

Supplementary Information

Nanoscale crystallization and thermal behaviour of 1,2,4,5-tetrabromobenzene

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Materials and methods

Materials: 1,2,4,5-Tetrabromobenzene (TBB) powder (97%, Sigma Aldrich) and toluene (HPLC grade, VWR Chemicals) were used to prepare the TBB crystals. Anodic aluminum oxide (AAO) membranes (Whatman Anodisc) with diameter of 13 mm, thickness of 60 μm , and pore size of 20, 100 and 200 nm were used as templates for fabricating cylindrical TBB nanocrystals. Sodium hydroxide (98%, Sigma Aldrich) was used for dissolving the AAO templates. The water used throughout all experiments was purified through a Millipore system (Milli-Q Integral 10).

Preparation of TBB crystals: A saturated solution of TBB in toluene was prepared at room temperature and filtered to remove any dust particles. The filtrate was transferred to amber vials which were then covered with aluminum foil. The vials were incubated at 50 $^{\circ}\text{C}$ for a week. This resulted in formation of prismatic crystals with dimensions ranging from few tens of microns to several hundred microns.

Preparation of TBB nanocrystals: Due to extremely low solubility of TBB in organic solvents, it was not possible to synthesize TBB nanocrystals by solution-casting in AAO templates. Thus, they were fabricated by melt-casting—by filling the AAO templates directly with molten TBB. The as-received AAO templates were sonicated in acetone and dried at 70 $^{\circ}\text{C}$ to remove any organic contaminants. In a typical process, the AAO template was sandwiched between small amounts of TBB crystals which were covered with microscopic glass slides. The whole assembly was placed directly on a hot plate preheated to 180 $^{\circ}\text{C}$. Within couple of minutes, the TBB crystals completely melted and filled the nanopores of AAO. Once the template became fully transparent and showed uniform distribution of the melt across the template, the assembly was removed from the hot plate and allowed to cool at room temperature. The extra frozen material on the AAO templates was cleaned by carefully scraping off with a scalpel blade until the template surface became smooth and shiny. The templates were then cleaned with pressurized nitrogen gas to remove any remaining debris. The rapid cooling from 180 $^{\circ}\text{C}$ to room temperature was necessary to trap the TBB melt inside the AAO nanopores; in our preliminary experiments, slow crystallization by gradual cooling of the AAO templates covered with TBB melt was not effective in filling the templates, and all TBB crystallized over the AAO template. In order to release the TBB nanocrystals, the AAO templates were immersed in 3 M aqueous sodium hydroxide for 3 hours. This resulted in formation of colorless opalescent suspension which was then filtered through Whatman Grade 4 filter paper. The filtrate was then washed at least 5 times with deionized water to obtain pure suspension of TBB nanocrystals in water. The fabrication procedure is schematically illustrated in Figure S1. The pH of the final suspension was found to be in the range of 7 to 8 by using pH paper, which confirmed almost complete removal of sodium hydroxide.

Morphological analysis: The morphology of the AAO templates and TBB nanocrystals was examined with FEI Scios scanning electron microscope (SEM) using the beam accelerating voltage and current of 5 kV and 25 pA, respectively. Due to charging issues, the surface of the AAO templates was coated with a thin layer of gold prior to the SEM analysis whereas the TBB nanocrystals were analyzed without any conductive coating.

FTIR analysis of TBB nanocrystals: The FTIR spectra of TBB nanocrystals were recorded using Model 670 IR spectrometer (Agilent) by directly drop-casting an aqueous suspension of TBB nanocrystals on to the diamond lens of the spectrometer. The water was allowed to completely evaporate until the lens surface was fully covered by TBB nanocrystals and the IR spectrum was collected in the transmission mode.

