

**“BABEȘ – BOLYAI” UNIVERSITY  
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING**

**CONTRIBUTIONS TO PERAZA CROWN  
ETHERS AND METAL ORGANIC  
FRAMEWORKS CHEMISTRY**

– Ph.D. Thesis Abstract –

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**Key words:** peraza crown ethers, macropolycyclic compounds, metal-organic framework, hydrogen storage, (metal organic framework)@(carbon structure) type composites

## **Introduction**

Peraza-crown ethers are the most studied group of polydentate macrocyclic compounds. The big interest manifested for these molecules is explained by their unique and selective properties to form complex compounds with cations, anions and organic molecules. These complexes have applications in many areas of human activity: the polluted water treatment, as artificial enzymes or contrast agents in NMR clinical investigations, for cancer or AIDS treatment, to mobilize the stem cells, as catalysts etc. They are also works as building blocks in synthesis of natural products with potential pharmaceutical properties.

Metal organic frameworks (MOF) are a new class of nanoporous materials which seems to be very attractive for certain application in gas separation and gas storage area due to their high surface area and pores volume.

The objectives of this work are the elaboration of new compounds and synthesis methods for peraza crown ethers and metal organic frameworks. The work is structured in two chapters: the first one contains the results obtained in peraza crown ethers synthesis and the second ones deals with metal organic frameworks studies.

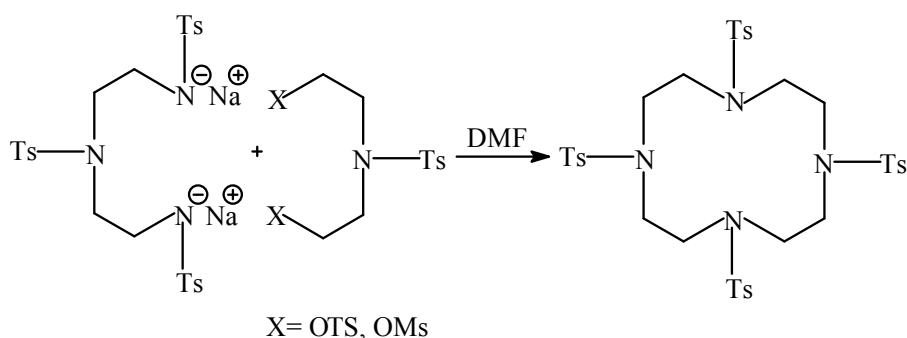
# I. Contributions to peraza crown ethers chemistry

## I.1 Synthesis methods and cyclization specific conditions

The most usual synthesis methods for peraza crown ethers are: the Richman-Atkins<sup>4</sup> reaction, the reaction of dichloride or diesters with polyamines<sup>29</sup>, „crab like” reaction<sup>39</sup> and Okahara<sup>42</sup> reaction. All these cyclization reaction are in competition with polymerization.

The azacrown synthesis methods can be classified in two categories: (1) reaction in which the product formation is controlled by the presence of a template metallic ion which interacts with heteroatoms; and (2) reactions carried out in ultra-dilution conditions without a template ion.

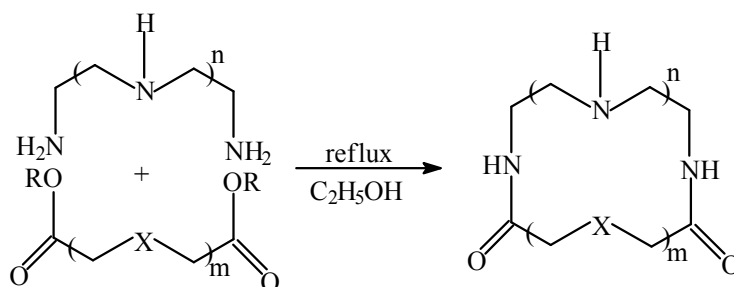
Richman and Atkins presented in 1974 the general preparation method of polyaza crown ethers from polysulphonamides, which implies their reaction with ditosyl ether or dimesyl esters (Scheme I.1.1.2)<sup>4</sup>.



**Scheme I.1.1.2**

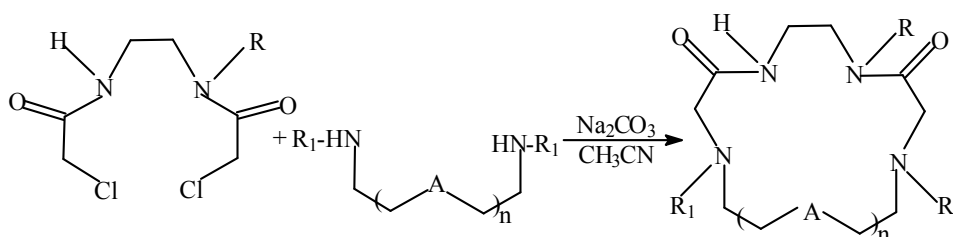
The polyamides tosyl groups are necessary in order to induce into the linear compound the conformation favorable for cyclization.

The cyclization of diesters is used to obtain 11-15 member rings. The yield of these synthesis is relatively poor, but permit the preparation of substituted ether rings<sup>34</sup>.



**Scheme I.1.2.1**

The “crab-like” cyclization permits the preparation of polyaza crown ethers with one or two unsubstituted nitrogen atoms by the reaction of bis- $\alpha$ -chloroamides with primary amines and bisamines (Scheme I.1.3.7)



**Scheme I.1.3.7**

## ***1.2. Original Contributions***

This chapter presents the original contribution brought by this paper in the peraza crown ethers area. The researches were focused in several directions:

- (i) The elaboration of a simple, rapid, economical efficient and less toxic synthesis method for peraza crown ethers;
- (ii) The preparation of poly macrocyclic compounds based on peraza crown ethers;
- (iii) The study of the potential catalytic properties of the peraza crown ethers complexes;

The results are organized in three sections:

- the new synthesis method of peraza crown ethers in the presence of  $\text{KF}/\text{Al}_2\text{O}_3$ ;
- the synthesis of new functionalized macrocyclic compounds based on 1,4,7-triazacyclononane și 1,4,7,10-tetraazacyclododecane;
- the catalytic activity of p-xylene-bis[[1,4,7-tris (hidroxyethyl)]cyclen} complex with  $\text{NaBH}_4$ .

## I.2.1 A peraza crown ethers new synthesis in the presence of $\text{KF}/\text{Al}_2\text{O}_3$

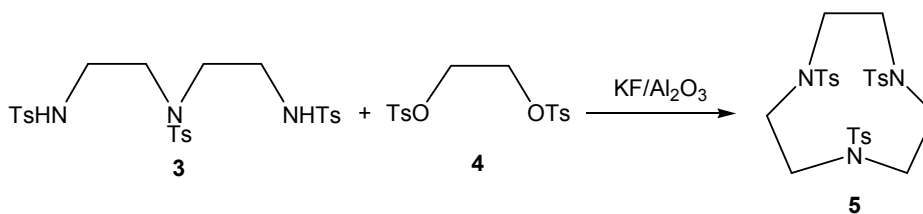
It is well known that the solid catalysts reactivity and/or selectivity can be modified by supporting them on the inorganic oxides as: alumina, silica, zeolites etc. The usage of  $\text{KF}/\text{Al}_2\text{O}_3$  was first reported in 1979<sup>60</sup> and proved itself to be a very efficient and advantageous reagent. The usage of  $\text{KF}/\text{Al}_2\text{O}_3$  joins together the advantages liquid solution reactions with the surface reactions: the supported reagent is separated from the reaction mixture by filtration (and then reused) and the reaction product is isolated by solvent removal. The reaction monitoring and the product analysis are made by standard procedure as: thin layer chromatography, NMR, IR spectroscopy, etc. Beside its unique properties, others advantages of using  $\text{KF}/\text{Al}_2\text{O}_3$  are: it is environmentally friendly, is not corrosive and has a low cost.

