Benzoic acid as a selector-modulator in the synthesis of MIL-88(Cr) and nano-MIL-101(Cr)†‡

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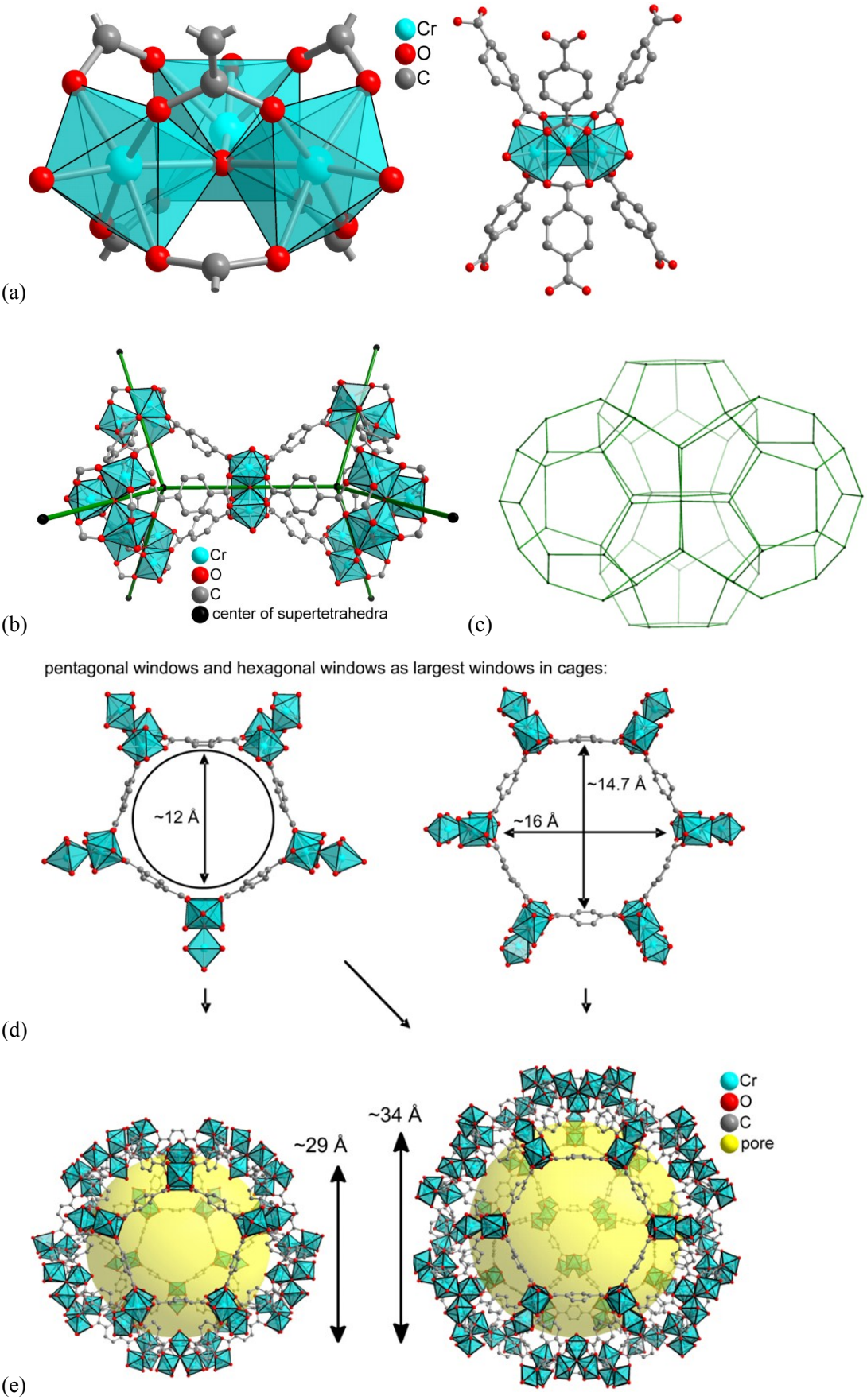

Fig. S1 The structure of MIL-101(Cr) consisting of {Cr_3O} secondary building units

