Computational Tuning of the Paddlewheel tcb-MOF Family for Advanced Methane Sorption

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Abstract

A series of metal-organic frameworks (MOFs) with **tcb** net topology and linkers of increasing size (combining triple bonds and benzene rings) is computationally designed using molecular mechanics and density functional theory. By grand canonical Monte Carlo simulations, we identify MOFs with outstanding methane total uptakes and working capacities, satisfying the targets of the US Department of Energy for automobile applications in cold weather regions (50 wt%, 263 cm³(STP)cm⁻³). For example, the **5B** MOF achieves at 298 K working capacities of 52.2 wt% at 5-65 bar and 61.9 wt% at 5-80 bar. The **3B** MOF exhibits at 298 K the most balanced (gravimetric vs. volumetric) total uptake and working capacity in the family of **tcb**-MOFs: 28.4 wt%, 160.9 cm³(STP)cm⁻³ at 35 bar and 23.0 wt%, 130.3 cm³(STP)cm⁻³ at 5-35 bar (exceeding the benchmarks of **rht**-MOF-7, IRMOF-6, IRMOF-9, PCN-14, Ni-MOF-74, Al-**soc**-MOF-1, MOF-205), 38.4 wt%, 218.0 cm³(STP)cm⁻³ at 65 bar and 33.0 wt%, 187.5 cm³(STP)cm⁻³ at 5-65 bar (exceeding the benchmarks of IRMOF-6, PCN-14, Ni-MOF-74, HKUST-1, NU-111, NOTT-101a), 41.6 wt%, 235.9 cm³(STP)cm⁻³ at 80 bar and 36.2 wt%, 205.3 cm³(STP)cm⁻³ at 5-80 bar (exceeding the benchmarks of Ni-MOF-74, MOF-5, MOF-205, HKUST-1).

Keywords: methane storage, metal-organic framework, material design, molecular mechanics, density functional theory, Monte Carlo

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Introduction

Metal-organic frameworks (MOFs) are crystalline materials^{1,2} with unique properties exploited in a range of applications: light harvesting^{3,4}, drug delivery⁵, biomedical imaging⁶, catalysis⁷⁻⁹, and gas separation and storage¹⁰⁻¹⁹. Their porosity combined with an easy tunability of the pore size results in outstanding potential in natural gas storage for automobile applications. Natural gas is superior to gasoline or diesel due to dramatically reduced release of dangerous pollutants such as NO_x, SO_x, CO, and CO₂²⁰. As natural gas consists mainly of methane, evaluating the methane total uptakes and working capacities of MOFs is of great interest. The latter is usually calculated as difference between the total uptake at a pressure of 35 bar, 65 bar, or 80 bar and that at a pressure of 5 bar⁸. Both variants of the total uptake and working capacity, gravimetric and volumetric, are important for characterizing the effectiveness of the methane storage^{21,22}. In 2009 the US Department of Energy (DoE) has announced targets for the methane storage in automobile applications: A gravimetric working capacity of 50 wt% and a volumetric working capacity of 350 cm³(STP)cm⁻³ at 298 K²³. The volumetric target takes into account the density of the adsorbent. Considering a 25% reduction due to the fact that MOF crystallites are pressed into pellets with lower density than a single crystal, the target becomes 263 cm³(STP)cm⁻³.

Due to advances in molecular simulations, modelling nowadays plays an invaluable role in predicting MOF structures and properties. Structure-property relationships can be obtained with high accuracy and much faster and cheaper than in real experiments²⁴⁻²⁸. Evaluation of different benchmarking materials has shown that classical force fields provide good agreement of the bulk modulus and linear thermal expansion coefficient with precise first-principles calculations²⁹. The flexibility of MOFs has been studied based on the assumption that the framework consists of rigid elements connected by hinges³⁰. Controlled release of methane molecules from Mg-MOF-74 by means of a molecular gate guided by an electric field has been predicted in Ref. 31 and a computational screening approach for MOF structure design from a library of chemical building blocks (of known compounds), with the target to enhance the methane working capacity, has been introduced in Ref. 32. A computational technique for evaluating structure-property relationships using algorithms from machine learning has been developed in Ref. 33, demonstrating fast and accurate identification of MOFs for efficient carbon dioxide storage (~300,000 hypothetical MOFs generated by combining 66 secondary building units and 19 functional groups). Screening of more than 20,000 candidates has led to the conclusion that the volumetric hydrogen total uptake is maximal for MOFs with surface areas in the range of 3100-4800 m²/g³⁴.

