Rapid defect engineering of UiO-67 (Zr) via microwave-assisted continuous-flow synthesis: Effects of modulator species and concentration on the toluene adsorption

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A B S T R A C T
Defect engineering is a promising approach for tailoring the physicochemical properties, such as stability, pore structure, and surface area, of metal–organic frameworks (MOFs). In this study, some defective Zr-based biphenyl dicarboxylate (UiO-67 (Zr)) MOFs were prepared via fast modulated synthesis under microwave-assisted continuous flow by using HCOOH, CH₃COOH, CH₂CH₂COOH, and C₆H₅COOH as modulators. A surface-modified UiO-67(Zr) framework with high porosity and crystallinity could be rapidly produced in a few minutes due to the incomplete exchange between the bridging ligand and the modulator. The defect concentration in the products was tuned by controlling both the modulator species and concentrations utilized. The adsorption ability toward toluene of the prepared UiO-67(Zr) MOFs was found to be related to their structural defects; the defective UiO-67(Zr) MOF synthesized with HCOOH as the modulator exhibited the highest toluene adsorption capacity (467 mg g⁻¹), surpassing also most of the previously reported adsorbent materials, such as zeolites, activated carbon, Zr-based dicarboxybenzene (UiO-66(Zr)), H₂N-UiO-66(Zr), zeolitic imidazolate, and copper benzenetricarboxylate. Moreover, the experimental dynamic adsorption data were mathematically modeled to predict the adsorption behaviors of defective UiO-67(Zr) MOFs.

1. Introduction

Metal–organic frameworks (MOFs) have recently gained considerable attention due to their excellent tunability of pore size, shape, and functionality [1–5]. Zr-based MOFs such as Zr-based dicarboxybenzene (UiO-66(Zr)) and biphenyl dicarboxylate (UiO-67(Zr)) are considered promising materials because of their attractive thermal, mechanical, and chemical stabilities [1,6–8]. Most of the MOFs, including UiO-66(Zr) and UiO-67(Zr), are generally prepared via solvothermal reaction in Teflon-lined stainless steel bomb reactors, which requires very long reaction times (from 12 h to a few days), with high energy consumption, and produces only small MOF amounts [9–16]. Microwave-assisted synthesis has recently emerged as an energy-effective MOF preparation approach due to its highly efficient heat transfer and short reaction time compared with conventional heating methods [17–19]. In addition, microwave irradiation usually decreases the crystal size by accelerating the nucleation and increasing the number of nuclei [7,20]. Microwave-assisted continuous-flow synthesis has been developed to rapidly prepare MOFs in large quantities and high yield. The continuous-flow condition can overcome the drawbacks of the batch process, such as low efficiency and lack of flexibility [21–24], and the microwave energy can heat the entire reaction media in a few minutes. Using this technique, multi-grams of UiO-66(Zr), MIL-53(Al), and copper benzenetricarboxylate (Cu-BTC) have been successfully synthesized within a short time (<1 h) [25]. Moreover, this approach is easily scalable without considerable changes in the operating conditions [25]. Vo et al. recently synthesized UiO-66 (Zr) within 5–10 min by using a microwave-assisted continuous

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tubular reactor at 120 °C, achieving a high production rate (≈ 6.10 g h⁻¹) along with high crystallinity and surface area (~ 1320 m² g⁻¹) [1].

Defect engineering is now considered a promising approach to tune the MOF properties, including pore structure and specific surface area, via the formation of missing linkers and/or clusters; such defects can be produced by surfactant additives or through linker substitution by secondary linkers or modulators [6,15,26]. Shearer et al. [26] could tune the crystal size, porosity, and composition of UiO-66 via modulated synthesis by using acetic acid, formic acid, and difluoroacetic acid. Schaate et al. [15] used monocarboxylic acids such as benzoic acid and acetic acid to augment the surface areas of various Zr-based MOFs, such as UiO-66(Zr), UiO-66(Zr)-NH₂, UiO-67(Zr), and UiO-68(Zr)-NH₂. Liang et al. [6] synthesized a defective UiO-66 framework by using HCl and HCOOH as modulators, improving the CO₂ and H₂O adsorption abilities compared with defect-free UiO-66(Zr). Vakili et al. [27] obtained defective UiO-67(Zr) by using hydrochloric acid and benzoic acid under microwave-assisted batch conditions. Zhang et al. [28] recently observed considerably higher toluene adsorption capacity in defective UiO-66(Zr) prepared with the cetyltrimethyl ammonium bromide surfactant with respect to its defect-free counterpart owing to the missing-linker defect sites and stronger π-π complexation. Fu et al. [29] prepared defective UiO-66(Zr)-NH₂ with improved photocatalytic activity by adjusting the reaction temperature in the modulated synthesis. Zhang et al. [30] reported that surface-modified UiO-66(Zr) prepared with polyvinylpyrrolidone (PVP) had 1.7 times higher toluene uptake capacity than the pristine UiO-66. All these studies demonstrated that defect-engineered MOFs could be promising materials with improved properties compared with pristine MOFs. As reported, missing-linker and cluster defects are mainly generated via the incomplete exchange between bridging ligands and modulators during the synthesis; the defect type and concentration are dependent on many experimental factors, such as modulator species and concentration as well as reaction temperature, reaction time, trace of water, or aging of reaction mixture [6,15,17,27,29,31–33]. Many investigations focused on fabricating surface-engineered MOFs via slow and small-scale solvothermal synthesis [6,15,26,29,31,32,34–36], which requires a long reaction time (typically, days). Furthermore, this synthetic approach is not suitable for large-scale production. Shortening the reaction time could potentially reduce the production costs [37–40]. Recently, Polyzoidis et al. [41] successfully prepared defective UiO-66(Zr) with HCl utilizing a continuous microreactor within a reaction time of 8–22 min. However, this approach was not proceeded with different types of modulator species, which might exhibit different behaviors depending on their characteristics such as molecular size, acidity, etc. [6,11,26]. As far as we know, report on the defect engineering of MOFs within a short reaction time under continuous-flow conditions is still limited, although this strategy could be highly promising for the production of surface-modified MOFs [1,25,41,42].