Though  $\text{KF}/\text{Al}_2\text{O}_3$  it is a successful reagent the source of its basicity and the identity of catalytic centers are still unknown. There are three basic species or three mechanisms to produce basic centers on the surface of KF-alumina:

- (i) the reactive  $\text{F}^-$  ions well dispersed and low coordinated;
- (ii)  $[\text{Al}-\text{O}^-]$  ion which in the water presence generate  $\text{OH}^-$ ;
- (iii) the concerted action of  $\text{F}^-$  ions and hydrated alumina surface,  $[\text{Al}-\text{OH}]$ , which can generate in-situ basic centers during the reaction<sup>77,78</sup>.

### I.2.2.1 1,4,7-triazacyclononane synthesis<sup>80</sup>:

$\text{N},\text{N}',\text{N}''$ -tris(p-toluene-sulfonyl)-1,4,7-triazacyclononane was synthesized in the presence of  $\text{KF}/\text{Al}_2\text{O}_3$  starting with tritosyl diethylenetriamine **3** and bistosyl ethylene glycol **4**, using different solvents (ethanol, acetonitrile and tetrahydrofuran – acetonitrile mixture (1:1) ( scheme I.2.1.2 )<sup>80</sup>.



Scheme I.2.1.2

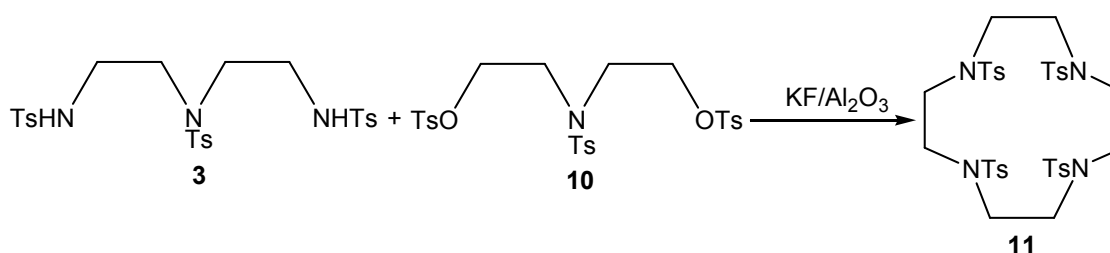
The reaction monitoring, the separation and purification of the products were made in the same way in all cases. For the reaction conducted in THF the apparition of few supplementary spots were observed, and were attributed to some secondary

products. The best yield for the preparation of N,N',N''-tris(p-toluene-sulfonyl)-1,4,7-triazacyclononane was obtained for the reaction conducted in CH<sub>3</sub>CN, 75%.

The tosyl groups were removed by acid hydrolysis in concentrated H<sub>2</sub>SO<sub>4</sub>.

### ***1.2.2.2 Cyclen synthesis*<sup>80</sup>:**

1,4,7,10-tetrakis(p-toluene-sulfonyl)-1,4,7,10-tetraazacyclododecane **11** was synthesized in the presence of KF/Al<sub>2</sub>O<sub>3</sub> starting with diethylenetriamine tristosylated **3** and diethanolamine bistosylated **10**, in acetonitrile with a yield of 61% (scheme 1.2.1.4)<sup>80</sup>.



**Scheme 1.2.1.4**

In conclusion, the utilization of KF/Al<sub>2</sub>O<sub>3</sub> as basis is a convenient, cheap and less toxic alternative for the synthesis of peraza crown ethers.

## **1.2.2 The synthesis of new polymacrocyclic compounds based on 1,4,7-triazacyclononane and 1,4,7,10-tetraazacyclododecane<sup>85</sup>**

Four new macrocyclic compounds (**21**, **24**, **27** and **28**) having different functional groups were synthesized by connected two molecules of cyclene and triazacyclononane, respectively through a rigid spacer, m-xylene.

The functional groups of the macrocyclic compounds can be introduced before synthesis by functionalization of the starting materials or after synthesis by functionalization of the skeleton. The macrocyclic compounds based on cyclen were functionalized after synthesis and in the case of triazacyclononane ones, one function was introduced before synthesis and the other one after synthesis.

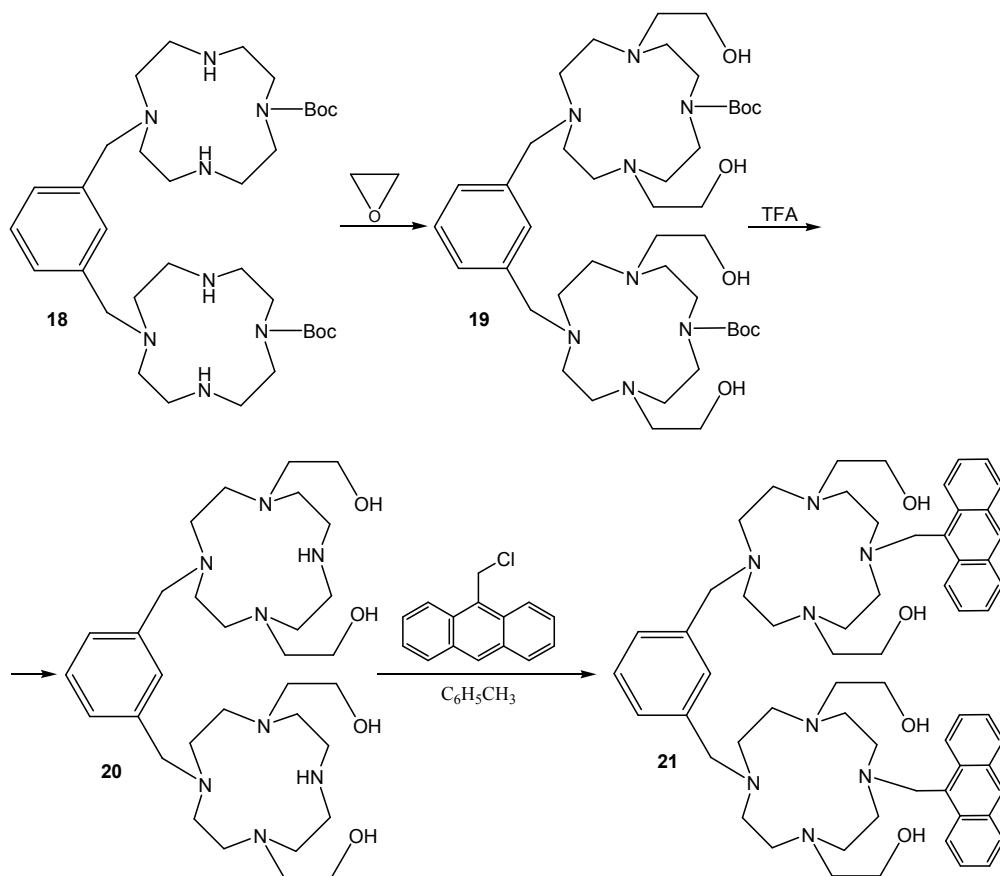
### ***1.2.2.1 1,1'-(m-Xylylene)-bis[4,10-di(hydroxyethyl)-7-methylantracene]-1,4,7,10-tetraazacyclododecane]* synthesis<sup>85</sup> (**21**)**

The preparation of **21** implies :

(i) the preparation of macropolycycle m-xylylene-bis(cyclen) skeleton



(ii) the functionalization of two cyclen rings after synthesis with two hydroxyl ethyl groups in 4 and 10 positions and one methylantracene group in 7 position (scheme I.2.2.1).