While it is difficult to achieve simultaneously both the gravimetric and volumetric US DoE targets for the methane working capacity, computational methods can point to new venues³⁵. For example, the Materials Genome Initiative,

a computational approach to screen databases, has been applied to nanoporous structures to identify limits for the methane working capacity²⁴ and hydrogen total uptake³⁶. Hypothetical frameworks have been proposed in Ref. 37 in order to minimize the framework density and maximize the void volume for methane molecules. The highest volumetric total uptake (80% of the US DoE target) has been found in the case of diamond-like networks. The properties of Al-soc-MOFs have been analyzed in Ref. 38 by a molecular simulation approach consisting of two steps, framework optimization on the molecular mechanics level of theory followed by evaluation of the working capacity. The results reveal a clear correlation between pore structure and methane storage properties: Shortening the linker leads to dramatic enhancement of the volumetric working capacity but lowers the gravimetric working capacity. In this work, molecular mechanics and first-principles approaches are employed to design a novel family of MOFs with **tcb** net topology (for which none of the known coordination polymers is interpenetrated) that satisfy the US DoE targets for automobile applications at low temperature and provide balanced methane total uptakes and working capacities.

Computational details

We analyze the topologies of paddlewheel coordination polymers by the TOPOS 4.0 Professional package³⁹. The **tcb** net topology occurs in several coordination polymers with metal-N and metal-O bonds⁴⁰⁻⁴⁵ but has not been reported in coordination polymers with polynuclear secondary building units, such as the paddlewheel cluster⁴⁶. The **tcb** net has orthorhombic symmetry with space group Pnna and incident edges forming an angle of 76.6°⁴⁷. As this geometry resembles the coordination figure of the metal atoms in the paddlewheel cluster, the **tcb** net is suitable for building new paddlewheel MOFs. There is only one type of vertex (uninodal net), i.e., the number of building units required to construct structures with **tcb** net is low, which is favorable both for design and synthesis. We build MOFs using the paddlewheel cluster and ditopic dicarboxylate linkers shown in Figure 1. All the linkers considered have been demonstrated to result in stable MOFs⁴⁸⁻⁵⁰. They are given names according to the number of triple bonds (**T**) and benzene rings (**B**) in the linker. Figure 2 shows the **tcb** net and the schematic structure of a MOF based on the paddlewheel cluster and the **B** linker. A paddlewheel cluster consists of two metal atoms linked by four bridging carboxylates. While paddlewheel clusters can be formed with various metals, resulting in different binding affinities, Cu is the most common choice and, at the same time, is available at low cost. For this reason, we consider Cu paddlewheel clusters.

Figure 1. Organic linkers used to obtain a series of **tcb**-MOFs.

Figure 2. (a) Topology (**tcb** net) and (b) schematic structure of a MOF based on the paddlewheel cluster and the **B** linker.

The MOF structures are built by estimating the three lattice vectors, placing the paddlewheel clusters onto the vertices of the net, and connecting them by the linkers. The paddlewheel clusters are oriented to connect with the four nearest-neighbor linkers. The atomic coordinates then are optimized at constant unit cell parameters employing molecular mechanics. We use the Forcite⁵¹ software with the universal force-field⁵² for describing the strong covalent interactions. The Smart algorithm of Forcite is employed with convergence criteria of 10^{-4} kcal/mol for the energy, $5 \cdot 10^{-3}$ kcal/mol/Å for the force, $5 \cdot 10^{-3}$ GPa for the stress, and $5 \cdot 10^{-5}$ Å for the atomic displacements. We verify the unit cell parameters by first-principles calculations (SIESTA⁵³ software), using finite-range pseudo-atomic orbitals (double- ξ with polarization) in the basis and the generalized gradient approximation⁵⁴. A fine real-space grid is employed, defined by an energy cutoff of 600 Ry. The atomic positions are optimized by the conjugate gradient algorithm until the Hellmann-Feynman forces are converged to 0.01 eV/Å. A series of calculations is performed for the **B** MOF with different unit cell parameters, changing the unit cell volume by up to 5%. The obtained energies are fitted to the Birch-Murnaghan equation of state⁵⁵ in order to find the volume that minimizes the total energy. The equilibrium volume is determined by optimizing the b/a and c/a ratios. We find excellent agreement of the results with those from molecular mechanics. For this reason, the unit cell parameters of

the other eleven predicted MOFs are optimized by molecular mechanics only (adopting a convergence criterion of 0.01 Å for the maximal change in the unit cell parameters).

