**Supplementary Materials**

**Single crystal structure analysis of two novel iron(II) coordination polymers with bridging 1,3,5-tris(1*H*-1,2,4-triazol-1-yl)methyl)benzene**

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**S1 Used chemicals**

**Table S1.** Overview of used chemicals.

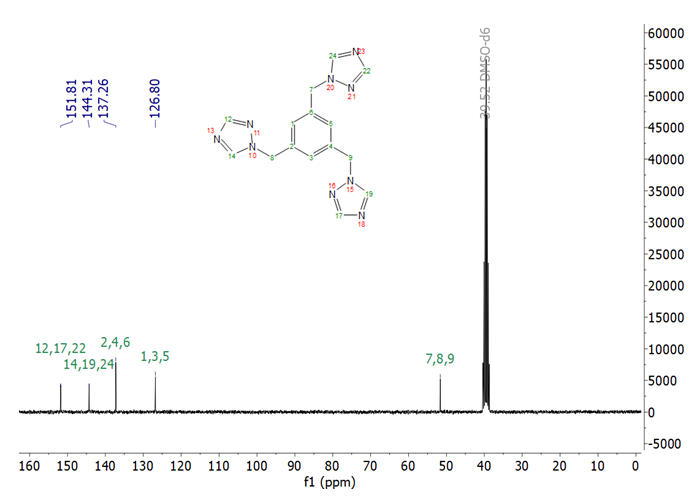
|  |  |  |
| --- | --- | --- |
| **Chemical** | **Supplier** | **Purity** |
| 1,2,4‑Triazole | BLDpharm | 97% |
| 1,3,5‑Tris(bromomethyl)benzene | BLDpharm | 99.44% |
| Acetonitrile | Riedel-de Haën | 99.9% |
| Ascorbic acid | Roth | 99% |
| Chloroform | Fisher | 99.8% |
| DSMO-d6 | Sigma-Aldrich | 99.9% |
| Ethanol | Chemsolute | 99.9% |
| Fe(BF4)2·6H2O | Merck | 97% |
| Fe(ClO4)2·xH2O | Sigma-Aldrich | 98% |
| KOH | Merck | p.a. |
| MgSO4 | Fisher Chemical | 99% |
| (NH4)2Fe(SO4)2·6H2O | Fluka | 99% |
| NH4SCN | Riedel‑de Haën | 99% |

**S2 Ligand analyses**

To eliminate the water signals in the spectrum, the sample was dried at 60 °C in vacuo before the analyses.

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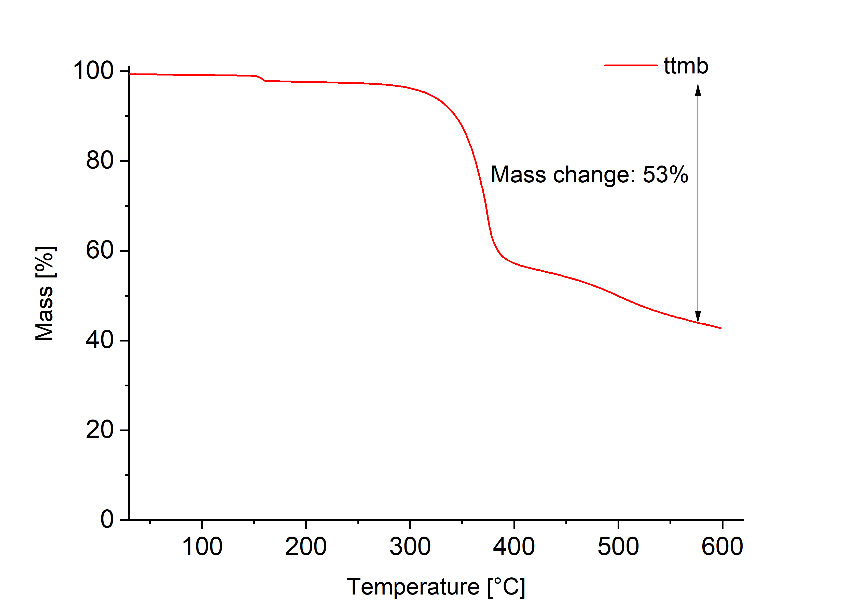
**Figure S1.** 1H-NMR spectrum (300 MHz, DMSO-d6) of ttmb. The water peak of the used DMSO-d6 is still visible since it is difficult to avoid the content of water in the solvent.

