

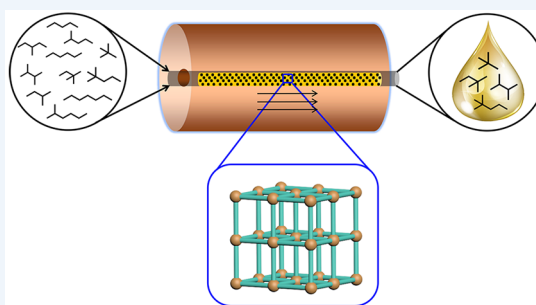
# Microporous Metal–Organic Frameworks for Adsorptive Separation of C5–C6 Alkane Isomers

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**CONSPECTUS:** The separation of alkane isomers, particularly C5–C6 alkanes, is of paramount importance in the petrochemical industry to achieve high quality gasoline. Upon catalytic isomerization reactions, less branched alkanes (with lower octane number) need to be separated from their more branched isomers (with higher octane number) in order to improve the octane rating of gasoline. To reduce the high energy input associated with distillations, the primary separation technique currently used in industry, adsorptive separation by porous solids has been proposed. For example, zeolite 5A has been used as the adsorbent material for adsorptive separation of linear alkanes from their branched isomers, as a supplement technology to distillations.



However, due to the limited number of zeolite structures and the lack of porosity tenability in these compounds, the task has not been fully fulfilled by using zeolites. Metal–organic frameworks (MOFs), in light of their structural diversity and high tunability in terms of surface area, pore size, and pore shape, offer new opportunities for resolving industrially relevant separation of alkanes through selective adsorption. This Account summarizes recent development of microporous MOFs for the separation of alkanes, with an emphasis on C5–C6 alkane isomers, including early examples of alkane separation by MOFs, as well as the latest advancement on tailor-made microporous MOFs for size sieving of C5–C6 alkane isomers.

The limitation of zeolite 5A as a sorbent material for the separation of C5–C6 alkane isomers lies in its relatively low adsorption capacity. In addition, it is not capable of separating branched alkanes, which is a crucial step for further improving the octane rating of gasoline. The high porosity and tunable pore size and pore shape of MOFs may afford them higher adsorption capacity and selectivity when used for alkane separation. MOFs with pore size slightly larger than the kinetic diameter of branched alkanes can effectively separate alkane isomers through thermodynamically controlled separation, as seen in the case of  $\text{Fe}_2(\text{bdp})_3$  ( $\text{bdp}^{2-} = 1,4\text{-benzenedipyrazolate}$ ). This MOF is capable of separating a mixture of hexane isomers by the degrees of branching, with higher adsorption capacity than zeolites under similar conditions but with relatively low selectivity. One effective strategy for obtaining MOFs with optimal pore size and pore shape for highly selective adsorption is to make use of reticular chemistry and precise ligand design. By applying topologically directed design strategy and precisely controlling the pore structure or ligand functionality, we have successfully synthesized a series of highly robust MOFs built on tetratopic carboxylate linkers that demonstrate high performance for the separation of C5–C6 alkane isomers. Zr-bptc ( $\text{bptc}^{4-} = 3,3',5,5'\text{-biphenyltetracarboxylate}$ ) adsorbs linear alkanes only and excludes all branched isomers. This size-exclusion mechanism is very similar to that of zeolite 5A. Yet, Zr-bptc has a significantly enhanced adsorption capacity for *n*-hexane, 70% higher than that of zeolite 5A under identical conditions. Zr-abtc ( $\text{abtc}^{4-} = 3,3',5,5'\text{-azobenzenetetracarboxylate}$ ) is capable of discriminating all three C6 alkane isomers via a thermodynamically controlled process, yielding a high separation factor for monobranched over dibranched isomers. MOFs with flexible framework may exhibit unexpected but desired adsorption properties.  $\text{Ca}(\text{H}_2\text{tcpb})$  ( $\text{tcpb}^{4-} = 1,2,4,5\text{-tetrakis(4-carboxyphenyl)-benzene}$ ) can fully separate binary or ternary mixtures of C5–C6 alkane isomers into pure form through selective molecular sieving as a result of its temperature- and adsorbate-dependent framework flexibility. The intriguing structural properties and exceptional tunability of these MOFs make them promising candidates for industrial implementation of adsorptive separation of alkane isomers.

## INTRODUCTION

Energy input associated with chemical separations takes up ~50% of industrial energy consumption.<sup>1</sup> The separations rely primarily on heat-driven processes such as distillations. Separating chemical mixtures using methods that are more energy-efficient could save billions of US dollars in energy costs and suppress millions of tons of carbon dioxide

emissions. Potential solutions such as adsorptive separation by simulated moving bed or membranes have been proposed as alternative or supplementary techniques to heat-driven technologies.<sup>2–4</sup>

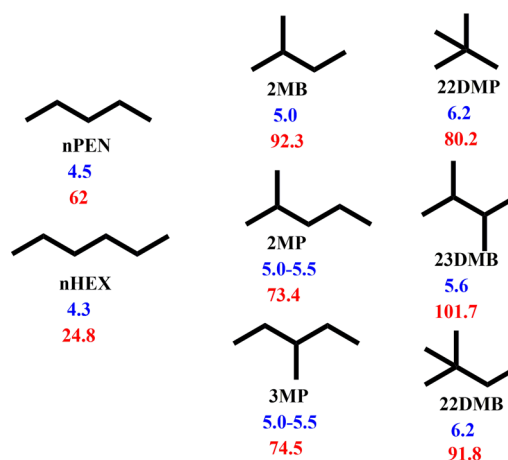
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The separation of alkane isomers, primarily C5–C6 alkanes, represents an important process in the petrochemical industry as it produces components of gasoline. During the oil refining process, catalytic isomerization reactions generate C5–C6 alkane isomers with different degrees of branching, which are subject to separation.<sup>5</sup> Less branched isomers, with lower octane number (such as *n*-hexane with an octane number of 30), are returned to catalytic isomerization reactors for cycling, and more branched isomers with higher octane number (such as 2,2-dimethylbutane with an octane number of 92) are used as gasoline ingredients. Currently zeolite 5A (LTA) is used as adsorbent for the adsorptive separation of linear and branched alkanes, as a supplement to distillations.<sup>6–9</sup> Zeolite 5A possesses one-dimensional channels with diameter of  $\sim 5$  Å. It adsorbs linear alkanes only and excludes all branched isomers and, thus, can separate them through selective molecular sieving. It would be, however, desirable to also recycle the monobranched paraffins to the isomerization reactor, in order to achieve further improvement of the average research octane number (RON) of the isomerate.<sup>10</sup> Zeolite 5A cannot accomplish this task as it does not adsorb any branched alkanes. In addition, the adsorption capacity for zeolite 5A is relatively low due to its low porosity. Thus, it is imperative to search for better adsorbent materials for the adsorptive separation of alkane isomers with higher performance yet lower energy input.

