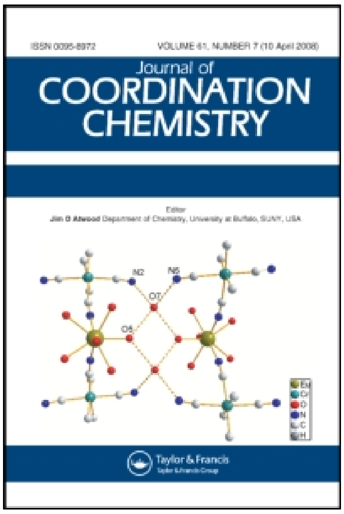

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Sonochemical syntheses and characterization of new nanorod crystals of mercury(II) metal–organic polymer generated from polyimine ligands

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Nanorod crystals of two new mercury(II) [Hg(II)] coordination polymers, $[Hg(4\text{-bpdh})Br_2]_n$ (**1**) and $[Hg(3\text{-bpdh})Br_2]_n$ (**2**) {4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene and 3-bpdh - 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene}, were prepared from the reaction of Hg(II) bromide with 4-bpdh and 3-bpdh by a sonochemical method. The nanorod crystals of **1** and **2** were characterized by scanning electron microscopy, X-ray powder diffraction, and IR spectroscopy. Compounds **1** and **2** were structurally characterized by single-crystal X-ray diffraction. The thermal stabilities of **1** and **2** were studied by thermal gravimetric and differential thermal analyses, which revealed that nanostructures of **1** and **2** are somewhat less stable than their bulk materials.

Keywords: Sonochemical; Nanoparticle; Mercury(II); 2,5-Bis(4-pyridyl)-3,4-diaza-2,4-hexadiene; 2,5-Bis(3-pyridyl)-3,4-diaza-2,4-hexadiene

1. Introduction

Inorganic polymeric substances have attracted intensive attention because of their potential applications as functional materials [1, 2]. Examples of nanoscale particles of metal–organic coordination polymers are limited [3–14]. Their preparation is challenging and requires tailoring of their physical and chemical properties through the deliberate selection [15] of metal and multifunctional ligands. In contrast to the coordination polymers of transition metals, the formation of polymers with heavy metals such as mercury(II) [Hg(II)] are sparse despite the use of Hg(II) compounds in the paper industry, paints, cosmetics, preservatives, thermometers, manometers, fluorescent lamps, and mercury batteries [4] (although limited due to its toxicity). Until recently, there have been only very few reports on Hg(II) complexes with rigid or flexible organic nitrogen donor-based ligands.

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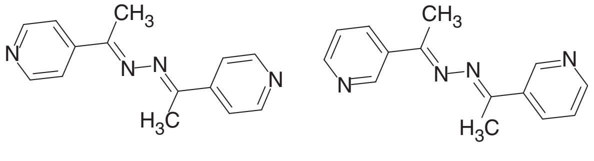


Figure 1. Ligands used in the construction of nanostructured mercury(II) bromide coordination polymers.

We have reported several Hg(II)-based organic/inorganic polymers based on *N*,*N*′-bidentate ligands, such as 4,4′-bipyridine (bipy), trans-1,2-bis(4-pyridyl)ethene (bpe), 1,2-bis(4-pyridyl)ethane (bpa), and 1,2-bis(4-pyridyl) propane (bpp) [6]. Very recently, coordination polymers with 1,4-bis(2-pyridyl)-2,3-diaza-1,3-butadiene, 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene, and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene have been synthesized and reported with several different metal ion-based organic/inorganic polymers [16–22].

This article focuses on the simple synthetic preparation of nanorod crystals of two new Hg(II) coordination polymers, $[Hg(4\text{-bpdh})Br_2]_n$ (**1**) and $[Hg(3\text{-bpdh})Br_2]_n$ (**2**), {4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene, and 3-bpdh = 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene} (figure 1).