Grand canonical Monte Carlo simulations are used for investigating the methane total uptake and working capacity (gravimetric and volumetric) at different temperatures (240 K, 258 K, 273 K, and 298 K) and pressures (up to 90 bar). The methane molecule is treated as united atom, with parameters taken from the TRAPPE force field⁵⁶ and Lennard-Jones parameters of $\sigma = 3.73$ Å and $\varepsilon/k_B = 148$ K (no charges considered). The MOF is assumed to be rigid and again described by the universal force field. For the van der Waals interaction a cut-off distance of 12.8 Å is used and periodic boundary conditions are applied. The MUSIC software⁵⁷ is employed for the grand canonical Monte Carlo simulations with $2.5 \cdot 10^7$ steps as equilibration period and $2.5 \cdot 10^7$ steps as production period. The fugacity coefficients are calculated by the Peng-Robinson equation of state⁵⁸. Previous studies have demonstrated excellent agreement between experiments and simulations using the methodology of the present work^{59,60}.

Results and Discussion

The Poreblazer program⁶¹ is employed for calculating the geometric surface area (using N as probe), pore volume (using He as probe), and framework density. The results, given in Table 1 together with the lattice parameters, show a strict trend: The longer the linker the larger are the geometric surface area and pore volume but the smaller is the framework density.

Table 1: Structural properties of the designed **tcb**-MOFs.

	geometric surface area (m ² /g)	pore volume (cm ³ /g)	framework density (g/cm ³)	unit cell parameters: a, b, c (Å)
T	69	0.170	1.690	13.80, 5.83, 17.16
B	321	0.441	1.219	16.07, 7.48, 20.64
TT	1759	0.621	0.914	16.09, 8.36, 21.55
TB	1838	0.721	0.826	16.16, 10.30, 24.31
BB	3040	1.094	0.641	20.64, 10.82, 28.20
2BT	4445	1.808	0.444	22.03, 13.61, 32.71
3B	5109	1.996	0.406	22.25, 15.67, 35.61
4T	6531	2.256	0.378	24.53, 11.09, 32.00
2B2T	7247	2.719	0.320	26.25, 14.81, 37.51
4B	7612	3.667	0.246	32.93, 16.81, 44.38
2T3B	8249	4.204	0.217	31.87, 17.96, 45.68
5B	7973	5.102	0.182	37.26, 20.25, 52.31

Figure 3. (a,c,e,g) Gravimetric and (b,d,f,h) volumetric sorption isotherms of **tcb**-MOFs.

Figure 4. (a,c,e) Total uptake and (b,d,f) working capacity of **tcb**-MOFs and benchmarking materials from the literature.

Methane sorption isotherms for the family of **tcb**-MOFs obtained at temperatures of 240 K, 258 K, 273 K, and 298 K by grand canonical Monte Carlo simulations for pressure up to 90 bar are shown in Figure 3. The **2BT** and **3B** MOFs exhibit the highest volumetric total uptakes at high pressure for all temperatures (Figure 3b,d,f,h) and, more importantly, the highest volumetric working capacities at 298 K for all pressure ranges (Figure 4b,d,f). The pore diameter is slightly larger than 10 Å (Figure S2) and the framework density turns out to be 0.444 g cm⁻³ and 0.406 g cm⁻³, respectively, which agrees with the finding of Ref. 22 that the highest volumetric working capacity is achieved for pore diameter ~11 Å and framework density 0.4-0.6 g cm⁻³. The methane sorption isotherms of the **T**, **B**, **TT**, **TB**, and **BB** MOFs exhibit saturation at comparably low pressures (Figure 3), because of small pore volumes (Table 1), such that no high pressure is required to fill the pores completely. The volumetric total uptake is

smaller at moderate pressure than expected from the high framework density. High gravimetric and volumetric total uptakes at 5 bar (Figure 3, zoomed view in Figure S1) lead to moderate working capacities at all temperatures studied. The **4T**, **2B2T**, **4B**, **2T3B**, and **5B** MOFs exhibit very high gravimetric total uptakes, due to large pore volumes and low framework density (Figure 3). Also, because of the low framework density, the volumetric total uptakes are slightly smaller than for the **2BT** and **3B** MOFs. It turns out that the volumetric isotherms of the **2BT**, **3B**, **4T**, **2B2T**, **4B**, **2T3B**, and **5B** MOFs approach each other for growing pressure, especially at low temperature (240 K and 258 K), when the methane sorption is enhanced. At 298 K the **5B** MOF shows the highest gravimetric total uptake, reaching 73 wt%, but moderate volumetric total uptake, due to the lowest framework density.

Figure 5. (a,c) Total uptake and (b,d) working capacity of **tcb**-MOFs and benchmarking materials from the literature.

