Electronic Supplementary Information

New Intermediate Polymorph of 1-Fluoro-adamantane and Its Second-Order-like Transition toward the Low Temperature Phase

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SI-1. (a) Purification procedure for 1-fluoro-adamantane.

1-Fluoro-adamantane (CAS registry number: 768-92-3) was purchased from ABCR in Germany. A saturated solution was prepared by dissolving the commercial 1-fluoro-adamantane in methanol (HPLC grade) at 40°C. The solution was filtrated at this temperature and put at room temperature in a glass vial. The crystals of 1-fluoro-adamantane were grown from the solution by slow evaporation.

(b) Purity checking process of purified 1-fluoro-adamantane.

Impurity levels in 1-fluoro-adamantane were monitored by Gas Chromatography (GC). Preliminary experiments made using a mass spectrometer detector allowed the identification of 1-adamantanol as the only detectable impurity in the commercial product. The impurity was quantified in 1-fluoro-adamantane samples according to the method described below:

Chromatographic conditions: GC measurements were carried out in an Agilent 7890B Series GC equipped with a flame ionization detector (FID) and an auto-sampler (10 µL syringe). The injector and detector temperatures were set at 300 °C. Hydrogen was used as carrier gas. A DB-35ms 30 m × 0.25 mm × 0.25 µm column was used for separations. The inlet split flow was 10 mL/min. The column outlet flow was 1.0 mL/min. Oven temperature was programmed from 50°C to 150°C at 5 °C/min. The FID was supplied with 30 mL/min hydrogen and 300 mL/min air. The acquisition rate was 200 Hz. For every solution, the injection volume was set at 1 µL - this volume was repeatable which allowed quantification by external standard calibration. In these conditions, 1-fluoro-adamantane and 1-adamantanol retention times were 14.80 min and 18.50 min, respectively.

FID calibration: The detector was calibrated by injecting 1-adamantanol solutions in acetone ranging from 10 to 100 ppm. Detector response (1-adamantanol peak area)

was modelled with respect to the concentration by a straight line ($y = 0.6594x + 0.582, R^2 = 0.998$).

1-adamantanol quantification: Sample solutions were prepared by dissolving ca. 8 mg 1-fluoro-adamantane in ca. 1 g acetone. After analysis by GC, 1-adamantanol concentration in the solution was determined using the calibration curve. The value was divided by the concentration of sample in the analysed solution to obtain 1-adamantanol level in the sample.

SI-2. DSC curve for the phase transitions of 1-F-A measured at 5 K/min heating/cooling rate.

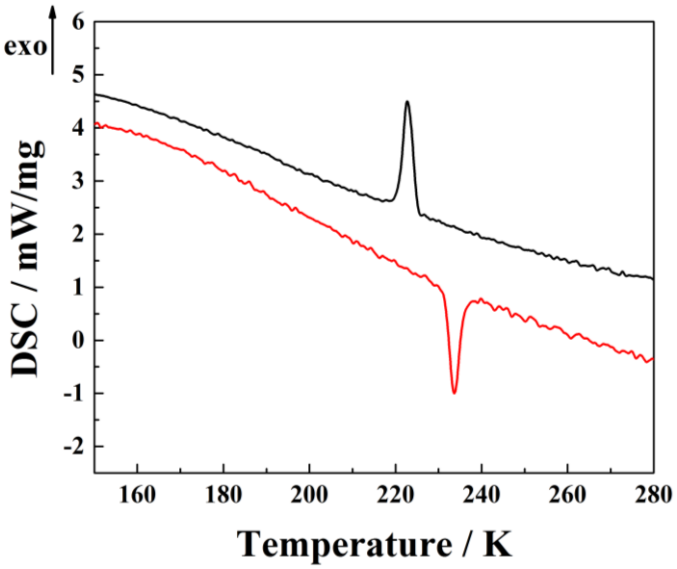


Figure SI-2. DSC measuring curves obtained for the phase transitions of 1-F-A. Black line: upon cooling (5 K/min), onset: 225.1K; red line, upon heating (5 K/min), onset: 231.5K.

