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Thermally Induced Disordering and Crystallization of DUT-67

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Introduction

Metal-organic frameworks (MOFs) are often considered purely crystalline materials¹. Zirconium based MOFs are different, as they require multiple specific solvents to guide the crystallization process. Without these solvents the frameworks become inherently disordered². DUT-67 is a zirconium MOF that owes its specific crystal structure to the addition of acetic acid during the solvothermal synthesis, which results in crystalline material with greater porosity than its polymorphs³. This also leads to an inherently unstable crystal structure, which is prone to disordering upon heating. DUT-67 showcases anomalous behavior which results in disordering and rearrangement of the structure into DUT-67 HT.

To understand the behavior and the properties of the disordered state, characterization with differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Fourier-transformed infrared spectroscopy (FT-IR), gas sorption, in-situ x-ray diffraction, and in-situ small angle x-ray scattering (SAXS) were performed.

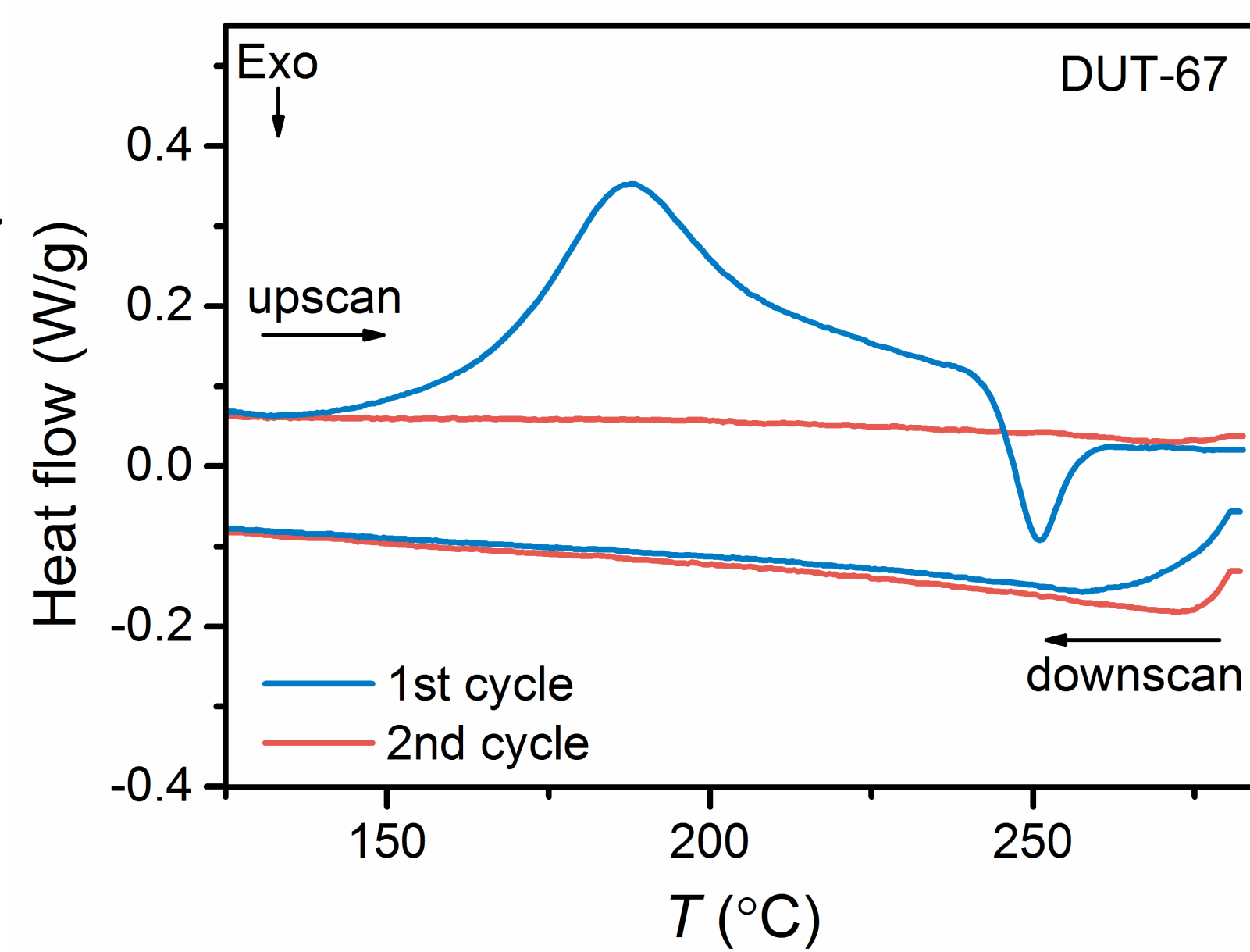
Thermal Behavior of DUT-67

Differential Scanning Calorimetry

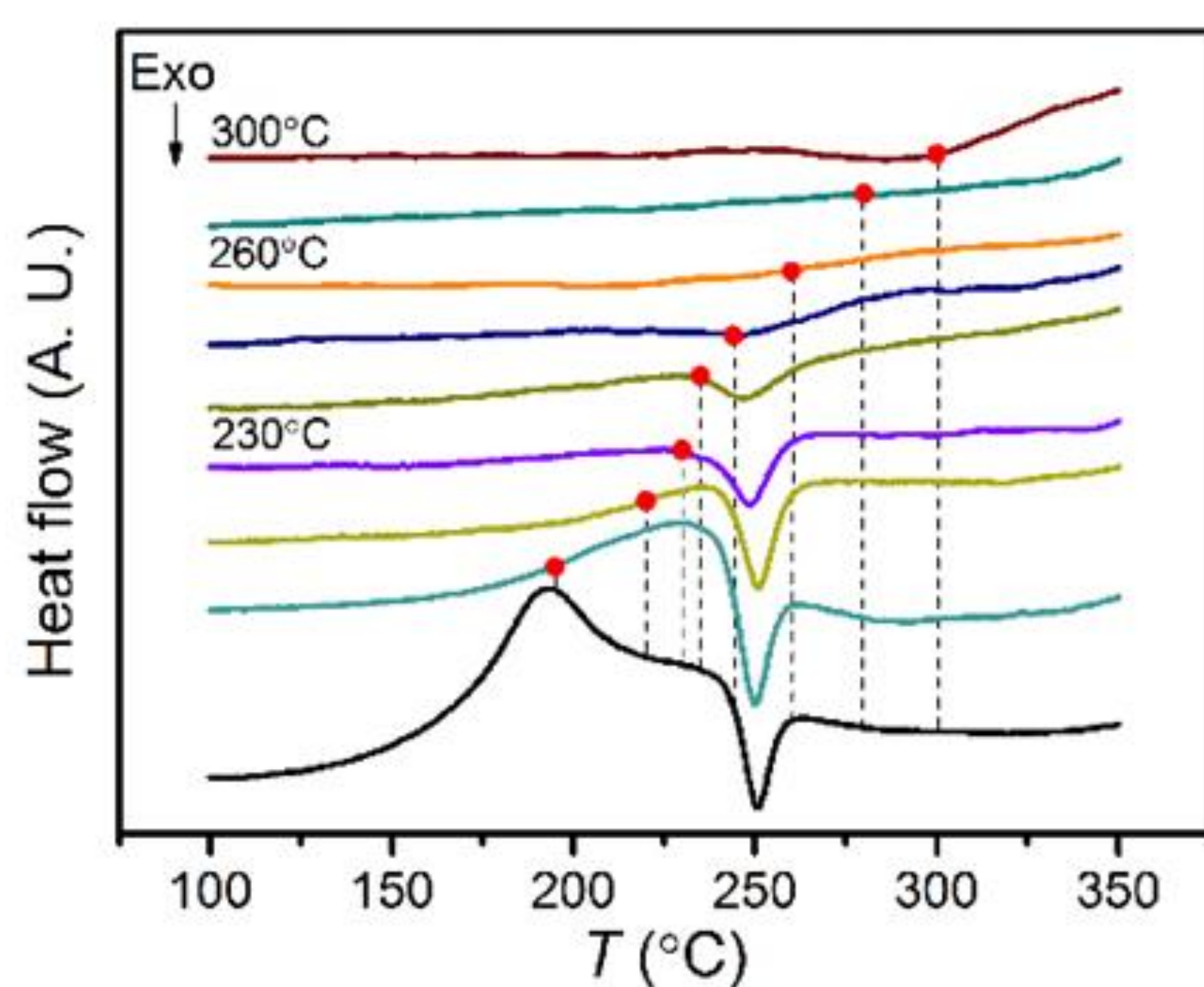
DSC measurements reveal an irreversible exothermic event at 250 °C.