MOFs have proven to be potentially useful for various applications, including gas storage and separation,<sup>11–15</sup> sensing and detection,<sup>16–18</sup> catalysis,<sup>19,20</sup> and lighting,<sup>21</sup> to name but a few. Among these applications, MOFs are particularly promising as adsorbents for the separation of hydrocarbons with high capacity and selectivity because they are highly porous and their pore size, pore shape, and surface functionality can be finely tuned. Using MOFs as adsorbents, scientists have made great advancements for the separation of C2–C4 hydrocarbons, such as propane/propylene,<sup>22</sup> ethane/ethylene,<sup>23–25</sup> ethylene/acetylene,<sup>26,27</sup> and C4 hydrocarbons.<sup>28</sup> In addition, the separation of alkane isomers, a crucial process in the petrochemical industry, has also been tested with various MOFs. Unlike the separation of C2–C4 hydrocarbons, which usually involves the removal of an impurity from a binary mixture, the separation of alkane isomers aims at discriminating components into groups with different degrees of branching. C5–C6 alkane isomers show differences in molecular size (kinetic diameter, see Scheme 1) and isomers with higher degree of branching are generally more bulky. MOFs with suitable pore aperture can potentially discriminate alkanes through kinetic separation or selective molecular sieving in an ideal scenario. In addition, due to the different shapes of alkane isomers, MOFs with slightly larger pores may be capable of their separation through thermodynamically controlled adsorption since the isomer molecules have different contacts with the pore surface, resulting in different adsorption affinity.<sup>29</sup> Early exploratory efforts focused on general adsorption properties of alkane isomers. Some of these materials can discriminate different isomers, but usually with relatively low capacity and/or selectivity since they were not specifically designed for target applications. Recent studies show that guided by material design strategies such as reticular chemistry, tailored MOF materials can be achieved for efficient separation of alkane isomers with high capacity and adsorption selectivity (Table 1). This Account summarizes recent research efforts in developing MOFs for the separation of

**Scheme 1.** Kinetic Diameter (blue number, in Å) and RON (red number) of C5/C6 Alkanes



alkane isomers, with a focus on material design strategy and separation mechanisms.

## ■ EARLY EXAMPLES

Exploratory studies using MOFs for separation of alkanes began more than 10 years ago.<sup>47,49</sup> In 2006, Chen et al. synthesized a microporous MOF,  $\text{Zn}(\text{bdc})(4,4'\text{-bipy})_{0.5}$  ( $\text{bdc}$  = 1,4-benzenedicarboxylic acid, 4,4'-bipy = 4,4'-bipyridine), and evaluated its capability for separating C5 and C6 alkanes.<sup>47</sup> A chromatographic column packed with the MOF sample displays separated peaks for different alkanes. In a followed up study, the authors explored column separation of alkane isomers on a derivative MOF,  $\text{Zn}(\text{bdc})(\text{dabco})$  ( $\text{dabco}$  = 1,4-diazabicyclo [2,2,2]octane), which reveals a kinetic separation mechanism.<sup>48</sup> Later, prototype MOFs were tested for the separation of alkane isomers,<sup>10,34,35,38,39,50</sup> among which ZIF-8 represents the most extensively investigated compound. With a formula of  $\text{Zn}(\text{mim})_2$  ( $\text{mim}$  = 2-methylimidazole), ZIF-8 features a sodalite (SOD) zeolite type structure. It has a surface area of 1813  $\text{m}^2$  and possesses cage-like pores with a large cavity ( $\sim 11.4$  Å) but narrow six-membered-ring window ( $\sim 3.4$  Å).<sup>51,52</sup> ZIF-8 is a representative member of the zeolitic imidazolate frameworks (ZIFs) family, with remarkable thermal and chemical stability. Yan et al. applied a ZIF-8 coated capillary for GC separation of linear C6 alkanes from their branched isomers.<sup>53</sup> The experiments show clear separation between *n*-hexane and its branched isomers though the branched isomers could not be well separated from each other (Figure 1a). Through various experiments, the authors concluded that the separation is based on a molecular sieving effect. It should be noted that although ZIF-8 has a pore window of  $\sim 3.4$  Å, it does not show a sharp cutoff at 3.4 Å with respect to guest inclusion. This is because ZIF-8 shows certain structural flexibility; thus it can accommodate adsorbate that is larger than 3.4 Å. Nevertheless, molecules larger than 5.4 Å are not able to pass the pore window of ZIF-8, as demonstrated by GC experiments, leading to the size sieving of linear alkanes and their branched isomers. In another work, Pirmgruber et al. studied the separation of C6 paraffins using ZIF-8 through multicomponent breakthrough measurements and made a comparison with zeolite 5A.<sup>10</sup> In their results, ZIF-8 behaves similarly to zeolite 5A, showing molecular sieving toward linear and monobranched hexanes (Figure 1b–d). However, zeolite 5A exhibits higher adsorption

Table 1. Adsorption and Separation of C5/C6 Alkane Isomers on Selected MOFs<sup>a</sup>

MOF	isomers tested (uptake, mmol·g <sup>-1</sup> )	T (°C)	separation mechanism <sup>b</sup>	experimental method	ref
Fe <sub>2</sub> (bdp) <sub>3</sub>	nHEX (1.32), 2MP (1.18), 3MP (1.27), 23DMB (1.37), 22DMB (1.22)	160	thermodynamic	adsorption isotherm/ breakthrough	29
Y-fum-fcu MOF	nPEN (1.87), 2MB (0)	20	molecular sieving	adsorption isotherm/ breakthrough	30
Zr-bptc	nHEX (1.51), 3MP (0.29), 23DMB (0)	150	molecular sieving	adsorption isotherm/ breakthrough	31
Zr-abtc	nHEX (1.28), 3MP (1.02), 23DMB (0.58)	150	thermodynamic	adsorption isotherm/ breakthrough	31
Ca(H <sub>2</sub> tcpb)	nHEX (1.62), 3MP (1.54), 22DMB (0.10)	60	molecular sieving	adsorption isotherm/ breakthrough	32
	nHEX (1.14), 3MP (0.12), 22DMB (0)	120			
Fe <sub>3</sub> (μ <sub>3</sub> -O)](6fdca) <sub>3</sub>	nHEX (0.75), 3MP (0.65), 22DMB (0.05)	25	kinetic	adsorption isotherm/ breakthrough	33
ZIF-8	nHEX (5.9), 2MP (1.05)	25	kinetic	adsorption isotherm/ breakthrough	34
ZIF-69	nHEX (3.95), 2MP (1.16)	25	kinetic	adsorption isotherm/ breakthrough	34
ZIF-8	nHEX, 3MP, 22DMB	125	kinetic	breakthrough	10
ZIF-76	nHEX, 3MP, 22DMB	125	thermodynamic	breakthrough	10
Zn <sub>2</sub> (Hbdc) <sub>2</sub> (dmtrz) <sub>2</sub>	nHEX (1.53), 3MP (1.40), 22DMB (0.40)	25	kinetic	adsorption isotherm/gas chromatography	35
ZIF-8	nHEX (2.63), 2MP (2.47), 23DMB (1.88), 22DMB (0.20)	100	kinetic	adsorption isotherm	36
MIL-53(Fe)-(CF <sub>3</sub> ) <sub>2</sub>	nHEX (0.37), 3MP (0.35), 22DMB (0.31)	40	kinetic	adsorption isotherm/ breakthrough	37
UiO-66	nHEX, 2MP, 3MP, 23DMB, 22DMB	100	thermodynamic	gas chromatography	38
MOF-CJ3	nHEX, 2MP, 22DMB	40	thermodynamic	gas chromatography	39
MIL-101(Fe)/(Cr)	nHEX, 2MP, 23DMB, 22DMB	80	thermodynamic	gas chromatography	40
MIL-101(Cr)	nHEX (10.2), 2MP (9.2), 22DMB (8.6), 23DMB (8.4)	40	thermodynamic	adsorption isotherm/gas chromatography	41
UiO-66-Br	nHEX, 3MP, 23DMB, 22DMB	70/150	thermodynamic	breakthrough	42
HKUST-1	nHEX, 2MP, 22DMB, 23DMB	25	thermodynamic	gas chromatography	43
MIL-125(Ti)	nHEX, 2MP, 22DMB, 23DMB	25	thermodynamic	gas chromatography	43
Al-fumarate	nHEX, 3MP, 23DMB	210	thermodynamic	gas chromatography	44
MIL-127(Fe)	nHEX, 3MP, 23DMB, 22DMB	70/100/150	kinetic	breakthrough	45
MIL-125(Ti)-NH <sub>2</sub>	nHEX, 3MP, 23DMB, 22DMB	70/100/150	thermodynamic	breakthrough	45
COK-18	nHEX, 2MP, 3MP, 23DMB, 22DMB, nPEN, 2MB,	100	thermodynamic	gas chromatography	46
Zn(bdc)(4,4'-bipy) <sub>0.5</sub>	nPEN, 2MB, nHEX, 2MP, 22DMB	40–150	thermodynamic	gas chromatography	47
Zn(bdc)(dabco) <sub>0.5</sub>	nHEX, 3MP, 22DMB	40	kinetic	adsorption isotherm/ breakthrough	48