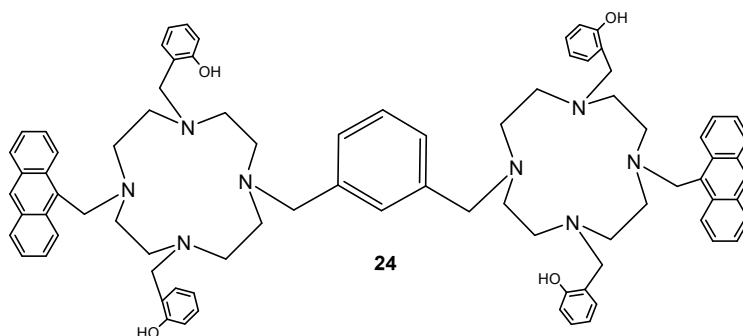


**Scheme I.2.2.1**

*1,1'-xylylene-bis[4,10-bis(hydroxyethyl)-7-t-butyloxycarbonyl-1,4,7,10-tetraazacyclododecane]* **19** is obtained by the reaction of compound **18** with ethylene oxide<sup>88</sup>. The protective groups, are removed from the compound **19**, by treating with trifluoroacetic acid resulting *1,1'-(m-Xylylene)-bis[4,10-di(o-hydroxyethyl)-1,4,7,10-tetraazacyclododecane]* **20**<sup>86</sup>. From this one, the introduction of methylantracene functions in 7 and 7' positions leads to *1,1'-(m-Xylylene)-bis[4,10-di(hydroxyethyl)-17-(methylantracene)-1,4,7,10-tetraazacyclododecane]* **21**<sup>89</sup>.

### I.2.2.2 *1,1'-(m-Xylylene)-bis[4,10-di(hydroxybenzyl)-7-(methylantracene)-1,4,7,10-tetraazacyclododecane] synthesis (24)*<sup>85</sup>

*1,1'-(m-Xylylene)-bis[4,10-di(o-hydroxybenzyl)-7-(metylantracene)-1,4,7,10-tetraazacyclododecane]* **24** has the same m-xylylene-bis(cyclen) skeleton as compound **21** (scheme I.2.2.2). The difference between the two macrocycles consist in the substituting groups from the 4 and 10 positions of the cyclen rings, which in the case of compound **24** are hydroxybenzyl groups. These substituents are inserted into the molecule through reaction of compound **18** with formaldehyde and phenol in inert medium<sup>90</sup>.



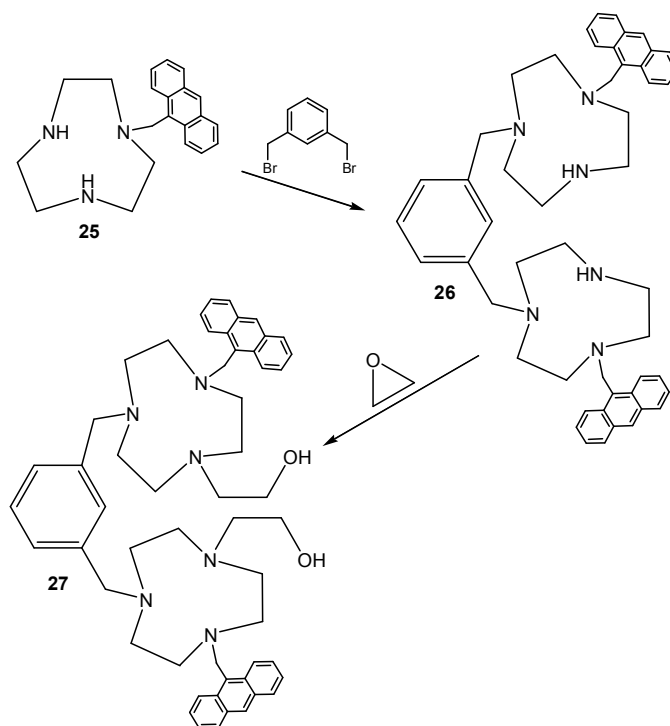
**Scheme I.2.2.2**

### I.2.2.3 *1,1'-(m-Xylylene)-bis[4-methylantracene-7-hydroxyethyl-1,4,7-triazacyclononane] synthesis (27)*<sup>85</sup>

For *1,1'-(m-Xylylene)-bis[4-methylantracene-7-hidroxyethyl-1,4,7-triazacyclononane]* **27** through the initial functionalization of construction unit 1,4,7-triazacyclononane, it is possible to design a strategy which does not imply deprotective steps. This strategy implies:

- (i) preparation of 1-methylantracene-1,4,7-triazacyclononane **25**,
- (ii) preparation of a macropolycycle m-xylylene-bis(triazacyclononane) skeleton
- (iii) after synthesis functionalization of the two triazacyclononane rings with hydroxyethyl groups in 7 and 7' positions (scheme I.2.2.3).

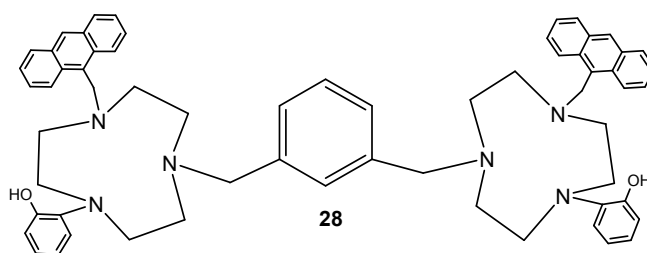
The methylantracene function is introduced before synthesis in the macrocycle **27** skeleton by triazacyclononane functionalization<sup>89</sup>. Condensing this molecule with dibromo-m-xylene the *1,1'-(m-Xylylene)-bis[4-methylantracene-1,4,7-triazacyclonone]* **26**<sup>87</sup> macrocycle skeleton is obtained. *1,1'-(m-Xylylene)-bis[4-methylantracene-7-hydroxyethyl-1,4,7-triazacyclononane]* **27** is obtained by the reaction of compound **26** with ethylene oxide<sup>90</sup>.



