# A Complete Separation of Hexane Isomers by a Functionalized Flexible Metal Organic Framework

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**The separation ability of branched alkane isomers (*n*HEX, 3MP, 22DMB) of the flexible and functionalized microporous iron(III) dicarboxylate MIL-53(Fe)-$(CF_3)_2$ solid is evaluated through a combination of breakthrough experiments (binary or ternary mixtures), adsorption isotherms, X-ray diffraction temperature analysis, quasi-elastic neutron scattering measurements and molecular dynamics simulations. A kinetically controlled molecular sieve separation between the di-branched isomer of hexane 22DMB from a mixture of paraffins is achieved. The reported total separation between mono- and di-branched alkanes which was neither predicted nor observed so far in any class of porous solids is spectacular and paves the way towards a potential unprecedented upgrading of the RON of gasoline.**

## 1. Introduction

The major applications related to the separation of hexane isomers by physisorption are in the so called total isomerization processes (TIP) from UOP[1–3] and more recently, the Ipsorb process[4,5] from Axens. Low Research Octane Number (RON) normal paraffins [e.g., *n*-hexane (*n*HEX; RON 24)] are thus separated from high RON branched hydrocarbons [e.g., 3-methylpentane (3MP; RON 74.5), 2,2-dimethylbutane (22DMB; RON 91.8)], using the molecular sieve zeolite 5A. Indeed, this zeolite has the ability to completely separate *n*-paraffins from the other branched hydrocarbons resulting in an efficient technology to increase the octane number of light straight run naphtha streams. However, in the final stream low RON hydrocarbons such as the mono-branched hexane isomer 3MP are usually still present and contribute to decrease the performance of the process. To overcome this drawback, there is a crucial need to search for alternative porous solids able to more selectively adsorb di-branched compounds such as the 22DMB from the mono-branched 3MP and linear nHEX.

As a typical example, it was demonstrated that zeolite BETA could be used to upgrade the actual TIP processes by partially separating mono from di-branched hexane isomers in a dual layer pressure swing adsorption (PSA) bed with 5A zeolite,[3] leading to an enhancement of the RON number of the final stream from 86 to 92, a value similar to the one obtained in the Hexsorb process of Axens. The achievement of higher upgrading thus calls for the design of more efficient porous adsorbents. Metal organic frameworks (MOFs) are the latest class of crystalline porous solids.[6] These are built up from the linkage of inorganic sub-units and organic ligands, and constitute a versatile class of porous materials due to their large chemical and structural diversity, paving the way for their use in many societally relevant applications (gas storage, separation, catalysis, sensing, biomedicine, etc.)[7,8] In the field of fluid separation, it was shown for instance that MOFs could be of a great interest to separate propane from propylene,[9] xylene or alkane isomers,[10] carbon dioxide from

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DOI: 10.1002/adfm.201401974

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nitrogen[11] or methane,[12] nitrogen from propylene[13] or acetylene from carbon dioxide,[14] among others. Regarding the separation of branched alkanes, it was evidenced that the microporous zirconium terephthalates UiO-66-type architecture or the mesoporous chromium trimesate MIL-100 structure type are able to discriminate the different alkane isomers with, however, a relatively low selectivity.[15,16] More interestingly, the small pores zinc imidazolate ZIF-8 solid was revealed to act as a molecular sieve to separate linear (*n*-hexane) from branched paraffins by kinetics with a much higher adsorption capacity,[17] making this MOF as an excellent alternative to zeolite 5A to improve the performance of the existing TIP processes.[1,2]

More recently, Long and co-workers demonstrated that a porous iron(III) bis-pyrazolate MOF ($Fe_2(BDP)_3$) based on a 1-D triangular corrugated micropores system is able to discriminate the different hexane isomers, one from each other, according to the degree of branching.[18] This resulted into much higher selectivities than the ones shown by zeolite BETA, the dibranched isomers being eluted first followed by the monobranched isomers and finally the linear *n*-hexane. Although the separation by the degree of branching of the isomers in $Fe_2(BDP)_3$ through competitive sorption is of interest, it still allows only a partial separation of the targeted species. Indeed, it is known that for industry the optimal candidate would be a porous material that completely segregates via a molecular sieve effect, monobranched from dibranched paraffins in a similar way than zeolite 5A proceeds for the separation of linear to branched hydrocarbons. To date, there is however no porous solid able to sieve the dibranched alkanes from the other hexane isomers.