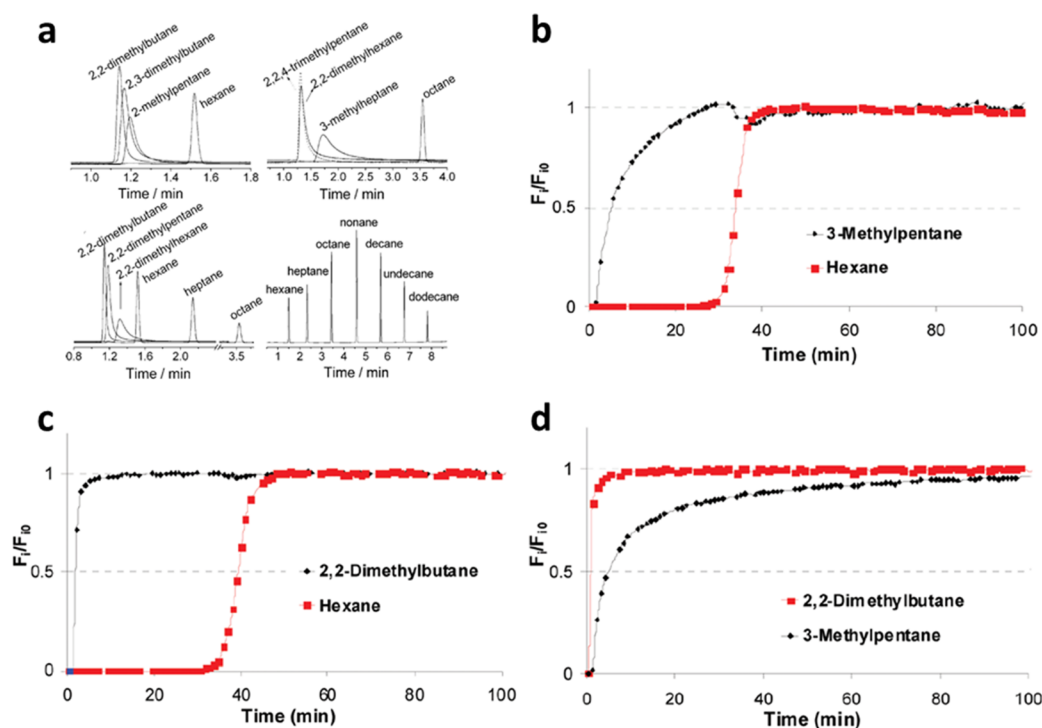
<sup>a</sup>Abbreviations: bdp<sup>2-</sup> = 1,4-benzenedipyrzolate; fum = fumarate; bptc<sup>4-</sup> = 3,3',5,5'-biphenyltetracarboxylate; abtc<sup>4-</sup> = 3,3',5,5'-azobenzenetetracarboxylate; tcpb<sup>4-</sup> = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene; 6fdca = 2,2-bis(4-carboxyphenyl)-hexafluoropropane; H<sub>2</sub>bdc = 1,4-benzenedicarboxylic acid; Hdmtz = 3,5-dimethyl-1H,1,2,4-triazole; 4,4'-bipy = 4,4'-bipyridine; dabco = 1,4-diazabicyclo[2,2,2]octane.

<sup>b</sup>Thermodynamic: separation based on different adsorption affinity and no or negligible difference in adsorption rate. Kinetic: obvious diffusional restrictions for at least one of the adsorbate and notable difference in diffusion rate between adsorbates. Molecular sieving: one or more components are adsorbed and the others are fully excluded.

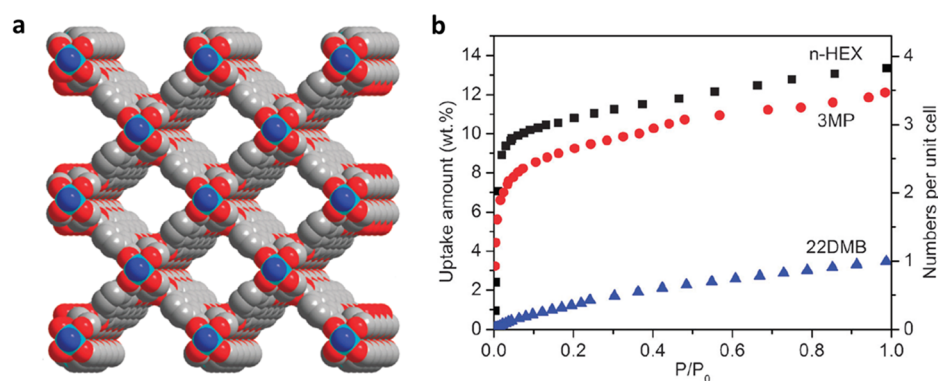
selectivity because ZIF-8 also adsorbs a small amount of monobranched alkanes, though with strong diffusional limitation. The authors attributed the tiny amount of monobranched alkanes adsorbed by ZIF-8 to the adsorption of their linear part of the hydrocarbon chain in the pore mouth rather than fully passing its pore window. Compared to zeolite 5A which fully excludes any branched alkanes, ZIF-8 can separate part of the monobranched alkanes from their dibranched isomers, but with very limited separation ability. Rothenberg et al.<sup>36</sup> investigated the equilibrium adsorption isotherms of hexane isomers on ZIF-8 at elevated temperature (373 K) using both experimental and theoretical techniques. Consistent with the previous reports, 2,2-dimethylbutane is totally excluded by ZIF-8. However, at 373 K, the monobranched hexane can be well adsorbed, suggesting its potential use for the separation of monobranched and dibranched alkane isomers at elevated temperature. Several

other groups also reported the adsorption and separation of alkane isomers by ZIF-8, with similar results.

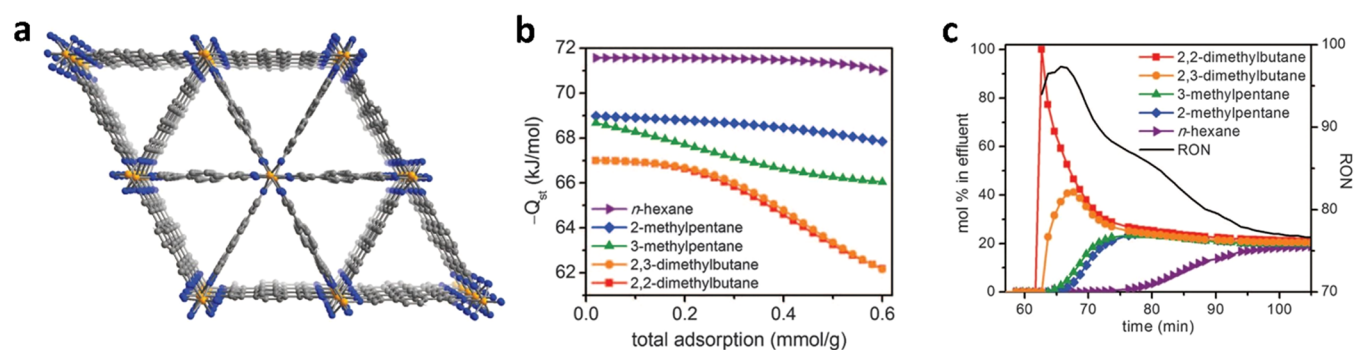
Zhao et al. reported a Zn-based MOF built on triazole and dicarboxylate ligands for selective adsorption of hexane isomers.<sup>54</sup> The compound, Zn<sub>2</sub>(Hbdc)<sub>2</sub>(dmtrz)<sub>2</sub> (H<sub>2</sub>bdc = 1,4-benzenedicarboxylic acid, Hdmtz = 3,5-dimethyl-1H,1,2,4-triazole) has a BET surface area of 552 m<sup>2</sup>·g<sup>-1</sup>, and 1D channels with a diameter of 6.7 Å (Figure 2a). Single-component vapor phase adsorption of *n*-hexane (nHEX), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB) was explored on Zn<sub>2</sub>(Hbdc)<sub>2</sub>(dmtrz)<sub>2</sub>. Its adsorption capacities for nHEX and 3MP are 13.3 and 12.1 wt %, respectively, at room temperature. In contrast, it can barely adsorb 22DMB, with a saturation uptake of 3.5 wt %, much lower than that of nHEX or 3MP (Figure 2b). These results suggest this material might be useful for the separation of dibranched alkanes from their linear and monobranched isomers. To explore its separation capability, the authors performed a GC separation experiment



