Solubility and crystallization studies of picolinic acid

Supplementary Materials

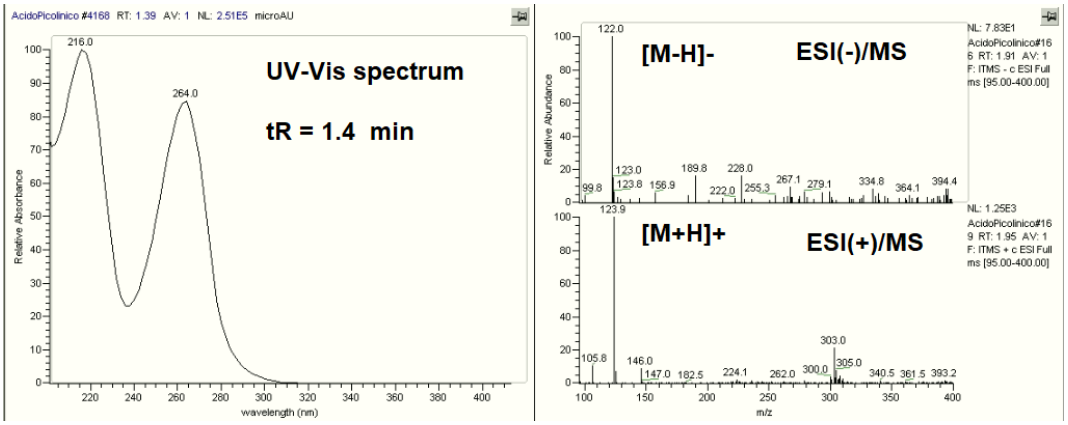

Figure S1 - UV-Vis and ESI mass spectra, in the positive and negative modes of picolinic acid (PA).

Figure S2 –Microscope image of PA crystals obtained through sublimation using a cold finger.

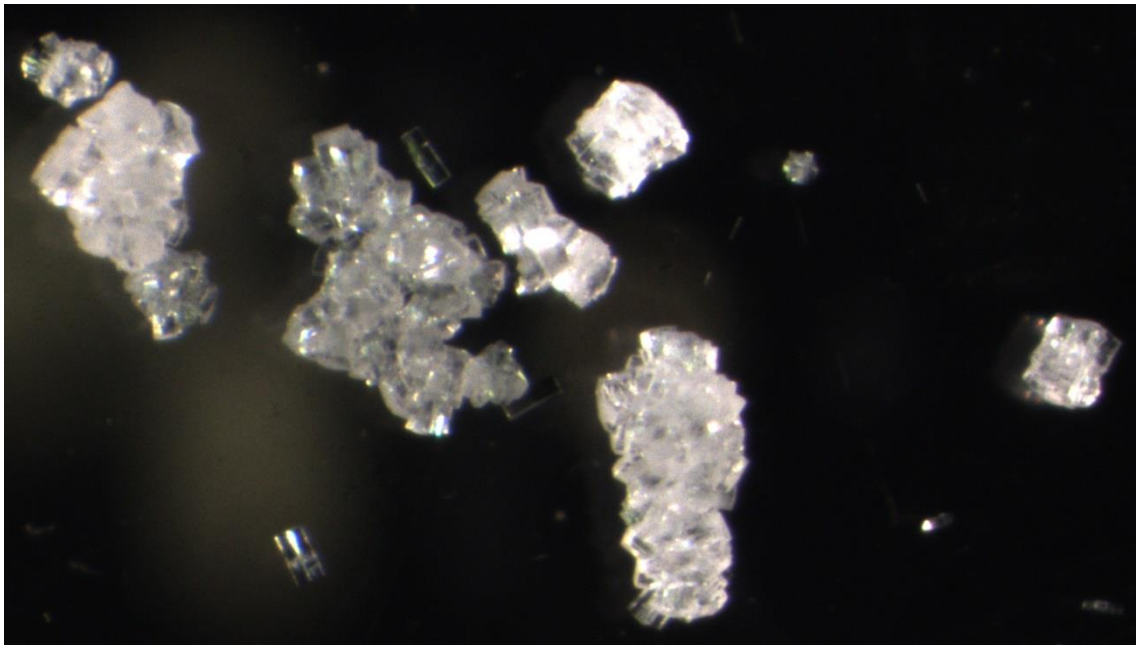

Figure S3 – Microscope image of PA crystals obtained through sublimation on a Petri dish used for SCXRD.

