<Supporting Information>

Microporous metal-organic framework containing cage-like pores with adjustable portal dimensions for adsorptive CO₂ separation

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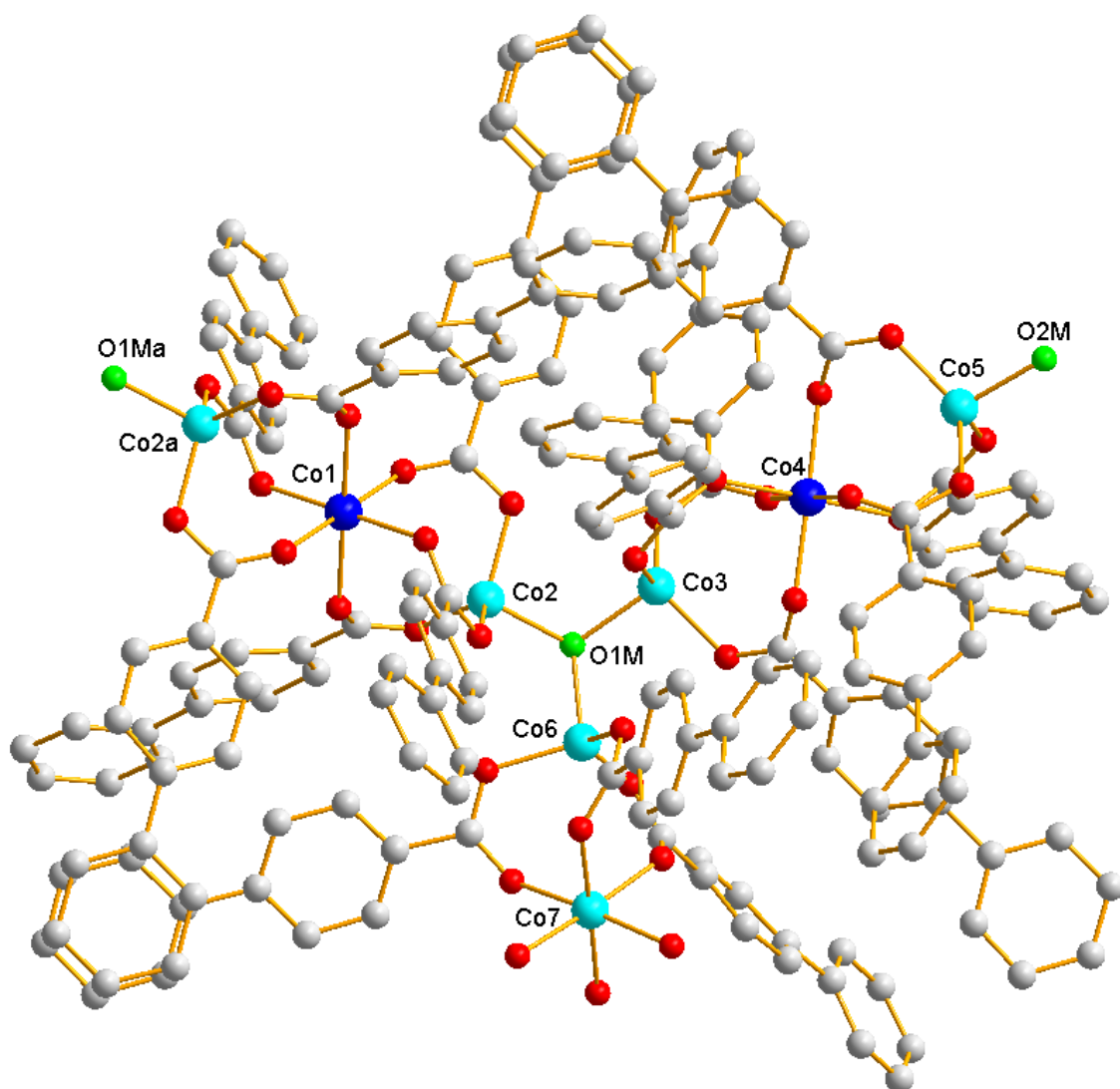
Figure S1. A ball-and-stick diagram of **1** showing three different cobalt carboxylate clusters and two different μ^3-OH groups. Color code: cobalt in the center of the linear trinuclear cobalt clusters, blue; the remaining cobalt, cyan; μ^3-OH, green; oxygen, red; carbon, gray. Symmetry code: a = –y, 1 + x – y, z.
