A new approach to enhancing the CO_2 capture performance of defective UiO-66 via post-synthetic defect exchange

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Electronic Supplementary Information

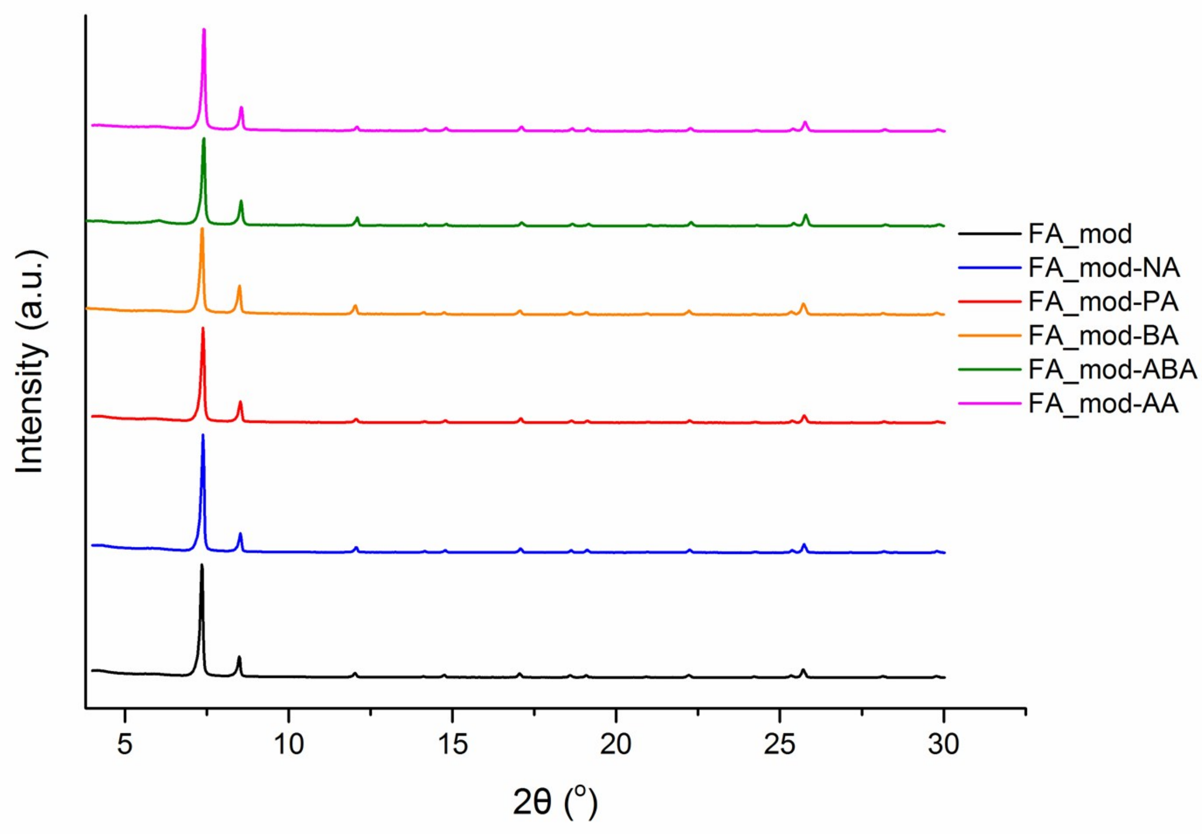

Figure S1. PXRD patterns of defective materials series.

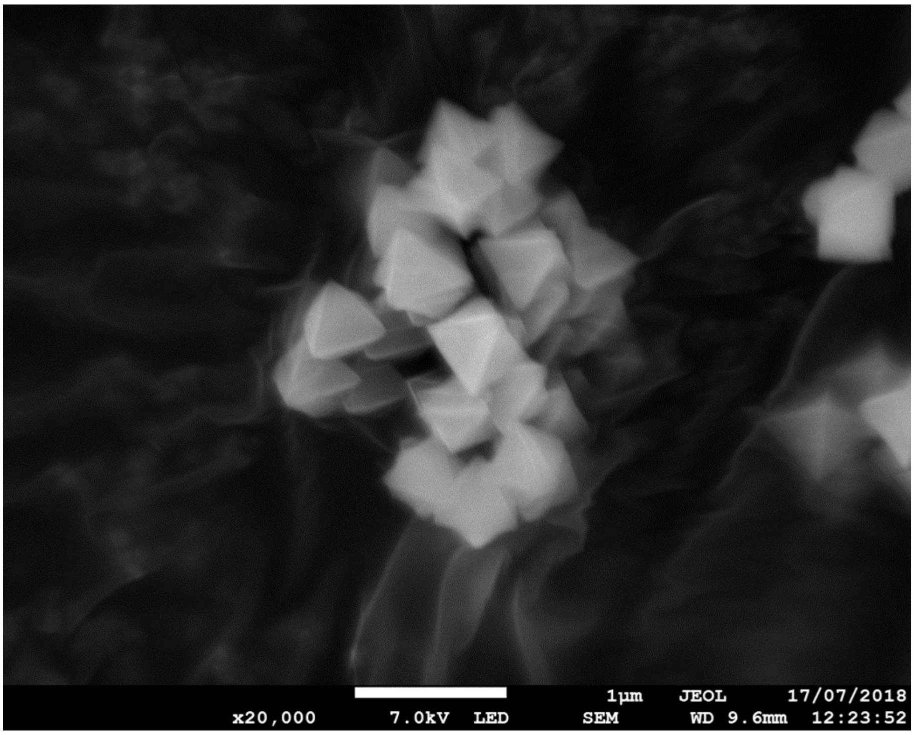

Figure S2. SEM micrograph of FA_mod. Scale bar is 1 μm.

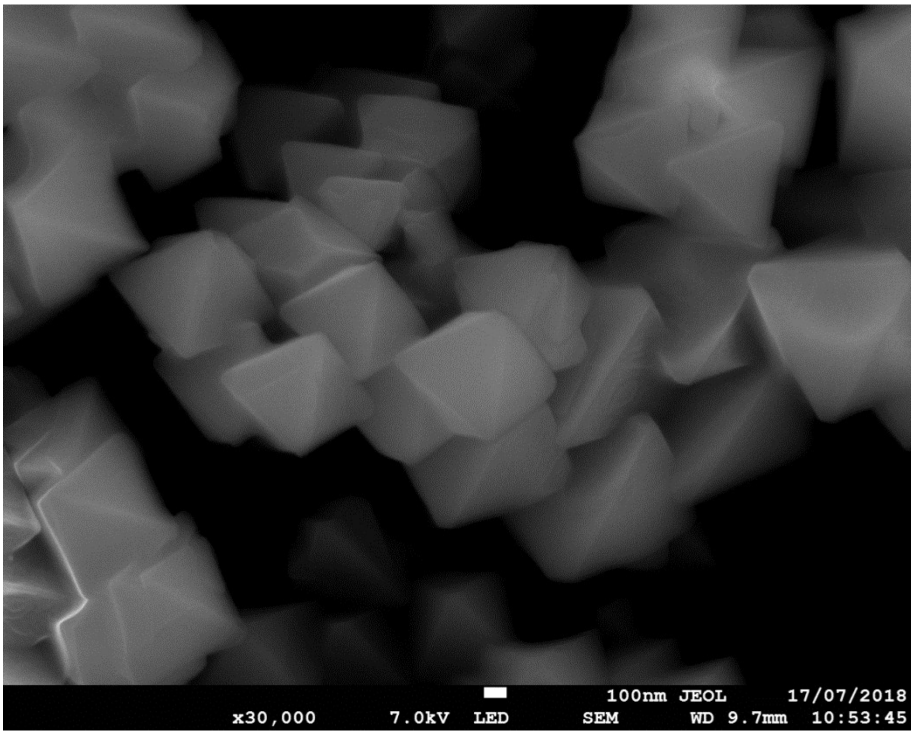

Figure S3. SEM micrograph of FA_mod-NA. Scale bar is 100 nm.

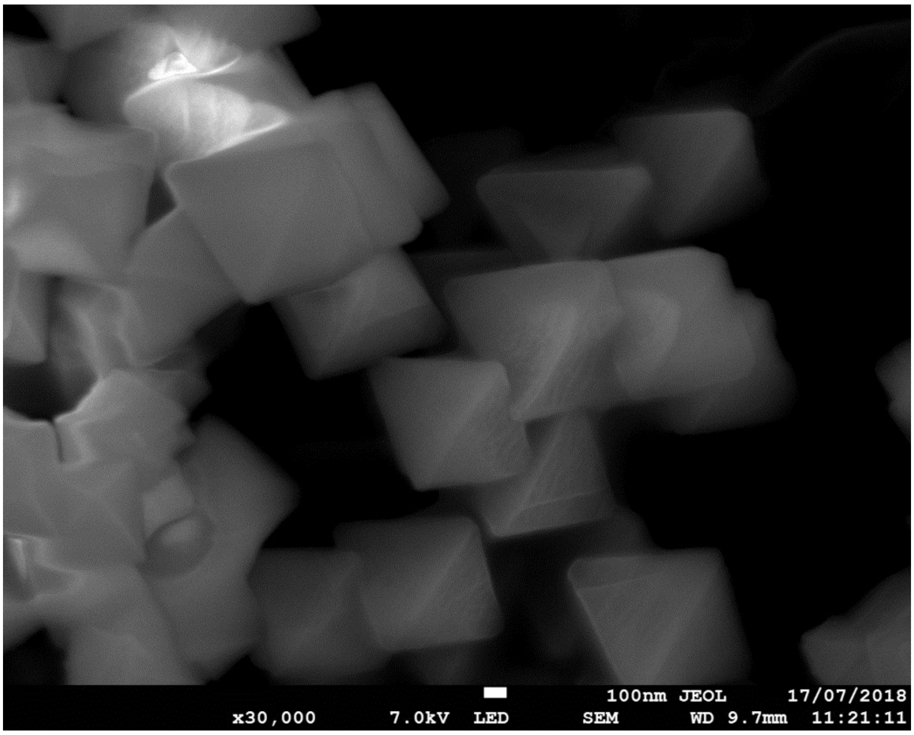

Figure S4. SEM micrograph of FA_mod-PA. Scale bar is 100 nm.

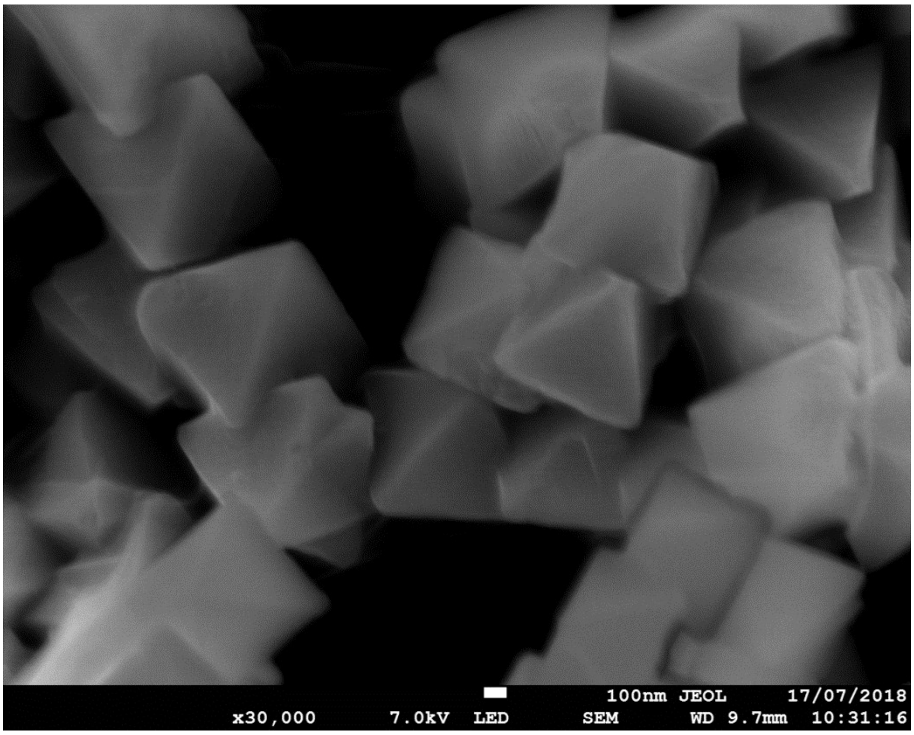

Figure S5. SEM micrograph of FA_mod-BA. Scale bar is 100 nm.

