Supporting Information for

Popcorn-shaped Fe_xO (Wüstite) Nanoparticles from a Single-Source Precursor: Colloidal Synthesis and Magnetic Properties

Christoph P. Guntlin,[†, §] Stefan T. Ochsenbein, [†, §] Michael Wörle,[†] Rolf Erni,[‡] Kostiantyn V. Kravchyk, [†, §] and Maksym V. Kovalenko,[, †, §]*

[†]Department of Chemistry and Applied Biosciences, ETH Zürich - Laboratory for Inorganic Chemistry, Vladimir Prelog Weg 1, CH-8093 Zürich, Switzerland

[§]Laboratory for Thin Films and Photovoltaics and [‡]Electron Microscopy Center, Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

[*]E-mail: mvkovalenko@ethz.ch

Structure determination

Crystallographic information for $[Fe_3(\mu_3\text{-}O)(CF_3COO)(\mu\text{-}CF_3COO)_6(H_2O)_2]\cdot CF_3COOH$ ("Fe_3OTFA")

Single crystals of "Fe_3OTFA" were grown from crude synthesis solution by keeping it at room temperature (RT) under N_2 flow for several days.

The crystals disintegrate when cooled to 100 K. Therefore, the single crystal XRD measurement was done at 250 K. All CF_3-groups are strongly disordered and a free refinement without restraints/constraints was not possible due to high correlation matrix elements. The final description of each of the CF_3-groups has been done with disorder over two sites, anisotropic displacement parameters and distance restraints, forcing the C-F, F-F and some C-C-distances equal.

An alternative description of the disorder over three or four sites with isotropic displacement parameters led to higher R-values and significant residual electron density close to the disordered fluorine sites. The hydrogen atoms were found in the difference map, however, a free refinement was only possible with the hydrogen atom H2 at the TFA, and the water molecules were refined as rigid groups.

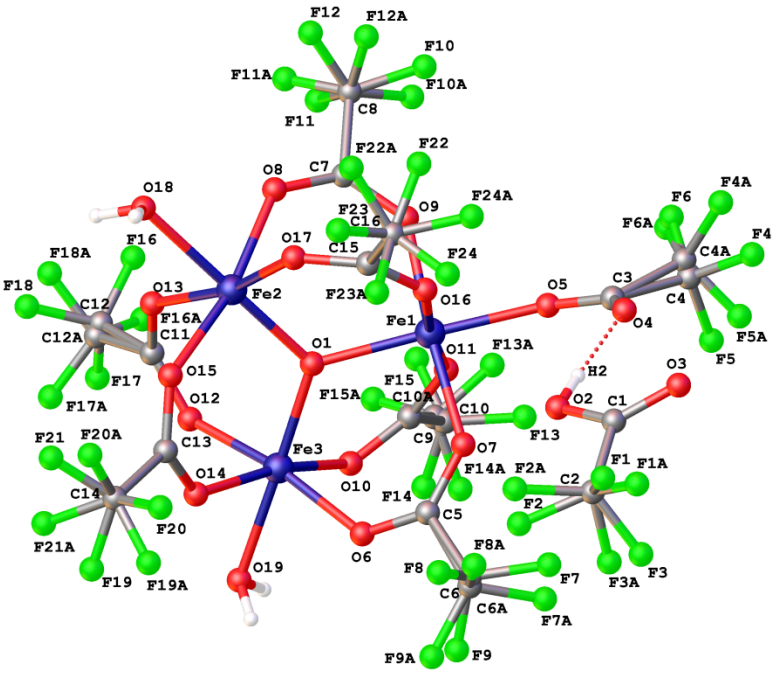

Figure S1. Crystal structure of "Fe_3OTFA". Because of large displacement parameters of fluorine, the structure is drawn with isotropic displacement parameters for clarity.

Table S1. Crystal data and structure refinement for "Fe_3OTFA".

CCDC number	**1559925**
Empirical formula	**$C_{16}H_5F_{24}Fe_3O_{19}$**
Formula weight / g mol^{-1}	**1124.75**
Temperature / K	**250**
Crystal system	**monoclinic**
Space group	***P*2$_1$/*n***
a / Å	**12.2131(19)**
b / Å	**15.207(2)**
c / Å	**20.901(4)**
α / °	**90**
β / °	**106.855(2)**
γ / °	**90**
Volume / $Å^3$	**3715.1(11)**
Z	**4**
ρ_{calc} / g cm^{-3}	**2.011**
μ / mm^{-1}	**1.347**
F(000)	**2188.0**
Crystal size / mm^3	**0.418 × 0.312 × 0.239**
Radiation	**Mo Kα (λ = 0.71073)**
2Θ range for data collection / °	**3.364 to 51.966**
Index ranges	**$-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$**
Reflections collected	**25309**
Independent reflections	**7200 [R_{int} = 0.0360]**
Data/restraints/parameters	**7200/846/801**
Goodness-of-fit on F^2	**1.043**
Final R indexes [I>=2σ (I)]	**R_1 = 0.0424, wR_2 = 0.1014**
Final R indexes [all data]	**R_1 = 0.0631, wR_2 = 0.1149**
Largest diff. peak/hole / e $Å^{-3}$	**0.37/-0.36**

Table S2. Bond lengths for "Fe_3OTFA".

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	1.959(2)	C14	F19	1.258(7)
Fe1	O5	1.944(2)	C14	F20	1.259(7)
Fe1	O7	2.018(2)	C14	F21	1.259(7)
Fe1	O9	2.009(3)	C15	C16	1.532(5)
Fe1	O11	2.002(2)	C16	F22	1.202(10)
Fe1	O16	2.014(2)	C16	F23	1.202(10)
Fe2	O1	1.885(2)	C16	F24	1.202(11)
Fe2	O8	1.989(3)	F4	C4	1.288(3)
Fe2	O13	2.017(2)	F5	C4	1.287(3)
Fe2	O15	2.003(3)	F6	C4	1.287(3)
Fe2	O17	2.000(2)	F7	C6	1.287(2)
Fe2	O18	2.064(2)	F8	C6	1.287(2)
Fe3	O1	1.904(2)	F9	C6	1.287(2)
Fe3	O6	1.990(2)	F13	C10	1.272(3)
Fe3	O10	2.002(2)	F14	C10	1.272(3)
Fe3	O12	2.010(2)	F15	C10	1.271(3)
Fe3	O14	2.004(3)	F16	C12	1.268(3)
Fe3	O19	2.048(2)	F17	C12	1.268(3)
O4	C3	1.224(4)	F18	C12	1.268(3)
O5	C3	1.238(4)	F4A	C4A	1.287(3)
O6	C5	1.226(4)	F5A	C4A	1.287(3)
O7	C5	1.232(4)	F6A	C4A	1.287(3)
O8	C7	1.234(5)	F7A	C6A	1.287(3)
O9	C7	1.224(4)	F8A	C6A	1.287(3)
O10	C9	1.233(4)	F9A	C6A	1.287(3)
O11	C9	1.214(4)	F13A	C10A	1.272(3)
O12	C11	1.227(4)	F14A	C10A	1.272(3)
O13	C11	1.227(4)	F15A	C10A	1.271(3)
O14	C13	1.227(5)	F16A	C12A	1.268(3)
O15	C13	1.223(5)	F17A	C12A	1.268(3)
O16	C15	1.226(4)	F18A	C12A	1.268(3)
O17	C15	1.231(4)	O2	C1	1.273(4)
C3	C4	1.530(9)	O3	C1	1.194(4)
C5	C6	1.508(10)	C1	C2	1.513(6)
C7	C8	1.537(6)	C2	F1	1.288(3)
C8	F10	1.276(5)	C2	F2	1.288(3)
C8	F11	1.277(5)	C2	F3	1.288(3)
C8	F12	1.277(5)	C2	F1A	1.288(3)
C9	C10	1.544(12)	C2	F2A	1.288(3)
C11	C12	1.532(12)	C2	F3A	1.288(3)
C13	C14	1.537(6)			