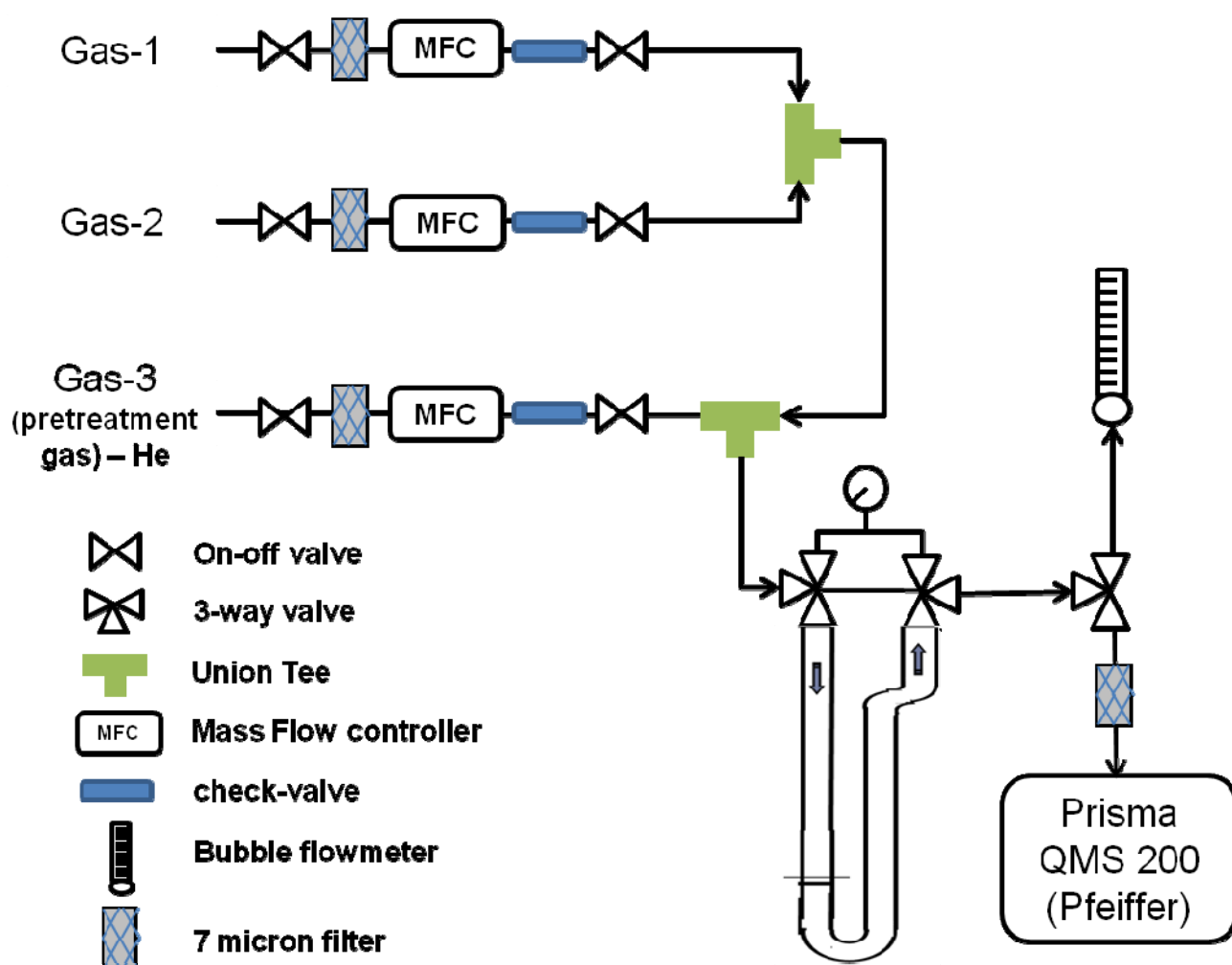
Figure S2. Schematic representation of breakthrough experiment apparatus.
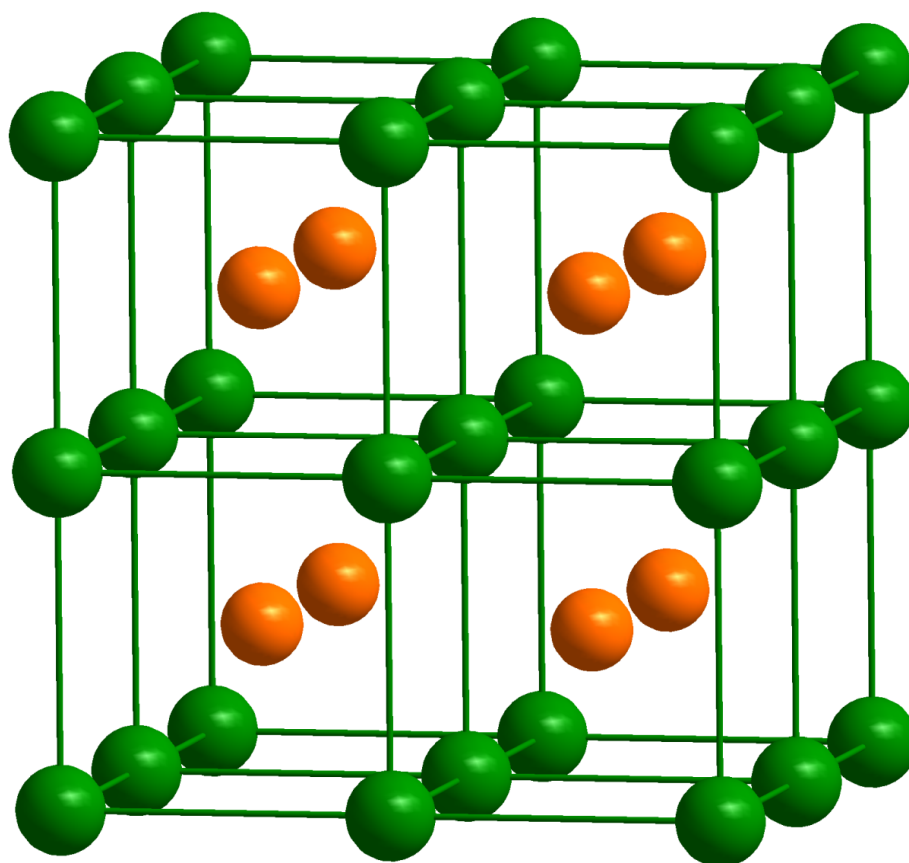
Figure S3. Schematic representation of the arrangement of the cages in **1**, where the green and the orange dummy balls represent the cavities of Cage A and Cage C, respectively. The surrounding Cage Bs around Cage As in AB_6 cage clusters were omitted for clarity.
