

Supporting Information (SI)

Thermal and *in Situ* X-ray Diffraction Analysis of a Dimorphic Co-crystal, 1:1 Caffeine-Glutaric Acid

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Figure S1. TGA trace of for CA-GA polymorphic forms, Forms I and II. Note the absence of solvent molecules in these crystalline phases.

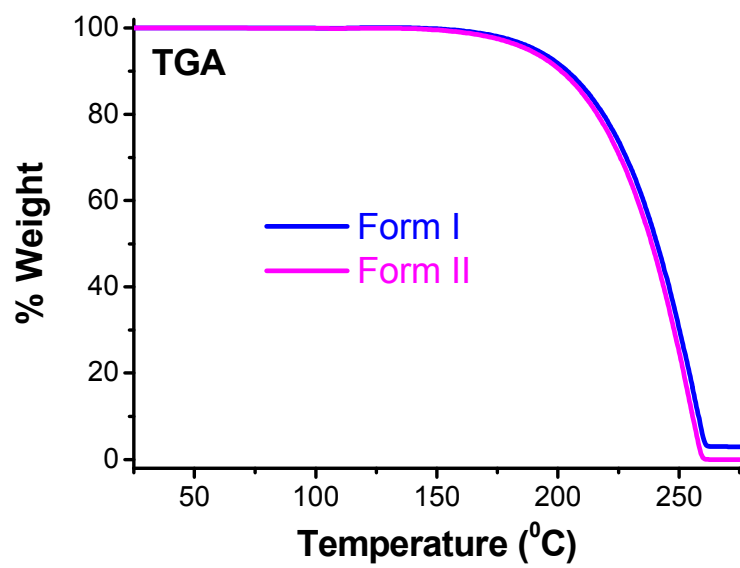


Figure S2. Variable temperature X-ray diffraction patterns of caffeine-glutaric acid Form II are shown in details.

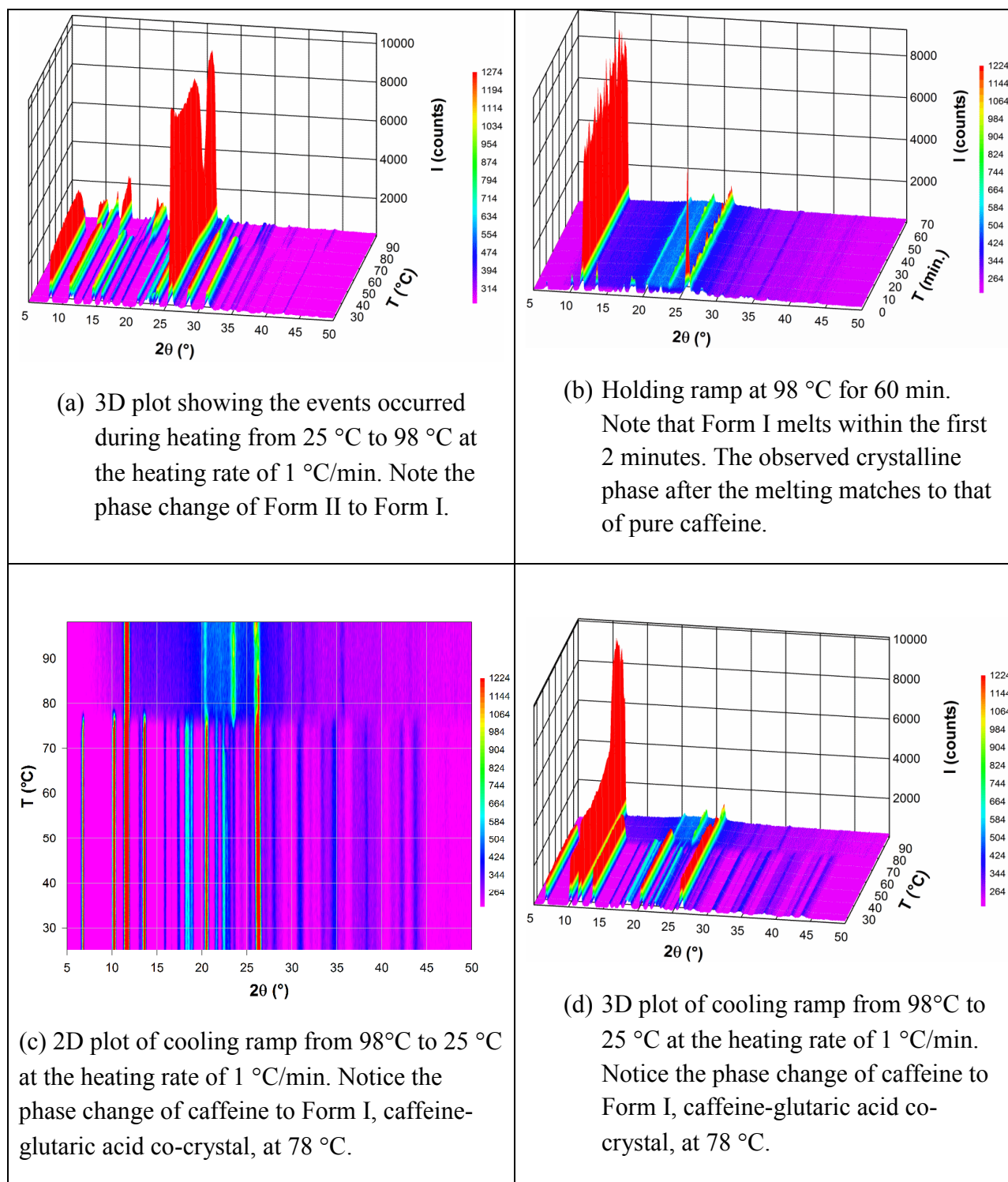


Figure S3. Variable temperature X-ray diffraction of caffeine-glutaric acid Form I from 25 °C to 95 °C at 1 °C/min. Next, it was held at 95 °C for 45 min. Subsequently, the sample was cooled to 25 °C at 1 °C/min.