(SBUs) bridged by benzene-1,4-dicarboxylate ligands. (a) The trinuclear $\{Cr_3(\mu_3\text{-}O)(RCOO)_6(F,OH)(H_2O)_2\}$ SBU; (b) A pair of supertetrahedra, which are constituting the structure of MIL-101 (c) A representative fragment of the MTN zeolite topology; (d) The largest aperture windows in the mesoporous cages delimited by the five- and six-membered rings; (e) The small cage with pentagonal windows and the large cage with pentagonal and hexagonal windows (the void volume is indicated by yellow spheres). The van-der-Waals diameters of the solvent accessible voids in the mesoporous cages are 29 or 34 Å respectively (the molecular graphics is computed using stuctural data with OCUNAK[1] CSD reference code by the DIAMOND program)[2]
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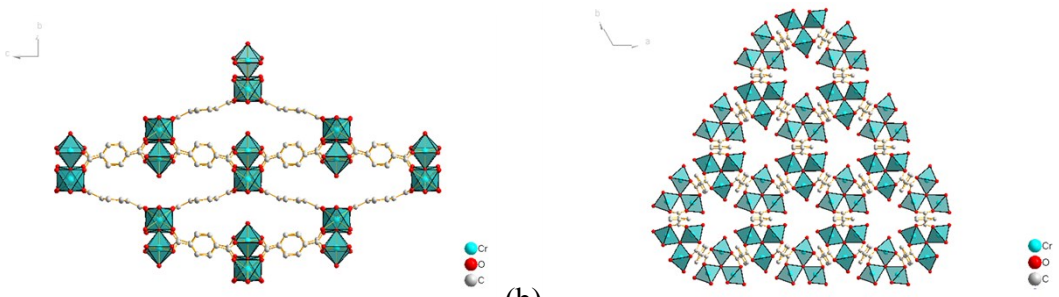


(a) (b)

Fig. S2 Schematic representation of the 'opened' high volume structure of the MIL-88(Cr): (a) View along 100 direction (c) View along 001 direction. The guest solvent molecules were not shown for clarity. (CSD-Refcode: YEDKOI)[3]