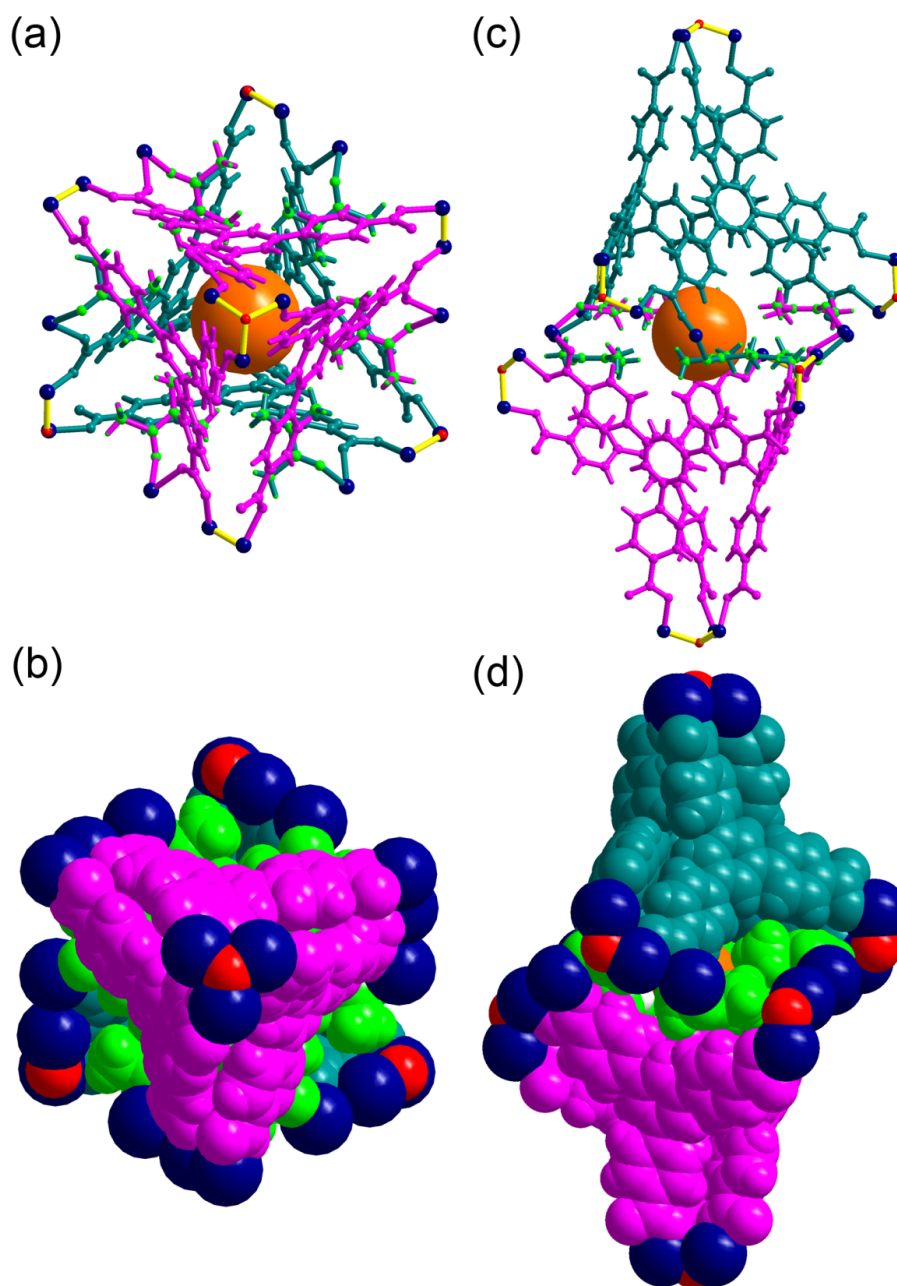
Figure S4. Ball-and-stick and space-filling models of Cage C with the portals between the dimeric one-face-open tetrahedra blocked by ligated DMA molecule. Top view of (a) the ball-and-stick and (b) space-filling models of Cage C. Side view of (c) the ball-and-stick and (d) space-filling models. Color code: DMA, green; BTB, pink and dark cyan; cobalt, dark blue; μ^3-O, red; dummy ball representing the cavity of Cage C, orange.