X-ray diffraction (XRD) analysis: X-ray microdiffraction (μ XRD) was performed on a D8 Discover GADDS microdiffractometer (Bruker) equipped with a VÅNTEC-2000 two-dimensional (2D) detector and a sealed Cu X-ray tube. The generated X-rays were monochromated with a graphite crystal and collimated with a 0.5 mm MONOCAP, which provided a focused spot beam ($\lambda = 1.54 \text{ \AA}$). The AAO template was mounted in a horizontal configuration on a sample stage affixed to an Eulerian $\frac{1}{4}$ cradle (Figure S3, left). The positions of the AAO membranes were aligned with aid of a laser-video accessory. Measurements were performed with ϑ_1 (incident angle of the X-ray beam) = ϑ_2 (detector angle) = 14° . The sample-to-detector distance was 150 mm and the exposure time was set to 10 minutes. The samples remained still during the data collection. This provided 2D microXRD (2D- μ XRD) patterns for the vertically aligned TBB nanocrystals inside the AAO templates. One-dimensional XRD (1D-XRD) patterns were generated by integrating the 2D-XRD images over the entire range of azimuthal angle ($\delta = 220\text{--}320^\circ$) and at the 2ϑ range of $10\text{--}49^\circ$ using the XRD2EVAL program (version 2009.5-0; Bruker AXS Inc., Madison, WI, 2009). In order to get the complete information of the TBB phase formed inside the AAO pores, the filled AAO membranes were gently crushed into small pieces and loaded in 0.8 mm Kapton capillaries for recording their PXRD patterns. For comparison, the PXRD patterns were also recorded in flat stage configuration (Figure S3, right) for the bulk TBB crystals used for loading the AAO pores. The temperature during the XRD measurements was controlled using DCS 350 Stage (Anton Paar) affixed to an Eulerian $\frac{1}{4}$ cradle (Figure S3, right). The PXRD patterns for the TBB filled crushed AAO templates and the bulk TBB crystals at -90°C and -170°C were recorded using D8 SMART APEXII single crystal diffractometer (Bruker) equipped with an APEXII CCD detector and a sealed Mo X-ray tube. The generated X-ray was monochromated with a graphite crystal and collimated with a 0.5 mm MONOCAP, which provided a focused spot beam ($\lambda = 0.71 \text{ \AA}$). The temperature was controlled using 700+ Cooler (Oxford Cryosystems). The finely ground powder of TBB crystals and each TBB-filled AAO template was filled in a 0.8 mm Kapton capillary for the measurements which were performed with $2\vartheta = -12^\circ$ and $\omega = -6^\circ$. The sample-to-detector distance was 150 mm while the exposure time was set to 5 or 2 minutes. The capillary spun 179° along the ϕ axis during the data collection.

Thermal analysis of TBB nanocrystals: The thermal behaviour of TBB nanocrystals was analyzed by heating the nanocrystals on a glass hot plate and viewed with optical microscope (Nikon LV100) using 100x lens. Thermogravimetric analysis (TGA) was performed using Simultaneous Thermal Analyzer SDT Q600 (TA Instruments) in the temperature range of 25 to 225°C at a heating rate $10^\circ\text{C}/\text{min}$. The measurements were performed on TBB-filled AAO templates placed in an aluminium pan. The differential scanning calorimetry (DSC) experiments were performed using TAM IV nanocalorimeter (TA Instruments) in the temperature range of 25 to 140°C while maintaining the heating rate at $2^\circ\text{C}/\text{h}$. The measurements were performed on isolated TBB nanocrystals that were loaded into the 1 mL glass ampules by directly transferring the concentrated aqueous suspension of TBB nanocrystals into the ampules. The nanocrystals were allowed to settle at the bottom of the ampules overnight followed by complete removal of water from the ampules by slow evaporation at 40°C overnight. The low-temperature DSC experiments were performed using DSC Q2000 (TA Instruments) in the temperature range of 25 to -150°C at a cooling rate $1^\circ\text{C}/\text{h}$. The measurements were performed on TBB nanocrystals loaded directly into the aluminium pan.

