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RESEARCH PAPER

# Synthesis and Crystal Structure of $[Pb(gly)_2]_n$; New lead(II) Coordination Polymer with Glycine Ligand

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**ABSTRACT**

$[Pb(gly)_2]_n$ (**1**) (gly is the abbreviation of Glycine) have been synthesized and characterized by elemental analyses, IR, $^1$H NMR and $^{13}$C NMR spectroscopy. The single crystal structure of **1** show the complex is 2D coordination polymer with octahedral environment that is formed into 3D supramolecule through hydrogen bond. Structural determination of compound **1** reveals the Pb(II) ion is four coordinated, bonded to a nitrogen, oxygen and two carbon atoms from the Glycine ligand. PbO nanoparticles were synthesized by calcinations of compound **1** at 500, 550 and 600 °C under air atmosphere. The PbO nanostructure was characterized by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). The thermal stability of compound **1** was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

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## INTRODUCTION

Coordination polymers are a new Stage of crystalline porous polymers that are formed by copolymerization of multi dentate ligands with transition metal ions or metal ion clusters[1]. They have zeolite-like properties, such as high surface, microporosity, well-defined structures and the ability to Accord pore size on Å scale. Three dimensional coordination polymers are porous materials and attractive materials because of their capability to space various guests (in gas or liquid phase) in high concentrations and homogeneously. The Incarcerate effect in such materials leads to strange properties such as high gas storage and separation, catalysis, controlled release or delivery of drug molecules etc [2-6]. The assembly of coordination polymers is affected by a combination of some factors, including the metal ion, organic ligand and auxiliary ligand, metal-to-ligand ratio, solvent and the reaction temperature[7-12]. The organic ligands are key to get some intriguing topologies and functional materials. The diffusion reaction is a Sensational method for the construction of coordination polymers with intriguing motifs [13-15]. We know that size, structure and shape have significant influence on properties of inorganic/organic materials, for Example optics, electrics, optoelectronics, gas-sensor, and magnetic properties [16-20]. Micro/nano-energetic materials

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with distinct structures and extremely small feature sizes also exhibit structure- and size-dependent properties, for Example thermal decomposition, sensitivity and operational performance [21, 22]. Controllable preparation of micro/nano-energetic materials with different morphologies and sizes is more importance for achieving desirable properties. It is more difficult for the synthesis of micro/nano-energetic materials than that of inorganic nano- structures because most of energetic compounds feature vander Waals or other weak intermolecular interactions among molecules, and they are dangerous explosives[23, 24].

To proceed, we describe the preparation of lead(II) coordination polymer, $[Pb(gly)_2]_n$ (1) from reaction between lead(II) nitrate and mixtures of Glycine and sodium hydroxide in methanol and conversion into nanostructured PbO by thermolyses at 500, 550 and 600 °C in air without any surfactant or capping molecules. PbO is a polar inorganic crystalline material with many applications. PbO is very fascinating because of its numerous phases, such as $Pb_2O$, $Pb_2O_3$, and $Pb_3O_4$.

## MATERIALS AND METHODS

Starting reagents for the synthesis were purchased and used without further purification from commercial suppliers (Sigma–Aldrich, Merck and others). IR spectra were recorded as nujol mulls using SHIMADZU 8900 and SEM Hitachi S4160 spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal (BI 9300) apparatus.$^1$H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz..

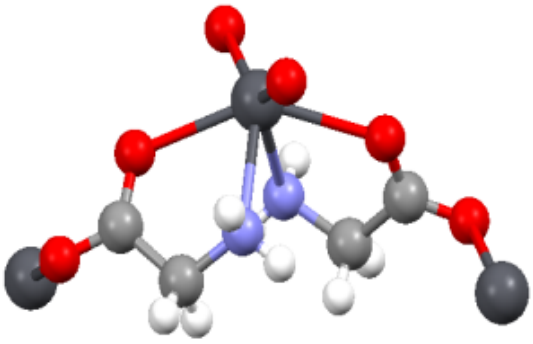

Fig. 1. The coordination environment of the compound $[Pb(gly)_2]_n$ (1).

*Synthesis of $[Pb(gly)_2]_n$ (1) as a single crystal*

Glycine (0.075g, 1mmol) and $Pb(NO_3)_2$ (0.331g, 1mmol) and Sodium hydroxide (0.04 g, 1mmol) were placed in one Bottom of a branched tube. Methanol was carefully added to fill tube, the tube sealed and the Bottom of branched tube immersed in a bath at 60 °C while the branched was at ambient temperature. After a week, crystals had deposited in the cooler arm which was filtered off, washed with Methanol, and air dried. Yield: 65 %, m.p. 218 °C is melting point.