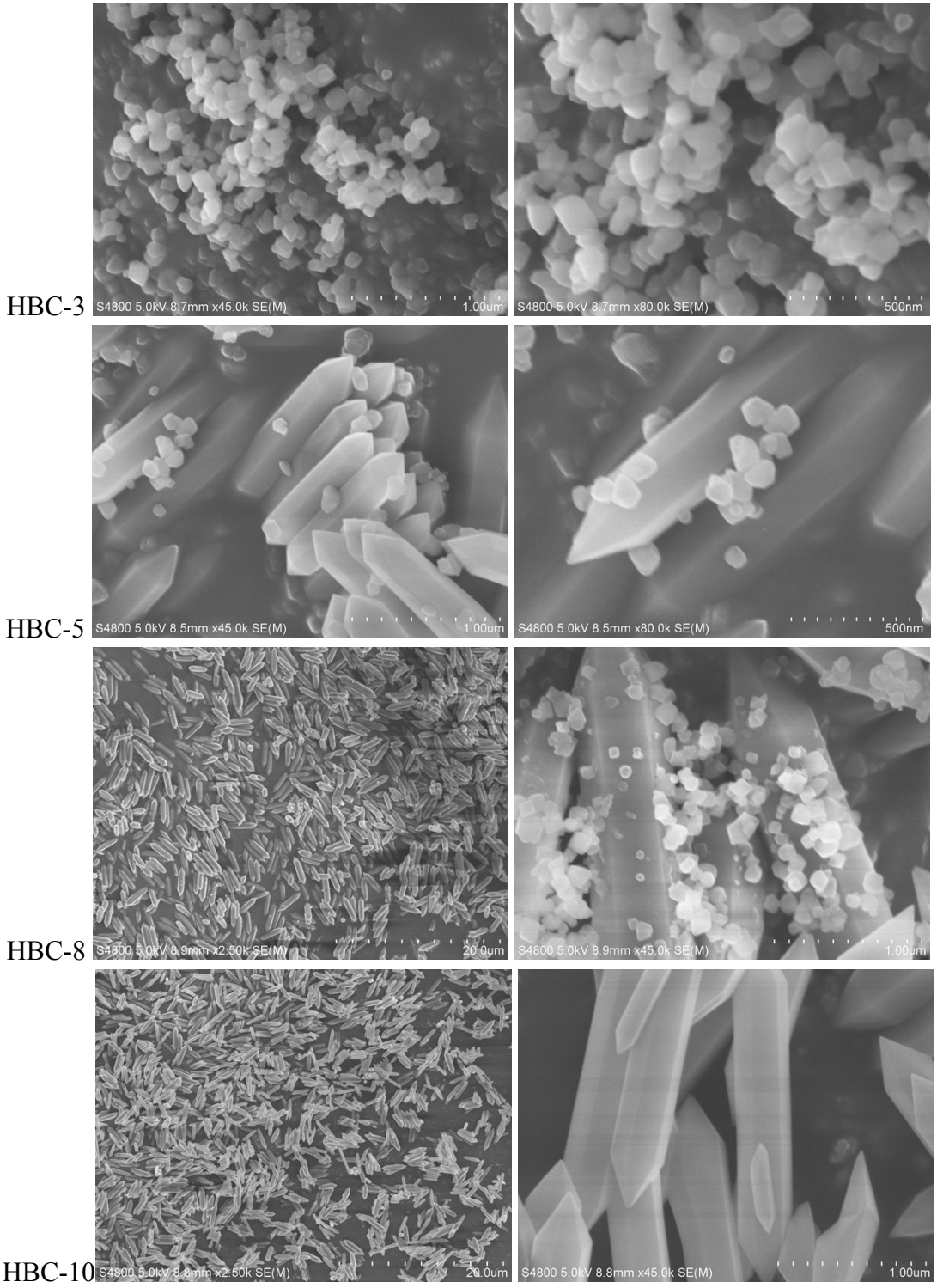


Fig. S3 SEM images of HBC-3, HBC-5, HBC-8 and HBC-10, the small particles represent nano-MIL-101(Cr) and the rod-like crystals are MIL-88(Cr).

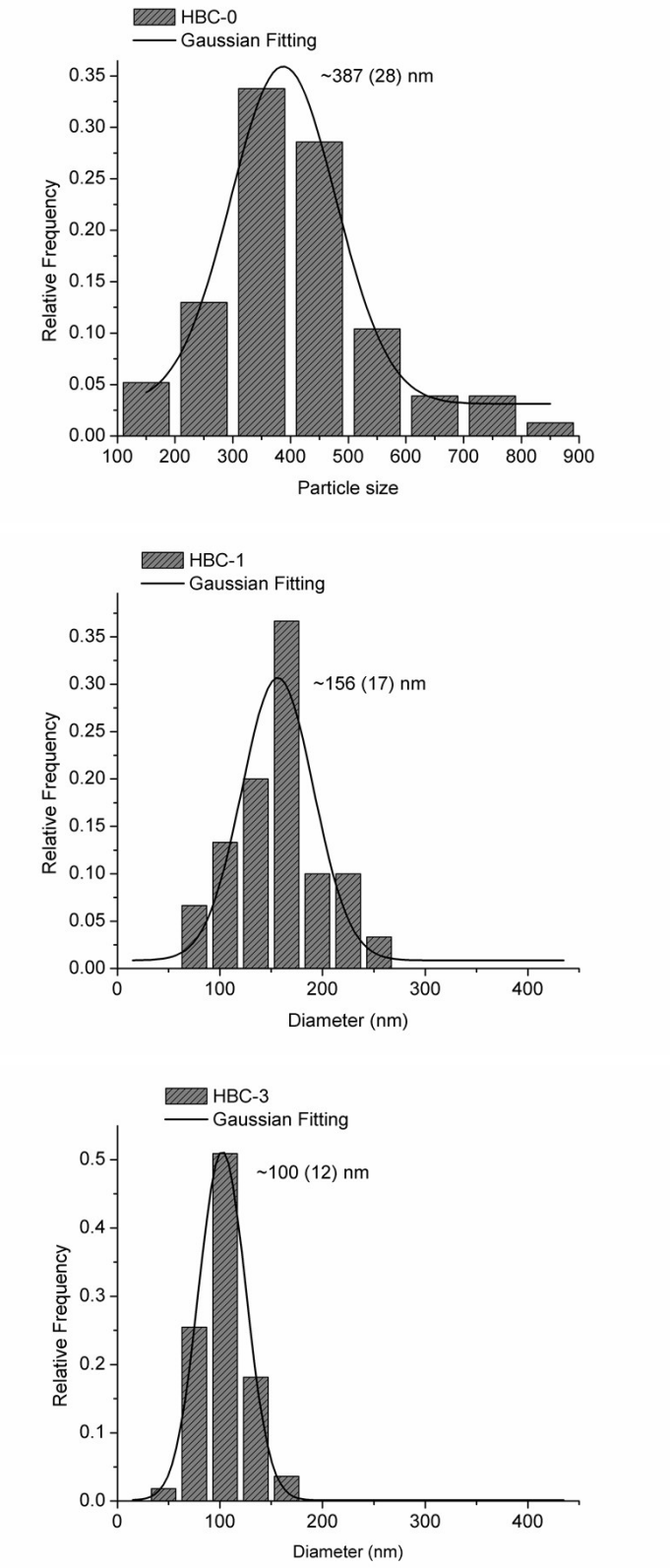
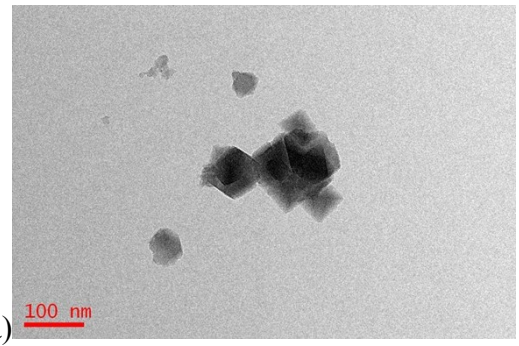


