Synthesis and optical behaviour of mesoporous silica functionalized by organometallic molecules

I. Laskowski\textsuperscript{1,2}, A. Kassiba\textsuperscript{1}, M. Makowska-Janusik\textsuperscript{2}, N. Errien\textsuperscript{1}, A. Mehdi\textsuperscript{3} and J. Swiatek\textsuperscript{2}

Laboratoire de Physique de l'Etat Condensé LPEC, UMR CNRS n° 6087, Université du Maine Avenue Olivier Messiaen 72085 - Le Mans CEDEX 9 France.
Institute of Physics, Jan długosz University, Al. Armii Krajowej 13/15, 42-200 Częstochowa, Poland
Institut Charles Gerhardt, UMR 5253 Chimie Moléculaire et Organisation du Solide, CC 1701 Université Montpellier II Place E. Bataillon, F-34095 Montpellier Cedex 5, France.

E-mail: m.makowska@ajd.czest.pl

Abstract. Mesoporous silica SBA-15 functionalized by (1,4,8,11-tetraazacyclotetradecane) cyclam groups chelating nickel ions (Ni-cyclam) were synthesized by two different approaches. Characterizations by transmission electron microscopy TEM and UV-VIS absorption spectroscopy were performed to monitor the structure and optical properties of the material with regard to the used synthesis methods. The assignment of the experimental UV-VIS absorption spectra is carried out by using the support of suitable numerical simulations based on quantum chemistry DFT codes developed on the modelled (Ni-cyclam) system as free molecule and also constrained in the pores of mesoporous silica matrices.

1. Introduction
Mesoporous silica functionalized by suitable active vectors are attractive architectures for fundamental understanding of physical phenomena at the interfaces or for potential magneto-optical, controlled drug delivery, bio-sensing, catalytic applications or other molecular engineering [1-7]. A wide synthesis activity has contributed to control the synthesis routines which are now well improved to obtain mesoporous silica with variable pore sizes (2-20 nm). Additionally, architectures based on several functional groups located either in the channels or in the silica network, were successfully obtained [7]. The incorporation of active groups inside the pores can be performed either by grafting the active molecules to the silica channels.
walls using organosilica chains or by direct synthesis methods. In this case, the guest groups are expected to be more regularly distributed in the channels leading to a homogeneous media. As matter of fact, the physical properties such as electronic, magnetic or optical, of mesoporous silica based composites can be tuned following the nature of the active groups.

The present work is devoted to cyclam moieties (1,4,8,11-tetraazacyclotetradecane) chelating nickel ions and used as functional groups in the mesoporous silica (SBA-15). Two main synthesis methods were developed based on sol-gel procedure. The performed physical investigations are devoted to shed light on the key features of the different classes of materials with the main criterion of homogeneous materials based on good dispersion of active groups in the host matrices. Experimental investigations of structure and optical properties were carried out by using TEM and UV-VIS absorption. Numerical simulations methods were introduced for the assignment of the absorption bands. The spatial organisation of Ni-cyclam groups inside the mesoporous silica matrices including agglomeration, dispersion or Ni-cyclam pairing, have also a great incidence on the probed properties. This fact justifies our approach based on comparative investigations of two mesoporous silica families.

2. Material Chemistry

Two mesoporous silica functionalized by Ni-Cyclam group were synthesized and referred below as SA and SB series. Both classes of samples had originally the same structure, but the procedure of preparing pre-functionalized silica-chlorine material (Cl-SBA, where SBA is the mesoporous silica) is different. For SA-series samples, chloropropyl groups were attached to mesoporous silica matrix by grafting in already prepared backbones whereas for SB material class, the pre-functionalized silica Cl-SBA samples, were obtained by a direct synthesis.

2.1 Procedure A: pre-functionlized [Cl-SBA₉] samples (SA)

The triblock copolymer (EO₂₀PO₇₀EO₂₀) Pluronic P123 (5.0 g) was dissolved in 150.0 mL of comparatively high acidic aqueous solution of HCl (2M). After about 1h stirring the clear solution was obtained. Amount of 134 g from the resulting solution was added to a tetraethylorthosilicate (7.50 g or 36.0 mmol). The mixture was vigorously stirred for 45 minutes at temperature of 40°C in hot oil bath in order to start polycondensation of silane groups. After this time a white suspension appeared indicating that a mesoporous material was formed. The second step deals with the grafting of the active groups through the 3-chloropropyltrimethoxysilane (0.79 g, 4.0 mmol) added to a suspension which contains hexagonal arranged mesoporous silica. In order to initialize grafting process, tightly closed flask with liquid was put into oven (90°C) for one night. The resulting white powder was filtered off and the surfactant was selectively removed by soxhlet extraction over ethanol for 24 hours. After drying at 120°C overnight under vacuum, Cl-SBA₉ were obtained as white powder according the scheme depicted in figure 1.