**IR** ($cm^{-1}$) selected bonds: 499*m*, 578m, 676 m, 717 m, 812 w, 888 m, 945 m, 1069*s*, 1167 w, 1327w , 1378 m, 1436 w, 1560 s, 2006 w, 2059w, 2166 w, 2267 w, 2329 w, 2359 w, 2456 w, 2493 w, 2926 m, 3152 m, 3227 s.

**$^1$H-NMR** (DMSO, δ): 2.091(*s*, $CH_2$), 3.334(*s*, $H_2O$), 3.331(*s*, $NH_2$). **$^{13}$CNMR** (DMSO, δ):30.666(*s*, $CH_2$).

*Synthesis of PbO nanoparticles*

Calcinations of the single crystals of compound **1** at 500, 550 and 600°C in a furnace and static atmosphere of air for 4h yields mixture of PbO orthorhombic and PbO tetagonal nanoparticls.

## RESULTS AND DISCUSSION

Reaction between lead(II) nitrate and mixtures of Glycine and sodium hydroxide in methanol

Table 1. Crystal data and refinement details of $[Pb(gly)_2]_n$ (1).

| Identification code | **1** |
|---|---|
| Empirical formula | $C_4H_8N_2O_4Pb$ |
| Formula weight | 355.324 |
| Temperature | 120(2) |
| Wavelength | 0.71073 |
| Space group | C2/c |
| unit cell dimensions | a=9.7165(6)Å<br>α=90°<br>b=5.9658(4)Å<br>β=101.336(5)°<br>c =12.9875(6)Å<br>γ =90° |
| Volume | 738.16 Å$^3$ |
| Z | 4 |
| Density (calculated) | 3.197 g cm$^{-3}$ |
| Absorption coefficient | 22.824 mm$^{-1}$ |
| Theta range for data collection | 0.015 to 0.046 |
| Index ranges | -12 ≤ h ≤ 12<br>-7≤ k ≤ 7<br>-16≤ l ≤ 16 |
| Reflections collected | 14393 |
| Independent reflections | 5181 |
| Absorption correction | multi-scan |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Final *R* indices [I>2σ (*I*)] | $R_1$ = 0.0186<br>$wR_2$ = 0.0234 |
| Largest diff. Peak, hole | 0.687 and 0.617 e Å$^{-3}$ |

provided the crystalline material $[Pb(gly)_2]_n$ (**1**). The structure of compound **1** was characterized by single-crystal X-ray techniques (Table 1). Determination of the structure of the **1** by X-ray crystallography showed each lead atom is chelated by nitrogen, oxygen and carbon atoms of "gly" ligands, therefore the coordination number in this complex is six (Fig. 1). Ortep diagram of compound **1** has been shown in Fig. 2**.**

The finest features on the construction of its 3D supramolecular architecture in **1** is that the hydrogen bonding serves to connect these 2D supramolecular sheets to 3D supramolecular Structure, as shown in Fig. 3. In the title compound, the Glycine molecules contribute to the formation of intermolecular hydrogen bonds involving lead atoms.

For compound **1** as single crystal IR ($cm^{-1}$) selected bands: the 578.70 (m), 1069.39 (s), 1167.05(w), 1378.48 . The IR spectrum of this compound show absorption bands resulting from Pb-O in the 578.70 $cm^{-1}$, single band CO in the 1069.39 and 1167.05 $cm^{-1}$, single band CH in the 1377.26 $cm^{-1}$, double band CO( in the COOH) in the 1559.16 $cm^{-1}$, single band CO( in the COOH) in the 1610 $cm^{-1}$, strain band in the 2925 $cm^{-1}$, $NH_2$ in the 3150 and 3272 $cm^{-1}$ and strain band in the 3459 $cm^{-1}$ shows the existence of Methanol molecule (Fig. 4).