**Figure 1.** Separation of alkane isomers on ZIF-8. (a) GC separation of alkanes with ZIF-8 coated capillary.<sup>53</sup> (b–d) Breakthrough curves of binary mixtures of C6 alkane isomers at 398 K.<sup>10</sup> Reprinted with permission from refs 10 and 53. Copyright 2012 and 2010 American Chemical Society.



**Figure 2.** (a) Three-dimensional crystal structure of [Zn<sub>2</sub>(Hbdc)<sub>2</sub>(dmtrz)<sub>2</sub>]. (b) Adsorption isotherm of nHEX, 3MP, and 22DMB at 298 K on [Zn<sub>2</sub>(Hbdc)<sub>2</sub>(dmtrz)<sub>2</sub>]. Reprinted with permission from ref 35. Copyright 2011 the Royal Society of Chemistry.

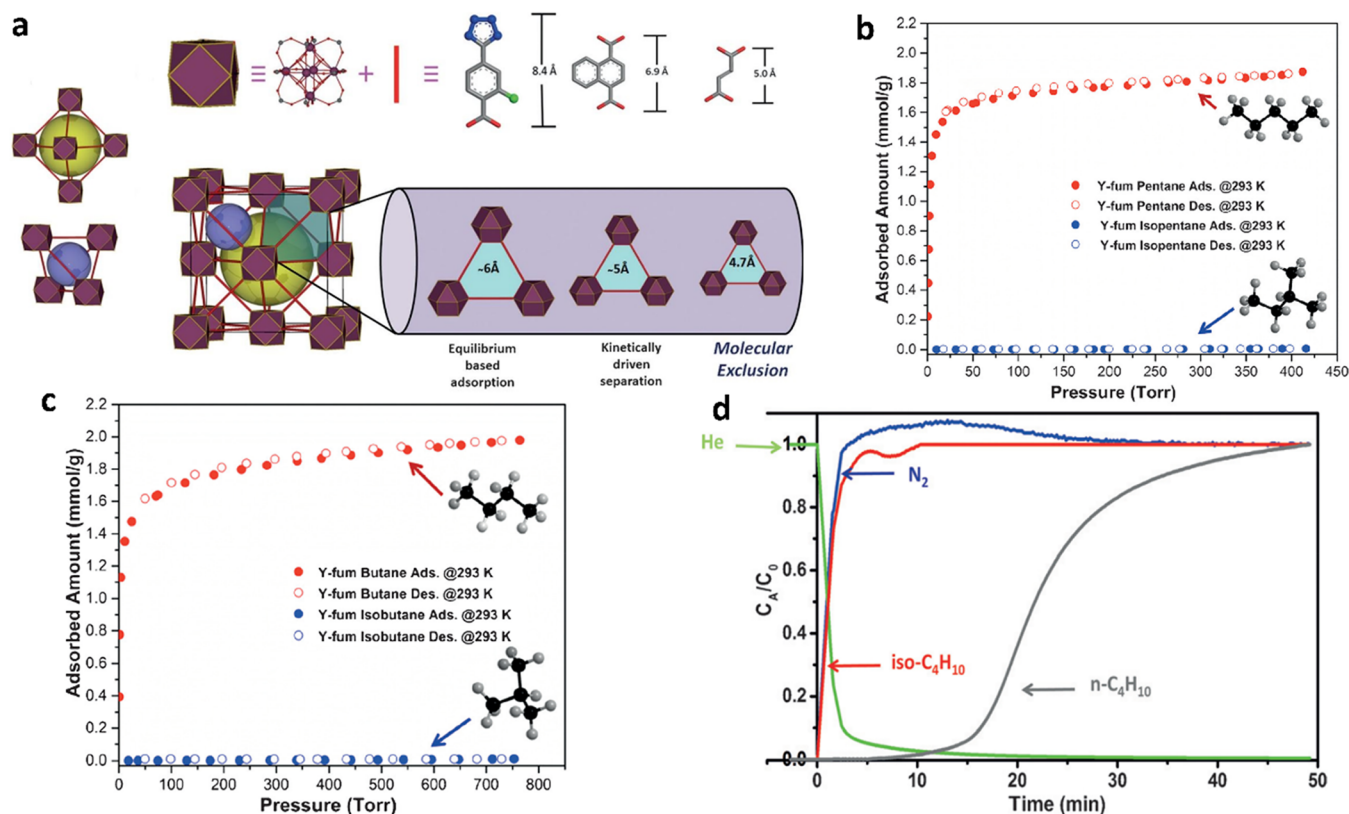


**Figure 3.** (a) Crystal structure of Fe<sub>2</sub>(bdp)<sub>3</sub>. (b) Isosteric heat of adsorption for C6 alkane isomers from single-component adsorption isotherm. (c) Multicomponent breakthrough curve of C6 alkane isomers for Fe<sub>2</sub>(bdp)<sub>3</sub>. Reprinted with permission from ref 29. Copyright 2013 American Association for the Advancement of Science.

for nHEX, 3MP, and 22DMB using a column filled with Zn<sub>2</sub>(Hbdc)<sub>2</sub>(dmtrz)<sub>2</sub>. The result demonstrates that 22DMB

can be well separated from the other two isomers. Unfortunately adsorption kinetics was not reported in this





**Figure 4.** (a) Schematic representation of the components of the RE fcu-MOFs platform including three possible organic linkers of different lengths and the resulting structures. (b, c) Adsorption isotherm of C5 and C4 alkane isomers at 293 K. (d) Column breakthrough test for the adsorption of mixed *n*-butane (5%) and isobutane (5%) in balance with  $N_2$ . Reprinted with permission from ref 30. Copyright 2015 John Wiley and Sons.