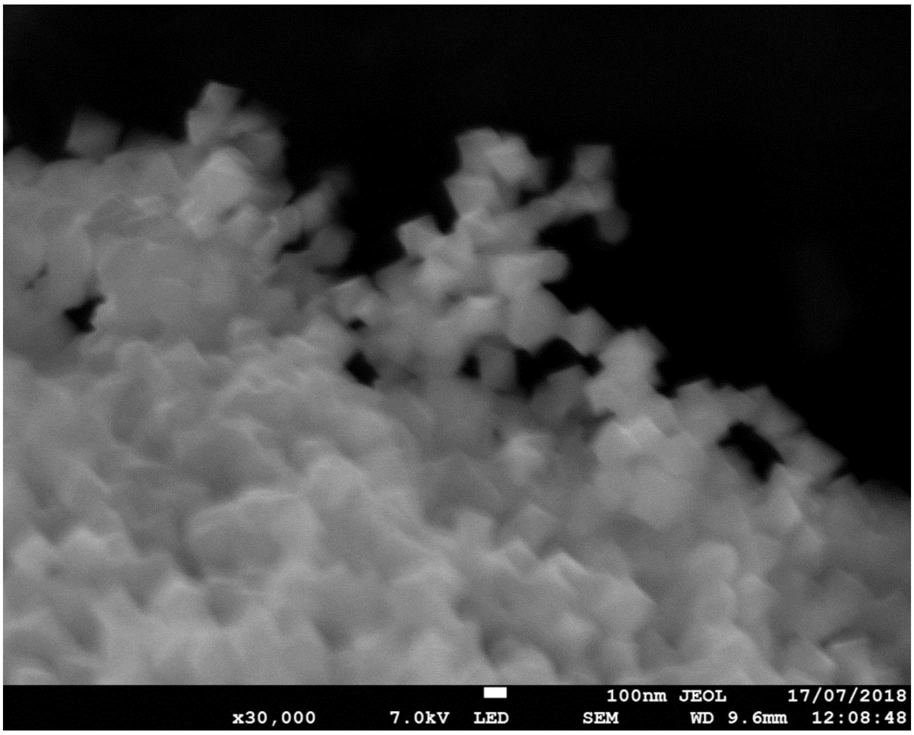

Figure S6. SEM micrograph of FA_mod-ABA. Scale bar is 100 nm.

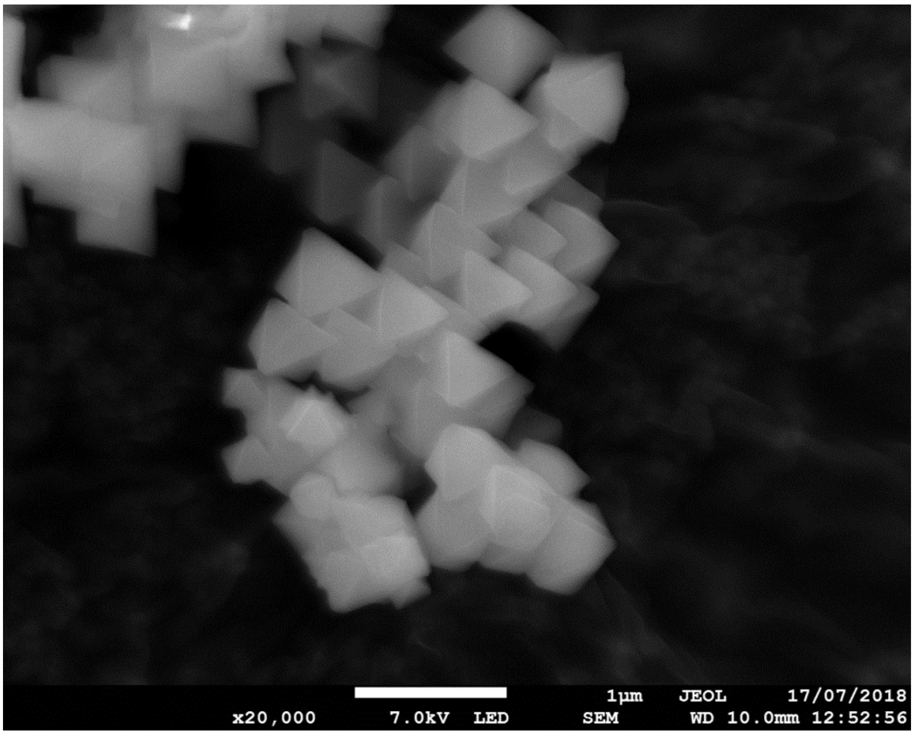

Figure S7. SEM micrograph of FA_mod-AA. Scale bar is 1 µm.

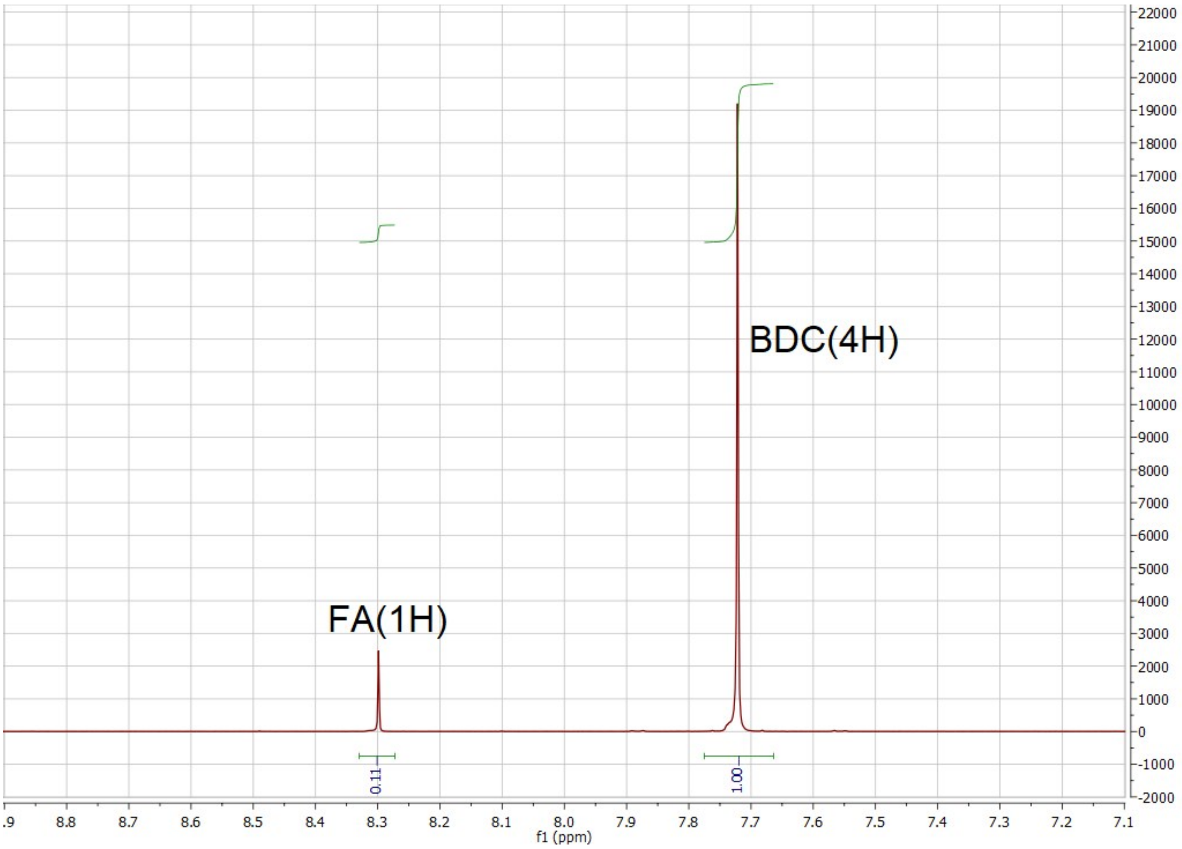

Figure S8. ^{1}H NMR spectrum of FA_mod. The signal of BDC accounts for four aromatic protons, therefore its integral (1.00) must be divided by four to obtain a value (0.25) comparable with that of FA (0.11), which accounts for one formyl proton. This leads to calculate a BDC/FA ratio of 2.27. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x}(FA)_{2x}$, the following can be written:

$$\frac{6-x}{2x} = 2.27$$

Solving the equation, a value of 1.08 is found for x. The proposed formula unit for FA_mod is therefore $Zr_6O_4(OH)_4(BDC)_{4.92}(FA)_{2.16}$.

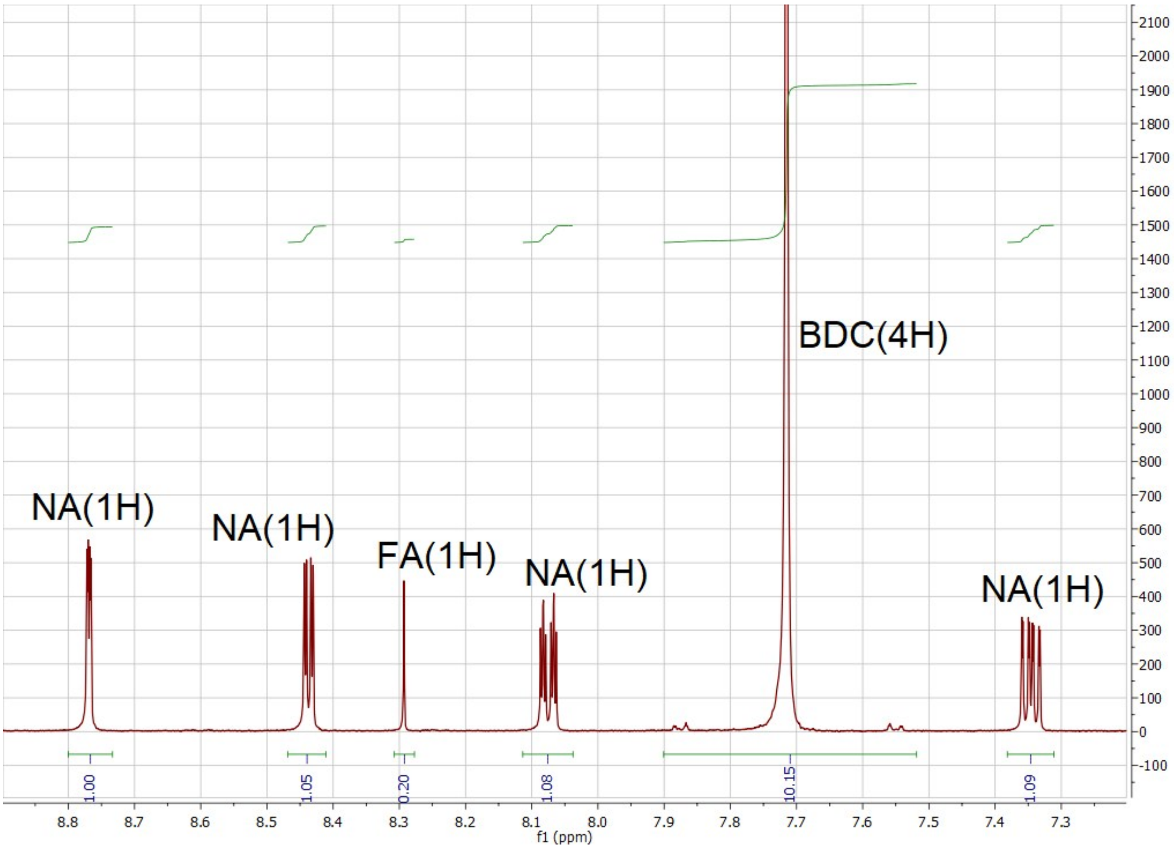

Figure S9. ^{1}H NMR spectrum of FA_mod-NA. The signal of BDC accounts for four aromatic protons, therefore its integral (10.15) must be divided by four to obtain a value (2.54) comparable with those of NA (1.06, average of four signals accounting for one aromatic proton each) and FA (0.20). This leads to calculate a BDC/NA ratio of 2.40 and a BDC/FA ratio of 12.70. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(NA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 12.70$$

$$\frac{6-x-y}{2y} = 2.40$$

Solving the system of equations, a value of 0.20 is found for x and a value of 1.00 is found for y. The proposed formula unit for FA_mod-NA is therefore $Zr_6O_4(OH)_4(BDC)_{4.80}(FA)_{0.40}(NA)_{2.00}$.

