Supplementary Materials

Cocrystals of 2-Aminopyrimidine with Boric Acid – Crystal Engineering of a Novel Nonlinear Optically (NLO) Active Crystal

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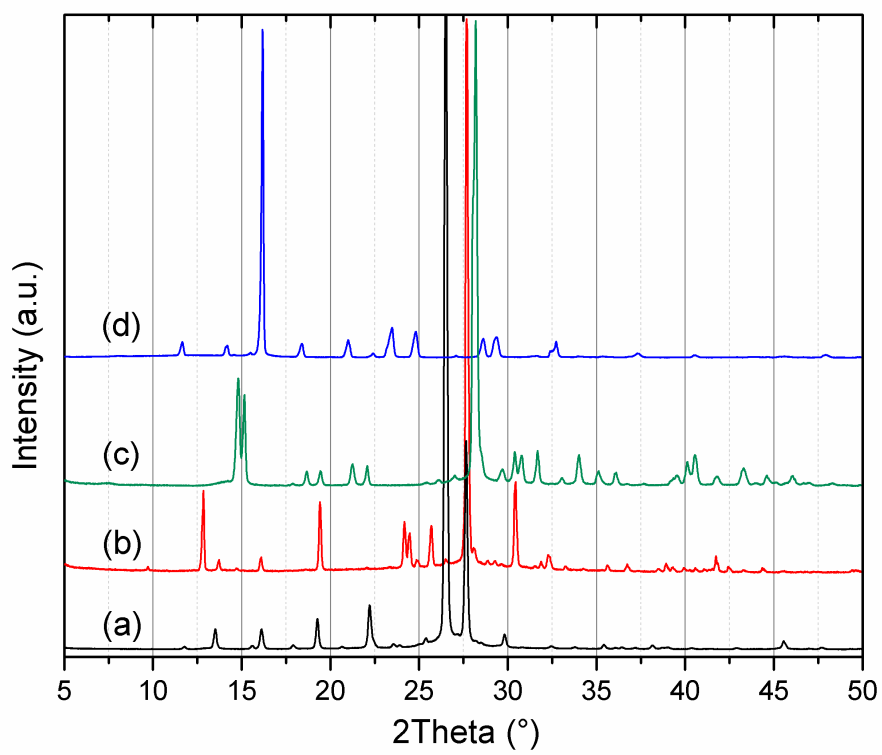

Figure S1. The comparison of recorded powder diffraction patterns of $(2\text{-AMP})_3(H_3BO_3)_2$ (**a**), $2\text{-AMP}(H_3BO_3)_2$ (**b**), boric acid (**c**) and 2-aminopyrimidine (**d**).

