

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

Aysenur Limon ¹, Dustin N. Jordan ¹, Till Strothmann ¹, Laure P. Cuignet ^{1,2}, Yann Garcia ², and Christoph Janiak ^{*,1}

¹ *Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität, Universitätsstraße 1, 40225 Düsseldorf, Germany*

² *Institute of Condensed Matter and Nanosciences, Molecular Chemistry, Materials and Catalysis (IMCN/MOST), Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium*

Emails: aysenur.limon@uni-duesseldorf.de, dustin.jordan@uni-duesseldorf.de, till.strothmann@uni-duesseldorf.de, laure.cuignet@sciensano.be, yann.garcia@uclouvain.be, janiak@uni-duesseldorf.de

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S1 Chemicals used

Table S1. Overview of chemicals used.

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-d ₆	Sigma-Aldrich	99.9%
Ethanol	Chemsolute	99.9%
Fe(BF ₄) ₂ ·6H ₂ O	Merck	97%
Fe(ClO ₄) ₂ ·xH ₂ O	Sigma-Aldrich	98%
KOH	Merck	p.a. ^{a)}
MgSO ₄	Fisher Chemical	99%
(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	Fluka	99%
NH ₄ SCN	Riedel-de Haën	99%

^{a)} p.a. = pro analysis (purity grade).

S2 Ligand analyses

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

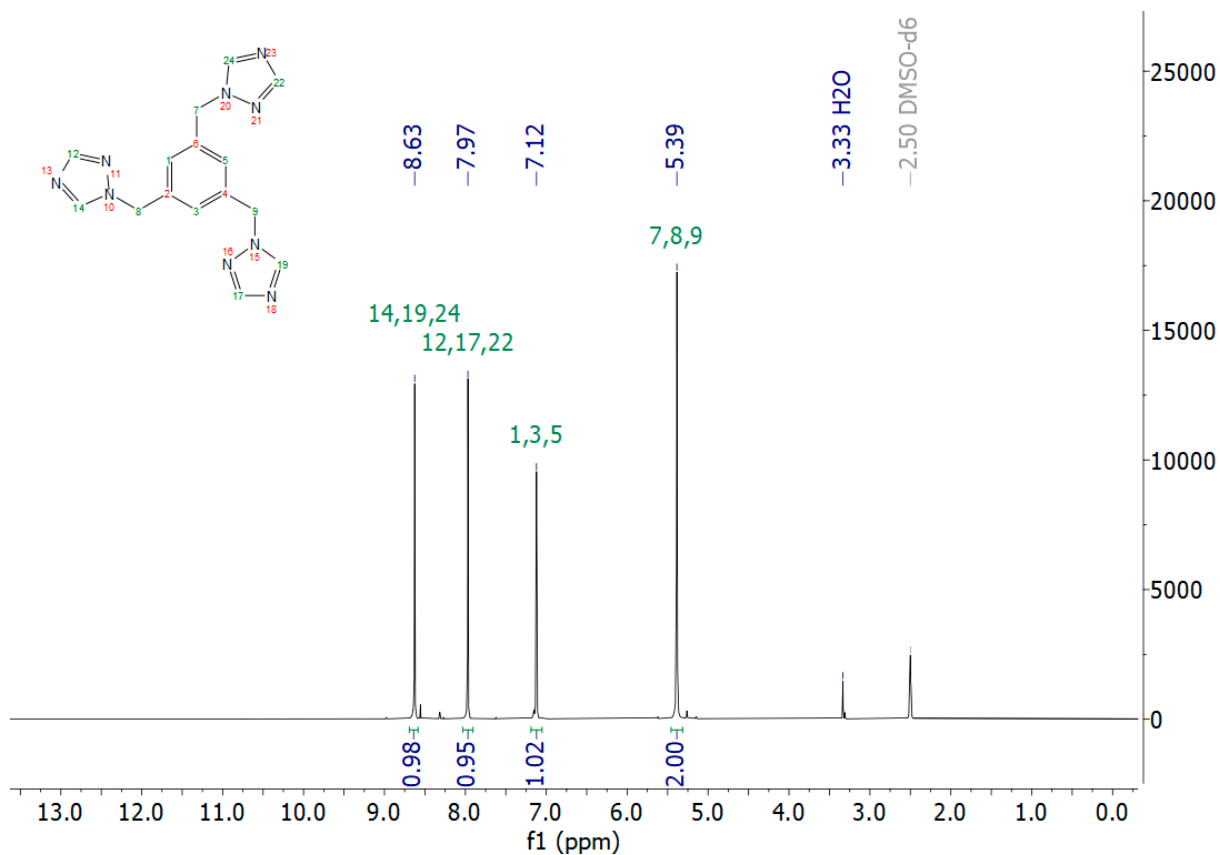


Figure S1. ¹H-NMR spectrum (300 MHz, DMSO-d₆) of ttmb. The water peak of the used DMSO-d₆ is still visible, as it is difficult to avoid the water in the solvent.

