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Calcium-based coordination polymers from a solvothermal synthesis of HKUST-1 in 3D printed autoclaves

Petr V. Primakov, Gleb L. Denisov, Valentin V. Novikov, Olga L. Lependina, Alexander A. Korlyukov and Yulia V. Nelyubina

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3D-printing of autoclaves. Open-source program OpenSCAD[S1] was used to model a cylindrical autoclave with a spherical cavity (Figure S1) in a SCAD format, which was then converted to a solid-body STL format.[S2] The volume of the spherical cavity was 1 ml, and all walls around it were at least 6 mm thick. Resulting STL model was sliced in Simplify3D program[S3] and prepared for 3D printing in GCODE.[S4]

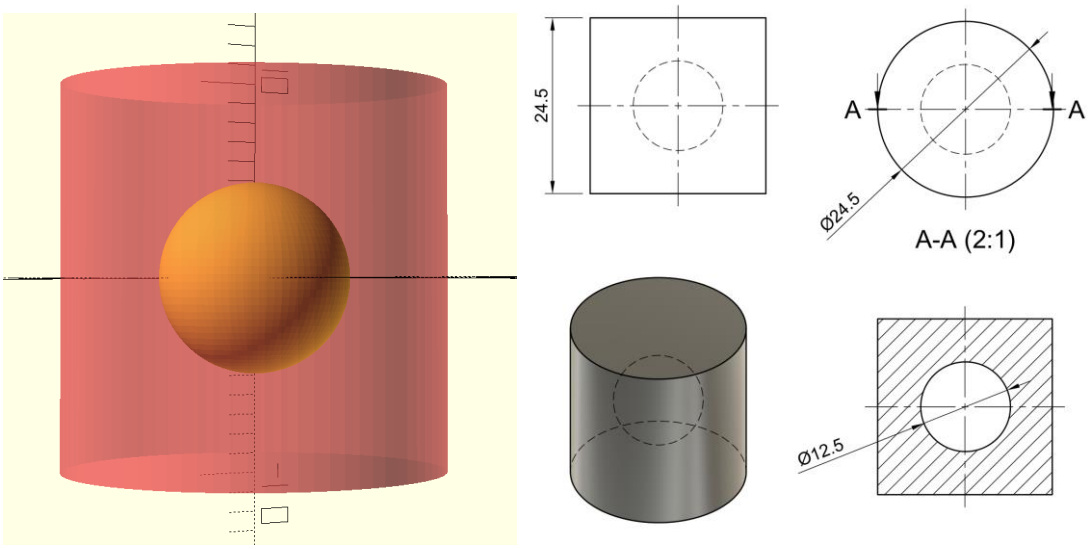

Figure S1 3D model of an autoclave in OpenSCAD program and its blueprint.

As a filament for 3D printing, polypropylene FL-33 (white) with a softening point around 160°C[S5] obtained commercially from top3Dshop[S6] as a standard 1 kg spool of polypropylene filament 1.75 mm in diameter (country of origin: China, no other information is available), was chosen owing to its high chemical and thermal stability under solvothermal conditions typically used for metal-organic frameworks (120°C, DMF).[S7] As its drawback, however, no sharp corners are allowed in an autoclave and it should be 3D-printed at a low speed, which results in a printing time for a single autoclave up to 5 hours. A poor adhesion of polypropylene to surfaces traditionally used for 3D-pronting, such as a warmed glass or a masking tape, requires the use of a cutting board made from polypropylene with a thickness of 5 mm as a printing bed during 3D-printing, complicating the separation of a finished autoclave from the surface of this bed.

For the 3D-printing of the autoclaves, Magnum 2 Uno printer[S8] was used with a maximum printing speed of 900 mm/min and a hot-end temperature of 230°C with each layer started from a random position. The other parameters of 3D-printing: the printing bed temperature of 25°C; nozzle diameter of 0.4 mm, layer height of 0.2 mm; concentric outer line form, 100%, 4 lines; wiggle inner line form, 100%; extrusion multiplier of 1.05.

The 3D-printing process was paused at about of 80% printing time to allow manually placing the reagents (see below) into an autoclave with a micropipette and then continued normally until the autoclave is properly seals. After this, the autoclaves were separated from the cutting board and moved to a heating oven, where they were heated to 55°C[S9] with a heating rate of 200°C/h, kept at this temperature for 3 days and then cooled to the room temperature with a cooling rate of 6°C/h. Cooled autoclaves were destructively opened using a hand-saw.

