Paraffin Separation

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Ultra-Tuning of the Rare-Earth fcu-MOF Aperture Size for Selective Molecular Exclusion of Branched Paraffins

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Abstract: *Using isoreticular chemistry allows the design and construction of a new rare-earth metal (RE)* ***fcu****-MOF with a suitable aperture size for practical steric adsorptive separations. The judicious choice of a relatively short organic building block, namely fumarate, to bridge the 12-connected RE hexanuclear clusters has afforded the contraction of the well-defined RE-*__*fcu*__*-MOF triangular window aperture, the sole access to the two interconnected octahedral and tetrahedral cages. The newly constructed RE (Y^{3+} and Tb^{3+})* ***fcu****-MOF analogues display unprecedented total exclusion of branched paraffins from normal paraffins. The resultant window aperture size of about 4.7 Å, regarded as a sorbate-size cut-off, enabled a complete sieving of branched paraffins from normal paraffins. The results are supported by collective single gas and mixed gas/vapor adsorption and calorimetric studies.*

Separation of light hydrocarbons is one of the most energy intensive and demanding process pertaining to the gas, oil, and fuel industries.[1] Principally, the separation of normal paraffins (such as *n*-pentane, *n*-hexane) from branched and cyclic paraffins is of prime interest for the production of high efficacy fuels in refineries, namely access to a high octane number (ON) gasoline and/or a high cetane number (CN) diesel. In point of fact, the octane number for a gasoline type fuel is directly correlated to the performance of an engine, and typically the more-valuable branched isomers, having a higher octane number, are added to gasoline while the less-valuable linear isomers are removed and/or fed back into the isomerization or reforming units.[2] In contrast, in the case of a diesel fuel, the normal paraffins, such as *n*-hexane and *n*-octane, are the essential components for a high CN diesel, therefore the selective separation of linear alkanes from branched and cyclic alkanes is of prime importance.

In addition to fuel upgrading, the cost-effective separation of branched paraffins from normal paraffins offers great benefits for practical industrial applications to produce LPG (liquefied petroleum gas) and isobutane referred to commercially, in its pure form, as R600a. Owing to their similar chemical and physical properties (boiling point, vapor pressure, etc), the conventional low-temperature fractional distillation technique is the currently used separation technology for the separation of normal paraffins from branched paraffins; however, this technology is recognized to be energy intensive and not cost effective.[3]

Accordingly, deployment of alternative cost-effective and energy efficient separation approaches is of prime industrial importance. Principally, adsorptive separation based on porous materials as separation agents is regarded as a prospective economically viable technology and a suitable alternate to the energy-intensive distillation-based separation. Nevertheless, the practicality of the adsorptive separation technology and its associated efficiency are strongly dependent and directly correlated to the intrinsic properties of the separation adsorbent employed. Adsorptive separation is accomplished by one of three processes, namely steric, kinetic, or equilibrium based mechanisms. In the case of the steric effect, originating from the molecular sieving property of the adsorbent, only relatively small and appropriately shaped molecules can diffuse into the adsorbent while the other molecules are totally excluded. In contrast, kinetic adsorption is based on the differences in diffusion rates of different adsorbate molecules. Note that a favorable close packing of a given guest molecule within a mismatched pore system was shown to be appropriate for molecular separation.[4] As a result of the difficulties in deliberately fine-tuning the aperture size of a typical purely inorganic or organic adsorbent, the equilibrium separation based on the equilibrium adsorption of the mixture remains the dominant industrial process.

Conventional microporous adsorbents, such as zeolites and activated carbons, have been used extensively as separation agents in pressure and/or temperature cyclic configurations. Nevertheless, their separation efficiency for linear/branched paraffins was asserted to be relatively low. Principally, hydrocarbons adsorption studies on the zeolite A adsorbents family (3A, 4A and 5A), a revolutionary adsorbent that impacted the oil, gas, and petrochemical industries as effective molecular sieves in the last decades, revealed moderate separation of hydrocarbons. Namely, zeolite 5A with a pore-opening diameter around 4.2 Å was found to adequately separate branched paraffins from linear C_{4+} paraffins.[5] Nevertheless, various reports showed that appreciable amounts of isopentane and isobutane were adsorbed in the α cages of the zeolite 5A[6] and thus lessening the separation efficiency.