**Scheme I.2.2.3**

***1,1'-(m-Xylylene)-bis[4-methylantracene-7-hydroxybenzyl-1,4,7-triazacyclononane] synthesis (28)***<sup>85</sup>

By bonding the hydroxybenzyl group to the **27** compound skeleton, the 1,1'-(m-xylylene)-bis[4-methylantracene-7-hydroxybenzyl-1,4,7-triazacyclononane] is obtained (number **28** in scheme I.2.2.4). This process takes place by the reaction of **27** compound with formaldehyde and phenol in inert medium<sup>90</sup>.

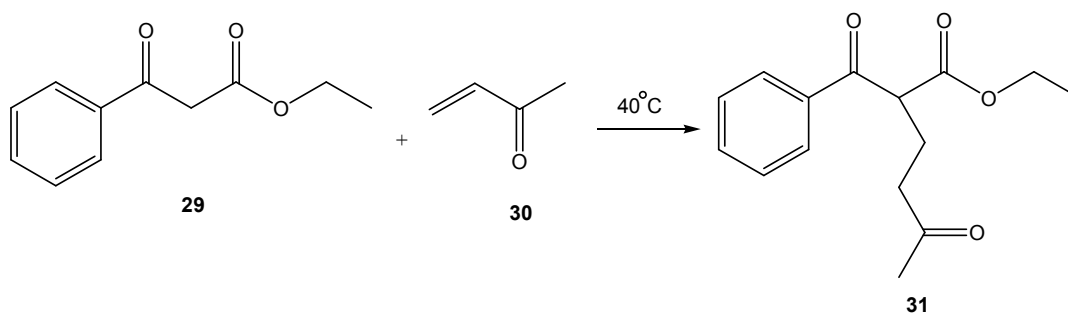


**Scheme I.2.2.4**

The compounds **18-24** and **26-28** were characterized by NMR spectroscopy (<sup>1</sup>H- and <sup>13</sup>C-) and elemental analysis.

### I.2.3 The catalytic activity of p-xylene-bis{[1,4,7-tris(hydroxyethyl)]cyclen} complex with NaBH<sub>4</sub>

The catalytic properties of the solvent free 2NaBH<sub>2</sub>·{p-xylene-bis[1,4,7-tris(hydroxyethyl)-cyclen]}<sup>88</sup> complex were tested to obtain ethyl 2 benzyl-5-oxo-hexanoate **31** from ethyl benzoyl-acetate **29** and methyl vinyl ketone **30** in different solvents (scheme I.2.5.1)<sup>91</sup>.



**Scheme I.2.3.1**

The complex proved to be basic enough to encourage the preparation of ethyl 2 benzyl-5-oxo-hexanoate.

## II. Contributions to metal organic frameworks chemistry

### *II.1 Cherchez la ?... MOF*

Metal organic frameworks, MOFs, represent a new class of hybrid porous crystalline compounds of special interest for both academia and industry. Basically, metal organic frameworks are polyatomic inorganic clusters which are three-dimensionally interconnected by organic linkers.

#### **Metal organic frameworks and/or coordination polymers?**

Species that involve metallic ions and organic ligands are denoted by metal organic frameworks<sup>11</sup>, coordination polymers<sup>7</sup>, metal organic coordinative networks, organic-inorganic hybrid materials<sup>8</sup>, or organic zeolites in the scientific literature. The first two terms are the most widely used ones. Although each term has pros and cons, there is no unanimous agreement able to eliminate confusions.

#### **Hydrogen storage in MOFs**

Due to their high porosity, metal organic frameworks are the best candidates from among porous materials for hydrogen storage by physisorption.

Hydrogen is the ideal energy vector: the value of its heat of combustion is almost three times larger than that corresponding to gasoline (120 MJ/kg compared to 44.5 MJ/kg), while water is the product of combustion. Several goals for hydrogen storage systems were established by the Department of Energy of the United States (DOE): storage capacity of 6% (weight %) and 45 g/l by 2010, and 9% and 81 g/l by 2015 respectively, at temperature ranges of (-40)-85°C and pressures below 100 atm<sup>19</sup>.

Metal organic frameworks reach the requirements of the DOE only at 77K, while the adsorption capacities are significantly lower at ambient temperature. The largest hydrogen adsorption capacities were recorded in the cases of: MOF-210 8.6%<sup>18</sup>, MOF-177 7.6% (66 bar)<sup>17</sup>, MOF-5 7.1% (40 bar)<sup>14</sup>, UMCM-2 (UMCM-2 stands for **U**niversity of **M**ichigan **C**rystalline **M**aterial-**2**) 6.9% (46 bar)<sup>21</sup>, IRMOF-20 6.7% (70 bar)<sup>22</sup>, MIL-101 (MIL stands for **M**aterials of the **I**nstitute **L**avoisier) 6.1% (60 bar)<sup>23</sup>.

The ability of metal organic frameworks to adsorb hydrogen is influenced by a series of factors such as: specific surface area, pore volume, pore dimensions, the

presence of open metallic coordinative positions, the structure of the ligand, catenation, chemical doping, and sample preparation. Except for the specific surface area, pore volume and sample preparation, the other factors have a direct influence on the adsorption enthalpy of hydrogen.

## **II.2 ORIGINAL CONTRIBUTIONS**

This chapter presents the original contributions to the development of metal organic frameworks with the aim to enhance their hydrogen storage capacity.

Research was focused upon several directions:

- (i) Development and optimization of a simpler, more rapid, and more economically efficient synthesis method in order to obtain metal organic frameworks with similar characteristics to those obtained by synthesis methods presented in the literature;
- (ii) Identification of synthesis factors to influence the textural characteristics (specific surface area, pore volume) of the metal organic frameworks;
- (iii) Preparation of a new type of composites, based on metal organic frameworks, for efficient hydrogen storage.

The obtained results are organized into four sections which present:

- a new synthesis method of metal organic frameworks in microwave field at atmospheric pressure;
- the influence of the autoclave filling grade upon the characteristics of MOF-5;
- a new type MOF@(carbon nanofibers) composite synthesis, and
- doping with Pd of the MOF@CNF composites.

### **II.2.1 Synthesis of metal organic frameworks in microwave field, at atmospheric pressure**

A new synthesis method was developed for the metal organic frameworks by activation in a microwave field at atmospheric pressure<sup>77</sup>. Synthesis of MOFs, at atmospheric pressure, in a power microwave field is achieved by using repetitive power microwave impulses, with a rate of 1 impulse per second, and a controllable filling factor. Each power impulse is characterized by a broad microwave frequency spectrum. In order to maintain a constant temperature during the reaction, the microwave energy is ensured by impulses, in a discontinuous mode.

MOF-5, IRMOF-8 and HKUST-1 were synthesized using this method. Syntheses were accomplished by using a microwave field processing installation fully designed, achieved and patented in the National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca<sup>78</sup>.

