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Rational Design of Non-Covalent Diamondoid Microporous Materials for Low Energy Separation of C₆-hydrocarbons.

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ABSTRACT: Selective separation of gases/vapors with similar physicochemical properties involves energetically costly distillation processes. Alternative separation processes based on shape selective molecular sieving, taking place on porous frameworks (or membranes), are less energy demanding but require an optimal balance between selectivity and diffusion kinetics (permeability). Herein, we report a rational strategy to select an optimal soft non-covalent microporous material (NPM) suitable for the low energy separation of C₆-hydrocarbons with kinetic diameters in the range of 4.3 – 6.3 Å. This strategy is based on a Cambridge Structure Database search of diamondoid NPMs with a low packing factor, leading to the selection of an oxidotetrazinc cluster based diamondoid NPM network named **DiaMM-1** containing tetrahedral voids of 336 Å³ (tetrahedron insphere diameter of 5.8 Å accessible through 8.2 Å triangular windows) suitable for this separation. Based on this result the fluorinated analogue **DiaMM-2** was designed and synthesized. **DiaMM-1** and **DiaMM-2** exhibit permanent porosity and high thermal stability. The optimal combination of molecular crystal softness, pore size and decoration of pore surface of **DiaMM-1,-2** leads to high adsorbate diffusivity and low adsorption energy allowing fast separation of hexane isomers and benzene/cyclohexane mixtures at low temperature.

INTRODUCTION

Separation processes account for about 50% of industrial energy consumption on a global scale with the separation of gases/vapors, possessing similar physicochemical properties, involving particularly costly energy intensive distillation processes. Separation of mixtures of lowfunctionality molecules, such as hexanes, which differ only in shape, for gasoline octanage enhancement, are prototypical examples of the limitation of the classical distillation method. Alternative separation processes, based on shape selective molecular sieving, taking place on porous frameworks (or membranes), are less energetically demanding but require an optimal balance between selectivity and diffusion kinetics (permeability).1 For porous materials, shape selectivity is usually accompanied by strong adsorbate-surface interactions. This requires high temperatures in order to achieve suitably fast diffusion kinetics.²

In the last two decades prominent examples of novel families of porous materials including metal-organic frameworks,³ covalent organic frameworks (COFs),⁴ and porous organic polymers (POPs),⁵ amenable to pore design, and exhibiting high potential for hydrocarbons separation have been studied. Indeed, some MOFs^{2,6-10} and intrinsically porous cage compounds^{11,12} display enhanced alkane separation capability compared to zeolites and mesoporous silica as a consequence of their fine pore shape tuning and soft crystal nature. Yet, the high adsorption energy for hexane isomers (-50 to -70 kJ/mol) implies the requirement for high temperature to perform the separation processes effectively (typically T > 423 K). Consequently, it is a challenge to find a novel class of much softer crystalline porous materials possessing lower adsorbate-adsorbent interaction energy, leading to higher adsorbate diffusivity for low energy efficient separation of challenging molecular mixtures. This can potentially be achieved in non-covalent porous materials (NPMs). However, the rational construction of porous structures based on van der Waals forces is challenging since discrete molecules tend to form close-packed solids with minimal void volume.^{13,14}

We have previously demonstrated that discrete zinc carboxylate and carbonate clusters can form diverse types of NPM structures ranging from zeolitic topologies to porous materials with voids or open channels,¹⁵ with the diamondoid **WUT-1** material being able to adsorb small probe gases.¹³ Thus, our working hypothesis was: 1) the diamondoid cubic lattice possesses the lowest packing density among prototypical networks (crystal packing factor of 34%, Fig. 1d); 2) tetrahedral clusters can favor the formation of diamondoid networks of NPMs with permanent porosity (Fig. 1b, c, d); 3) the soft nature of the van der Waals interactions building up the NPM crystals should favor high adsorbate diffusivity. Herein, we report a rational strategy to select optimal soft non-covalent

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Diamondoid Microporous Materials (DiaMM) (Fig. 1c), suitable for the



Figure 1. (a) Schematic representation of hexane isomers interaction with pore surface of NMPs **DiaMM-1** and its fluorinated analogue **DiaMM-2**. (b) Schematic representation of the self-assembly of T_d discrete molecules into diamondoid NMPs. (c) Histogram showing the comparison of accessible volume per cage (in Å³) in potential NPMs with diamondoid lattice based on the CSD search. The preferred pore size range, defined as the insphere diameter of tetrahedral voids, namely 4.3 Å for *n*-hexane as the lower limit and 6.3 Å for 2,2-dimethylbutane as the upper limit, is shown as red horizontal lines at 138 and 433 Å³, respectively. (d) Packing of equal spheres in the diamond cubic unit cell.