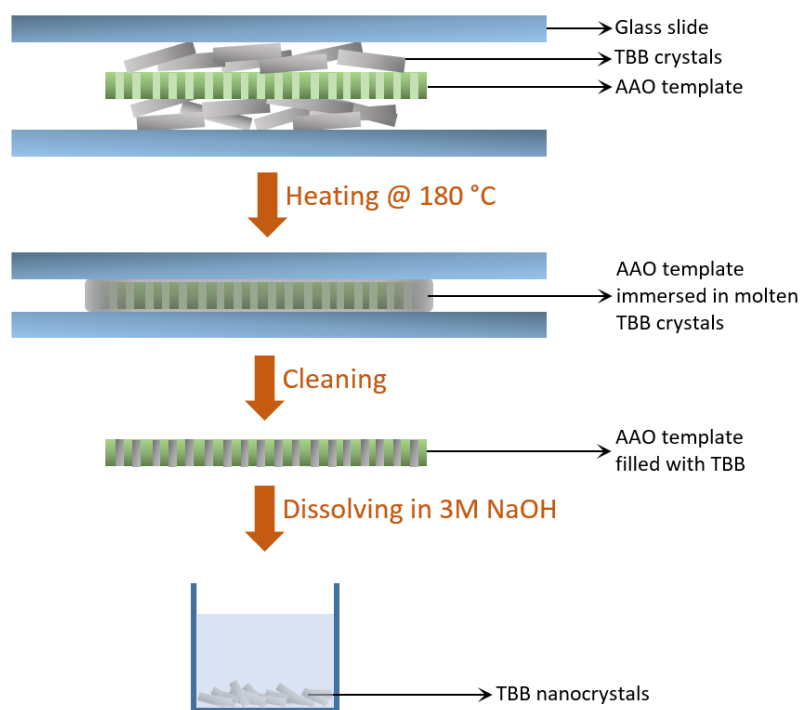


Figure S1. Schematic of the procedure used to fabricate TBB nanocrystals.

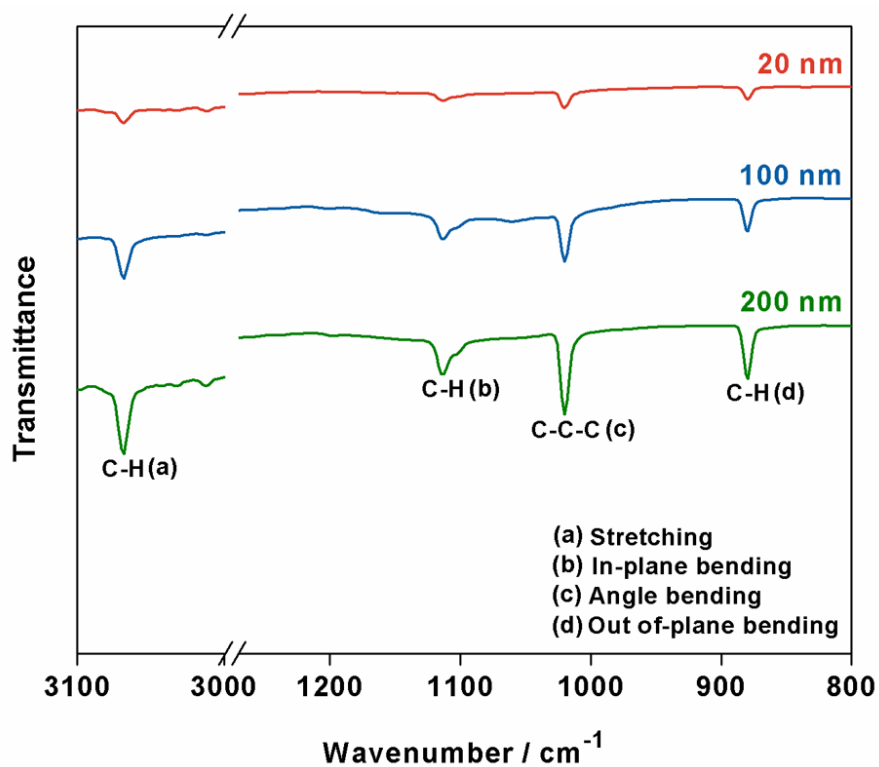


Figure S2. FTIR spectra of TBB nanocrystals with varying diameter.

