

Facile synthesis of the new tripodal tetramine ligand tris(thiazolylmethyl) amine, and full characterization of two ferrous complexes.

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Electronic Supplementary Information

Single crystals: These were obtained by slow diffusion of diisopropyl ether (or diethyl ether) in a sealed tube containing a solution of [(TTA)FeCl₂] in CH₃CN or [(TTA)Fe(OTf)₂] in CH₂Cl₂.

X-ray analysis. Single crystals of [(TTA)FeCl₂] and [(TTA)Fe(OTf)₂] were mounted on a Bruker APEX II DUO Kappa-CCD area detector diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal-detector distance was 38mm. The cell parameters were determined (APEX2 software) (*M86-E01078 APEX2 User Manual*, Bruker AXS Inc., Madison, USA, 2006) from reflections taken from three sets of 12 frames, each at 10 s exposure. The structures were solved by Direct methods using the programme SHELXS-97 (G. M. Sheldrick, 1990, "SHELXS-97 Program for Crystal Structure Determination", *Acta Crystallogr.*, A46, 467-473). The refinement and all further calculations were carried out using SHELXL-97 (Sheldrick, G. M. *SHELXL97*, Program for the refinement of crystal structures; University of Göttingen: Germany, 1997). The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . A semi-empirical absorption correction was applied using SADABS in APEX2; transmission factors: $T_{\min}/T_{\max} = 0.511/0.697$ for [(TTA)FeCl₂] and $T_{\min}/T_{\max} = 0.658/0.764$ for [(TTA)Fe(OTf)₂].

Crystal data for [(TTA)FeCl₂]: green crystals, monoclinic, space group P 21/c, $a = 8.3621(3) \text{ \AA}$, $b = 16.1372(7) \text{ \AA}$, $c = 15.1144(5) \text{ \AA}$, $\beta = 122.684(2)^\circ$, $V = 1716.61(11) \text{ \AA}^3$, $D_{\text{calcd}} = 1.684 \text{ g.cm}^{-3}$, $Z = 4$. For 5953 unique reflections, 5287 observed reflections with $I > 2\sigma(I)$ and 199 parameters, the discrepancy indices are $R [I > 2\sigma(I)] = 0.0274$ and $R_w (\text{all data}) = 0.0640$.

Crystal data for [(TTA)Fe(OTf)₂]: yellow crystals, monoclinic, space group P 21/c, $a = 8.3064(3) \text{ \AA}$, $b = 18.8237(8) \text{ \AA}$, $c = 16.1232(6) \text{ \AA}$, $\beta = 106.251(2)^\circ$, $V = 2420.25(16) \text{ \AA}^3$, $D_{\text{calcd}} = 1.818 \text{ g.cm}^{-3}$, $Z = 4$. For 8357 unique reflections, 6650 observed reflections with $I > 2\sigma(I)$ and 325 parameters, the discrepancy indices are $R [I > 2\sigma(I)] = 0.0581$ and $R_w (\text{all data}) = 0.1760$.

Experimental Section

General considerations: Chemicals were purchased from Aldrich and Maybridge Chemicals and used as received. All the solvents used during the metalation reactions and workup were distilled and dried according to: W. L. F. Armarego.; D. D. Perrin, Purification of Laboratory Chemicals, 4th ed.; Pergamon Press: Oxford, 1997ref.

Analytical anhydrous FeCl₂ was obtained as a white powder by treating iron powder (ACS grade) with hydrochloric acid in the presence of methanol in an argon atmosphere. Preparation and handling of all the compounds were performed in an argon atmosphere by using the Schlenk technique following standard procedures. The purity of the dry dioxygen was 99.999% (grade 5). Mass spectrometric experiments were carried out by the Service Commun de Spectrométrie de Masse de l'Institut de Chimie de Strasbourg. The structural determinations were carried out by the Service de Diffraction des Rayons X, Institut de Chimie (Université de Strasbourg).

Physical methods: The ¹H NMR data were recorded in CD₃CN and CD₂Cl₂ for the complexes and CDCl₃ for the ligands at ambient temperature on a Bruker AC 300 spectrometer at 300.1300 MHz with the residual signal of CD₂HCN (CHCl₃) as a reference for calibration. The UV/Vis spectra were recorded on a Varian Cary 05 E UV/Vis NIR spectrophotometer equipped with an Oxford instrument DN1704 cryostat with optically transparent Schlenk cells. The cyclic voltammetry measurement was obtained from a PAR 173A potentiostat in a 0.1M solution of TBACl (supporting electrolyte) in acetonitrile using platinum electrodes and saturated calomel electrode as the reference. For each measurement, the potential was checked by the addition of a small amount of ferrocene (Fc/Fc⁺ = 0.450 V versus SCE) in the cell. Magnetic susceptibility data were acquired from powder samples on a Quantum Design MPMS-XL SQUID magnetometer operating between 1.8 and 298 K. Field-dependent magnetization measurements at a given temperature confirm the absence of ferromagnetic impurities.