Evidently, ultra-fine-tuning of the size aperture of the aforementioned zeolite to completely exclude (full sieving)

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the appropriate hydrocarbons will potentially permit the achievement of the practical and desired separation efficiency. Nevertheless, such a precise structural control in the case of purely inorganic microporous zeolite materials remains an ongoing challenge owing to the manifest difficulties in maintaining the same topology while altering the window size, shape, and circumference exposed functionalities. Such a looked-for chemical process, that enables the expansion, contraction, decoration, and functionalization of a set porous material topology, is referred to as isoreticular chemistry and it is a common practice in the fast burgeoning field of metal–organic frameworks (MOFs).[7]

In fact, MOFs owing to their hybrid character and modular nature are regarded as new generation of porous materials with great prospective to address current challenges pertinent to energy and environmental sustainability.[8]

Principally, the successful practice of isoreticulation in MOF crystal chemistry permits unparalleled control of the pore system at the molecular structure level, by judiciously selecting the appropriate building blocks,[6a,8] and subsequently offers potential to develop new highly effective microporous materials with fine-tuned aperture sizes that can permit selective molecular exclusion of branched paraffins from normal paraffins, in other words, complete molecular sieving (Figure 1). Such a conceivable selective molecular exclusion in MOFs would be ideal for gas/vapor separation of isomers with similar physical–chemical properties.

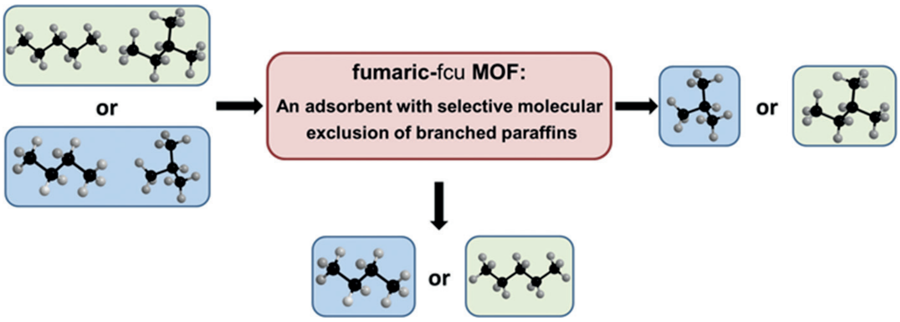

Figure 1. The concept of using molecular sieve materials in the highly selective separation of paraffin from isoparaffins.

Encouraged by our recent results on the successful utilization of an isoreticular rare-earth metal (RE) **fcu**-MOF with deliberately fine-tuned triangular windows for kinetic adsorption based separation of alkanes, we elect to expand our strategy and explore the promise of the **fcu**-MOF platform for the selective molecular exclusion of branched paraffins from normal paraffins. Rationally, the **fcu**-MOF platform is ideal for exploring the selective molecular exclusion as it holds some unique desired features, namely it encloses only equilateral triangular windows that are the sole access to the pore system which is composed of interconnected tetrahedral and octahedral cages sharing triangular faces. The tetrahedron and the octahedron are the only two edge-transitive polyhedra comprising solely triangular faces. Accordingly, construction of an isoreticular **fcu**-MOF with a relatively shorter linker will permit the anticipated contraction of the triangular window aperture with nominal reduction in the overall porosity, permitting the realization of the size cut-off for molecular discrimination of isomers with favorable diffusion of the adsorbed isomer (Figure 1).

