Electronic Supplementary Material (ESI) for CrystEngComm.

Laser-induced nucleation promotes crystal growth of anhydrous sodium bromide

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Supporting Information

1. Sample vials

Samples were prepared using two sizes of glass vial: small vials with a nominal volume of 4 mL and a diameter of 15 mm, which were filled with approximately 2 mL of solution; and large vials with a nominal volume of 7 mL and a diameter of 20 mm, which were filled with approximately 5 mL of solution. The size of the vial did not significantly affect the mean pulse energy densities or peak power densities.

2. Laser parameters

Laser	Wavelength / nm	Pulse duration / ns	Beam diameter / mm
Continuum Surelite II-10	532	5.0	3.0
Quantel Brilliant	1064	5.6	4.0

Table S1. Laser wavelengths, pulse durations and beam diameters used during NPLIN experiments. Beam diameters were achieved using a Galilean telescope.

Laser	Pulse energy density / J cm^{-2}			Peak power density / GW cm^{-2}		
	Incident	Exit	Mean	Incident	Exit	Mean
Continuum Surelite II-10	1.0	2.5	1.7	0.18	0.45	0.32
Quantel Brilliant	0.60	1.5	1.1	0.10	0.25	0.18

Table S2. Pulse energy densities and peak power densities used during NPLIN experiments. The power was controlled using a Glan-laser polarizer. The cylindrical shape of the vials caused them to act as a lens, slightly focusing the beam. The energy densities at the exit point of the vials were determined by ray tracing, and the mean energy density and corresponding peak power densities were calculated.

3. Experimental conditions

Concentration *(C)* / mol kg^{-1}	**Temperature (*T*) / °C**	**Supersaturation (*S*)**
11.5	60	1.004 (AH)
11.5	55	1.01 (AH)
11.5	50	1.02 (DH) 1.01 (AH)
11.5	45	1.06 (DH) 1.01 (AH)
10.0	21	1.12 (DH) 0.89 (AH)
10.9	21	1.22 (DH) 0.97 (AH)
11.5	21	1.29 (DH) 1.02 (AH)

Table S3. Summary of experimental solution conditions, showing concentrations, temperatures and supersaturations. Supersaturations are given with respect to the anhydrous (AH) and dihydrate (DH) solid forms of sodium bromide at each condition.

Temperature (*T*) / °C	**$C_{sat}(T)$ [DH] / mol kg^{-1}**	**$C_{sat}(T)$ [AH] / mol kg^{-1}**
21 (in H_2O) 21 (in D_2O)	8.93 8.80	11.29 10.83
60		11.46
55		11.42
50	11.28	11.39
45	10.82	11.36

Table S4. Saturation concentrations (C_{sat}) obtained from fitting solubility data of Eddy and Menzies, J. Phys. Chem. 1940, **44** (2), 207–235. The solid crystal form is indicated (AH = anhydrous; DH = dihydrate).

4. Seeding procedures

Solutions were seeded using crystals from a sample of solid AH sodium bromide (Acros Organics, ≥ 99%). One to three crystals (size < 0.5 mm) were picked using tweezers and dropped into a vial containing solution with concentration C = 11.5 mol kg^{-1} at T = 21 °C where the supersaturation was S = 1.29 (DH) or 1.02 (AH). Examples of the seeding process are shown in videos S1 and S2.

5. X-ray analysis

Crystals were extracted from solutions using hot tweezers and quickly transferred to an inert oil (Paratone or Fomblin). Single crystal X-ray diffraction was carried out using an Rigaku Oxford Diffraction SuperNova diffractometer with Atlas detector. Data collection and refinement were obtained using CrysAlis PRO 1.171.40.84a (Rigaku Oxford Diffraction, 2020), XT (Sheldrick, 2015), XL (Sheldrick, 2008) and Olex2 (Dolomanov et al., 2009). The solid form (AH or DH) was verified by single crystal diffraction. DH crystals were stable during the collection and a full dataset could be collected; however, it was found that AH crystals degraded rapidly once isolated from the sample solution and a full dataset could not be collected. Data sufficient for indexing purposes was collected and the unit cell obtained was consistent with the expected cell for AH NaBr as shown in Tables S5 and S6, respectively. The data are included with this Supporting Information as a zipped file **NaBr_XRD_data.zip**.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339-341; Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112-122; Sheldrick, G. M. (2015). *Acta Cryst.* **A71**, 3-8.

Chemical formula	$NaBr.2H_2O$
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature	120 K
a, *b*, *c*	6.5805(4), 10.3617(4), 6.7018(4) Å
β	114.303(7)°
V	416.47(4) $Å^3$
Z	4
μ	9.78 mm^{-1}
Crystal size	0.43 × 0.20 × 0.03 mm
Crystal description	plate, colourless
Formula mass M_r	138.93 g mol^{-1}

Table S5. Data from single-crystal X-ray analysis for sodium bromide dihydrate (DH).

Chemical formula	NaBr
Crystal system	Cubic
Space group	Fm-3m
Temperature	120 K
a	5.9291(3) Å
V	208.43(2) $Å^3$
Z	4
μ	2.45 mm^{-1}
Crystal size	0.35 × 0.33 × 0.28 mm
Crystal description	block, colourless
Formula mass M_r	102.90 g mol^{-1}

Table S6. Data from single-crystal X-ray analysis for anhydrous sodium bromide (AH).

5. Supporting videos

Video S1. Seeding of a sample vial of NaBr in H_2O showing slow growth of plate-like crystals. Solution conditions: C = 11.5 mol kg^{-1}, T = 21 °C, S = 1.29 (DH) or 1.02 (AH).

Video S2. Similar to Video S1, but showing fast growth of plate-like crystals.

Video S3. Nucleation of NaBr in H_2O by mechanical shock, showing plate-like crystals growing from the solution–air interface. Solution conditions: C = 11.5 mol kg^{-1}, T = 21 °C, S = 1.29 (DH) or 1.02 (AH).

Video S4. Example of nucleation of NaBr by mechanical shock, showing plate-like crystals growing throughout the solution. Solution conditions: C = 11.5 mol kg^{-1}, T = 21 °C, S = 1.29 (DH) or 1.02 (AH).

Video S5. Example of nucleation of NaBr in D_2O by laser-trapping. The location of the laser focus is indicated by the red circle (laser spot size is not to scale). The horizontal field of view is 120 μm. Solution conditions: C = 9.51 mol kg^{-1}, T = 21 °C, S = 1.08 (DH) or 0.88 (AH).