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# Structural landscape of multicomponent solids of 5-aminosalicylic acid

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**Experimental Procedures**

**$(ASA^+)_2\cdot(SO_4^{2-})\cdot H_2O$**, **1**. ASA (0.7 mmol, Sigma-aldrich>99%) was dissolved in 15 mL of distilled water followed by the addition of sulphuric acid (0.7 mmol, Fischer Scientific 95-98% w/w) slowly. The resulting clear solution was filtered and heated on a water bath at around 60-65 °C till colorless crystals of **1** were obtained.

**$(ASA^+)\cdot(HSO_4^-)\cdot H_2O$**, **2**. ASA (0.7 mmol) was dissolved in 10 mL of distilled water and sulphuric acid (0.7 mmol) was added slowly. The resulting clear solution was kept at room temperature for slow evaporation. Needle shaped colorless crystals of **2** were obtained after 12 days.

**$(ASA^+)\cdot(NO_3^-)\cdot H_2O$**, **3**. $HNO_3$ (0.7 mmol, Fischer scientific 68-70% w/w) was added rapidly to a 10 mL of ASA (0.7 mmol) solution. The resulting solution was filtered and kept at room temperature for slow evaporation. Plate shaped colorless crystals of **3** were obtained after 8 days.

**$(ASA^+)\cdot(CCl_3COO^-)$**, **4**. ASA (0.7 mmol) was ground with $CCl_3COOH$ (0.7 mmol) in a mortar-pestle for around 10 minutes. The ground material was dissolved in water-acetone (1:1) and the solution was kept at room temperature for slow evaporation. Plate shaped colorless crystals were obtained after 5 days.

**$(ASA^+)\cdot(CH_3SO_3^-)$**, **5**. Methanesulphonic acid (0.7 mmol) was added to ASA (0.07 mmol) in a mortar-pestle and the mixture was ground for about 10 minutes. The ground material was dissolved in water-acetone (1:1) and kept aside for slow evaporation at room temperature. Plate shaped yellow crystals were obtained after 5 days.

**$(ASA^-)\cdot(pip^{2+})$**, **6**. ASA (0.07 mmol) was ground with piperazine (0.07 mmol) in a mortar-pestle for about 10 minutes. The ground product was dissolved in 10 mL of water and kept at room temperature for slow evaporation. Plate shaped colorless crystals were obtained after a week.

**$(ASA)_2$·(bpy)**, **7**. 10 mL water-acetone (1:1) solution of *bpy* (0.7 mmol) was added to a 10 mL water-acetone (1:1) solution of ASA (0.7 mmol). The resulting solution was kept at room temperature for slow evaporation. Plate shaped yellow crystals of **7** were obtained after 15 days.

**$(ASA^-)$·(bpee)·$(bpee^+)$ 8**. To a 10 mL solution of ASA (0.7 mmol) in water-acetone (1:1) was added a solution of *bpee* (0.7 mmol) in 10 mL solution in water-acetone (1:1). The resulting solution was filtered and kept at room temperature for slow evaporation. Plate shaped red crystals were obtained after 10 days.

**$(ASA^-)$·$(bpp^+)$**, **9**. ASA (0.07 mmol) was ground for 10 minutes with *bpp* (0.07 mmol) in a mortar-pestle for about 10 minutes. The resulting material was dissolved in 10 mL of water-acetone (1:1) and kept the solution at room temperature slow evaporation. Plate shaped yellow crystals were obtained after 8 days.

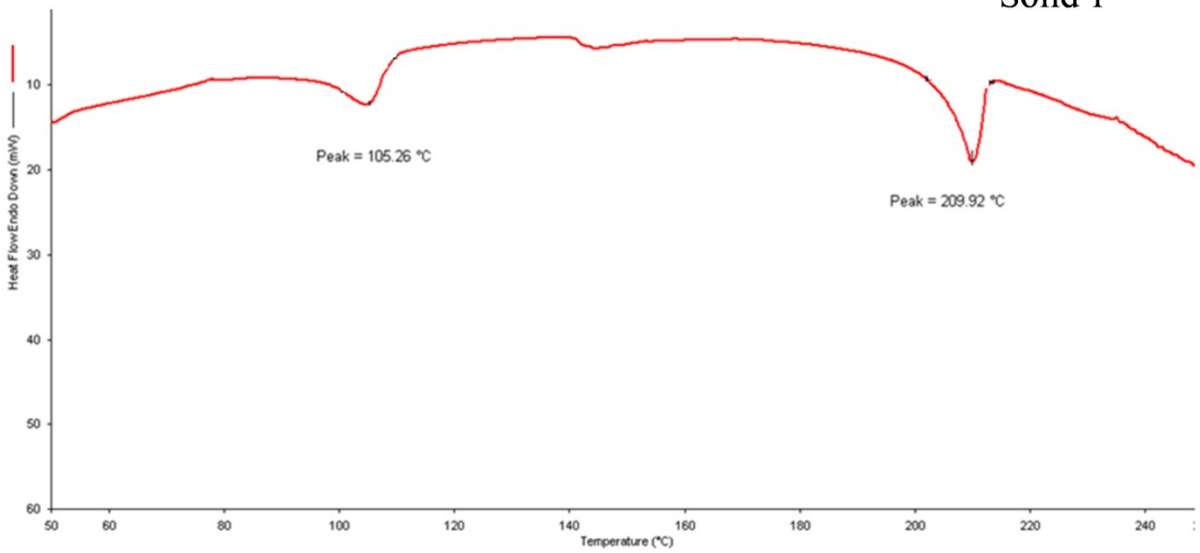
**$(ASA^-)$·$(4\text{-}apy^+)$**, **10**. ASA (0.07 mmol) and 4-*apy* (0.07 mmol) were ground in a mortar-pestle for about 10 minutes. The ground material was dissolved in 10 mL of water-acetone (1:1). Plate shaped red crystals were obtained after 8 days of slow evaporation.

**Solid 11**. 2-*apy* (0.07 mmol) and ASA (0.07 mmol) were ground in a mortar-pestle for approximately 10 minutes. The ground material was characterized through PXRD, ATR and DSC.

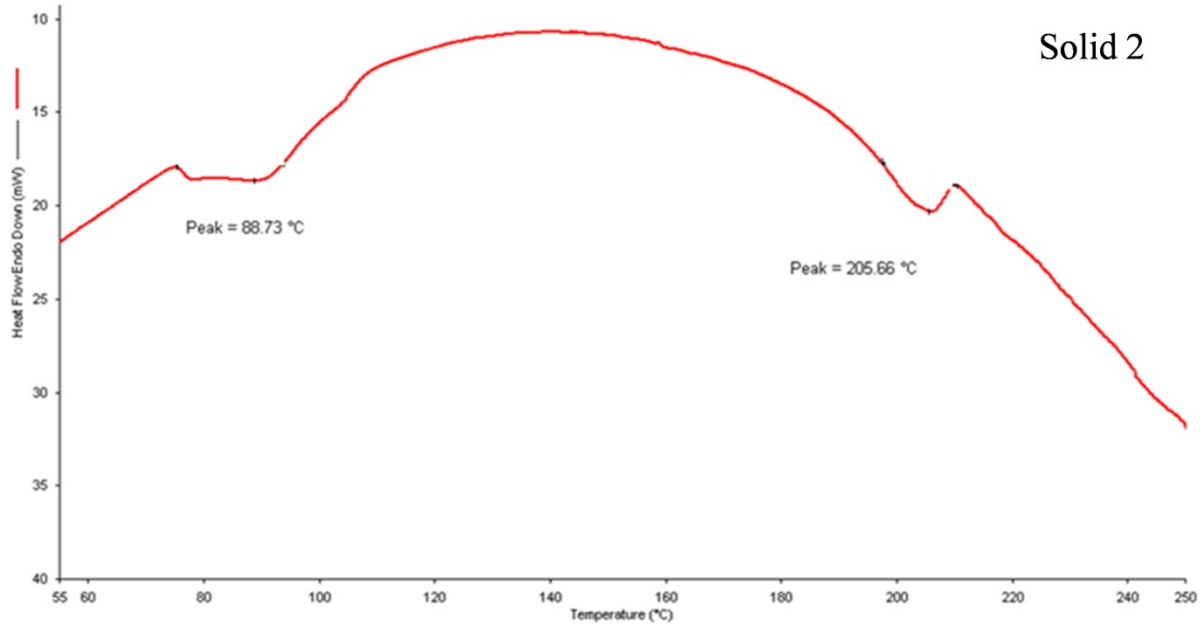
**Table S1:** Melting points of the ASA based solids (based on DSC) and coformers (reported) considered in the present study.

| Solid form | Melting point of drug/coformer (°C) | Melting point of solid forms (°C) |
|---|---|---|
| **ASA** | NA | 280-283 °C |
| $(ASA^{+})_2 \cdot (SO_4^{2-}) \cdot H_2O$ (**1**) | NA | 210 |
| $ASA^{+} \cdot HSO_4^{-} \cdot H_2O$ (**2**) | NA | 206 |
| $ASA^{+} \cdot NO_3^{-} \cdot H_2O$ (**3**) | NA | 133 |
| $ASA^{+} \cdot CCl_3COO^{-}$ (**4**) | NA | 269 |
| $ASA^{+} \cdot CH_3SO_3^{-}$ (**5**) | NA | 229 |
| $(ASA^{-})_2 \cdot (pip^{2+})$ (**6**) | 106 °C | 207 |
| $(ASA)_2 \cdot bpy$ (**7**) | 114 °C | 242 |
| $(ASA^{-}) \cdot (bpee)\ (bpee^{+})_{0.5}$ (**8**) | 148-152 °C | 206 |
| $ASA^{-} \cdot bpp^{+}$ (**9**) | 53-56 °C | 129 |
| $ASA^{-} \cdot 4\text{-}apy^{+}$ (**10**) | 155 °C | 227 |