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**Figure S2.** 13C{1H}-NMR spectrum (75 MHz, DMSO-d6) of ttmb.

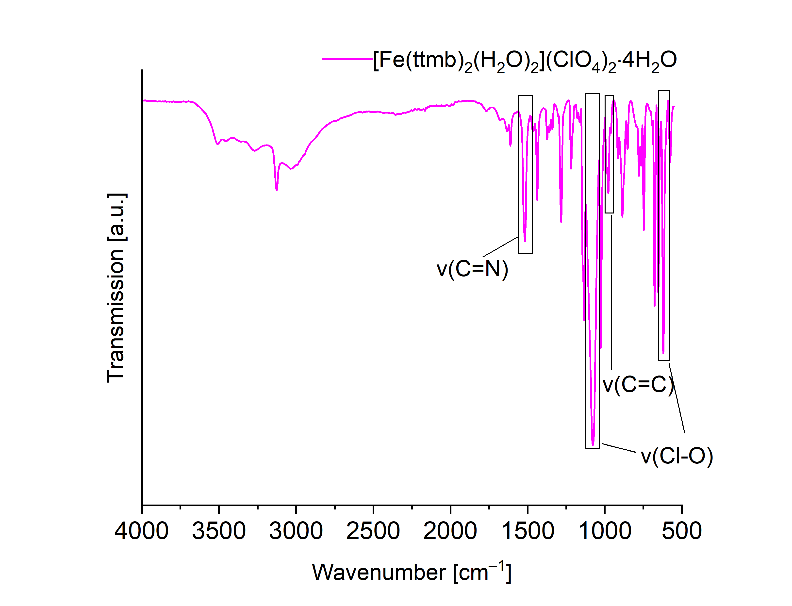
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**Figure S3.** IR spectrum of ttmb (ATR).

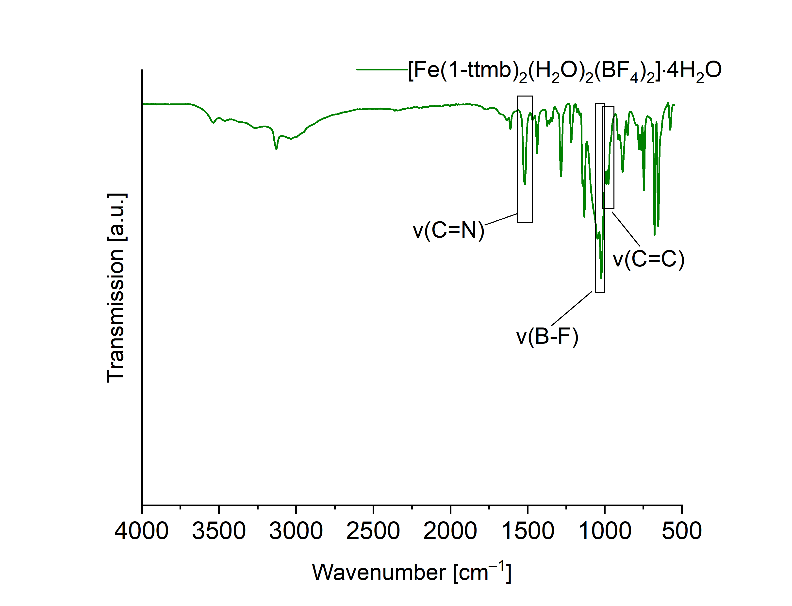


**Figure S4.** TGA of ttmb (heating rate 5 K min–1).

**S3 Infrared spectra of 1-3**

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**Figure S5.** IR spectrum of **1** (ATR).