Crystallographic information for $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CF_3COO)_6(H_2O)_3][FeCl_4]$

The same synthesis conditions as for "Fe_3OTFA", but reducing the synthesis temperature to 60 °C after water addition, yields a different molecule, which crystallizes by slow cooling after re-dissolving it in TFA at 50 °C as $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CF_3COO)_6(H_2O)_3][FeCl_4]$ (Figure S2, Table S3-4). This molecule has the same core structure as "Fe_3OTFA" with three Fe(III) atoms in an octahedral environment sharing one oxygen atom, but with a water molecule on each Fe(III) atom trans to the Fe-μ_3O bond. The triangular core is thus positively charged, the $[FeCl_4]^-$ complex providing charge balance. Due to the lower reaction temperature of 60 °C a certain amount of the reactant ($FeCl_3$) remain in the system as well as some chlorine anions (coming from reacted $FeCl_3$). At this low temperature, the built $[FeCl_4]^-$ complex is meta stable coordinated to the positive charged $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CF_3COO)_6(H_2O)_3]^+$.

Most of the CF_3-groups show a considerable amount of disorder, leading to the pronounced anisotropy of the corresponding displacement parameters. The hydrogen atom positions were found in the difference Fourier map, however a free refinement of the positional and displacement parameters (with exception of a restraint forcing both O-H-distances equal) was only possible for the hydrogen atoms attached to O4, one of which forms a hydrogen bond to Cl1 of the $[FeCl_4]^-$ ion.

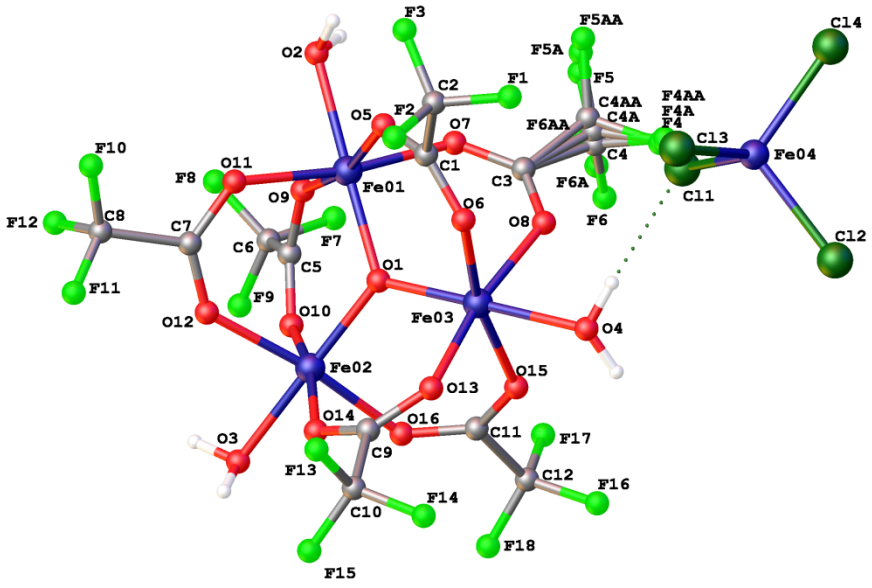

Figure S2. Asymmetric unit of $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CF_3COO)_6(H_2O)_3][FeCl_4]$. Because of large displacement parameters of fluorine, the structure is drawn with isotropic displacement parameters for clarity.

Table S3. Crystal data and structure refinement for $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CF_3COO)_6(H_2O)_3][FeCl_4]$.

CCDC number	**1559926**
Empirical formula	**$C_{12}H_6Cl_4F_{18}Fe_4O_{16}$**
Formula weight / g mol^{-1}	**1113.42**
Temperature / K	**100.0**
Crystal system	**monoclinic**
Space group	***P*21/*c***
a / Å	**13.5360(7)**
b / Å	**15.0772(7)**
c / Å	**17.4768(8)**
α / °	**90**
β / °	**109.9420(10)**
γ / °	**90**
Volume / $Å^3$	**3352.9(3)**
Z	**4**
ρ_{calc} / g cm^{-3}	**2.206**
μ / mm^{-1}	**2.179**
F(000)	**2160.0**
Crystal size / mm^3	**0.235 × 0.163 × 0.135**
Radiation	**Mo Kα (λ = 0.71073)**
2Θ range for data collection / °	**3.2 to 56.728**
Index ranges	**$-18 \le h \le 17$, $-20 \le k \le 20$, $-22 \le l \le 23$**
Reflections collected	**52179**
Independent reflections	**8306 [R_{int} = 0.0547]**
Data/restraints/parameters	**8306/192/540**
Goodness-of-fit on F^2	**1.055**
Final R indexes [I>=2σ (I)]	**R_1 = 0.0380, wR_2 = 0.0885**
Final R indexes [all data]	**R_1 = 0.0515, wR_2 = 0.0942**
Largest diff. peak/hole / e $Å^{-3}$	**0.88/-0.42**