Several different synthetic approaches have been offered for the preparation of coordination polymers: (1) slow diffusion of the reactants into a polymeric matrix, (2) diffusion from the gas phase, (3) evaporation of the solvent at ambient or reduced temperatures, (4) precipitation or recrystallization from a mixture of solvents, (5) temperature-controlled cooling, and (6) hydrothermal synthesis. In this article we describe a simple sonochemical preparation of the nanostructures of new coordination polymers. Sonochemistry uses powerful ultrasound radiation (20 KHz–10 MHz) [23]. Ultrasound induces chemical changes as a result of cavitation phenomena involving the formation, growth, and instantaneously implosive collapse of the bubbles in liquid, which can generate local hot spots having a temperature of 5000°C, pressure of 500 atm, and a lifetime of a few microseconds [24]. These extreme conditions can drive chemical reactions to fabricate a variety of nanocompounds [23]; many nanomaterials have been prepared by this method [25–34].

2. Experimental

With the exception of the nitrogen ligands, which were prepared according to literature procedures [35], all reagents and solvents for the synthesis and analysis were commercially available and were used as received. A multiwave ultrasonic generator (Sonicator_3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 24 kHz with a maximum power output of 600 W, was used for ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a

Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behavior was measured with a PL-STA 1500 apparatus. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer manufactured by X'pert with monochromated Cu-Kα radiation and simulated XRD powder patterns based on single crystal data were prepared using Mercury [36]. Crystallite sizes of the selected samples were estimated using the Sherrer method. The samples were characterized using a scanning electron microscope (SEM) with gold coating. Single crystal diffraction measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. Intensity data were collected using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using the SHELXTL suite of programs [37]. Molecular structure plots were prepared using ORTEPIII [38]. Crystal data for **1**: Triclinic space group $P\bar{1}$, $a = 7.1976(7)$ Å, $b = 8.6555(9)$ Å, $c = 14.4555(15)$ Å, $\alpha = 92.781(2)°$, $\beta = 97.789(2)°$, $\gamma = 104.666(2)°$, $V = 859.95(15)$ Å^3, $Z = 2$, $T = 298(2)$ K. The refinement of 192 parameters on the basis of 2988 independent reflections (of a total of 4544) converged at $R_1 = 0.0623$, $wR_2 = 0.1260$. Crystal data for **2**: Monoclinic space group $P2/n$, $a = 19.0250(16)$ Å, $b = 4.1701(4)$ Å, $c = 20.0902(17)$ Å, $\beta = 98.3290(10)°$, $V = 1577.1(2)$ Å^3, $Z = 4$, $T = 100(2)$ K. The refinement of 193 parameters on the basis of 3924 independent reflections (of a total of 14957) converged at $R_1 = 0.0267$, $wR_2 = 0.0627$. The observed anisotropic thermal parameters, the calculated structure factors, and the full lists of bond distances, bond angles, and torsion angles are given in the "Supplementary material".

To prepare the nanostructured **1** and **2**, 10 mL of a 0.3 M solution of Hg(II) bromide in EtOH was posited in an ultrasonic bath. Into this solution, 10 mL of a 0.3 M solution of the ligand 4-bpdh or 3-bpdh was added in drops. The obtained precipitates were filtered, subsequently washed with EtOH and then dried.

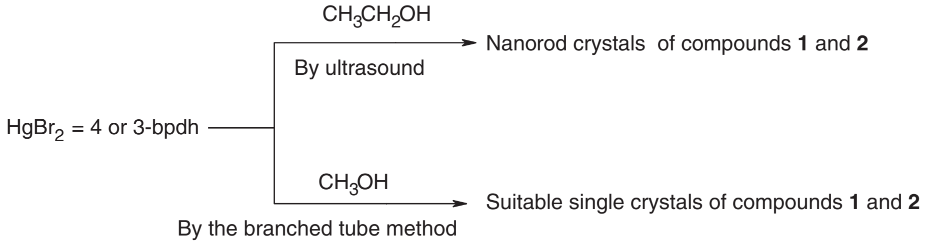
For **1**: Found (%): C, 29.50; H, 2.60; N, 9.60. Calcd for $C_{14}H_{14}Br_2HgN_4$ (%): C, 28.06; H, 2.34; N, 9.35. IR (cm^{-1}) selected bands: 568(m), 631(m), 741(m), 818(m), 1002(m), 1055(w), 1210(m), 1361(m), 1407(m), 1594(s), 1695(w), 3430(m).

