

The Effects of Methane Storage Capacity Using Telmisartan Organotin (IV) Complex

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Abstract

The fabrication of porous dibutylorganotin (IV) complex as methane storage was successful. Interesting physicochemical properties for diorganotin (IV) complex were observed using a combination of several techniques such as scanning electron microscopy, Brunauer–Emmett–Teller and nitrogen adsorption–desorption isotherm, Barrett–Joyner–Halenda and H-sorb 2600 analyzer. The mesoporous complex exhibit tunable porosity with Brunauer–Emmett–Teller surface area (SABET = 130.357 m².g⁻¹), pore volume (0.162 cm³.g⁻¹) and narrow pore size distribution; the complex was found to has high physico-chemical stability. At 323 K and 50 bars, the complex has methane uptake (up to 1.116 cm³.g⁻¹). The field emission scanning electron microscopy images, at different 100 and 50 μm magnification powers were confirmed, the morphological images of the polymeric film showed a rough surface.

Keywords: Gas storage; Methane capture; Diorganotin (IV) complex; Field emission scanning electronic microscope.

Introduction

Porous organic polymers (POPs) are emerging with great promise for a wide range of applications, especially those involving gas storage and separation [1, 2]. By virtue of their remarkable physicochemical stability, POPs are well suited for gas capture and separation applications wherein high temperature, moisture, and acidic gases are typically encountered [3]. Emerging as a new type of porous materials, porous metal–organic frameworks (MOFs), also known as porous coordination polymers, have been one of the fastest growing fields in chemistry during the past decade [4].

Porous MOFs are highly crystalline inorganic–organic hybrids, and they are constructed by assembling metal-containing clusters known as secondary building units (SBUs) with multi-dentate organic ligands (such as carboxylates) via coordination bonds into a three-dimensional structure [5]. As with hydrogen, methane is also considered a clean energy gas. Compared to petroleum oil, it can provide much more energy because of its higher hydrogen-to-carbon ratio, and has

much lower carbon emission. In addition, deposits of methane-containing natural gas are more widespread globally than those of petroleum oil, and its refinement (purification) to an energy fuel is much simpler than that of crude petroleum oil to gasoline or diesel fuels. Methane is also produced by decomposition of organic waste and by bacteria in the guts of ruminants and termites. In terms of near-term practical utilization and innovations necessary for commercialization, methane appears to be a more promising alternative for mobile applications [6, 7].

The first reported measurement of methane uptake by a porous MOF could date back to as early as 1997 reported by Kitagawa and coworkers but with very limited methane uptake. However, the field of methane storage on MOFs has not developed as quickly as the hydrogen-storage field, and studies on methane storage in porous MOFs are far less numerous than hydrogen [8]. A wide variety of adsorbents with large surface areas such as metal-organic frameworks

(MOFs) and activated carbon are being investigated for methane storage. Zhou et al. [9]. Recently, we reported porous and robust organotin (IV) complexes that contain both aliphatic (butyl) and aromatic (phenyl) substituents using simple and efficient procedures with exceptionally high CO₂ and H₂ uptake [10].

The dibutyl organotin (IV) complex was the most efficient carbon dioxide and hydrogen storage medium, having a gas uptake up to 7.1 wt%, 1.1 wt% for CO₂ and H₂, respectively at 323 K and 50 bars. With the purpose of

optimizing its performance further, herein, we expected to exhibit the improved capacity and selectivity for CH₄ sorption owing to the interactions between dibutyl organotin (IV) complex and gas molecules.

Experimental

Dibutyl organotin (IV) complex **1** was synthesized as previously reported [9]. The reaction of telmisartan (two mole equivalents) and dibutyltin (IV) chloride in methanol under reflux for 8 h gave the corresponding *bis* (telmisartan) diorganotin (IV) complex **1** in 89% yield (Figure 1).

