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A survey on the effects of ultrasonic irradiation, reaction time and concentration of initial reagents on formation of kinetically or thermodynamically stable copper(I) metal-organic nanomaterials

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ABSTRACT

In order to evaluation the effects of ultrasonic irradiations, concentration of initial reagents and reaction time on formation $[Cu_4(MBT)_4]$ or $[Cu_6(MBT)_6]$ copper(I) metal-organic nanomaterials, [HMBT = 2-Mercaptobenzothiazole], we designed some experiments and synthesized six samples under different conditions. These nanostructures were characterized by IR spectroscopy, X-ray powder diffraction (XRD) and Scanning Electron Microscopy (SEM). It seems that the tetranuclear cluster of $[Cu_4(MBT)_4]$ (**2**) is the kinetically stable product which is formed at the initial time of the reaction and as the time went, it converts to thermodynamically stable product of $[Cu_6(MBT)_6]$ (**1**) with hexanuclear cluster unit. In the samples which synthesized with low concentration of initial reagents, against to those synthesized with high concentration of initial reagents, the ultrasonic irradiation does not have any effect on formation of any special morphology.

1. Introduction

Metal–organic materials are found to be a fascinating novel class of functional nanomaterials [1]. The miniaturization of metal–organic materials down to the nanometer length scale is therefore a unique opportunity to develop a new class of highly tailor able nanoscale materials that combine the rich diversity of compositions, structures and properties of classical metal–organic materials with the obvious advantages of nanomaterials that opening up avenues for technological and biomedical applications in many areas, including drug-delivery, catalysis, diagnostics, solar cells, etc [2–4]. The extensive application of nano-scale material is related their unique properties like high adsorption capacity, fast mass transfer and high surface area to mass ratio, can differ from those in the micro and macro world and even depend not only on the chemical composition and phase but also on the size of the given materials [5]. The limitless combinations between inorganic and organic building blocks enable researchers to synthesize metal–organic discrete nanostructures with varied compositions, morphologies and sizes. Metal-organic materials have been prepared by a variety of synthetic methods, including gas phase techniques, liquid phase methods and mixed phase approaches [6]. Among a variety of approaches, the utilization of ultrasound for materials synthesis has been extensively examined over many years, and is now positioned as one of the most powerful tools in nanostructured materials synthesis [7]. Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation, that is, the formation, growth and collapse of micrometrical bubbles, formed by the propagation of a pressure wave through a liquid [8]. Ultrasound, and its secondary effect, cavitation (nucleation, growth and transient collapse of tiny gas bubbles) improve the mass transfer through convection pathway that is emerged from physical phenomena such as microstreaming, micro-turbulence, acoustic (or shock) waves and micro jets without significant change in equilibrium characteristics of the adsorption/desorption system [9]. High-intensity ultrasound can induce a wide range of chemical and physical consequences [10]. The study of chemical effects of ultrasound is a rapidly growing research area. Some of the most important recent aspects of sonochemistry have been its applications in the synthesis and modification of both organic and inorganic materials [6,11–15]. In addition to the power, frequency, duration of the ultrasound, the vapor pressure of both reactants and solvent are crucial parameters for the preparation of these kinds of materials. The volatility of the precursors is a key because the sonochemical reaction begins

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within the vapor of the collapsing bubble [16]. The chemical effects of ultrasound fall into three areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis. Applications of ultrasound to materials chemistry are found in all of these categories [17]. Physical effects of high-intensity ultrasound, which often have chemical consequences, include enhanced mass transport, emulsification, bulk thermal heating and a variety of effects on solids [18–20]. In this article, we wish to report the effects of ultrasonic irradiations, concentration of initial reagents and reaction time on formation kinetically ($[Cu_4(MBT)_4]$) or thermodynamically ($[Cu_6(MBT)_6]$) stable copper(I) metal-organic nanomaterials. Selection of this compound (Cu(MBT)) is due to its possibility to exist in two forms of kinetically and thermodynamically stable products. On the other hand, sonochemical synthesis is a simple, cost effective and environmentally friendly approach to nanoscale coordination supramolecular compounds which can also be considered as green synthetic method because of shorter reaction time and higher yield in comparison with thermal synthesis.

