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12th July 2016,
Accepted 5th September 2016

DOI: 10.1039/c6nj02169g

www.rsc.org/njc

Positive effect of the fluorine moiety on the oxygen storage capacity of UiO-66 metal–organic frameworks†

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Two series of fluorine-containing UiO-66 have been synthesized, replacing the 1,4-benzodicarboxylic acid linker with increasing amounts of 2-fluoro-1,4-benzodicarboxylic acid or 2-trifluoromethyl-1,4-benzodicarboxylic acid. The capacity to store oxygen and nitrogen within these MOFs has been tested, which revealed a positive correlation between the fluorine content and the oxygen storage performances.

Metal–organic frameworks (MOFs) have attracted the attention of the scientific community in the last fifteen years,¹ giving rise to an extraordinary amount of work in terms of fundamental research. These microporous materials, due to their exceptional properties (surface area, pore volume and tunability), indeed have potential application in a wide variety of technological fields ranging from gas storage and separation² to catalysis,³ luminescence,⁴ drug delivery⁵ and sensing.⁶ Regarding the storage of gases in porous materials, different industrial sectors, related to energy, environmental technology and health care, are seeking new technological solutions that are able to ensure the safe storage of considerable amounts of gases into units with reduced volumes.⁷ The properties of MOFs as a storage medium for H₂,⁸ CO₂⁹ and CH₄¹⁰ have been extensively studied. Commercial implementations are expected to happen in the near future.

Differently, only a limited amount of scientific reports have dealt with the use of MOFs for oxygen storage, which may be utilized in the future by medical or aerospace industries as well as in some military applications.

A typical strategy to design a MOF with enhanced affinity between the gas (guest) and the crystalline framework (host) consists of introducing ligands that contain selected uncoordinated functional groups (–NH₂, –COOH or –OH).¹¹ According to this

methodology, by using fluorine-containing linkers, it should be possible to increase the adsorption enthalpy in the MOFs, and consequently, their storage performances.¹² Several fluorinated MOFs and porous materials have been prepared,¹³ and investigated,¹⁴ and it has been demonstrated that fluorinated MOFs have remarkable gas storage capacities,¹⁵ although some divergent results have also been reported.¹⁶ The superior adsorption capacity of fluorinated MOFs for selected hydrocarbons has also been observed¹⁷ and can be applied in future hydrocarbon separations.¹⁸ The synthesis of some fluoro-MOFs for gas storage applications have already been covered by a patent, which illustrates the relevance of fluorinated MOFs beyond academic interest.¹⁹

The introduction of fluorinated functional groups into the crystalline framework may provide a technological solution to enhance the performances of MOFs as oxygen storage media. Farha *et al.* recently demonstrated that, compared to porous carbons and zeolites, the MOFs NU-125 and HKUST-1 provide substantially increased performances. These materials were selected after a simulation process that involved 10 000 MOF candidates,²⁰ confirming the potential of MOFs in oxygen storage applications. Nevertheless, a systematic study of oxygen adsorption in fluorinated MOFs is still missing.

Among the numerous MOFs described in the literature, UiO-66 represents one of the most investigated materials due to its outstanding stability²¹ and easily reproducible preparation.^{22,23} UiO-66 is undoubtedly a readily available MOF since several alternative straightforward routes allow its synthesis. Additionally, the introduction of a functional group into the benzodicarboxylic acid linker permits the easy preparation of tagged UiO-66 derivatives with specific properties (acidity, basicity, and polarity).²⁴ Herein, a series of two fluorine-containing UiO-66 MOFs have been synthesized and high pressure oxygen and nitrogen adsorption capacities have been measured and correlated with the amount of fluorine.