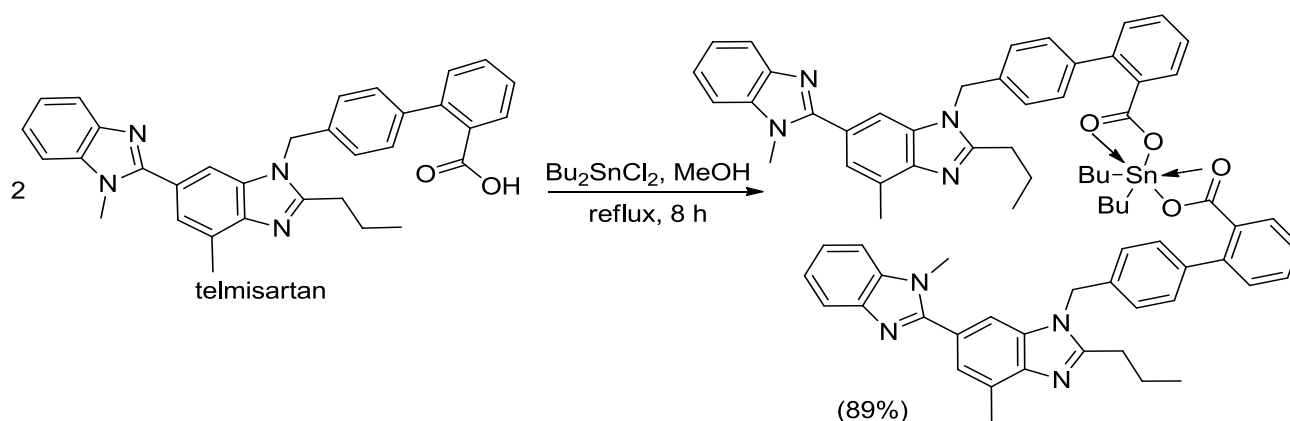


Figure 1: Synthesis of dibutyl organotin (IV) complex **1**

Results and Discussion

The permanent porosity of dibutyl organotin (IV) complex **1** has been investigated by N₂ adsorption experiments at 77 K. The BET surface area estimated by N₂ adsorption to be 130.357 m².g⁻¹ [10]. In Fig. 2, the N₂

adsorption and desorption isotherms of dibutyl organotin(IV) complex **1** show the formation of mesoporous structures and type III nitrogen sorption isotherms. Such isotherms have no identifiable monolayer formation [10, 11].

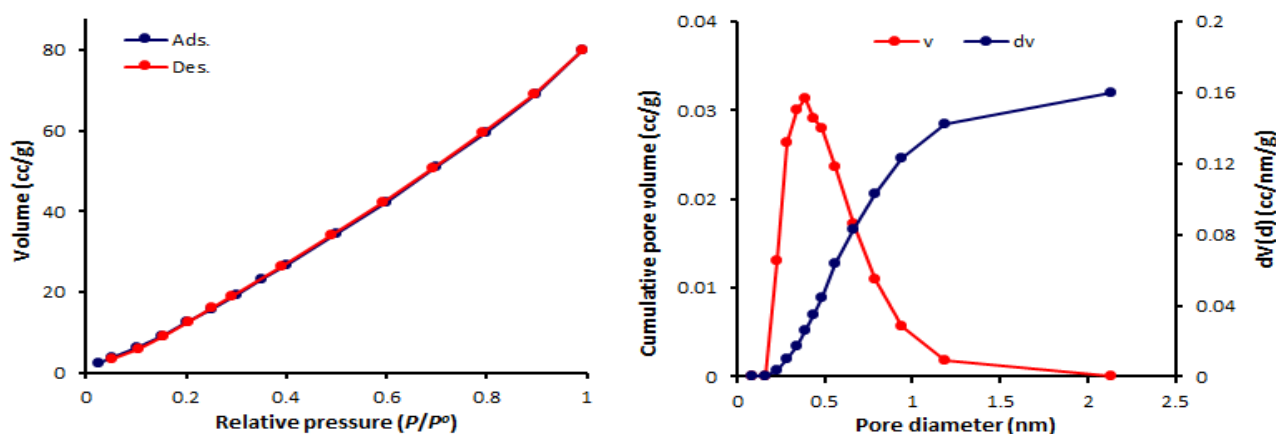


Figure 2: N₂ isotherms and pore diameters of **1**

Organotin (IV) complex **1** has small mesopores with consistent pore sizes (2.429 nm) and the pore volume (0.162 cm³.g⁻¹) of the organotin (IV) complexes [10]. The sorption of complex **1** was investigated at a constant temperature (323 K) and pressure (50 bars). Complexes **1** showed a high CO₂ uptake, possibly as a result of the strong van

der Waals interaction between such complexes and CO₂. The quantity of adsorbed CO₂ was 35.0 cm³.g⁻¹ for complex **1**. However, adsorption for H₂ (1.1 cm³.g⁻¹) under identical conditions to those used for the CO₂ uptake. Such behavior could be due to the weak interaction between the complexes and H₂ [10]. CH₄ adsorption

isotherms were obtained using a High Pressure Volumetric Analyzer (HPVA-II Micrometrics) which employs a static volumetric technique and uses pure CH₄ (99.95%) for adsorption. After degassing the sample, sample holder was attached to the analysis port and the system was purged with helium gas followed by free space measurement. It is noted from Figure 3 that

CH₄ uptake increases with pressure for complex 1. The difference in behavior of adsorption between gases can also be related to pores adsorption, the uptake is lower than that of CO₂ at the same conditions, the quantity of adsorbed CH₄ was 1.116 cm³·g⁻¹ for complex 1. Clearly, complex 1 has the highest CH₄ uptake capacity (0.08 wt %) of the organotin (IV) complex.