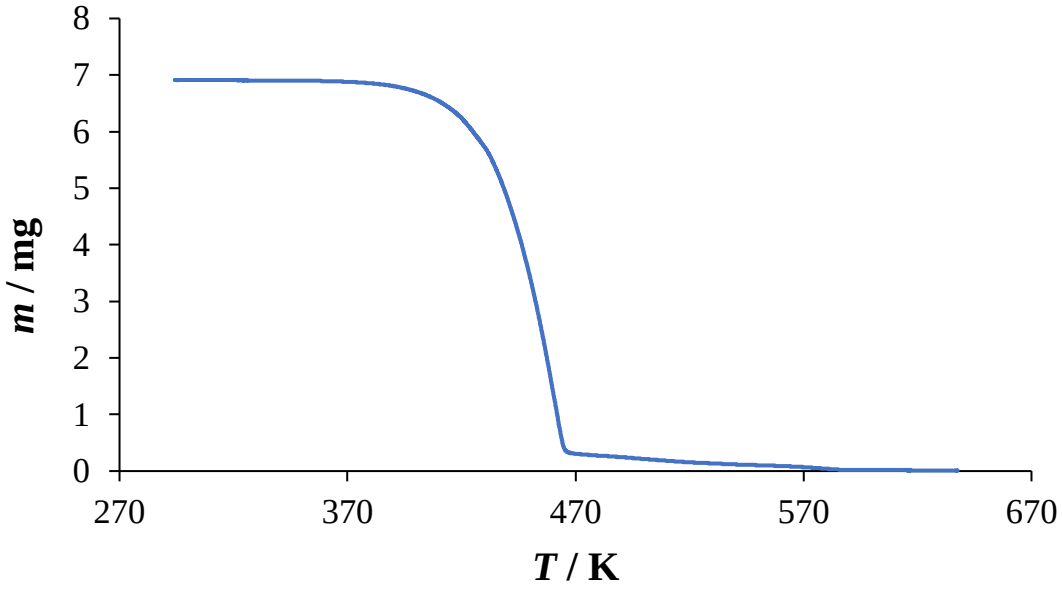

Figure S4 – Thermogram obtained through the thermogravimetric analysis (TGA) of PA.

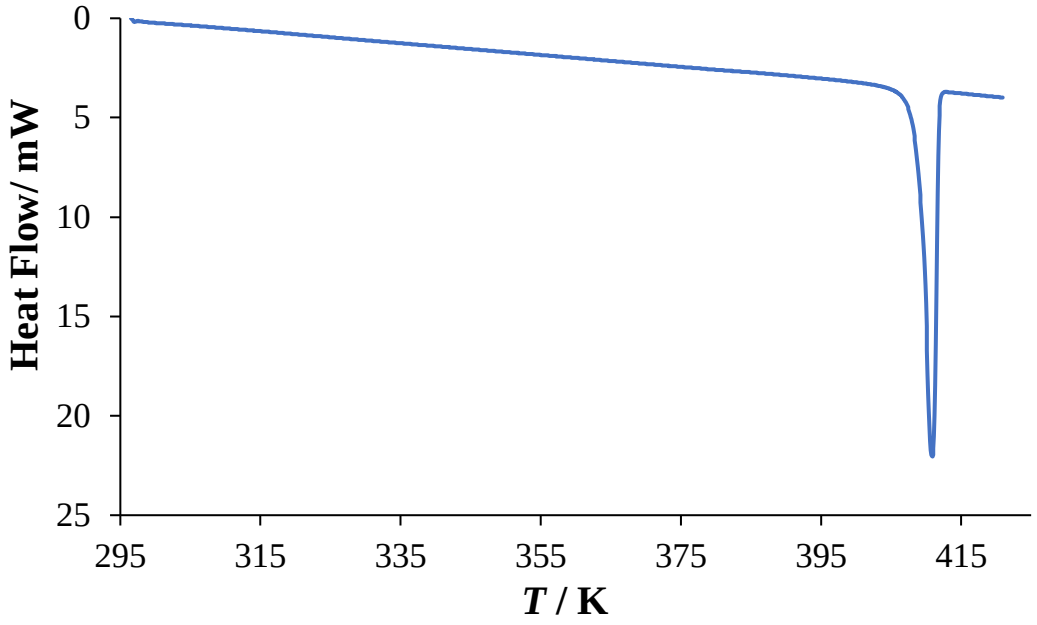

Figure S5 - Thermogram obtained through differential scanning calorimetry (DSC) in the temperature range of 298 – 423 K of PA.

