

Supporting Information for

First Example of Ugi's Amine as a Platform for Construction of Chiral Coordination Polymers: Synthesis and Properties

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Experimental section

General Considerations. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry argon. Anhydrous diethyl ether was obtained from commercial sources and used as supplied. ¹H (400.13 MHz), ¹³C (100.16 MHz), and ³¹P (500 MHz) NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 20 °C in CDCl₃ and referenced to tetramethylsilane (TMS). Powder X-ray diffraction (PXRD) experiments were carried out at room temperature using STOE STADI P diffractometer with Cu-Kα1 radiation (λ = 1.54059 Å) and a 2D detector (Mythen, Dectris) in transmission geometry. The thermal stabilities were investigated by thermogravimetry (TG) analysis using NETZSCH (Selb, Germany) STA409 instrument. Approximately 5–6 mg of sample was placed into an Al₂O₃ crucible with a pre-hole on the lid and heated from 25 °C to 1000 °C (heating rate of 5 °C/min, under Ar atmosphere). SEM analysis was carried out using 2 kV acceleration voltage and a working distance of 21.7 mm on a Hitachi SU8020. FT-IR spectra were recorded on a Bruker Vertex 70 in the range from 4000 to 600 cm⁻¹ (resolution 2 cm⁻¹, ATR). CHN analysis was performed on a EuroEA elemental Analyser.

R,Sp/S,Rp-2-(N,Ndimethyl-α-aminoethyl)ferrocenylphosphinic acid (1) synthesis. To a solution of N,N-dimethyl-1-ferrocenylethylamine (5 g, 19.45 mmol) in diethyl ether at RT was slowly added ⁿBuLi (7.8 ml, 21.4 mmol, 2.5M in *n*-hexane). The resulting solution was stirred for 8 h. Then it was cooled down on *i*-pr/N₂ bath and bis(N,N-diethylamino)chlorophosphine (4.1 ml, 21.4 mmol) was added dropwise. Cold bath was removed in 30 min and reaction continued for more 6 h. Afterwards Et₂O was evaporated, brown oily residue was dissolved in chloroform and hydrolyzed with 4 equivalents of 30% acetic acid. Reaction mixture was refluxed for 5 h. Brown oily residue was washed thoroughly with Et₂O and recrystallized from acetone giving a yellow powder. Yield: 3 g (48%). ¹H NMR: δ = 1.56 (d, 3H, 3JHH = 6.27, CH₃), 2.50 (s, v br, 6H, NMe₂), 4.26 (s, 5H, Cp), 4.29 (s, 1H, Cp), 4.37 (s, 1H, Cp), 4.66 (qv, 1H, 3JHH = 6.27, CH), 4.78 (s, 1H, Cp) 8.00 (d, ¹J_{HP} = 540, P-H). ¹³C{¹H} NMR: δ = 70.34 (s), 76.61 (s), 77.04 (s), 77.46 (s). ³¹P{¹H} NMR: δ = 14.8 (s, 1P, ¹J_{HP} = 549). FT-IR: 2300 cm⁻¹ (P-H stretch), 1644 cm⁻¹ (P-OH stretch), 1178 cm⁻¹ (P=O stretch), 1110-914 cm⁻¹ (P-Ar stretch and Cp-ring groups). EA: calcd.: C 49.58 %, H 6.54 %, N 4.13 %, P 9.13 %, found: C 48.99 %, H 6.84%, N 3.44%, P 8.79%.

Synthesis of **2**: Ni(NO₃)₂·6H₂O (0.0136 g, 0.046 mmol), acid **1** (0.03 g, 0.092 mmol), and 4,4'-bipyridine (0.0146 g, 0.092 mmol) were dissolved in water (2 ml). The mixture was heated to 90 °C for 24 h in a Pyrex tube. After cooling to room temperature the product was isolated by decanting the mother liquid and washed with water. Yield: 49%.

The phase purity of the product was confirmed by X-ray powder diffraction analysis (Fig. S1), TG and SEM/EDS analysis. FT-IR: 2300 cm⁻¹ (P-H stretch), 1604 cm⁻¹ (P-OH stretch), 1165 cm⁻¹ (P=O stretch), 1096-

941 cm⁻¹ (P-Ar stretch and Cp-ring groups), EA for [Ni(bpy)₂L₂·7H₂O]_n: calcd.: C 50.69 %, H 6.03 %, N 7.39 %, P 5.45 %, found: C 52.78 %, H 5.65 %, N 5.09 %, P 4.90 %.