One of the plausible routes to modulate both the adsorption/separation performances of porous MOFs solids is to functionalize their organic constitutive moieties. The series of metal(III) terephthalate MIL-53(M) type solids (M = Fe, Al, Cr...) or MIL-88B (M = Fe, Sc) are the most spectacular illustrations of classes of breathing porous solids (MIL for Materials from Institut Lavoisier),[19] whose direct ligand functionalization strongly impacts the flexible character of the framework.[20] A large number of studies have already explored the consequences of such a functionalization in terms of (unusual) sorption behavior associated sometimes with performances of interest in the field of gas separation or drug delivery.[21] Here, we report how grafting specific bulky perfluoro $–CF_3$ groups on the terephthalate linker of the MIL-53(Fe) solid strongly impacts not only the accessibility of the pores for the different hexane isomers but also the diffusivity of these species. This porous solid can thus be considered as the first sorbent being ever able to efficiently sieve the di-branched isomers from the other components, paving the way for future improvements of the RON of gasoline.

## 2. Results and Discussion

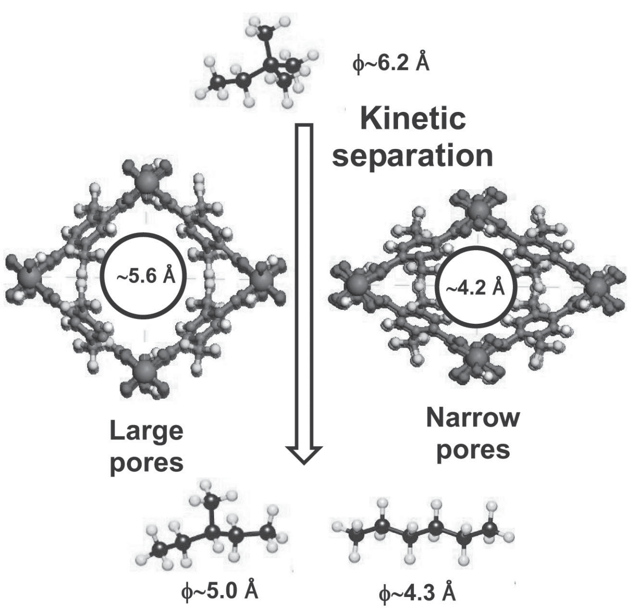

**Figure 1.** Illustration of the three isomers with their kinetic diameters andthe 1D-type channel MIL-53(Fe) $(CF_3)_2$ and their corresponding pore sizes (left: large pore, right : narrow pore).

The BDC-$(CF_3)_2$ linker (or 2,5 diperfluoro-1,4 benzene dicarboxylic acid) was selected to prepare a functionalized version of the iron terephthalate MIL-53(Fe) (**Figure 1**), denoted here as MIL-53(Fe)-$(CF_3)_2$, for separation tests of mixtures of hexane isomers : *n*-hexane (*n*HEX), 3-methyl-pentane (3MP) and 2,2 dimethylbutane (22DMB). The choice of this grafted ligand amongst others, was set-up in order to narrow down the pore aperture of the pristine MIL-53(Fe), ≈7.6 Å in its large pore (LP) form (see Figure S16 in the Supporting Information (SI) for the corresponding calculated pore size distribution (PSD)), too large for an efficient separation. The aim here was to tune the pore size of this solid for an optimal separation of *n*HEX and mono-branched 3MP from a mixture also containing the di-branched 22DMB. The pore diameters of the MIL-53(Fe)-$(CF_3)_2$ in its LP and NP forms calculated from the corresponding crystal structures, reported in the literature,[20a] are 5.6 Å and 4.2 Å respectively (see SI for the corresponding pore size distributions). These pore sizes range below the kinetic diameter of the 22DMB (6.2 Å) while remaining close to the dimensions of both linear *n*HEX (4.3 Å) and 3MP molecules (5.0 Å). This observation suggests that grafting $-2CF_3$ functions on this porous solid is expected to favor the separation of the alkane isomers from a steric standpoint, this becoming even more true if the structure is present in a NP version upon hexane isomer adsorption. The separation performance of this solid for a mixture of hexane isomers was then assessed by performing several separation tests in a breakthrough apparatus at 313 K over the 0.5–20 kPa pressure range. Noteworthy, MIL-53(Fe)-$(CF_3)_2$ is able to discriminate the three isomers as seen from the breakthrough experiments conducted with an equimolar ternary mixture of *n*HEX/3MP/22DMB and various pressures (**Figure 2**; Table S1, SI). A complete separation between 22DMB and both mono-branched 3MP and linear *n*HEX is achieved in all experiments, with an elution of the 22DMB, practically similar to the one obtained during the blank experiments, except at a very low pressure of 0.5 kPa where the mono-branched 3MP elutes similarly to 22DMB (see Figure S2, SI). This observation strongly supports that the di-branched alkane