Synthesis. All synthetic manipulations were carried out on air. Solvents were purchased from commercial sources and purified by distilling from conventional drying agents under an argon atmosphere prior to use. In all cases, a modified procedure for the synthesis of **HKUST-1** reported to produce large single crystals was used.[S9]

HKUST-1 + 2: $Cu(OAc)_2 \cdot H_2O$ (20.3 mg, 0.1014 mmol) and H_3BTC (12.0 mg, 0.0571 mmol) were dissolved in 0.45 ml of a 1:1:1 mixture of dimethylformamide, ethanol and water. Then, 0.3 ml of glacial acetic acid were added to the resulting mixture, which was put into a 1ml polypropylene autoclave and heated at 55°C for three days to yield a mixture of blue cubic and pale-green needle-like crystals. They were dispersed in ethanol, and the resulting dispersion was centrifuged and washed with ethanol 10 times. The solid residue was dried in vacuum at room temperature for 4 h and then at 55° for two days in air atmosphere.

***3*:** H_3BTC (12.0 mg, 0.0571 mmol) was dissolved in 0.45 ml of a 1:1:1 mixture of dimethylformamide, ethanol and water. Then, 0.3 ml of glacial acetic acid were added to the resulting mixture, which was put into a 1ml polypropylene autoclave and heated at 55°C for three days to yield a few pale-green needle-like crystals. Yield < 1 mg.

***HKUST-1*:** $Cu(OAc)_2 \cdot H_2O$ (30.4 mg, 0.1521 mmol) and H_3BTC (18.0 mg, 0.0857 mmol) were dissolved in 0.68 ml of a 1:1:1 mixture of dimethylformamide, ethanol and water in a 1.5 ml glass vial. Then, 0.45 ml of glacial acetic acid were added to the resulting mixture, which was put into an autoclave and heated at 55°C for three days to yield blue cubic crystals. They were dispersed in ethanol, and the resulting dispersion was centrifuged and washed with ethanol 10 times. The solid residue was dried in vacuum at room temperature for 4 h and then at 55° for two days in air atmosphere. Yield: 22.4 mg (79%).

Powder X-ray diffraction. The measurements of the dried samples of **HKUST-1 + 2** and **HKUST-1** were carried out using a Bruker D8 Advance diffractometer (λ[CuKα] = 1.5418 Å, Ni filter, Bragg–Brentano geometry, 1D-detector LynxEye) in a Θ/2Θ scanning mode from 4° to 60° with a step size of 0.02°. The data were processed by EVA[S10] and TOPAS 4.2[S11] program packages.

Elemental analysis. The elemental analysis of a polypropylene sample as a 3D-printed 39 mm x 39 mm square was carried out by non-destructive X-ray spectrometry using a FRX PFX-101 spectrometer equipped with LiF200, Ge111 and AXO3 crystals and a rhodium anode X-ray tube operating at 60 kV. Found (%): Si, 2.91; Mg, 3.27; Ca, 0.47; Ti, 0.099. Other elements with a contribution below 10^{-2} — 10^{-3}% are Al, Fe, P and S.

Supplementary References:

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S6. Top3DShop Top3DShop. https://top3dshop.ru/.
S7. P. J. Kitson, S. Glatzel, W. Chen, C.-G. Lin, Y.-F. Song and L. Cronin, *Nature Prot.,* 2016**, *11***, 920.
S8. *Magnum3D*, 2017.
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S11. A. Coelho, *TOPAS 4.2*, Bruker AXS GmbH: Karlsruhe, Germany, 2009.

