### Accepted Manuscript

Sonochemical synthesis of a nano-structured zinc(II) amidic pillar metal-organic framework

Mina Bigdeli, Ali Morsali

PII:	S1350-4177(15)00163-7
DOI:	http://dx.doi.org/10.1016/j.ultsonch.2015.05.034
Reference:	ULTSON 2893
To appear in:	Ultrasonics Sonochemistry
Received Date:	18 April 2015
Revised Date:	24 May 2015
Accepted Date:	25 May 2015



Please cite this article as: M. Bigdeli, A. Morsali, Sonochemical synthesis of a nano-structured zinc(II) amidic pillar metal-organic framework, *Ultrasonics Sonochemistry* (2015), doi: http://dx.doi.org/10.1016/j.ultsonch.2015.034

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

### Sonochemical synthesis of a nano-structured zinc(II) amidic pillar metal-organic framework

Mina Bigdeli, Ali Morsali\*

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-4838, Tehran, Islamic Republic of Iran

Tel: +98-21-82883449, Fax: +98-21-8009730

#### Abstract

A facile and environmentally friendly nano-scale synthesis of a Zn(II) metal-organic framework (MOF), { $[Zn_4(BDC)_4(bpta)_4] \cdot 5DMF \cdot 3H_2O$ }<sub>n</sub> (1) (bpta = N,N'-bis(4-pyridinyl)-1,4-benzenedicarboxamide, BDC = 1,4-dicarboxylate, DMF = N,N-dimethylformamide), with nanorods morphology under ultrasonic irradiation at ambient temperature and atmospheric pressure has been explored. This MOF has been characterized by scanning electron microscopy (SEM), powder X-ray diffraction (PXRD) and IR spectroscopy. Some parameters such as concentration of initial reagents, power ultrasound irradiation and time effects on size and morphology of nano-structured compound 1 have been studied.

Keywords: metal-organic framework, sonochemical, amidic pillar, nano-structure;

#### 1. Introduction

Metal-organic frameworks (MOFs) are porous organic-inorganic hybrid materials, that are constructed by joining metal-containing units with organic linkers, using strong bonds to create open crystalline frameworks with permanent porosity [1, 2]. Because of their porosity and tunable chemical functionality, they have been used in diverse areas such as gas storage [3, 4], adsorption [5], separation [6], catalysis [7], magnetism [8, 9] and drug delivery [10]. The key to the design of intriguing MOFs [11] lays in the intelligent ligand design, the proper choice of metal center and counter ions. Hydrogen bonding, on the other hand, plays a crucial role in the crystal engineering of organic solids [12]. Combination of both metal–ligand coordination (MLC) and hydrogen bonding in designing MOFs should be considered an

attractive design strategy because of the possibility of structural variations and guest entrapment induced by specific hydrogen bonding interactions. The amide group is a fascinating functional group because it possesses two types of hydrogen-bonding sites: the -NH moiety acts as an electron acceptor and the -C=O group acts as an electron donor. These multifunctional moieties of amide groups tend to form hydrogen bonds among themselves and interact negligibly with guest molecules after construction of MOFs [13]. These structural frameworks have been utilized in applications such as chemical sieving, sensing, and catalysis, and much progress has been made in all of these areas [14]. By decreasing the size of metal-organic frameworks in nano-size, surface area would be increased. Hence making MOFs in nano-scale is certainly a major step forward toward the technological applications of these new materials [15, 16].