In the present work, the defective UiO-67(Zr) framework was quickly generated within 10 min under microwave-assisted continuous-flow condition. Various monocarboxylic acids (HCOOH, CH₃COOH, CH₃CH₂COOH, and G₂H₅COOH) were used as modulators to evaluate their defect formation abilities. The effects of the modulator species and concentration on the UiO-67(Zr) defectivity were systematically investigated by scanning electron microscopy, Fourier-transform infrared (FTIR) spectroscopy, N₂ porosimetry, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Then, the defective UiO-67(Zr) samples were used as adsorbents to investigate the effect of their defects on their toluene adsorption ability; the toluene adsorption kinetics was also analyzed. Furthermore, consecutive adsorption−desorption cycles were performed to evaluate the regenerability of these adsorbents.

**2. Experimental**

### 2.1. Synthetic procedure

The microwave-assisted continuous-flow synthesis adopted is described in detail in Ref. [1] and schematized in Fig. 1. Briefly, ZrCl₄ (3.5 g, 99.8%, Sigma-Aldrich) and 4,4'-biphenyl dicarboxylic acid (BPDC) (4.0 g, 97%, Sigma-Aldrich) were separately dissolved in N, N'-dimethylformamide (DMF) via sonication; then, a calculated amount of the modulator (that is, formic acid, acetic acid, propionic acid, or benzoic acid) was added to the as-obtained solution. A tubular reactor consisting of a polytetrafluoroethylene (PTFE) tube (diameter: 2 mm; length: 8 m) coiled around a laboratory-made PTFE stand was built. Microfluidic syringe pumps (Pico Plus Elite, Harvard Apparatus, USA) were utilized to transport the metal salt and ligand solutions into the microwave oven, which was set at 120 °C. The tubular reactor was filled with DMF before injecting the precursor solutions, whose residence time, that is, the time the reaction mixture stayed in the microwave oven, was fixed at 10 min. The resulting product was centrifuged and successively washed with DMF and ethanol at 70 °C for 6 h. The samples synthesized with formic acid, acetic acid, propionic acid, and benzoic acid were denoted as UiO-67(Zr)-HFO, UiO-67(Zr)-HAc, UiO-67(Zr)-HPF, and UiO-67(Zr)-Benzo, respectively; different amounts of formic acid, that is, HCOOH/Zr⁴⁺ of 40, 50, 60, and 80 equiv, were used and, thus, the UiO-67(Zr)-HFO samples were further distinguished as UiO-67(Zr)-HFO-40, UiO-67(Zr)-HFO-50, UiO-67(Zr)-HFO-60, and UiO-67(Zr)-HFO-80, respectively.

### 2.2. Characterization

The crystallinity of the synthesized defective UiO-67(Zr) samples was analyzed by using an X-ray diffractometer (MiniFlex 600, Rigaku, Japan) with a Cu Kα radiation source (λ = 1.54 Å). FTIR spectra were collected with an infrared spectrometer (TENSOR 27, Bruker, Germany). TGA was performed in flowing air at a heating rate of 5 K min⁻¹ with a thermogravimetric analyzer (Q50, TA Instruments, USA). Nitrogen adsorption−desorption isotherms were measured by using a N₂ porosimeter (Tristar 3020, Micromeritics, USA) at 77 K; the samples were degassed at 150 °C for 12 h under vacuum before this analysis. The surface areas were calculated via the standard Brunauer−Emmett−Teller equation. The mesoporous and microporous structures were determined through, respectively, Barrett–Joyner–Halenda plots and the Horvath–Kawazoe method. The chemical states of Zr, O, and C were identified with an X-ray photoelectron spectrometer (K-Alpha, Thermo Scientific, USA).