Table S4. Bond lengths for $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CF_3COO)_6(H_2O)_3][FeCl_4]$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe01	O1	1.9103(18)	O5	C1	1.251(3)
Fe01	O2	2.0365(18)	O6	C1	1.239(3)
Fe01	O5	2.0102(18)	O7	C3	1.242(3)
Fe01	O7	2.0093(18)	O8	C3	1.244(3)
Fe01	O9	2.0051(18)	O9	C5	1.249(3)
Fe01	O11	2.0358(18)	O10	C5	1.243(3)
Fe02	O1	1.9096(17)	O11	C7	1.256(3)
Fe02	O3	2.0493(18)	O12	C7	1.239(3)
Fe02	O10	2.0267(18)	O13	C9	1.246(3)
Fe02	O12	2.0134(18)	O14	C9	1.248(3)
Fe02	O14	2.0070(18)	O15	C11	1.239(3)
Fe02	O16	2.0101(18)	O16	C11	1.246(3)
Fe03	O1	1.9155(17)	C1	C2	1.542(4)
Fe03	O4	2.0712(19)	C3	C4AA	1.542(4)
Fe03	O6	1.9935(18)	C3	C4	1.542(4)
Fe03	O8	2.0173(19)	C3	C4A	1.542(4)
Fe03	O13	1.9970(19)	C5	C6	1.538(4)
Fe03	O15	2.0135(18)	C7	C8	1.547(4)
F1	C2	1.299(3)	C9	C10	1.545(4)
F2	C2	1.314(3)	C11	C12	1.546(4)
F3	C2	1.299(3)	F4AA	C4AA	1.322(2)
F7	C6	1.313(4)	F5AA	C4AA	1.322(3)
F8	C6	1.319(4)	F6AA	C4AA	1.322(3)
F9	C6	1.302(3)	Fe04	Cl1	2.1852(9)
F10	C8	1.325(3)	Fe04	Cl2	2.2069(9)
F11	C8	1.298(3)	Fe04	Cl3	2.1907(8)
F12	C8	1.304(4)	Fe04	Cl4	2.1827(8)
F13	C10	1.316(3)	F6	C4	1.322(3)
F14	C10	1.321(3)	F6A	C4A	1.322(2)
F15	C10	1.317(3)	F4	C4	1.322(3)
F16	C12	1.336(3)	F4A	C4A	1.322(2)
F17	C12	1.310(3)	F5	C4	1.322(12)
F18	C12	1.327(3)	F5A	C4A	1.322(3)

Crystallographic information for $[Fe_4(\mu_3\text{-}O)_2(CF_3COO)_4(\mu\text{-}CF_3COO)_4(H_2O)_6]\cdot 2H_2O$

Single crystals of two different compounds were grown by treating "Fe_3OTFA" differently after the synthesis. One was determined as $[Fe_4(\mu_3\text{-}O)_2(CF_3COO)_4(\mu\text{-}CF_3COO)_4(H_2O)_6]\cdot 2H_2O$ (Figure S3, Table S5-6). It crystallizes in the space group *P*21/*n* after dissolving "Fe_3OTFA" in toluene at 60 °C, followed by slowly cooling this solution to RT and keeping it in air for one week. The structure can be described as two oxygen-centered triangles sharing one side forming an Fe(III) rhombus, and has been published before by Ponomarev et al.[1]

One CF_3-group was strongly disordered and had to be described by 4 partially occupied sites with isotropic displacement parameters, the C-F and C-C-distances were restrained to be equal. All hydrogen atom positions were found in the difference Fourier map and refined independently with exception of two water molecules, where the O-H-distances were restrained to be equal (O10 and O13).

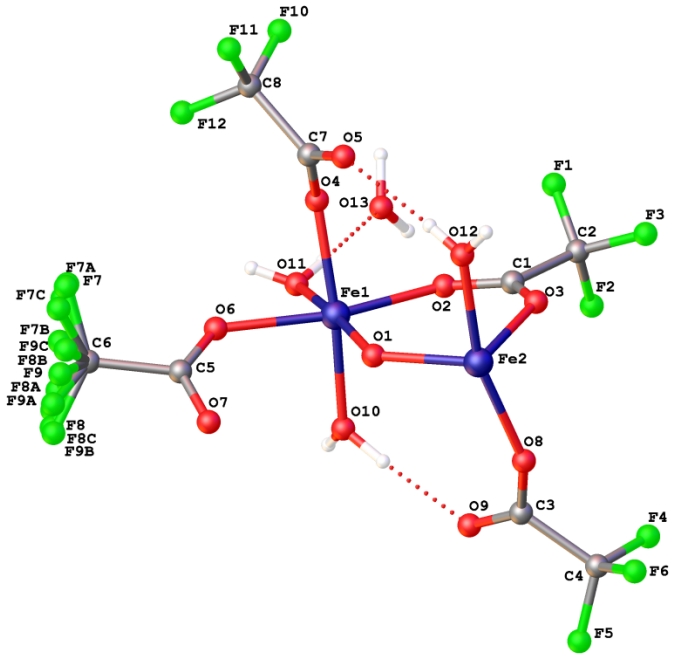

Figure S3. Asymmetric unit of $[Fe_4(\mu_3\text{-}O)_2(CF_3COO)_4(\mu\text{-}CF_3COO)_4(H_2O)_6]\cdot 2H_2O$. Because of large displacement parameters of fluorine, the structure is drawn with isotropic displacement parameters for clarity.

Table S5. Crystal data and structure refinement for $[Fe_4(\mu_3\text{-}O)_2(CF_3COO)_4(\mu\text{-}CF_3COO)_4(H_2O)_6]\cdot 2H_2O$.

CCDC number	**1559927**
Empirical formula	**$C_{16}H_{16}F_{24}Fe_4O_{26}$**
Formula weight / g mol^{-1}	**1303.78**
Temperature / K	**102**
Crystal system	**monoclinic**
Space group	**$P2_1/n$**
a / Å	**12.9152(9)**
b / Å	**8.3225(5)**
c / Å	**19.2599(13)**
α / °	**90**
β / °	**103.8230(10)**
γ / °	**90**
Volume / $Å^3$	**2010.2(2)**
Z	**2**
ρ_{calc} / g cm^{-3}	**2.154**
μ / mm^{-1}	**1.615**
F(000)	**1280.0**
Crystal size / mm^3	**0.4 × 0.21 × 0.12**
Radiation	**Mo Kα (λ = 0.71073)**
2Θ range for data collection / °	**3.452 to 53.096**
Index ranges	**$-16 \le h \le 16$, $-10 \le k \le 10$, $-24 \le l \le 24$**
Reflections collected	**26832**
Independent reflections	**4183 [R_{int} = 0.0494]**
Data/restraints/parameters	**4183/32/360**
Goodness-of-fit on F^2	**1.064**
Final R indexes [I>=2σ (I)]	**R_1 = 0.0359, wR_2 = 0.0863**
Final R indexes [all data]	**R_1 = 0.0447, wR_2 = 0.0904**
Largest diff. peak/hole / e $Å^{-3}$	**0.77/-0.46**

Table S6. Bond lengths for $[Fe_4(\mu_3\text{-}O)_2(CF_3COO)_4(\mu\text{-}CF_3COO)_4(H_2O)_6]\cdot 2H_2O$. [1]1-X,1-Y,1-Z

