Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

A thermally derived and optimized structure from ZIF-8 with giant enhancement in CO_2 uptake

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Material synthesis:

The ZIF-8 sample was synthesized at room temperature by magnetic stirring of a methanol solution of $Zn(NO_3)_2.6H_2O$ and 2-methylimidazole. Firstly, 2-methyl imidazole of 6.7873 g was dissolved in 250 ml methanol, and the solution was constantly stirred at room temperature, $Zn(NO_3)_2.6H_2O$ of 6.1467 g was dissolved in 250 ml methanol, and then slowly added to the former solution (see supporting information). The mixed solution continued to be stirred for a few hours, during which a milk-like solution was formed from the clear solution of precursors (**Figure S1**). Later the stirring was stopped and the solution was left for 24 h to settle. The top clear solution was drained out and the white sample precipitation was collected by centrifugation. A clean sample was obtained after a few cycles of methanol washing and centrifugation, which was then dried at room temperature and later activated at 180 °C under dynamic vacuum for 24 h. The thermal annealing of ZIF-8 at various temperatures was carried out by the placement of $\approx$ 150 mg ZIF-8 sample in an alumina boat in a horizontal tube furnace under continuous N_2 flow. Before being heated to the target temperature at 5 °C per minute, the furnace with the sample was purged with dry N_2 to make sure that no air or moisture residue remain that could degrade sample quality. After being cooled to room temperature, the sample was collected in a glass vial in ambient air. All samples for further characterizations were handled in ambient air.

Characterization:

The combined thermogravimetric analysis (TGA, on Setsys from Setaram) and mass spectrometry (MS, on OmniStar from Pfeiffer Vacuum) were carried out on a dry sample under Ar flow after purging; after reaching the target temperature at a ramping rate of 5 °C per minute, the annealing step was carried out under an isothermal step for a suitable period of time, up to 24 h. The TGA mass-loss was recorded after background correction to empty alumina crucible. Powder X-ray diffraction (PXRD, on Stoe Stadi-P, Cu-K-alpha) was carried out by filling the sample in a 0.5 mm diameter glass capillary at ambient. Fourier-transform Infrared (FTIR, on Perkin-Elmer) data was obtained at room temperature by KBr pellet transmission method with background correction. X-ray Photoemission spectroscopy (XPS, on Al-K-alpha, Thermo Scientific) data were obtained on the samples depositing on carbon tape. Transmission electron microscope (TEM, Jeol) images were obtained on the samples depositing on carbon coated copper TEM grid. The gas adsorption-desorption isotherm measurements at 77 K and 298 K using liquid nitrogen and water bath, respectively, were carried out using a Quantachrome Autosorb-iQC. The specific surface area was measured from the 77 K N_2 desorption isotherm in the relative pressure range between 0.01 and 0.2, according to the Brunauer-Emmett-Teller (BET) method. QSDFT (quenched solid density functional theory) method with slit/cylindrical pores was applied to desorption isotherm to obtain pore size distribution and cumulative pore volume. The high-pressure CO_2 adsorption-desorption isotherms at 0 °C, 25 °C and 50 °C (maintained by ice bath and precisely controlled temperature tube furnace) were measured on a PCTPro 2000. The isosteric heat of adsorption (Q_{st}) was determined from the isotherms measured at three different temperatures of 0 °C, 25 °C and 50 °C using the Clausius-Clapeyron equation, (please see ref. 21b). The CO_2 uptake cycling test was carried out on TGA under continuous CO_2 flow at ≈ 1 bar and 25.5 °C. As the entire sample handling was in air, the sample was degassed at 150 °C overnight under dynamic vacuum before all the actual gas adsorption measurements. IAST (ideal adsorbed solution theory) is applied to calculate the CO_2/N_2 selectivity, $S_{CO2/N2}$. IAST predicts the mixture adsorption equilibriums using single-component adsorption isotherms and is defined as;

S_{IAST} (selectivity of CO_2/N_2) = $(q_1/q_2)/(p_1/p_2)$,

where q_1 and q_2 are the CO_2 and N_2 uptake capacities in mmol g^{-1} at partial pressures of p_1 (=0.15 bar) and p_2 (=0.85 bar), respectively [[D. Lee, C. Zhang, C. Wei, B. L. Ashfeld and H. Gao, Hierarchically porous materials via assembly of nitrogen-rich polymer nanoparticles for efficient and selective CO_2 capture, *J. Mater. Chem. A*, 2013, **1**, 14862; W. M. Bloch, R. Babarao, M. R. Hill, C. J. Doonan and C. J. Sumby, Post-synthetic Structural Processing in a Metal−Organic Framework Material as a Mechanism for Exceptional CO_2/N_2 Selectivity, *J. Am. Chem. Soc.*, 2013, **135**, 10441].