The molecular building block (MBB) approach[7c] has been employed to form the RE-**fcu**-MOF platform constructed from the assembly of unique RE hexanuclear clusters with a series of fluorinated and nonfluorinated, heterofunctional as well as fluorinated homofunctional linkers assisted by the modulator and structural directing agent (SDA), namely 2-fluorobenzoic acid (2-FBA).[9]

In light of the large aperture size of the RE-**fcu**-MOFs (Figure 2), the adsorption of gases (such as, CO_2, C_2H_6 and C_3H_8) was mainly driven by the difference in adsorption energetics (equilibrium based separation) while no noticeable differences were observed in their adsorption kinetics as a result of increasing the size of the adsorbate.[9,10]

Whereas, altering the triangular widow size and functionality by substituting the relatively longer H_2FTZB ligand by the shorter and bulkier linker, namely 1,4-naphthalenedicarboxylate (1,4-NDC) (Figure 2 and Figure S1 in the Supporting Information) allowed us to construct the isoreticular RE-1,4-NDC-**fcu**-MOF with tuned adsorption/kinetic properties arising from the consequential contracted pore size.[10] The resultant RE-NDC-**fcu**-MOF showed favorable adsorption kinetics for n-C_4H_{10} and n-C_5H_{12} versus their branched isomers. However, their final adsorption equilibrium capacities were identical in the entire pressure range (Figure S16) and consequently prohibited the attainment of the desired highly efficient n-paraffin/isoparaffin separation.

To address this challenge, we opted to target the n-paraffin/isoparaffin separation by virtue of selective molecular exclusion of branched paraffins from mono and/or di-branched paraffins (Figure 1). Accordingly, we targeted the assembly of an isoreticular RE **fcu**-MOF based on a ligand shorter than 1,4-NDC, namely fumarate (fum) (Figure 2). Indeed, predetermined reaction conditions for the assembly of the RE-**fcu**-MOF platform were employed in the presence of fumaric acid and have allowed the isolation for the first time of the new 12-connected RE (Y^{3+} and Tb^{3+}) fumarate based **fcu**-MOF with much contracted aperture size (Figure 2) and affording an unprecedented selective molecular exclusion of branched paraffins from normal paraffins. Reactions between fumaric acid and yttrium nitrate hexahydrate in N,N'-dimethylformamide (DMF)/water solution yielded transparent octahedral shaped crystals, formulated by single-crystal X-ray diffraction (SCXRD) as $(|(CH_3)_2NH_2)_2|[Y_6(\mu_3\text{-}OH)_8(fum)_6(H_2O)_6]\cdot(DMF)_5$ (**1**). The chemical formula was confirmed by elemental analysis (Table S1), ^{1}H NMR analysis (Figure S14), and thermogravimetric measurements (Figure S10 and S11) validating the good agreement between the theoretical and the experimental weight-loss values. Furthermore, the presence of five DMF

