

A green route approach to the synthesis of Ni(II) and Zn(II) templated metal–organic frameworks

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Abstract A new synthetic route involving mixing of solid reactants followed by heating has been developed for the preparation of two templated metal–organic frameworks (MOFs). $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$ (**1**) was obtained by mixing together $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4,4-bipyridine and pyrene followed by heating at 85 °C for 4 h, while $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ (**2**) was synthesized by mixing together $\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$, fumaric acid and 4,4-bipyridine followed by heating at 160 °C for 16 h. The materials were characterized by elemental analysis, FT-IR spectroscopy and X-ray powder diffraction analysis (XRPD). Comparison of XRPD patterns of the materials with patterns simulated from the single crystal X-ray diffraction data, obtained from Cambridge Structural database, allowed identification of the products. Conversion of solid reactants to MOFs occurs spontaneously even when reactants are not mechanically stressed. Overall, the study suggests that MOFs can be synthesized in solid state simply by mixing together appropriate reactants without co-mill (ball-mill). Compared with traditional synthetic techniques such as solvothermal, ball-milling and solution-based, this method is environmentally friendly and highly efficient in the manufacture of these MOFs on a large scale.

Introduction

The main goal of green chemistry approach to synthesis is to produce functional materials through a process that reduce or eliminate hazardous waste generation which are harmful to human health and the environment [1, 2]. Furthermore, concerns about costs of solvents and the long-term harmful effects on the environment when solvents are discarded after use have led investigations into solvent-free synthetic method as a form of green chemistry [3]. Continued interests in metal–organic frameworks (MOFs) during the past decade stems from their unique properties such as large pore volume, apparent surface area, tuneable structures and controllable functionalities [4]. Therefore, many applications have been proposed for MOFs; however, these applications are still in their infancy stage and have not yet been commercialized. A lot of MOFs have been synthesized by a variety of solvent-based methods, ranging from solvothermal conditions over several days to reflux for several hours at reaction temperature ranging between room temperature and approximately 220 °C [5–8]. A number of parameters such as different metal salts, solvent or mixture of solvents, presence of additives, molar ratios of the starting materials, reaction temperature and reaction time can be varied to investigate the mechanism of reactions. Recently, alternative synthetic methods such as electrochemical, sonochemical, microwave heating and mechanochemistry have been employed to introduce energy into the reaction systems [9, 10].

The first solvent-free mechanochemical synthesis of a microporous MOF $[\text{Cu}(\text{INA})_2]$ using ball-mill was reported in 2006 [11]. Since then, there is continued interest in the use of mechanochemical method to prepare MOFs and metal complexes. Most of the studies carried out on synthesis of MOFs in solid state involved the use of ball-mills

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[12–16]. Unfortunately, ball-mills suffer some limitations such as temperature control, low yields and contamination of the products by ball materials. Also, application of this method in large scale in industries remains a distant goal. Developing highly efficient and environmentally friendly synthetic processes for MOFs has therefore become an emerging challenge.

Furthermore, mechanism and principles of the synthesis of coordination polymers in the solid state are still not well established. To provide effective alternative routes to the synthesis of the MOFs, new techniques which are simple and efficient are being developed. The main objective of this study therefore is to discover more facile synthetic approach to the reported MOFs $[\text{Zn}_2(\text{Fumarate})_2(\text{bipy})]$ [17] and $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$ [18]. These compounds have been prepared previously using ball-mill and solvent-based techniques [16–20]. With this study, we wish to draw the attention of chemistry community to the fact that MOFs can be synthesized in the solid state simply by mixing together appropriate reactants followed by heating. The procedure is simple; it requires no complex apparatus and allows large scale preparation of the MOFs materials.