Single crystal X-ray diffraction

The X-ray diffraction data for the single crystal of **1** was collected on a Bruker AXS Smart Apex diffractometer at 296(2) K using Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using APEX3¹ for data collection, SAINT² for data reduction, SADABS³ for multi-scan absorption correction, SHELXT⁴ for structure solution, SHELXL⁴ for structure refinement by full-matrix least-squares against F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at carbon atoms were placed into calculated positions and refined as “riding” atoms. Hydrogen atoms of the water molecule were revealed from difference Fourier series and refined isotropically. CCDC 1996849 contains the supplementary crystallographic data for this paper.

Crystal data for **1**: formula C₁₄H₂₂FeNO₃P, $M = 339.14$ g/mol, monoclinic, space group P2₁/c (No. 14), $Z = 4$, $a = 16.210(8)$ Å, $b = 7.525(4)$ Å, $c = 12.606(6)$ Å, $\beta = 97.855(6)^\circ$, $V = 1523.3(13)$ Å³, $\rho_{\text{calc}} = 1.479$ g·cm⁻³, $\mu = 1.101$ mm⁻¹, 13163 reflections collected ($-21 \leq h \leq 21$, $-10 \leq k \leq 9$, $-16 \leq l \leq 16$), θ range = 2.537° to 28.325°, 3732 independent ($R_{\text{int}} = 0.0922$) and 1762 observed reflections [$I \geq 2 \sigma(I)$], 200 refined parameters, $R_1 = 0.0584$, $wR_2 = 0.1418$, max (min) residual electron density 0.745 (−0.472) e Å⁻³.

Table S1. Details of hydrogen bonds in **1**.

D–H···A	D–H, Å	H···A, Å	D···A, Å	angle D–H···A
N13–H13···O2	0.92(5)	1.76(5)	2.665(5)	166(4)
O1W–H1WB···O2	0.85(1)	1.97(3)	2.777(6)	159(6)
O1W–H1WA···O1*	0.878(10)	1.975(17)	2.811(5)	169(7)

O1* is at equivalent position (1− x , −1− y , 1− z)

The dataset on single crystal of **2** was collected on Bruker Kappa APEX2 diffractometer, equipped with a 4-circle goniometer, long-focus X-ray tube with Mo-anode and graphite monochromator ($\lambda = 0.071073$ nm). The dataset was collected at 296 K. The images were integrated using the SAINT routine.⁵⁻⁸ The corrections for Lorentz, polarization and absorption effects were performed with the help of SADABS software.⁵⁻⁸ The crystal structure was solved by direct methods and refined by full matrix least-squares on F^2 using SHELXT-2014/5 and SHELXL-2018/3.⁴ All non-hydrogen atoms were refined in the anisotropic approximation. Hydrogen atoms were refined in geometrically calculated positions using a “riding model” with $U_{\text{iso}}(H) = 1.2U_{\text{iso}}(C)$. The occupancies of disordered P1 and Fe1 were refined freely and fixed in the last refinement cycle. CCDC-2021806 contain the supplementary crystallographic data for **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for [Ni(bpy)₂L₂·7H₂O]_n·(**2**): C₄₈H₅₄Fe₂N₆NiO₄P₂·7H₂O, $M = 1137.32$ g mol⁻¹, tetragonal, $I4/mmm$ (No. 139), $a = 11.3027(7)$ Å, $c = 17.8993(13)$ Å, $V = 2286.7(3)$ Å³, $Z = 2$, $d_c = 1.469$ gcm⁻³, $\mu = 1.155$ mm⁻¹, 2θ range 2.131 - 26.40°, reflections collected/unique 26.400/711, $R_{\text{int}} = 0.0585$, reflections/parameter 711/44, $R_1(I/I(\sigma) > 2) = 0.1200$, $wR_2(\text{all data}) = 0.3158$, $S = 1.537$, largest diff. peak 1.060 eÅ⁻³ and hole - 0.349 eÅ⁻³.