There are several different synthetic approaches for the preparation of metal-organic frameworks such as slow diffusion, hydrothermal, and solvothermal synthesis methods [17-19]. In many cases, these methods are needed long reaction times, high temperatures and pressures. Also, because of the big potential of MOFs for industrial applications, it is important to develop novel and techno-economically approaches, such as mechanochemical [20-23], microwave (MW) [24-27], electrochemical synthesis [28, 29] and sonochemical approach. In recent years many kinds of nano-sized materials have been prepared by sonochemical method [30-34]. With using ultrasonic irradiation, various chemical reactions, even some reactions that were previously difficult to realize by other traditional methods, can also proceed at room temperature easily [35-37]. Sonochemical methods can lead to homogeneous nucleation and a substantial reduction in crystallization time compared with conventional oven heating when nanomaterials are prepared [38]. Many researchers have investigated the effect of ultrasound on chemical reactions, and most theories imply that the chemical or physical effects of ultrasound originate from acoustic cavitation within collapsing bubbles, which generates extremely localized hot spots having temperatures of roughly 5000 K, pressures of about 500 atm, and a lifetime of a few microseconds. 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 [39]. The use of high-intensity ultrasound to enhance the reactivity of metals as a stoichiometric reagent has become a synthetic technique for many heterogeneous organic and organometallic reactions [40-46]. Ultrasonic irradiation is considered a green energy source because of shorter reaction times and higher yields in comparison with thermal energy sources [47] and this method is more convenient, cost effective and environmentally friendly approach to nano-scale coordination supramolecular compounds and easily controlled [39, 48, 49]. As a part of our ongoing efforts in the design and synthesis of facile and environmentally friendly nano-scale materials, we wish to report nano-structure herein the of MOF. on synthesis a porous  $\{[Zn_4(BDC)_4(bpta)_4] \cdot 5DMF \cdot 3H_2O\}_n$ (1), (bpta= N,N'-bis(4-pyridinyl)-1,4benzenedicarboxamide, BDC=1,4-dicarboxylate) [50], which is synthesized by the reaction of zinc(II) acetate dehydrate, N,N'-bis(4-pyridinyl)-1,4-benzenedicarboxamide and 1,4dicarboxylate under ultrasonic irradiation at ambient temperature and atmospheric presure. MOF 1 was synthesized in three different concentrations of initial reagents (0.006, 0.01 and 0.04 M) and two different reaction times of 15 and 30 min. MOF 1 was also synthesized using the ultrasonic method at two different ultrasound powers (12 and 24 W). This metalorganic framework has potential uses in the context of molecular recognition, catalysis, sizeselective guest transportation, optical materials, molecular magnetism, semiconductors, and conductors [51].

Because of the unique properties of nano-particles, they have been used in electrical, optical, magnetic and chemical features which are entirely different from their bulk counterparts [40, 52-55], in particular nanoscale metal–organic frameworks (NMOFs), have potential in templating, biosensing, magnetic resonance imaging and drug delivery [56, 57].

#### 2. Experimental

#### 2.1. Materials and physical techniques

Except bpta ligand that was synthesized, all reagents and solvents for the synthesis and analysis were commercially available and were used as received. Powder X-ray diffraction (PXRD) of compound **1** was carried out on a diffractometer of Philips Company with X'pert monochromatized Cu k $\alpha$  radiation. Simulated XRD powder patterns were calculated using

Mercury based on the single crystal data [50]. FT-IR spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500–4000 cm<sup>-1</sup> using the KBr disk technique. Ultrasonic generator was carried out on a TECNO-GAZ, S.p.A., Tecna 6, input: 50–60 Hz/305 W.

#### 2.2. Synthesis of bpta ligand

The N,N'-bis(4-pyridinyl)-1,4-benzenedicarboxamide ligand of bpta is synthesized according to literature method [58].(Fig.1)

200 mL of  $CH_2Cl_2$  and 3 mL of  $NEt_3$  were successively added to a 500 mL flask containing terephthaloyl chloride (0.5 g, 2.46 mmol) and 4-aminopyridine (0.48 g, 5.20 mmol). The resulting mixture was stirred at room temperature for 24 h. The resulting white precipitate was collected, washed with water (50 mL) and  $CH_2Cl_2$  (50 mL), and dried. IR (cm<sup>-1</sup>) selected bond: 594(m), 835(m), 1118(m), 1296(s), 1416(m), 1505(vs), 1594(vs), 1663(s), 3533(s).

#### 2.3. Synthesis of $\{[Zn_4(BDC)_4(bpta)_4]$ .5DMF.3H<sub>2</sub>O $\}_n$ (1) as single crystal

According to reported method [50], colorless block crystals of compound **1** were obtained from a mixture of ZnCl<sub>2</sub> (20.5 mg, 0.15 mmol), H<sub>2</sub>BDC (24.9 mg, 0.15 mmol), bpta (47.8 mg, 0.15 mmol), DMF (7 mL) and H<sub>2</sub>O (0.5 mL) in Teflon-lined stainless steel autoclave under autogenous pressure and heated at 120 °C for 72 h and then slowly cooled to 30 °C. m.p. > 300 °C. IR (cm<sup>-1</sup>) selected bond: 532(s), 601(m), 748(m), 831(s), 1103(s), 1296(m), 1384(s), 1508(vs), 1595(vs), 1671(s), 3077(m), 3263(m).