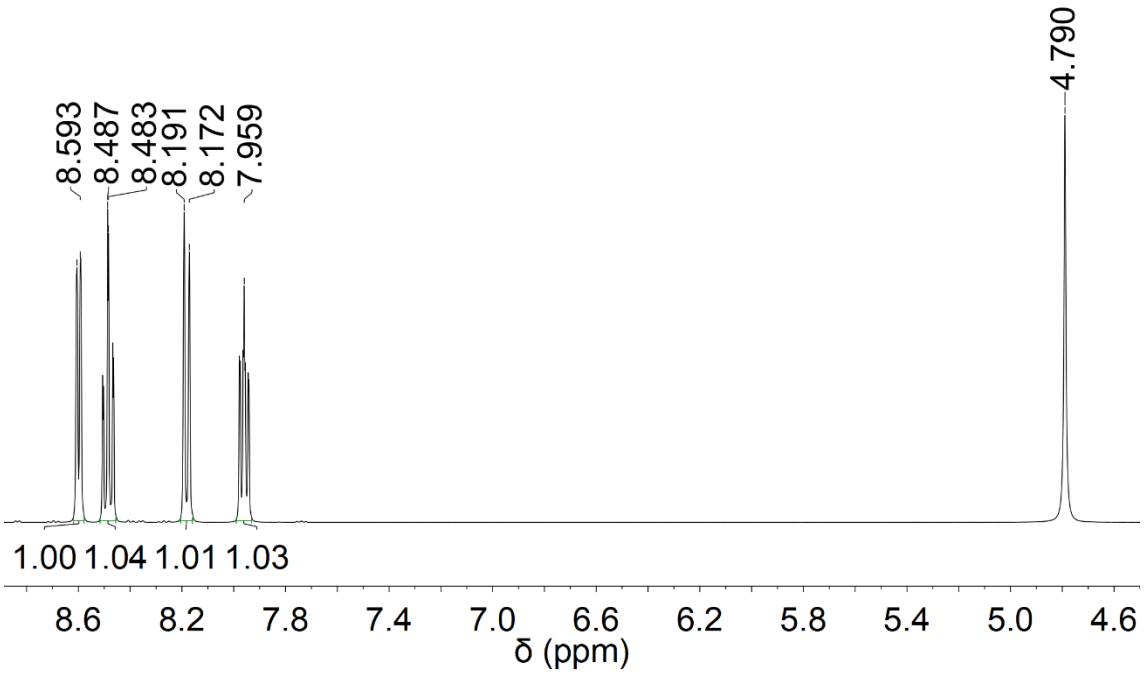

Figure S6 –^{1}H-NMR spectrum of a solution of PA in D_2O with a concentration of 126.28 $g \cdot kg^{-1}$.

Table S1. Provenance and mass fraction purity of the materials used in this work.

Material	CAS #	Supplier	Mass fraction purity
Picolinic acid	98-98-6	Alfa Aesar	0.99999[a]
Ethanol	64-17-5	Carlo Erba Reagents	0.999[b]
Acetonitrile	75-05-8	Chem-Lab	0.999[b]

[a] Mass fraction given by HPLC-ESI/MS analysis, after the purification procedure carried out in this work; [b] Given by the supplier.

Table S2 - Indexation of the X-ray Powder Diffraction Pattern of PA, as supplied, recorded at 298±2 K, in the range $7° \leq 2\theta \leq 35°$; Crystal system: Monoclinic; Space group: C2/c; a = 21.2215 Å, b = 3.8295 Å, c = 13.9497 Å, β = 108.08°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.829	8.760
-2	0	2	13.42	13.50
4	0	0	17.63	17.57
-4	0	2	18.56	18.49
1	1	1	25.00	24.95
-6	0	2	25.61	25.70
-3	1	1	26.58	26.58
-3	1	2	28.06	28.07
-1	1	3	30.31	30.27
-3	1	3	30.99	31.03
-6	0	4	31.49	31.45
3	1	2	31.88	31.86
6	0	2	33.38	33.39
-8	0	2	33.87	33.86
5	1	1	34.28	34.34
3	1	3	36.17	36.17
4	0	4	36.74	36.74

Table S3- Indexation of the X-ray Powder Diffraction Pattern of PA, obtained through sublimation using a cold finger, recorded at 298±2 K, in the range $7° \leq 2\theta \leq 35°$; Crystal system: Monoclinic; Space group: C2/c; a = 21.2215 Å, b = 3.8295 Å, c = 13.9497 Å, β = 108.08°.

h	k	l	2θ(Obs.) /°	2θ(Calc.) / °
2	0	0	8.835	8.756
-2	0	2	13.42	13.51
4	0	0	17.62	17.56
-4	0	2	18.56	18.50
-1	1	1	24.24	24.20
1	1	1	24.99	24.96
-3	1	1	26.60	26.58
0	0	4	26.91	26.87
-3	1	2	28.07	28.08
-1	1	3	30.28	30.27
2	0	4	30.85	30.85
-3	1	3	31.05	31.05
-6	0	4	31.46	31.47
3	1	2	31.88	31.86
6	0	2	33.36	33.36
-8	0	2	33.85	33.86
5	1	1	34.23	34.34

Table S4 – Solubility of the picolinic, nicotinic and isonicotinic acid isomers in water (H_2O), ethanol (EtOH) and acetonitrile (MeCN) at 25 and 30 °C in mol·dm^{-3}.

