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Synthesis of Metal–Organic Frameworks through Enzymatically Recycled Polyethylene Terephthalate

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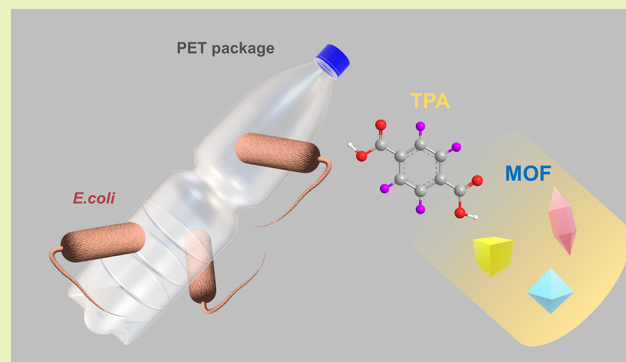
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Supporting Information

ABSTRACT: Polyethylene terephthalate (PET) as one of the most produced plastics contributes to global waste pollution. Upcycling PET into value-added products therefore is of environmental and economic interest. Terephthalic acid (TPA), the monomer of PET, is a common linker for metal–organic framework (MOF) synthesis; thus, PET-to-MOF upcycling raises much research attention. However, conventional PET-to-MOF upcycling often requires PET depolymerization with strong acids or bases and high temperatures, which can lead to environmental and energy penalties. As an alternative, PETase offers a sustainable approach to depolymerizing PET under mesophilic and mild pH conditions. Here we report UiO-66, MOF-5, and MIL-101 syntheses using enzymatically recycled TPA as linkers. The enzymatically recycled TPA demonstrated low impurity, and the obtained MOFs possessed comparable crystallinity, thermal stability, and surface area. These results reveal the feasibility of MOF synthesis by using enzymatically recycled PET.

KEYWORDS: Metal–organic frameworks, PET-to-MOF, upcycling, PETase, recycling, enzyme



INTRODUCTION

Plastics are used in various sectors of our everyday lives and have become an essential part of our economy. The production of plastics has grown explosively from 2 million metric tons (Mt) in 1950 to over 400 Mt in 2018, resulting in global challenges in waste pollution.^{1,2} Only 9% of plastic waste was recycled due to low value-added products and difficulties in sorting.³ Polyethylene terephthalate (PET), as one of the most produced plastics, is extensively employed in single-use bottles, textiles, packaging, etc. Notably, it may take up to 48 years to degrade PET bottles under ambient conditions, leading to a huge burden on the environment.^{4,5} Current PET recycling is through mechanical, thermal, or chemical approaches.^{6–8} These methods can be energy-consuming or generate secondary pollutants.^{9,10} Consequently, enzymatic recycling of PET has raised massive attention ever since the discovery of PET depolymerase (IsPETase) from *Ideonella sakaiensis* in 2016, as this process could depolymerize PET into its monomers terephthalic acid (TPA), 2-hydroxyethyl terephthalic acid (MHET), and ethylene glycol (EG) with high specificity in mesophilic conditions.¹¹ Efforts have since been made to elevate the efficiency of PETase through rational designing,¹² directed evolution,¹³ and machine learning,¹⁴ as the cost of enzymatically recycled TPA (\$1.93/kg) is predicted to be comparable to that of the virgin TPA (\$1.0–1.5/kg).¹⁵ Furthermore, over 69% of supply chain energy and 17% of

greenhouse gas emissions could be potentially reduced by replacing virgin TPA with enzymatically recycled TPA.¹⁵ PETase is reported to be capable of depolymerizing debris-contaminated PET and colored PET, which could be favorable for its integration to the PET recycling stream.^{11,14} Currently, the enzymatic depolymerization of PET has been performed from microliter to 3 L bioreactors in laboratory studies.¹⁶ By using larger bioreactors, the enzymatic depolymerization reaction could potentially be scaled up. Moreover, enzymes have the potential to be recycled by ultrafiltration and immobilization.^{17–20} Therefore, upcycling PET waste into a value-added product through enzymatic recycling fashion is highly relevant to sustainability and circular economy.²¹

Metal–organic frameworks (MOFs) are emerging porous materials with crystalline structures and versatile functionality. With a nanoscale particle size, designable geometry, and tailorable chemical composition, MOFs demonstrate great potential for various applications, such as gas storage, gas separation, catalysis, sensing, and drug delivery.²² MOFs have