# 2.3. Synthesis of $\{[Zn_4(BDC)_4(bpta)_4]$ .5DMF.3H<sub>2</sub>O $\}_n$ (1) nano-structure by a sonochemical process

To prepare { $[Zn_4(BDC)_4(bpta)_4]$ .5DMF.3H<sub>2</sub>O}<sub>n</sub> (1) nanopowder, Zn(OAC)<sub>2</sub>.2H<sub>2</sub>O (0.01 M), BDC and bpta with molar ratio 1:1:1 were added to the one-necked flask that contain 25 ml DMF as solvent and treated by ultrasound irradiation in ultrasonic bath. The obtained precipitates were filtered off, washed with DMF several times and then dried in air, m.p. > 300 °C. IR bands are: 534(s), 602(m), 748(m), 833(s), 1104(s), 1297(m), 1385(s), 1508(vs), 1596(vs), 1671(s), 3079(m), 3267(m).

To investigate the role of initial reagent concentrations on size and morphology of nano structured compound **1**, the above processes were done with different concentrations (0.04, 0.01 and 0.006 mol  $L^{-1}$ ). For monitoring the role of power ultrasound irradiations on size and morphology of compound **1** the process with the initial reagents concentration 0.01 M has been done in three different ultrasound power (12 and 24 W). Sonochemical syntheses of **1** for the reaction times of 15 and 30 min were carried out under ultrasonic irradiation too.

#### 3. Results and discussion

The hydrothermal reaction of zinc(II) chloride with 1,4-dicarboxylate (BDC) and N,N'-bis(4pyridinyl)-1,4-benzenedicarboxamide (bpta) as amidic pillar in 1:1:1 mole ratio at 120 °C for 72 h yields colorless crystals of compound **1**, which is suitable for X-ray crystallography, while nano-structures of compound **1** were obtained in DMF by ultrasonic irradiation at room temperature. Scheme 1 gives an overview of the methods used for the synthesis of  $\{[Zn_4(BDC)_4(bpta)_4].5DMF.3H_2O\}_n$  (**1**) using the two different routes.

The IR spectrum of the nano-structures produced by the sonochemical method and of the bulk material produced by the solvothermal method were compared with each other in Fig. 2. The structure of compound **1** was characterized by single-crystal X-ray diffraction techniques [50]. The molecular structure of the fundamental building unit for **1** is shown in Fig. 3. The asymmetric unit consists of four Zn(II) atoms, four BDC<sup>2–</sup> ligands, four bpta linkers, five DMF, and three water guest molecules. The framework is constructed from a six-connected dinuclear {Zn<sub>2</sub>N<sub>4</sub>O<sub>6</sub>} node, which is octahedrally bound to four BDC ligands and two double-bpta-deckered pillars. Each BDC<sup>2–</sup> ligand acts as a  $\mu_3$ -bridge to link three Zn(II) atoms, in which one carboxylate group exhibits a  $\mu_2$ - $\eta_1$ : $\eta_1$ -bridging coordination mode, while the other adopts a monodentate structure (Fig. 3).

Fig. 4 shows the simulated XRD pattern from single crystal X-ray data of compound **1** in comparison with the XRD pattern of the as synthesized nano-structure of compound **1** by the sonochemical process. Acceptable matches were observed between the simulated and experimental XRD patterns. This indicates that the compound obtained by the sonochemical

process as nano-structures is identical to that obtained by single crystal diffraction. The significant broadening of the peaks indicates that the particles are of nanometer dimensions.