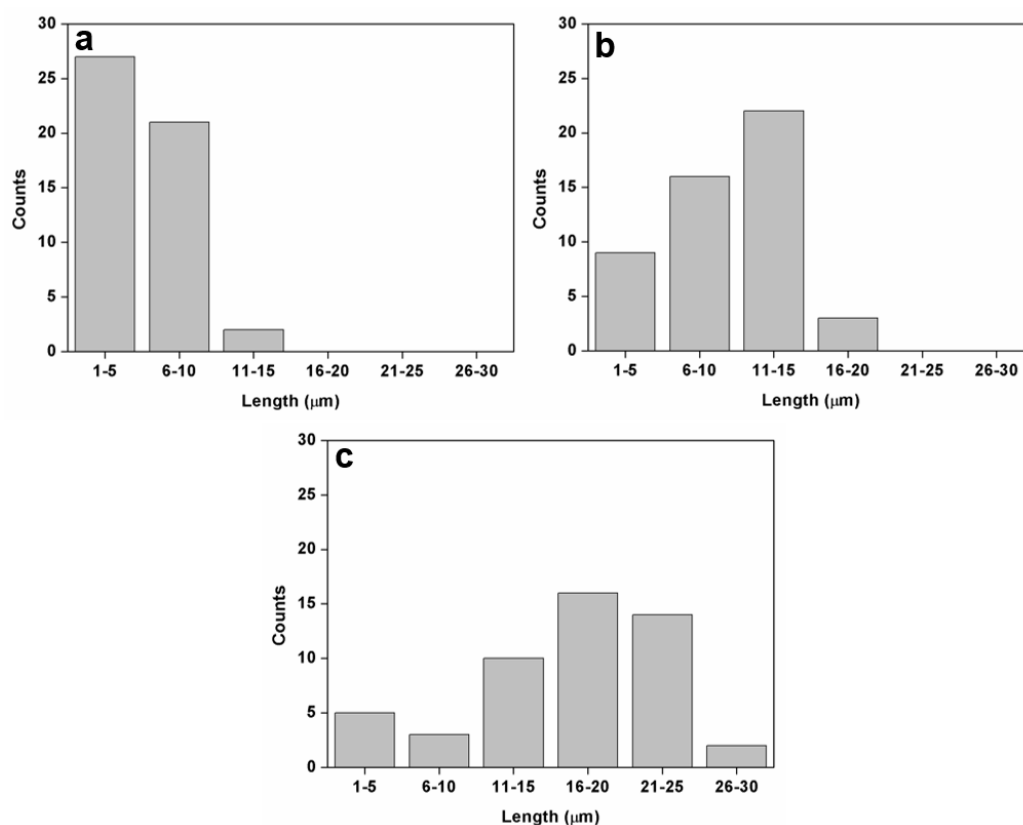


Figure S3. Histograms showing the length distribution of TBB nanocrystals having a diameter of (a) 20 nm, (b) 100 nm and (c) 200 nm (sample size = 50).

