

Supplementary Information for

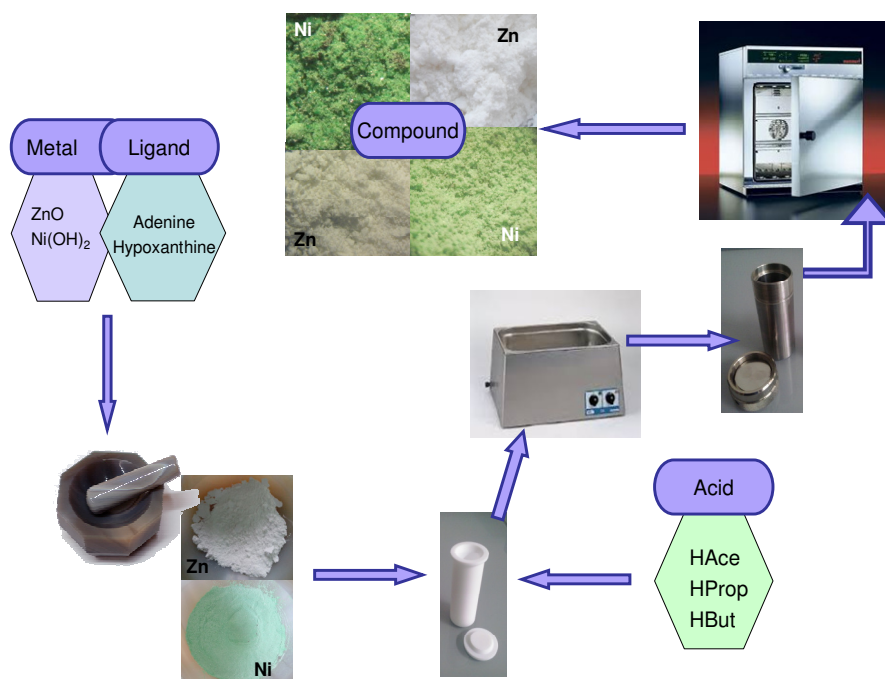
Towards multicomponent MOFs via solvent-free synthesis under conventional oven and microwave assisted heating

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Antonio Luque^a and Sonia Pérez-Yañez^a

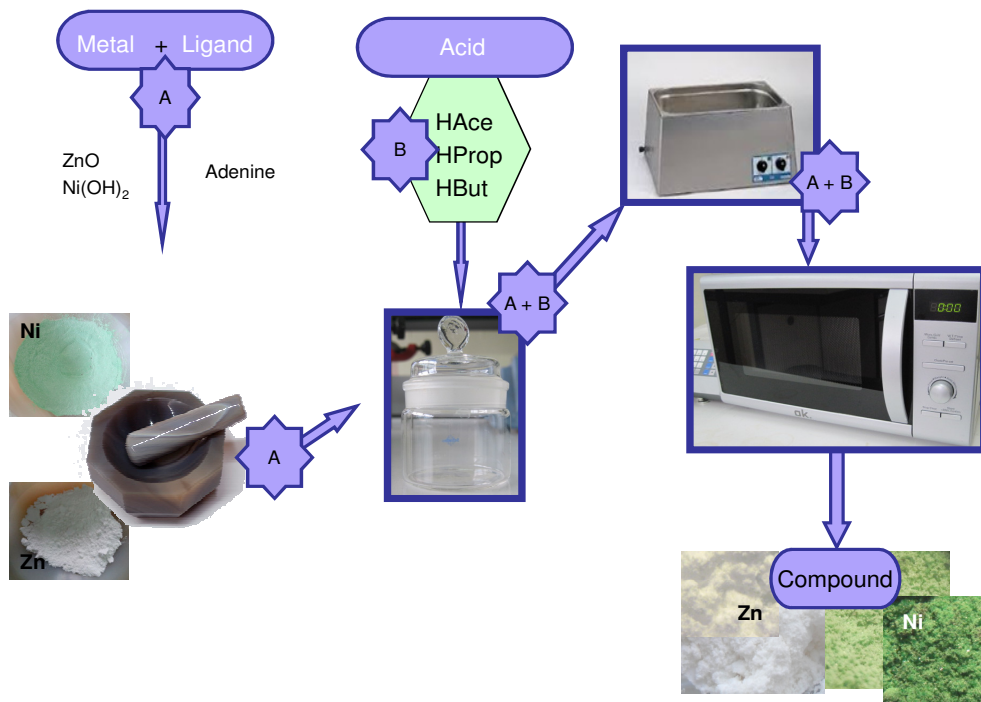
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S1. SOLVENT-FREE SYNTHESIS BY OVEN HEATING AND MICROWAVE IRRADIATION



Conventional oven-heating



Microwave assisted heating

S2. SYNTHESIS CONDITIONS AND CHARACTERIZATION OF THE SAMPLES

1_Ni@Prop

Synthesis: 0.7420 g (8 mmol) Ni(OH)₂

1.0920 g (8 mmol) Adenine

2 mL (27 mmol) propanoic acid

Formula: [Ni₂(C₅H₄N₅)₂(C₃H₅O₂)₂]_n·2.5(CH₃CH₂OH)
=C₁₆H₁₈Ni₂N₁₀O₄·(C₂H₆O)_{2.5} (646.94 g/mol)

Yield: 97.3% (based on the metal)

