



Mild, fast and solvent-driven room-temperature synthesis of lamellar $\text{Zn}_2(\text{bim})_4$

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Abstract

A rapid, additive-free, and environmentally friendly synthesis of the two-dimensional metal–organic framework $\text{Zn}_2(\text{bim})_4$ (ZIF-7-III) is achieved in a variety of green solvents. The reaction proceeds rapidly within 10 min at room temperature, eliminating the need for additives, elevated temperatures, or toxic solvents. Lamellar $\text{Zn}_2(\text{bim})_4$ was obtained in water, ethanol, n-propanol, i-propanol, butanol, acetone and selected solvent mixtures. The produced metal–organic framework was characterized by powder X-ray diffraction, Raman spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The results reveal a pronounced solvent-dependent influence on both product yield and particle morphology. Water affords the highest yield (55%) and spherical particles, whereas alcohols and acetone favor the formation of plate- to disc-like morphologies. Notably, the synthesis and all subsequent washing steps were performed using non-toxic solvents, aligning the process with green chemistry principles. This work establishes a fast, energy-efficient, and sustainable route for producing lamellar $\text{Zn}_2(\text{bim})_4$, highlighting solvent choice as a key parameter for controlling material properties for various applications.

Keywords $\text{Zn}_2(\text{bim})_4$ · Solvent-dependent morphology · Green synthesis · Room-temperature MOF synthesis

Introduction

Two-dimensional metal–organic frameworks (2D MOFs) have gained considerable interest owing to their mechanical flexibility, controllable pore architectures, and highly versatile chemical and functional tunability (Adegoke et al. 2022; Xie et al. 2024), enabling applications in sensing, electronics, energy storage and conversion, gas separation, and biocatalysis (Li et al. 2018; Gao et al. 2023; Shu et al. 2023; Liu et al. 2024; Song et al. 2024).

Among these materials, $\text{Zn}_2(\text{bim})_4$ (bim = benzimidazole) is a two-dimensional Zn–imidazolate framework first structurally reported in 2008 (Yang et al. 2008). It consists

of tetrahedrally coordinated Zn(II) centers linked by bim ligands into layered grids, rather than the three-dimensional zeolitic topology characteristic of ZIF-7 polymorphs. While $\text{Zn}_2(\text{bim})_4$ and ZIF-7 share the same Zn:bim stoichiometry, they are crystallographically distinct. This compositional similarity has led to ambiguity in the nomenclature. To avoid confusion, we refer to this compound as lamellar $\text{Zn}_2(\text{bim})_4$ throughout this work.

Traditionally, lamellar $\text{Zn}_2(\text{bim})_4$ is synthesized solvothermally by reacting Zn precursors with benzimidazole in toxic, polar, high-boiling organic solvents such as N,N-dimethylformamide (DMF) (Zhao et al. 2014; Park et al. 2020; Peng et al. 2014). The selection of the solvents originates from the optimal solubility of the precursors in these solvents, favoring the crystallization process. Several by-products can be obtained in this reaction, such as ZIF-7 or $[\text{Zn}_2(\text{PhIm})_3(\text{OH})(\text{H}_2\text{O})] \cdot (\text{DMF})(\text{H}_2\text{O})_3$ (Zhao et al. 2014), lowering the purity of the product. An alternative involves the hydrothermal transformation of ZIF-7 via the hydrolysis of Zn–N bonds (Zhao et al. 2014; Peng et al. 2014; Li et al. 2022). However, this approach requires prior ZIF-7 synthesis, which is also commonly produced using DMF