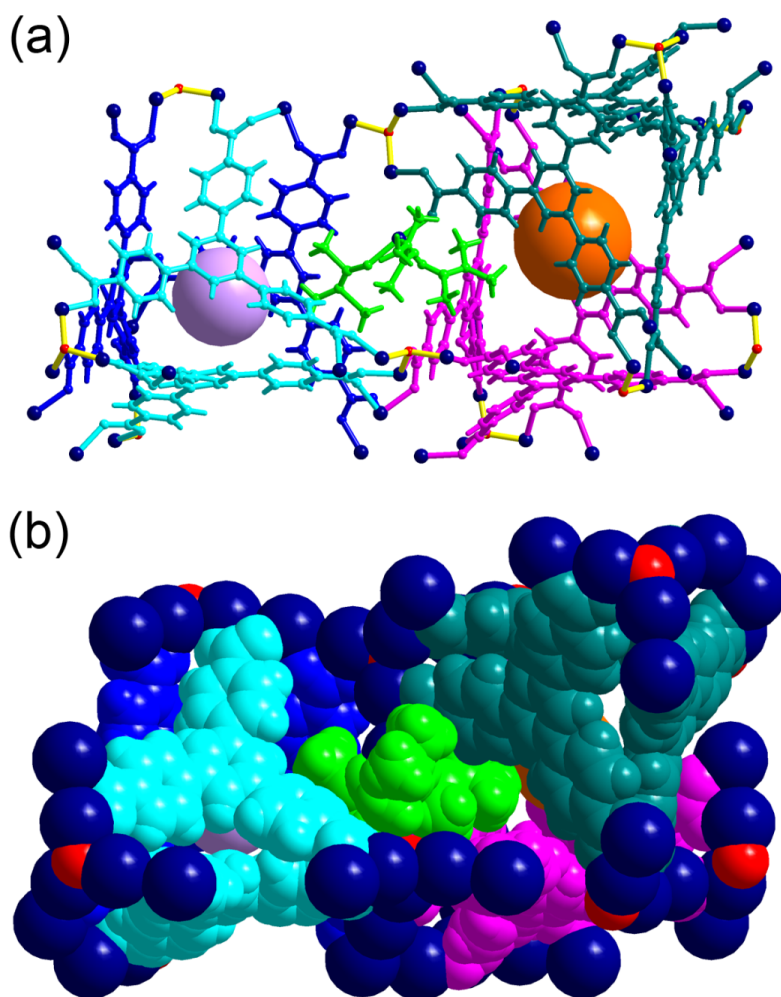
Figure S5. Ball-and-stick and space-filling models showing the passages between the pores of Cage B and Cage C blocked by ligated DMA molecule. Top view of (a) the ball-and-stick and (b) space-filling models of Cage C. Side view of (c) the ball-and-stick and (d) space-filling models. Color code: DMA, green; BTB, blue, cyan, pink, and