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Accepted Article

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Post-synthetic ligand exchange in zirconium-based metal-organic frameworks: beware of the defects!

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Abstract: Post-synthetic ligand exchange in the prototypical zirconium-based metal-organic framework UiO-66 was investigated by *in situ* solution ¹H nuclear magnetic resonance. Samples of UiO-66 having different degrees of defectivity were exchanged using solutions of several terephthalic acid analogues in a range of conditions. Linker exchange only occurred in defect-free UiO-66, whereas monocarboxylates grafted at defective sites were found to be preferentially exchanged with respect to terephthalic acid over the whole range of conditions investigated. A 1:1 exchange ratio between the terephthalic acid analogue and modulator was observed, providing evidence that the defects had missing-cluster nature. *Ex situ* characterisation of the MOF powders after exchange corroborated these findings and evidenced that the physical-chemical properties of the MOF depend on whether the functionalisation occurs at defective sites or on the framework. N₂ sorption analysis showed that, upon exchange, defective samples underwent significant decrease of surface area and disappearance of large pores, associated with the presence of missing-cluster defects in the starting material. CO₂ sorption studies displayed the different impact of pure defect functionalisation and pure framework functionalisation on isosteric heat of adsorption and CO₂/N₂ selectivity.

Post-synthetic modification (PSM) is a trademark tool of metal-organic frameworks (MOF) chemistry that has been extensively employed to tailor the physical-chemical properties of the porous framework towards a range of applications.^[1] Post-synthetic ligand exchange (PSE) is a PSM method that was first reported in 2012 by Cohen and co-workers,^[2] who demonstrated that exchange of linkers in the prototypical zirconium-based MOF (Zr-MOF) UiO-66^[3] could occur either between two solids soaked in a polar solvent (solid-solid PSE) or between a solid and a solution of a terephthalic acid analogue in a polar solvent (solid-liquid PSE). PSE has since been demonstrated to be a simple, yet powerful, tool to introduce functionalities in the crystal structure of highly stable Zr-MOFs that are not accessible *via*

direct synthesis.^[4] Recent reports have shed some light onto microstructural aspects, evidencing that either homogeneous solid solutions^[5] or core-shell architectures^[6] can be formed upon PSE, mainly depending on crystal size. The possible role of defects during PSE has not yet been the object of thorough investigation, even though it is now well established that Zr-MOFs can contain a large number of defects.^[7] Defects reduce the connectivity of the [Zr₆O₄(OH)₄]¹²⁺ clusters by substitution of bridging dicarboxylate linkers with terminal groups, usually monocarboxylates derived from crystallisation modulators used during the synthesis.^[8] Recent reports have evidenced that monocarboxylates grafted at defective sites can be readily exchanged with other monocarboxylates^[8c, 9] or even with phosphonates^[10], phosphinates^[11] and sulfate.^[12] So far, it was assumed that PSE purely involved replacement of the linker, but this holds true only for defect-free Zr-MOFs (Figure 1a). During PSE on defective Zr-MOFs, exchange could involve both framework linkers and defect-compensating groups in a competitive manner, with different outcomes depending on the nature of defects being either missing linkers^[8a] (Figure 1b-c) or missing clusters^[13] (Figure 1d-e), as highlighted in a recent review.^[7] In the case of missing linkers, PSE (Figure 1b) would compete with the replacement of two monocarboxylic modulators attached to adjacent clusters with the incoming linker, a process we term post-synthetic defect healing (PSDH, Figure 1c).^[7] PSDH would occur with a 1:2 linker/modulator exchange ratio, leading to a less defective MOF product with slightly decreased porosity. In the case of missing clusters, PSE (Figure 1d) would compete with the replacement of one monocarboxylic modulator by coordination of the incoming linker through only one of its carboxylic groups, a process we term post-synthetic defect exchange (PSDE, Figure 1e).^[7] PSDE would occur with a 1:1 linker/modulator exchange ratio and would not affect the defectivity of the framework. However, there would be a decrease in porosity due to the exchange of small modulator units with bulky linker molecules. Grafting of the linker at defective sites during PSDE would leave free carboxylic groups in the pores, with potential impact on the physical-chemical properties of the framework. Given the ubiquitous nature of modulated synthesis for the preparation of Zr-MOFs,^[14] it is imperative to understand the possible involvement of defects in PSE, if one wishes to wisely employ this synthetic method to produce functional MOFs with tailored properties. To shed light on this, we have investigated solid-liquid PSE in the prototypical Zr-MOF UiO-66 (based on terephthalic acid as a linker) by monitoring the composition of the liquid phase during the exchange process using *in situ* ¹H nuclear magnetic spectroscopy (NMR). This was complemented with *ex situ* characterisation of the MOF samples before and after exchange, thus providing further understanding of PSE in defective Zr-MOFs.