low energy separation of C₆-hydrocarbons (Fig. 1c). This strategy is based on a Cambridge Structural Database search of diamondoid NPMs (Fig. 1c) with a low packing factor, leading to the selection of **DiaMM-1** and its fluorinated analogue **DiaMM-2**. Noteworthily, the results show that **DiaMM-n** (n = 1 or 2)(Figs. 1a and 2) exhibit permanent porosity and very high thermal stability, with the pore surface functionalization having crucial influence on the robustness and C₆-hydrocarbons separation efficiency.

EXPERIMENTAL SECTION

All air- or water-sensitive reactions were carried out under a dry nitrogen atmosphere using Schlenk techniques. Chemicals were purchased from Fluorochem, POCh and Aldrich Chemicals Co. (Milwaukee, WI) and used without further purification. The synthesis of N,N'di(*p*-tolyl)formamidine (L1) and N,N'-bis(*p*-(trifluoromethyl)phenyl)formamidine (L2) is described in the Supporting Information.

Synthesis of DiaMM-1. Et₂Zn (4.97 mL, 4.97 mmol, 1M in hexane) was added to a suspension of L1 (1.674 g, 7.46 mmol) in THF (8 mL) at -78 °C and then the reaction mixture was allowed to warm to room temperature, and stirred for an additional 1 h. Then the solution of H₂O in THF (0.73 mL, 1.24 mmol, 1.7 M) was added to the reaction mixture and the solution was stirred for additional 12 h at room temperature. The obtained microcrystalline solid was decanted and washed with a mixture of THF/hexane (5 mL, 1:10 v/v) and then with pure hexane three times (5 mL). Isolated yield 1.25 g (62%). **DiaMM-1** is stable in the dry air atmosphere. **Synthesis of DiaMM-2.** Et₂Zn (2.00 mL, 2.00 mmol), 1M in hexane) was added to a suspension of L2 (0.997 g, 3.00 mmol) in THF (6 mL) at -78 °C and then the reaction mixture was allowed to warm to room temperature, and stirred for an additional 12 h. Then solution of H₂O in THF (0.29 mL, 0.5 mmol, 1.7 M) was added to the reaction mixture and the solution was stirred for additional 12 h at room temperature. The obtained microcrystalline solid was decanted and washed with a mixture of THF/hexane (3 mL, 1:10 v/v) and then with pure hexane 3 times (3 mL). Isolated yield 0.69 g (61%). **DiaMM-2** is stable in the dry air atmosphere.

Thermal activation of DiaMM-n. Prior to the gas and vapor sorption measurements, the samples were degassed at 100 °C (**DiaMM-1**) or 150 °C (**DiaMM-2**) for 12 h under dynamic vacuum of 10⁻¹ Pa (oil pump).

RESULTS AND DISCUSSION

Presynthesis selection and design of NPMs. With the design principles laid out, we first proceeded with screening of the structures deposited in the Cambridge Structural Database (CSD) in order to identify potential NPMs possessing pore sizes in the 138 and 433 Å³ range (Fig. 1c and Supplementary Information). This pore range corresponds to 4.3 - 6.3 Å insphere diameter of tetrahedral voids (Fig. S1), suitable for the molecular sieving of the target C₆-hydrocarbons with kinetic diameters in the range of 4.3 - 6.3 Å (Table 1). We have identified a suitable candidate exhibiting voids and diamondoid packing: tetrakis(N,N'-di(*p*-tolyl)formamidinate)oxidotetrazinc(II) (CSD refcode QAGMUH) containing potential voids of 336 Å³ (tetrahedron insphere diameter of 5.8 Å, accessible

through triangular windows of innercircle diameter of 8.2 Å), being named as **DiaMM-1** (Fig. 2). We also targeted the fluorinated analogue denoted as **DiaMM-2** containing the N,N'-bis(*p*-(trifluoromethyl)phenyl)formamidinate ligand, as



Figure 2. (a) Composition of molecular clusters **DiaMM-1** and **DiaMM-2**. (b) View of the supertetrahedral structure based on intermolecular CH₃···CH₃ or CF₃···CF₃ interactions leading to the formation of diamondoid non-covalent porous networks **DiaMM-1** and its fluorinated analogue **DiaMM-2**. (c) Projection of the unit cell in **DiaMM-1** or -2 along *a* axis, cavities are represented as spheres: small (yellow), large (orange). Note that the diamondoid unit cell contains 24 cavities (8 large and 16 small).

promising soft porous material for separation of challenging C₆-hydrocarbon mixtures.