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	1.8477(18)	O4	C7	1.249(3)
Fe1	O2	2.0205(19)	O5	C7	1.234(3)
Fe1	O4	2.0044(19)	O6	C5	1.246(3)
Fe1	O6	2.0338(18)	O7	C5	1.247(3)
Fe1	O10	2.0376(19)	O8	C3	1.252(3)
Fe1	O11	2.062(2)	O9	C3	1.224(3)
Fe2	O1	1.9232(18)	C1	C2	1.542(4)
Fe2	O1[1]	1.9502(17)	C3	C4	1.542(4)
Fe2	O3	2.0690(18)	C5	C6	1.541(4)
Fe2	O7[1]	2.0472(19)	C6	F7A	1.299(9)
Fe2	O8	1.9936(18)	C6	F8A	1.387(9)
Fe2	O12	2.008(2)	C6	F9A	1.324(8)
F1	C2	1.324(4)	C6	F7	1.368(6)
F2	C2	1.317(3)	C6	F8	1.306(5)
F3	C2	1.316(3)	C6	F9	1.349(5)
F4	C4	1.323(4)	C6	F7C	1.313(7)
F5	C4	1.336(3)	C6	F8C	1.325(7)
F6	C4	1.318(3)	C6	F9C	1.348(7)
F10	C8	1.316(4)	C6	F7B	1.33(2)
F11	C8	1.326(3)	C6	F8B	1.33(2)
F12	C8	1.327(4)	C6	F9B	1.36(2)
O2	C1	1.244(3)	C7	C8	1.534(4)
O3	C1	1.238(3)			

Crystallographic information for $[Fe_3(CF_3COO)_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_2(H_2O)_2(\mu\text{-}H_2O)_2]\cdot 2CF_3COOH$

The second structure grown post-synthetically, $[Fe_3(CF_3COO)_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_2(H_2O)_2(\mu\text{-}H_2O)_2]\cdot 2CF_3COOH$ (Figure S4, Table S7-8), was determined from a single crystal grown out of a TFA/toluene solution of "Fe_3OTFA", which was stored for 2 weeks in a closed vial. It contains three Fe(II) ions in a row, neighboring ions being bridged by two trifluoroacetates and one water molecule. The coordination spheres of the two outer Fe(II) ions each are completed by a non-bridging trifluoroacetate, a TFA molecule and a water molecule. Such a core structure was found before in a complex with naphthyridine-functionalized ferrocenes trans to the two water molecules on the outer two Fe(II) ions.[2]

The crystal under investigation was twinned by a rotation of -3.64° around the [100] direction (real space). The ratio of the twin individuals is 0.286(11):0.714. Four of the nine CF_3-groups showed strong disorder and were described by three partially occupied sites each. The C-F-distances and for two of them also the C-C-distances were restrained to be equal. The hydrogen atoms at the terminal water molecule as well as at the oxygen atom O11 were found in the difference map and were subsequently placed at calculated positions and refined as a rigid group or using the riding model, respectively. The charge of the iron cations cannot be determined unambiguously, since the hydrogen atoms at O1 and O9 cannot be located in the difference Fourier map. Nevertheless, in order to fulfill the electroneutrality condition (assuming exclusively Fe(II)), they were introduced at calculated positions and refined according to the riding-hydrogen model (O9) or with O-H (donor), O-H (acceptor) and H-H distance restraints for the water molecule.

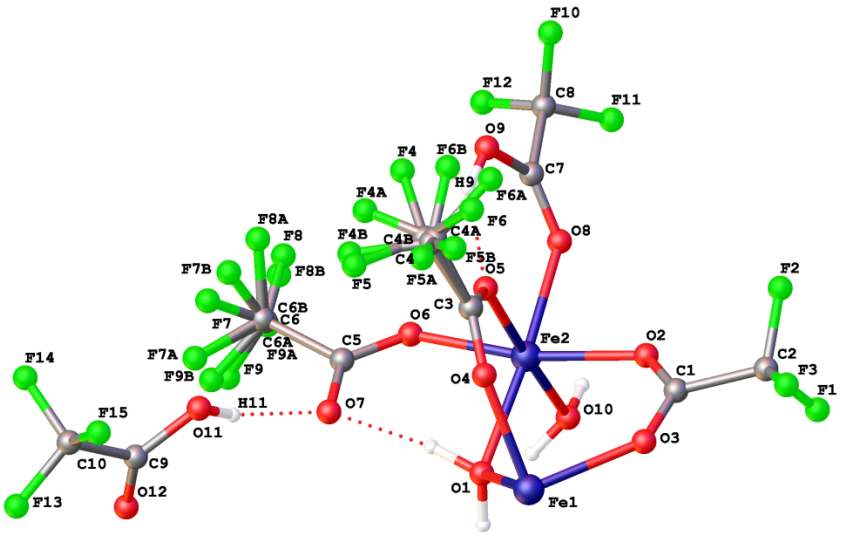

Figure S4. Asymmetric unit for $[Fe_3(CF_3COO)_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_2(H_2O)_2(\mu\text{-}H_2O)_2]\cdot 2CF_3COOH$. Because of large displacement parameters of fluorine, the structure is drawn with isotropic displacement parameters for clarity.

Table S7. Crystal data and structure refinement for $[Fe_3(CF_3COO)_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_2(H_2O)_2(\mu\text{-}H2O)_2]\cdot 2CF_3COOH$.

CCDC number	**1559928**
Empirical formula	**$C_{20}H_{12}F_{30}Fe_3O_{24}$**
Formula weight / g mol^{-1}	**1373.85**
Temperature / K	**250**
Crystal system	**triclinic**
Space group	***P*-1**
a / Å	**9.201(5)**
b / Å	**10.484(6)**
c / Å	**12.232(6)**
α / °	**84.900(14)**
β / °	**71.634(14)**
γ / °	**81.897(14)**
Volume / $Å^3$	**1107.5(10)**
Z	**1**
ρ_{calc} / g cm^{-3}	**2.060**
μ / mm^{-1}	**1.177**
F(000)	**672.0**
Crystal size / mm^3	**0.376 × 0.172 × 0.128**
Radiation	**Mo Kα (λ = 0.71073)**
2Θ range for data collection / °	**3.512 to 53.076**
Index ranges	**$-10 \le h \le 11$, $-12 \le k \le 12$, $0 \le l \le 15$**
Reflections collected	**4731**
Independent reflections	**4731 [R_{int} = merged]**
Data/restraints/parameters	**4731/564/476**
Goodness-of-fit on F^2	**0.924**
Final R indexes [I>=2σ (I)]	**$R_1 = 0.0653$, $wR_2 = 0.1362$**
Final R indexes [all data]	**$R_1 = 0.1413$, $wR_2 = 0.1619$**
Largest diff. peak/hole / e $Å^{-3}$	**0.88/-0.53**