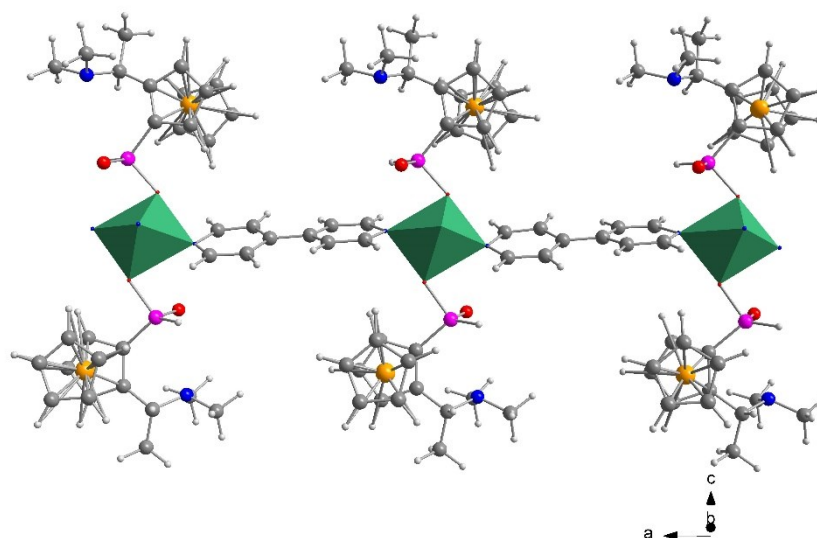


Figure S1. Simulated crystal structure of **2** in *P1*: view on Ni(bpy)₂L₂ layers along *b* crystallographic direction. Color code: C - grey, N - blue, O - red, P - pink, Fe - orange, Ni polyhedra - green. **Powder X-ray diffraction**

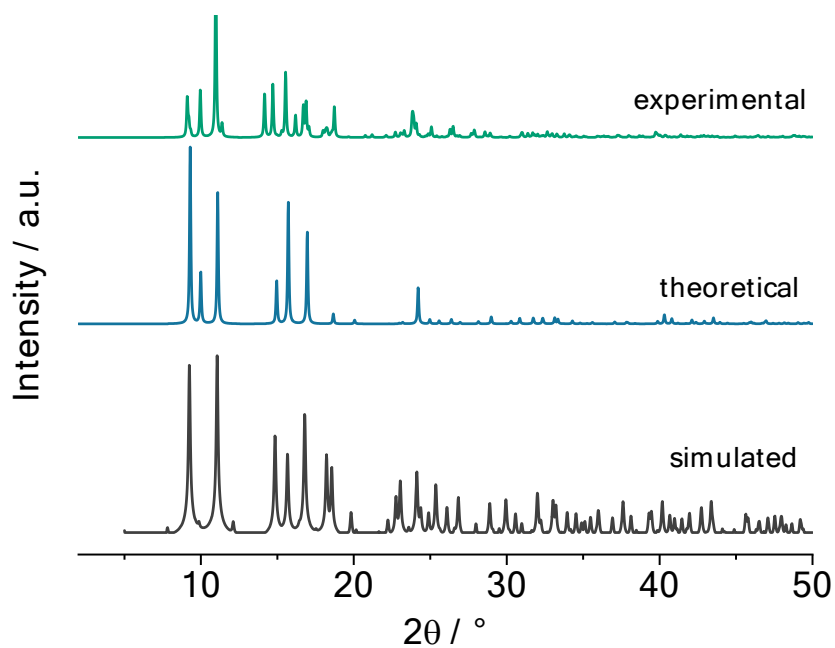


Figure S2. Powder X-ray diffraction patterns of **2**: calculated from the simulated structure (black), calculated from the crystal structure (blue), as-made material (green).