Experimental

Materials and instrumentation

All reagents were commercially sourced from Sigma-Aldrich chemical company and were used as received. The reactants were ground separately at room temperature using mortar and pestle in air. About 500 mg of reactant was ground for 30 s. Infra-red spectra were obtained from samples in the form of KBr pellets using a Perkin Elmer FT-IR spectrometer. Metal analyses were carried out by atomic absorption spectroscopy with a Perkin Elmer Spectrometer, model 3110. The analyses of carbon, hydrogen and nitrogen were carried out on a Perkin Elmer 204C microanalyser. Powder XRD analysis was performed on a Syntag PADS diffractometer at 294 K using $\text{Cu } K_\alpha$

radiation ($\lambda = 1.54059 \text{ \AA}$). Ball-mill apparatus was a RetchMM2000.

Synthesis

The two MOFs were prepared using two different techniques, the ball-mill and mixing of ground solid reactants followed by heating (MHSFR). For the ball-mill method, the procedure described in the literature was adopted [11]. For MHSFR techniques, mixtures were prepared using reactants in the molar ratios reported in literature for the ball-mill method [11].

Synthesis of $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$ (1)

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (291 mg, 1 mmol), 4,4-bipyridine (312 mg, 2 mmol) and pyrene (404 mg, 2 mmol) which have been previously ground separately were mixed in a vial till homogenous mixture was obtained (about 5 min). The mixture was characterized by FT-IR spectroscopic and X-ray powder diffraction (XRPD) techniques prior to heating. The mixture was then heated at 85°C for 4 h on oil bath. The resulting product was allowed to cool to room temperature (Scheme 1).

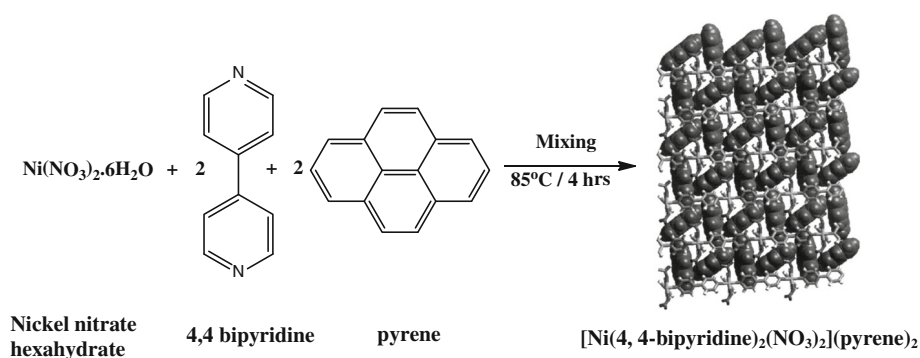
Synthesis of $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ (2)

$\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (440 mg, 2 mmol), fumaric acid (232 mg, 2 mmol) and 4,4-bipyridine (156 mg, 1 mmol) which have been previously ground separately were mixed together in a vial. Mixture was characterized by FT-IR and XRPD prior to heating. The mixture was then heated at 160°C for 16 h using an oil bath. The resulting product was allowed to cool to room temperature (Scheme 2).

Results and discussion

Introduction of an organic compound that will not coordinate to the metal centre but instead act as a template

Scheme 1 Solvent-free reaction to form $[\text{Ni}(\text{4,4-bipyridine})_2(\text{NO}_3)_2](\text{pyrene})_2$ and the structure of $[\text{Ni}(\text{4,4-bipyridine})_2(\text{NO}_3)_2](\text{pyrene})_2$ reproduced from Biradha et al. [18] with permission of The Royal Society of Chemistry



Scheme 2 Solvent-free reaction to form $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ and the structure of $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ reprinted from Ma et al. [17] with permission of The American Chemical Society