The total uptakes and working capacities of the designed **tcb**-MOFs are compared to outstanding existing MOFs with different topologies (**rht**-MOF-7⁶², **IRMOF**-6⁶³, **IRMOF**-9⁶³, **PCN**-14^{64,65}, **Ni-MOF**-74^{64,66,67}, **HKUST**-1^{64,67,68}, **Al-soc**-MOF⁶⁹, **UTSA**-76⁷⁰, **MOF**-5⁶³, **MOF**-177³⁸, **MOF**-205³⁸, **MOF**-210³⁸, **NU**-111⁷¹, and **NOTT**-101a⁷²) for a variety of thermodynamic conditions in Figures 4 and 5 to evaluate their suitability for automobile applications. The **4B**, **2T3B**, and **5B** MOFs exceed the gravimetric total uptakes (at 35 bar, 65 bar, and 80 bar) and working capacities (at 5-35 bar, 5-65 bar, and 5-80 bar) of the benchmarking materials. At 298 K the **5B** MOF reaches impressive values of 33.1 wt% at 35 bar, 28.2 wt% at 5-35 bar, 57.1 wt% at 65 bar, 52.2 wt% at 5-65 bar, 66.9 wt%

at 80 bar, and 61.9 wt% at 5-80 bar, thus satisfying the US DoE targets for automobile applications from the gravimetric point of view. The highest volumetric working capacity of $177.2 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ is obtained for the **4B** MOF at 5-80 bar. The excellent performance of the **4B**, **2T3B**, and **5B** MOFs is explained by the combination of a light structure with a moderate total uptake at 5 bar, see above. The **3B** MOF exhibits the most balanced (gravimetric vs. volumetric) total uptake and working capacity in the family of **tcb**-MOFs at 298 K, see Figure 4. Values of 28.4 wt%, $160.9 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ at 35 bar and 23.0 wt%, $130.3 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ at 5-35 bar exceed the performance of **rht**-MOF-7, IRMOF-6, IRMOF-9, PCN-14, Ni-MOF-74, Al-**soc**-MOF-1, and MOF-205; values of 38.4 wt%, $218.0 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ at 65 bar and 33.0 wt%, $187.5 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ at 5-65 bar exceed those of IRMOF-6, PCN-14, Ni-MOF-74, HKUST-1, NU-111, and NOTT-101a; values of 41.6 wt%, $235.9 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ at 80 bar and 36.2 wt%, $205.3 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ at 5-80 bar exceed those of Ni-MOF-74, HKUST-1, MOF-5, and MOF-205.

Figure 5a,b addresses the influence of the temperature by giving results at 273 K, restricted to the total uptake at 65 bar and working capacity at 5-65 bar as for other pressures no data for comparison are available in the literature. The **4B**, **2T3B**, and **5B** MOFs exhibit again the highest gravimetric total uptakes, reaching a maximum of 72.2 wt% in the case of the **5B** MOF, and the **3B** MOF achieves the most balanced performance. In terms of the working capacity, the **2BT**, **3B**, and **2B2T** MOFs outperform the benchmarking materials PCN-14, Ni-MOF-74, HKUST-1, UTSA-76, and NU-111. At further reduced temperature of 240 K we observe for the **T** and **B** MOFs saturation of the methane sorption at a pressure of about 5 bar (Figure S1). Thus, the working capacity is very low, especially from the gravimetric point of view (Figure 5c,d). Both the **2BT** and **3B** MOFs exhibit balanced total uptakes and working capacities significantly higher than those of the benchmarking materials PCN-14, Ni-MOF-74, HKUST-1, and UTSA-76. The **4T**, **2B2T**, **4B**, **2T3B**, and **5B** MOFs are characterized by outstanding gravimetric total uptakes (107.4 wt% in the case of the **5B** MOF) and relatively high volumetric uptakes of at least $260.0 \text{ cm}^3(\text{STP})\text{cm}^{-3}$. The volumetric working capacities fall in a narrow range between $240.0 \text{ cm}^3(\text{STP})\text{cm}^{-3}$ and $266.0 \text{ cm}^3(\text{STP})\text{cm}^{-3}$, while the gravimetric working capacities vary strongly from 48.1 wt% in the case of the **4T** MOF to 97.1 wt% in the case of the **5B** MOF. Low volumetric total uptakes at 5 bar lead to impressive working capacities outperforming the benchmarking materials PCN-14, Ni-MOF-74, HKUST-1, and UTSA-76. The US DoE targets are almost satisfied from both the gravimetric and volumetric points of view. The comparison to higher pressure in Figure 5c,d shows that larger pore volume enhances both the total uptake and working capacity. In particular, the **4T**, **2B2T**, **4B**, **2T3B**, and **5B** MOFs satisfy the US DoE targets for automobile applications. The **5B** MOF reaches an outstanding gravimetric working capacity of 107.4 wt%.