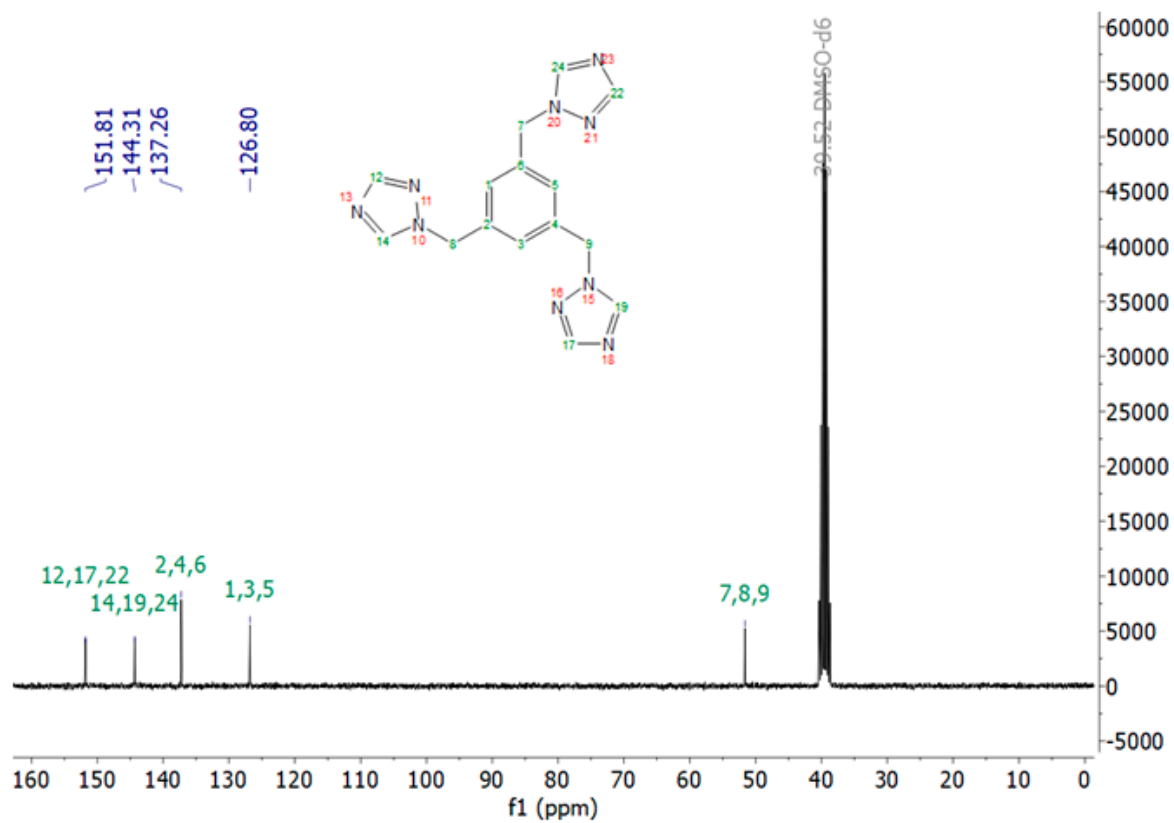


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (75 MHz, DMSO- d_6) of tmb.

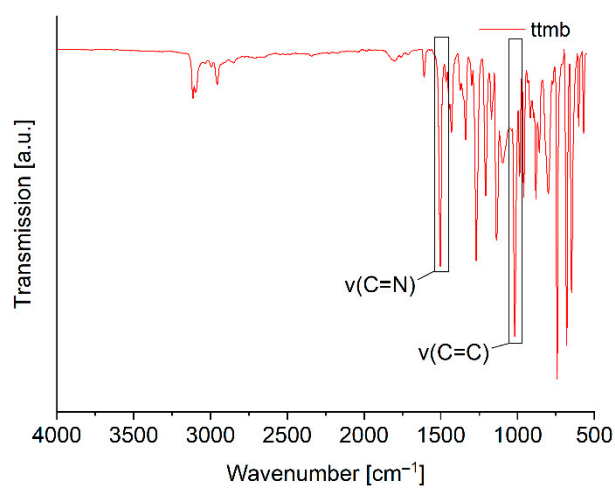


Figure S3. IR spectrum of tmb (attenuated total reflection, ATR).