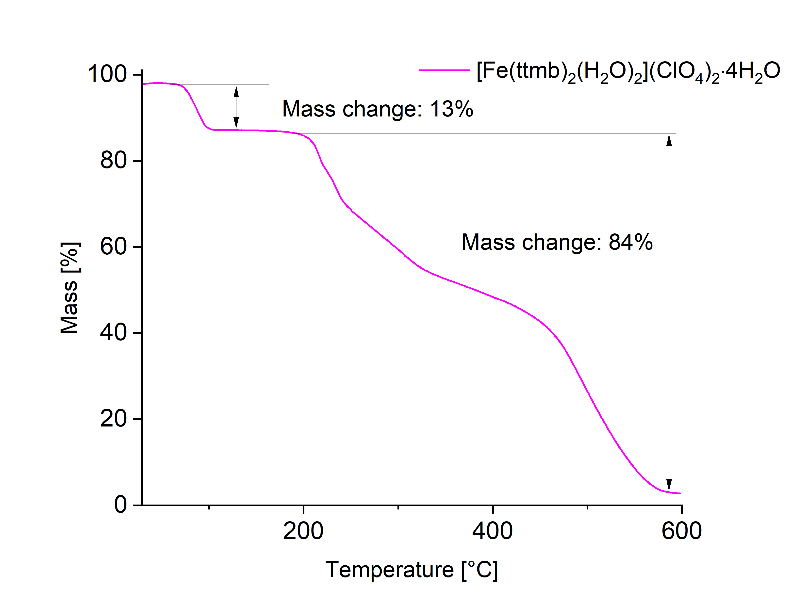


**Figure S6.** IR spectrum of **2** (ATR).

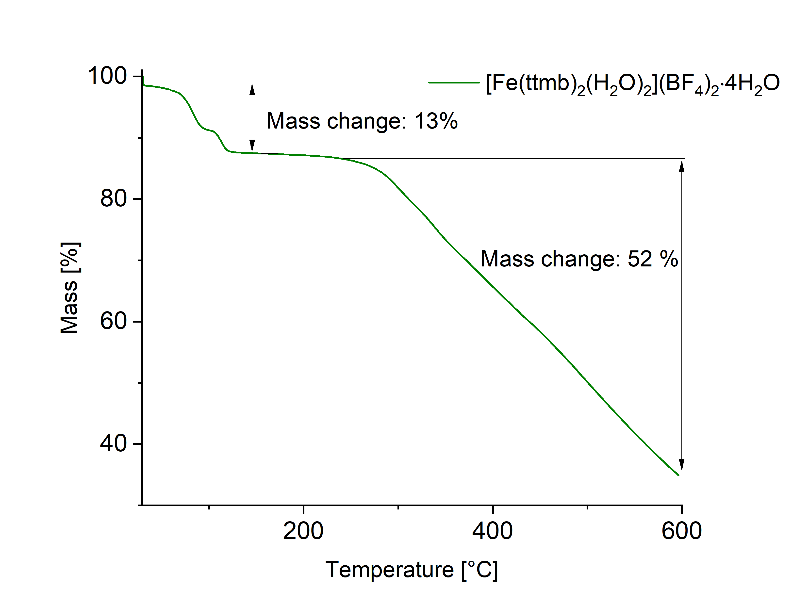
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**Figure S7.** IR spectrum of **3** (ATR).

**S4 Thermogravimetric analyses of 1-3**



**Figure S8.** TGA of **1** (heating rate 5 K min–1). Caution! If **1** is dried at 60 °C in vacuo before the TGA, an explosion is visible at 200 °C.