Compound	*t* / °C	Solvent	c / mol·dm^{-3}	References
PA	25	H_2O	4.5620	This work
NA			0.1371	[1]
IA			0.0477	[2]
			0.0467	[3]
PA	30	H_2O	4.7982	This work
NA			0.1569	[2]
			0.1525	[1]
IA			0.0639	[2]
PA	25	EtOH	0.3785	This work
NA			0.0631	[1]
IA			0.0098	[3]
PA	30	EtOH	0.4745	This work
NA			0.0720	[1]
PA	25	MeCN	0.1417	This work
NA			0.0035	[1]
PA	30	MeCN	0.0298	This work
NA			0.0051	[1]

Table S5 – Indexation of the X-ray Powder Diffraction Pattern of PA, in H_2O at 293.15 K recorded at 298±2 K, in the range 7° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group: C2/c; a = 21.2646 Å, b =3.8317 Å, c =13.9725 Å, β =107.97°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.765	8.736
0	0	2	13.33	13.31
4	0	0	17.55	17.52
-4	0	2	18.46	18.47
1	1	0	23.65	23.61
-1	1	1	24.17	24.18
1	1	1	24.93	24.93
4	0	2	25.20	25.18
-2	0	4	25.52	25.48
-3	1	1	26.53	26.55
0	0	4	26.79	26.81
-4	0	4	27.16	27.17
1	1	2	27.87	27.88
-3	1	2	28.07	28.05
-1	1	3	30.28	30.23
2	0	4	30.77	30.78
-3	1	3	30.99	31.01
-6	0	4	31.42	31.41
3	1	2	31.80	31.80
5	1	0	32.17	32.15
6	0	2	33.29	33.28
-8	0	2	33.78	33.79
5	1	1	34.23	34.28

Table S6 - Indexation of the X-ray Powder Diffraction Pattern of PA, in EtOH at 293.15 K recorded at 298±2 K, in the range 7° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group: C2/c; a =21.2048 Å, b =3.8293 Å, c =13.9294 Å, β =107.96°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
0	0	2	13.40	13.35
-4	0	2	18.56	18.52
4	0	2	25.30	25.26
-3	1	1	26.60	26.58
0	0	4	26.86	26.89
-4	0	4	27.24	27.25
1	1	2	27.90	27.91
3	1	1	28.66	28.62
-3	1	3	31.08	31.06
-6	0	4	31.50	31.51
3	1	2	31.88	31.86
5	1	0	32.23	32.20
6	0	2	33.38	33.37
-8	0	2	33.89	33.89
5	1	1	34.24	34.34

Table S7 - Indexation of the X-ray Powder Diffraction Pattern of PA, in MeCN at 293.15 K recorded at 298±2 K, in the range 7° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group: C2/c; a =21.2451 Å, b =3.8301 Å, c =13.9532 Å, β =108.02°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.725	8.734
0	0	2	13.32	13.30
4	0	0	17.52	17.52
-4	0	2	18.46	18.46
1	1	0	23.57	23.59
-1	1	1	24.17	24.15
1	1	1	24.92	24.91
4	0	2	25.17	25.18
-2	0	4	25.45	25.47
-1	1	2	26.49	26.49
0	0	4	26.79	26.79
-4	0	4	27.16	27.15
1	1	2	27.83	27.85
-3	1	2	28.04	28.03
3	1	1	28.56	28.56
-1	1	3	30.21	30.21
2	0	4	30.78	30.77
-3	1	3	30.97	30.98
-5	1	1	31.38	31.38
3	1	2	31.80	31.78
5	1	0	32.12	32.13
6	0	2	33.27	33.27
-8	0	2	33.78	33.78
-5	1	3	34.18	34.18

Table S8 - Indexation of the X-ray Powder Diffraction Pattern of PA, in H_2O at 298.15 K recorded at 298±2 K, in the range 7° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group: C2/c; a =21.2451 Å, b =3.8301 Å, c =13.9532 Å, β =108.02°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.775	8.747
0	0	2	13.32	13.34
4	0	0	17.57	17.55
-4	0	2	18.53	18.48
-1	1	1	24.19	24.19
1	1	1	24.96	24.94
4	0	2	25.26	25.23
-2	0	4	25.55	25.52
-1	1	2	26.50	26.53
0	0	4	26.80	26.86
-4	0	4	27.22	27.19
-3	1	2	28.07	28.07
-1	1	3	30.27	30.26
2	0	4	30.83	30.84
-3	1	3	31.04	31.03
-6	0	4	31.46	31.44
3	1	2	31.87	31.84
5	1	0	32.16	32.18
6	0	2	33.36	33.33
-8	0	2	33.75	33.82
-5	1	3	34.21	34.22