The first series of fluoro-MOF was prepared by replacing the 1,4-benzodicarboxylic acid linker with increasing amounts of 2-fluoro-1,4-benzodicarboxylic acid. Four different MOFs with

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6nj02169g



increasing amounts of 2-fluoro-substituted linker (UiO-66-F), 25%, 50%, 75% and 100% mol mol⁻¹, respectively, were synthesized and fully characterized. Synthesis proceeded only in the presence of HCl as a modulating agent,²² whilst the reaction between ZrCl₄ and the selected linkers²⁵ without any modulator resulted in an amorphous solid. XRD analyses confirmed that partially or completely replacing 1,4-benzodicarboxylic acid with the 2-fluoro-substituted linker leads to the formation of crystalline structure isomorphs to UiO-66 (see ESI,†). Moreover, the

strong electron withdrawing effect of the fluorine does not reduce the thermal stability of these fluoro-MOFs, as observed by thermogravimetric analysis (TGA) (see ESI,†). Since the final residues from TGA can be considered, with reasonable confidence, to be ZrO₂, the number of linker units per Zr can be calculated as reported.²⁶ The prepared MOFs presented some defects; however, they all contain a comparable amount of linker per Zr (3.7–4.2). The presence of increasing amounts of fluorine-containing linker in the synthesized MOFs has been proven by FT-IR analyses. B.E.T. surface area and total pore volume are reported in Table 1.

High pressure gas adsorption isotherms measurements were carried out employing a magnetic suspension balance. Samples were activated at 200 °C for 6 h under vacuum. TGA does not show any additional weight loss after 200 °C for all the investigated samples, hence no residual solvent was expected to be trapped in the pores after the activation procedure. Fig. 1a reports the oxygen adsorption isotherms (20 °C) for the series of UiO-66-F, compared with a standard UiO-66 sample (prepared using the same synthetic procedure). The structural stability of the UiO-66-F series appears to be reduced compared to the fluorine-free UiO-66. In fact, the adsorption isotherms followed

Table 1 B.E.T. surface area and total pore volume of synthesized MOFs

Entry	B.E.T. surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
UiO-66	1571	0.6036
UiO-66-F 25	1152	0.4555
UiO-66-F 50	1173	0.4618
UiO-66-F 75	1129	0.4462
UiO-66-F 100	1126	0.4453
UiO-66-CF ₃ 25	1345	0.5275
UiO-66-CF ₃ 50	1249	0.4992
UiO-66-CF ₃ 75	1000	0.3927
UiO-66-CF ₃ 100	909	0.3657