**Figure S9.** TGA of **2** (heating rate 5 K min–1).

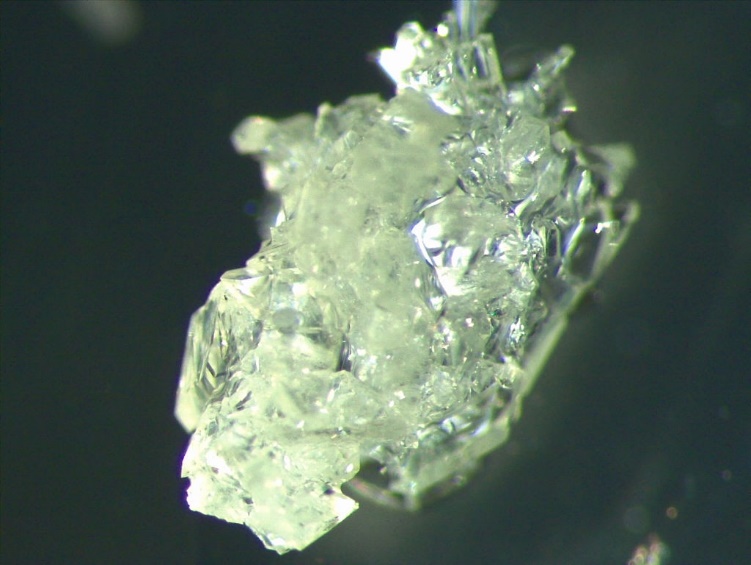


**Figure S10.** TGA of **3** (heating rate 5 K min–1).

**S5 Crystal images of 1-3**

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**Figure S11.** Crystal image of **1**.

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**Figure S12.** Crystal image of **2**.

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**Figure S13.** Crystal image of **3**.

**S6 Crystal data of 1-3**

**Table S2.** Crystal data for compounds **1-3**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **1** | **2** | **3** |
| CCDC no. | 2297073 | 2297074 | 2297075 |
| Empirical formula | C30H34FeN18O2·2(ClO4)·4(H2O) | C30H34FeN18O2·2(BF4)·4(H2O) | C32H30FeN20S2 |
| Mr [g/mol] | 1005.56 | 980.28 | 814.73 |
| Temperature [K] | 294 | 273 | 298 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | *P*21/*n* | *P*21/*n* | *P* |
| a [Å] | 8.9918(1) | 8.9379(8) | 8.5918(4) |
| b [Å] | 18.0165(2) | 17.9291(16) | 9.4947(3) |
| c [Å] | 13.4614(2) | 13.4514(13) | 11.7005(3) |
| α [°] | 90 | 90 | 80.490(2) |
| β [°] | 91.565(1) | 91.562(4) | 85.194(3) |
| γ [°] | 90 | 90 | 89.497(3) |
| Volume [Å3] | 2179.94(5) | 2154.8 | 938.05 |
| Z | 2 | 2 | 1 |
| ρcalc [g/cm3] | 1.532 | 1.511 | 1.442 |
| μ [mm–1] | 4.64 | 0.45 | 4.72 |
| F(000) | 1040 | 1008 | 420 |
| Crystal size [mm3] | 0.37 × 0.19 × 0.08 | 0.5 × 0.2 × 0.2 | 0.13 × 0.07 × 0.06 |
| Wavelength [Å] | 1.54184 | 0.71073 | 1.54184 |
| No. of unique reflections | 3890 | 4915 | 3321 |
| No. of total reflections | 16794 | 15411 | 10116 |
| Rint | 0.040 | 0.024 | 0.039 |
| R[F2 > 2s(F2)] | 0.045 | 0.044 | 0.038 |
| wR(F2) | 0.127 | 0.138 | 0.104 |