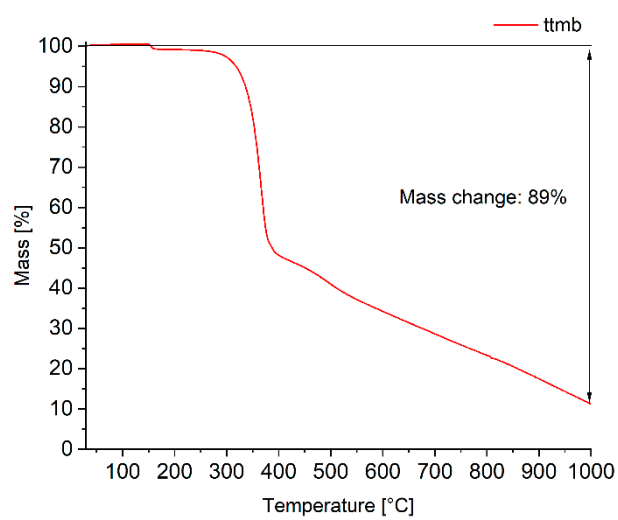


Figure S4. TGA of tmb (heating rate 5 K min⁻¹).

S3 Infrared spectra of compounds 1–3

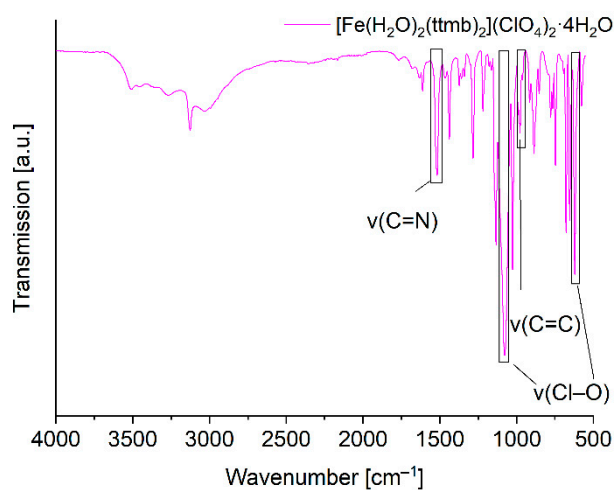


Figure S5. IR spectrum of compound 1 (ATR).

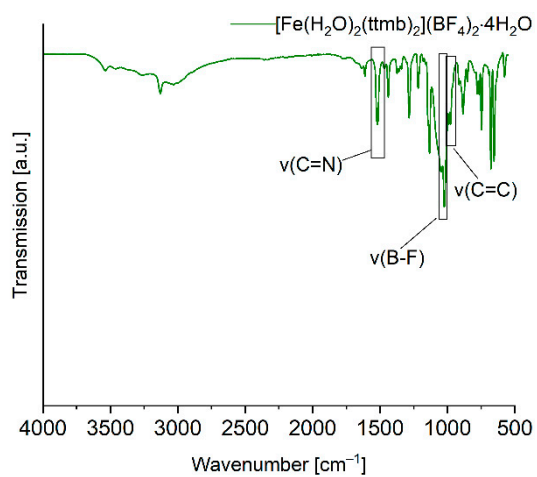


Figure S6. IR spectrum of compound 2 (ATR).

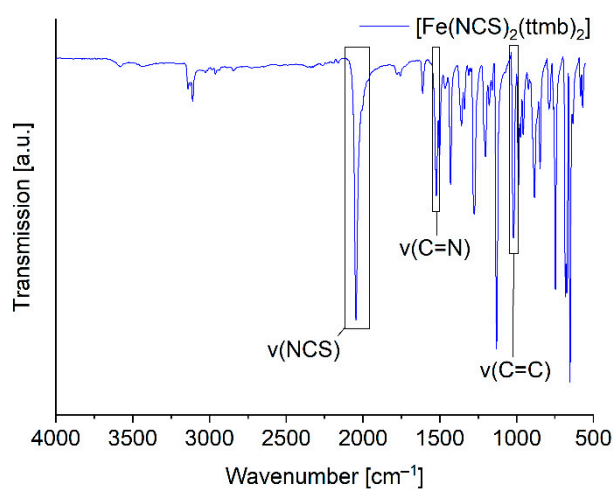


Figure S7. IR spectrum of compound 3 (ATR).