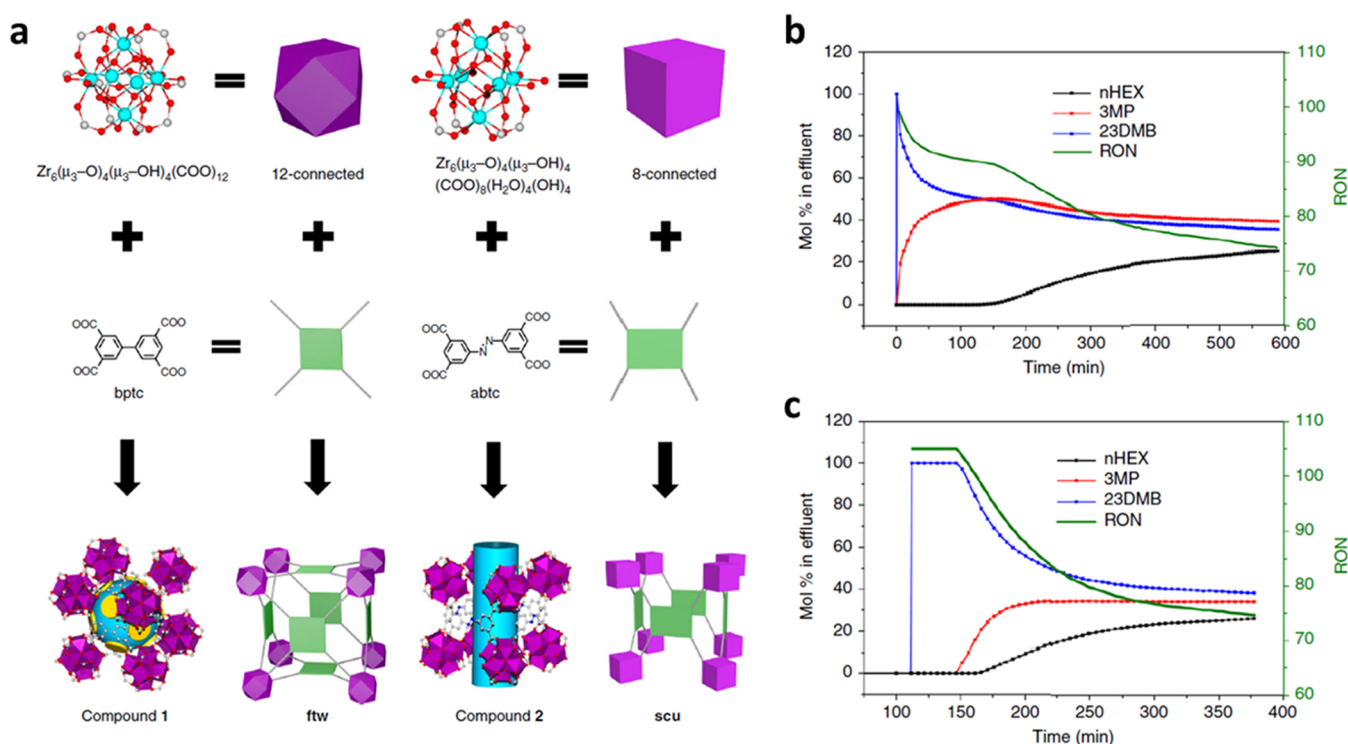
work; thus it is not very clear whether the separation is a result of differences in adsorption affinity or diffusion rate for different isomers. Considering the pore size of the material (6.7 Å), it is reasonable to speculate that 22DMB may encounter some diffusional restrictions under these experimental conditions.

In a proof of concept study, Long and co-workers reported a comprehensive work on the separation of hexane isomers in a microporous MOF, namely,  $Fe_2(bdp)_3$ .<sup>29</sup> The structure is built on octahedral iron(III) centers that are linked via pyrazolate units to form 1D chains, which are further propagated to 3D framework by  $bdp^{2-}$  linkers (Figure 3a). The organic ligands define the 1D triangle channels, which are sufficiently large to accommodate all hexane isomers. The authors studied the adsorption of all five hexane isomers, including *n*-hexane (nHEX), 2-methylpentane (2MP), 3-methylpentane (3MP), 2,3-dimethylbutane (23DMB), and 2,2-dimethylbutane (22DMB). Adsorption isotherms of single-component hexane isomers at elevated temperature (130–200 °C) show that  $Fe_2(bdp)_3$  adsorbs a similar amount of each isomer but with different adsorption strength. Isothermic heats of adsorption follow the order of  $nHEX > 2MP > 3MP > 23DMB \approx 22DMB$  (Figure 3b). The authors conclude that the channel can maximize van der Waals contacts for linear alkanes but not for their branched isomers, leading to higher adsorption affinity toward the former. Difference in adsorption affinity endows  $Fe_2(bdp)_3$  with the capability of separating these isomers as a function of degrees of branching. Multi-component column breakthrough experiments indicate that dibranched isomers, with the weakest interaction with the

material, elute first followed by monobranched isomers, while nHEX, with the highest adsorption affinity, is retained in the column for the longest time (Figure 3c). It suggests that  $Fe_2(bdp)_3$  is able to produce hexane blends with a RON higher than 90, meeting the industrial standard. Hexane isomers are separated by  $Fe_2(bdp)_3$  through a thermodynamically controlled mechanism: although all isomers can diffuse into its channel, their difference in adsorption affinity leads to the separation.

## SEPARATION BY TAILORED MOFs

In the above-mentioned early examples, while a number of MOFs were explored for the potential of separating alkane isomers, they generally suffer from limited adsorption capacity or selectivity. This could be partly because early studies focused more on general adsorption properties of MOFs rather than targeted functionality. However, applying rational design strategy, tailor-made materials may be achieved for the separation of alkane isomers with high performance. Fine tuning of pore structure of MOFs can be realized by making use of reticular chemistry and ligand design. Through this strategy, a number of tailored MOFs have been synthesized that show excellent performance for the separation of industrially relevant mixtures. In general, molecular sieving mechanism is favored over thermodynamically controlled or kinetically controlled separation since it offers the highest selectivity. It is for this reason that zeolite 5A has been used for industrial separation of alkane isomers. However, separating a mixture through selective molecular sieving has a stringent requirement for matching between the pore



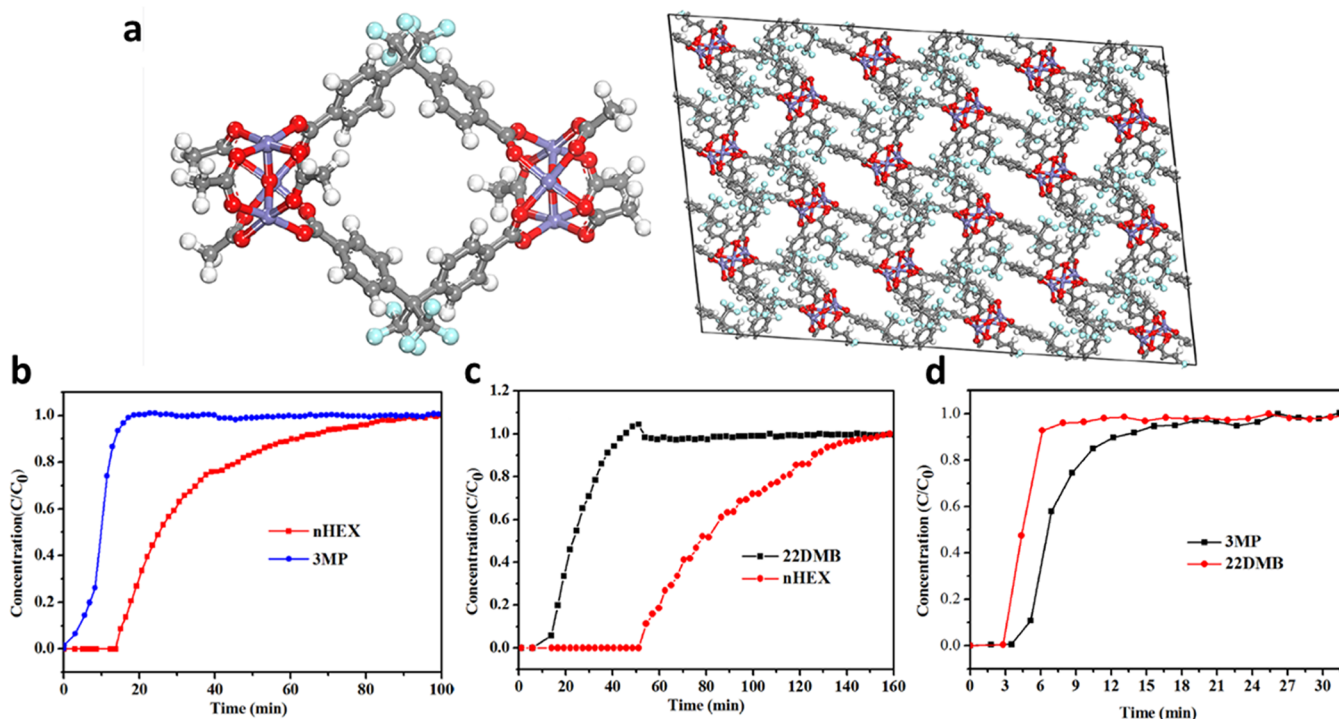
**Figure 5.** (a) SBUs, organic ligands, crystal structures, and topology of Zr-btpc and Zr-abtc. (b, c) Breakthrough curves of ternary mixture of C<sub>6</sub> alkane isomers for Zr-btpc and Zr-abtc. Reprinted with permission from ref 31. Copyright 2018 Nature Publishing Group.