For **2**: Found (%): C, 29.60; H, 2.50; N, 9.50. Calcd for $C_{14}H_{14}Br_2HgN_4$ (%): C, 28.06; H, 2.34; N, 9.35. IR (cm^{-1}) selected bands: 560(m), 638(m), 748(m), 820(m), 1026(m), 1050(w), 1214(m), 1331(m), 1417(m), 1593(s), 1695(w), 3435(m).

To isolate the single crystals of **1** and **2**, 4-bpdh or 3-bpdh (0.5 mmol, 0.115 g) and Hg(II) bromide (0.180 g, 0.5 mmol) were placed in the main arm of a branched tube reactor. Methanol was carefully added to fill the arms, the tube was sealed, and the ligand and mercury salt containing arm was immersed in an oil bath at 60°C, while the other arm was kept at an ambient temperature. After 4–5 days, colorless crystals had deposited in the cooler arm, which were isolated, filtered off, washed with acetone and ether, and air dried (0.118 g, yield 45% for **1** and 0.110 g, yield 43% for **2**).

For **1**: Found (%): C, 28.20; H, 2.30; N, 9.50. Calcd for $C_{14}H_{14}Br_2HgN_4$ (%): C, 28.06; H, 2.34; N, 9.35%. IR (cm^{-1}) selected bands: 568(m), 631(m), 741(m), 818(m), 1002(m), 1055(w), 1210(m), 1361(m), 1407(m), 1594(s), 1695(w), 3430(m).

For **2**: found (%): C, 29.10; H, 2.40; N, 9.95. Calcd for $C_{14}H_{14}Br_2HgN_4$ (%): C, 28.06; H, 2.34; N, 9.35%. IR (cm^{-1}) selected bands: 561(m), 637(m), 748(m), 820(m), 1026(m), 1050(w), 1214(m), 1331(m), 1417(m), 1595(s), 1693(w), 3435(m).



Scheme 1. Reaction of 4-bpdh and 3-bpdh with mercury(II) bromide by two different routes.

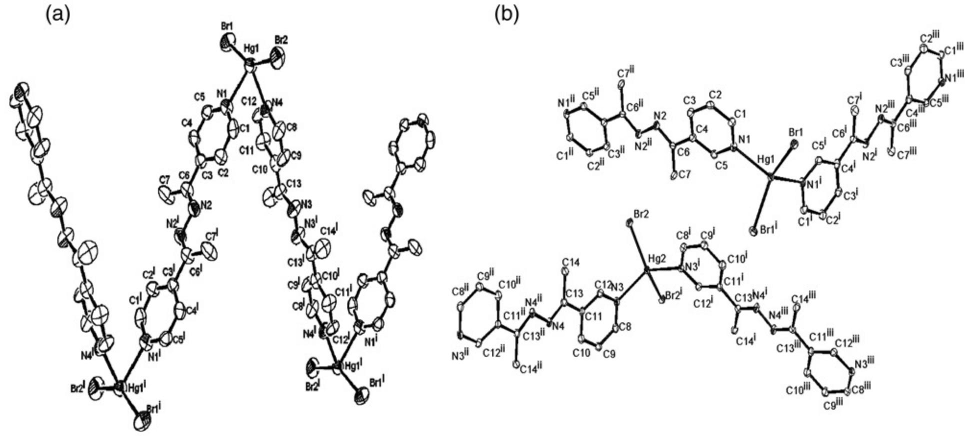


Figure 2. ORTEP diagram and representation of Hg^{II} environment (a) [Hg(4-bpdh)Br$_2$]$_n$ (**1**), i: $-x$, $-y$, $-z$ and (b) [Hg(3-bpdh)Br$_2$]$_n$ (**2**). i: $-x+1/2$, y, $-z+1/2$; ii: $-x$, $-y$, $-z$; iii: $x+1/2$, $-y$, $z+1/2$.

