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High-yield, fluoride-free and large-scale synthesis of MIL-101(Cr)

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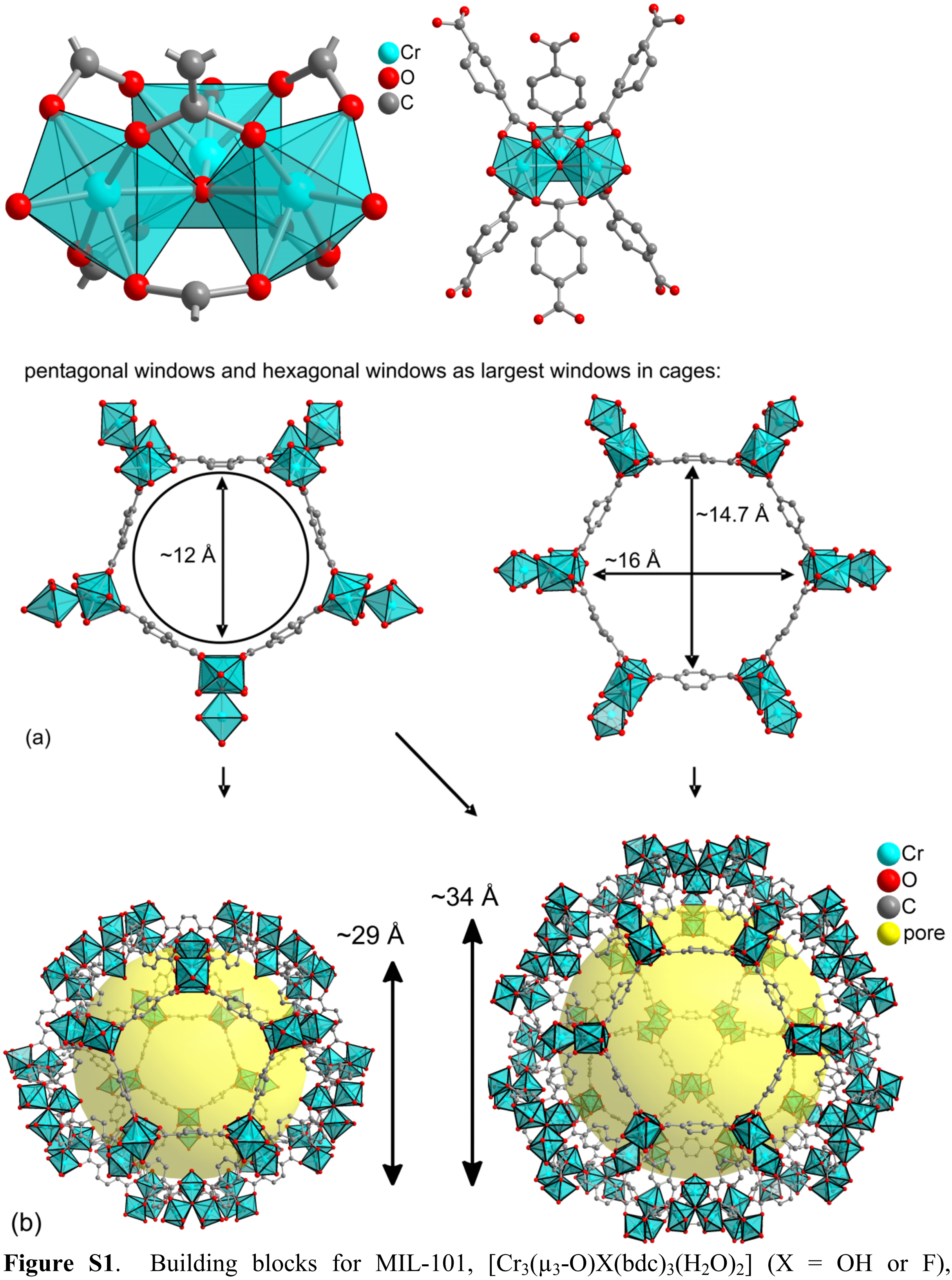

