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Synthesis of silica nanoparticles incorporating triazolyl macrocycle

Raghda Mahdi Ameer Alziadi

Chemistry department, faculty of sciences, university of Kufa, An-najaf, Iraq

Abstract---Incorporating of silica nanoparticles with crown ethers is of interest regarding the excellent stability of these inorganic polymers against various acidic and basic conditions. The attachments of silica nanoparticles to macrocycles are involved many reactions to attach the active site of crown ether with modified silica nanoparticles. To achieve the goal, the selection of 3,5-dihydroxybenzoic acid as a model for the synthesis of macrocycle base the reaction of esterification of acid residue followed by etherification with propargyl chloride and finally the cyclization reaction with di azide residue to form macrocycle 4. From the other side, the silica nanoparticle both magnetic and mesoporous were prepared in different size and properties according to the literature. The final step involving the attachment of macrocycle to the silica nanoparticles of different type, two methods are used. First method was included the crafting of macrocycle with the ready synthesized nanoparticles under basic medium. Second method is the one-pot synthesis of nanoparticles and adding the macrocycle 4, directly before finish the reaction. All the compounds have been characterized by the instrumental techniques include FT-IR, ¹H NMR, ¹³C NMR, EXD, XRD, FESEM, TEM and BET.

Keywords---nanoparticles, crown ethers, macrocycles, silica, cyclization.

Introduction

The current research interests are focus mainly on the smart materials.[1] The term smart materials, also sometimes called responsive materials[2], can be refer to the substances which are designed materials that have one or more properties that can be significantly changed in a controlled process by outside stimuli, such as moisture, electrical field, light, pH or heat. These materials are the base of various applications, including but not limited to chemical sensors and actuators, synthetic muscle tissues. [3] Moreover, the nanomaterials is unique substances that possess interesting smart properties that found in the different research

fields, such as, medicine, pharmaceuticals[4], drug delivery[5], catalysts, artificial additives[6], food industry, cosmetics, agriculture[7], and .. etc. A nanoparticle is referring to a particle of matter that has a diameter between one and one hundred nanometers (*nm*)[8]. Nanoparticles are usually differ from microparticles (one to one thousand μm), "fine particles", because they are smaller size, and as a result, the chemical and physical properties are totally different[9].

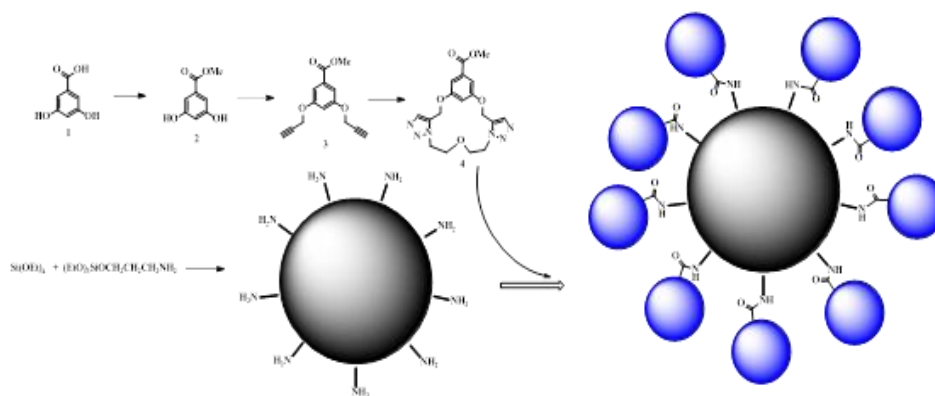
Silica nanoparticles (MSNs), also known as silicon dioxide nanoparticles, are the source for a great deal of medical and pharmaceutical researches based on their stability, low toxicity and the ability of functionalization of a wide range of materials.[10] The (MSNs) have simply functionalized surface and amusing textural properties, in which the adjustable pore size (2–20 nm) and enormous surface area ($>1000 \text{ m}^2.\text{g}^{-1}$).[11] Macrocycles are special class of compounds that grew up numerously in the last few decades[12]. These compounds can be define as cyclic compounds containing at least nine atoms in their structures[13], with at least three heteroatoms, such as oxygen, sulfur, nitrogen and so on[14]. Indeed, their unique structures and properties make them of interest in variety of research fields[15], including but not limited to separation of different organic or inorganic species, chiral recognitions asymmetric synthesis, enantio-selective and stereo-selective reactions, pharmaceuticals, extractions and so on[16]. This family of compounds when incorporating with meso-porous silica nanoparticle will form a unique materials in term of their structure and properties. [17]

Result and Discussion

In this study, three types of silica nanoparticles have been prepared, these are, mesoporous silica nanoparticles (mSNP), magnetic silica nanoparticles (MSNP) and mesoporous magnetic silica nanoparticles (mMSNP). In addition, three types of the silica nanoparticles involving macrocycle have been synthesized in two different procedures. Firstly, after synthesize the nanoparticles the crafting of surface with macrocycle 4 could be perform by basic amide coupling(ester and amino groups) to craft the silica nanoparticles with macrocycle by amide linkage was successfully synthesized. All the silica nanoparticle types have been characteristic by the available techniques to evaluate their morphology and surface modifications.

