Supplementary Material

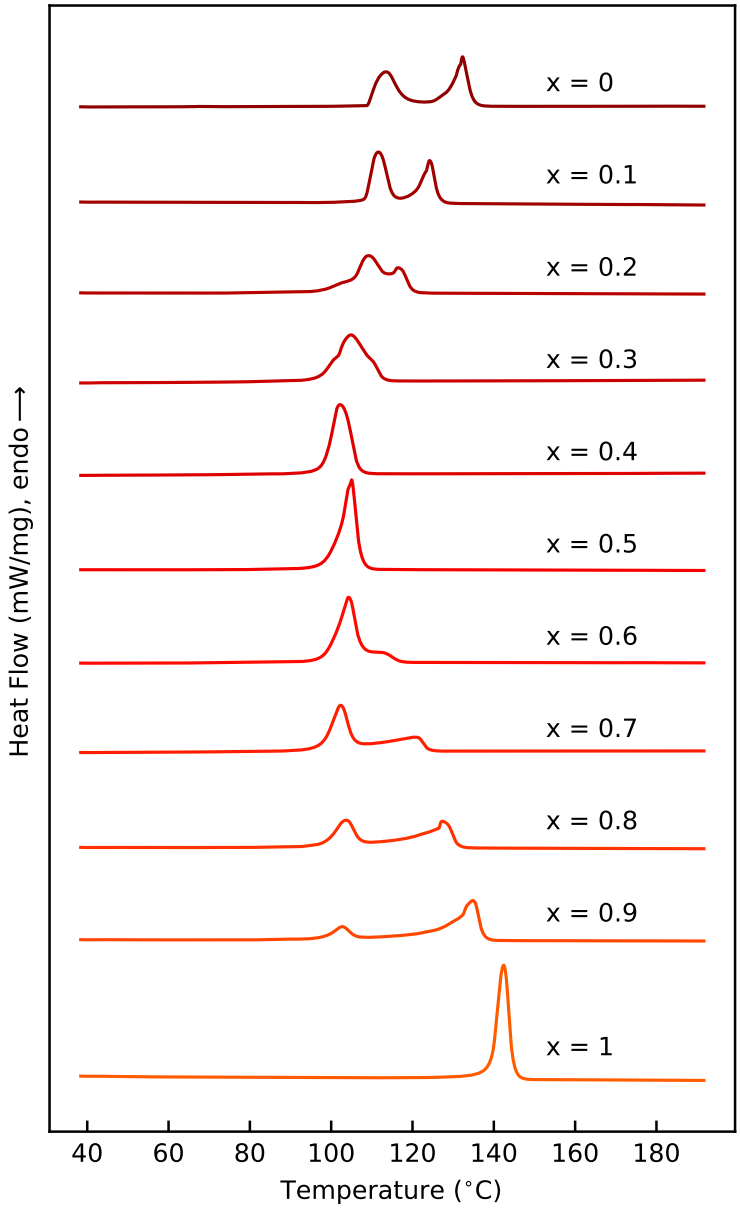

Figure S1: The first DSC heating cycle of the $TPA_xTBA_{1-x}FBC$ samples.

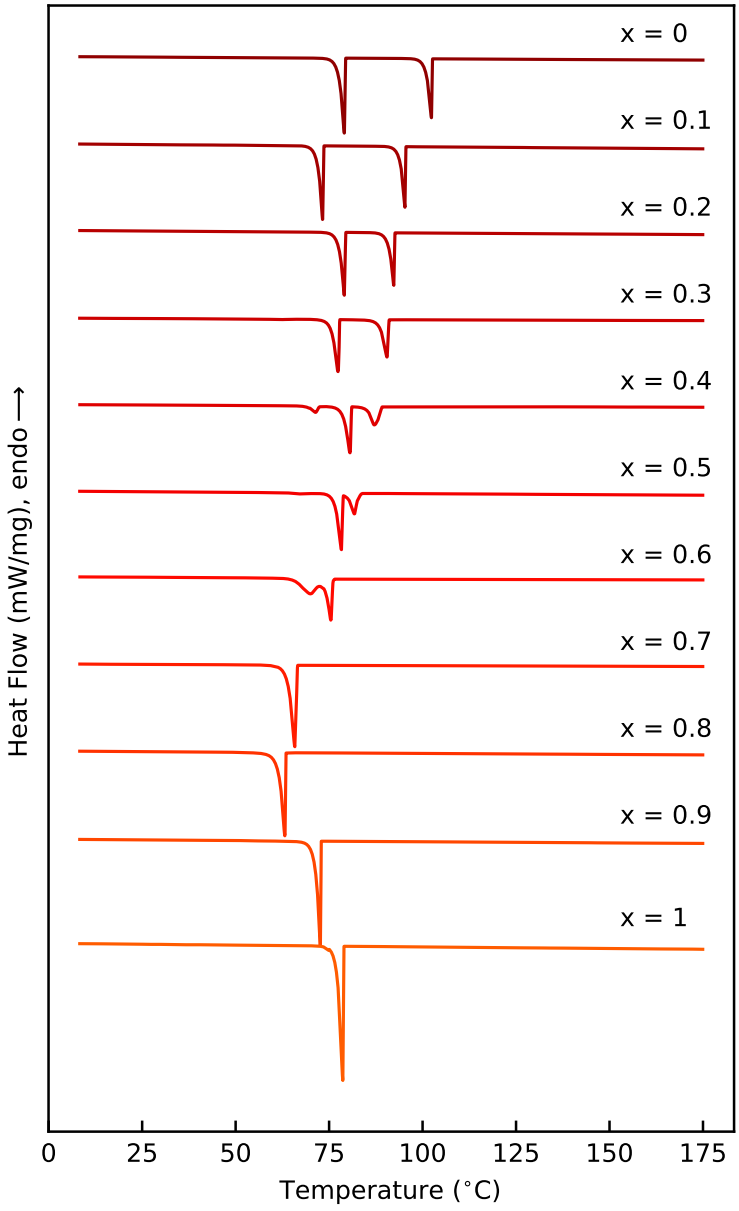

Figure S2: The first DSC cooling cycle of the $TPA_xTBA_{1-x}FBC$ samples.