Figure S1. Building blocks for MIL-101, $[Cr_3(\mu_3\text{-}O)X(bdc)_3(H_2O)_2]$ (X = OH or F), generated from the deposited X-ray data file at the Cambridge Structure Database (CSD-Refcode OCUNAK)[1] using the program DIAMOND.[2] Trinuclear $\{Cr_3(\mu_3\text{-}O)X(H_2O)_2\}$ building units and bridging benzene-1,4-dicarboxylate ligands form pentagonal and hexagonal rings (a) which are assembled into mesoporous cages. The yellow spheres in the mesoporous cages with diameters of 29 or 34 Å, respectively, take into account the van-der-Waals radii of the framework walls (water-guest molecules are not shown). The different objects in this figure are not drawn to scale.

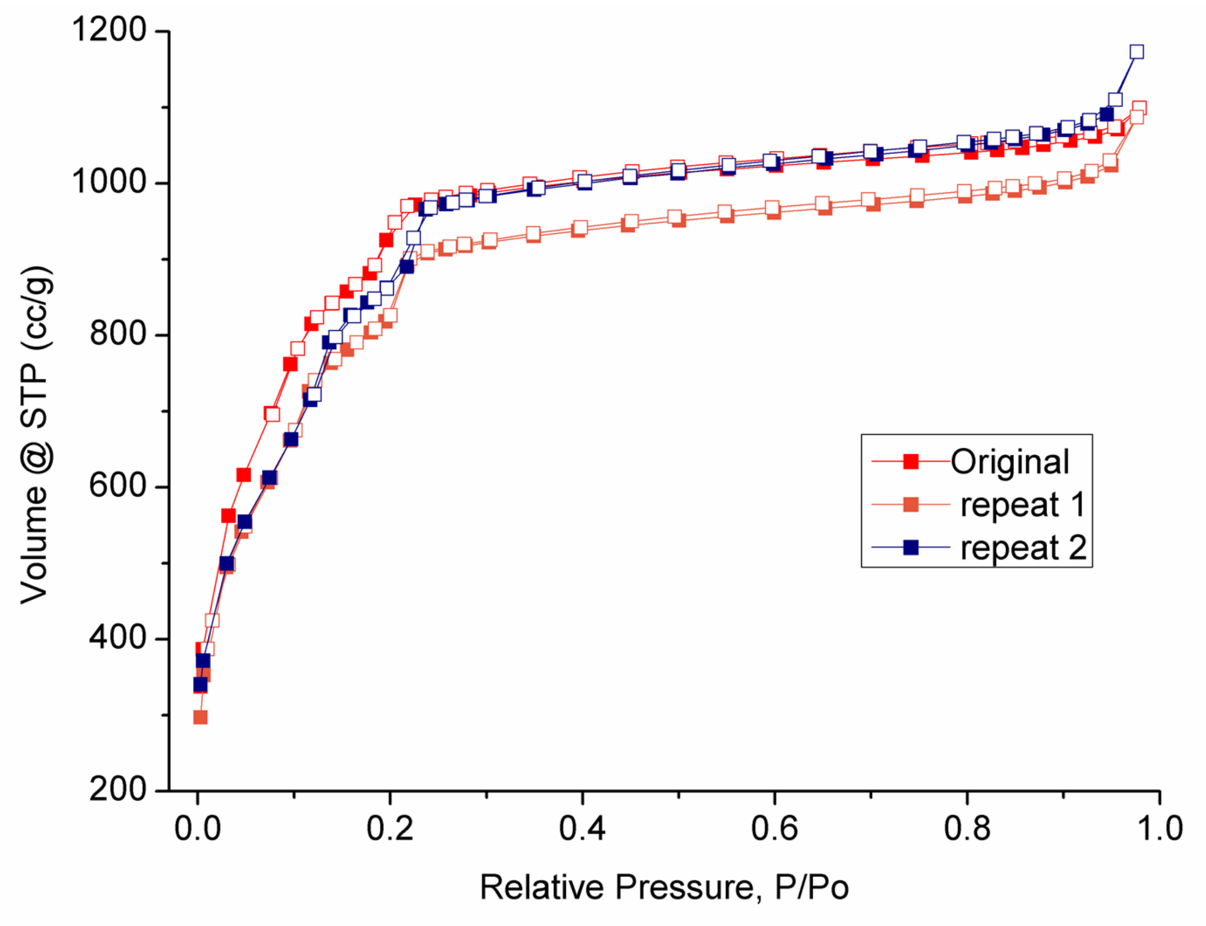

Fig. S2 N_2 sorption isotherms of repeated MIL-101(Cr) synthesis experiments with 1 eq. HNO_3; filled symbols are for adsorption, empty symbols for desorption.

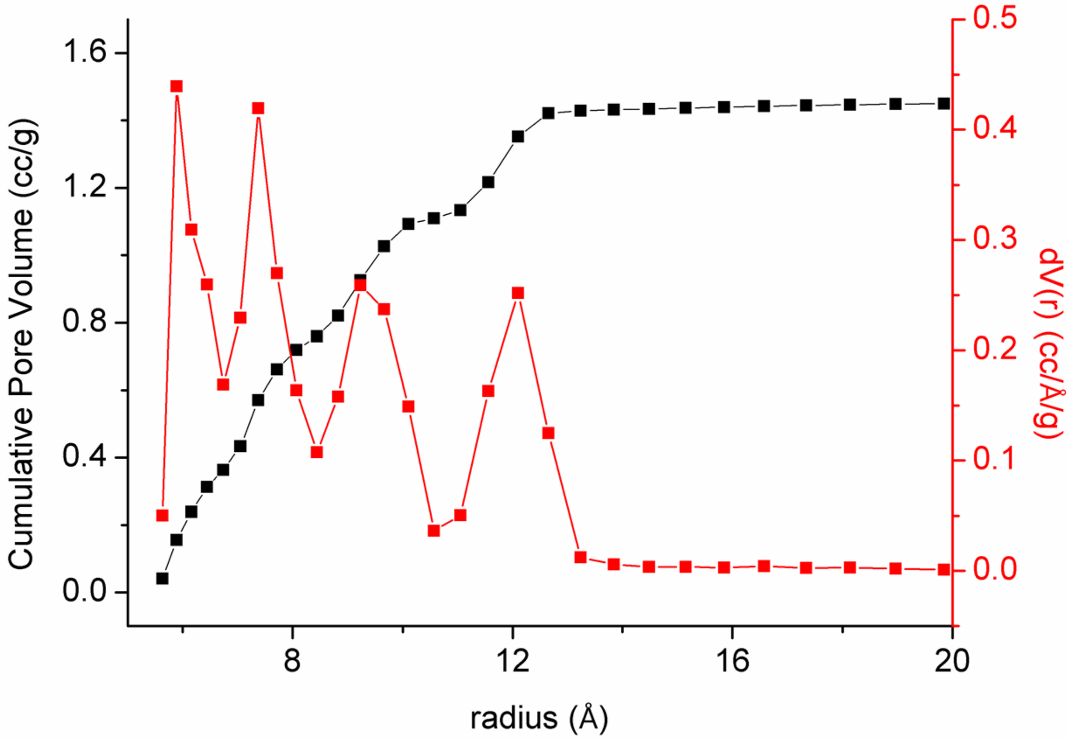

Fig. S3 Pore size distribution curve and cumulative volume curve of MIL-101(Cr) with 1.0 eq. HNO_3 (N-1.0) calculated with 'N$_2$ at 77 K on carbon, slit pore, NLDFT equilibrium' model.