Synthesis of the silica nanoparticle cragted macrocycle 6

The chosen of ditriazoles cyclization instead of other methods is performed to minimize the polymerization reaction that normally occur when the synthesis of macrocycles is applied. The combination of high dilution methods with some templating could increase the cyclization, which was performing in this strategy (scheme I) successfully to get a certain macrocycle with reasonable yield (63%).



Scheme (1) synthesis of grafted polymeric macrocycles

The strategy of synthesis of macrocycle 4 was started by the esterification of carboxylic acid with methanol in acidic medium, followed by the etherification of phenolic hydroxyl with propargyl bromide under slightly basic condition, i.e., sodium carbonate to obtain compound 3. The macrocycle 4 was prepared by treatment of compound 3 with di-azide derivative 5 under Huisgen 1,3-dipolar cycloaddition in good yield. The ¹HNMR spectrum of macrocycle 5 is confirmed the formation of it through the absent of propargylic proton and appear of new signals for (CH₂O) groups at the region 3-4 ppm as well as the triazole ring protons at 8.1 ppm (Fig 1).

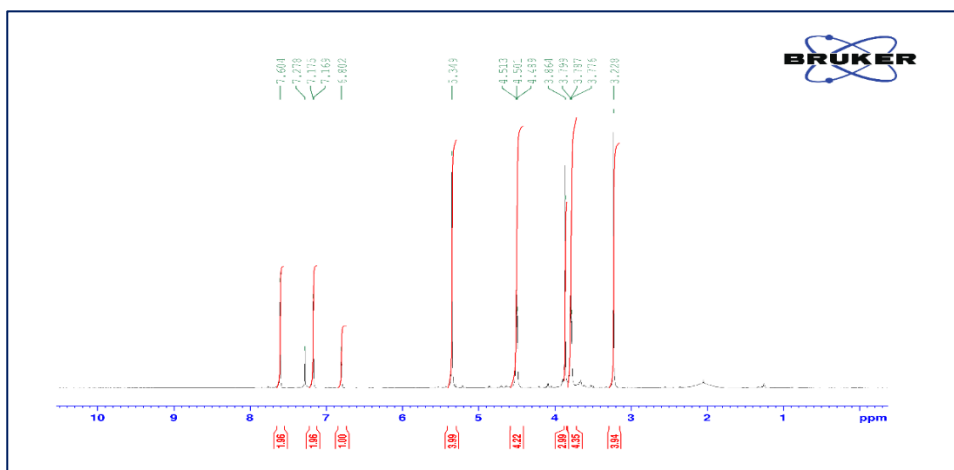


Figure 1: the ^1H NMR spectrum of compound 5

In addition, the ^{13}C NMR spectrum of **5** is showed the disappearance of propargylic carbons at 78 and 81 ppm and appear of some additional peaks at the region of 70-80 ppm for the CH_2O carbons. The spectrum also showed the signals at 143 and 132 ppm which is assigned to the carbons of triazole ring (Fig. 2).

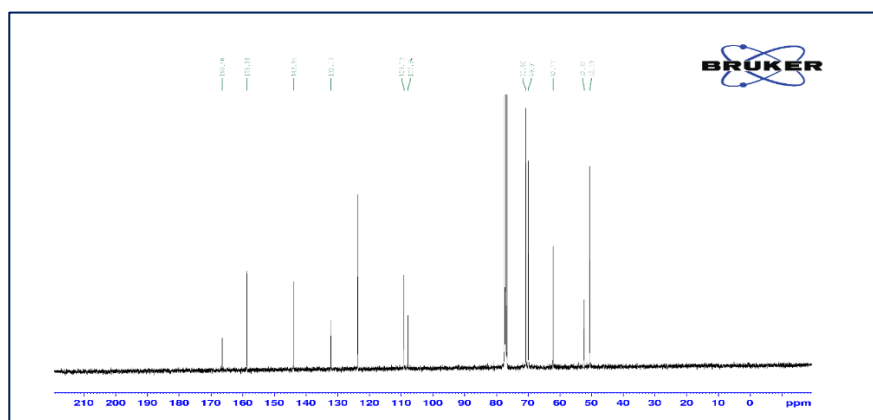


Figure 2: the ^{13}C NMR spectrum of compound 4

The assignments of carbons and protons of compound 5 is confirmed by the two-dimension HSQC experiment (Fig. 3)