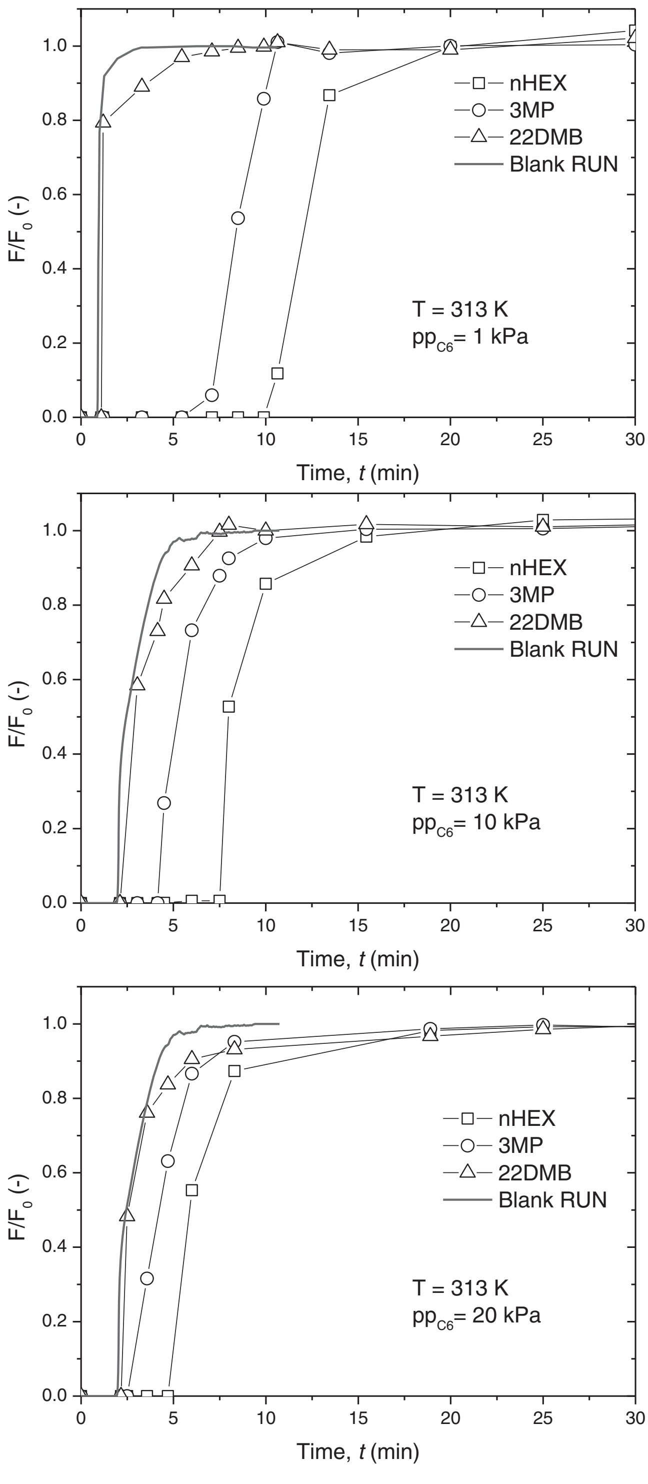

**Figure 2.** Ternary breakthrough curves for 22DMB/3MP/*n*HEX in MIL-53(Fe)-$(CF_3)_2$ at 313 K and partial pressures of 1, 10 and 20 kPa.

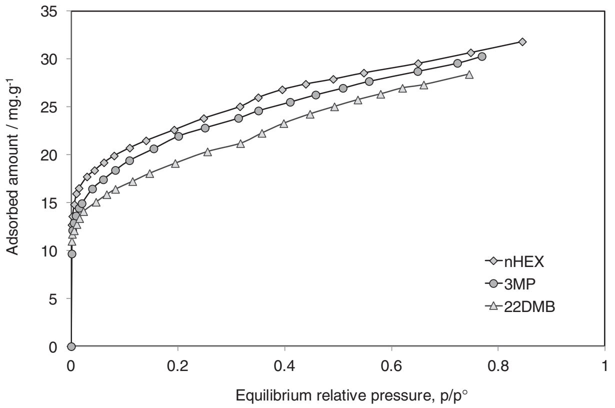

**Figure 3.** Hexane isomers single component adsorption isotherms at 313 K in MIL-53(Fe)-$(CF_3)_2$.

is not adsorbed at all within the porosity of MIL-53(Fe)-$(CF_3)_2$ in a fixed bed flow dynamic system from the ternary mixture (22DMB/3MP/*n*HEX) at 313 K, being consistent with its dimension exceeding the pore aperture of the selected solid, as mentioned above.