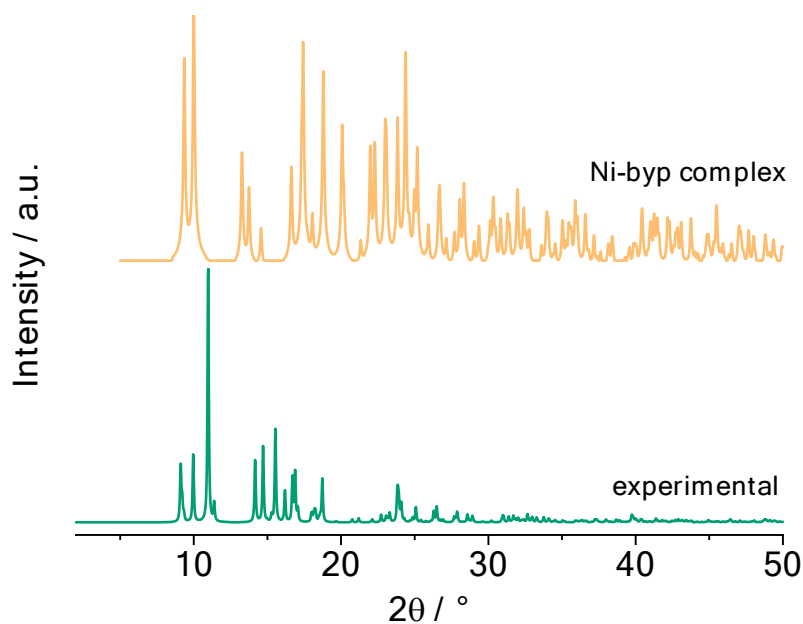


Figure S3. Powder X-ray diffraction patterns of **2** and pre-organized Ni-bipyridine framework $[(\text{Ni}(\text{bipy})_2(\text{NO}_3)_2)_n]$ (CCDC 182/1136).¹⁰

Electrochemistry

Electrochemical measurements were taken on a BASiEpsilonE2P electrochemical analyzer (USA). The program concerned Epsilon-EC-USB-V200 waves. A conventional three-electrode system was used with glassy carbon for carbon paste electrode (CPE) solutions for powder samples as the working electrode, the Ag/AgCl system was served as reference electrode, and a Pt wire as the counter electrode. 0.1 M Et_4NBF_4 was used as the supporting electrolyte to determine the current–voltage characteristics. To study the powder samples, a modified CPE working electrode was used, which was prepared as follows: the carbon particles/phosphonium salt (dodecyl(tri-tert-butyl)phosphonium tetrafluoroborate) composite electrode was prepared using a grinding a mixture of graphite powder and phosphonium salt with a 90/10 (w/w) ratio in mortar giving it a homogeneous mass. A modified electrode was also devised in a similar manner except that a portion (ca. 5%) of the graphite powder was replaced by the CPs under study. As a result, a portion of the resulting paste was packed firmly into the (3 mm in diameter) a Teflon holder cavity.⁹

Energy dispersive spectroscopy (EDS) of **2**.

The chemical composition of Ni coordination polymer was studied using energy dispersive spectroscopy (EDS) in addition to the elemental analysis. The EDS pattern confirms the presence of Ni, Fe, and P in the synthesized compound. Quantitative analyses of the EDS result show, that **2** contains 23.6 wt.% Ni, 39.5 wt.% f Fe and 36.9 wt.% P.

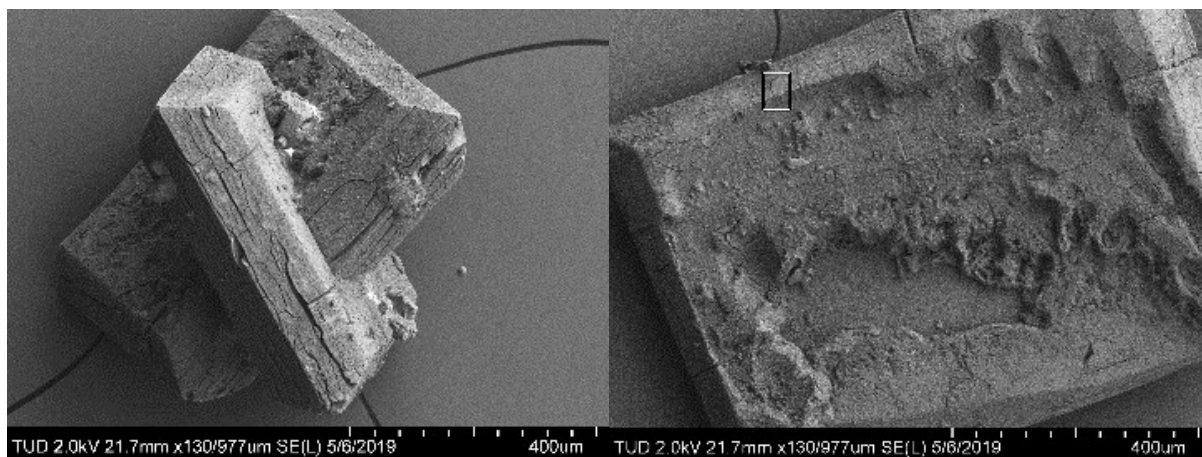


Figure S4. SEM image of **2**.

Thermogravimetry (TGA)

The thermal stability of **2** was investigated by thermogravimetric (TG) analysis using NETZSCH (Selb, Germany) STA449 F3 instrument. Approximately 5–6 mg of sample was placed into an Al₂O₃ crucible with a pre-hole on the lid and heated from 30 to 1000 °C. The same empty crucible was used as the reference. High-purity argon was used with a gas flow rate of 50 mL min⁻¹. TG measurement was performed at the heating rates of 10 °C min⁻¹.