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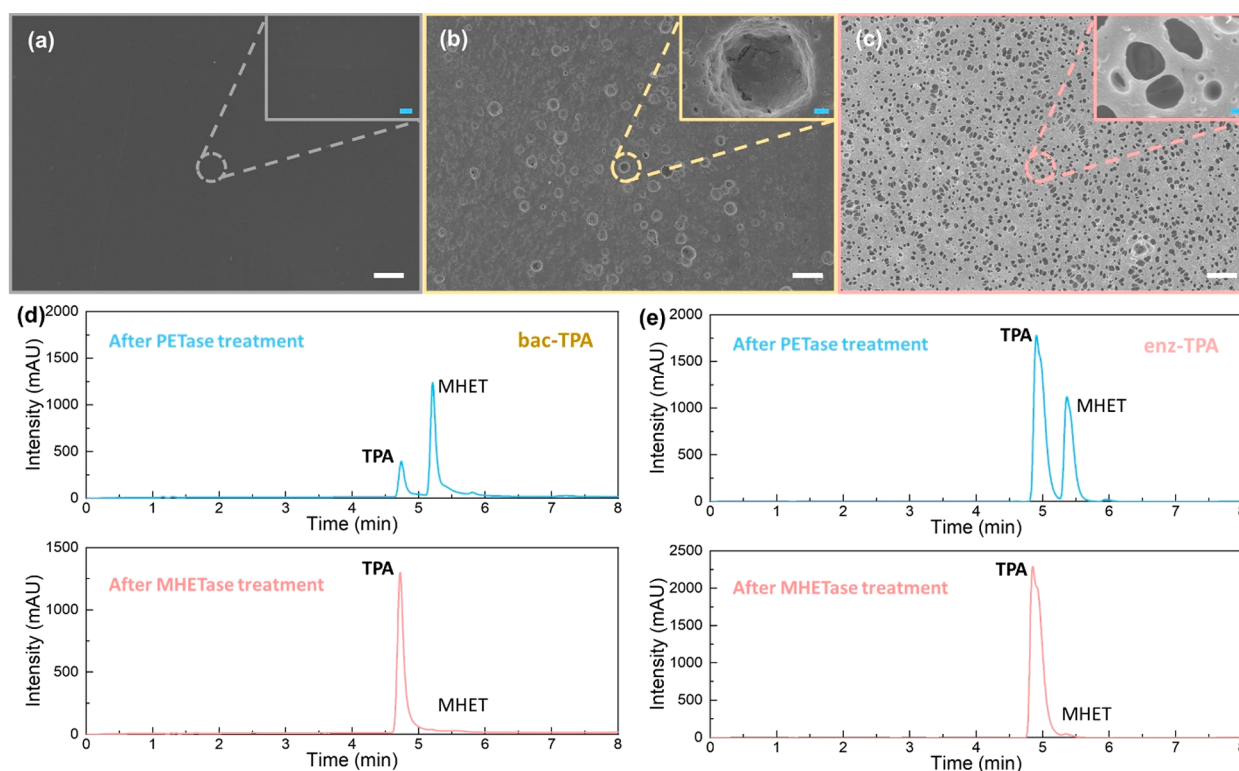


Figure 1. SEM images of PET based yogurt container lid: (a) in the buffer without PETase 48 h, (b) after 48 h degradation with bacterial lysate, (c) after 48 h degradation with purified PETase; scale bar 500 nm (blue, inner figures) and 10 μm (white). HPLC results of (d) bac-TPA (produced using bacterial lysate) and (e) enz-TPA (produced using purified PETase) after PETase and MHETase treatments sequentially.

been produced on a large scale owing to their extraordinary performance.^{23–25} Organic linkers as one main cost driver of MOF production, therefore, would face increasing demands.

TPA (also known as benzene-1,4-dicarboxylic (BDC) acid), as one of the main monomers of PET, is a common linker for MOF synthesis.²⁶ Over 3000 crystal structures contain BDC according to the Cambridge Structure Database (CSD).²⁷ For instance, MOF-5,²⁸ UiO-66,²⁹ MIL-47,³⁰ MIL-53,³¹ MIL-88B,³² and MIL-101,³³ consist of BDC as the organic linker. These MOFs have been widely investigated in sustainable applications, such as CO₂ capture, hydrogen storage, and water remediation.^{34,35} Therefore, upcycling PET waste into MOFs has attracted many investigations recently.⁷ The previously reported work has validated the feasibility of the PET-to-MOF conversion.³⁶ With the development, one-pot PET-to-MOF synthesis has been reported for several MOFs, including MIL-47, MIL-53, and UiO-66.^{37,38} Nonetheless, the PET depolymerization process typically involves strong acids/bases (e.g., nitric acid, sodium hydroxide) and with high temperature (>150 °C) in the reported MOF synthesis,^{39–41} which necessitates considerable energy use and results in the generation of liquid waste. Enzymatic PET depolymerization could be a benign substitute considering the sustainable sourcing and mesophilic conditions of enzymes. However, no record trials of MOF synthesis using enzymatically recycled TPA have been found to date, and the feasibility of enzymatic PET-to-MOF upcycling remains elusive.

