Electronic Supplementary Material (ESI) for RSC Advances.

Content

Tab. S1: Crystal Data and Structure Refinement for **1**.

Empirical Formula	$C_{16}H_{24}F_6N_2O_4Fe$
Formular weight	478.22 Da
Density (calculated)	1.509 g · cm^{-1}
F (000)	984
Temperature	100(2) K
Crystal size	0.322 x 0.156 x 0.098 mm
Crystal appearance	red tablet
Wavelenght (MoK_α)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell volume	a = 8.2798(9) Å b = 26.236(3) Å c = 10.1171(11) Å α = 90° β = 106.7333(16)° γ = 90°
Unit cell volume	2104.6(4) $Å^3$
Z	4
Cell measurement refections used	9940
ϑ range for cell measurement	2.24° to 24.80°
Diffractometer used for measurement	Bruker D8 KAPPA II (APEX II detector)
Diffractometer control software	BRUKER APEX3 (v2019.1-0)
Measurement method	Data collection strategy APEX 3/QUEEN
ϑ range for data collection	2.613° to 30.749°
Completeness to ϑ = 25.242° (to ϑ_{max})	99.9% (99.5%)
Index ranges	$-11 \leq h \leq 11$ $0 \leq k \leq 37$ $0 \leq l \leq 14$
Computing data reduction	BRUKER APEX3 (v2019.1-0)
Absorption correction	Semi-empirical form equivalents
Absorption coefficient	0.792 mm^{-1}
Absorption correction computing	TWINABS
Max./min. transmission	0.75/0.61

R_{merg} before/after correction	0.0678/0.0551 and 0.0902/0.0653
Computing structure solution	BRUKER APEX3 (v2019.1-0)
Computing structure refinement	SHELXL-2017/1 (Sheldrick, 2017)
Refinement method	Full-matrix least-squares on F^2
Reflections collected	117073
Independent reflections	6534 (R_{int} = 0.0797)
Reflections with I > 2σ (I)	5293
Data / retraints / parameter	6534 / 142 / 324
Goodness-of-fit on F^2	1.075
Weighting details	$\omega = 1/[\sigma^2(F_0^2) + (0.0395P)^2 + 0.9427P]$ where $P = (F_0^2 + 2F_c^2)/3$
R indices [I > 2σ (I)]	$R1$ = 0.0416 $\omega R2$ = 0.0866
R indices [all data]	$R1$ = 0.0605 $\omega R2$ = 0.0931
Largest diff. peak and hole	0.591 and –0.299 Å^{-3}

Tab. S2: Crystal Data and Structure Refinement for **2**.

Empirical Formula	$C_{16}H_{24}F_6N_2O_4Ni$
Formular weight	481.08 Da
Density (calculated)	1.552 g · cm^{-1}
F (000)	992
Temperature	100(2) K
Crystal size	0.350 x 0.216 x 0.208 mm
Crystal appearance	blue tablet
Wavelenght (MoK_α)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell volume	a = 8.1121(5) Å b = 20.0344(13) Å c = 12.6691(8) Å α = 90° β = 91.0753(15)° γ = 90°
Unit cell volume	2058.6(2) $Å^3$
Z	4
Cell measurement refections used	9716
ϑ range for cell measurement	3.17° to 33.32°
Diffractometer used for measurement	Bruker D8 KAPPA II (APEX II detector)
Diffractometer control software	BRUKER APEX3 (v2019.1-0)
Measurement method	Data collection strategy APEX 3/QUEEN
ϑ range for data collection	1.902° to 33.425°
Completeness to ϑ = 25.242° (to ϑ_{max})	99.9% (99.8%)
Index ranges	$-12 \leq h \leq 12$ $-30 \leq k \leq 31$ $-19 \leq l \leq 13$
Computing data reduction	BRUKER APEX3 (v2019.1-0)
Absorption correction	Semi-empirical form equivalents
Absorption coefficient	1.020 mm^{-1}
Absorption correction computing	SADABS
Max./min. transmission	0.75/0.66

R_{merg} before/after correction	0.0445/0.0352
Computing structure solution	BRUKER APEX3 (v2019.1-0)
Computing structure refinement	SHELXL-2017/1 (Sheldrick, 2017)
Refinement method	Full-matrix least-squares on F^2
Reflections collected	82511
Independent reflections	8019 (R_{int} = 0.0226)
Reflections with I > 2σ (I)	7248
Data / retraints / parameter	8019 / 53 / 327
Goodness-of-fit on F^2	1.046
Weighting details	$\omega = 1/[\sigma^2(F_0^2) + (0.0353P)^2 + 0.6264P]$ where $P = (F_0^2 + 2F_c^2)/3$
R indices [I > 2σ (I)]	$R1$ = 0.0245 $\omega R2$ = 0.0642
R indices [all data]	$R1$ = 0.0286 $\omega R2$ = 0.0667
Largest diff. peak and hole	0.557 and –0.353 Å^{-3}

Tab. S3: Crystal Data and Structure Refinement for **3**.

Empirical Formula	$C_{16}H_{24}F_6N_2OCu$
Formular weight	495.91 Da
Density (calculated)	1.541 g · cm^{-1}
F (000)	996
Temperature	100(2) K
Crystal size	0.362 x 0.325 x 0.110 mm
Crystal appearance	green plate
Wavelenght (MoK_α)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell volume	a = 9.7772(10) Å b = 15.3822(16) Å c = 14.6761(15) Å α = 90° β = 108.4413(16)° γ = 90°
Unit cell volume	2093.9(4) $Å^3$
Z	4
Cell measurement refections used	9810
ϑ range for cell measurement	2.56° to 32.98°
Diffractometer used for measurement	Bruker D8 KAPPA II (APEX II detector)
Diffractometer control software	BRUKER APEX3 (v2019.1-0)
Measurement method	Data collection strategy APEX 3/QUEEN
ϑ range for data collection	2.220° to 33.481°
Completeness to ϑ = 25.242° (to ϑ_{max})	100% (99.3%)
Index ranges	$-15 \leq h \leq 15$ $-23 \leq k \leq 23$ $-22 \leq l \leq 22$
Computing data reduction	BRUKER APEX3 (v2019.1-0)
Absorption correction	Semi-empirical form equivalents
Absorption coefficient	1.119 mm^{-1}
Absorption correction computing	SADABS
Max./min. transmission	0.75/0.60

R_{merg} before/after correction	0.0647/0.0448
Computing structure solution	BRUKER APEX3 (v2019.1-0)
Computing structure refinement	SHELXL-2017/1 (Sheldrick, 2017)
Refinement method	Full-matrix least-squares on F^2
Reflections collected	70229
Independent reflections	8143 (R_{int} = 0.0384)
Reflections with I > 2σ (I)	6554
Data / retraints / parameter	8143 / 349 / 353
Goodness-of-fit on F^2	1.053
Weighting details	$\omega = 1/[\sigma^2(F_0^2) + (0.0348P)^2 + 0.9588P]$ where $P = (F_0^2 + 2F_c^2)/3$
R indices [I > 2σ (I)]	$R1$ = 0.0291 $\omega R2$ = 0.0696
R indices [all data]	$R1$ = 0.0448 $\omega R2$ = 0.0782
Largest diff. peak and hole	0.623 and –0.657 Å^{-3}

Tab. S4: Crystal Data and Structure Refinement for **4**.

Empirical Formula	$C_{16}H_{24}F_6N_2O_4Zn$
Formular weight	487.74 Da
Density (calculated)	1.437 g · cm^{-1}
F (000)	1000
Temperature	100(2) K
Crystal size	0.541 x 0.359 x 0.190 mm
Crystal appearance	colourless tablet
Wavelenght (MoK_α)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell volume	a = 8.323(19) Å b = 20.79(5) Å c = 13.03(3) Å α = 90° β = 90.27(4)° γ = 90°
Unit cell volume	2254(9) $Å^3$
Z	4
Cell measurement refections used	4056
ϑ range for cell measurement	3.69° to 30.34°
Diffractometer used for measurement	Bruker D8 KAPPA II (APEX II detector)
Diffractometer control software	BRUKER APEX3 (v2019.1-0)
Measurement method	Data collection strategy APEX 2/COSMO
ϑ range for data collection	3.826° to 31.386°
Completeness to ϑ = 25.242° (to ϑ_{max})	98.8% (93.9%)
Index ranges	$-9 \leq h \leq 11$ $-29 \leq k \leq 29$ $-19 \leq l \leq 18$
Computing data reduction	BRUKER APEX3 (v2019.1-0)
Absorption correction	Semi-empirical form equivalents
Absorption coefficient	1.160 mm^{-1}
Absorption correction computing	SADABS
Max./min. transmission	0.75/0.62

R_{merg} before/after correction	0.1676/0.0869
Computing structure solution	BRUKER APEX3 (v2019.1-0)
Computing structure refinement	SHELXL-2017/1 (Sheldrick, 2017)
Refinement method	Full-matrix least-squares on F^2
Reflections collected	43803
Independent reflections	6974 (R_{int} = 0.0450)
Reflections with I > 2σ (I)	5203
Data / retraints / parameter	6974 / 132 / 324
Goodness-of-fit on F^2	1.090
Weighting details	$\omega = 1/[\sigma^2(F_0^2) + (0.0475P)^2 + 1.6161P]$ where $P = (F_0^2 + 2F_c^2)/3$
R indices [I > 2σ (I)]	$R1$ = 0.0538 $\omega R2$ = 0.1364
R indices [all data]	$R1$ = 0.0739 $\omega R2$ = 0.1459
Largest diff. peak and hole	0.585 and –0.309 Å^{-3}

Tab. S5: Overview on intermolecular contacts in **1**-**4**.

Compound	H···H	H···F	F···F	C-H···O
$Fe(acac)_2(TMEDA)$	2.226			2.623
$Ni(acac)_2(TMEDA)$	2.274 2.262 2.312 2.045 2.312			
$Zn(acac)_2(TMEDA)$	2.311 2.394 2.381			
$Fe(tfac)_2(TMEDA)$ **1**		2.059 2.268		
$Ni(tfac)_2(TMEDA)$ **2**	2.386	2.608 2.633 2.622	2.768	
$Cu(tfac)_2(TMEDA)$ **3**	2.352	2.452 2.625 2.567 2.601		
$Zn(tfac)_2(TMEDA)$ **4**	---	---	---	
$Fe(hfac)_2(TMEDA)$		2.658	2.816	
$Ni(hfac)_2(TMEDA)$		2.586	2.764	
$Cu(hfac)_2(TMEDA)$		2.476 2.596 2.629 2.653		
$Zn(hfac)_2(TMEDA)$		2.540 2.656 2.577 2.575 2.613	2.928	

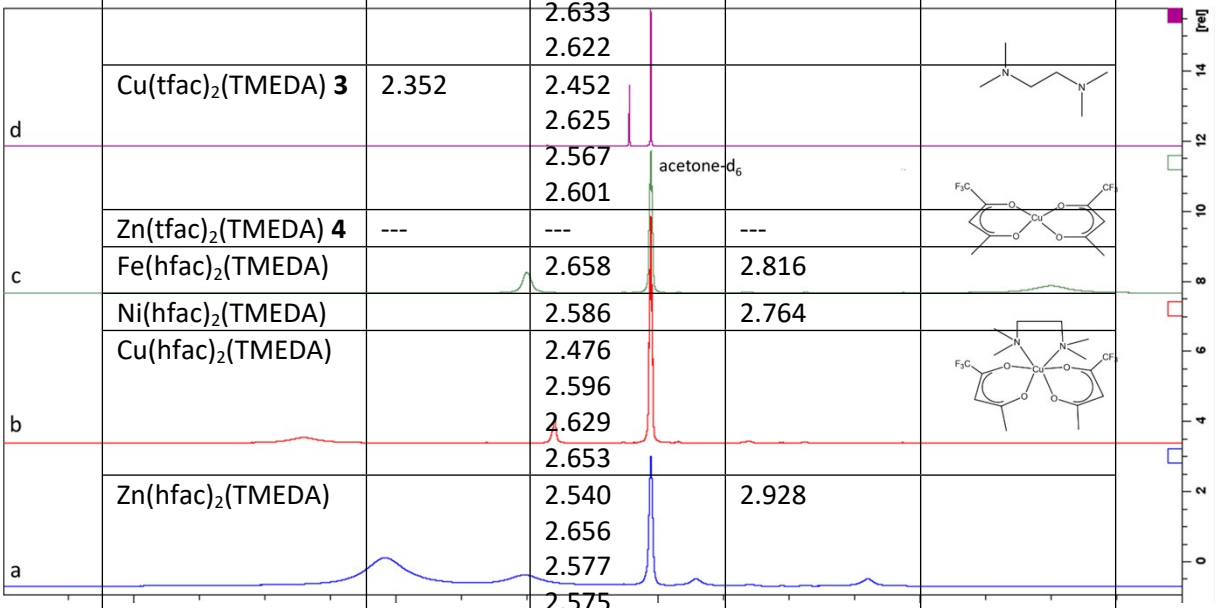

Fig. S1: ^{1}H-NMR of the black residue after heating **3** at 120 °C for 3 h under inert conditions at atmospheric pressure. (a). The comparison with the spectrum of **3** (b) shows the complete degradation of the starting material. Further comparison with the spectra of $Cu(tfac)_2$ (c) and TMEDA (d) excludes the loss of TMEDA as decomposing pathway. All spectra were recorded in aceton-d_6.

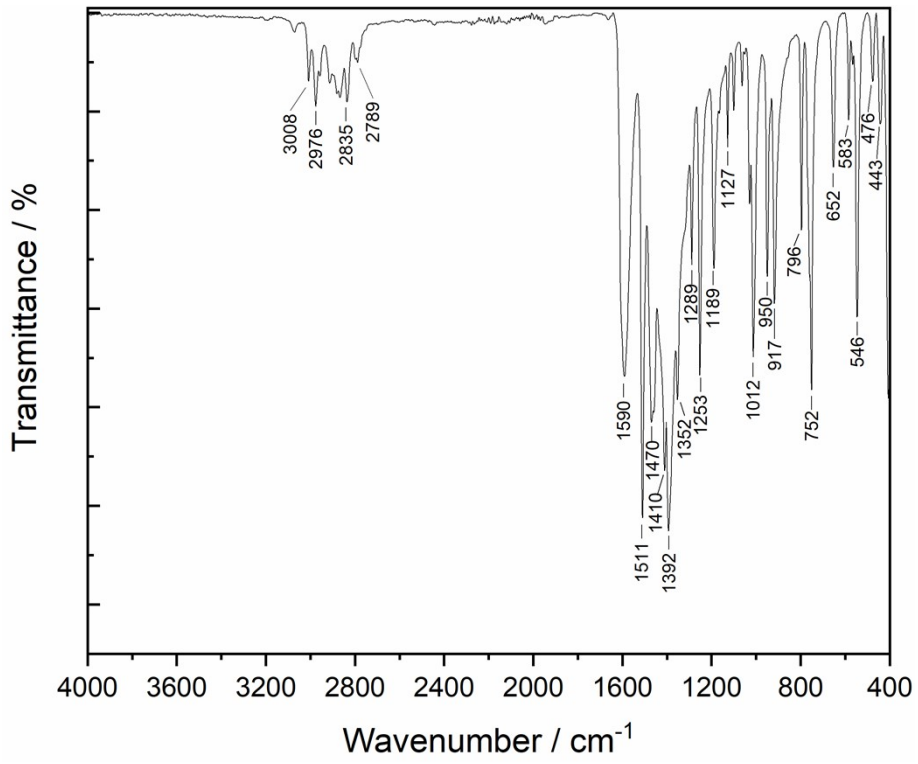

Fig. S2: ATR-IR spectrum of $Fe(acac)_2(TMEDA)$.