Mass change in the range of 25 - 242 °C is due to loss of the solvent (water) molecules. Further mass losses correspond to decomposition of linker molecules – Fc fragment and bpy. The residual mass of 35.75% fits to the mass of products remaining after combustion to Fe₂O₃, NiO and P₂O₅ (found 35.75%, calculated 30.72%).

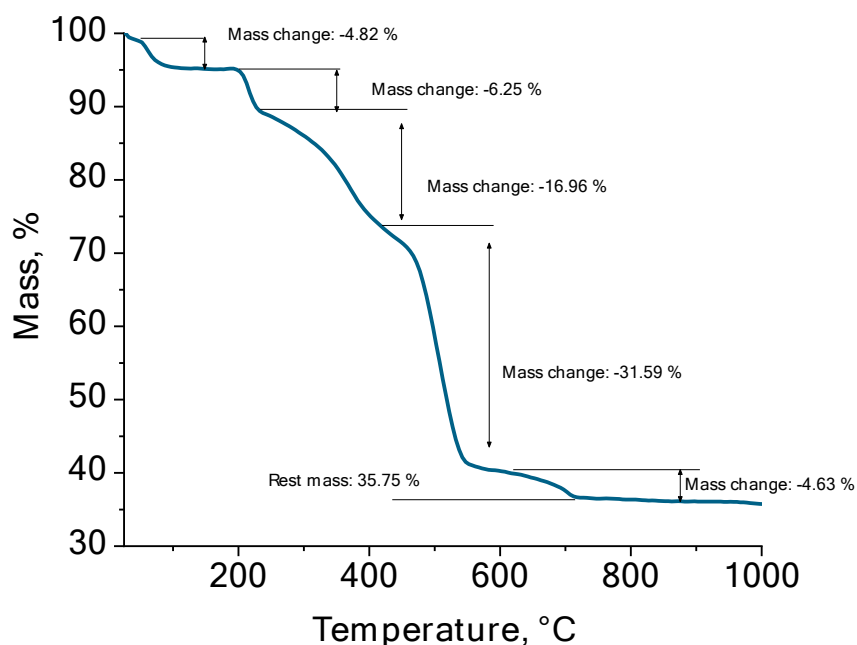


Figure S5. Thermogravimetric analysis data of **2**.

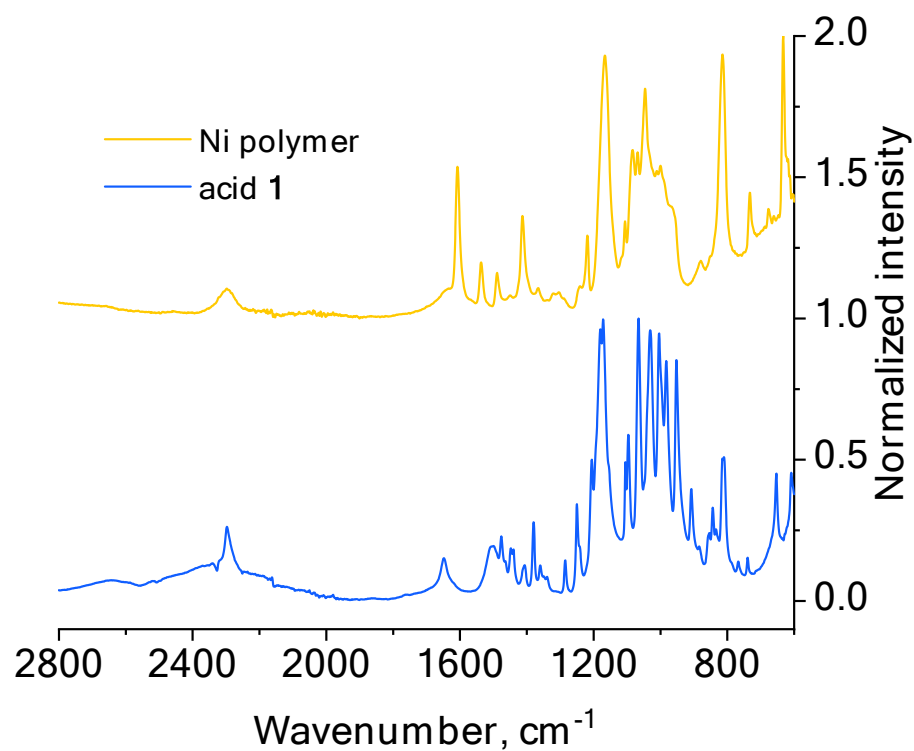


Figure S6. IR spectra for 1 (in blue) and 2 (in orange).