In this study, PET plastics were depolymerized to TPA by enzymes. The purity of the enzymatically recycled TPA was characterized by high-performance liquid chromatography (HPLC) and nuclear magnetic resonance spectroscopy (NMR). Three representative MOFs with BDC linkers, i.e.,

UiO-66(Zr), MOF-5(Zn), and MIL-101(Fe) (SI, Section S1) were synthesized by enzymatically recycled TPA and compared with samples from commercial TPA (comm-TPA). Our results cast light on the obstacle of MOF synthesis from PET waste through a biological approach.

RESULTS AND DISCUSSION

PET-based yogurt container lids were collected from domestic waste as the raw material and rinsed with 1% sodium dodecyl sulfate (SDS), 70% ethanol, and deionized water sequentially to remove debris and then dried at room temperature. The cleaned PET lids were cut into small pieces (30 × 30 mm², ~0.3 g) for the following experiments. The crystallinity level of the collected PET is low according to the X-ray diffraction (XRD) patterns (SI, Section S2).

The PET plastics were depolymerized into TPA by ThermoPETase, which is the IsPETase^{S121E/D186H/R280A} variant and has 14-fold enhanced activity at 40 °C compared to the original IsPETase wild-type.¹² ThermoPETase was overexpressed and purified from *Escherichia coli* BL21 (DE3) (SI, Section S3). PET pieces were depolymerized for 48 h with PET-to-buffer ratio at 15 g/L under 2 different conditions: (1) with the bacterial lysate and (2) with the purified PETase. The TPA produced using bacterial lysate and purified enzymes are denoted as bac-TPA and enz-TPA, respectively (SI, Section S4). To obtain purified PETase, protein purification is essential, which is time-consuming and requires special reagents or instruments. Combinations of filtration or different chromatography approaches are used to separate the target protein fraction from cellular debris, nucleic acids, and other contaminants.⁴² Therefore, bac-TPA was used as the main

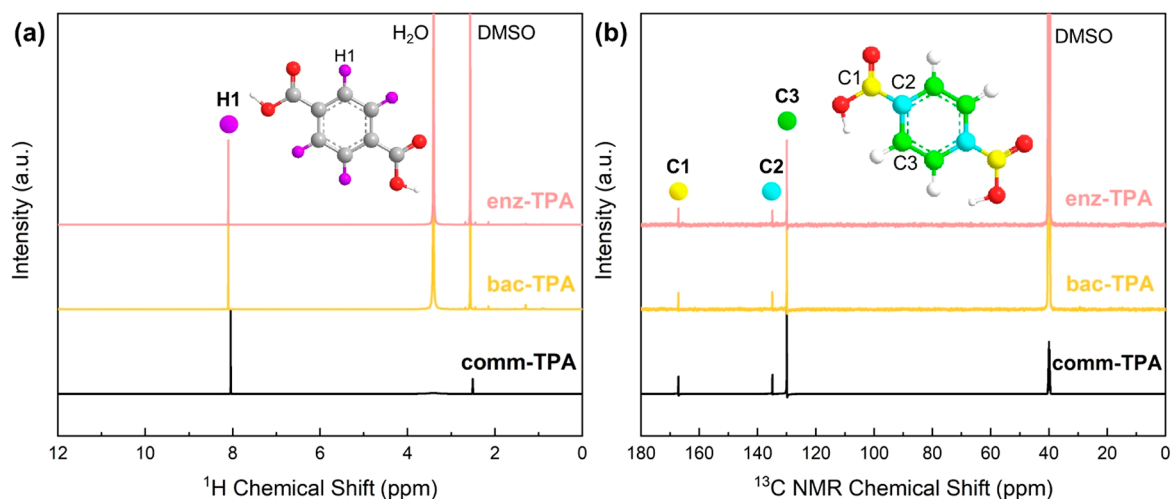


Figure 2. (a) ^1H and (b) ^{13}C NMR spectra of commercial terephthalic acid (comm-TPA), bac-TPA (produced using bacterial lysate), and enz-TPA (produced using purified PETase).

enzymatically recycled TPA for MOF synthesis in this study, while enz-TPA has been tested only for UiO-66 synthesis.

