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Elucidation of crystal growth mechanism of melamine-cyanuric acid by using real time *in situ* atomic force microscopy.

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Electronic Supplementary Information

Materials. M, CA, sodium citrate (Sigma-Aldrich, St. Louis, MO, USA) and citric acid monohydrate (BDH, West Chester, PA, USA) were purchased and used as obtained without further purification. All solutions were prepared using deionized water purified by a Direct-Q 3 water purification system purchased by Millipore (Molsheim, France).

Hydrothermal M-CA crystallization. M-CA crystals were prepared by a hydrothermal method, in which 15 ml of a solution of 0.1 mmol of M and 0.1 mmol of CA were placed in a Parr acid digestion vessel (Parr Instrument Company, Moline, IL, USA) with a stainless steel body and a 45 ml Teflon PTFE removable liner. The solution was maintained at 180 ^{o}C for one hour in a SS-00AB gravity and mechanical convection oven purchased from MTI Corporation and cooled slowly over four hours to room temperature.

Buffer preparation. Buffer solutions were prepared by dissolving citric acid and sodium citrate in deionized water, adjusting opportunely the pH to a value of 4 ± 0.1 with addition of citric acid or sodium citrate and measuring it using an Orion-3 Star pH meter purchased by Thermo Electron Corporation (Beverly, MA, USA).

M-CA growth solution for AFM experiments. Growth solutions of M-CA were prepared by dissolving 0.02 mmol of M and 0.02 mmol of CA in 50 ml of buffer solution at 180 ^{o}C for 2 hours under reflux.

AFM. M-CA crystals prepared by hydrothermal method were harvested by filtration of the crystallization media and then transferred to a specimen disk that had been coated with partially cured (approximately 45 seconds under a Blak-RayB100 bulb at a distance of 6 in.) UV-curable thiolene adhesive (NOA-81, Norland Products, Inc.). After surplus particles on the disk were removed using a gentle nitrogen gas stream, the optical cement was completely cured by exposing the specimen to UV radiation for another 2min. The azimuthal orientation of the crystals with respect to the AFM image frame was identified using an optical microscope above the AFM cell. In situ AFM was performed in buffered solutions by contact mode using a Nanoscope IIIa Multimode system (Digital Instruments, Santa Barabara, CA, USA), a quartz glass liquid cell, a J-scanner (Digital Instruments, Santa Barabara, CA, USA) with a maximum *x*-*y* scan range of 125 μm, and a Si_3N_4 cantilever tip with a force constant of approximately 0.12 N/m.

X-ray single crystal diffraction. Single crystal X-ray diffraction was performed by Dr. Chunhua Hu of the Department of Chemistry X-ray diffraction facility at New York University. A M-CA crystal (0.05 × 0.05 × 0.84 mm_3) was selected for geometry and intensity data collection with a Bruker SMART ApexII CCD area detector on a D8 goniometer at 100 K. The temperature during the data collection was -173 ˚C, and it was controlled with an Oxford Cryosystems Series 700 plus instrument. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. The crystal faces were determined by APEXII/Crystal Faces (APEX II, version 2009.5). Data were collected using graphite-monochromated and 0.5mm-MonoCap-collimated Mo-Kα radiation (λ = 0.71073 Å) with the ω scan method (APEX II, version 2009.5). Data were processed with the SAINT+ program (SAINT+, version 7.60A) for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SADABS program for area detector. The structure was solved by the direct method (SHELXS-97) and refined on F2 (SHELXL-97). Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.93 or 0.96 Å) and included as riding with Uiso(H) = 1.2 or 1.5 Ueq(non-H).