Scanning Electron Microscopy (SEM)

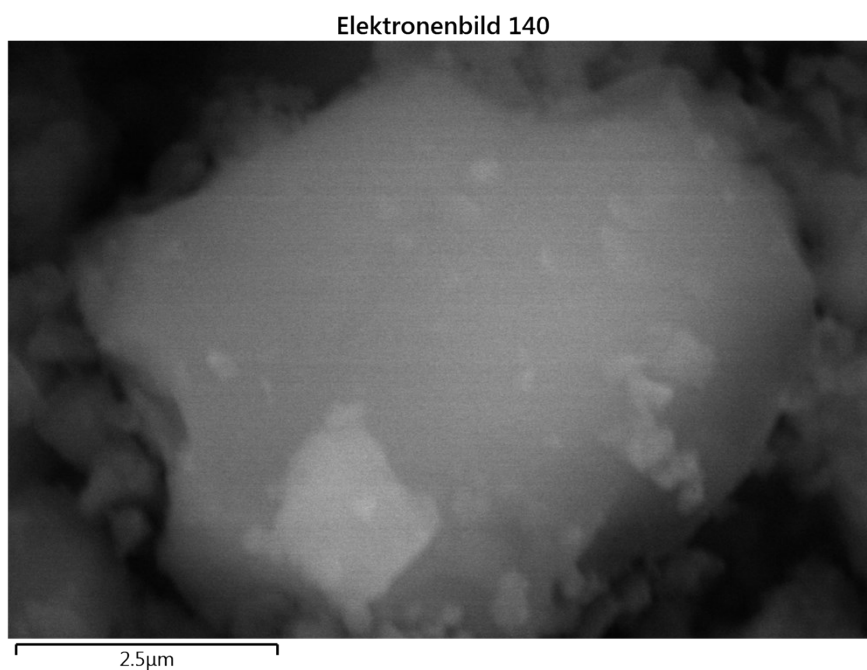
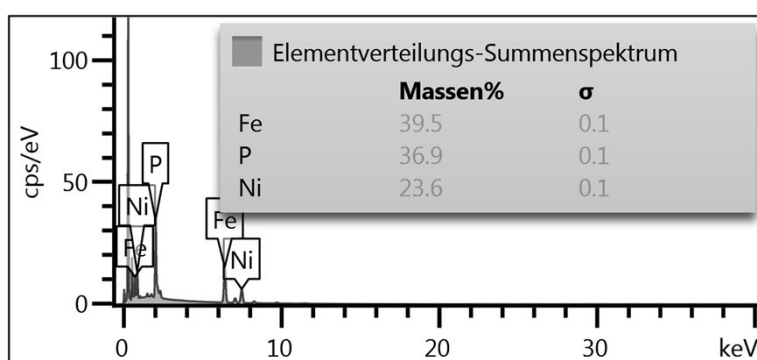


Figure S7. EDS analysis for 2.

Name:	Electron image140
Collected:	16.06.2020 11:42:52
Input signal:	Sig1
Resolution (width):	1024 pixels
Resolution (height):	704 pixels
Image width:	8.33µm
Image height:	5.72µm
Table tilt degree:	0.00°
Sample tilt in degrees:	0.00°
Software tilt correction:	Not applied
Enlargement:	15000 x
Number of frames averaged:	1
Dwell time:	10µs



Element	Line type	Quantification	Area	Sigma	Fit index
P	K series	Yes	710123.35	1788.38	430.36
Fe	K series	Yes	542660.67	1279.14	4.36
Fe	L series	No	178889.56	1541.72	11680.94
Ni	K series	Yes	226185.07	902.70	4.27
Ni	L series	No	233656.29	1263.17	7193.90
Al	K series	No	27725.92	757.63	123.73
	Noise 1	No	173323.57	4095.56	10193.55
	Noise 2	No	-210762.85	7639.02	1879.84
	Noise 3	No	113081.57	3971.10	1762.41