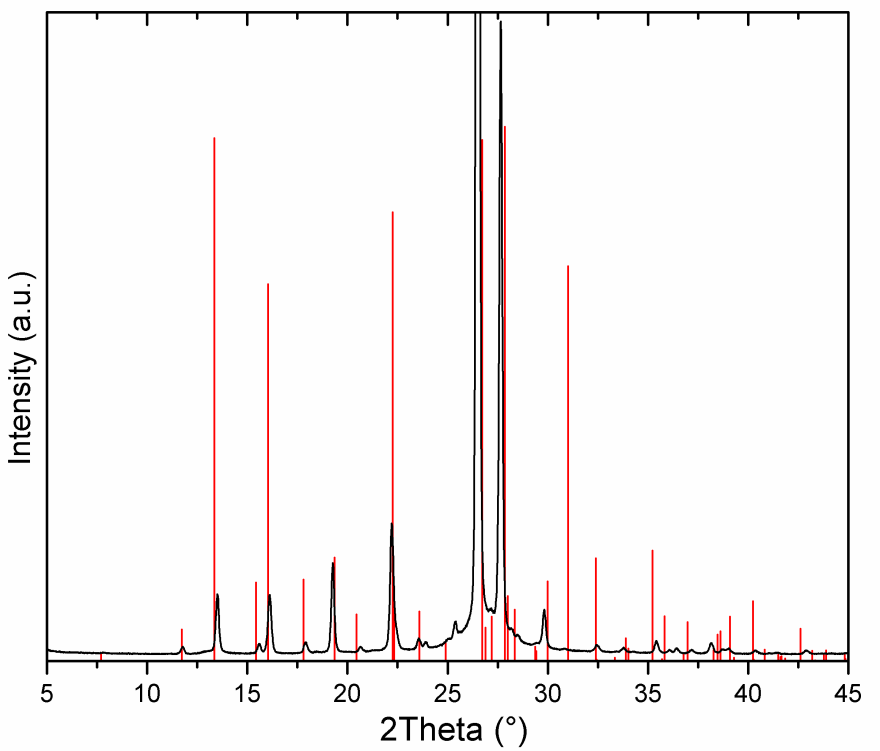

Figure S2. The comparison of recorded (298 K) powder diffraction pattern of $(2\text{-AMP})_3(H_3BO_3)_2$ with theoretical diffraction pattern (red lines) calculated from single-crystal X-ray diffraction data (150 K).
Note: The observed differences for intensities and positions of some diffractions are related to preferential orientation of the powdered sample (intensities) and different temperatures used for powder and single-crystal measurements (positions).

Table S1. Experimental powder diffraction data for $(2\text{-AMP})_3(H_3BO_3)_2$.

2 Theta (°)	d (Å)	Intensity (%)	2 Theta (°)	d (Å)	Intensity (%)
11.79	7.51	1	29.81	3.00	3
13.53	6.55	4	30.83	2.90	1
15.60	5.68	1	32.43	2.76	1
16.12	5.50	4	33.79	2.65	1
17.91	4.95	2	35.41	2.53	2
19.27	4.61	5	36.42	2.47	1
20.66	4.30	1	38.12	2.36	1
22.18	4.01	6	38.70	2.33	1
23.57	3.78	2	39.05	2.31	1
23.91	3.72	2	45.56	1.99	2
25.42	3.50	2	47.65	1.91	1
26.51	3.36	100	54.36	1.69	1
27.64	3.23	28	55.02	1.67	2
28.21	3.16	2	56.30	1.63	1
28.50	3.13	2			

Table S2. Experimental powder diffraction data for 2-AMP(H_3BO_3)$_2$

2 Theta (°)	d (Å)	Intensity (%)	2 Theta (°)	d (Å)	Intensity (%)
9.72	9.10	1	29.68	3.01	1
12.85	6.89	15	30.37	2.94	14
13.74	6.45	2	30.45	2.93	17
16.04	5.52	2	31.53	2.84	1
16.11	5.50	3	31.87	2.81	2
19.40	4.57	13	32.26	2.78	3
24.17	3.68	10	33.24	2.70	1
24.41	3.64	6	35.61	2.52	1
24.49	3.63	7	36.74	2.45	1
24.85	3.58	2	38.91	2.31	1
25.71	3.47	9	39.28	2.29	1
26.50	3.36	2	39.91	2.26	1
27.65	3.22	100	41.74	2.16	3
28.12	3.17	4	42.42	2.13	1
28.86	3.09	2	44.35	2.04	1
29.30	3.05	2	50.80	1.80	9

Table S3. Calculated and recorded vibrational frequencies (cm^{-1}) of 2-aminopyrimidine.