Purity: 99% (sample outgassed)

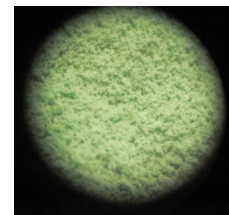
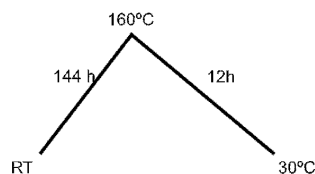
CSD Code: IZUMUM, IZUNAT (isostructural)

Topology: lvt

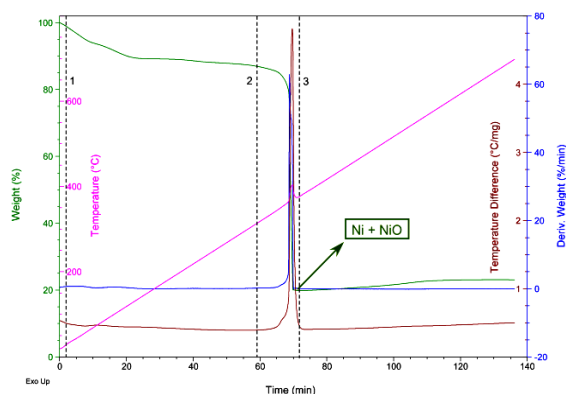
Elemental Analysis: Cal(%): C 38.99; H 5.14; N 21.65; Ni 18.14 Exp(%): C 38.76; H 5.46; N 21.41; Ni 18.19.

Main FTIR bands (cm⁻¹, KBr pellets): 3350s, 3200s, 2980m, 1658vs, 1606vs, 1578vs, 1541s, 1508m, 1468vs, 1442s, 1428s, 1400s, 1372m, 1347m, 1317m, 1303m, 1278m, 1244m, 1211s, 1147m, 1078w, 1036w, 997w, 953sh, 939w, 900w, 808m, 797m, 739m, 700m, 667m, 642m, 580m, 558m.

Thermal program



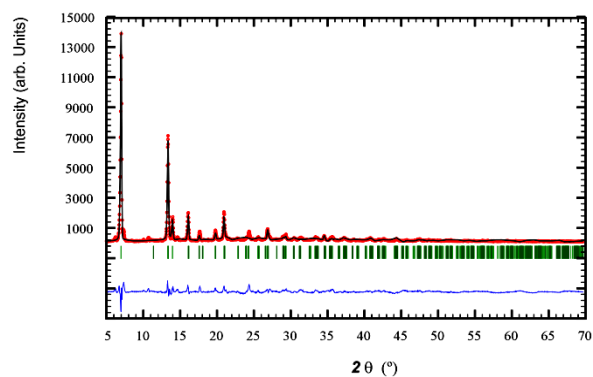
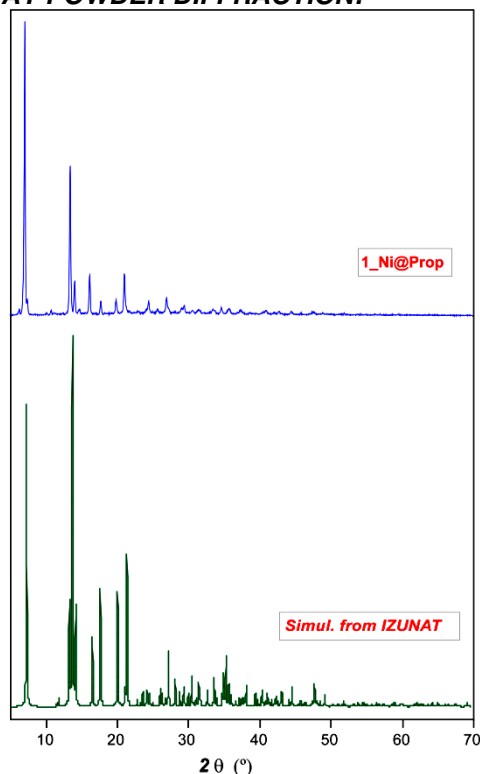
TG/DTA:



Step	T _i (°C)	T _f (°C)	T _{peak} (°C)	ΔH
1	24	155		ENDO
2	316	411	403	EXO
3	411	641		EXO

Step	Δm (%)	Δm (Teor)	Lost	Residue
1	13.14	17.74	-2.5EtOH	
2	67			
3	-3.24			
Res.	23.10	23.02		NiO

X-RAY POWDER DIFFRACTION:



IZUNAT		1_Ni@Prop	
Space group	I 4 ₁ /a		
a (Å)	15.348(5)	a (Å)	15.581(1)
c (Å)	22.702(5)	c (Å)	21.930(1)
V (Å ³)	5348(3)	V (Å ³)	5323.7
T (K)	100	R _f	29.8
		R _b	17.9
		R _p	18.4
		R _{wp}	25.0
		χ ²	18.4

1_Zn@Prop

Synthesis: 0.6640 g (8 mmol) ZnO
1.0920 g (8 mmol) Adenine
2 mL (27mmol) propanoic acid

Formula $[\text{Zn}_2(\text{C}_5\text{H}_4\text{N}_5)_2(\text{C}_3\text{H}_5\text{O}_2)_2]_n \cdot 0.9(\text{CH}_3\text{CH}_2\text{OH})$
 $= \text{C}_{16}\text{H}_{18}\text{Zn}_2\text{N}_{10}\text{O}_4 \cdot (\text{CH}_3\text{CH}_2\text{OH})_{0.9}$
(588.63 g/mol)