Tris(thiazolylmethyl)amine (TTA): An equimolar amount of 1,3-thiazole-2-carboxaldehyde (991 mg, 8.76 mmol) and 2-(aminomethyl)thiazole (1 g, 8.76 mmol) were mixed in dichloromethane and stirred at RT overnight. Then, 3 equivalents of sodium triacetoxyborohydride were added to the mixture. After one night under stirring, a saturated aqueous sodium hydrogen carbonate solution was added. 30 minutes later, an extraction of the mixture using DCM was performed. The organic phases were collected and dried with anhydrous MgSO₄. The solvents were removed under reduced pressure. The crude product (DTA) was used directly without any further purification.

The pale solid (1.5 g, 7.11 mmol) was then solubilized in a small amount of DCM and one equivalent of 1,3-thiazole-2-carboxaldehyde (804.3 mg, 7.11 mmol) was added and the solution was stirred overnight at RT. 3 equivalents of sodium triacetoxyborohydride were added to the mixture and after one night under stirring, a saturated aqueous sodium hydrogen carbonate solution was added. 30 minutes later, an extraction of the mixture using DCM was performed. The organic phases were collected and dried with anhydrous MgSO₄. The solvents were removed under reduced pressure. The product was further purified by flash chromatography over silica eluting with a gradient of 100% Et₂O to 95% Et₂O / 5% methanol. TLC's were visualized by UV. Evaporation of the solvents in vacuo yielded the ligand TTA as a beige solid, with a 54 % yield. ¹H NMR (300 MHz, CDCl₃, 25°C): δ (ppm) = 7.73 (d, 3H; J = 3,3Hz), 7.34 (d, 3H; J = 3,3Hz), 4.17 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 55.5, 119.9, 142.7, 169.4; HRMS (ES, positive mode): m/z: 309.03 [L+H]⁺, 331.01 [L+Na]⁺

Preparation of the [(TTA)FeX₂] (X = Cl or OTf) complexes: Details are given for [(TTA)FeCl₂], but the following procedure applies to both complexes: Free TTA (200 mg, 0.65 mmol) was dissolved in a Schlenk tube containing dry degassed CH₃CN (7 mL). Anhydrous FeCl₂ (82.6 mg, 0.65 mmol)

was dissolved in a second Schlenk tube containing dry, degassed CH₃CN (7 mL). The solution of FeCl₂ in CH₃CN was transferred under argon in the Schlenk tube containing the solution, which was stirred overnight. The addition of diethyl ether afforded a yellow solid, which was washed thoroughly with this solvent, prior to drying under vacuum. [(TTA)FeCl₂] was obtained (200 mg, 70 %) and showed good analytical and spectroscopic data, which are detailed in the following pages.

Elemental analysis:

[(TTA)FeCl₂], % calc. C: 33.1, H:2.8, N:12.9; found C: 32.6, H:3.3, N:12.6.

[(TTA)Fe(OTf)₂]: % calc. C: 25.4, H:1.8, N: 8.5; found C: 25.1, H: 2.2, N: 8.4.

Magnetic susceptibility (298 – 100K):

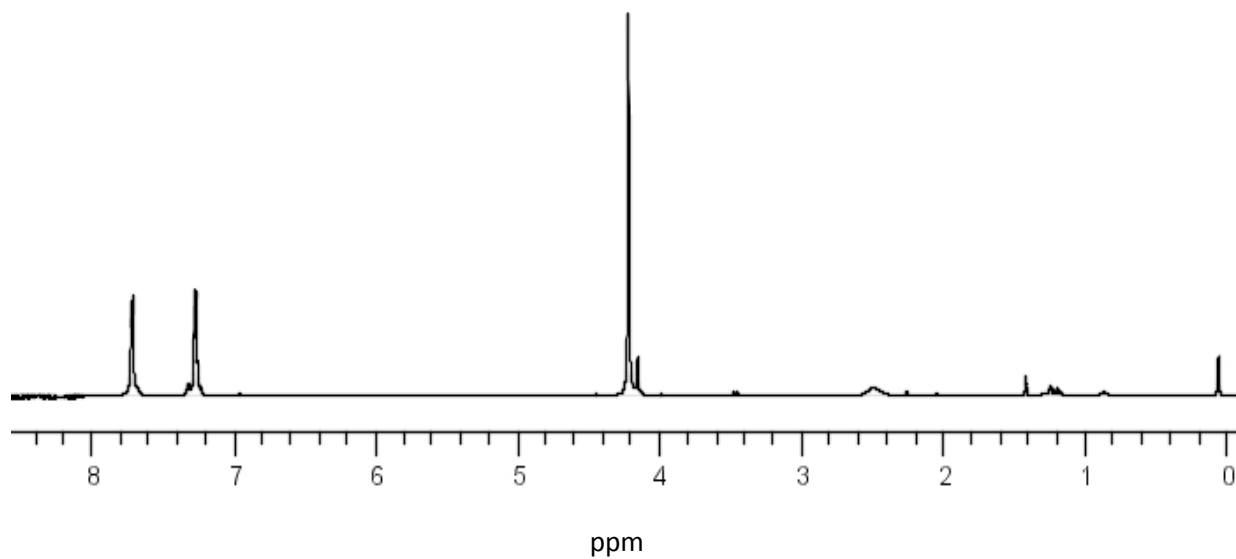
[(TTA)FeCl₂]: $\chi T = 3,36 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$

