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## Preparation of Value-added Metal-organic Frameworks (MOFs) Using Waste PET Bottles as Source of Acid Linker

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### Abstract

Metal-organic frameworks (MOFs) have been considered with various novel applications and the development of cost-effective processes is essential for further practices. In this work, waste PET bottles were demonstrated as the source of acid linker to prepare value-added metal-organic frameworks UiO-66(Zr), and the texture properties as well as hydrogen storage capacity are comparable to those derived from commercial chemicals. This process offers an economically attractive strategy for eliminating waste PET stream while making value-added materials.

**Keywords:** metal-organic framework, waste PET, UiO-66(Zr), hydrogen storage

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## Abstract

Metal-organic frameworks (MOFs) have been considered with various novel applications and the development of cost-effective processes is essential for further practices. In this work, waste PET bottles were demonstrated as the source of acid linker to prepare value-added metal-organic frameworks UiO-66(Zr), and the texture properties as well as hydrogen storage capacity are comparable to those derived from commercial chemicals. This process offers an economically attractive strategy for eliminating waste PET stream while making value-added materials.

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## 1. Introduction

Metal-organic frameworks (MOFs) have been considered extensively in a wide array of applications, which include, catalysis, biological imaging, drug delivery and gas adsorption, in particular MOFs are emerging as potential materials for hydrogen storage [1–3]. However, the MOF products at BASF and Aldrich are still being sold expensively to the market and only small amounts are available for certain MOFs [4]. Zr-based MOF such as UiO-66(Zr) has been explored as one of the most important prototypical MOFs for a variety of applications such as gas sorption [5], separation [6], catalysts [7,8], sensor [9] owing to their high moisture and thermal stabilities [10]. As BDC is a principal component in the synthesis of UiO-66(Zr), the development of a successful strategy where BDC can be derived from waste PET with the goal of using the BDC to synthesize UiO-66(Zr) materials would be an economically attractive approach towards recycling waste PET. Such a strategy would contribute to a suitable route for eliminating waste PET landfilling, decrease overall consumption of crude oil, and maintain the chemical value of polyester while producing high-value materials at 40-50% energy consumption when compared to the utilization of virgin resin [11]. In this study, UiO-66(Zr) materials were prepared both from PET-derived BDC and commercial BDC (98%, Sigma-Aldrich) for comparison. The PET-derived UiO-66(Zr) materials are expected to have comparable textural properties and hydrogen storage capacities to those derived from commercial BDC. This work is a follow up on the successful one-pot conversion of waste PET bottles to Cr-MOF materials conducted in our laboratory but in this case the synthesis was conducted as a two-step process [12].

Polyethylene terephthalate (PET) is a condensation polymer made by the reaction of terephthalic acid (BDC) and ethylene glycol (EG) [13]. Since 1960s, PET materials have been used as packaging materials [14]. Statistics show that globally, consumption of PET exceeds 24 million tons per year and this number continues to take an upward trend [15]. The durability of PET is advantageous but when PET is disposed as a waste, it may take 500 years to biodegrade in landfills by themselves. Regarding the present practices for PET recycling, most of the developing countries have lower recycling rates, while the recycling rates are higher in the developed countries. Furthermore, the price of virgin PET stays low, which imposes further pressure on the PET recycling industries [16]. It will be of tremendous economic value to produce some high value-added products from waste PET materials.

## 2. Materials and methods

### 2.1. Reagents and Chemicals

Zirconium tetrachloride ( $ZrCl_4$ , Sigma-Aldrich, 99.5+%), terephthalic acid (Sigma-Aldrich, 98%), formic acid (HCOOH, Sigma-Aldrich, 95+%), ethylene glycol ( $HOCH_2CH_2OH$ , Sigma-Aldrich, 99.8%), de-ionized water and N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%) were purchased and used without further purification. Waste PET water bottles were collected from the 5<sup>th</sup> CSIR Conference, South Africa. After the removal of the caps, rings and labels, the cleaned bottle bodies were cut into small flakes with scissors.