Table S8. Bond lengths for $[Fe_3(CF_3COO)_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_2(H_2O)_2(\mu\text{-}H2O)_2]\cdot 2CF_3COOH$. [1]1-X,1-Y,1-Z

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1[1]	2.153(3)	F8A	C6A	1.328(15)
Fe1	O1	2.153(3)	F9B	C6B	1.327(13)
Fe1	O3	2.037(4)	F9A	C6A	1.328(15)
Fe1	O3[1]	2.037(4)	F10	C8	1.293(9)
Fe1	O4	2.047(4)	F11	C8	1.295(9)
Fe1	O4[1]	2.047(4)	F12	C8	1.278(8)
Fe2	O1	2.180(4)	O2	C1	1.235(7)
Fe2	O2	2.066(4)	O3	C1	1.225(6)
Fe2	O5	2.084(4)	O4	C3	1.230(7)
Fe2	O6	2.041(4)	O5	C3	1.253(7)
Fe2	O8	2.141(4)	O6	C5	1.248(7)
Fe2	O10	2.012(4)	O7	C5	1.227(7)
F1	C2	1.310(8)	O8	C7	1.182(8)
F2	C2	1.328(8)	O9	C7	1.320(8)
F3	C2	1.308(7)	C1	C2	1.520(8)
F4B	C4B	1.314(5)	C3	C4A	1.510(9)
F4	C4	1.336(8)	C3	C4B	1.510(9)
F4A	C4A	1.313(7)	C3	C4	1.510(9)
F5A	C4A	1.313(7)	C5	C6B	1.542(9)
F5B	C4B	1.314(5)	C5	C6A	1.542(9)
F5	C4	1.336(8)	C7	C8	1.505(10)
F6A	C4A	1.313(7)	F13	C10	1.325(8)
F6B	C4B	1.314(5)	F14	C10	1.284(9)
F6	C4	1.336(8)	F15	C10	1.275(8)
F7A	C6A	1.328(15)	O11	C9	1.297(7)
F7B	C6B	1.327(13)	O12	C9	1.193(7)
F8B	C6B	1.327(13)	C9	C10	1.512(10)

Materials Characterization

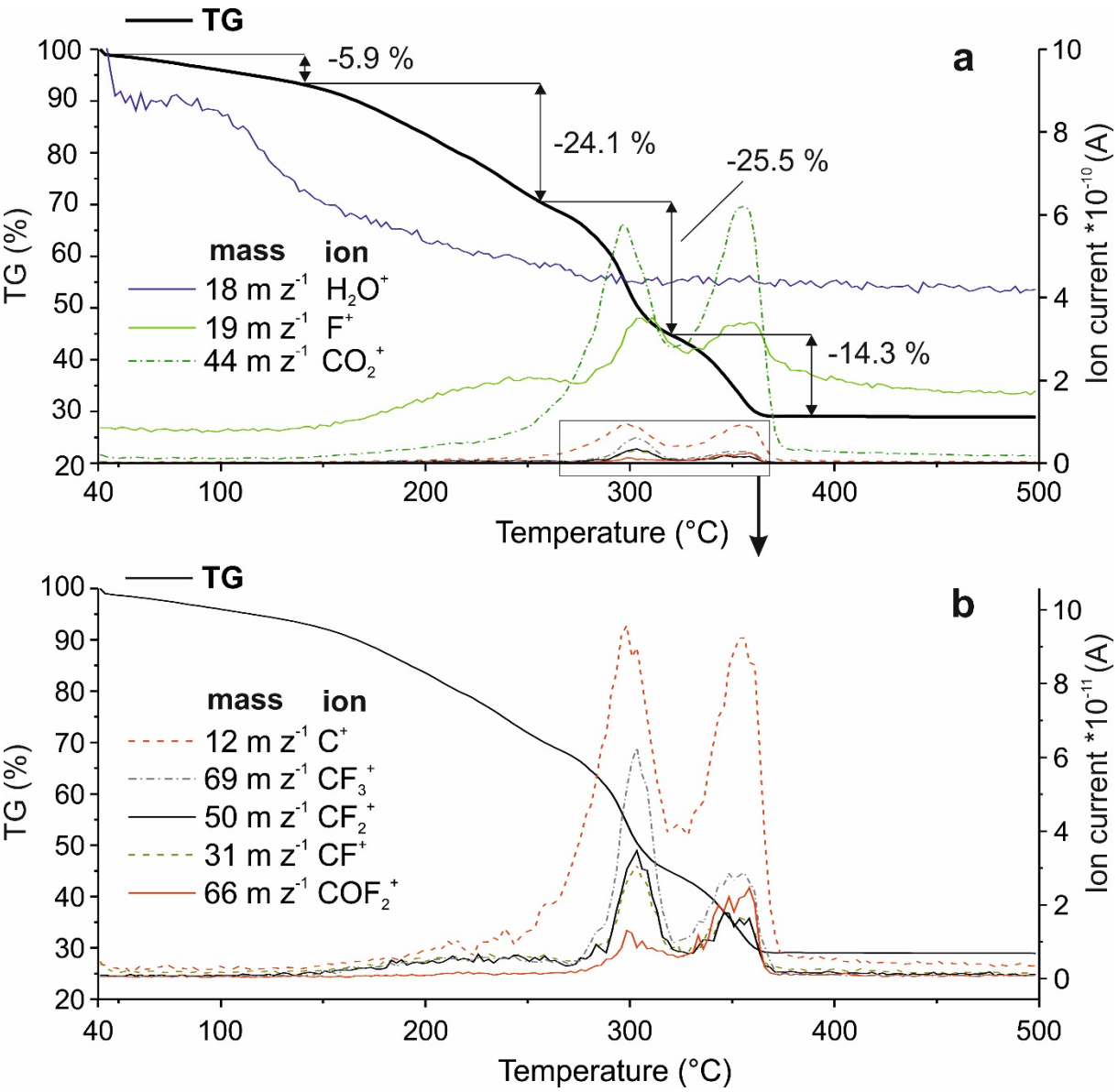

Figure S5. TGA-MS measurement of "Fe_3OTFA" between 40 and 500 °C with a heating rate of 5 °C min^{-1} under Ar flow (40 ml min^{-1}). a) "Fe_3OTFA" decomposes in four steps. First, water is released (-5.9%, calculated -3.2%) followed by the decomposition of 3 TFA ligands (-24.1%, calculated -25.1%). The remaining 5 TFA ligands are decomposed in 2 pronounced steps at 297 °C (-25.5%, calc. -25.1%) and 355 °C (-14.3%, calc. -16.7%). The remaining mass of 28.9% corresponds to 3Fe 1O 6F (calc. 26.5%). The main decomposition gases are H_2O, fluorine and CO_2 as analyzed by MS. b) By zooming to lower ion current, the spectra of the minor decomposition gases become visible. Those are CF_x (x = 1 – 3) and COF_2. Interestingly, the CF_x decomposition products appear mostly at 297 °C, whereas COF_2 appears more intensely at 355 °C.