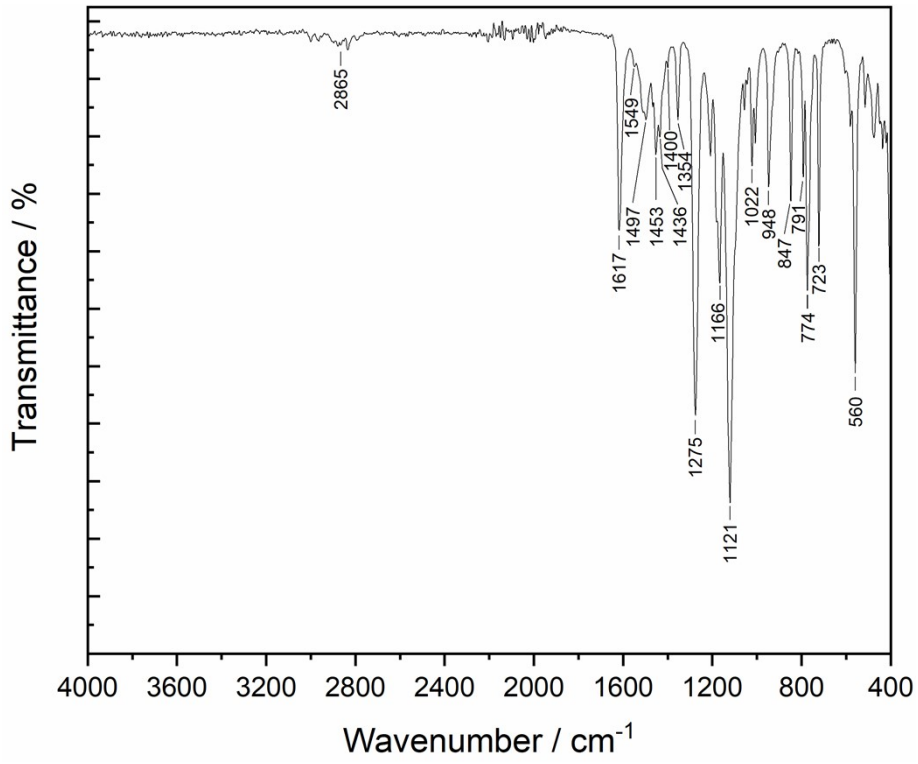

Fig. S3: ATR-IR spectrum of $Fe(tfac)_2(TMEDA)$ **2**.

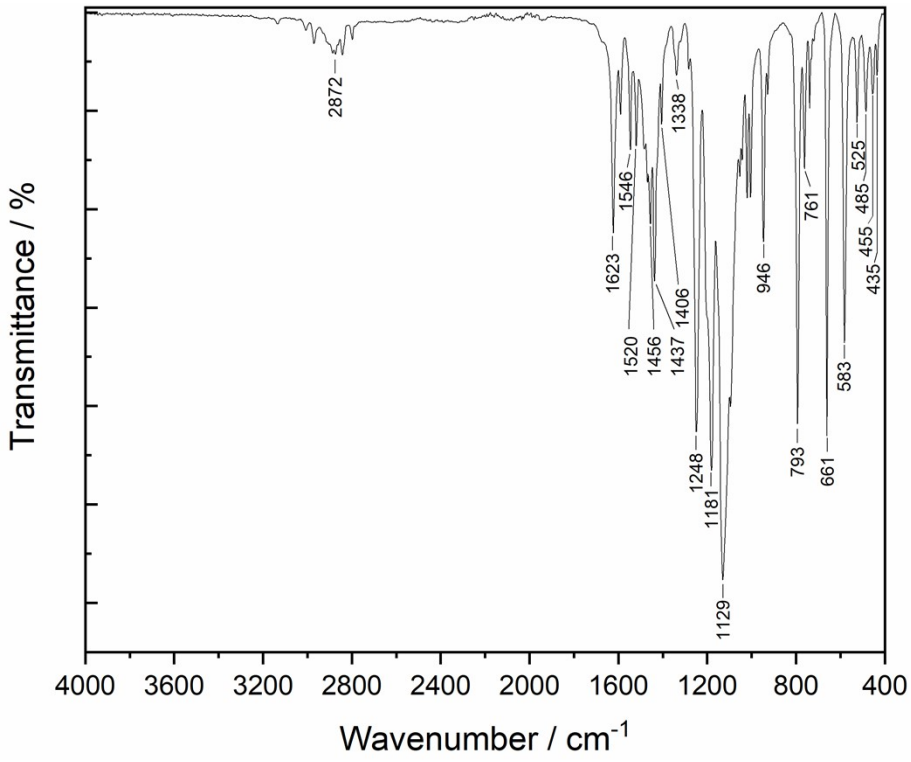

Fig. S4: ATR-IR spectrum of $Fe(hfac)_2(TMEDA)$.

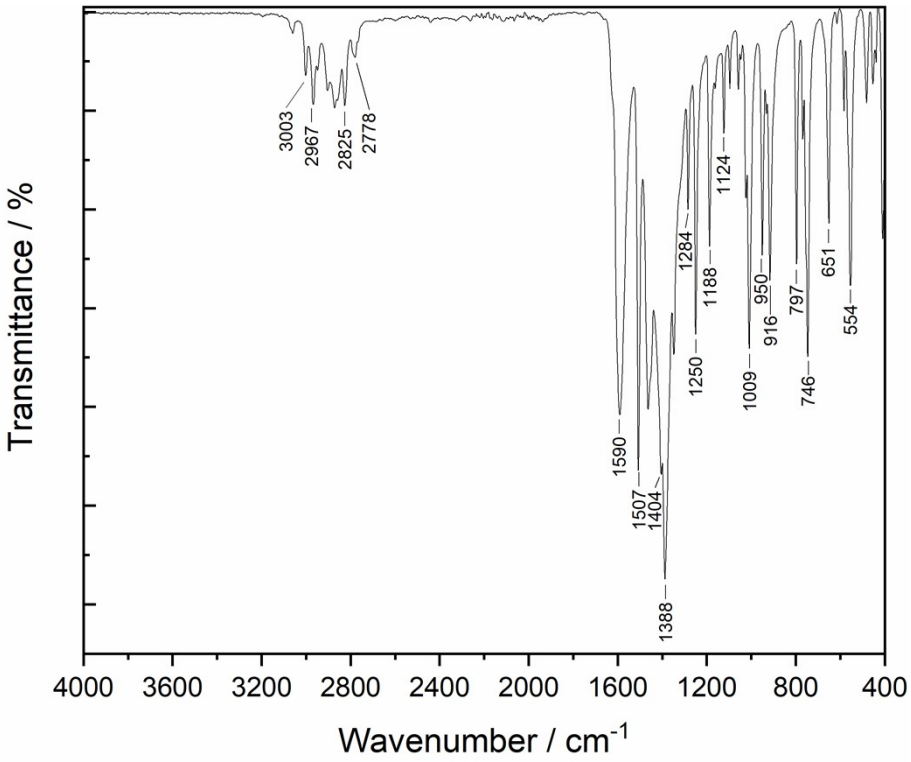

Fig. S5: ATR-IR spectrum of $Ni(acac)_2(TMEDA)$.

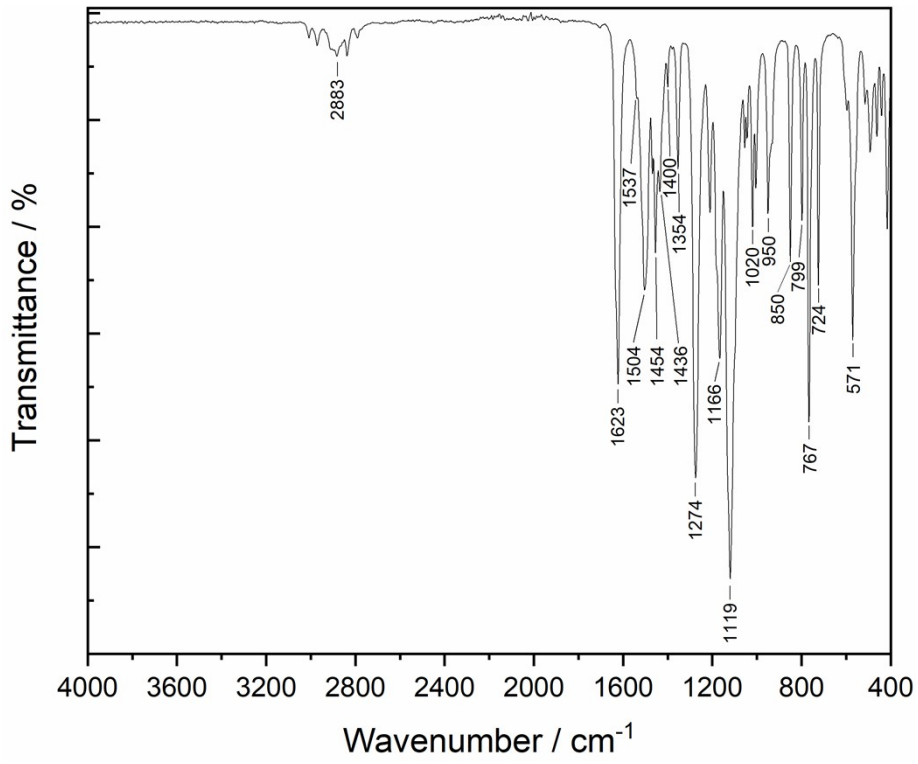

Fig. S6: ATR-IR spectrum of Ni(tfac)$_2$(TMEDA) **2**.

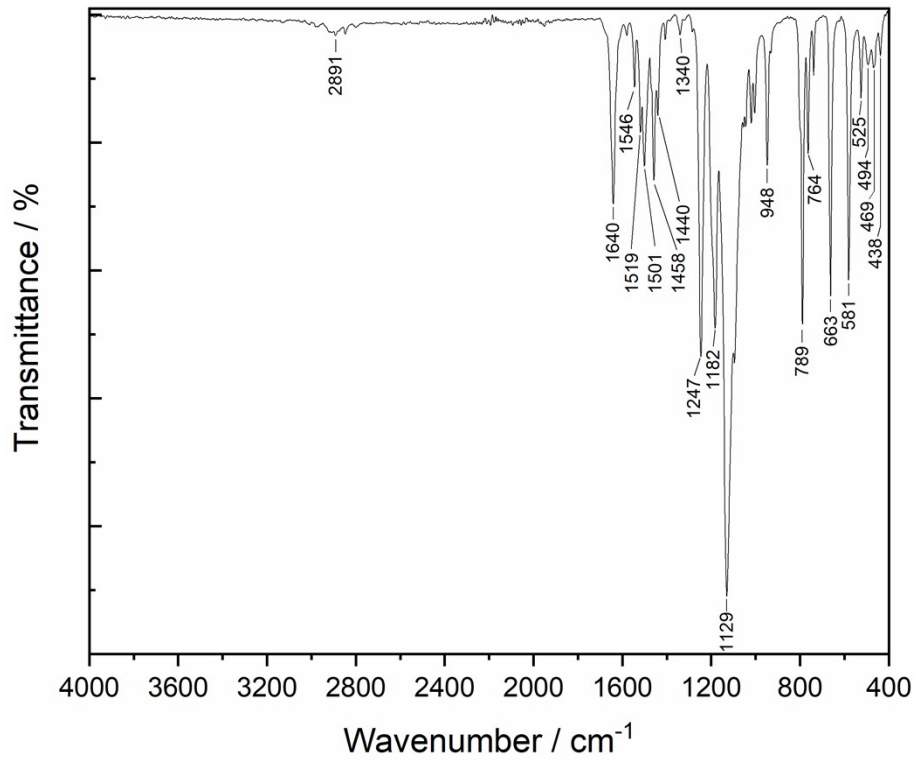

Fig. S7: ATR-IR spectrum of Ni(hfac)$_2$(TMEDA).

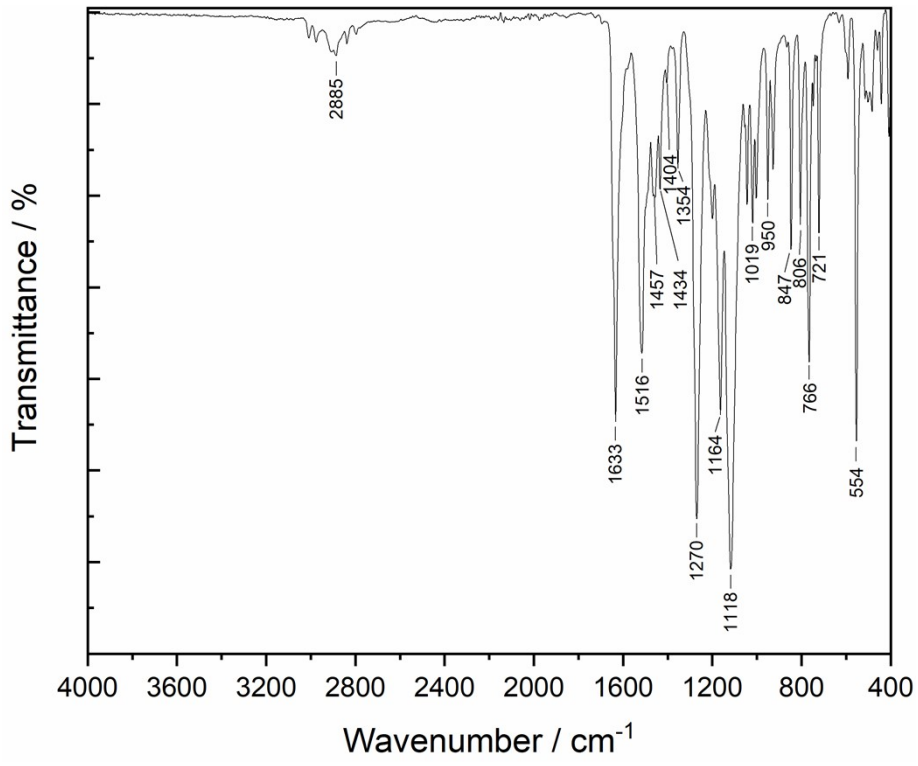

Fig. S8: ATR-IR spectrum of Cu(tfac)$_2$(TMEDA) **3**.

