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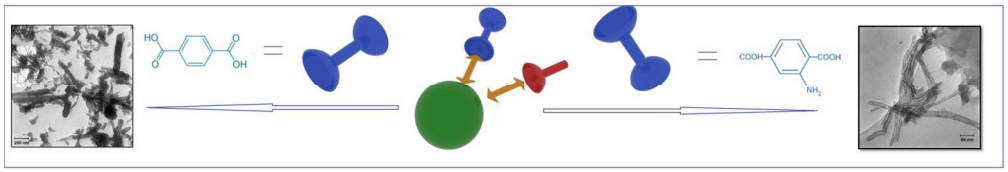

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ARTICLE

Synthesis and Characterization of different Nanostructured Copper(II) Metal-organic Frameworks by Ligand Functionalization and Modulation Method

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Nanorods of *{[Cu_2(BDC)$_2$(dabco)].2DMF.2H_2O}* ***(1)*** and Nanotubes *{[Cu_2(BDC-NH_2)$_2$(dabco)].2DMF.2H_2O}* ***(2)*** have been synthesized via reaction of *copper(II) acetate* with terephthalic acid and aminoterephthalic acid, in presence of triethylenediamine as pillar ligand and acetic acid as modulator, respectively. Formation of the unexpected nanotubes morphology instead of nanorods was evidenced when *amino benzene-1,4-dicarboxylate* [*BDC-NH_2*] was used instead of *benzene-1,4-dicarboxylate* (*BDC*) ligand. Nanorods and Nanotubes of compounds ***1*** and ***2*** were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and *BET* analyses.

Introduction

Well-designed porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) are produced by assembly of organic linkers with metal ions.[1-6] Their well-defined porosity and tunable chemical functionality make them extremely attractive for applications in gas storage[7, 8], catalysis[9] and separation.[10] Reducing the size of PCP crystals to nanometer scale via functionalization of the crystal interfaces will provide further opportunities to integrate novel functions without changing characteristic features of the parent PCP crystal. Besides, it will allow correlation between porous properties and interfacial structures of nanocrystals to be investigated.[11-14] Despite the advantages of nano PCPs, growth processes responsible for establishment of universal methodology are still unclear because there is no suitable defining protocol. [11, 14-18] In this regard, understanding crystal growth of framework materials, promises to determine the fundamental requirements for bottom-up self-assembly processes.

Formation of *[Cu(ndc)(dabco)$_{0.5}$]* nanocrystals through reaction of *ndc=1,4-naphthalene dicarboxylate* and *dabco=1,4-diazabicyclo[2.2.2]octane* in presence of acetic acid as modulator was previously reported by *Kitagawa et al.*[19]. *Zhang and co-workers* have synthesized nanoscale *Ln(BTC)(H_2O)*, where *Ln* = Dy^{3+} , Eu^{3+} , or Tb^{3+} and *BTC = 1,3,5-benzenetricarboxylate*, using sodium carboxylates (sodium formate, sodium acetate, or sodium oxalate) as capping agents to control crystal size and morphology.[20] However in these reports the linker were carboxylate ligand with no functional groups or substitutes and only the effect of modulator or capping agent on MOF growth mechanism have been investigated. In this work, modulation method is used to prepare one dimensional nanorods of *{[Cu_2(BDC)$_2$(dabco)].2DMF.2H_2O} (1)* and nanotubes of *{[Cu_2(BDC-NH_2)$_2$(dabco)].2DMF.2H_2O} (2) where BDC= benzene-1,4-dicarboxylate and BDC-NH_2= amino benzene-1,4-dicarboxylate.* Interestingly, replacing *BDC* ligand with *BDC-NH_2* changes the morphology from nanorod to nanotube.