![Fig. 1. Synthetic procedure (DMF: N,N'-dimethylformamide; BPDC: 4,4'-biphenyl dicarboxylic acid, UiO-67(Zr): Zr-based biphenyl dicarboxylate).](image-url)
Table 1  Production and physical properties of the synthesized Zr-based biphenyldicarboxylate (UIO-67(Zr)) samples (90%: Brunauer–Emmett–Teller surface area).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (%)</th>
<th>Production rate (g h⁻¹)</th>
<th>BET (m² g⁻¹)</th>
<th>Micropore volume (cm³ g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without modulator</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UIO-67(Zr)-Benzo (60 equiv)</td>
<td>65</td>
<td>4.89</td>
<td>2502</td>
<td>1.07</td>
<td>1.46</td>
</tr>
<tr>
<td>UIO-67(Zr)-HFo (60 equiv)</td>
<td>61</td>
<td>4.59</td>
<td>2449</td>
<td>0.89</td>
<td>1.33</td>
</tr>
<tr>
<td>UIO-67(Zr)-HAc (60 equiv)</td>
<td>59</td>
<td>4.44</td>
<td>2375</td>
<td>0.83</td>
<td>1.30</td>
</tr>
<tr>
<td>UIO-67(Zr)-HFo (60 equiv)</td>
<td>76</td>
<td>5.72</td>
<td>1904</td>
<td>0.69</td>
<td>0.95</td>
</tr>
<tr>
<td>UIO-67(Zr)-HAc (60 equiv)</td>
<td>68</td>
<td>5.12</td>
<td>2450</td>
<td>0.78</td>
<td>1.29</td>
</tr>
<tr>
<td>UIO-67(Zr)-HFo (60 equiv)</td>
<td>65</td>
<td>4.89</td>
<td>2502</td>
<td>1.07</td>
<td>1.46</td>
</tr>
<tr>
<td>UIO-67(Zr)-HFo (60 equiv)</td>
<td>45</td>
<td>3.39</td>
<td>2051</td>
<td>0.77</td>
<td>1.22</td>
</tr>
</tbody>
</table>

*Unsuccessful synthesis.

2.3. Toluene recovery test

The toluene vapor adsorption test was conducted in a continuous-flow fixed bed reactor under atmospheric pressure. Synthesized adsorbents were preliminarily activated at 150 °C for 12 h under vacuum condition (10⁻² kPa). Toluene gas (1000 ppm) balanced with air passed through the fixed bed with a flow rate of 0.3 L min⁻¹, which was monitored by a mass flow controller (EL-FLOW classic series, Brokhorst High-tech BV, The Netherlands). The inlet and outlet toluene concentrations were measured every 3 min with a gas chromatography–flame ionization detector (YL6500GC, Younglin Co., Ltd., Republic of Korea) until reaching the equilibrium. The toluene adsorption and desorption capacities of the synthesized samples were derived from the breakthrough and desorption curves as follows [28,43,44]:

\[ q_{\text{ads}} = \frac{FC_{\text{i}}}{m} \left( \frac{C_{\text{i}}}{C_{\text{f}}} - \int_{0}^{t} \frac{C_{\text{i}}}{C_{\text{f}}} dt \right) \]  \hspace{1cm} (1)

and

\[ q_{\text{deso}} = \frac{F}{m} \int_{0}^{t} C_{\text{s}} 10^{-6} dt \] \hspace{1cm} (2)

where \( q_{\text{ads}} \) and \( q_{\text{deso}} \) (in mg g⁻¹) are the equilibrium adsorption and desorption capacities, \( F \) (in mL min⁻¹) is the gas flow rate, \( t_i \) and \( t_d \) (in min) are the adsorption equilibrium and desorption times, respectively, \( m \) (in g) is the adsorbent weight, \( C_i \) and \( C_f \) (in mg m⁻³) are the inlet and outlet toluene concentrations, respectively, and \( C_s \) (in mg m⁻³) is toluene concentration collected during the desorption.