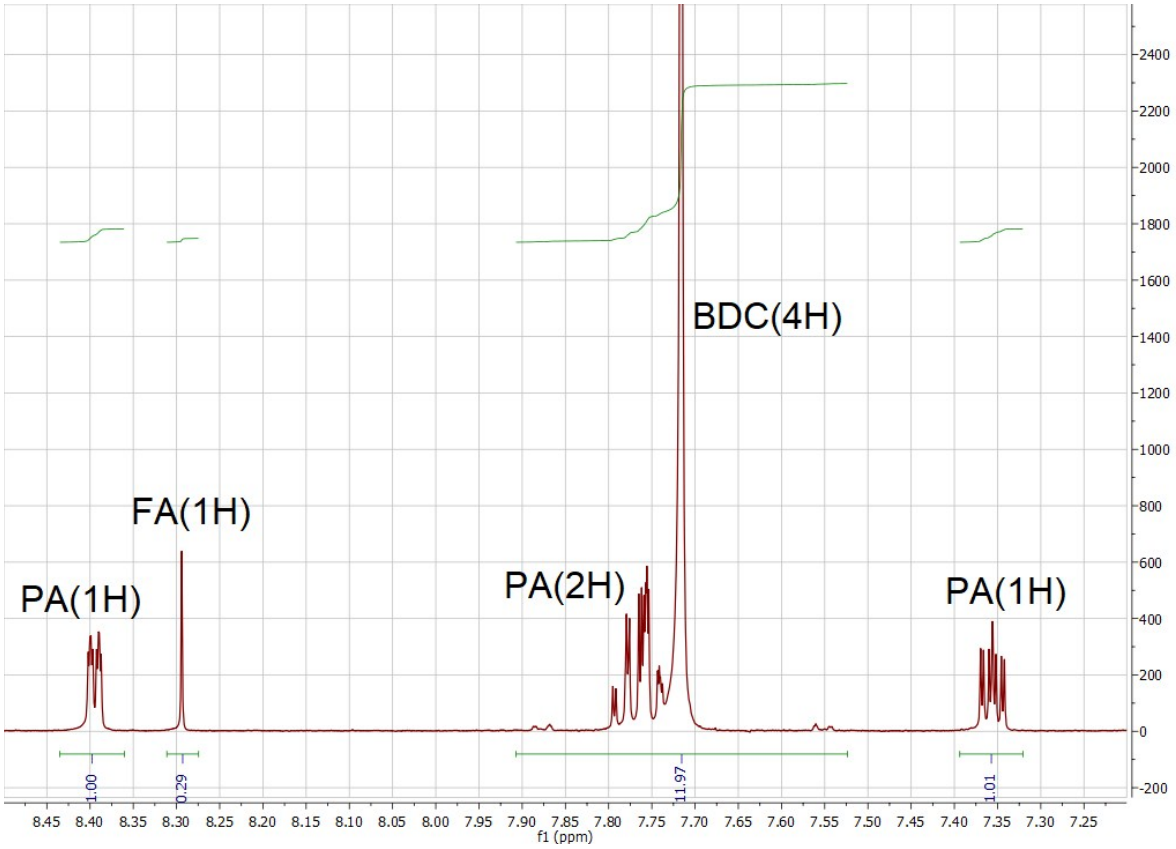

Figure S10. ^{1}H NMR spectrum of FA_mod-PA. The signal of BDC superimposes with two of the signals of PA (each accounting for one aromatic proton), therefore the value of the integral of BDC (2.49) is derived by subtracting the sum of the PA integrals (2.00) from 11.97 and dividing the result (9.97) by four. This leads to calculate a BDC/PA ratio of 2.49 and a BDC/FA ratio of 8.60. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(PA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 8.60$$

$$\frac{6-x-y}{2y} = 2.49$$

Solving the system of equations, a value of 0.26 is found for x and a value of 0.96 is found for y. The proposed formula unit for FA_mod-PA is therefore $Zr_6O_4(OH)_4(BDC)_{4.78}(FA)_{0.52}(PA)_{1.92}$.

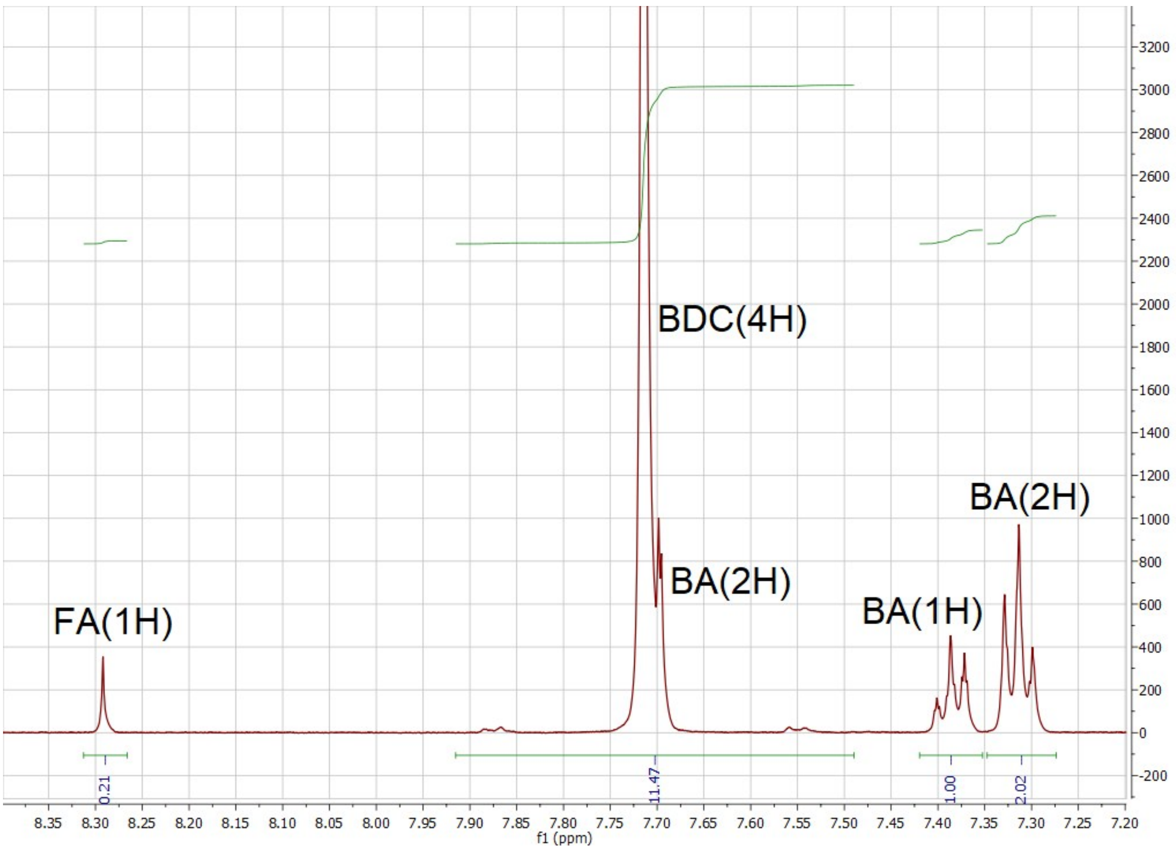

Figure S11. ^{1}H NMR spectrum of FA_mod-BA. The signal of BDC superimposes with one of the signals of BA (accounting for two aromatic protons), therefore the value of the integral of BDC (2.37) is derived by subtracting that of BA (2.00) from 11.47 and dividing the result (9.47) by four. This leads to calculate a BDC/BA ratio of 2.37 and a BDC/FA ratio of 11.29. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(BA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 11.29$$

$$\frac{6-x-y}{2y} = 2.37$$

Solving the system of equations, a value of 0.21 is found for x and a value of 1.01 is found for y. The proposed formula unit for FA_mod-BA is $Zr_6O_4(OH)_4(BDC)_{4.78}(FA)_{0.42}(BA)_{2.02}$.

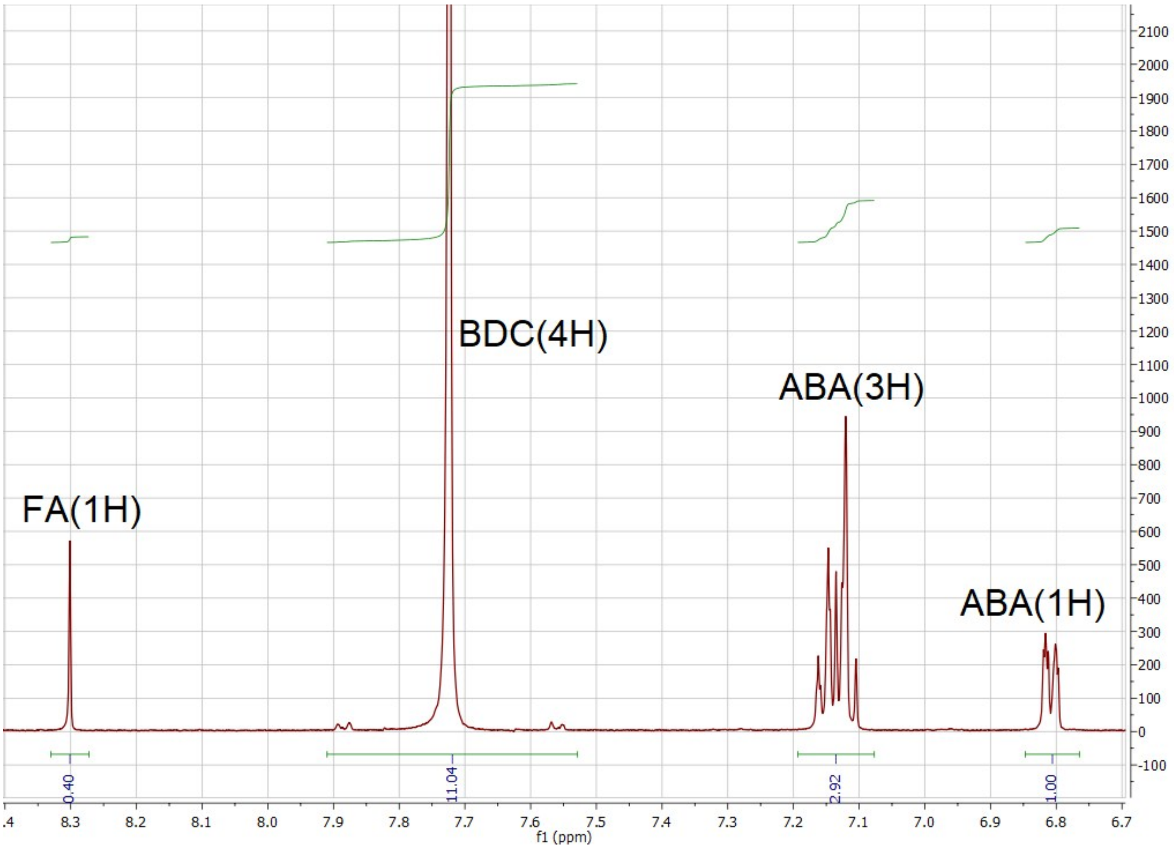

Figure S12. ^{1}H NMR spectrum of FA_mod-ABA. The signal of BDC accounts for four aromatic protons, therefore its integral (11.04) must be divided by four to obtain a value (2.76) comparable with those of ABA (0.98, average of two signals accounting for three and one aromatic protons, respectively) and FA (0.40). This leads to calculate a BDC/ABA ratio of 2.82 and a BDC/FA ratio of 6.90. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(ABA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x}=6.90$$

$$\frac{6-x-y}{2y}=2.82$$

Solving the system of equations, a value of 0.35 is found for x and a value of 0.85 is found for y. The proposed formula unit for FA_mod-ABA is therefore $Zr_6O_4(OH)_4(BDC)_{4.80}(FA)_{0.70}(ABA)_{1.70}$.