Experimental

Materials and Physical Techniques

All reagents and solvents for the synthesis and analysis were commercially available from Merck and used as received. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with mono chromatized Cukα radiation. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating and also a transmission electron microscope (TEM) (LEO912AB) at an accelerating voltage of 120 kV. FTIR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers and *BET* (*Brunauer-Emmett-Teller*) surface area of the samples were determined from N_2 adsorption–desorption isotherms using a Surface Area Analyzer (*BELSORP*).

General procedure for synthesis of compounds *1* and *2*

Nanotubes and nanorods of *PCP [$Cu_2(BDC)_2(dabco)$].2DMF.2H_2O} **(1)**, {[$Cu_2(BDC\text{-}NH_2)_2(dabco)$].2DMF.2$H_2O$} **(2)*** were prepared by the coordination modulation method. A solution of *$Cu(OAc)_2{\cdot}H_2O$* (0.06 M) and CH_3COOH (0.6 and 1M) in DMF was heated at 100ºC in a two-necked flask. When the temperature of the solution reached to 100ºC, *$H_2BDC\text{-}NH_2$* or *H_2BDC* (0.63 mmol) and *dabco* (0.035 mmol) was added to the solution (Table 1). After the reaction had run for 24 h, the resulting samples were filtered through a glass microfiber filter, washed with DMF several times, and dried using a vacuum pump. Anal. calc. for compound ***1***: C, 44.58; H, 5.04; N, 7.43; found; C, 46.07; H, 4.66; N, 7.05% and anal. calc. for compound ***2***: C, 42.87; H, 5.01; N, 10.7; found; C, 43.84; H, 4.18; N, 9.96 %. To confirm the effect of modulator reagent (acetic acid) on the morphology and crystal sizes of *PCP* a sample was prepared in the reaction conditions of *{[$Cu_2(BDC)_2(dabco)$].2DMF.2H_2O} **(1)** and {[$Cu_2(BDC\text{-}NH_2)_2(dabco)$].2DMF.2$H_2O$} **(2)*** in the absence of acetic acid.

Table1: Experimental condition to prepare ***{[$Cu_2(BDC)_2(dabco)$].2DMF.2H_2O}*** (***1***) nanorods and ***{[$Cu_2(BDC\text{-}NH_2)_2(dabco)$].2DMF.2$H_2O$}*** (***2***) nanotubes.

Sample	*$Cu(OAc)_2.H_2O$*	*BDC*	*$BDC\text{-}NH_2$*	*Dabco*	*CH_3COOH*
1	*0.6 mmol*	*0.6 mmol*	----------	*0.3 mmol*	*0.6 M*
2	*0.6 mmol*	*0.6 mmol*	----------	*0.3 mmol*	*1 M*
3	*0.6 mmol*	*0.6 mmol*	----------	*0.3 mmol*	----------
4	*0.6 mmol*	----------	*0.6 mmol*	*0.3 mmol*	*0.6 M*
5	*0.6 mmol*	----------	*0.6 mmol*	*0.3 mmol*	*1 M*
6	*0.6 mmol*	----------	*0.6 mmol*	*0.3 mmol*	---------
7	*0.3 mmol*	----------	*0.3 mmol*	*0.15 mmol*	*0.6 M*
8	*0.3 mmol*	----------	*0.3 mmol*	*0.15 mmol*	*0.3M*
9	*1 mmol*	----------	*1 mmol*	*0.5 mmol*	*0.6 M*

Results and discussion

To confirm the preparation of MOFs with paddle-wheel motifs, X-ray powder diffraction and elemental analyses are performed. Both compounds ***1***(*Nanorod*) and ***2***(*Nanotube*) have very similar PXRD patterns with the reported isostructure compounds, ([$Zn_2(BDC)_2(TED)$]·2DMF·0.2H_2O and [$Zn_2(BDC\text{-}NH_2)_2$ (TED)]·xDMF·yH_2O,[21] (*Figure 1*) confirming that the pillared 3D structure is retained upon ligand functionalization. So, modulation method does not change the phase and structure in compounds 1 and 2. For each MOF these analyses were done in the presence of 0.6 and 1 M of acetic acid (Figure 2). As it can be seen, in compound 2, by replacing BDC with $BDC\text{-}NH_2$ crystalinity is reduced. Besides, in compound 1, by increase the acetic acid concentration from 0.6 to 1M, crystalinity reduces but in compound 2 crystalinity increases. It seems that interactions of acetate ions with amino groups blocks them, improves the crystalinity, and affects growth of motifs in one-dimensional.