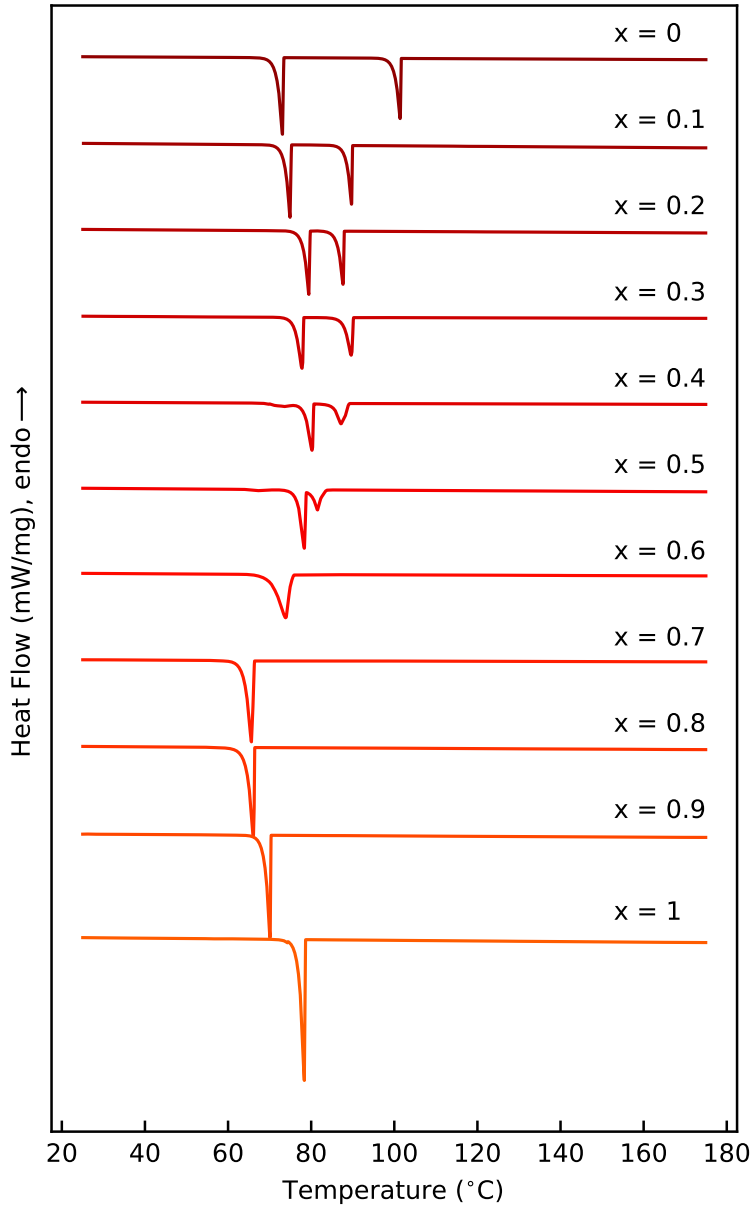

Figure S3: The second DSC cooling cycle of the $TPA_xTBA_{1-x}FBC$ samples.

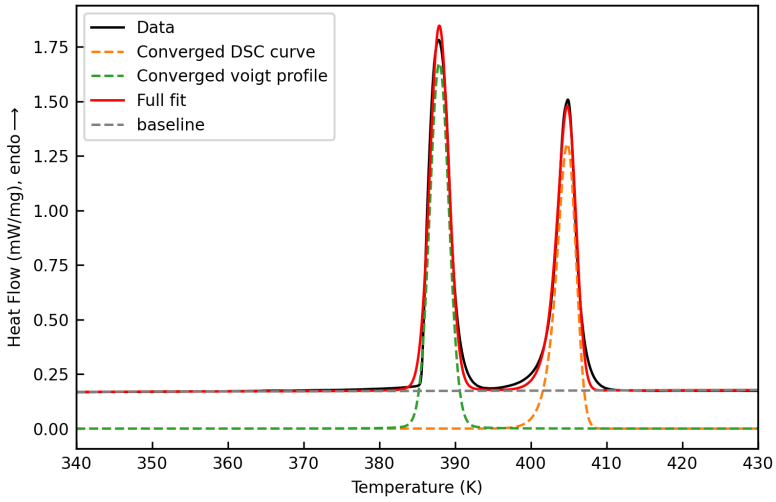

Figure S4: The peak fitting of the TBA FBC DSC data, from the second heating cycle.

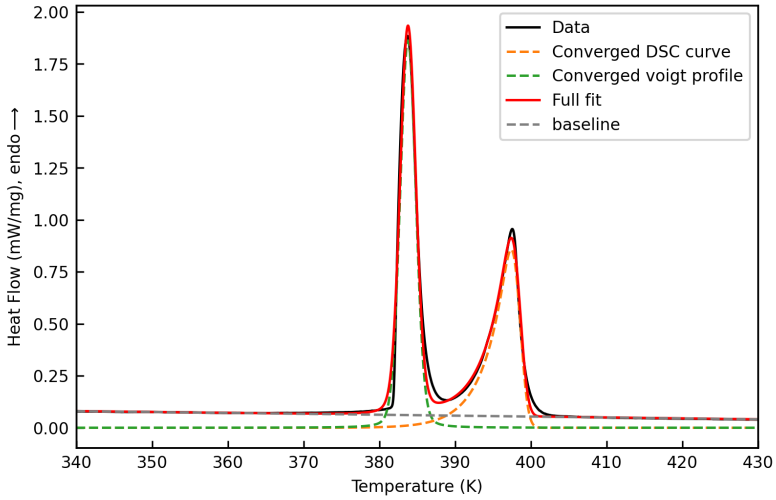

Figure S5: The peak fitting of the $TPA_{0.1}TBA_{0.9}$FBC DSC data, from the second heating cycle.

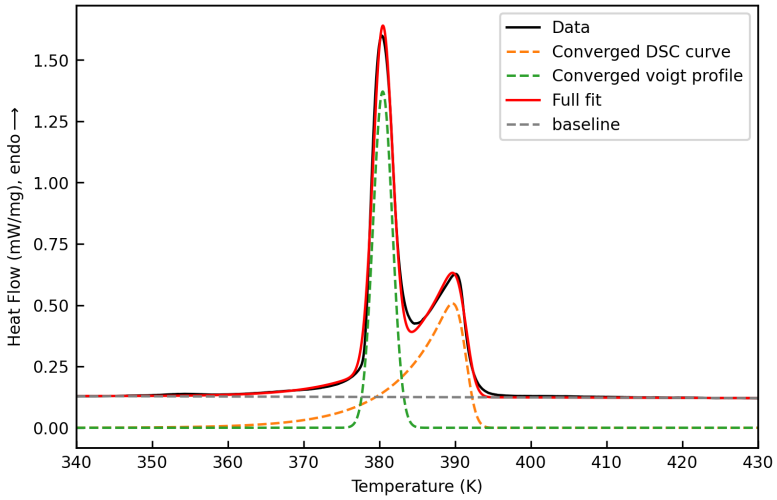

Figure S6: The peak fitting of the $TPA_{0.2}TBA_{0.8}FBC$ DSC data, from the second heating cycle.

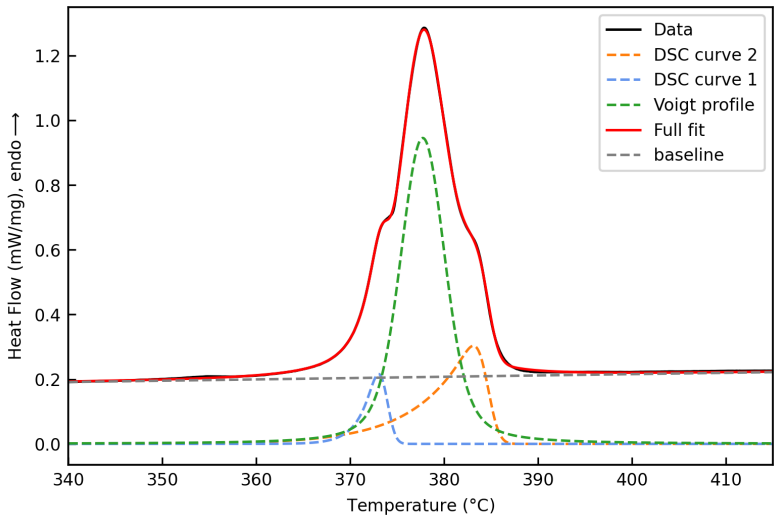

Figure S7: The peak fitting of the $TPA_{0.3}TBA_{0.7}FBC$ DSC data, from the second heating cycle.

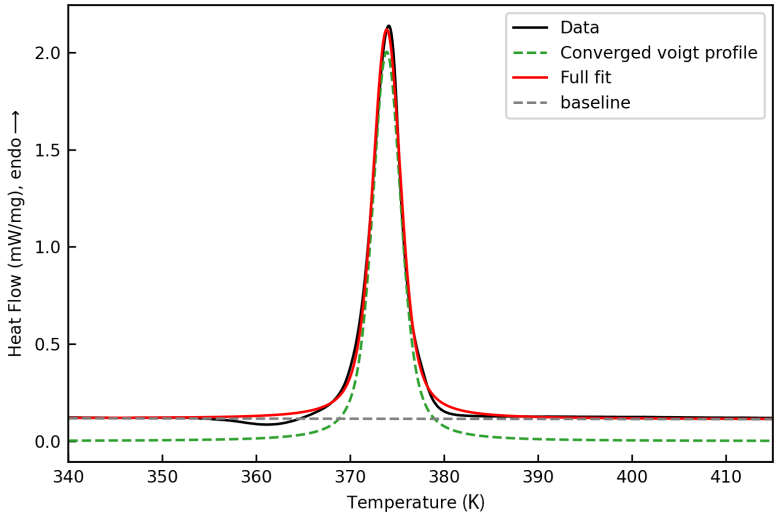

Figure S8: The peak fitting of the $TPA_{0.5}TBA_{0.5}FBC$ DSC data, from the second heating cycle.