3. Results and discussion

3.1. Microwave-assisted continuous-flow synthesis of UIO-67(Zr)

In modulated synthesis, the modulators form bondings with the metal ion clusters that modulate the MOF crystallization [36]. In this study, various carboxylic acids, that is, HCOOH, CH₃COOH, CH₂CH₂COOH, and C₆H₅COOH, were used as modulators. UIO-67(Zr) was not obtained without the modulator in the adopted microwave-assisted approach, probably due to the high heating rate of the microwave irradiation, which accelerated the zirconia gel production in the initial reaction stage [31,45]. When using HCOOH, CH₃COOH, or CH₂CH₂COOH as the modulator, a white powder was rapidly formed. In contrast, the use of benzoic acid maintained a clear solution without any solid crystals, suggesting that the reaction did not occur in this case; however, in previous studies, the UIO-67(Zr) framework has been successfully prepared using the same C₆H₅COOH/Zr⁴⁺ equivalence at 120 °C via microwave-assisted batch synthesis within 2.5 h [27] or solvothermal synthesis within 24 h [46]. This indicates that the UIO-67(Zr) crystallization might require a longer reaction time (>10 min) when using benzoic acid as the modulator in the proposed synthetic path. Table 1 summarizes the yields and production rates of the various UIO-67(Zr) samples, showing only slight changes depending on the modulator species at the same modulator concentration. Nonetheless, the concentration of formic acid strongly influenced the yield and production rate, which both decreased with increasing its concentration; the highest UIO-67-HFo yield and production rate were obtained when using a HCOOH/Zr⁴⁺ molar ratio of 40 equiv. The decrease in the UIO-67(Zr) yield when increasing the concentration of the monocarboxylic acid modulator has also been previously reported [27]. The possible explanation is that a high amount of modulator could slow...
down the nucleation process and the exchange between coordinated modulators and linkers, reducing the UiO-67(Zr) yield [31, 45].

Fig. 2(a) illustrates the XRD patterns of the UiO-67(Zr)-HFO, UiO-67(Zr)-HAc, and UiO-67(Zr)-HPPr samples, revealing in all cases a highly crystalline nature and good agreement with the simulated pattern of UiO-67(Zr), implying the formation of a cubic close-packed structure regardless of the monocarboxylic acid type; moreover, at the same modulator concentration, all the samples showed similar intensities, suggesting similar crystallinities. Fig. 2(b) displays the XRD patterns of the UiO-67(Zr)-HFO samples prepared with different HCOOH concentrations. In this case, the XRD peak intensities; thus, the crystallinity gradually increased along with the modulator concentration; in addition, the full width at half maximum decreased with increasing modulator concentration, indicating an increase in the crystallite size.

The bond formation and chemical identity of the prepared samples were verified via FTIR analysis (Fig. 3(a and b)). The FTIR spectra of all the UiO-67(Zr) samples exhibited similar characteristic peaks. The vibrational modes detected at 1589 and 1400 cm\(^{-1}\) were ascribed to the COO\(^{-}\) asymmetric and symmetric stretches, respectively, in the terephthalate linker [12]. The signal at around 1500 cm\(^{-1}\) resulted from the vibration of the C=O bonding in the benzene ring. The small peak at 550 cm\(^{-1}\) was attributed to the stretch vibrations of Zr–O–C [47], while the bands at around 660 and 480 cm\(^{-1}\) came from the \(\mu_3\)-O and \(\mu_3\)-OH stretch, respectively [12, 48].

Then, the morphologies of the defective UiO-67(Zr) samples were analyzed. As shown in Fig. S1, they all consisted of octahedral crystals without apparent surface defects; moreover, the UiO-67(Zr)-HAc and UiO-67(Zr)-HPPr samples exhibited more clear facets with sharper edges than the UiO-67(Zr)-HFO sample. Fig. 4 illustrates the strong effect of the formic acid concentration on the crystal morphology. The UiO-67(Zr)-HFO-40 sample showed extremely small irregular particles with low crystallinity; with increasing the modulator concentration, the defective UiO-67(Zr)-HFO crystals grew in size, revealing a typical octahedral morphology, along with well-defined facets and edges. This occurred because the higher HCOOH concentration intensified the competition between bridging ligand and modulator molecules as well as diminished the nuclei number, resulting in larger crystals [26, 27]. The same phenomenon had been reported for the acid-promoted synthesis of UiO-66 (Zr) under solvothermal conditions for 24 h [11].

Fig. 5 displays the \(N_2\) adsorption-desorption isotherms and the pore size distributions of the synthesized UiO-67(Zr) samples. The nitrogen adsorption capacity varied depending on the modulator type and concentration. The difference in \(N_2\) uptake was clearly observed at low relative pressure (inset of Fig. 5(a)), revealed the following order: UiO-67(Zr)-HFO > UiO-67(Zr)-HAc > UiO-67(Zr)-HPPr. In the UiO-67(Zr) framework, there are small tetrahedral cages (1.2 nm) and large octahedral cages (1.6 nm) [27, 49]. The pore size distribution showed maxima at approximately 0.9 and 1.9 nm (Fig. 5(b)), which indicates the defect formation resulting from the missing linkers. Both the nitrogen uptake capacity and the pore size distribution were enormously affected by the modulator concentration used (Fig. 5(c and d)). The \(N_2\) uptake capacity increased with increasing HCOOH/Zr\(^{4+}\) molar ratio from 40 to 60 equiv, but it decreased when this ratio is further raised to 80 equiv. This suggests that the UiO-67(Zr) pore structure and porosity might be controlled by the modulator species because the tested monocarboxylic acids have different molecular weight and acidity.