The morphology and size of compound 1 prepared by the sonochemical method was characterized by scanning electron microscopy (SEM). Fig. 5 shows the SEM of the compound 1 prepared by ultrasonic generator 12W in concentration of initial reagents  $[Zn^{2+}]$ = [BDC] = [bpta] = 0.04 mol L<sup>-1</sup>. Also different concentrations of zinc(II), 1,4benzenedicarboxylate and N,N'-bis(4-pyridinyl)-1,4-benzenedicarboxamide solution (0.01 and 0.006 mol  $L^{-1}$ ) were tested (Figs. 6 and 7). In order to investigate the role of concentration of initial reagents on the nature of products, reactions were performed with three different concentrations of initial reagents. Comparison between the samples with different concentrations shows that high concentrations of initial reagents decreased particles size. Thus, particles sizes produced using lower concentrations of initial reagents (0.006 mol  $L^{-1}$ , Fig. 7) are bigger than particles size produced using higher concentrations (0.04 and 0.01 mol  $L^{-1}$ , Figs. 5 and 6, respectively). More interestingly that, as shown in Fig. 7, decreasing of concentration of initial reagents ultimate to prepared rod-like nano-structure compound 1 (Fig. 7). The morphologies and size of nano-structure of the as-prepared samples for different reaction times were characterized by SEM. Fig. 8 shows the SEM image of compound 1 with reaction time of 30 min ( $Zn(II) = BDC = bpta = 0.006 \text{ mol } L^{-1}$ , 12 W). The results show that the size of the nanoparticles increased with increasing reaction times. Thus, smaller particles (for 15 min, see Fig. 7) were achieved by sonocrystallization at shorter times when compared with 30 min (Fig. 8). To investigate the role of power ultrasound irradiation on the nature of products, reactions were performed under diverse power ultrasound irradiation too (Zn(II) = BDC = bpta =  $0.006 \text{ mol } L^{-1}$ , 12 and 24W). Comparison between the samples with different powers ultrasound irradiation shows that increasing of power from 12 to 24W leads to decreasing of sizes of the nanoparticles (Fig. 9). Table 1 gives an overview of the comparison of the concentration of initial reagents, times effect and different powers of ultrasonic irradiation on the morphologies and sizes of nano-structure of the compound 1. Thermogravimetric analysis of 1 showed that guest molecules are eliminated from the network (calcd 16.1%; found 16.5%, which correspond to loss of 20 DMF molecules and 12

 $H_2O$  molecules per unit cell) when the temperature is increased from room temperature to about 270 °C [50].

#### 4. Conclusions

Nanoparticles and nanorods of porous metal-organic framework,  $\{[Zn_4(BDC)_4(bpta)_4].5DMF.3H_2O\}n$ (1) ,(bpta N,N'-bis(4-pyridinyl)-1,4-= benzenedicarboxamide, BDC = 1,4-dicarboxylate, DMF = N,N-dimethylformamide) have been synthesized under ultrasound irradiation. Structural information of the nanoparticles was compared with the structural information of crystals of compound 1. Morphology and sizes of the nano-structures were investigated in different concentrations of initial reagents, different powers of ultrasonic irradiation and various reaction times. Results show an increase in the particles size as the concentrations of initial reagents is decreased. It is an interesting point that low concentration of initial reagents leaded to rod-like nano-structures morphology. Also the shorter reaction times and using of different powers of ultrasonic irradiation lead to decreasing the size of nano-structures.

#### Acknowledgement

C

Support of this investigation by Tarbiat Modares University is gratefully acknowledged.



Fig. 1. bpta ligand



Fig. 2. IR spectrum of (a) nanostructures of compound 1 produced by sonochemical method and (b) bulk materials of 1.



**Fig. 3.** Molecular-packing diagram of  $\{[Zn_4(BDC)_4(bpta)_4].5DMF.3H_2O\}_n$  (1) viewed along the *b*-axis, Zn(yellow), O(red), N(blue), C(purple and green), H(grey).



Fig. 4. XRD patterns of simulated pattern based on single crystal data of compound 1 (blue), as synthesized and nanostructures of 1 prepared by sonochemical process (red)



Fig. 5. SEM photographs of compound 1 nanoparticles prepared by ultrasonic generator 12W in concentration of initial reagents  $[Zn^{2+}] = [bpta] = 0.04 \text{ mol } L^{-1}$ .



Fig. 6. SEM photographs of compound 1 nanoparticles prepared by ultrasonic generator 12W in concentration of initial reagents  $[Zn^{2+}] = [bpta] = 0.01 \text{ mol } L^{-1}$ .