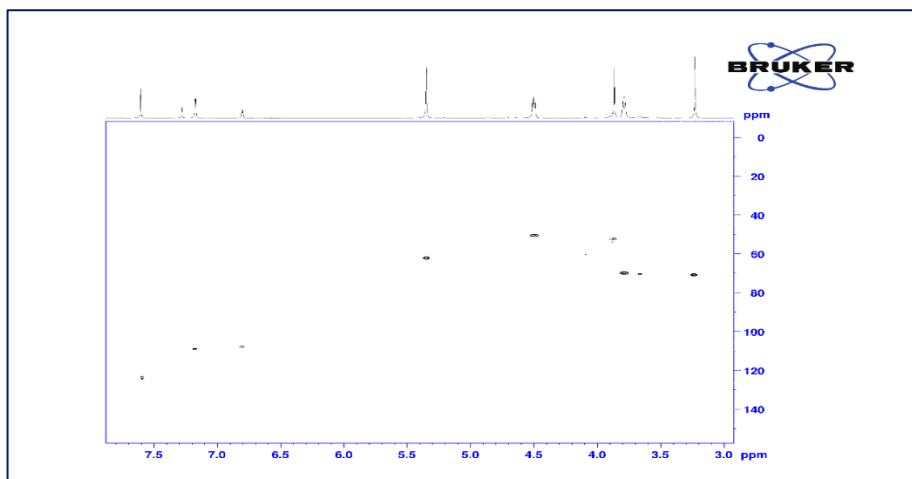
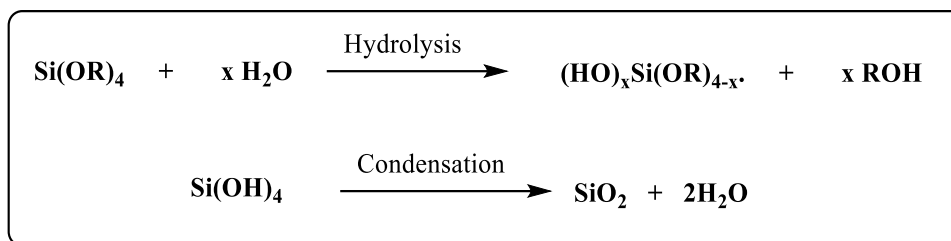


Figure 3: the HSQC spectrum of compound 4

From the other side, the silica nanoparticles were obtained by the treatment of tetraethoxysilane and 3-aminopropyltriethoxysilane [$\text{Si}(\text{OEt})_4$ and $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$] with basic medium in water/ethanol. Finally, the silicananoparticle crafted macrocycle was synthesized by the amide coupling of ester and amine residues of both macrocycle and amine in the silica respectively in refluxed DMF. It is clear that the reaction will allow the crafting of macrocycles on silica according to the nature of spherical original poly functional structure with only single functional group of macrocycle 4. The size of macrocycle would result in homogeneity of distribution along the polymeric spherical shape of silicananoparticles.



Scheme **Error! No text of specified style in document.**3-1 : Synthesis of silica nanoparticles via Stöber approach

The size of the silica particles formed from the Stöber process is primarily controlled by the relative contribution from nucleation and growth of particles; these phenomena are themselves dependent on the hydrolysis and condensation of TEOS, controlled by the reaction conditions.

Characterization techniques

The standard characterization of mesoporous silica nanoparticles include use of electron microscopies (scanning electron microscopy; SEM, transmission electron microscopy; TEM), small angle X-ray diffraction (SAXD), gas adsorption analysis, thermogravimetric analysis (TGA) and dynamic light scattering (DLS). The particle morphology is typically studied by SEM, while the ordered arrangement of pores can be detected by TEM.

FTIR spectroscopy

The FT-IR spectrum of the Fe_3O_4 nanoparticles has only weak absorption at 1508, 1488 and 1347 cm^{-1} (**Error! Reference source not found.** 4). The FT-IR spectrum of mSNP (**Error! Reference source not found.**4) showed a very strong band at 1060 cm^{-1} resulting from the stretching vibration of the (O-Si-O) bonds in both symmetric and asymmetric vibrations. Interestingly, the result peaks from Fe_3O_4 is disappeared when coated with silica to form mesoporous silica nanoparticles (mMSNP) and (MSNP) and appear the strong absorption at 1060 cm^{-1} respectively.