The differences in the porosity among the UiO-67(Zr)-HFO, UiO-67(Zr)-HAc and UiO-67(Zr)-HPPr samples (Table 1) might be attributed to their different defect concentrations. Several studies on the modulated synthesis of Zr-based MOFs have demonstrated that the deprotonated modulator can compete with the ligand to generate missing-linker and/or missing-cluster defects, eventually increasing the surface area and pore volume of the products [6, 26, 27]. Shearer et al. investigated the effect of the acidity of various monocarboxylic acids (formic acid, acetic acid, difluoroacetic acid, and trifluoroacetic acid) on the solvothermal synthesis of UiO-66(Zr), reporting an increase in the MOF porosity along with the modulator acidity; the modulator acidity influenced its deprotonating ability in solution and, thus, also its competition with the ligand [26]. The \(pK_a\) values of formic acid, acetic acid, and propanoic acid are 3.77, 4.74, and 4.87, respectively. Therefore, in our experiment, the deprotonated modulator concentration in the mixed synthesis solution followed the order of HCOO\(^{-}\) > CH\(_3\)COO\(^{-}\) > CH\(_3\)CH\(_2\)COO\(^{-}\). The higher concentration of formate in the solution could favor its competition ability with the H\(_3\)PBDC linker compared to the partners. Thus, more defects were formed in the UiO-67(Zr)-HFO sample than in the UiO-67(Zr)-Ac and UiO-67(Zr)-Pr ones (discussed later based on the TGA analysis). When increasing formic acid concentration from 40 to 60 equiv, the surface area and pore volume of the products correspondingly increased, but the further increase to 80 equiv resulted in a decrease of both parameters (Table 1); this can be attributed to a more porous structure generated by the defects formed when using a high modulator concentration [50].

The elemental changes in the UiO-67(Zr) framework when varying the experimental conditions were explored via XPS analysis. Fig. 6(a–c) compare the XPS C, O, and Zr spectra of the UiO-67(Zr) samples synthesized with the different modulators under microwave-assisted continuous flow at 120 °C for 10 min. All the Zr 3d spectra exhibited two peaks at 181.5 (Zr 3d\(_{5/2}\)) and 184 eV (Zr 3d\(_{3/2}\)), similarly to zirconia [51]; this suggests the formation of a well-grown UiO-67(Zr) crystal lattice with Zr\(_6\)O\(_8\) clusters in the Zrk(\(\mu_3\)-O)(\(\mu_3\)-OH)\(_4\)CO\(_2\)\(_2\) second building unit [52] by using the various modulators. The O 1s spectra showed one peak between the binding energy values for Zr–O (530.1 eV) [53] and O–C=O (532.2 eV) [54], indicating a hybrid framework in solution [52]. The C 1s spectra revealed two peaks at around 185 and
289 eV corresponding to C in the hydrocarbon (C–H and C–C) and carboxylate (O–C=O) [54] groups, respectively. Furthermore, these peaks were slightly shifted toward higher binding energies for UiO-67 (Zr)-HFO and UiO-67(Zr)-HAc compared with UiO-67(Zr)-HPro. Among the investigated modulators, HCOOH led to the stronger shifts in the C1s and O1s spectra. This behavior might be related to the difference in the monocarboxylate concentration and their incoordination to metal cluster during the synthesis. Fig. 6(d–f) illustrate the XPS results for the various UiO-67(Zr)-HFO samples. The Zr 3d peaks gradually shifted toward higher binding energy of zirconium hydroxide with increasing the modulator concentration; a similar trend was observed in the O1s and C1s spectra also. This could be because of an undesired coordination of the modulator with the Zr$^{4+}$ cation and a certain extent of ligand vacancies [55], which changed the affected atom surroundings [29].