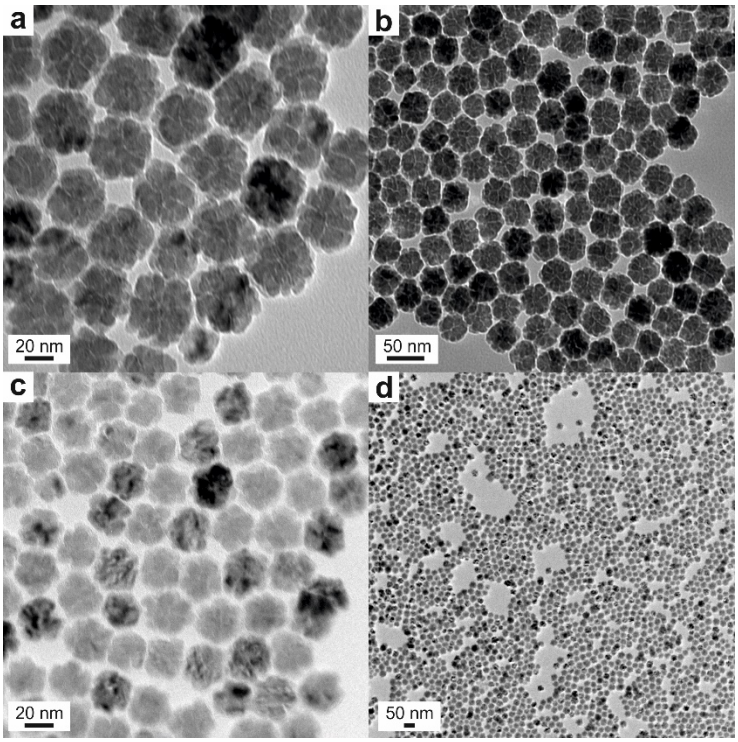

Figure S6. Size-variation of popcorn-shaped Fe_xO NPs based on different "Fe_3OTFA" concentrations synthesized at 260 °C for 20 min. TEM images of a), b) NPs synthesized with 0.3 mmol "Fe_3OTFA", 3.6 mmol OA, 5.4 mmol HDA in 10 mL TOP/squalane (1:1), and of c), d) NPs synthesized with 0.4 mmol "Fe_3OTFA", 3.6 mmol OA, 5.4 mmol HDA in 10 mL TOP/squalane (1:1).

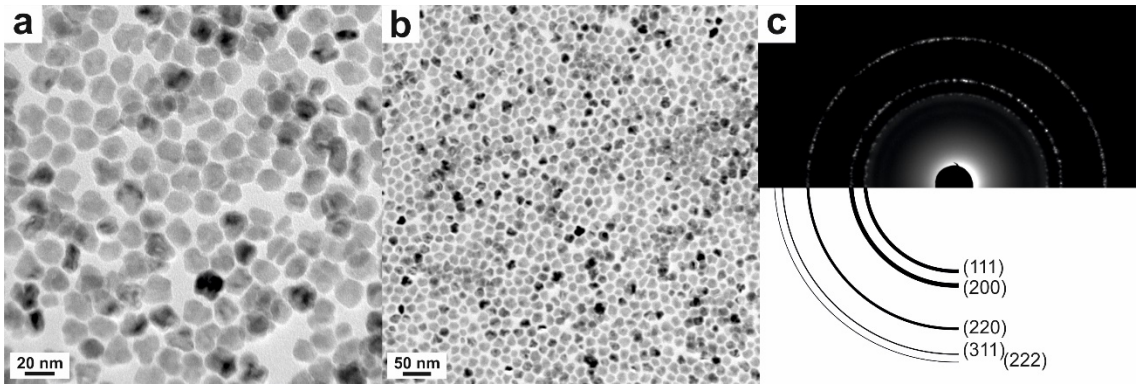

Figure S7. a), b) TEM images of fragmented Fe_xO popcorn-shaped particles obtained in a synthesis with increased HDA/OA ratio. c) SAED pattern of such Fe_xO NPs.

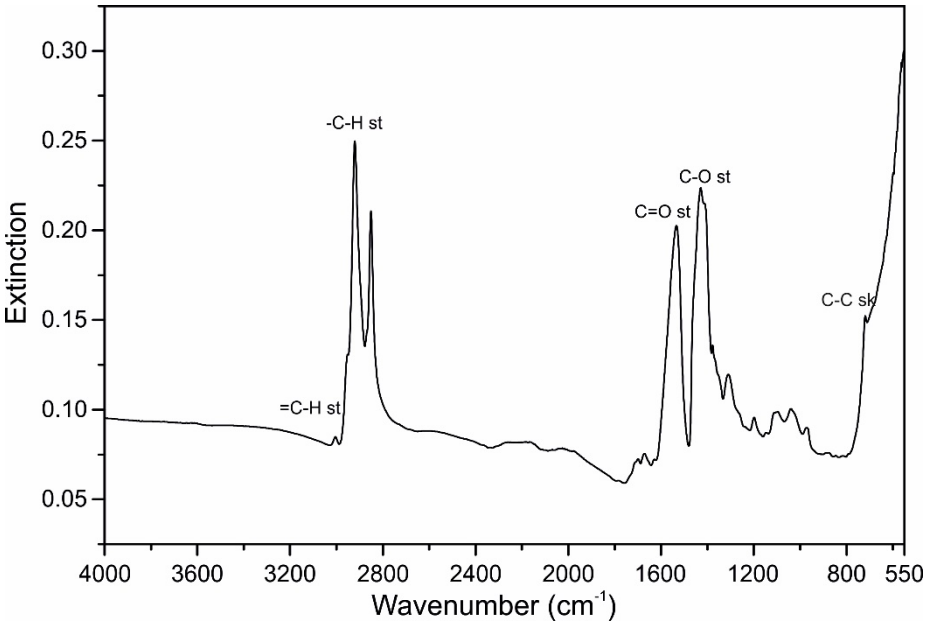

Figure S8. FTIR spectrum of popcorn-shaped wüstite NPs. The predominant surface ligand is oleate.