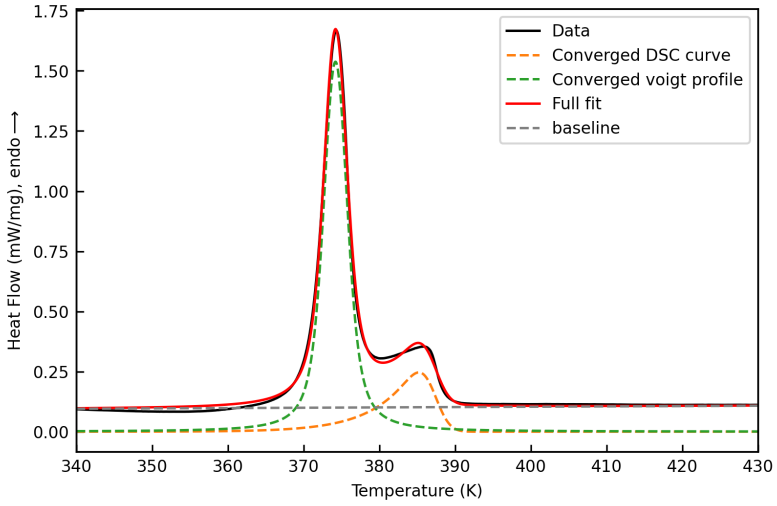

Figure S9: The peak fitting of the $TPA_{0.6}TBA_{0.4}FBC$ DSC data, from the second heating cycle.

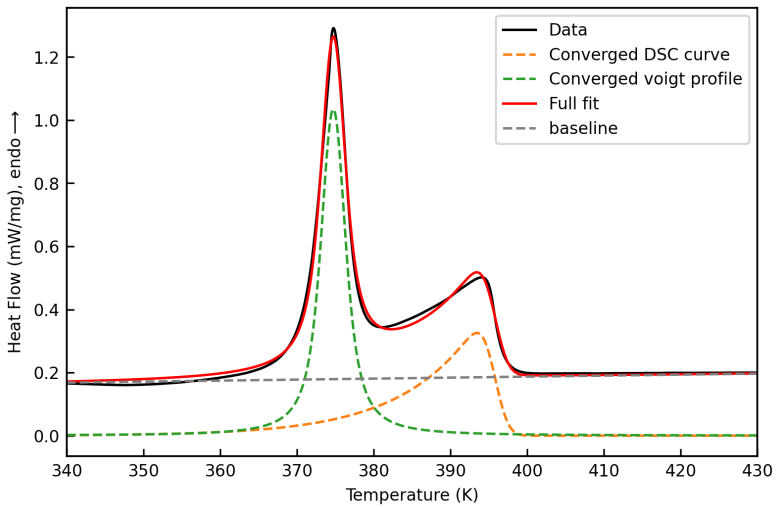

Figure S10: The peak fitting of the $TPA_{0.7}TBA_{0.3}FBC$ DSC data, from the second heating cycle.

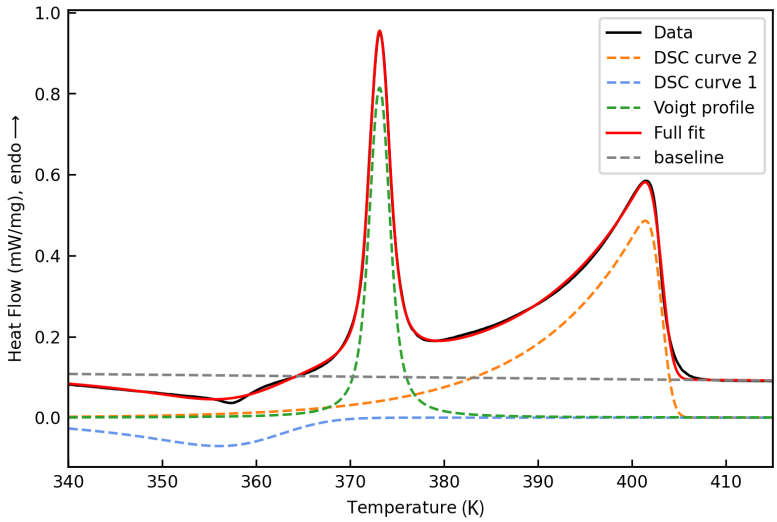

Figure S11: The peak fitting of the $TPA_{0.8}TBA_{0.2}FBC$ DSC data, from the second heating cycle.

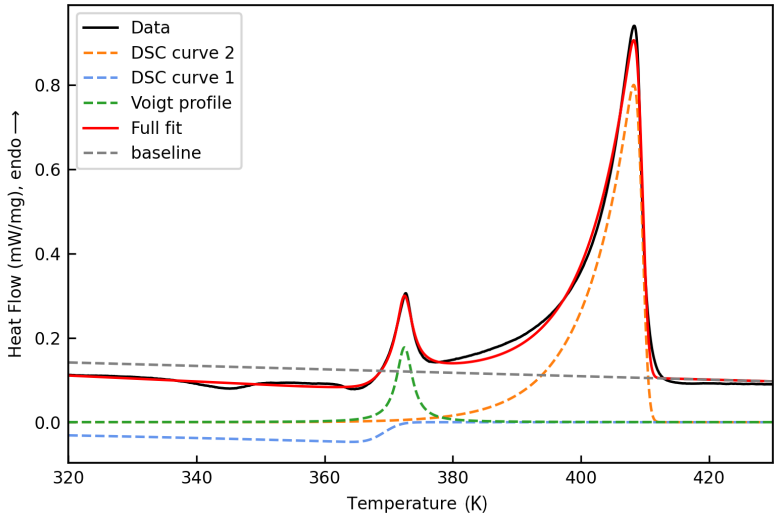

Figure S12: The peak fitting of the $TPA_{0.9}TBA_{0.1}FBC$ DSC data, from the second heating cycle.

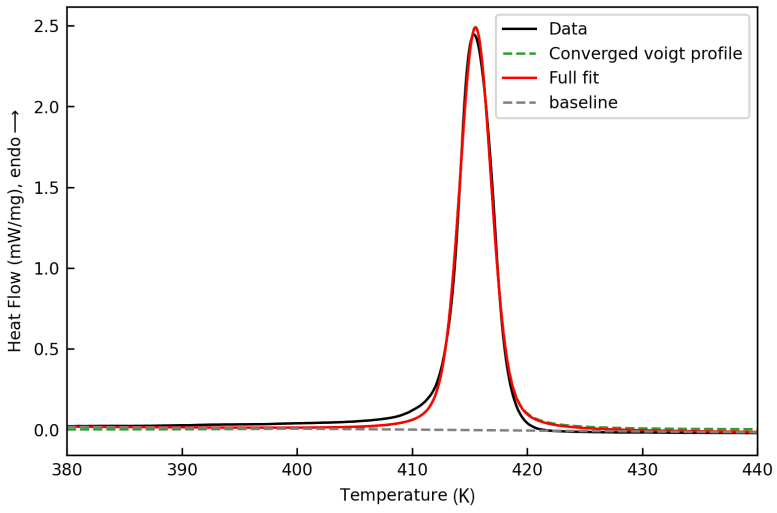

Figure S13: The peak fitting of the TPA FBC DSC data, from the second heating cycle.