S4 Thermogravimetric analyses of compounds 1–3

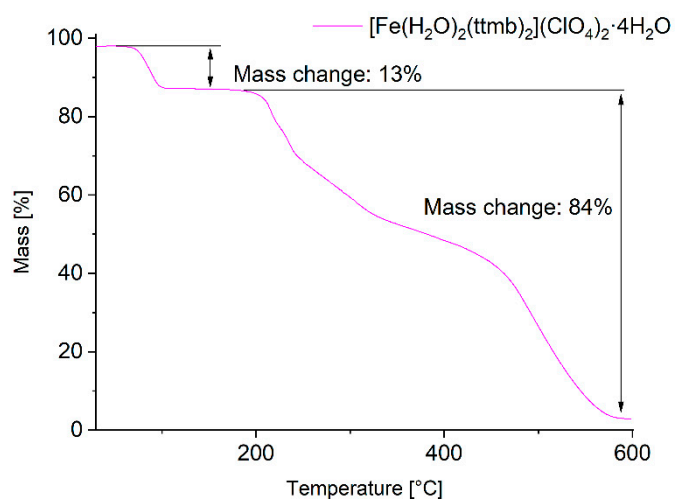


Figure S8. TGA of compound **1** (heating rate 5 K min⁻¹). Caution! If compound **1** is dried at 60 °C in vacuo before the TGA, an explosion will occur at 200 °C.

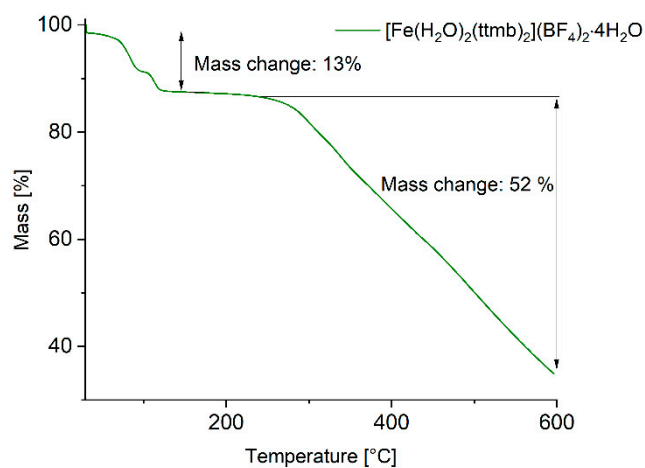


Figure S9. TGA of compound **2** (heating rate 5 K min⁻¹).

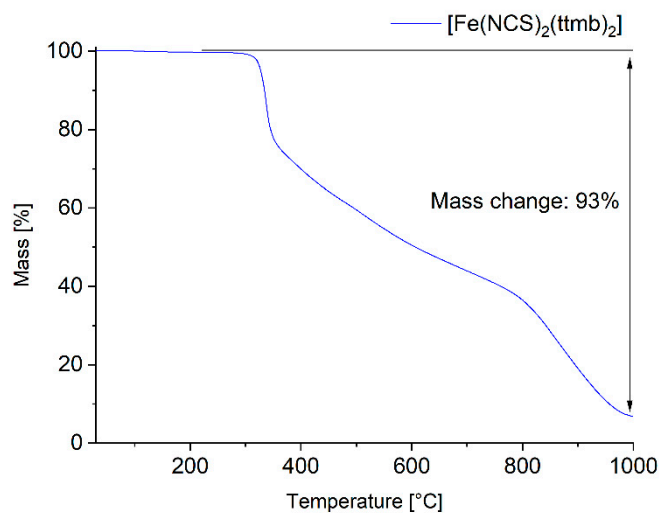


Figure S10. TGA of compound **3** (heating rate 5 K min⁻¹).

S5 Crystal images of compounds 1–3

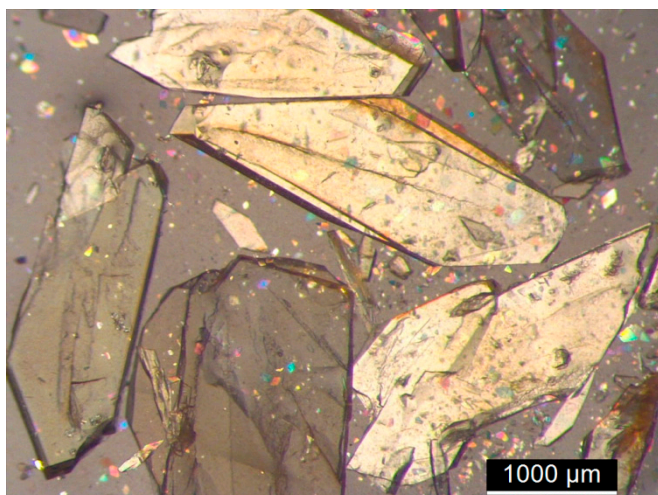


Figure S11. Crystal image of compound 1.

