



## Facile synthesis of highly luminescent nanowires of a terbium-based metal–organic framework by an ultrasonic-assisted method and their application as a luminescent probe for selective sensing of organoamines

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### ABSTRACT

In this paper, we report on a facile and environmentally friendly large-scale synthesis of metal–organic framework (MOF) nanowires by using an ultrasonic method without the introduction of any seeds, polymers, or surfactants. Highly luminescent nanowires of a one-dimensional terbium benzenetricarboxylate MOF,  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  (1,3,5-btc = benzene-1,3,5-tricarboxylate), with an average diameter of 50 nm and lengths of up to a few micrometers can be easily obtained in a relatively high yield under ultrasound irradiation at 70 °C and under atmospheric pressure. The structure and morphology of the as-synthesized MOF nanowires were characterized by powder X-ray diffractometry (PXRD) and field emission scanning electron microscopy (FE-SEM), respectively. The  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  nanowires obtained show strong luminescence emission at 548 and 492 nm, and exhibit high selectivity for sensing of aromatic amines, such as aniline and *p*-phenylenediamine, in comparison with alkylamines (e.g. methylamine, ethylamine, *n*-propylamine, *n*-butylamine and triethylamine). Such a significantly selective luminescence quenching effect of  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  nanowires for aromatic amines makes the nanostructured Tb-MOF-based sensing materials potential for sensing of aromatic amines in a mixture solution of organoamines.

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Nanoscale materials, which are of great fundamental and technological interests, exhibit a wide range of magnetic, electrical, and optical properties [1,2]. Among them nanowires are especially attractive, due to the fact that they have shown a variety of interesting properties that make them useful for a wide range of applications including catalysts, magnetic devices, and sensors [3–5]. A variety of methods have been used for fabrication of nanowires, among them solution-phase synthesis has the advantage that it can be scaled-up to produce very large quantities of nanowires from a diversified range of materials at reasonably low costs.

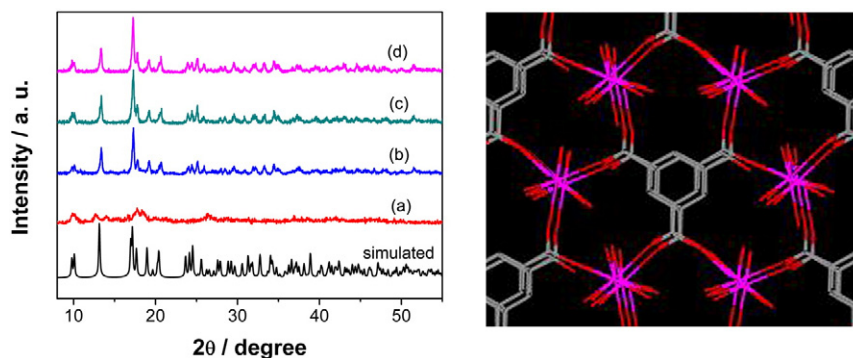
Metal–organic frameworks (MOFs) are a new class of crystalline materials built from metal ions (or metallic clusters) with well-defined coordination geometry and various polyfunctional organic ligands [6–9]. They have attracted extensive attention in recent years owing to their intriguing variety of architectures and topologies and their tremendous potential applications in catalysis [10], adsorption [11], magnetism [12], photonics [13], and molecular sensing [14]. Recently, increased efforts have been put into the synthesis of nanoscale metal–organic frameworks (NMOFs), because such a novel

type of nanomaterial has potential in templating, biosensing, magnetic resonance imaging, and drug delivery [15,16]. MOF nanocrystals with various morphologies, such as nanocubes, nanospheres, nanorods, nanosheets, and nanotubes, have been fabricated by precipitation, microemulsion, solvothermal techniques, as well as microwave-assisted methods [17,18]. Recently, we attempted for the first time to synthesize highly luminescent MOF nanocrystals (e.g. nanospheres, nanorods, nanosheets and nanotubes) by using sonochemical methods [19–22]. The results reveal that ultrasonic synthesis is a simple yet highly efficient approach for the fabrication of NMOFs, and the as-synthesized luminescent MOF nanocrystals possess superior sensing properties over its counter micro-scaled crystals for highly sensitive and selective chemical sensing [19–23]. This makes them potential for designing novel sensing devices with low cost, high sensitivity and selectivity.