3. Results and discussion

Scheme 1 shows the reaction between Hg(II) bromide and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh) or 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) for **1** and **2**, respectively, in two different conditions. The nanorod crystals of **1** and **2** were obtained by ultrasonic irradiation in methanolic solution and single crystalline material was obtained using a heat gradient applied to a solution of the reagents (the "branched tube method"). IR spectra of the nanorod crystals and of the single crystalline material are indistinguishable.

Single crystal X-ray analysis reveals that **1** crystallizes in triclinic space group $P\bar{1}$ as a 1-D polymeric unit of [Hg(4-bpdh)Br$_2$] (figure 2a). The terminal nitrogens of 4-bpdh are linked to two different mercury's, resulting in 1-D polymeric units in the solid state. The coordination environment of Hg is distorted tetrahedral with 4-bpdh, thus generating angular nodes at the metal resulting in the 1-D zig-zag chains. The Hg···Hg distance is 16.01(2) Å. The N–Hg1–N and Br–Hg1–Br angles are 79.98(2)° and 148.14(2)°, respectively. Individual 1-D chains in **1** are almost parallel and further linked by weak nonclassical Br···HC hydrogen bonds (figure 3). The Br···HC bond distances in **1** are 2.845 Å (Br1···C11 = 3.638 Å and ∠BrHC = 143.67°).

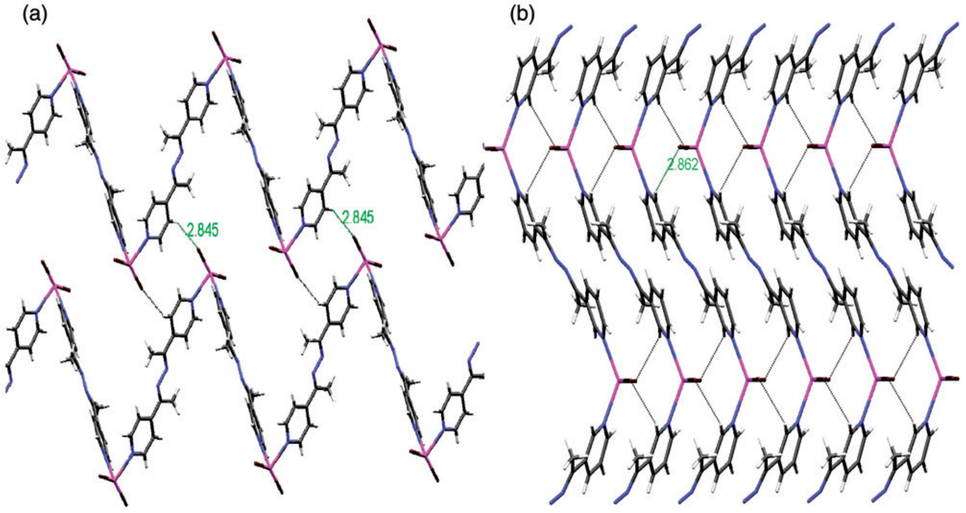


Figure 3. A fragment of the 2-D polymer (a) **1** and (b) **2**.

These interactions of Br with the C–H hydrogens of adjacent molecules grow the 1-D chains into 2-D networks (figure 3a).

$[Hg(3\text{-bpdh})Br_2]_n$ (figure 2b) crystallizes in the monoclinic space group *P2/n* as a polymeric species containing two 1-D coordination polymers with Hg1 and Hg2. In both chains,the structure is a coordination polymer of Hg(II) consisting of zig-zag chains formed by bridging 3-bpdh. There are two different Hg(II) ions, Hg1 and Hg2, coordinated by two bromides and two nitrogens from 3-bpdh, resulting in a four-coordinate complex with HgN_2Br_2. Although the coordination geometry around Hg(II) is irregular, presumably associated with steric constraints arising from the shape of 3-bpdh, it is best described as a distorted tetrahedron. The two individual, adjacent 1-D chains in **2** are almost parallel and further linked by weak $Br \cdots H$ (figure 3b) with the bond distances of 2.862(2) Å ($Br1 \cdots C5 = 3.531$ Å and $<BrHC = 128.35°$). The weak $Br \cdots H_{py}$ interactions in **2** extend the structure into 2-D supramolecules (figure 3b). A similar 1-D Hg(II) coordination polymer, $\{[HgI_2(pbbm)] \cdot (DMF)_{1/2}\}_n$ (pbbm = 1,1′-(1,5-pentanediyl)bis-1*H*-benzimidazole), with zig-zag chains has been reported [39].