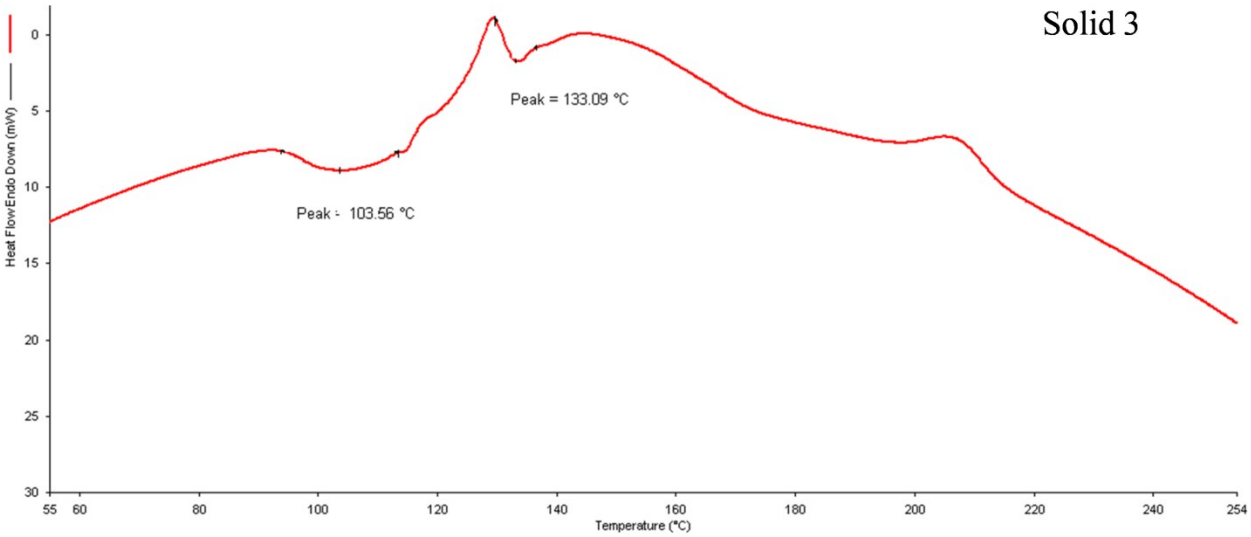
Solid 1



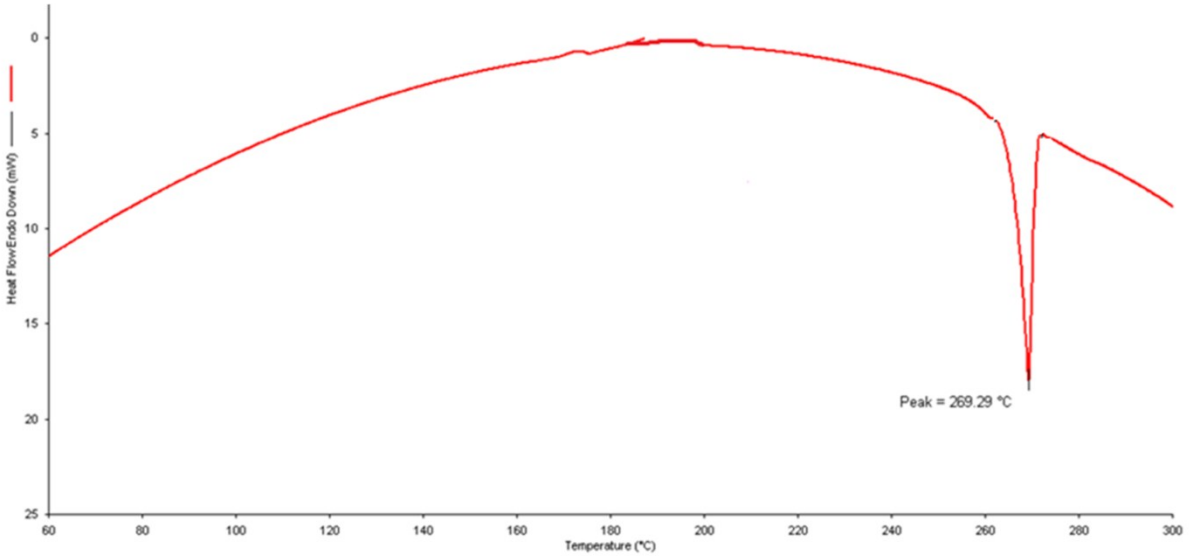

Solid 2



Solid 3

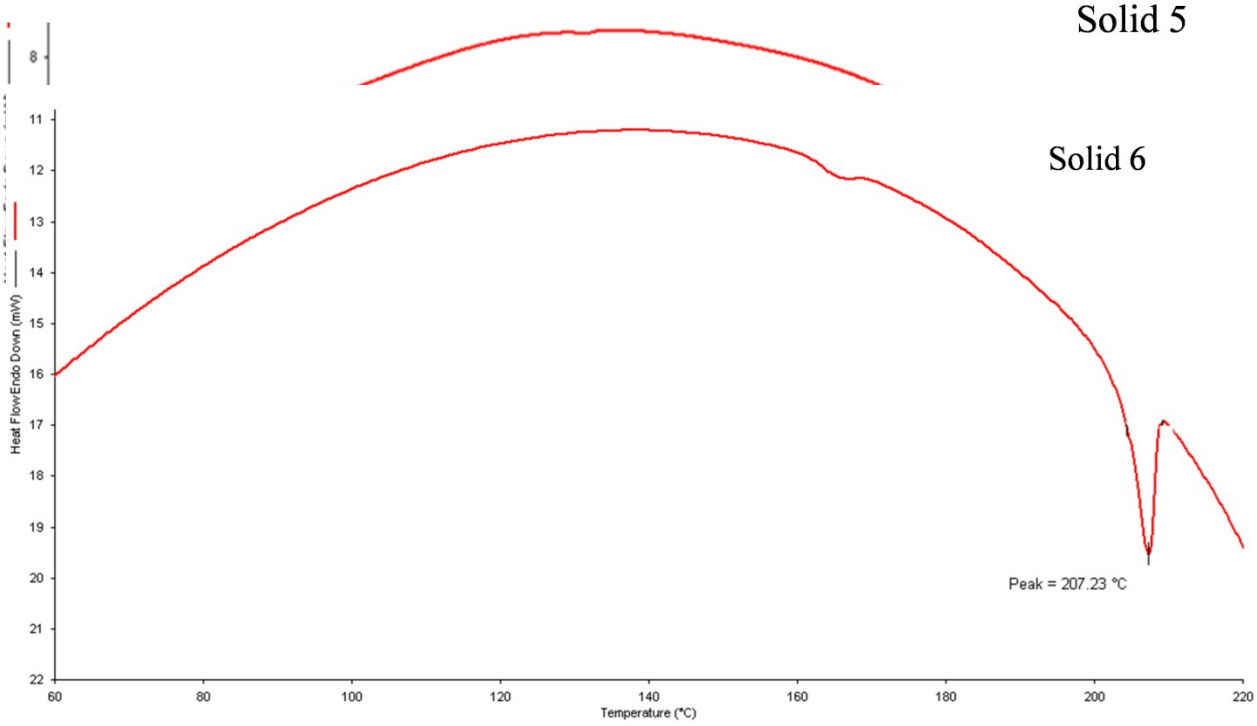



Solid 4

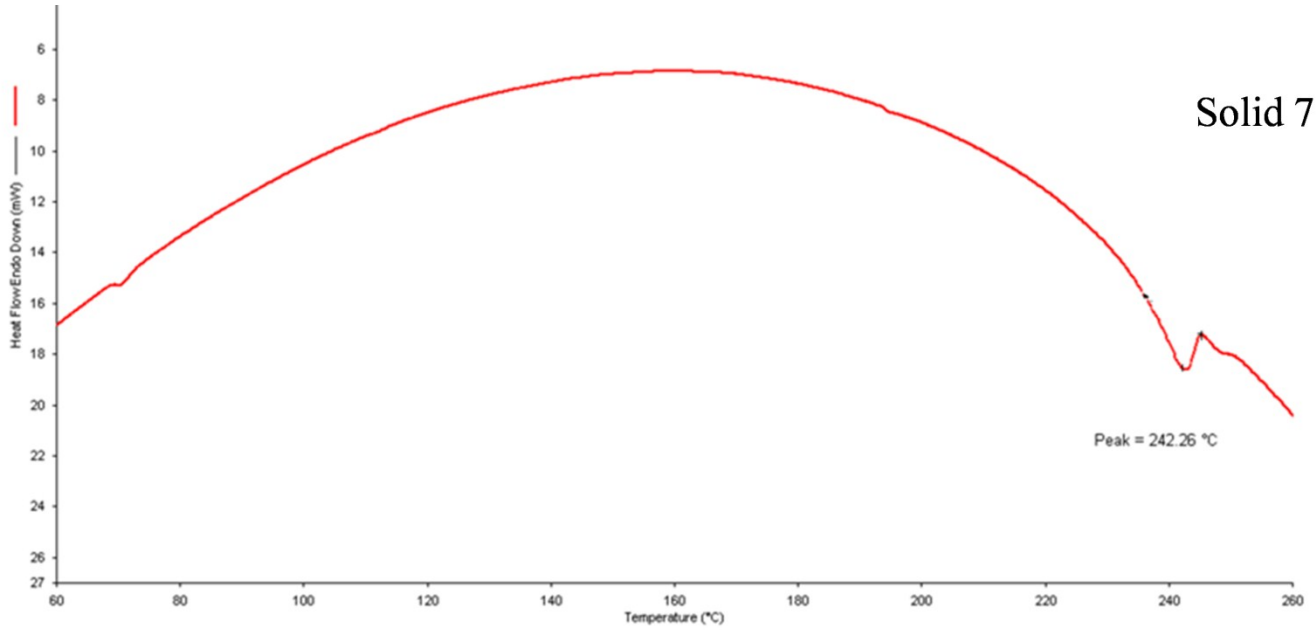


Solid 5

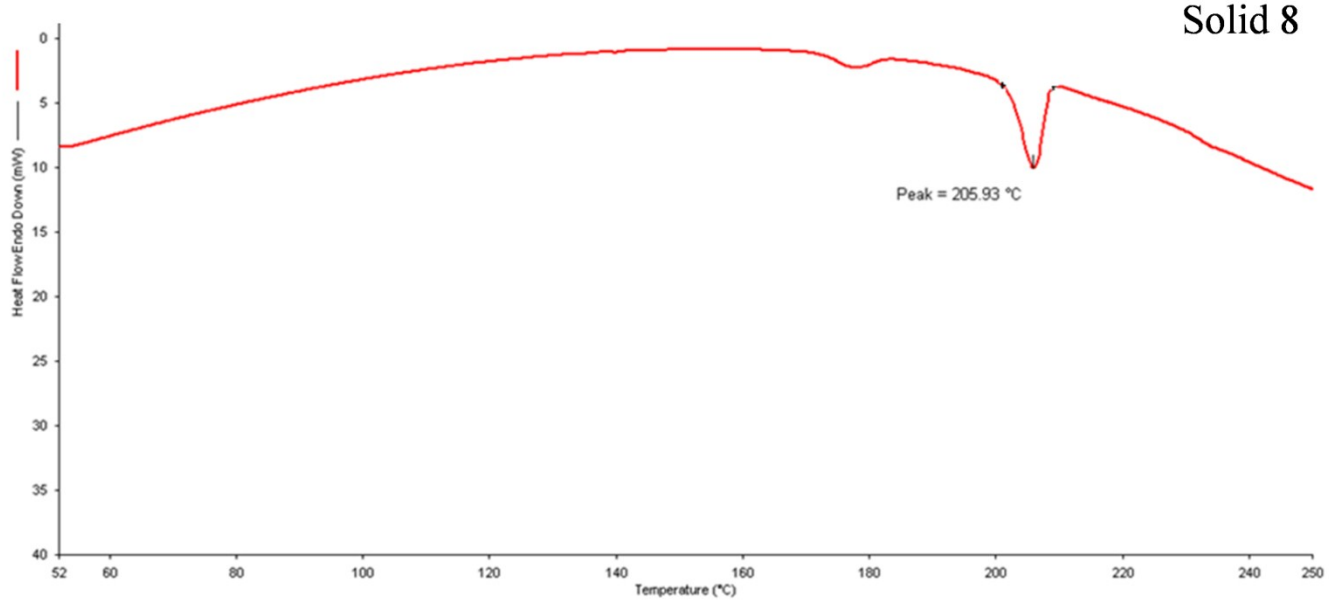