SI-3. TR-SHG curve obtained for 1-fluoro-adamantane by annealing at 213K for 10h.

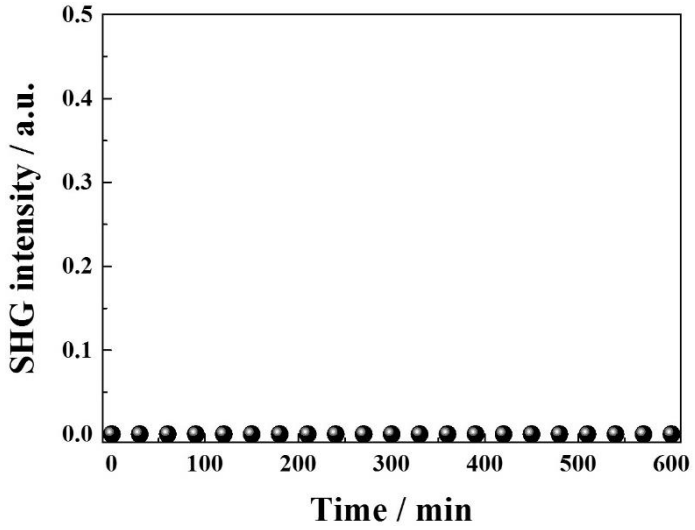


Figure SI-3. TR-SHG curve obtained for 1-fluoro-adamantane by annealing at 213K for 10h. No SH signal was detected after 10h of annealing. Suggested that no LT phase was crystallized at 213K.

SI-4. TR-SHG curve obtained for 1-fluoro-adamantane by annealing at 167K for 10h (inset).

The TR-SHG measurements were performed while annealing the sample at 167K. The SH signal was recorded every 2min. After 10h, no evolution of the SH signal was observed.

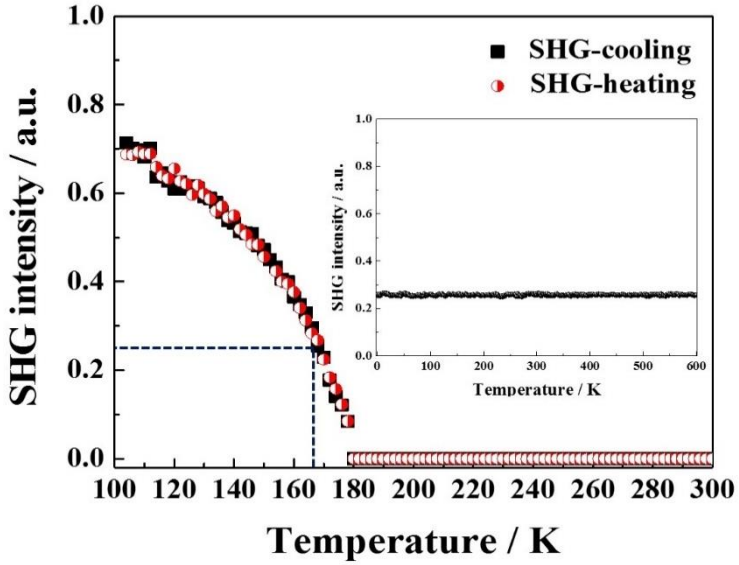


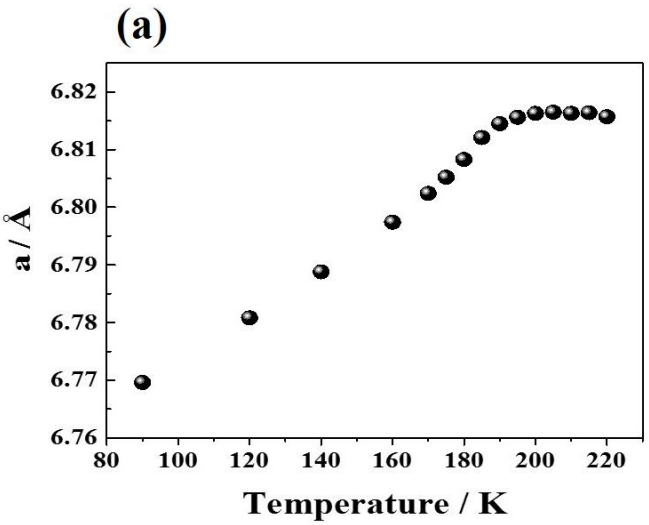
Figure SI-4. TR-SHG curve obtained for 1-fluoro-adamantane by annealing at 167K for 10h (inset). After 10h, no evolution of the SH signal was observed. Indicates that the maximum amount of LT phase was