To gain further understanding, separation tests using equimolar binary mixtures of 3MP/22DMB and 22DMB/*n*HEX under similar temperature (313 K) and pressure (from 0.5 to 20 kPa) conditions were carried out. These measurements confirmed (SI, Figure S3,S4, Table S2,S3) that MIL-53(Fe)-$(CF_3)_2$ behaves as a molecular sieve to separate linear *n*HEX and mono-branched 3MP from the di-branched isomer 22DMB, at 313 K for partial pressures above 0.5 kPa. As far as we know, such a spectacular behavior has never been reported to such an extent before in any type of porous solid. These findings might be of a great importance in octane enhancement technologies due to the differences in the octane number of 22DMB (RON 91.8) and 3MP (RON 74.5). In addition to this outstanding separation performance, Table S1 (SI) shows that this solid adsorbs reasonable amounts of *n*HEX (4 wt%) and 3MP (3 wt%).

In order to shed light into this unusual separation behavior, complementary experiments were coupled with molecular simulations and the so-obtained conclusions were further compared with the ones collected on other related MOFs.

The single component adsorption isotherms of each of the three isomers have been first obtained at 313 K (**Figure 3**). It appears that all isomers are adsorbed in MIL-53(Fe)-$(CF_3)_2$ with sorption capacities of the same order of magnitude, that is, within the [3–3.5] wt% range at saturation in fair agreement with the quantities deduced from the breakthrough experiments. The adsorption isotherms for all isomers remain of I-shape type characteristic of a microporous solid, their slopes at low pressure ($P/P^o$ below 0.05) increasing in the sequence *n*HEX>3MP>22DMB. This clearly emphasizes that the affinity of this solid for the alkanes decreases when their degree of branching increases. Obtaining however a significant adsorption of 22DMB seems, at first sight, contradictory with the breakthrough experiments also performed at 313 K, which evidenced no adsorption of this isomer over the same pressure range. A first plausible explanation would be that 22DMB is not adsorbed at 313 K during the breakthrough experiments due to a much shorter contact time in the bed (passage time L/v) compared with the time constant of diffusion ($15D_c/r_c^2$) of 22DMB within the narrow and corrugated pores of MIL-53(Fe)-$(CF_3)_2$. In the adsorption experiments, the equilibrium time is much

**Table 1.** Cell parameters of MIL-53(Fe)-$(CF_3)_2$ at different pressures of *n*HEX (*T* = 303 K).

| *n*HEX partial pressure $P/P_0$ | *a* [Å] | *b* [Å] | *c* [Å] | Beta [°] | Cell volume [Å$^3$] | Space group |
|---|---|---|---|---|---|---|
| 0* | 19.429(1) | 10.355(1) | 6.911(1) | 108.57(1) | 1317.9(1) | C2/c (n°15) |
| | 16.490(1) | 13.653(1) | 6.883(1) | —— | 1549.5(3) | Imcm (n°74) |
| 0.1 | 19.43(1) | 10.32(1) | 6.89(1) | 108.6(1) | 1310.0(2) | C2/c (n°15) |
| | 16.39(1) | 13.51(1) | 6.91(1) | —— | 1529.3(3) | Imcm (n°74) |
| 0.7 | 19.45(1) | 10.28(1) | 6.90(1) | 108.9(1) | 1306.1(2) | C2/c (n°15) |
| | 16.42(1) | 13.50(1) | 6.90(1) | —— | 1530.5(3) | Imcm (n°74) |

(*) According to Devic et al.[20a]

higher, of ≈2 h per point, and this would explain why 22DMB is adsorbed. This distinct behavior can be also understood by a careful analysis of the structure of this solid in different conditions by means of X-ray powder diffraction (XRPD). First, temperature dependent XRPD tests were carried out for the MIL-53(Fe)-$(CF_3)_2$ solid. The sample was soaked with each of the three isomers in their liquid state and loaded within glass capillaries (Figure S10–S12, SI). It was evidenced previously that in the presence of polar or apolar liquids, the MIL-53 solids exhibit a variable pore opening.[20a] More particularly, it was shown that the solvent loaded MIL-53(Fe)-$(CF_3)_2$ exhibits a full LP form which evolves towards a mixture of empty LP and contracted narrow pore (NP) upon thermal treatment concomitant with the departure of the solvent.[20a] In our case, during the sample preparation, the powders start drying and thus the XRPD pattern does not show only the signature of a fully open LP form but rather a phase coexistence with a contracted NP structure reminiscent of the one previously evidenced (Figure S10, SI). Once hexane isomers are adsorbed, a mixture of LP and NP forms is observed in all cases (Figure S11,S12, SI) whose cell parameters are very similar to the ones already obtained for the dry state (**Table 1**).

As from a steric hindrance point of view, 22DMB or 3MP are expected to hardly enter the pores of the MIL-53(Fe)-$(CF_3)_2$ NP form (see comments above on the pore size dimensions of the solids vs the kinetic diameters of the adsorbates), adsorption and separation occurs mainly within the LP form while *n*HEX can be adsorbed in both NP and LP forms.