**Table S3.** Selected bond lengths and bond angles for **1-3**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound 1** | | | |
| **Bond lengths [Å]** | | | |
| Fe1—O1 | 2.0745(19) | Fe1—N1i | 2.2014(19) |
| Fe1—O1i | 2.0746(19) | Fe1—N7ii | 2.227(2) |
| Fe1—N1 | 2.2014(19) | Fe1—N7iii | 2.227(2) |
| **Bond angles [°]** | | | |
| O1—Fe1—O1i | 180.00(4) | O1—Fe1—N7ii | 91.48(8) |
| O1i—Fe1—N1 | 93.54(8) | N1—Fe1—N1i | 180.0 |
| O1i—Fe1—N1i | 86.46(8) | N1i—Fe1—N7ii | 93.34(7) |
| O1—Fe1—N1 | 86.46(8) | N1—Fe1—N7ii | 86.66(7) |
| O1—Fe1—N1i | 93.54(8) | N1i—Fe1—N7iii | 86.66(7) |
| O1i—Fe1—N7ii | 88.52(8) | N1—Fe1—N7iii | 93.34(7) |
| O1i—Fe1—N7iii | 91.48(8) | N7ii—Fe1—N7iii | 180.00(11) |
| O1—Fe1—N7iii | 88.52(8) |  |  |
| Symmetry transformations: i = -x+1, -y+1, -z; ii = -x+1, -y+1, -z+1; iii = x, y, z-1; iv = x, y, z+1. (v) -x+2, -y+1, -z+1; vi = x-1/2, -y+3/2, z-1/2; vii = -x+3/2, y-1/2, -z+3/2; viii = x+1, y, z+1. | | | |

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound 2** | | | |
| **Bond lengths [Å]** | | | |
| Fe1—O1i | 2.0781(14) | Fe1—N1 | 2.1940(15) |
| Fe1—O1 | 2.0781(14) | Fe1—N9ii | 2.2179(16) |
| Fe1—N1i | 2.1940(15) | Fe1—N9iii | 2.2179(16) |
| **Bond angles [°]** | | | |
| O1i—Fe1—O1 | 180.0 | O1i—Fe1—N9ii | 91.60(7) |
| O1—Fe1—N1 | 93.72(6) | N1—Fe1—N1i | 180.00(8) |
| O1—Fe1—N1i | 86.28(6) | N1i—Fe1—N9ii | 93.50(6) |
| O1i—Fe1—N1 | 86.28(6) | N1—Fe1—N9ii | 86.50(6) |
| O1i—Fe1—N1i | 93.72(6) | N1—Fe1—N9iii | 93.50(6) |
| O1—Fe1—N9ii | 88.40(6) | N1i—Fe1—N9iii | 86.50(6) |
| O1—Fe1—N9iii | 91.60(7) | N9ii—Fe1—N9iii | 180.0 |
| O1i—Fe1—N9iii | 88.40(6) |  |  |
| Symmetry transformations: i = −x+2, −y+1, −z+2; ii = −x+2, −y+1, −z+1; iii = x, y, z+1; iv = x, y, z−1; v = −x+1, −y+1, −z+1; vi = −x+3/2, y+1/2, −z+3/2. | | | |

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound 3** | | | |
| **Bond lengths [Å]** | | | |
| Fe1—N1i | 2.1813(17) | Fe1—N7iii | 2.2150(17) |
| Fe1—N1 | 2.1813(17) | Fe1—N10 | 2.143(2) |
| Fe1—N7ii | 2.2150(17) | Fe1—N10i | 2.143(2) |
| **Bond angles [°]** | | | |
| N1i—Fe1—N1 | 180.0 | N10i—Fe1—N1i | 90.09(7) |
| N1—Fe1—N7ii | 95.59(6) | N10—Fe1—N1 | 90.09(7) |
| N1i—Fe1—N7iii | 95.59(6) | N10—Fe1—N7ii | 89.32(7) |
| N1—Fe1—N7iii | 84.41(6) | N10i—Fe1—N7iii | 89.32(7) |
| N1i—Fe1—N7ii | 84.41(6) | N10i—Fe1—N7ii | 90.68(7) |
| N7ii—Fe1—N7iii | 180.00(9) | N10—Fe1—N7iii | 90.68(7) |
| N10—Fe1—N1i | 89.91(7) | N10—Fe1—N10i | 180.0 |
| N10i—Fe1—N1 | 89.91 (7) |  |  |
| Symmetry transformations: i = -x+1, -y+2, -z; ii = x, y+1, z-1; iii = -x+1, -y+1, -z+1; iv = x, y-1, z+1; v = -x, -y+1, -z+1; vi = x, y-1, z. | | | |