dark cyan; cobalt, dark blue; μ^3-O, red; dummy balls representing the cavities, violet and orange.
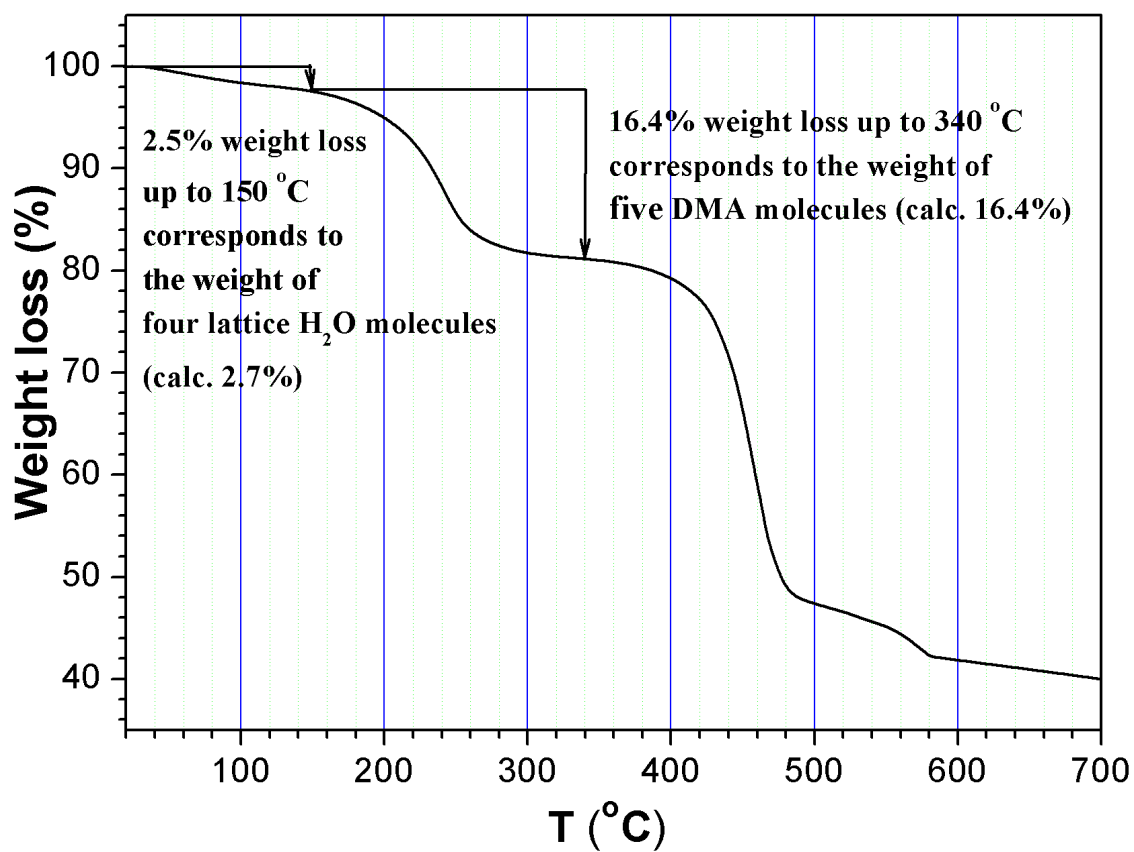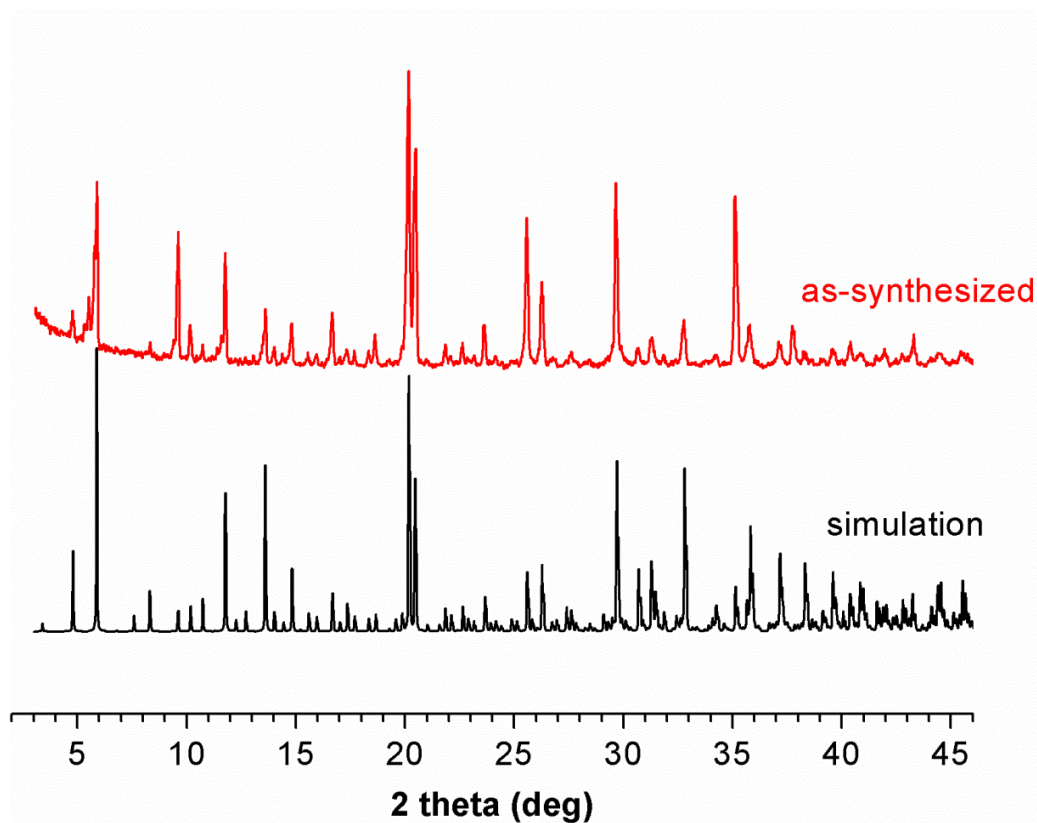
Figure S6. TGA data of as-synthesized **1**.

Figure S7. PXRD patterns of the simulated sample from the single-crystal structure (black) and of as-synthesized **1** (red).