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as solvent. The multiple synthesis steps reduce the overall reaction yields to around 60% for the first step and 75% for the second step (Cai et al. 2014). Alternative water-based methods have recently been proposed, such as rapid synthesis under ammonia atmosphere (Ebrahimi and Mansournia 2017) or the steam-assisted conversion using water vapor and 4A zeolite templates (Silva et al. 2025) or aqueous formation at 40 °C using high benzimidazole excess in 12 h (Andriotou et al. 2025). Although promising, these approaches still require elevated temperature, high ligand excess, additives, or extended reaction times. Therefore there remains a need for a mild, fast, and simple synthesis route that avoids toxic solvents, external base, and multi-step processing. Given the relevance of lamellar $\text{Zn}_2(\text{bim})_4$ in the field of membrane separation and sensors, a better understanding of the influence of the solvent on the MOF morphology is desired to prepare 2D crystals or nanosheets with homogeneous particle size distribution. Round-shaped $\text{Zn}_2(\text{bim})_4$ particles can be synthesized at room temperature in 24 h using methanol as the solvent (Jin et al. 2016). The formation of a $\text{Zn}_2(\text{bim})_4$ thin film consisting of horizontally oriented $\text{Zn}_2(\text{bim})_4$ crystals on a graphene substrate in only 10 min was also achieved at room temperature in water (Song et al. 2024). However, the ultradilute aqueous conditions required for this method limit its applicability to bulk powder synthesis and restrict it to low-surface-area and graphene-modified substrates. These findings highlight that the room-temperature synthesis of lamellar $\text{Zn}_2(\text{bim})_4$ is possible but strongly influenced by the choice of solvent, which can govern not only the feasibility of powder and layer formation but also the resulting crystal purity and morphology.

This study aims to investigate the influence of different solvents and a reduced reaction time on the synthesis of lamellar $\text{Zn}_2(\text{bim})_4$ powders at room temperature, with a particular focus on crystallinity, morphology, and thermal stability. In a typical procedure, solutions of zinc(II) nitrate hexahydrate (1 mmol) and benzimidazole (6 mmol) were dissolved in single solvents or solvent mixtures, which are listed in Table 1. Upon mixing the Zn^{2+} and benzimidazole

precursor solutions, a white precipitate immediately formed, indicating the rapid nucleation and growth of lamellar $\text{Zn}_2(\text{bim})_4$ crystals. In contrast to literature procedures employing an external base, benzimidazole here serves both as ligand and proton acceptor. This self-buffering behavior was confirmed by ^1H NMR spectroscopy and pH measurements of the reaction filtrates (Fig. S1, Table S1). The NMR spectra show downfield-shifted benzimidazole-derived aromatic resonances, consistent with protonated and/or hydrogen-bonded species, while the filtrates are acidic (pH ~5 in water and ~3.8 in ethanol for $\text{bim}:\text{Zn}=6:1$). These observations demonstrate that protons released during Zn-benzimidazolate formation are accommodated in the liquid phase and partially buffered by excess benzimidazole. This behavior differs from base-assisted syntheses reported in the literature, where rapid and extensive deprotonation promotes the formation of three-dimensional ZIF-7 frameworks. The milder and self-regulated generation of benzimidazolate under the present conditions is therefore consistent with the selective formation of lamellar $\text{Zn}_2(\text{bim})_4$.

Additional syntheses with lower Zn:bim ratios (Table S3) further support this interpretation. Reducing the ligand excess from 1:6 to 1:2 leads to a marked decrease in isolated yield (from 55.0% to 35.9% in water and from 23.0 to 5.8% in ethanol), indicating that excess benzimidazole plays a key role in promoting efficient product formation under these additive-free conditions, consistent with its dual function as ligand and proton acceptor.

The suspension was aged for 10 min and washed with ethanol and water. After centrifugation, the solids were collected in deionized water and dried at 70 °C overnight. The detailed synthesis and characterization procedures are given in the Supporting Information. Table 1 summarizes the solvents, molar ratios, phases obtained, and resulting particle morphologies. The synthesized powders were systematically labelled as ZNBIM-solvent, where solvent denotes the pure solvent or solvent mixture used during the synthesis.