Synthesis and characterization of DiaMM-n. Our target NPMs can be obtained by a one-pot reaction under mild synthetic conditions. Briefly, the reaction of 2 equiv. of Et₂Zn with 3 equiv. of N,N'-di(p-tolyl)formamidine (L1) or N,N'-bis(p-(trifluoromethyl)phenyl)formamidine (L2) in tetrahydrofuran and the subsequent addition of 1 equiv. of degassed water resulted in immediate formation of oxidotetrazinc formamidinate white crystalline powders of **DiaMM-1** and **DiaMM-2**, respectively (Fig. 2). Thus obtained powders are stable in the solid state at ambient temperature under N₂ or dry air.¹⁶

The composition of both compounds was confirmed by spectral and X-ray diffraction studies.¹⁷ The powder X-Ray diffraction (PXRD) patterns of the bulk phases of **DiaMMn** match perfectly those simulated based on single crystal data (Figs. 3a,b). The morphology of the bulk samples of **DiaMM-n** was examined by scanning electron microscopy (SEM, Fig. 3f and Figs. S23, S24). The SEM images show well-shaped octahedral microcrystals with the size below 20 µm. **DiaMM-1** and **DiaMM-2** are isostructural and crystallize in the cubic space group $Fd\overline{3}$. The molecular structures are built of the tetrahedral oxidotetrazinc core $[Zn_4(\mu_4-O)]^{6+}$ stabilized by six bidentate formamidinate ligands, and exhibit propeller-like symmetry of the cluster (Figs. S13, S14). A detailed analysis of the crystal structures of **DiaMM-1** and **DiaMM-2** revealed that tetrahedral nanoclusters self-assemble through weak cooperative noncovalent interactions CH₃…CH₃ (2.67 Å) and CF₃…CF₃ (2.87 Å), respectively, extended into a porous 3D diamondoid network (Figs. 2b,c). The accessible void fraction in



Figure 3. Comparison of simulated and experimental PXRD patterns (a) **DiaMM-1** and (b) **DiaMM-2**, (c) VT-PXRD studies for **DiaMM-2**, (d) TGA profiles of as-synthesized materials, (e) experimental N₂ isotherms of **DiaMM-n** obtained at 77 K with Poreblazer pore distribution as inset, (f) SEM micrograph of microcrystalline sample of **DiaMM-1**.

DiaMM-1 and **DiaMM-2** was estimated to 36.8% and 35.5% of the unit cell volume, respectively,¹⁸ distributed in two types of alternating cavities: for **DiaMM-1** the cavity diameters are 7.5 and 9.1 Å, and for **DiaMM-2**, 7.2 and 8.8 Å, accessible through 8.0 Å triangular windows (Fig. 2b,c). In this regard, the analysis of the critical diameters of C₆-hydrocarbons (Table 1) is indicative that the porosity in **DiaMM-n** should be accessible for all hexane isomers and cyclohexane/benzene.

Having in hand well-defined and phase-pure crystalline samples of **DiaMM-n** we studied the thermal stability by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and variable temperature PXRD (VT-PXRD) (Fig. 3c,d and S17-S22). The TGA profiles, under oxidative atmosphere (N_2/O_2 = 60:40), for the as-synthesized **DiaMM-n** demonstrate that **DiaMM-1** is thermally stable up to 473 K, whereas **DiaMM-2** does not show signs of decomposition up to 600 K. The above superior thermal stability was further confirmed by variable-temperature PXRD measurements. We note that **DiaMM-2** does not show any phase transition up to 603 K,

whereas DiaMM-1 transforms into a dense crystalline phase above 473 K. The high thermal stability of DiaMM-2 is unique for porous molecular crystals¹⁹ with the weak intermolecular interactions of the CF₃ residues playing a fundamental role in hampering the formation of the dense phase.²⁰ Moreover, the type I nitrogen adsorption isotherms at 77 K for DiaMM-n shown in Fig. 3e confirm the permanent porosity, microporosity and isostructural nature of the two materials. The maximum uptake of N₂ at 77 K is 243.4 and 249.3 cm3/cm3 STP respectively, which result in the total pore volume of 0.38 cm3/cm3 based on a dual pore distribution of 7 and 9 Å pore diameters. The calculation of Brunauer-Emmett-Teller surface area (SBET) for DiaMM-1 and DiaMM-2 resulted in SBET values of 831 and 904 m²/cm³, respectively, which are in excellent agreement with accessible surface area (ASA) values of 846 m²/cm³ and 921 m²/cm³, calculated with Poreblazer²¹.