TEM analysis was used to investigate growth of the unexpected nanotubes. As expected, in the presence of 0.6 M and 1 M acetic acid for samples No 1 and 2, respectively, nanorods of compound **1**

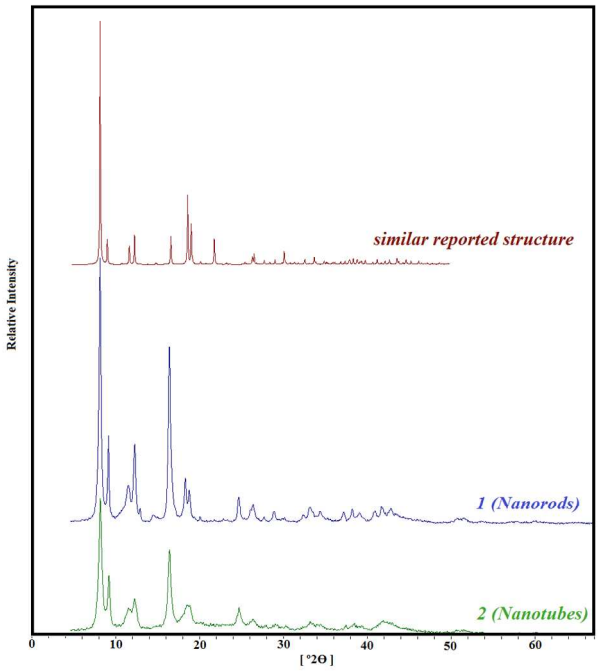

Figure 1. XRD pattern of compounds ***1*** and ***2*** as well as compound [$Zn_2(bdc)_2(ted)$]·2 DMF·0.2H_2O (similar reported structure)

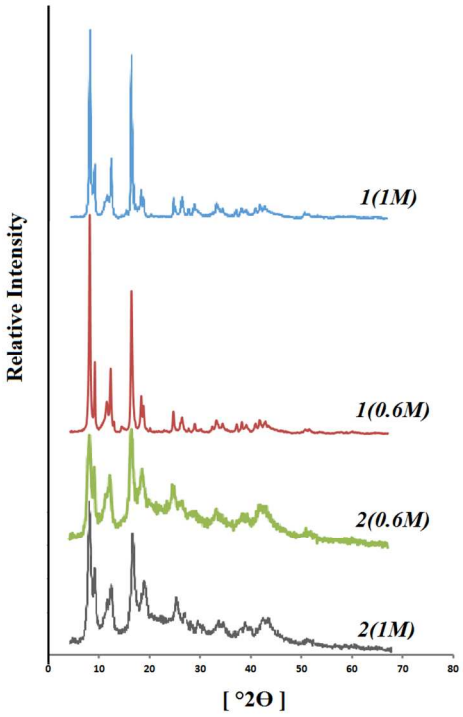

Figure 2. XRD patterns of compounds 1 and 2 in the presence of 0.6 and 1 M concentration of acetic acid.

are prepared (*Figure 3a-d*). Replacing BDC with $BDC\text{-}NH_2$ (compound **2**) the morphology is changed to nanotubes (*Figure 3e-h*). To investigate the role of modulator on the morphology of

compound **2,** three further experiments (*samples No. 7, 8 and 9*) were done. Comparison of the TEM images of samples No. 4 and 7 (Figures 3e,f and 4a,b, respectively) shows that by decreasing the concentration of metal ions and linkers a few nanotubes has been prepared. As it can be seen in *Figure 4 c,d* there is no sign of nanotubes in prepared compound **2** by decreasing the concentration of modulator till 0.3 M (Sample No.8). Figure 4e,f shows TEM images of sample No. 9 and confirms that increasing or decreasing the concentration of metal ions and linkers has the same results and a few nanotubes has been growth in these conditions.