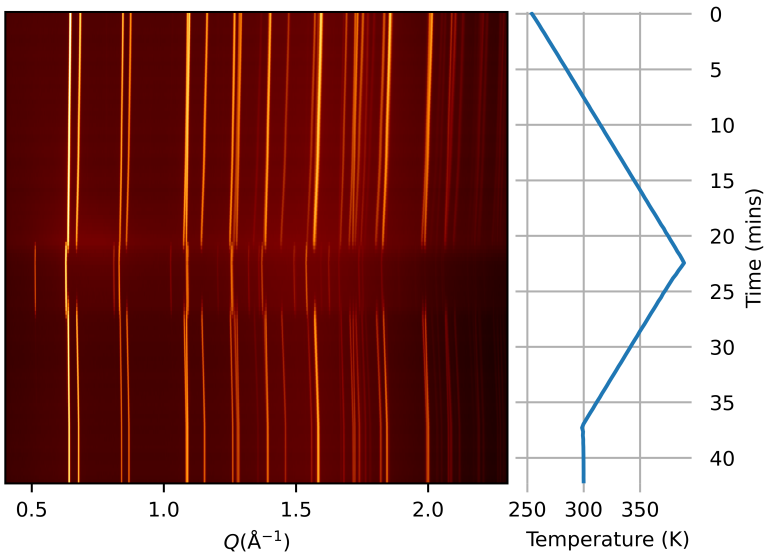

Figure S14: In-situ synchrotron XRD data for $TPA_{0.1}TBA_{0.9}FBC$.

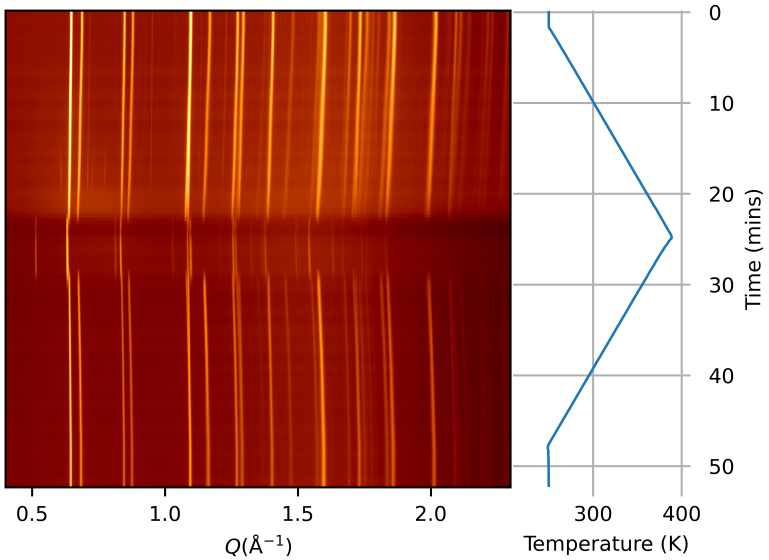

Figure S15: In-situ synchrotron XRD data for $TPA_{0.2}TBA_{0.8}FBC$.

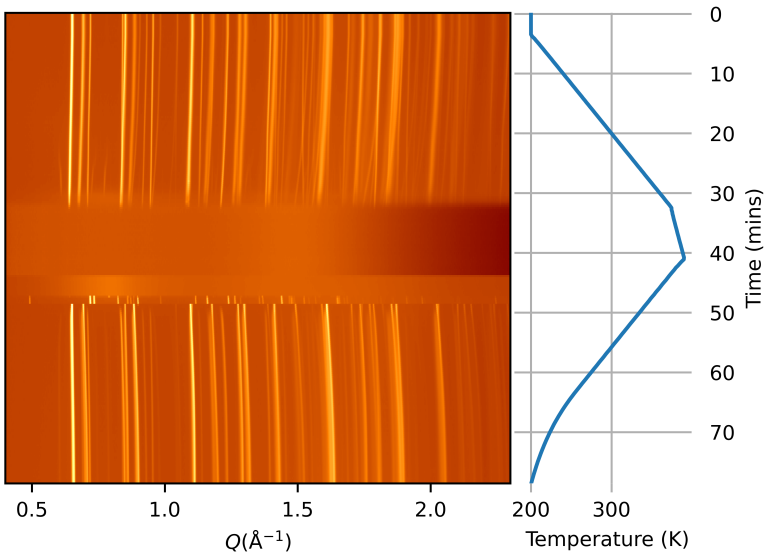

Figure S16: In-situ synchrotron XRD data for $TPA_{0.5}TBA_{0.5}FBC$.

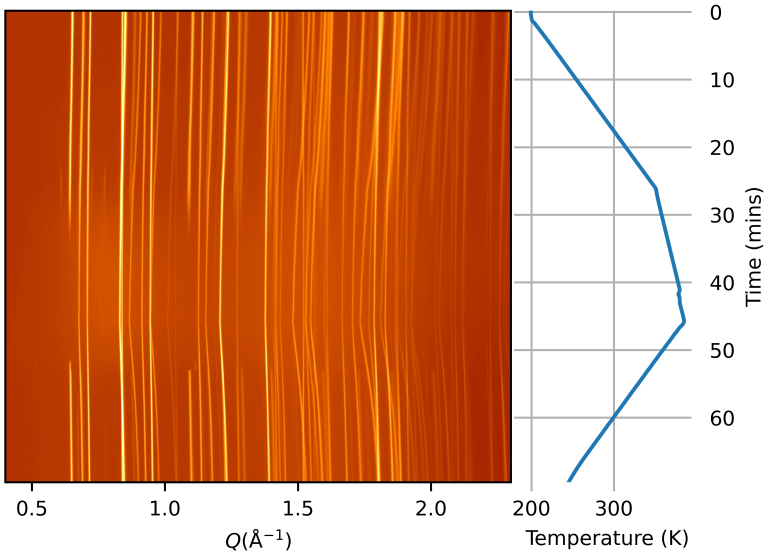

Figure S17: In-situ synchrotron XRD data for $TPA_{0.8}TBA_{0.2}FBC$.

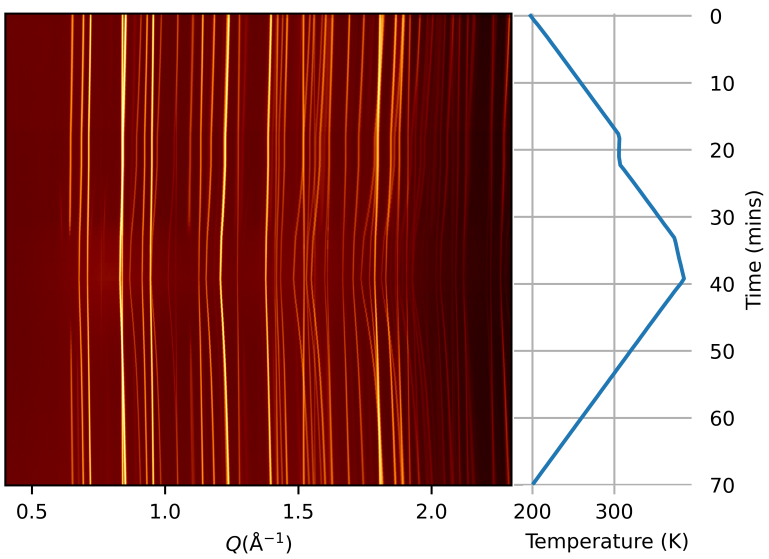

Figure S18: In-situ synchrotron XRD data for $TPA_{0.9}TBA_{0.1}FBC$.