### 2.2. Depolymerization of waste PET bottles

The experiments were carried out in a 250 ml teflon-lined Berghof high-pressure reactor (Heizung, Germany). 5 g of PET flakes were put into the reactor together with 5 ml ethylene glycol (EG) and

100 ml H<sub>2</sub>O, then the reactor was heated up to 210 °C and maintained at that temperature for 8 h. After the reaction, the product was centrifuged off, washed twice with ethanol and dried at 100 °C for 24 h.

### 2.3. Synthesis of UiO-66(Zr) materials

The synthesis of Zr-MOFs was based on a previously reported procedure [17] with some amendments. Experiments were conducted using a 250 ml round-bottom flask and an oil bath to provide constant reaction temperature. In a typical procedure, 0.68 g (4.54 mmol) of PET-derived BDC (or commercial BDC) and 1.06g (4.54 mmol) zirconium tetrachloride were dissolved in 50 ml of DMF solvent. Meanwhile, 0.454 mol of formic acid (17.13 ml) was added as modulator. The flask was sealed, put into an oil bath, heated up to 120 °C and maintained at that temperature for 4 h. Then the solid was filtered off, washed with ethanol and dried under vacuum at room temperature for 24 h.

### 2.4. Characterization

X-ray diffraction (XRD) patterns were obtained at room temperature by using a PANalytical X'Pert Pro powder diffractometer with Pixcel detector using Ni-filtered Cu-K  $\alpha$  radiation (0.154 nm) in the range of  $2\theta = 1-80^\circ$ , and at a scanning rate of  $0.1^\circ \cdot s^{-1}$ . The exposure time of sample to environment was about 20 min including the sample preparation and testing procedure. An Auriga Cobra Focused-Ion Beam Scanning Electron Microscope (FIB-SEM) was used to study the morphology of the obtained Zr-MOF samples. All the samples were mounted on a carbon tape and coated with gold prior to measurement. Surface area and pore characteristics measurements were carried out on an ASAP 2020 HD analyzer (Micromeritics) using N<sub>2</sub>, and the BET surface areas were obtained from the N<sub>2</sub> isotherms. Hydrogen adsorption isotherms at 77 K and pressure up to 1 bar were also measured on the ASAP 2020 instrument. All gas sorption isotherms were obtained using ultra-high purity grade (99.999%) gases. Considering that the as-prepared MOF samples may contain free carboxylic acid within the pores, before analysis, MOF samples (0.2–0.3 g) were first solvent-exchanged using ethanol, pre-treated in an oven and then outgassed in the analysis tube under vacuum (down to  $10^{-7}$  bar) with heating up to 200 °C, which is sufficient to remove impurities without causing thermal decomposition or loss of framework crystallinity.

## 3. Results and discussion

Fig. 1a-c shows the XRD pattern and SEM image of PET flakes from the collected PET bottles. Some earlier work has revealed from thermodynamic approximations that the weakest chemical bond in the PET chain is the ester link, pointed out by the red arrow in Fig. 1d [18]. This implies less energy is needed to break this bond and therefore the attack mechanisms of the degrading agents mainly focus on the ester link [19–22]. This is the working principle of PET depolymerisation process.

Five characteristic reflection signals in Fig. 2a positioned at  $2\theta = 17.21, 25.01, 27.64, 29.53$  and  $39.51^\circ$  confirmed PET-derived BDC when compared to Fig. 2b. The relative crystallinity of PET-derived BDC is much lower than commercial BDC (Sigma-Aldrich). Fig. 2c-d shows the morphologies of the BDC samples from PET bottles and Sigma-Aldrich.

In Fig. 3a-b, three characteristic reflection signals confirmed the successful synthesis of UiO-66 when compared to the simulated XRD pattern [23]. However, the crystallinity of UiO-66 product from PET-derived BDC is much lower than that derived from commercial BDC (Sigma-Aldrich), indicating the necessity for purification of the PET-derived BDC. Fig. 3c-d shows the SEM images with similar morphologies for both UiO-66 samples. It can also be seen that the sizes of UiO-66 (PET-derived BDC) crystals are larger than those of UiO-66 (BDC, Sigma-Aldrich) crystals.