Figure 3 illustrates the similarity in diameters of nanotubes and nanorods, confirming the influence of ligands on structure of MOF and showing that the synthesis conditions are optimized for both of the systems.

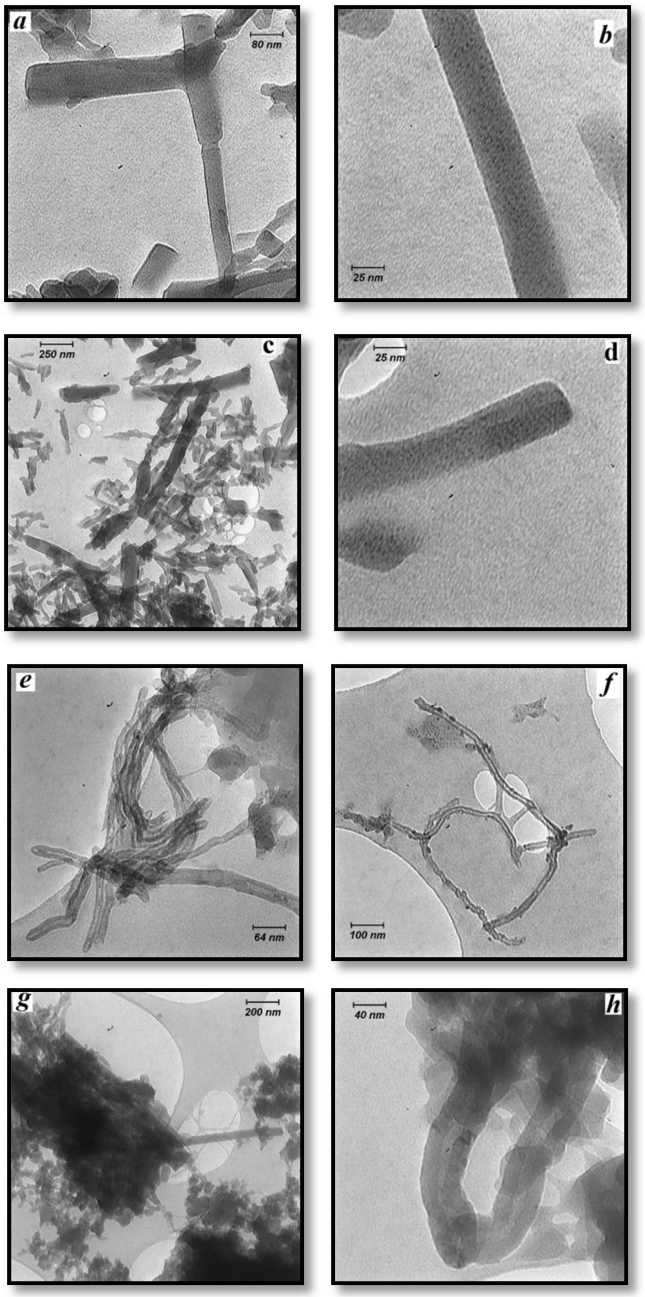

Figure 3. TEM analysis of samples No. ***a, b)*** 1, ***c,d)*** 2**,** ***e,f)*** 4 and ***g,h)*** 5.