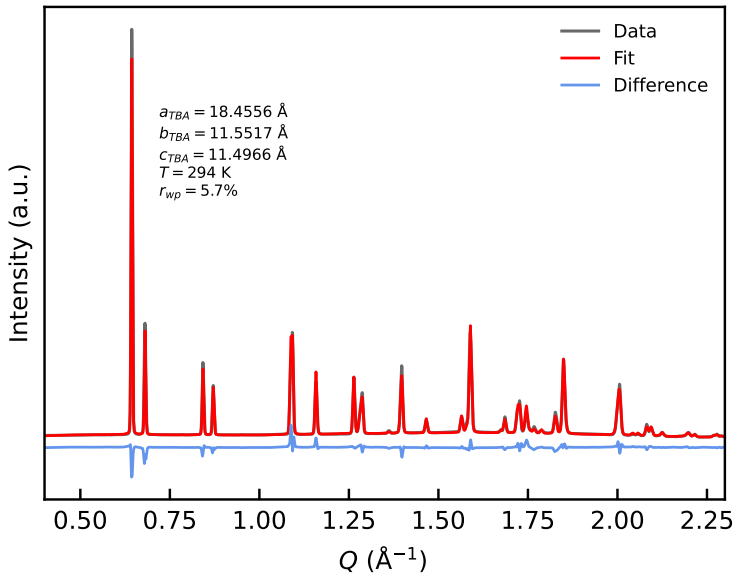

Figure S19: XRD data and fitted structure from Rietveld refinement of $TPA_{0.1}TBA_{0.9}FBC$. The data was fitted with the TBA FBC *Pnna* structure.

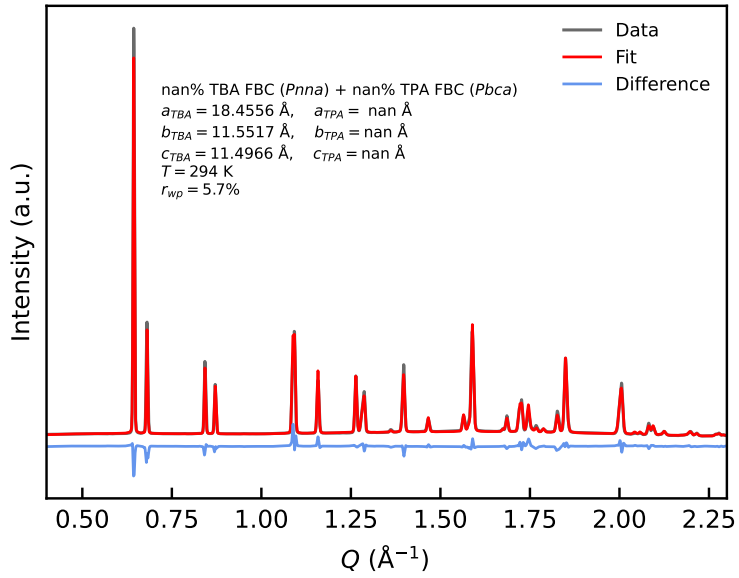

Figure S20: XRD data and fitted structure from Rietveld refinement of $TPA_{0.5}TBA_{0.5}FBC$. The data was fitted with the TBA FBC *Pnna* and TPA FBC *Pbca* structure. Both phases are assumed to exist as a solid solution with guest molecules from the other phase.

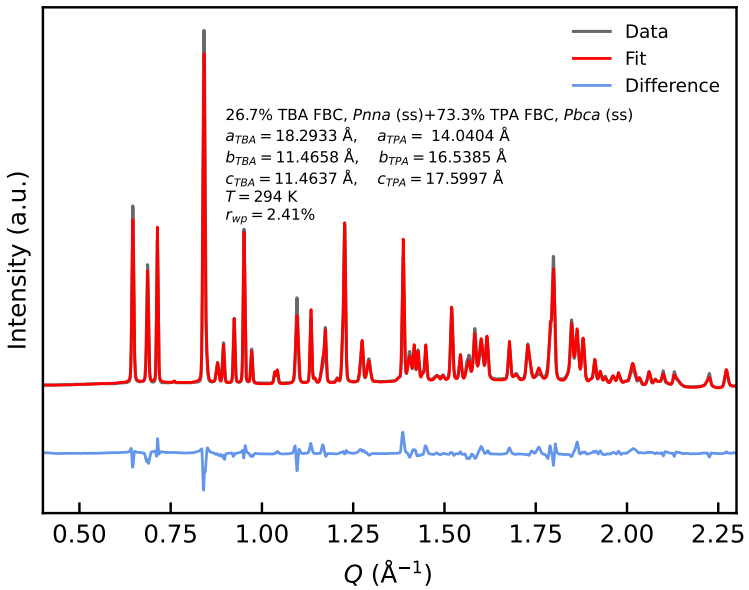

Figure S21: XRD data and fitted structure from Rietveld refinement of $TPA_{0.8}TBA_{0.2}FBC$. The data was fitted with the TBA FBC *Pnna* and TPA FBC *Pbca* structure. Both phases are assumed to exist as a solid solution with guest molecules from the other phase.

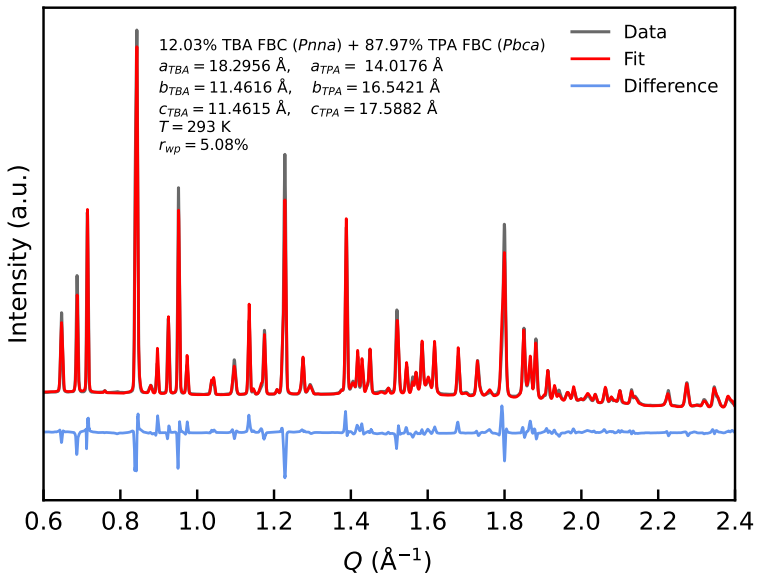

Figure S22: XRD data and fitted structure from Rietveld refinement of $TPA_{0.9}TBA_{0.1}FBC$. The data was fitted with the TBA FBC *Pnna* and TPA FBC *Pbca* structure. Both phases are assumed to exist as a solid solution with guest molecules from the other phase.

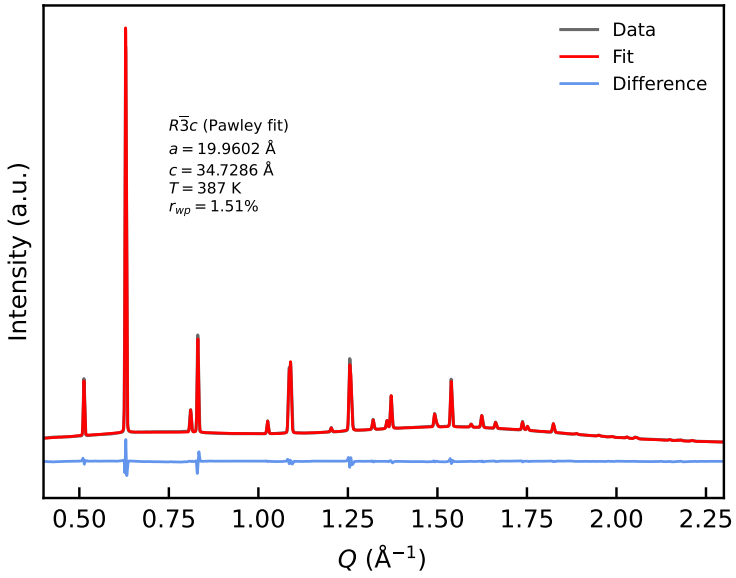

Figure S23: XRD data and Pawley fit of $TPA_{0.1}TBA_{0.9}FBC$ high-temperature plastic crystal phase.