$$\mu_{\text{eff}} = (8\chi T)^{1/2} = 5.18 \mu_{\text{B}}$$

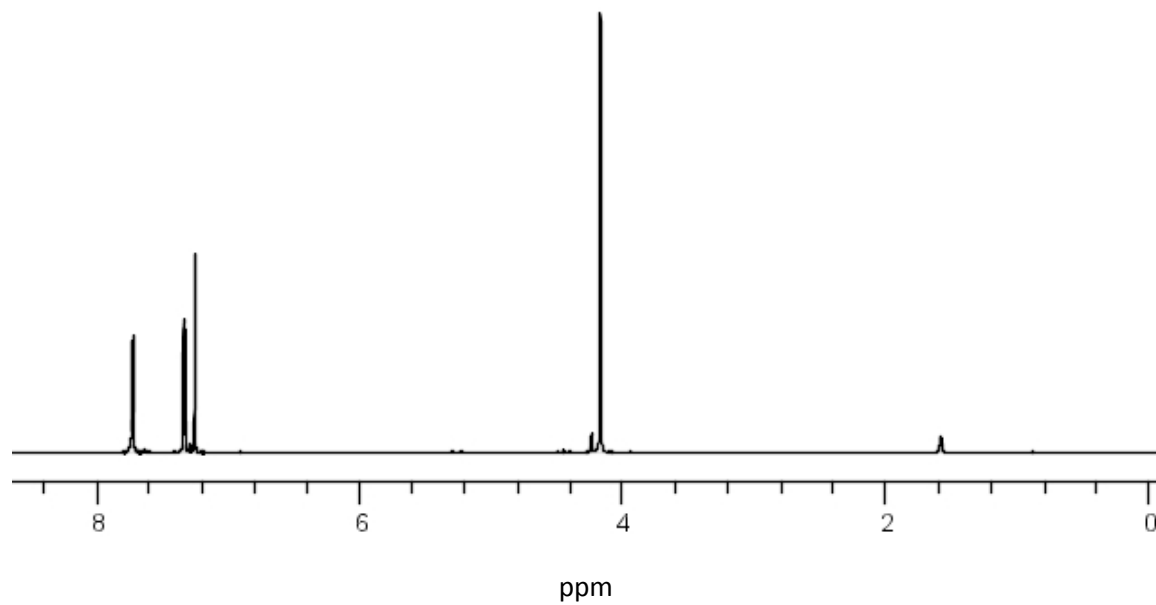
[(TTA)Fe(OTf)₂]: $\chi T = 3,66 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$