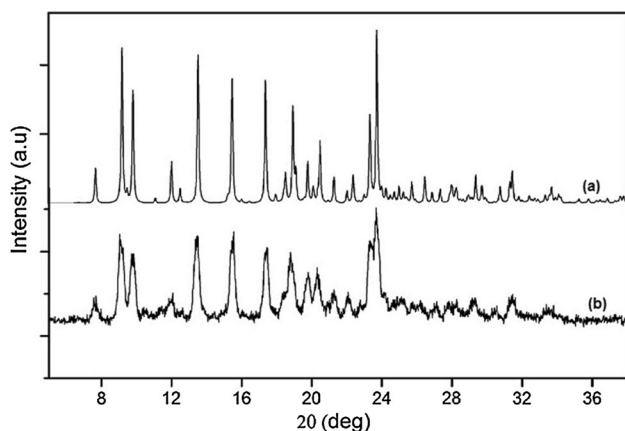
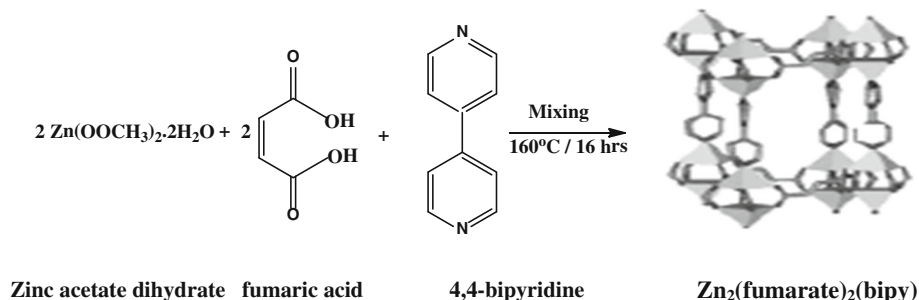


Fig. 1 Comparison of XRPD patterns of $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$ *a* pattern simulated from X-ray single crystal data (CSD Code: GOSSEM) and *b* product **1**

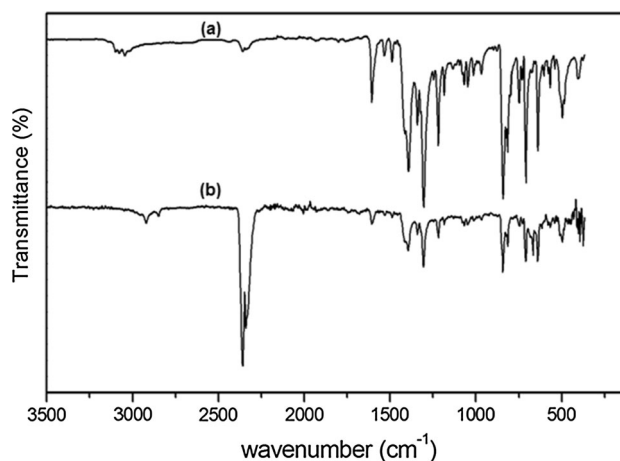


Fig. 2 Comparison of FT-IR spectra of $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$ *a* product **1** and *b* product obtained from the ball-mill method

during crystal growth to direct the formation of the overall topology are usually carried out using solution-based and mechanochemical methods [15–20]. Reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 4,4-bipyridyl and pyrene in 1:2:2 ratio gave $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$. The mixture obtained after mixing reactants prior to heating consists of starting materials, with some additional peaks suggesting no clear evidence of reaction as shown in Fig. S1. Figure S2 shows the appearance of **1** as a function of temperature and time. There is phase evolution of $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$ as temperature increases at a reaction time of 4 h. The optimum temperature required for the complete product formation is 85 °C at this reaction time as shown in Fig. S2. The heating lead to acceleration both at the stage of nucleation and crystal growth. It can be seen in Fig. S2 that there are no unreacted or partially reacted starting materials in the product. The XRPD patterns of material **1** matched well with the pattern of the product obtained from ball-mill method as shown in Fig. S3. The single crystal diffraction data for $[\text{Ni}(\text{NO}_3)_2(\text{bipy})_2](\text{pyrene})_2$ reported in Ref 18 was obtained from the Cambridge Structural database (CSD code GOSSEM). Its XRPD pattern was simulated from the single crystal data using mercury 1.3 software and compared to that of

