## Polymorphism and Solid-to-Solid Phase Transitions of a

## Simple Organic Molecule, 3-Chloroisonicotinic Acid

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SUPPORTING INFORMATION



**Figure S1**. DSC for forms I and II with a heating rate of 1° C/min. A phase transition for form II at around 135 ° C indicates solid-to-solid phase transition from form II to form I.



**Figure S2**. DSC for forms I and II with a heating rate of 10 ° C/min. The solid-to-solid phase transition from form II to form I has a higher onset temperature compared with that with a heating rate of 1 ° C/min.



Figure S3. DSC for forms I and II with a heating rate of 30 ° C/min.



**Figure S4**. Heating-cooling-heating cycle for form I. After heating form I to its phase transition temperature, it was cooled down to 195  $^{\circ}$  C and then it was reheated to 260  $^{\circ}$  C. It can be seen that the sample did not revert to the original form during cooling.



**Figure S5**. Heating-cooling-heating cycle for form I. After heating form I to its phase transition temperature, it was cooled down to 50  $^{\circ}$  C and then it was reheated to 260  $^{\circ}$  C. It can be seen that the sample reverted back to the original form during cooling.



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**Figure S6**. DSC for forms I, II and III with a heating rate of 10 ° C/min. The difference from Figures S1 and S2 is here hermetic lid with a pinhole was used. Sublimation is greatly reduced.



**Figure S7**. MTDSC of form I. The phase transition at 220 ° C consists of two events, one is reversible and the other not reversible.



**Figure S8**. MTDSC of form II. The phase transition is nonreversible, likely solid-to-solid phase transition.



Figure S9. MTDSC of form III. The phase transition is nonreversible, likely solid-to-solid.



**Figure S10**. Solid-to-solid phase transition of form III to form I observed by hot-stage microscopy during heating: 35.6 (a), 153.3 (b), 171.3 (c), and 178.3 °C (d).



**Figure S11.** shows the powder X-ray diffraction (PXRD) patterns of the three polymorphs collected at room temperature (RT) as well as simulated patterns that are based on the single crystal structures determined at 90 K. The shift of peaks are likely due to the temperature difference (RT for experimental PXRD and 90 K for simulated PXRD). The missing of some peaks for form III is likely because of preferred orientation of the crystals. And the presence of a peak at 24.2 20 for form I probably means phase impurity.



**Figure S12**. Solvent drop grinding experiment. When a mixture of forms I and III were ground manually in the presence of a few drops of MeOH, the PXRD pattern matched that of a physical mixture of forms I and III.