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Synthesis of Nanocrystals of Dysprosium Benzenedicarboxylate Metal-Organic Framework for Sensing of Nitroaromatic Explosives†

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In this paper, we present a morphology-controlled synthesis of nanoscale metal-organic frameworks (NMOFs) by using a surfactant-assisted method for fluorescent sensing of nitroaromatic explosives. Nanocrystals of dysprosium-containing MOF, Dy-BDC (**1**) (BDC = 1,4-benzene dicarboxylate), was synthesized under different conditions. Transmission electron microscopy (TEM) images of Dy-BDC reveal that size and shape of nanocrystals can be tuned by varying the reaction time. Fluorescence sensing of 2-nitrotoluene, 4-nitrotoluene, 2,4-dinitrotoluene and 2,6-dinitrotoluene by using Dy-BDC nanorods have been studied. The results indicate that Dy-BDC nanocrystals are highly sensitive to nitroaromatic compounds. The results may be helpful for designing novel fluorescence sensor for the sensing of explosives.

Key Words: Metal-organic frameworks, Nanocrystals, Nitroaromatic compounds, Fluorescence sensing, Explosive detection.

INTRODUCTION

Due to the critical antiterrorism situation worldwide and the increased use of explosive materials in terrorism, the development of a detection method for trace explosive materials is highly desirable and urgently necessary in the field of security screening nowadays[1-3]. Fluorescence-quenching is proven to be one of the most sensitive and convenient methods for the rapid detection of ultra-trace analytes from explosives[4]. This method offers a simple, exquisitely sensitive and rapid detection of explosives in the vapour phase and is now an established technology.

In recent years, much interest has been focused on the design and synthesis of metal-organic frameworks (MOFs)[5,6]. In contrast to traditional porous materials, these porous metal-organic frameworks built from metal ions with well defined coordination geometry and organic bridging ligands[7]. Especially, lanthanide-containing metal-organic frameworks often exhibit intense fluorescence and are potentially interesting for the design of luminescent materials and devices[8]. More recently, increased effort was put into synthesis of the controlled nano- and micro-scaled metal-organic frameworks[9] due to this novel type of nano- and micro-scaled material has potential in a variety of imaging, biosensing and biolabeling and drug delivery applications. Some traditional techniques, such as reverse microemulsion[10], microwave[11] and ultrasound-assisted synthesis[10] are commonly applied to prepare these nanoscale metal-organic frameworks. Herein, we not only present a surfactant-assisted precipitation reaction of a nanorods of Dy-BDC (1, BDC = 1,4-benzenedicarboxylate), but also report on a highly sensitive to nitroaromatic compounds, such as 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT), 2,4-dinitrotoluene and 2,6-dinitrotoluene (2,4-DNT and 2,6-DNT). The results reveal that nanocrystals of Dy-BDC shows high sensitivity and selectivity for the sensing of nitroorganic compounds, it may be helpful for designing novel fluorescence sensor for potential detection of explosives.

EXPERIMENTAL

Nanocrystalline powders of metal-organic frameworks were obtained by mixing stoichiometric amounts of a dysprosium chloride and cetyltrimethyl ammonium bromide (CTAB) in water with the disodium salt of terephthalic acid. Precipitation immediately occurred. Continue stirring for a desired reaction time (10, 30, 180 or 420 min). The nanocrystals were separated by filtration and washed with deionized water (5 mL × 5 mL) and alcohol (5 m L × 5 mL) and then dried in air. The white

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precipitates were filtered and dried in air. The yields of the reactions are close to 100 %.

RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of the resulting products obtained for different reaction times, indicating that the sample is of high crystallinity. All samples prepared for the reaction time of 10, 30, 180 and 420 min of the diffraction peaks can be assigned to the crystalline Dy-BDC and no obvious peaks of impurities can be detected in these XRD patterns.

