Facile synthesis of nanocrystals of a microporous metal–organic framework by an ultrasonic method and selective sensing of organoamines†

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In this work we present the rapid synthesis of nanocrystals of a fluorescent microporous metal-organic framework using an ultrasonic method, and their utility for selective sensing of organoamines.

Microporous metal–organic frameworks (MOFs)[1] have attracted extensive attention in recent years owing to their intriguing structural motifs and their potential applications in catalysis,[2] adsorption,[3] magnetism,[4] photonics,[5] and molecular sensing.[6] Compared with traditional porous materials, MOFs are synthesized under mild conditions and allow the systematic engineering of chemical and physical properties through modifications of their components.[1] Very recently, increasing investigations have been focused on the design and construction of nanoscale MOFs[7,8] because this novel type of nanoscale material has potential in a variety of imaging, biosensing, biolabeling, and drug delivery applications.

Compared with the solvent diffusion approach to the construction of nanocrystalline MOFs,[7] in which long reaction times (over 2 days) and a large amount of solvent are needed, microwave and reverse micromulsion methods have been demonstrated to be more efficient. However, no evidence shows that dimensionality of the nanocrystals of MOFs could be tuned using the microwave method, although the size of the particles is tunable by varying the reaction time and the concentration of the precursor.[7] In the case of the reverse micromulsion method, although good control over the dimensions of the nanoscale materials can be realized,[7] removal of the surfactants from the nanoparticle surface can require harsh conditions or multiple washings to remove unwanted materials. Especially for sensing applications such as luminescence or surface-enhanced Raman scattering that require analyte adsorption to the surface of the materials, the presence of residue from the synthesis on the nanoparticle surface may be a significant interferent.[9] Furthermore, synthesis of nanomaterials on a large scale using the reverse micromulsion method may lead to environmental pollution and a high cost of the product due to the large amount of surfactants used in these systems.

Herein, we present a facile and environmentally friendly synthesis of nanocrystals of MOF with "clean" surfaces under ultrasonic irradiation. Although the ultrasonic approach has been widely used for organic synthesis[10] and the preparation of nanosized materials,[11] to date the application of the ultrasonic method for the construction of MOFs remains unexplored. In this work, we describe the rapid synthesis of nanocrystals of a fluorescent microporous MOF, $Zn_3(BTC)_2\cdot 12H_2O$ (**1**, Fig. 1) and selective sensing of organoamines using nanocrystals of **1**. The results reveal that ultrasonic synthesis is a simple, efficient, low cost, and environmentally friendly approach to nanoscale MOFs. Particularly, nanocrystals of MOF **1** shows high sensitivity and selectivity for the sensing of ethylamine. To the best of our knowledge, this is the first example of synthesis of MOF using the ultrasonic method.

MOF **1** was synthesized using the ultrasonic method at an ambient temperature and atmospheric pressure for different reaction times of 5, 10, 30, and 90 min, respectively. A control experiment was also carried out to synthesize compound **1** using the hydrothermal method,[12] and the structures were confirmed by IR, elemental analysis and Rietveld analysis of the powder X-ray diffraction (XRD) patterns using WinPLOTR and Fullprof[13] (see ESI†). Surprisingly, the reaction of zinc acetate dihydrate with benzen-1,3,5-tricarboxylic acid (H_3BTC) in 20% of ethanol in water (*v*/*v*) under ultrasonic irradiation at ambient temperature and pressure for 5 min gave **1** in a remarkably high yield (75.3%, based on H_3BTC). Also, the yield of **1** increased gradually from

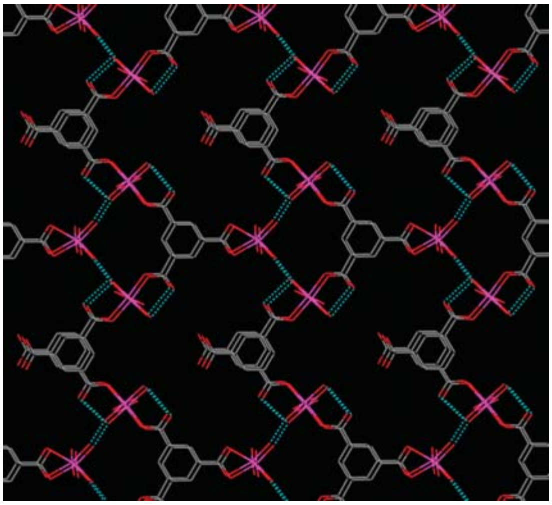

Fig. 1 Molecular-packing diagram of **1** viewed along the *c*-axis, showing open metal sites in 1-D channels created in 3-D supramolecular metal-organic framework.

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78.2% to 85.3% with increasing the reaction time from 10 to 90 min. This result suggests that rapid synthesis of MOF can be realized in a significantly high yield using ultrasonic method. Compared with hydrothermal synthesis of the same compound MOF **1**, which is carried out at 140 °C at high pressure for 24 h,[12] ultrasonic synthesis is found to be a highly efficient method with high yield and low cost.

