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Triptycene-modified linkers of MOFs for methane sorption enhancement: A molecular simulation study

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ABSTRACT

We computationally study the effect of triptycene incorporation in linkers of metal–organic framework on methane adsorption properties. Geometry optimization at molecular mechanics level of theory has been performed for creation of triptycene-based MOFs. Grand Canonical Monte Carlo simulations have been employed for methane sorption properties calculations of triptycene-modified MOFs. The results obtained are compared favourably with known MOF material of similar structure and topology. This provides a viable linker modification method, which has a potential in uptake enhancement of methane and other gas molecules. These results indicate that linkers' modification by triptycene is efficient for methane adsorption enhancement.

1. Introduction

Metal–organic frameworks (MOFs) are crystalline porous materials [1,2], which have attracted a substantial amount of interest as prospective materials for different applications: light harvesting [3,4], drug delivery [5], biomedical imaging [6], catalysis [7–9], chemical sensing [10], gas separation and storage [11–18]. MOFs have unique physical and chemical properties such as large pore volumes and high surface areas [19,20] which are necessary for gas storage applications. In particular, MOFs show great promise for mobile methane sorption and storage applications which has fuelled a wave of research in this area.

The Advanced Research Projects Agency–Energy of the U.S. Department of Energy (DOE) has recently started a program with new methane storage targets: volumetric storage capacity of 263 cm^3 (STP) cm^{-3}, which is equivalent to that of compressed natural gas at 250 bar and 298 K, and gravimetric storage capacity of 0.5 g (CH_4) g^{-1} (adsorbent) at room temperature [21]. The feature of the working capacity is that it requires high uptake at high pressures and low uptake at low pressures.

Methane cannot form multilayers at $T > 191$ K, therefore the surface area has to be enlarged to achieve higher methane sorption values at room temperature. Surface area and the size of linkers must be properly enhanced through molecular design in order to help methane molecules occupy the void space of pores. Several theoretical approaches have been utilized to increase MOF surface area: for example Duren et al. proposed to use linkers with 'wings' [22] and Froudakis proposed to use linkers of larger size with functionalization [23].

Triptycene and its derivatives with three-dimensional rigid framework, have been widely used as building blocks for creation new supramolecular systems [24–26]. Triptycene-based polymers have been constructed using coupling reaction: triptycene–triptycene and showed surface area (1990 m^2 g^{-1}) acceptable for gas storage purposes [27]. It was demonstrated that the triptycene structure was suitable to the adsorption of H_2 from the theoretical study [28]. Very recently it was shown that triptycene-based microporous polyimides have high selectivity for CO_2 capture [29]. Metal–organic frameworks with triptycene- and pentiptycene-based ligands were studied recently for efficient gas storage purposes [30,31].

The synthesis of new MOFs is challenging and time consuming process. Computer simulation is a powerful tool for MOF structure simulation: it is possible to create a series of MOFs containing different linkers and nodes with idealized properties. Snurr et al. developed a technique for the creation of hypothetical MOFs [32] using a generic procedure that recombined different building blocks from experimental data of synthesized MOFs. Another strategy of building new MOFs with desirable properties has been employed by Martin [33–35], where the actual ligands and nodes of MOFs were replaced by geometrical, so-called alchemical, building blocks.

Methane sorption in several series of advanced MOFs was studied using Grand Canonical Monte Carlo simulations and the conclusion has been made that to design a new desirable material

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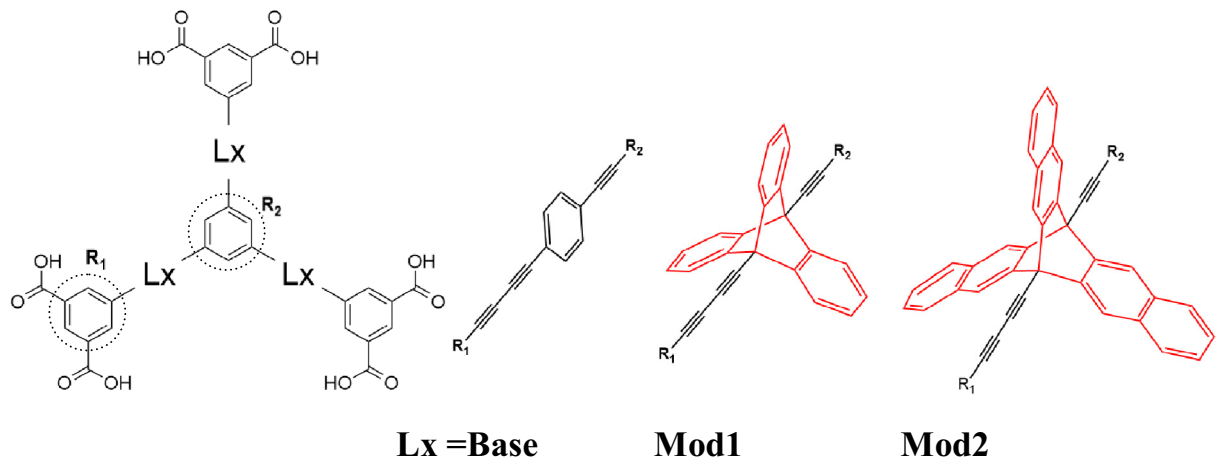

Fig. 1. Hexa-protonated precursor and three linker fragments: original one - Base, and two modified: mod1 and mod2.

for methane storage, a framework with larger accessible surface area and free volume, low density of framework has to be considered [36].