Computed vibrational frequencies (cm^{-1})	Dual scaling[a] (cm^{-1})	WLS scaling[b] (cm^{-1})	Relative intensity IR/Raman[c]	Assignment	Observed FTIR (cm^{-1})	Observed Raman (cm^{-1})
				external mode		120vs
177	180	178	1/6	γrg, γC-NH_2		193s
274	279	275	47/26	ωNH_2		
407	415	408	3/3	δNCN		408m
415	423	416	0/5	γrg	471m	456m
521	531	521	0/2	τNH_2	525m	522w
531	541	531	0/1	γCH, γrg	567mb	
600	611	599	0/42	δrg, δNCN	604mb	588m
654	666	653	1/14	δrg, δNCN	644m	650m
797	812	794	4/5	γCH	788m	779m
					803s	814m
821	837	817	5/2	γrg, γCN_3		
889	906	884	0/100	$\nu_s$rg, $\delta_s$rg, νC-NH_2	868w	871vs
992	1011	985	0/4	γCH	999w	985s
1002	1021	995	0/0	γCH		
1005	1024	997	1/32	νrg, δrg		
1032	1052	1024	0/0	ρNH_2, δCH	1040w	1047sh
1092	1058	1082	0/59	δCH, νrg	1078w	1078s
1138	1103	1127	0/21	δCH, ρNH_2	1132w	1131s
					1180m	1186w
					1209w	
1260	1221	1245	3/0	νrg, δrg, ρNH_2	1224m	1226w
1332	1291	1315	1/3	δCH, ρNH_2	1303w	1307w
1382	1339	1363	0/5	δCH, νC-NH_2	1358m	1356m
1475	1429	1453	0/0	δCH, νrg , δNCN	1444s	1443w
1480	1434	1457	44/6	νC-NH_2, δNH_2, δNCN, δCH	1457s	
					1480s	1477w
					1514w	
1595	1545	1568	20/1	νrg, δrg, δNCN, ρNH_2, δCH	1561s	1558sh
1619	1569	1591	0/12	δNH_2, νC-NH_2, νrg	1577s	1579s
1642	1591	1613	100/45	δNH_2, νC-NH_2, νrg	1649s	1651m
3145	3047	3012	3/44	νCH	2958m	3000w
3147	3049	3014	4/27	νCH	3027m	3026m
						3050m
						3088m
3209	3109	3070	1/45	νCH		3120m
3611	3499	3431	14/32	νNH	3170s	3160m
3741	3625	3546	10/8		3240m	
					3330s	
					3350s	

Note: Abbreviation and Greek symbols used for vibrational modes: rg, ring; $_s$, symmetric; ν, stretching; δ, deformation or in-plane bending; γ, out-of-plane bending; ρ, rocking; ω, wagging; τ, twisting.

[a]Scaling factors 1.0189 (below 1035 cm^{-1}) and 0.9689 (above 1035 cm^{-1}) [24].

[b]According to [25]: $\nu_{obs}/\nu_{calc} = 1.0087 - 0.0000163 \cdot \nu_{calc}$.

[c]Raman intensities were calculated using RAINT programme [22] for a 1064 nm excitation wavelength.

Table S4. Selected bond lengths [Å] and angles [°] for $(2\text{-AMP})_3(H_3BO_3)_2$.

Bond/Angle	Value (Å/°)	Angle	Value (°)
N1A-C1A	1.329(2)	N2A-C3A-H3A	118
N2A-C1A	1.355(2)	C3A-C4A-H4A	122
N2A-C3A	1.3293(17)	C4A-C3A-H3A	119.95(13)
C3A-C4A	1.377(2)	C1B-N2B-C3B	116.79(12)
N1B-C1B	1.3338(16)	C1B-N6B-C5B	116.63(10)
N2B-C3B	1.3274(16)	C1B-N1B-H12B	118.3(11)
N2B-C1B	1.3526(15)	H11B-N1B-H12B	126.2(16)
N6B-C5B	1.3299(16)	C1B-N1B-H11B	115.5(12)
N6B-C1B	1.3544(17)	N2B-C1B-N6B	124.35(10)
C3B-C4B	1.377(2)	N1B-C1B-N2B	117.69(12)
C4B-C5B	1.3838(18)	N1B-C1B-N6B	117.96(10)
O1-B1	1.3667(19)	N2B-C3B-C4B	123.25(11)
O2-B1	1.3594(16)	C3B-C4B-C5B	115.74(11)
O3-B1	1.3707(16)	N6B-C5B-C4B	123.23(13)
B1-O1-H1	112.8(17)	N2B-C3B-H3B	118
B1-O2-H2	112.9(12)	C4B-C3B-H3B	118
B1-O3-H3	111.9(14)	C3B-C4B-H4B	122
C1A-N2A-C3A	116.79(12)	C5B-C4B-H4B	122
H11A-N1A-H11A[a]	131.3(18)	C4B-C5B-H5B	118
C1A-N1A-H11A	114.4(14)	N6B-C5B-H5B	118
N2A-C1A-N2A[a]	123.95(13)	O1-B1-O2	120.28(11)
N1A-C1A-N2A	118.03(13)	O1-B1-O3	119.75(11)
N2A-C3A-C4A	123.28(15)	O2-B1-O3	119.95(13)
C3A-C4A-C3A[a]	115.91(14)		
Hydrogen bonds			
D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
O1-H1...N2A[a]	0.85(2)	1.90(2)	2.7461(17)	176(2)
O2-H2...N2B	0.85(2)	1.92(2)	2.7623(16)	173.9(18)
O3-H3...N6B[b]	0.86(2)	1.97(2)	2.8222(15)	171.3(16)
N1A-H11A...O2[c]	0.88(2)	2.04(2)	2.9231(17)	176.0(15)
N1B-H11B...O1[d]	0.900(18)	2.039(18)	2.9385(15)	178.2(15)
N1B-H12B...O3	0.86(2)	2.15(2)	2.9995(17)	168.1(15)