### ***II.2.1.3 Synthesis of tetra- $\mu_2$ -trimesato-dicopper (II) ( $Cu_3[C_6H_3(COO)_3]_2$ , HKUST-1)<sup>77</sup>***

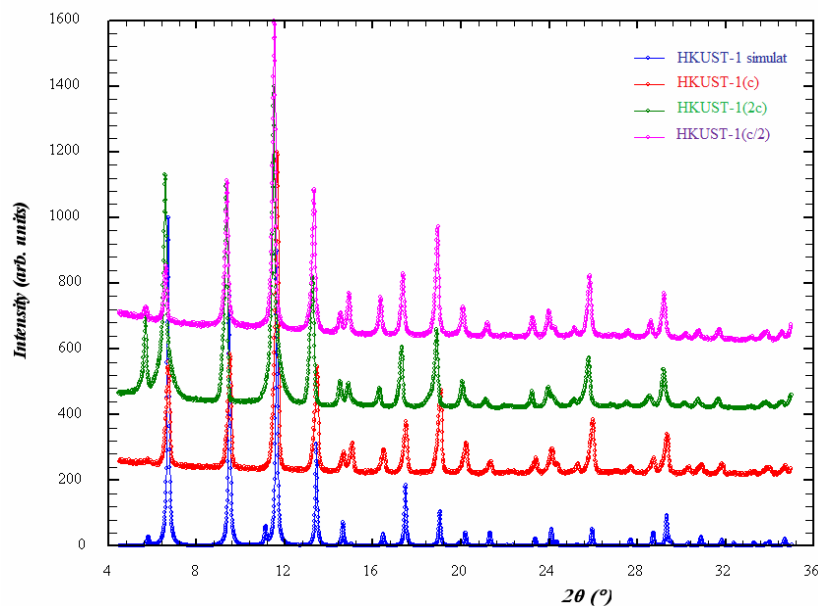
The effect of different synthesis parameters was studied as follows: concentration (samples c/2, c, 2c), solvents (c, s1, s2), temperature (2c, t1, t2), exposure time in the microwave field (2c,  $\theta_1$ ,  $\theta_2$ ), power of the microwave field (2c, p1, p2), activation (c, a), and the synthesis method of HKUST-1 in a power microwave field, at atmospheric pressure was optimized.

The identity of HKUST-1 samples, prepared under different conditions, was confirmed by comparing powder X ray diffractograms with simulated diffractograms from monocrystal data<sup>88</sup>. The compounds were characterized by nitrogen adsorption/desorption at liquid nitrogen temperature, and by thermo gravimetric analysis.

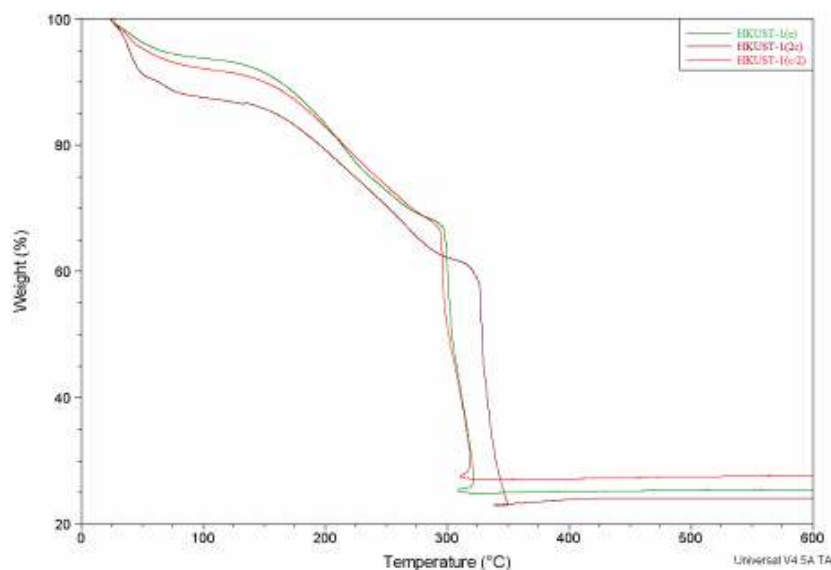
In order to study *the effect of the concentration*, the following samples denoted with HKUST-1(c), HKUST-1(2c) and HKUST-1(c/2) were synthesized. The high correspondence degree between the powder X ray diffractograms of the samples (c), (2c) and (c/2) and those simulated from monocrystal data<sup>88</sup> confirms the fact that the obtained metal organic frameworks have crystalline structure (figure II.2.1.3.7). Sample (2c) has crystallites of smaller dimensions, as Bragg reflections are broader than that corresponding to samples (c) and (c/2).

The thermal behavior of the studied samples is similar (Fig. II.2.1.3.8.). HKUST-1(c) and HKUST-1(c/2) have almost identical behavior and thermal decomposition occurs in the temperature range of 290-325°C. The TGA curve of HKUST-1(2c) has a similar shape, but the temperature range corresponding to the decomposition of this structure is shifted towards temperatures ranging 310 and 350°C.

N<sub>2</sub> adsorption isotherms of these three samples were measured volumetric at 77K, after degassing at 200°C for 3 hours. As shown in Fig. II.2.1.3.9, samples HKUST-1(c) and HKUST-1(2c) present type I adsorption isotherms, which means that both compounds are microporous. The adsorption isotherm in case of HKUST-1(c/2) is of type II. This type of isotherm is associated to the monolayer-multilayer adsorption on the surfaces of nonporous, macroporous or to some extent to microporous powders<sup>101</sup>.



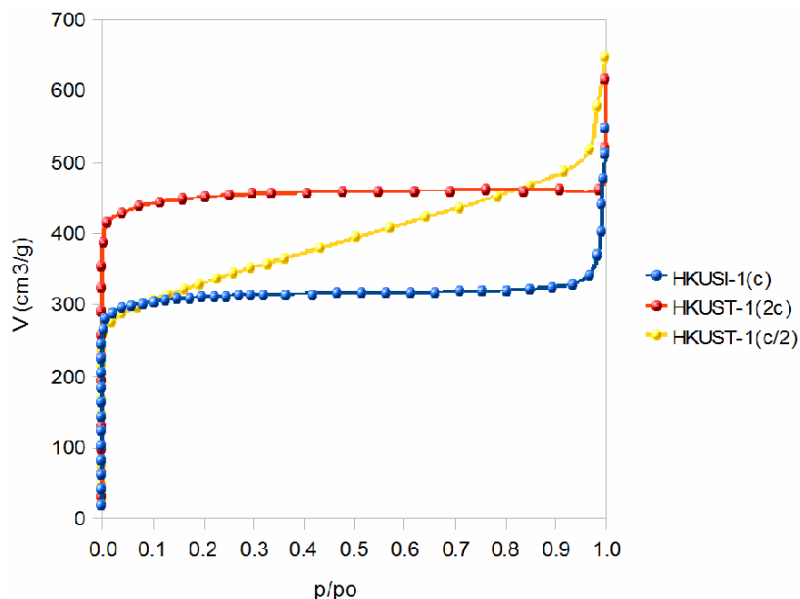
**Fig. II.2.1.3.7** Comparison of powder X ray diffractograms of HKUST-1(c) (red), HKUST-1(2c) (green) and HKUST-1(c/2) (violet) to the simulated diffractogram resulted from monocrystal data (blue)<sup>88</sup>.



**Fig. II.2.1.3.8.** TGA curves corresponding to HKUST-1(c) (green), HKUST-1(2c) (brown) and HKUST-1(c/2) (red).

The adsorption isotherm of HKUST-1(c/2) is linear in the  $p/p_0$  range of 0.0416-0.9157, which indicates the formation by adsorption of a layer that thickens as the relative pressure  $p/p_0$  rises towards 1. Each of the three isotherms presents a type  $H_1$  hysteresis which is characteristic for adsorbents with a narrow distribution of the uniform pores.