Computational methods:

First-principles density-functional theory (DFT) calculations were performed using the Quantum-Espresso package.[1] We used Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 820 eV and a 2×2×2 k-point mesh (generated using the Monkhosrt-Pack scheme) were found to be enough for total energy to converge within 0.01 meV/atom. We first optimized the ZIF-8 structure. Hypothetic structures with a Zn or a $–CH_3$ vacancy were then calculated. Energies of the free Zn atom and a $–CH_3$ radical were also obtained. Bond dissociation enthalpies are the energy differences.

1. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, *J. Phys.: Condens. Matter*, 2009, **21**, 395502.

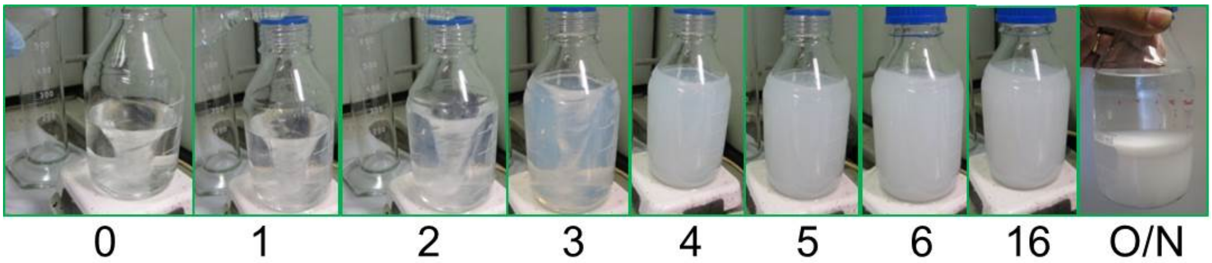

Figure S1. Showing the ZIF-8 synthesis method by room temperature magnetic stirring from methanol solutions of precursors; $Zn(NO_3)_2.6H_2O$ and 2-methylimidazole. $Zn(NO_3)_2.6H_2O$ dissolved in methanol is slowly added to 2-methylimidazole methanol solution while stirring. The numbers on the pictures are in minutes counted from the moment of adding solvents. Stirred for few hours and left overnight (O/N) for settling.