Powder X-ray diffraction analysis was conducted to characterize the synthesized products (Fig. 1). All diffraction

Table 1 Overview of the solvents used, molar ratios applied and particle morphology for the $\text{Zn}_2(\text{bim})_4$ samples produced at room temperature

Sample code	Solvent	$\text{Zn}^{2+}/\text{bim}/\text{solvent(s)}$	Particle morphology	Yield (%)
ZNBIM-Ace	Acetone	1/6/1400	Square plates (up to 3 μm)	24
ZNBIM-BOH	Butanol	1/6/1400	Square plates (up to 6 μm)	24
ZNBIM-isoPOH	Iso-propanol	1/6/1400	Square plates (up to 6 μm)	24
ZNBIM-nPOH	n-propanol	1/6/1400	Square/round shape plates (up to 6 μm)	25
ZNBIM-EtOH	Ethanol	1/6/1400	Square/round shape plates (up to 3 μm)	27
ZNBIM-EtOH: Ace	31 v/v% EtOH: Acetone	1/6/500/900	Square plates (up to 12 μm)	21
ZNBIM-EtOH: H_2O	65 v/v% EtOH: H_2O	1/6/500/900	Square plates (up to 3 μm)	15
ZNBIM- H_2O	Water	1/6/1400	Imperfect spheres (up to 6 μm)	55

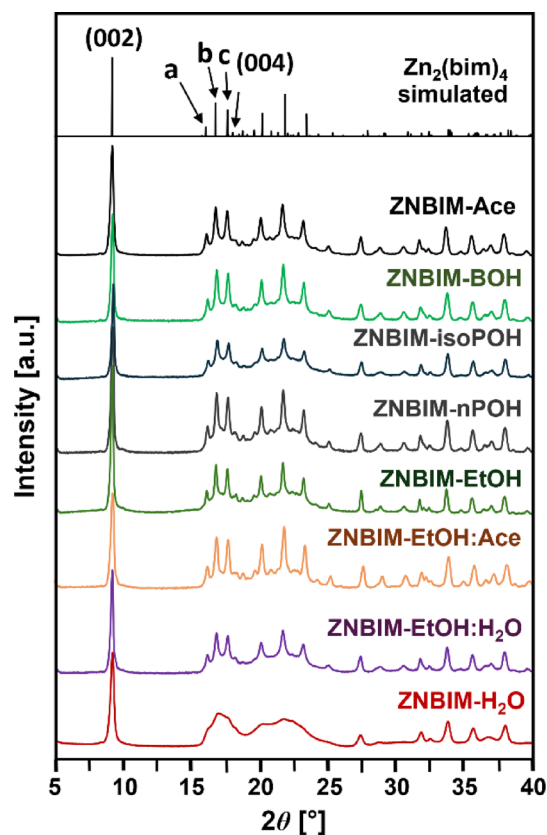


Fig. 1 Powder X-ray diffraction patterns of the $\text{Zn}_2(\text{bim})_4$ (ZIF-7-III) powders, prepared in different solvents. For explanation of the sample codes, see Table 1. The notations a, b, and c refer to the Miller indices (22–1), (221), and (22–2), respectively

patterns match the reported reference for lamellar $\text{Zn}_2(\text{bim})_4$ (ZIF-7-III) (CCDC 675375). No secondary crystalline phases from the derivatives ZIF-7-I and ZIF-7-II, or impurities, like ZnO, were observed. Notably, the result obtained for the sample ZNBIM- H_2O , synthesized using water, displayed a pronounced peak broadening at $2\theta \sim 19$ and 23° , which could be the result of small particle size, also observed during the synthesis of $\text{Zn}_2(\text{bim})_4$ using water as a solvent and NaOH as a base (Silva et al. 2025). Elemental analysis of $\text{Zn}_2(\text{bim})_4$ (Table S2) samples prepared in water and ethanol gave comparable C, H, and N contents of 57.0, 3.4, and 19.1 wt% and 56.8, 3.2, and 18.5 wt%, respectively, with C/N ratios close to the theoretical value of $\text{Zn}_2(\text{bim})_4$, supporting the conclusion of the formation of a relatively pure product.