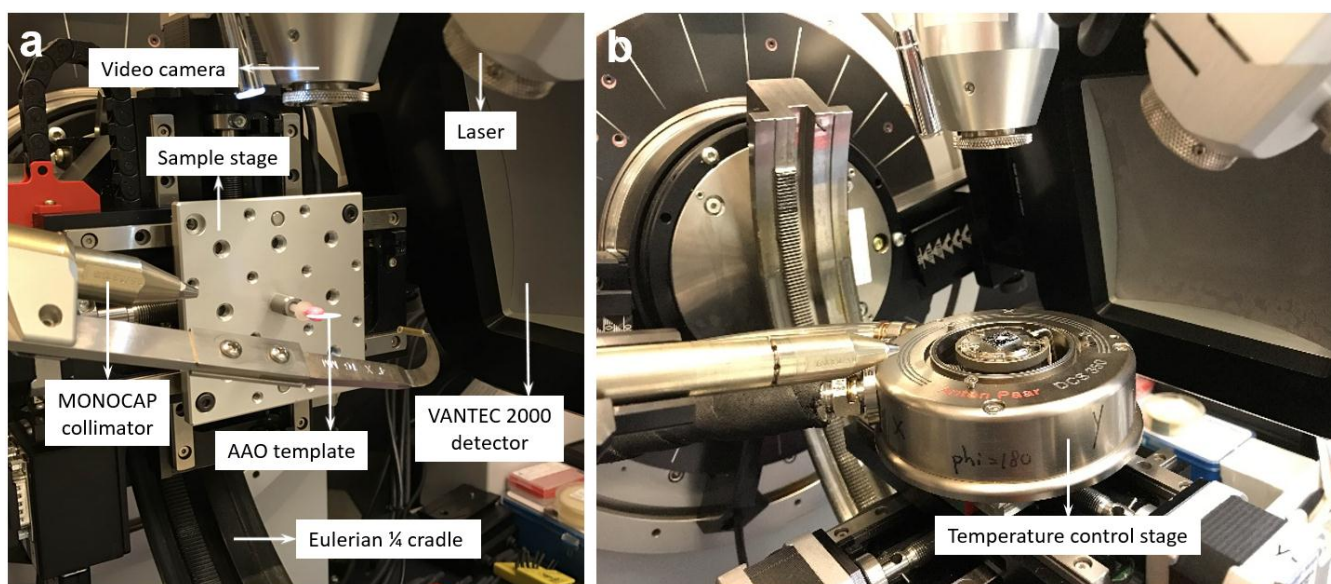


Figure S4. Setups for Bruker D8 Discover GADDS X-ray microdiffractometer used to study the TBB nanocrystals inside AAO templates (a) and the temperature control stage used for low- and high-temperature XRD measurements (b).

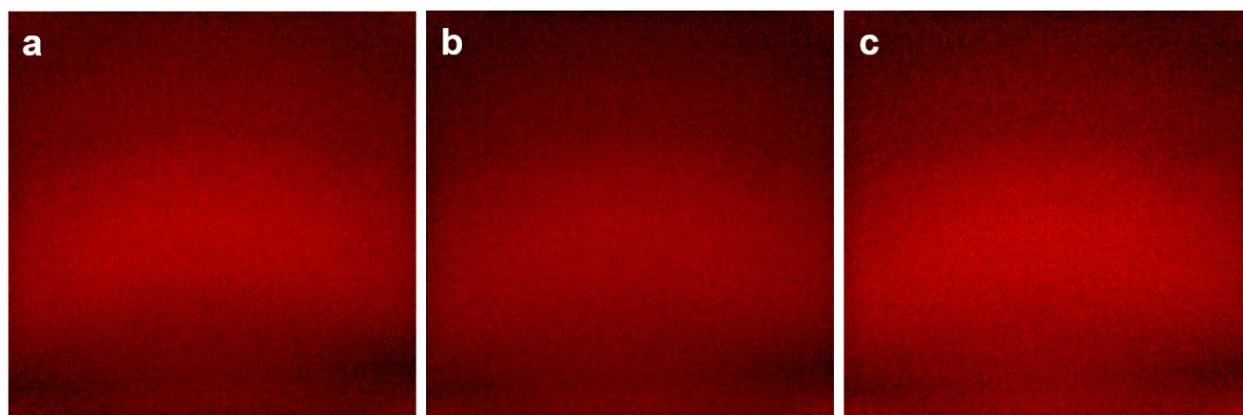


Figure S5. 2D- μ XRD images collected from empty AAO templates with pore size of 20 nm (a), 100 nm (b), and 200 nm (c) in horizontal configuration.