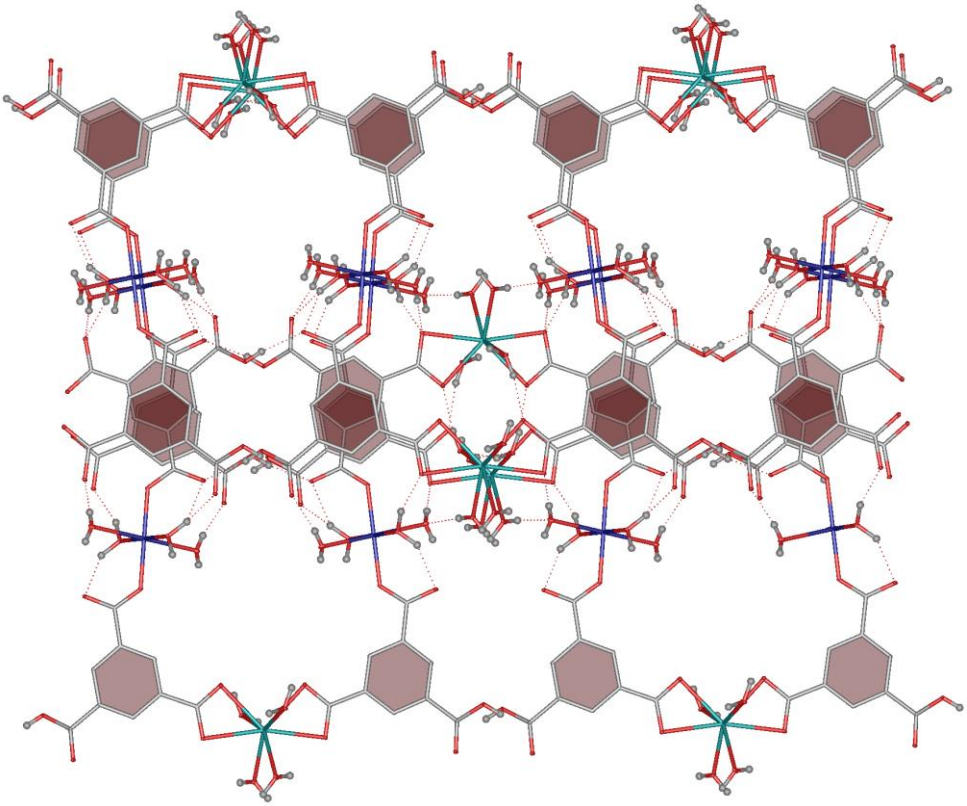

Figure S2 General view of **2** illustrating the formation of a 3D hydrogen-bonded framework from 1D folded polymer chains. Hydrogen bonds are shown by dashed lines, benzene moieties of the anions involved in stacking interactions are highlighted by pink color.

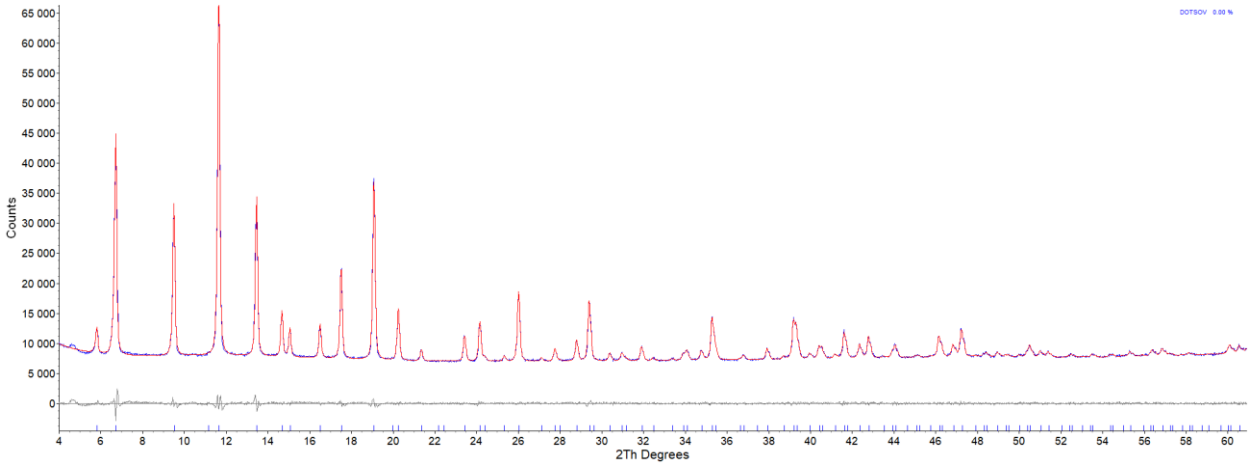

Figure S3 X-ray diffractograms collected from a dried sample of **HKUST-1 + 2** (blue line) and calculated for **HKUST-1** (red line) and their difference (black line).