To assess the possible presence of ZIF-7-I or its thermally induced amorphous phase (ZIF-7-II), Raman spectroscopy was conducted. The Raman spectra originate from the various vibrational modes of both the bim ligand and the framework lattice. The tetrahedral vibrational mode of the lattice and the torsional mode of the imidazolate ring can be seen in Fig. 2I–II. Importantly, the peak typically associated with

the C–H in-plane bending vibration of the benzimidazole ring for ZIF-7-I at 870 cm^{-1} is not visible (Fig. 2III). These results, together with the distinctive Raman bands from the $\text{Zn}_2(\text{bim})_4$ compared to the ZIF-7-I and ZIF-7-II phases, confirm the high phase purity of the products obtained. The full Raman spectrum can be found in the supporting information (Fig. S2).

SEM images of $\text{Zn}_2(\text{bim})_4$ powders synthesized in different solvents are shown in Fig. 3a–h. Samples prepared in organic solvents exhibit the plate-like morphology typical for the lamellar $\text{Zn}_2(\text{bim})_4$ phase, although particle sizes and thicknesses varied with the solvent. Powders synthesized in acetone consisted of comparatively thin plate-like particles, with thicknesses up to $\sim 500\text{ nm}$ and lateral dimensions up to $6\text{ }\mu\text{m}$. In contrast, particles obtained from butanol, n-propanol, and isopropanol showed similar lateral dimensions (up to $6\text{ }\mu\text{m}$) but are considerably thicker, exceeding $10\text{ }\mu\text{m}$. Ethanol-derived powders were generally smaller but appeared relatively thick, and in some regions exhibited rounded particles similar to those reported for methanol-synthesized $\text{Zn}_2(\text{bim})_4$ (Jin et al. 2016). In contrast, the water-derived sample does not consist of smooth spheres but rather of spherical agglomerates composed of smaller crystallites (Fig. 3h and S3). Longer reaction times in water promote the formation of more uniform and well-defined spherical assemblies of these crystallites (Fig. S3) as well as thinner plate-like particles compared to those obtained in pure ethanol (see Fig. 3h). The emergence of this sphere-like morphology in an aqueous medium is attributed to their lower surface-to-volume ratio and reduced interfacial contact between the hydrophobic $\text{Zn}_2(\text{bim})_4$ crystals and the aqueous medium. A summary of the observed morphologies is presented in Table 1. Overall, these results confirm that particle morphology is strongly influenced by the solvent.

To quantify the trapped solvent in the MOF structure, the samples were analyzed by thermogravimetric analysis (TGA). Figure S4 shows TGA weight loss curves for the $\text{Zn}_2(\text{bim})_4$ powders synthesized in different solvents. All samples exhibit no weight loss below $\sim 200^\circ\text{C}$, confirming the absence of loosely bound solvents. A distinct weight loss at $\sim 200^\circ\text{C}$ appeared due to strongly bound pore solvents. The weight loss varied slightly by synthesis solvent, suggesting incomplete solvent exchange influenced by solvent size, for example the smaller molecular size of water leads to higher retention and enables deeper pore infiltration. Framework degradation began at $\sim 600^\circ\text{C}$, consistent with literature (Sherman et al. 2023). The isolated yields obtained using different solvents are summarized in Table 1. Water gave the highest isolated yield (55%), whereas the organic solvents resulted in lower but comparable yields of 24–27%. One possible explanation is the lower solubility of benzimidazole in water compared with the organic solvents.