The XRD patterns simulated from the single crystal X-ray data of **1** and **2**, respectively, of bulk materials as synthesized and of typical samples prepared by sonochemical process are shown in the "Supplementary material". Acceptable matches are observed for both compounds, indicating the presence of only one crystalline phase in the samples prepared using the sonochemical process. The estimation of particle sizes from the Sherrer formula from broadening of XRD peaks ($D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at a half maximum of an observed peak, respectively [40]) at 2θ in 16 and 12 gives 180 and 250 nm for **1** and **2**, respectively, in agreement with the value obtained from SEM images (figures 4 and 5). We examined other solvents such as water, acetonitrile, dichloromethane, benzene, and chloroform in the sonochemical process, but the particle sizes of the compounds were not in nanoscale.

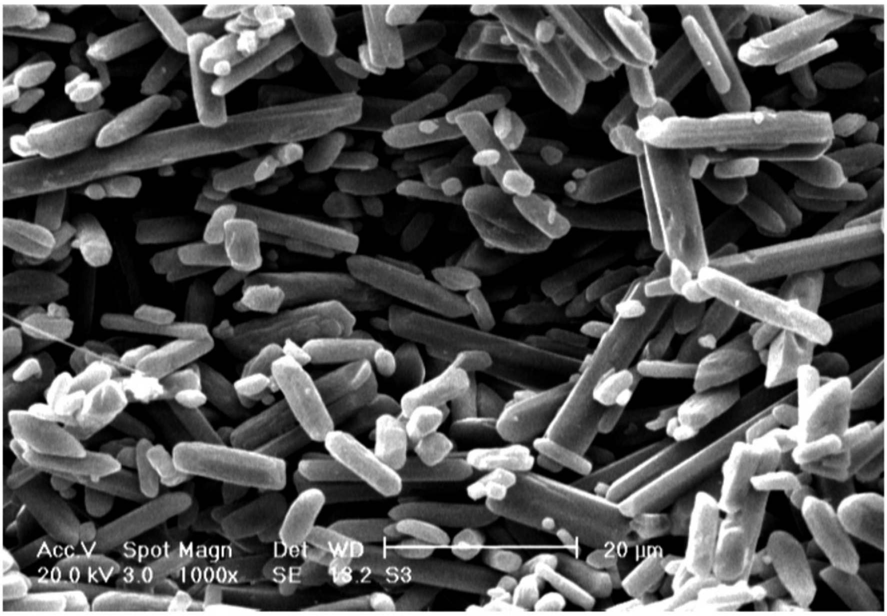


Figure 4. SEM photographs of **1** nanorod crystals.