The initial peak and is due to the desolvation of solvents used during the synthesis.

Irreversible transitions are expected of MOFs if it is related to rearrangement of the linkers into a denser state (disordering, melting, collapse).



Annealing



Annealing at various temperatures demonstrates that the initial desolvation event is unrelated to the exothermic event.

The energy released by the exothermic event decreases when annealing at 230 °C.

The exothermic event seems to be an inherent feature of DUT-67, related to linker rearrangement.

Thermal Stability of DUT-67

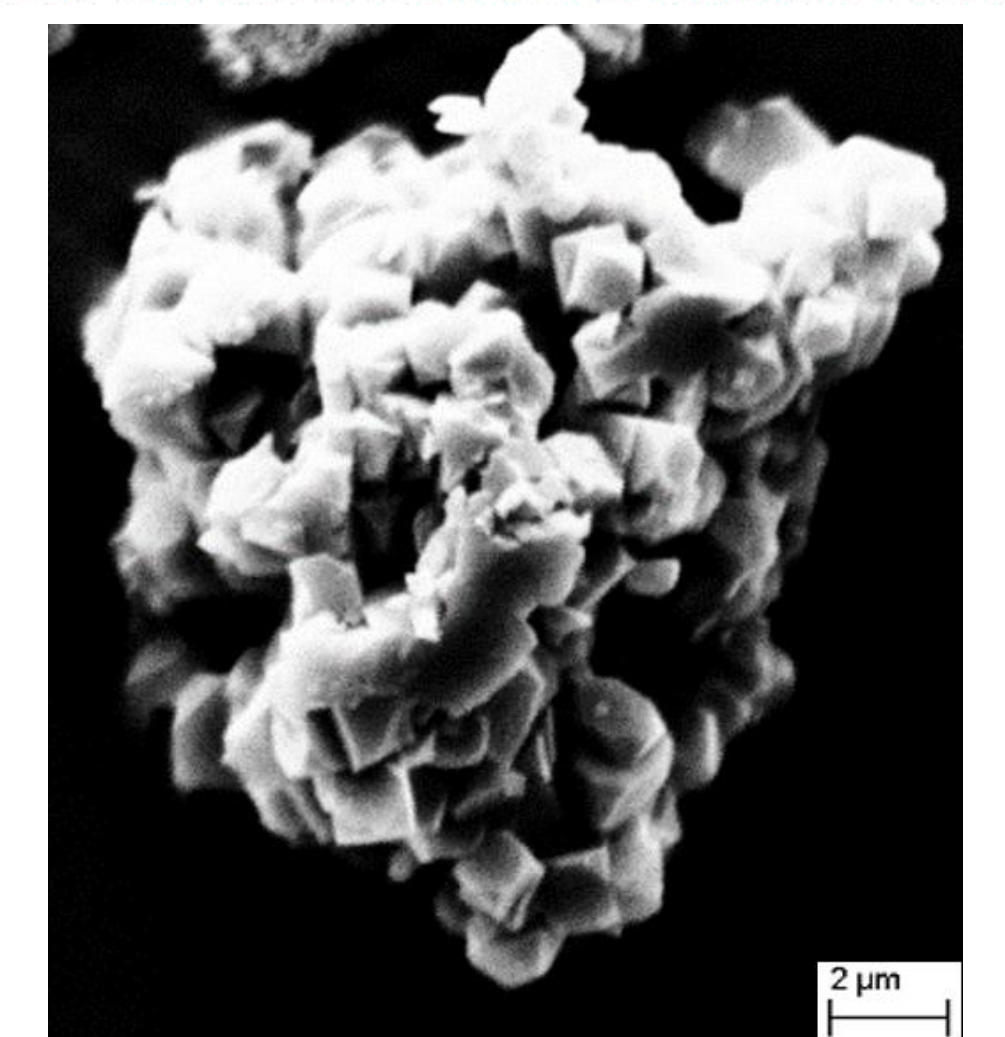
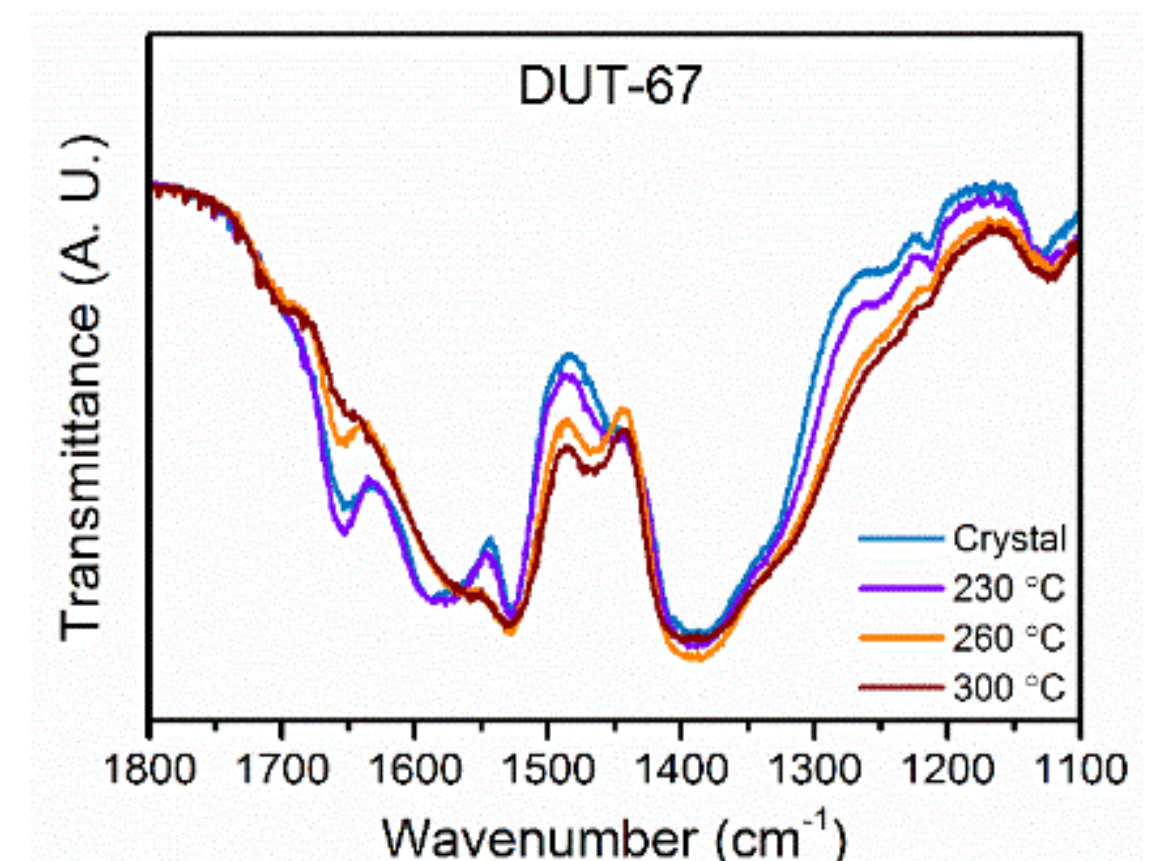
The chemical signatures of the linkers remain intact, confirming that no decomposition occurs during disordering or the transition.