To highlight if when increasing the pressure of alkane, as observed typically with flexible MIL-53 MOFs, the NP form of MIL-53(Fe)-$(CF_3)_2$ switches to a LP form, leading to a system with a single phase LP structure, two glass capillaries with the MIL-53(Fe)-$(CF_3)_2$ 2$CF_3$ solid loaded at two different partial pressures of *n*HEX were collected at the ESRF at 303 K (**Figure 4**). It confirmed first that if at low *n*HEX pressure, the solid is mainly present in its NP form with a cell volume very close to the one observed for the dried solid (Table 1), allowing hardly any adsorption of the 2,2DMB; increasing the vapor pressure leads to a pore opening with the solid mainly in its LP form, once again with a cell volume very close to the one observed for the dried solid (Table 1), which lets 22DMB diffuses within its pores, making the separation less effective. Note that here the NP and LP form keep similar cell parameters whatever the pressure of *n*HEX at room temperature (Figure S13,S14, SI; Table 1).

Quasi-elastic neutron scattering (QENS) experiments were further coupled with Molecular Dynamics (MD) simulations to probe the diffusivity of all isomers as single components for a loading of 1 molecule/u.c at various temperatures. A 1D normal diffusion mechanism was first experimentally assessed for both *n*HEX and 3MP (Figure S15, SI), indicating that these molecules are able to pass each other in the narrow channels of MIL-53(Fe)-$(CF_3)_2$.[24] This mechanism was confirmed by the MD calculations which showed that whatever the structures considered for MIL-53(Fe)-$(CF_3)_{2,}$ that is, the LP or the NP forms, the molecules diffuse along the direction of the tunnel within a corridor section primarily centered in the middle of the pore (see Figure S18, SI). However, while in the LP form, 3MP and *n*HEX tend to glide along the channel, a jump sequence occurs for 22 DMB due to a steric barrier created by the inclusion of the grafted functional group (Figure S19, SI). This later scenario is also observed for 3MP and *n*HEX in the NP form due the decrease of the pore size.

Due to the presence of the bulky grafted function, the self-diffusion coefficients extracted from QENS experiments were found (**Figure 5**) to be two orders of magnitude smaller in comparison with a related structure, the porous vanadium terephthalate MIL-47(V) existing in a LP form.[25] Indeed, at 370 K,

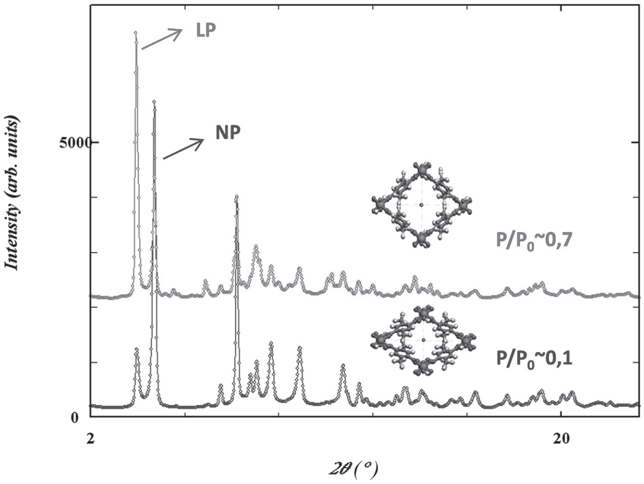

**Figure 4.** X-ray powder diffraction patterns of MIL-53(Fe)-$(CF_3)_2$at 303 K loaded under partial pressure of *n*HEX of ≈0.1 and 0.7 ($\lambda \approx 0.70128$ Å).