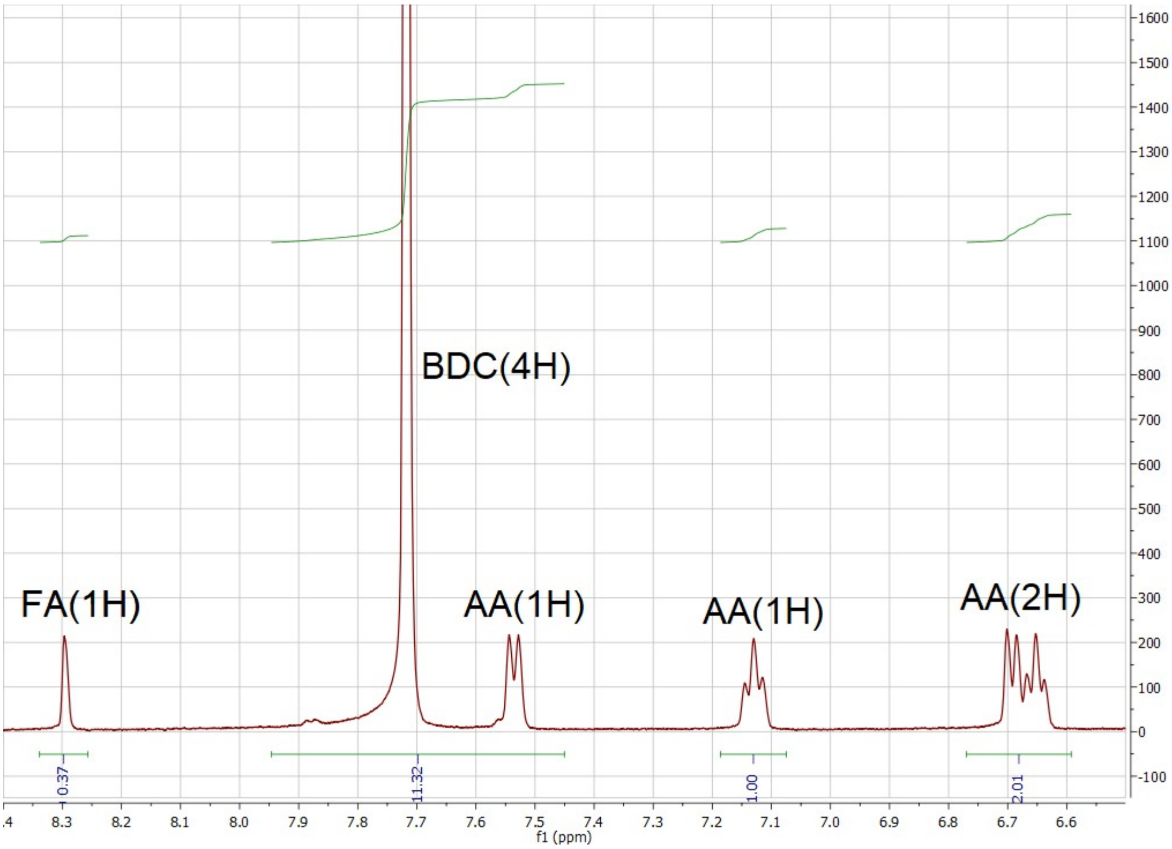

Figure S13. ^{1}H NMR spectrum of FA_mod-AA. The signal of BDC superimposes with one of the signals of AA (accounting for one aromatic proton), therefore the value of the integral of BDC (2.58) is derived by subtracting that of AA (1.00) from 11.32 and dividing the result (10.32) by four. This leads to calculate a BDC/AA ratio of 2.58 and a BDC/FA ratio of 6.97. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(FA)_{2x}(AA)_{2y}$, the following can be written:

$$\frac{6-x-y}{2x} = 6.97$$

$$\frac{6-x-y}{2y} = 2.58$$

Solving the system of equations, a value of 0.34 is found for x and a value of 0.87 is found for y. The proposed formula unit for FA_mod-AA is therefore $Zr_6O_4(OH)_4(BDC)_{4.74}(FA)_{0.68}(AA)_{1.84}$.

Unit cell content calculation for defective samples

The formula units proposed in Figures S8-S13 provide an average information on the chemical composition of the compounds in object, however, they do not account for the actual unit cell content. This information is useful to convert the uptake values from mol per kg (a bulk unit of measurement) into CO_2 molecules per unit cell (a microscopic unit of measurement), thus providing further insight into the effect of functionalization on the adsorption properties of the frameworks.

Based on previous literature,[1] we assume that defects in these samples are exclusively of missing-cluster nature. In the case of FA_mod, this means that the framework can be thought as being constituted of non-defective unit cells having **fcu** topology and content $Zr_{24.0}O_{16.0}(OH)_{16.0}(BDC)_{24.0}$, and defective unit cells having **reo** topology and content $Zr_{18.0}O_{12.0}(OH)_{12.0}(BDC)_{12.0}(FA)_{12.0}$. Knowing that the formula unit for FA_mod is $Zr_6O_4(OH)_4(BDC)_{4.92}(FA)_{2.16}$, one can easily determine the fraction of **fcu** cells (*x*) and the fraction of **reo** cells (*y*) in the framework of FA_mod by solving the following:

$$x + y = 1$$

$$\frac{BDC}{FA} = \frac{24.0x + 12y}{12y} = \frac{4.92}{2.16}$$

This yields *x* of 0.39 and *y* of 0.61. By multiplying *x* times the content of the **fcu** unit cell and *y* times the content of the **reo** unit cell and adding up the resulting values, the following unit cell content is determined for FA_mod: $Zr_{20.3}O_{13.6}(OH)_{13.6}(BDC)_{16.7}(FA)_{7.3}$.

Similar procedure can be employed for the functionalized derivatives of FA_mod. The procedure is here explained only for FA_mod-NA, but it is straightforward to apply for the other compounds. In FA_mod-NA, the **fcu** cell has the same content as detailed above for FA_mod, whereas the **reo** cell has content $Zr_{18.0}O_{12.0}(OH)_{12.0}(BDC)_{12.0}(FA)_{2.0}(NA)_{10.0}$. The FA and NA indexes in this formula are determined such that the NA/FA ratio is consistent with that derived from the formula unit $Zr_6O_4(OH)_4(BDC)_{4.80}(FA)_{0.40}(NA)_{2.00}$. The fraction of **fcu** cells (*x*) and the fraction of **reo** cells (*y*) in the framework of FA_mod-NA is derived by solving the following:

$$x + y = 1$$

$$\frac{BDC}{NA} = \frac{24.0x + 12y}{10y} = \frac{4.80}{2.00}$$

This yields *x* of 0.33 and *y* of 0.67. By multiplying *x* times the content of the **fcu** unit cell and *y* times the content of the **reo** unit cell and adding up the resulting values, the following unit cell content is determined for FA_mod-NA: $Zr_{20.0}O_{13.3}(OH)_{13.3}(BDC)_{16.0}(FA)_{1.3}(NA)_{6.7}$.

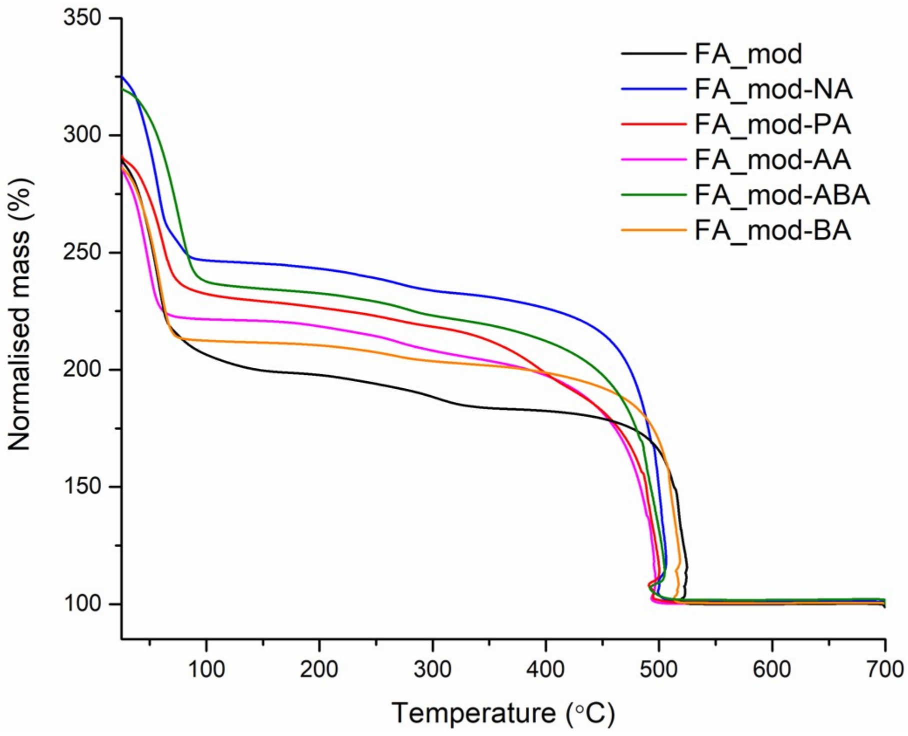

Figure S14. Comparison of the TGA curves of the defective materials.

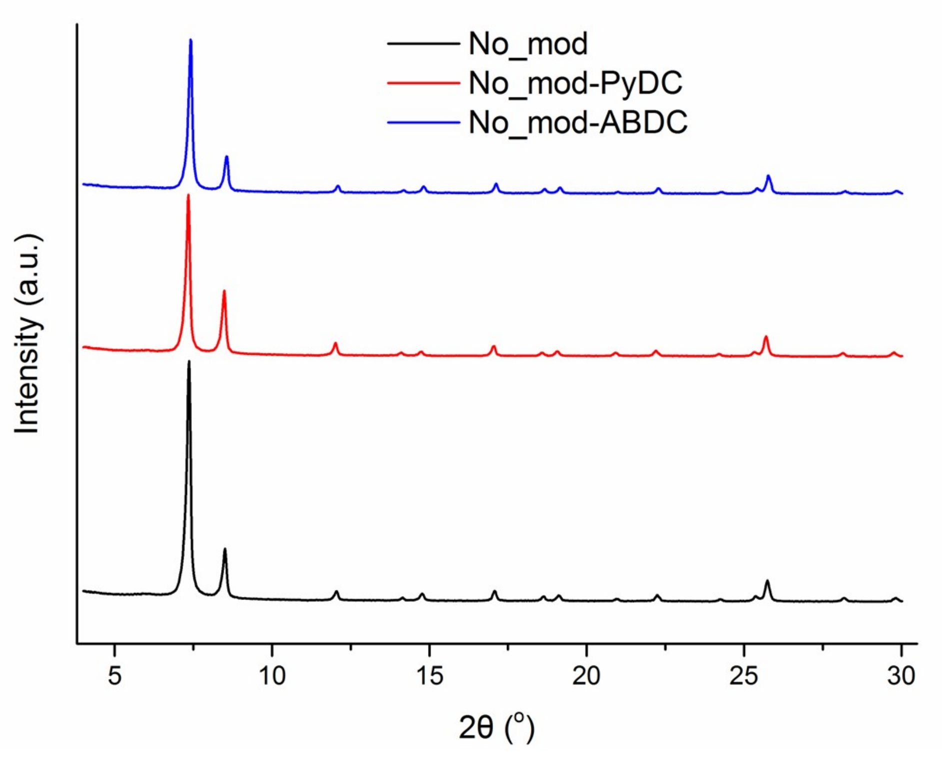

Figure S15. PXRD patterns of non-defective materials series.

