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 \( \text{Cr}_3(\mu_3-O)(RCOO)_6(F,OH)(H_2O)_2 \) 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)\(^2\).
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)
**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.
Fig. S5 TEM images of the nano-MIL-101(Cr) (a: HBC-3) and MIL-88(Cr) (b: HBC-10).
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 N₂ 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\textsuperscript{3} (120 °C, 250 °C) and the MIL-88B(Cr)-'closed' form\textsuperscript{4} (350 °C).
**Fig. S9** TGA weight loss curves of the samples prepared with different amounts of benzoic acid as a modulator.