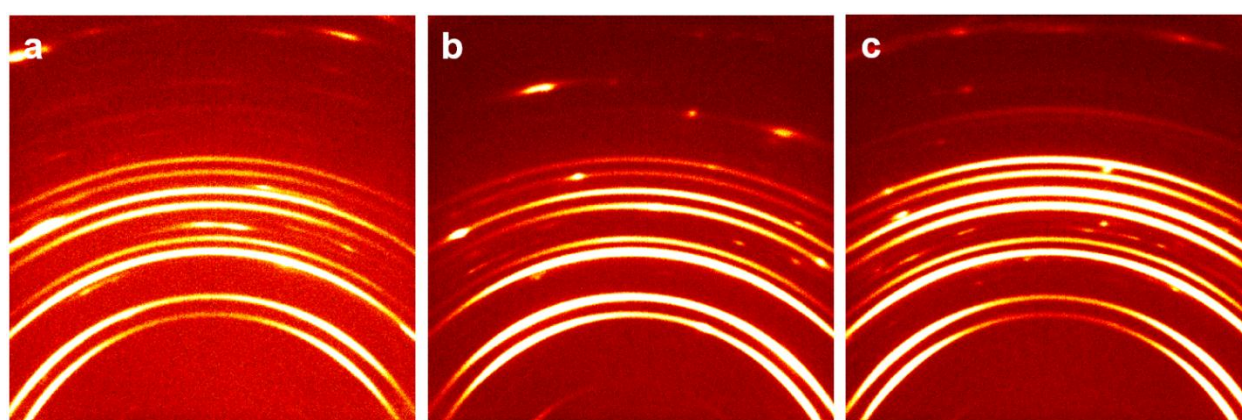


Figure S6. 2D- μ XRD images collected from TBB-filled AAO templates with pore size of 20 nm (a), 100 nm (b), and 200 nm (c) in vertical configuration.

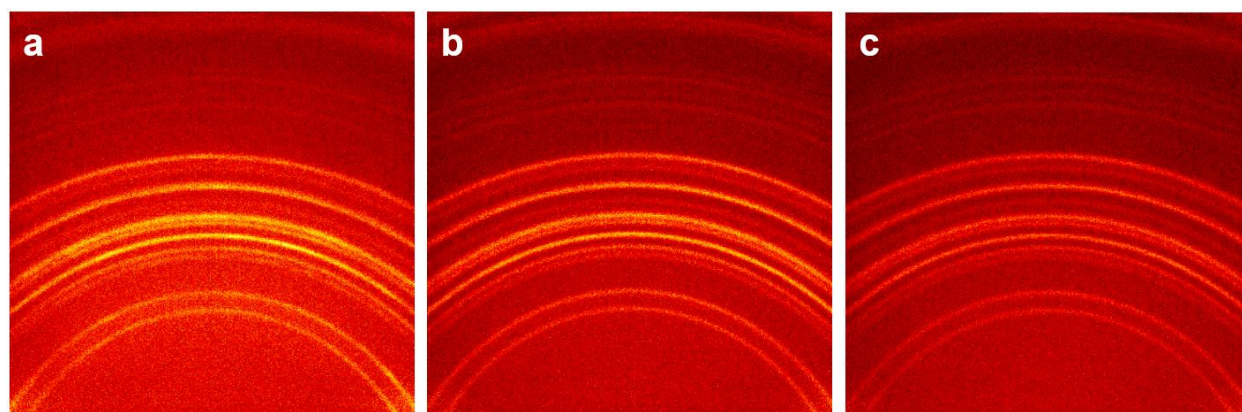


Figure S7. 2D- μ XRD images collected from crushed TBB-filled AAO templates with pore size of 20 nm (a), 100 nm (b), and 200 nm (c) in capillary.