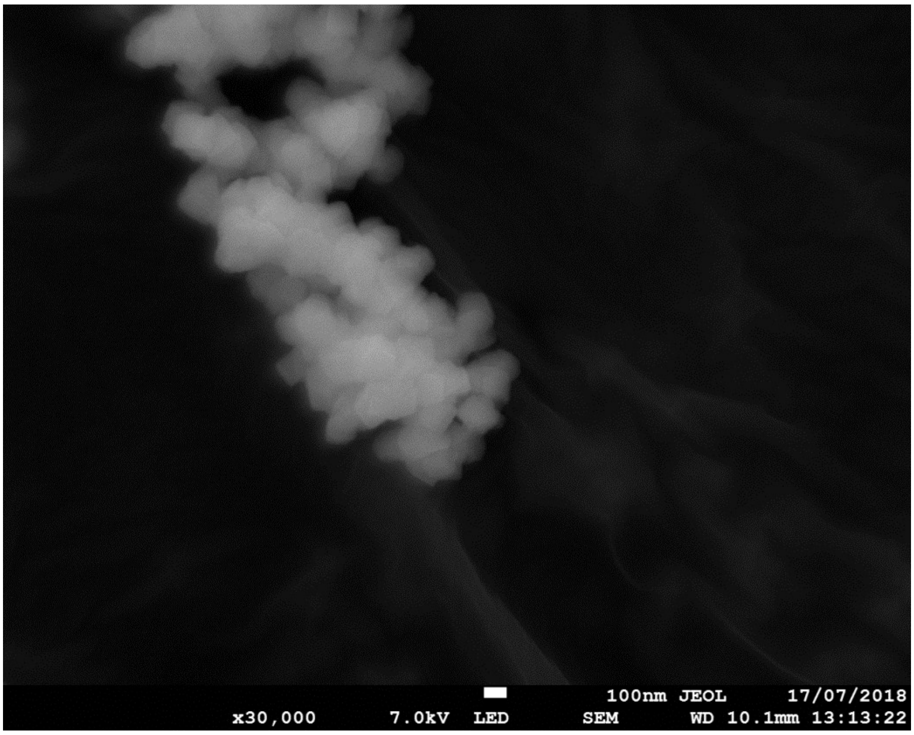

Figure S16. SEM micrograph of No_mod. Scale bar is 100 nm.

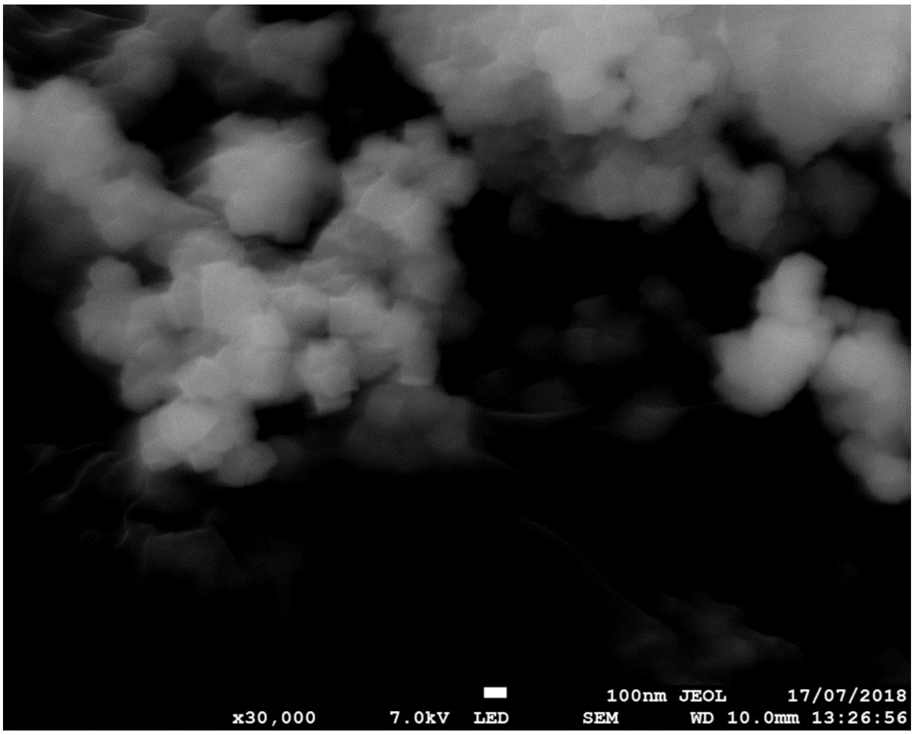

Figure S17. SEM micrograph of No_mod-PyDC. Scale bar is 100 nm.

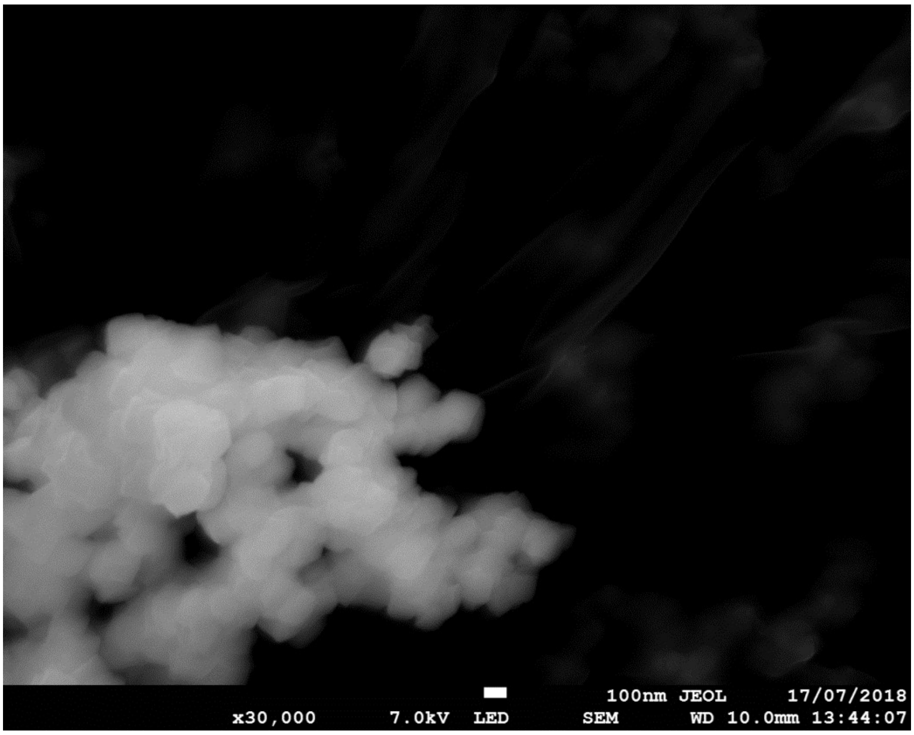

Figure S18. SEM micrograph of No_mod-ABDC. Scale bar is 100 nm.

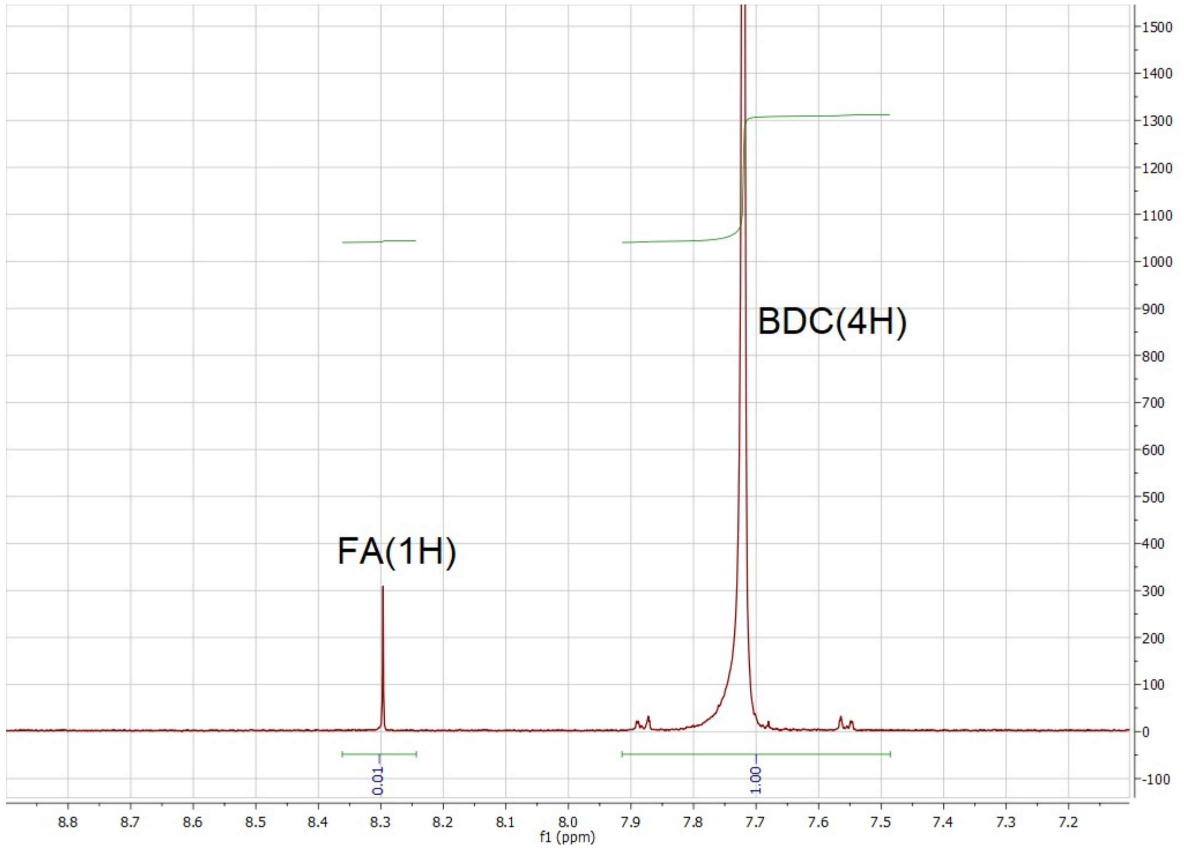

Figure S19. ^{1}H NMR spectrum of No_mod. The signal of BDC accounts for four aromatic protons, therefore its integral (1.00) must be divided by four to obtain a value (0.25) comparable with that of FA (0.01), which accounts for one formyl proton. This leads to calculate a BDC/FA ratio of 25.00. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x}(FA)_{2x}$, the following can be written:

$$\frac{6-x}{2x} = 25.00$$

Solving the equation, a value of 0.12 is found for x. The proposed formula unit for No_mod is therefore $Zr_6O_4(OH)_4(BDC)_{5.88}(FA)_{0.24}$.