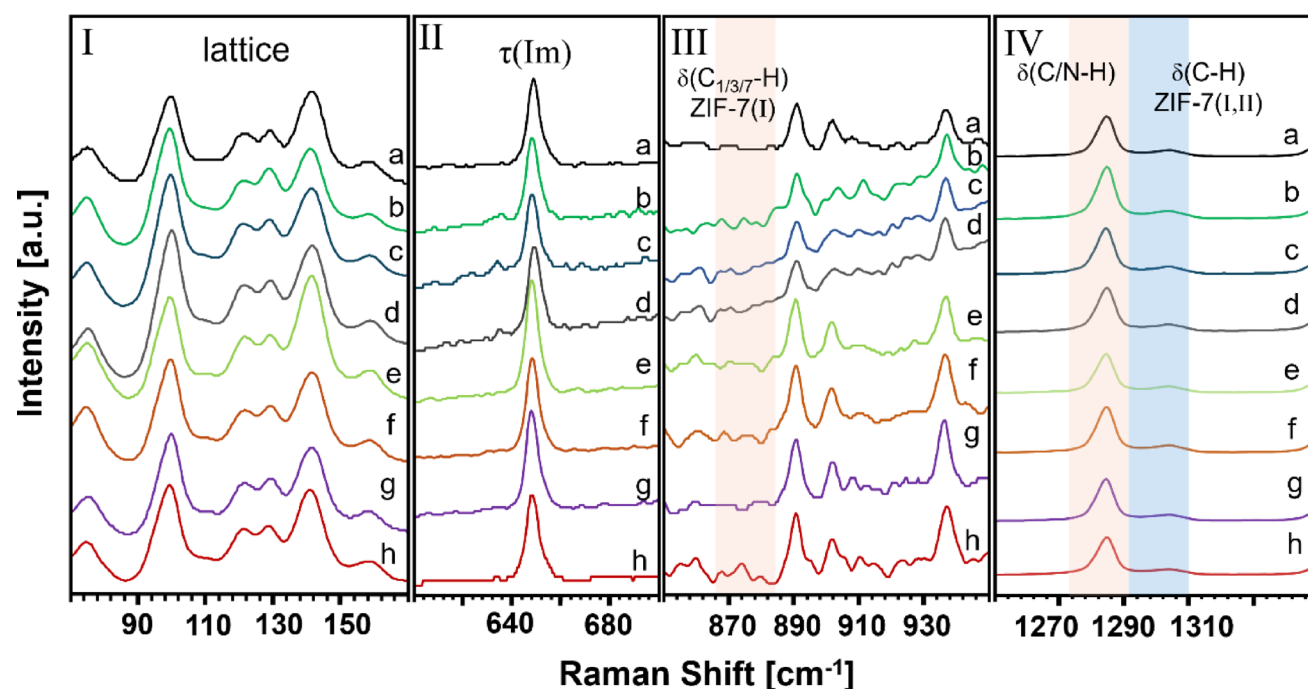


Fig. 2 Raman spectra in the region 70–170 (I), 600–700 (II), 850–950 (III) and 1250–1350 cm^{-1} (IV) of the $\text{Zn}_2(\text{bim})_4$ powders prepared in: **a** acetone, **b** butanol, **c** iso-propanol, **d** n-Propanol, **e** ethanol, **f**

31 v/v% EtOH:Acetone, g 65 v/v% EtOH:H₂O mixture, h water. The orange zone indicates the area where vibration bands are expected for the ZIF-7-I or ZIF-7-II phases

In organic media, the better dissolution and more homogeneous distribution of benzimidazole may stabilize soluble Zn–bim species or small nuclei for longer, thereby delaying precipitation and reducing the amount of recoverable solid. In contrast, the limited solubility of benzimidazole in water may promote local supersaturation, faster nucleation, and agglomeration of small crystallites, resulting in a larger recoverable product fraction. This interpretation is consistent with the spherical agglomerates observed for the water-derived sample and the broadened PXRD reflections, which indicate smaller coherent crystallite sizes. Under highly diluted conditions, however, direct hydrolysis of ZIF-7 may be favored. In such cases, the reduced agglomeration minimizes shielding effects, allowing smaller particles, which degrade faster, to undergo more efficient transformation (Velásquez-Hernández et al. 2019). $\text{Zn}_2(\text{bim})_4$ is often described as the “dense” or more hydrophilic phase relative to ZIF-7 (Zhao et al. 2014; Navarro et al. 2025). The higher density likely reduces its exposure to water, stabilizing the framework. Additionally, the pore size of lamellar $\text{Zn}_2(\text{bim})_4$ is significantly smaller than the pore size of ZIF-7-I, reducing the ability of water to infiltrate the structure (Peng et al. 2014; Xiao and Liu 2019).