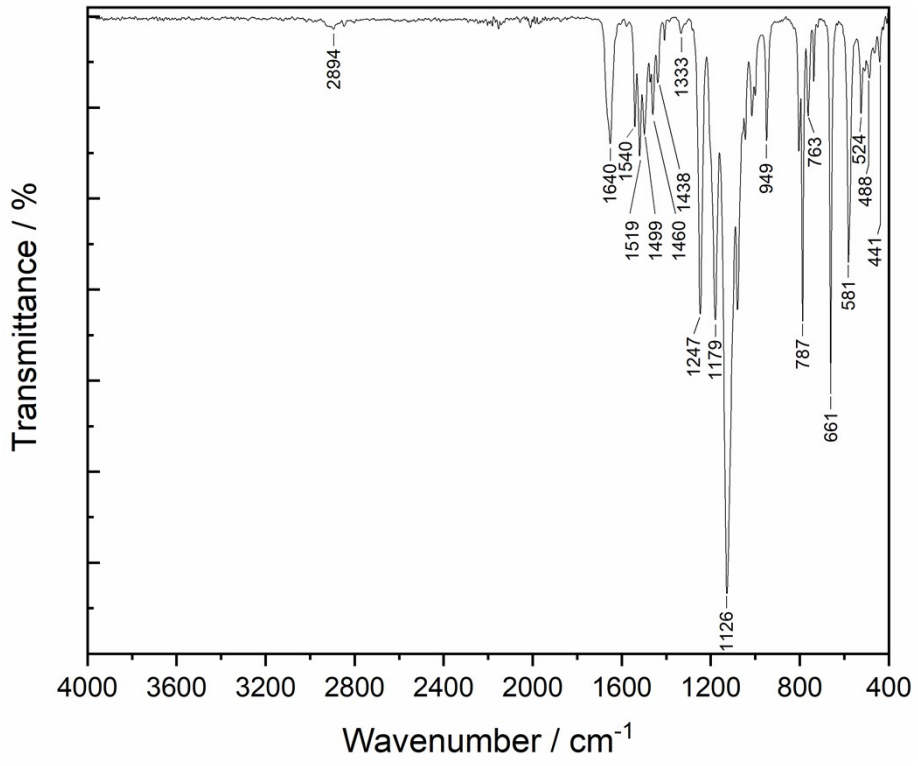

Fig. S9: ATR-IR spectrum of Cu(hfac)$_2$(TMEDA).

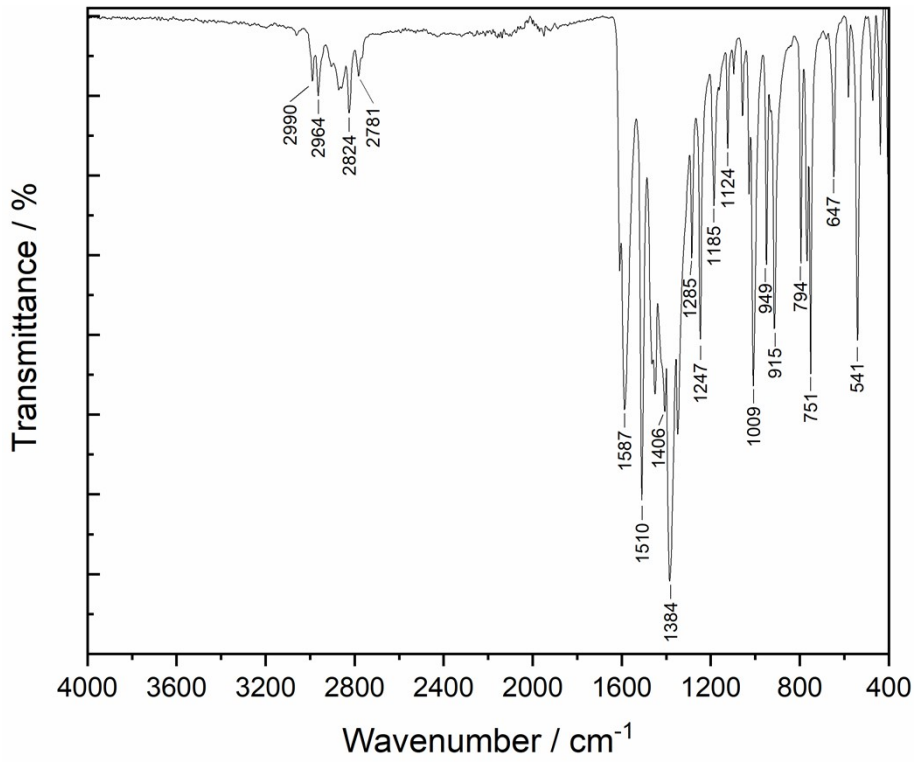

Fig. S10: ATR-IR spectrum of $Zn(acac)_2(TMEDA)$.

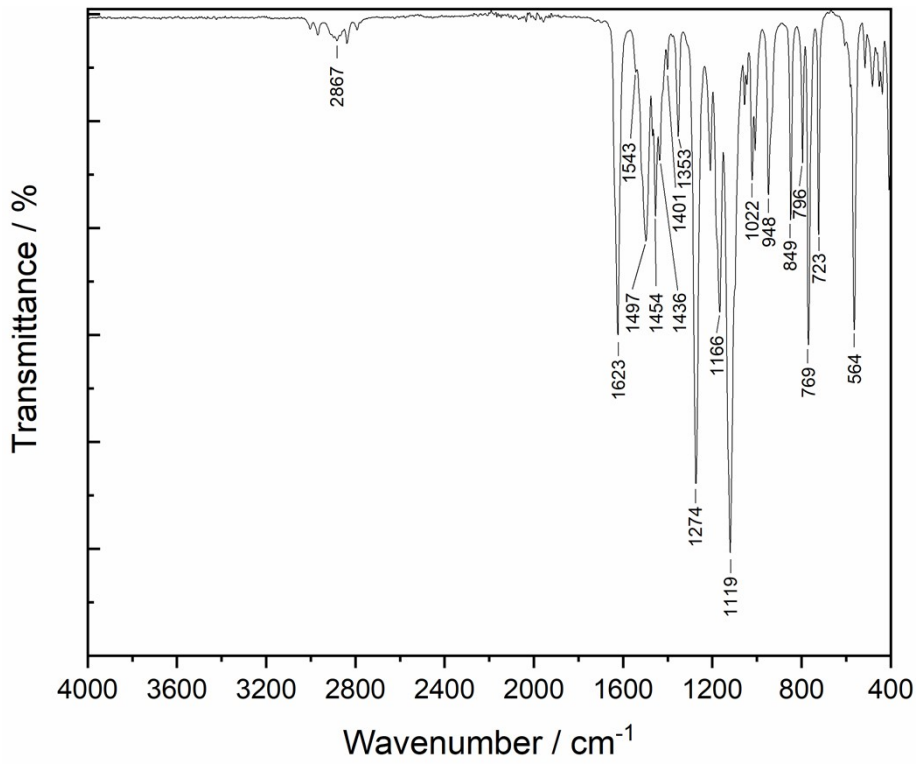

Fig. S11: ATR-IR spectrum of $Zn(tfac)_2(TMEDA)$ **4**.

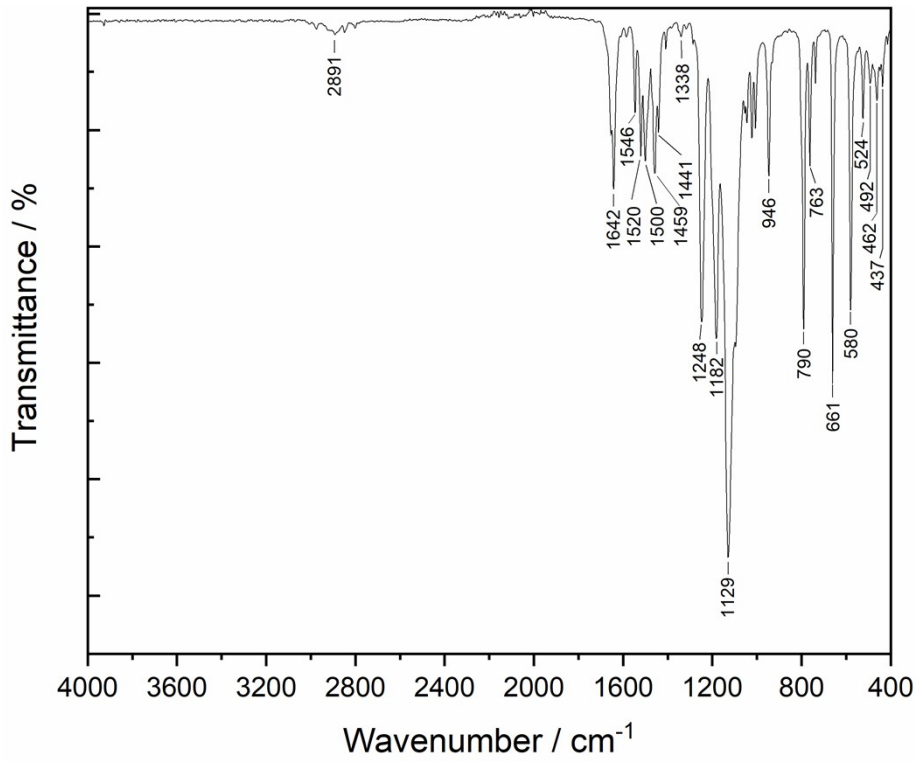

Fig. S12: ATR-IR spectrum of $Zn(hfac)_2(TMEDA)$.

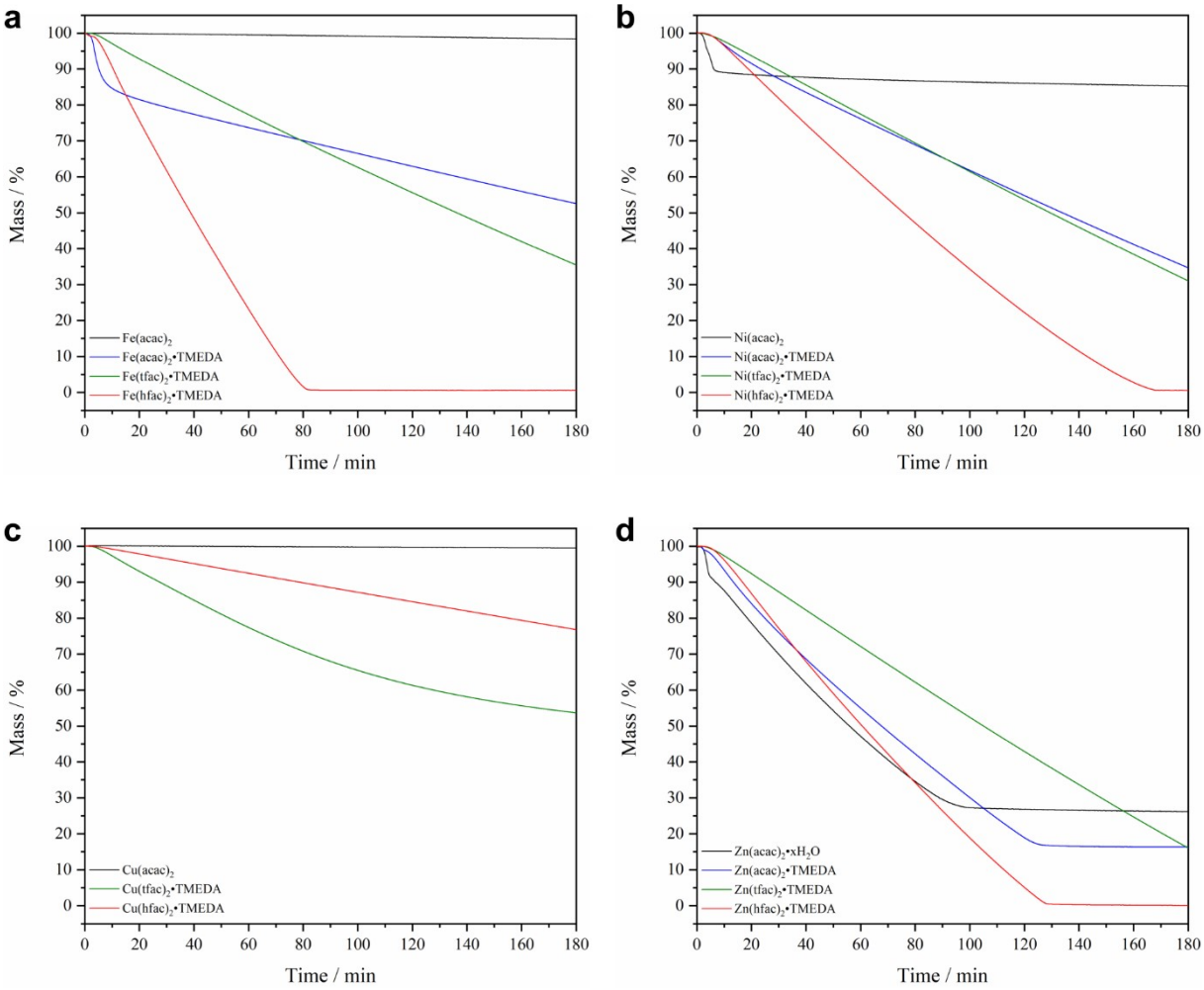

Fig. S13: Isothermal TGA curves (125 °C) for $M(acac)_2$, $M(acac)_2(TMEDA)$, $M(tfac)_2(TMEDA)$ and $M(hfac)_2(TMEDA)$ (M = Fe (a), Ni (b), Cu (c) and Zn (d)).

For the PXRD analysis of **1**-**4**, crystalline samples were grinded and measured with Cu-Kα radiation. Theoretical X-ray pattern were calculated from the crystal structures using the Mercury software (Version 4.2.0, Cambridge Crystallographic Data Centre) and displayed as vertical red and blue bars. While for **1** a mixture of two polymorphic structures was observed, good agreements were found between the calculated and the experimental X-ray pattern for **2**-**4**, excluding the presence of polymorphs.

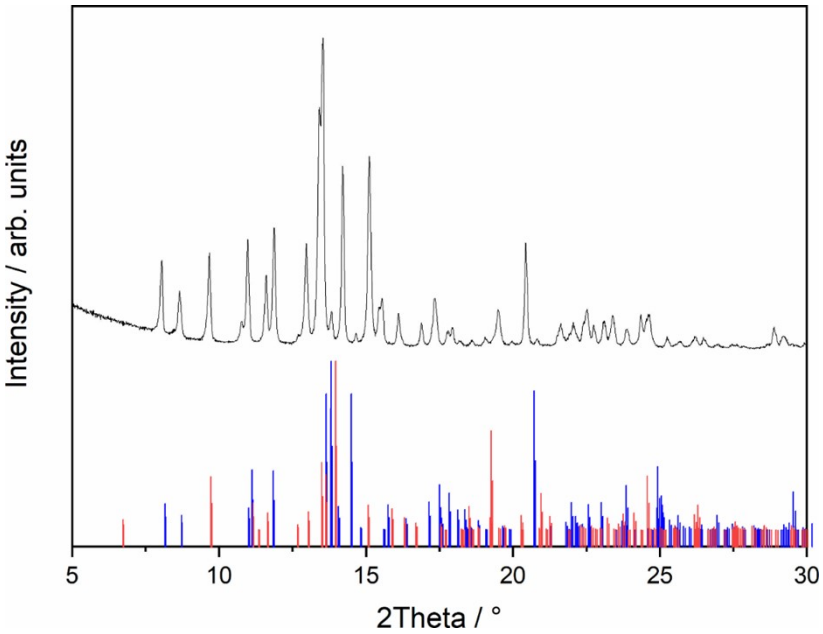

Fig. S14: PXRD of **1**. Calculated position of the reflections from the crystal structure as vertical bars. **1** (red) and $Fe(tfac)_2(TMEDA)$[1] (blue).