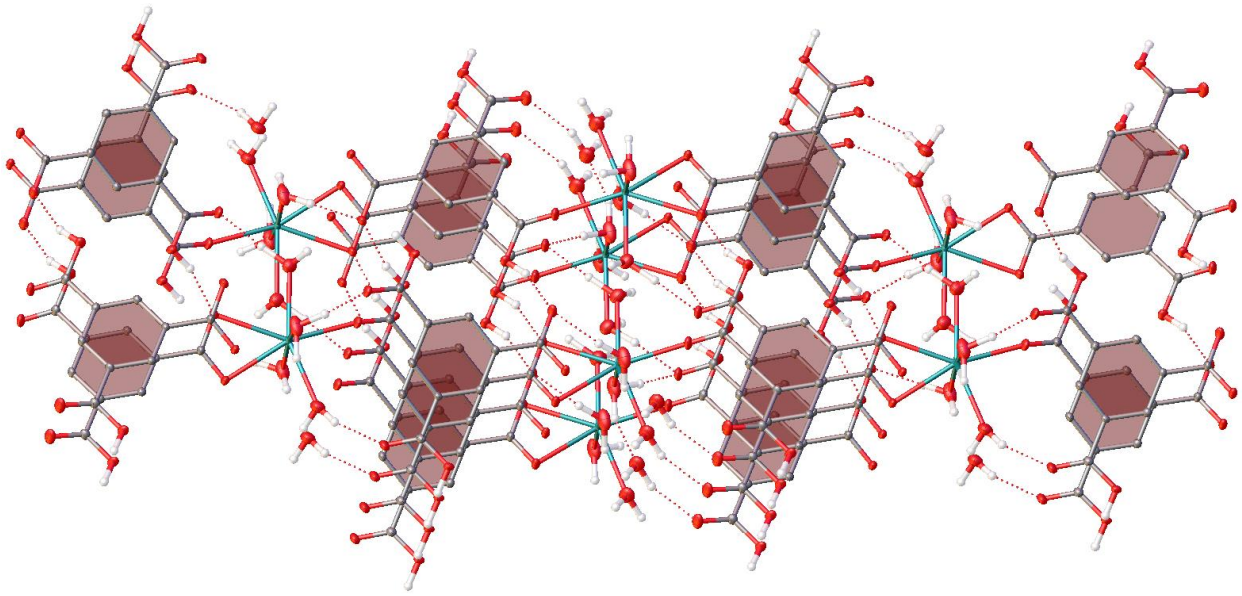

Figure S4 General view of **3** illustrating the formation of a 3D hydrogen-bonded framework from 1D zig-zag polymer chains. Hydrogen bonds are shown by dashed lines, benzene moieties of the anions involved in stacking interactions are highlighted by pink color.

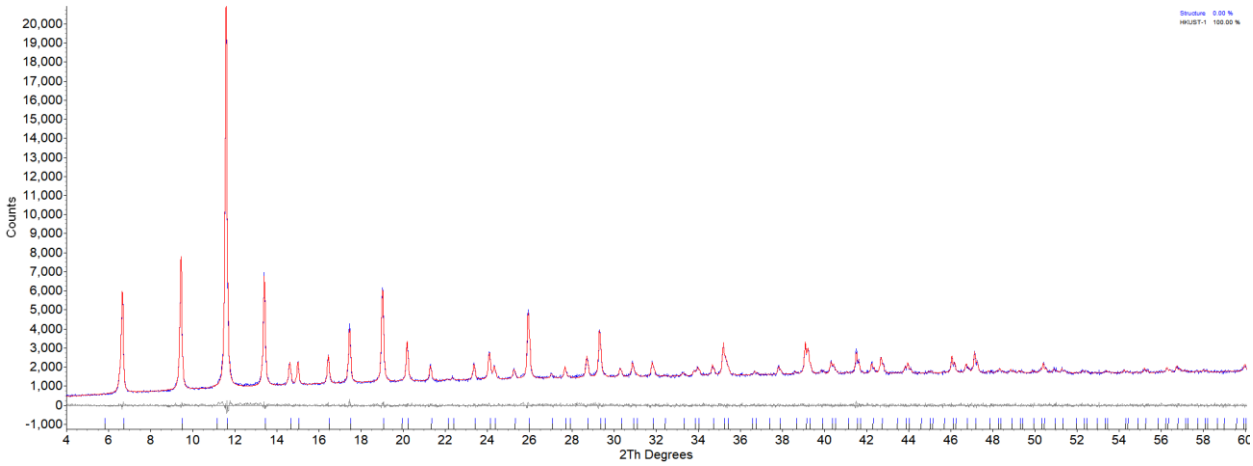

Figure S5 X-ray diffractograms collected from a dried sample of **HKUST-1** (blue line) and calculated for **HKUST-1** (red line) and their difference (black line).