The $^{13}$CNMR spectrum of the DMSO and $CH_2$ solution of **1** display a distinct absorption band at 30.666 ppm and 80 ppm respectively. The $^{1}$HNMR spectrum of the DMSO solution of **1** displays a distinct absorption band at 2.507 ppm. Spectrum of the $H_2O$

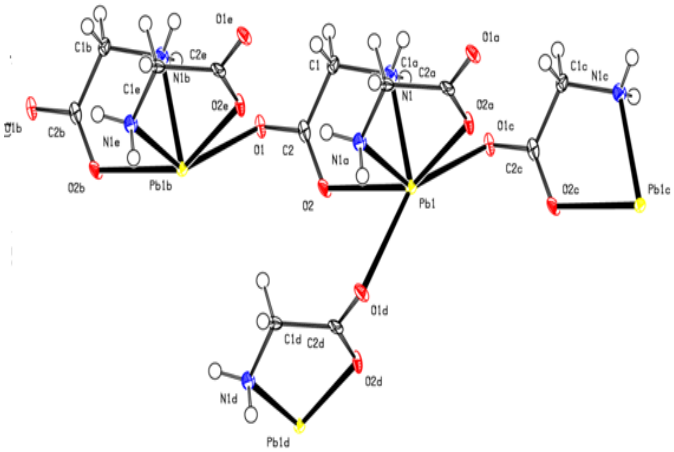


Fig. 2. Ortep diagram of $[Pb(gly)_2]_n$ (1).

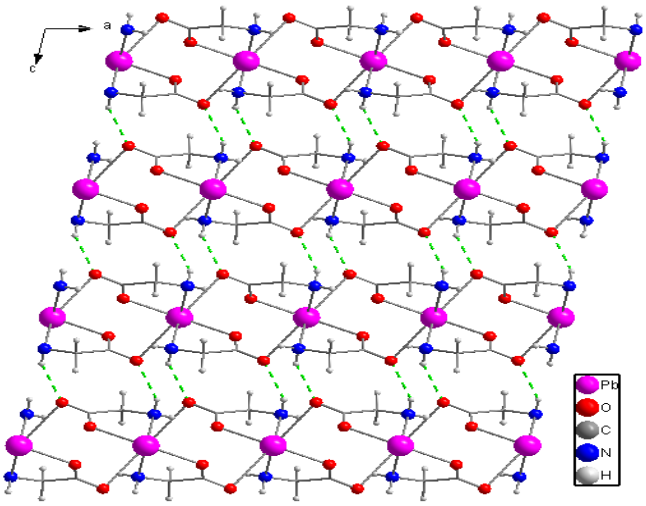


Fig. 3. A supramolecular Structure of $[Pb(gly)_2]_n$ (1), viewed along b direction.

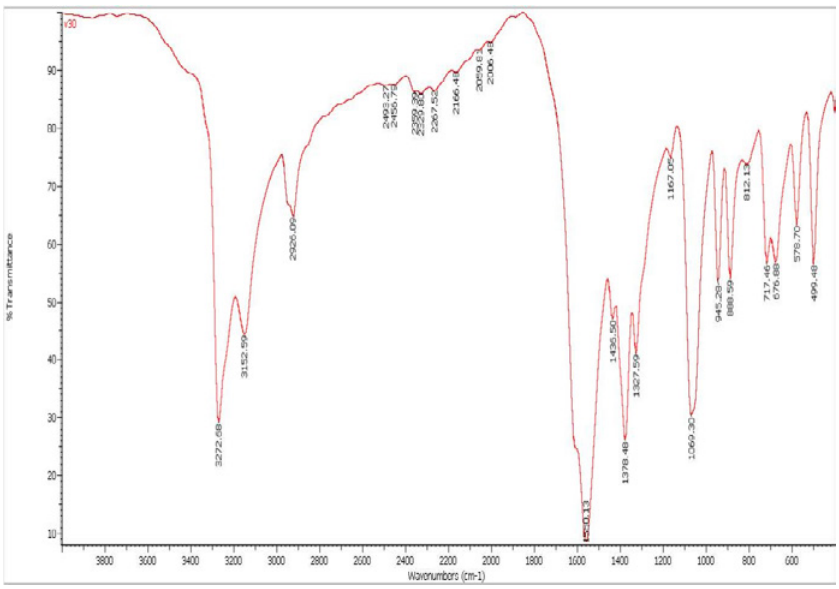


Fig. 4. IR spectra of the compound $[Pb(gly)_2]_n$ (1).

solution of **1** display at 3.334 ppm, 3.311 ppm and 2.091 ppm is show respectively distinct absorption band of $NH_2$ and $CH_2$. To Study the thermal stability of the single crystals of compound $[Pb(gly)_2]_n$ (**1**), thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 50 and 700°C under argon flow (Fig. 5). The compound **1** destruction 100 until 200°C. Decomposition of compound **1** occurs between 100 and 200°C and between 200°C and 480°C with a mass loss of 52.5%. The DTA curve displays one distinct endothermic effect at 180°C for the single crystals of compound **1**.