[1] M. Klotzsche, D. Barreca, L. Bigiani, R. Seraglia, A. Gasparotto, L. Vanin, C. Jandl, A. Pöthig, M. Roverso, S. Bogialli, G. Tabacchi, E. Fois, E. Callone, S. Dirèe, C. Maccato, Dalton. Trans.; 2021, 50, 10374–10385.

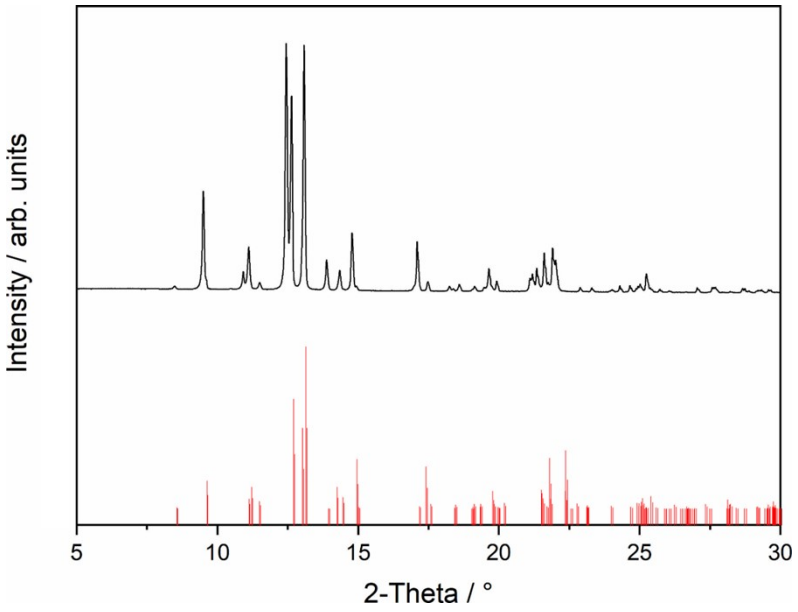

Fig. S15: PXRD of **2**. Calculated position of the reflections from the crystal structure as vertical bars.

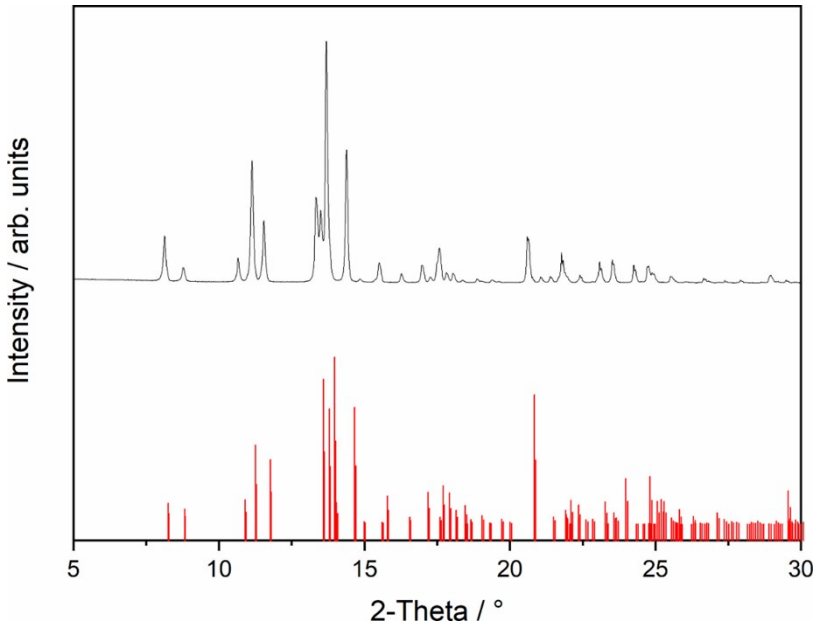

Fig. S16: PXRD of **3**. Calculated position of the reflections from the crystal structure as vertical bars.

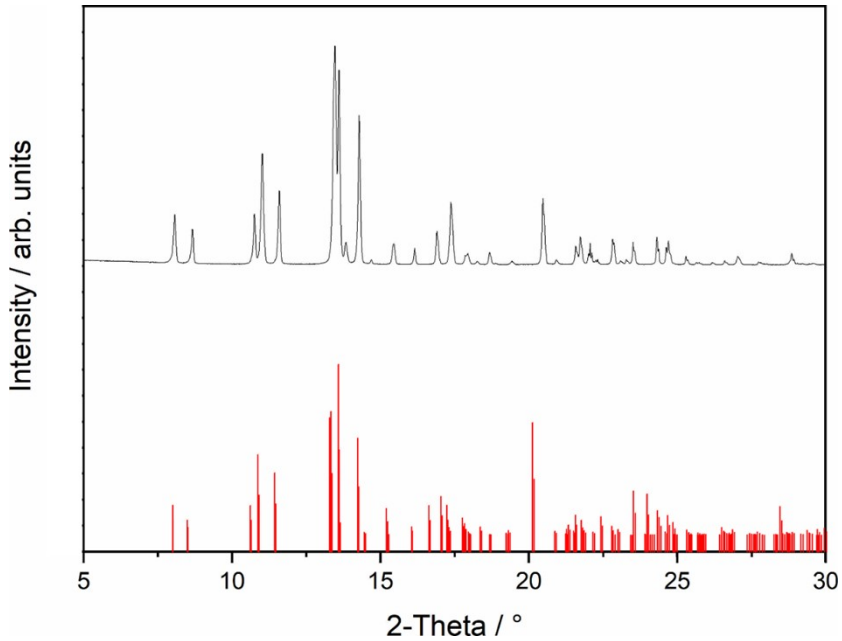

Fig. S17: PXRD of **4**. Calculated position of the reflections from the crystal structure as vertical bars.

Tab. S6: Experimental conditions.

sample name	precursor	evaporation temperature [°C]	deposition temperature [°C]	deposition pressure [mbar]	deposition time [min]	substrate
1_Al	$Fe(tfac)_2(TMEDA)$	100	500	0.35	20	Al_2O_3 (0001)
1_Si	$Fe(tfac)_2(TMEDA)$	100	300-500	0.35	20	Si (100)
2_Al	$Ni(tfac)_2(TMEDA)$	100	500	0.35	20	Al_2O_3 (0001)
2_Si	$Ni(tfac)_2(TMEDA)$	100	300-500	0.35	20	Si (100)
3_Al	$Cu(tfac)_2(TMEDA)$	100	500	0.35	20	Al_2O_3 (0001)
3_Si	$Cu(tfac)_2(TMEDA)$	100	300-500	0.35	20	Si (100))
4_Si	$Zn(tfac)_2(TMEDA)$	100	500	0.35	20	Al_2O_3 (0001)
4_Si	$Zn(tfac)_2(TMEDA)$	100	300-500	0.35	20	Si (100)

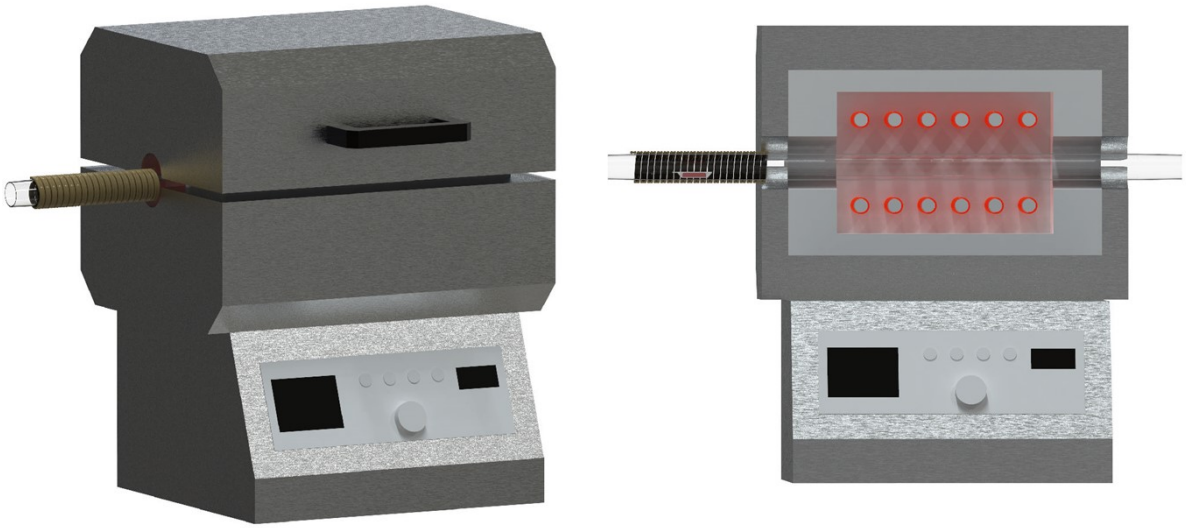

Fig. S18: 3D model of the reactor used in this paper. Side view (left) and front view with cross section (right). Gas supply system and vacuum system are not shown.

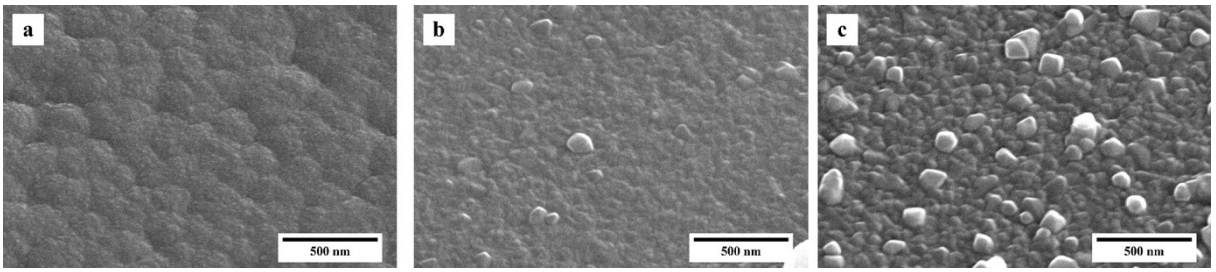

Fig. S19: SEM of **1_Si** at 300 °C (a), 400 °C (b) and 500 °C (c).

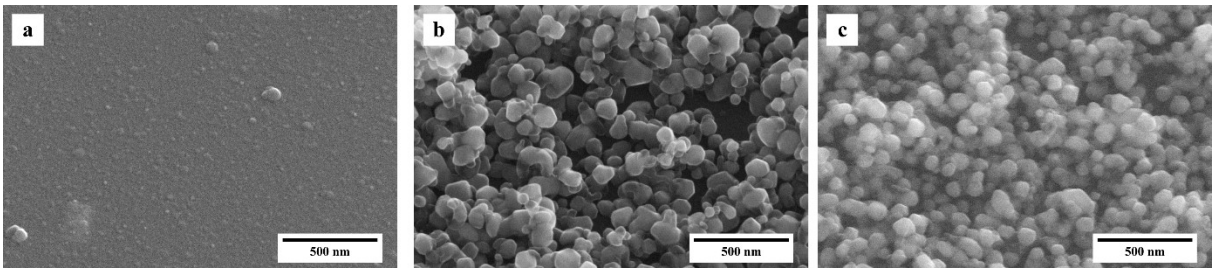

Fig. S20: SEM of **2_Si** at 300 °C (a), 400 °C (b) and 500 °C (c).

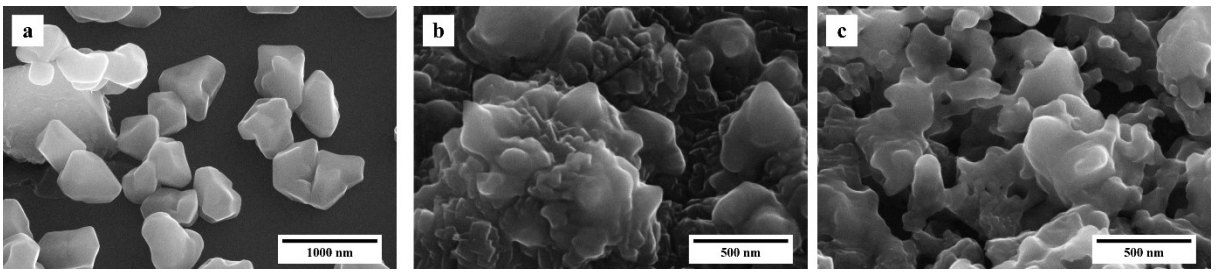

Fig. S21: SEM of **3_Si** at 300 °C (a), 400 °C (b) and 500 °C (c).

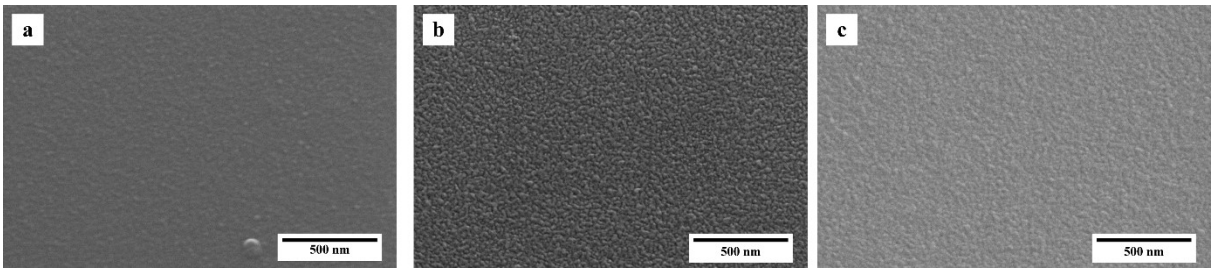

Fig. S22: SEM of **4_Si** at 300 °C (a), 400 °C (b) and 500 °C (c).

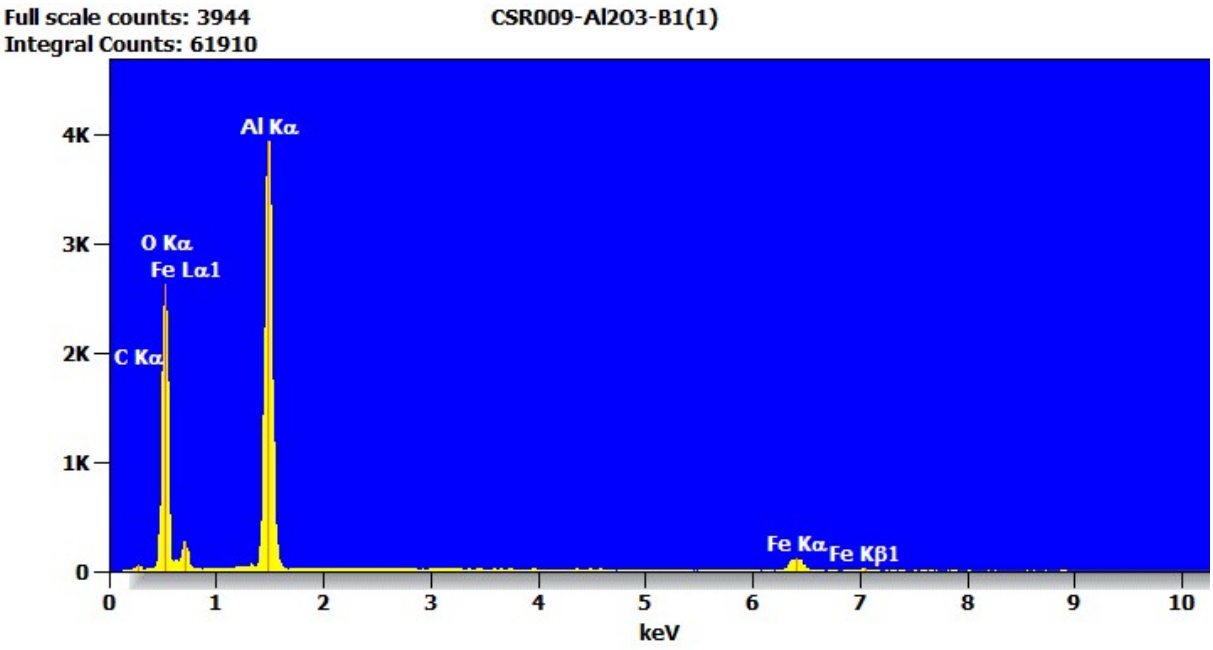

Fig. S23: EDX spectrum of **1_Al**.