**Table S4.** Hydrogen-bond geometry for **1-3**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound 1** | | | | |
| ***D*—H···*A*** | ***D*—H [Å]** | **H···*A* [Å]** | ***D*···*A* [Å]** | ***D*—H···*A* [°]** |
| C1—H1···N8v | 0.93 | 2.50 | 3.346 (3) | 151 |
| C2—H2···O6vi | 0.93 | 2.44 | 3.264 (4) | 148 |
| C10—H10A···N2ii | 0.97 | 2.65 | 3.572 (4) | 158 |
| C12—H12···O6vii | 0.87 (4) | 2.51 (4) | 3.279 (5) | 148 (4) |
| C13—H13A···O2viii | 0.97 | 2.59 | 3.436 (4) | 145 |
| C15—H15···O7 | 0.93 | 2.54 | 3.386 (5) | 152 |
| O2—H2A···N5 | 1.03 | 2.31 | 2.904 | 115 |
| O3—H3C···N2 | 0.96 | 2.17 | 3.020 | 148 |
| O1—H1A···O2 | 0.74 | 1.90 | 2.643 | 176 |
| O2—H2A···O7 | 1.03 | 2.50 | 3.435 | 151 |
| O2—H2B···O3 | 0.91 | 1.87 | 2.745 | 160 |
| O3—H3D···O4 | 1.04 | 2.57 | 3.050 | 108 |
| O3—H3D···O5 | 1.04 | 2.48 | 3.424 | 152 |
| Symmetry transformations: ii = -*x*+1, -*y*+1, -*z*+1; v = -*x*+2, -*y*+1, -*z*+1; vi = *x*-1/2, -*y*+3/2, *z*-1/2; vii = -*x*+3/2, *y*-1/2, -*z*+3/2; viii = *x*+1, *y*, *z*+1. | | | | |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound 2** | | | | |
| ***D*—H···*A*** | ***D*—H [Å]** | **H···*A* [Å]** | ***D*···*A* [Å]** | ***D*—H···*A* [°]** |
| C1—H1···F4Bi | 0.93 | 2.50 | 3.218(7) | 134 |
| C1—H1···F4Ai | 0.93 | 2.47 | 3.308(8) | 151 |
| C2—H2···N8v | 0.93 | 2.49 | 3.329(3) | 151 |
| C10—H10A···N3ii | 0.97 | 2.61 | 3.537(3) | 161 |
| C12—H12···F4Biv | 0.93 | 2.45 | 3.362(9) | 167 |
| C12—H12···F2Aiv | 0.93 | 2.55 | 3.290(9) | 136 |
| C12—H12···F4Aiv | 0.93 | 2.40 | 3.196(6) | 144 |
| C13—H13A···O2v | 0.97 | 2.58 | 3.419(3) | 145 |
| C14—H14···F2Bvi | 0.93 | 2.46 | 3.243(8) | 142 |
| C14—H14···F2Avi | 0.93 | 2.51 | 3.357(10) | 152 |
| O2—H2A···N5 | 0.85 | 2.32 | 2.895(27) | 125 |
| O3—H3C···N3 | 0.85 | 2.36 | 3.025(34) | 136 |
| O1—H1A···O2 | 0.85 | 1.78 | 2.626(27) | 177 |
| O2—H2B···O3 | 0.85 | 1.88 | 2.723(40) | 170 |
| Symmetry transformations: i = −x+2, −y+1, −z+2; ii = −x+2, −y+1, −z+1; iv = x, y, z−1; v = −x+1, −y+1, −z+1; vi = −x+3/2, y+1/2, −z+3/2. | | | | |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound 3** | | | | |
| ***D*—H···*A*** | ***D*—H [Å]** | **H···*A* [Å]** | ***D*···*A* [Å]** | ***D*—H···*A* [°]** |
| C2—H2···N8v | 0.93 | 2.45 | 3.256 (3) | 146 |
| C12—H12···N2iii | 0.93 | 2.64 | 3.484 (4) | 152 |
| C13—H13B···S1vi | 0.97 | 2.75 | 3.668 (2) | 157 |
| C15—H15···S1iii | 0.93 | 2.98 | 3.877 (2) | 163 |
| Symmetry transformations: iii = -x+1, -y+1, -z+1; v = -x, -y+1, -z+1; vi = x, y-1, z. | | | | |