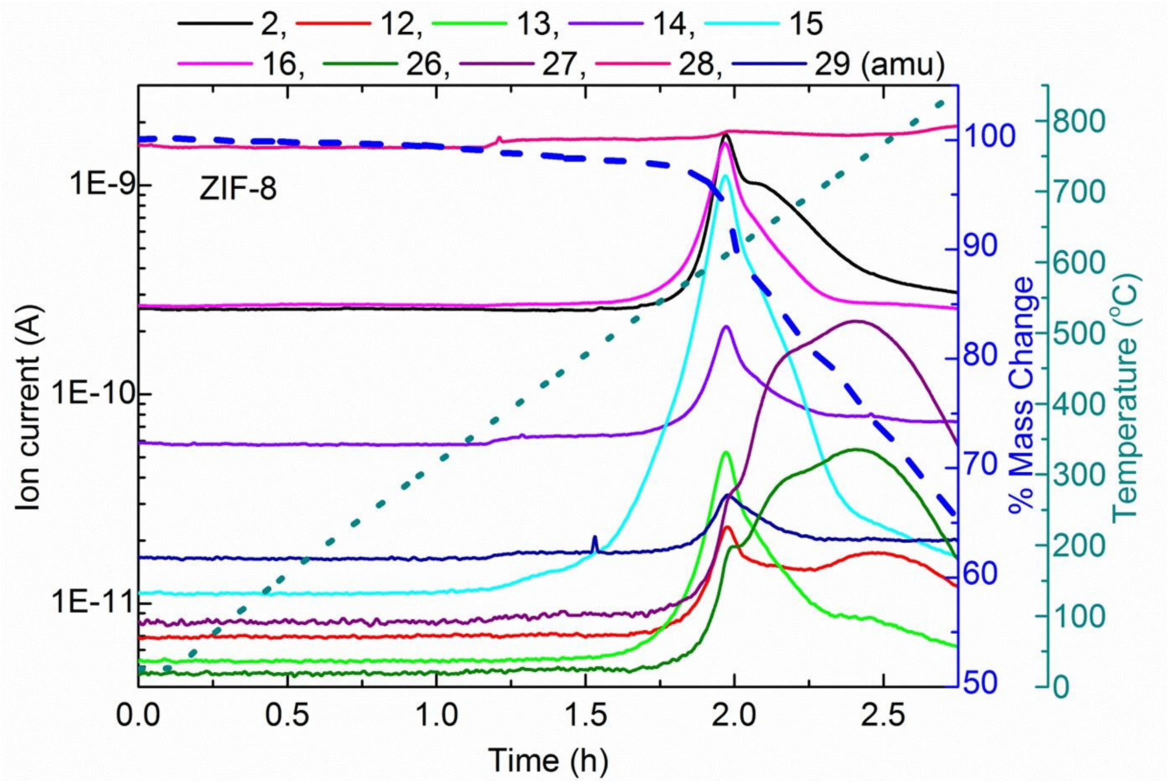

Figure S2. Simultaneous thermogravimetric (TG) (blue dashed line for blue axis) and mass spectroscopic (MS) (left axis) analysis plotted against temperature (dark cyan, right axis) ramping (5 °C per minute) rate. MS signals in atomic mass unit (amu; 2-H_2, 12-C, 13-CH, 14-CH_2, 15-CH_3, 16-CH_4, 26-C_2H_2, 27-HCN, 28, N_2 / H_2CN, 29- H_2CNH) represent the evolution of decomposed gaseous species during TG analysis. The evolutions of various signals can be attributed the recombination of fragmented charged particles which are generated during decomposition of ZIF-8 framework. Note that CH_3 mass signal starts appear well before actual decomposition temperature and which is the high intense mass signal compared to any other.