Yield: 96.5% (based on the metal)

Purity: 98.9% (sample outgassed)

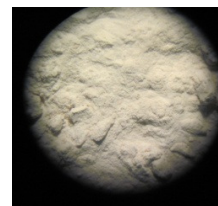
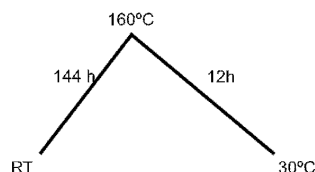
CSD Code: IZUMUM, IZUNAT (isostructural)

Topology: *1t*

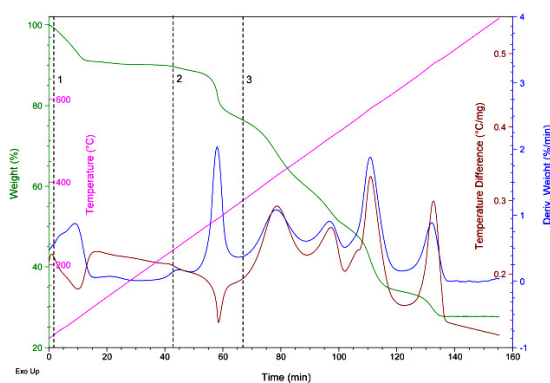
Elemental Analysis: Cal(%): C 36.44; H 4.02; N 23.88; Zn 22.29 Exp(%): C 36.18; H 4.37; N 23.72; Zn 22.35.

Main FTIR bands (cm^{-1} , KBr pellets): 3340s, 3200s, 2980m, 2940m, 2880m, 1660vs, 1651vs, 1602vs, 1587vs, 1547f, 1464vs, 1436vs, 1400vs, 1371s, 1349s, 1302m, 1276s, 1213s, 1150s, 1080m, 1043m, 1000m, 933w, 890w, 810w, 797m, 740m, 700m, 640m, 577m, 553m.

Thermal program:

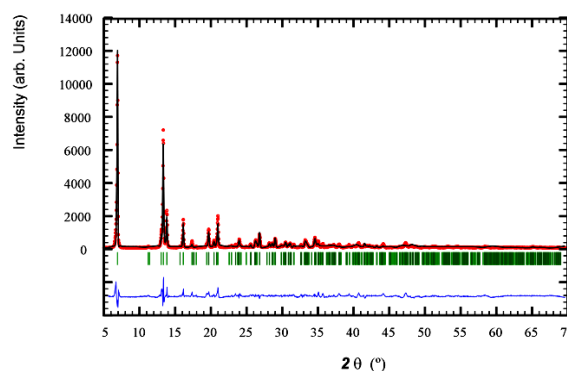
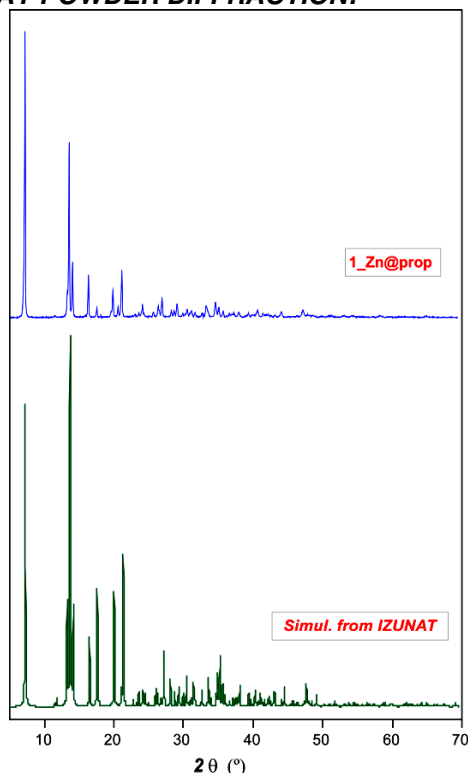


TG/DTA:



Step	$T_i (^{\circ}\text{C})$	$T_E (^{\circ}\text{C})$	$T_{\text{peak}} (^{\circ}\text{C})$	ΔH
1	27	104		ENDO
2	256	355	313	ENDO
3	355	720	416/508 /579/686	EXO
Step	$\Delta m(\%)$	$\Delta m(\text{Teor})$	Lost	Residue
1	9.1	7.04	-0.9EtOH	
2	14.4	---		
3	48.78			
Res.	27.72	27.65		ZnO

X-RAY POWDER DIFFRACTION:



IZUNAT		1_Zn@Prop	
Space group	$I4_1/a$		
a (Å)	15.348(5)	a (Å)	15.548(1)
c (Å)	22.702(5)	c (Å)	22.630(1)
V (Å ³)	5348(3)	V (Å ³)	5470.4
T (K)	100	R _f	24.3
		R _b	31.6
		R _p	20.8
		R _{wp}	29.4
		χ^2	21.4

1_Ni@But

Synthesis: 0.7420 g (8 mmol) Ni(OH)₂
1.0920 g (8 mmol) Adenine
2.5 mL (27 mmol) Butanoic acid