Solid 6



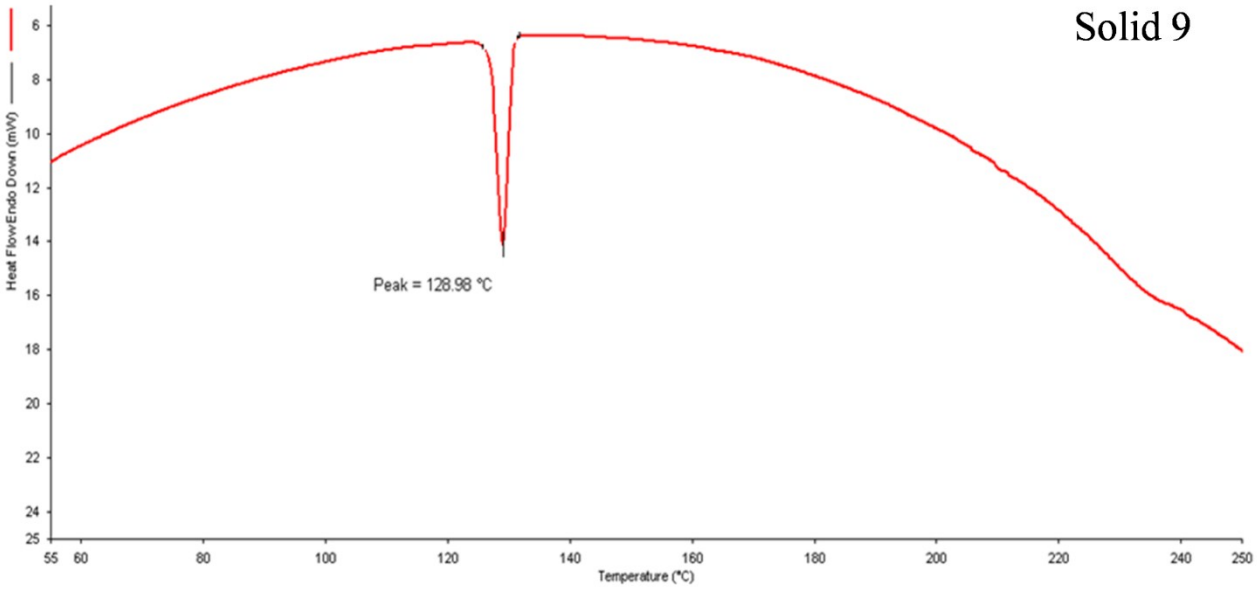
Solid 7



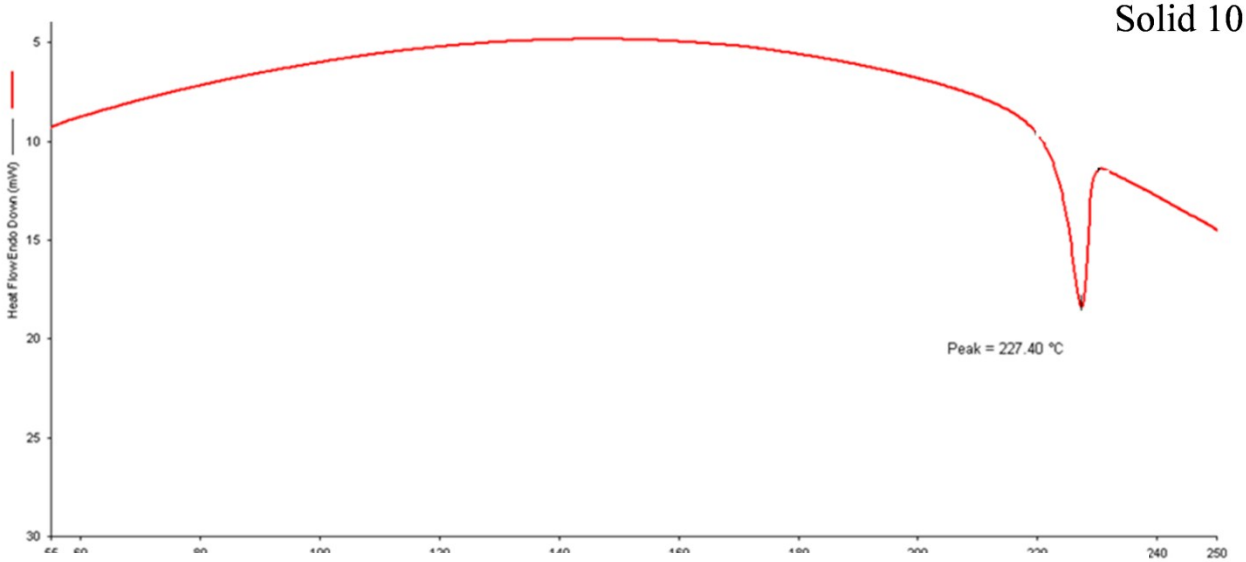

Solid 8



Solid 9




Solid 10




Solid 11

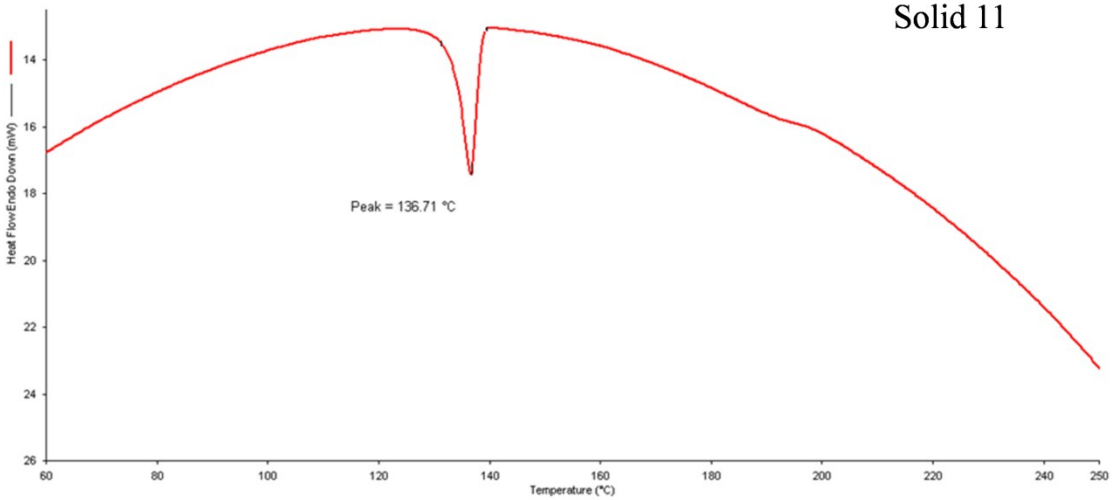
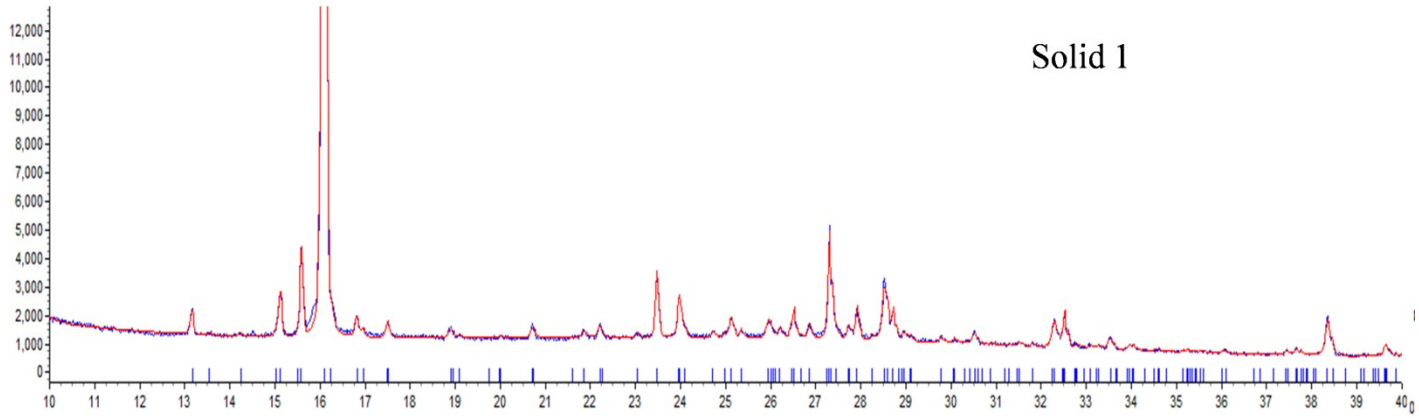