The microstructure of the PET lid of the yogurt container after 48 h degradation was characterized with scanning electron microscopy (SEM). As shown in Figure 1a, the PET lid maintained its smooth morphology after 48 h in buffer without any PETase. In contrast, in Figure 1b,c, many holes were observed in the PET lid after 48 h in the buffer of bacterial lysate and purified PETase, showing the degradation of PET. Notably, the PET lid possessed denser and deeper holes when using purified PETase compared to using bacterial lysate, suggesting a higher level of PET degradation with purified PETase.

HPLC analysis in Figure 1d,e shows that 0.7 mM TPA and 1.8 mM MHET were obtained within the bacterial lysate buffer and 4.1 mM TPA and 2.1 mM MHET using the purified PETase. MHET can be further hydrolyzed by MHET hydrolase (MHETase) into TPA and EG to enhance the TPA concentration.⁴³ After the MHETase treatment, most of the MHET was converted and the bac-TPA and enz-TPA reached 2.5 mM and 6.2 mM, respectively, which is similar to reported studies.^{12,14,44} Though the purified enzymes and cell lysate originate from the same volume of cell culture, the purification process facilitates the concentration of the enzymes. In contrast, the cell lysate ultimately maintains a volume that is 10-fold greater than that of the purified enzyme, attributable to the ample volume of lysis buffer required to ensure comprehensive cell lysis during sonication. Additionally, the potential interference of secondary metabolites, nucleotides, lipids, lipopolysaccharides, inorganic ions, and other residual proteins present in the cell lysate mixture may further hinder the depolymerization efficiency of ThermoPETase,⁴⁵ which also leads to lower TPA yield in bac-TPA than enz-TPA. Those impurities in the PET degradation supernatant could impede the MOF synthesis (SI, Section S5), and one-pot MOF synthesis using enzymatically recycled TPA requires further optimization. Therefore, following the reported methods,^{8,36} both bac-TPA and enz-TPA were protonated, washed, and collected for the MOF synthesis (SI, Section S6).

The ^1H and ^{13}C NMR spectra shown in Figure 2 confirm that both bac-TPA and enz-TPA possess the same structure as that of the comm-TPA, as indicated by the aryl proton (H1)

peak at 8.1 ppm in ^1H NMR spectrum, and carbonyl carbon (C1), quaternary aromatic carbon (C2), and aromatic carbon (C3) peaks at 167.1, 135.0, and 130.1 ppm, respectively, in ^{13}C NMR spectrum. To address the substantial water peak in the NMR spectra, we performed thermogravimetric analysis (TGA) to determine the water content of the enzymatic recycled TPA, where bac-TPA (0.8 wt %) was found to have similar water content as comm-TPA (0.7 wt %) (SI, Section S7). Both HPLC and NMR results suggest the obtained bac-TPA and enz-TPA with low organic impurity, whereas some thermal/chemical PET degradation approaches could lead to the mixture of oligomers with monomers, which could potentially impact the MOF synthesis.^{46–48}

UiO-66(Zr), MOF-5(Zn), and MIL-101(Fe) were synthesized based on reported solvothermal synthesis conditions (SI, Section S1). All of the obtained MOFs were characterized with powder X-ray diffraction (PXRD) and SEM. According to the PXRD patterns as shown in Figure 3, UiO-66 synthesized from bac-TPA and enz-TPA (denoted as bac-UiO-66 and enz-UiO-66) matches the characteristic peaks of the UiO-66 synthesized from comm-TPA (denoted as comm-UiO-66) and the

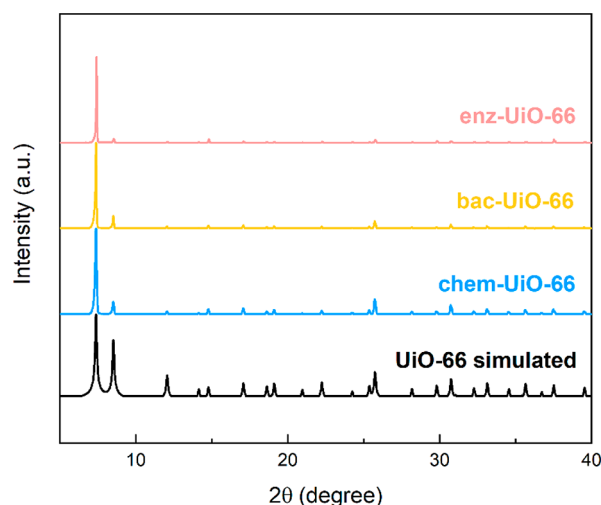


Figure 3. PXRD patterns of simulated UiO-66 (CCDC: RUB-TAK04), comm-UiO-66, bac-UiO-66, and enz-UiO-66.