The N<sub>2</sub> and H<sub>2</sub> sorption isotherms presented in Fig. 4 indicate that the PET-derived UiO-66 material had relatively lower N<sub>2</sub> and H<sub>2</sub> adsorption levels, but the values are comparable to other developed MOF materials [24].

From the results in Table 1, the PET-derived UiO-66 product has comparable textural properties to those obtained from commercial BDC (Sigma-Aldrich), which indicates the successful employment of waste PET bottles as BDC linker source for producing high value UiO-66 materials. Moreover, UiO-66 was also synthesized brown coloured PET bottle as BDC source; this was done to determine the effects of additives and colourants (used in PET bottles) on the textural properties of the prepared MOFs. From experimental results it was concluded that the prepared MOFs had comparable textural properties to the MOFs prepared using BDC derived from colourless PET bottles and commercial BDC.

### Acknowledgements

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**Table 1**

Physical properties and H<sub>2</sub> uptake capacities of the desolvated UiO-66 samples obtained from PET-based synthesis and commercial BDC (Sigma-Aldrich).

Sample	Size (nm) <sup>a</sup>	Density (g/cm <sup>3</sup> ) <sup>b</sup>	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> ) <sup>c</sup>	Pore vol. (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>d</sup>	Micropore vol. (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>e</sup>	H <sub>2</sub> uptake (wt.%) <sup>f</sup>
UiO-66 (BDC, PET-derived)	800	1.6	814	0.33	0.28	1.2
UiO-66 (BDC, Sigma-Aldrich)	400	1.55	1171	0.45	0.39	1.5

<sup>a</sup> Estimated from SEM images. <sup>b</sup> Determined by pycnometer. <sup>c</sup> BET surface area. <sup>d</sup> From H-K analysis. <sup>e</sup> From H-K analysis. <sup>f</sup> Absorbed at 77 K and 1 bar.

**Fig. 1.** (a) Collected PET bottles, (b) surface morphology of PET flakes, (c) XRD pattern of PET flakes, and (d) working principle of PET depolymerization.

**Fig. 2.** XRD patterns (a-b) and SEM images (c-d) of samples of BDC (PET-derived) and BDC (Sigma-Aldrich).

**Fig. 3.** (a) XRD patterns (a-b) and SEM images (c-d) of samples: UiO-66 (PET-derived BDC) and UiO-66 (BDC, Sigma-Aldrich).

**Fig. 4.** (a) N<sub>2</sub> and (b) H<sub>2</sub> sorption isotherms of samples: UiO-66 (PET-derived BDC) and UiO-66 (BDC, PET-derived BDC).