**Fig. 7.** SEM photographs of compound **1** nanoparticles prepared by ultrasonic generator 12W in concentration of initial reagents  $[Zn^{2+}] = [bpta] = 0.006 \text{ mol } L^{-1}$ .



Fig. 8. The SEM image of compound 1 with reaction time of 30 min ( $Zn(II) = bpta = 0.006 \text{ mol } L^{-1}$ , 12 w).



**Fig. 9.** SEM photographs of compound 1 nanoparticles prepared by ultrasonic generator 24W in concentration of initial reagents  $[Zn^{2+}] = [bpta] = 0.006 \text{ mol } L^{-1}$ .

					•
Concentration	Time	Power	Size		
Concentration (M)	Time (min)	Power (W)	Size (nm)	Morphology	
Concentration (M) 0.04	Time (min) 15	Power (W) 12	Size (nm) 74	Morphology spherical	
Concentration (M) 0.04 0.01	Time (min) 15 15	Power (W) 12 12	Size (nm) 74 85	Morphology spherical nanorod	
Concentration (M) 0.04 0.01 0.006	Time (min) 15 15 15	Power (W) 12 12 12 12	Size (nm) 74 85 109	Morphology spherical nanorod nanorod	
Concentration (M) 0.04 0.01 0.006 0.006	Time (min) 15 15 15 30	Power (W) 12 12 12 12 12 12	Size (nm) 74 85 109 135	Morphology spherical nanorod nanorod nanorod	

**Table 1.** Comparison of the concentration of initial reagents, times effect and different powers of ultrasonic irradiation on the morphologies and sizes of nano-structure of the compound 1.

PCC

#### Reference

[1] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, The chemistry and applications of metal-organic frameworks, Science, 341 (2013) 1230444.

[2] H.-L. Jiang, T.A. Makal, H.-C. Zhou, Interpenetration control in metal–organic frameworks for functional applications, Coord. Chem. Rev, 257 (2013) 2232-2249.

[3] M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann, J.R. Long, Hydrogen storage in a microporous metal-organic framework with exposed Mn<sup>2+</sup> coordination sites, J. Am. Chem. Soc, 128 (2006) 16876-16883.
[4] X. Zhao, B. Xiao, A.J. Fletcher, K.M. Thomas, D. Bradshaw, M.J. Rosseinsky, Hysteretic adsorption and desorption of hydrogen by nanoporous metal-organic frameworks, Science, 306 (2004) 1012-1015.

[5] K. Biradha, M. Fujita, A Springlike 3D-Coordination Network That Shrinks or Swells in a Crystal-to-Crystal Manner upon Guest Removal or Readsorption, Angew, Chem, 114 (2002) 3542-3545.

[6] L. Pan, D.H. Olson, L.R. Ciemnolonski, R. Heddy, J. Li, Separation of hydrocarbons with a microporous metal–organic framework, Angew. Chem, 118 (2006) 632-635.

[7] K.H. Park, K. Jang, S.U. Son, D.A. Sweigart, Self-supported organometallic rhodium quinonoid nanocatalysts for stereoselective polymerization of phenylacetylene, J. Am. Chem. Soc, 128 (2006) 8740-8741.
[8] M.A. Abu-Youssef, A. Escuer, D. Gatteschi, M.A. Goher, F.A. Mautner, R. Vicente, Synthesis, structural characterization, magnetic behavior, and single crystal EPR spectra of three new one-dimensional manganese azido systems with FM, alternating FM-AF, and AF coupling, Inorg. Chem, 38 (1999) 5716-5723.

[9] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M.G. Pini, M.A. Novak, Cobalt (II)-Nitronyl Nitroxide Chains as Molecular Magnetic Nanowires, Angew. Chem. Int. Ed, 40 (2001) 1760-1763.

[10] J. An, S.J. Geib, N.L. Rosi, Cation-triggered drug release from a porous zinc- adeninate metal- organic framework, J. Am. Chem. Soc, 131 (2009) 8376-8377.