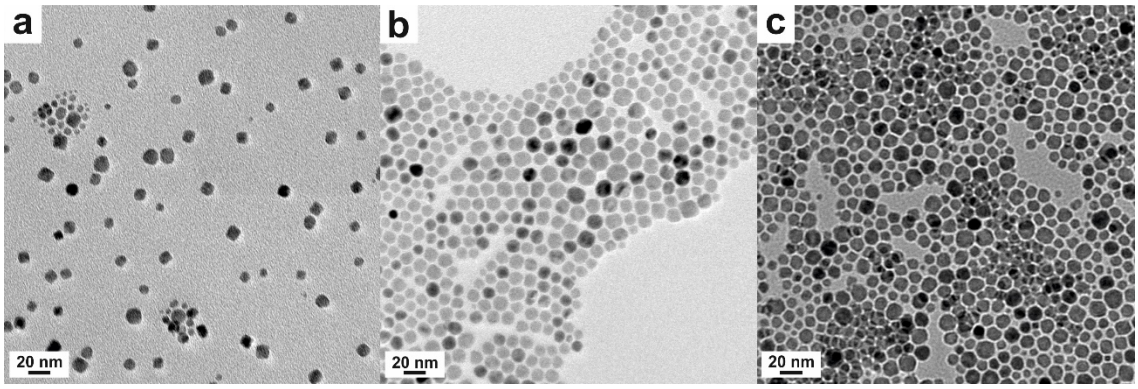

Figure S9. TEM images of particles synthesized by adding the precursor after the drying period of 1.5 h at 110 °C. The synthesis was performed at 260 °C for a) 20 min, b) 40 min, and c) 60 min. No popcorn-shaped particles are observed, if the precursor is added after the drying period, thus not catalyzing amide-formation or undergoing a structural change.

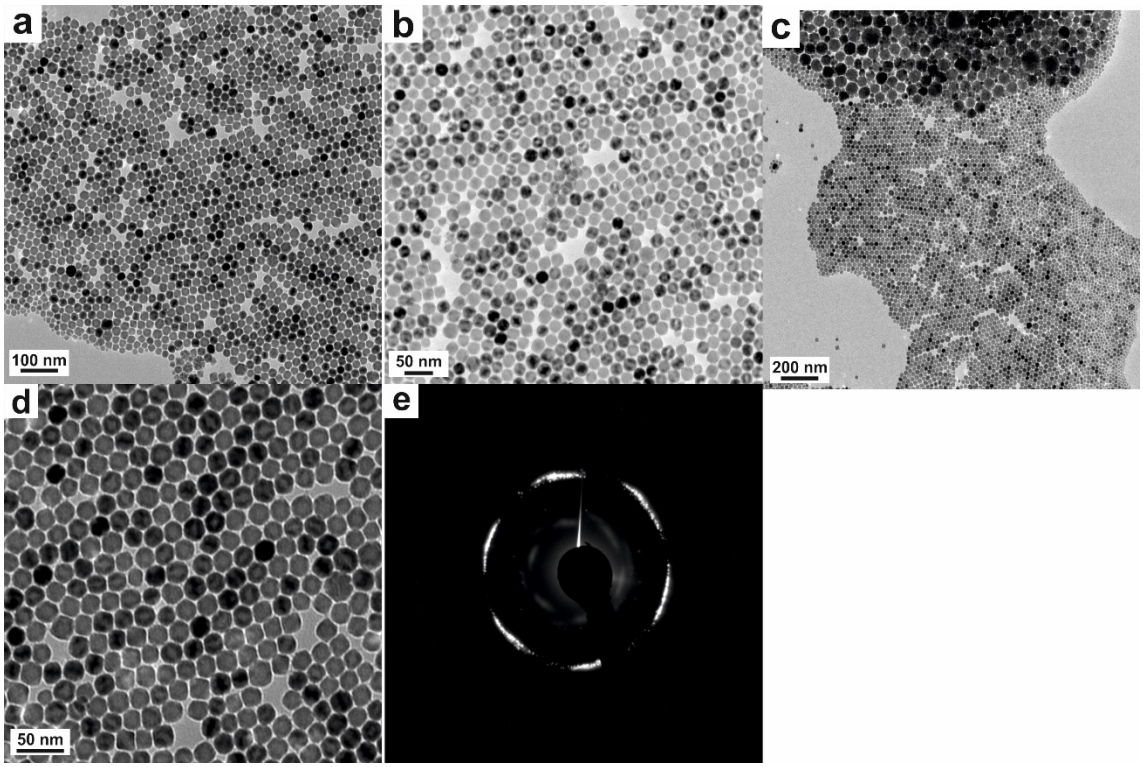

Figure S10. Monodisperse wüstite NPs (probably deltoidal icositetrahedron shaped) synthesized with increased amount of OA/HDA (13x/19x) and reaction time at 260 °C to 1 h. Calculated to 0.3 mmol "Fe_3OTFA" in the same TOP/squalene 1:1 solvent. a) – d) LRTEM images and e) SAED spectra of the monodisperse deltoidal icositetrahedron shaped wüstite NPs.

Rietveld refinement. The composition of the Fe_xO (x~0.94) NPs was analyzed based on the powder XRD pattern **(**Cu $K\alpha_1$ radiation, λ= 1.540598 Å) by a Rietveld refinement with the GSAS program[3-5] (Figure S11). For the refinement a reference Fe_xO structure[6] was used with the following parameters: space group *Fm*-3*m*, Z = 4, Fe: (x, y, z) = (0,0,0), occupancy = 0.944, U_{iso} = 0.00032 Å^2; O: (x, y, z) = (0.5,0.5,0.5), occupancy = 1, U_{iso} = 0.00032 Å^2. The stoichiometry of Fe_xO revealing x~0.94 was calculated[7] based on the unit cell parameter obtained by the refinement, a = 4.3095(1) Å. The figures of merit of the fit were χ^2 = 0.3184, wR_p = 0.0091 R_p = 0.0066, RF^2 = 0.1053. The peak asymmetry and the broadening of the (222)-reflection (60°) can be attributed to the non-homogeneous strain field caused by the Fe(III)-distribution vacancies.[8] The large background is largely related to the polymer film used for sample preparation.

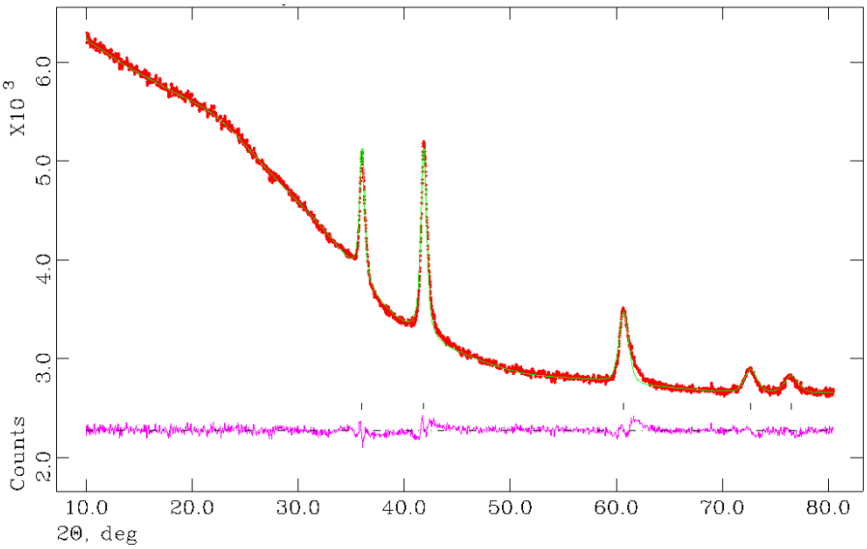

Figure S11. Rietveld refinement of popcorn-shaped Fe_xO (x~0.94) NPs with space group *Fm*-3*m*. Experimental powder XRD (red), refinement (green) using a starting reference[6] and the residuals (purple).