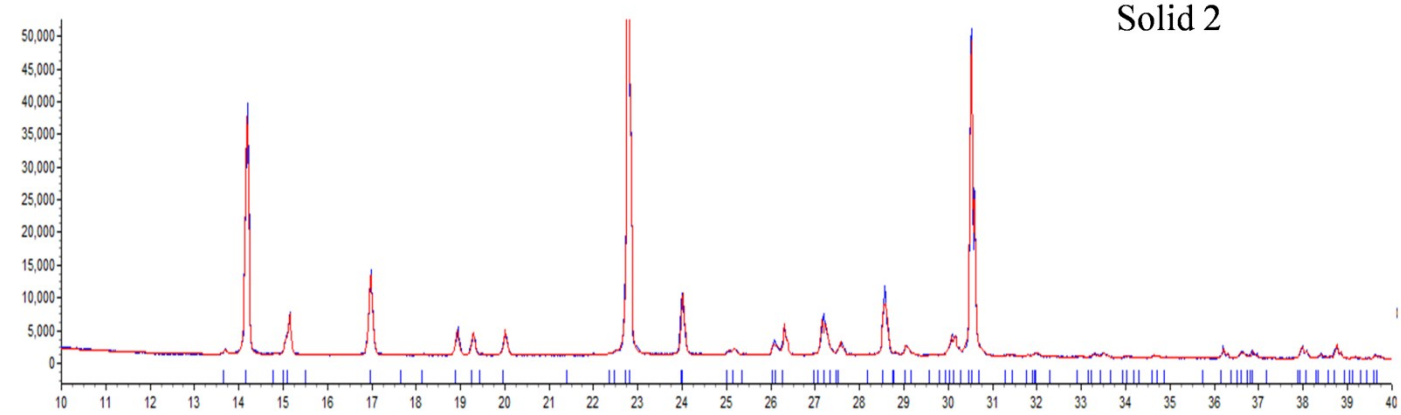
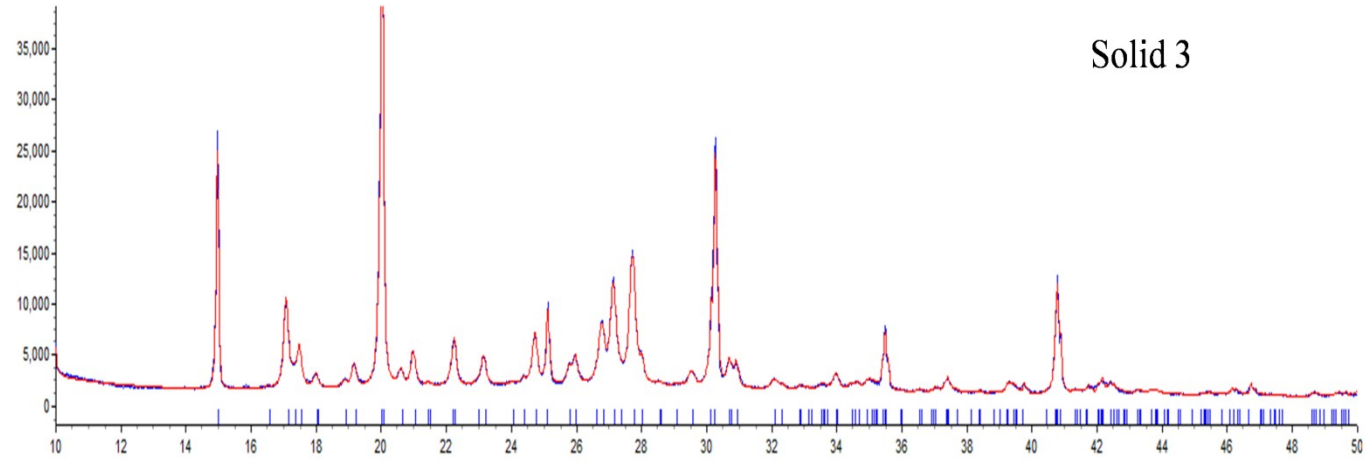


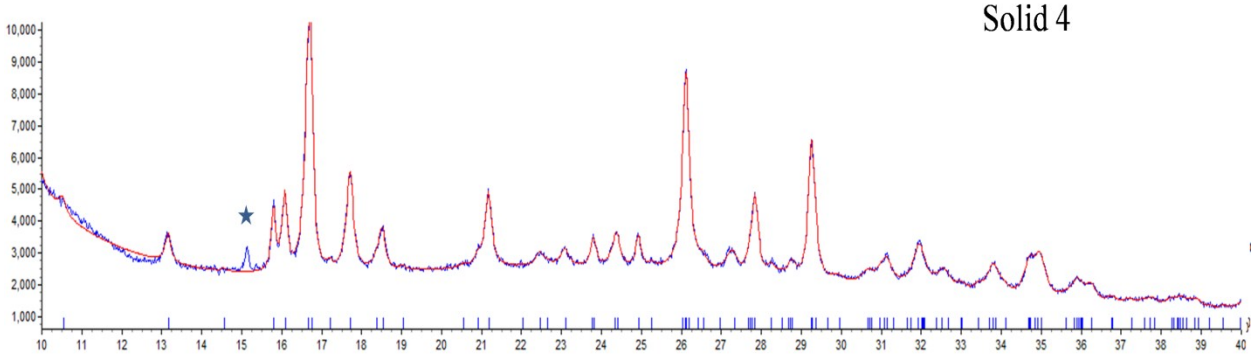
**Figure S1**. DSC scans of solids **1-11** showing an endothermic peak corresponding to its melting points.