[11] N. Adarsh, D.K. Kumar, P. Dastidar, Metal–organic frameworks derived from bis-pyridyl-bis-amide ligands: Effect of positional isomerism of the ligands, hydrogen bonding backbone, counter anions on the supramolecular structures and selective crystallization of the sulfate anion, CrystEngComm, 11 (2009) 796-802.
[12] G.R. Desiraju, Supramolecular synthons in crystal engineering—a new organic synthesis, Angew. Chem. Int. Ed, 34 (1995) 2311-2327.

[13] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, Threedimensional porous coordination polymer functionalized with amide groups based on tridentate ligand: selective sorption and catalysis, J. Am. Chem. Soc, 129 (2007) 2607-2614.

[14] B.C. Tzeng, T.H. Chiu, B.S. Chen, G.H. Lee, Novel Single-Crystal-to-Single-Crystal Anion Exchange and Self-Assembly of Luminescent d<sup>10</sup> Metal (Cd<sup>II</sup>, Zn<sup>II</sup>, and Cu<sup>I</sup>) Complexes Containing C<sub>3</sub>-Symmetrical Ligands, Chem. Eur. J, 14 (2008) 5237-5245.

[15] T. Uemura, S. Kitagawa, Nanocrystals of coordination polymers, Chem. Lett, 34 (2005) 132-137.
[16] V. Safarifard, A. Morsali, Sonochemical syntheses of nano lead (II) iodide triazole carboxylate coordination polymer: Precursor for facile fabrication of lead (II) oxide/iodide nano-structures, Inorg. Chim. Acta, 398 (2013) 151-157.

[17] W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula, K. Müllen, A zone-casting technique for device fabrication of field-effect transistors based on discotic hexa-peri-hexabenzocoronene, Adv. Mater, 17 (2005) 684-689.

[18] S.S.-Y. Chui, S.M.-F. Lo, J.P. Charmant, A.G. Orpen, I.D. Williams, A chemically functionalizable nanoporous material [Cu<sub>3</sub>(TMA)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>, Science, 283 (1999) 1148-1150.

[19] O. Yaghi, H. Li, T. Groy, Construction of porous solids from hydrogen-bonded metal complexes of 1, 3, 5benzenetricarboxylic acid, J. Am. Chem. Soc, 118 (1996) 9096-9101.

[20] S.L. James, C.J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K.D. Harris, G. Hyett, W. Jones, Mechanochemistry: opportunities for new and cleaner synthesis, Chem. Soc. Rev, 41 (2012) 413-447.
[21] H. Sakamoto, R. Matsuda, S. Kitagawa, Systematic mechanochemical preparation of a series of coordination pillared layer frameworks, Dalton trans, 41 (2012) 3956-3961.

[22] T. Friščić, D.G. Reid, I. Halasz, R.S. Stein, R.E. Dinnebier, M.J. Duer, Ion-and Liquid-Assisted Grinding: Improved Mechanochemical Synthesis of Metal–Organic Frameworks Reveals Salt Inclusion and Anion Templating, Angew. Chem, 122 (2010) 724-727.

[23] T. Friščić, L. Fábián, Mechanochemical conversion of a metal oxide into coordination polymers and porous frameworks using liquid-assisted grinding (LAG), CrystEngComm, 11 (2009) 743-745.

[24] L. Hashemi, A. Morsali, Microwave assisted synthesis of a new lead (ii) porous three-dimensional coordination polymer: study of nanostructured size effect on high iodide adsorption affinity, CrystEngComm, 14 (2012) 779-781.

[25] J. Klinowski, F.A.A. Paz, P. Silva, J. Rocha, Microwave-assisted synthesis of metal–organic frameworks, Dalton Trans, 40 (2011) 321-330.

[26] Z. Ni, R.I. Masel, Rapid production of metal-organic frameworks via microwave-assisted solvothermal synthesis, J. Am. Chem. Soc, 128 (2006) 12394-12395.

[27] S.H. Jhung, J.H. Lee, P.M. Forster, G. Férey, A.K. Cheetham, J.S. Chang, Microwave Synthesis of Hybrid Inorganic–Organic Porous Materials: Phase-Selective and Rapid Crystallization, Chem. Eur. J, 12 (2006) 7899-7905.