Subtle changes to the FT-IR spectra could be related to bending and stretching of the linkers during structural rearrangement.

SEM of DUT-67 HT shows that the morphology of the original crystals remain unchanged during disordering.

There is no visible formation of new crystals corresponding to the new Bragg peaks.

DUT-67 HT is expected to have retained its original chemical functionality.



Permanent Porosity and Density

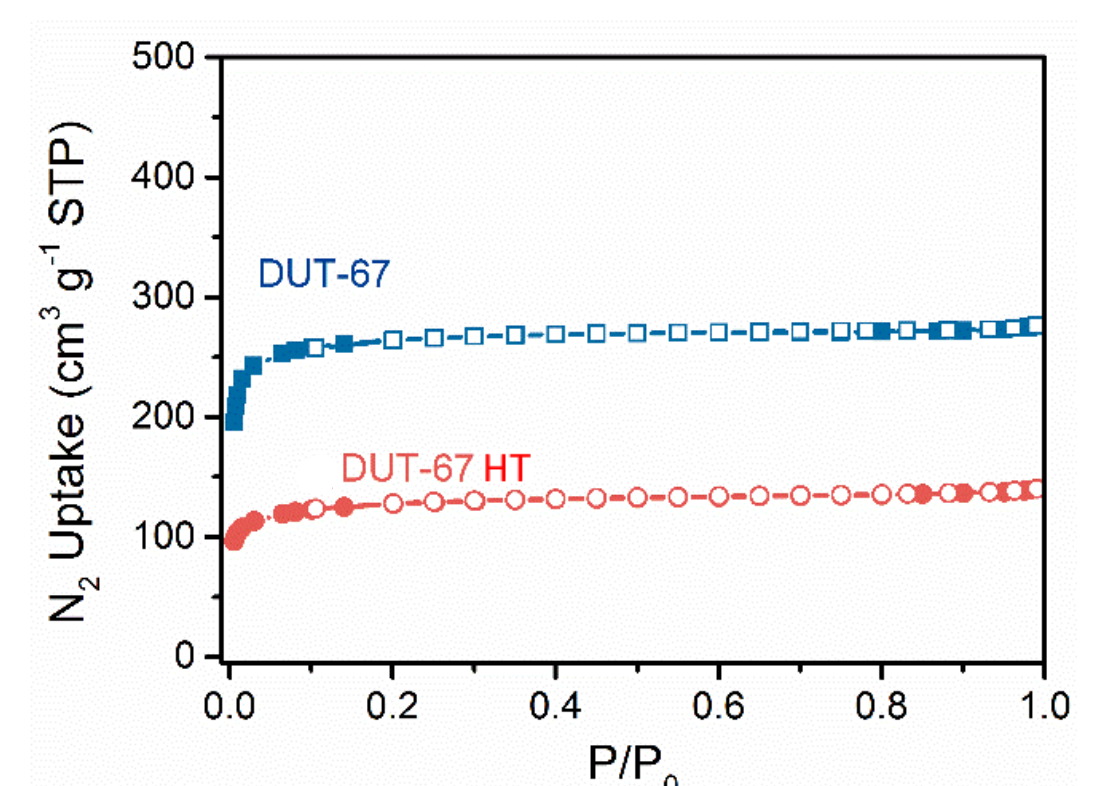
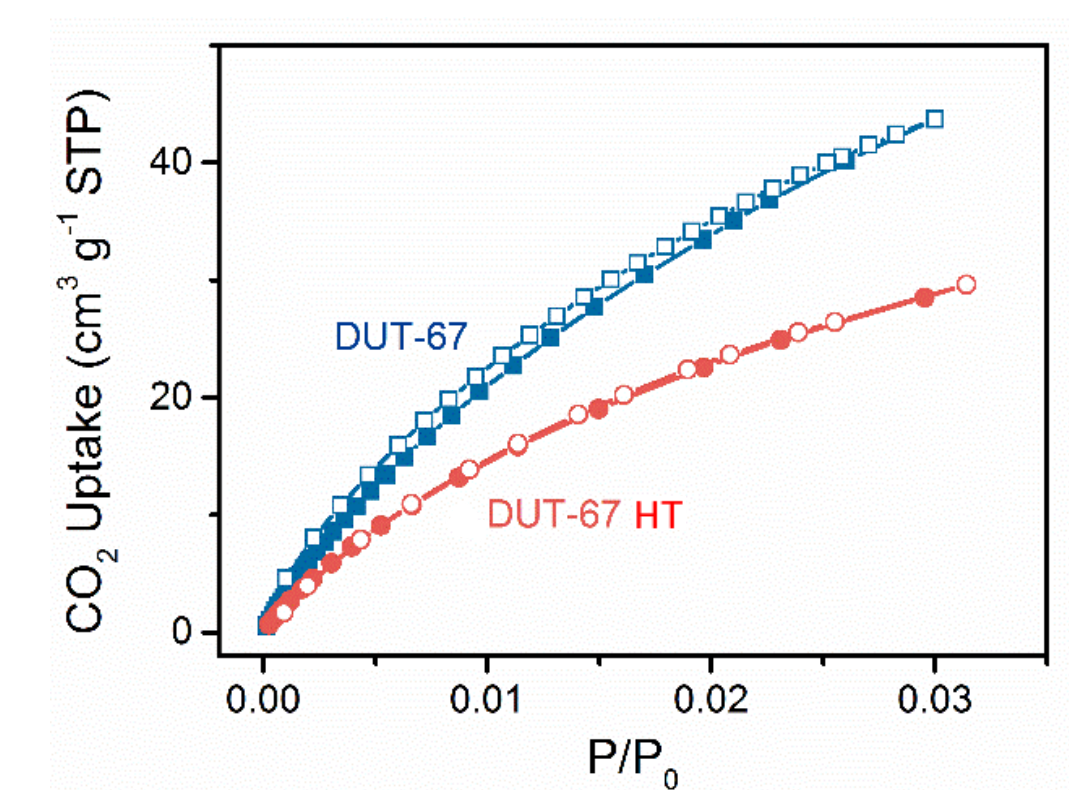
Disordering of the structure results in partial collapse of the pore structure.