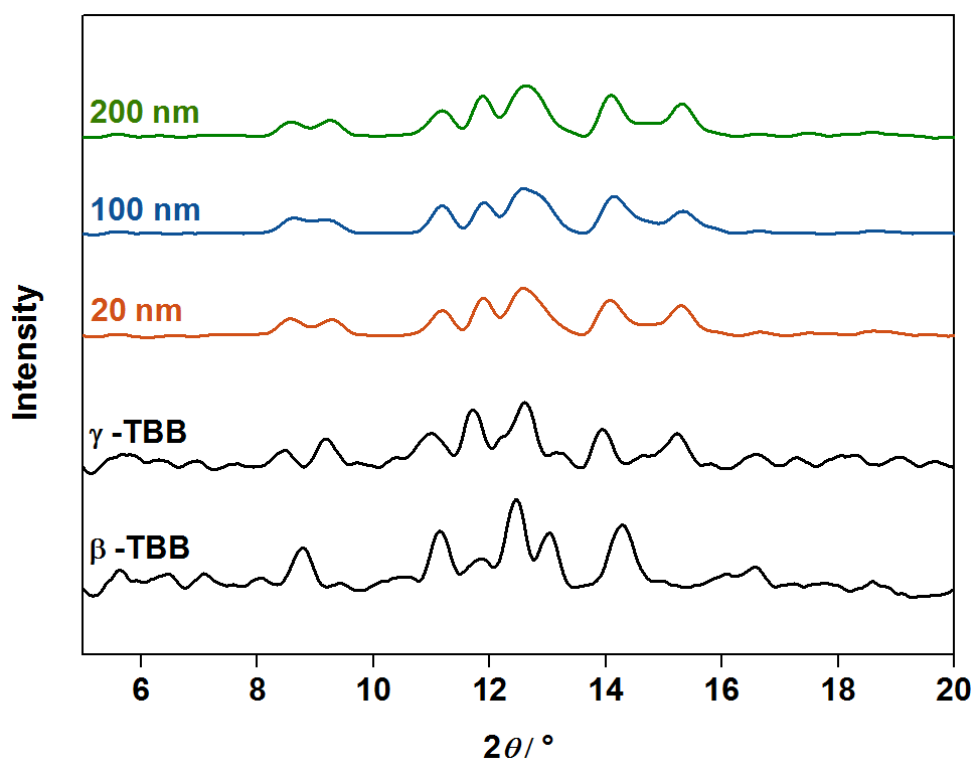


Figure S8. PXRD patterns of crushed AAO templates of varying pore size filled with TBB at $-170\text{ }^{\circ}\text{C}$. The PXRD patterns of the bulk TBB crystals in β and γ phase are also shown for comparison. The data was collected using $\text{MoK}\alpha$ radiation ($\lambda = 0.71\text{ \AA}$).