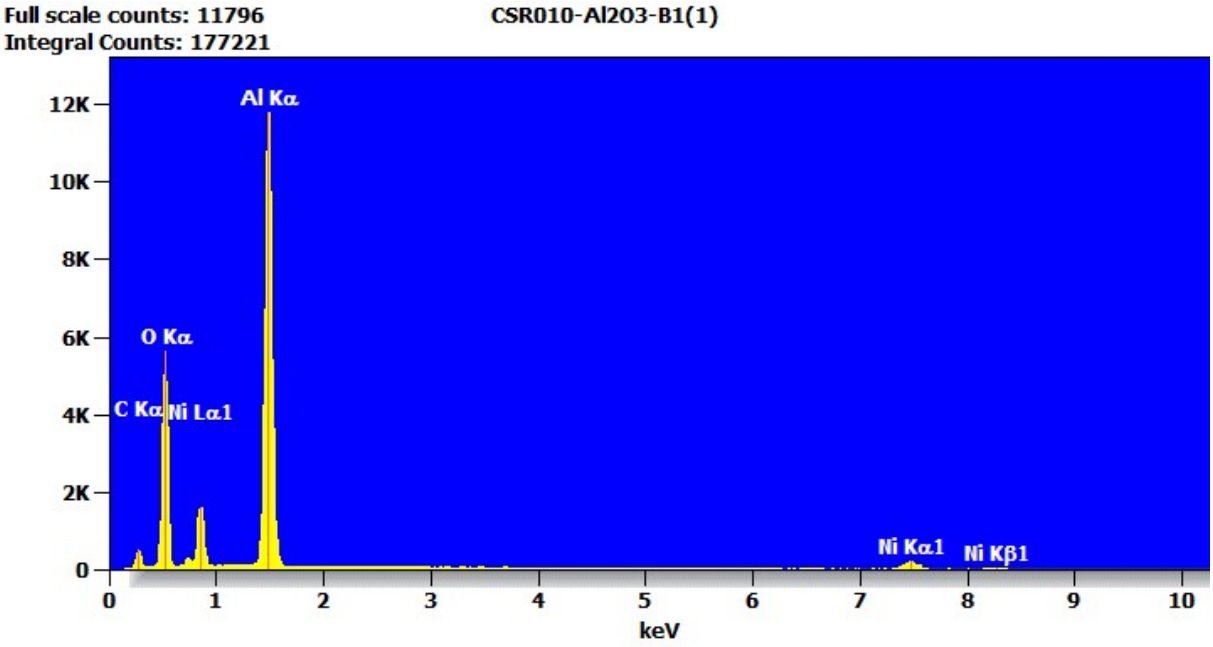

Fig. S24: EDX spectrum of **2_Al**.

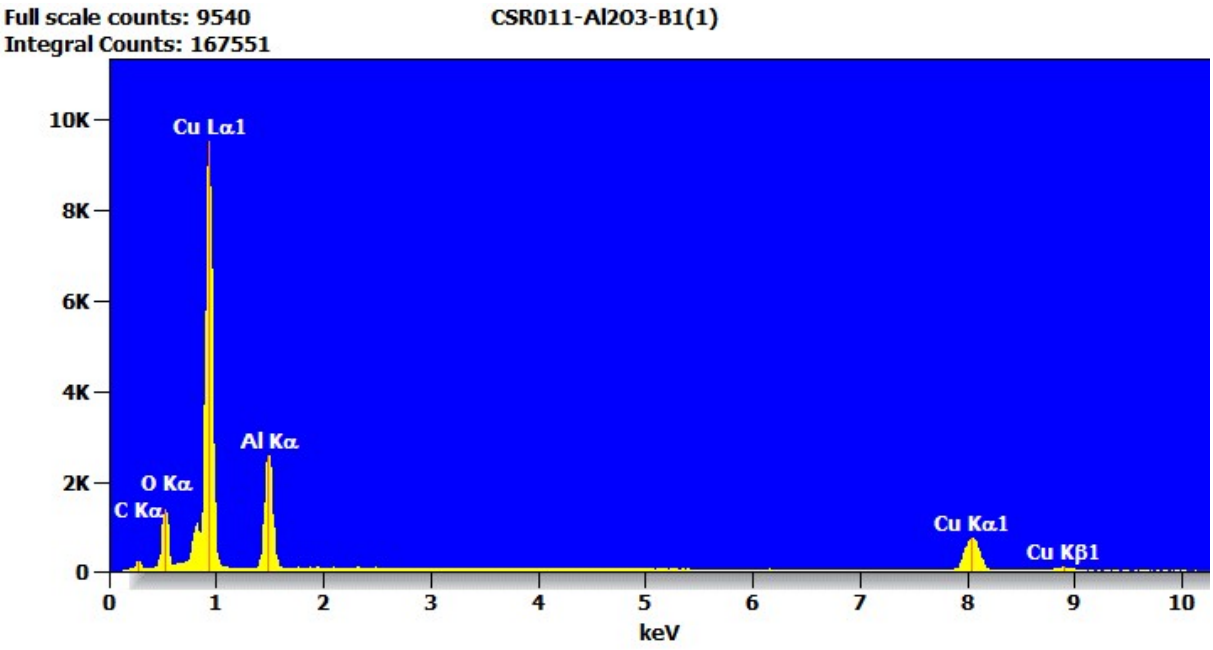

Fig. S25: EDX spectrum of **3_Al**.

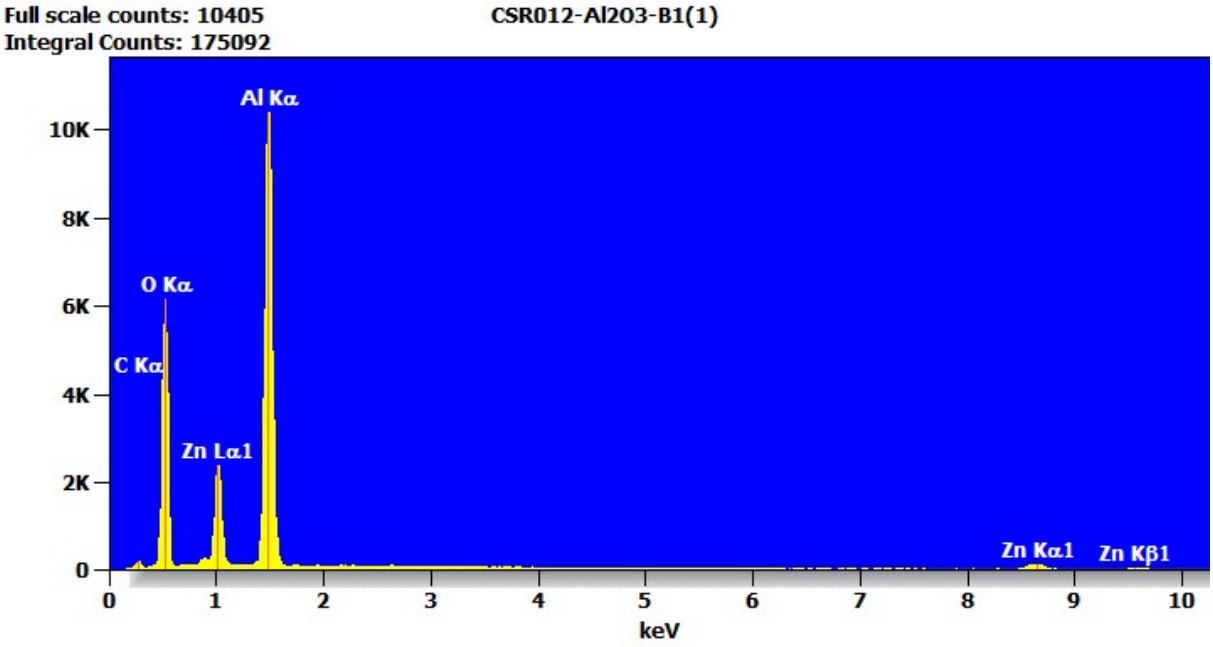

Fig. S26: EDX spectrum of **4_Al**.

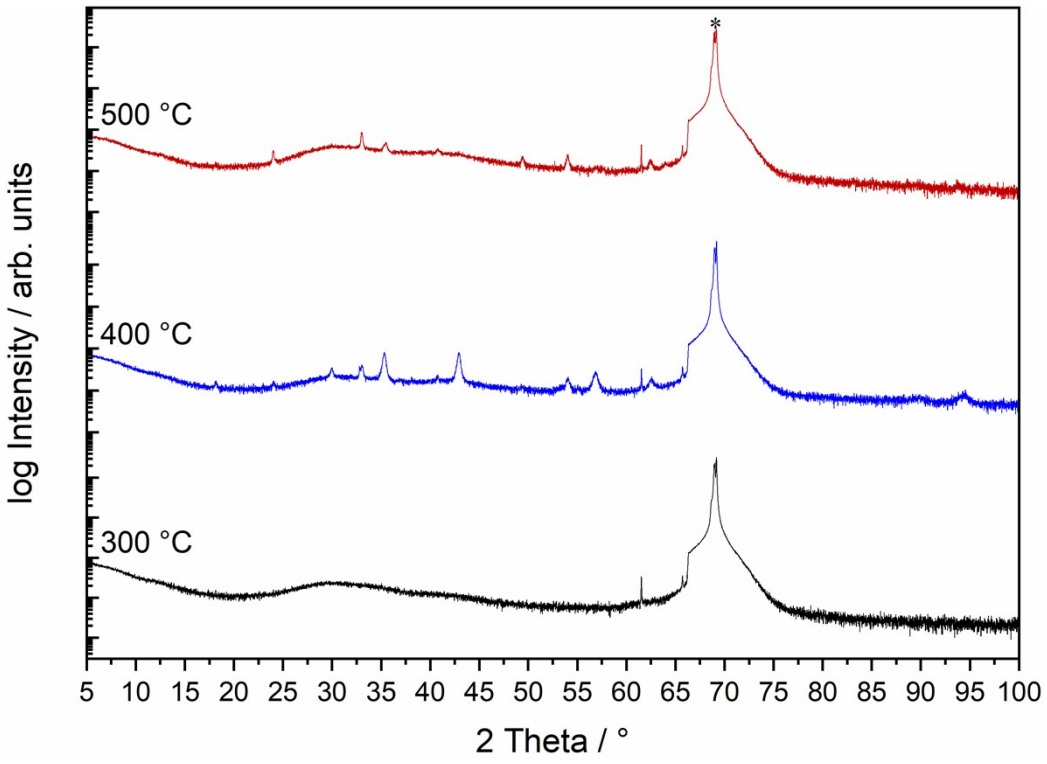

Fig. S27: XRD of **1_Si**.

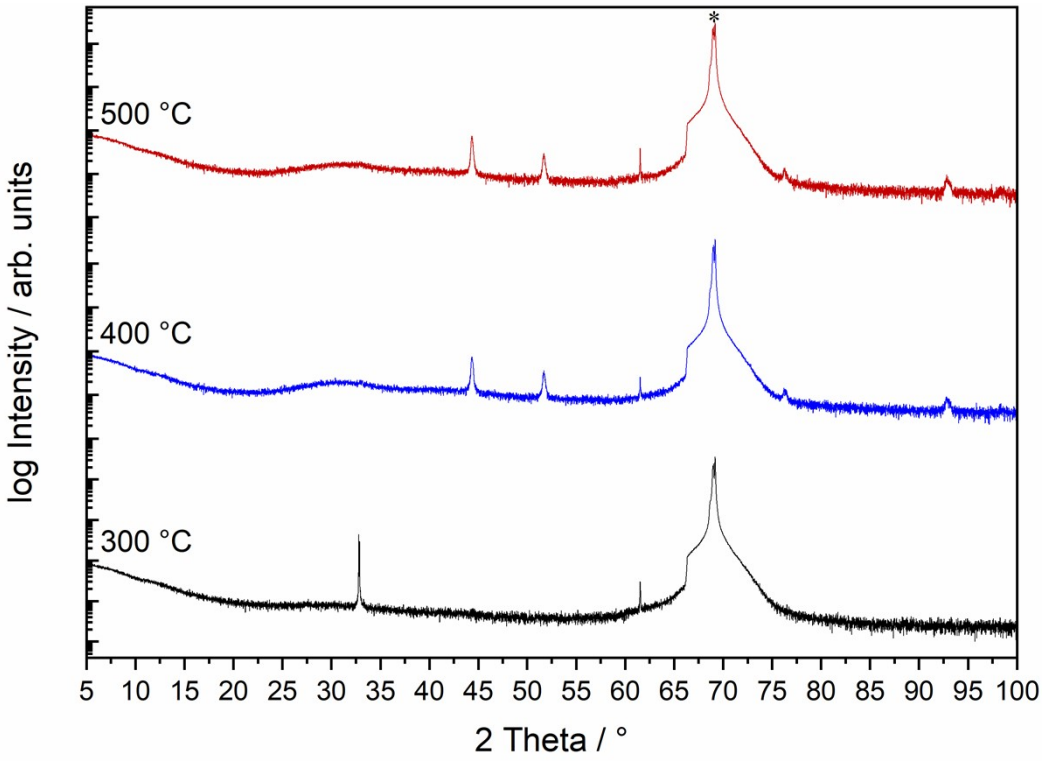

Fig. S28: XRD of **2_Si**.