Fig. S4 Particle size distributions for the samples predominantly consisting of MIL-101.

(a) 

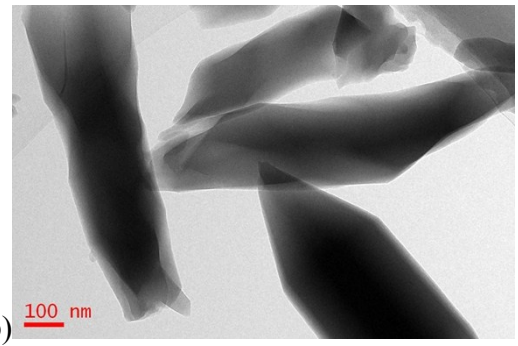
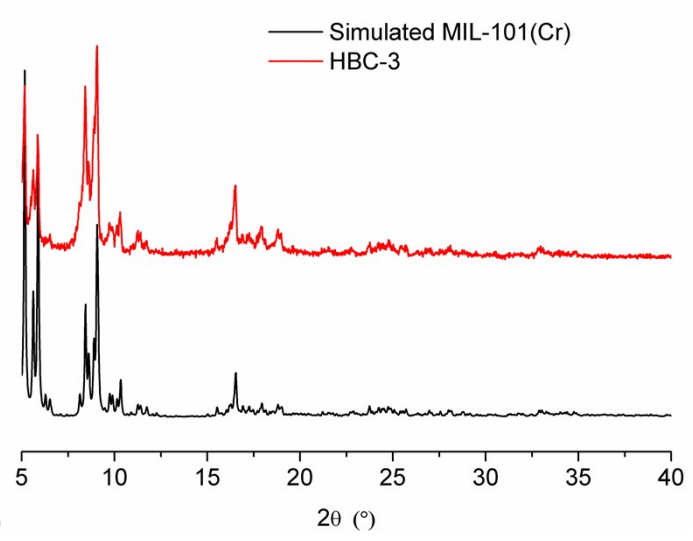
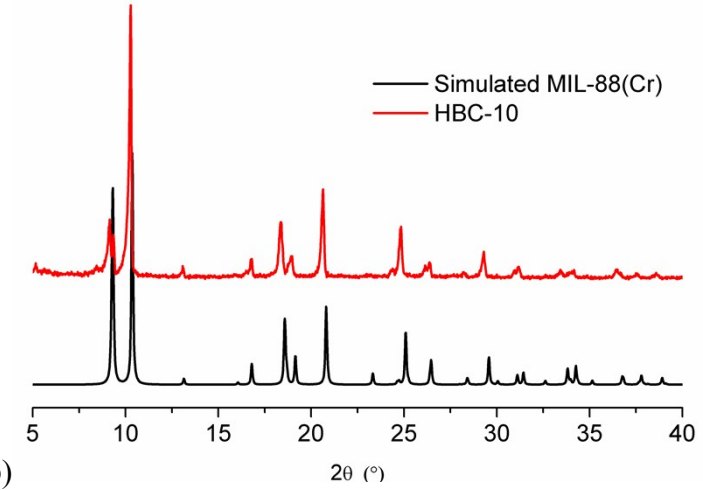
(b) 