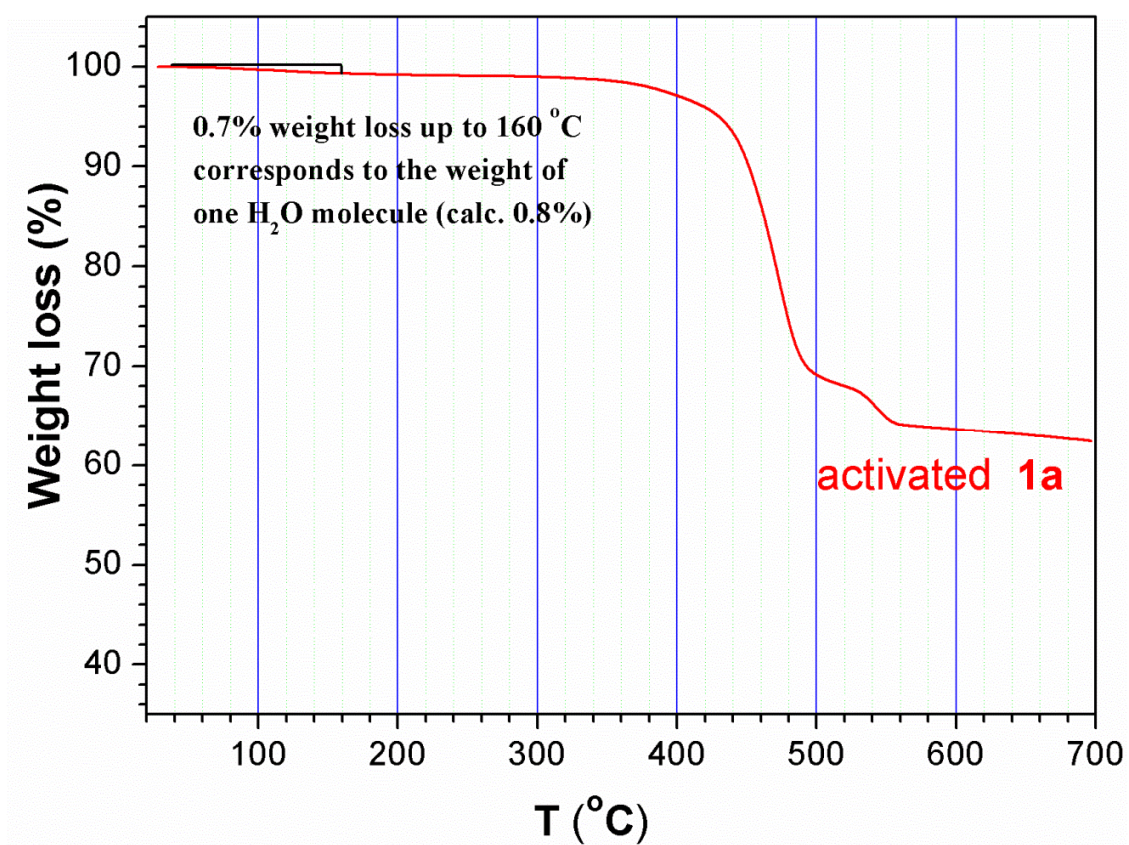
The figure shows a TGA plot with Weight loss (%) on the y-axis (from ~35 to 100) and T (°C) on the x-axis (100 to 700). Text within the plot reads:

0.7% weight loss up to 160 °C corresponds to the weight of one H_2O molecule (calc. 0.8%)

activated 1a

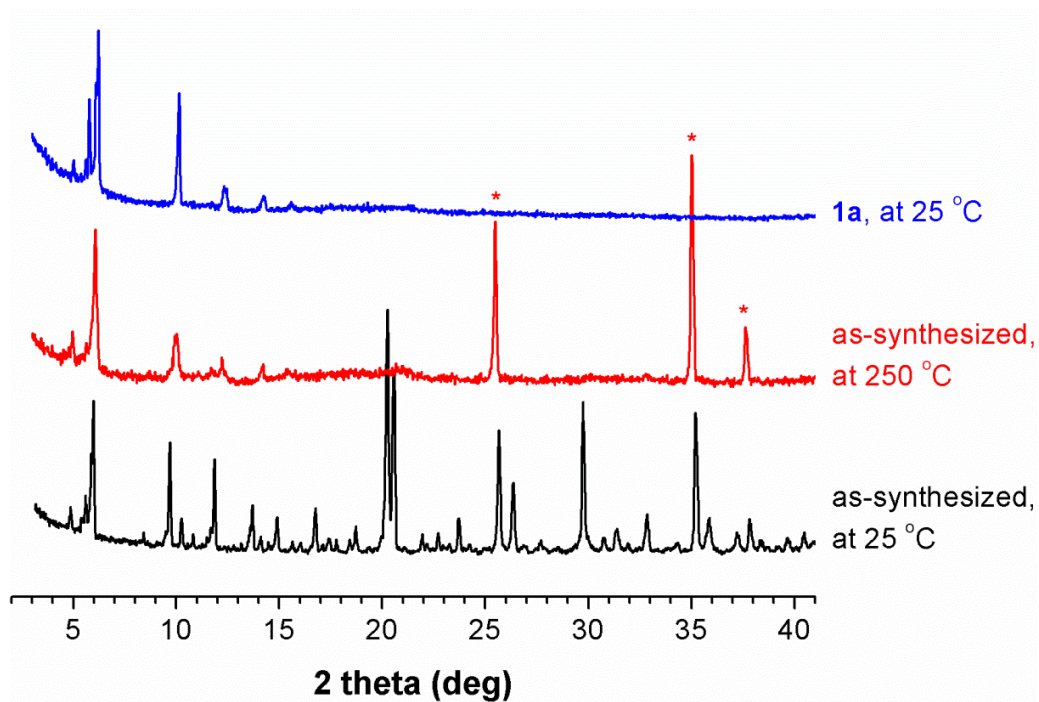**Figure S8.** TGA data of activated **1a** exposed to air for 30 min.