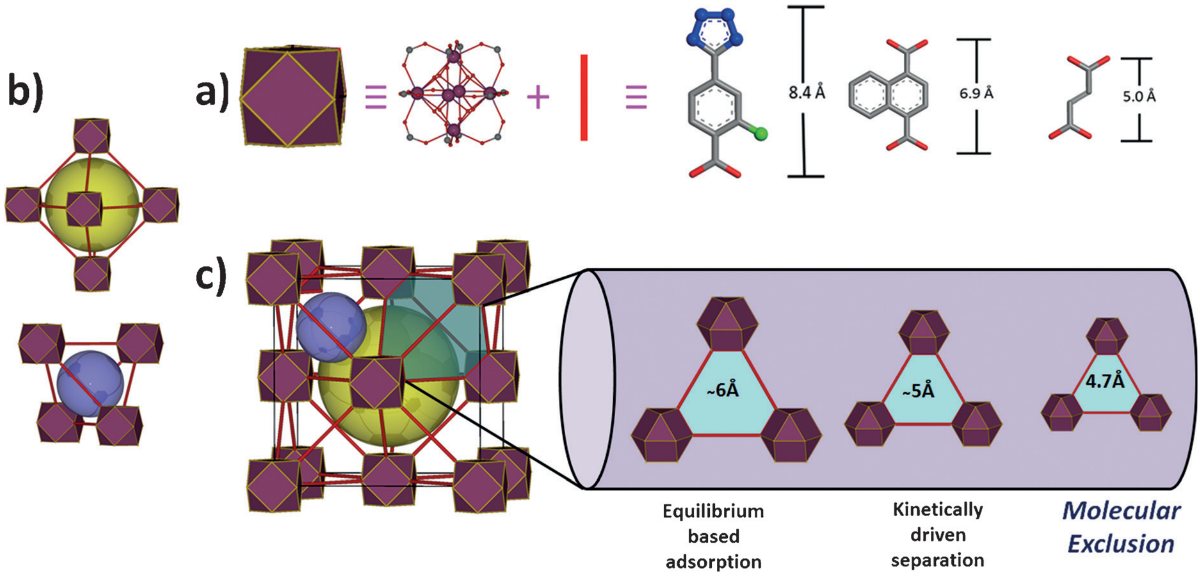

Figure 2. Schematic representation of the components of the RE **fcu**-MOFs platform including three possible organic linkers of different lengths (a). The RE **fcu**-MOFs consist of two types of cages one with octahedral shape and the other with tetrahedral shape (b), both of them accessible through triangular windows (c). The judicious choice of the organic building block allowed to isolate the new **fcu**-MOF with smallest aperture.

molecules per mole of the MOF was evidenced by the resulting 5:12 ratio for the integration of formyl proton of DMF to the fumarate olefinic protons. The presence of *N*,*N*-dimethylammonium ions, balancing the charge of the anionic framework, is supported by the presence of distinct methyl proton signals which are clearly separated from the signals for the methyl protons of DMF. Furthermore, the methyl proton signals associated with DMA cations are preserved in the ethanol-exchanged and fully evacuated fum-**fcu**-MOF sample while the DMF signals disappear (Figure S14). These results were further supported by CHN elemental analysis of both as-synthesized and activated samples of **1** and **2** (Table S1).

Compound **1** crystallizes in a cubic crystal system $Pn\bar{3}$ space group with the unit cell parameter $a = 18.5353(9)$ Å. In **1**, each yttrium cation (Y^{3+}) is surrounded by four oxygen atoms from four μ_3-OH groups, four oxygen atoms from carboxylate groups belonging to three crystallographically independent fumarate ligands, and one terminal water molecule. The adjacent Y ions are bridged by μ_3-OH and deprotonated carboxylate groups in a bis-monodentate fashion giving rise to the 12-coordinated hexanuclear molecular building block (MBB), $[Y_6(\mu_3\text{-OH})_8(O_2C\text{-})_{12}]$ (Figure 2 and Figure S1). Each hexanuclear MBB is connected to 12 fumarate ligands to generate a 3-periodic MOF.

Topological analysis of the resultant crystal structure confirmed that the topology of **1** corresponds to the expected **fcu** net, the only 12-connected edge transitive net. The hexanuclear cluster $[Y_6(\mu_3\text{-OH})_8(O_2C\text{-})_{12}]$ MBBs, where the carbons atoms of the carboxylate moieties act as points of extension, coincide with the cuboctahedron vertex Figure of the **fcu** net.[11]

As anticipated, the terbium analogue $(|(CH_3)_2NH_2)_2|[Tb_6(\mu_3\text{-OH})_8(\text{fum})_6(H_2O)_6]\cdot(\text{DMF})_5$ (**2**) has been isolated under similar reaction conditions when using $Tb(NO_3)_3\cdot5H_2O$ as the rare-earth metal source. It must be noted that different RE metals (i.e., Yb, Sm, Er, Ho, Dy, Gd) analogues have also been successfully synthetized (Figure S2) but herein only compound **1** and **2** are investigated for hydrocarbons adsorption and separation (Figure S19 and S20).