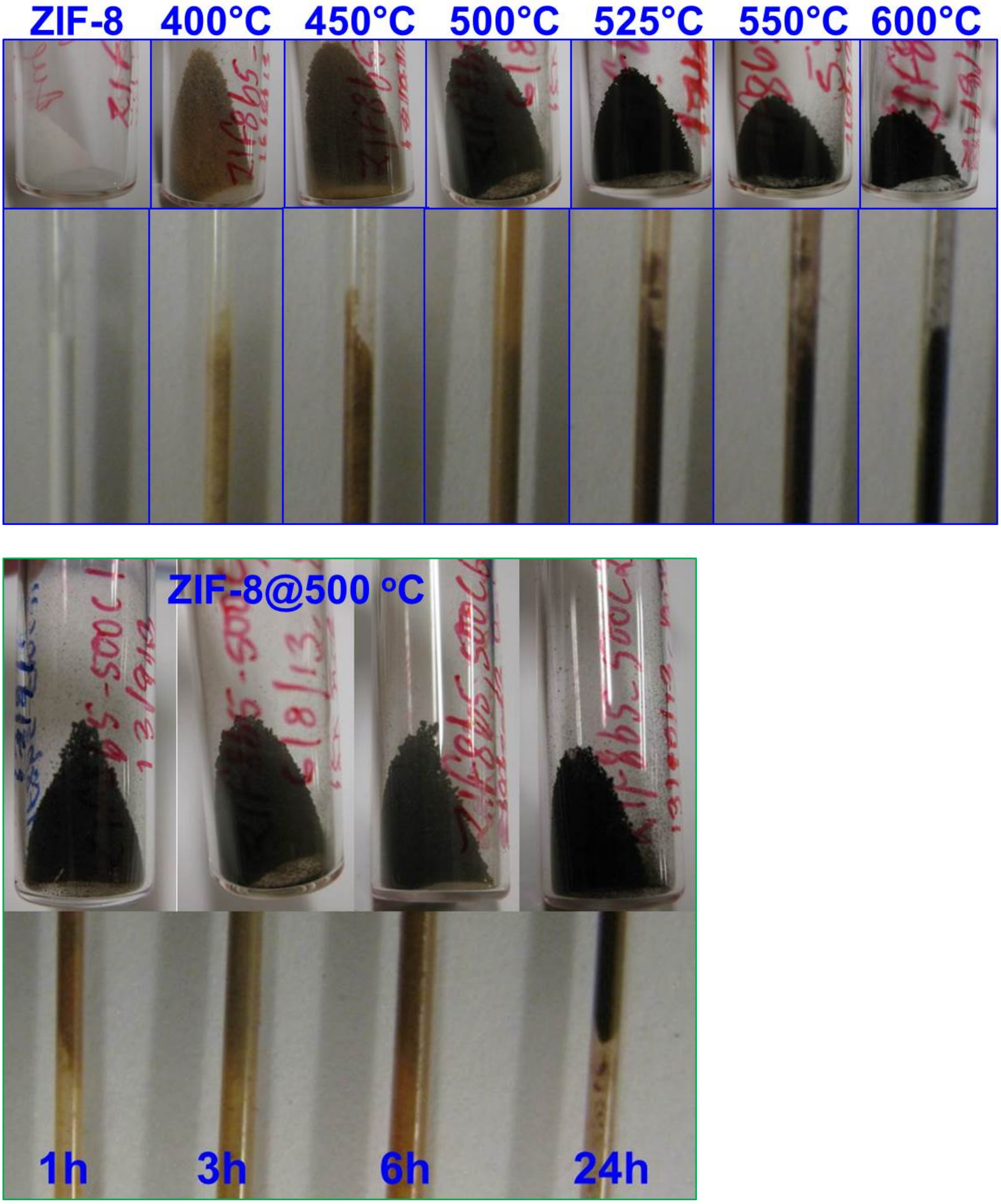

Figure S3. Digital photographs of the ZIF-8 and annealed samples; as obtained (in vials) and ground powder (in 0.5 mm XRD glass capillaries). Top: each sample is annealed for 3h at a given temperature. Bottom: sample is annealed at same 500 °C for different times; 1h, 3h, 6h & 24h.