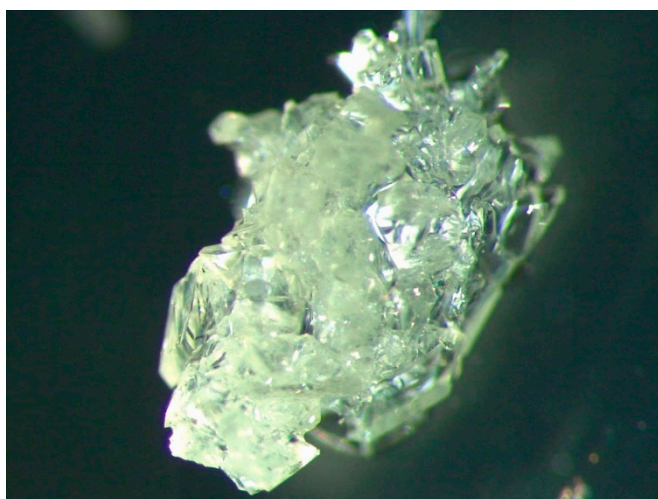


Figure S12. Crystal image of compound 2.

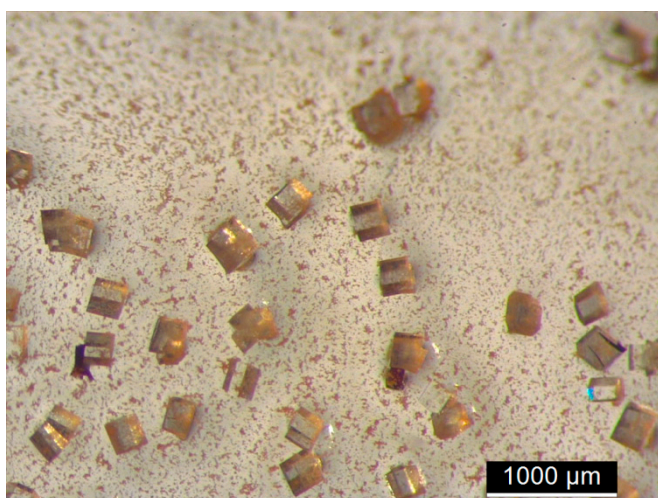


Figure S13. Crystal image of compound 3.

S6 Crystal data of compounds 1–3

Table S2. Crystal data for compounds 1–3.

Compound	1	2	3
CCDC no.	2297073	2297074	2297075
Empirical formula	C ₃₀ H ₃₄ FeN ₁₈ O ₂ ·2(ClO ₄)·4(H ₂ O)	C ₃₀ H ₃₄ FeN ₁₈ O ₂ ·2(BF ₄)·4(H ₂ O)	C ₃₂ H ₃₀ FeN ₂₀ S ₂
M _r [g/mol]	1005.56	980.28	814.73
Temperature [K]	294	273	298
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
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 [Å ³]	2179.94(5)	2154.8	938.05
Z	2	2	1
Q _{calc} [g/cm ³]	1.532	1.511	1.442
μ [mm ⁻¹]	4.64	0.45	4.72
F(000)	1040	1008	420
Crystal size [mm ³]	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
R _{int}	0.040	0.024	0.039
R[F ² > 2σ(F ²)]	0.045	0.044	0.038
wR(F ²)	0.127	0.138	0.104

Table S3. Selected bond lengths and bond angles for compounds 1–3.