Figure S9. PXRD pattern of **1a**. Peaks with stars represent the α-Al_2O_3 of the high-temperature sample holder.
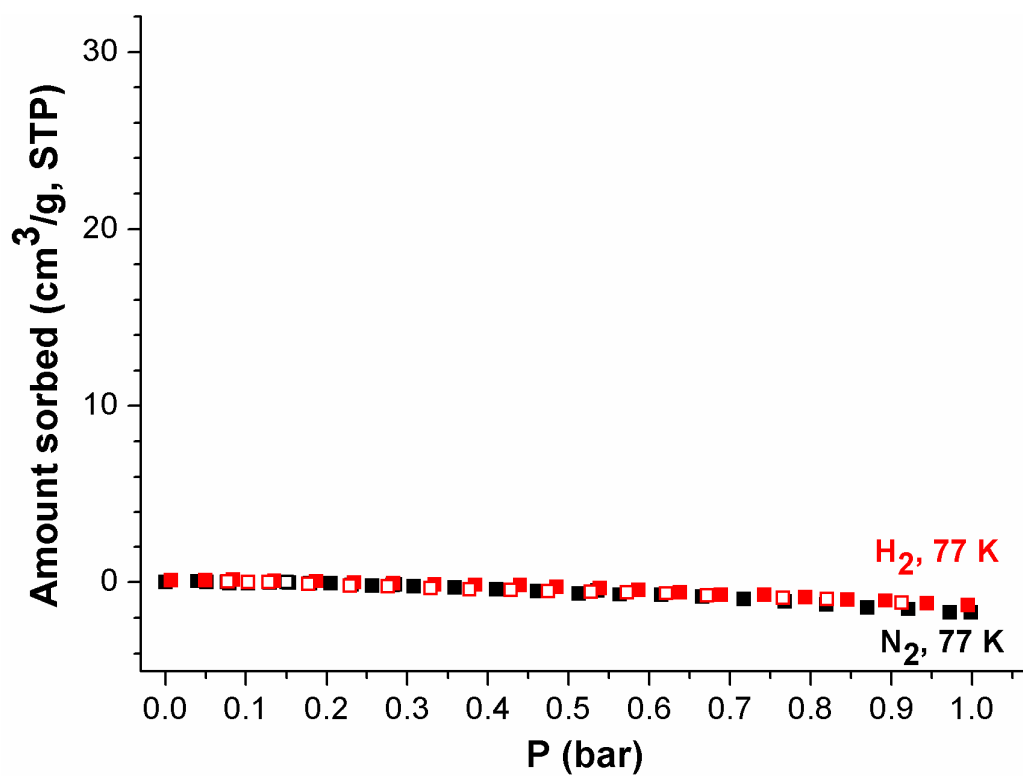
Figure S10. Gas sorption isotherms of N_2 (black) and H_2 (red) on **1a** at 77 K. Solid and open shapes represent adsorption and desorption, respectively.