Typically, both compound **1** and **2** displays classical octahedral and tetrahedral cages with the diameter of the largest spheres that can fit into these cages (taking into account the Van der Waals surface) being about 7.6 and 5.2 Å, respectively. This is further supported by pore size distribution analysis from low-pressure Argon adsorption isotherms (Figure S17b and S18b). The judicious choice of fumaric acid as a linker permits the precise control of the access to the cages through triangular windows. Compounds **1** and **2** display a window aperture of approximately 4.7 Å which is slightly larger than linear paraffins (e.g. *n*-butane ca. 4.3 Å) and shorter that most of mono and dibranched paraffins (e.g. isobutane ca. 5 Å). The corresponding solvent-accessible free volumes for **1** and **2** were estimated to be 46 and 47%, respectively, using PLATON software.[12]

The phase purity of the bulk crystalline materials was confirmed by similarities between the calculated powder X-ray diffraction (PXRD) pattern from the associated SCXRD data and the experimental PXRD pattern of as-synthesized material (Figure S2,S3). In addition, analysis of the variable-temperature PXRD patterns and thermogravimetric experiments revealed that compounds **1** and **2** are highly thermal stable (Figure S8–S11), which is an important parameter for potential practical use of porous MOFs in gas/vapor separation applications. The materials were also soaked in various organic and inorganic solvents for long periods of time and showed appreciable stability (Figure S4 and S5). The stability of RE fum-**fcu**-MOF to moisture was evaluated by exposing the materials to different levels of humidity and no alteration in crystallinity nor the porosity was observed for **1** and **2** (Figure S6 and S7). The water adsorption isotherms at room temperature (Figure S15) were recorded for both **1** and **2** and revealed high water adsorption capacity and fast adsorption kinetics.

The permanent porosity of the materials was confirmed by low-pressure Ar adsorption experiments prior performing the targeted hydrocarbons adsorption studies. Ar adsorption isotherms recorded at 87 K for the activated **1** and **2** showed fully reversible type-I isotherms (Figure S17a and S18a), characteristic of microporous materials with permanent porosity. The apparent BET area based on Ar were estimated to be 691 and 503 $m^2 g^{-1}$ and the total pore volumes were calculated to be 0.28 and 0.21 $cm^3 g^{-1}$ for **1** and **2**, respectively.

Further investigation of the adsorption of normal paraffins, such as *n*-pentane and *n*-butane, was carried out at 293 K. The single-component adsorption isotherms of *n*-pentane and *n*-butane showed a fully reversible type-I behavior for both compound **1** and **2** (Figure S19) with fast adsorption kinetics (Figure S23). In contrast, investigation of mono-branched paraffins at 293 K showed that no adsorption was observed for isobutane and isopentane with both **1** and **2** (Figure S19). In light of these results, we anticipate no adsorption of all other mono and di-branched isomers of hexane, heptane, octane, etc.

This finding is a breakthrough discovery, thanks to isoreticular chemistry applied to RE-**fcu**-MOF platform, as it has been possible to design and discover suitable rigid separation agents with the appropriate aperture affording complete sieving of branched paraffins from normal paraffins, translated into infinite selectivity toward normal paraffins.

The combination of contracted pore aperture size of approximately 4.7 Å and the relative rigidity in comparison to other MOFs (such as, ZIF-8, ZIF-7)[13] allowed **1** and **2** to exhibit a perfect cut-off aperture size for the total separation of *n*-pentane/isopentane, *n*-butane/isobutane and paraffins/branched paraffins in general.

The selective molecular exclusion (total exclusion) of isobutane from *n*-butane was confirmed further by performing simultaneous thermal gravimetric and calorimetric measurements (TG-DSC) for **1** (Figure 3 and Figure S21). In fact, the enthalpy (ΔH) of n-C_4H_{10} adsorption was found to be 56 $kJ mol^{-1}$, while no noticeable exothermic effect was observed for isobutene (Figure 4). Evidently, such a distinct adsorption behavior confirms the selective molecular exclusion of the iso-C_4H_{10} and corroborates the unique molecular sieving properties of **1**.