Compound 1			
Bond lengths [Å]			
Fe1—O1	2.0745(19)	Fe1—N1 ⁱ	2.2014(19)
Fe1—O1 ⁱ	2.0746(19)	Fe1—N7 ⁱⁱ	2.227(2)
Fe1—N1	2.2014(19)	Fe1—N7 ⁱⁱⁱ	2.227(2)
Bond angles [°]			
O1—Fe1—O1 ⁱ	180.00(4)	O1—Fe1—N7 ⁱⁱ	91.48(8)
O1 ⁱ —Fe1—N1	93.54(8)	N1—Fe1—N1 ⁱ	180.0
O1 ⁱ —Fe1—N1 ⁱ	86.46(8)	N1 ⁱ —Fe1—N7 ⁱⁱ	93.34(7)
O1—Fe1—N1	86.46(8)	N1—Fe1—N7 ⁱⁱ	86.66(7)
O1—Fe1—N1 ⁱ	93.54(8)	N1 ⁱ —Fe1—N7 ⁱⁱⁱ	86.66(7)
O1 ⁱ —Fe1—N7 ⁱⁱ	88.52(8)	N1—Fe1—N7 ⁱⁱⁱ	93.34(7)
O1 ⁱ —Fe1—N7 ⁱⁱⁱ	91.48(8)	N7 ⁱⁱ —Fe1—N7 ⁱⁱⁱ	180.00(11)
O1—Fe1—N7 ⁱⁱⁱ	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—O1 ⁱ	2.0781(14)	Fe1—N1	2.1940(15)
Fe1—O1	2.0781(14)	Fe1—N9 ⁱⁱ	2.2179(16)
Fe1—N1 ⁱ	2.1940(15)	Fe1—N9 ⁱⁱⁱ	2.2179(16)
Bond angles [°]			
O1 ⁱ —Fe1—O1	180.0	O1 ⁱ —Fe1—N9 ⁱⁱ	91.60(7)
O1—Fe1—N1	93.72(6)	N1—Fe1—N1 ⁱ	180.00(8)
O1—Fe1—N1 ⁱ	86.28(6)	N1 ⁱ —Fe1—N9 ⁱⁱ	93.50(6)
O1 ⁱ —Fe1—N1	86.28(6)	N1—Fe1—N9 ⁱⁱ	86.50(6)
O1 ⁱ —Fe1—N1 ⁱ	93.72(6)	N1—Fe1—N9 ⁱⁱⁱ	93.50(6)
O1—Fe1—N9 ⁱⁱ	88.40(6)	N1 ⁱ —Fe1—N9 ⁱⁱⁱ	86.50(6)
O1—Fe1—N9 ⁱⁱⁱ	91.60(7)	N9 ⁱⁱ —Fe1—N9 ⁱⁱⁱ	180.0
O1 ⁱ —Fe1—N9 ⁱⁱⁱ	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—N1 ⁱ	2.1813(17)	Fe1—N7 ⁱⁱⁱ	2.2150(17)
Fe1—N1	2.1813(17)	Fe1—N10	2.143(2)
Fe1—N7 ⁱⁱ	2.2150(17)	Fe1—N10 ⁱ	2.143(2)
Bond angles [°]			
N1 ⁱ —Fe1—N1	180.0	N10 ⁱ —Fe1—N1 ⁱ	90.09(7)
N1—Fe1—N7 ⁱⁱ	95.59(6)	N10—Fe1—N1	90.09(7)
N1 ⁱ —Fe1—N7 ⁱⁱⁱ	95.59(6)	N10—Fe1—N7 ⁱⁱ	89.32(7)
N1—Fe1—N7 ⁱⁱⁱ	84.41(6)	N10 ⁱ —Fe1—N7 ⁱⁱⁱ	89.32(7)
N1 ⁱ —Fe1—N7 ⁱⁱ	84.41(6)	N10 ⁱ —Fe1—N7 ⁱⁱ	90.68(7)
N7 ⁱⁱ —Fe1—N7 ⁱⁱⁱ	180.00(9)	N10—Fe1—N7 ⁱⁱⁱ	90.68(7)
N10—Fe1—N1 ⁱ	89.91(7)	N10—Fe1—N10 ⁱ	180.0
N10 ⁱ —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 compounds 1–3.

Compound 1				
<i>D</i> —H... <i>A</i>	<i>D</i> —H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> —H... <i>A</i> [°]
C1—H1...N8 ^v	0.93	2.50	3.346 (3)	151
C2—H2...O6 ^{vi}	0.93	2.44	3.264 (4)	148
C10—H10A...N2 ⁱⁱ	0.97	2.65	3.572 (4)	158
C12—H12...O6 ^{vii}	0.87 (4)	2.51 (4)	3.279 (5)	148 (4)
C13—H13A...O2 ^{viii}	0.97	2.59	3.436 (4)	145
C15—H15...O7	0.93	2.54	3.386 (5)	152
O1—H1A...O2	0.75 (5)	1.90 (5)	2.643 (3)	176 (5)
O1—H1B...N4 ^{ix}	0.86 (5)	1.95 (5)	2.785 (3)	165 (4)
O2—H2A...N5 ⁱ	1.03 (7)	2.31 (7)	2.904 (3)	116 (5)