Note. Equivalent positions: (a) -y,x-y,1/3+z; (b) x-y,1-y,2/3-z; (c) -x+y,-x,-1/3+z; (d) 1+x-y,1-y,2/3-z

Table S5. Selected bond lengths [Å] and angles [°] for 2-AMP(H_3BO_3)$_2$.

Bond/Angle	Value (Å/°)	Angle	Value (°)
N1-C1	1.344(2)	H1A-N1-H1A[a]	124.7(15)
N2-C1	1.3456(10)	N2-C1-N2[a]	124.72(12)
N2-C2	1.3311(13)	N1-C1-N2	117.64(6)
C2-C3	1.3810(13)	N2-C2-C3	122.71(10)
O1-B1	1.3677(14)	C2-C3-C2[a]	116.24(11)
O2-B1	1.3633(14	N2-C2-H2A	119
O3-B1	1.3725(13)	C3-C2-H2A	119
B1-O1-H1	111.4(11)	C2-C3-H3A	122
B1-O2-H2	114.4(12)	O1-B1-O2	120.08(9)
B1-O3-H3	108.6(12)	O1-B1-O3	120.97(9)
C1-N2-C2	116.81(9)	O2-B1-O3	118.95(9)
C1-N1-H1A	117.7(11)		
Hydrogen bonds			
D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
O1-H1...O3[a]	0.833(18)	1.965(18)	2.7976(11)	177.5(15)
N1-H1A...O1	0.902(18)	2.443(18)	3.3345(9)	169.8(15)
O2-H2...N2[b]	0.838(18)	1.864(18)	2.6878(11)	167.3(18)
O3-H3...O2[c]	0.857(18)	1.865(18)	2.7208(11)	176.6(17)

Note. Equivalent positions: (a) 2-x,-y,2-z ; (b) 1-x,y,3/2-z; (c) 5/2-x,1/2-y,2-z

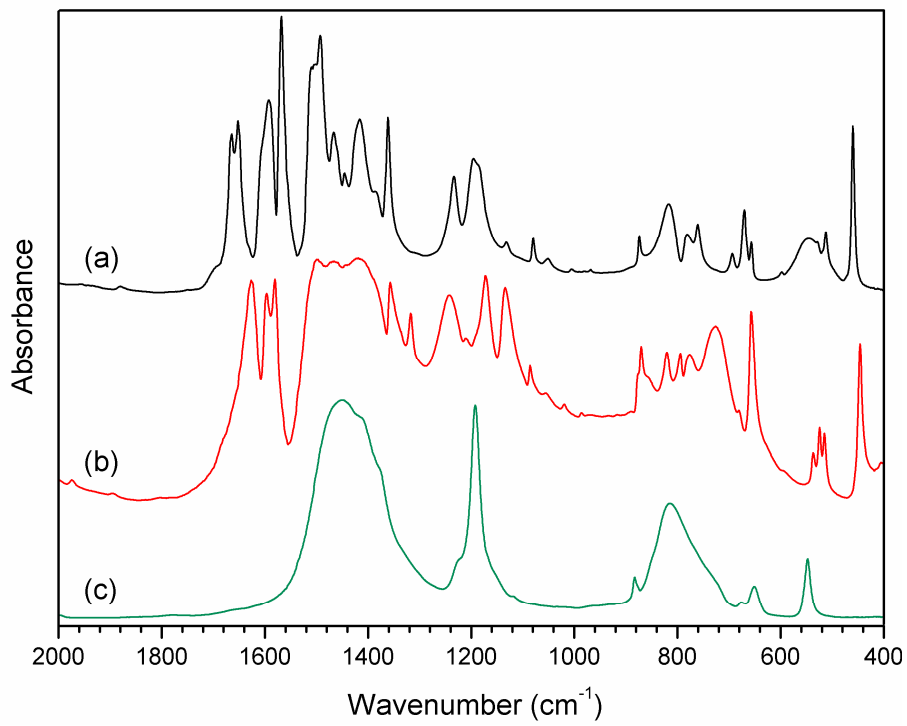

Figure S3. The comparison of recorder IR spectra (compiled from nujol and fluorolube mulls) of (2-AMP)$_3$(H_3BO_3)$_2$ (**a**), 2-AMP(H_3BO_3)$_2$ (**b**) and boric acid (**c**).