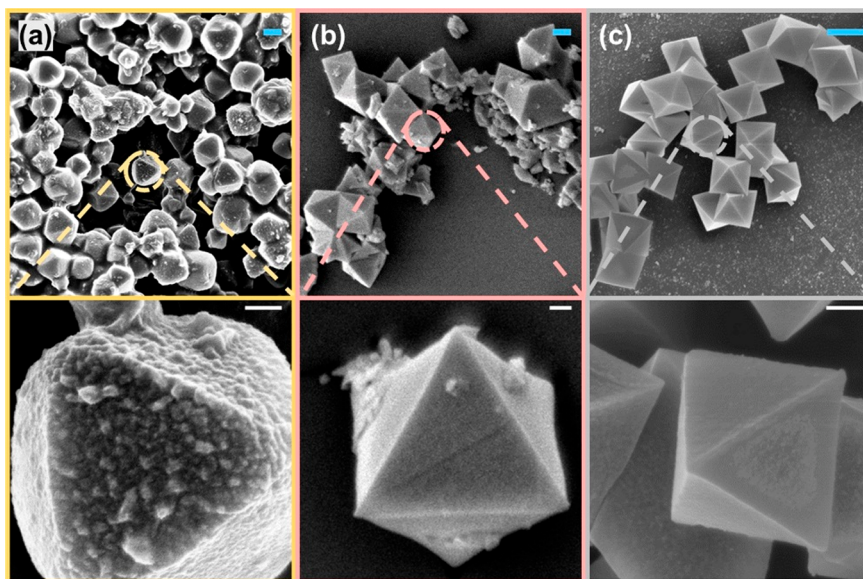


Figure 4. SEM images of (a) bac-UiO-66, (b) enz-UiO-66, and (c) comm-UiO-66 at different scales; scale bar 1 μm (blue, top row) and 200 nm (white, bottom row).

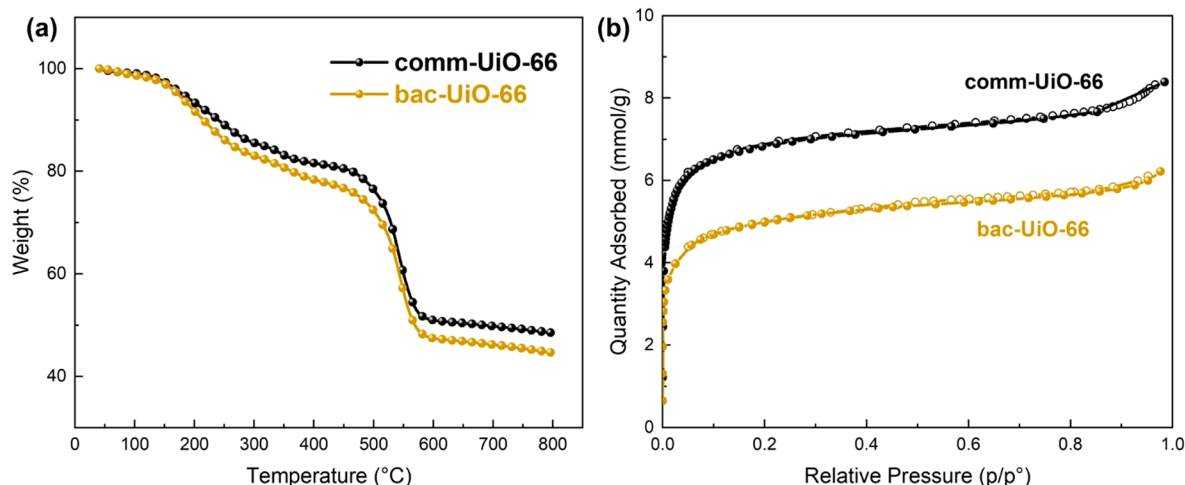


Figure 5. (a) Thermogravimetric analysis for comm-UiO-66 and bac-UiO-66. (b) N_2 adsorption–desorption isotherms of comm-UiO-66 and bac-UiO-66, filled circle for adsorption and open circle for desorption

simulated UiO-66 pattern (CCDC: RUBTAK04), which revealed the crystallization of UiO-66 for all three obtained powders. Similar results were found for the MOF-5 and MIL-101 (SI, Section S8 and S9). The PXRD results confirmed the feasibility of using enzymatically recycled PET (bac-TPA and enz-TPA) as an organic linker for MOF synthesis.