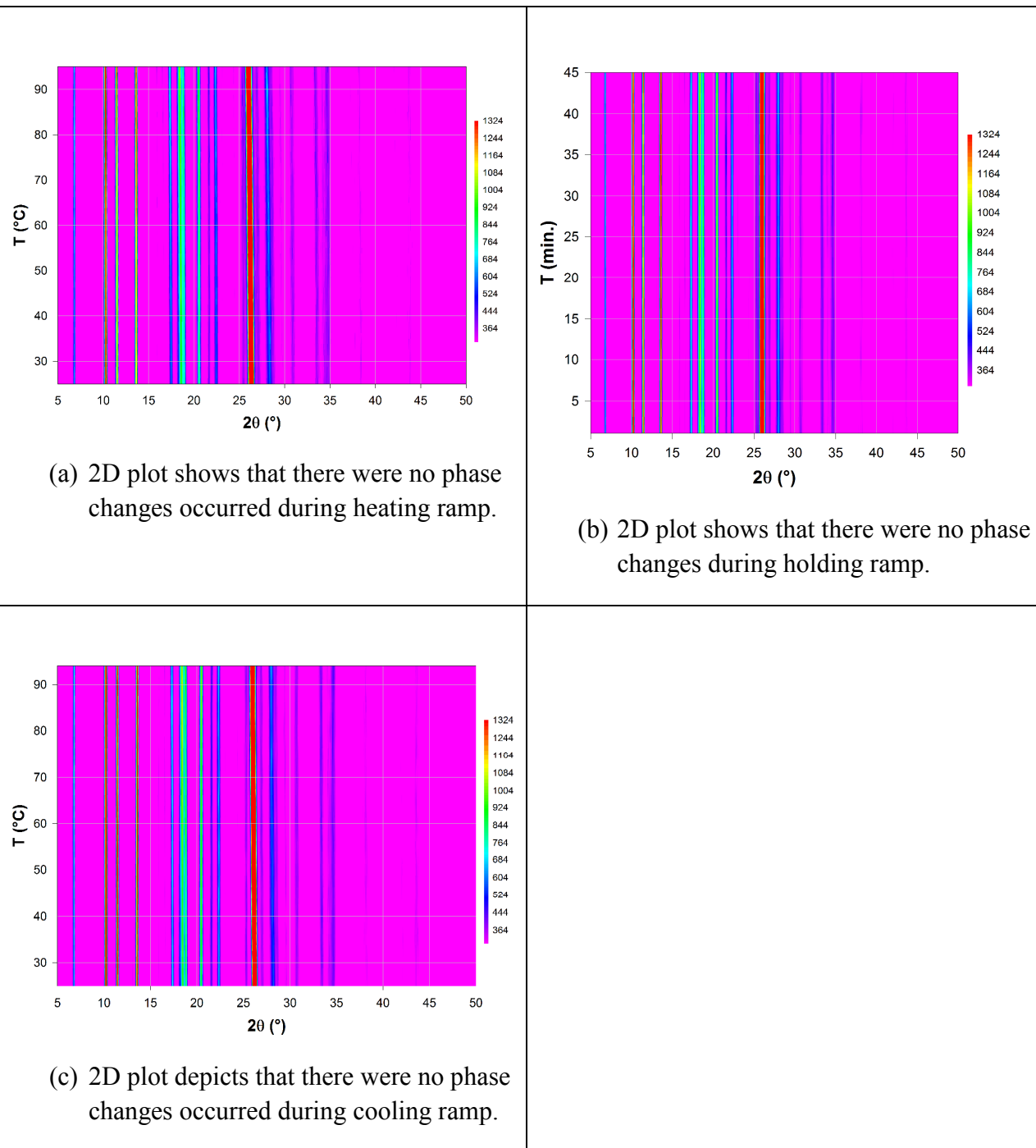


Figure S4. DSC heat-cool-heat profiles of CA-GA Form II at 10 °C/min heating rate. Heating cycle 1 involved heating of sample from room temperature to 170 °C and the melt was subjected to cooling cycle 1 (170 °C to -5 °C), which was followed by heating cycle 2 (-5 °C to 170 °C). The heating cycle 2 results suggest that Form II transformed to Form I during heating followed by melting of Form I at 98.2 °C which indicates that during cooling cycle 1, initially Form I was formed (VTXRD results support this) and upon further cooling to -5 °C, Form I could have converted to Form II. Hence, CA-GA dimorphs, Forms I and II, are enantiotropically related.