Table S9- Indexation of the X-ray Powder Diffraction Pattern of PA, in EtOH at 298.15 K recorded at 298±2 K, in the range 7° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2469 Å, b =3.8295 Å, c =13.9557 Å, β =108.97°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.755	8.744
0	0	2	13.34	13.33
24	0	0	17.61	17.54
-4	0	2	18.53	18.48
1	1	0	23.67	23.63
-1	1	1	24.20	24.19
1	1	1	24.99	24.95
-3	1	1	26.58	26.57
0	0	4	26.84	26.84
-4	0	4	27.17	27.20
1	1	2	27.94	27.90
3	1	1	28.48	28.60
-1	1	3	30.29	30.26
2	0	4	30.83	30.82
-6	0	4	31.43	31.44
6	0	2	33.33	33.31
-8	0	2	33.81	33.82
5	1	1	34.25	34.30

Table S10 - Indexation of the X-ray Powder Diffraction Pattern of PA, in MeCN at 298.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2800 Å, b =3.8399 Å, c =13.9944 Å, β =107.94°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.685	8.728
0	0	2	13.30	13.29
4	0	0	17.50	17.51
-4	0	2	18.44	18.45
1	1	0	23.54	23.56
-1	1	1	24.14	24.13
1	1	1	24.86	24.88
4	0	2	25.16	25.15
-2	0	4	25.42	25.44
-1	1	2	26.47	26.46
0	0	4	26.78	26.76
-4	0	4	27.12	27.13
1	1	2	27.79	27.82
-3	1	2	28.02	28.00
-1	1	3	30.16	30.17
2	0	4	30.73	30.73
-3	1	3	30.97	30.95
-5	1	1	31.33	31.35
3	1	2	31.74	31.74
-5	1	2	32.10	32.06
6	0	2	33.26	33.23
-8	0	2	33.75	33.77
-5	1	3	34.20	34.15

Table S11 - Indexation of the X-ray Powder Diffraction Pattern of PA, in H_2O at 303.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2426 Å, b =3.8353 Å, c =13.9625 Å, β =107.97°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.735	8.745
0	0	2	13.35	13.32
4	0	0	17.47	17.54
2	0	2	18.09	18.09
-4	0	2	18.51	18.48
-1	1	1	24.21	24.16
1	1	1	24.88	24.91
4	0	2	25.22	25.21
-2	0	4	25.48	25.50
-3	1	1	26.51	26.54
3	1	0	26.73	26.73
0	0	4	26.82	26.83
-4	0	4	27.19	27.19
-3	1	2	28.05	28.04
-1	1	3	30.20	30.23
2	0	4	30.81	30.81
-3	1	3	31.04	31.00
-5	1	1	31.39	31.40
3	1	2	31.82	31.80
6	0	2	33.34	33.31
-8	0	2	33.85	33.83
-5	1	3	34.19	34.20

Table S12 - Indexation of the X-ray Powder Diffraction Pattern of PA, in EtOH at 303.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2966 Å, b =3.8373 Å, c =13.9742 Å, β =108.01°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.740	8.725
0	0	2	13.31	13.31
4	0	0	17.51	17.50
-4	0	2	18.43	18.44
-1	1	1	24.14	24.14
1	1	1	24.92	24.90
-6	0	0	26.37	26.38
3	1	0	26.73	26.70
-4	0	4	27.14	27.15
1	1	2	27.91	27.85
-3	1	2	28.00	28.01
-1	1	3	30.19	30.21
2	0	4	30.82	30.78
-3	1	3	30.93	30.97
-5	1	1	31.31	31.35
3	1	2	31.77	31.77
6	0	2	33.21	33.25
-8	0	2	33.79	33.74
-5	1	3	34.17	34.16

Table S13 - Indexation of the X-ray Powder Diffraction Pattern of PA, in MeCN at 303.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2736 Å, b =3.8401 Å, c =13.9747 Å, β =108.08°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.695	8.738
4	0	0	17.49	17.53
-4	0	2	18.44	18.45
1	1	0	23.53	23.56
-1	1	1	24.10	24.13
1	1	1	24.82	24.88
4	0	2	25.18	25.21
-6	0	0	26.44	26.42
3	1	0	26.76	26.70
-4	0	4	27.13	27.15
1	1	2	27.93	27.84
-3	1	2	28.03	28.00
-1	1	3	30.17	30.19
2	0	4	30.84	30.81
-5	1	1	31.36	31.35
3	1	2	31.76	31.78
6	0	2	33.31	33.31
-8	0	2	33.79	33.77
-5	1	3	34.16	34.15

