

SUPPORTING INFORMATION

of

**Structural Characterization, Proton Conductivity
and Furfural Catalysis of Novel Polyfunctional
Zirconium Phosphonates**

Montse Bazaga-García,^{a,b} Rosario M. P. Colodrero,^{a,c} Álvaro Vilchez-Cózar,^{a,c} Pascual

Olivera-Pastor,^{a,c} Juan A. Cecilia,^{a,d} Łukasz Kurowski,^e Jan K. Zaręba,^{,e}*

Aurelio Cabeza^{a,c,}*

^a Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias,
Universidad de Málaga, Campus Teatinos s/n 29071-Málaga, Spain

^b Departamento de Química Inorgánica, Universidad de Salamanca, Plaza de los Caídos s/n,
37008 Salamanca, Spain.

^c Instituto Universitario de Materiales y Nanotecnología, IMANA, Universidad de Málaga,
Campus Teatinos s/n 29071-Málaga, Spain

^d Instituto de Investigación de Biorrefinerías “I3B”, Facultad de Ciencias, Universidad de
Málaga, Campus Teatinos s/n 29071-Málaga, Spain

^e Department of Chemistry, Wrocław University of Technology, 27 Wybrzeże
Wypianskiego Str., 50-370 Wrocław, Poland.

Table of contents

Figures

Figure S1. Rietveld plot for $\text{Zr}(\text{O}_3\text{P-NH-C}_5\text{H}_3\text{-COOH})_2\text{F}_2$ (**Zr-PNA**).

Figure S2. Rietveld plot for $\text{Zr}[(\text{H}_2\text{O}_3\text{PCH}_2)(\text{O}_3\text{PCH}_2)_2\text{-C}_6\text{H}_3]\cdot\text{H}_2\text{O}$ (**Zr-BTTMP**).

Figure S3. XPS spectra of (a) F 1s and (b) N 1s for **Zr-PiPhtA** (red) and **Zr-PNA** (blue).

Figure S4. FT-IR spectra for **Zr-PNA** (blue), **Zr-BTTMP** (violet) and **Zr-PiPhtA** (red).

Figure S5. Thermal analysis for **Zr-PNA** (blue), **Zr-BTTMP** (violet) and **Zr-PiPhtA** (red).

Figure S6. X-ray thermodiffraction patterns of (a) **Zr-BTTMP** and (b) **Zr-PiPhtA**.

Figure S7. SEM images for (a, b) **Zr-PiPhtA**, (c, d) **Zr-PNA** and (e, f) **Zr-BTTMP**.

Figure S8. (a) X-ray powder diffraction (XRPD) patterns and (b) TG analysis for **Zr-PiPhtA** (blue), **Zr-PiPhtA_NH₃** (green), and post-impedance **Zr-PiPhtA** (red) and **Zr-PiPhtA_NH₃** (violet) samples.

Figure S9. (a) X-ray powder diffraction (XRPD) patterns and (b) TG analysis for **Zr-PNA** (blue), **Zr-PNA_NH₃** (green), and post-impedance **Zr-PNA** (red) and **Zr-PNA_NH₃** (violet) samples.

Figure S10. (a) X-ray powder diffraction (XRPD) patterns and (b) TG analysis for: **Zr-BTTMP** before (blue), **Zr-BTTMP_NH₃** (green), and post-impedance **Zr-BTTMP** (red) and **Zr-BTTMP_NH₃** (violet) samples.

Figure S11. FT-IR spectra of **Zr-PiPhtA** as synthesized (blue) and **Zr-PiPhtA_NH₃** (green).

Figure S12. FT-IR spectra for **Zr-PNA** as synthesized (blue) and **Zr-PNA_NH₃** (green).

Figure S13. SEM images for (a, b) **Zr-PiPhtA_NH₃** and (c, d) **Zr-PNA_NH₃**.

Figure S14. FT-IR spectra for (a) **Zr-PiPhtA**, (b) **Zr-BTTMP** and (c) **Zr-PNA** as synthesized (red) and pyridine-adsorbed samples (blue).

Figure S15. Plot of complex impedance plane for (a) **Zr-PiPhtA** and (b) **Zr-PiPhtA_NH₃** compound at 75% (left) and 95% (right) of relative humidity (RH) at different temperatures: 80 (black), 70 (red), 60 (green), 50 (blue) and 40 °C (cyan).

Figure S16. Plot of complex impedance plane for (a) **Zr-PNA** and (b) **Zr-PNA_NH₃** compound at 75% (left) and 95% (right) of relative humidity (RH) at different temperatures: 80 (black), 70 (red), 60 (green), 50 (blue) and 40 °C (cyan).

Figure S17. Plot of complex impedance plane for (a) **Zr-BTTMP** and (b) **Zr-BTTMP_NH₃** at 75% (left) and 95% (right) of relative humidity (RH) at different temperatures: 80 (black), 70 (red), 60 (green), 50 (blue) and 40 °C (cyan).

Figure S18. Arrhenius plots at 95% RH of first (closed symbols) and second (open symbols) cycle samples: (a) **Zr-PiPhtA_NH₃** (circle) and (b) **Zr-PNA_NH₃** (square).

Tables

Table S1. Rietveld analysis for **Zr-BTTMP** at different conditions under N_2 from thermodiffraction ($Cu_{K\alpha 1}$) data.

Table S2. Conversion and product yields for FUR transformation on Zr-based catalysts.

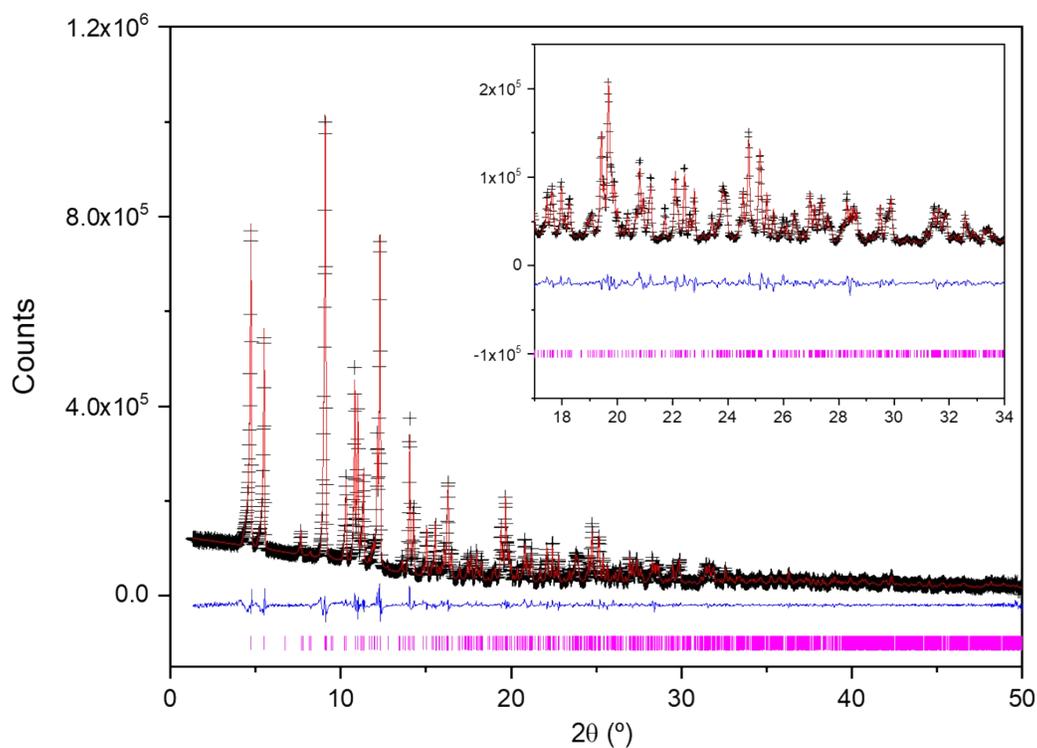


Figure S1. Rietveld plot for $\text{Zr}(\text{O}_3\text{P-NH-C}_5\text{H}_3\text{-COOH})_2\text{F}_2$ (**Zr-PNA**).

