TMEDA β -spin HOMO-1 orbital. Atom color codes as in Figure S5.



Figure S8. Left panel: optimized structure of the fragment $Fe(hfa)_2$ obtained from $Fe(hfa)_2$ •TMEDA by loss of the TMEDA ligand. Right panel: optimized structure of the fragment Fe(hfa)•TMEDA⁺ obtained from $Fe(hfa)_2$ •TMEDA by loss of a hfa ligand. Atom color codes as in Figure S5.

Thermal properties of Fe(hfa)₂•TMEDA



Figure S9. Isothermal studies carried out at different temperatures for Fe(hfa)₂•TMEDA.

SIMS analysis of β-Fe₂O₃ nanodeposits on SiO₂



Figure S10. SIMS depth profile of a β -Fe₂O₃ nanodeposit on SiO₂.