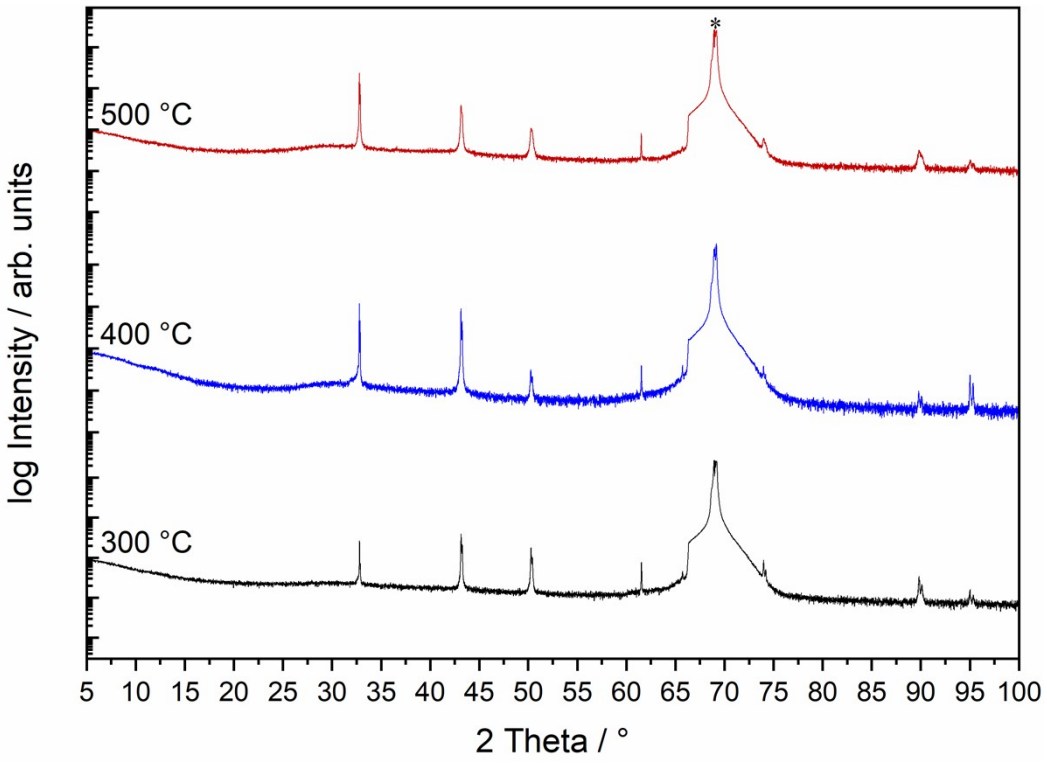

Fig. S29: XRD of **3_Si**.

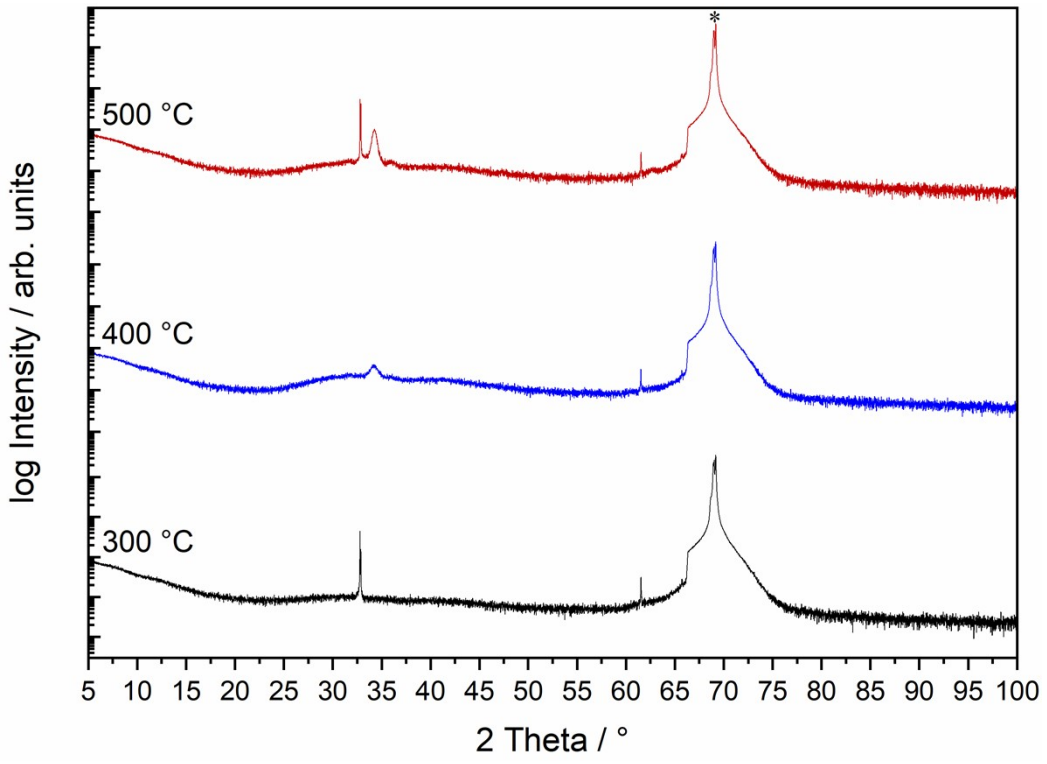

Fig. S30: XRD of **4_Si**.

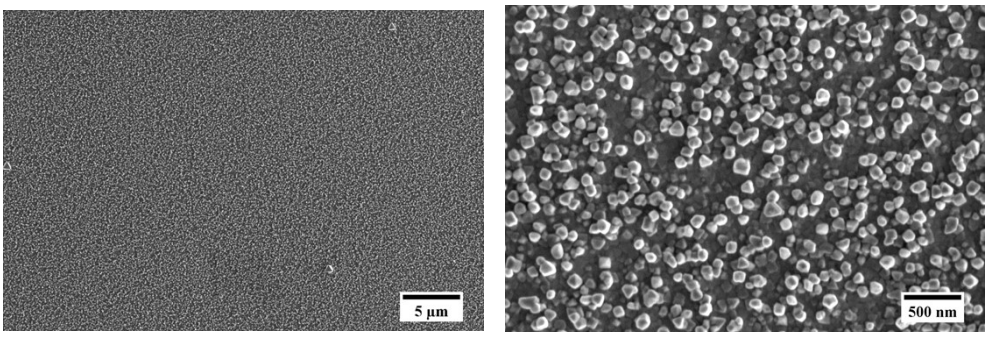

Fig. S31: SEM image of **1_Al**.

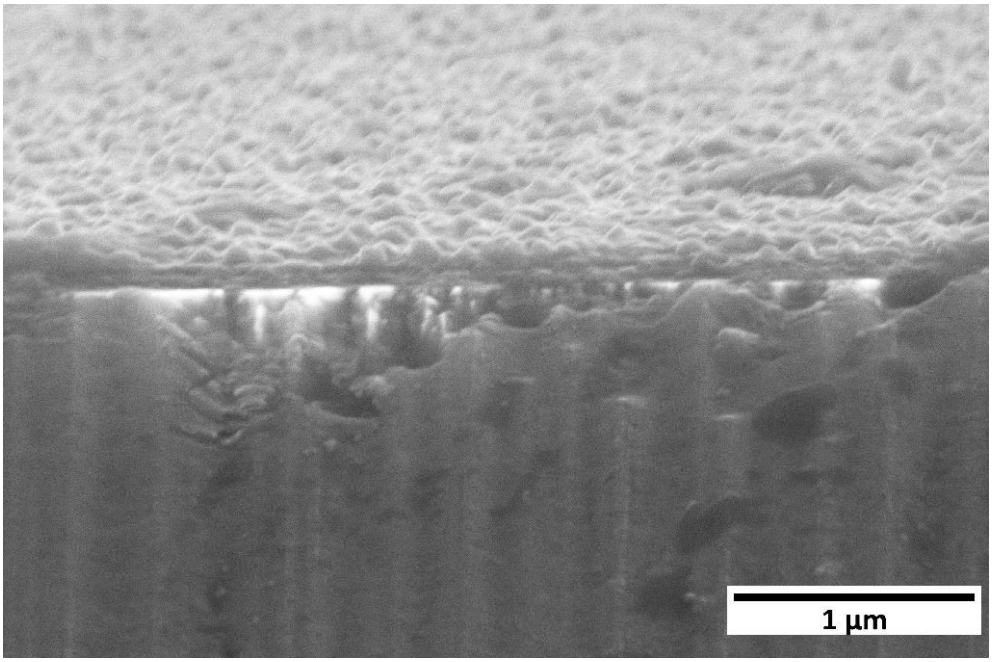

Fig. S32: Cross section SEM image of **1_Al**.

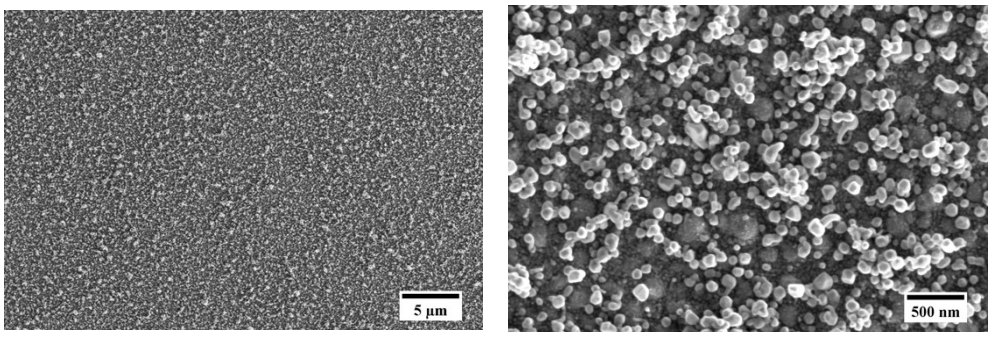

Fig. S33: SEM image of **2_Al**.

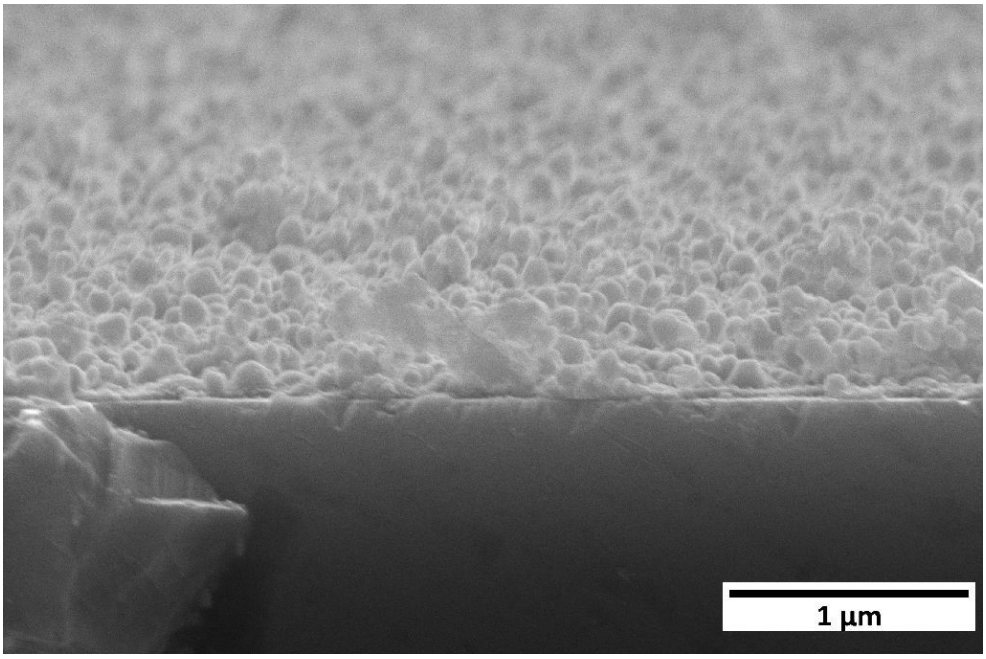

Fig. S34: Cross section SEM image of **2_Al**.

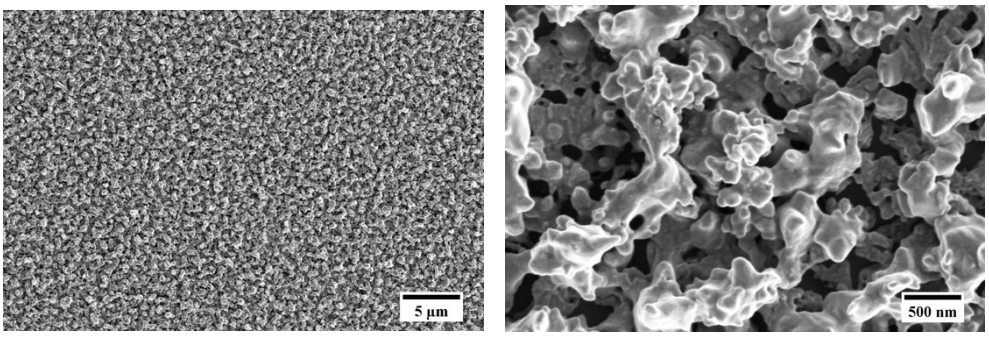

Fig. S35: SEM image of **3_Al**.

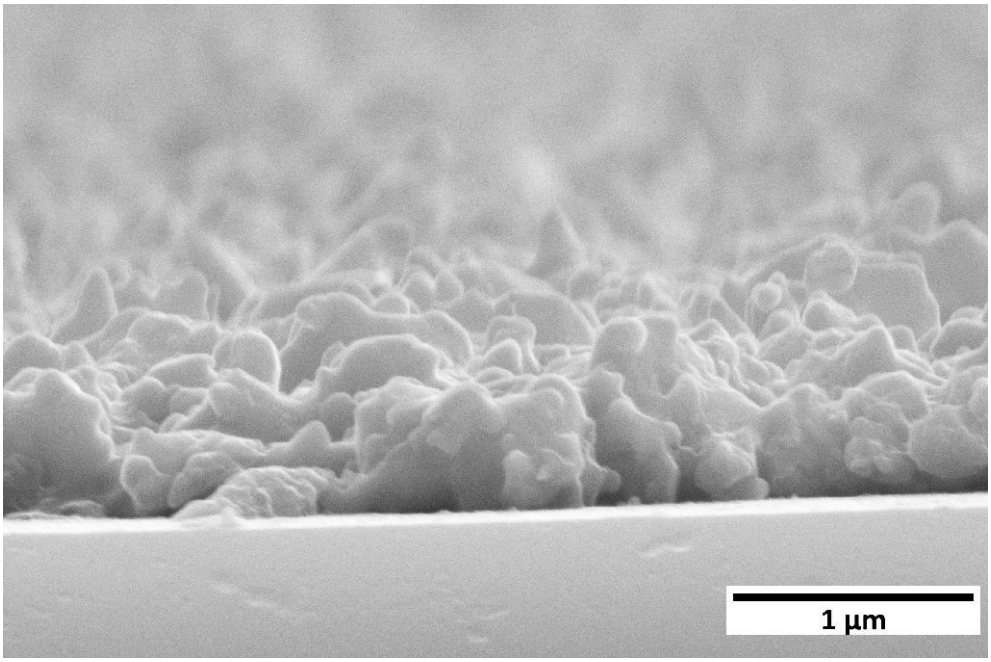

Fig. S36: Cross section SEM image of **3_Al**.

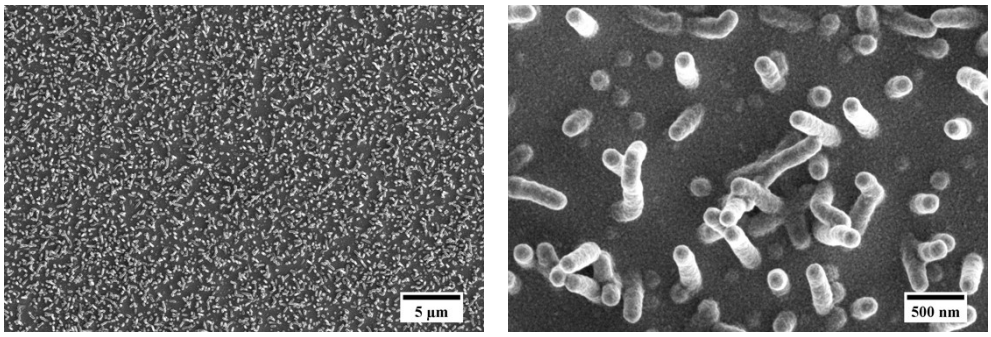

Fig. S37: SEM image of **4_Al**.