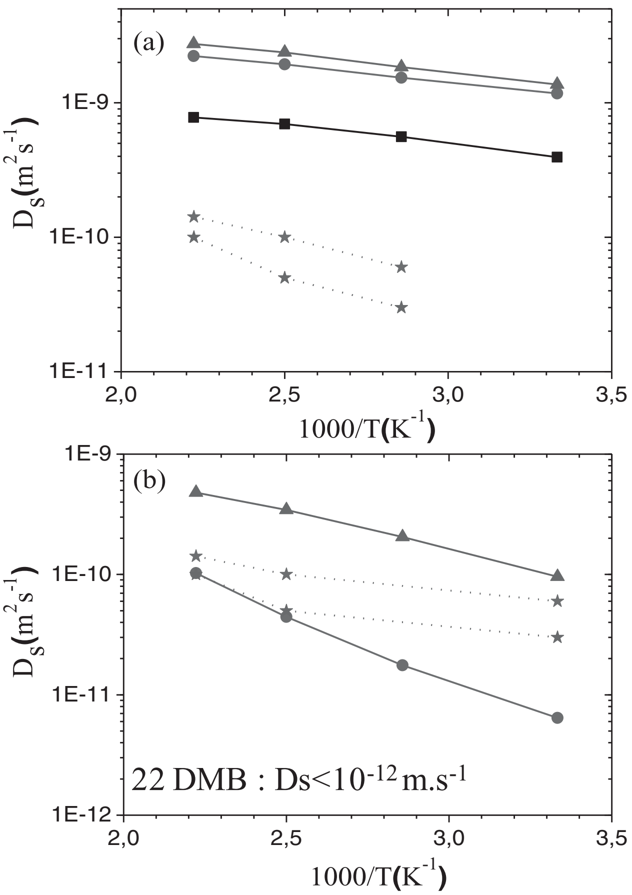

**Figure 5.** Self-diffusion coefficients for *n*HEX (triangles), 3MP (circles), and 22DMB (squares) in a) MIL-53(Fe)-$(CF_3)_2$ LP form and b) MIL-53(Fe)-$(CF_3)_2$ NP structures. The stars and dotted lines correspond to the experimental QENS data (lower: *n*HEX; upper: 3MP). The simulated and experimental data are estimated within an error bar of 10% and 50%, respectively.

the orientationally averaged self-diffusivities of *n*HEX and 3MP are respectively of $4 \times 10^{-11}$ and $8 \times 10^{-11}$ m$^2$ s$^{-1}$ in MIL-53(Fe) $-(CF_3)_2$, while they are of $6 \times 10^{-9}$ and $4 \times 10^{-9}$ m$^2$ s$^{-1}$ in MIL-47(V) for the same temperature. Figure 5 also reports the simulated self-diffusivities obtained in both the LP and the NP forms of MIL-53(Fe)-$(CF_3)_2$. Compared to the scenario in the LP form, the diffusivities of *n*HEX and its mono-branched isomer in the NP structure are slower and become closer to the QENS values. This trend holds also true for the corresponding simulated activation energies (Ea) (Table S4, SI) which agree quite well with the experimental data. As a typical illustration for *n*HEX, the calculated Ea of 12.6 kJ mol$^{-1}$ in the NP structure (vs 5.3 kJ mol$^{-1}$ in the LP form) matches rather well the experimental value (15.5 kJ mol$^{-1}$). This whole observation supports that the diffusivity of both isomers is experimentally probed in the contracted phase. It is also noticeable that the QENS diffusivity of 3MP is slightly faster than the one measured for *n*HEX but the difference stands within the standard deviation. Thus, one can estimate that the separation between 3MP and *n*HEX is not kinetically driven, at 313 K but rather related to the difference of adsorption as deduced from the isotherms (Figure S13, SI). Noteworthy, the situation is not the same for 22DMB whereas broadenings were too small to test the single-file diffusion model and to derive diffusivities. Complementary MD calculations were performed by forcing the inclusion of 22DMB molecules within the pores of the LP and the NP forms. No $D_s$ values were able to be extracted from these MD runs due to an extremely restricted mobility of these molecules even for long MD runs up to 50 ns (Figure S20, SI). All these results thus converge towards a kinetic separation of 22DMB from the other isomers as illustrated by the difference between the results of the the breakthrough experiments at low temperature (313 K) or pressure (1 kPa). Figure 5a further shows that in contrast to the situation in the NP form, 22 DMB is predicted to diffusive within the pore of the LP form which is consistent with a decrease of the separation performance of this solid when occurs an opening of its structure triggered by the hexane pressure (see above) or by the temperature (see below).

The impact of the temperature over the separation was further evaluated on MIL-53(Fe)-$(CF_3)_2$ using binary or ternary mixtures of the isomers at pressure between 1 and 20 kPa. A decrease in the separation ability and sorption capacity of the solid is observed (Figure S5–S7, SI). This trend could be thus at first sight attributed to the decrease in the adsorbed amounts of 3MP and *n*HEX when the temperature increases as expected. Another explanation relies on the flexible character of the MOF. It was shown above (Figure S15,S16, SI) that the pores further expand when the pressure increases. In addition as observed previously with the parent MIL-53(Cr, Al, or Fe) analogues,[26,27] an increase in temperature for the MIL-53(Fe) derivatives might induce here a contraction of the pores that would here significantly decrease the sorption capacity of the isomers.[27]

From a practical point of view, a sorbent shall be recyclable. Thus, we have investigated the effect of temperature over the desorption of a previously saturated bed around a partial pressure of the isomers of 1 kPa at 303 K. Using the desorption time of the blank experiment as a reference, it is confirmed that the title solid MIL-53(Fe)-$(CF_3)_2$ can be easily regenerated after adsorption of the alkane mixture. Indeed, the desorption time of 22DMB is close to the one of the blank which further proves that this compound is not adsorbed at all. The other isomers (nHEX, 3MP) also come out from the bed very fast which was expected due to their very high diffusivities. Moreover, it also indicates that it is easier to regenerate *n*HEX than 3MP which can be explained through a higher diffusivity of nHEX over 3MP. One can also point out that as the temperature increases, the washing time decreases related to the lower adsorption capacity of this MOF.