Unlike glassy ZIF-4 and ZIF-62, the disordered DUT-67 retains permanent porosity.

50% retention of N₂ uptake is expected due to lowered surface area and pore volume.

73% retention of CO₂ uptake indicates that the chemically functional sites remain mostly accessible in the disordered state.

Higher density and lower pore volume correspond to framework collapse.



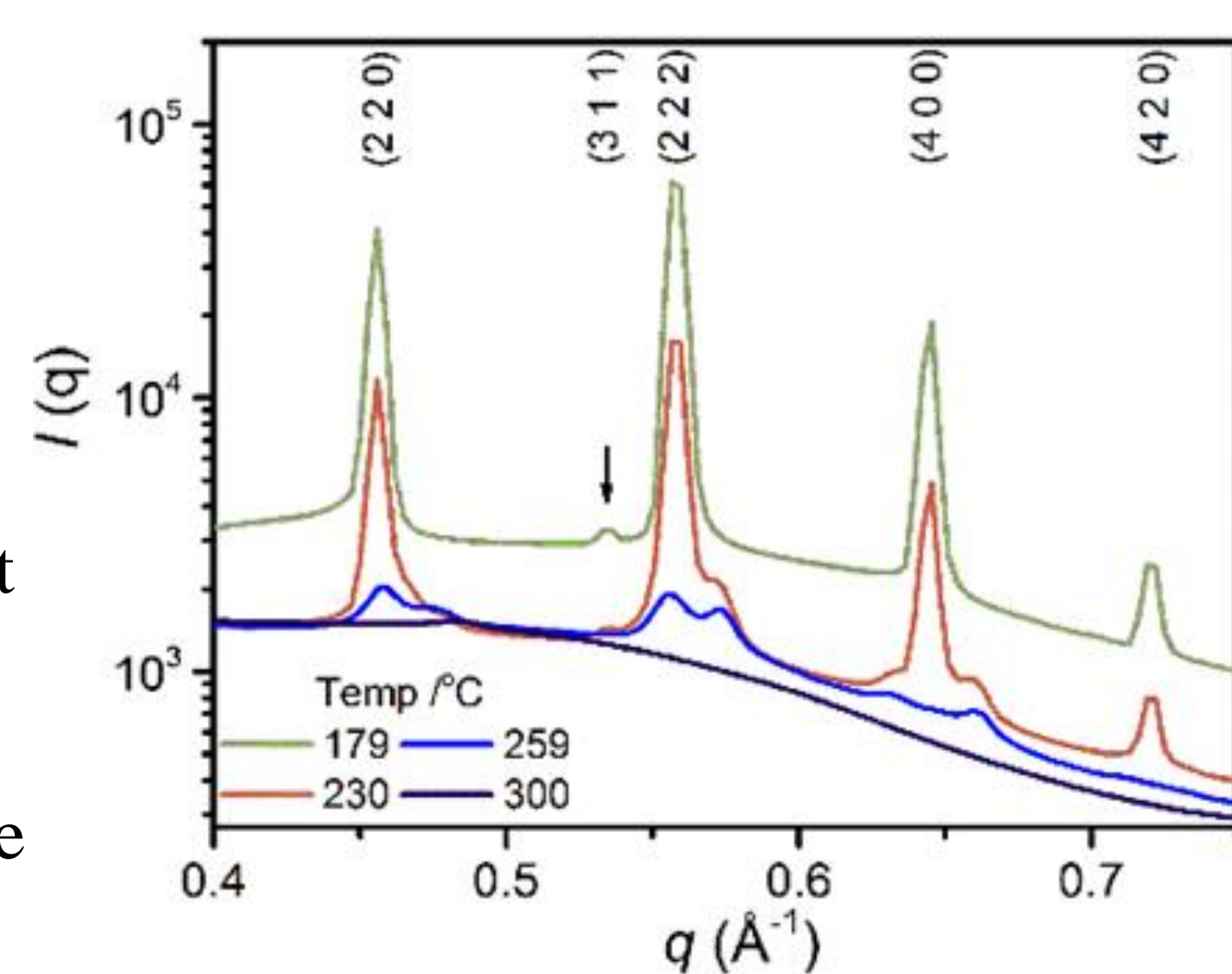
Confirmation of Structural Changes

In-situ XRD

Decreasing intensity of Bragg peaks indicates gradual disordering of the crystal structure

New Bragg peaks appear during the exothermic event. Hinting at rearrangement of the linkers into a denser conformation.

Original and new peaks coexist and become fully disordered at higher temperatures.