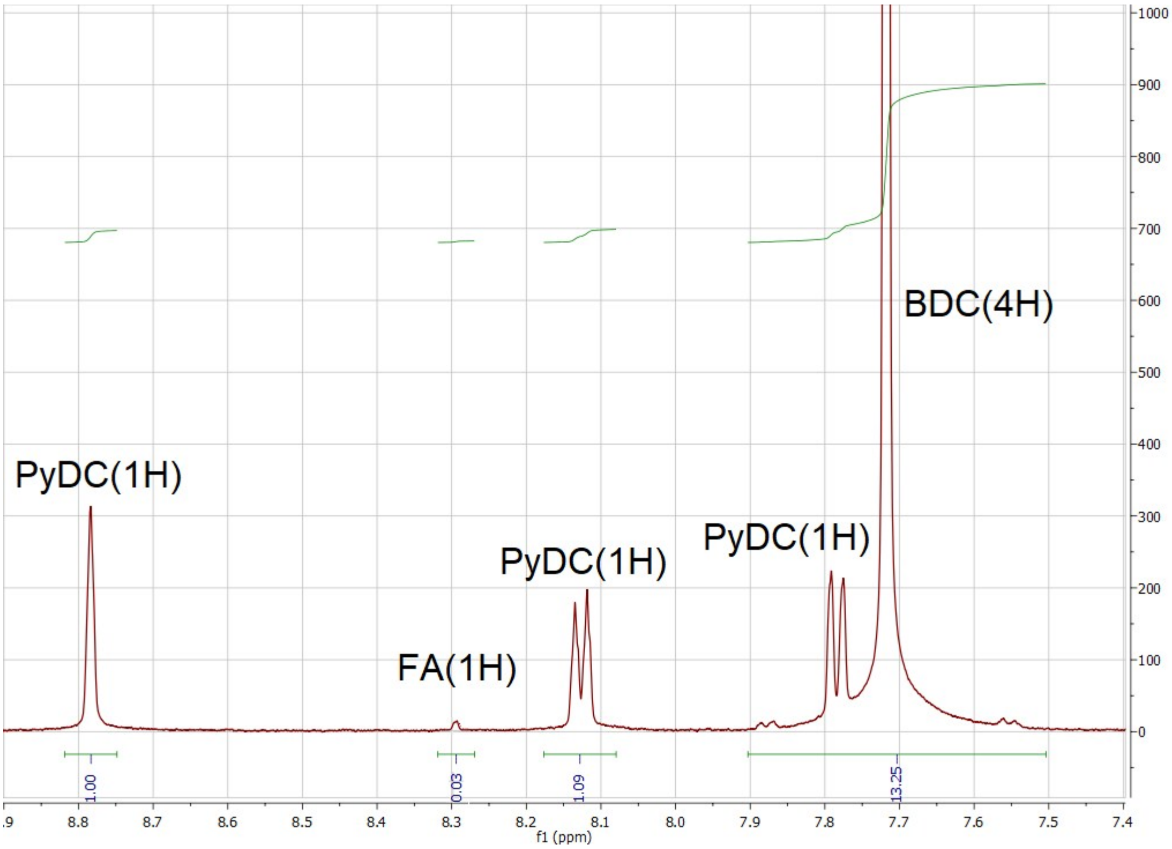

Figure S20. ^{1}H NMR spectrum of No_mod-PyDC. The signal of BDC superimposes with one of the signals of PyDC (accounting for one aromatic proton), therefore the value of the integral of BDC (3.06) is derived by subtracting the PyDC integral (1.00) from 13.25 and dividing the result (12.25) by four. This leads to calculate a BDC/PyDC ratio of 3.06 and a BDC/FA ratio of 102.00. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6\text{-}x\text{-}y}(PyDC)_x(FA)_{2y}$, the following can be written:

$$\frac{6-x-y}{x}=3.06$$

$$\frac{6-x-y}{2y}=102.00$$

Solving the system of equations, a value of 1.47 is found for *x* and a value of 0.03 is found for *y*. The proposed formula unit for No_mod-PyDC is therefore $Zr_6O_4(OH)_4(BDC)_{4.50}(PyDC)_{1.47}(FA)_{0.06}$.

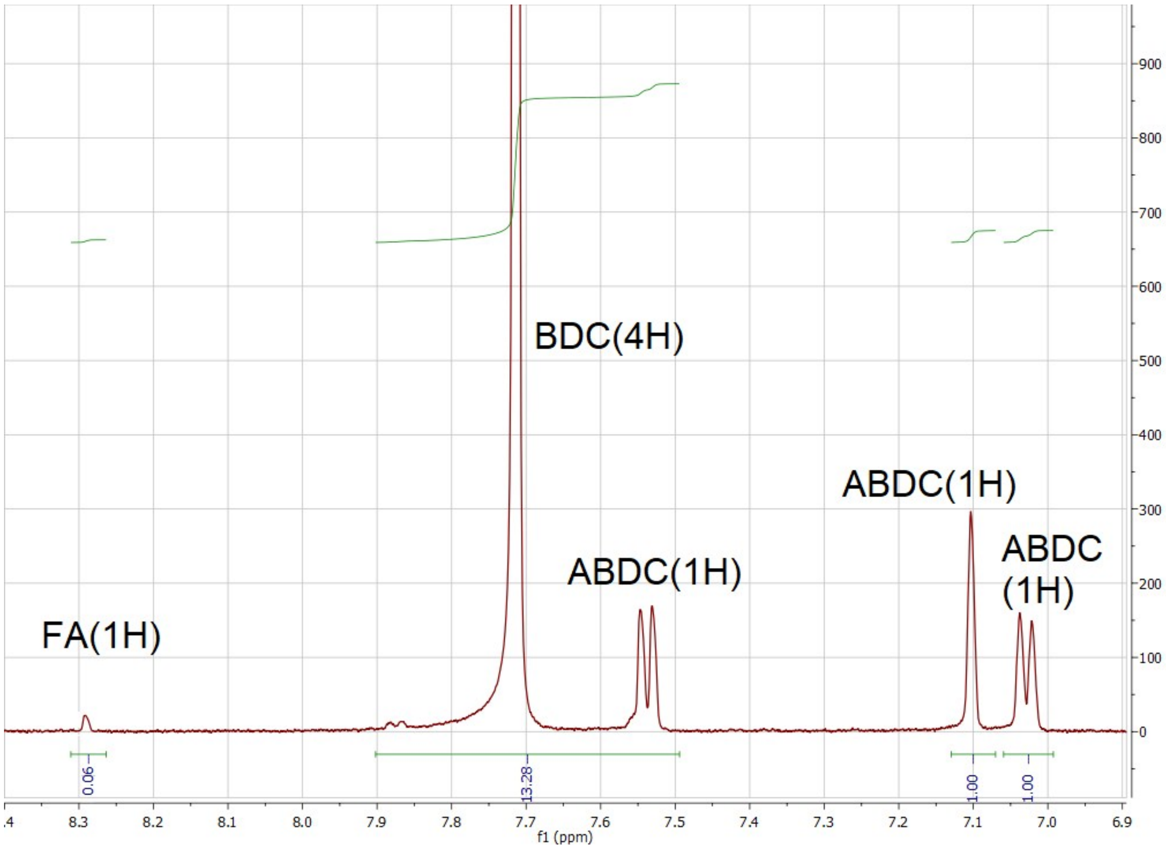

Figure S21. ^{1}H NMR spectrum of No_mod-ABDC. The signal of BDC superimposes with one of the signals of ABDC (accounting for one aromatic proton), therefore the value of the integral of BDC (3.07) is derived by subtracting the ABDC integral (1.00) from 13.28 and dividing the result (12.28) by four. This leads to calculate a BDC/ABDC ratio of 3.07 and a BDC/FA ratio of 51.17. Assuming a general formula $Zr_6O_4(OH)_4(BDC)_{6-x-y}(ABDC)_x(FA)_{2y}$, the following can be written:

$$\frac{6-x-y}{x} = 3.07$$

$$\frac{6-x-y}{2y} = 51.17$$

Solving the system of equations, a value of 1.46 is found for x and a value of 0.04 is found for y. The proposed formula unit for No_mod-ABDC is therefore $Zr_6O_4(OH)_4(BDC)_{4.50}(ABDC)_{1.46}(FA)_{0.08}$.

Unit cell content calculation for non-defective samples

Different from defective samples, the unit cell content for non-defective samples is calculated in a more straightforward manner. In this case, all the unit cells in the framework are assumed to have **fcu** topology and small amounts of FA, as observed in the case of No_mod, are attributed to the presence of a few missing-linker defects, which only affect the organic content in the unit cell by substitution of one with BDC with two FAs. The unit cell content for No_mod can therefore be derived by simply multiplying by 4 the formula unit $Zr_6O_4(OH)_4(BDC)_{5.88}(FA)_{0.24}$, thus obtaining $Zr_{24.0}O_{16.0}(OH)_{16.0}(BDC)_{23.5}(FA)_{1.0}$. The unit cell content for the amino-functionalized derivatives No_mod-PyDC and No_mod-ABDC is determined with an analogous procedure.

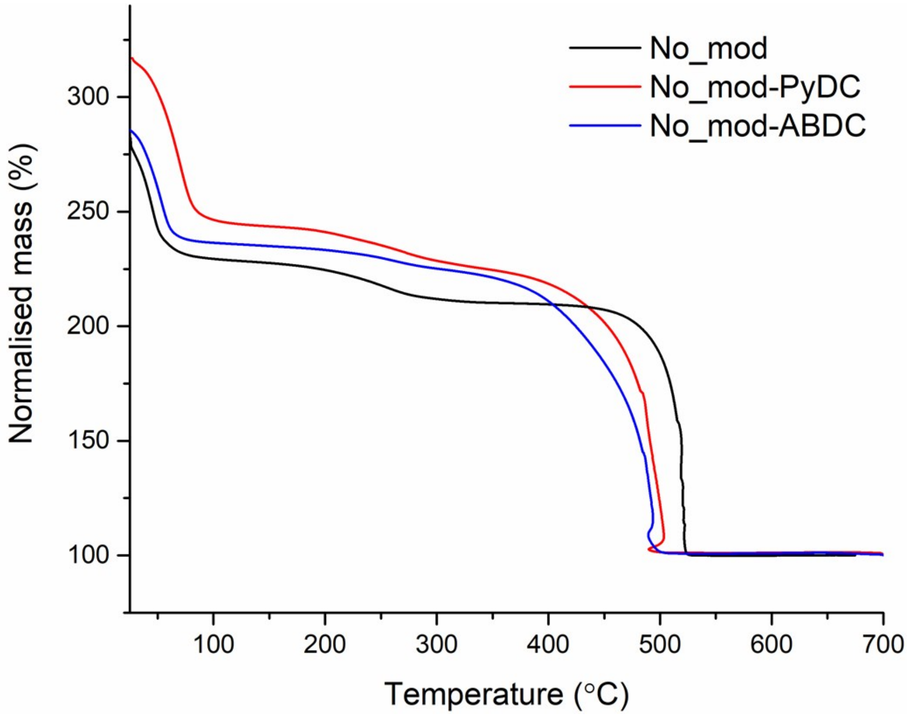

Figure S22. Comparison of the TGA curves of the non-defective series.

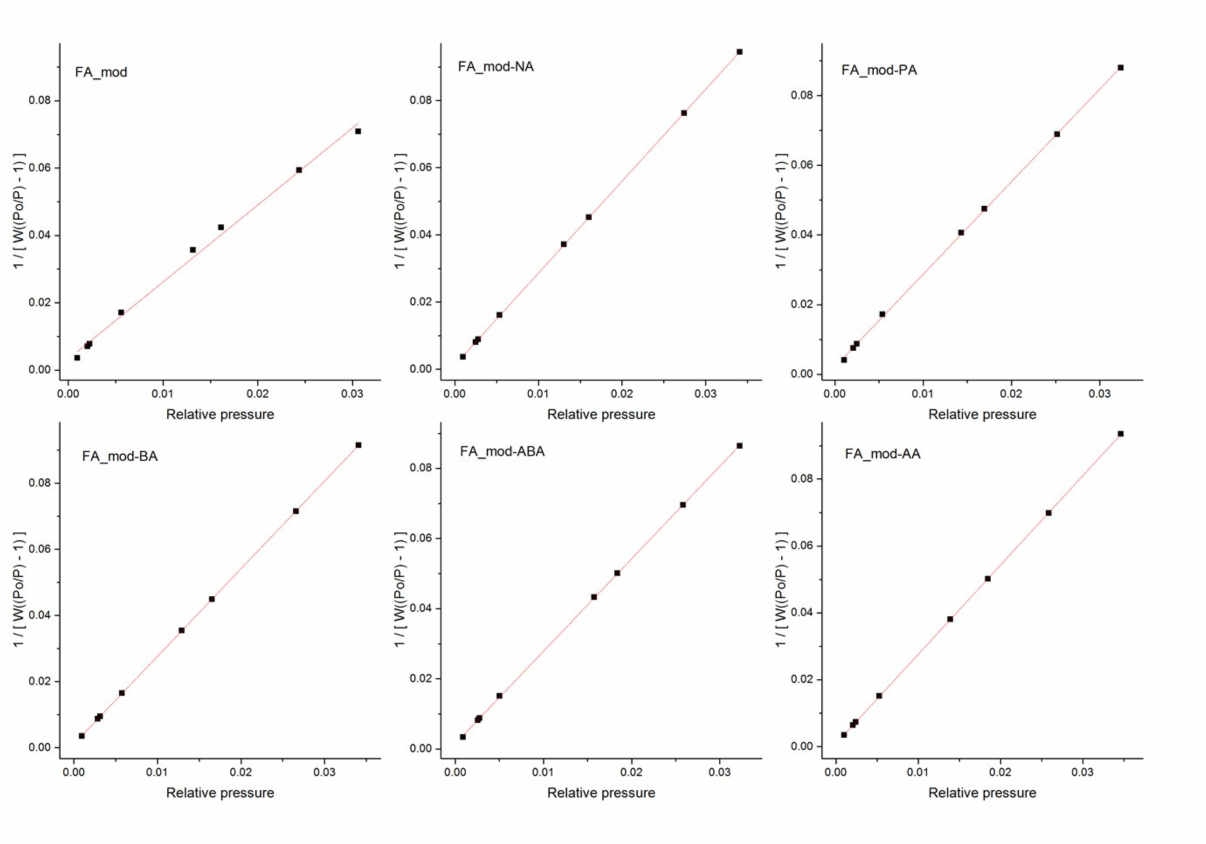

Figure S23. Linearization of the N_2 adsorption isotherms of the defective materials according to the BET model.