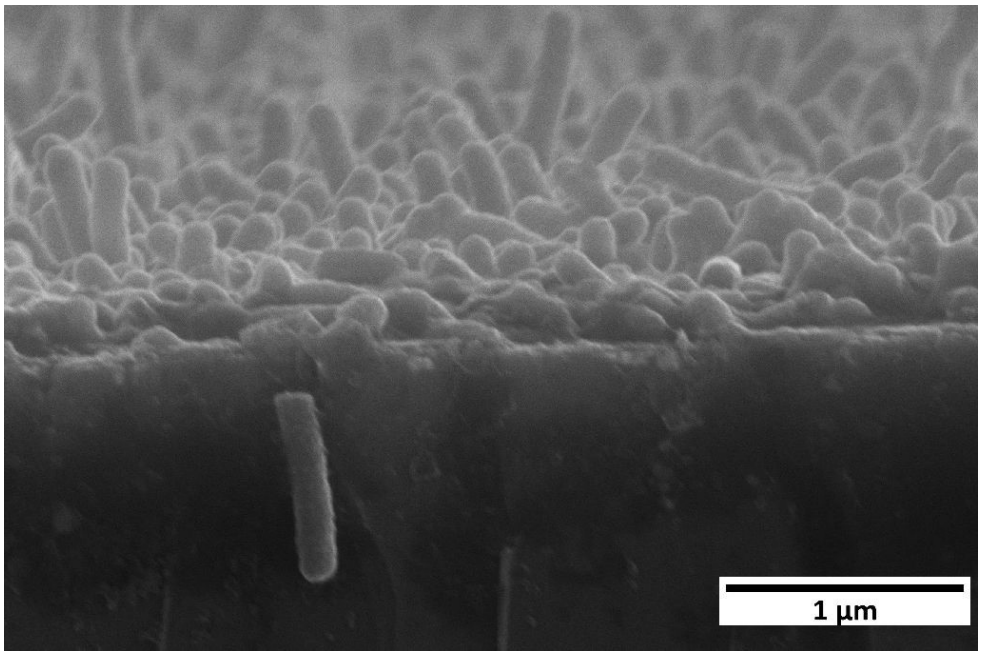

Fig. S38: Cross section SEM image of **4_Al**.

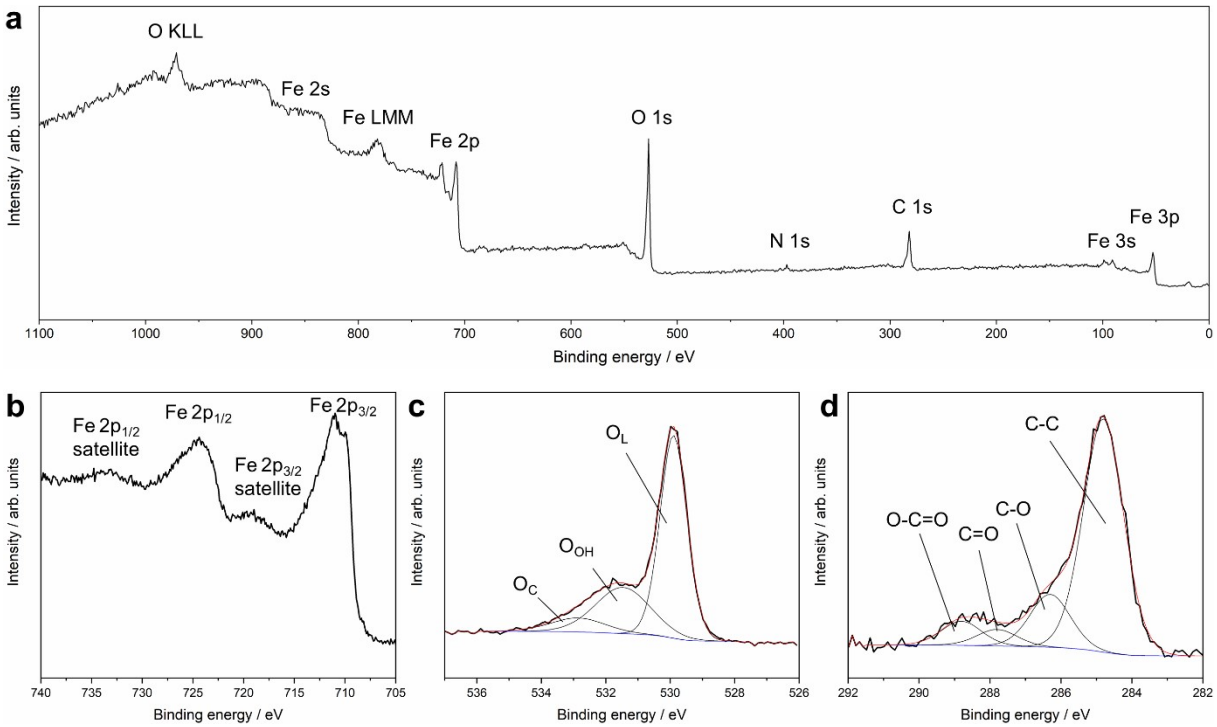

Fig. S39: XPS of **1_Al**. Survey (a), Fe 2p (b), O 1s (c) and C 1s (d).

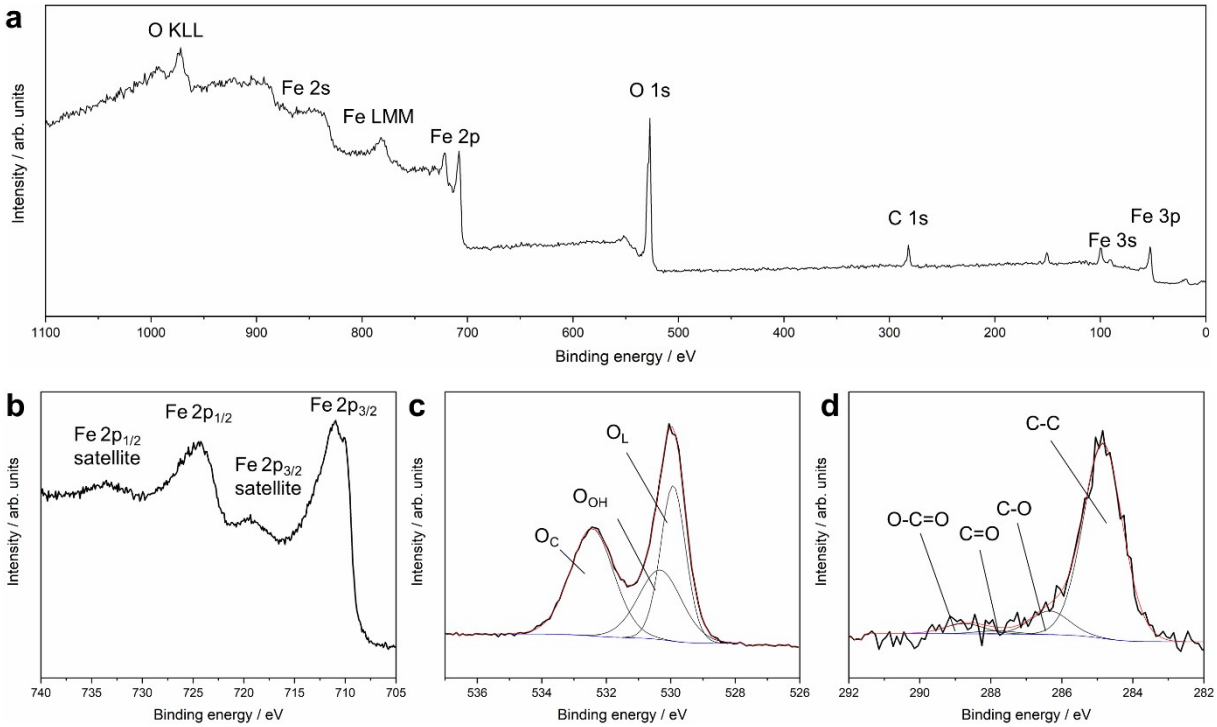

Fig. S40: XPS of **1_Al** after calcination. Survey (a), Fe 2p (b), O 1s (c) and C 1s (d).

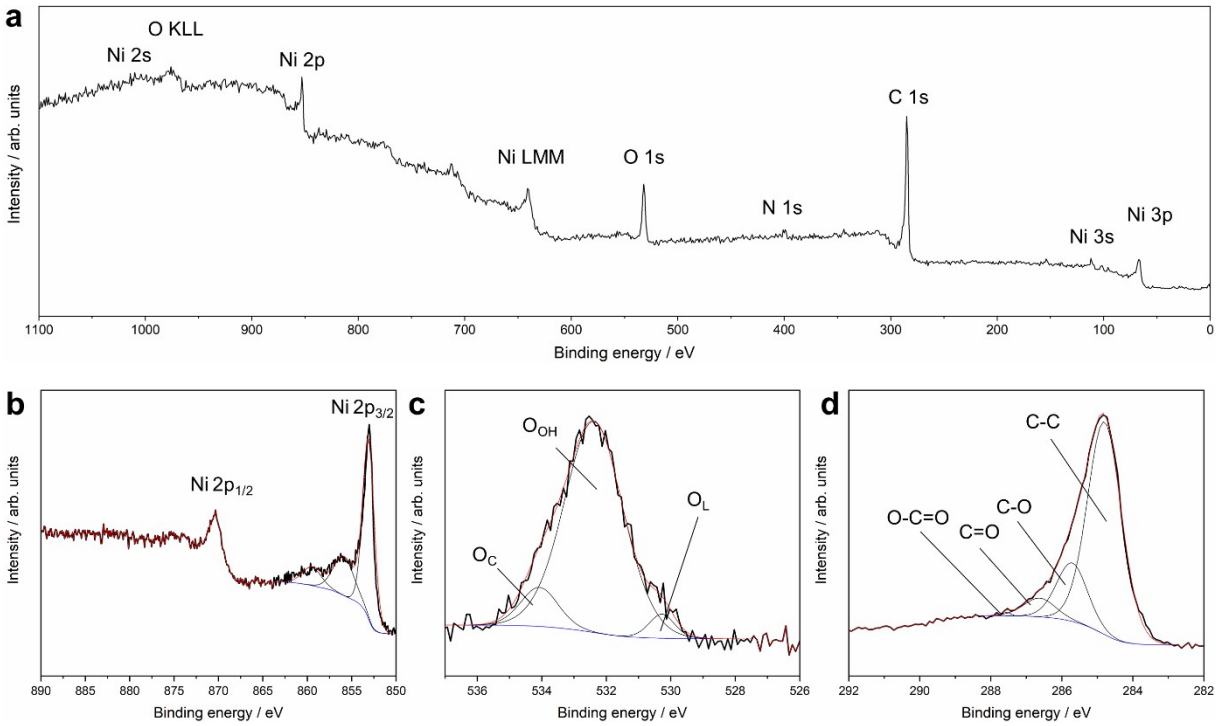

Fig. S41: XPS of **2_Al**. Survey (a), Ni 2p (b), O 1s (c) and C 1s (d).

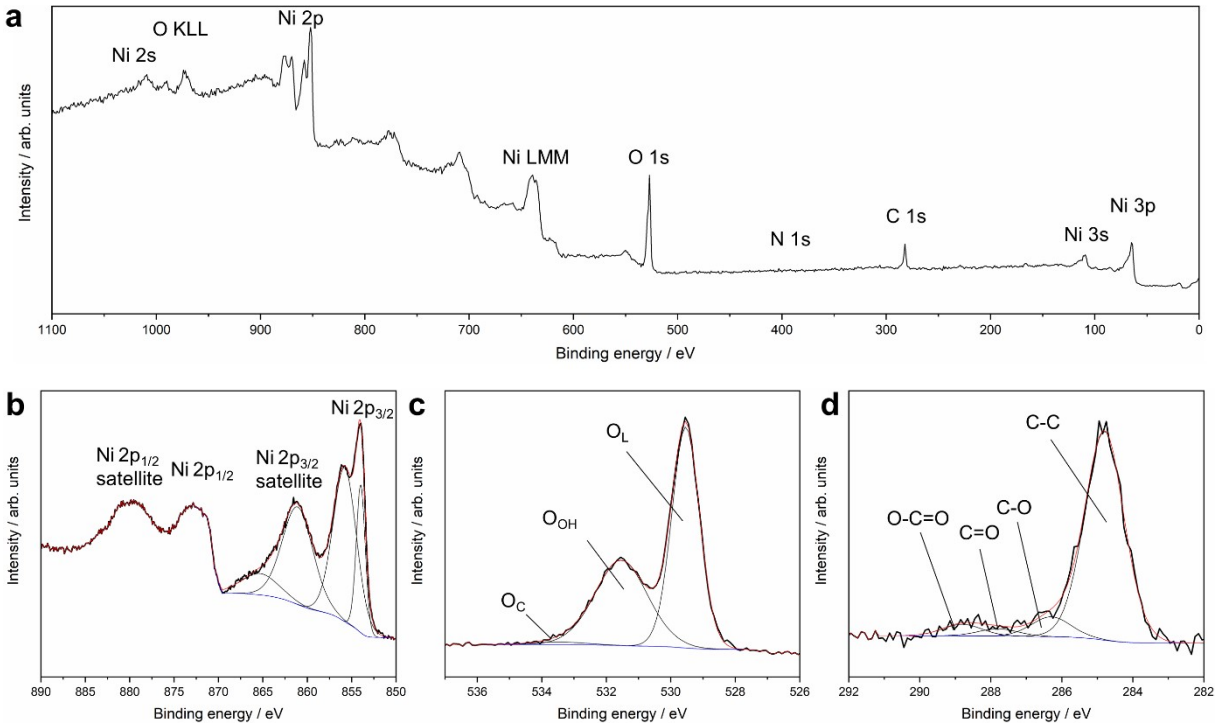

Fig. S42: XPS of **2_Al** after calcination. Survey (a), Ni 2p (b), O 1s (c) and C 1s (d).