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Static and dynamic sorption studies of C₆hydrocarbons in DiaMM-n. Having proved the structural robustness and pore accessibility of the **DiaMM-n** systems we proceed to evaluate the accessibility of their micropores to C₆-hydrocarbons (hexane isomers, cyclohexane and benzene) by means of static single component equilibrium isotherms at 293 K, dynamic variable temperature pulse gas chromatography, breakthrough curves, solid state ¹³C and ¹⁹F cross polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR) and computational modelling (Fig. 4). For hexane isomers, the adsorption isotherms demonstrate the accessibility of the microporous network to all molecules. Based on the calculations from the maximum uptake we found that both materials can adsorb very similar numbers of alkane molecules. Moreover, in the low pressure region of the alkane adsorption isotherms (Fig. 4a,b), one can observe the arrangement of sorption isotherms according to the bulkiness of adsorbate molecules, in other words, linear alkanes interact much weaker with the pore walls, whereas more branched and bulky alkanes interact stronger.



Figure 4. Adsorption and separation of hexane isomers and benzene/cyclohexane mixtures on **DiaMM-n** systems. Experimental single-component isotherms at 293 K: (a) alkanes on **DiaMM-1**, (b) alkanes on **DiaMM-2**, (c) cyclohexane/benzene on **DiaMM-1** and **DiaMM-2**, insets show low-pressure range (p/po < 0.1 for alkanes and p/po < 0.5 for cyclohexane/benzene) in a logarithmic scale. Pulse gas chromatograms at 373 K of vapor mixture of: C_5 - C_6 alkanes on 10 cm columns (4 mm inner diameter) packed with microcrystalline **DiaMM-1** (d), and **DiaMM-2** (e); benzene-cyclohexane mixture on **DiaMM-1** (f, top), and **DiaMM-2** (f, bottom). The insets show the respective van't Hoff plots for the studied materials. Computational simulation of accommodation of 2,3-dimethylbutane (g) and *n*-hexane (h) on **DiaMM-2**. The larger pores are shown as orange spheres with the loaded alkanes in sticks while the alkanes loaded in the smaller pores are shown with the van der Waals radii. (i) Breakthrough curves at 293 K for 1:1

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benzene/cyclohexane mixture on **DiaMM-n**. (j) Solid state ¹⁹F CP-MAS NMR spectra for **DiaMM-2** in the presence of C₆-hydrocarbons.

	DiaMM-1 (DiaMM-2)					
Studied adsorbates	B.P.	Size	$-\Delta H_{iso}$	-ΔS	-ΔG	
	(K)	(Å)	(kJ/mol)	(J/Kmol)	(kJ/mol)	$\alpha_{X/Y}$
pentane	309	4.3	24.8 (33.7)	67.4 (104.2)	-0.30 (-7.75)	0.37 (0.44)
hexane	341	4.3	38.4 (39.4)	95.5 (111.7)	2.80 (-5.06)	1 (1)
2-methylpentane	333	5.4	43.1 (39.5)	106.9 (110.7)	3.23 (-4.54)	1.1 (1.16)
3-methylpentane	336	5.4	44.0 (42.6)	107.5 (117.0)	3.93 (-4.01)	1.36 (1.40)
2,3-dimethylbutane	331	5.8	46.1 (40.7)	111.3 (110.0)	4.57 (-3.06)	1.66 (1.82)
2,2-dimethylbutane	323	6.3	46.4 (38.4)	111.7 (103.6)	4.70 (-2.80)	1.72 (1.89)
benzene	353.1	5.8	35.9 (32.5)	84.8 (87.0)	4.31 (-2.15)	1 (1)
cyclohexane	353.7	6.2	40.3 (36.1)	87.9 (89.3)	7.49 (0.51)	2.81 (2.41)

Table 1. Summary of physical characteristics of the studied hydrocarbons and thermodynamic characterization of the adsorption process on DiaMM-1 and DiaMM-2 from variable temperature pulse gas chromatography.