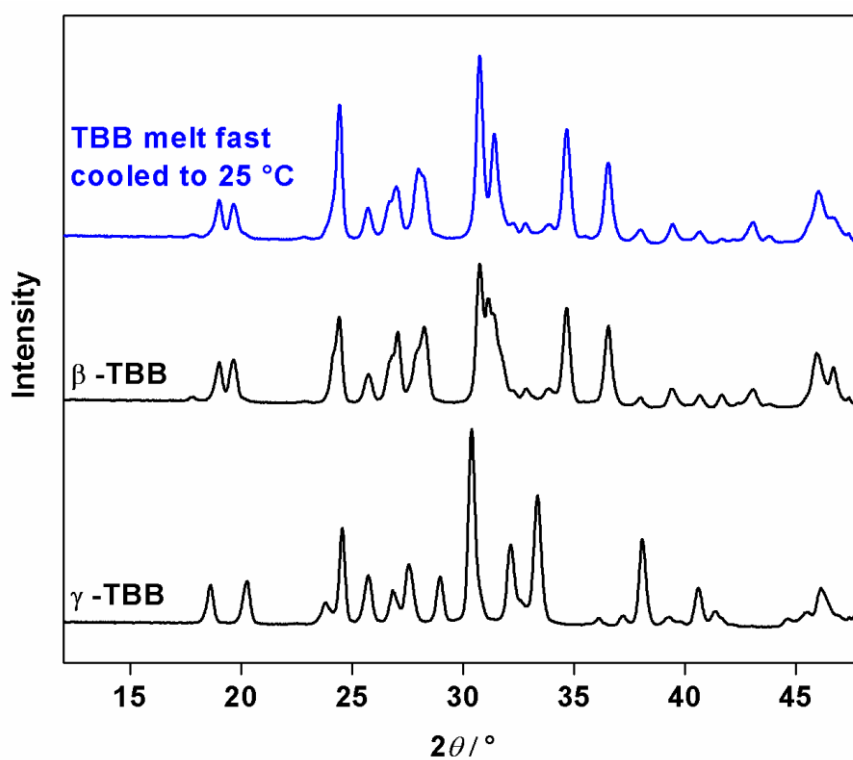


Figure S9. PXRD pattern of TBB crystals obtained after rapid solidification of TBB melt. PXRD patterns for the β and γ phase TBB crystals are also shown for comparison. The data was collected using $\text{CuK}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$).

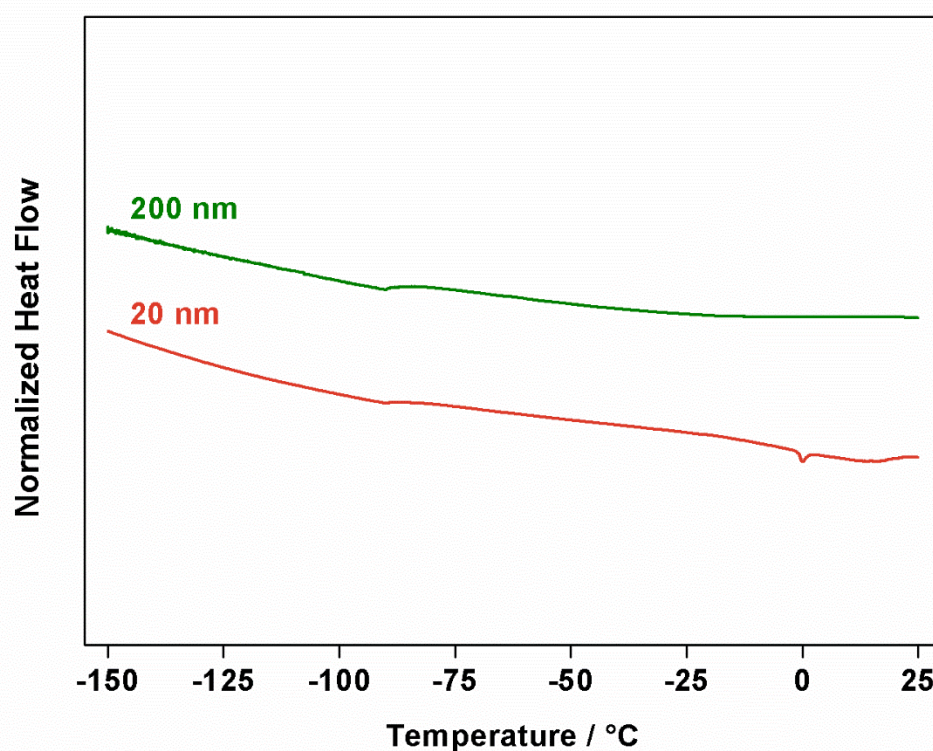


Figure S10. Low-temperature DSC curves for 20 and 200 nm TBB nanocrystals. The small peak around 0 °C is due to melting of frost, and the plateau-like feature around -90 °C is an artifact that was also observed when an empty aluminum pan was used as a sample.

Legends to the supplementary movies

Movie S1. Sublimation of 100 nm TBB nanocrystals.

Movie S2. Sublimation of 200 nm TBB nanocrystals.