1 obtained by MHSFR. Comparing the XRPD patterns of product **1** with those of the simulated one, the XRPD pattern of product **1** revealed major peaks at $2\theta = 6.78, 8.22, 8.92, 11.12, 12.64, 14.64, 16.42, 17.98, 18.90, 19.56, 20.36, 21.20, 22.38, 22.92, 28.42, 30.54$ and 32.62 , while those of the simulated pattern were found at $6.78, 8.30, 8.86, 11.12, 12.56, 14.58, 16.48, 18.06, 18.90, 19.60, 20.38, 21.14, 22.44, 22.82, 28.48, 30.56$ and 32.80 . It can be observed from the 2θ values that the XRPD pattern of product **1** and the simulated pattern are in close agreement as shown in Fig. 1.

Comparison of the IR spectra of **1** before and after heating revealed that the latter shows additional peaks (Fig. S4). The spectra are not similar; this shows that heating is necessary for the formation of product. The IR spectra of **1** and the one obtained from the ball-mill method closely matched, this further proved that resulting compounds from both methods are similar as shown in Fig. 2. The elemental analysis data for C, H and N shown in Table S1 are in close agreement and consistent with the formula unit of product **1**.

Reaction of $\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$ with fumaric acid and 4,4-bipyridine in 2:2:1 molar ratio using MHSFR technique gave $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ (**2**) in quantitative yield. Formation of **2** required heating the mixed reactants at 160 °C

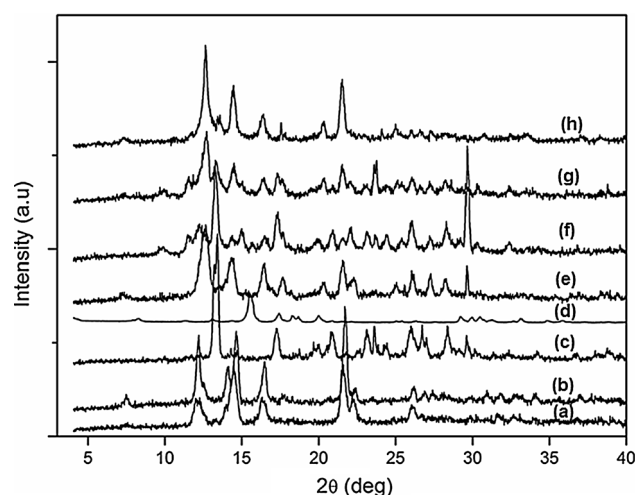


Fig. 3 XRPD patterns showing progress of reaction for the formation of $\text{Zn}_2(\text{fumarate})_2(\text{bipy})$ *a* ball-milling product, *b* 160 °C/16 h, *c* mixture, *d* 65 °C/16 h, *e* 100 °C/16 h, *f* 110 °C/16 h, *g* 130 °C/16 h, and *h* 150 °C/16 h

for 16 h and the identity of the MOFs formed was established by comparing the XRPD patterns of the starting materials and the mixture prior to heating as shown in Fig. S5. The patterns are different from those of starting materials this indicated formation of new phase, while the appearance of some peaks attributable to the starting materials indicated that the reaction has not gone fully to completion at this stage. The progress of the reaction was monitored by XRPD analysis as shown in Fig. 3. There were formations of new phases as temperature increases at constant time. The results showed that the product at 150 °C for 16 h still contains small traces of both starting materials, indicating that the reaction has not fully gone to completion. However, at a temperature of 160 °C all the traces of starting materials have disappeared. Therefore, the MHSFR technique requires a reaction time of 16 h at 160 °C to get a single phase of $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$. It can also be observed that the XRPD patterns of the material obtained from ball-mill and product **2** are similar.