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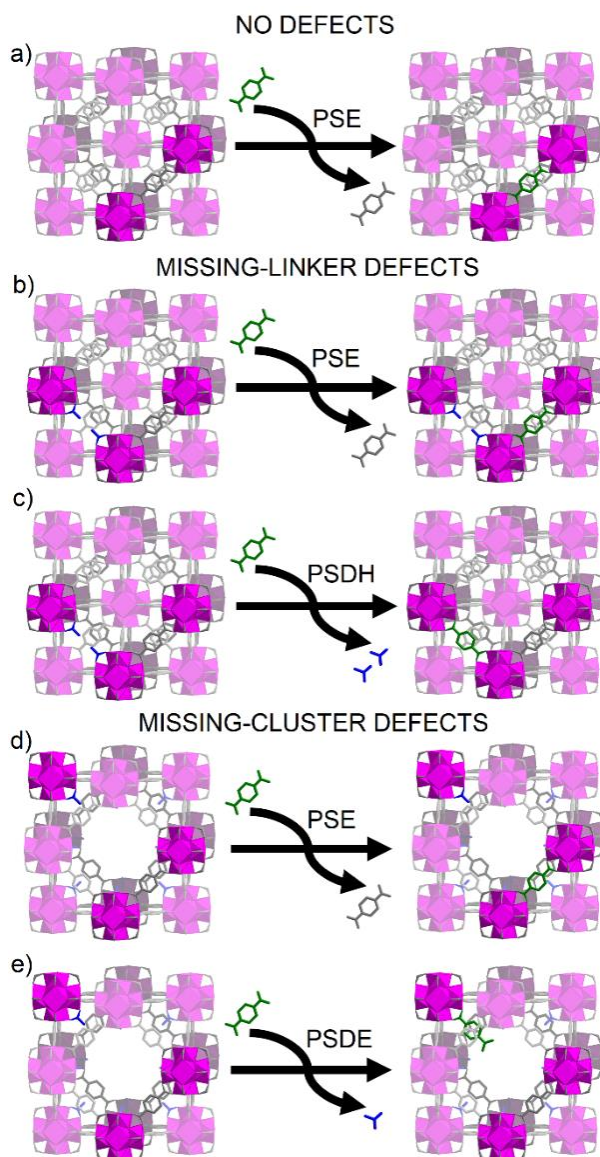


Figure 1. Possible outcomes of exchange reactions of a terephthalic acid analogue (represented in green) on UiO-66: defect-free UiO-66 can only undergo PSE, exchanging one terephthalate linker (represented in grey) per incoming linker (a). UiO-66 containing missing-linker defects can either undergo PSE (b) or PSDH, exchanging two modulator units (represented in blue) per incoming linker (c). UiO-66 containing missing-cluster defects can either undergo PSE (d) or PSDE, exchanging one modulator unit per incoming linker (e). Clusters not undergoing any change are shaded for the sake of clarity.