Morphology and particle sizes of the nanostructures depend on the the calcinations method at different temperature and investigated by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). SEM image obtained from calcination of compound **1** at 500°C (Fig. 6), 550°C (Fig. 7) and 600°C (Fig. 8) shows the nanoparticle of lead(II) oxide (at 550°C nanorod and nanoparticle have been obtained) .

For further demonstration, the EDAX of nanoparticle in 550°C has been shown in Fig. 9. The spectrum shows the presence of Pb as the only element component.

To investigate the composition and phase information of the final products, X-ray diffraction (XRD) was carried out in Fig. 10 that shows the XRD pattern of the residue obtained from calcination of compound **1** at 600 °C. The spectrum shows the presence of pb as the only element component.

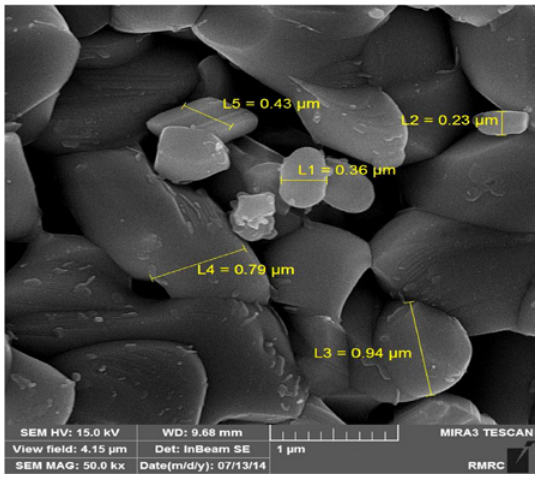


Fig. 6. The SEM image of PbO nanostructure produced by calcination of 1 at 500°C.

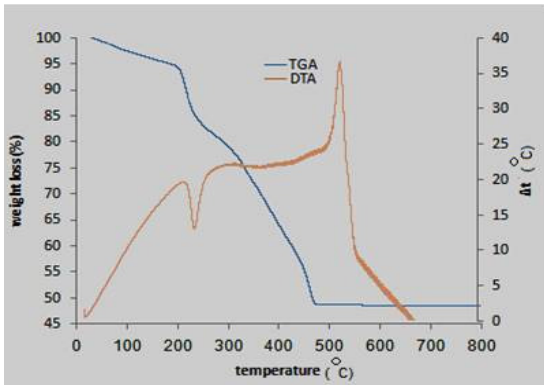


Fig. 5. Thermal behavior of compound $[Pb(gly)_2]_n$ 1.

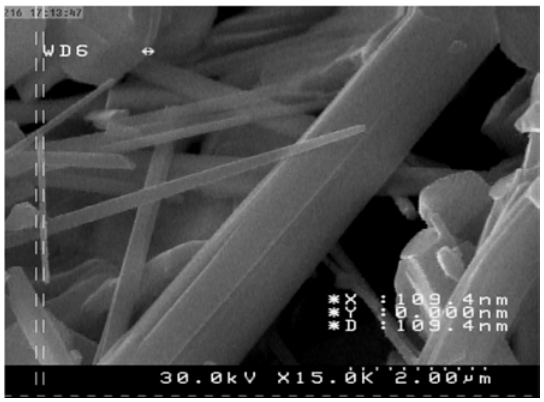


Fig. 7. SEM images of PbO nanostructure prepared by calcination of 1 at 550°C.

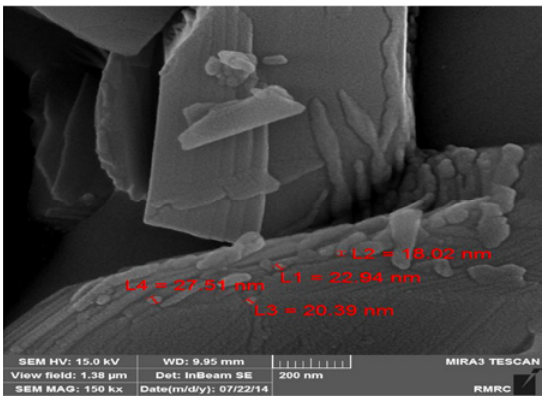


Fig. 8. SEM images of PbO nanostructure prepared by calcination of 1 at 600°C.