Table S14 - Indexation of the X-ray Powder Diffraction Pattern of PA, in H_2O at 308.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2620 Å, b =3.8286 Å, c =13.9528 Å, β =107.99°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
0	0	2	13.28	13.33
-2	0	2	13.42	13.50
4	0	0	17.63	17.52
-4	0	2	18.44	18.47
1	1	0	23.65	23.63
1	1	1	24.98	24.95
4	0	2	25.19	25.20
-6	0	2	25.58	25.66
-3	1	1	26.58	26.57
0	0	4	26.89	26.85
-4	0	4	27.20	27.19
1	1	2	27.89	27.90
-3	1	2	28.08	28.07
-1	1	3	30.25	30.27
2	0	4	30.86	30.82
-6	0	4	31.46	31.43
3	1	2	31.84	31.83
5	1	0	32.17	32.16
6	0	2	33.25	33.29
-8	0	2	33.84	33.78
5	1	1	34.24	34.29

Table S15 - Indexation of the X-ray Powder Diffraction Pattern of PA, in EtOH at 308.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2445 Å, b =3.8314 Å, c =13.9553 Å, β =108.00°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.775	8.746
0	0	2	13.36	13.33
4	0	0	17.56	17.54
-4	0	2	18.51	18.48
1	1	0	23.64	23.62
-1	1	1	24.18	24.18
1	1	1	24.95	24.94
4	0	2	25.23	25.22
-2	0	4	25.55	25.52
-3	1	1	26.53	26.56
0	0	4	26.84	26.85
-4	0	4	27.18	27.19
1	1	2	27.89	27.89
-3	1	2	28.06	28.06
3	1	1	28.59	28.59
-1	1	3	30.25	30.25
2	0	4	30.82	30.83
-3	1	3	31.03	31.02
-6	0	4	31.43	31.44
5	1	0	32.17	32.17
6	0	2	33.32	33.32
-8	0	2	33.81	33.82
5	1	1	34.31	34.30

Table S16 - Indexation of the X-ray Powder Diffraction Pattern of PA, in MeCN at 308.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2368 Å, b =3.8269 Å, c =13.9427 Å, β =108.03°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.830	8.751
-2	0	2	13.42	13.51
4	0	0	17.62	17.55
-4	0	2	18.53	18.49
1	1	0	23.68	23.64
-1	1	1	24.24	24.21
1	1	1	25.00	24.97
-2	0	4	25.56	25.54
-3	1	1	26.54	26.59
0	0	4	26.91	26.88
-4	0	4	27.22	27.21
-3	1	2	28.10	28.09
3	1	1	28.63	28.62
-1	1	3	30.29	30.28
2	0	4	30.85	30.86
-3	1	3	31.06	31.05
-6	0	4	31.44	31.45
3	1	2	31.87	31.86
5	1	0	32.19	32.20
6	0	2	33.36	33.35
-8	0	2	33.83	33.83
5	1	1	34.24	34.34

Table S17 - Indexation of the X-ray Powder Diffraction Pattern of PA, in H_2O at 313.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2676 Å, b =3.8351 Å, c =13.9517 Å, β =108.02°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.770	8.738
0	0	2	13.37	13.34
4	0	0	17.57	17.53
-4	0	2	18.50	18.47
-1	1	1	24.20	24.16
1	1	1	24.95	24.91
4	0	2	25.25	25.21
-2	0	4	25.52	25.52
-3	1	1	26.52	26.53
3	1	0	26.65	26.72
0	0	4	26.86	26.86
-4	0	4	27.20	27.19
1	1	2	27.88	27.87
-3	1	2	28.06	28.04
-1	1	3	30.26	30.24
2	0	4	30.82	30.84
-6	0	4	31.40	31.42
3	1	2	31.80	31.81
6	0	2	33.29	33.31
-8	0	2	33.78	33.79
-5	1	3	34.17	34.19

Table S18 - Indexation of the X-ray Powder Diffraction Pattern of PA, in EtOH at 313.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2598 Å, b =3.8370 Å, c =13.9720 Å, β =108.02°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.765	8.739
0	0	2	13.33	13.32
4	0	0	17.55	17.53
-4	0	2	18.49	18.47
1	1	0	23.56	23.58
-1	1	1	24.16	24.15
1	1	1	24.91	24.90
4	0	2	25.21	25.20
-2	0	4	25.50	25.49
-1	1	2	26.48	26.48
0	0	4	26.82	26.81
-4	0	4	27.16	27.17
1	1	2	27.81	27.85
-3	1	2	28.03	28.02
3	1	1	28.59	28.55
-1	1	3	30.21	30.21
2	0	4	30.79	30.79
-3	1	3	30.99	30.98
-6	0	4	31.39	31.41
3	1	2	31.80	31.79
5	1	0	32.12	32.13
6	0	2	33.28	33.29
-8	0	2	33.79	33.80
-5	1	3	34.20	34.18