Name:	Element distribution sum spectrum
Element list type:	Current spectrum
Processing option:	All elements
Coating element:	No
Automatic line selection:	Activated
Normalization:	Activated
Limit value determination:	Disabled
Elements to be deployed:	Al
Selected standards:	Quant Standardizations (Extended Set) [default]
Pulse pileup correction:	Successfully carried out
Detector file:	X-Max 8
Efficiency:	File based

General information	
Name	Element distribution sum spectrum
Recording date	16.06.2020 11:43:13
Conditions for registration	
Measurement time (seconds)	230.7
Real time (seconds)	426.0
Process time	5
Energy range (keV)	40
Number of channels	2048
Energy per channel (eV)	20.0
Acceleration voltage (kV)	25.0
Enlargement	15000.0
Working distance (mm)	14.8
Sample tilt (degree)	0.0
Spectrum information	
Spectrum range (counts)	7554266.0
Spectrum Count Rate (cps)	17732.7
Pulse pileup correction	Successfully carried out
Strobe information	
Strobe resolution (eV)	44.05
Strobe area (counts)	5808900.0
Energy calibration information	
Calibration date	05.10.2015 15:36:32
Calibration peak	Nickel K-Series
Gain Calibration (eV / Channel)	19.9966
Beam calibration information	
Calibration date	05.10.2015 15:32:59
Calibration peak	Nickel K-Series
Peak integral (impulses)	310238.0
Process time	5
Measurement time (seconds)	12.3
System configuration	
Detector type	X-Max
serial number	65977-X080
Window type	SATW
Processor type	XStream2
Azimuth (degrees)	0.0
Inclination (degree)	30.0

EDS-Überlagerungsbild 130

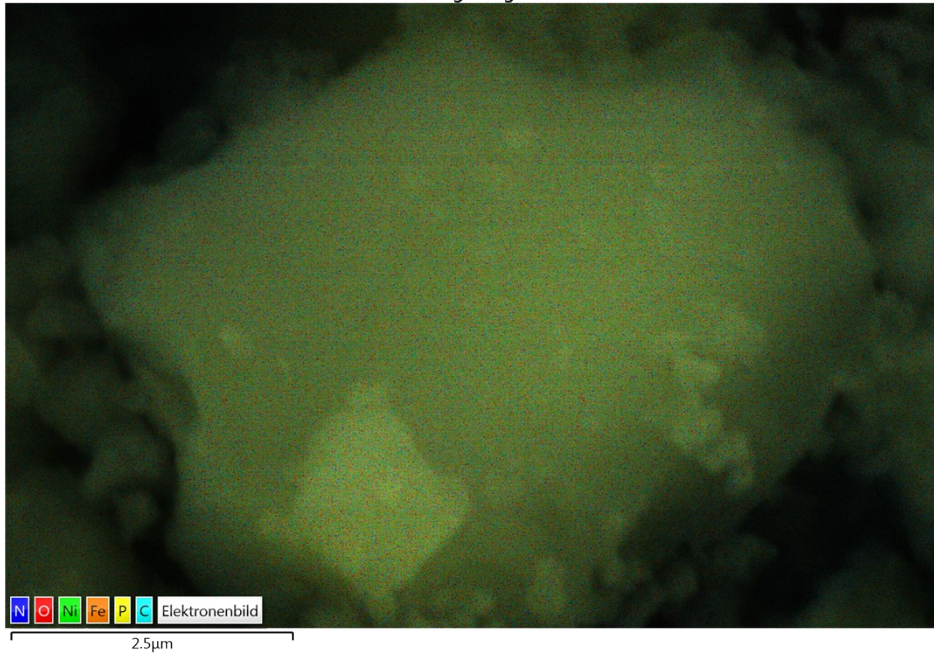
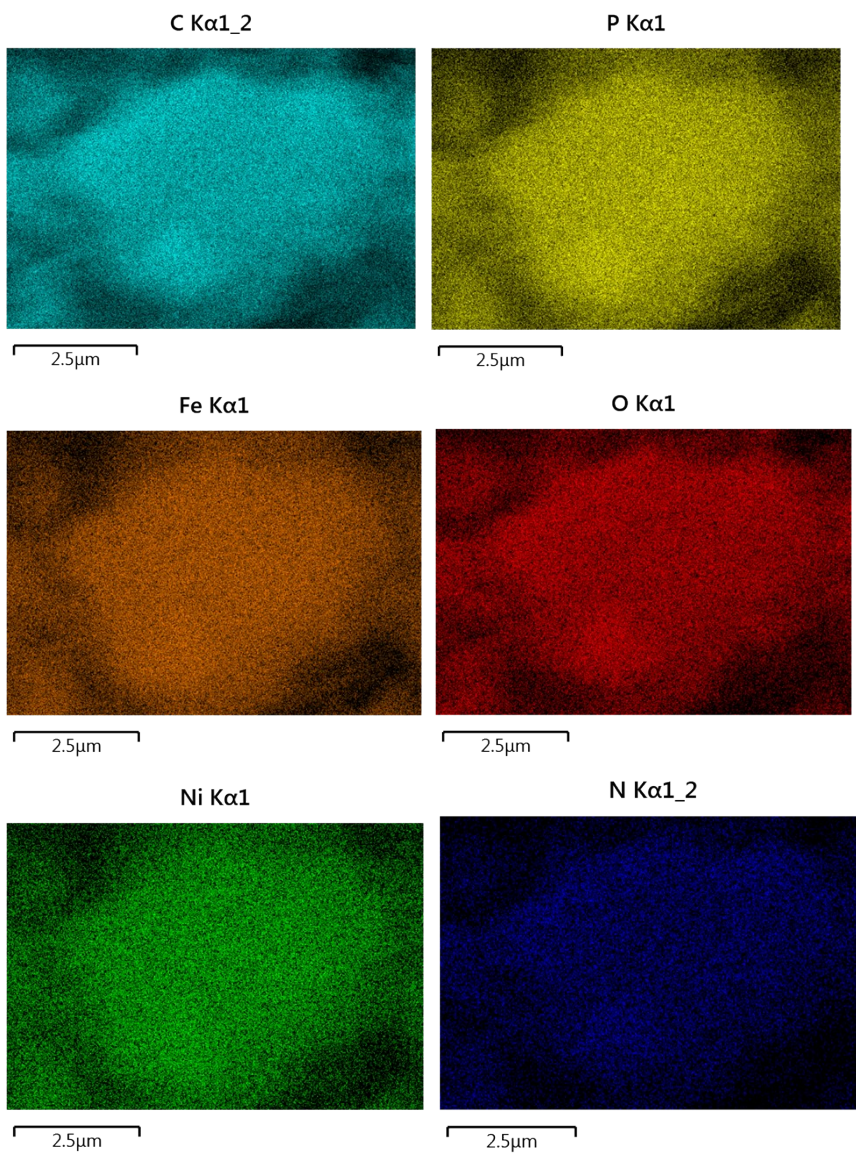