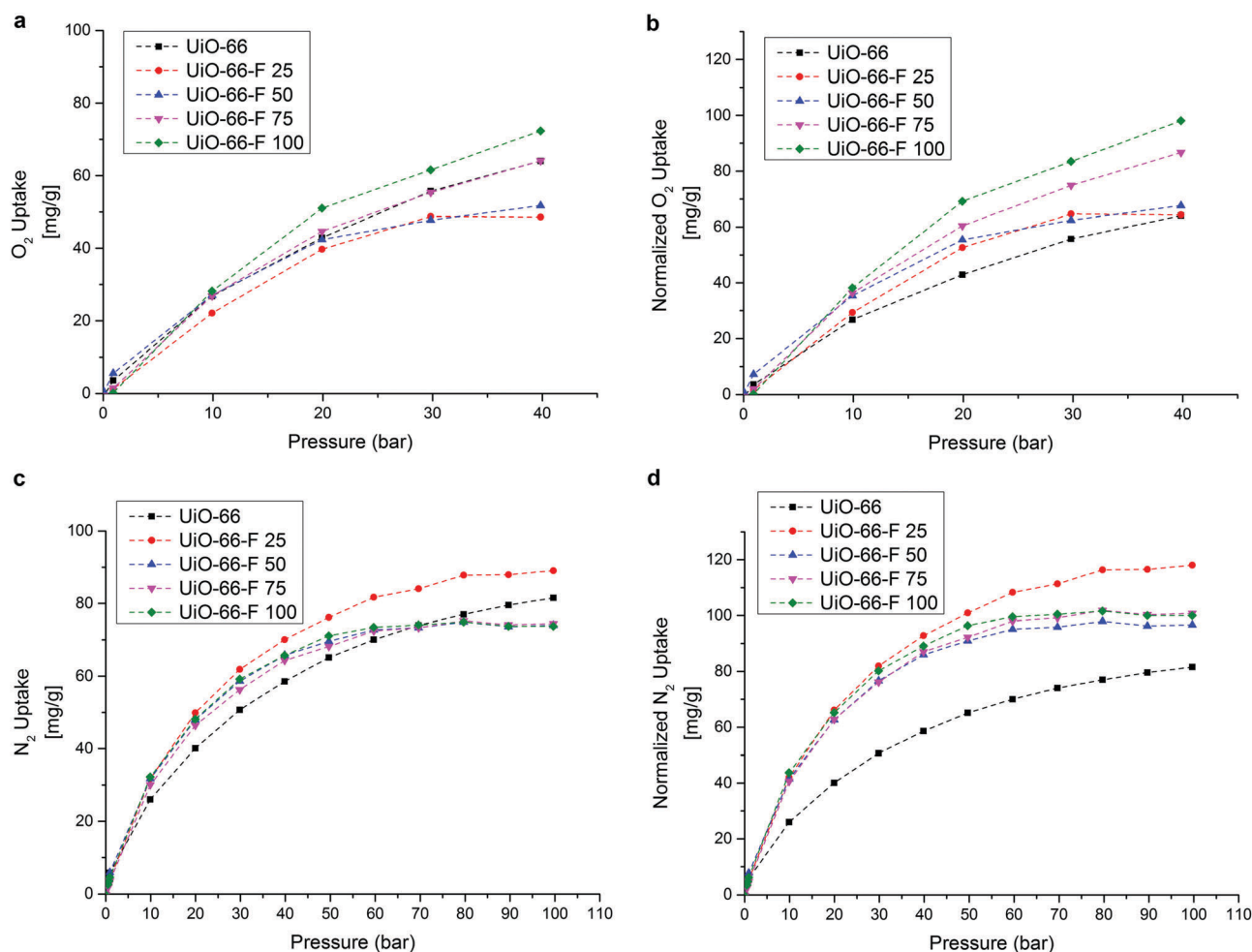


Fig. 1 (a) Oxygen adsorption isotherms for UiO-66 and UiO-66-F series; (b) normalized oxygen adsorption isotherms for UiO-66 and UiO-66-F series; (c) nitrogen adsorption isotherms for UiO-66 and UiO-66-F series; (d) normalized nitrogen adsorption isotherms for UiO-66 and UiO-66-F series.



a normal trend up to 40 bar of oxygen, for higher pressures an unexpected reduction of the uptake was observed for UiO-66-F 25, UiO-66-F 50 and UiO-66-F 75 (complete oxygen adsorption isotherms are reported in the ESI†).

The UiO-66-F 100, containing only the 2-fluoro-1,4-benzodicycarboxylic acid linker, shows a noteworthy oxygen adsorption capacity, storing 72 mg of oxygen per gram of MOF at 40 bar, higher than the standard UiO-66. Similar performances were obtained by UiO-66-F 75 (64 mg g⁻¹). Slightly lower oxygen adsorptions were recorded for UiO-66-F 50 (51 mg g⁻¹) and UiO-66-F 25 (48 mg g⁻¹).

Nevertheless, the UiO-66-F series had considerably lower pore volumes compared to the standard UiO-66 (due to the steric effect of the functional group), which has a significant influence on the oxygen adsorption capacity. Since the gas adsorption isotherms were performed at high pressure (up to 100 bar) it is expected that the guest molecules are adsorbed not only on the external surface of the MOFs, but they also occupy all of the available pore volume. In Fig. 1b the oxygen

adsorption isotherms were normalized with reference to the total pore volume of each MOF (mg of adsorbed gas · total pore volume of UiO-66/total pore volume of UiO-66-F). In this plot, the correlation between the oxygen adsorption performances and the fluorine content can be identified.

The observed trend provides evidence that the fluorine has a positive interaction with oxygen; indeed, in the case of UiO-66-F 100 (where this effect is maximized due to the higher amount of fluorine) the absolute adsorbed amount of oxygen is higher than in the UiO-66, despite a substantially reduced available volume (Fig. 1a).

To corroborate this hypothesis, the nitrogen adsorption isotherms for the series of UiO-66-F and for the standard UiO-66 were also measured. In this case it was possible to quantify the gas adsorption up to 100 bar. These adsorption isotherms follow a regular trend, confirming that all samples have permanent porosity. Fig. 1c shows that, although all the UiO-66-F can adsorb more nitrogen than the standard UiO-66, no direct correlation between the fluorine content and the storage capacity was observed.