Figure 6. (a,c) Gravimetric and (b,d) volumetric total uptakes of **tcb**-MOFs at temperatures of 240 K and 298 K.

Figure 6 illustrates for temperatures of 240 K and 298 K (Figure S3 for temperatures of 258 K and 273 K) how much the gravimetric and volumetric total uptakes at 5 bar (red bars) reduce the working capacities. For the **T** and **B** MOFs the impact is massive, because the pore volume is small (Table 1) and the sorption saturates at relatively low pressure. It turns out that the presence of triple bonds in the linker increases the working capacity. While the linkers of the **B**, **TT**, and **TB** MOFs have similar size (implying that the size of the unit cell is also similar), the **TT** MOF exhibits at 258 K, 273 K, and 298 K the lowest total uptake at 5 bar from both the gravimetric and volumetric points of view. The gravimetric and volumetric total uptakes at 35 bar, 65 bar, and 80 bar increase with the length of the linker (except for 240 K, where the **TT** MOF shows higher total uptake than the **B** and **TB** MOFs). The **4T** MOF exhibits at 5 bar one of the smallest total uptakes from both the gravimetric and volumetric points of view at all temperatures (Figure S1). This agrees with previous reports on positive effects of triple bonds on the working capacity of porous materials^{59,73}. Moreover, the **4T** MOF has higher geometric surface area and pore volume but lower framework density than the **2BT** and **3B** MOFs (see Table 1). The MOFs with the longest linkers and, therefore, lowest framework densities (**2B2T**, **4B**, **2T3B**, and **5B**) exhibit similar gravimetric total uptakes at 5 bar as the other MOFs, while the volumetric total uptakes are much lower. Figure 6 demonstrates for all MOFs and temperatures that the methane gain from 35 bar to 65 bar is higher than that from 65 bar to 80 bar. For the **T**, **B**, **TT**, **TB**, and **BB** MOFs (small pore volume) the methane gain from 65 bar to 80 bar, in fact, is almost negligible,

while the **2B2T**, **4B**, **2T3B**, and **5B** MOFs (large pore volume) exhibit large gains. In addition, the methane gain from 65 bar to 80 bar is smaller at lower temperature, because the pores are saturated at lower pressure.

The dependence of the volumetric uptake on the length of the linker is addressed in Figure 7a, revealing a distinct maximum at each temperature. Interestingly, the maxima follow in good approximation a linear law, which makes it possible to estimate the optimal length of the linker at given temperature. According to Figure 7b, the maximum volumetric uptake depends almost linearly on the temperature. The isosteric heat of adsorption is calculated from the sorption isotherms at different temperatures. According to Figure 8, the values increase for growing loading. Due to small pores, the values obtained for the **T** and **B** MOFs exceed those reported for PCN-14, UTSA-20, and HKUST-1 [67]. The **3B** and **2BT** MOFs exhibit at low loading similar values as Al-soc-MOF [11]. As expected, larger pore volume correlates with lower isosteric heat of adsorption.

Figure 7. (a) Dependence of the volumetric uptake on the length of the linker at 240 K (red), 258 K (green), 273 K (blue), and 298 K (orange). The full lines are results of third order polynomial regression at constant temperature.

The maxima (black circles) follow in good approximation a linear law (black dashed line). (b) Maximum volumetric uptake as function of the temperature, demonstrating a linear dependence.

Figure 8. Isosteric heat of adsorption as function of loading.

Conclusions

A family of MOFs with **tcb** net topology has been designed by computational means and the properties have been evaluated in detail for identifying candidates that excel in methane storage. Several members of the family exhibit outstanding total uptakes and working capacities. Specifically, the **4T**, **2B2T**, **4B**, **2T3B**, and **5B** MOFs perform well at low temperature, satisfying the US DoE targets for automobile applications. The highest gravimetric working capacity at 298 K is observed for the **5B** MOF with 52.2 wt% at 5-65 bar and 61.9 wt% at 5-80 bar. The **3B** MOF exhibits the most balanced (gravimetric vs. volumetric) total uptake and working capacity at 298 K and all pressures studied. It outperforms many benchmarking materials.

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Supporting Information

Gravimetric and volumetric sorption isotherms of **tcb**-MOFs at low pressure. Pore size distribution of **tcb**-MOFs. Gravimetric and volumetric total uptakes of **tcb**-MOFs at temperatures of 258 K and 273 K.

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