Comparing of the TEM images confirm that a small change in the linker, from BDC to BDC-NH_2, affects the morphology. Preparation of one-dimensional nanorods in the presence of modulator reagents was explained earlier by Kitagawa et al.[19] In fact, acetic acid has functionalities similar to dicarboxylate linker and the competition between them leads to production of one-dimensional nanorods of MOFs. The nanorods grow by the oriented attachment of the nanocubes by collision of nanocubes in solution.[19, 22-24] The mechanism of anisotropic crystal growth is clearly explained by oriented attachment. The coordination modulation method affords perfect framework regularity in PCP nanocrystals, which allows the nanocrystals to be applied as crystalline porous materials.[19] Furthermore, functionalization of the dicarboxylate linker by amino group in this investigation opens up a new way to prepare the nanotubes of the same MOFs. It seems that amino groups interfere during self-assembly of MOFs and lead to production of nanotubes.

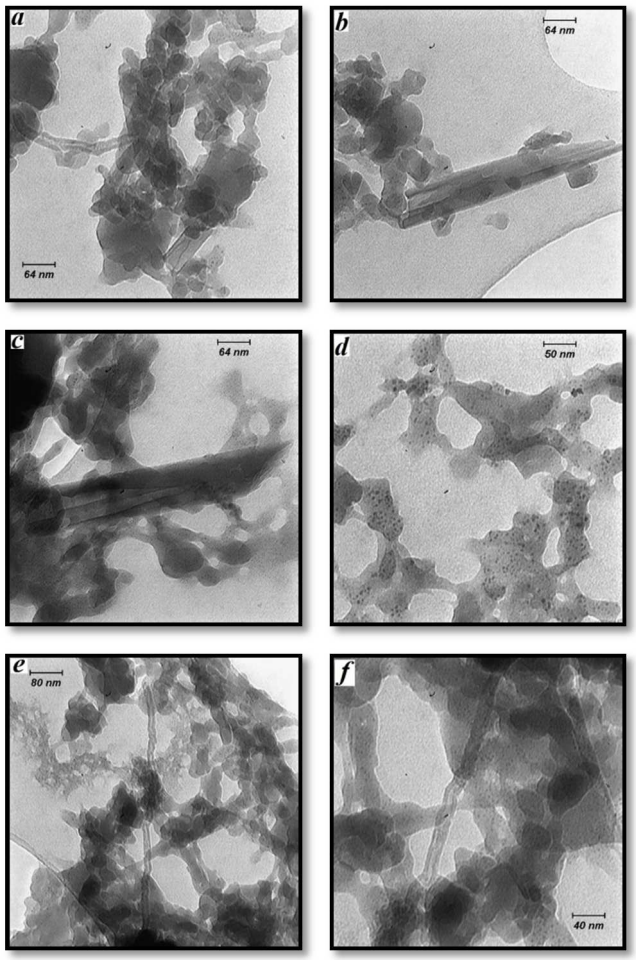

Figure 4. TEM images of samples ***a,b)*** No.7, ***c,d)*** No.8 and ***e,f)*** No.9.

Figure 5 shows SEM images of samples No. 1-8. As we expected in the presence of modulator reagent (samples No.1, 2, 4 and 5) nanostructures were grown and separated but in the absence of modulator reagent (samples No. 3 and 6) agglomeration of particles has been prepared.