A sample of defective UiO-66, prepared in the presence of formic acid (FA) as a modulator (hereafter FA_mod; see SI for details on synthesis and characterisation of all the materials examined throughout the manuscript; Figures S1-5), was introduced in an NMR tube and soaked in a 0.025 M solution of 2,5-pyridinedicarboxylic acid (PyDC, a terephthalic acid analogue) in d_7 -*N,N*-dimethylformamide (d_7 -DMF) for 24 hours. Three experiments were performed at different temperatures (303 K, 323 K, 353 K) and ^1H NMR spectra were collected every five minutes. Figure 2 shows the stacked NMR spectra for each

experiment and the extracted concentration vs time profiles of PyDC, FA and terephthalic acid (BDC). In all experiments, a decrease in the intensity of peaks of PyDC is accompanied by the appearance of the peaks of FA and BDC, whose intensity gradually increases (Figure 2a-c), proving that exchange is taking place. FA is always exchanged at a much higher rate than BDC, regardless of the temperature. After 24 hours at 303 K, the small amount of PyDC disappeared from the solution has exclusively exchanged FA at defective sites. The PyDC/FA exchange occurs with a 1:1 ratio, which is evidence that PSDE is taking place and defects have missing-cluster character. Increasing the temperature, the exchange process is accelerated and at 353 K an appreciable amount of BDC is also replaced. The higher inertness of BDC towards exchange might be the result of the combination of two factors: 1) replacing one FA requires to break two Zr-O bonds on the same cluster, whereas exchanging one BDC involves a total of four Zr-O bonds on two opposite clusters, thus also requiring PyDC to be oriented in an appropriate manner; 2) FA groups are exposed on the surface of the large pores generated by a missing-cluster defect and are presumably more accessible than the BDC linkers constituting the framework. Kinetic information for the variable-temperature experiments was extracted using the initial rates method (see SI for details on kinetic analysis; Figures S7-14). The enthalpy and entropy of activation (ΔH^\ddagger and ΔS^\ddagger , respectively) were calculated using the Eyring equation (Figure S14), obtaining values of 86.5 kJ mol $^{-1}$ for ΔH^\ddagger and -72 J K $^{-1}$ mol $^{-1}$ for ΔS^\ddagger (Table S1). The enthalpic contribution to the free energy of activation is dominant over the whole range of investigated temperatures, indicating that the bond breaking and formation process plays a crucial role. The negative value of ΔS^\ddagger indicates that the activated complex for the rate-determining step has associative nature and that exchange likely occurs in a concerted manner, analogous to an S $_N2$ reaction.

Effect of the solvent was evaluated by using d_6 -dimethylsulfoxide (d_6 -DMSO, Figure S15). PSDE is again favoured over PSE, although d_6 -DMSO slows down the exchange process, if compared with d_7 -DMF. This result is apparently in contradiction with the seminal report of Cohen and co-workers,^[2] who observed that more polar solvents are more effective in promoting exchange. DMSO is slightly more polar than DMF (relative polarity: DMF = 0.386, DMSO = 0.444, in a scale where water = 1.000),^[15] therefore one would expect the exchange to be more effective in d_6 -DMSO, if polarity were the only factor to take into account. Kinetic analysis (Table S2; Figures S16-17) reveals values of 53.7 kJ mol $^{-1}$ for ΔH^\ddagger and -186 J K $^{-1}$ mol $^{-1}$ for ΔS^\ddagger . d_6 -DMSO appears indeed to assist bond breaking/formation better than d_7 -DMF, in agreement with its higher polarity. However, the process is more entropically demanding in d_6 -DMSO, which eventually yields systematically higher free energy of activation and slower exchange rate than in d_7 -DMF. This could be explained on the basis of the higher viscosity of DMSO (at 298 K: DMF = 0.79 cP, DMSO = 1.99 cP),^[16] which can negatively influence its ability to both diffuse inside the porous framework and transport solute species, thus increasing the entropic demand of the process. The poor solubility of both PyDC and BDC prevented us from investigating the process in other common polar solvents (e.g., H $_2$ O, CH $_3$ OH, CH $_3$ CN).