Solid 1

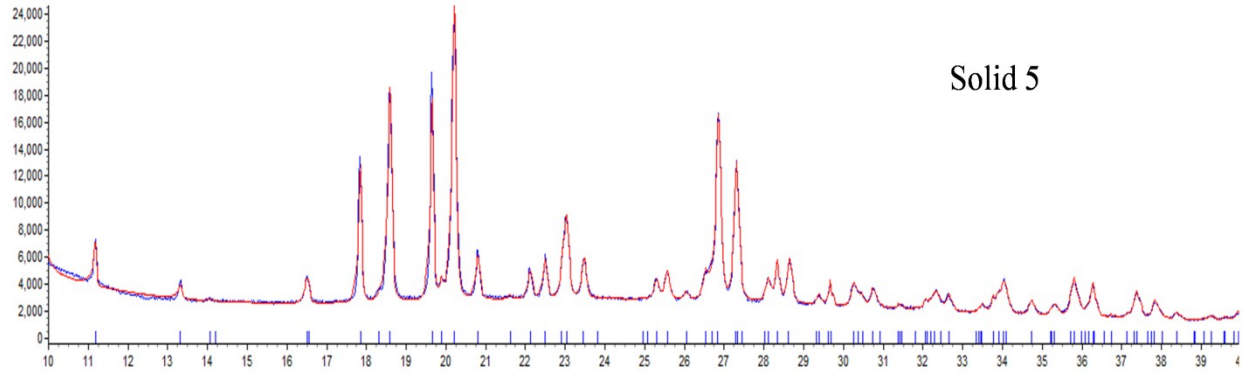

Solid 2


Solid 3

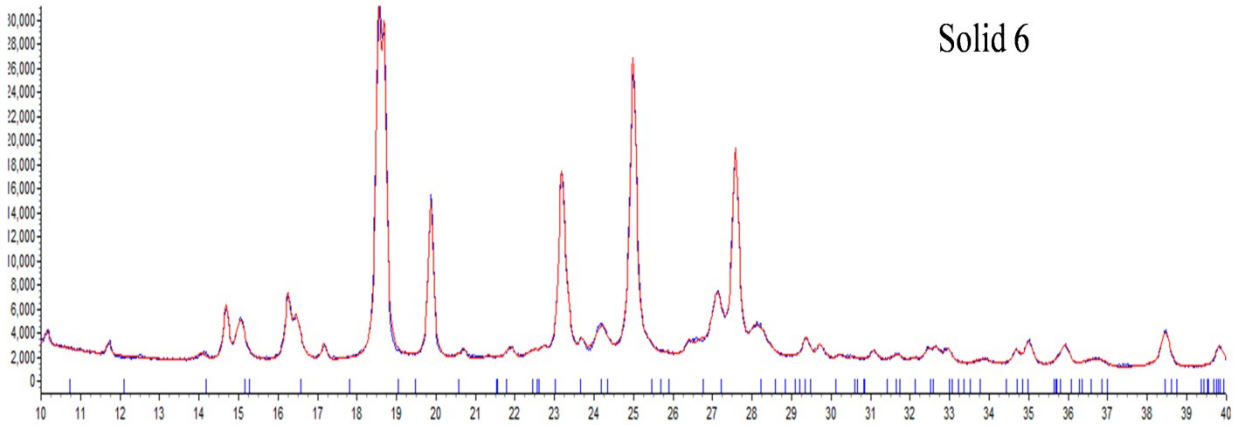
Solid 4

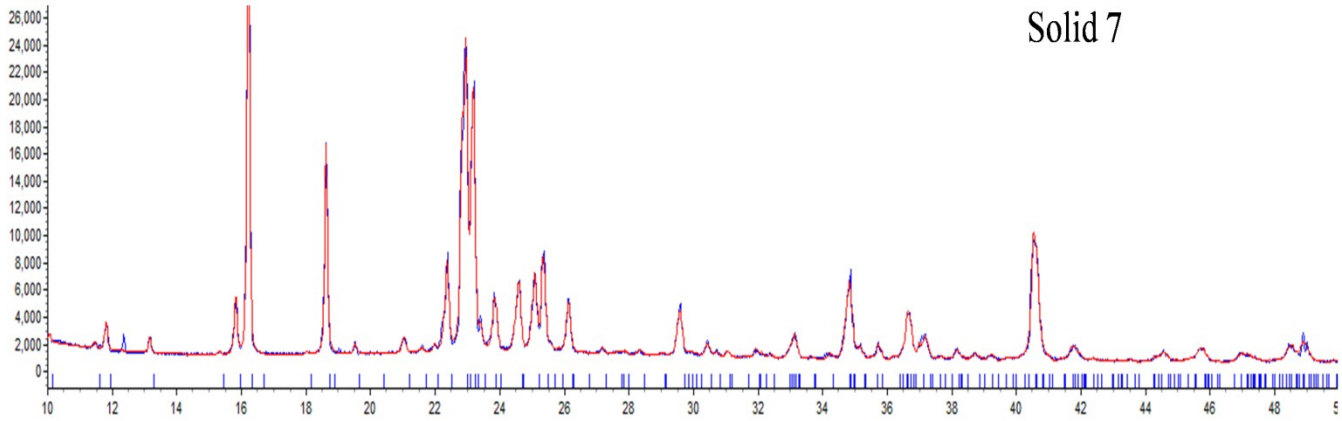


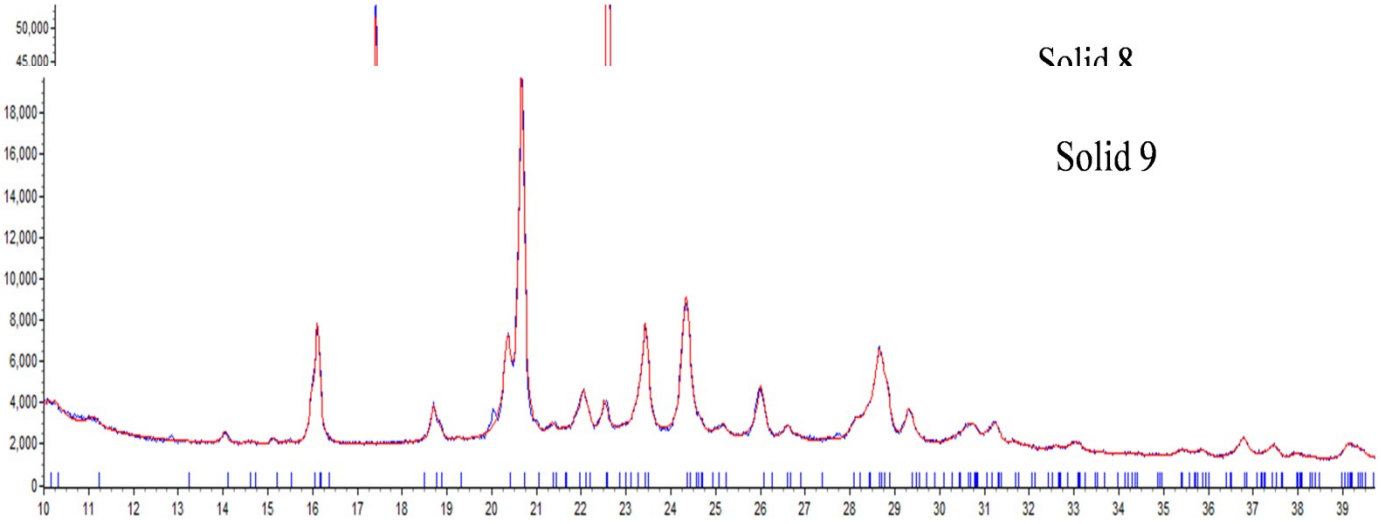
Solid 5



Solid 6




Solid 7


Solid 8
Solid 9

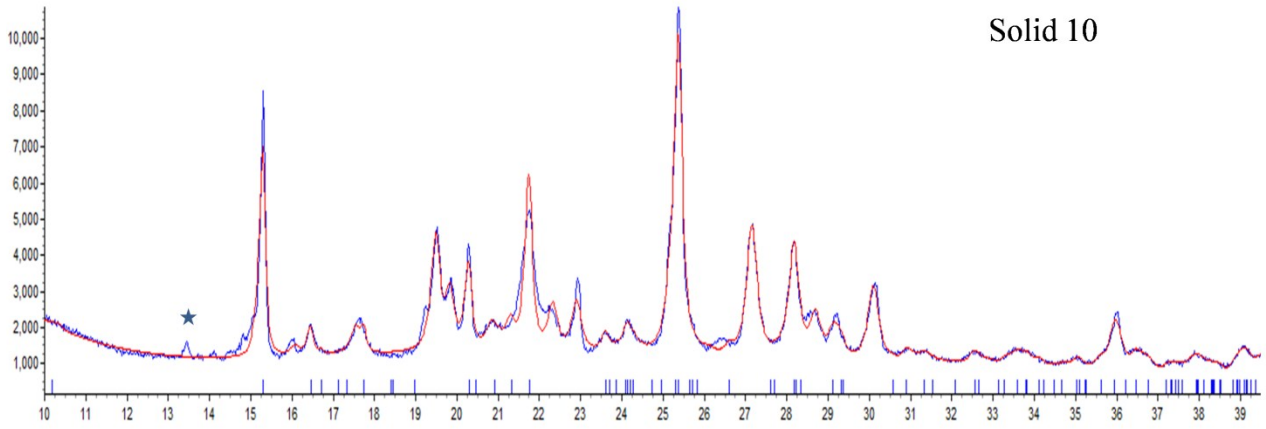



**Figure S2**. Rietveld refinement plots for **1-10**, indicating the homogeneity of the bulk samples except for solids **4** and **10**. The plot shows the experimental powder XRD profile (blue line), the calculated (red line), and blue tick lines shows Bragg positions in the bottom.

Footnote: *Peak(s) marked with asterisk correspond to an unidentified phase.