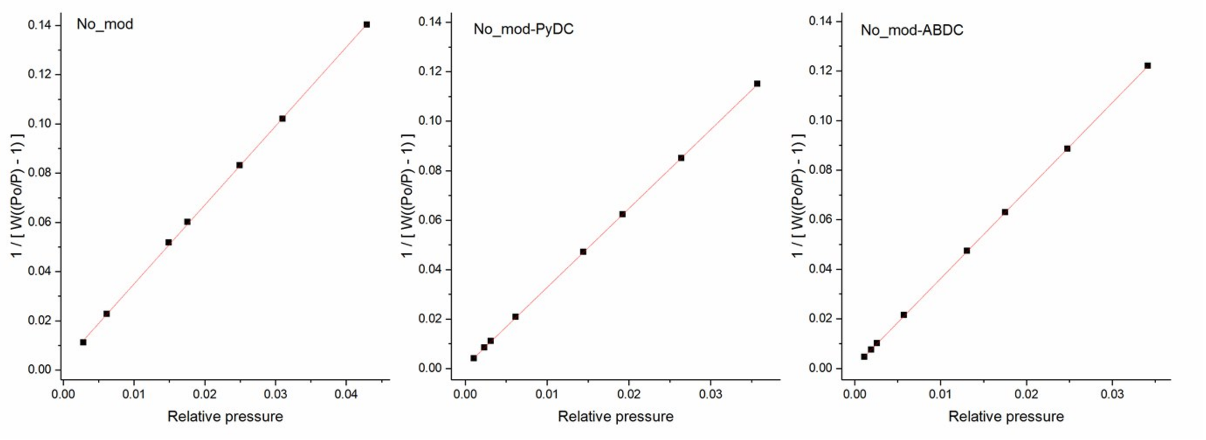

Figure S24. Linearization of the N_2 adsorption isotherms of No_mod, No_mod-PyDC and No_mod-ABDC according to the BET model.

Conversion procedure of uptake values from mol kg^{-1} to molecules per unit cell

The procedure is here explained only for FA_mod, but it is straightforward to apply for the other compounds. Assuming an uptake of 1 mol of CO_2 per kg of FA_mod, the following applies:

$$Unit\ cells\ in\ 1\ kg\ of\ FA\_mod = \frac{1000\ g\ of\ FA\_mod}{\frac{Average\ unit\ cell\ weight\ (in\ g\ mol^{-1})}{6.02 \times 10^{23}\ unit\ cells\ per\ mol}} =$$

$$= \frac{1000 \times\ 6.02 \times 10^{23}}{Average\ unit\ cell\ weight} = \frac{6.02 \times 10^{26}}{Average\ unit\ cell\ weight}$$

Considered that 1 mol of CO_2 contains 6.02×10^{23} molecules, the following can be written:

$$Molecules\ of\ CO_2\ per\ unit\ cell\ of\ FA_{mod} = \frac{6.02 \times 10^{23}}{\frac{6.02 \times 10^{26}}{Average\ unit\ cell\ weight}} == Average\ unit\ cell\ weight \times 10^{-3}$$

Introducing the value of the average unit cell weight reported in Table 1 (5363.3 g mol^{-1}), one calculates that an uptake of 1 mol kg^{-1} equates to 5.36 molecules of CO_2 per unit cell. Applying the same procedure, the values reported in table S1 are obtained for all the compounds investigated in this work.

Table S1. Conversion of CO_2 uptake from 1.0 mol kg^{-1} to molecules per unit cell for the samples in this study.

Sample	CO_2 Uptake	
	mol kg^{-1}	Molecules/unit cell
FA_mod	1.0	5.36
FA_mod-NA		5.75
FA_mod-PA		5.71
FA_mod-BA		5.73
FA_mod-ABA		5.76
FA_mod-AA		5.75
No_mod		6.61
No_mod-PyDC		6.64
No_mod-ABDC		6.72

Isosteric Enthalpies of Adsorption calculation

In order to calculate the isosteric enthalpies of adsorption (IEA) the dual-site Langmuir model (Equation 1) was used to fit the CO_2 adsorption isotherms at 283, 298 and 313 K with the

Origin software. IEA values were then determined using the integrated form of the Clausius-Clapeyron equation (Equation 2) by calculating the slope of ln(p) vs 1/T for each loading.[2] The standard deviation for the error of the linear regression equation was also calculated using Microsoft Excel.

$$n = \frac{q_{sat,A}\, k_A\, p}{1 + k_A\, p} + \frac{q_{sat,B}\, k_B\, p}{1 + k_B\, p} \qquad (1)$$

$$\ln p_n = \left(\frac{IEA}{R}\right)\left(\frac{1}{T}\right) + C \qquad (2)$$

where n is the loading in mol/kg, q_{sat} is the saturation loading for site A or B, k_A and k_B are the Langmuir parameters associated with site A and B respectively (bar^{-1}), p is the pressure (bar) and T the temperature (K).

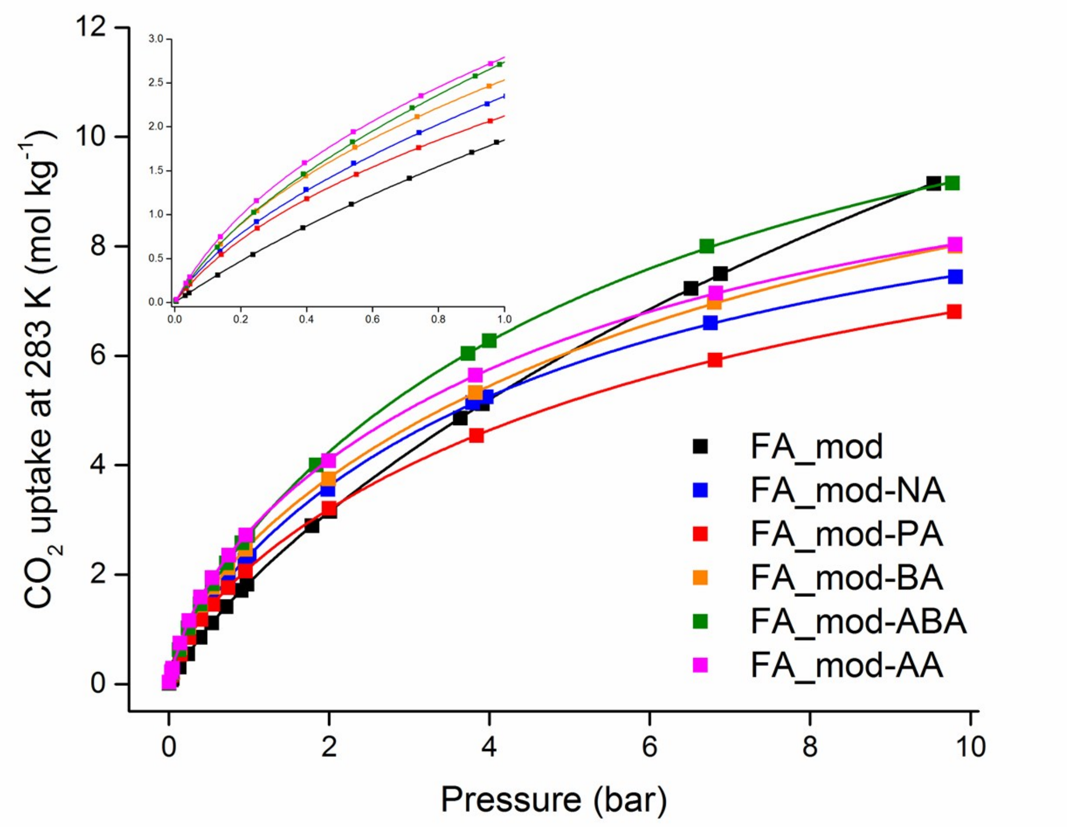

Figure S25. CO$_2$ excess adsorption isotherms at 283 K of the defective materials.

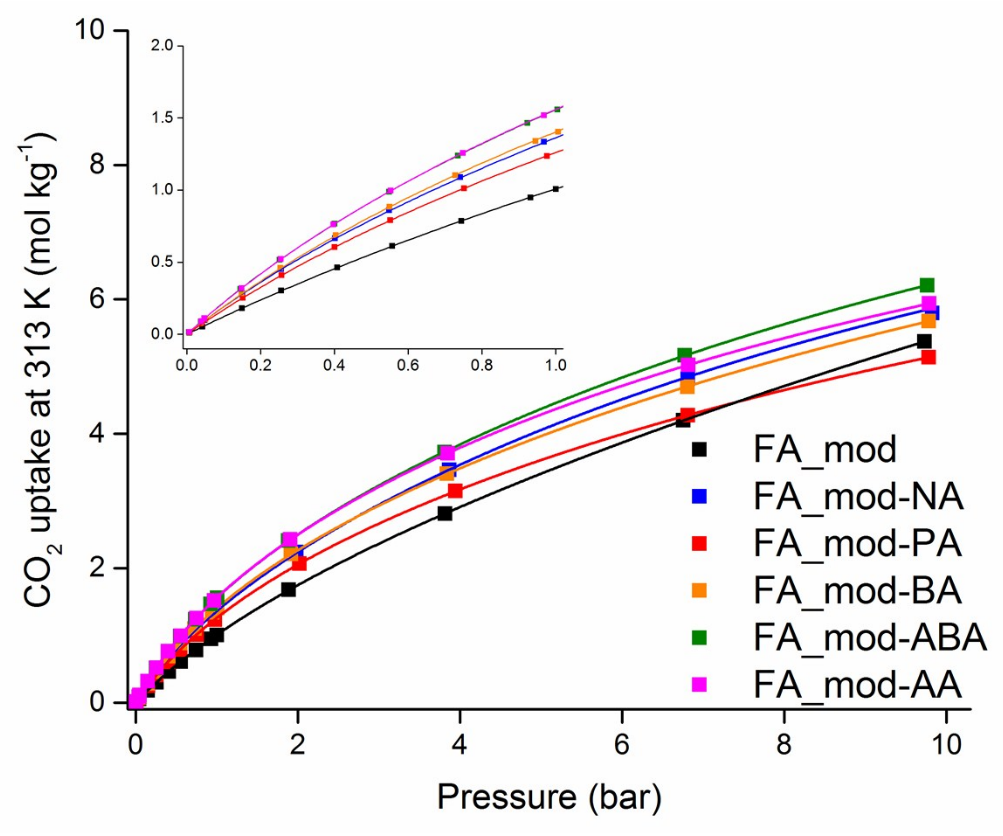

Figure S26. CO$_2$ excess adsorption isotherms at 313 K of the defective materials.