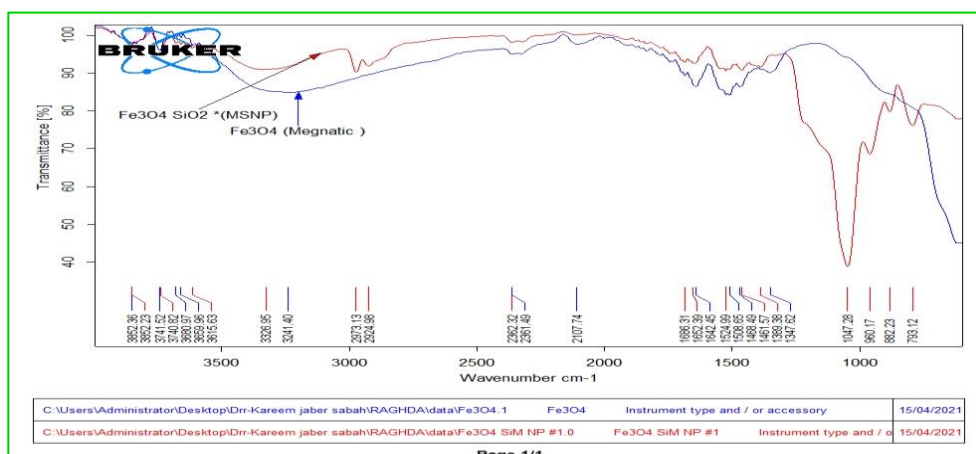


Figure 4: The combination of FTIR spectra of Fe_3O_4 and mSNP nanoparticles. In addition, when coating the silica nanoparticle with macrocycle **5** the spectrum showed the characteristic peaks of both silica and macrocycles bands, for example, the peaks at 1600, 1500 cm^{-1} (Figure **Error! No text of specified style in document.**5-7) can be attributed to stretching vibration of C=C or aromatic aromatic group on macrocycle. in the same context, the strong peak at 1047 cm^{-1} can be assigned to the (O-Si-O) stretching vibration.

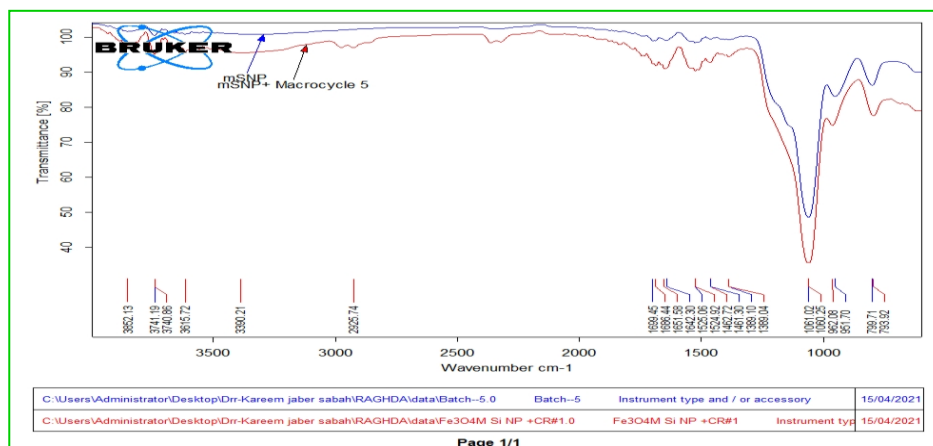


Figure **Error! No text of specified style in document.**5: The combination of FTIR spectra of mSNP and mSNP crafting compound **5**