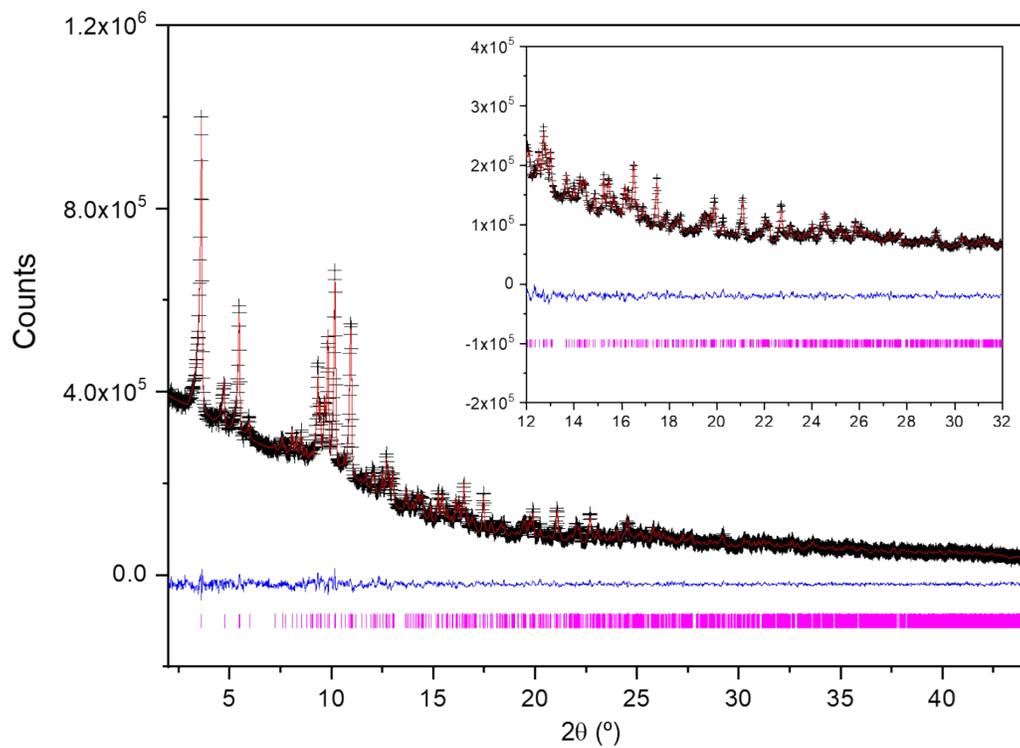


Figure S2. Rietveld plot for $\text{Zr}[(\text{H}_2\text{O}_3\text{PCH}_2)(\text{O}_3\text{PCH}_2)_2\text{-C}_6\text{H}_3]\cdot\text{H}_2\text{O}$ (**Zr-BTTMP**).

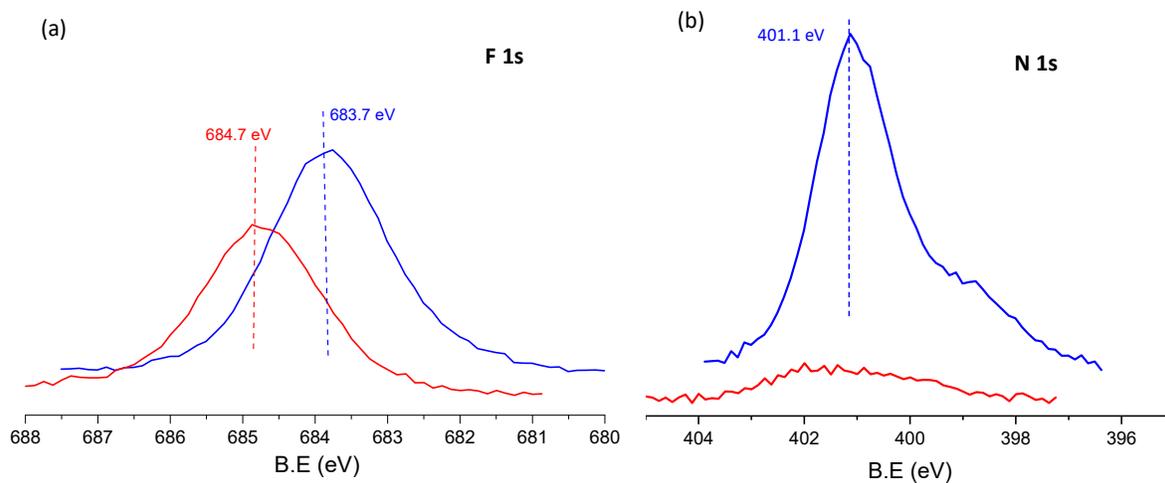


Figure S3. XPS spectra of (a) F 1s and (b) N 1s for **Zr-PiPhTA** (red) and **Zr-PNA** (blue).

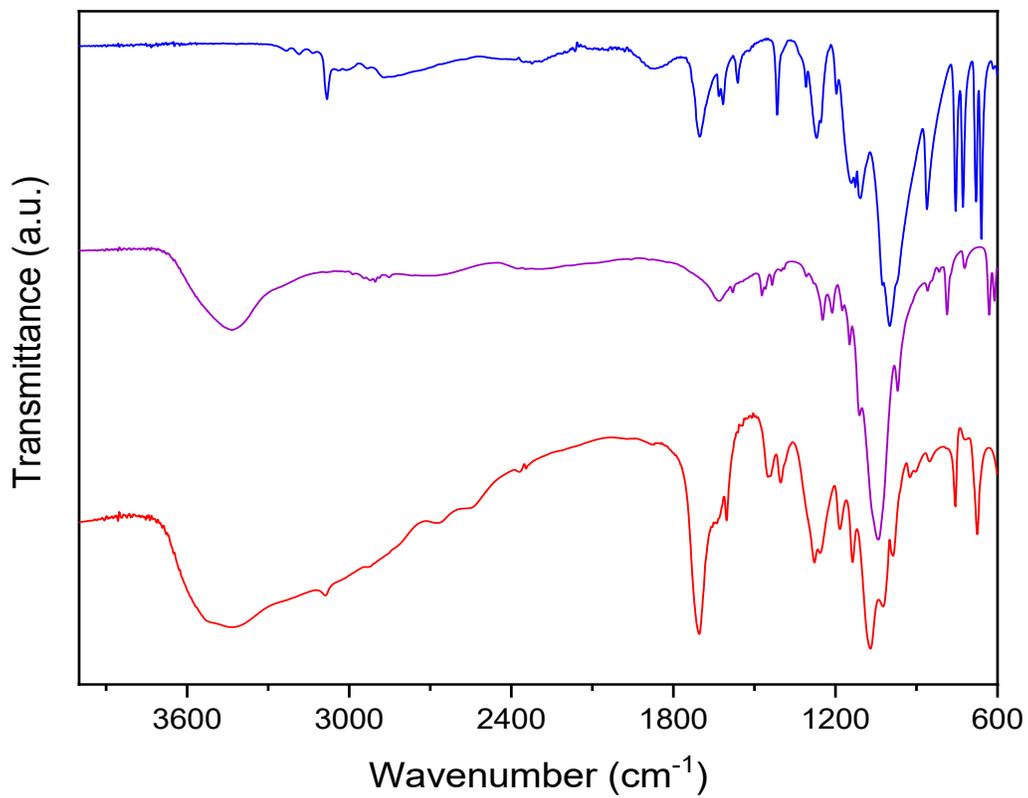


Figure S4. FT-IR spectra for **Zr-PNA** (blue), **Zr-BTTMP** (violet) and **Zr-PiPhTA** (red).