In a last step, the performances of both the parent MIL-53(Fe) and its functionalized form MIL-53(Fe)-$(CH_3)_2$ were assessed for the same separation test. Note that this later solid has never been reported previously. Its synthesis and characterization as well as the analysis of its flexible character are reported in the SI (Figures S22-S27). In both cases, neither significant adsorption nor separation ability of the hexane isomers was evidenced at 313 K (Figure S28,S29, SI). It was established previously that MIL-53(Fe) exhibits upon drying a closed pore form with hardly any adsorption, at low pressure, for linear alkane vapors (C6-C9) at 303–313 K, mainly due to diffusion limitations within the narrow 1D pore system.[27] In the case of the dimethyl functionalization, we show here (Figure S22, SI) that the dried form exhibits also very narrow pores considering the cell volume (≈1060 Å$^3$). To assess such assumption, the simulated crystal structures of the two NP forms were analyzed and their PSD calculated. While the crystal structure for MIL-53(Fe) was taken from our previous contribution,[20] the one forthe dried MIL-53(Fe)-2CH$_3$ NP form was constructed using a computational assisted structure determination approach based on the cell parameters deduced from ex situ XRPD (Figure S22, SI). The corresponding pore diameters of MIL-53(Fe) and MIL-53(Fe)-2CH$_3$ are 1.8 and 3.0 Å, respectively, therefore ruling out any significant adsorption at low partial pressure of hexane isomers (even if one could expect a pore opening at higher vapor pressure). In a second step, the behavior of the pseudo-polymorph of MIL-53(Fe)-(CF$_3$)$_2$, denoted MIL-88B-(CF$_3$)$_2$ was also assessed for the same separation. This compound possesses a structure (Figure S1, SI) built up from another type of inorganic sub-unit, that is, oxocentered trimers of iron(III) octahedra, resulting in a highly flexible architecture with a 3D (micro-) pores system. It was shown previously that this type of MOFs, despite its very narrow pore form once dried associated with a low nitrogen surface area, could adsorb significant amounts of linear alkanes at 313 K, with in some cases a slight increase in the pore opening (e.g., pentane).[28] In a first step, adsorption isotherms of the pure components were performed at 313 K resulting into differences in terms of shape of isotherms and amounts of adsorbed guests (Figure S8, SI), much more significant and over a much larger pressure range compared to MIL-53(Fe)-(CF$_3$)$_2$, with a clear-cut *n*HEX>3MP>22DMB order of selectivity. Thus, one could expect an improved separation ability of this material compared with the MIL-53 polymorphs.

In a last step, breakthrough separation tests of the paraffins mixture were carried out using this solid at different temperatures (313, 393 K) and pressures (1–20 kPa) (**Figure 6** and Figure S6–S8, SI). If a separation is noticeable at low pressure and temperature, the selectivity is however poor, that is, much lower than the one of its MIL-53(Fe)-(CF$_3$)$_2$ polymorph, and in addition with almost no separation between the branched isomers. One possible explanation would be that upon adsorption of *n*HEX, a tiny pore expansion occurs during the very first step of alkane adsorption, as observed previously with *n*-pentane, that makes easier the diffusion of the isomers leading to almost no separation effect between the branched paraffins.[28]