O2—H2A···O7 ⁱⁱⁱ	1.03 (7)	2.50 (7)	3.435 (6)	151 (5)
O2—H2B···O3	0.91 (3)	1.87 (2)	2.745 (4)	159 (5)
O3—H3C···N2 ^{vi}	0.95 (2)	2.17 (6)	3.020 (4)	148 (8)
O3—H3D···O5 ^{vi}	1.03 (10)	2.48 (8)	3.423 (7)	152 (7)

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 = $x + 1, y, z + 1$; ix = $-x + 3/2, y + 1/2, -z + 1/2$.

Compound 2

<i>D</i> —H··· <i>A</i>	<i>D</i> —H [Å]	H··· <i>A</i> [Å]	<i>D</i> ··· <i>A</i> [Å]	<i>D</i> —H··· <i>A</i> [°]
C1—H1···F4B ⁱ	0.93	2.50	3.218(7)	134
C1—H1···F4A ⁱ	0.93	2.47	3.308(8)	151
C2—H2···N8 ^v	0.93	2.49	3.329(3)	151
C10—H10A···N3 ⁱⁱ	0.97	2.61	3.537(3)	161
C12—H12···F4B ^{iv}	0.93	2.45	3.362(9)	167
C12—H12···F2A ^{iv}	0.93	2.55	3.290(9)	136
C12—H12···F4A ^{iv}	0.93	2.40	3.196(6)	144
C13—H13A···O2 ^v	0.97	2.58	3.419(3)	145
C14—H14···F2B ^{vi}	0.93	2.46	3.243(8)	142
C14—H14···F2A ^{vi}	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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H [Å]	H··· <i>A</i> [Å]	<i>D</i> ··· <i>A</i> [Å]	<i>D</i> —H··· <i>A</i> [°]
C2—H2···N8 ^v	0.93	2.45	3.256 (3)	146
C9—H9···N5 ^v	0.93	2.67	3.500 (3)	149
C12—H12···N2 ⁱⁱⁱ	0.93	2.64	3.484 (4)	152
C13—H13B···S1 ^{vi}	0.97	2.75	3.668 (2)	157
C15—H15···S1 ⁱⁱⁱ	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 compounds 1–3

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

ζ parameter [2]: $\zeta = \sum_{i=1}^6 |d_i - d_{mean}|$

d_i : individual M–L bond distance

d_{mean} : mean metal-ligand bond distance

Σ parameter [3]: $\Sigma = \sum_{i=1}^{12} |90 - \phi_i|$

ϕ_i : individual cis angle

θ parameter [4]: $\theta = \sum_{i=1}^{24} |60 - \theta_i|$

θ_i : 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 $90 - \phi_i$ and 24 differences $60 - \theta_i$, respectively, in the octahedron. The angles ϕ_i and θ_i are 90° and 60° , respectively, giving the parameters Σ and θ as zero for a perfect octahedron [1]. However, a very small deviation in ϕ_i and θ_i by only 1° will already result in $\Sigma = 12^\circ$ and $\theta = 24^\circ$.

The Fe(II) atoms in compounds **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 Photophysical spectra of ttmb and compounds 1–3

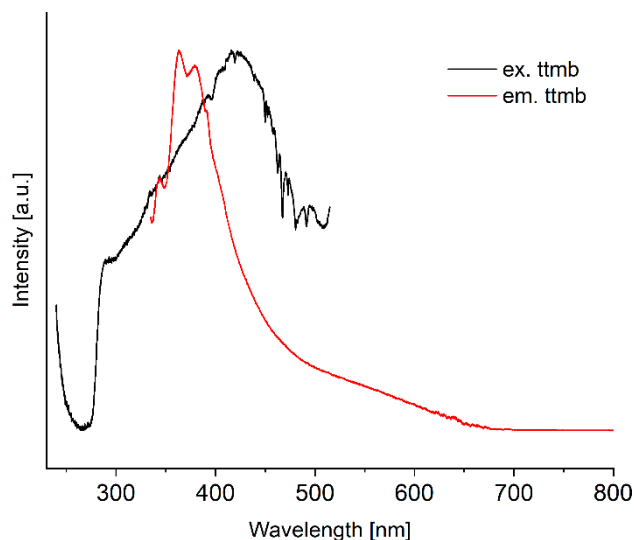


Figure S14. Excitation ($\lambda_{\text{em}} = 550 \text{ nm}$) and emission spectra ($\lambda_{\text{exc}} = 320 \text{ nm}$) of solid-phase ttmb at $T = 293 \text{ K}$.