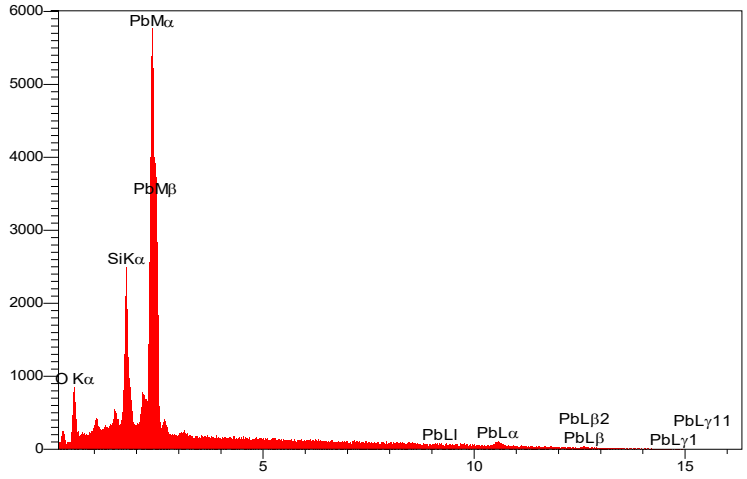


Fig. 9. EDX pattern of PbO nanostructure prepared by calcination of compound 1 at 550°C.

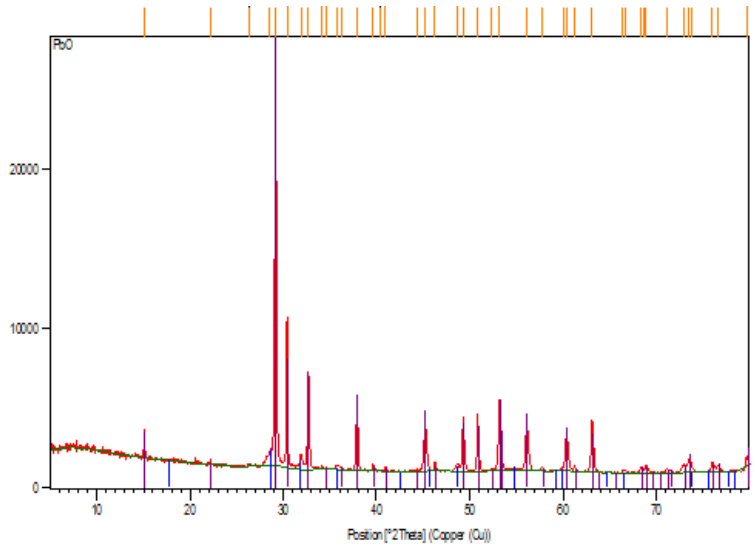


Fig. 10. XRD pattern of orthorhombic and tetragonal PbO nanostructure prepared by calcination of compound 1 at 600 °C

## CONCLUSION

A new Pb(II) coordination polymer, {[$Pb(gly)_2$]$_n$ (**1**)(gly is the abbreviation of Glycine)}, has been synthesized using branched tube method. Compound **1** was structurally characterized by single crystal X-ray diffraction, IR spectroscopy and Thermal gravimetric (TG) and differential thermal analysis (DTA). The crystal structure of compound **1** consists of a 3D supramolecular compound and shows the coordination number in the Pb(II) ions is six. Calcination of the compound **1** at 500, 550 and 600°C under air atmosphere yields mixture of orthorhombic and tetragonal PbO nanoparticles and nanorods.

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## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