Table S19 - Indexation of the X-ray Powder Diffraction Pattern of PA, in MeCN at 313.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2165 Å, b =3.8285 Å, c =13.9368 Å, β =107.96°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.825	8.756
0	0	2	13.40	13.35
4	0	0	17.62	17.56
-4	0	2	18.54	18.51
1	1	0	23.63	23.63
-1	1	1	24.24	24.20
1	1	1	24.99	24.96
4	0	2	25.26	25.24
-3	1	1	26.56	26.59
0	0	4	26.88	26.88
-4	0	4	27.22	27.24
1	1	2	27.91	27.92
-3	1	2	28.12	28.09
3	1	1	28.64	28.62
2	0	4	30.84	30.86
-3	1	3	31.06	31.06
-6	0	4	31.49	31.49
3	1	2	31.88	31.85
5	1	0	32.20	32.20
6	0	2	33.37	33.35
-8	0	2	33.85	33.87
5	1	1	34.23	34.33

Table S20 - Indexation of the X-ray Powder Diffraction Pattern of PA, in toluene a 313.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2334 Å, b =3.8324 Å, c =13.9707 Å, β =108.02°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.790	8.752
0	0	2	13.37	13.32
4	0	0	17.57	17.55
-4	0	2	18.50	18.48
1	1	0	23.60	23.61
-1	1	1	24.21	24.17
1	1	1	24.97	24.93
4	0	2	25.23	25.23
-3	1	1	26.52	26.56
3	1	0	26.76	26.75
-4	0	4	27.17	27.17
1	1	2	27.83	27.88
-3	1	2	28.06	28.05
-1	1	3	30.26	30.23
2	0	4	30.78	30.81
-3	1	3	31.04	31.00
-6	0	4	31.43	31.42
3	1	2	31.82	31.82
5	1	0	32.15	32.17
6	0	2	33.33	33.33
-8	0	2	33.84	33.84
-5	1	3	34.19	34.21

Table S21 - Indexation of the X-ray Powder Diffraction Pattern of PA, in cyclohexane a 313.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2472 Å, b =3.8349 Å, c =13.9574 Å, β =107.95°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.785	8.742
0	0	2	13.36	13.33
4	0	0	17.56	17.54
-4	0	2	18.48	18.49
1	1	0	23.63	23.59
-1	1	1	24.19	24.16
1	1	1	24.92	24.91
4	0	2	25.21	25.20
-2	0	4	25.55	25.51
-3	1	1	26.51	26.54
0	0	4	26.82	26.84
-4	0	4	27.19	27.20
1	1	2	27.85	27.87
-3	1	2	28.07	28.04
-1	1	3	30.21	30.23
2	0	4	30.80	30.81
-3	1	3	31.02	31.01
-6	0	4	31.44	31.45
3	1	2	31.81	31.80
5	1	0	32.16	32.15
6	0	2	33.31	33.30
-8	0	2	33.82	33.82
5	1	1	34.23	34.28

Table S22 - Indexation of the X-ray Powder Diffraction Pattern of PA, in H_2O at 318.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2605 Å, b =3.8304 Å, c =13.9365 Å, β =108.04°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.810	8.741
-2	0	2	13.40	13.35
4	0	0	17.49	17.53
-4	0	2	18.13	18.13
1	1	0	18.51	18.48
-1	1	1	23.63	23.62
1	1	1	24.20	24.19
-2	0	4	24.96	24.95
-3	1	1	25.26	25.24
0	0	4	25.53	25.55
-4	0	4	26.54	26.56
-3	1	2	26.75	26.75
3	1	1	26.89	26.89
-1	1	3	27.22	27.21
2	0	4	27.90	27.91
-3	1	3	28.08	28.07
-6	0	4	30.25	30.27
3	1	2	30.86	30.87
5	1	0	31.46	31.44
6	0	2	31.87	31.84
-8	0	2	33.34	33.33
5	1	1	33.78	33.80
-5	1	3	34.22	34.22

Table S23- Indexation of the X-ray Powder Diffraction Pattern of PA, in EtOH at 318.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.1969 Å, b =3.8276 Å, c =13.9535 Å, β =107.93°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.720	8.762
0	0	2	13.31	13.33
-2	0	2	13.45	13.51
-4	0	2	18.56	18.52
1	1	0	23.67	23.64
1	1	1	24.95	24.96
-3	1	1	26.58	26.60
0	0	4	26.82	26.84
-4	0	4	27.23	27.22
-1	1	3	30.29	30.27
2	0	4	30.85	30.82
-6	0	4	31.50	31.49
3	1	2	31.88	31.85
6	0	2	33.38	33.36
5	1	1	34.29	34.34