^aPartition coefficients between a given alkane (X) vs *n*-hexane (Y). In the case of cyclohexane (X) and benzene (Y).

This trend can be observed for both materials, however for the more omniphobic DiaMM-2 all isotherms are shifted to higher p/po values indicative of considerably weaker adsorbate-adsorbent interactions. Solid state ¹³C CP-MAS NMR spectra of DiaMM-1 (Figs. S10, S11) show that the line width of the carbon signals corresponding to the benzene residues decreases while the signals corresponding to the methyl groups shift downfield on going from *n*-hexane to bulkier 2,3-dimethylbutane. These results are indicative of stiffening of the structure upon loading with the most strongly binding alkanes.²² In the case of DiaMM-2, the ¹⁹F CP-MAS NMR spectra (Fig. 4j and Fig. S12) show that the ¹⁹F signal shifts with concomitant reduction in the line width upon hydrocarbon guest adsorption, which is consistent with the decrease in 19F-19F dipolar coupling: the more alkane enters the pores, the more spatially separated the CF₃ moieties are and the smaller, on average, the ¹⁹F-¹⁹F dipolar coupling.

Variable temperature pulse gas chromatography carried out on 10 cm chromatographic columns packed with DiaMM-n materials, in the 363-423 K temperature range, further proved the selective adsorbate-adsorbent interactions between C6-alkanes and DiaMM-n under dynamic conditions (Fig. 4d,e). The results indicate that both materials are effective in separating both linear alkanes (n-pentane vs. n-hexane), and branched alkane isomers (hexanes). The elution time of alkanes on DiaMM**n** systems follows the sequence: *n*-pentane < *n*-hexane < 2methylpentane < 3-methylpentane < 2,3-dimethylbutane < 2,2-dimethylbutane. We ascribe it to the reverse separation *hierarchy*, whereby the linear isomers are eluted before the more branched ones. This elution trend is in agreement with the monocomponent isotherms (see Fig. 4a,b) and has also been observed for microporous framework materials, especially with pore voids in the range of 6–8 Å, including UiO-66²³, and ZIF-76²⁴. This behavior can be rationalized by preferential lodging of dibranched alkanes within tetrahedral cages. We note that, **DiaMM-2** gives rise to faster (7 times) and better separation of the alkane mixture ($\alpha_{X/Y}$ partition coefficients) compared to **DiaMM-1** (Table 1). Indeed, **DiaMM-2** is able to fully resolve the *n*hexane and 2-methylpenthane mixture and partially the 2,3-dimethylbutane, 2,2-dimethylbutane mixture while **DiaMM-1** performs more poorly. The $\alpha_{X/Y}$ partition coefficients values found for **DiaMM-2** material are comparable to those found for reverse shape selective UiO-66 system²⁵, however, the separation is 6 fold faster which should be related to higher gas diffusivity on **DiaMM-2** material (see below).

To gain additional insight into the interaction forces between the adsorbate molecules and the pores of **DiaMM-n**, the enthalpy and entropy of adsorption were calculated using van't Hoff plots and are summarized in Table 1. The heat of adsorption, $-\Delta H_{iso}$, is in the range of 25-46 kJ/mol and considerably smaller than the values typically found for porous framework materials (50-70 kJ/mol), namely, MOFs7,9,23, mesoporous silicas²⁶ and zeolites²⁷ and intrinsically porous cages¹². For **DiaMM-1** the adsorption enthalpy for the linear isomers is smaller than for the branched ones while for DiaMM-2 the entropic term appears to be more relevant in the separation process, which is likely related to the dynamics of the adsorbate molecules in the pores. Overall, in both cases, the high research octane number (RON) 2,3-dimethyl- (105) and 2,2-dimethylbutane (92) isomers are the ones that are most strongly associated with the structures of the studied materials.