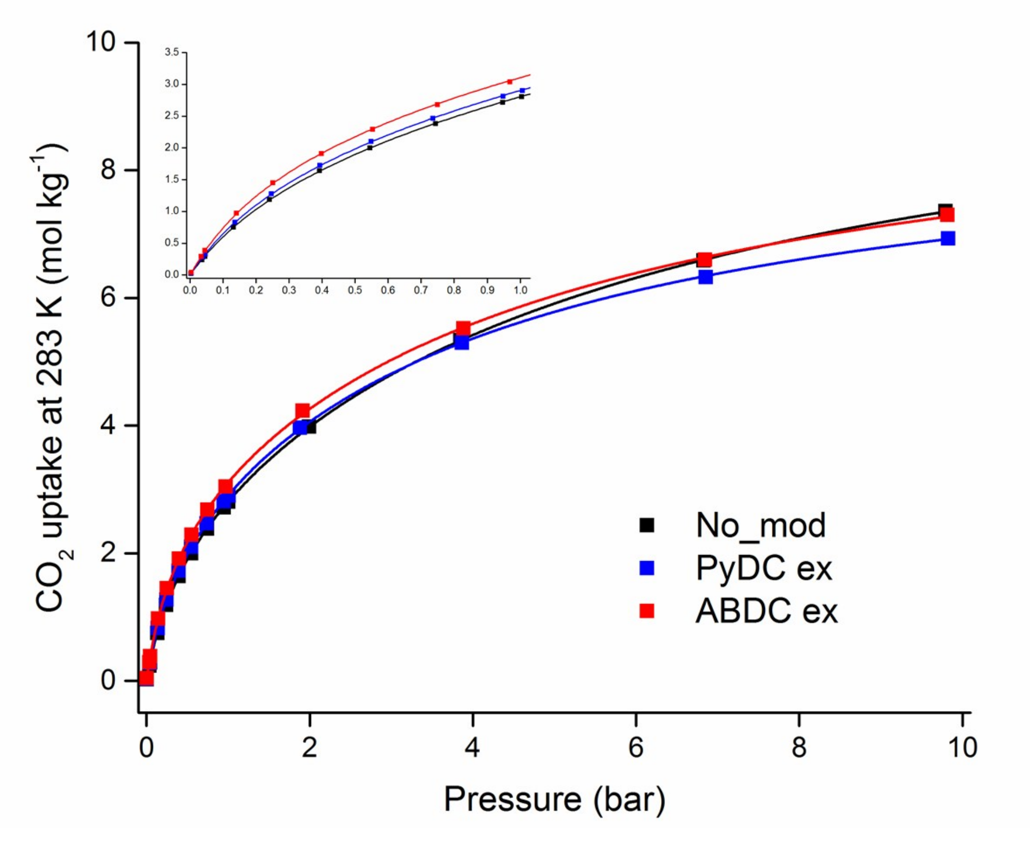

Figure S27. CO$_2$ excess adsorption isotherms at 283 K of the non-defective materials.

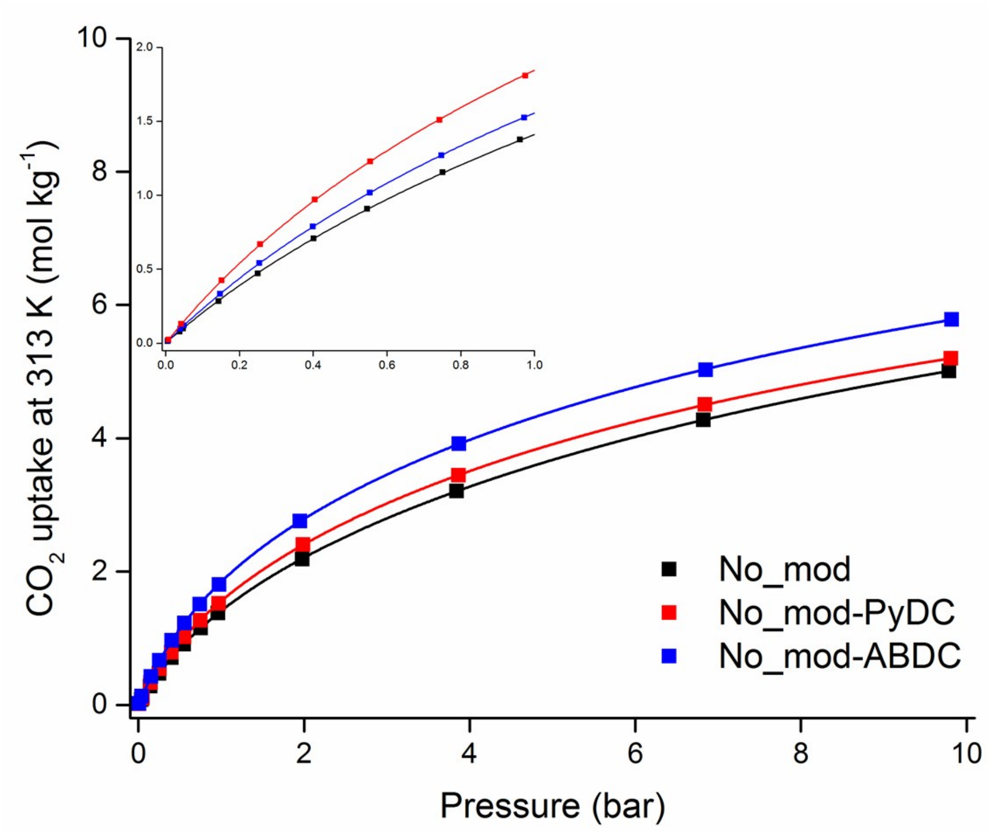

Figure S28. CO$_2$ excess adsorption isotherms at 313 K of the non-defective materials.

Ideal Adsorbed Solution Theory

The most popular model proposed for extracting gas co-adsorption and adsorption selectivity from single-gas isotherms is the Ideal Adsorbed Solution Theory (IAST). Adsorbates are considered to behave as ideal solutions in equilibrium with the gas phase.[3] CO$_2$ and N$_2$ single-component adsorption isotherms measured at 298 K and then fitted using suitable adsorption equations. Molar fraction of each species in the adsorbed phase is calculated by solving equation 3:

$$\int_{t=0}^{\frac{P y_1}{x_1}} F_1(t) d\ln t = \int_{t=0}^{\frac{P y_2}{x_2}} F_2(t) d\ln t \qquad (3)$$

where t is a dummy variable, x_i is the molar fraction of component i in adsorbed phase, y_i is the molar fraction of component i in gas phase, F_i is adsorption isotherm function for pure component, and P is the total pressure.

Selectivity is defined as:

$$\frac{\frac{x_1}{y_1}}{\frac{x_2}{y_2}}$$

The model was implemented by IAST^{++} software.[4]

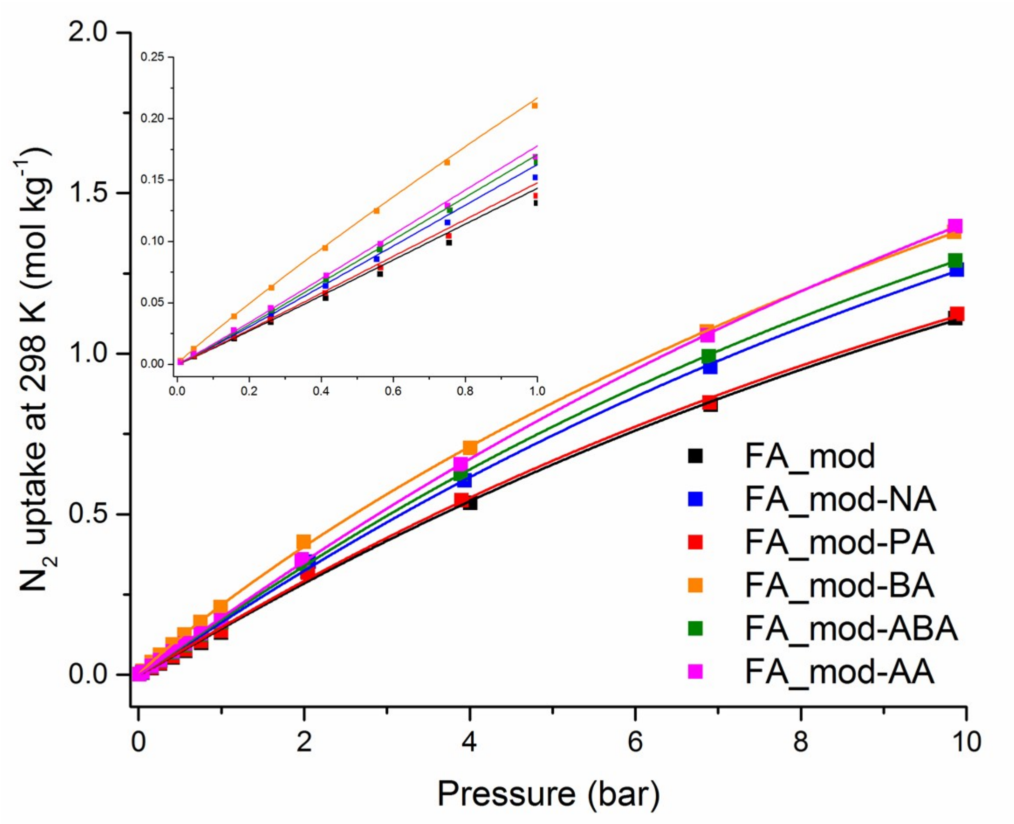

Figure S29. N$_2$ excess adsorption isotherms at 298 K of the defective materials.

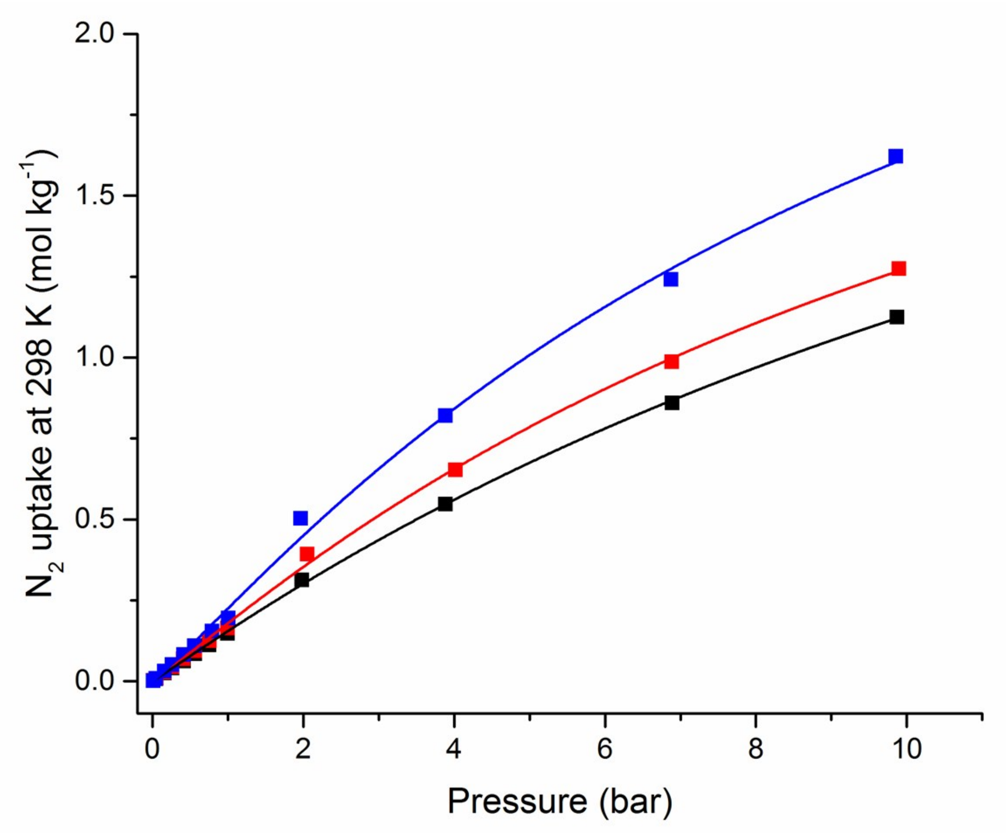

Figure S30. N_2 excess adsorption isotherms at 298 K of the non-defective materials.

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