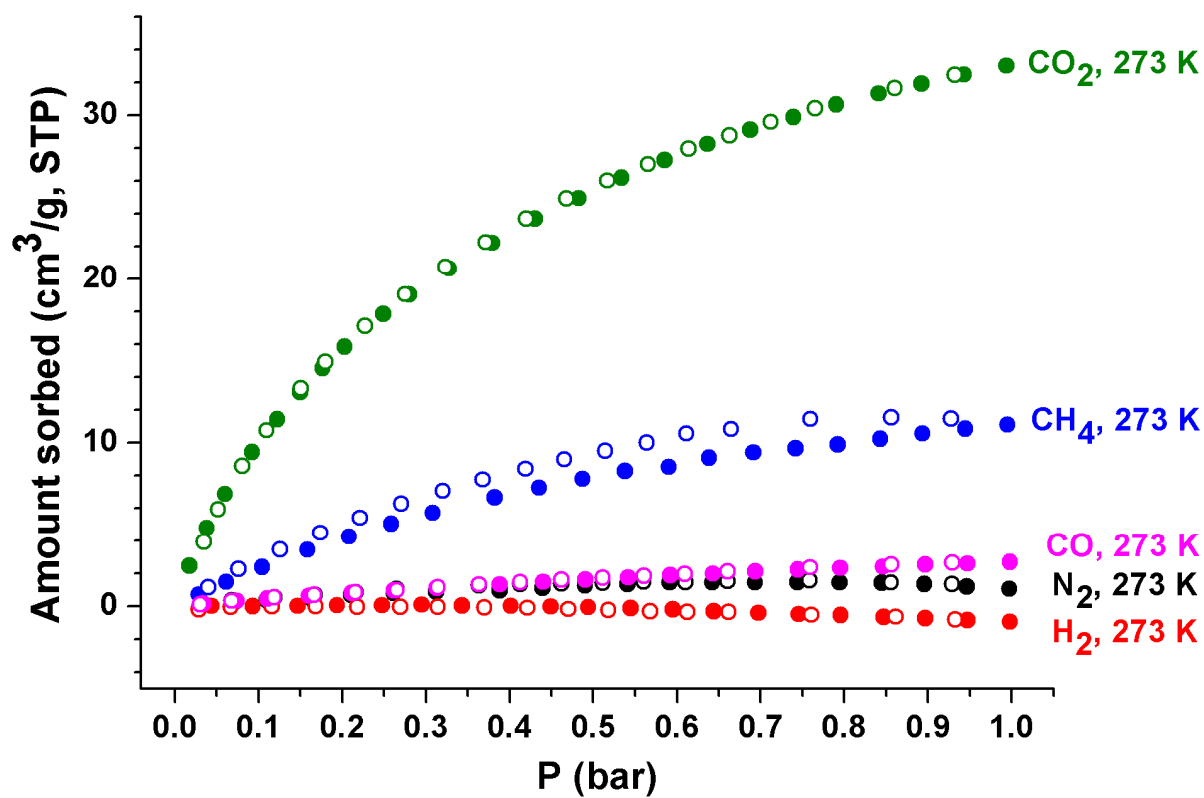
Figure S11. Gas sorption isotherms of CO_2 (green), CH_4 (blue), CO (pink), N_2 (black), and H_2 (red) on **1a** at 273 K. Solid and open shapes represent adsorption and desorption, respectively.

Figure S12. Gas sorption isotherms of CO_2 (green), CH_4 (blue), CO (pink), N_2 (black), and H_2 (red) on **1a** at 293 K. Solid and open shapes represent adso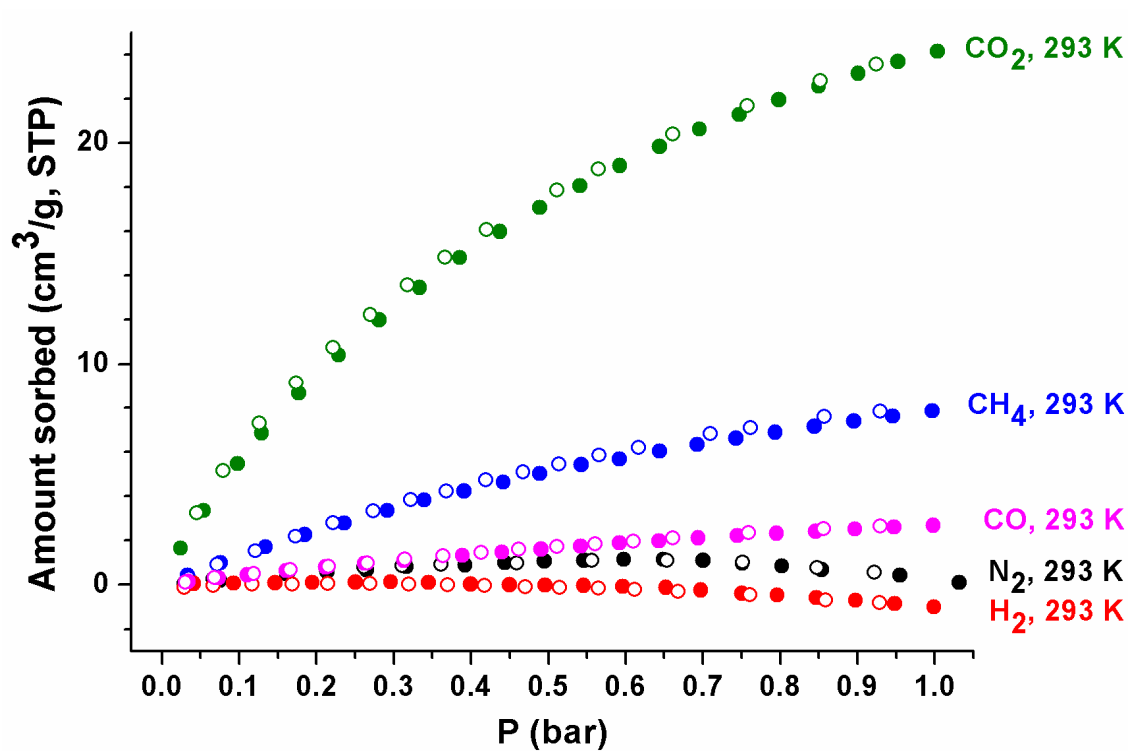rption and desorption, respectively.