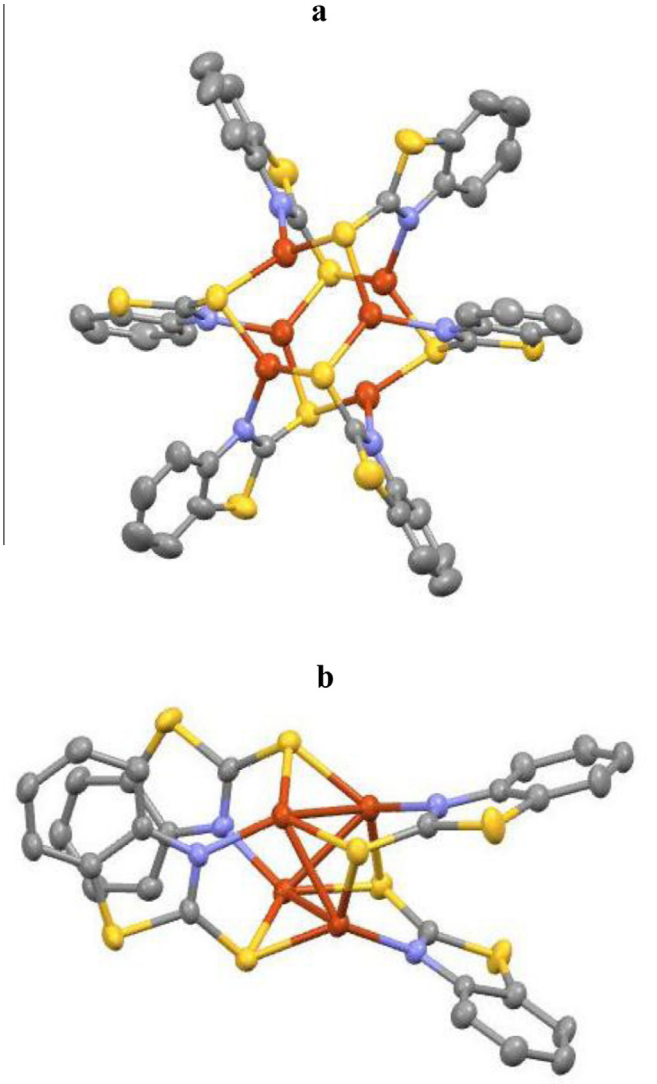

Fig. 1. a) Structural building units of a) $[Cu_6(MBT)_6]$ (**1**) and b) $[Cu_4(MBT)_4]$ (**2**), (Cu = orange, S = Yellow, N = blue and C = gray, H atoms have been omitted for clarity). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and were used as received from Merck chemical company. The molecular structure plots were prepared using Mercury. PARSONIC 15S ultrasonic bath (with the frequency of 28 kHz and the maximum power of 200 W) was used for the ultrasonic irradiation. Melting points were measured on an Electro thermal 9100 apparatus and are uncorrected. IR spectra were recorded using an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) in ATR form, in the range of 400–4000 cm^{-1} with 4.0 cm^{-1} resolution and the 16 scan's numbers. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by Philips with monochromatized Cuk_α radiation and simulated XRD powder patterns based on single crystal data were prepared using the Mercury software. The samples were characterized with a scanning electron microscope (Philips XL 30) with gold coating.

2.2. Bulk and sonochemical reaction between 2-Mercaptobenzothiazole and $CuCl_2$ with low concentration of initial reagents

To prepare the nano-structures of $[Cu_6(MBT)_6]$ (**1**) and/or $[Cu_4(MBT)_4]$ (**2**) by sonochemical process we used ultrasonic bath with 0.025:0.025 M concentrations of initial reagents (HMBT:$CuCl_2$) and the power of 28 kHz with the reaction times of 20 (LCU20) and 60 (LCU60) minutes. To the solution of HMBT in MeOH (20 cc), a solution of $CuCl_2$ in MeOH (20 mL) was added in a drop wise manner under the ultrasonic irradiation. The obtained greenish yellow precipitates were filtered, subsequently washed with water and then dried. d.p. = above 300 °C, Yield: 0.063 g and 0.073 g (55.5% and 63.5% based on Cu(MBT)) for LCU20 and LCU60, respectively.

For synthesis the bulk sample (LC60), 0.025 M solution of HMBT in 20 cc MeOH was heated and stirred with solution of 0.025 M of $CuCl_2$ in 20 cc MeOH for 60 min. The greenish yellow precipitate was formed, and then the solution was cooled to room temperature. The obtained precipitate was filtered subsequently washed with MeOH and then dried. d.p. = above 300 °C, Yield: 0.071 g (62.0% based on Cu(MBT)).

Table 1
A summary of reaction conditions for synthesis six samples of **1** by considering the effects of ultrasonic irradiation, reaction time and concentration of initial reagents.

Compound Label	Reaction Time (minutes)	Ultrasonic Irradiation	Concentrations of Initial Reagents (M)	Products
LCU20	20	Yes	0.025	Mainly $[Cu_6(MBT)_6]$ (**1**) mixed with low amounts of $[Cu_4(MBT)_4]$ (**2**)
LCU60	60	Yes	0.025	Pure $[Cu_6(MBT)_6]$ (**1**)
LC60	60	No	0.025	Pure $[Cu_6(MBT)_6]$ (**1**)
HCU20	20	Yes	0.25	Mixture of $[Cu_6(MBT)_6]$ (**1**) and $[Cu_4(MBT)_4]$ (**2**)
HCU60	60	Yes	0.25	Mixture of $[Cu_6(MBT)_6]$ (**1**) and $[Cu_4(MBT)_4]$ (**2**)
HC60	60	No	0.25	Mixture of $[Cu_6(MBT)_6]$ (**1**) and $[Cu_4(MBT)_4]$ (**2**)

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