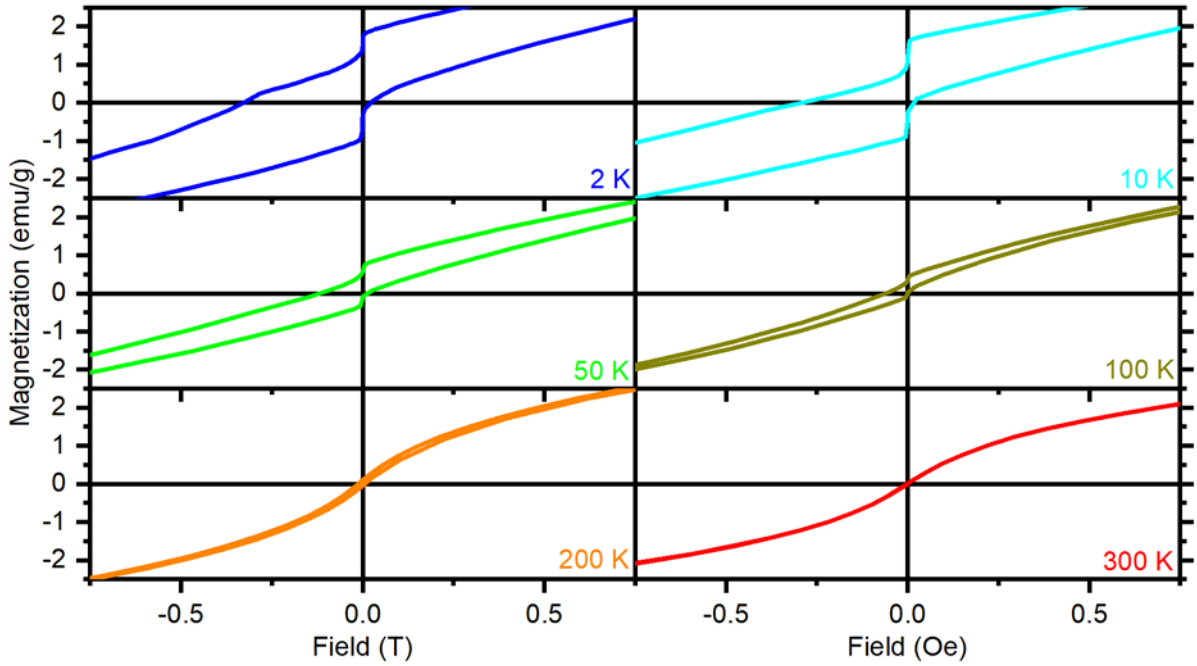

Figure S12. The low-field region of the magnetic hysteresis curves of Fe_xO NPs after cooling in a magnetic field of 1 T, clearly showing exchange bias.

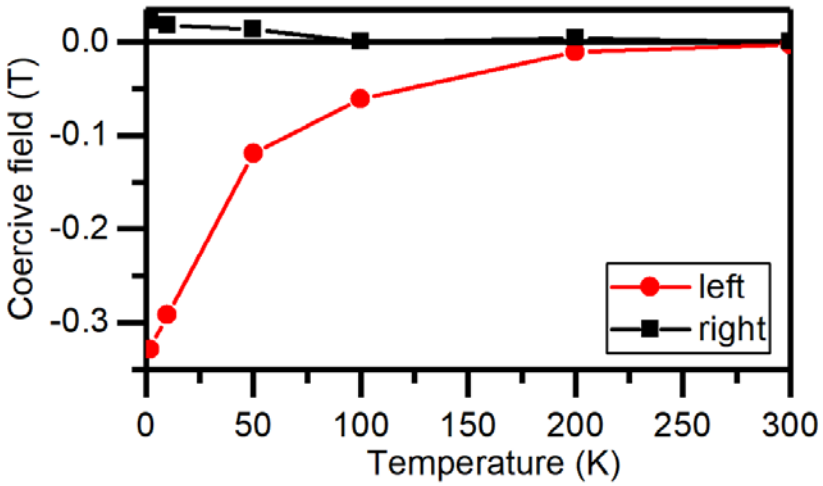

Figure S13. The coercive field of the Fe_xO NPs after cooling in a magnetic field of 1 T determined from the data in Figure S13. Left and right indicate the coercive field after decreasing the field from 9 T and increasing the field from -9 T, respectively.

References

1. Ponomarev, V. I.; Atovmyan, L. O.; Bobkova, S. A.; Turte, K. I., A New Tetranuclear Complex of Fe(III)-Crystal- and Molecularstructur of $[Fe_4O_2(CF_3COO)_8(H_2O)_6]\cdot 2H_2O$ at 300 K. *Dokl. Akad. Nauk SSSR* **1984,** 274, 368.
2. Sadhukhan, N.; Sarkar, M.; Ghatak, T.; Rahaman, S. M.; Barbour, L. J.; Bera, J. K., Reactions of Acids with Naphthyridine-Functionalized Ferrocenes: Protonation and Metal Extrusion. *Inorg. Chem.* **2013,** 52, 1432-1442.
3. Rietveld, H. M., The Rietveld Method: a Retrospection. *Z. Kristallogr.* **2010,** 225, 545-547.
4. Larson, A. C.; Von Dreele, R. B., General Structure Analysis System (GSAS). *LAUR* **1994**, 86-748.
5. Brian, T., EXPGUI, a Graphical User Interface for GSAS. *J. Appl. Crystallogr.* **2001,** 34, 210-213.
6. Jette, E. R.; Foote, F., An X-Ray Study of the Wüstite (FeO) Solid Solutions. *J. Chem. Phys* **1933,** 1, 29-36.
7. McCammon, C. A.; Liu, L. G., The Effects of Pressure and Temperature on Nonstoichiometric Wüstite, Fe_xO: The Iron-rich Phase Boundary. *Phys. Chem. Minerals* **1984,** 10, 106-113.
8. Balzar, D., X-Ray Diffraction Line Broadening: Modeling and Applications to High-Tc Superconductors. *J. Res. Natl. Inst. Stand. Technol.* **1993,** 98.