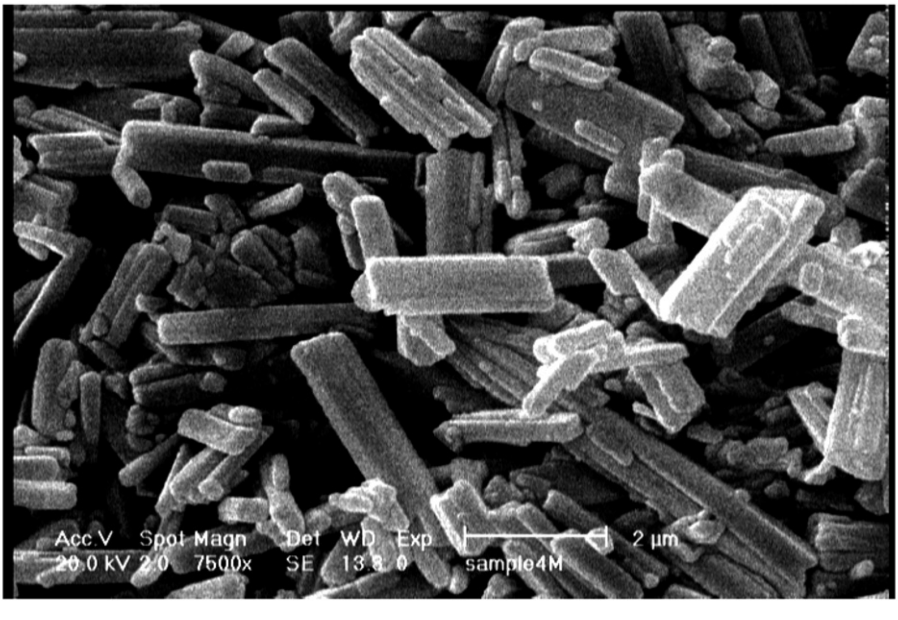


Figure 5. SEM photographs of **2** nanorod crystals.

The morphology of **1** and **2** prepared by sonochemistry (figures 4 and 5) shows nanorod crystals with a uniform diameter of around 180 nm and a length up to 2000 nm, with an aspect ratio of 100, larger than the other reported nanorods [41–44]. Very few isotropic nanoparticles can be found in the products, indicating that this synthetic method is effective for the high-yield synthesis of coordination polymer nanorods. The specific formation mechanism of the Hg(II) coordination polymer nanorod crystals warrants further investigation. There is no report about the synthesis of coordination polymer nanomaterials using sonochemical method. Here, the formation of 1-D Hg(II) coordination polymer may play an important role in the formation of the nanorod crystals.

Compounds **1** and **2** are stable up to 235°C at which temperature the ligands 4-bpdh or 3-bpdh with one endothermic effect, 255°C and 240°C, and one exothermic effect, 270°C and 260°C for **1** and **2**, respectively, begin to be removed (Supplementary material). The solid formed at 250°C is suggested to be the ligand-free $HgBr_2$ (observed 39.70, Calcd: 38.41%), that is stable up to 550°C. It is decomposed only at higher temperatures, ultimately giving solid that appears to be HgO, which at higher temperature is evaporated. Thermogravimetric analysis (TGA) shows that both frameworks have similar thermal stability, not melting and only decomposing above 240–250°C. The TGA curves of nanostructured materials have the same general appearance as their single crystalline counterparts but are somewhat less stable and gradually decompose at *ca*. 200°C. The decomposition of **1** and **2** nanostructures starts at 40° lower than single crystals, suggesting the reduction of the particle size of the coordination polymers to a few dozen nanometers results in lower thermal stability.

4. Conclusion

Two new Hg(II) coordination polymers, $[Hg(4\text{-bpdh})Br_2]_n$ (**1**) and $[Hg(3\text{-bpdh})Br_2]_n$ (**2**), have been synthesized using a thermal gradient approach and by a sonochemical method. Compounds **1** and **2** were structurally characterized by single-crystal X-ray diffraction. The crystal structures of **1** and **2** consist of 1-D polymers with the coordination number of Hg^{II} four. The reduction of the particle size of the coordination polymers results in lower thermal stability compared to the single crystalline samples. Coordination polymers may be suitable precursors for the preparation of nanoscale materials with their packing producing different and interesting morphologies. This is the first report of the synthesis of nanorods of coordination polymers and one of the few samples using sonication as an alternative synthetic procedure to form coordination polymers. This preparation takes place in shorter reaction times, produces better yields, and also produces coordination polymer at nanosize. Further systematic studies of coordination polymers with different metal ions are going on in our laboratory, which may offer new insights into metal–organic supramolecular assembly and nanochemistry.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 703754-703755 for **1** and **2**, respectively. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44–1223/336033; Email: deposit@ccdc.cam.ac.uk].

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