Formula: [Ni₂(C₅H₄N₅)₂(C₄H₇O₂)₂]_n·1.7CH₃CH₂OH
= C₁₈H₂₂Ni₂N₁₀O₄·(CH₃CH₂OH)_{1.7}
(638.13 g/mol)

Yield: 98.2% (based on the metal)

Purity: 99.4% (sample outgassed)

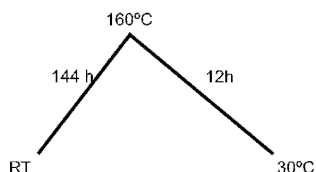
CSD Code: IZUMUM, IZUNAT (isostructural)

Topology: *1t*

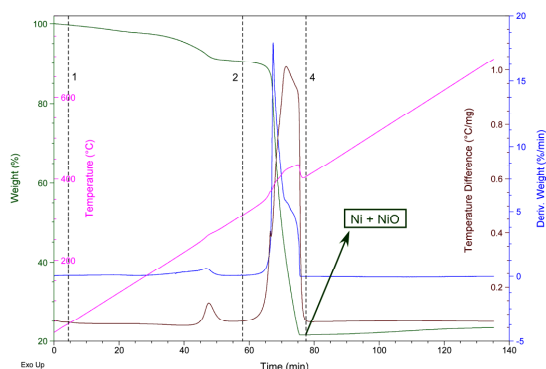
Elemental Analysis: Cal(%): C 40.28%; H 5.09%; N 21.95%; Ni 18.39% Exp(%): C 40.28%; H 5.35%; N 21.74%; Ni 18.39%

Main FTIR bands (cm⁻¹, KBr pellets): 3350s, 3200s, 2980m, 2940vw, 1658vs, 1606vs, 1578vs, 1541s, 1508m, 1468vs, 1442s, 1428s, 1400s, 1372m, 1347m, 1317m, 1303m, 1278m, 1244m, 1211s, 1147m, 1078w, 1036w, 997w, 939w, 900w, 808m, 797m, 739m, 700m, 667m, 642m, 580m, 558m

Thermal program:



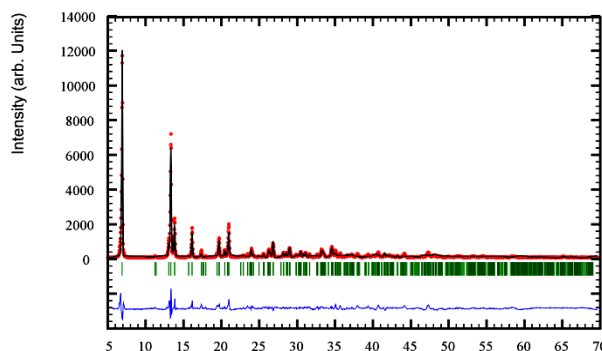
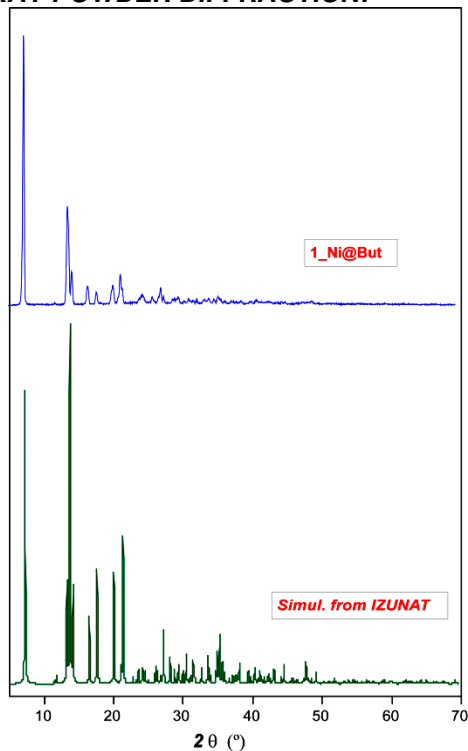
TG/DTA:



Step	<i>T_i</i> (°C)	<i>T_f</i> (°C)	<i>T_{peak}</i> (°C)	Δ <i>H</i>
1	50	286	262	EXO
2	325	439	423	EXO
3	439	693		EXO

Step	Δ <i>m</i> (%)	Δ <i>m</i> (Teor)	Lost	Residue
1	10.18	12.2	-1.7EtOH	
2	69.2			
3	-1.71			
Res.	23.33	23.18		NiO

X-RAY POWDER DIFFRACTION:



	IZUNAT		1_Ni@But
Space group	<i>I</i> 4 ₁ /a		
<i>a</i> (Å)	15.348(5)	<i>a</i> (Å)	15.313(1)
<i>c</i> (Å)	22.702(5)	<i>c</i> (Å)	22.110(1)
<i>V</i> (Å ³)	5348(3)	<i>V</i> (Å ³)	5247.0
<i>T</i> (K)	100	<i>R_f</i>	7.66
		<i>R_b</i>	1.78
		<i>R_p</i>	11.3
		<i>R_{wp}</i>	14.2
		χ ²	5.63

1_{MW}_Ni@Pro

Synthesis: 0.7420 g (8 mmol) Ni(OH)₂

1.0920 g (8 mmol) Adenine

2 mL (27 mmol) propanoic acid

Formula: [Ni₂(C₅H₄N₅)₂(C₃H₅O₂)₂]_n 1.5(CH₃CH₂OH)
=C₁₆H₁₈Ni₂N₁₀O₄·(C₂H₆O)_{1.5} (600.87 g/mol)