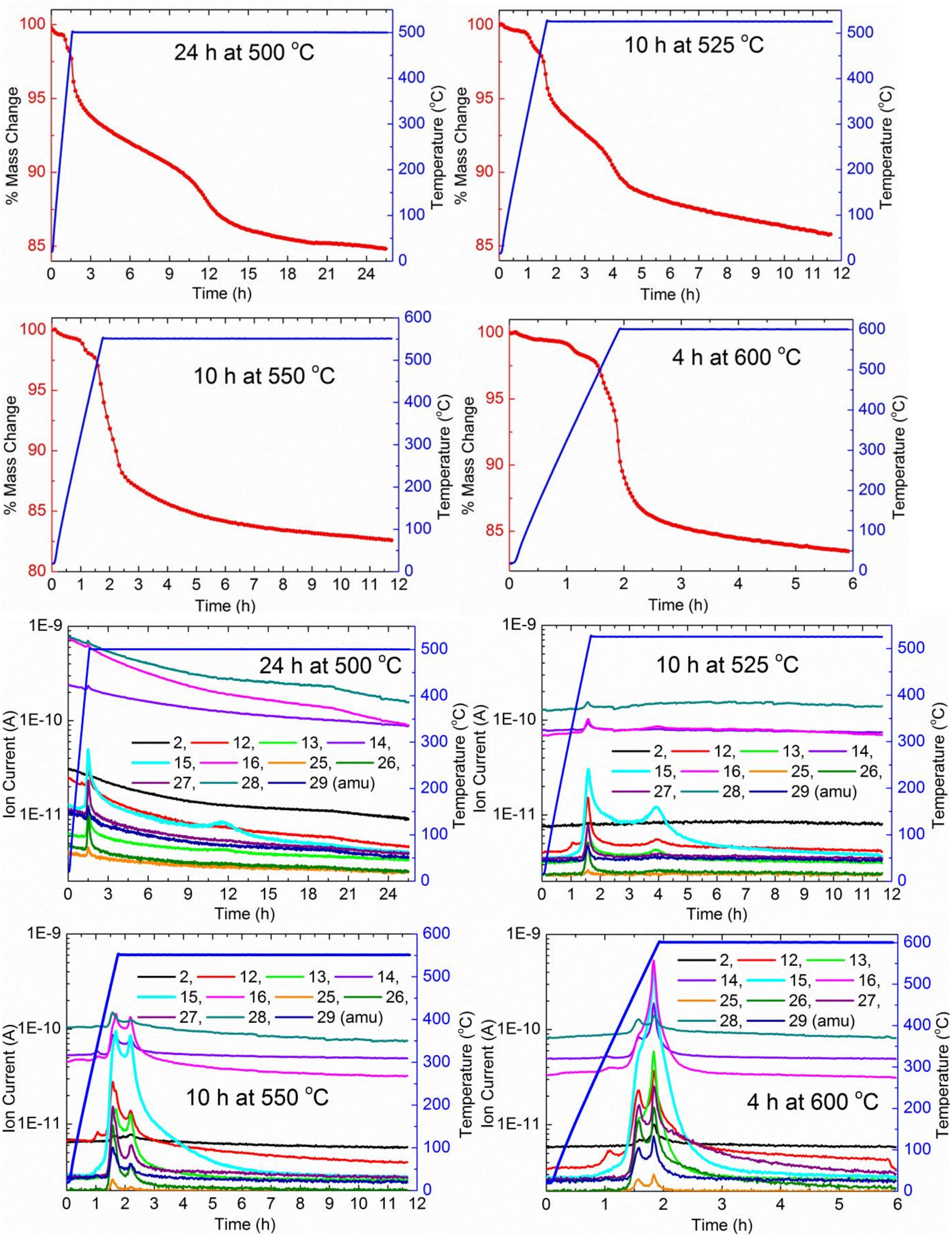

Figure S4. Simultaneous thermogravimetric (top four) (Red data symols for left Y axis) and mass spectroscopic (bottom four) (left Y axis) analysis plots against temperature (blue, right Y axis in all 8 plots) ramping rate (5 °C per minute) and isothermal process time (X-axis). Note that the temperature ramping is up to target temperature and after that the isothermal process is maintained up to 4 h (at 600 °C), 10 h (at 550 °C and 525 °C) and 24 h (at 500 °C).

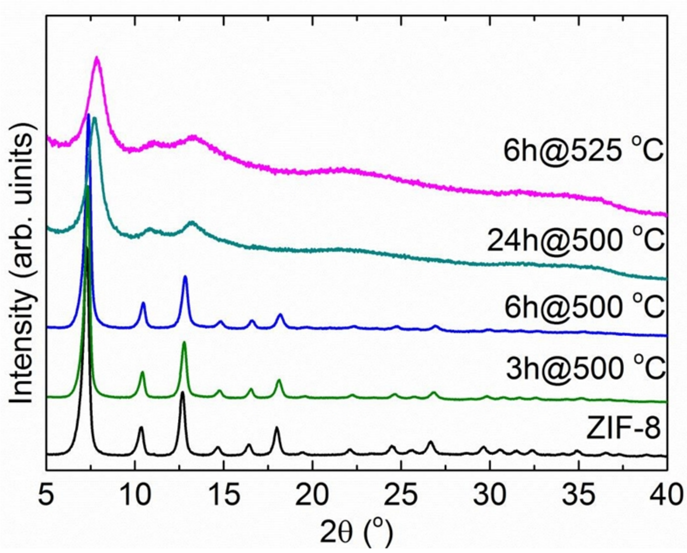

Figure S5. PXRD patterns of thermal annealed ZIF-8 samples. The corresponding labels represent the respective annealing temperature and period. It is worth noting that there are no zinc oxide related peaks, mainly in the two-theta region of 30-40.

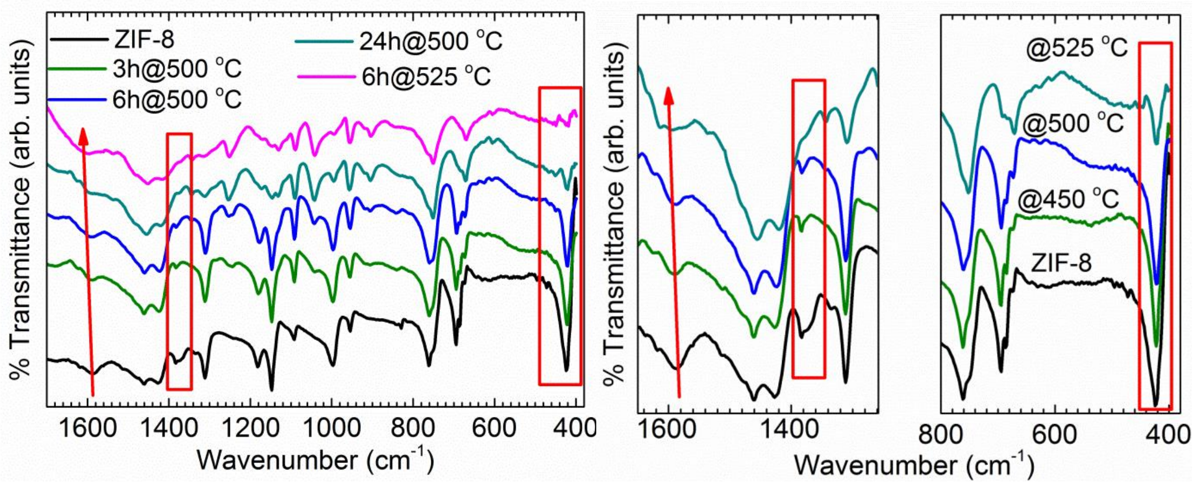

Figure S6. FTIR spectra of thermal annealed ZIF-8 samples. Left: the corresponding labels represent the respective annealing temperature and period. Right: samples annealed for 3 h at a given temperature. The red arrow and rectangular boxes show clear changes in C=N stretch mode at 1584 cm^{-1}, δ CH_3 IR mode at 1384 cm^{-1} and Zn−N stretching at 422 cm^{-1}.