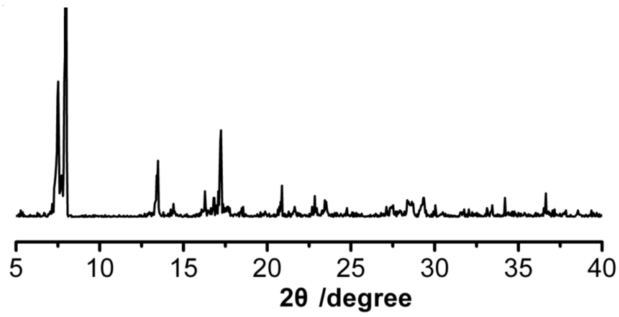
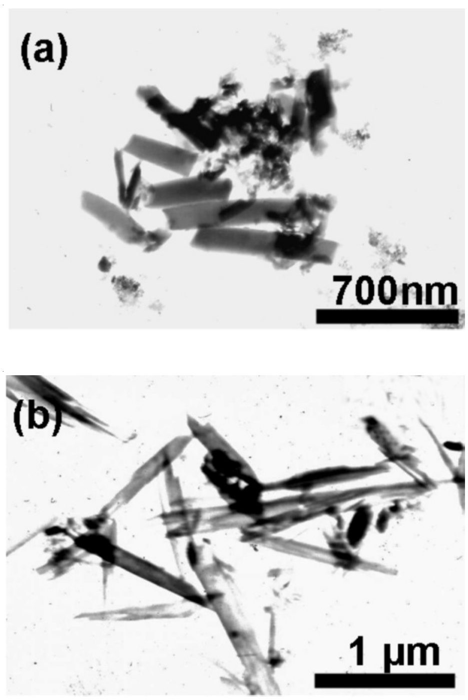
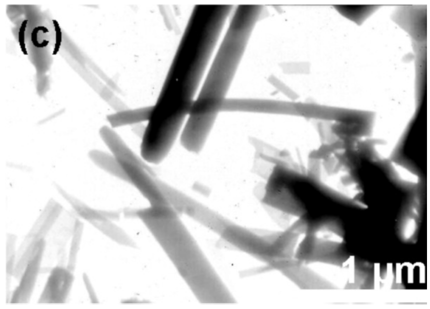


Fig. 1. Powder XRD patterns of Dy-BDC nanocrystals

The morphologies and size or nanostructure of the as-prepared samples for different reaction times were characterized by TEM (Fig. 2). Nanosheets of Dy-BDC with a width of 50-100 nm and a length of 200-500 nm were obtained. With increasing the time from 10-30 min, nanobelts were formed. Further increased of the reaction time led to the growth of nanobelts to nanorods. When the reaction time increased to 420 min, nanorods with large dimensions could be detected, the diameter of nanorods increased to 0.3-0.5 μm. These results suggest that the reaction time and the presence of CTAB are crucial to the final morphology and size. For example, in the present work, the addition of CTAB leads to a distinct difference in the size and morphologies of the products. Hence, it





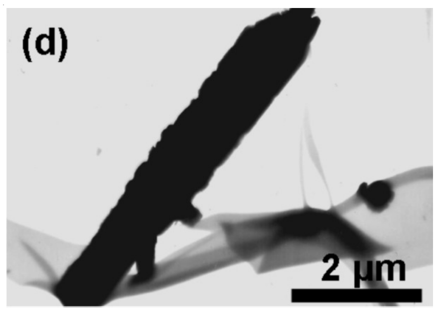


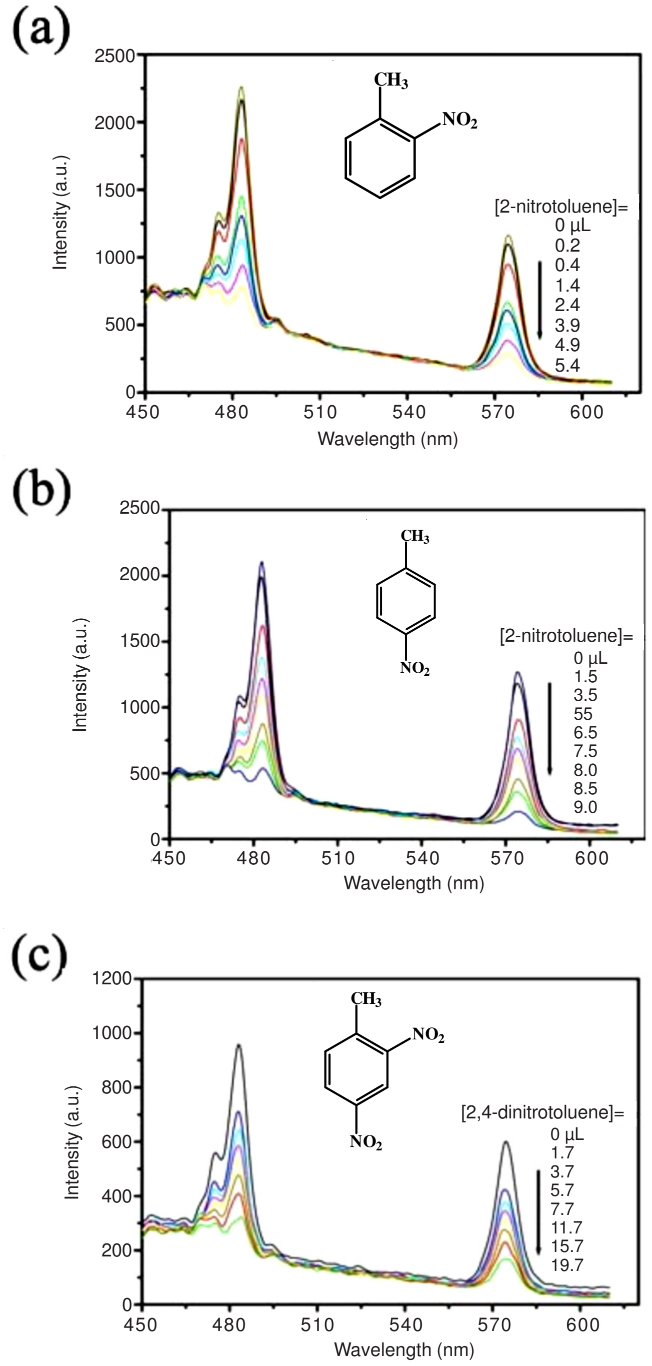
Fig. 2. TEM images of Dy-BDC in the presence of CTAB for various reaction times: (a) 10, (b) 30, (c) 180, (d)