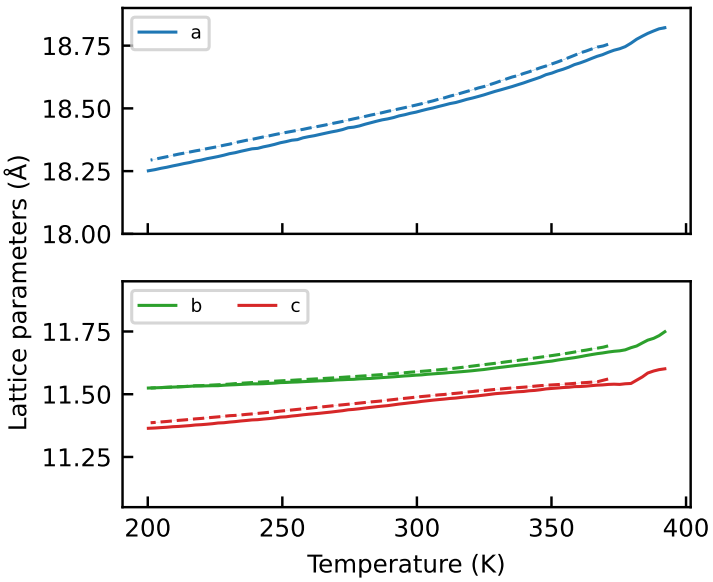

Figure S24: TBA FBC (*Pnna*) Lattice parameters from Rietveld refinement of in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

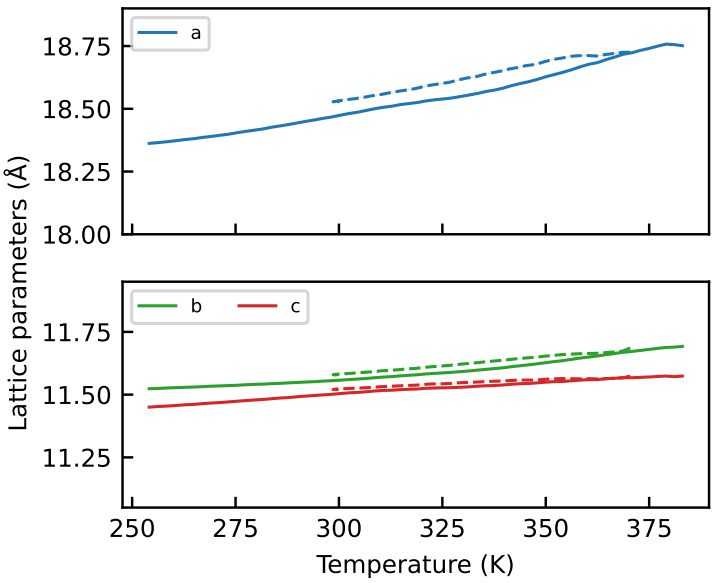

Figure S25: TBA FBC (*Pnna*) Lattice parameters from Rietveld refinement of $TPA_{0.1}TBA_{0.9}FBC$ in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

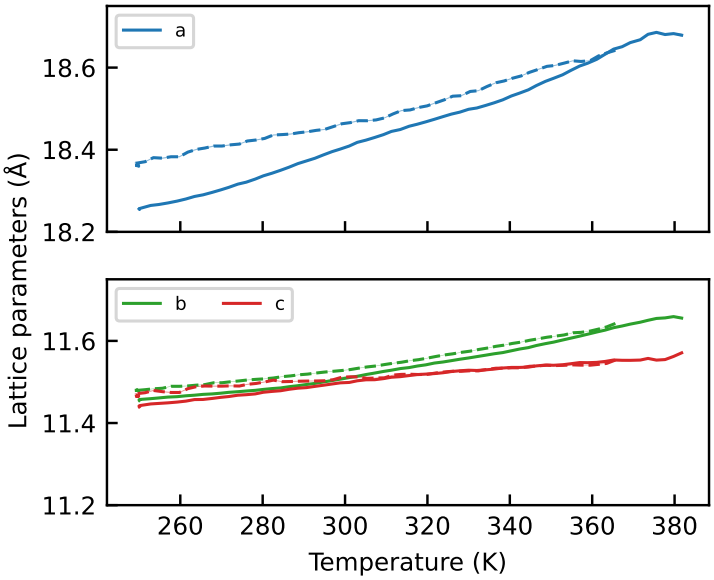

Figure S26: TBA FBC (*Pnna*) Lattice parameters from Rietveld refinement of $TPA_{0.2}TBA_{0.8}$FBC in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

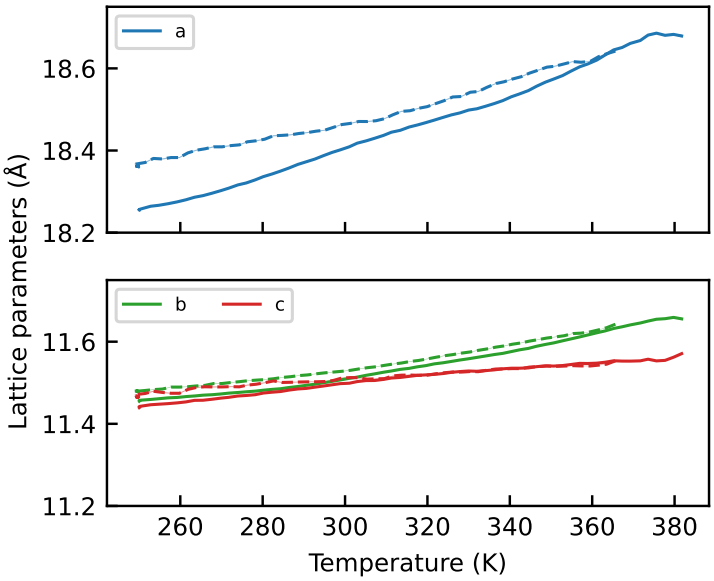

Figure S27: TPA FBC (*Pbca*) Lattice parameters from Rietveld refinement of $TPA_{0.2}TBA_{0.8}$FBC in-situ XRD data. Solid lines denote heating data. The TPA FBC diffraction lines disappeared upon heating and did not reappear on cooling.

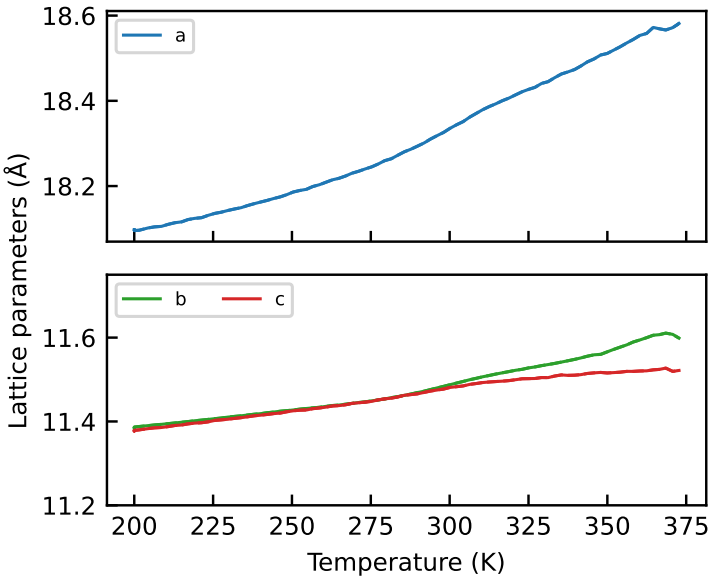

Figure S28: TBA FBC (*Pnna*) Lattice parameters from Rietveld refinement of $TPA_{0.5}TBA_{0.5}FBC$ in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