Fig. S4. The picture of the 3 L of autoclave used in large-scale MIL-101(Cr) syntheses.

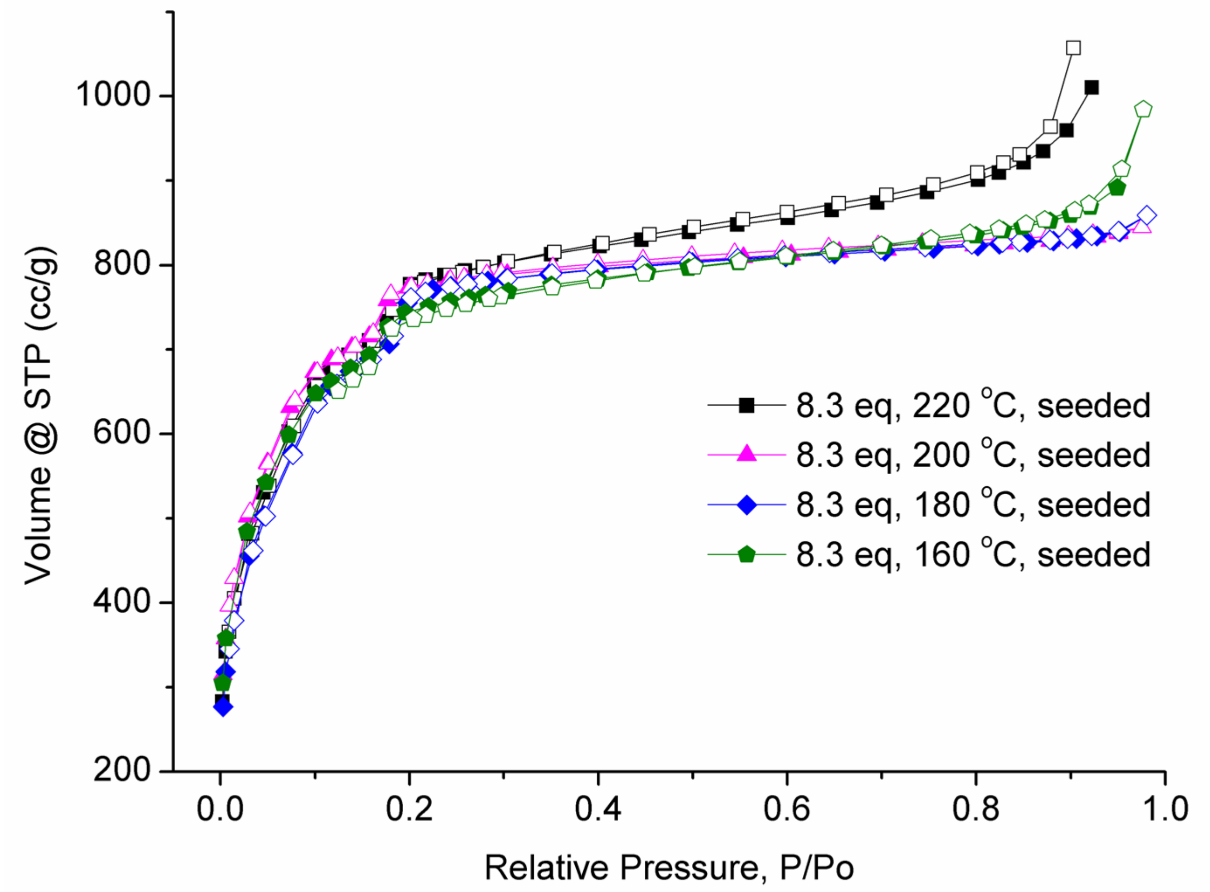

Fig. S5 Nitrogen sorption isotherms for "seeded" samples with different synthesis temperature, filled symbols are for adsorption, empty symbols for desorption.