**Fig. II.2.1.3.9** N<sub>2</sub> adsorption isotherms for HKUST-1(c) (blue), HKUST-1(2c) (red) and HKUST-1(c/2) (yellow), at 77K.

BET and Langmuir specific surface areas, as well as pore specific volumes corresponding to all HKUST-1 synthesized samples were estimated from the N<sub>2</sub> adsorption isotherms at 77K. The largest values were recorded in the case of HKUST-1(2c) (table II.2.1.3.3)

**Table II.2.1.3.3** The textural characteristics of HKUST-1(2c).

Nr. crt.	Compound	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>Langmuir</sub> (m <sup>2</sup> /g)	V <sub>pores</sub> (cm <sup>3</sup> /g)
2	HKUST-1(2c)	1736	2005	0.71

The optimum synthesis conditions for HKUST-1 by activation with microwaves at atmospheric pressure are:

- 0.1M concentrations of trimesic acid in solvent mixture DMF:C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O=1:1:1;
- filling factor of the pulse at 40%;
- 70°C temperature;
- total exposure time of 10 minutes;
- purification with anhydrous DMF and activation with anhydrous CH<sub>2</sub>Cl<sub>2</sub>.

## II.2.2 The filling grade of the autoclave for the solvothermal synthesis of MOF-5

Different values for the specific surface area and for the pore volumes were reported for MOF-5, which is explained by the influence of the synthesis conditions (concentration, solvents, temperature, reaction time, purification and activation method) over the physico-chemical properties of the product.

Another factor to influence the properties of the product is the filling factor of the autoclave<sup>103</sup>. Four samples denoted with MOF-5(a), MOF-5(b), MOF-5(c) and MOF-5(d) were synthesized starting from reaction mixtures obtained from identical reactants and solvents, with the same stoichiometric ratio, but at different filling grades of the autoclave, that is 0.196, 0.365, 0.551, and 0.926.

Samples (a), (b) and (c) are MOF-5, as confirmed by the comparison of powder X ray diffractograms and those simulated using monocystal data<sup>88</sup>.

N<sub>2</sub> adsorption/desorption isotherms were measured at 77K for the four samples. BET and Langmuir specific surface areas, as well as pore specific volumes were estimated from adsorption data (table II.2.2.1). One can observe that a greater filling factor of the autoclave leads to a decrease of the specific surface area, as well as of the specific pore volume of the sample.

**Table II.2.2.1** Textural characteristics and H<sub>2</sub> adsorption capacities for MOF-5 samples

Sample	Filling grade of the autoclave	S <sub>BET</sub> / S <sub>Lang</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	Q <sub>H2 ads.</sub> (weight %)
MOF-5(a)	0.196	3019 / 3501	1.35	5.2, 60 bar, 77K
MOF-5(b)	0.365	2680 / 3153	1.14	4.8, 66.7 bar, 77K 0.68, 88 bar, 298K
MOF-5(c)	0.551	2151 / 2470	1.24	-
MOF-5(d)	0.926	1099 / 1235	0.41	-

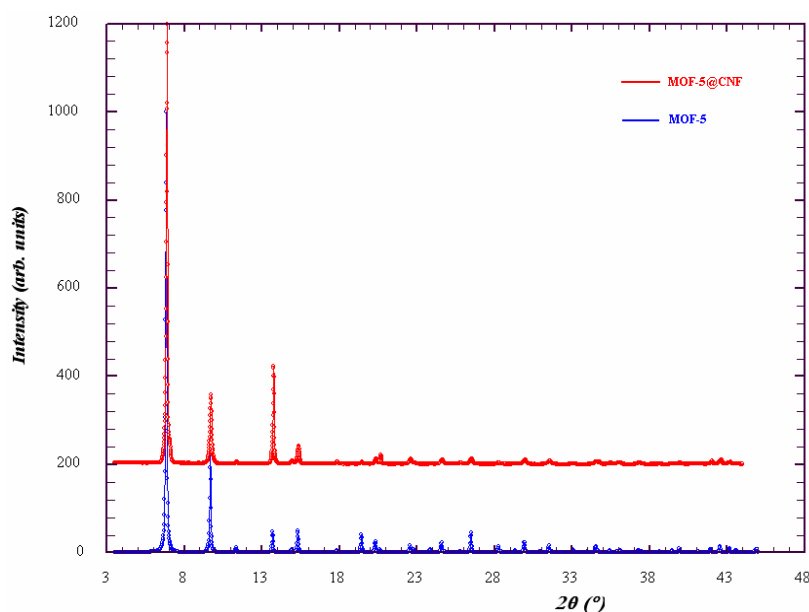
## II.2.3 Composites (metal organic framework)@(carbon nanofibres)

Composites of the type MOF-5@CNF<sup>112</sup> and HKUST-1@CNF<sup>118</sup> were synthesized and characterized.

### II.2.3.1 MOF-5@CNF

Characterization of MOF-5@CNF was made by IR spectroscopy, powder X-ray diffraction, thermogravimetric analysis, N<sub>2</sub> adsorption/desorption at 77K, and H<sub>2</sub> adsorption at 77K and 293K.

Powder X ray diffractogram of the composite compared to that simulated from crystallographic data<sup>15</sup>, shows each Bragg reflection which is characteristic for MOF-5. This means that use of carbon nanofibres in MOF-5 does not disturb and damage the crystalline structure of the metal organic framework.



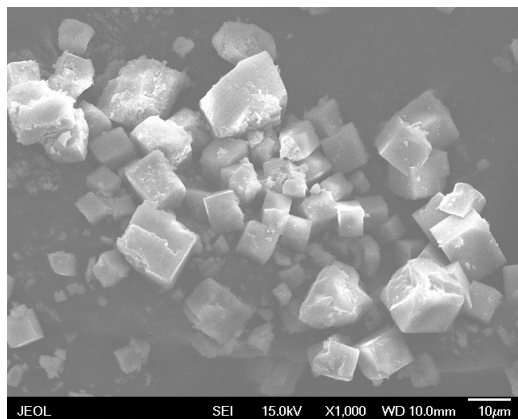
**Fig. II.2.3.1.4** Comparison of the powder X ray diffractogram of MOF-5@CNF composite with the simulated diffractogram from crystallographic data<sup>15</sup>.

Table II.2.3.1.2 comparatively presents the estimated BET and Langmuir specific surface areas, as well as hydrogen adsorption capacities of MOF-5(s), CNF, and MOF@CNF.