The morphology of the synthesized UiO-66 particles is revealed by the SEM images in Figure 4. The characteristic octahedral structure was found in all obtained UiO-66, suggesting the formation of UiO-66 crystals, which is consistent with their PXRD patterns. However, the geometry and particle size are more uniform in comm-UiO-66, compared with bac-UiO-66 and enz-UiO-66. Furthermore, the edges of bac-UiO-66 were not as sharp as those of enz-UiO-66 and comm-UiO-66. The roughness of the surface of bac-UiO-66 particles is visibly higher compared to the other two counterparts, suggesting relatively lower crystallinity and suboptimal synthesis conditions for bac-UiO-66. This could result from bac-TPA containing more impurities from the

bacterial lysate such as metal cations and residual proteins. Nevertheless, the bac-UiO-66 and enz-UiO-66 upcycled by an enzymatical approach demonstrate superior regular and sharp octahedral geometry than some of the counterparts via other approaches, e.g., thermal hydrolysis.⁴⁹ This could be attributed to the high specificity of the PETase and MHETase for the PET degradation.

To further investigate the performance of the obtained MOFs, TGA and Brunauer–Emmett–Teller (BET) surface analysis were performed. As shown in Figure 5a, the bac-UiO-66 demonstrated similar thermal stability as the comm-UiO-66 with the decomposition temperature around 480 $^{\circ}\text{C}$, which is close to other reported UiO-66.⁵⁰ The N_2 adsorption–desorption isotherms of comm-UiO-66 and bac-UiO-66 in Figure 5b show type I isotherms, revealing their microporous structure. Bac-UiO-66 demonstrates a reduced BET surface area of 417 $\text{m}^2 \text{g}^{-1}$, compared to comm-UiO-66 at 602 $\text{m}^2 \text{g}^{-1}$. The reduction of the BET surface area of bac-UiO-66 could result from its relatively low crystallinity and impurities, as

suggested from the SEM images in Figure 4a. Nevertheless, the comparable thermal stability, surface area, and microporous structure of the bac-UiO-66 suggest that the enzymatically upcycled PET-to-MOF could be a potential substitute for the MOF obtained with commercial TPA in many applications, such as gas sorption/separation and catalysis.⁵¹

To conclude, we demonstrated the feasibility of upcycling PET waste into value-added MOFs through a sustainable enzymatic approach. PET waste was degraded into the monomer TPA after PETase and MHETase treatment under mesophilic and mild pH conditions. Three different MOFs were successfully synthesized using enzymatically recycled TPA as linkers. The bac-TPA produced UiO-66 demonstrated comparable PXRD pattern, microstructure, thermal stability, and surface area with the commercial TPA produced UiO-66, suggesting a low penalty of the performance with enzymatic PET-to-MOF upcycling. Considering the enzymatically recycled TPA could reduce supply chain energy use and greenhouse gas emissions compared with virgin TPA production¹⁵ and avoid hazardous catalysts and harsh process conditions compared with other PET recycling methods,²¹ we believe enzymatic PET-to-MOF upcycling can provide a novel view to promote sustainability and circular economy.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c05222>.

Materials, experimental methods, enzyme overexpression, TPA recovery and collection, water content in TPA, PXRD, and SEM of MOF-5(Zn) and MIL-101(Fe) (PDF)

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Author Contributions

Z.C. and X.F. contributed equally. Z.C. conceptualized the study. Z.C. and X.F. wrote the original draft. Z.C, X.F. and H.L. performed experiments. I.M., A.Z., F.M.A.N., and L.Ö. supervised the study. All authors reviewed and edited the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PET, polyethylene terephthalate; MOF, metal–organic framework; TPA, terephthalic acid; MHET, 2-hydroxyethyl terephthalic acid; BDC, benzene-1,4-dicarboxylic; HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance spectroscopy; XRD, X-ray diffraction; SEM, scanning electron microscopy; BET, Brunauer–Emmett–Teller; TGA, thermogravimetric analysis

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