structure of the adsorbent and the size and shape of the adsorbates. It sometimes requires fine-tuning of the MOF pore size at a subangstrom level, which is only possible through topologically directed material design strategies. Guided by this powerful strategy, we and others have obtained a number of MOFs that are capable of selective molecular sieving toward alkane isomers.

By fine-tuning of the aperture size of rare-earth (RE) based fcu-MOFs, Eddaoudi et al. achieved molecular sieving of linear C<sub>4</sub> or C<sub>5</sub> alkanes from their branched isomers.<sup>30</sup> The fcu structure is a prototype MOF topology that has been commonly observed for Zr or RE based structures, such as UiO-66. The fcu-MOFs possess octahedral cages that are interconnected through smaller tetrahedral cages. For both types of cages, inorganic metal clusters occupy the vertexes and organic linkers reside at the edges connecting the metal clusters. Thus, the accessible pore size of fcu-MOFs is the triangular window size of the tetrahedral (or octahedral) cages. Obviously the length of the organic linker dictates the limiting pore size of an fcu-MOF. To fine-tune the pore size of the material while keeping its topology intact, the authors designed a series of three organic linkers with similar functionality but decreasing molecular length, namely, 2-fluoro-4-(1H-tetrazol-5-yl)benzoate (ftzb), 1,4-naphthalenedicarboxylate (1,4-ndc), and fumarate (fum) (Figure 4a). As expected, targeted MOF structures with the selected organic linkers and RE metals were obtained, and experimental evidence shows that they indeed possess accessible pore size closely related to the length of the organic linkers. RE-ftzb-fcu-MOF, built on the longest linker, show equilibrium based adsorption toward linear and branched alkanes, where all isomers can penetrate into its pores without noticeable diffusional limitations. With a slightly shorter linker, RE-ndc-fcu-MOF exhibits favorable adsorption kinetics for n-

C<sub>4</sub>H<sub>10</sub> and n-C<sub>5</sub>H<sub>12</sub> versus their branched isomers while their equilibrium-based adsorption capacities are identical, leading to kinetically controlled separation. As hypothesized, the use of fum, the shortest linker, leads to the formation of RE-fum-fcu-MOF with further contracted pore size. This MOF displays equilibrium adsorption toward linear C<sub>4</sub>/C<sub>5</sub> alkanes at room temperature but fully excludes their branched isomers, resulting in separation through selective molecular sieving (Figure 4b,c). Multicomponent column breakthrough experiments confirm that the material is capable of separating *n*-butane from isobutane where isobutane eluted out from the column immediately while *n*-butane was retained in the column for a substantially longer time (Figure 4d). In this study, the authors were able to ultratune the accessible pore aperture of a targeted series of MOFs and finally achieved a MOF that shows selective molecular exclusion of branched alkanes over their linear isomers.

In industry, adsorptive separation of alkane isomers is typically carried out at elevated temperature (100–200 °C) to facilitate mass transfer. The selective molecular exclusion behavior of zeolite 5A toward C<sub>5</sub>–C<sub>6</sub> alkane isomers is fully retained at elevated temperature as a result of its rigid structure. At 150 °C, branched alkanes are excluded by zeolite 5A, but it adsorbs their linear isomers with fast kinetics. However, its adsorption capacity, which is determined by its pore volume, needs to be improved to boost the separation efficiency. In this context, we attempted to fine-tune the pore structure of ftw-based Zr-MOFs for the separation of C<sub>6</sub> alkane isomers with the following considerations: (1) Zr-MOFs typically possess high stability with respect to thermal or water treatment as a result of their strong Zr–O bonds and multinuclear SBUs with high connectivity. High stability is a prerequisite for an adsorbent to be suitable for industrial separations. (2) Zr-MOFs with ftw topology feature 3D



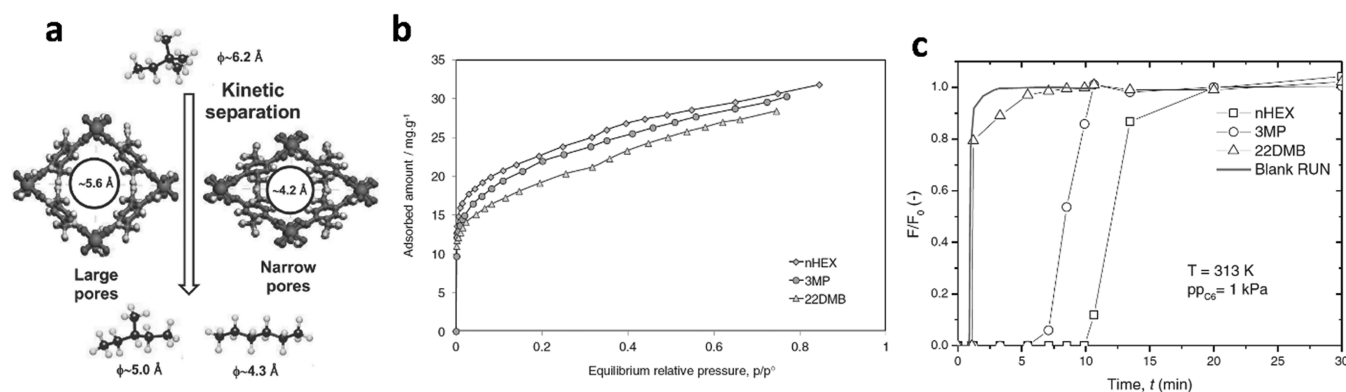
**Figure 6.** (a) Crystal structure of  $[\text{Fe}_3(\mu_3\text{-O})](6\text{fdca})_3$ . (b–d) Breakthrough curves of binary mixtures of C6 alkane isomers for  $[\text{Fe}_3(\mu_3\text{-O})](6\text{fdca})_3$  at room temperature. Reprinted with permission from ref 33. Copyright 2018 American Chemical Society.