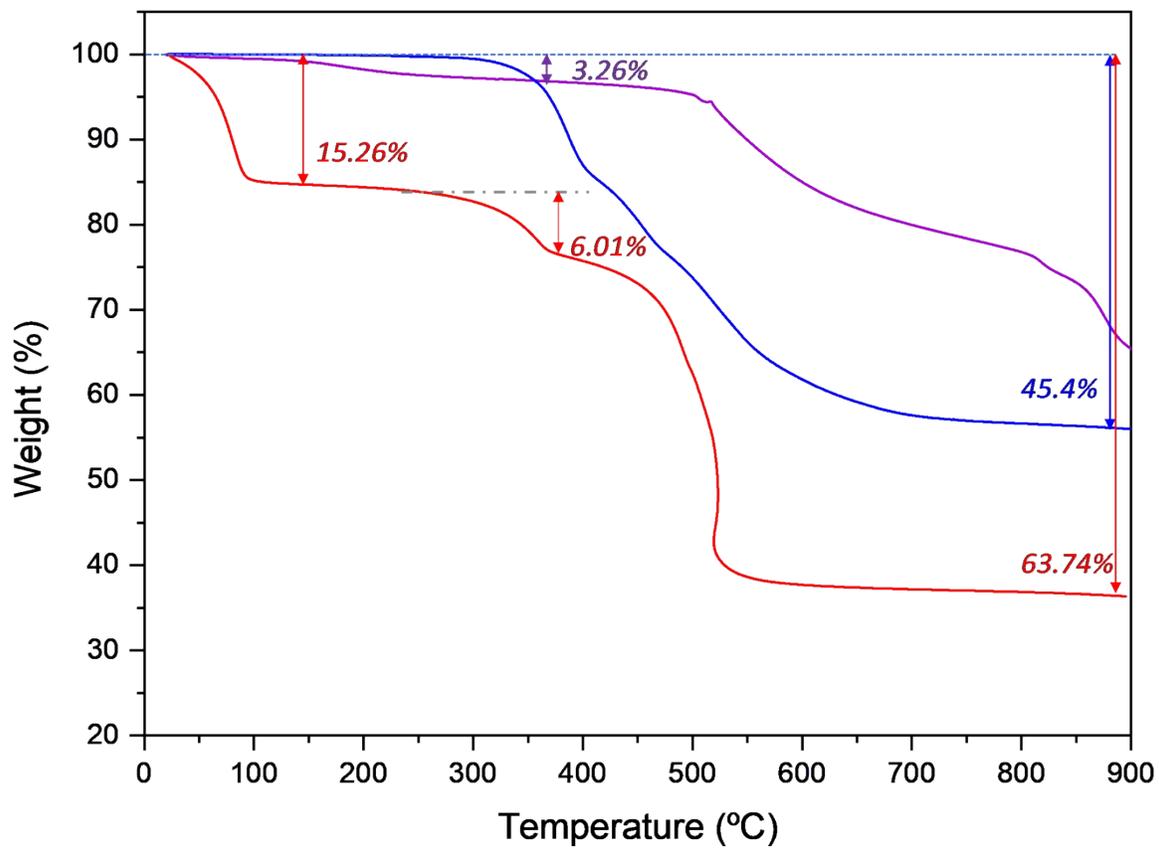


Figure S5. Thermal analysis for **Zr-PNA** (blue), **Zr-BTTMP** (violet) and **Zr-PiPhtA** (red).

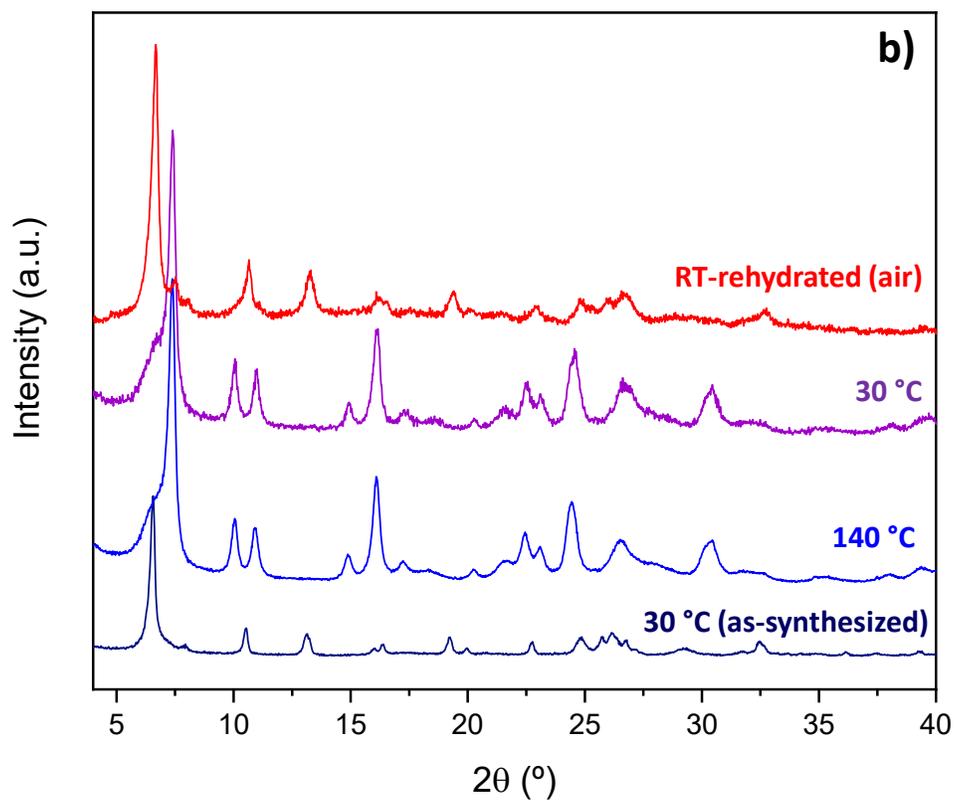
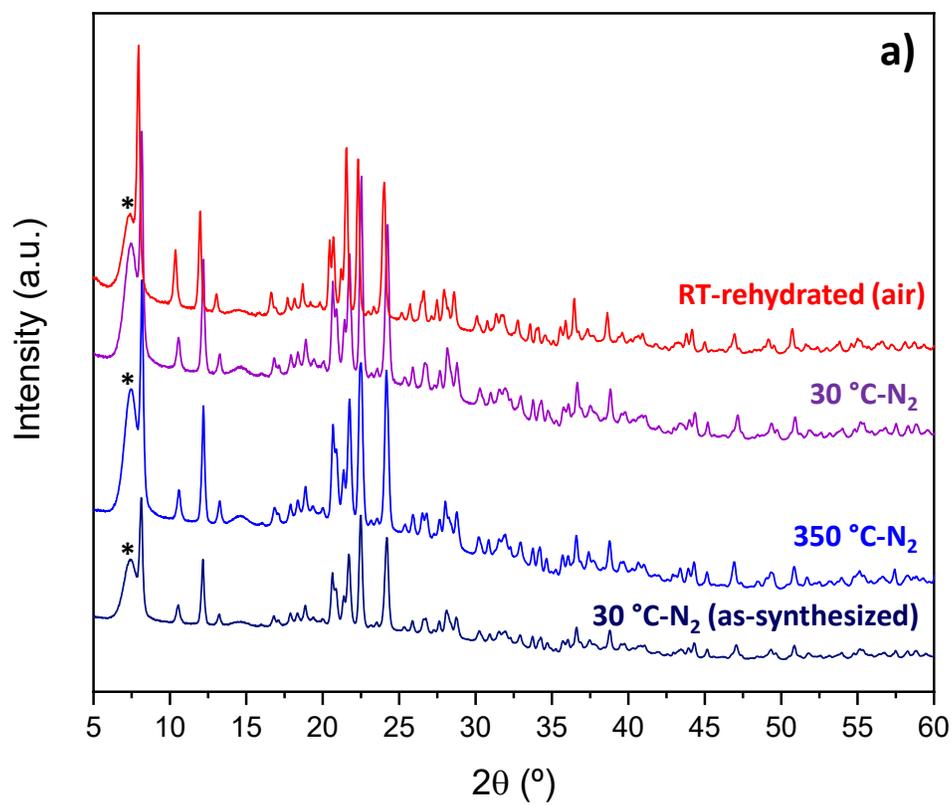


Figure S6. X-ray thermodiffraction patterns of (a) Zr-BTTMP and (b) Zr-PiPhTA. (*peak corresponding to the chamber).