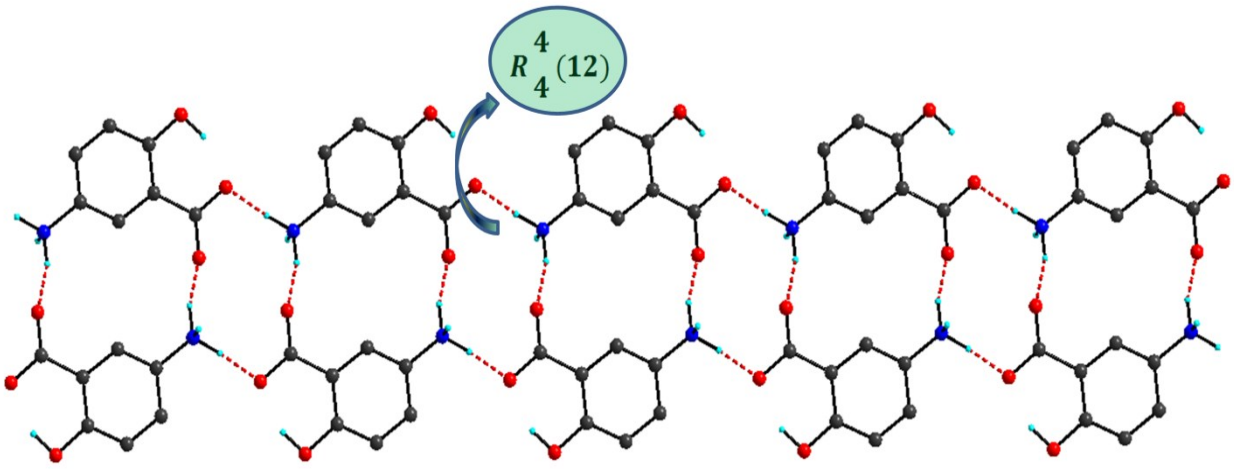



**Figure S3**. The chains of zwitterionic ASA molecules linked to each other through twelve-membered ring $R_4^4(12)$.

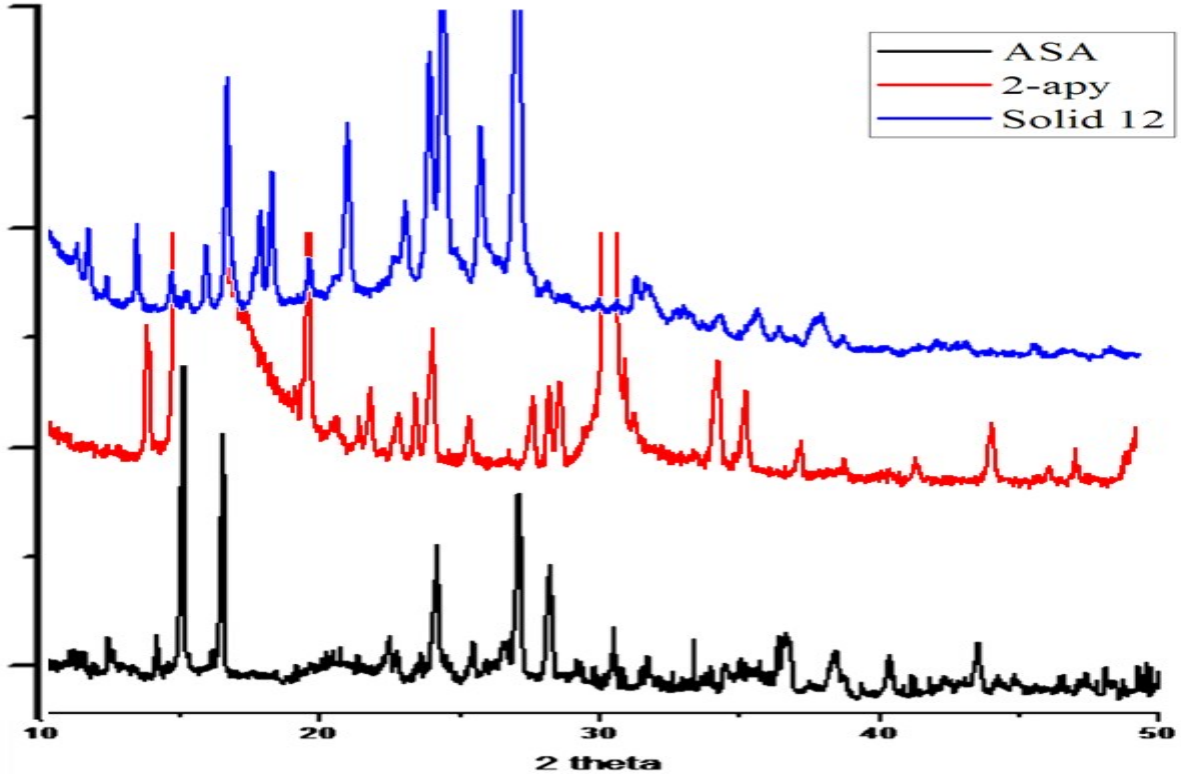