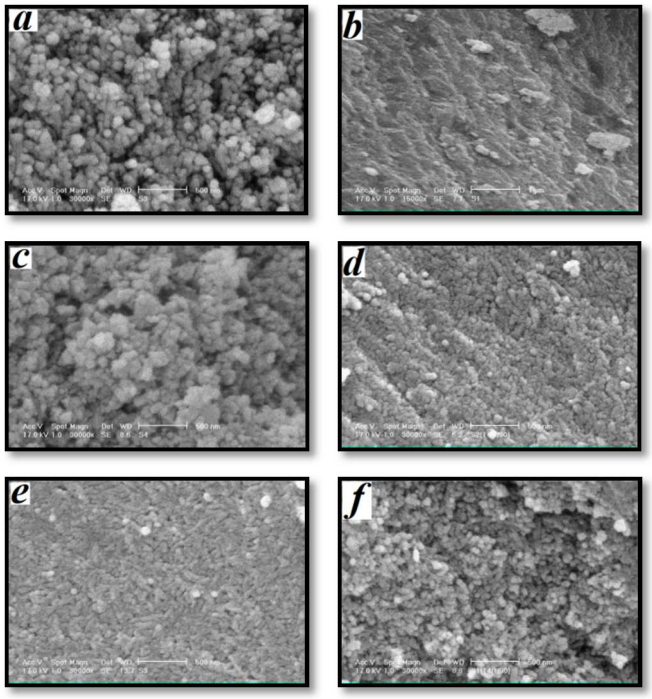

Figure 5. SEM images of samples **a)** No.1, **b)** No.2, **c)** No.3, **d)** No.4, **e)** No.5 and **f)** No.6.

High resolution SEM (HR-SEM) analysis for samples No. 5 and 9 were done (Figure 6). Figure 6a shows one-dimensional structures for sample No 5 that in agreement with TEM analysis. HR-SEM images shows a few one-dimensional structures for sample No.9 (Figure 6b). Comparing the TEM and HR-SEM images for sample No. 9 confirms that by increasing the starting material concentration modulator reagent did not affect properly and a few nanotubes has been prepared.

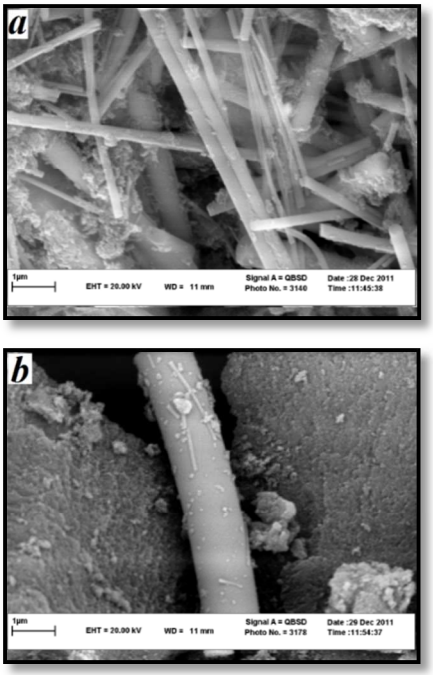

Figure 6. HR-SEM images of samples **a)** No. 4, **b)** No. 5.

Adsorption of N_2 is studied for both the nanorods of compound **1** and nanotubes of compound **2** to analyze porosity based on *Brunauer-Emmett-Teller* (BET) method. Comparing of the adsorption isotherms corresponding to highly crystalline nanorods of *compound **1***, nanotubes of *compound **2***, prepared with 0.6 M acetic acid, and less-crystalline aggregated crystals, prepared in absence of acetic acid, clearly indicates that nanorods are the superior sorbers of nitrogen (Figures 7). The competitive interaction of the *BDC–copper* or *BDC-NH_2-copper* and the *acetate–copper* is essential to reduce the rate of framework construction. This allows anisotropic growth of nanocrystals and formation of MOF structures with high crystalinity. The lower sorption amount of the aggregated crystals is most likely attributed to the lower crystalinity and critical number of defects which allow blocking of the channels.[19] The adsorption branches are completely flat up to p/p° = 0.8 discarding the occurence of such a porosity. The prepared materials are therefore essentially microporous. The hysteresis loop observed is likely due to some interparticular voids which desorb at low pressure, that is p/p° = 0.42. Moreover, the isotherm *b* looks like type IV, not type I. This may be attributed to the presence of the nanotubes which provides some mesoporosity in the compound 2.