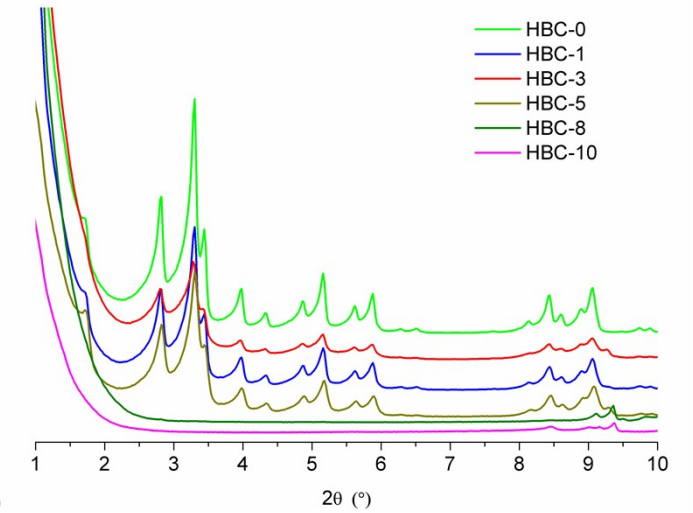
Fig. S5 TEM images of the nano-MIL-101(Cr) (a: HBC-3) and MIL-88(Cr) (b: HBC-10).



(a)



(b)



(c)

Fig. S6 The PXRD patterns of (a) nano-MIL-101(Cr) (HBC-3) and (b) MIL-88(Cr) (HBC-10) compared with the corresponding simulated patterns. (c) The low-angle region of the PXRD patterns of all samples.

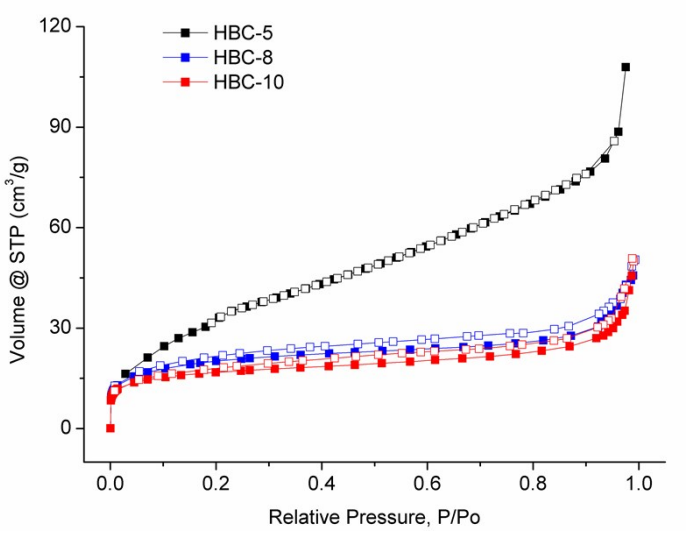


Fig. S7 N_2 adsorption-desorption isotherms for the HBC-5, HBC-8 and HBC-10 samples after activation at 350 °C; filled symbols stands for adsorption, empty symbols for desorption.