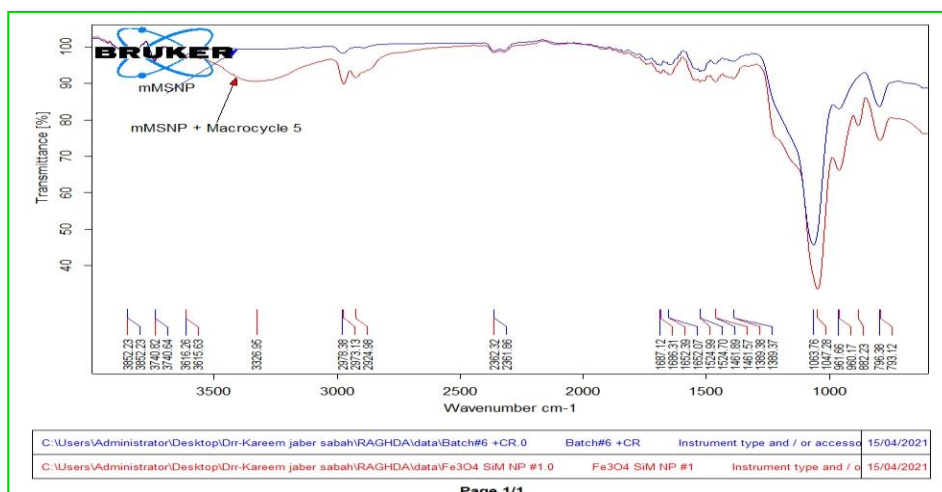


Figure 6: The combination of FTIR spectra of mMSNP and mMSNP crafting compound 5

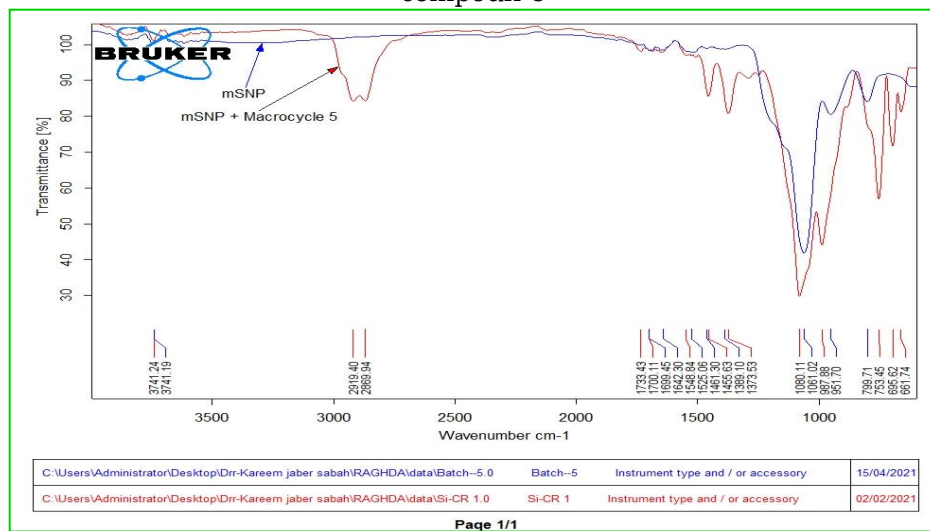


Figure 7: The combination of FTIR spectra of mSNP and mSNP crafting compound 5

Field Emission scanning electron microscopy (FESEM) study

The FESEM images of magnetic silica nanoparticles (MSNP) show sphere particles below 50 nm in diameters (Figure **Error! No text of specified style in document.**8a). In addition, the crafting of MSNP with macrocycle **5** indicates there are aggregation on particles appear more clearly in its FESEM image. also the SEM observation of the particles confirmed a robust kind of attachment of the particles to each other because of modification, as seen in (Figure **Error! No text of specified style in document.**8b).

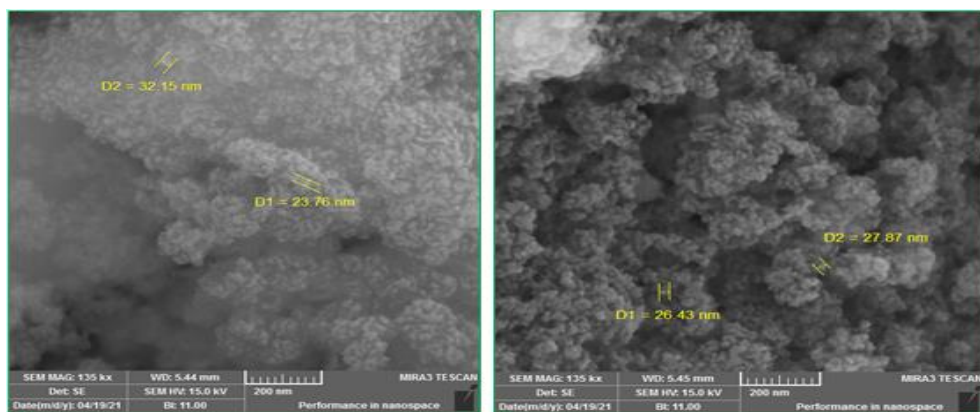


Figure **Error! No text of specified style in document.8:** a) FESEM image of MSNP, b) FESEM of MSNP crafting macrocycle 5

That is may be attributed to dispersion of surfactant CTAB is not regular in the solution upon preparation of mesoporous silica coated the Fe_3O_4 nanoparticles. However, the crafting with compound 5 also showed the particles to be closer by the act of macrocycle attachment on their surfaces. Furthermore, the mesoporous silica nanoparticles (mSNP) morphology is showed spherical particles below 500 nm in diameter. The FESEM image of mSNP crafted macrocycle 5 had the morphology of few aggregation of

Transmission electron microscopy (TEM) study

The TEM image of MSNP and its crafting macrocycle 5 (Figure 9: TEM image of MSNP and its crafting Macrocycle 5), show an aggregation of the particles which are small enough to interact with each other forming fine powder. Unfortunately the image is not magnifying properly to investigate the surface of the particles.

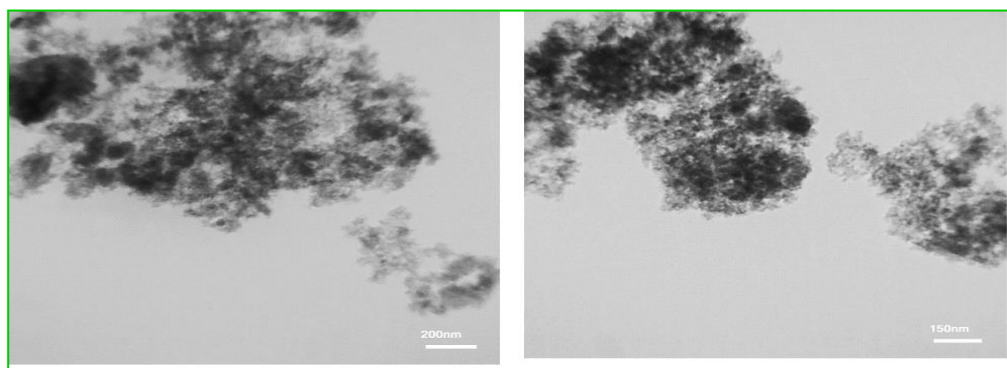


Figure 9: TEM image of MSNP and its crafting Macrocycle 5

In addition, the TEM images of mMSNP and its corresponding crafting macrocycle 5 (Figure 10), showed a spherical particles that are varied