Fig. 7 and Fig. S2 display the TGA results of the prepared UiO-67(Zr) samples. The TGA curves consisted of three steps: the solvent elimination (25–150 °C), the dehydroxylation and removal of the monocarboxylate ligand from the zirconium cluster (150–350 °C), and the framework decomposition (~450 °C). This is consistent with previously reported results [27,48,55]. The structural unit of defect-free UiO-67 (Zr) is Zr$_6$O$_{44}$(OH)$_{34}$(BPDC)$_{18}$. Hence, the dehydroxylation and removal of the monocarboxylate ligand would result in an inner Zr$_6$O$_{33}$(BPDC)$_{18}$ cluster and the decomposition of the BPDC linker would finally form only the solid product of ZrO$_2$. Thus, the weight at around 450 °C for Zr$_6$O$_{33}$(BPDC)$_{18}$ should ideally be ~64.5% of the initial value. However, the experimental results showed weights much below this theoretical value for all the samples, implying the presence of abundant missing-linker and/or cluster defects in the synthesized frameworks. The use of different modulators resulted in a slightly different magnitude of the decomposition weight loss; in particular, the experimental weight losses of UiO-67(Zr)-HFO, UiO-67(Zr)-HAc, and UiO-67(Zr)-HPro were 43.87%, 45.51%, and 46.89%, respectively. By dividing these values by the theoretical one per each linker of 10.75% (6 linkers for UiO-67) [27], the real numbers of the BPDC linkers per Zr$_6$ formula unit for UiO-67 (Zr)-HFO, UiO-67(Zr)-HAc, and UiO-67(Zr)-HPr were 4.08, 4.23, and 4.36, respectively. This suggests that the defecitivity of the prepared samples slightly increased along with the modulator acidity. As regards the samples prepared with different amounts of formic acid, the modulator concentration strongly influenced their defecitivity although the reaction time was very short; the weight loss decreased with increasing the modulator amount from 40 to 50, 60, and 80 equiv. As a result, the real numbers of the BPDC linkers per Zr$_6$ formula unit were 4.98, 4.32, 4.08, and 3.82, respectively. These data were used to calculate the number of linker deficiencies per Zr$_6$ formula unit for the dehydroxylated molecular formula of Zr$_{6-x}$O$_{33}$x(BPDC)$_{18-x}$ [26,27]; the results were presented in Table 2. The linker deficiency increased along with the modulator acidity and concentration, in agreement with previous reports on the modulated synthesis of Zr-based frameworks via the microwave batch (2.5 h) or the slow solvothermal approach (24 h) [1, 26, 27].

### 3.2. Toluene adsorption and desorption

Fig. 8(a and b) show the breakthrough curves for toluene sorption and the derived toluene adsorption capacities for the various UiO-67(Zr) samples. The breakthrough points were observed after approximately 10 min for all the samples, but the adsorption equilibrium was reached after 85, 70, and 65 min for UiO-67(Zr)-HFO, UiO-67(Zr)-HAc, and UiO-67(Zr)-HPr, respectively. The observed changes in the toluene adsorption capacities could be attributed to the different porosity of the samples, which was related to their linker deficiencies in the following order: UiO-67(Zr)-HFO (467 mg g$^{-1}$) > UiO-67(Zr)-HAc (420 mg g$^{-1}$) > UiO-67(Zr)-HPr (404 mg g$^{-1}$). The results confirmed the tunability of the toluene uptake capacity of the UiO-67(Zr) adsorbents by the modulator species in the microwave-assisted continuous-flow synthesis for 10 min, showing that the type of modulator used in a modulated synthesis of MOFs can influence the sorption ability of the produced adsorbent. Liang et al. [6] found that defective UiO-66(Zr) prepared by using HCl and HCOOH as modulators exhibited greater CO$_2$ and H$_2$O
adsorption abilities than defect-free UiO-66(Zr) and the adsorbate affinities were determined by the modulator species. Table S1 compares the toluene adsorption capacities of various adsorbent materials. The defective UiO-67(Zr) adsorbents rapidly prepared in this study showed remarkably higher capacity than conventional adsorbents such as zeolite (200 mg g$^{-1}$) and activated carbon (183 mg g$^{-1}$), which had lower porosity. Compared with other MOF-based adsorbents, the prepared defective UiO MOFs exhibited considerably higher toluene capacity than most of previously reported materials such as UiO-66(Zr) (130 mg g$^{-1}$), CTAB-modified UiO-66(Zr) (275 mg g$^{-1}$), PVP-modified UiO-66(Zr) (259 mg g$^{-1}$), UiO-66(Zr)–NH$_2$ (252 mg g$^{-1}$), ZIF-8(139 mg g$^{-1}$), ZIF-67(224 mg g$^{-1}$), and Cu-BTC(234 mg g$^{-1}$). This could be due to the fact that the defect-engineered UiO-67(Zr) had higher surface area and pore volume than those of other counterparts. Among the comparative MOFs, only MIL-101(Cr) exhibited a considerably higher toluene adsorption capacity owing to its considerably high surface area and pore volume (Table S1). It is noteworthy that the defect-engineered UiO-67(Zr) adsorbent can be rapidly prepared by a facile and an easily scalable route that makes it more promising material. Fig. 8(c) illustrates the breakthrough curves for the toluene adsorption on the various UiO-67(Zr)-HFo samples; the equilibrium time for UiO-67(Zr)-HFo-40, UiO-67(Zr)-HFo-50, UiO-67(Zr)-HFo-60, and UiO-67(Zr)-HFo-80 was 60, 68, 85, and 70 min, respectively. The toluene sorption ability of the adsorbents was clearly enhanced by increasing the modulator concentration from 40 to 60 equiv. However, the further modulator content increase to 80 equiv reduced this ability. This could be due to the lower surface area of UiO-67(Zr)-HFo-80 compared with UiO-67(Zr)-HFo-60 (Table S1) [56].