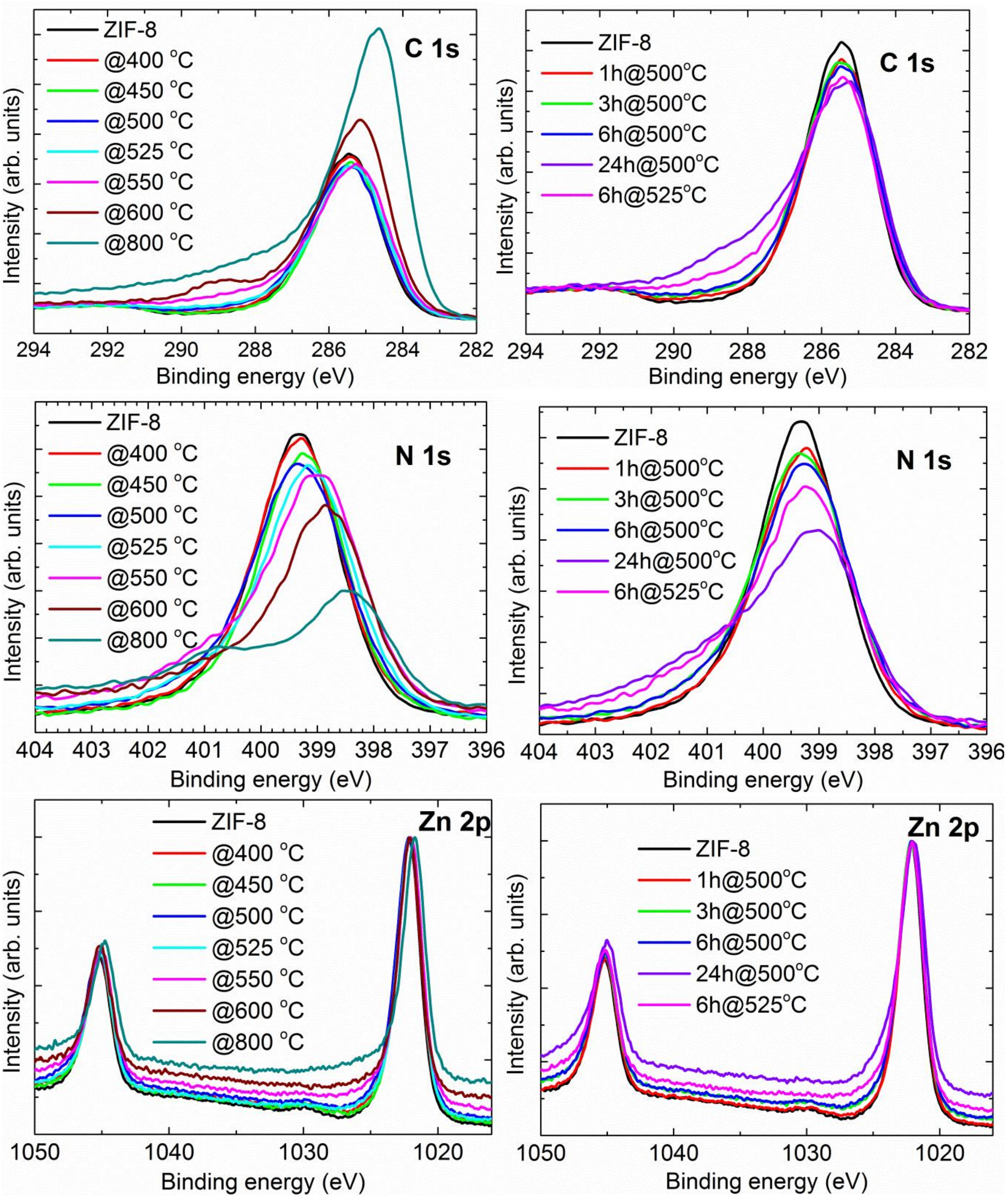

Figure S7. XPS C 1s, N 1s and Zn 2p core level spectra of thermal annealed ZIF-8 samples at various temperatures and periods. Left, top-bottom: samples annealed for 3 h at each temperature.

