

SI1 Materials and methods

MIL-103(Sm) was synthesized following a literature procedure (Micro. Meso. Mater. 2011, 140, 25-33): 1 mmol of 1,3,5-Tris(4-carboxyphenyl)benzene (Sigma-Aldrich) and 1 mmol $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to 12.5 ml water and 1 ml of a 2M NaOH solution in a 50 ml Schott[®]-bottle. After stirring for 2 min, 12.5 ml of 50 °C cyclohexanol was added. After stirring the solution for 10 min, the Schott[®]-bottle was closed and placed in an oven at 100°C for 5 days. MIL-103 was recovered as a beige solid by filtration and extensively washed with water and ethanol after which the material was measured with SHG-microscopy.

The light source is a Ti:Sapphire laser (Spectra-Physics, Tsunami, ~100 fs pulses with a repetition rate of 80 MHz). The wavelength of 800 nm is chosen. A Glan-Taylor polarizer is placed in the beam path, after which a zero-order half wave plate for 800 nm (Thorlabs) is placed. Via rotation the half wave plate the plane of polarization of the laser light incident on the sample is chosen. A long pass red filter (Schott, RG665, 1mm) blocks transmittance of second-harmonic light generated by the optics earlier in the beam path and inside the laser. A lens ($f = 7.5\text{cm}$) is positioned such that the spot illuminated in the sample plane has a diameter of ~ 500 μm . The sample is placed in a stage that can rotate in the sample plane. The following parts are part of an inverted microscope (Olympus, IX71): the objective, a filter carousel and a tube to which the camera is connected. As objective a 15x objective with a N.A. of 0.32 (Thorlabs, LMU-15X-NUV) was used. The filter set for the second-harmonic light consists of a band pass filter (Schott, BG39, 2mm) and an interference filter (Melles-Griot, F10-400, centre wavelength 400 nm, FWHM 10 nm). If applicable, a Glan-Taylor analyzer was placed in front of the filter set. The transmitted light is detected by an EM-CCD camera (Hamamatsu, C9100-13). Data were collected and analyzed with the HoKaWo software package provided with the camera. For the measurements in which the sample was rotated, the images were aligned with the plug-in Stackreg for ImageJ (IEEE

Transactions on Image Processing 1998, 7, 27-41). Calculations and simulations were performed with Mathematica.