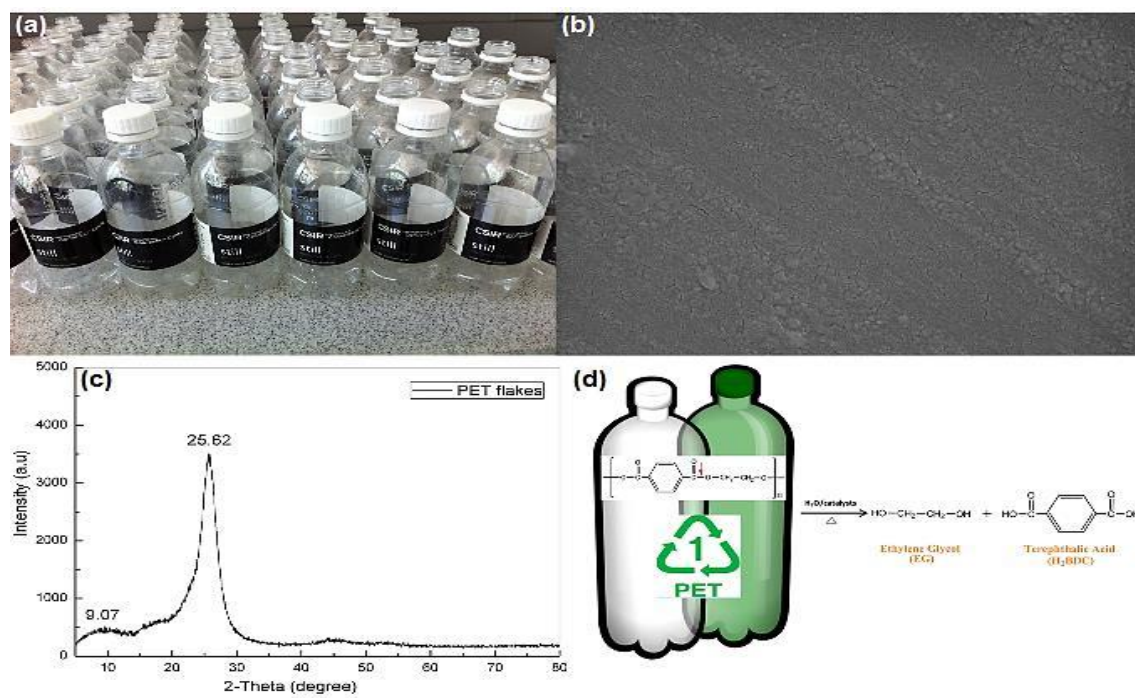


Figure 1



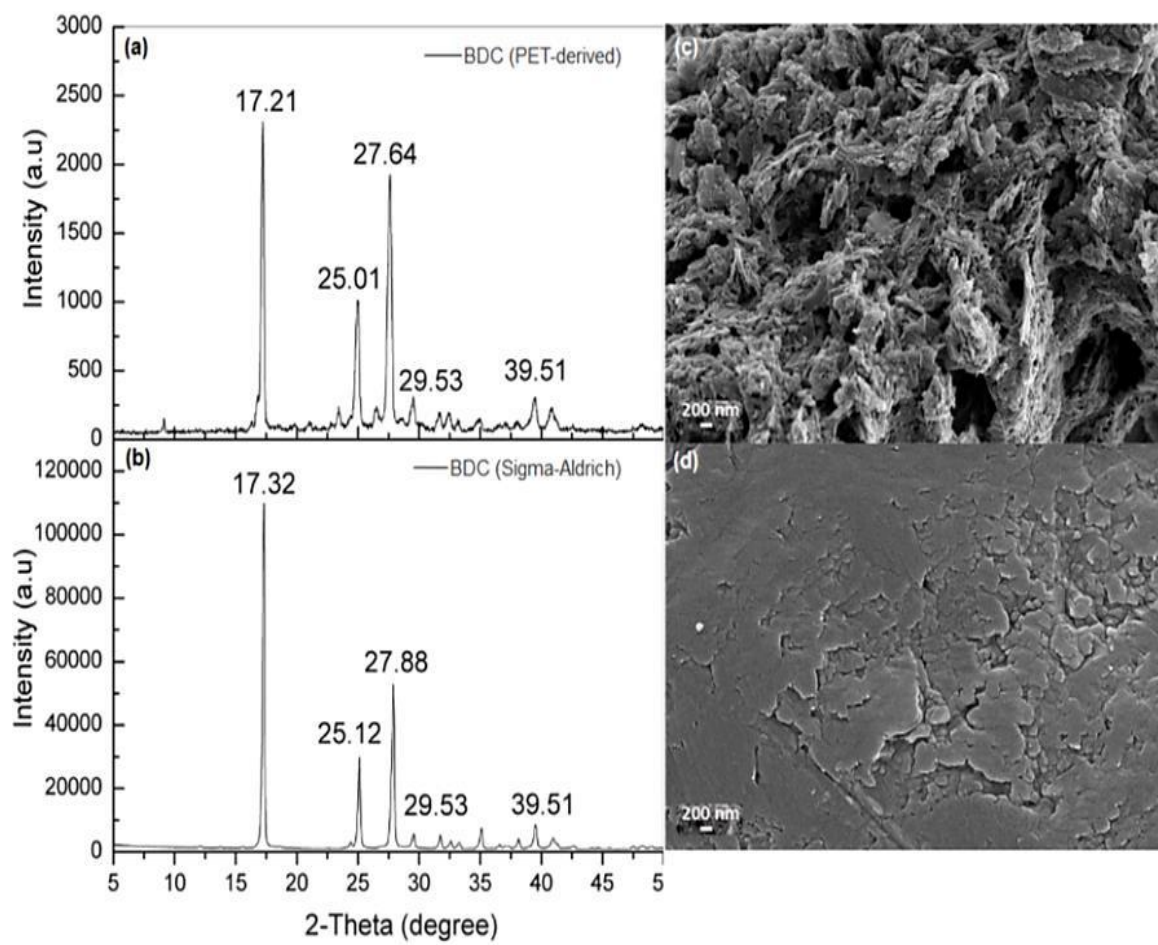