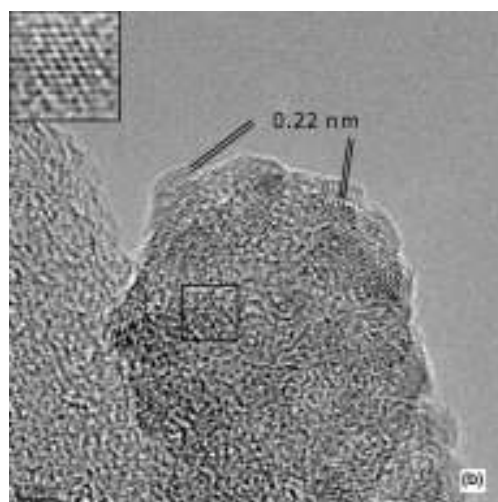
**Table II.2.3.1.2** Comparison of MOF-5, CNF, MOF-5@CNF and MOFMC characteristics

Material	S <sub>BET</sub> /S <sub>Lang.</sub> [m <sup>2</sup> /g]	Max. adsorption, 77K [%H]	Adsorption, 298K [%H]
MOF-5(s)	2681 / 3153	4.8 (55.12 bar)	0.42 (91.0 bar)
CNF	234 / 354	0.33 (55.99 bar)	0.13 (70.0 bar)
MOF@CNF	2494 / 2856	4.11 (55.93 bar)	0.56 (93.0 bar)

The morphology of the MOF-5@CNF composite particles was analyzed by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).



**Fig. II.2.3.1.8** SEM image of MOF-5@CNF



**Fig. II.2.3.1.11** TEM image of the pore structure of MOF-5@CNF.

The crystals of the composites reflect the cubic symmetry and are well structured with well defined edges, and clean facets, aspects that characterize the synthesis of a good quality product (Fig. II.2.3.1.8).

Although TEM images of the cubic crystals of the composite couldn't be obtained due to the sensibility of the metal organic framework to the electron flux, images of the pore structure and of the square section of the cubic pores of MOF-5 were obtained for the first time (figure II.2.3.1.11). The values of the interplanar distances for MOF-5 and carbon nanofibres were determined using (figure II.2.3.1.11) FFT (Fast Fourier Transform) of 0.22, and 0.32 nm.

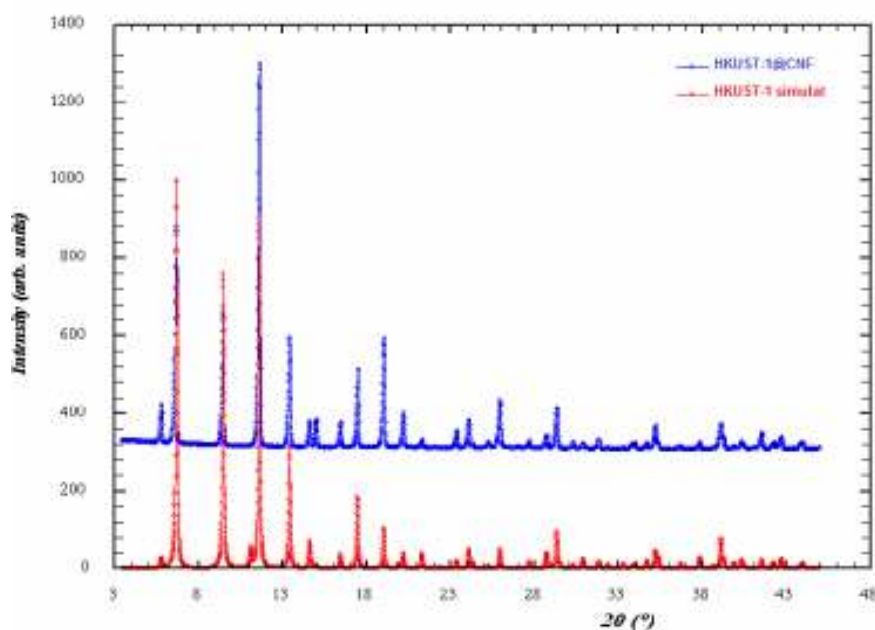
In conclusion, a new hybrid composite was synthesized, denoted with MOF-5@CNF, which is characterized by high specific surface area and pore volume. Introduction of carbon nanofibres in the crystals of the metal organic framework made possible the acquisition of the images of the pore structure and of the MOF-5 pore section for the first time.

### **II.2.3.2 HKUST-1@CNF<sup>118</sup>**

The characterization of the product was made by IR spectroscopy, powder X ray diffraction, thermogravimetric analysis, N<sub>2</sub> adsorption/desorption at 77K, scanning

electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM).

HKUST-1 formation into a composite is confirmed by powder X ray diffraction compared to the corresponding simulated diffractogram for HKUST-1<sup>88</sup> (Fig. II.2.3.2.2).



**Fig. II.2.3.2.2** Powder X ray diffractogram of HKUST-1@CNF (blue) and of the simulated HKUST-1 diffractogram from crystallographic data (red)<sup>88</sup>.

BET and Langmuir specific surface areas were estimated from N<sub>2</sub> adsorption data by using the specific multiple point BET equation, and Langmuir equation. Thus, Bet surface area was evaluated at 1270 m<sup>2</sup>/g, Langmuir surface area corresponds to 1471 m<sup>2</sup>/g, while the specific pore volume was evaluated at 0.67 cm<sup>3</sup>/g.

Figure II.2.3.2.5 shows the presence of octahedral shape crystals which are specific for HKUST-1. Carbon nanofibres wind among them.

Figure II.2.3.2.6 presents the TEM image of the successive planes of the HKUST-1 crystalline. The interplanar distance evaluated by FFT is 0.24 nm, compared to the 0.32 nm distance obtained for CNF.

In conclusion, the hybrid HKUST-1@CNF composite was synthesized and characterized. Due to the presence of carbon nanofibres, images of the crystalline structure planes and of the pore structure of HKUST-1 were recorded for the first time.

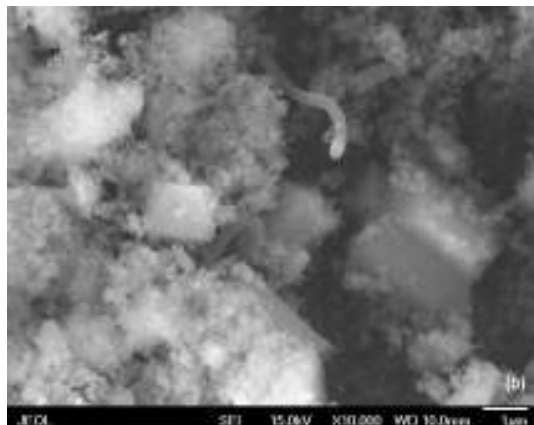


Fig. II.2.3.2.5 SEM image of HKUST-1@CNF.

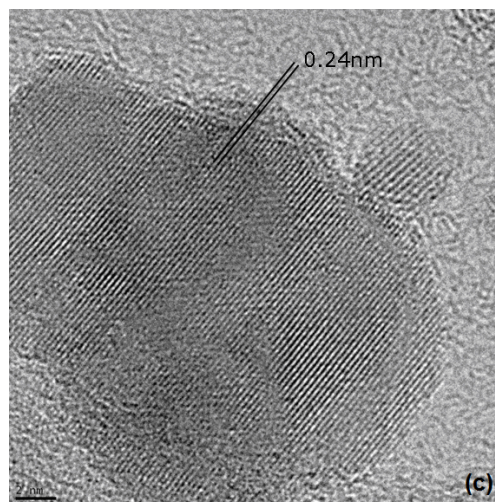


Fig. II.2.3.2.6 TEM image of HKUST-1@CNF.