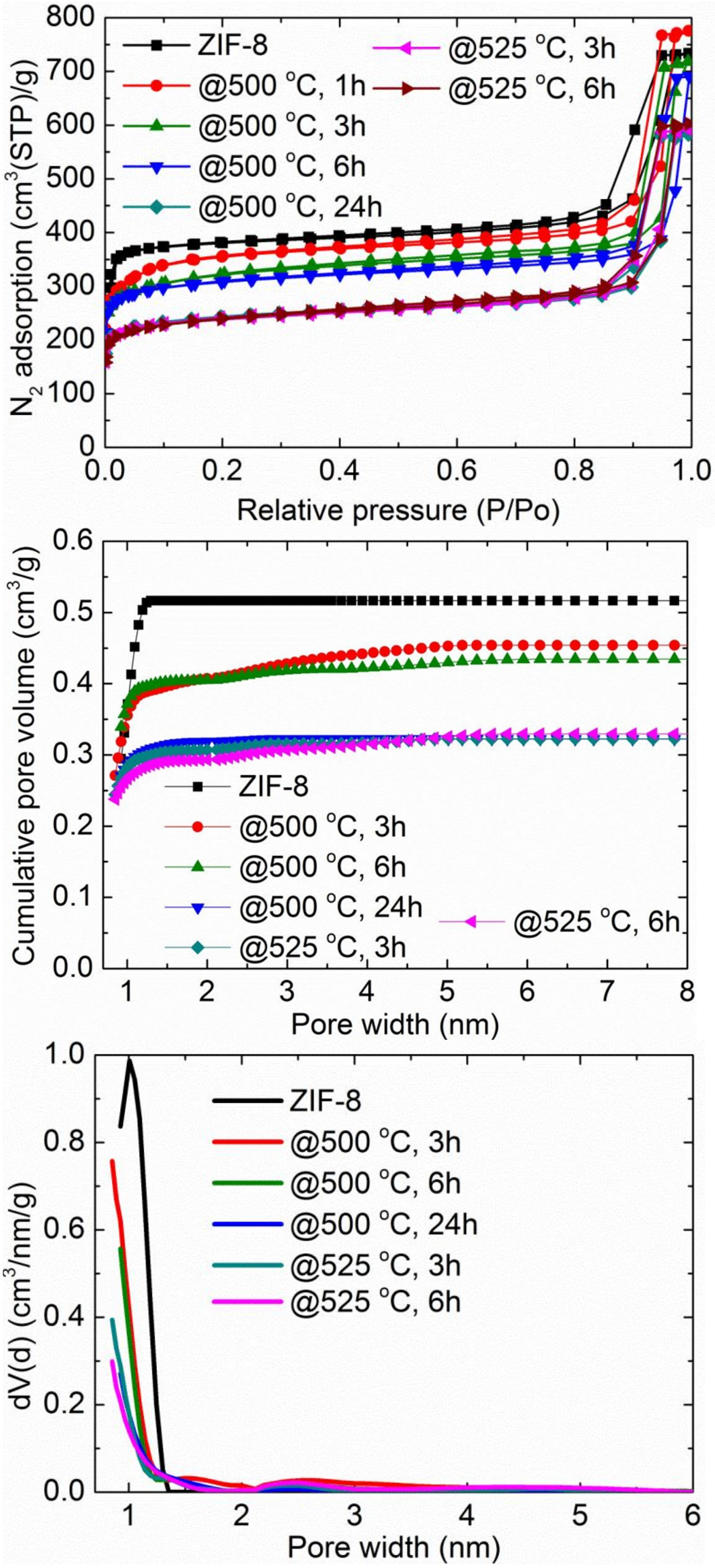

Figure S8. Top: 77 K N_2 adsorption-desorption isotherms of thermal annealed ZIF-8 samples measured on Quantachrome Autosorb-iQC. Midle-bottom: Cumulative pore volume and pore size distribution plots derived from N_2 desorption isotherm by applying QSDFT model.

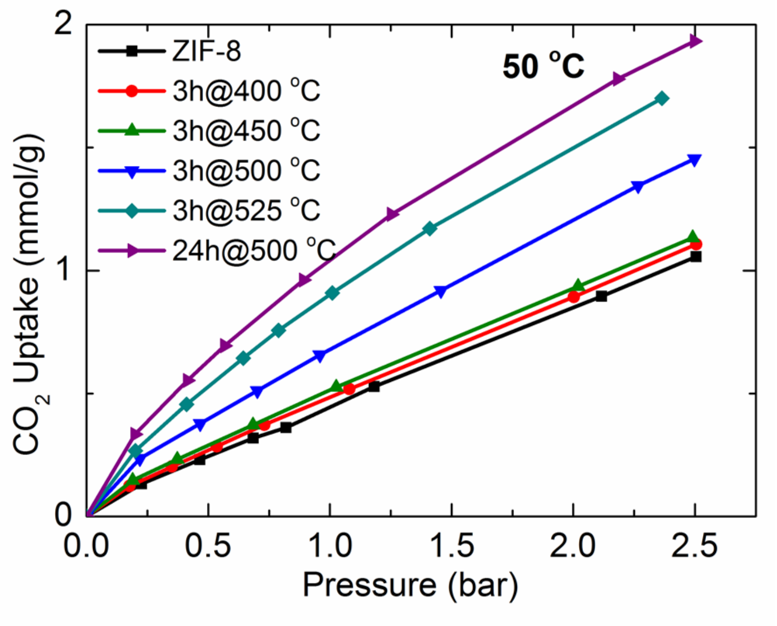

Figure S9. CO$_2$ uptake isotherms up to 2.5 bar of thermal annealed ZIF-8 samples measured at 50 °C on high-presure PCTPro2000.