**S7 Distortion of the Fe coordination polyhedra of 1-3**

The indices for distortion were calculated using OctaDist software [1]. The distortion parameters were calculated as follows:

ζ parameter [2]:

di: individual M–L bond distance

dmean: mean metal-ligand bond distance

Σ parameter [3]:

: individual cis angle

θ parameter [4]:

θi: individual angle between two vectors of two twisting face

These parameters are zero for a perfect octahedron.

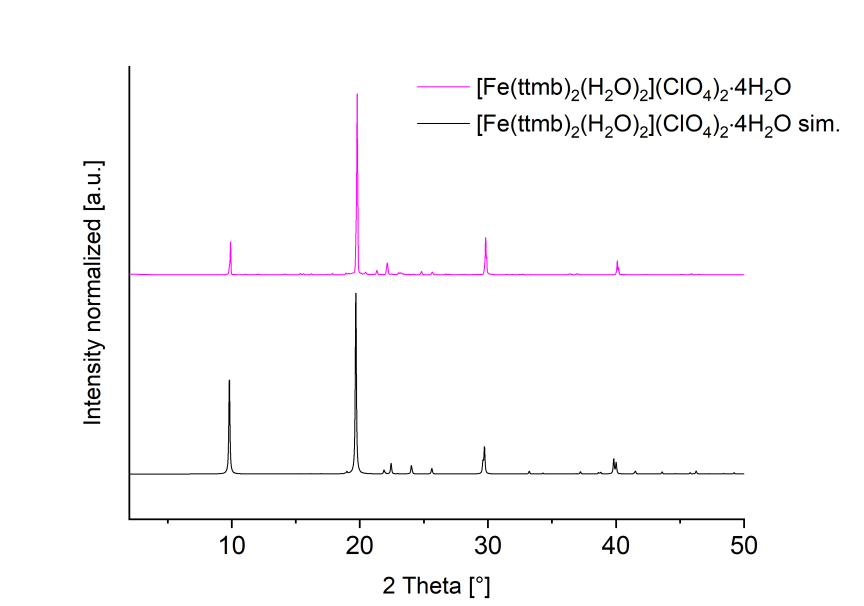
The values Σ and θ are derived by summation over the absolute values of all 12 differences 90 – ϕi and 24 differences 60 – θi, respectively, in the octahedron. The angles ϕi and θi are 90° and 60°, respectively, giving the parameters Σ and θ as zero for a perfect octahedron [1]. However, a very small deviation in ϕi and θi by only 1° will already result in Σ = 12° and θ = 24°.

The Fe(II) atoms in compound **1-3** are in a somewhat distorted coordination environment [5] (Table S5).