Computational modelling of sorption of C₆**hydrocarbon in DiaMM-n.** Computational modelling of 24 bulky 2,3-dimethylbutane molecules distributed in 24

cavities of the pore network (Fig. 4g) indicates good size matching. A similar loading of the linear hexane (or bent conformations) isomer leads to loose arrangement of the guest molecules in the cavities (Fig. 4h) which accounts for the stronger interactions of branched isomers with the pores. The pore diffusion coefficients of the adsorbate molecules at 370 K in DiaMM-1 were obtained from dynamic computational modelling.²⁸ The calculated values: 2.05×10^{-8} m²/s, 1.95×10^{-8} m²/s, 1.83×10^{-8} m²/s. 1.54×10^{-8} m²/s for *n*-hexane, 2-methylpentane, 3methylpentane and 2,3-dimethylbutane, respectively, are one to three orders of magnitude higher than in flexible porous framework materials.² These values indicate that adsorbate diffusion in the porous network is not a limiting factor of the separation process pointing that the separation takes place under thermodynamic equilibrium regime. These results highlight the importance of network plasticity of molecular crystals in the separation process allowing fast, efficient and low energy separation of alkane isomers. Moreover, the decoration of the pore surface with weakly interacting -CF₃ groups (instead of -CH₃) is responsible for a further reduction of up to 8 kJ/mol in the adsorption enthalpy values leading to faster and more efficient separation process (Fig. 4e).

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Benzene/Cyclohexane separation on DiaMM-n. We have been able to contend that the separation capacity of the DiaMM-n systems can be extended to the difficult separation of benzene/cyclohexane mixtures possessing similar boiling points (0.7 K difference). Indeed, static adsorption isotherms (Fig. 4c), ¹³C and ¹⁹F CP-MAS NMR (Figs. 4j, S9-S12), variable temperature pulse gas chromatography (Fig. 4f), room temperature breakthrough experiments (Fig. 4i) and computational modelling demonstrated the ability of DiaMM-n systems to separate vapor mixtures of these two compounds at low temperatures. The calculated diffusion coefficients at 370 K for benzene $(2.29 \times 10^{-8} \text{ m}^2/\text{s})$ and cyclohexane $(1.93 \times 10^{-8} \text{ m}^2/\text{s})$ m²/s) on DiaMM-1 are very high. The enthalpy and entropy of adsorption (Table 1), obtained by analyzing the van't Hoff plots (Figs. S35, S36), show stronger interaction of bulkier cyclohexane than benzene with the microporous network. Also in this case, CF, decoration is responsible for a significant reduction of 4 kJ/mol in the enthalpy of adsorption. Computational modelling also shows good size matching of cyclohexane in the network pores compared to looser arrangement of benzene molecules (Figs. S₃₇, S38). Solid state ¹³C MAS-NMR (Fig. S10) shows 0.9 and 1.4 ppm respective downfield shifts of the methyl group resonances upon exposure to benzene and cyclohexane vapor indicative of an atomic-level interaction of the adsorbate molecules with these residues.²² Similarly, for DiaMM-2, the ¹⁹F CP-MAS NMR spectra (Fig. 4j and Fig. S12) show ¹⁹F signal shifts and decrease in line width on going from benzene to cyclohexane which is consistent with the stronger interaction of the latter with the porous network (see above). In addition, DiaMM-2 is capable of separating the benzene/cyclohexane mixture almost 5 times faster than the more lipophilic **DiaMM-1** (Fig. 4f). The corresponding breakthrough curves show that

cyclohexane and benzene are initially co-adsorbed, however, after adsorbent saturation is achieved, the cyclohexane replaces the weakly adsorbed benzene. This behavior is more pronounced in **DiaMM-2** compared to **DiaMM-1** (Fig. 4i).

CONCLUSIONS

In summary, we have applied a rational strategy, based on a Cambridge Structure Database search of diamondoid non-covalent microporous materials (DiaMM-n) with low packing efficiency, which has allowed us to select an optimal system for the low energy separation of C₆-hydrocarbons. The selected **DiaMM** and its fluorinated analogue possess permanent porosity with superior thermal stability (up to 600 K) based solely on weak van der Waals methane...methane (or trifluoromethane...trifluoromethane) interactions between tetrahedral oxidotetrazinc building units. Furthermore, these weak interactions are responsible for the formation of a highly plastic porous network possessing an optimal balance between high adsorbate diffusivity and shape selectivity for the low temperature. fast and efficient reverse hierarchical separation of volatile organic compounds.

ASSOCIATED CONTENT

Supporting Information. Materials, synthesis and characterization methods, synthesis and characterizations of proligands and clusters. Solution ¹H and ¹³C NMR spectra, solid-state ¹³C and ¹⁹F CP-MAS NMR spectra, TGA and DSC data, VT PXRD studies SEM/EDS images, static and dynamic sorption data and computational simulations for C₆-hydrocarbons. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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