In conclusion, lamellar $\text{Zn}_2(\text{bim})_4$ was successfully synthesized rapidly at room temperature using a variety of polar solvents, selected for their low toxicity and favorable environmental profile compared to more toxic standard solvents, like DMF and methanol. All solvents led to a high-purity product without traces of ZIF-7-I or ZIF-7-II. Water promoted the formation of isotropic, spherical particles with high yield (55%), while the organic solvents used in this study lead to thin plate-like morphologies. The ability to tailor particle morphology through solvent selection could be particularly advantageous for applications in catalysis or membrane fabrication, where surface area or the ability to form a thin layer is critical. The washing procedure was done without the use of toxic solvents. While the use of excess benzimidazole reduces atom efficiency, preliminary experiments indicate that the reaction filtrate can be reused by addition of fresh zinc precursor, enabling further recovery of $\text{Zn}_2(\text{bim})_4$. This approach highlights a potential route to improve the overall sustainability of the process and will be the subject of future investigation. By reducing the need for toxic solvents and high temperatures, this approach aligns well with green chemistry principles, making it possible to produce lamellar $\text{Zn}_2(\text{bim})_4$ on a large scale for application in catalysis, membranes, or sorbent materials.

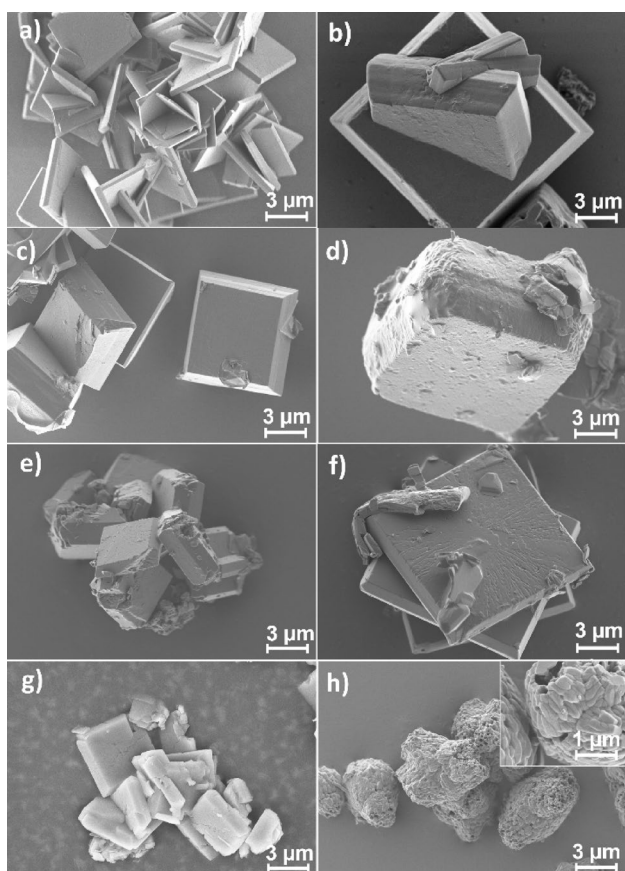


Fig. 3 FE-SEM images made of $\text{Zn}_2(\text{bim})_4$ powders prepared using different solvents: **a** acetone, **b** butanol, **c** iso-propanol, **d** n-propanol, **e** ethanol, **f** 31 v/v% ethanol and acetone, **g** 65 v/v% ethanol and water, and **h** water

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Data availability The data are available upon request.

Declarations

Conflict of interest The authors declare no competing interests.

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