Figure 2

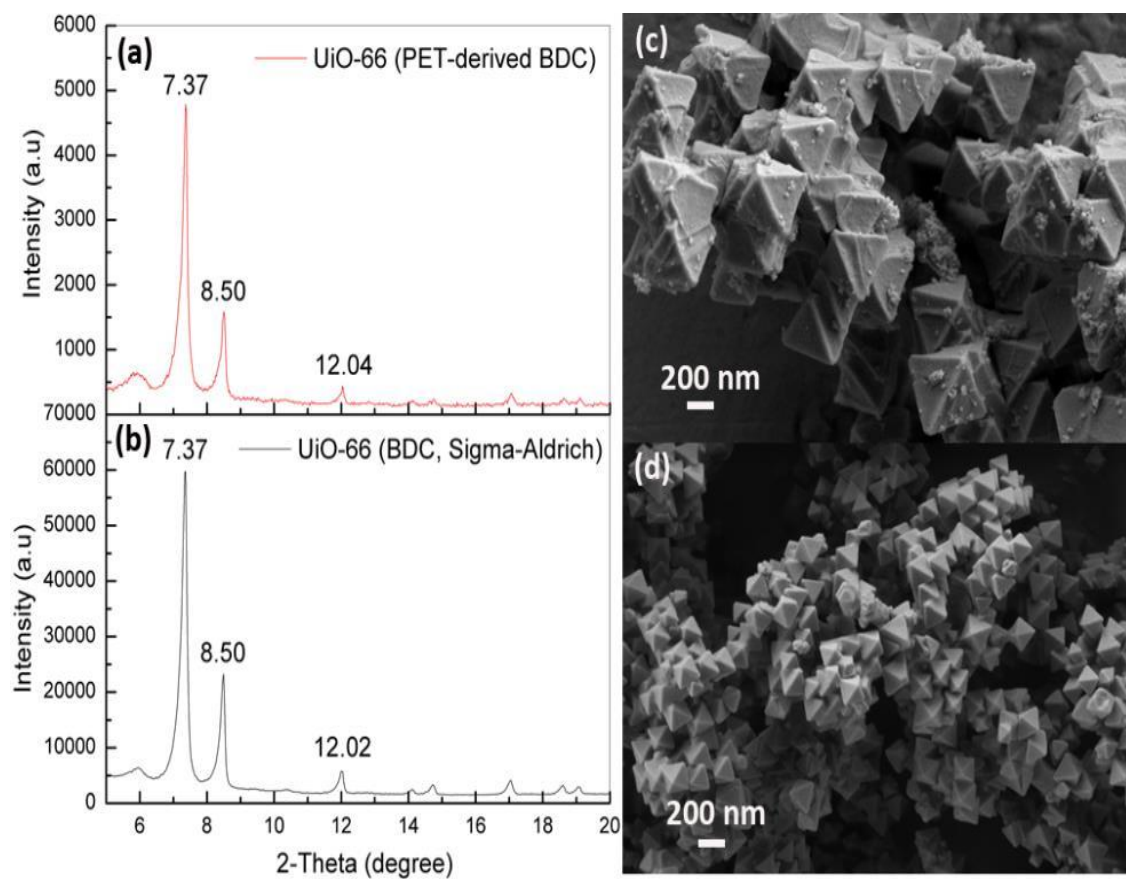


Figure 3

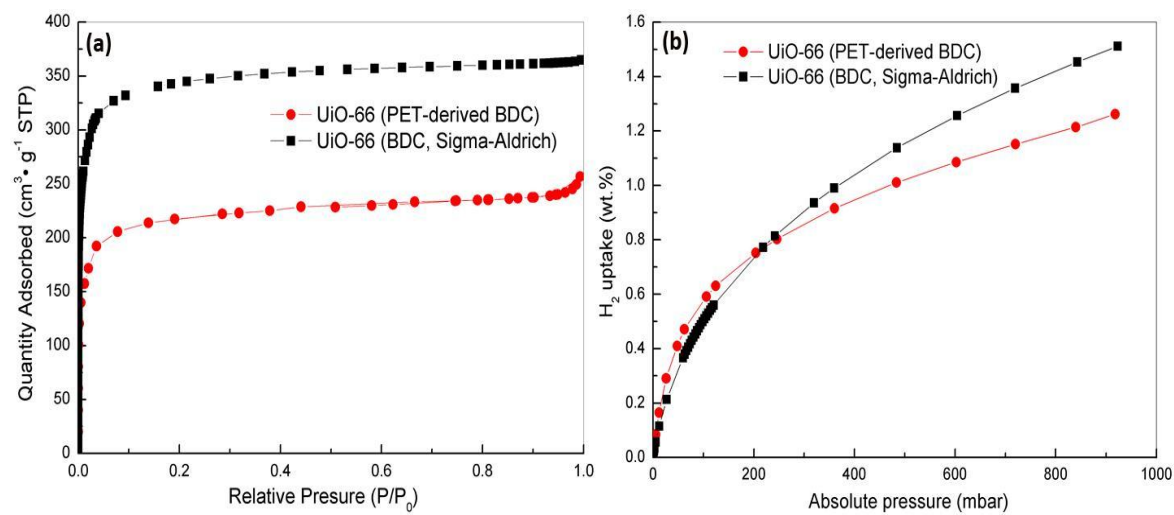