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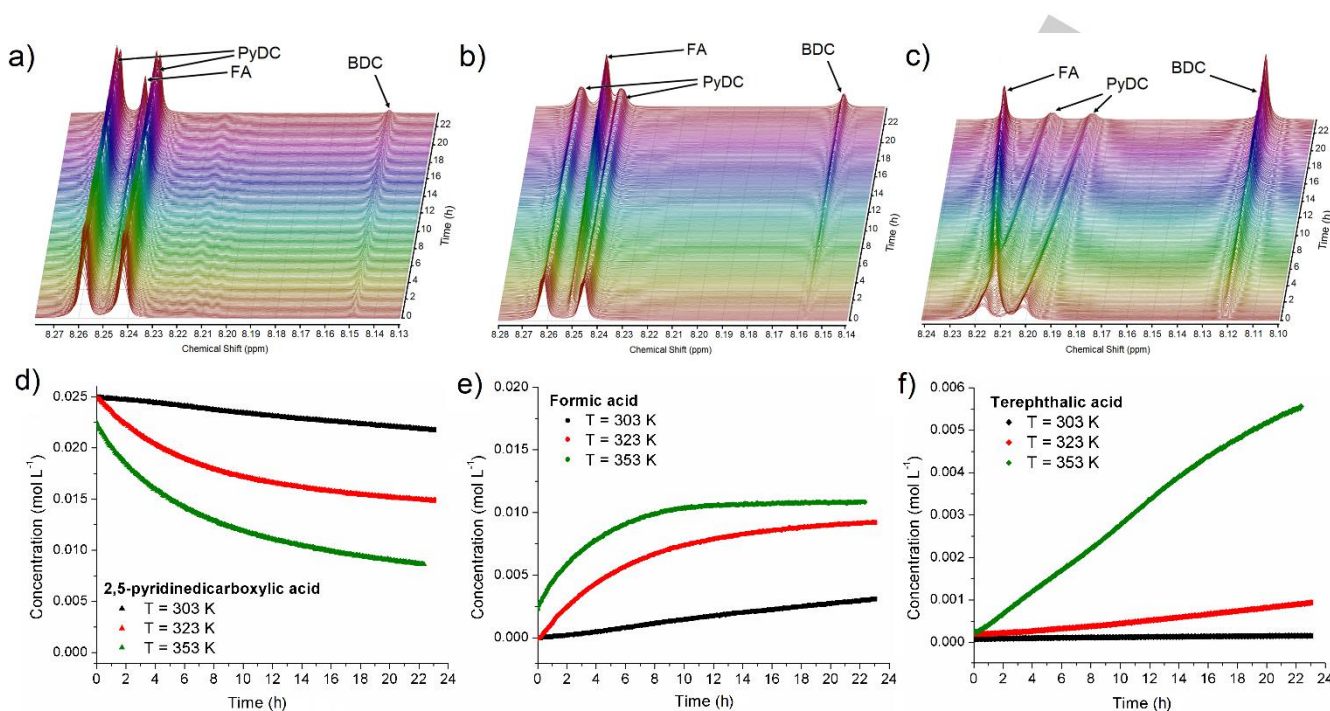


Figure 2. Stacked ¹H NMR spectra collected during exchange reactions performed at 303 K (a), 323 K (b) and 353 K (c) soaking FA_{mod} in a 0.025 M solution of PyDC in *d*₇-DMF. The signals of FA, PyDC and BDC in (c) all display continuous shifts during the experiment. This is most likely due to a combination of the changes affecting the solution composition, as the exchange process occurs over time, and the increase of the ionisation constant at higher temperature, eventually leading to small changes in the protonation state of the solute species. The relative concentration vs time profiles extracted for PyDC (d), FA (e) and BDC (f).

Exchange of a range of terephthalic acid analogues in FA_{mod} was investigated employing 2-aminoterephthalic acid (NH₂-BDC), 2-bromoterephthalic acid (Br-BDC) and 2-nitroterephthalic acid (NO₂-BDC) (Figures S18-26). All these linkers display much lower reactivity towards exchange than PyDC. Relevant changes in the composition of the solution within 24 hours only took place at 353 K, and in all cases FA was the species preferentially exchanged. The exchange proceeded at the same rate for NH₂-BDC, Br-BDC and NO₂-BDC, suggesting that acidity of the linker is not a key parameter. The higher reactivity of PyDC compared to NH₂-BDC, Br-BDC and NO₂-BDC could be explained by the fact that PyDC is the only linker that can exist in zwitterionic form, which probably makes its carboxylate group more available for coordination to the clusters (Figure S27).