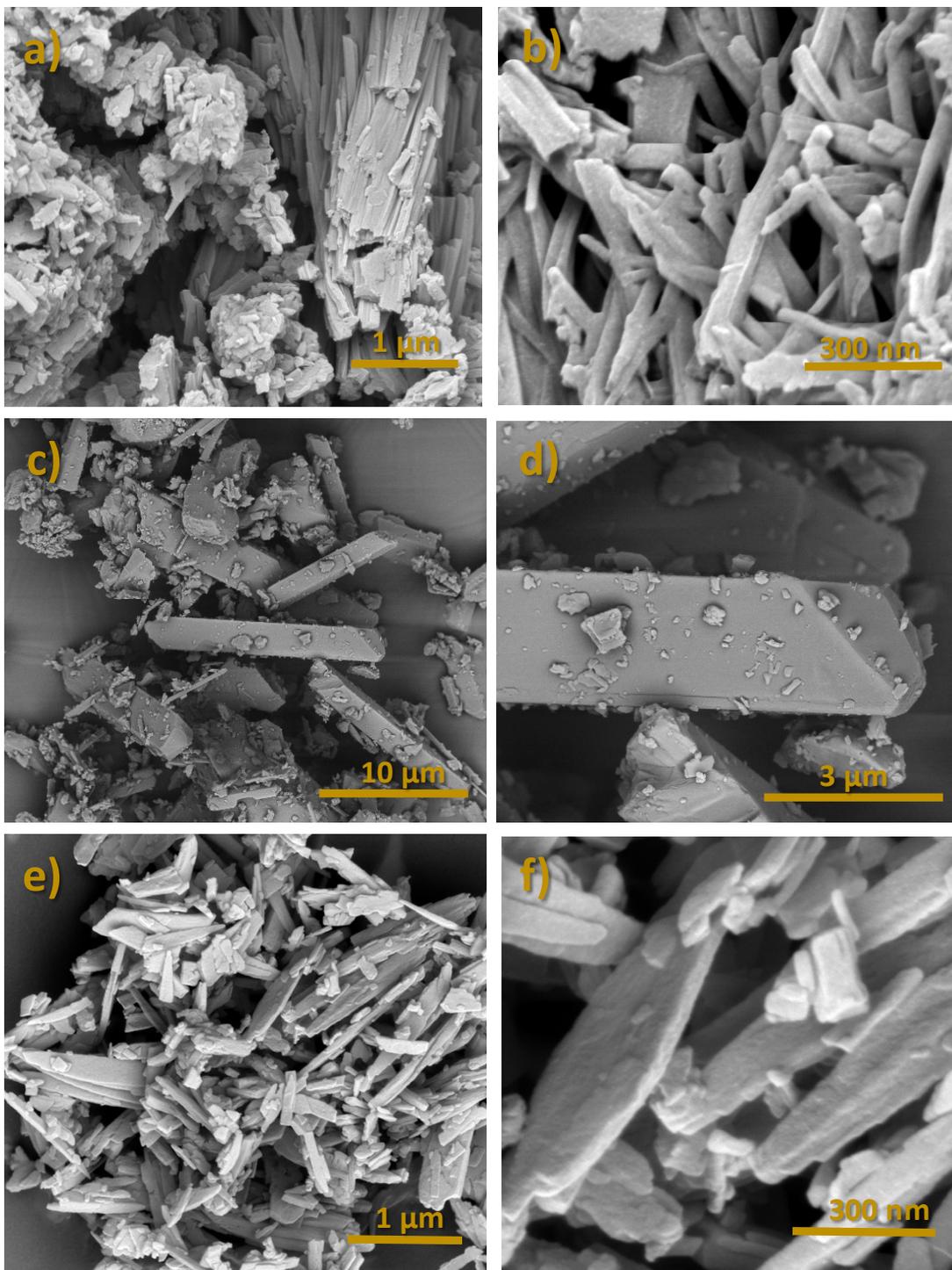


Figure S7. SEM images for (a, b) Zr-PiPhtA, (c, d) Zr-PNA and (e, f) Zr-BTTMP.

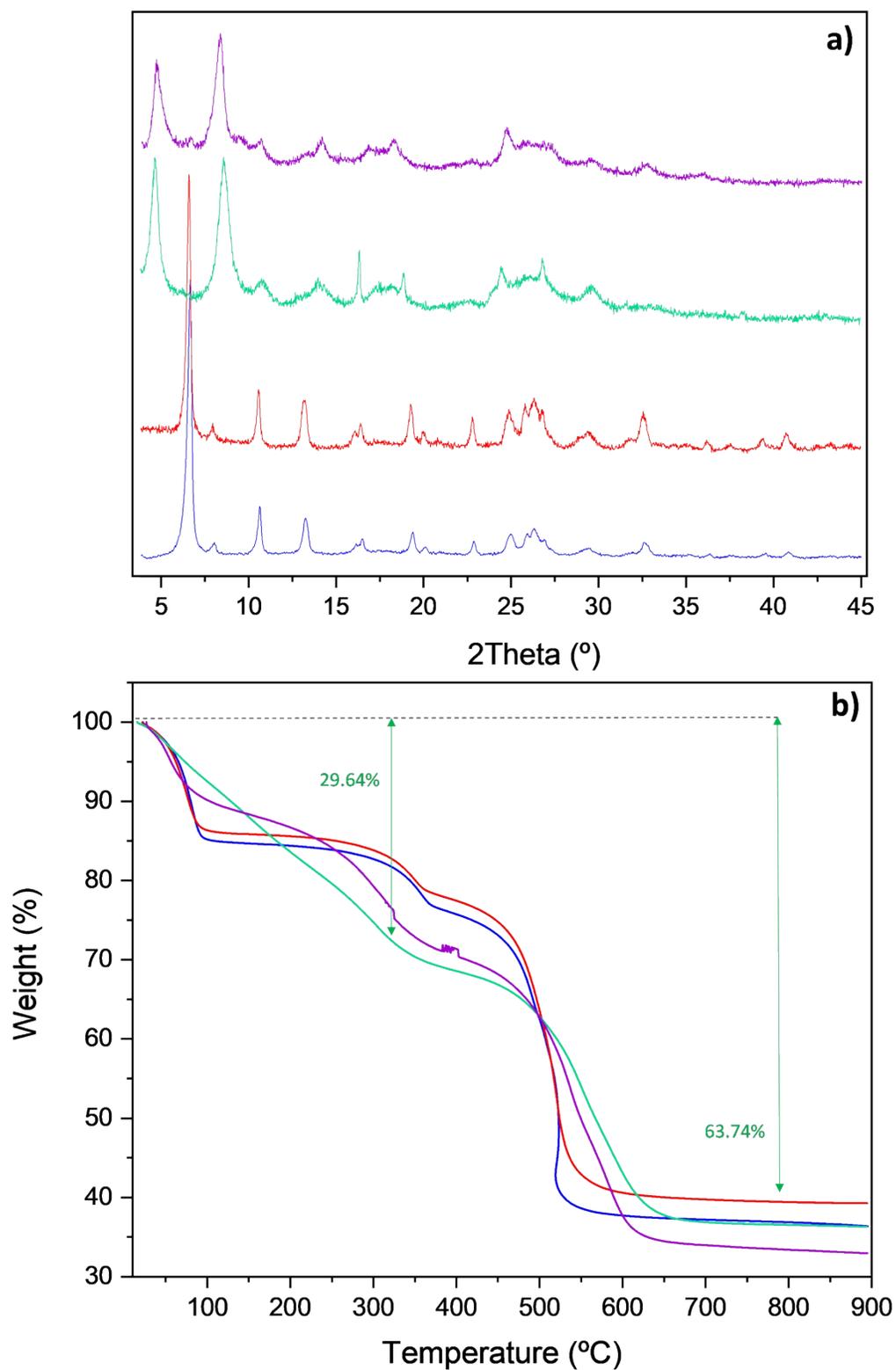


Figure S8. (a) X-ray powder diffraction (XRPD) patterns and (b) TG analysis for **Zr-PiPhtA** (blue), **Zr-PiPhtA_NH₃** (green), and post-impedance **Zr-PiPhtA** (red) and **Zr-PiPhtA_NH₃** (violet) samples.