porous structures containing cage-like pores with large cages connected through small windows. This type of pore structure is particularly ideal for molecular separation as large cages ensure high adsorption capacity, while small windows may function as “gates” that can discriminate different adsorbates leading to selective adsorption. (3) Zr-MOFs with ftw topology are built on planar tetratopic carboxylates, and their pore aperture is closely related to the distance between adjacent carboxylates of the linkers (or adjacent SBUs). With judicious design and selection of organic linkers that fit into the topology, one can precisely control the pore aperture of the MOFs. Keeping this in mind, we did a literature survey of the reported ftw based Zr-MOFs and found that their pore sizes are all too large for efficient alkane separation as they are all built on large linkers such as porphyrin- or pyrene-based molecules. In order to downsize the pore aperture of Zr-MOFs with ftw topology, we deliberately selected isophthalate based tetratopic linkers with appropriate dimensions for the purpose of reducing the distance between adjacent SBUs and consequently the pore window (Figure 5a). With the smallest linker, bptc, we did obtain the expected MOF, Zr-bptc, with ftw topology. It has a surface area of  $1030 \text{ m}^2/\text{g}$ , higher than that of zeolite 5A.<sup>31</sup> Similar to other reported ftw-MOFs, Zr-bptc also features cage-like pores with  $\sim 12 \text{ \AA}$  cages connected through  $\sim 4.5 \text{ \AA}$  tetrahedral windows, which are notably smaller than those of the reported analogues. It is worth mentioning that Zr-bptc possesses exceptional thermal and water stability. Adsorption measurements reveal that Zr-bptc is capable of separating hexane isomers in a similar fashion to that of zeolite 5A. It adsorbs nHEX but excludes its monobranched and dibranched isomers, with a capacity of  $130 \text{ mg/g}$  for nHEX at  $150^\circ\text{C}$ , which is substantially higher than that of zeolite 5A ( $77 \text{ mg/g}$ ) under identical conditions. Multicomponent column breakthrough measurements agree well with single-component adsorption results that Zr-bptc is

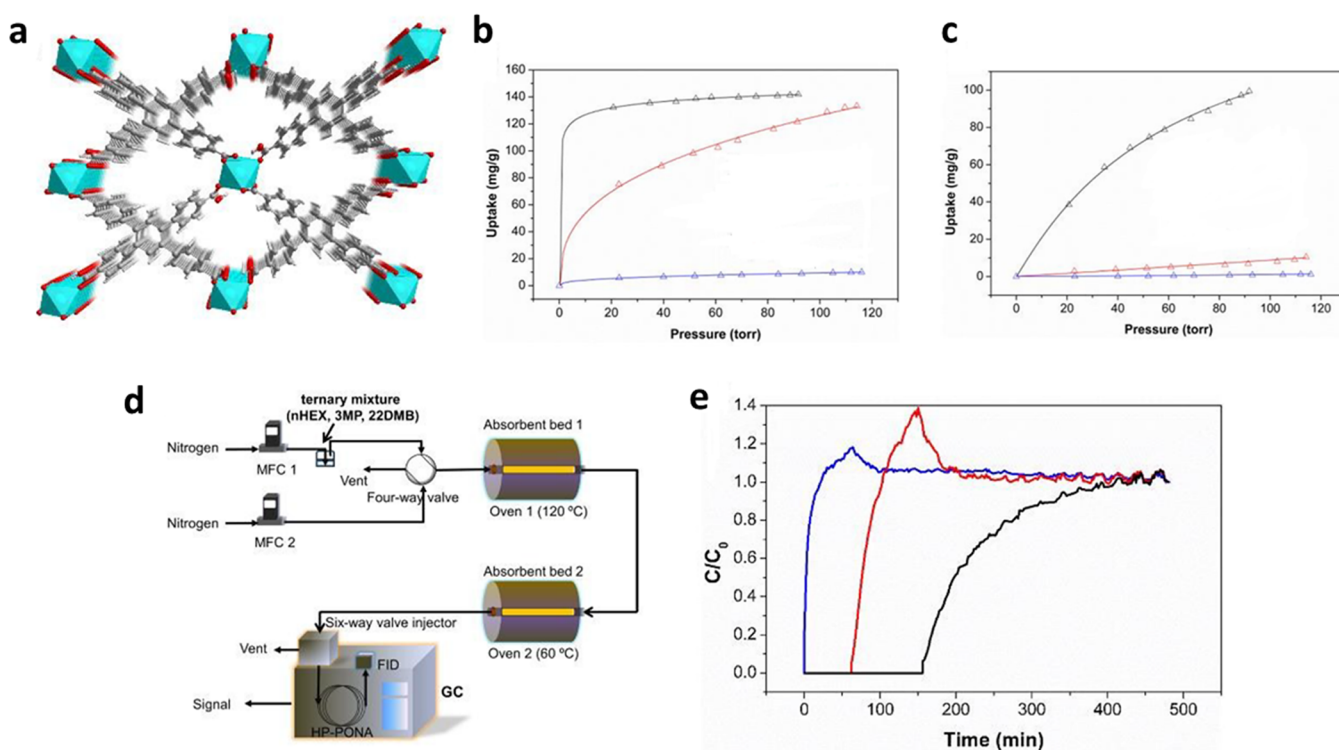
capable of separating hexane isomers through selective molecular exclusion with a much higher adsorption capacity compared to zeolite 5A (Figure 5b). This example confirms that through a topology-directed approach, with judicious ligand selection and design one can achieve MOFs with tailored pore structure for targeted separations. We also attempted to tune the pore structure of the MOFs by using a slightly longer linker, abtc, with the same geometry and functionality but a larger aspect ratio compared to bptc. Not surprisingly, the use of abtc with Zr did not afford another ftw MOF due to its high aspect ratio making it difficult to fit into the ftw topology. Instead, it features a 4,8-connected scu topology, a derivative net of ftw with organic linkers along one direction missing. Consequently, the cage-like pores in Zr-bptc transform into 1D channels with a diameter of  $\sim 7 \text{ \AA}$  in Zr-abtc. As expected, adsorption experiments revealed that it can accommodate linear and branched hexane isomers but with different strength and kinetics. It shows the highest adsorption capacity and rate for nHEX. We believe the underlying mechanism may be similar to that in the case of  $\text{Fe}_2(\text{bdp})_3$ : linear alkanes can maximize contact with the 1D channels leading to higher adsorption affinity. Interestingly, Zr-abtc displays better separation of 23DMB from its linear and monobranched isomers compared to  $\text{Fe}_2(\text{bdp})_3$ , possibly because there is a small diffusional restriction for 23DMB in Zr-abtc (Figure 5c). A combined thermodynamic and kinetic effect affords Zr-abtc a high separation factor of 1.3 for 3MP and 23DMB calculated from multicomponent breakthrough measurements, making it promising for producing alkane blends with improved RON.

Moisture commonly acts as a competing adsorbate during adsorptive separation because it is ubiquitous and most adsorbent materials are hydrophilic. To minimize the competing adsorption from water and to enhance water stability of the material, we assembled a fluorine-rich linker





**Figure 7.** (a) Illustration of the three isomers with their kinetic diameters and the 1D-type channel MIL-53(Fe)-(CF<sub>3</sub>)<sub>2</sub> and their corresponding pore sizes. (b) Hexane isomer single component adsorption isotherms at 313 K in MIL-53(Fe)-(CF<sub>3</sub>)<sub>2</sub>. (c) Ternary breakthrough curves for 22DMB/3MP/nHEX in MIL-53(Fe)-(CF<sub>3</sub>)<sub>2</sub> at 313 K and partial pressures of 1 kPa. Reprinted with permission from ref 37. Copyright 2014 John Wiley and Sons.



**Figure 8.** (a) Crystal structure of Ca(H<sub>2</sub>tcpb). (b, c) Adsorption isotherms of nHEX (black), 3MP (red), and 22DMB (blue) at 60 °C (b) and 120 °C (c). (d, e) Schematic representation (d) and results (e) of breakthrough of ternary mixture of C<sub>6</sub> alkane isomers for Ca(H<sub>2</sub>tcpb). Reprinted with permission from ref 32. Copyright 2018 the Royal Society of Chemistry.

into a hydrophobic MOF through a precursor-based synthesis strategy. The use of preformed building blocks [Fe<sub>3</sub>(μ<sub>3</sub>-O)(CH<sub>3</sub>COO)<sub>6</sub>] can avoid the formation of unpredictable building blocks that commonly occurs in conventional one-pot reactions. By combining [Fe<sub>3</sub>(μ<sub>3</sub>-O)(CH<sub>3</sub>COO)<sub>6</sub>] precursors and 2,2-bis(4-carboxyphenyl)-hexafluoropropane (6fdca), we achieved a microporous MOF, [Fe<sub>3</sub>(μ<sub>3</sub>-O)](6fdca)<sub>3</sub>, with the SBU well maintained in the resulting framework (Figure 6a).<sup>33</sup> The material exhibits high stability in aqueous solutions and a hydrophobic nature, which should be attributed to the high density of fluorine atoms in the channels. While equilibrium adsorption isotherms reveal it can accommodate linear, monobranched, and dibranched hexane isomers, the compound shows different adsorption kinetics for them with the

highest adsorption rate for nHEX and the lowest for 22DMB. Multicomponent column breakthrough experiments confirmed its capability of separating hexane isomers as a function of degrees of branching (Figure 6b). This study indicates a possible solution for improving MOF adsorbent hydrophobicity and water stability.