## II.2.4 (Metal Organic Framework)@(Carbon Nanofibres) composites doped with Pd

### II.2.4.1 MOF-5@(Pd/CNF)

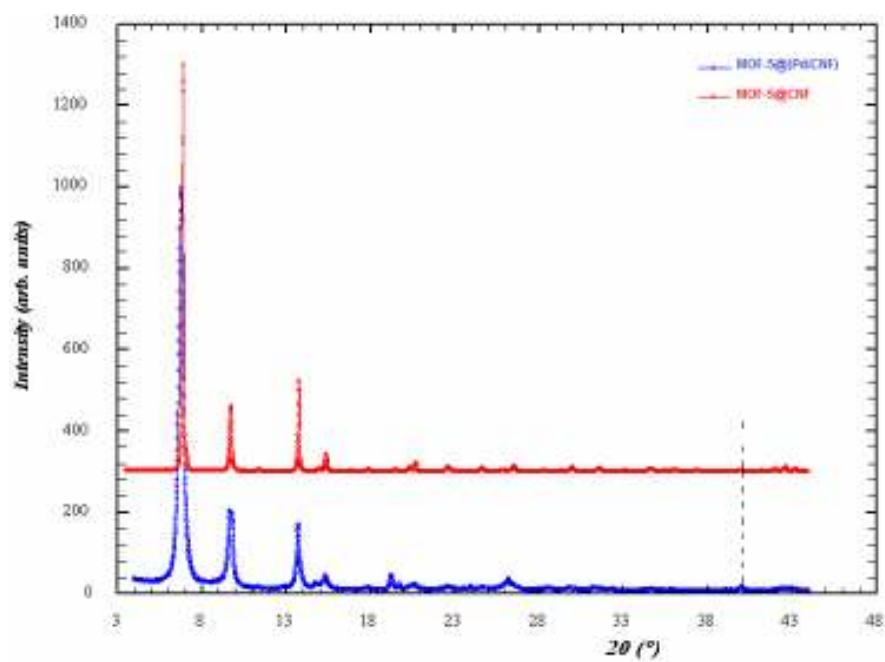
MOF-5@(Pd/CNF) composite is a variation of the MOF-5@CNF but with Pd doping.

The identity of the product was confirmed by powder X ray diffraction (Fig. II.2.4.1.1). Powder XRD of MOF-5@(Pd/CNF) revealed all Bragg reflections from the undoped composite. The diffractogram of the doped composite presents at  $2\theta = 40^\circ$  the (111) reflection characteristic for metallic Pd<sup>5,7</sup>.

N<sub>2</sub> and H<sub>2</sub> adsorption isotherms were measured. BET and Langmuir specific surface areas estimated from N<sub>2</sub> adsorption data are presented in Table II.2.4.1.1, compared to the undoped MOF-5@CNF composite.

Table II.2.4.1.1 Textural characteristics of MOF-5@(Pd/CNF) and MOF-5@CNF

Material	S <sub>BET</sub> / S <sub>Lang.</sub> ( m <sup>2</sup> /g )	V <sub>pore</sub> (cm <sup>3</sup> /g)	Q <sub>H2 ads.</sub> (weight %), 77K
MOF-5@(Pd/CNF)	1474 / 1695	0.63	2.87 (58.98 bar)
MOF-5@CNF	2494 / 2856	1.06	4.11 (70.62 bar)



**Fig. II.2.4.1.1** Powder X ray diffraction of MOF-5@(Pd/CNF) (blue) compared to that of MOF-5@CNF (red).

### III. Conclusions

1. A new method for peraza crown ethers synthesis was elaborated and perfected, using as base  $\text{KF/Al}_2\text{O}_3$ . 1,4,7-tris(p-toluene-sulfonyl)-1,4,7-triazacyclononane **5** and 1,4,7,10-tetrakis(p-toluene-sulfonyl)-1,4,7,10-tetraazacyclododecane **11** were synthesized using this new method. An advantage of this method is that there are avoided the restrictions of working in inert medium and with big quantities of solvents, as in the classical Richman-Atkins method. The new synthesis method is more energetic efficient and more environmentally friendly.

2. Several macropolycyclic compounds having different substituting groups were prepared based on:

(a) m-xylylene-bis(cyclen) - compounds **21** and **24** and intermediates **18**, **19**, **20**, **22**, **23**;

(b) m-xylylen-bis(triazacyclononane) compounds **27** and **28** and intermediate **26**.

The compounds were characterized by elemental analysis and NMR spectroscopy ( $^1\text{H}$ - and  $^{13}\text{C}$ -).

3. The catalytic activity of  $2\text{NaBH}_2\cdot\{\text{p-xylylene-bis}[1,4,7\text{-tris}(\text{hydroxiethyl})\text{-cyclen}]\}$  complex was determined for the preparation of ethyl 2-benzyl-5-oxo-hexanoate **31** from ethyl benzoyl-acetate **29** and methyl vinyl ketone **30**, in different solvents.

4. A new method for metal organic framework synthesis was elaborated using microwave field and atmospheric pressure. This new method is simple, rapid and energetic efficient, and represent a good alternative to solvo- and hydrothermal methods. The reaction time varies from few second to few minutes comparing to many hours and even days for the solvo- and hydrothermal methods. Another advantage is working at atmospheric pressure which reduces the risk of explosions when nitrates and volatile solvents are heated. The resulting crystals have qualities very similar with that obtained by solvo- and hydrothermal methods. The syntheses at atmospheric pressure by activation in microwave fields are selective and reproducible.

5. MOF-5 and IRMOF-8 were synthesized by microwave activation at atmospheric pressure. The identity of the samples was confirmed by comparison of powder X-ray diffractograms with simulated ones from monocystal data. The compounds were



characterized by vibrational spectrometry, nitrogen adsorption/desorption at 77K and thermogravimetric analysis.

6. The effect of different synthesis parameters was studied: concentration (samples c/2, c, 2c), solvents (c, s1, s2), temperature (2c, t1, t2), exposure time in the microwave field (2c,  $\theta_1$ ,  $\theta_2$ ), power of the microwave field (2c, p1, p2), and activation (c, a). Moreover, the HKUST-1 synthesis method in power microwave field, at atmospheric pressure was optimized. The identity of the samples was confirmed by comparison of powder X ray diffractograms with simulated ones from monocrystal data. The compounds were characterized by IR spectrometry, nitrogen adsorption/desorption at 77K and thermogravimetric analysis.

7. A new synthesis method was developed for a new type of composites: (porous metal organic frameworks)@(carbon structures).

8. New MOF-5@CNF and HKUST-1@CNF composites were prepared. Characterization of the composites was accomplished by powder X ray diffraction, IR spectroscopy, N<sub>2</sub> adsorption/desorption at 77K, H<sub>2</sub> adsorption at 77K and at 298K. The morphology of the particles of the 2 composites was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

9. The introduction of carbon nanofibres into the crystals of MOF-5 made possible the recording of TEM images of the pore structure and of the pore section of MOF-5, for the first time.

10. For the first time, images of the crystalline structure planes and of the pore structure of HKUST-1 were recorded, due to the presence of carbon nanofibres.

11. MOF-5@(Pd/CNF) composite was synthesized as a doped variation of MOF-5@CNF. The composite was characterized by powder X ray diffraction, N<sub>2</sub> adsorption/desorption at 77K and H<sub>2</sub> adsorption at 77K.

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