Yield: 94.0% (based on the metal)

Purity: 97.8% (sample outgassed)

CSD Code: IZUMUM, IZUNAT (isostructural)

Topology: lvt

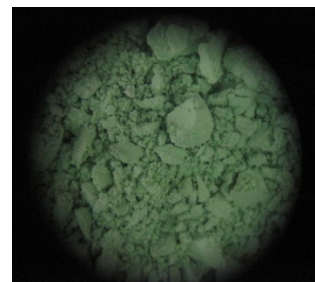
Elemental Analysis: Cal(%): C 37.98%; H 4.53%; N 23.23%; Ni 19.54% Exp(%): C 37.71%; H 4.84%; N 23.12%; Ni 19.61%

Main FTIR bands (cm⁻¹, KBr pellets): 3341s, 3275sh, 3201s, 2978m, 2942m, 2716sh, 2689w, 1899w, 1794w, 1657vs, 1604vs, 1575vs, 1543s, 1510m, 1468vs, 1442s, 1429s, 1400vs, 1372s, 1347s, 1318sh, 1304m, 1277m, 1250m, 1240m, 1211s, 1147m, 1081m, 1036w, 997w, 939w, 911sh, 900w, 872w, 847w, 808w, 797m, 739m, 724m, 700m, 642m, 580m, 558m, 543m

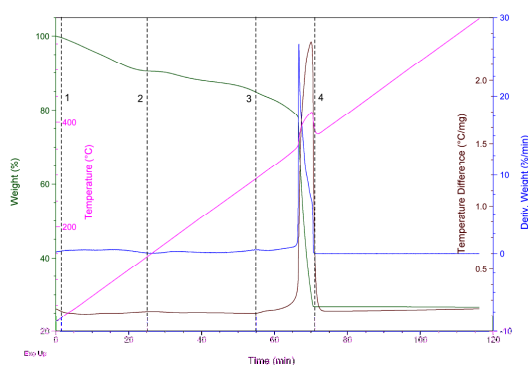
Microwave irradiation:

Power output

50%, 12 min



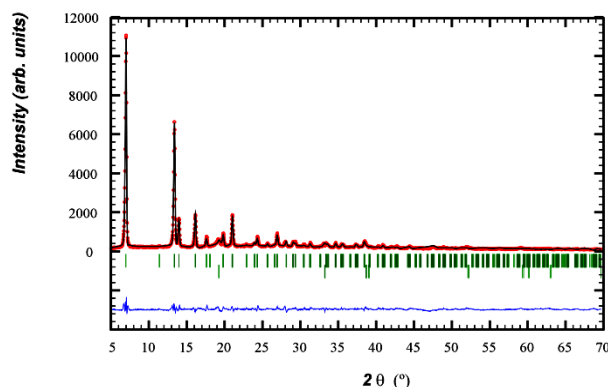
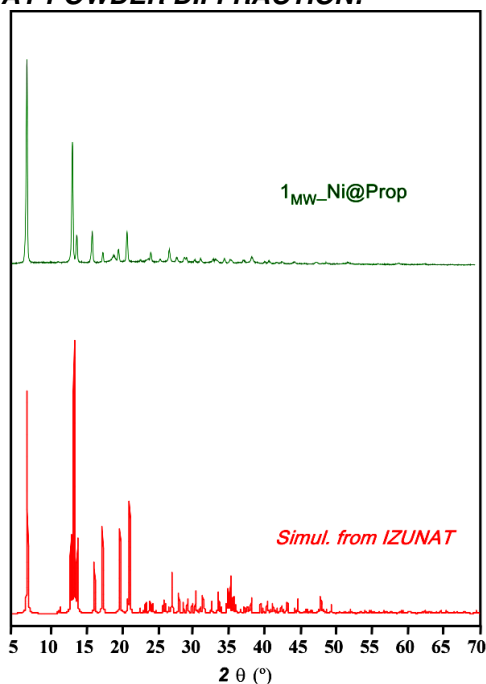
TG/DTA:



Step	T _i (°C)	T _F (°C)	T _{peak} (°C)	ΔH
1	20	143		
2	143	293		
3	293	423	418	EXO
4	424	700		EXO

Step	Δm (%)	Δm (Teor)	Lost	Residue
1	9.74	11.46	1.5 EtOH	
2	5.65			
3	58.05			
4	-0.1			
Res.	26.66	24.77		NiO

X-RAY POWDER DIFFRACTION:



IZUNAT		1 _{MW} _Ni@Prop	
Space group	I 4 ₁ /a		
a (Å)	15.348(5)	a (Å)	15.549(1)
c (Å)	22.702(5)	c (Å)	21.939(1)
V (Å ³)	5348(3)	V (Å ³)	5304.3
T (K)	100	R _f	5.09
		R _b	1.76
		R _p	10.0
		R _{wp}	14.3
		χ ²	6.38

1_{MW}_Zn@Pro

Synthesis: 0.6640 g (8 mmol) ZnO
1.0920 g (8 mmol) Adenine
2 mL (27mmol) propanoic acid