[28] A. Martinez Joaristi, J. Juan-Alcañiz, P. Serra-Crespo, F. Kapteijn, J. Gascon, Electrochemical synthesis of some archetypical Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Al<sup>3+</sup> metal organic frameworks, Cryst. Growth Des, 12 (2012) 3489-3498.
[29] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, Metal–organic frameworks—prospective industrial applications, J. Mater. Chem, 16 (2006) 626-636.

[30] N. Soltanzadeh, A. Morsali, Sonochemical synthesis of a new nano-structures bismuth (III) supramolecular compound: new precursor for the preparation of bismuth (III) oxide nano-rods and bismuth (III) iodide nano-wires, Ultrason. Sonochem, 17 (2010) 139-144.

[31] M.Y. Masoomi, G. Mahmoudi, A. Morsali, Sonochemical syntheses and characterization of new nanorod crystals of mercury (II) metal–organic polymer generated from polyimine ligands, J. Coord. Chem, 63 (2010) 1186-1193.

[32] M.A. Alavi, A. Morsali, Syntheses and characterization of  $Sr(OH)_2$  and  $SrCO_3$  nanostructures by ultrasonic method, Ultrason. Sonochem, 17 (2010) 132-138.

[33] L. Hashemi, A. Morsali, Sonichemical Synthesis of a New Ethylene Diamine Lead (II) Coordination Polymer as Precursor for Preparation of PbO Nano-Structure, Journal of Inorganic and Organometallic Polymers and Materials, 22 (2012) 272-277.

[34] L. Hashemi, A. Morsali, Sonichemical Synthesis of a New Ethylene Diamine Lead (II) Coordination Polymer as Precursor for Preparation of PbO Nano-Structure, Journal of Inorg. Organomet. Polym, 22 (2012) 272-277.

[35] Y. Kojima, S. Koda, H. Nomura, Effects of sample volume and frequency on ultrasonic power in solutions on sonication, Jpn. J. Appl. Phys, 37 (1998) 2992.

[36] S. Koda, T. Kimura, T. Kondo, H. Mitome, A standard method to calibrate sonochemical efficiency of an individual reaction system, Ultrason. Sonochem, 10 (2003) 149-156.

[37] G. Cravotto, L. Boffa, S. Mantegna, P. Perego, M. Avogadro, P. Cintas, Improved extraction of vegetable oils under high-intensity ultrasound and/or microwaves, Ultrason. Sonochem, 15 (2008) 898-902.

[38] W.-J. Son, J. Kim, J. Kim, W.-S. Ahn, Sonochemical synthesis of MOF-5, Chem. Comm, (2008) 6336-6338.

[39] L.-G. Qiu, Z.-Q. Li, Y. Wu, W. Wang, T. Xu, X. Jiang, Facile synthesis of nanocrystals of a microporous metal–organic framework by an ultrasonic method and selective sensing of organoamines, Chem. Comm, (2008) 3642-3644.

[40] A. Aslani, A. Morsali, M. Zeller, Nano-structures of two new lead (II) coordination polymers: New precursors for preparation of PbS nano-structures, Solid State Sci, 10 (2008) 1591-1597.

[41] M.A. Alavi, A. Morsali, Syntheses and characterization of  $Mg(OH)_2$  and MgO nanostructures by ultrasonic method, Ultrason. Sonochem, 17 (2010) 441-446.

[42] A. Askarinejad, A. Morsali, Synthesis of cadmium (II) hydroxide, cadmium (II) carbonate and cadmium (II) oxide nanoparticles; investigation of intermediate products, Chem. Eng. J, 150 (2009) 569-571.
[43] V. Safarifard, A. Morsali, S.W. Joo, Sonochemical synthesis and characterization of nano-sized lead (II) 3D coordination polymer: Precursor for the synthesis of lead (II) oxybromide nanoparticles, Ultrason. Sonochem, 20 (2013) 1254-1260.

[44] V. Safarifard, A. Morsali, Sonochemical syntheses of a nano-sized copper (II) supramolecule as a precursor for the synthesis of copper (II) oxide nanoparticles, Ultrason. Sonochem, 19 (2012) 823-829.

[45] A.R. Abbasi, K. Akhbari, A. Morsali, Dense coating of surface mounted CuBTC Metal–Organic Framework nanostructures on silk fibers, prepared by layer-by-layer method under ultrasound irradiation with antibacterial activity, Ultrason. Sonochem, 19 (2012) 846-852.