Effect of the nature of the defect-compensating species was evaluated employing a defective UiO-66, prepared using benzoic acid (BA) as a modulator (hereafter BA_{mod}; Figures S28-32), as a matrix for exchange (Figures S33-34). In this case, PyDC disappears from the solution faster than for FA_{mod}, especially at lower temperature, again preferentially replacing the modulator over BDC. This could be due to two factors: 1) BA_{mod} contains more modulator than FA_{mod} (BDC/modulator ratio: 1.14 for BA_{mod}; 2.27 for FA_{mod}), increasing the probability of exchanging BA over BDC; 2) BA is a better leaving group than FA. We can reasonably exclude influence of the porosity of the

framework: despite being more defective, BA_{mod} has very similar Brunauer-Emmett-Teller surface area (BET s.a.) and micropore volume (1577 m² g⁻¹ and 0.60 cm³ g⁻¹, respectively) to FA_{mod} (BET s.a. = 1570 m² g⁻¹; micropore volume = 0.63 cm³ g⁻¹). Extracting kinetic information for the experiments involving BA_{mod} was not possible (see SI for details; Figures S35-37).

Finally, an almost defect-free sample of UiO-66, prepared without modulator (hereafter No_{mod}; Figures S38-42), was used as a matrix for PSE in the same conditions as FA_{mod}. Exchange exclusively involved BDC with a 1:1 ratio and proceeded at a slower rate than in FA_{mod} throughout the investigated temperature range (Figures S43-44). Kinetic analysis (Table S3; Figures S45-47) gives values of 84.9 kJ mol⁻¹ for ΔH[‡] and -105 J K⁻¹ mol⁻¹ for ΔS[‡], indicating that the enthalpic contribution to the free energy of activation in No_{mod} is basically the same as in FA_{mod}, but the entropic term is more relevant. This is likely due to the need of breaking Zr-O bonds on opposite sides of BDC at the same time, making the process demanding in terms of correct orientation of the incoming linker. Increased diffusion limitations, due to the lower porosity of No_{mod} (BET s.a. = 1189 m² g⁻¹; micropore volume = 0.41 cm³ g⁻¹) compared to FA_{mod}, could also be responsible for the lower rates observed.

Ex situ experiments were performed to confirm that the observations made *in situ* effectively mirror the actual process occurring in the MOF. PyDC was exchanged into FA_{mod} in DMF at 323 K and 353 K over 24 hours, yielding two solids named

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FA_mod-PSE-50 and FA_mod-PSE-80, respectively (Figures S48-52). The porosity of FA_mod-PSE-50 (BET s.a. = 1100 m² g⁻¹; micropore volume = 0.39 cm³ g⁻¹) is significantly lower than that of FA_mod (Figure 3a). Pore size distribution analysis clearly shows disappearance of pores having half width of 7.4 Å, associated with missing cluster defects and well visible in FA_mod (Figure 3b). ¹H NMR analysis of hydrolysed FA_mod-PSE-50 confirms that no exchange of BDC has occurred and all the exchanged PyDC has replaced FA at missing-cluster defective sites, in line with the result of the *in situ* experiment. This is good evidence that no significant diffusion limitations exist and exchange occurs homogeneously throughout the crystallites (see at the bottom of SI for a detailed discussion of microstructural aspects of PSE). The porosity of FA_mod-PSE-80 (BET s.a. = 1081 m² g⁻¹; micropore volume = 0.39 cm³ g⁻¹) is identical to that of FA_mod-PSE-50 (Figure 3a). Given the nearly identical molecular weight and steric bulk of PyDC and BDC, no further loss of porosity is expected if PyDC is incorporated in the framework. Experimental evidence confirms this. ¹H NMR analysis of hydrolysed FA_mod-PSE-80 proves that in this case a significant amount of the total exchanged PyDC (33%) is incorporated in the framework, substituting 21% of BDC. CO₂ sorption isotherms were collected on FA_mod and FA_mod-PSE-50 at 298 K and 313 K, observing slight increase in uptake at low pressure (from 1.50 to 1.57 mmol g⁻¹ at 298 K and 1 bar, Figure 3c) and in CO₂/N₂ selectivity (from 14 to 17, for a 0.15:0.85 CO₂/N₂ mixture at 1 bar and 298 K, Figures S53-55) in the exchanged MOF. The replacement of FA with PyDC has a notable effect on