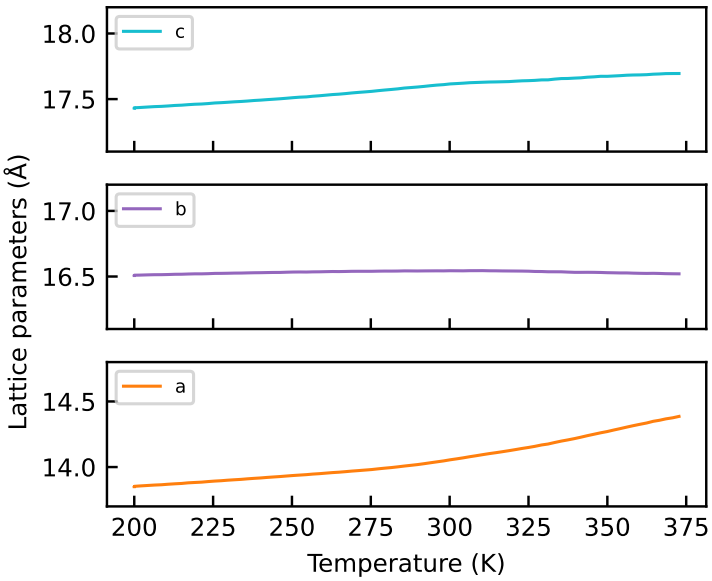

Figure S29: TPA FBC (*Pbca*) Lattice parameters from Rietveld refinement of $TPA_{0.5}TBA_{0.5}FBC$ in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

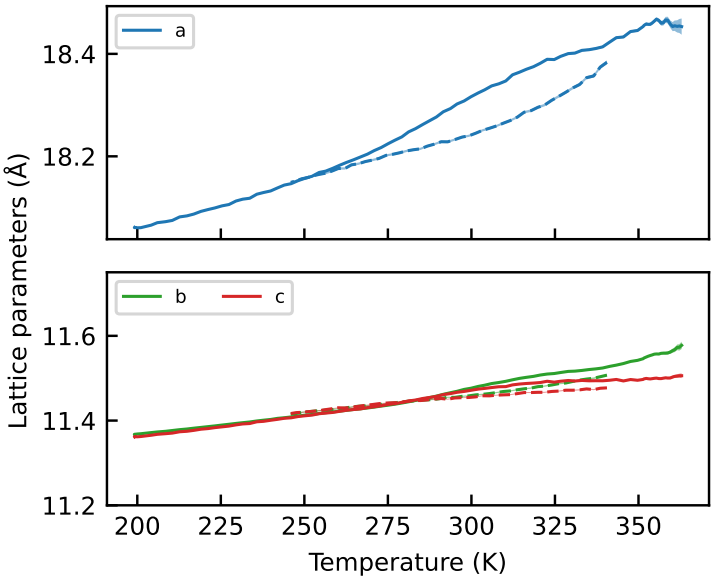

Figure S30: TBA FBC (*Pnna*) Lattice parameters from Rietveld refinement of $TPA_{0.8}TBA_{0.2}FBC$ in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

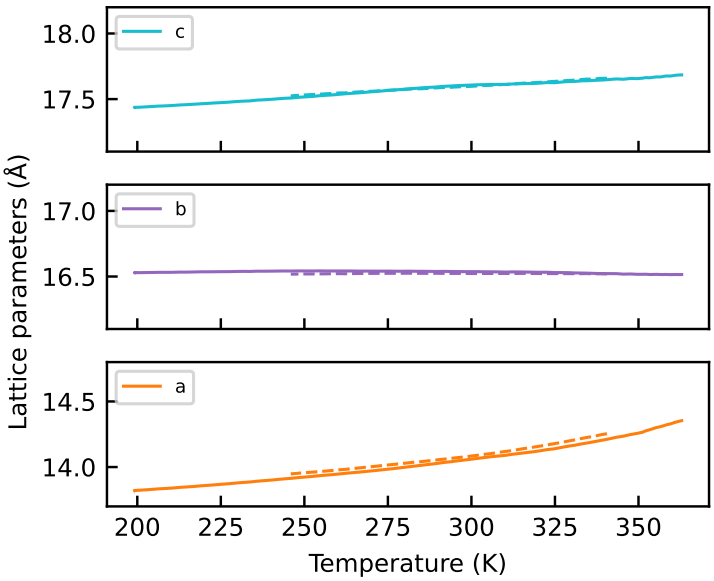

Figure S31: TPA FBC (*Pbca*) Lattice parameters from Rietveld refinement of $TPA_{0.8}TBA_{0.2}FBC$ in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

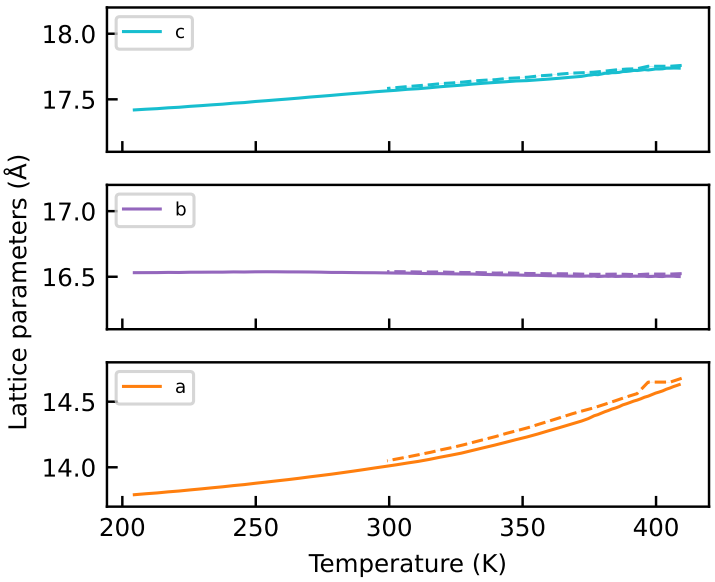

Figure S32: TPA FBC (*Pbca*) Lattice parameters from Rietveld refinement of in-situ XRD data. Solid lines denote heating data, and dashed lines denote cooling data. A break occurs in the data because the diffraction lines disappeared and reappered during the experiment.

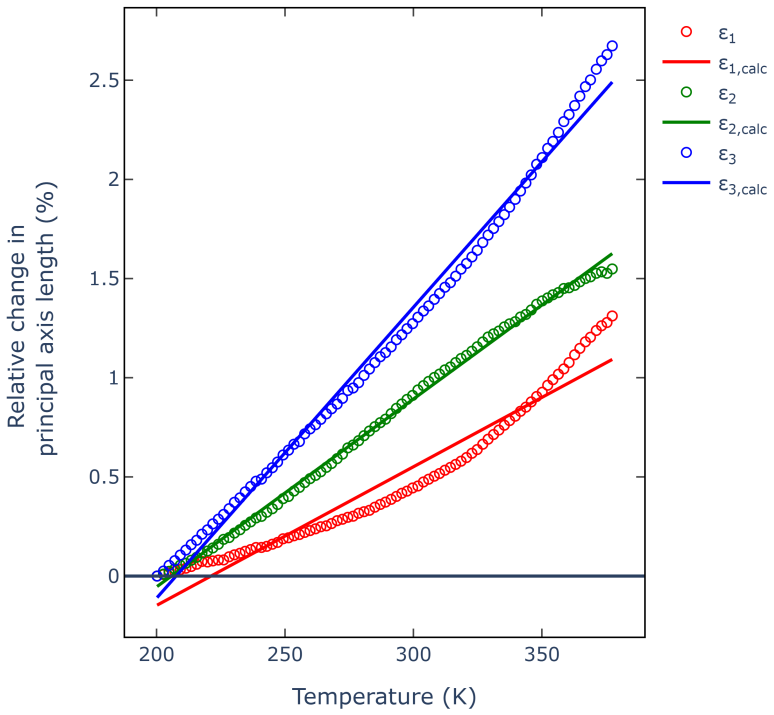

Figure S33: Relative change in principal axis length for TBA FBC (*Pnna*), calculated with PASCal.