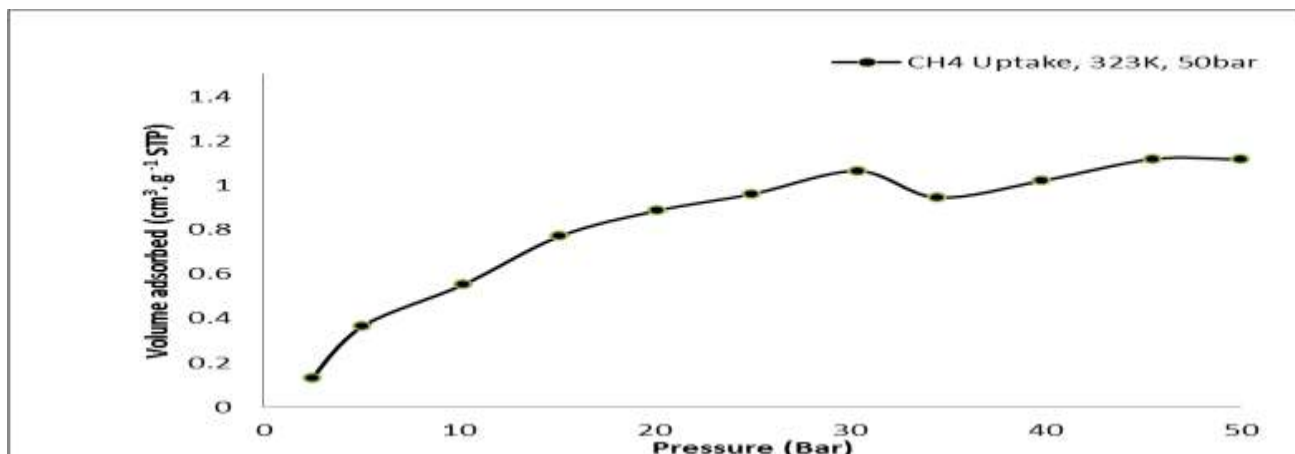


Figure 3: Adsorption isotherms of CH₄ for complex 1

To observe the particle size and morphology, field-emission scanning electron microscopy (FE-SEM) was performed. As expected, this

complex showed similar morphology formed by inter-linking of irregular shapes with a wide range of size distribution (Fig. 4 and 5).