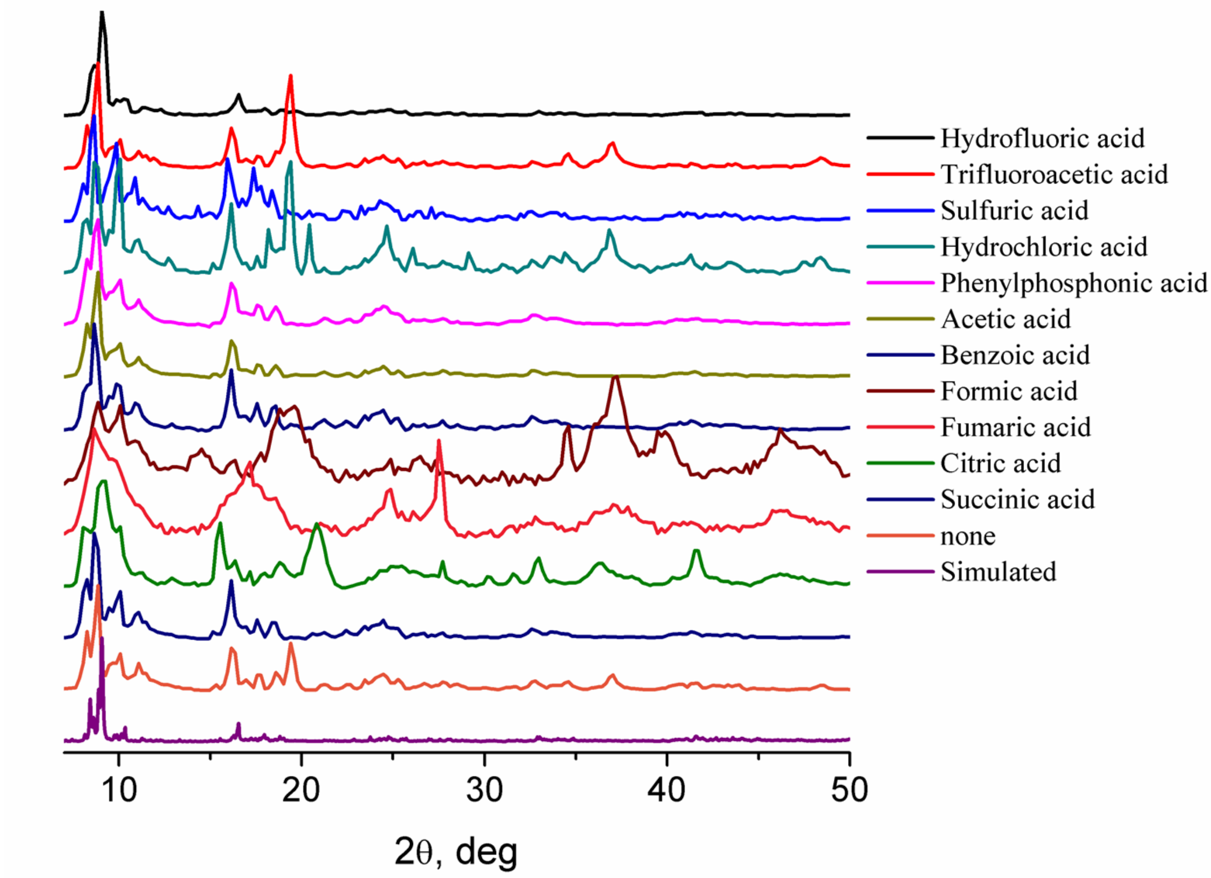

Fig. S6 Powder X-ray diffractograms of MIL-101(Cr) obtained with different additive acids.

1 Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surble, S.; Margiolaki, I. A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science*, 2005, **309**, 2040-2042.

2 Brandenburg, K. Diamond (Version 3.2), crystal and molecular structure visualization, Crystal Impact.Brandenburg, K.; PutzGbr, H. Bonn, Germany, 2007-2012.