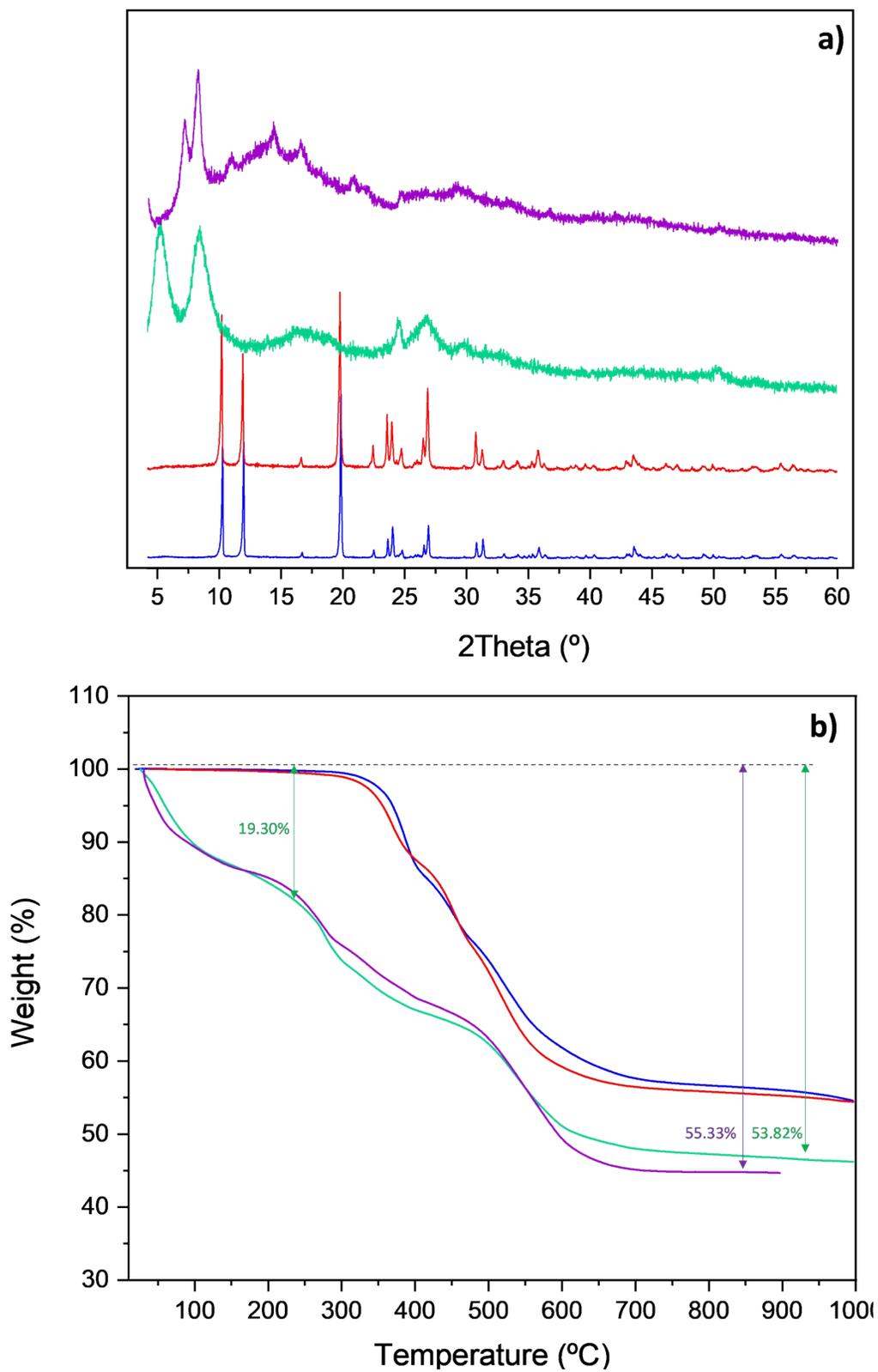


Figure S9. (a) X-ray powder diffraction (XRPD) patterns and (b) TG analysis for **Zr-PNA** (blue), **Zr-PNA_{NH₃}** (green), and post-impedance **Zr-PNA** (red) and **Zr-PNA_{NH₃}** (violet) samples.

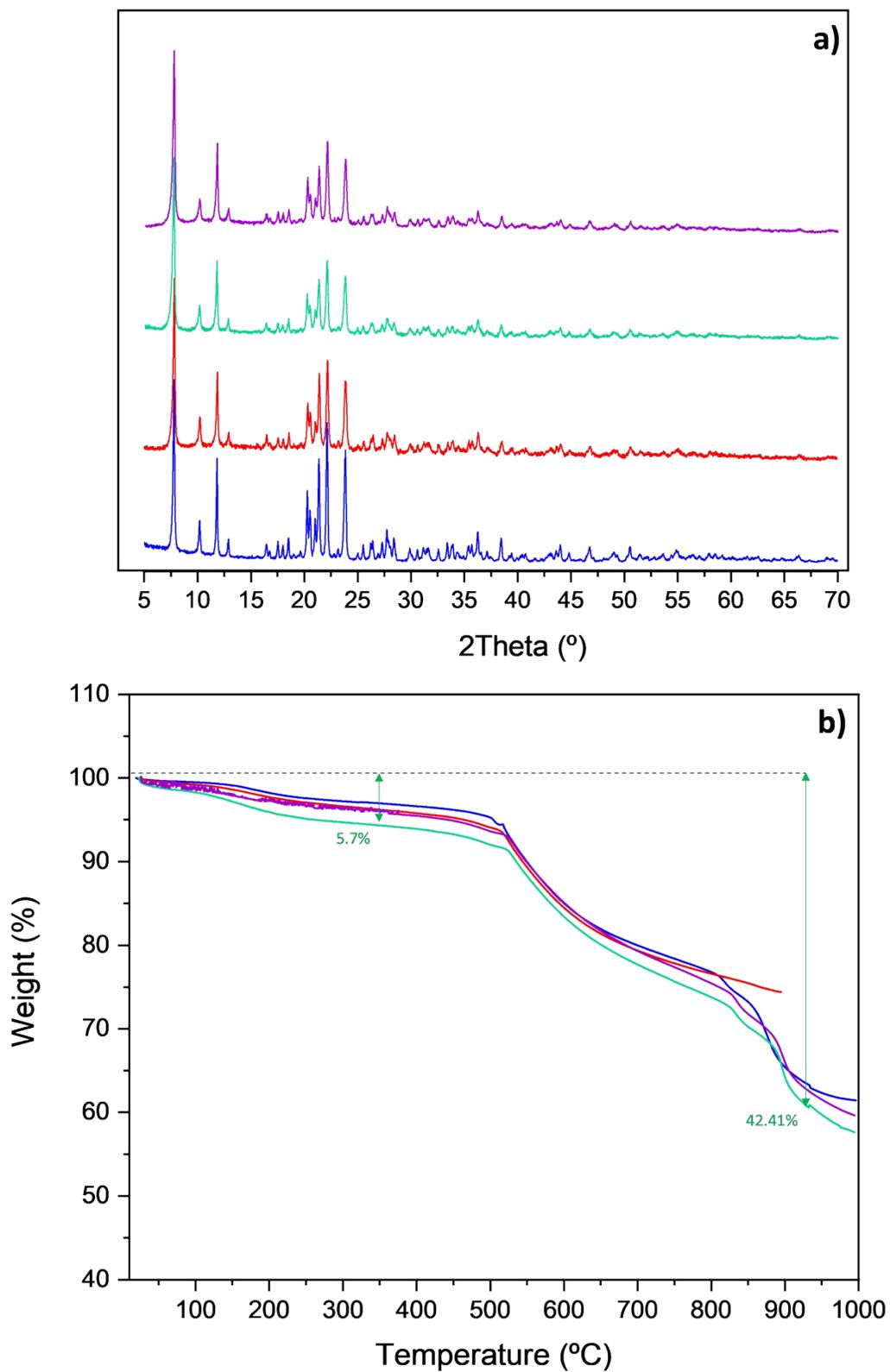


Figure S10. (a) X-ray powder diffraction (XRPD) patterns and (b) TG analysis for: **Zr-BTTMP** before (blue), **Zr-BTTMP_NH₃** (green), and post-impedance **Zr-BTTMP** (red) and **Zr-BTTMP_NH₃** (violet) samples.

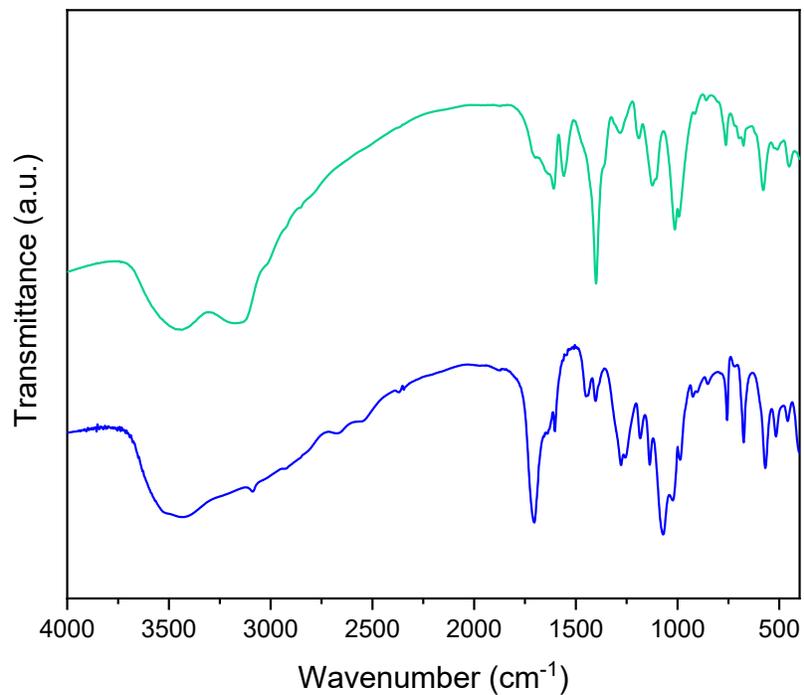


Figure S11. FT-IR spectra of **Zr-PiPhtA** as synthesized (blue) and **Zr-PiPhtA_NH₃** (green).