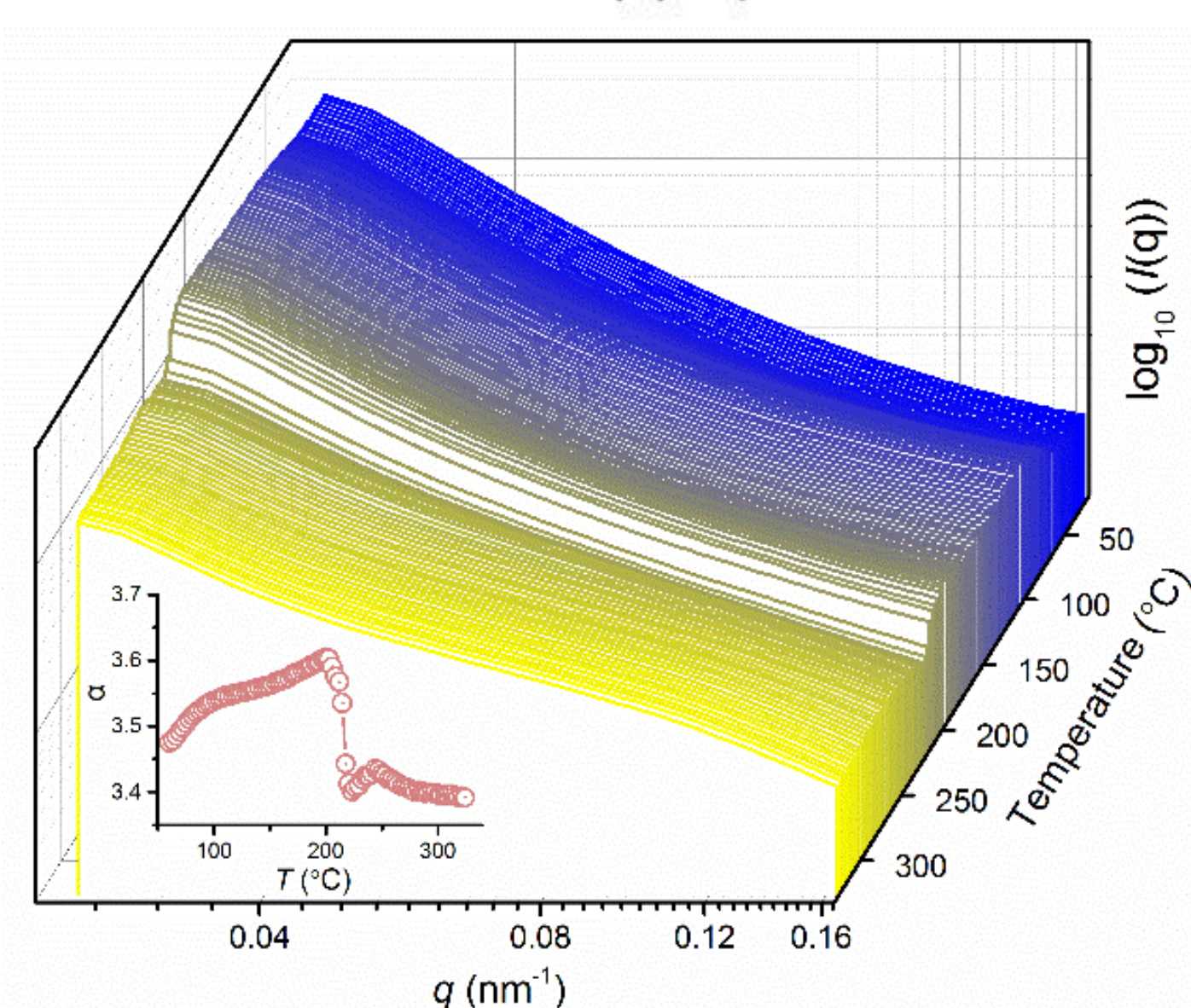


In-situ SAXS

SAXS intensity decreases at 210 °C, confirming that disordering occurs before the exothermic transition.

Disordering changes the pore structure, indicated by the Porod exponent α .

The weak crystallization event at 240 °C can be noted from both the intensity and α .



| Sample | BET Surface area /m ² g ⁻¹ | Micropore volume /cm ³ g ⁻¹ | N ₂ uptake /cm ³ g ⁻¹ (STP) | CO ₂ uptake /cm ³ g ⁻¹ (STP) | Density /g cm ⁻³ |
|-----------|--|---|--|---|-----------------------------|
| DUT-67 | 1038 | 0.428 | 276.4 | 40.7 | 2.074 (6) |
| DUT-67 HT | 490 | 0.217 | 140.3 | 29.6 | 2.554 (8) |

Conclusions

We have investigated the thermally induced transition of DUT-67 through calorimetric and structural analysis. We found that the framework showcases anomalous disordering of the structure when compared to other zirconium MOFs. We ascribe the behavior to the framework having a high pore volume and internal surface area, while possessing lower linker connectivity, greater reliance on structure guiding solvents, and less rigid linkers than other zirconium MOFs.

Our work highlights the permanent porosity of the disordered phase without changing the chemical properties of the material, which could have interesting implications for catalytic or energy storage applications.

Acknowledgments

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