The temperature-dependent toluene adsorption by UiO-67(Zr)-HFo-60 was also measured (Fig. S3), revealing a rapid decrease with increasing the temperature; in particular, the toluene adsorption capacities at 25, 50, 75, and 100 °C were 467, 125, 31, and 25 mg g$^{-1}$, respectively. This indicates that the toluene adsorption onto defective UiO-67(Zr) adsorbents is an exothermic reaction, suggesting the significance of the physisorption mechanism between defective UiO-67(Zr) and gaseous toluene molecules [57]. The same phenomenon has been reported for the toluene adsorption on other Zr-based MOFs [1,28,57]. To learn more about the regenerability of the synthesized UiO-67(Zr)-HFo-60, three consecutive adsorption–desorption cycles were performed by switching between gaseous toluene and N$_2$ at 25 °C under atmospheric pressure (Fig. 9). The toluene desorption was slower than its adsorption. Approximately 80% of the adsorbed toluene was desorbed during the first adsorption–desorption cycle; the toluene adsorption capacities at the second and third runs were 283 and 269 mg g$^{-1}$, respectively. This suggests the presence of a strong force between toluene and UiO-67(Zr) framework and the requirement of a higher temperature to swing the adsorption process under atmospheric pressure.

Fig. 5. (a,c) Nitrogen adsorption–desorption isotherms and (b,d) pore size distributions of defective Zr-based biphenyl dicarboxylate (UiO-67(Zr)) samples prepared with different modulators (HPr: propionic acid; HAc: acetic acid; HFo: formic acid) and different concentrations of HFo as the modulator.
The surface area and pore structure of the adsorbents played an important role in their adsorption of volatile organic compounds. The size of their micropores was beneficial for the toluene adsorption because it was similar to the dynamic size of toluene [43,58,59]. As mentioned above, the use of different modulator species and concentrations for the rapid defect engineering of UiO-67(Zr) resulted in drastic changes in their surface area and pore structure, which could affect their toluene adsorption mechanism. The toluene diffusion mechanism in the defective UiO-67(Zr) samples was investigated via the following equation [43]:

\[ q_i = K_i t^{1/2} + C_i \]

where \( q_i \) (in mg g\(^{-1}\)) is adsorption capacity at the time \( t \) (in min), \( K_i \) is the rate constant of the \( i \)-stage, and \( C_i \) is the intercept of the \( i \)-section.

Fig. 6 shows the fitted curves, which revealed a multi-linear structure containing three stages, suggesting that the adsorption process can be divided into three steps: external surface adsorption, particle diffusion, and equilibrium phase [43,60]. Table 3 lists the corresponding fitting parameters. In the external surface adsorption stage, toluene diffuses into the tubular capillaries of the adsorbents; at this stage, the rate followed the order of UiO-67(Zr)-HFo-60 > UiO-67(Zr)-HFo-50 > UiO-67(Zr)-HFo-80 > UiO-67(Zr)-HFo-40, consistently with the trend of the surface area. This indicates that the surface area is a major influencing factor in this stage. In the particle diffusion stage, the adsorption was mainly controlled by the adsorption force between adsorbent and adsorbate; at this stage, the adsorption rate followed the order of UiO-67(Zr)-HFo-60 > UiO-67(Zr)-HFo-50 > UiO-67(Zr)-HFo-80 ~ UiO-67.
The high adsorption rates of UiO-67(Zr)-HFO-60 and UiO-67(Zr)-HFO-50 could be due to their higher micropore volumes, which promoted the toluene diffusion into the pores. The adsorption rate increased along with the total pore volume, implying that this stage was mainly controlled by the pore structure and volume. In the equilibrium adsorption stage, many pores were already saturated and the sorption was dominated by the multilayer adsorption. At this stage, the adsorption rate followed the order of UiO-67(Zr)-HFO-60 > UiO-67(Zr)-HFO-50 > UiO-67(Zr)-HFO-40. These results suggest that the toluene adsorption behavior of defective UiO-67(Zr) was strongly affected by the modulator concentration despite the extremely fast modulated synthesis compared with the slow solvothermal method.