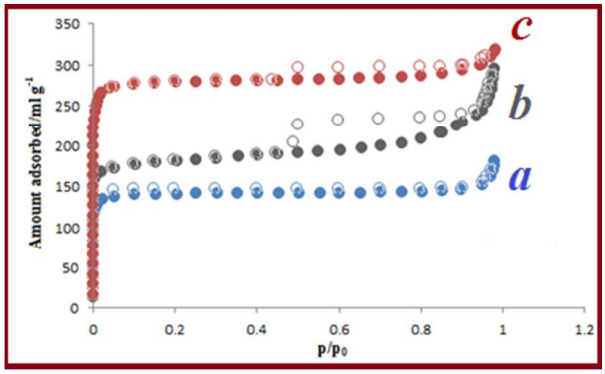

Figure 7. Nitrogen adsorption-desorption diagram of samples ***a***) 3, ***b***) 4 and ***c***) 1.

The pore size distributions for samples No.1, 3 and 4 are shown in Figure 8. For *compound **1*** and ***2*** one peak is observed at 6 Å, indicating that the obtained MOFs have uniform micropores.

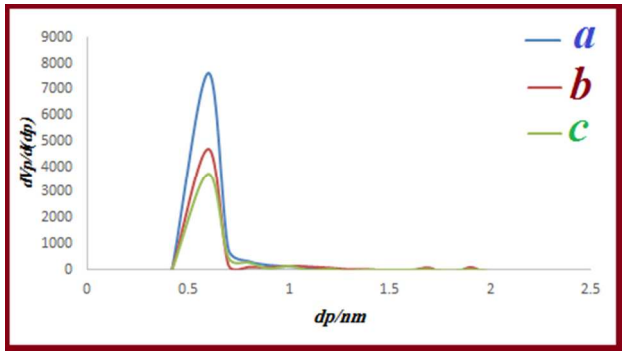

Figure 8. Pore size distribution of samples a) No.1, b) No.4 and c) No.3.

Thermal gravimetric analysis of compounds ***1*** and ***2*** is illustrated as Figure 9. As it can be seen for compound 1, three major losing weights at 145, 250, 350 °C are due to DMF+ H_2O (17%), dabco (14%), and terephthalic acid (43%), respectively. The results are the

same for compound ***2*** but weight losses occur at different temperatures, i.e. at 145°C DMF and H_2O (16%), and dabco (13%) and NH_2-BDC (46%) at 250°C and 290°C , respectively. So the results are in agreements with structural formula of $[Cu_2(BDC)_2(dabco)].2DMF.2H_2O\}$ for compound ***1*** and $\{[Cu_2(BDC\text{-}NH_2)_2(dabco)].2DMF.2H_2O\}$ for compound ***2***.

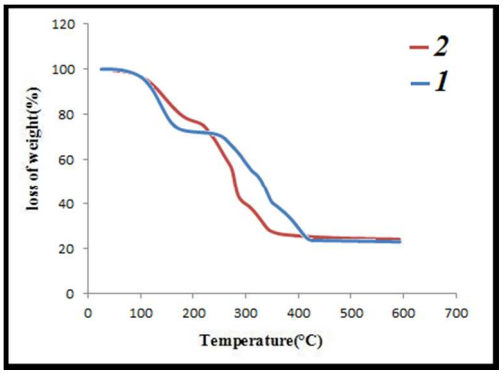

Figure 9. TGA analysis of compounds 1 and 2.

Conclusions

One-dimensional nanostructure, i.e. nanorods and nanotubes, of *compounds* $\{[Cu_2(BDC)_2(dabco)].2DMF.2H_2O\}$, ***(1)*** *and* $\{[Cu_2(BDC\text{-}NH_2)_2(dabco)].2DMF.2H_2O\}$ ***(2)*** have been synthesized via modulation method. Formation of the unexpected nanotubes morphology instead of nanorods was evidenced when *amino benzene-1,4-dicarboxylate* (*BDC-*NH_2) was used instead of *benzene-1,4-dicarboxylate* (*BDC*) ligand. This investigation shows that by functionalizing the linker with amino group in presence of modulator, the morphology changes from one-dimensional nanorods to nanotube. This is the first report for preparation nanotube of $\{[Cu_2(BDC\text{-}NH_2)_2(dabco)].2DMF.2H_2O\}$ ***(2)*** by modulation method.

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