the isosteric heat of CO₂ adsorption (Q_{st} , Figure 3d): at near-zero loading, FA_mod-PSE-50 displays higher Q_{st} than FA_mod (26.4 kJ mol⁻¹ vs 23.7 kJ mol⁻¹, respectively), but this quickly decreases by 6 kJ mol⁻¹ as the loading reaches 2 mmol g⁻¹, whereas it remains almost constant for FA_mod. This effect is likely due to a combination of the modified textural properties of the framework and the introduction of pyridine rings and carboxylic acid groups in the pores upon PSE.

Exchange of PyDC in No_mod was performed in DMF at 323 K and 353 K over 24 hours, yielding two solids named No_mod-PSE-50 and No_mod-PSE-80, respectively (Figures S56-60). Porosity of both No_mod-PSE-50 (BET s.a. = 1055 m² g⁻¹; micropore volume = 0.37 cm³ g⁻¹) and No_mod-PSE-80 (BET s.a. = 1097 m² g⁻¹; micropore volume = 0.40 cm³ g⁻¹) (Figure 3d) is comparable to that of No_mod, as expected upon replacement of BDC with PyDC. ¹H NMR analysis of the hydrolysed No_mod-PSE-50 and No_mod-PSE-80 confirms that PSE has effectively occurred, although to a different extent: 5% of BDC is exchanged at 323 K, 17% is exchanged at 353 K. CO₂ sorption isotherms collected on No_mod and No_mod-PSE-80 show increased uptake (from 1.90 to 2.18 mmol g⁻¹ at 298 K and 1 bar, Figure 3g) and identical CO₂/N₂ selectivity (Figures S61-63) in the exchanged MOF. The plot of Q_{st} versus loading for the two MOFs (Figure 3h) shows the same trend, with slightly higher affinity in the case of No_mod-PSE-80. Different from FA_mod, this is likely due to pure chemical modification of the surface upon PSE, without affecting the textural properties of the framework.