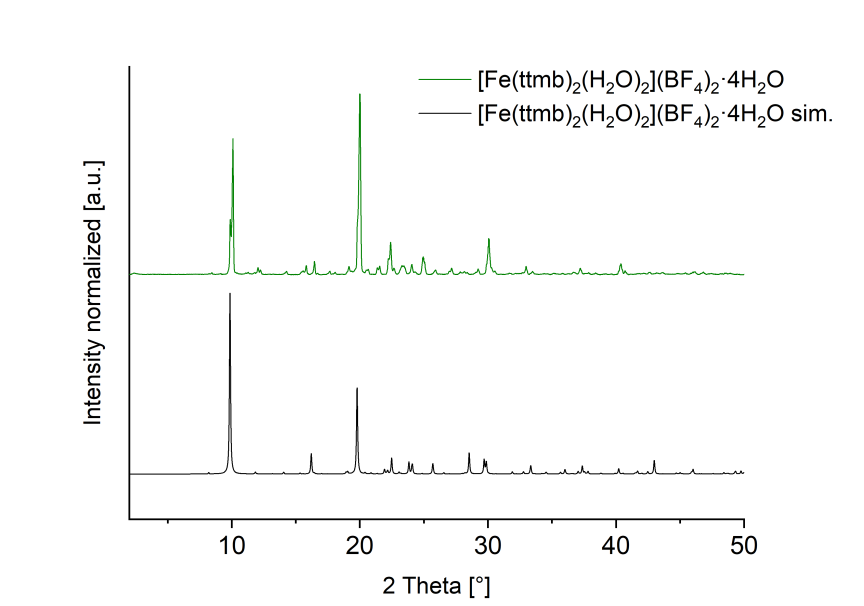
**Table S5.**Mean M–L distance and values for distortion indices of the metal atom coordination environment in compounds **1-3**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Compound | M | Mean distance  <D> [Å] | Distance distortion  ζ [Å] | Angle distortion  Σ [°] | Torsional distortion  θ [°] |
| **1** | Fe1 | 2.17 | 0.37 | 33.47 | 89.64 |
| **2** | Fe1 | 2.16 | 0.34 | 35.27 | 93.84 |
| **3** | Fe1 | 2.18 | 0.15 | 25.52 | 103.91 |

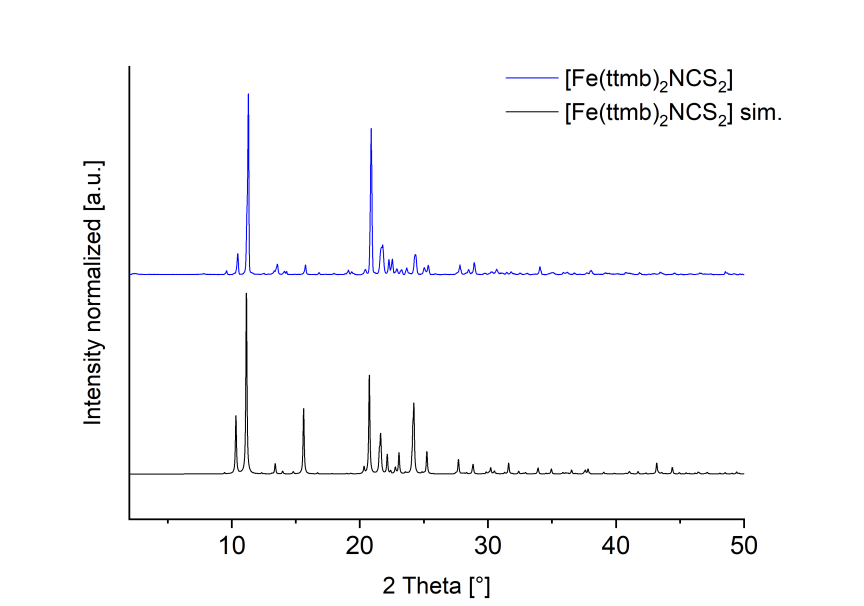
**S8 Powder X-ray diffraction patterns of 1-3**



**Figure S14.** Powder X-ray diffraction pattern of **1** compared to the simulation with preferred orientation (h = -7, k = 0, l = -6, March-Dollase = 10).



**Figure S15.** Powder X-ray diffraction pattern of **2** compared to the simulation with preferred orientation (h = -6, k = 0, l = -3, March-Dollase =5).



**Figure S16.** Powder X-ray diffraction pattern of **3** compared to the simulation with preferred orientation (h = -2, k = 8, l = -16, March-Dollase = 3).

**S9 References**

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