$$\mu_{\text{eff}} = 5.41 \mu_{\text{B}}$$

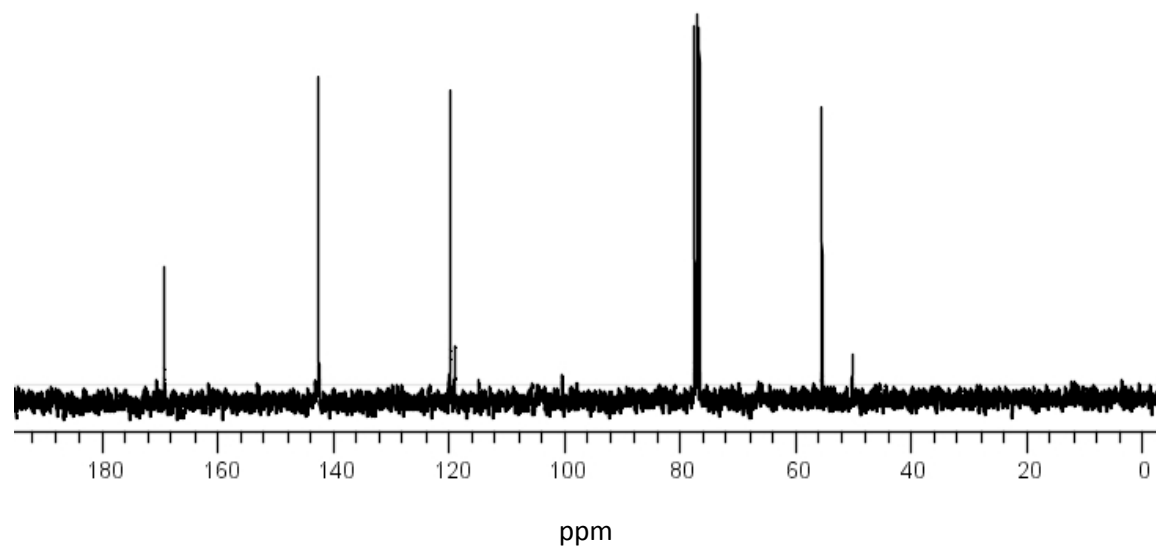
These values correspond to high-spin Fe(II) centers ($S = 2$) with a weak to moderate orbital contribution.



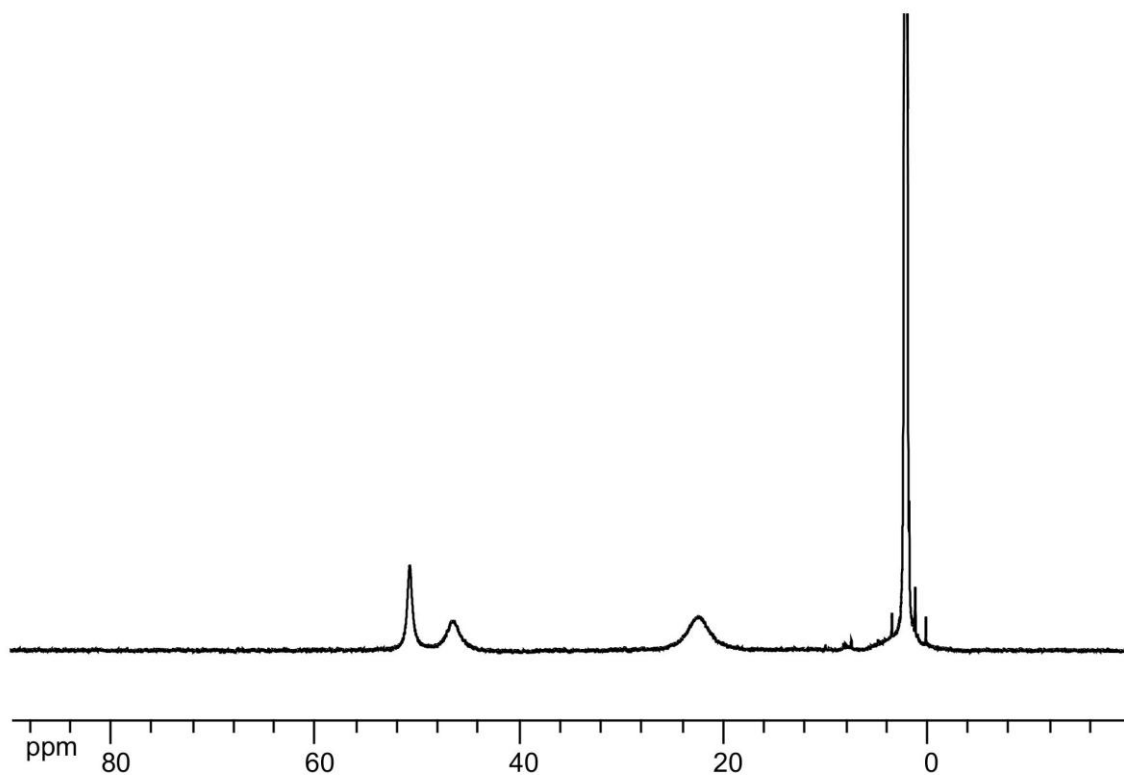
E.S.I. 01 : ¹H NMR spectrum of the DTA intermediate in CDCl₃.