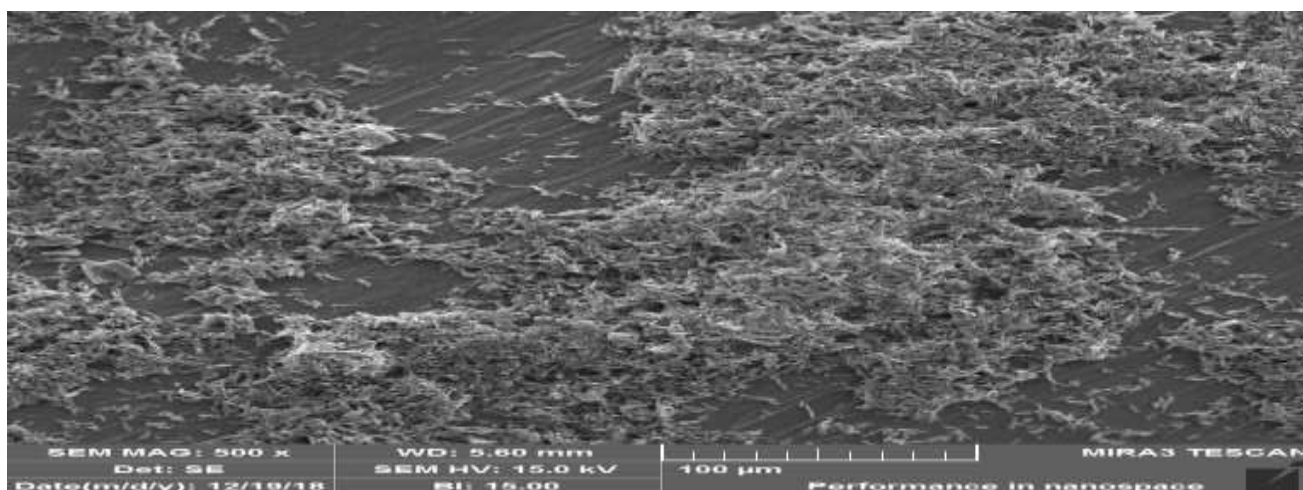


Figure 4: Field emission scanning electron microscopy (FESEM) images 100 μm of 1

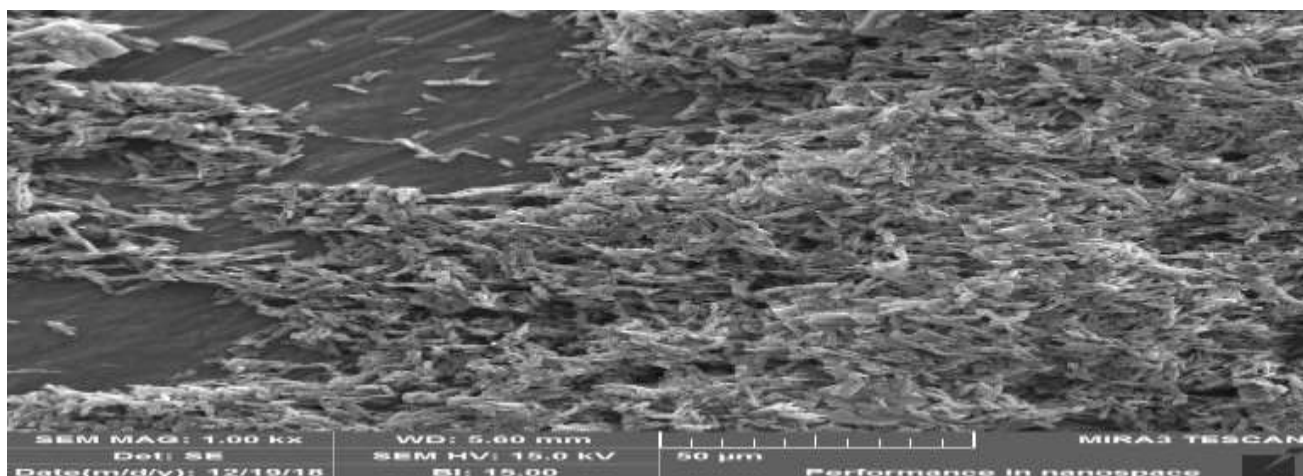


Figure 4: Field emission scanning electron microscopy (FESEM) images 50 μm of 1

Conclusion

Organotin (IV) complex containing telmisartan was used as methane storage media. The chemical structures of organotin (IV) complex were confirmed by SEM, BET, BJH and H-sorb2600 analyzer. The analysis of N₂ sorption isotherms reveals that the

complex has type III isotherm and quite narrow pore size distribution. The coordinated organotin (IV) complex has mesopores and heteroatom-rich structures. The outstanding storage of CH₄ gas a promising potential in clean energy applications.

References

1. Dawson R, Cooper AI, Adams DJ (2012) *Prog. Polym. Sci.*, 37(4): 530-563.
2. Zou X, Ren H, Zhu G (2013) *Chem. Commun.*, 49 (38): 3925-3936.
3. Rabbani MG, El-Kaderi HM (2012) *Chem. Mater.*, 24 (8): 1511-1517.
4. JR Long, OM Yaghi (2009) *Chem. Soc. Rev.*, 38, 1213-1214.
5. M Eddaoudi, DB Moler, H Li, B Chen, TM Reineke, M O'Keeffe, OM Yaghi (2001) *Acc. Chem. Res.*, 34: 319-330.
6. DJ Collins, S Ma, H-C Zhou (2009) *Metal-Organic Frameworks Design and Application*, ed. L. MacGillivray, Wiley-VCH, Hoboken, New Jersey, USA.
7. S Ma PhD (2008) Dissertation "Gas Adsorption Applications of Porous Metal-Organic Frameworks", Miami University.
8. M Kondo, T Yoshitomi, K Seki, H Matsuzaka, S Kitagawa (1997) *Angew. Chem., Int. Ed. Engl.*, 36: 1725-1727.
9. W Zhou, H Wu, MR Hartman, T Yildirim (2007) Hydrogen and methane adsorption in metalorganic frameworks: A high-pressure volumetric study, *J. Phy. Chem. C.*, 111: 16131-16137.
10. Angham G Hadi 1, Khudheyer Jawad 1, Emad Yousif 2*, Gamal A El-Hiti, Mohammad Hayal Alotaibi 4, Dina S Ahmed (2019) Synthesis of Telmisartan Organotin(IV) Complexes and their use as Carbon Dioxide Capture Media. *Molecules*, 24: 16-31.
11. Ahmed DS, El-Hiti GA, Yousif E, Hameed AS, Abdalla M (2017) New eco-friendly phosphorus organic polymers as gas storage media. *Polymers*, 9: 336. doi: 10.3390/polym9080336.