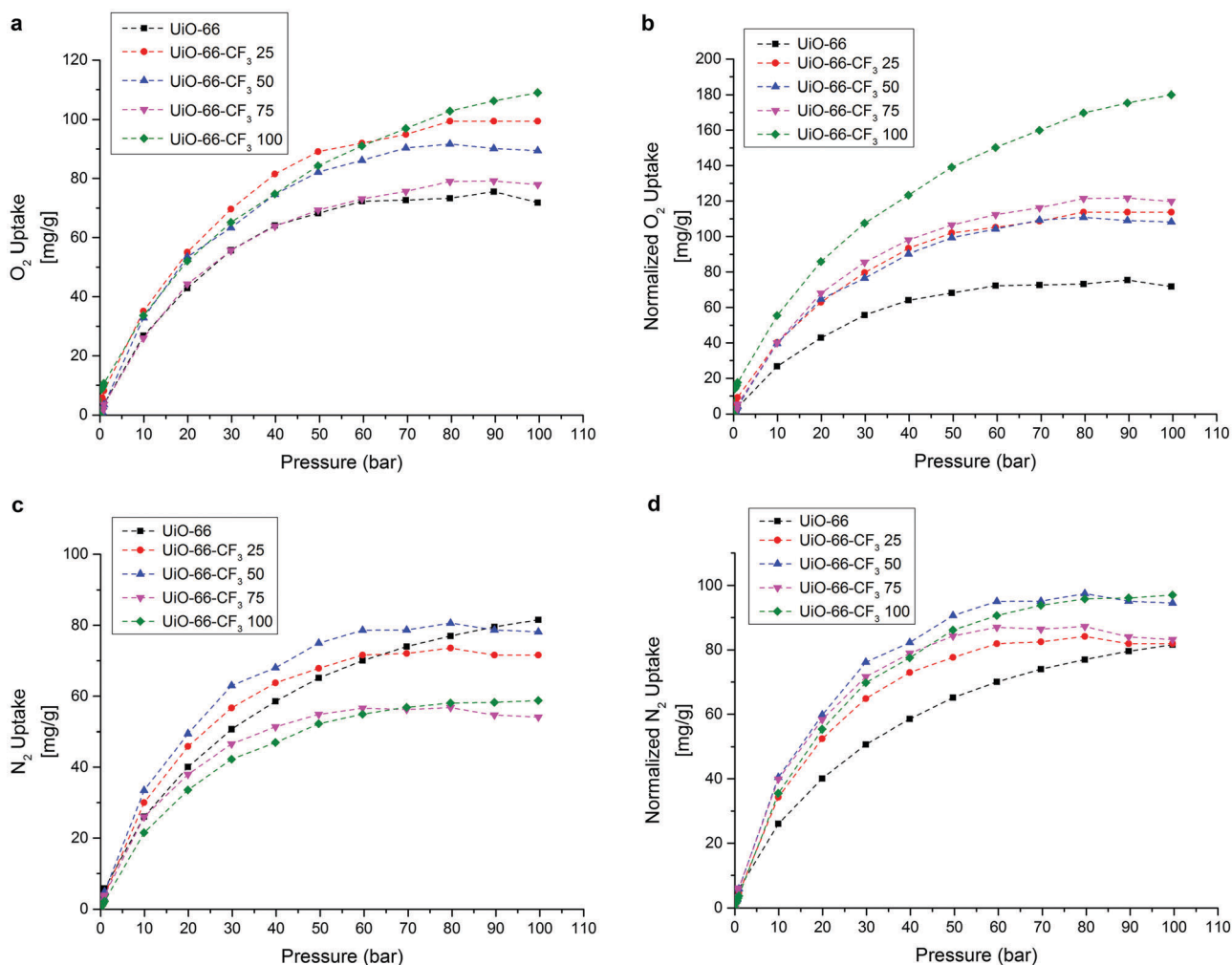


Fig. 2 (a) Oxygen adsorption isotherms for UiO-66 and UiO-66-CF₃ series; (b) normalized oxygen adsorption isotherms for UiO-66 and UiO-66-CF₃ series; (c) nitrogen adsorption isotherms for UiO-66 and UiO-66-CF₃ series; (d) normalized nitrogen adsorption isotherms for UiO-66 and UiO-66-CF₃ series.