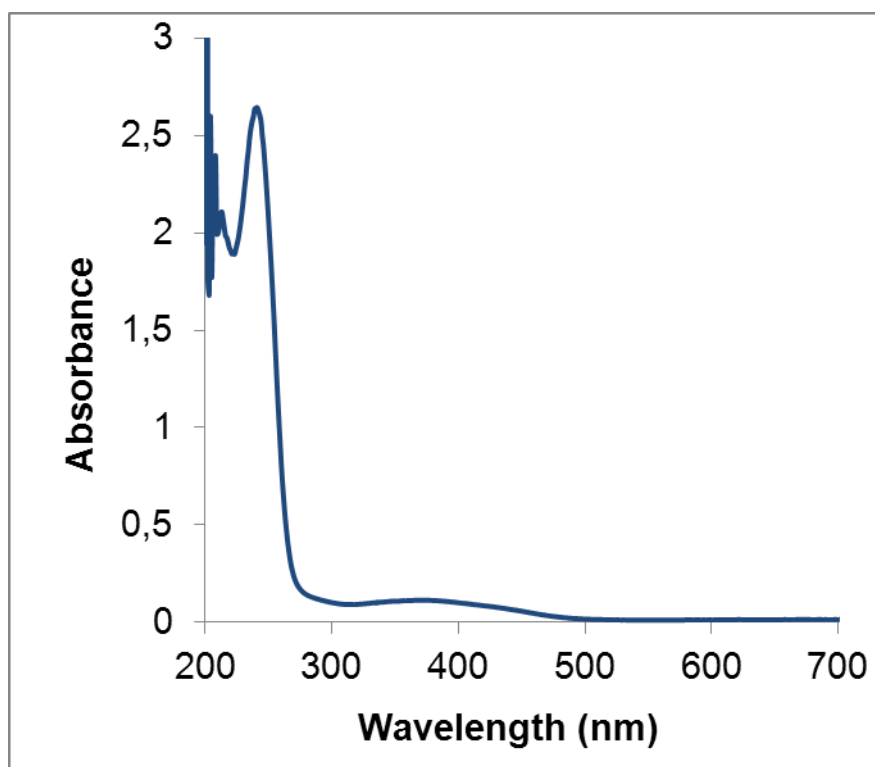
E.S.I. 02 : ^1H NMR spectrum of the ligand TTA in CDCl_3 .



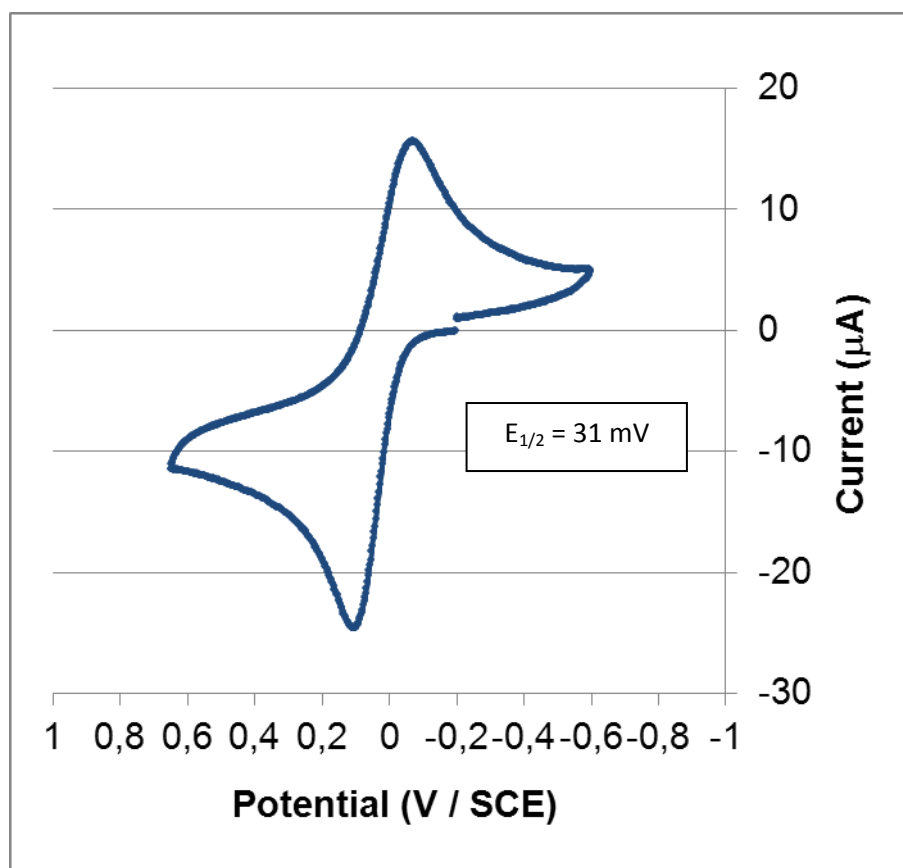
E.S.I. 03 : ^{13}C NMR spectrum of the ligand TTA in CDCl_3 .