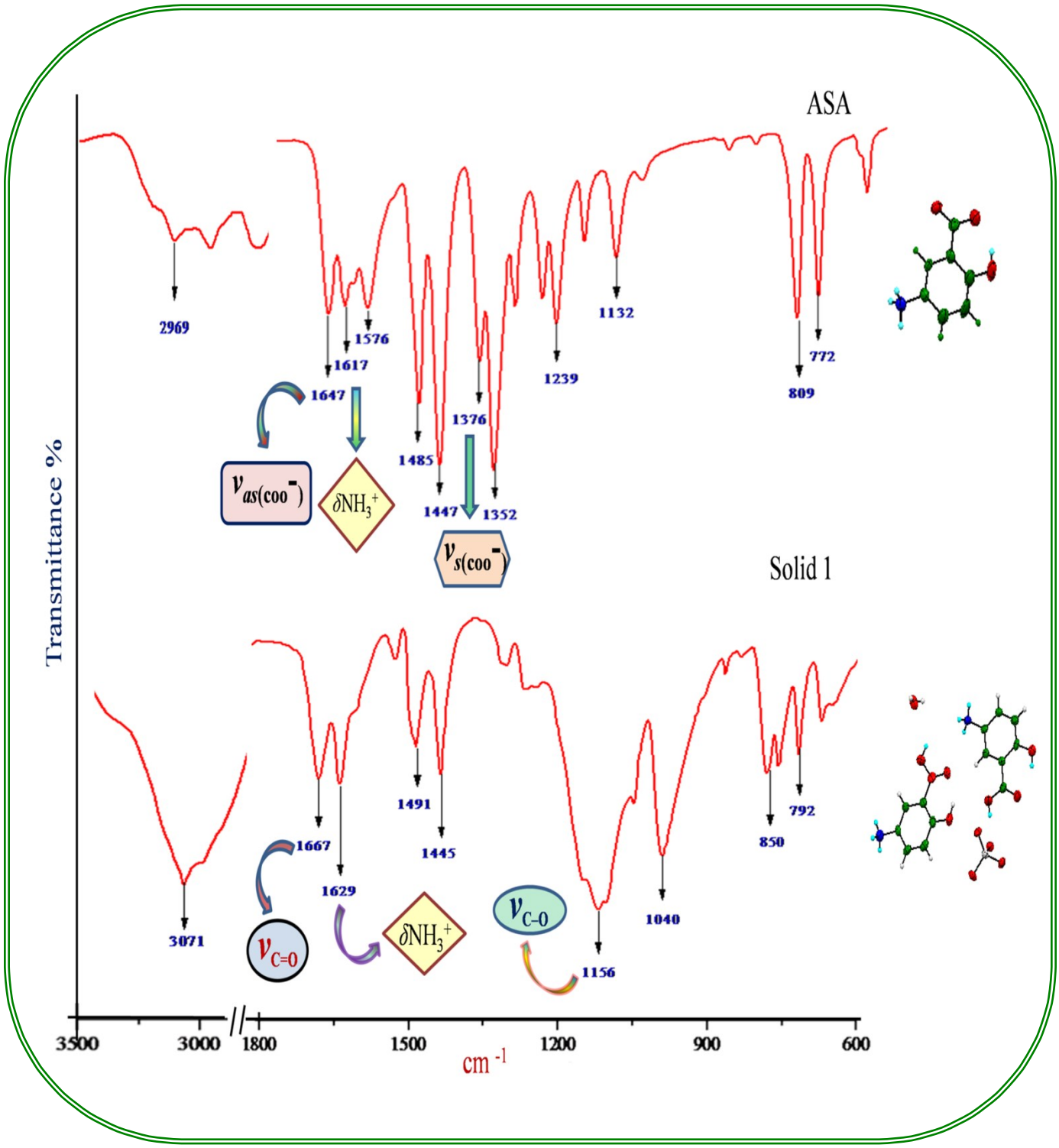
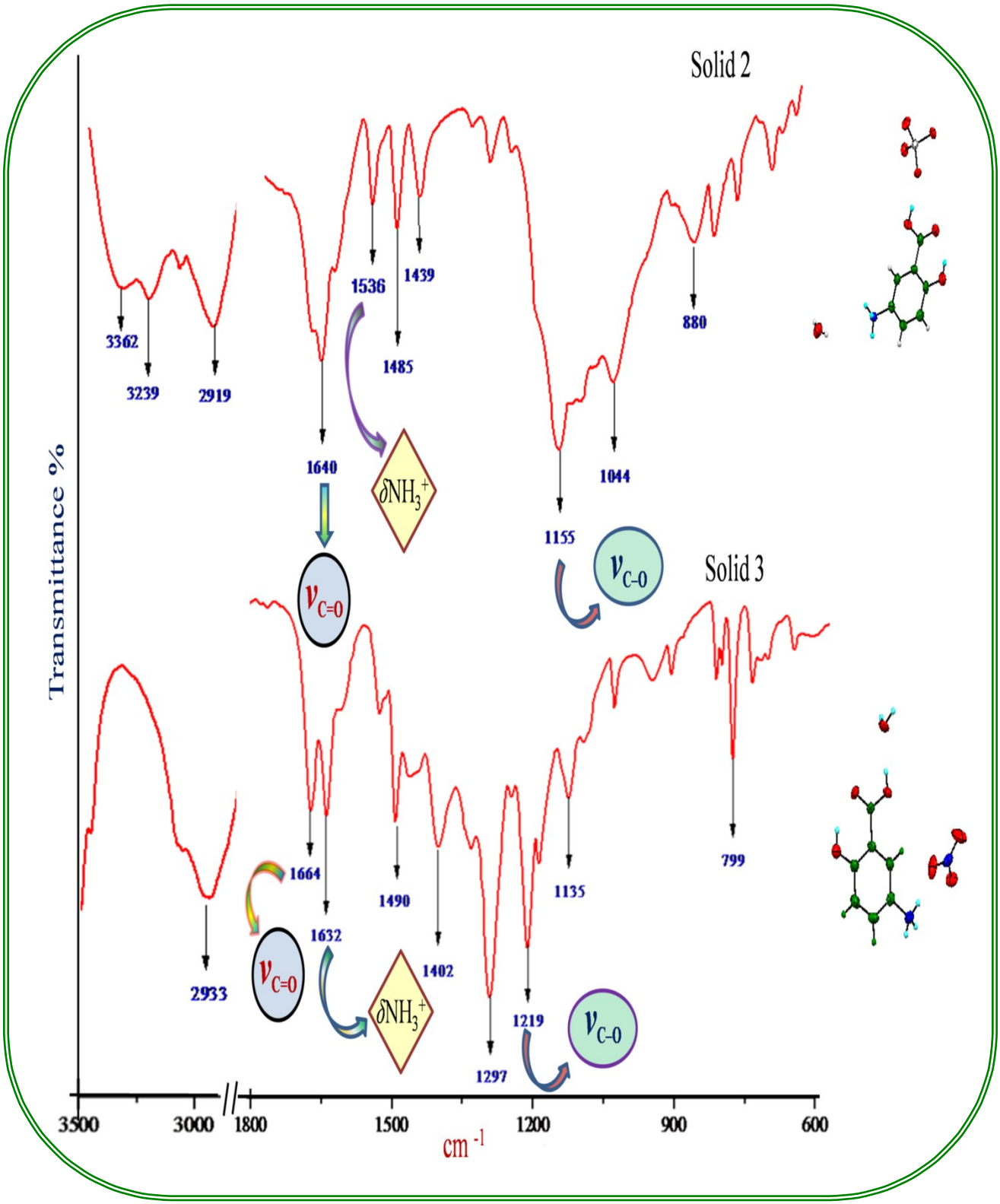
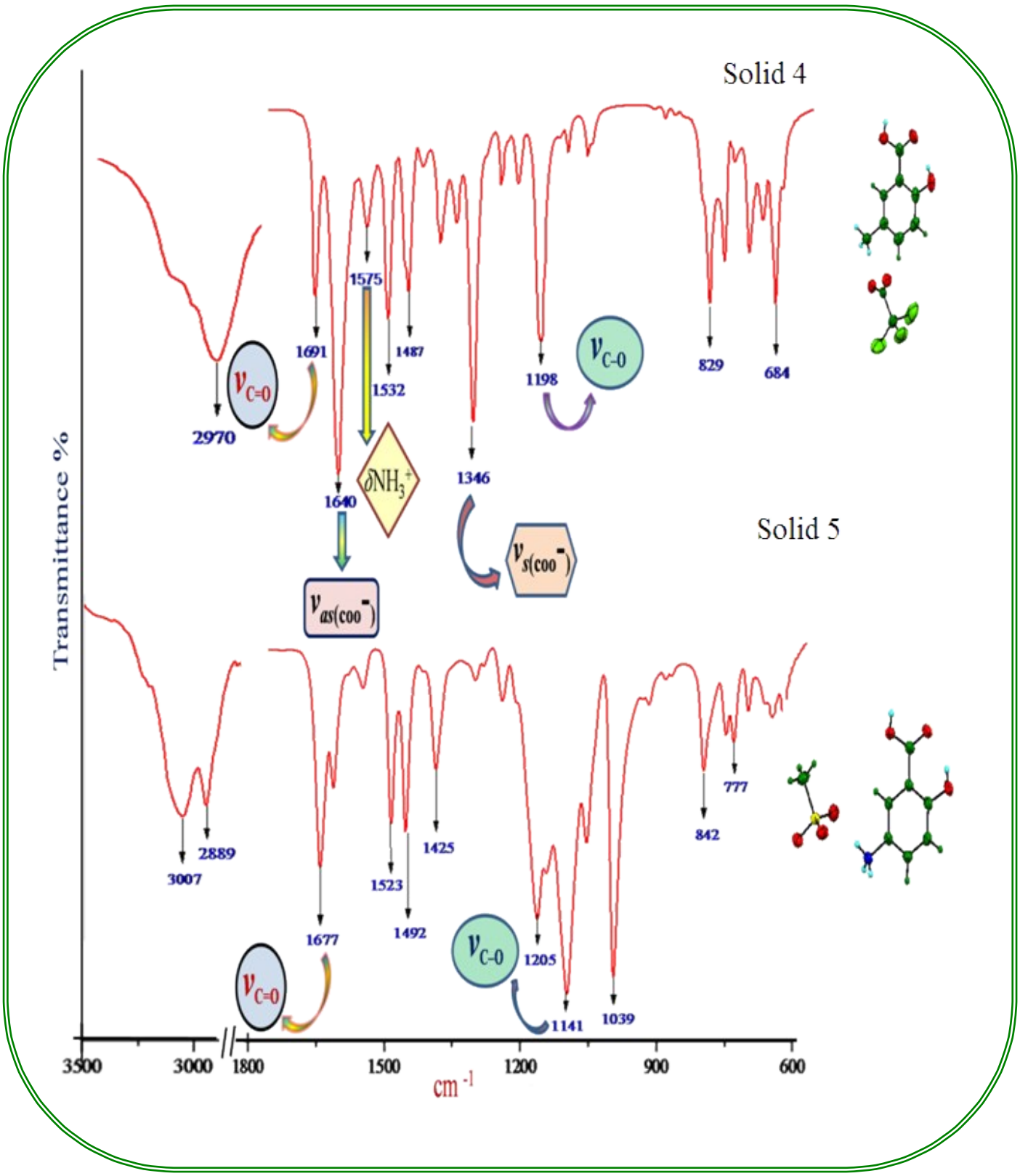
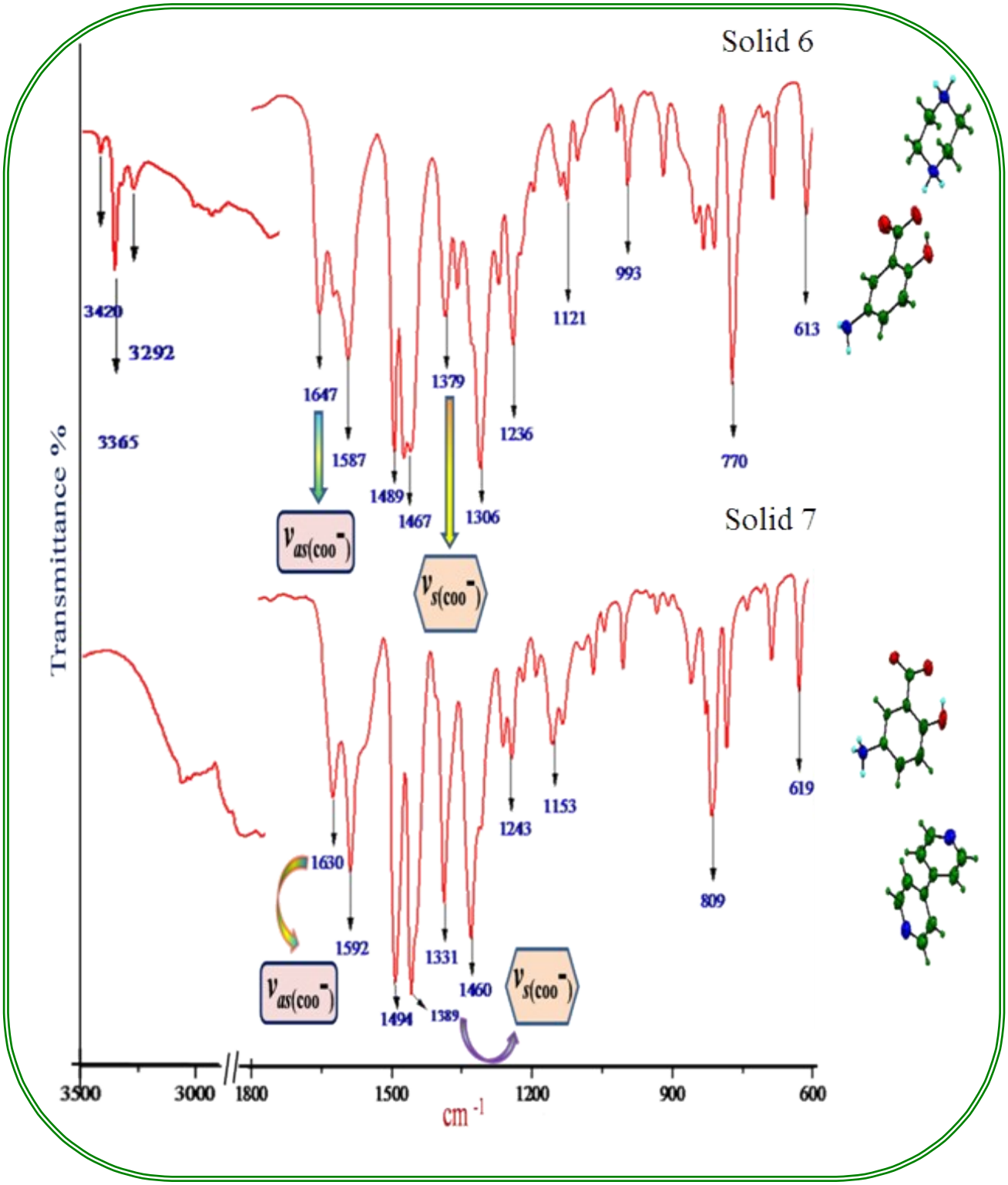