The single crystal diffraction data for $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ reported by Ma et al. [17] was also obtained from the Cambridge Structural database (CSD code MAVNUT01). The XRPD pattern was simulated from the single crystal data using mercury 1.3 software. The XRPD pattern of product **2** and that of the simulated pattern were also compared with those of the starting materials as shown in Fig. S6. From the figure, one can observe that XRPD pattern of the product and that of the simulated pattern were identical but quite different from those of the starting materials. Furthermore, three XRPD patterns (Fig. S7) of reaction products at (160 °C/16 h, 150 °C/16 h and 100 °C/16 h) were selected and compared with simulated

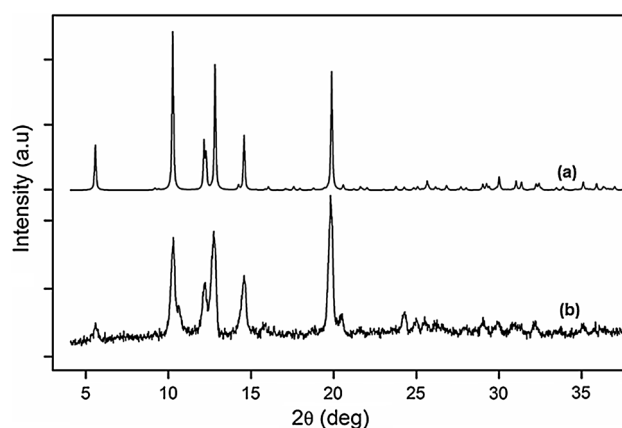


Fig. 4 Comparison of XRPD patterns for $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ *a* simulated pattern obtained from the X-ray single crystal data CSD code MAVNUT01 and *b* product **2**

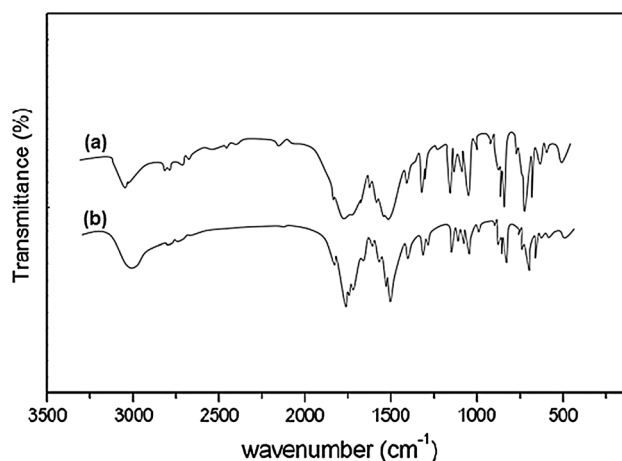


Fig. 5 Comparison of FT-IR spectra of $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ *a* product **2** and *b* the product obtained from the ball-mill technique

pattern. It was revealed that a single phase of $[\text{Zn}_2(\text{fumarate})_2(\text{bipy})]$ was successfully obtained after the mixture was heated at 160 °C for 16 h. Quantitative estimation of the 2θ of XRPD pattern of the product and that of the simulated pattern was carried out. The major peaks in the XRPD pattern of product **2** were observed at $2\theta = 5.60, 10.18, 12.28, 12.74, 14.54, 15.88, 19.80, 20.44, 29.04, 29.88$ and 32.26 , while those of the simulated pattern were observed at $2\theta = 5.58, 10.26, 12.16, 12.82, 14.58, 16.06, 19.88, 20.56, 29.02, 30.02, 32.08$ and 32.24 . The closeness of the 2θ values as shown in Fig. 4 indicates that the two compounds are essentially the same.

The IR spectrum of **2** was compared with that of the ball-mill product and the results that there is no significant difference in the spectra of the two samples (Fig. 5). The elemental analysis data for both products are

identical as presented in Table S2 and also supports the formula unit.

Conclusion

In summary, two known templated MOFs were synthesized by mixing solid reactants followed by heating without co-milling or ball-milling. We have demonstrated in this study that the method is an efficient and environmentally friendly route to the synthesis of these MOFs under solvent-free condition. The method is able to compete with the mechanochemical technique by ball-mill and solution-based methods with gains in simplicity and efficiency.

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