## REFERENCES

1. Rowsell JLC, Yaghi OM. Metal–organic frameworks: a new class of porous materials. Microporous and Mesoporous Materials. 2004;73(1-2):3-14.
2. Kitagawa S, Kitaura R, Noro S-i. Functional Porous Coordination Polymers. Angewandte Chemie International Edition. 2004;43(18):2334-75.
3. Tranchemontagne DJ, Mendoza-Cortés JL, O'Keeffe M, Yaghi OM. Secondary building units, nets and bonding in the chemistry of metal–organic frameworks. Chemical Society Reviews. 2009;38(5):1257.
4. Lee J, Farha OK, Roberts J, Scheidt KA, Nguyen ST, Hupp JT. Metal–organic framework materials as catalysts. Chemical Society Reviews. 2009;38(5):1450.
5. Murray LJ, Dincă M, Long JR. Hydrogen storage in metal–organic frameworks. Chemical Society Reviews. 2009;38(5):1294.
6. Horcajada P, Serre C, Maurin G, Ramsahye NA, Balas F, Vallet-Regí Ma, et al. Flexible Porous Metal-Organic Frameworks for a Controlled Drug Delivery. Journal of the American Chemical Society. 2008;130(21):6774-80.
7. Ma L-F, Wang L-Y, Lu D-H, Batten SR, Wang J-G. Structural Variation from 1D to 3D: Effects of Temperature and pH Value on the Construction of Co(II)-H2tbip/bpp Mixed Ligands System. Crystal Growth & Design. 2009;9(4):1741-9.
8. Luo F, Luo M-b, Liu Y-h. Temperature-controlled structure diversity observed in the Zn(ii)-oxalate-4,4'-bipyridine three-member system. CrystEngComm. 2010;12(6):1750.
9. Li S-L, Tan K, Lan Y-Q, Qin J-S, Li M-N, Du D-Y, et al. pH-Dependent Binary Metal–Organic Compounds Assembled from Different Helical Units: Structural Variation and Supramolecular Isomers. Crystal Growth & Design. 2010;10(4):1699-705.
10. Chen M, Lu Y, Fan J, Lv G-C, Zhao Y, Zhang Y, et al. High structural diversity controlled by temperature and induction agent. CrystEngComm. 2012;14(6):2015.
11. Zhang Y, Yang J, Yang Y, Guo J, Ma J-F. Syntheses, Structures, and Luminescent Properties of a Series of Coordination Compounds Based on (4-Carboxylphenyl) (4-(2'-Carboxylphenyl)benzyl) Ether and Different N-Donor Ligands. Crystal Growth & Design. 2012;12(8):4060-71.
12. Luo R, Xu H, Gu H-X, Wang X, Xu Y, Shen X, et al. Four MOFs with 2,2'-dimethoxy-4,4'-biphenyldicarboxylic acid: syntheses, structures, topologies and properties. CrystEngComm. 2014;16(5):784-96.
13. Zhu X, Liu X-G, Li B-L, Zhang Y. Solvent-controlled assembly of supramolecular isomers: 2D (4,4) network, 1D ribbons of ring, and both 2D (4,4) networks and 1D ribbons of rings polycatenated in a 3D array. CrystEngComm. 2009;11(6):997.
14. Ling Y, Zhang L, Li J, Du M. A robust porous PtS-type Cu(ii) metal–organic framework: single-crystal-to-single-crystal transformation with reversible guest intercalation accompanied by colour change. CrystEngComm. 2011;13(3):768-70.
15. Moon SY, Noh TH, Jung O-S. Insight into the crystallization process: relationships between crystal structures and properties of copper(ii) coordination polymers containing dimethylbis(4-pyridyl)silane. CrystEngComm. 2013;15(19):3854.
16. Jenekhe SA. Self-Assembly of Ordered Microporous Materials from Rod-Coil Block Copolymers. Science. 1999;283(5400):372-5.
17. Whitesides GM. Self-Assembly at All Scales. Science. 2002;295(5564):2418-21.
18. Tian ZR, Voigt JA, Liu J, McKenzie B, McDermott MJ, Rodriguez MA, et al. Complex and oriented ZnO nanostructures. Nature Materials. 2003;2(12):821-6.
19. Park S. Self-Assembly of Mesoscopic Metal-Polymer Amphiphiles. Science. 2004;303(5656):348-51.
20. Yeats AL, Schwab AD, Massare B, Johnston DE, Johnson AT, de Paula JC, et al. Photoconductivity of Self-Assembled Nanotapes Made frommeso-Tri(4-sulfonatophenyl) monophenylporphine. The Journal of Physical Chemistry C. 2008;112(6):2170-6.
21. Yongxu Z, Dabin L, Chunxu L. Preparation and Characterization of Reticular Nano-HMX. Propellants, Explosives, Pyrotechnics. 2005;30(6):438-41.
22. Khasainov BA, Ermolaev BS, Presles HN, Vidal P. On the effect of grain size on shock sensitivity of heterogeneous high explosives. Shock Waves. 1997;7(2):89-105.
23. Manaa MR, Reed EJ, Fried LE, Goldman N. Nitrogen-Rich Heterocycles as Reactivity Retardants in Shocked Insensitive Explosives. Journal of the American Chemical Society. 2009;131(15):5483-7.
24. Gökçınar E, Klapötke TM, Bellamy AJ. Computational study on 2,6-diamino-3,5-dinitropyrazine and its 1-oxide and 1,4-dioxide derivatives. Journal of Molecular Structure: THEOCHEM. 2010;953(1-3):18-23.