Formula $[\text{Zn}_2(\text{C}_5\text{H}_4\text{N}_5)_2(\text{C}_3\text{H}_5\text{O}_2)_2]_n \cdot 2.4(\text{CH}_3\text{CH}_2\text{OH})$
 $= \text{C}_{16}\text{H}_{18}\text{Zn}_2\text{N}_{10}\text{O}_4 \cdot (\text{CH}_3\text{CH}_2\text{OH})_{2.4}$
(655.72 g/mol)

Yields: 99.2% (based on the metal)

Purity: 99.8% (sample outgassed)

CSD Code: IZUMUM, IZUNAT (isostructural)

Topology: *lvt*

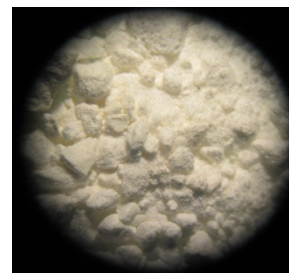
Elemental Analysis: Cal(%): C 38.10%; H 4.98%; N 21.36%; Zn 19.94% Exp(%): C 38.01%; H 5.29%; N 21.28%; Zn 19.91%

Main FTIR bands (cm⁻¹, KBr pellets): 3343s, 3273s, 3207s, 2978m, 2938m, 2880m, 2717w, 1900w, 1800w, 1656vs, 1602vs, 1587vs, 1547s, 1464vs, 1424m, 1400vs, 1371s, 1349s, 1302m, 1273s, 1213s, 1152s, 1080m, 1043m, 1000m, 933w, 890w, 847w, 810m, 799m, 739m, 700m, 643m, 578m, 554m.

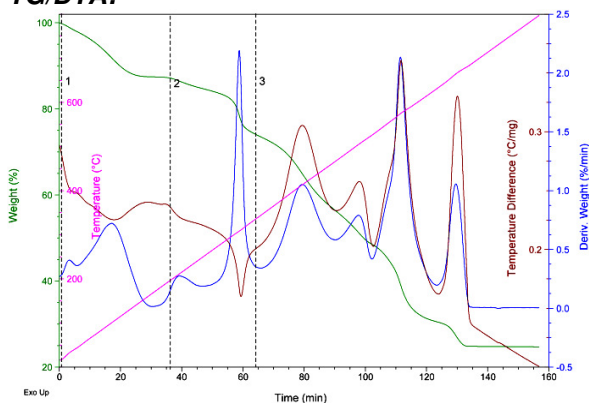
Microwave irradiation:

Power output

50%, 12 min

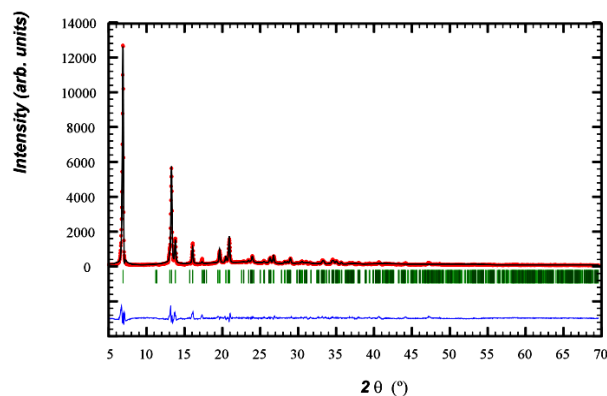
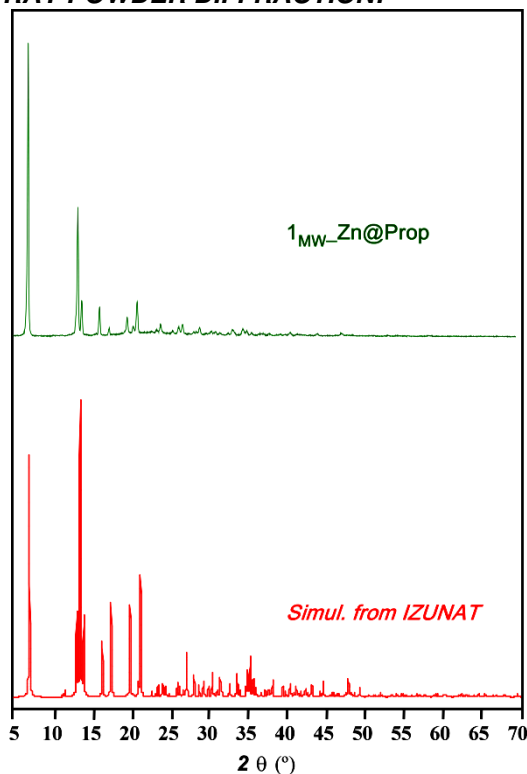


TG/DTA:



Step	T_i (°C)	T_F (°C)	T_{peak} (°C)	ΔH
1	17	167		ENDO
2	193	341	311	ENDO
3	341	695	412/505 /575/656	EXO
Step	$\Delta m(\%)$	Δm (Teor)	Lost	Residue
1	17.33	16.8	-2.4EtOH	
2	8.88	---		
3	49.03			
Res.	24.76	24.73		ZnO

X-RAY POWDER DIFFRACTION:



IZUNAT		1 _{MW} _Zn@Prop	
Space group	<i>I</i> 4 ₁ /a	a (Å)	15.598(1)
a (Å)	15.348(5)	c (Å)	22.600(1)
c (Å)	22.702(5)	V (Å ³)	5498.8
V (Å ³)	5348(3)	R _f	2.80
T (K)	100	R _b	1.27
		R _p	13.9
		R _{wp}	20.4
		χ^2	9.97