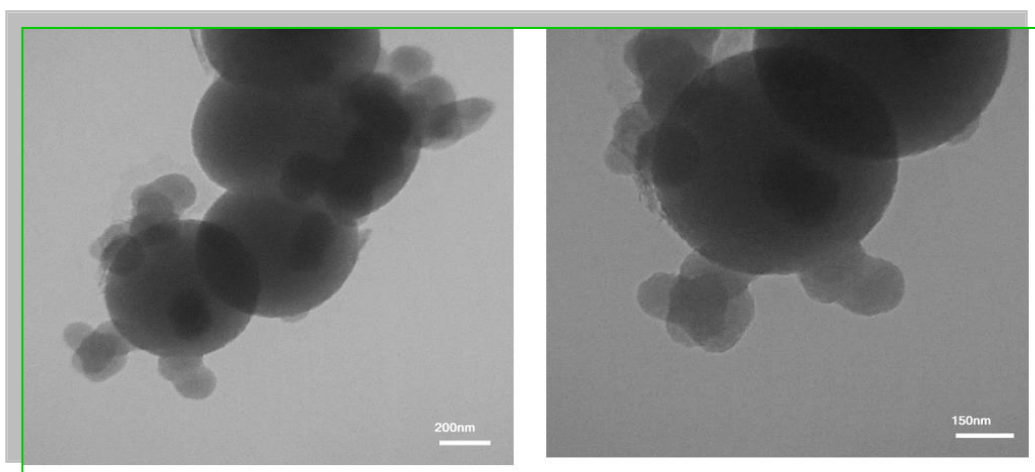


Figure 10 : TEM image of mMSN and its crafting Macrocycle 5

in the size, with clear mesoporous structure in the surface. The image is magnified enough to see clearly the porosity of the particles in deep. Finally, the FESEM and TEM images show that the large particles are fully covered by small ones; however, TEM images suggest that the small particles surrounding the large ones are not properly-defined, making the raspberry-like particles appear ill-defined, or 'fluffy', rather than with the desired roughness.

X-ray diffraction (XRD) study

The XRD patterns of the the nanoparticles MSNP, mMSN and mSNP coating macrocycle **5**, were shown in (Figure 11) respectively. The XRD patterns of MSNP showed two main characteristic peaks at $2\theta = 23.15$ to 23.62 and the other at 44.80 to 45.82 . The broadening and noise of observed peaks were probably attributed to the effect of structural changes from homogeneity of nanoparticles that coating with macrocycle **5**. The strongest reflection at smallest 2θ is assigned to crystal forms II and the weaker peak appeared at higher 2θ attributed to crystal forms I.

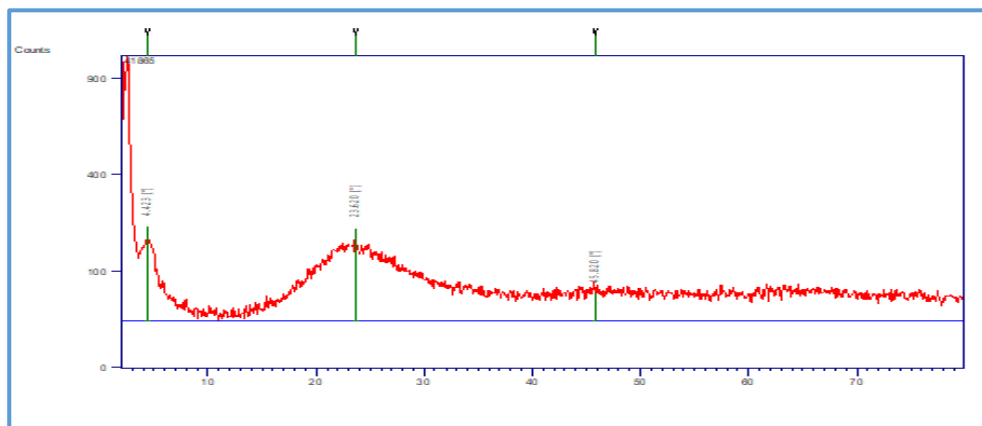


Figure **Error! No text of specified style in document.** 11: XRD plot of mSNP crafted Macrocycle 5

Peak List			
Height[cts]	d-spacing[?]		Rel.Int.[%]
23.6200	186.30	1.0298	97.21
45.8200	36.00	0.0900	18.78

Nitrogen sorption analysis (BET) study

Gas adsorption measurements are of major importance for the characterization of various porous materials, as specific surface area, specific pore volume, pore size and its distribution can be determined using this technique. The nitrogen physisorption process is described quantitatively by an adsorption/desorption isotherm, representing the amount of adsorbed/desorbed Nitrogen at a fixed temperature as a function of partial pressure of N_2 .