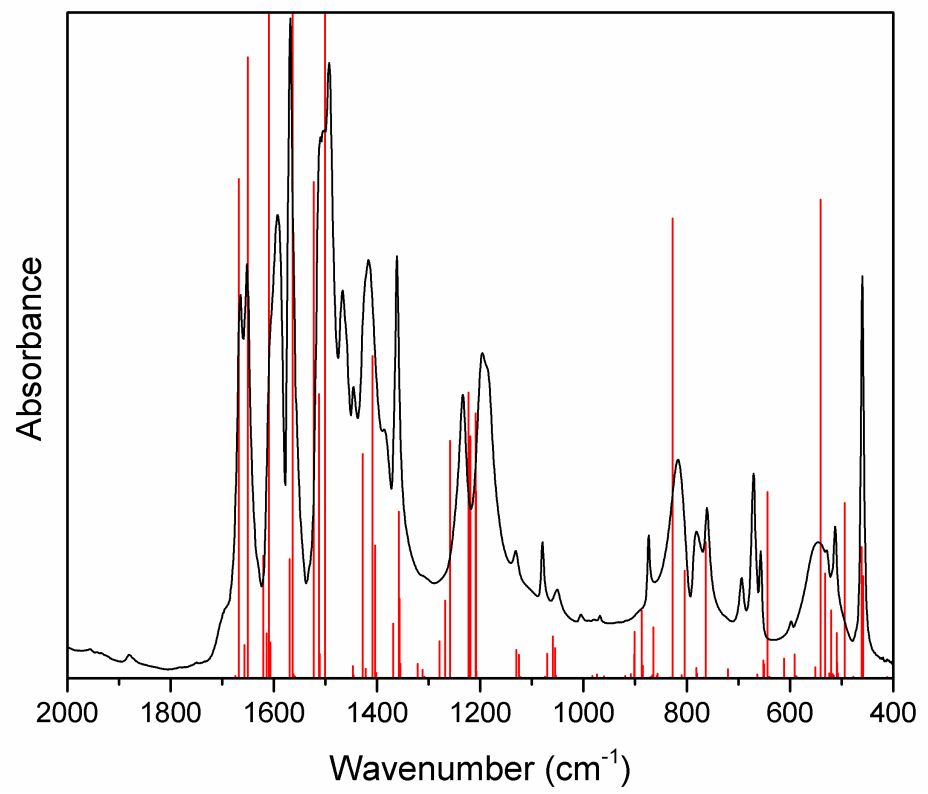

Figure S4. The comparison of calculated (CRYSTAL17 programme) vibrational modes (red lines) with recorded IR spectrum (compiled from nujol and fluorolube mulls) of $(2\text{-AMP})_3(H_3BO_3)_2$.