Ultrasonic irradiation must play an important role during the formation of MOF **1** because no product was obtained by mixing zinc acetate with H_3BTC in the same reaction medium at ambient temperature and pressure in the absence of ultrasound. Many researchers have investigated the effect of ultrasound on chemical reactions, and most theories imply that the chemical effect of ultrasound originate from acoustic cavitation within collapsing bubbles, which generates localized hot spots with an exceedingly high transient temperature (5000 K), pressure (1800 atm), and cooling rate (10^{10} K s^{-1}).[10,11,14] Between the microbubble and the bulk solution, the interfacial region around the bubble has very large gradients of temperature, pressure, and the rapid motion of molecules leading to the production of excited states, bond breakage, the formation of free radicals, mechanical shocks, and high shear gradients.[10] As a result, many kinds of chemical reactions, even some reactions that were previously difficult to realize by other traditional methods, can also proceed using ultrasonic irradiation.[10,14] In this work, high transient temperatures and pressures should play important roles in the activation and the coordination reaction between metal ions and H_3BTC, although other special effects of ultrasonic irradiation may also affect the reaction and crystallization.[15]

Transmission electron microscopy (TEM) images of MOF **1** revealed nanoparticles in a size range of 50–100 nm for short reaction times (5 and 10 min, see Fig. 1(a) and (b)), and the size of the nanoparticles increased with increasing reaction times. Interestingly, when the reaction time increased to 30 min, nanocrystals of **1** with a diameter of 100–200 nm and a length of up to 100 μm or more were obtained in a high yield (Fig. 2(c)). When the reaction time increased as long as 90 min, the diameter of nanocrystals of **1** increased to 700–900 nm (Fig. 2(d)). These results may be useful for scientists to control the dimensionality of nanoscale MOFs with tunable size and shape by varying the reaction time.

All products of MOF **1** obtained using the ultrasonic method for 5–90 min exhibited strong blue solid state fluorescence at room temperature with an emission maximum at 414 nm upon excitation at 327 nm, which could be assigned to the fluorescence from intra-ligand emission excited state.[16] Selective sensing of organoamines was examined based on the solid state fluorescence response of nanocrystals of **1** to amines. Amines are one of the most poisonous pollutants in waste water. Although some kinds of sensors have been developed for the determination of organoamines, their low selectivity and sensitivity toward amines make them impractical.[17] Consequently, the development of sensitive and reversible sensors and simple monitoring systems distinguishing molecular species would be extremely useful in environmental technology.

The sensing of organoamines in an acetonitrile solution was quantitatively analyzed by a fluorescence spectrometric titration experiment. Although all nanoscale MOF **1** showed similar fluorescence emission, nanocrystals of **1** synthesized for 90 min were used for the sensing experiments. The variation of emission intensity with the concentration of organoamine was obtained by injecting different amounts of amine into a 1 cm cuvette containing 2.00 mL of acetonitrile, in which a slice of glass coated with nanocrystals of **1** was fixed (Fig. S1, see ESI†), and the results are shown in Fig. 3. No response of emission intensity to ethylamine was observed when its amount was lower than 1.25 μL. Upon increasing the volume of ethylamine from 2.5 to 13.75 μL, corresponding to contents from 0.125% and 0.683% (*v*/*v*), respectively, the emission intensity decreased gradually from approximately 7500 to 6100 a.u. However, a remarkable decrease of emission intensity was observed when the volume of ethylamine added into acetonitrile was larger than 13.75 μL; a significant fluorescence quenching effect was observed when 17.50 μL (0.867%, *v*/*v*) of ethylamine was added. This result suggests

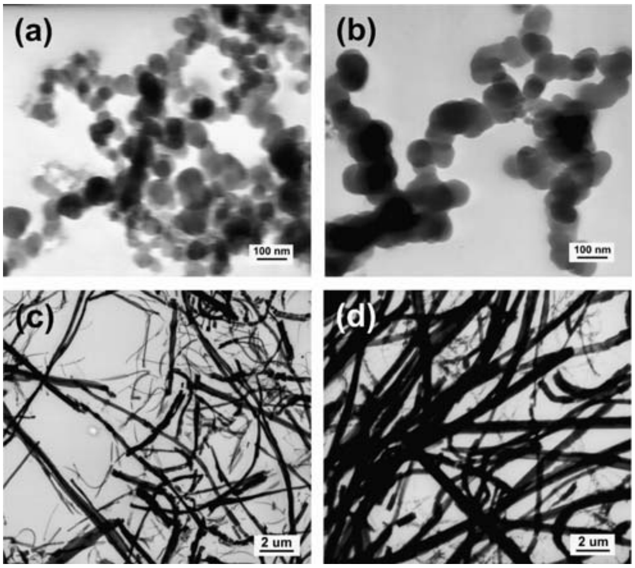

Fig. 2 TEM images of **1** synthesized using ultrasonic method for various reaction times: (a) 5, (b) 10, (c) 30, and (d) 90 min.