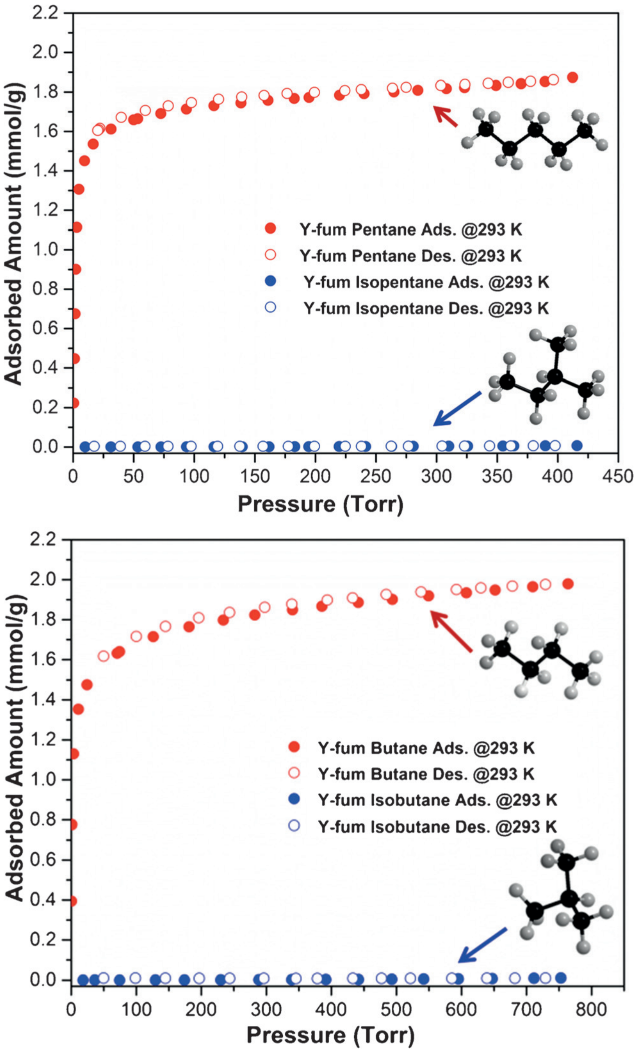

Figure 3. Adsorption isotherms for **1** collected at 293 K. Top: *n*-pentane and isopentane. Bottom: *n*-butane and isobutane.

To further confirm this unprecedented selective molecular exclusion of iso-C_4H_{10}, a column (filled with 408 mg of **2**) breakthrough adsorption test using n-C_4H_{10}/iso-C_4H_{10}/N_2: 5/5/90 gas mixture was carried out at 298 K and 1 bar total pressure (Figure 4). The choice of this specific mixture in balance with N_2 is motivated by the negligible N_2 uptake as compared to n-C_4H_{10} and its use as a reference non-adsorbable gas. As anticipated, iso-C_4H_{10} was not retained in the column similarly to the reference gas N_2, confirming that iso-C_4H_{10} is not adsorbed (Figures S24–S26). Conversely, using 8 $mL min^{-1}$ gas mixture flow, n-C_4H_{10} was retained in the column for ca. 17 min with the n-C_4H_{10} adsorbed amount (0.8 $mmol g^{-1}$) in the bed which is in a good agreement with the n-C_4H_{10} single adsorption data (Figure S19) at 35 torr partial pressure. It is important to note that the breakthrough curves were normalized by taking into account the overlap of mass fragmentation intensities m_{29} and m_{39} associated to *n*-butane and isobutane respectively.

Single gas breakthrough tests of n-C_4H_{10} and iso-C_4H_{10} (Figure S27 and S28) are another evidence supporting the ability of fumaric based **fcu**-MOF to fully sieve branched paraffins from their linear isomers. It must be highlighted that it is the first time that a relatively rigid material, in solid-state chemistry, exhibits the selective molecular exclusion of mono-branched paraffins (full molecular exclusion) from the linear ones. For illustration purposes, zeolite 5A, which was the best material to date and used in industry, was shown to partially sieve *n*-butane as 3–4% of isobutane was shown to be adsorbed.