An investigation has been carried out recently into a rather 'conventional' screening for hydrogen storage capacity [37]. Hypothetical MOF models have been optimized using molecular mechanics. In this work a computational study has been carried out to investigate the influence of linker modification by triptycene on the storage of methane sorption in MOFs. The purpose of this work is to use bulky linkers to obtain denser structures in order to increase methane uptake at relatively low pressure and gain higher volumetric uptake.

Two MOFs with *rht*-topology have been theoretically designed and their methane adsorption properties have been investigated.

2. Approach

This research focuses on (3,24)-paddlewheel – connected MOF networks (*rht*-topology) used by groups of Schröder [39,40], Eddaoudi [41] and Zaworotko [41], Zhou [42,43] and Hupp

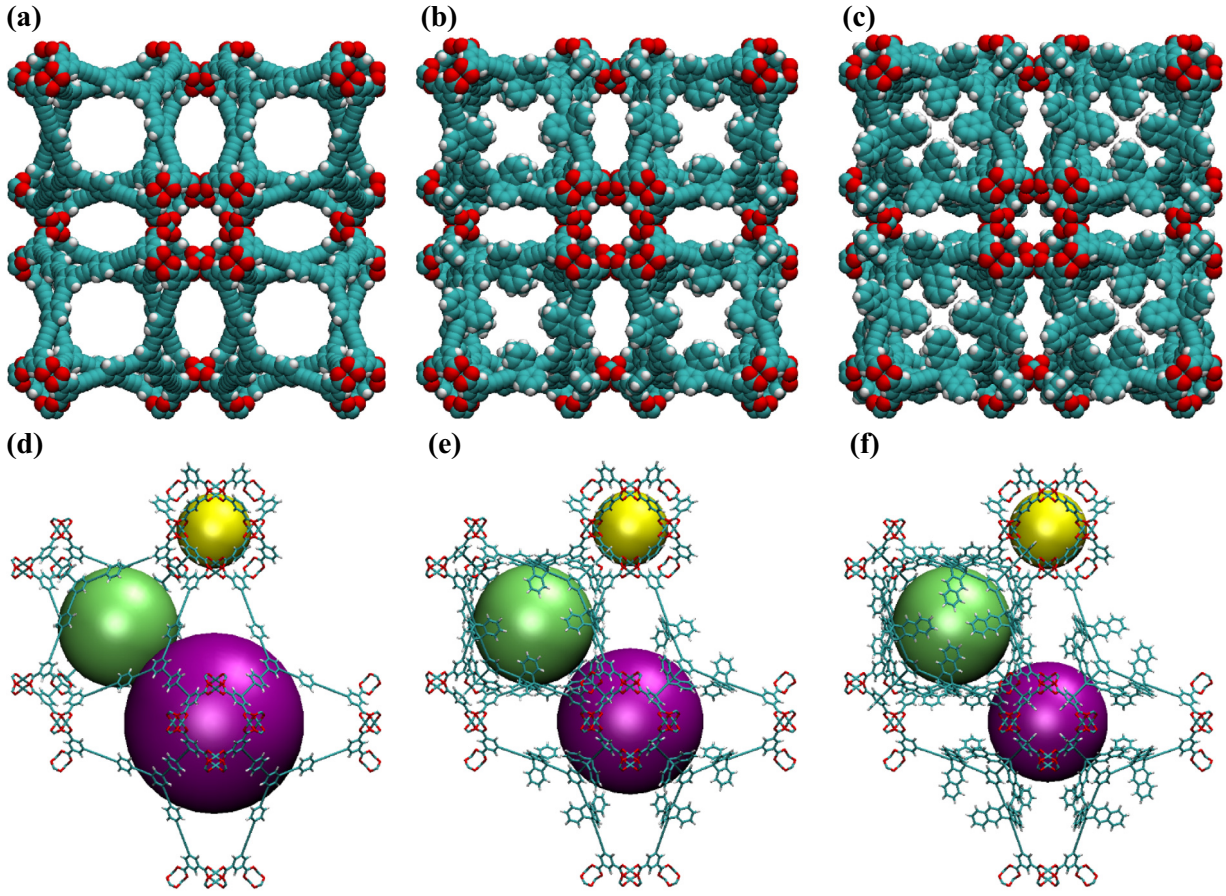

Fig. 2. There are frameworks (a) base, (b) mod1, (c) mod2, where atoms are presented as Van der Waals spheres. In order to further explore internal volume of MOFs the spheres of different colours are included to separate the three cages in MOFs: (d) base, (e) mod1, (f) mod2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)