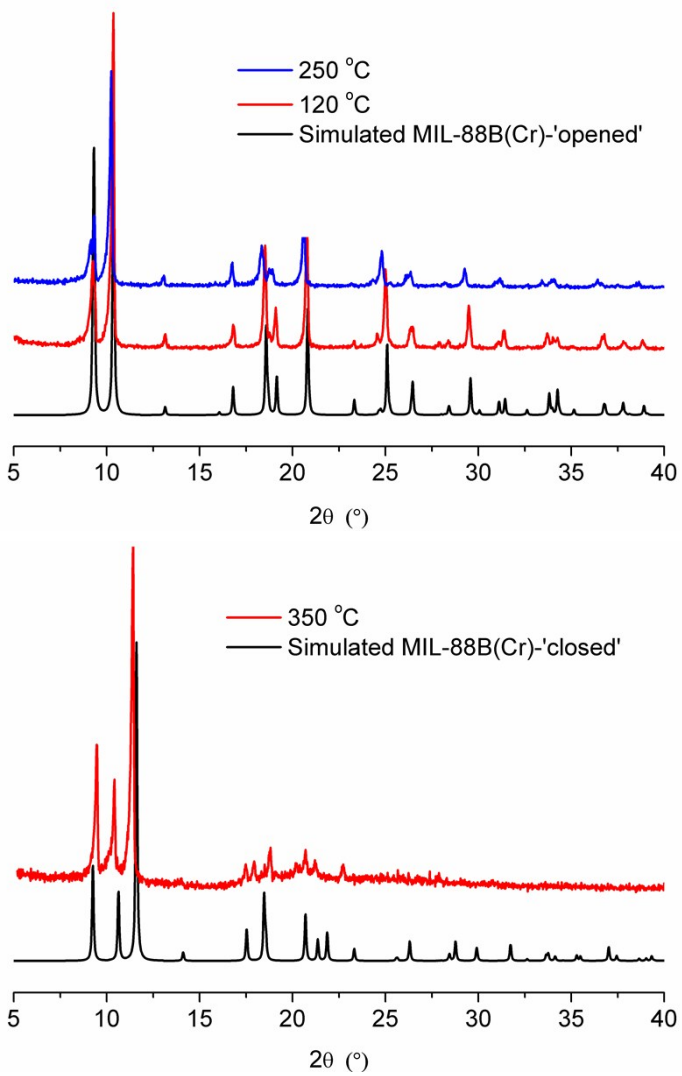


Fig. S8 The PXRD patterns of HBC-10 after different activation temperatures compared with the simulated MIL-88B(Cr)-'opened' form[3] (120 °C, 250 °C) and the MIL-88B(Cr)-'closed' form[4] (350 °C).

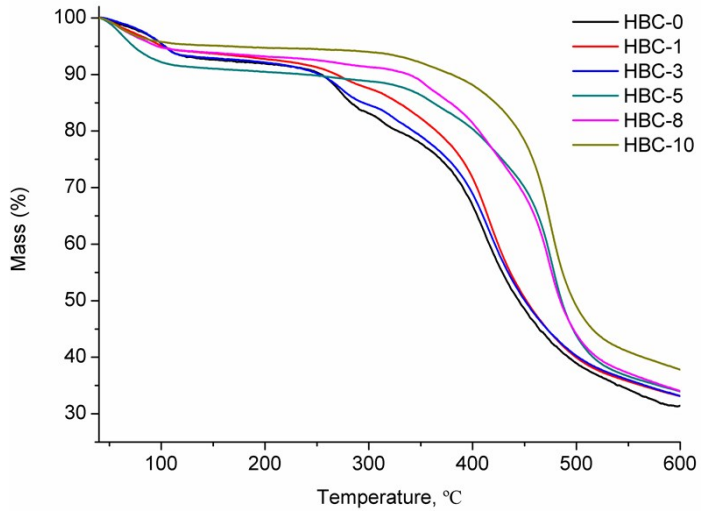


Fig. S9 TGA weight loss curves of the samples prepared with different amounts of benzoic acid as a modulator.

1 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.

2 K. Brandenburg, Diamond (Version 3.2), crystal and molecular structure visualization, Crystal Impact, K. Brandenburg & H. Putz Gbr, Bonn, Germany, 2007–2012.

3 S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millangea, G. Férey, *Chem. Commun.*, 2006, **3**, 284-286.

4 C. Serre, C. Mellot-Draznieks, S. Surble, N. Audebrand, Y. Filinchuk, and G. Ferey, *Science*, 2007, **315**, 1828–1831. The actually used atom coordinates were taken from the RASPA software database: D. Dubbeldam, S. Calero, D. E. Ellis, and R. Q. Snurr, *Mol. Simul.*, 2016, **42**, 81–101.