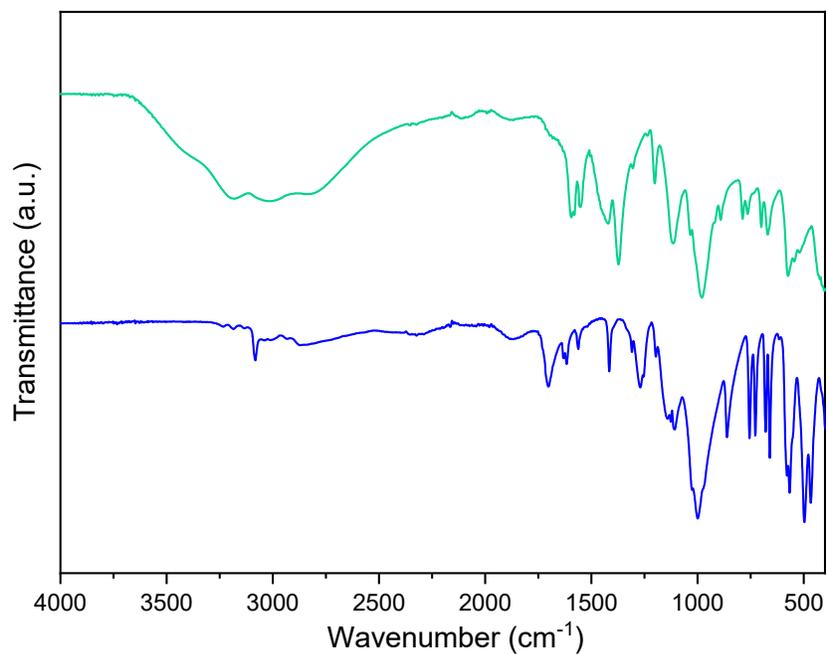


Figure S12. FT-IR spectra for **Zr-PNA** as synthesized (blue) and **Zr-PNA_NH₃** (green).

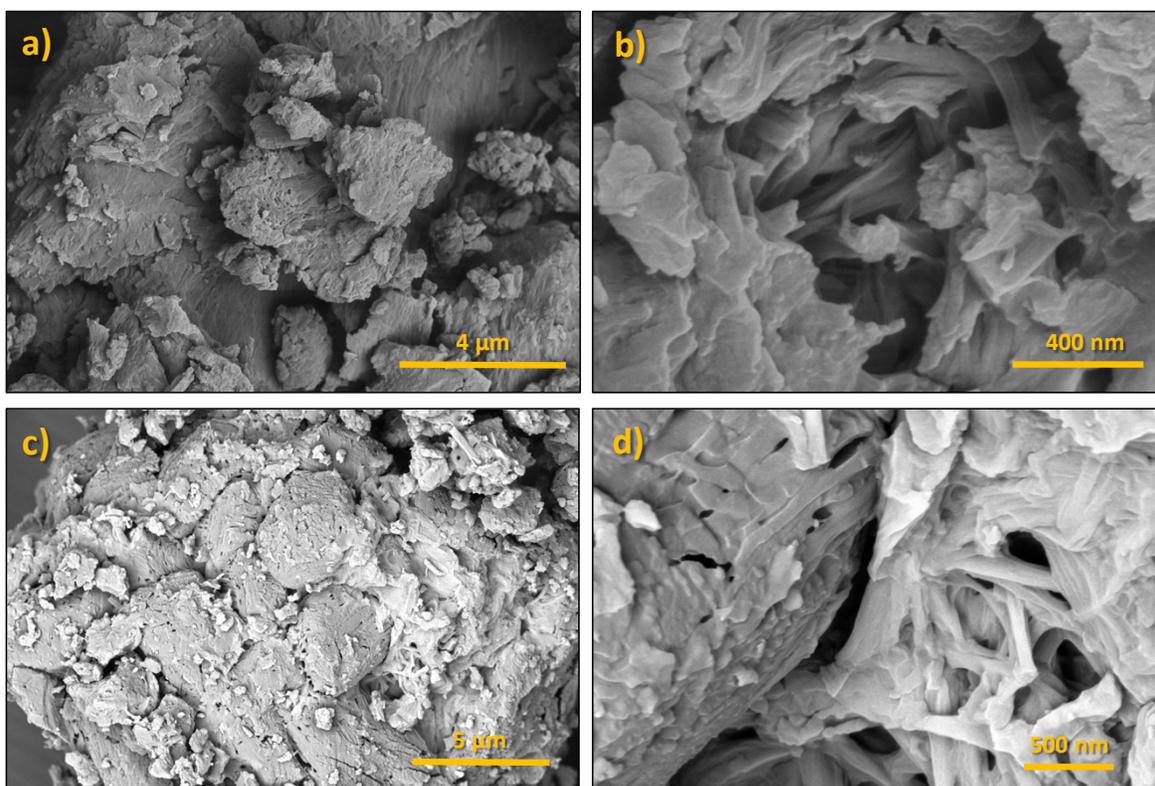


Figure S13. SEM images for (a, b) Zr-PiPhtA_NH₃ and (c, d) Zr-PNA_NH₃.

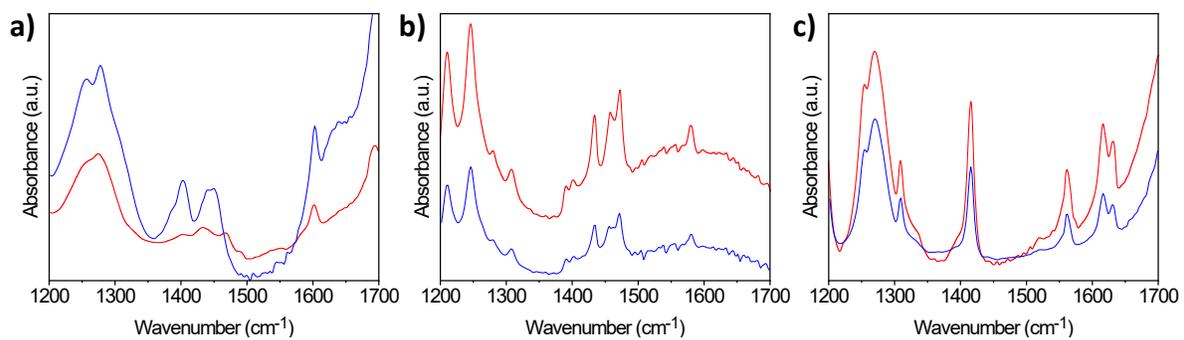


Figure S14. FT-IR spectra for (a) Zr-PiPhtA, (b) Zr-BTTMP and (c) Zr-PNA as synthesized (red) and pyridine-adsorbed samples (blue).