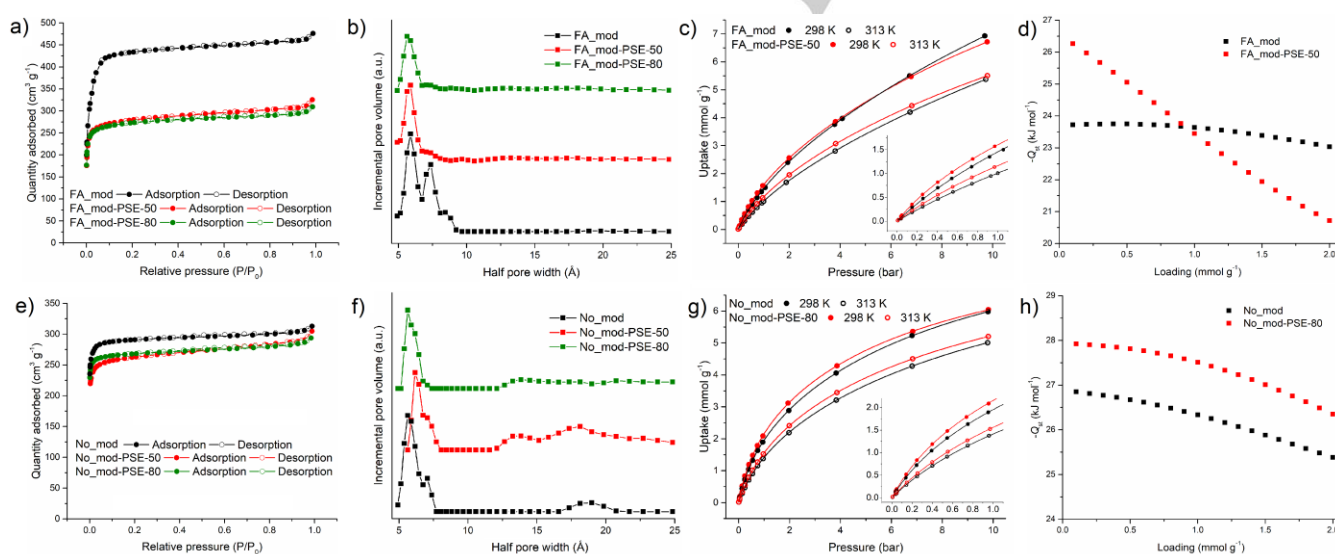


Figure 3. Characterisation of the products of *ex situ* experiments: nitrogen sorption isotherms at 77 K (a) and pore size distributions (b) of FA_mod (black), FA_mod-PSE-50 (red) and FA_mod-PSE-80 (green); CO₂ sorption isotherms at 298 K and 313 K (c) and isosteric heat of CO₂ adsorption as a function of loading (d) of FA_mod (black) and FA_mod-PSE-50 (red); nitrogen sorption isotherms at 77 K (e) and pore size distributions (f) of No_mod (black), No_mod-PSE-50 (red) and No_mod-PSE-80 (green); CO₂ sorption isotherms at 298 K and 313 K (g) and isosteric heat of CO₂ adsorption as a function of loading (h) of No_mod (black) and No_mod-PSE-80 (red).

This study demonstrates that *in situ* solution NMR is a simple, yet effective, method to gain insight into a process, such as PSE, occurring at the interface between the solution and the MOF. We found that defective UiO-66 soaked in a solution of a terephthalic

acid analogue always undergoes preferential exchange of monocarboxylic species grafted at defective sites, regardless of temperature, solvent, nature of the terephthalic analogue and nature of the defect-compensating species. By demonstrating that

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the exchange between the incoming linker and the modulator occurs with a 1:1 ratio, our work provides evidence in favour of the recently proposed model of defective UiO-66 exclusively featuring missing clusters.^[8b] As a consequence, most of the exchanged linker coordinates through only one of its carboxylic groups, decreasing the porosity and leaving the second carboxylate uncoordinated and exposed in the pores. This has repercussions on the properties of the MOF, as proved by the different CO₂ sorption behaviour of framework- and defect-functionalised UiO-66. These findings will be paramount to increase the awareness of researchers performing future work involving PSE in defective Zr-MOFs and to better understand the properties of the resulting materials. Building on these results, ongoing work in our group is focused on exploring defect functionalisation as an alternative method to classical linker modification for tuning the CO₂ affinity of Zr-MOFs.

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Conflict of interest

The authors declare no conflict of interest.

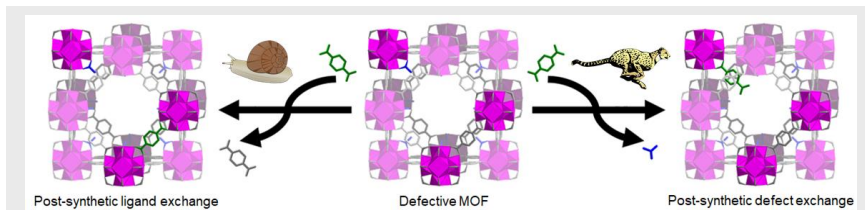
Keywords: metal-organic frameworks • defects • post-synthetic exchange • NMR spectroscopy

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Athanasios Koutsianos, Enrico Andreoli,
and Andrew R. Barron

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Title

Defects matter: a combination of *in situ* NMR investigation and *ex situ* characterisation proves that post-synthetic ligand exchange on defective UiO-66 occurs preferentially at missing-cluster defective sites.

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