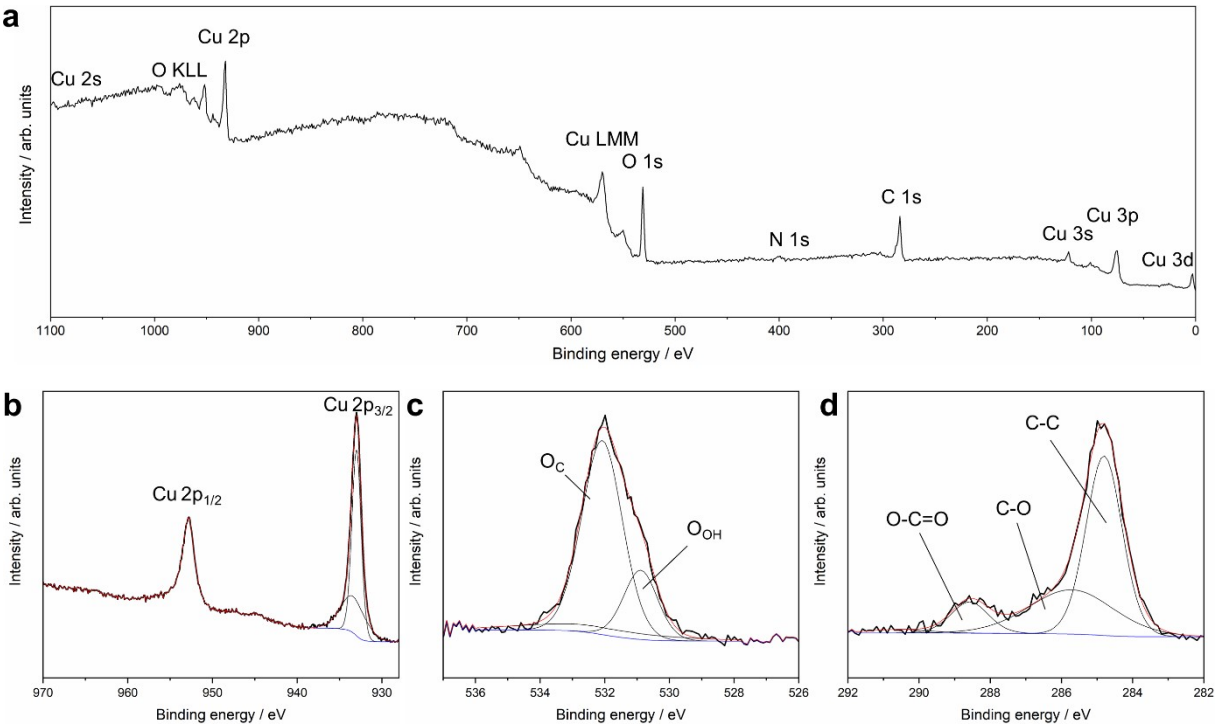

Fig. S43: XPS of **3_Al**. Survey (a), Cu 2p (b), O 1s (c) and C 1s (d).

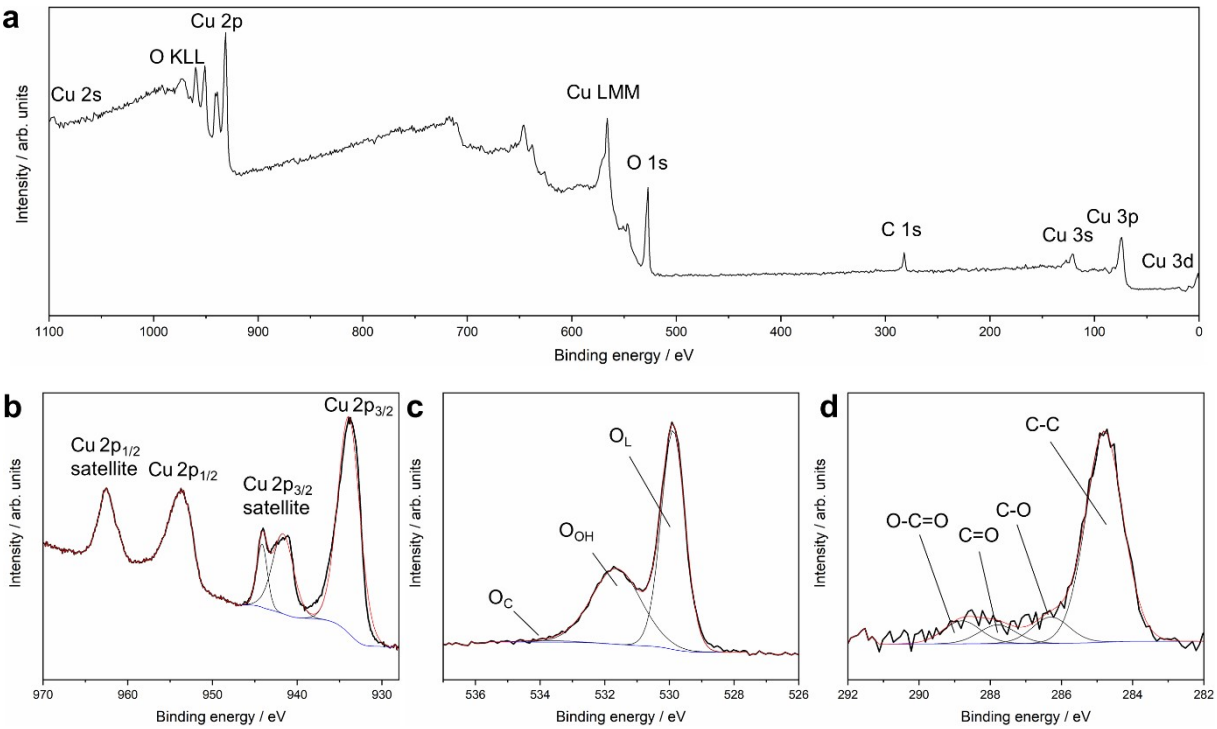

Fig. S44: XPS of **3_Al** after calcination. Survey (a), Cu 2p (b), O 1s (c) and C 1s (d).

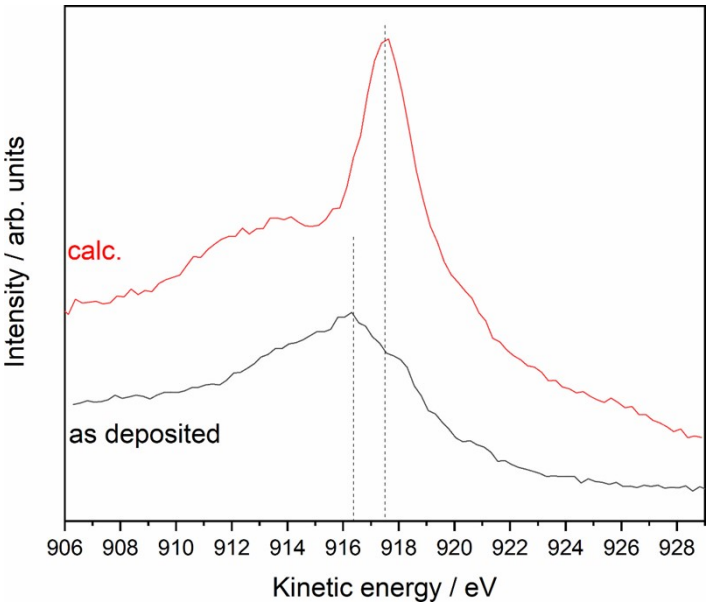

Fig. S45: Cu LMM spectra of **3_Al** before and after calcination.

Tab. S7: Calculation of the mod. Auger parameter for **3_Al**

	Cu $2p_{3/2}$ (eV)	Zn LMM (eV)	Mod. Auger parameter (eV)	Mod. Auger parameter (eV) Reference[2]
3_Al	933.0	916.4	1849.4	1849.2 (Cu_2O)
3_Al_calc	933.7	917.6	1851.3	1851.3 (CuO)

[2] M. C. Biesinger, Surf. Interface Anal., 2017, 49, 1325–1334.

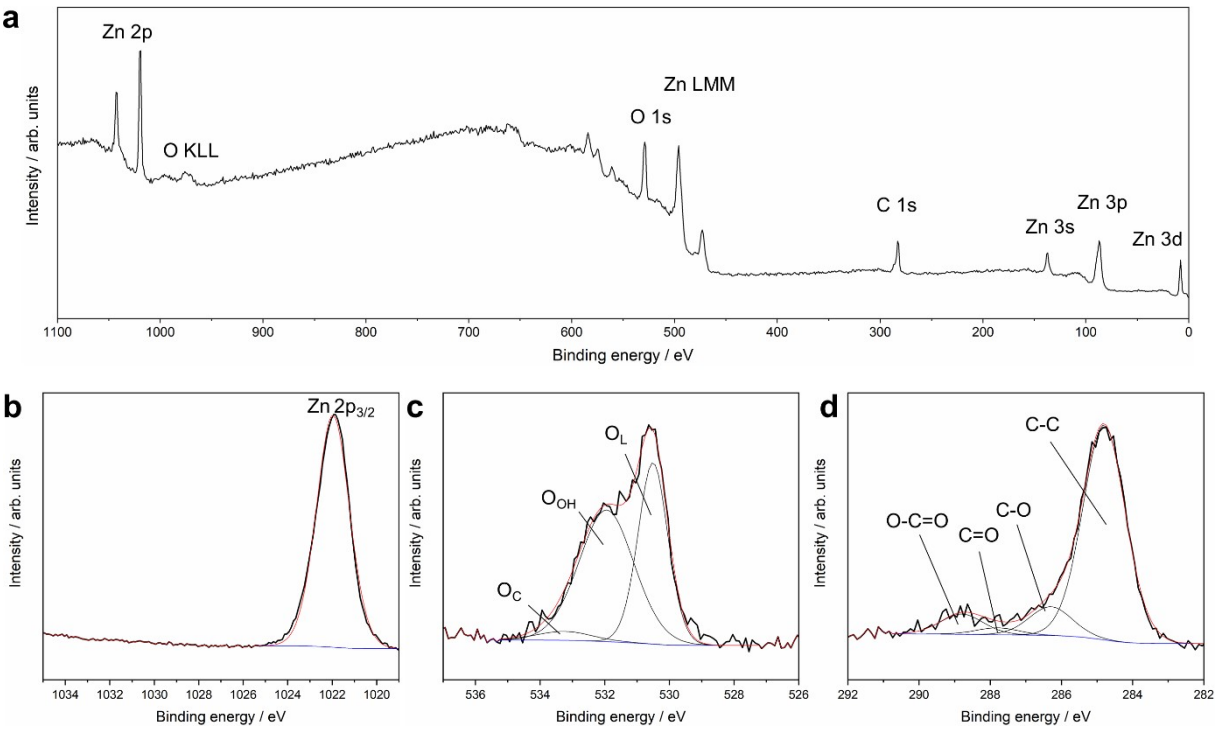

Fig. S46: XPS of **4_Al**. Survey (a), Zn 2p (b), O 1s (c) and C 1s (d).

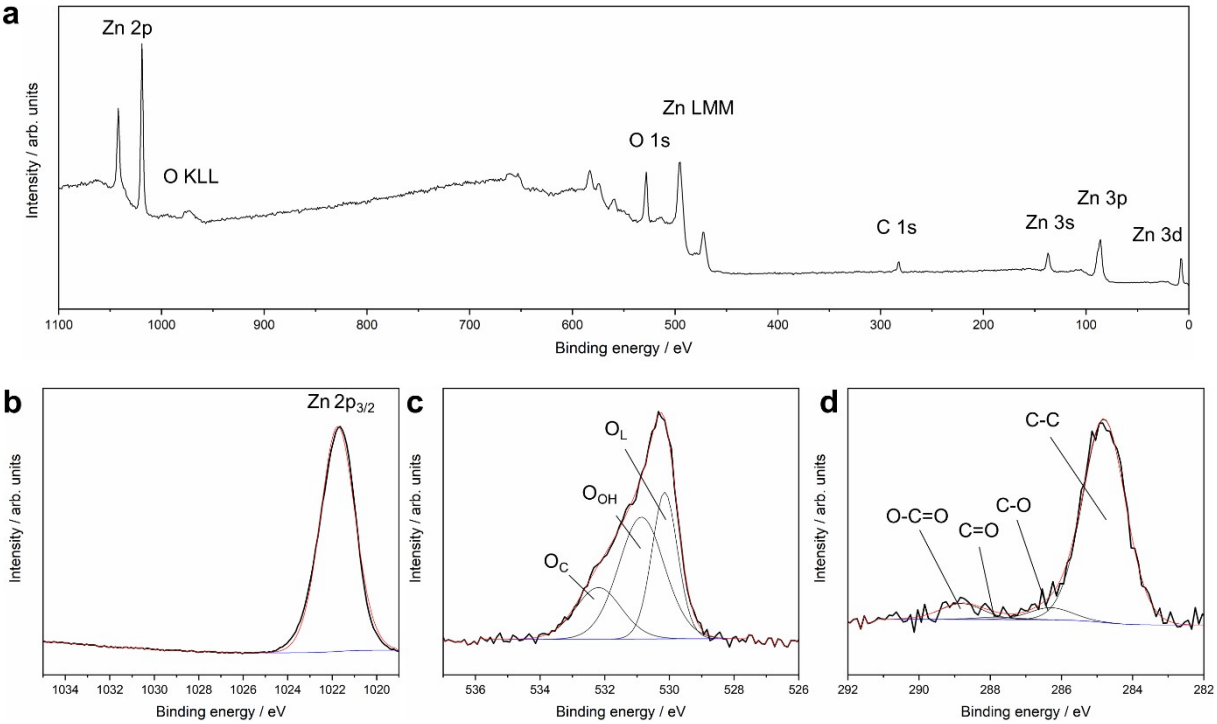

Fig. S47: XPS of **4_Al** after calcination. Survey (a), Zn 2p (b), O 1s (c) and C 1s (d).

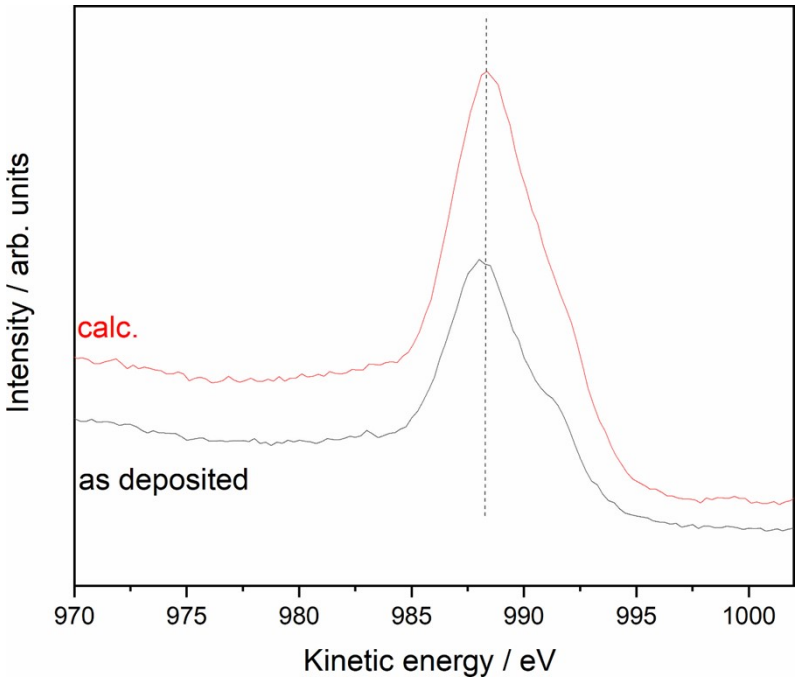

Fig. S48: Zn LMM spectra of **4_Al** before and after calcination.

Tab. S8: Calculation of the mod. Auger parameter for **3_Al**

	Zn $2p_{3/2}$ (eV)	Zn LMM (eV)	Mod. Auger parameter (eV)	Mod. Auger parameter (eV) Reference[3]
4_Al	1021.9	988.0	2009.9	2010.4 (ZnO)
4_Al_calc	1021.7	988.3	2010.0	2010.4 (ZnO)

[3] M. C. Biesinger, L. W. M. Lau, A. R. Gerson, R. S. C. Smart, *Appl. Surf. Sci.* **2010**, *257*, 887–898.