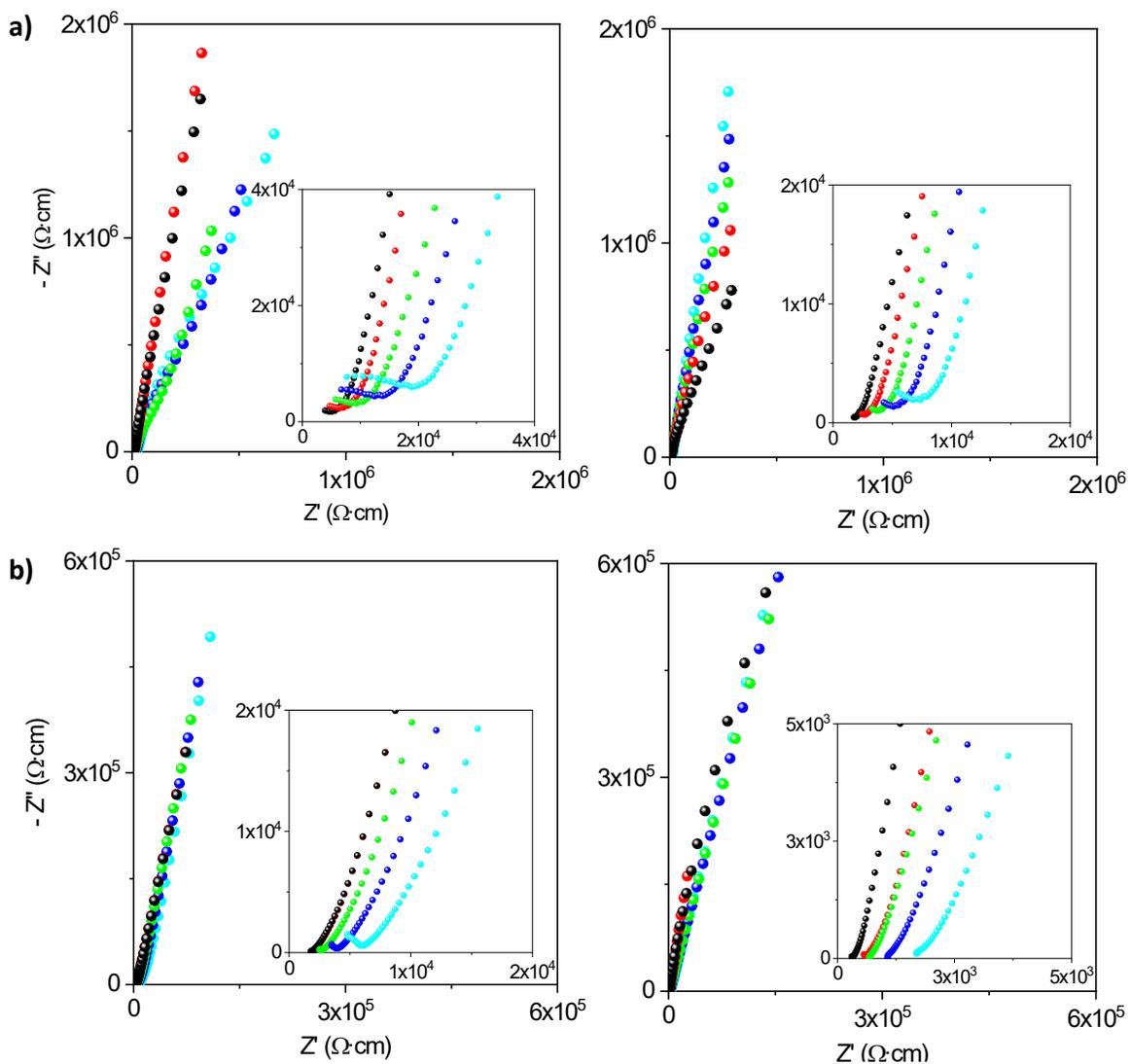


Figure S15. Plot of complex impedance plane for (a) Zr-PiPhtA and (b) Zr-PiPhtA_NH₃ compound at 75% (left) and 95% (right) of relative humidity (RH) at different temperatures: 80 (black), 70 (red), 60 (green), 50 (blue) and 40 °C (cyan).

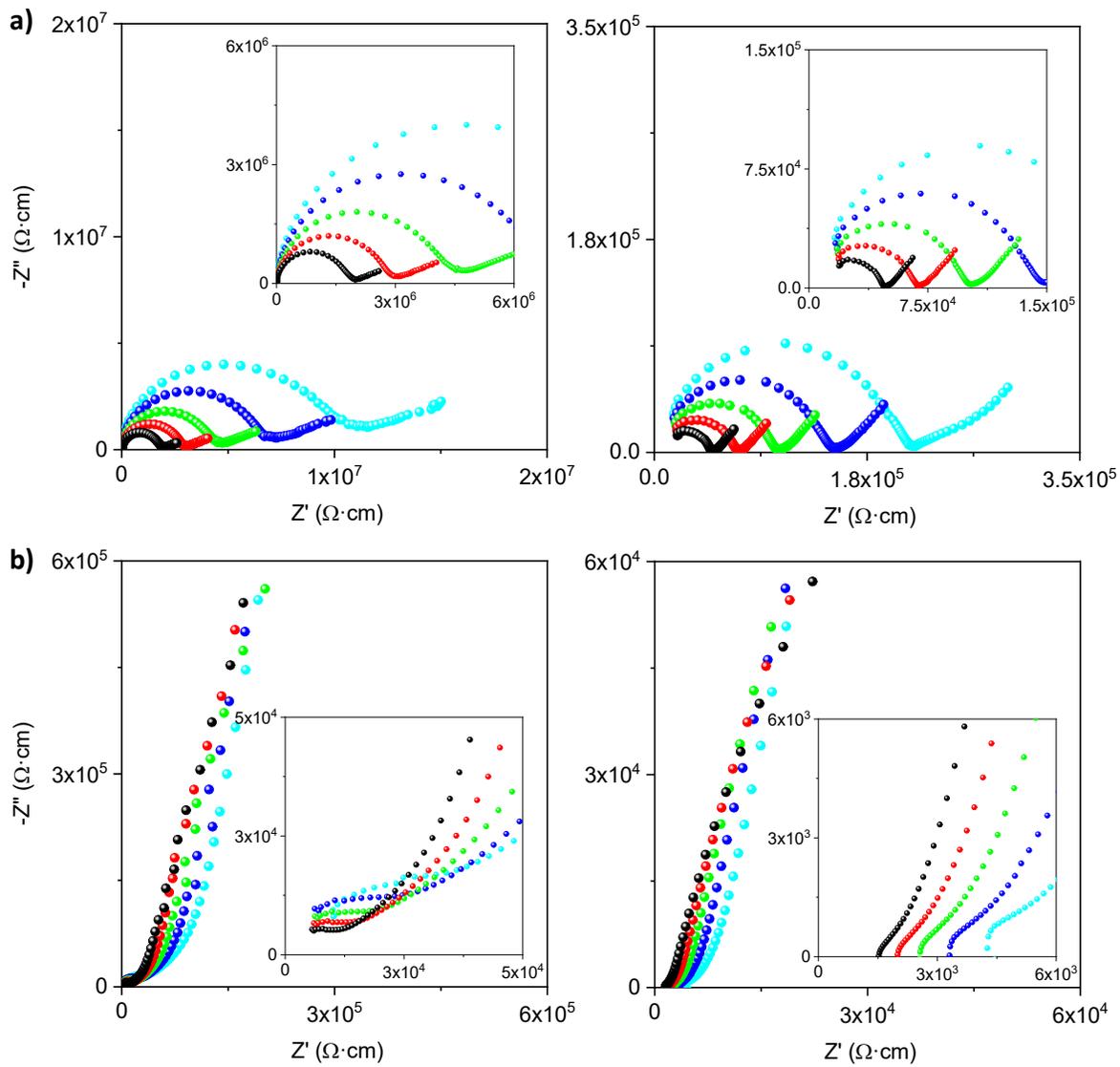


Figure S16. Plot of complex impedance plane for (a) Zr-PNA and (b) Zr-PNA_NH₃ compound at 75% (left) and 95% (right) of relative humidity (RH) at different temperatures: 80 (black), 70 (red), 60 (green), 50 (blue) and 40 °C (cyan).