### Dynamic adsorption of toluene

For designing a continuous adsorption process, parameters such as uptake capacity and breakthrough point are key factors. The toluene adsorption behaviors of the prepared UiO-67(Zr) adsorbents were predicted on the basis of their desorption breakthrough curves. The mathematical models of Yan and Thomas, which are commonly used to analyze the column behavior of adsorbent-adsorbate systems \[44, 61, 62\], were utilized to fit the experimental breakthrough data. The following equations were used \[44, 65\]:

\[
\frac{C'_t}{C'_0} = 1 - \frac{1}{1 + \left(\frac{C'_t}{C'_0}\right)}
\]  

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental weight loss (%)</th>
<th>Number of linkers per Zr₆ formula unit</th>
<th>Linker deficiency</th>
<th>Defective dehydroxylated formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-67-HFO</td>
<td>43.87</td>
<td>4.08</td>
<td>1.92</td>
<td>Zr₆O₁₂₂(BPDC)₄₁₃₁</td>
</tr>
<tr>
<td>(60 equiv)</td>
<td></td>
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<tr>
<td>UiO-67-HAC</td>
<td>45.51</td>
<td>4.23</td>
<td>1.77</td>
<td>Zr₆O₁₂₇(BPDC)₄₂₃</td>
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<td>(60 equiv)</td>
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</tr>
<tr>
<td>UiO-67-HPR</td>
<td>46.89</td>
<td>4.36</td>
<td>1.64</td>
<td>Zr₆O₁₂₄(BPDC)₄₃₆</td>
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</tr>
<tr>
<td>UiO-67-HFO-40</td>
<td>53.51</td>
<td>4.98</td>
<td>1.02</td>
<td>Zr₆O₁₂₂(BPDC)₄₆₈</td>
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<td>(60 equiv)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>UiO-67-HFO-50</td>
<td>46.52</td>
<td>4.33</td>
<td>1.67</td>
<td>Zr₆O₁₂₅(BPDC)₄₃₁</td>
</tr>
<tr>
<td>(60 equiv)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>UiO-67-HFO-60</td>
<td>43.87</td>
<td>4.08</td>
<td>1.92</td>
<td>Zr₆O₁₂₂(BPDC)₄₃₈</td>
</tr>
<tr>
<td>(60 equiv)</td>
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<tr>
<td>UiO-67-HFO-80</td>
<td>41.87</td>
<td>3.62</td>
<td>2.18</td>
<td>Zr₆O₆₂₈(BPDC)₅₈₂</td>
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<td>(60 equiv)</td>
<td></td>
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</tr>
</tbody>
</table>
and

$$C_t = \frac{1}{1 + \exp \left( \frac{A_t C_0}{K_t C_0} - K_t C_0 / \right)} \tag{5}$$

where $t$ is the operation time (in min), $A_t$ and $K_t$ are the constants of the Yan and Thomas models, respectively, and $Q_t$ and $Q_n$ (in mg g$^{-1}$) are the uptake capacities estimated by the Yan and Thomas models, respectively. The experimental data were fitted to Equations (3) and (4) via nonlinear least square fitting by using the MATLAB software. The mathematical modeling of the toluene adsorption on UiO-67(Zr)
Table 3
Parameters of the internal toluene diffusion model for defective Zr-based biphenyl dicarboxylate (UIO-67(Zr)) adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(K_1) (mg g(^{-1})min(^{1/2}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UIO-67(Zr)-HFo-40</td>
<td>2.89</td>
<td>0.9235</td>
</tr>
<tr>
<td>UIO-67(Zr)-HFo-50</td>
<td>4.25</td>
<td>0.9894</td>
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<tr>
<td>UIO-67(Zr)-HFo-60</td>
<td>5.84</td>
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<tr>
<td>UIO-67(Zr)-HFo-80</td>
<td>3.84</td>
<td>0.9854</td>
</tr>
</tbody>
</table>

4. Conclusions

Defective UIO-67(Zr) materials with modified pore structure and surface area were successfully prepared through rapid moderated synthesis by using a microwave-assisted continuous-flow tubular reactor. The results showed the quick formation (within 10 min) of high defect concentrations inside the UIO-67(Zr) framework; the missing linker/cluster concentration could be tuned by controlling the modulator acidity and concentration, which allows also the porosity tunability of the synthesized samples. The highest surface area and pore volume (2502 m\(^2\) g\(^{-1}\) and 1.46 cm\(^3\) g\(^{-1}\), respectively) were exhibited by the UIO-67(Zr)-HFo-60 sample. The toluene adsorption on the defective UIO-67(Zr) adsorbents was influenced by their structural defects; high surface area and micropore volumes favored the toluene capture. The prepared defect-engineered UIO-67(Zr) samples exhibited a toluene adsorption capacity up to 467 mg g\(^{-1}\), surpassing most of the reported adsorbents, such as UIO-66(Zr), UIO-66(Zr)-NH\(_2\), ZIF-67, Cu-BTC, zeolites, and activated carbon. Furthermore, the toluene dynamic adsorption on defective UIO-67(Zr) could be predicted well by using the Yan and the Thomas models. These findings indicate fast modulated synthesis with a microwave-assisted continuous-flow system as a promising approach to quickly produce defective UIO-67(Zr) materials; more importantly, this study provides a cost-effective and scalable route to systematically tuning the defectivity in frameworks to obtain novel materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement


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Appendix A. Supplementary data

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References