is reasonable to speculate that the cationic surfactant CTAB plays important roles in controlling the size and morphology of Dy-BDC.

To demonstrate the ability of Dy-BDC for detection of explosives, the sensing of nitroorganic compounds in an acetonitrile solution was quantitatively analyzed by a fluorescence spectrometric titration experiment. The results of emission intensity with concentration of nitroorganic compounds was shown in Fig. 3. It can be observed that the fluorescence intensity of Dy-BDC decreases sharply in response to 2-NT, 4-NT, 2,4-DNT and 2,6-DNT, respectively. A significantly decrease of emission intensity was observed when 1 μL nitroaromatics was added into acetonitrile. Further increase of volume of nitroaromatics solution led to a gradual decrease in fluorescence intensities until 5.4-20 μL of stock solution of nitroaromatics were added, at which significant fluorescence quenching effect was observed. All these results suggest that the fluorescence intensity of the as-prepared Dy-BDC nanorods is highly sensitive to nitrobenzene. Such fluorescence properties of Dy-BDC nanorods are of interest for the sensing of the nitroaromatic and the materials may serve as an ideal candidate for applications in nitroaromatic explosives detection, because many explosive materials, such as the infamous 2,4,6-trinitrotoluene, are based on nitroaromatic compounds.

Conclusion

In summary, we described a surfactant-assisted method for the synthesis of nanoscale dysprosium-containing metal-organic framework and fluorescent sensing of nitroaromatic compounds. The surfactant was found to play an important role in the sizes and shapes controlling of metal-organic framework nanocrystals and such the surfactant-assisted methodology can be widely applied to synthesize other nanoscale metal-



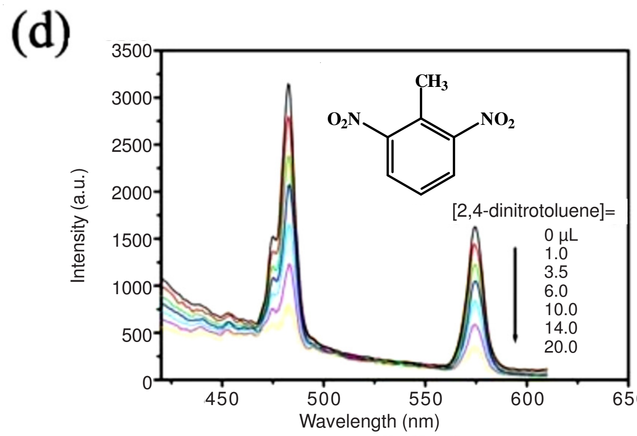


Fig. 3. Variation of emission spectra of Dy-BDC nanorods with the volume of 0.78 M of nitroaromatics (a) 2-NT, (b) 4-NT, (c) 2,4-DNT and (d) 2,6-DNT in 2 mL of acetonitrile

organic frameworks. The fluorescence properties of these metal-organic framework nanorods were found to be highly sensitive to nitroaromatics such as 2-NT, 4-NT, 2,4-DNT and 2,6-DNT. The result is helpful for the design of low cost and highly sensitive sensors for nitroaromatic explosives, due to the fact that the used materials are inexpensive and the morphology-controlled preparation of metal-organic frameworks nanocrystals can be easily realized as described in this work.

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