Table S24 - Indexation of the X-ray Powder Diffraction Pattern of PA, in MeCN at 318.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.3248 Å, b =3.8414 Å, c =13.982 Å, β =108.26°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.645	8.726
-4	0	2	18.37	18.40
1	1	0	23.54	23.55
-1	1	1	24.08	24.12
1	1	1	24.83	24.88
-6	0	0	26.40	26.39
3	1	0	26.69	26.68
0	0	4	26.77	26.84
-4	0	4	27.11	27.09
1	1	2	27.95	27.84
-1	1	3	30.13	30.19
2	0	4	30.89	30.84
-3	1	3	30.98	30.92
-5	1	1	31.31	31.31
3	1	2	31.79	31.79
-5	1	3	34.13	34.09

Table S25 - Indexation of the X-ray Powder Diffraction Pattern of PA, in H_2O at 323.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2426 Å, b =3.8353 Å, c =13.9625 Å, β =107.97°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.735	8.745
0	0	2	13.35	13.32
4	0	0	17.47	17.54
2	0	2	18.09	18.09
-4	0	2	18.51	18.48
-1	1	1	24.21	24.16
1	1	1	24.88	24.91
4	0	2	25.22	25.21
-2	0	4	25.48	25.50
-3	1	1	26.51	26.54
3	1	0	26.73	26.73
0	0	4	26.82	26.83
-4	0	4	27.19	27.19
-3	1	2	28.05	28.04
-1	1	3	30.20	30.23
2	0	4	30.81	30.81
-3	1	3	31.04	31.00
-5	1	1	31.39	31.40
3	1	2	31.82	31.80
6	0	2	33.34	33.31
-8	0	2	33.85	33.83
-5	1	3	34.19	34.20

Table S26 - Indexation of the X-ray Powder Diffraction Pattern of PA, in EtOH at 323.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.2484 Å, b =3.8323 Å, c =13.9589 Å, β =107.97°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.795	8.743
0	0	2	13.36	13.33
4	0	0	17.58	17.54
-4	0	2	18.49	18.48
1	1	0	23.62	23.61
-1	1	1	24.20	24.18
1	1	1	24.94	24.93
4	0	2	25.22	25.21
-3	1	1	26.54	26.56
3	1	0	26.75	26.74
0	0	4	26.85	26.84
-4	0	4	27.20	27.19
1	1	2	27.87	27.88
-3	1	2	28.05	28.05
3	1	1	28.59	28.58
-1	1	3	30.25	30.24
2	0	4	30.78	30.81
-3	1	3	31.02	31.02
-6	0	4	31.45	31.44
3	1	2	31.81	31.82
5	1	0	32.15	32.16
6	0	2	33.30	33.31
-8	0	2	33.80	33.82
-5	1	3	34.20	34.22

Table S27 - Indexation of the X-ray Powder Diffraction Pattern of PA, in MeCN at 323.15 K recorded at 298±2 K, in the range 7 ° ≤ 2θ ≤ 35°; Crystal system: Monoclinic; Space group C2/c; a =21.1984 Å, b =3.8264 Å, c =13.9548 Å, β =107.96°.

h	k	l	2θ(Obs.) / °	2θ(Calc.) / °
2	0	0	8.830	8.763
-2	0	2	13.41	13.51
4	0	0	17.62	17.58
-4	0	2	18.56	18.52
1	1	0	23.66	23.65
-1	1	1	24.24	24.21
1	1	1	24.98	24.97
4	0	2	25.27	25.24
-3	1	1	26.57	26.60
0	0	4	26.82	26.84
-4	0	4	27.23	27.21
1	1	2	27.94	27.92
3	1	1	28.66	28.63
-1	1	3	30.30	30.27
2	0	4	30.85	30.83
-3	1	3	31.08	31.05
-6	0	4	31.50	31.48
3	1	2	31.83	31.86
5	1	0	32.23	32.22
6	0	2	33.37	33.36
-8	0	2	33.88	33.90
5	1	1	34.25	34.35

References:

[1] Gonçalves, E.M.; Minas da Piedade, M.E. J. Chem. Thermodynamics 2012, 47, 362–371.

[2] Katscher, E.; Moroz, W. *Process for the separation of nicotinic and isonicotinic acid* US Patent, US3147269A, International Chemical Corp, New York, 1964.

[3] Abraham, M.H.; Acree, W.E. *J. Chem. Thermodynamics* **2013**, *61*, 74–78.