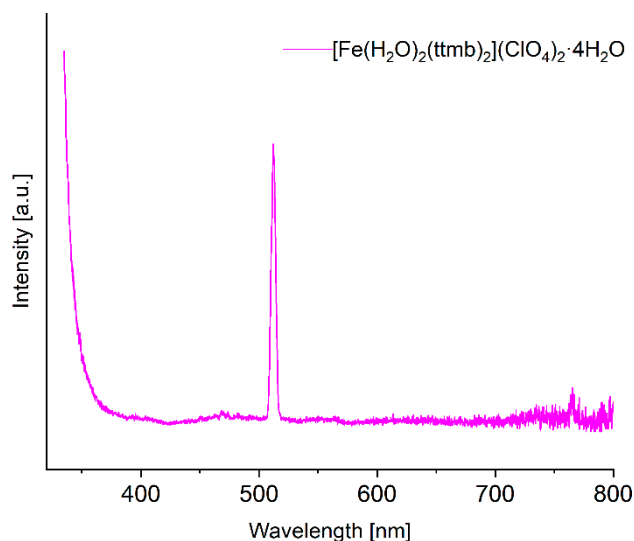


Figure S15. Emission spectrum ($\lambda_{\text{exc}} = 320 \text{ nm}$) of solid-phase compound **1** at $T = 293 \text{ K}$. The sharp peak at 512 nm is due to the xenon lamp.

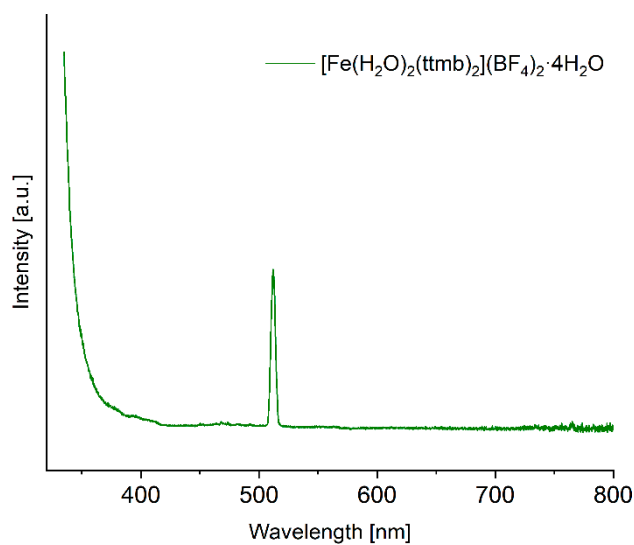


Figure S16. Emission spectrum ($\lambda_{\text{exc}} = 320 \text{ nm}$) of solid-phase compound **2** at $T = 293 \text{ K}$. The sharp peak at 512 nm is due to the xenon lamp.

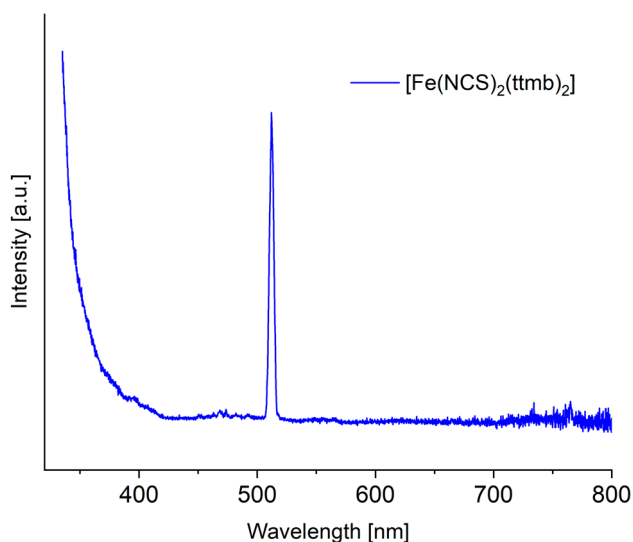


Figure S17. Emission spectrum ($\lambda_{\text{exc}} = 320$ nm) of solid-phase compound **3** at $T = 293$ K. The sharp peak at 512 nm is due to the xenon lamp.

S9 References

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