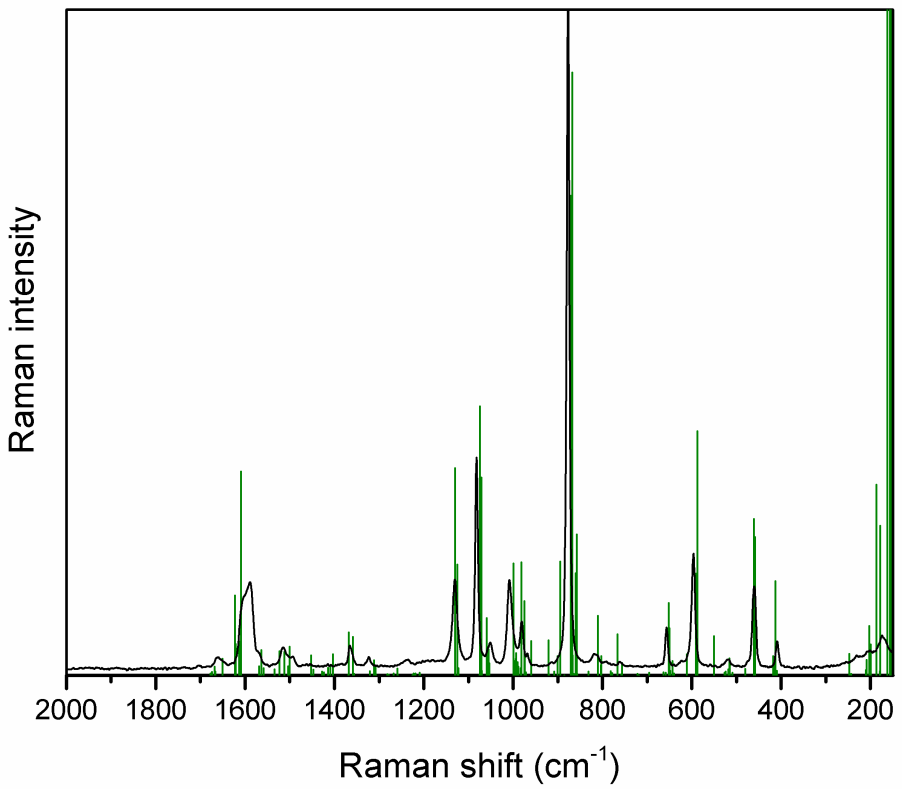

Figure S5. The comparison of calculated (CRYSTAL17 programme) vibrational modes (green lines) with recorded Raman spectrum of $(2\text{-AMP})_3(H_3BO_3)_2$.

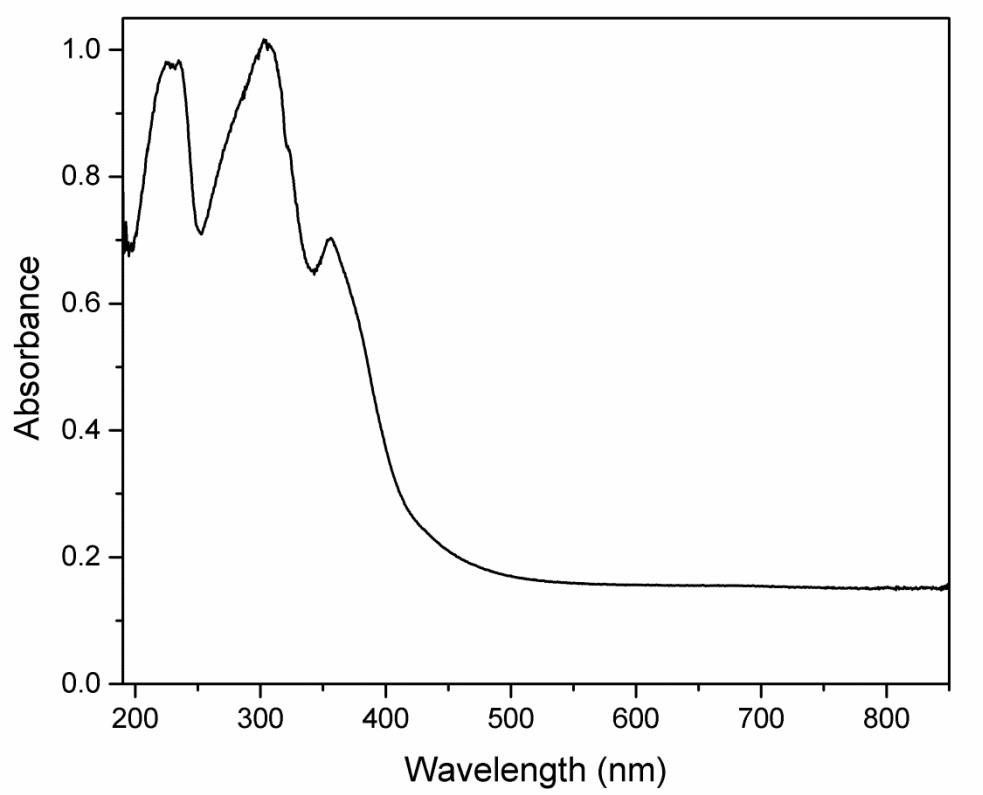

Figure S6. The UV-Vis spectrum of polycrystalline $(2\text{-AMP})_3(H_3BO_3)_2$.