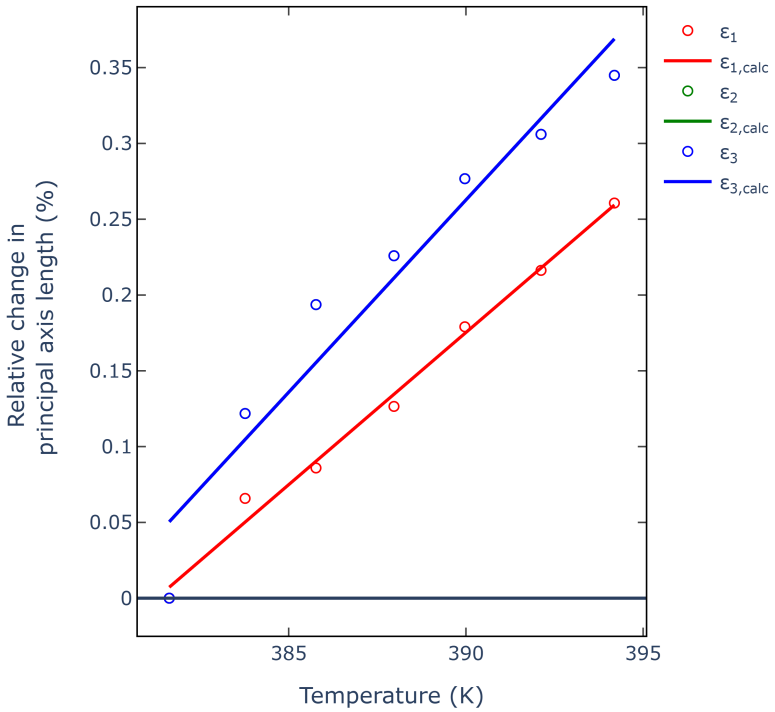

Figure S34: Relative change in principal axis length for TBA FBC ($R\bar{3}c$), calculated with PASCal.

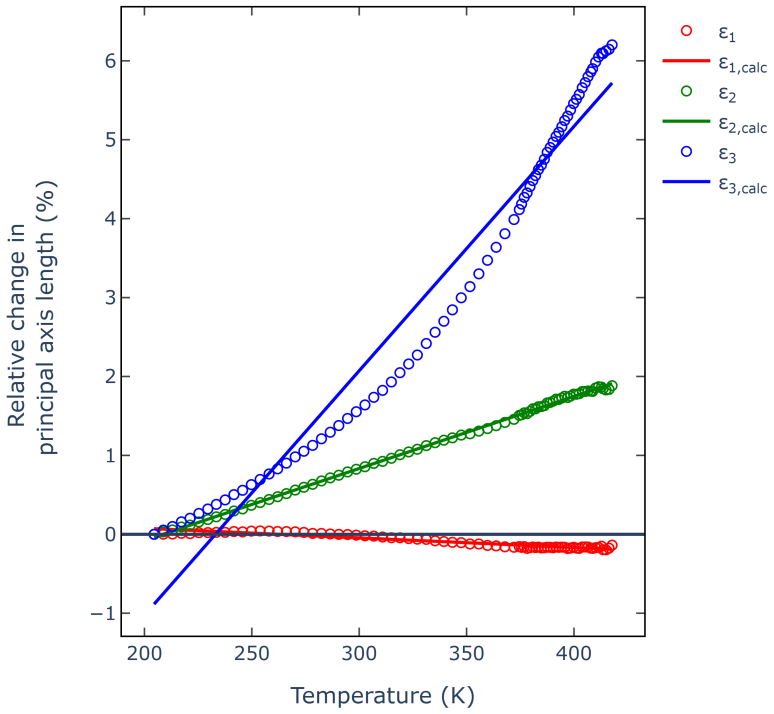

Figure S35: Relative change in principal axis length for TPA FBC, calculated with PASCal.

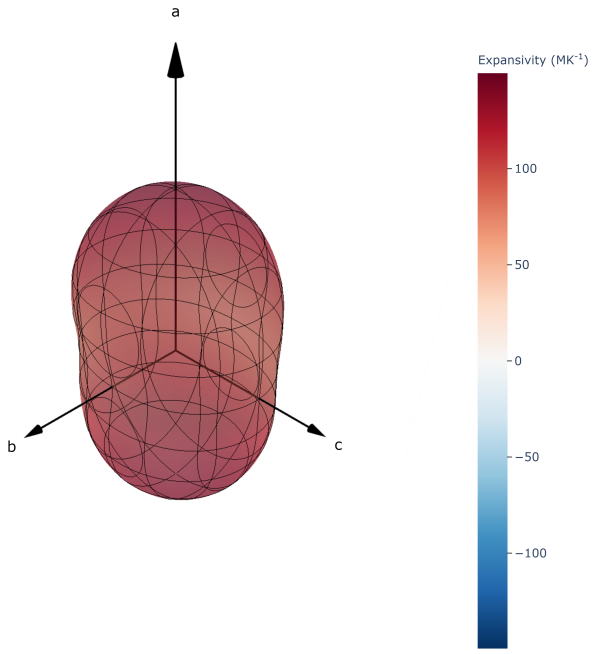

Figure S36: Indicatrix plot (visual representation of principal axis thermal expansion coefficients) for TBA FBC (*Pnna*), derived from PASCal.

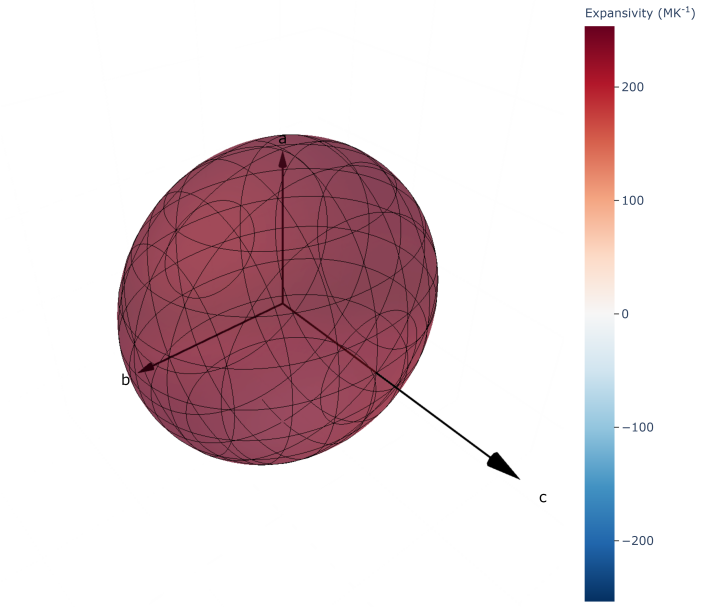

Figure S37: Indicatrix plot (visual representation of principal axis thermal expansion coefficients) for TBA FBC (*Pnna*), derived from PASCal.

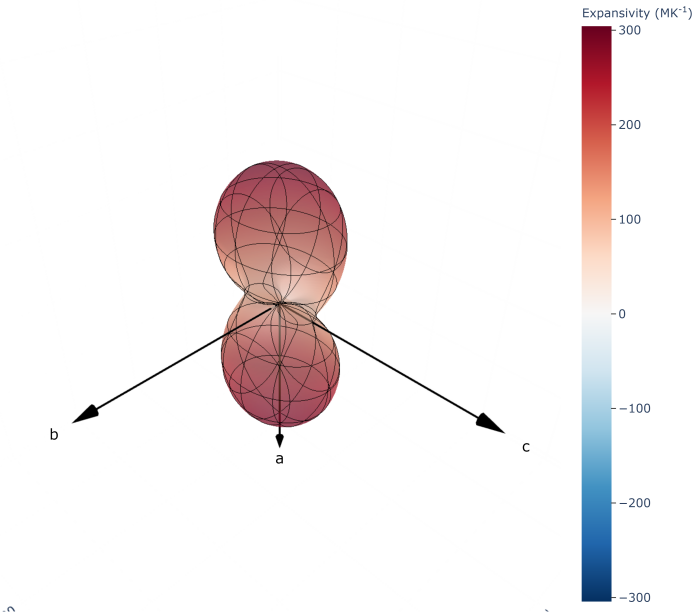

Figure S38: Indicatrix (visual representation of principal axis thermal expansion coefficients) plot for TPA, derived from PASCal.