## SEPARATION BY FLEXIBLE MOFs

Flexible MOFs represent a unique group of MOF materials that exhibit dynamic structural change upon inclusion and removal of guest molecules (or other external stimuli, such as heating or pressure). Structural flexibility can sometimes contribute to unexpected adsorption and separation properties. Mendes et al. reported the use of a flexible MOF for the



separation of hexane isomers of different degrees of branching (Figure 7a).<sup>37</sup> It was found that MIL-53(Fe)-(CF<sub>3</sub>)<sub>2</sub> adsorbs similar amounts of nHEX, 3MP, and 22DMB at 313 K under equilibrium conditions (Figure 7b). However, breakthrough experiments with a feed of a nHEX/3MP/22DMB ternary mixture with a total pressure of 1 kPa at 313 K revealed that the material shows nearly complete separation of 22DMB from the alkane mixture due to their different adsorption rates (Figure 7c). This is an intriguing property as materials that can efficiently separate monobranched and dibranched alkanes are very rare. Further studies indicate that the adsorption and separation is highly temperature and pressure dependent, and the separation performance becomes worse at different temperatures and pressures. Nevertheless, this study provides some clue on making use of flexible MOFs for challenging separations.

In an effort to develop MOF materials with the capability of highly efficient separation of monobranched and dibranched alkanes, a critical step in the production of gasoline blends with desired RON, we have recently moved our focus to flexible MOFs because of their unique adsorption behavior and separation capability. Through a careful screening of selected flexible MOFs, we discovered that Ca(H<sub>2</sub>tcpb) (tcpb = 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene), a flexible microporous MOF,<sup>55</sup> exhibits highly efficient separation not only for monobranched and dibranched alkanes, but also for a ternary mixture of linear, monobranched, and dibranched isomers.<sup>32</sup> Ca(H<sub>2</sub>tcpb) is built on CaO<sub>6</sub> octahedra connected through H<sub>2</sub>tcpb<sup>2-</sup> linkers, forming a 3D framework with 1D open channels with a diameter of ~5.5 Å, which is close to the kinetic diameters of branched C5–C6 alkanes (5.0–6.2 Å) (Figure 8a).<sup>11</sup> Ca(H<sub>2</sub>tcpb) exhibits slight structural flexibility indicated by the PXRD patterns of the as synthesized and activated samples. The unique adsorption profiles of Ca-(H<sub>2</sub>tcpb) toward hexane isomers confirmed its flexible structure feature. The adsorption is highly dependent on temperature (relative pressure), and the material exhibits a temperature-dependent selective molecular sieving behavior. It adsorbs nHEX and 3MP but fully excludes 22DMB at 60 °C, and when temperature is increased to 120 °C only nHEX could be adsorbed (Figure 8b,c). This represents the first adsorbent material that can fully separate monobranched and dibranched alkanes through selective molecular exclusion. Multicomponent column breakthrough measurements confirm the separation capability of the material. Breakthrough curves of binary mixtures indicate nHEX/3MP and 3MP/22DMB mixtures are completely separated at 120 and 60 °C, respectively, with one component eluting out immediately while the other is retained in the column for substantially longer time. Inspired by the temperature-dependent adsorption behavior of Ca(H<sub>2</sub>tcpb), we designed a two-column breakthrough system aimed at separating alkane isomers as a function of degree of branching. As expected, a ternary mixture of nHEX, 3MP, and 22DMB was fully separated into pure components (Figure 8d,e). Further study indicated the separation capability of the material was well retained under humid conditions or after several adsorption–desorption cycles.

## ■ CONCLUSIONS AND PERSPECTIVES

Adsorptive separation of gas/liquid mixtures by porous solids at temperatures around ambient temperature represents a promising supplementary or alternative technology to

cryogenic distillations for producing industrially needed pure components with lower energy input and suppressed carbon dioxide emission. Adsorptive separation of alkane isomers has proved a promising solution for the separation of alkane isomers aimed at upgrading gasoline RON. The current separation technology relies on heat-driven distillations or a combination of distillations and adsorptive separation by zeolite 5A. To improve the separation efficiency, adsorbent materials with high adsorption capacity or with the capability of separating monobranched and dibranched alkanes need to be developed. In light of their high porosity and tunable pore structure, MOFs are potentially useful as adsorbents for separating alkane isomers with high efficiency. In this Account, we have overviewed the main progress in using MOFs for alkane isomer separation over the past several years, from early examples to recent studies on design of tailored materials. To develop new MOF materials with desired separation performance, one should take advantage of their systematically tunable and precisely controllable pore shape and size. With judicious selection of inorganic SBUs and organic linkers and in combination with topology-directed design strategy, it is possible to achieve MOF adsorbents with optimal performance for highly selective adsorptive separation.

After 20 years since they were first reported, MOFs have proven to be the most promising candidates for molecular separation. Their exceptional selectivity and uptake capacity often outperform zeolites. In general, the following aspects must be taken into consideration when selecting MOF materials for a specific industrial separation processes: (1) Adsorption capacity. One of the limitations of zeolite 5A for the separation of alkane isomers is its relatively low adsorption capacity, determined by its small pore volume. Many MOFs are intrinsically highly porous, and they can potentially address this issue. However, MOFs with large pore aperture or composed of complex linkers may not be suitable as these features may sacrifice adsorption selectivity or stability or lead to high cost. (2) Adsorption selectivity. Selectivity usually depends on the pore size and shape and surface functionality of the adsorbents. With the help of reticular chemistry, MOFs can be designed and systematically tuned with respect to their pore structures and surface functionality so that adsorbents with desirable adsorption and separation performance can be obtained. Typically, adsorbents showing highly selective adsorption toward the targeting adsorbates are required for industrial separations, for example separation through selective molecular exclusion, as in the case of alkane isomer separation by zeolite 5A. By topology-directed ligand and SBU design, pore size and shape of MOFs can be finely tuned to achieve optimal molecular separation performance. (3) Stability. Stability, including water or moisture and thermal stability, is a crucial requirement for an adsorbent to be suitable for industrial separations. Zeolites are highly stable, while MOFs generally suffer from relatively poor stability due to their inorganic–organic hybrid nature. However, the incorporation of early transition metals including Zr, Cr, and Y, to name a few, can substantially improve the stability of MOFs, especially those built on multinuclear SBUs. In addition, other strategies such as using hydrophobic linkers may also lead to moisture-stable MOFs. In addition, stability toward impurities in industrial gases (e.g., H<sub>2</sub>S) and stability toward abrasion may also need to be taken into consideration. (4) Cost. Cost is another key factor that needs to be taken into account when considering an adsorbent for industrial use. Cost of MOFs

depends mainly on the organic linkers. Thus, MOFs built on inexpensive, commercially available ligands are advantageous for industrial applications. MOFs have exhibited enormous potential in the separation of alkane isomers; however, new materials that can fully address the limitation of currently used benchmark adsorbents are much needed. In addition, future efforts should also be focused on lowering the cost of the MOF candidates so that their commercialization can be realized.

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### Notes

The authors declare no competing financial interest.

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