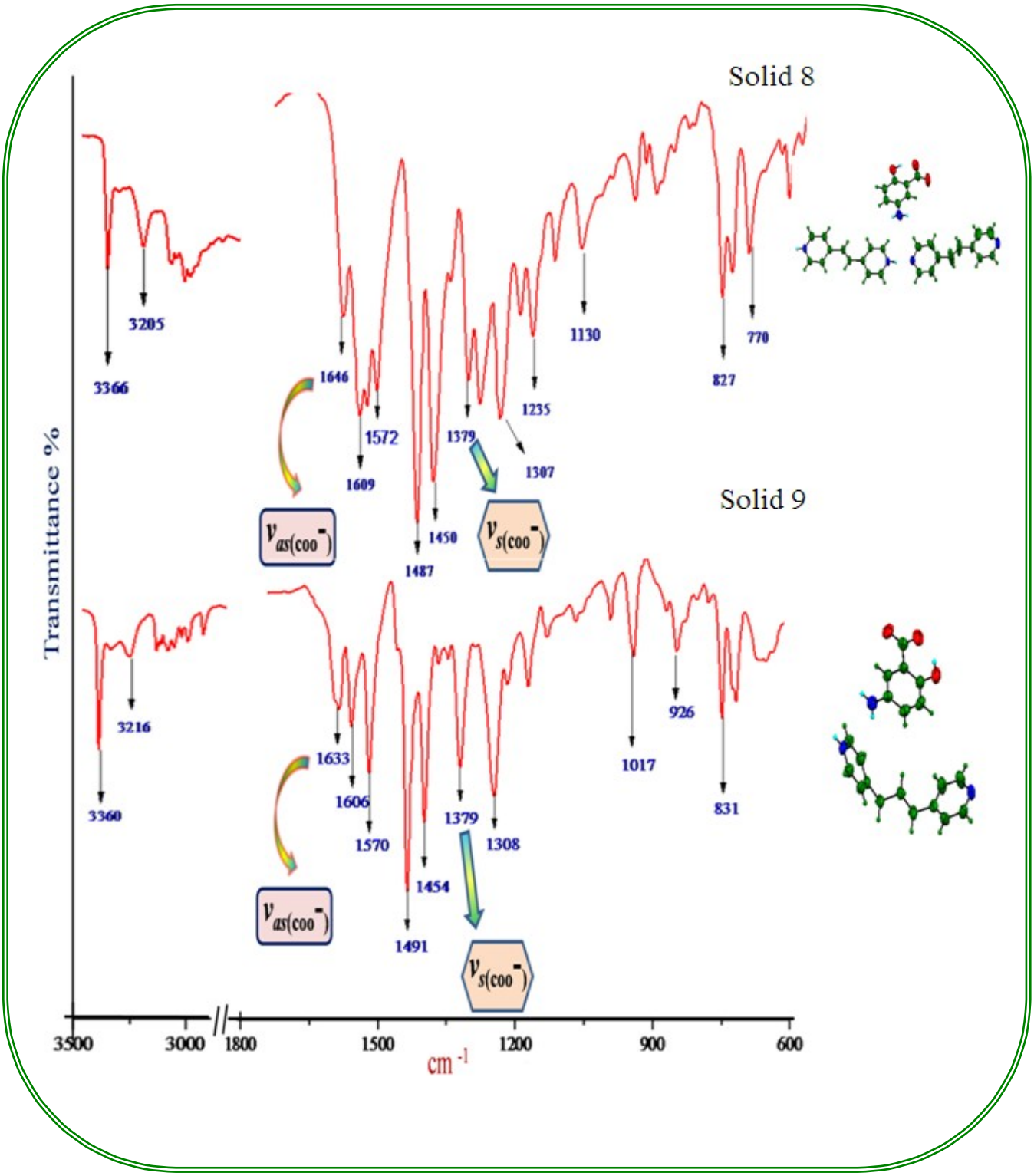

**Figure S4.** The powder pattern of solid **11** is different than the reacting components.


ASA
Solid 1
Transmittance %
cm -1
3500
3000
1800
1500
1200
900
600
2969
1617
1576
1647
1485
1376
1447
1352
1239
1132
809
772
$\nu_{as(coo^-)}$
$\delta NH_3^+$
$\nu_{s(coo^-)}$
3071
1667
1629
1491
1445
1040
850
792
1156
$\nu_{C=O}$
$\delta NH_3^+$
$\nu_{C-O}$


Solid 2
Solid 3
Transmittance %
3362
3239
2919
1640
1536
1485
1439
1155
1044
880
2933
1664
1632
1490
1402
1297
1219
1135
799
$\nu_{C=0}$
$\delta NH_3^+$
$\nu_{C-0}$
3500
3000
1800
1500
1200
900
600
cm $^{-1}$


Solid 4
Solid 5
Transmittance %
2970
1691
1575
1532
1487
1640
1346
1198
829
684
$\nu_{C=O}$
$\delta NH_3^+$
$\nu_{as(coo^-)}$
$\nu_{s(coo^-)}$
$\nu_{C-O}$
3007
2889
1677
1523
1492
1425
1205
1141
1039
842
777
3500
3000
1800
1500
1200
900
600
cm $^{-1}$


Solid 6
3420
3292
3365
1647
1587
1489
1467
1379
1306
1236
1121
993
770
613
$v_{as(coo^-)}$
$v_{s(coo^-)}$
Solid 7
1630
1592
1494
1389
1331
1460
1243
1153
809
619
$v_{as(coo^-)}$
$v_{s(coo^-)}$
Transmittance %
3500
3000
1800
1500
1200
900
600
cm -1


Solid 8
Solid 9
Transmittance %
3366
3205
1646
1572
1609
1487
1450
1379
1235
1307
1130
827
770
$v_{as(coo^-)}$
$v_{s(coo^-)}$
3360
3216
1633
1606
1570
1491
1454
1379
1308
1017
926
831
$v_{as(coo^-)}$
$v_{s(coo^-)}$
3500
3000
1800
1500
1200
900
600
cm -1

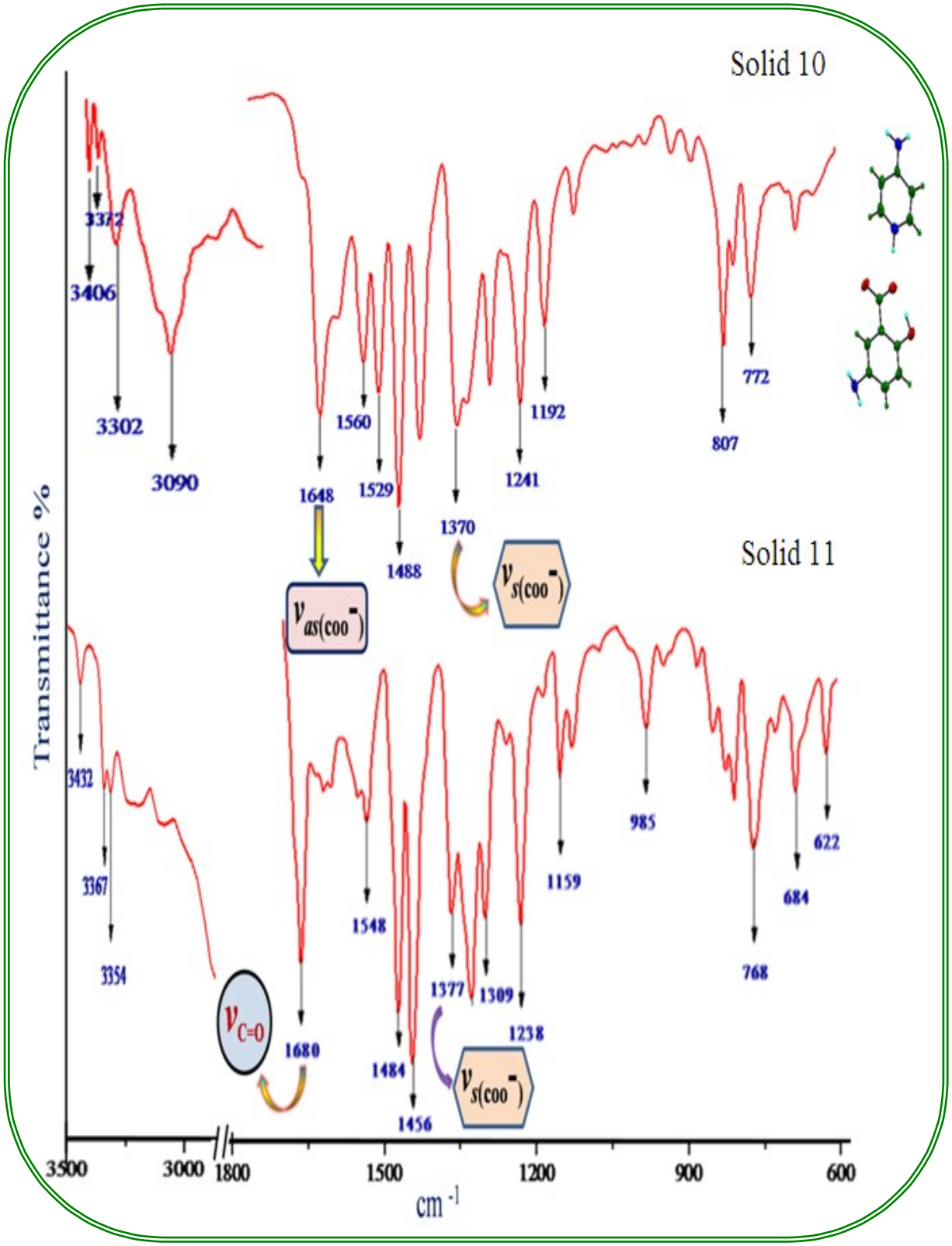



**Figure S5**. ATR spectra of solids **1-11**.