In summary, we have successfully employed isoreticular chemistry approach with our RE-**fcu**-MOF platform and synthesized new series of RE fumarate-based **fcu**-MOF analogues with the smallest apertures in the family of RE-

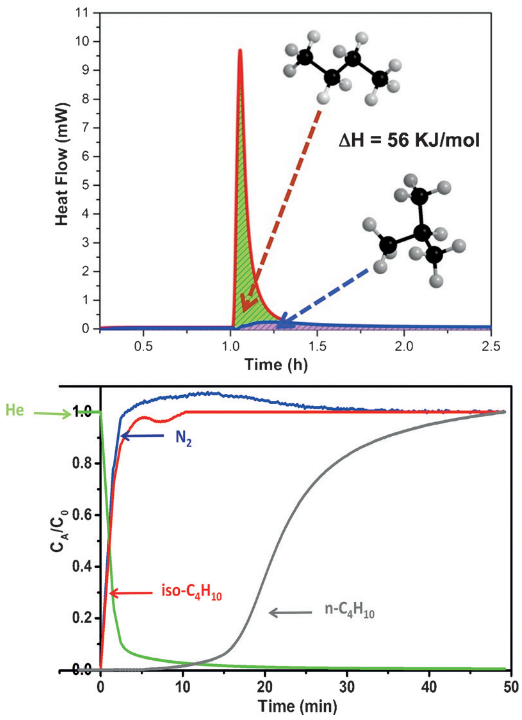

Figure 4. Top: Heat-flow (in mW) for the adsorption of *n*-butane (red) and isobutane (blue) on **1** obtained by TG-DSC analysis. Bottom: Column breakthrough test for the adsorption of mixed *n*-butane (5 %) and isobutane (5 %) in balance with N_2 (n-C_4H_{10}/iso-C_4H_{10}/N_2: 5/5/90 mixture) on **2**.

fcu-MOFs. Yttrium and terbium fumarate-based **fcu**-MOF analogues, namely Y-fum-**fcu**-MOF and Tb-fum-**fcu**-MOF were selected for extensive structural–adsorption properties studies. The judicious choice of fumarate as bridging linker combined with the control of in situ formation of the RE hexanuclear cluster have allowed the fabrication of a microporous material with the required characteristics (cut-off window size of ca. 4.7 Å) that afford the selective molecular exclusion of the branched paraffins, complete sieving of linear/mono-branched paraffins. The *n*-pentane/isopentane and *n*-butane/isobutane adsorption studies, based on various complimentary techniques such as single and mixed gas adsorption calorimetry, suggests for the first time that it is indeed possible to employ a MOF for the gasoline-diesel upgrading and for the isobutane (R600a) purification. These relevant and unique applications, resulting from the selective molecular exclusion of branched paraffins, are unique to MOFs as such performances were not observed nor achieved, to our knowledge, with any other class of porous materials. Further work is underway to 1) fine tune the window size to allow the passing of mono-branched paraffins and exclusion of di-branched paraffins and 2) explore other applications, such as separation of isopropanol from water and other alcohol driven mainly by size/sieving.

Experimental Section

All the starting materials used were purchased and used without further purification. The experimental details for different characterizations and adsorption measurements are described in the Supporting Information. MOFs were prepared solvothermally by heating solutions containing lanthanide salts, fumaric acid, and 2-fluorobenzoic acid modulating agent as described in the Supporting Information. The components were combined in a 20 mL scintillation vial, sealed and heated to 115 °C for 72 h, and cooled to room temperature. The colorless polyhedral crystals were collected and air dried. Further details are described in the supporting information.

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Keywords: hydrocarbons · isoreticular chemistry · metal–organic frameworks · molecular sieves · separation

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