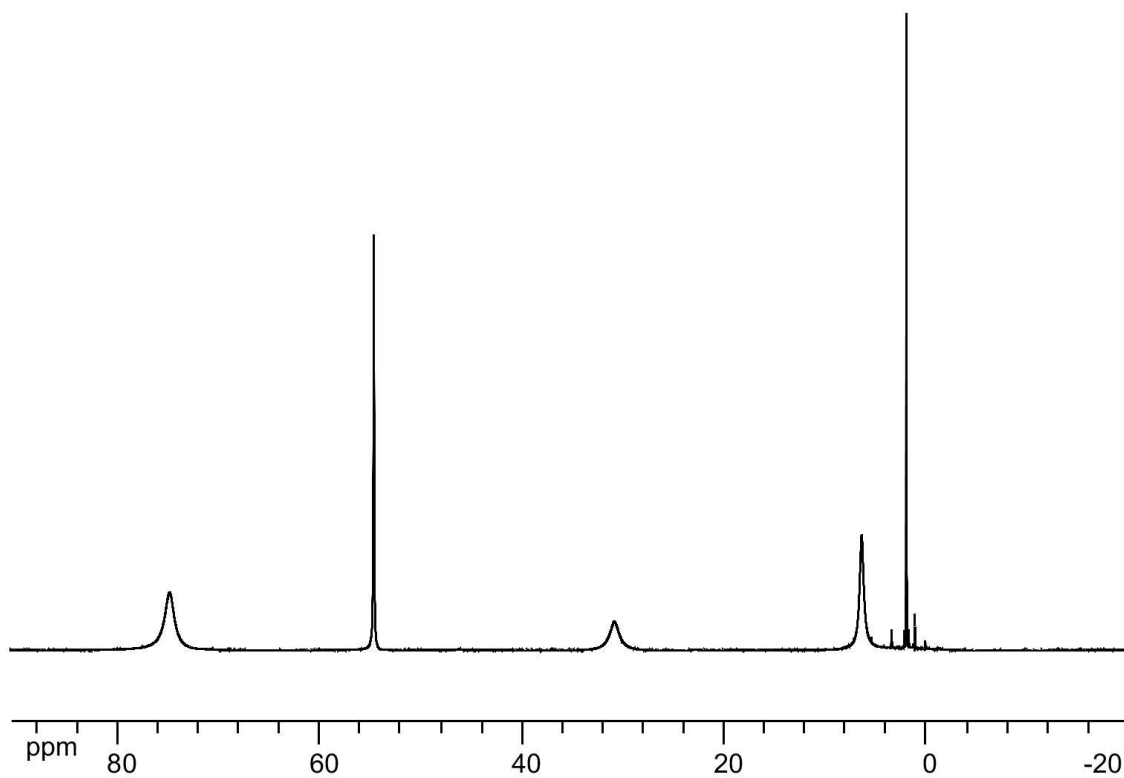
E.S.I. 04: ¹H NMR spectrum of [(TTA)FeCl₂] in CD₃CN at room temperature.



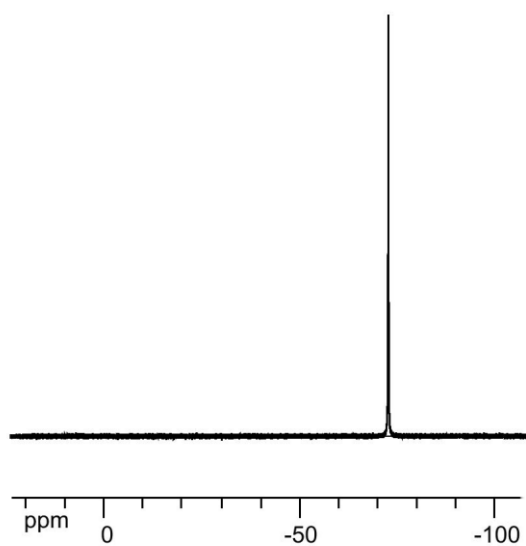
E.S.I. 05 : UV-visible spectrum of [(TTA)FeCl₂] (1.15 mM) in CH₃CN, R.T.