reached at 167K.

SI-5. Cold-stage microscopy observations of the phase transition of 1-fluoro-adamantane.

Single crystal was grown on the cap of a closed vial by sublimation at 160°C. The crystal was cooled down at 1K/min to 153K, and was heated at 1K/min. The video was recorded during heating from 153K to 243K. No phenomenon was observed at ca. 178K (the temperature of second-order transition). At ca. 230K, the transition begins. One can observe the propagation of the transition front and the slight change of the volume, which indicate the first-order transition.

SI-6. Variations of (a) the unit cell parameter *a*, (b) the unit cell parameter *c*, and (c) the volume of 1-fluoro-adamantane in the temperature range of 90K to 220K.



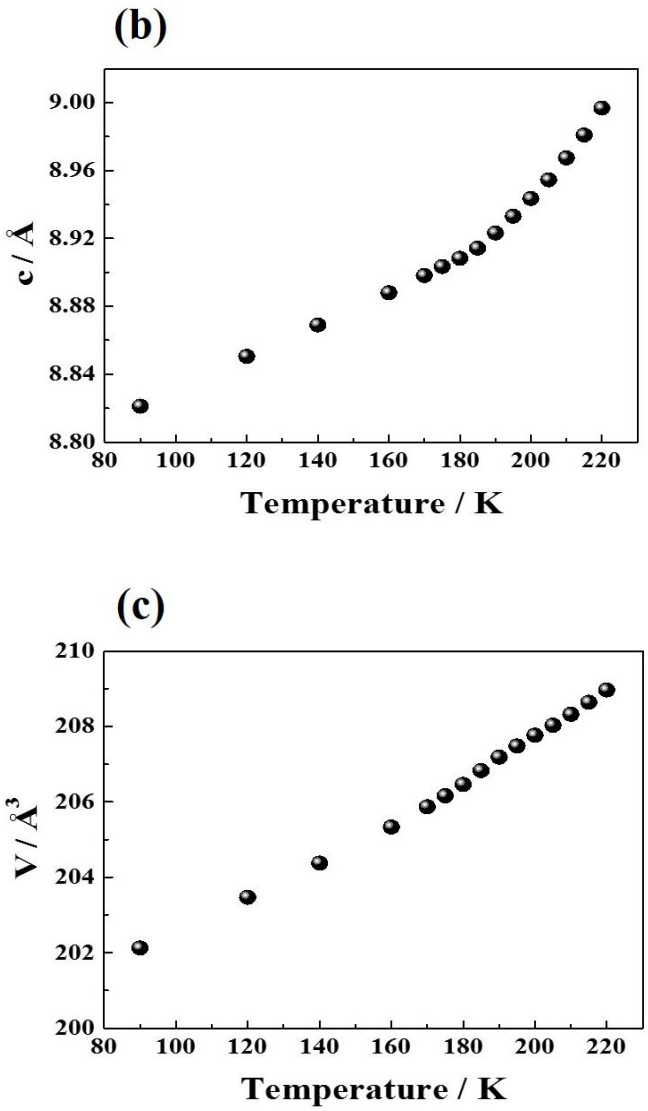


Figure SI-6. Variations of (a) the lattice parameter *a* and (b) the lattice parameter *c* and (c) the volume of 1-fluoro-adamantane in the temperature range of 90K to 220K. The continuity in the variation of the parameters and the volume as a function of temperature confirms the second-order transition.