1_{MW}_Ni@But

Synthesis: 0.7420 g (8 mmol) Ni(OH)₂
1.0920 g (8 mmol) Adenine
2.5 mL (27 mmol) Butanoic acid

Formula: [Ni₂(C₅H₄N₅)₂(C₄H₇O₂)₂]_n·3(CH₃CH₂OH)
= C₁₈H₂₂Ni₂N₁₀O₄·(CH₃CH₂OH)₃
(698.02 g/mol)

Yields: 58.8% (based on the metal)

Purity: 88.2% (sample outgassed)

CSD Code: IZUMUM, IZUNAT (isostructural)

Topology: 1vt

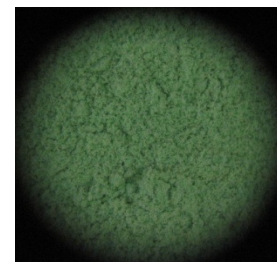
Elemental Analysis: Cal(%): C 41.30%; H 5.78%; N 20.10%; Ni 16.82 % Exp(%): C 40.56%; H 5.72%; N 19.73%; Ni 17.61 %

Main FTIR bands (cm⁻¹, KBr pellets): 3640m, 3330m, 3207f, 2970m, 2937m, 2874m, 2690w, 1900w, 1656vs, 1597vs, 1581vs, 1543s, 1506m, 1464vs, 1420s, 1397vs, 1363s, 1347s, 1317s, 1336s, 1311s, 1278s, 1256m, 1207vs, 1147s, 1093m, 1078m, 1053m, 1033m, 993m, 939m, 906m, 893m, 872m, 846w, 797m, 739m, 722m, 698m, 667m, 643s, 580m, 558m, 540m, 464w, 437w.

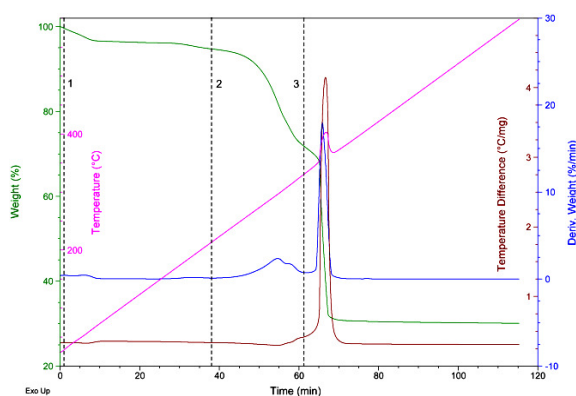
Microwave irradiation:

Power output

50%, 12 min

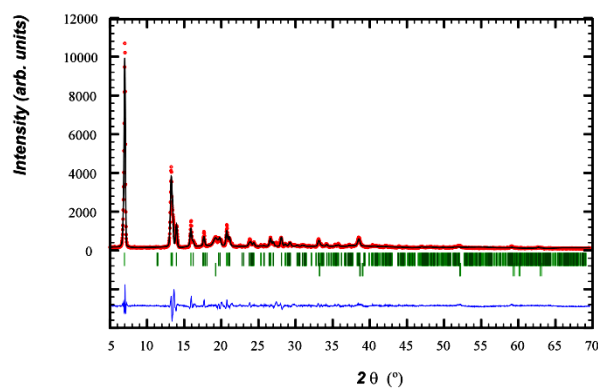
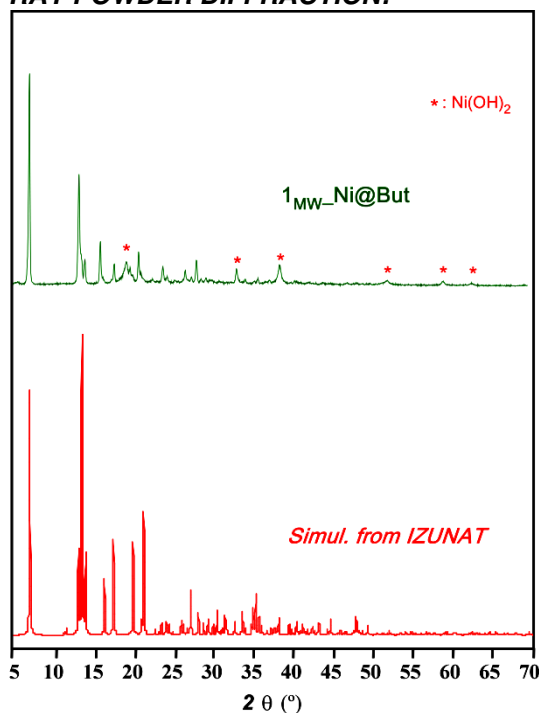


TG/DTA:



Step	T_i (°C)	T_F (°C)	T_{peak} (°C)	ΔH
1	26	81		
2	217	335		ENDO
3	335	409	402	EXO
Step	Δm (%)	Δm (Teor)	Lost	Residue
1	3.48	2.02	-3EtOH	
2	25.39			
3	41.06			
Res.	30.07	21.34		NiO

X-RAY POWDER DIFFRACTION:



IZUNAT		1 _{MW} _Ni@But	
Space group	$I 4_1/a$		
a (Å)	15.348(5)	a (Å)	15.463(1)
c (Å)	22.702(5)	c (Å)	22.293(1)
V (Å ³)	5348(3)	V (Å ³)	5330.8
T (K)	100	R _f	8.02
		R _b	2.47
		R _p	12.5
		R _{wp}	17.2
		χ^2	8.29

Compound 2

Synthesis: 0.6640 g (8 mmol) ZnO
1.0920 g (8 mmol) Adenine
500 μ L (8.6 mmol) Acetic acid

Formula: $[\text{Zn}_3(\text{C}_5\text{H}_4\text{N}_5)_2(\text{OOCCH}_3)_4]_n \cdot 3\text{H}_2\text{O}$
 $= \text{C}_{18}\text{H}_{26}\text{Zn}_3\text{N}_{10}\text{O}_{11}$ (754.63 g/mol)

Yields: 93.5% (based on the metal)

Purity: 97.6% (sample outgassed)

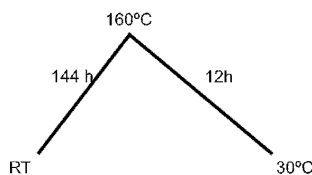
CSD Code: This work

Topology: *sql*

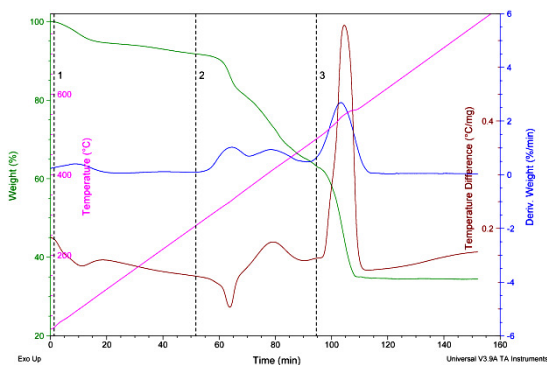
Elemental Analysis: Cal(%): C 28.65%; H 3.47%; N 18.56%; Zn 25.99% Exp(%): C 28.55%; H 3.45%; N 18.52%; Zn 26.15%

Main FTIR bands (cm^{-1} , KBr pellets): 3379m, 3300s, 3237m, 3125s, 2929m, 2846sh, 2733w, 1687s, 1640vs, 1613vs, 1586vs, 1472m, 1403vs, 1387s, 1307s, 1278m, 1220s, 1161m, 1056m, 1017m, 1000m, 950w, 940w, 933m, 907w, 800m, 744m, 672m, 644m, 617m, 589m, 561m, 517m, 500m

Thermal program:

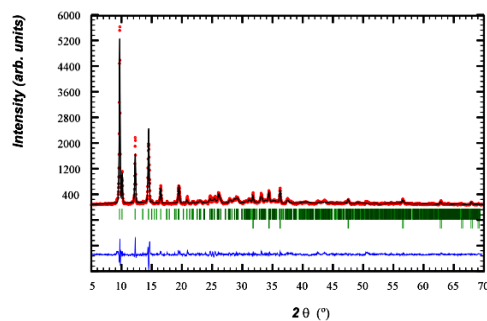
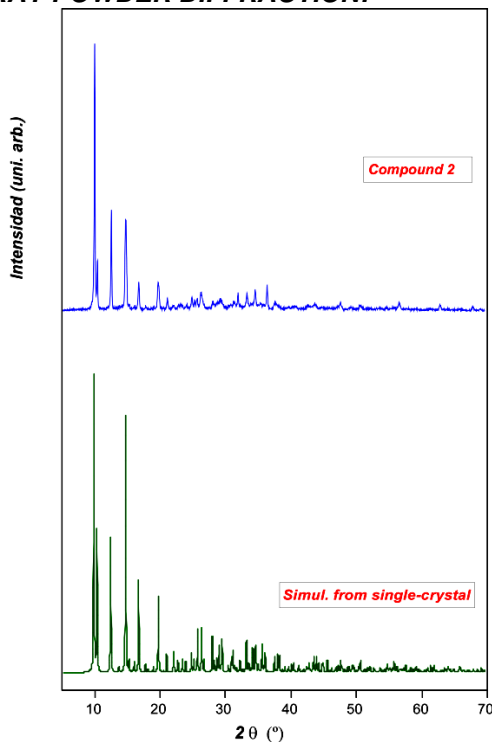


TG/DTA:



Step	T_i (°C)	T_F (°C)	T_{peak} (°C)	ΔH
1	19	284		ENDO
2	284	466	332/409	ENDO/EXO
3	466	588	548	EXO
Step	Δm (%)	Δm (Teor)	Lost	Residue
1	8.42	7.15	-3H ₂ O	
2	26.23			
3	32.11			
Res.	33.24	32.35		ZnO

X-RAY POWDER DIFFRACTION:



Single-crystal		Compound 2	
Space group	$P 2_1/c$	a (Å)	9.196(1)
a (Å)	9.1709(4)	b (Å)	11.801(1)
b (Å)	11.7306(4)	c (Å)	13.180(1)
c (Å)	12.9958(4)	β (°)	95.972(1)
β (°)	96.400(3)	V (Å ³)	1422.6
V (Å ³)	1389.38(9)	R_f	11.0
T (K)	100	R_b	3.43
		R_p	11.2
		R_{wp}	14.4
		χ^2	3.83