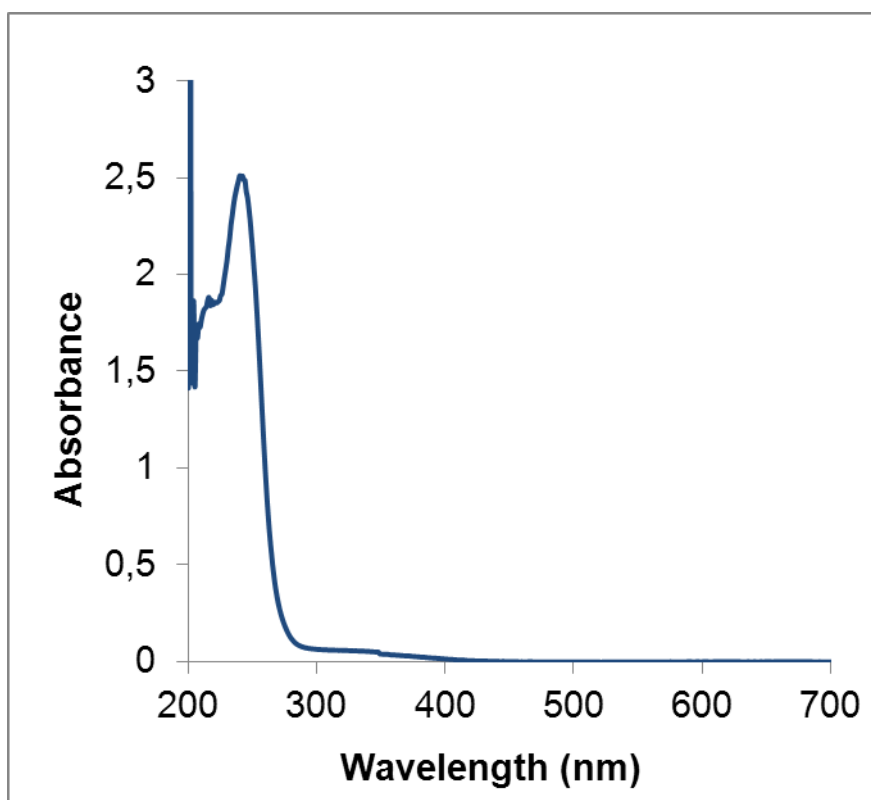
E.S.I. 06 : Cyclic voltammogram of $[(TTA)FeCl_2]$ ($C=2,1$ mM), CH_3CN , R.T., TBACl 0.1 M, 200 mV/s. At the end of the measurement, the potentials (given in text versus SCE) were calibrated by addition of a small amount of ferrocene.



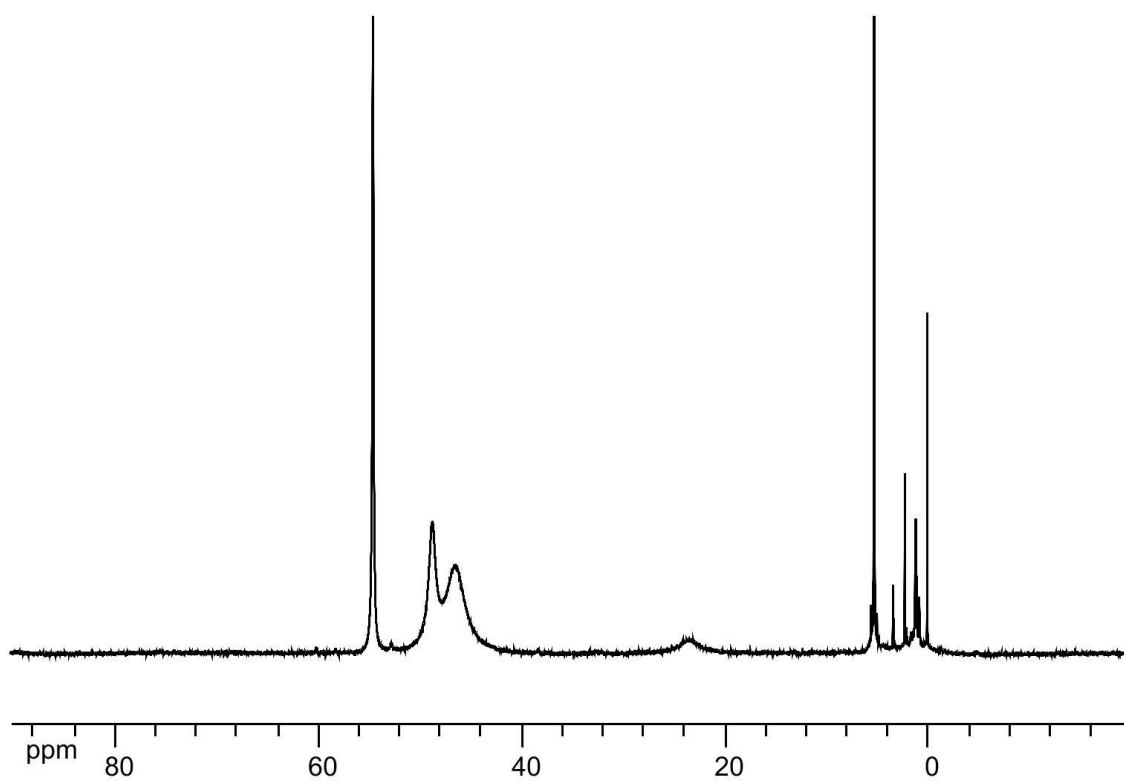
ESI 07: ¹H NMR spectrum of [(TTA)Fe(OTf)₂] in CD₃CN at room temperature.