[46] Z.-Q. Li, L.-G. Qiu, T. Xu, Y. Wu, W. Wang, Z.-Y. Wu, X. Jiang, Ultrasonic synthesis of the microporous metal–organic framework  $Cu_3(BTC)_2$  at ambient temperature and pressure: an efficient and environmentally friendly method, Mater. Lett, 63 (2009) 78-80.

[47] A. Alizadeh, H. Sedighian, R. Ghanbaripour, An Approach to the Synthesis of

7-Amino-6-imino-9-phenyl-6H-benzo [c] chromene-8-carbonitrile Derivatives via a Three-Component Reaction under Ultrasonic Irradiation, Helv. Chim. Acta, 97 (2014) 447-452.

[48] A.R. Armstrong, P.G. Bruce, Synthesis of layered LiMnO<sub>2</sub> as an electrode for rechargeable lithium batteries, Nature, 381 (1996) 499-500.

[49] V. Safarifard, A. Morsali, Sonochemical syntheses of a new fibrous-like nano-scale manganese (II) coordination supramolecular compound; precursor for the fabrication of octahedral-like  $Mn_3O_4$  nano-structure, Ultrason. Sonochem, 21 (2014) 253-261.

[50] C.-H. Lee, H.-Y. Huang, Y.-H. Liu, T.-T. Luo, G.-H. Lee, S.-M. Peng, J.-C. Jiang, I. Chao, K.-L. Lu, Cooperative Effect of Unsheltered Amide Groups on CO<sub>2</sub> Adsorption Inside Open-Ended Channels of a Zinc (II)–Organic Framework, Inorg. Chem, 52 (2013) 3962-3968.

[51] Z. Qin, M.C. Jennings, R.J. Puddephatt, Self-assembly in palladium (II) and platinum (II) chemistry: The biomimetic approach, Inorg. Chem, 42 (2003) 1956-1965.

[52] M. Martos, J. Morales, L. Sanchez, R. Ayouchi, D. Leinen, F. Martin, J.R. Barrado, Electrochemical properties of lead oxide films obtained by spray pyrolysis as negative electrodes for lithium secondary batteries, Electrochim. Acta, 46 (2001) 2939-2948.

[53] A.V. Murugan, R. Sonawane, B. Kale, S. Apte, A.V. Kulkarni, Microwave–solvothermal synthesis of nanocrystalline cadmium sulfide, Mater. Chem. Phys, 71 (2001) 98-102.

[54] S.-H. Yu, J. Yang, Z.-H. Han, Y. Zhou, R.-Y. Yang, Y.-T. Qian, Y.-H. Zhang, Controllable synthesis of nanocrystalline CdS with different morphologies and particle sizes by a novel solvothermal process, J. Mater. Chem, 9 (1999) 1283-1287.

[55] H. Shi, L. Qi, J. Ma, H. Cheng, Polymer-directed synthesis of penniform BaWO<sub>4</sub> nanostructures in reverse micelles, J. Am. Chem. Soc, 125 (2003) 3450-3451.

[56] W. Lin, W.J. Rieter, K.M. Taylor, Modular synthesis of functional nanoscale coordination polymers, Angew. Chem. Int. Ed, 48 (2009) 650-658.

[57] R.K. Bhakta, J.L. Herberg, B. Jacobs, A. Highley, R. Behrens Jr, N.W. Ockwig, J.A. Greathouse, M.D. Allendorf, Metal– Organic Frameworks As Templates for Nanoscale NaAlH<sub>4</sub>, J. Am. Chem. Soc, 131 (2009) 13198-13199.

[58] S.-S. Sun, A.J. Lees, P.Y. Zavalij, Highly sensitive luminescent metal-complex receptors for anions through charge-assisted amide hydrogen bonding, Inorg. Chem, 42 (2003) 3445-3453.

- Nanorods of a Zinc(II) metal-organic framework were synthesized
- The morphology of the nanorods depend on the concentration of initial reagents
- Low concentrations of initial reagents leaded to rod-like morphology
- The time effect on size of nano-structured MOF have been studied
- re MARANA • The shorter reaction times lead to decreasing the size of nano-structures