Similarly, the normalization of the adsorption isotherms according to the pore volumes does not allow for defining a trend (Fig. 1d). Therefore, the interaction between oxygen and fluorine has a decisive effect on the gas storage capacity of the MOFs.

Moving forward in the field of fluorine containing UiO-66 MOFs, another new series of porous materials has been prepared and tested for oxygen adsorption. In this case, the 1,4-benzodicyclohexane dicarboxylic acid linker was replaced by increasing amounts of 2-trifluoromethyl-1,4-benzodicyclohexane dicarboxylic acid. Four different MOFs (UiO-66-CF₃) containing 25%, 50%, 75% and 100% mol mol⁻¹ of 2-trifluoromethyl-1,4-benzodicyclohexane dicarboxylic acid linker, respectively, were synthesized and fully characterized. The syntheses were carried out again using HCl as a modulating agent, producing fluorine-containing crystalline materials stable up to 400 °C (XRD patterns, FT-IR spectra and TGA are reported in the ESI†). B.E.T. surface area and total pore volume are reported in Table 1.

Fig. 2a displays the oxygen adsorption isotherms (20 °C) for the series of UiO-66-CF₃, compared with a standard UiO-66 sample. These MOFs exhibit regular adsorption behavior, allowing the measurement of oxygen adsorption up to 100 bar. In all cases, the fluorine-containing MOFs have a higher oxygen capacity compared to the standard UiO-66, but a direct correlation between the fluorine content and the oxygen capacity is not clearly noticeable. UiO-66-CF₃ 100 is able to adsorb up to 109 mg of oxygen (≈3 mmol) per gram of porous material, achieving the best result between all the MOFs investigated in this experimental work. It should be noted that the reduction of the pore volume for the UiO-66-CF₃ series, in comparison to the normal UiO-66, is undoubtedly significant due to the size of the trifluoromethyl group (Table 1). Indeed, normalizing the oxygen adsorption capacity according to the pore volume of each MOF, an obvious tendency is observable (Fig. 2b). UiO-66-CF₃ 100 shows the highest (normalized) oxygen adsorption capacity followed by UiO-66-CF₃ 75, UiO-66-CF₃ 50 and UiO-66-CF₃ 25. All the UiO-66-CF₃ series MOFs have similar performances, but they are still better than that of the standard UiO-66.

The nitrogen adsorption isotherms (20 °C) for the UiO-66-CF₃ series are reported in Fig. 2c and d. Also in this case, the experimental data does not allow for determining an evident effect of the fluorine moiety on the gas adsorption capacity. The normalized patterns of the fluorinated MOFs have higher values compared to the UiO-66 (Fig. 2d), yet the fluorine content cannot be associated with the performances.

The reported results highlight the positive effect of fluorine on the oxygen adsorption capacity of UiO-66-type MOFs. Since this special effect has not been observed for N₂ adsorption, it can be attributed more specifically to the oxygen/fluorine interaction rather than a general functional group/guest interaction. The UiO-66-CF₃ series provides an oxygen adsorption ranging from 64 to 81 mg of oxygen per gram of MOF at 40 bar (90 to 123 mg g⁻¹ normalized amount), sensitively higher than the UiO-66-F series, which allows an adsorption ranging between 49 and 72 mg of oxygen per gram of MOF at 40 bar (64 to 98 mg g⁻¹ normalized amount). Higher amounts of fluorine in the CF₃ series can, therefore, be associated with higher oxygen adsorption capacity. Further studies on different porous coordination

polymers are needed to confirm the generality of these findings, paving the way for the design and realization of new materials with enhanced oxygen storage capacities.

The authors are grateful to W. Schweikert, H. Schuppler and M. Herrmann for measuring and discussing IR, HP N₂ and O₂ adsorption isotherms, TGA and XRD data.

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