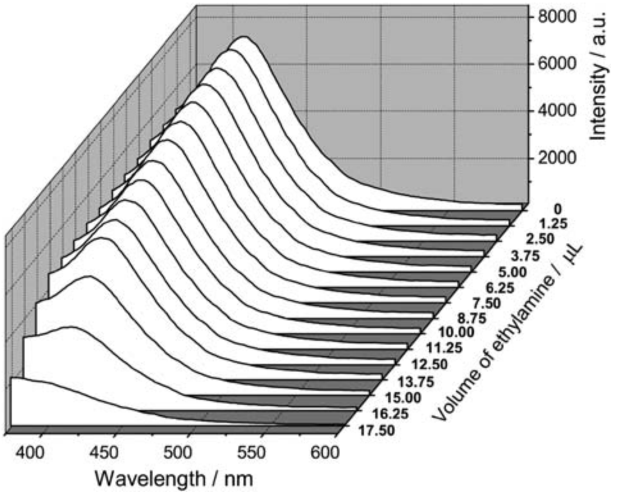

Fig. 3 Variation of emission spectra of **1** with the volume of ethylamine in 2 mL of acetonitrile. The excitation wavelength is 327 nm.

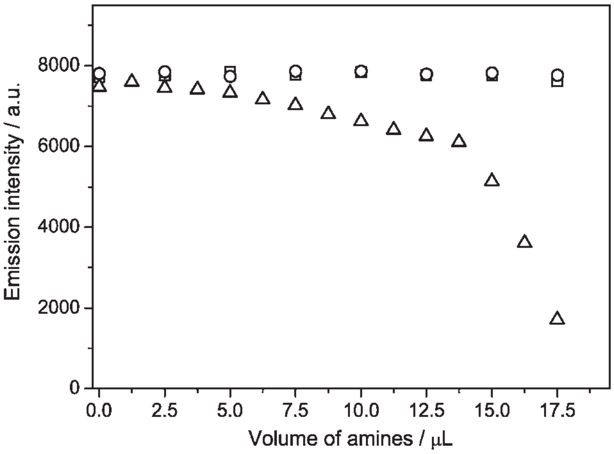

Fig. 4 Emission intensity of **1** at 414 nm against volume of ethylamine (△), *n*-butylamine (□), and aniline (○) in 2 mL of acetronitrile, showing high sensitivity for the sensing of ethylamine.

that the fluorescence intensity of MOF **1** is highly sensitive to ethylamine.

To investigate the influence of other organoamines on the sensing of ethylamine, the effects of three other amines with different molecular sizes, *i.e.* *n*-propylamine, *n*-butylamine and aniline, on the fluorescent emission intensity of **1** were also studied. As shown in Fig. 4 the emission intensity of the nanocrystals of **1** is insensitive to *n*-butylamine and aniline even when the volume of *n*-butylamine and aniline added is larger than 17.50 μL (0.867%, *v*/*v*), although weak fluorescence quenching effects were also observed at higher concentrations (Fig. S4, see ESI†). In the case of *n*-propylamine, no influence was found when the volume of propylamine is lower than 7.50 μL (0.374%, *v*/*v*), above which weak fluorescence quenching effect was also observed (Fig. S5, see ESI†).

As mentioned above, there exists both a 1-D channel system and open metal sites (*i.e.* coordinatively unsaturated metal sites in open channels) in MOF **1**. The fluorescence-responsive properties of the framework can be attributed to interactions between the open metal sites and the guest molecules which diffuse into the channels. Accordingly, guest molecules with large sizes, whose diffusion may be constrained by the channel, would show no or only a weak effect on the fluorescence property of the framework. Although propylamine and butylamine are also able to diffuse into channels of the framework, MOF **1** exhibits remarkable size-selectivity for the sensing of ethylamine due to the constraint effect of the channels in MOF **1** on the diffusion of propylamine and butylamine.

Another challenge for designing novel sensors is to develop sensors with excellent reversibility, which is crucial for their practical application. As a result, additional experiments were carried out to investigate the reversibility of the fluorescence properties of MOF **1**. After the spectrometric titration experiment for detecting ethylamine using nanocrystals of **1**, the specimen was dried at 70 °C for 4 h in a vacuum (0.01 MPa), and its fluorescence spectra was determined again. An obvious blue shift and a remarkable fluorescence quenching effect were found when 17.50 μL of ethylamine was added as mentioned above. After the drying process, however, the sample showed reversibly maximum fluorescence emission at 414 nm upon excitation at 327 nm (Fig. S6, see ESI†), suggesting highly reversible fluorescence property of MOF **1**.

In summary, we have demonstrated that rapid synthesis of MOF can be realized by using the ultrasonic method. A type of reversible fluorescent sensor for size-selective sensing of organoamines has been developed using nanocrystals of **1**. We have also begun to investigate whether other MOFs can also be synthesized using the ultrasonic method, and preliminary results show that it is possible to prepare other MOFs, *e.g.* $[Cu_3(BTC)_2(H_2O)_3]_n$,[18] a 3-D MOF with 3-D channels, by the reaction of cupric acetate and H_3BTC under similar conditions as used for MOF **1**. All these results reveal that ultrasonic synthesis can be employed successfully as a simple and very promising method for the fabrication of nanoscale MOFs.

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