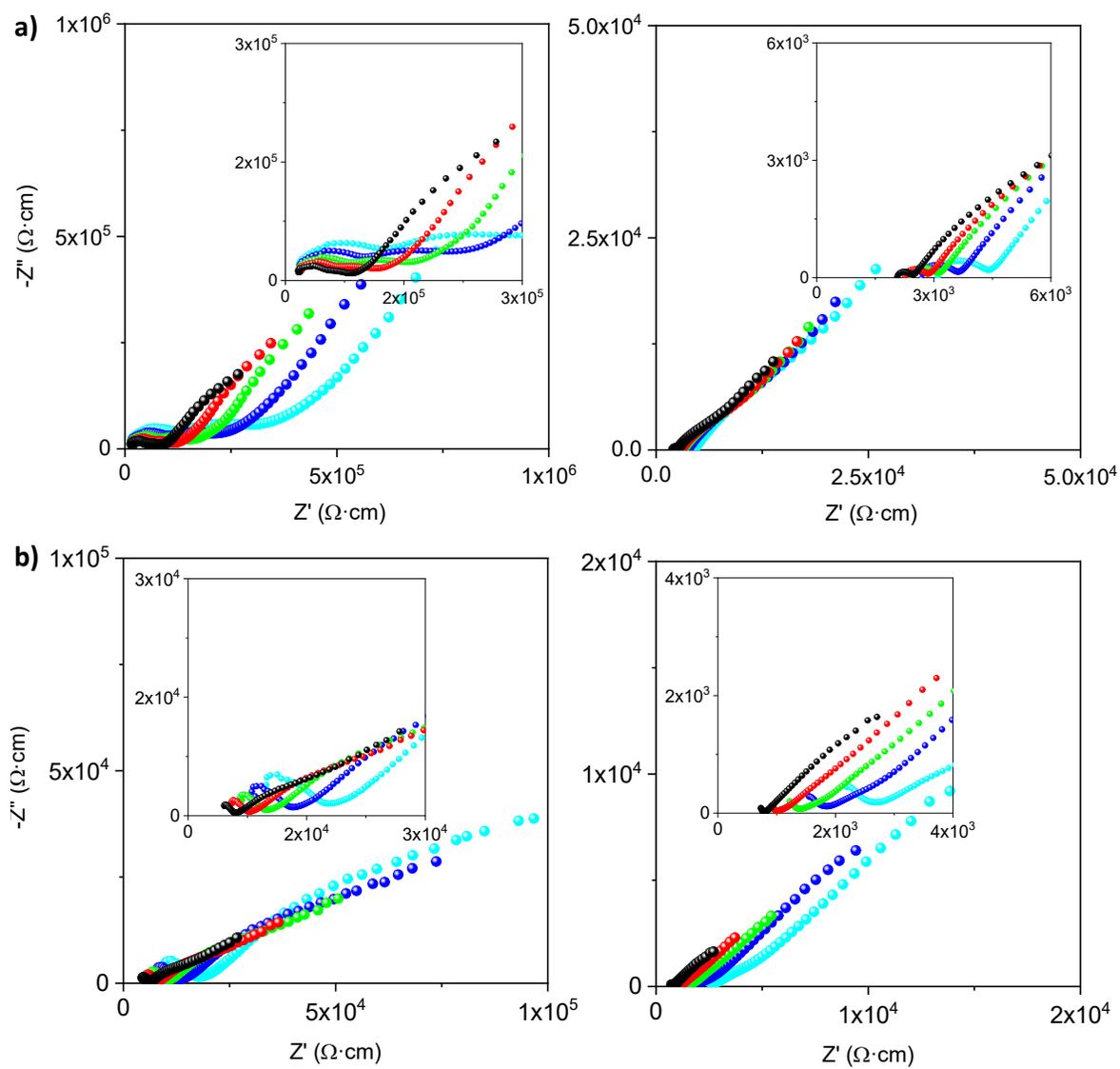


Figure S17. Plot of complex impedance plane for (a) **Zr-BTTMP** and (b) **Zr-BTTMP_NH₃** at 75% (left) and 95% (right) of relative humidity (RH) at different temperatures: 80 (black), 70 (red), 60 (green), 50 (blue) and 40 °C (cyan).

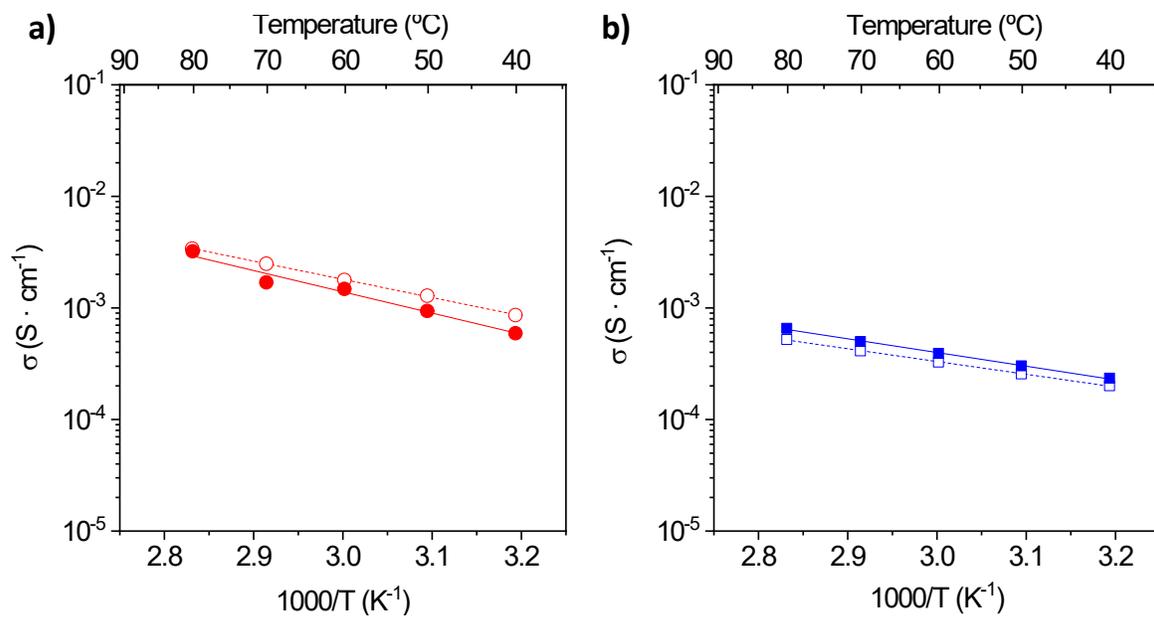


Figure S18. Arrhenius plots at 95% RH of first (closed symbols) and second (open symbols) cycle samples: (a) **Zr-PiPhtA_NH₃** and (b) **Zr-PNA_NH₃**.

Table S1. Rietveld analysis for **Zr-BTTMP** at different conditions under N₂ from thermodiffraction (Cu_{Kα1}) data.

Compound	As-synthesized	350 °C-N₂	30 °C-N₂
<i>a</i> (Å)	15.0070(30)	15.0451(28)	14.9954(30)
<i>b</i> (Å)	17.2903(21)	17.3074(20)	17.2805(21)
<i>c</i> (Å)	5.3002(8)	5.3164(7)	5.2968(8)
<i>β</i> (°)	95.483(7)	95.293(6)	95.547(7)
Volume (Å³)	1369.0(4)	1378.4(4)	1366.1(4)
<i>Z</i>	4	4	4
<i>ρ</i> _{calc} (g·cm ⁻³)	2.1166	2.1060	2.1210
2θ range (°)	7.3–67.1	7.3–67.1	7.3–67.1
Data/restraints/parameters	2991/525/99	3582/526/99	2986/525/99
<i>R</i> _{wp}	7.05	6.53	6.40
<i>R</i> _p	5.32	4.85	4.82
<i>R</i> _F	5.67	5.43	5.44

Table S2. Conversion and product yields for FUR transformation on Zr-based catalysts

Catalyst	Reaction time (h)	FUR conversion (%)	Yields (%)			
			FOL	IpFE	IpL	ND*
Zr-PNA	0	0	0	0	0	0
	3	6.5	3.7	2.3	0	0.4
	6	19.2	5.4	3.1	0.4	10.3
	9	24.1	6.7	4.0	1.2	12.2
	12	28.0	7.4	6.9	2.6	11.1
	24	37.1	7.6	13.9	4.5	11.1
Zr-PiPhtA	0	0	0	0	0	0
	3	28.6	9.1	14.9	1.8	2.8
	6	40.5	14.1	18.2	3.7	4.4
	9	54.2	19.0	21.7	4.4	9.1
	12	63.4	19.7	29.1	7.4	7.3
	24	81.2	18.9	37.6	12.4	13.1
Zr-BTTMP	0	0	0	0	0	0
	3	40.4	13.7	19.0	3.6	4.1
	6	49.4	15.6	22.1	5.5	6.2
	9	64.3	23.3	23.4	5.4	12.2
	12	81.9	19.6	34.6	9.6	18.1
	24	100	17.2	44.4	16.6	21.8
Zr₃(PO₄)₄	0	0	0	0	0	0
	3	17.2	11.5	0	0	5.7
	6	32.3	24.8	0	0	7.5
	9	38.5	21.4	3.9	1.4	11.8
	12	46.7	19.0	7.2	8.3	16.3
	24	63.0	18.8	12.9	12.3	19.0

*ND: non-detected products