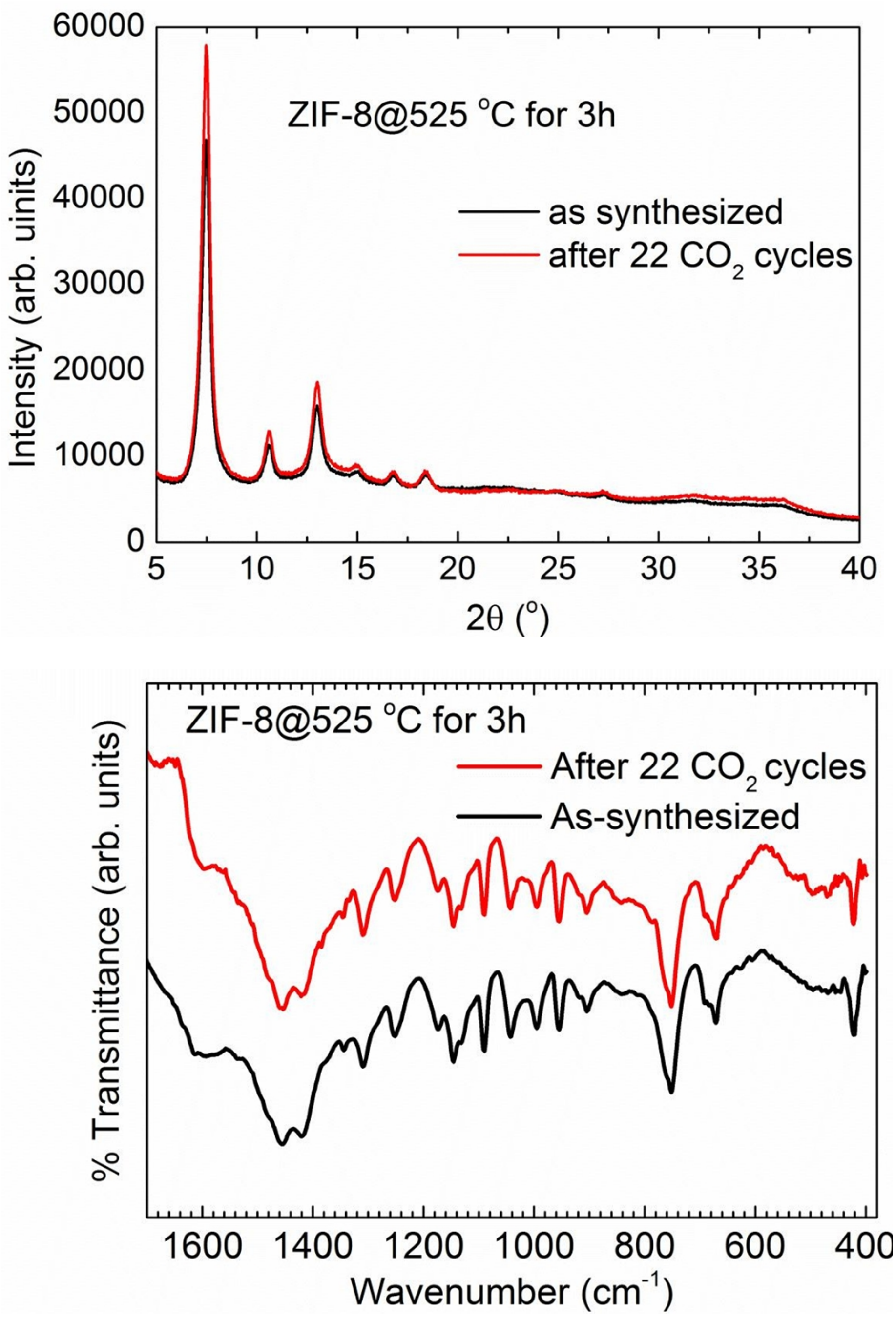

Figure S10. Powder XRD patterns (top) and FTIR spectra (bottom) of ZIF-8 sample annealed at 525 °C for 3 h, recorded on fresh sample and sample after CO$_2$ uptake cycling tests.