According to IUPAC, the pores can be classified according to their sizes¹⁷⁶:

- (i) macropores: pore width > 50 nm
- (ii) mesopores: pore width 2 - 50 nm
- (iii) micropores: pore width 0.7 - 2 nm
- (iv) ultramicropores: pore width < 0.7 nm

The amount of gas adsorbed by the mass of solid is dependent on the equilibrium pressure, the temperature, and the nature of the gas-solid system. These relationships are represented in what is called the adsorption isotherm. MSNP crafted macrocycle **5** was subjected to the BET test to measure the pore size of the porosity in addition to get the surface area of the particles. The Table 1, showed that the surface area is $2716 \text{ m}^2 \cdot \text{g}^{-1}$, while the pore diameter in the average of 1.88 nm. These results indicate that MSNP crafted macrocycle consider as microporous nanoparticles figure 12.

Table 1: BET data and pore size for MSNP involving macrocycle 5

V_m	624.11	$[\text{cm}^3(\text{STP}) \text{ g}^{-1}]$
$a_{s,\text{BET}}$	2716.4	$[\text{m}^2 \text{ g}^{-1}]$
C	1.1117	
Total pore volume	1.2779	$[\text{cm}^3 \text{ g}^{-1}]$
Average pore diameter	1.8817	$[\text{nm}]$
<i>Langmuir plot</i>		
V_m	358.63	$[\text{cm}^3(\text{STP}) \text{ g}^{-1}]$
$a_{s,\text{Lang}}$	1560.9	$[\text{m}^2 \text{ g}^{-1}]$
B	0.1027	

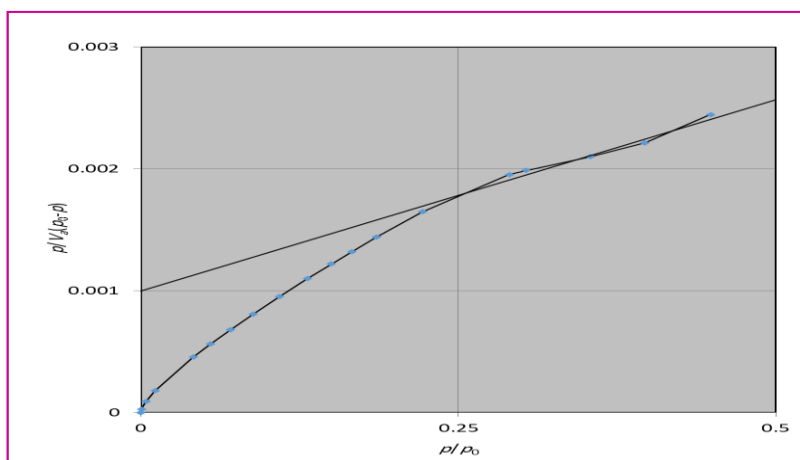


Figure **Error! No text of specified style in document.**12 : BET plot of mMSNPs
crafted macrocycle **5**

Experimental

Synthesis of Silica nanoparticles

The synthesis of several types of silica nanoparticles were achieved by manipulating several factors as described below

Method (A) using CTAB as surfactant Batch 1

The mixture of Cetyl Trimethylammonium bromide CTAB (0.3 g), ammonia (10 ml) and water (120 ml) is subject to heating to 80°C for 15 minutes to reach pH 12.3. Tetraethoxysilane TEOS (1 mL) was added rapidly with moderate stirring about (400-500 rpm). A white solid is observed after few mins of constant stirring. The temperature is kept constantly at 80°C for 2 hours. The solid are isolated from its hot solution by filtration, washed with water (10 ml ×3 times) and methanol (10 ml). The surfactant CTAB was removed from the mesoporous nanoparticles by acid medium. A mixture of methanol (100 ml), conc. HCl (1 ml) was added to the particles sample (1.0 g) and heated tot 60°C for 8 hours using hot plate. The particles was filtered off and washed extensively with water, followed by methanol to obtain a white solid.

Method (C) synthesis of Magnetic silica nanoparticles

The $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.30 g, 21.62 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (11.68 g, 43.1 mmol) were dissolved under a N_2 atmosphere in of deionized water (200 mL) with rapid stirring at 85 °C. Afterwards, 25 mL of an aqueous solution of ammonia NH_4OH (25%) was added slowly to the vessel, and then the solution color changed rapidly to black (from original orange color of iron salts solution). The obtained Fe_3O_4 nanoparticles were collected, washed with deionized water (3 x 25 mL) and finally with sodium chloride (100 mL, 0.2 M) and dispersed in deionized water for further use.