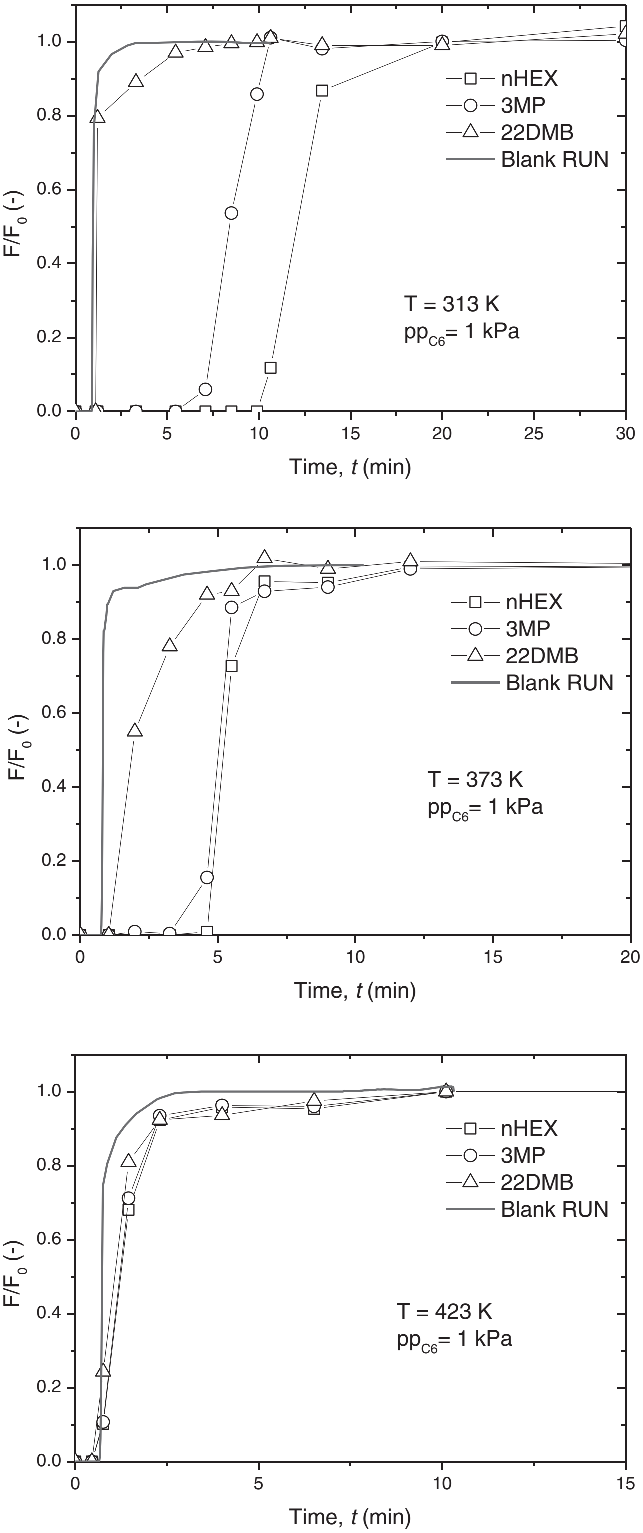

**Figure 6.** Breakthrough curves of *n*C6/3MP/2,2DMB over MIL-53(Fe)-(CF$_3$)$_2$ at 303, 373, and 423 K at a partial pressure of 1 kPa.

In conclusion, our multidisciplinary approach clearly evidenced that a 1D-pore type hybrid porous solid (MOF) functionalized with bulky CF$_3$ groups, is able to completely sieve, at low pressure and 313 K, the dibranched isomer of hexane from a mixture of paraffins in a view of upgrading the RON of gasoline. This phenomenon was shown to be kinetically controlled, that is, related to a difference of diffusivity between the dibranched isomer and the 3MP and *n*HEX molecules. This is the first time that an adsorbent exhibits such a spectacular separation behavior. If previously zeolites or other MOFs did exhibit a certain degree of separation between the dibranched and the other isomers, this has never reached a total exclusion magnitude as shown by MIL-53(Fe)-(CF$_3$)$_2$ (**Table 2**). Our results open thus a new route in the field of adsorbents to achieve such a complex separation. Indeed,

**Table 2.** Classification of the separations performances of zeolites and MOFs for the hexane isomers obtained from experimental data.

| | Zeolite 5A[22] | Zeolite BETA[23] | MOF $Fe_2(BDP)_3$[18] | MOF ZIF-8[17b,c] | MOF IM-22[17b] | MOF MIL-53(Fe)-$(CF_3)_2$* |
|---|---|---|---|---|---|---|
| Separation Linear/ Branched | Total (Sieve effect) | Partial (Equilibrium based) | Partial (Equilibrium based) | Total (Kinetic based) | Partial (Kinetic based) | Partial (Kinetic/Equilibrium Based) |
| Separation mono/ di-Branched | None | Partial (Equilibrium based) | Partial (Equilibrium based) | Partial (Kinetic based) | Partial (Kinetic based) | Total (Kinetic based) |

(*)This work

due to the high degree of chemical and structural diversity of this class of flexible solids, based on the use of a wide range of metal(III) cations (Fe, Al, Sc, V, In, Ga) and dicarboxylate linkers (functionality, spacer) or structures (MIL-53, MIL-88, etc.) available, one can reasonably expect that our future investigation will lead to the design of an optimized sorbent to maintain the dibranched sieving effect at high temperature (>400 K) in order to produce an upgraded RON.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The research leading to these results has received funding from the Franco-Portuguese PAUILF program 2008–2011 and the European Community's Seventh Framework Program (FP7/2007–2013) under grant agreement n° 228862. G.M. thanks the Institut universitaire de France for its support. ESRF SNBL Beamline and its staff members for the ex situ XRPD data collection.

Received: June 16, 2014
Revised: September 11, 2014

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