Figure S8. EDS overlay image for 2



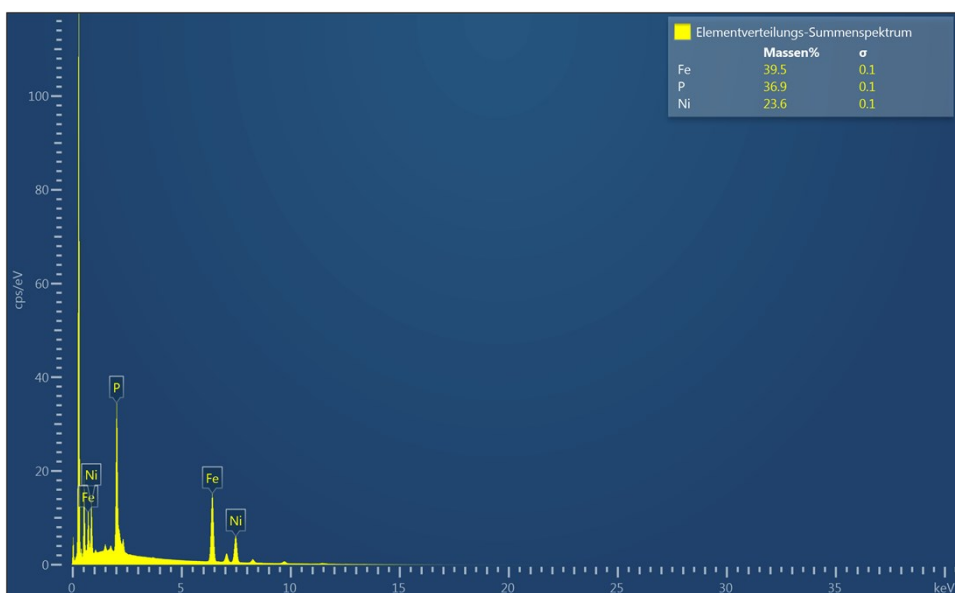


Fig. S9. Element distribution sum spectrum and mass %.

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