The silica coated Fe_3O_4 magnetic nanoparticles were synthesis as follow. The prepared magnetite suspension (25 mL) placed in a round bottom flask, and exposed to external magnet. After removing the supernatant, of aqueous solution of TEOS (8.0 g dissolved in 80 mL water) was added, followed by glycerol (60 mL) and the pH of the mixture was approximately allowed to be 4.6 using glacial acetic acid. Then, the suspension was heated and stirred for two hours under the inert atmosphere at 90 °C. The mixture was cooled to room temperature and the particles were separated by filtration. Finally, the silica-coated magnetic nanoparticles, washed with deionized water (500 mL) and ethanol (500 mL) several time, and dispersed in deionized water for further use.

Methyl 3,5-bis(prop-2-yn-1-yloxy) benzoate 3

Methyl 3,5-dihydroxybenzoate (3.36 g, 20 mmol), Propargyl bromide (4.72 g, 40 mmol) and sodium carbonate in acetone (150 mL) were refluxed for 12 hours. After the TLC showed disappearance of starting material, the mixture was cooled down to room temperature and the acetone was evaporated on vacuum. The residue was dissolved in dichloromethane 100 mL and washed extensively with water, the organic solvent was dried over magnesium sulfate and evaporated to produce a white solid (yield: 4.86 g, 95%). ^1H NMR (400 MHz, Chloroform- d) δ 7.34 – 7.28 (m, 2H) (Ph), 6.83 (q, J = 2.3, 1.6 Hz, 1H) (Ph), 4.74 (d, J = 2.3 Hz, 4H) ($\text{CH}_2\text{-C}\equiv\text{C-H}$), 3.93 (s, 3H; OCH_3), 2.57 (t, J = 2.3, 1.7 Hz, 2H, $\text{C}\equiv\text{C-H}$). ^{13}C NMR (101 MHz, Chloroform- d) δ 166.48 (C=O), 158.47 (Phenyl C-O), 132.12, 108.82, 107.48 (Ph), 77.94 ($\text{C}\equiv\text{C-H}$), 76.02 ($\text{C}\equiv\text{C-H}$), 56.10 ($\text{OCH}_2\text{-C}\equiv\text{C-H}$), 52.42 (O-CH_3).

Synthesis of methyl 3,5-[15-crownether-5] ditraizole benzoate 4

Compound 3 (2.44 g, 10 mmol), sodium ascorbate (g, 2 mmol) and cuprous chloride (g, 1 mmol) were dissolved in dichloromethane and stirred for 30 minutes. The solution of 1,2- bis(2-azidoethoxy) (2.0 g, 10 mmol) in dichloromethane (100 mL) was added dropwise to the mixture and the stirring was continued for 48 hours. The catalyst was removed by filtration and the residue was washed extensively with water, dried over magnesium sulfate and the dichloromethane was evaporated. The macrocycles 5 was obtain after purification on column chromatography on silica gel to get yellowish brown solid (2.8 g, 71 %), m.p 155-156 °C. ^1H NMR (400 MHz, Chloroform- d) δ : 7.6 (s, 2H; H-triazole), 7.17 (d, J = 2.3 Hz, 2H; H-2 and H-6 on Ph), 6.80 (t, J = 2.3 Hz, 1H-4 Ph), 5.35 (s, 4H, 2 $\text{CH}_2\text{-O}$), 4.51 (m, 2H, CH_2O), 3.81(s, 3H; OCH_3), 3.78 (m, 2H, CH_2O), 3.23 (s, 4H, 2 CH_2N). ^{13}C NMR (100 MHz, Chloroform- d) δ 166.48 (C=O), 158.47 (Phenyl C-O), 143.81 (C-triazole), 132.12, (Ph), 123.46 (CH-triazole), 108.82, 107.48 (Ph), 70.70 (2 CH_2N), 69.82 (2 CH_2O), 62.16 (2 OCH_2), 52.75 (O-CH_3), 50.56 (OCH_2).

synthesis of silica nanoparticle incorporating macrocycle 6

Silica nanoparticles and macrocycle **5** was stirred in DMF at 80 °C for 72 hours. After what the TLC showed disappearance of macrocycles **5** completely, the mixture was filter out through harsh funnel and wash extensively with water followed by acetone to furnish the desired nanoparticles involving macrocycles.

Conclusion

The macrocycle containing a triazolyl residue has been achieved in good yield without polymerization product. This type of macrocycle containing an ester residue is ready to react with an amino group to form amide. In other word the silica and mesoporous silica nanoparticles were synthesized using simple techniques are possess an amino groups in their structures. So simple reaction in the more polar aprotic solvent is good enough to form an amide coupling and imobilized the macrocycle on silica nanoparticles surfaces. The structures of materials are characterized with IR, Mass and one and two dimensions NMR techniques. The mesoporous and magnetic silica nanoparticles were characterized by several techniques include, FESEM, TEM, BET, XRD, FTIR and EDX. The BET study showed extremely surface area of the pore of silica nanoparticles exceeds 1600 m²/g.

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