Herein, we present a simple, rapid, and easy scale-up synthetic method for the fabrication of MOF nanowires and their application for selective sensing of aromatic amines. MOF nanocrystals with different morphologies, such as nanorods and nanowires, of a luminescent MOF,  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$ , were prepared by using an ultrasonic method. Selective sensing of organoamines was tested using nanowires of  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  based on selective luminescence response of the as-prepared MOF nanowires to organoamines. The results suggest

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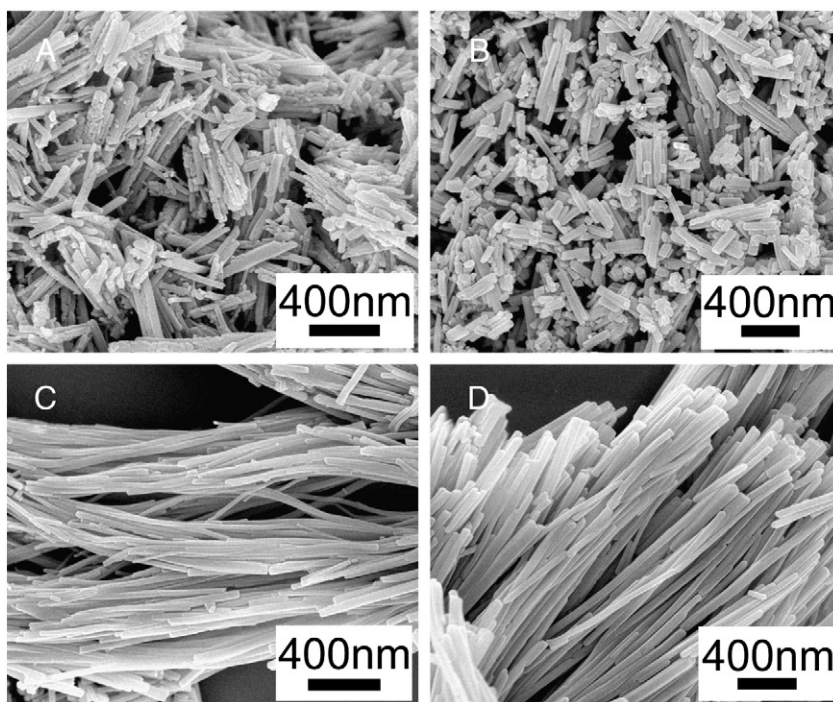
**Fig. 1.** X-ray diffraction patterns simulated from the crystallographic data of  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$ , and (a)–(d)  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  synthesized by using ultrasonic method for 30, 60, 90, and 140 min, respectively (left); molecular-packing diagram of  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  viewed along the *c*-axis (right).

that the ultrasonic synthesis is a highly efficient and environmentally friendly method for preparing MOF nanocrystals. Furthermore, luminescence emission of the as-prepared MOF nanowires was found to be selectively sensitive to aromatic amines. This makes luminescent MOF nanocrystals useful in various applications such as selective sensing of aromatic amines in a mixture solution of organoamines.

Ultrasonic syntheses of  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  for the reaction times of 30, 60, 90, and 140 min were carried out under ultrasonic irradiation at a frequency of 40KHz (JK-3200, JINNIKE Ultrasonic) at 70 °C and under atmospheric pressure, respectively [24]. The crystal structure and phase purity of the products obtained for different reaction times were characterized by powder X-ray diffraction (PXRD), as shown in Fig. 1. All the diffraction peaks can be well indexed to a known bulk phase of  $[\text{La}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  [25] for samples prepared for the reaction time of 60, 90, and 140 min. However, only a few of diffraction peaks with comparatively low intensities could be observed for the sample synthesized under ultrasound irradiation for 30 min (see Fig. 1a), suggesting incomplete crystallization of MOF crystals at a short ultrasonic time. To further confirm crystal structures of the Tb-btc nanowires obtained at various reaction times, crystallographic data of the as-synthesized samples were calculated by X-ray diffraction Rietveld analysis using WinPLOTR and

Fullprof [26,27]. The results (see Table S1 in the ESI) agree well with this obtained from single-crystal X-ray diffraction data of  $[\text{La}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  (monoclinic,  $a = 11.5289 \text{ \AA}$ ,  $c = 7.3507 \text{ \AA}$ ,  $V = 1329.59 \text{ \AA}^3$ ) [25]. For comparison, the reaction of  $\text{Tb}(\text{NO}_3)_3$  with  $\text{H}_3\text{btc}$  was also carried out at 70 °C for 140 min without ultrasound irradiation. To the best of our knowledge, however, its XRD pattern cannot be indexed to any known phases of a compound related to Tb and btc (see Fig. S1 in the ESI) [25].

The morphology of the  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  prepared using ultrasonic method for different reaction times was studied using scanning electron microscopy (SEM). As can be seen from Fig. 2, size of  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  nanocrystals changes significantly with increasing the reaction time from 30 to 140 min. The formation of a large quantity of short MOF nanorods with a diameter of 30–50 nm and a length of 300–500 nm is verified under ultrasound irradiation for 30 and 60 min (see Fig. 2A, B). Further increases of the reaction time led to continued crystal growth after the formation of MOF nanorods. However, no short MOF nanorods could be observed after further prolonging the reaction time to 90 or 140 min, as shown in Fig. 2C and D. In contrast, a large quantity of MOF nanowires with an average diameter of 50 nm and lengths of up to a few micrometers was obtained in a relatively high yield, suggesting



**Fig. 2.** SEM images of  $[\text{Tb}(1,3,5\text{-btc})(\text{H}_2\text{O})_6]_n$  synthesized using ultrasonic method for various reaction times: (A) 30, (B) 60, (C) 90, and (D) 140 min.

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