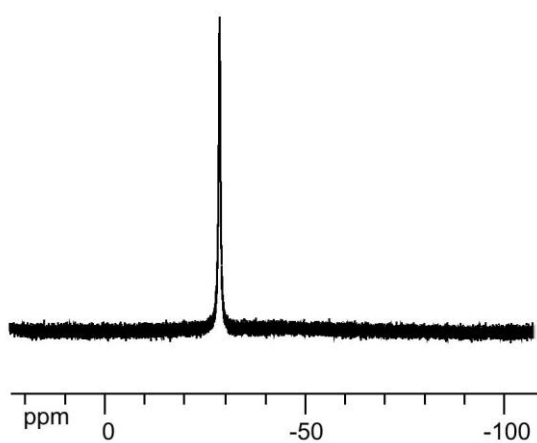
ESI 08: ¹⁹F NMR spectrum of [(TTA)Fe(OTf)₂] in CD₃CN at room temperature.



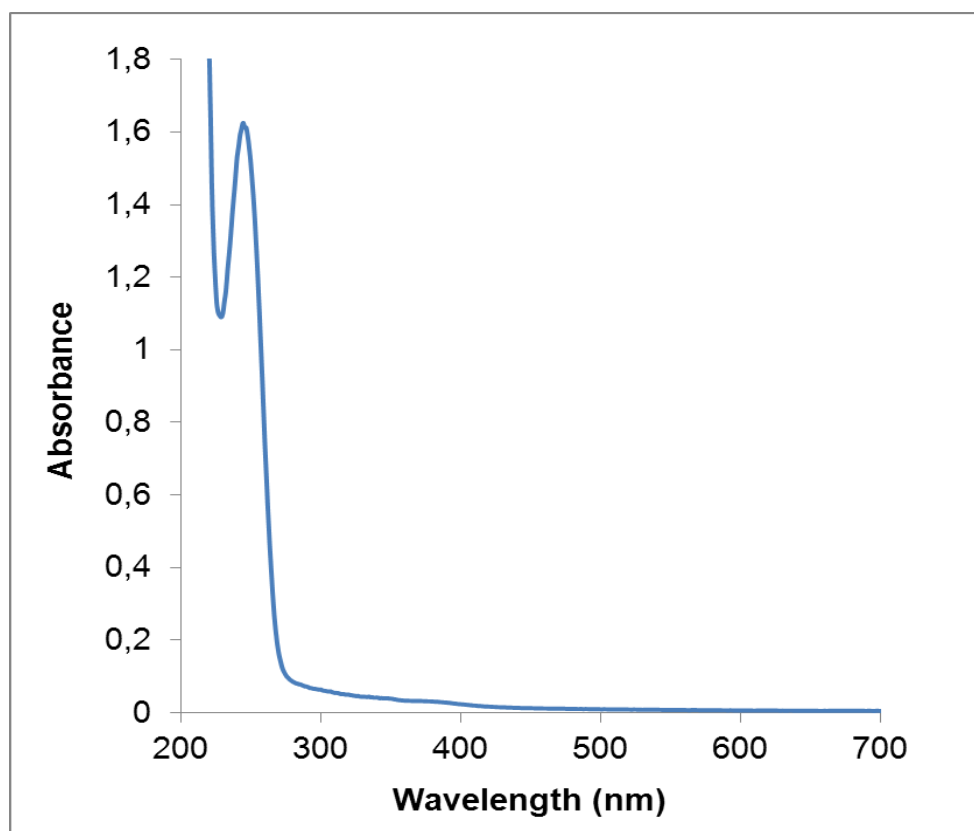
E.S.I. 09: UV-visible spectrum of [(TTA)Fe(OTf)₂] (1.06 mM) in CH₃CN, R.T.



ESI 10: ^1H NMR spectrum of $[(\text{TTA})\text{Fe}(\text{OTf})_2]$ in CD_2Cl_2 at room temperature.



ESI 11: ^{19}F NMR spectrum of $[(\text{TTA})\text{Fe}(\text{OTf})_2]$ in CD_2Cl_2 at room temperature.



E.S.I. 12: UV-visible spectrum of [(TTA)Fe(OTf)₂] (ca. $7 \cdot 10^{-4}$ M) in CH₂Cl₂, R.T.