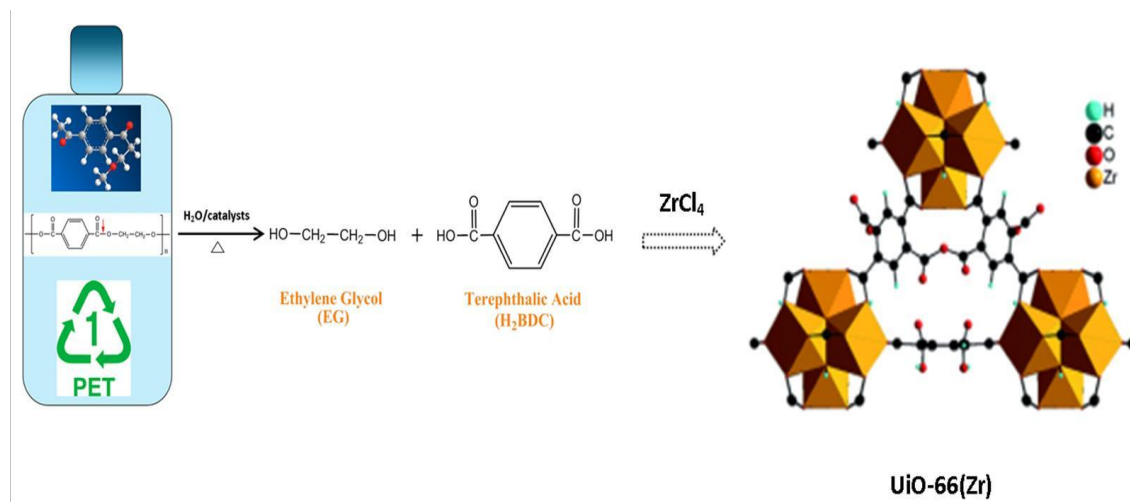


Figure 4



Graphical abstract