![Figure 1: Steps of the mesoporous silica synthesis by procedure A](image-url)
2.2 Procedure B: Preparation of Cl-SBA₉ (SB)
According the well defined protocol [7], the triblock copolymer (EO₂₀PO₇₀EO₂₀) Pluronic P123 (4.0 g) was dissolved in 160 mL of an aqueous solution of HCl (pH=1.5). The resulting clear solution was then added to a mixture of 3-chloropropyltrimethoxysilane (0.84 g, 4.49 mmol) and tetraethylorthosilicate (8.41 g, 40.41 mmol). The mixture was vigorously stirred for 3 hours at room temperature until a transparent solution appeared. The solution was transferred in a hot oil bath at 60°C and NaF (76.0 mg, 1.80 mmol) and then immediately added to induce the polycondensation. A white precipitate appeared within a few minutes and the resulting suspension was further stirred for 2 days at 60°C. The resulting white powder was filtered off and the surfactant was selectively removed by soxhlet extraction over ethanol for 24 hours. After drying at 120°C overnight under vacuum, 2.89 g (94%) of Cl-SBA₉ were obtained as white powder. The main steps of the procedure were depicted on figure 2.

2.3 Reactivity of chloropropyl groups toward cyclam.

After the above steps, the phase of functionalization aims to locate cyclam groups grafted in the mesoporous silica channels. The substitution reactions within the different solids, obtained by procedures A and B, have been carried out and the preparation of cycl-SBA₉ is given below as an example.

2.4 Preparation of cycl-SBA
A mixture of cyclam (0.42 g, 2.09 mmol), Cl-SBA₉ (1.00 g, 1.49 mmol), 90 mL of acetonitrile and triethylamine 1.1 g, (10.9 mmol) was heated under reflux and stirring for 2 days. The white solid was quantitatively recovered by filtration and washed 5 times with hot chloroform and 3 times with hot ethanol to remove the excess of cyclam. After drying at 120°C overnight under vacuum, cycl-SBA₉ were obtained as a white powder.

2.5 Complexation of cycl-SBA₉ by nickel salts
1.00g (1.49 mmol) of cycl-SBA₉ was added to a solution of NiCl₂ (0.017 M, 123 mL) dissolved in ethanol. The resulting suspension was heated overnight under reflux with stirring. The solid was quantitatively recovered by filtration and washed by dry ethanol several times to remove the excess of nickel salt. After drying at 120°C overnight under vacuum, functionalised mesoporous silica as cycl-SBA₉₉ were obtained as a green powder.
3. Physical characterizations

3.1 Transmission electron microscopy (TEM)

TEM observations were carried out in order to check the homogeneity and morphology of the mesoporous silica. JEOL 2010 equipment with accelerating voltage of 200 kV was used as well as liquid nitrogen anticontamination trap devoted to improve the vacuum around the sample. All TEM images were taken by using a contrast diaphragm. The sample preparation consists in small amount of powder, grinded in pure ethanol. One droplet of the suspension was then deposited on copper grid covered by amorphous carbon membrane. The sample resists quite well to the electron beam and the shape of the mesoporous silica can be resolved in very precise way. As shown in figure 3, elongated grains are clearly seen and testify the achievement of the synthesis of the appropriate mesoporous silica structures.

![Figure 3. TEM images of mesoporous silica](image)

The morphology of the mesoporous grains is marked by alternating clear and dark fringes with a periodicity about 10 nm. Such contrast reveals the porous structure of the sample with parallel and well aligned pores. However, with regard to the functional (molecular) group dimensions (Ni-cyclam), it wasn’t easy to evaluate their presence in the host silica.

3.2 UV-VIS reflectance measurements and band assignment

Room temperature UV–visible diffuse reflectivity spectra were collected on a finely grinded sample with a Cary 5G spectrometer (Varian). This instrument was equipped with a Cary Praying Mantis Diffuse Reflectance accessory and computer control using the “Scan” software. The absorption in diffuse reflectance versus wavelength measurements were made in the 250–800 nm range with a 2 nm step using a mirror as reference (100% reflectance).

Fig. 4. shows the absorption reflectance measurement recorded for the SA and SB samples, pure mesoporous silica as well as bare Ni-Cyclam powders.
The bare mesoporous silica did not show any absorption band in the 250 nm – 800 nm region. SB sample exhibits more or less resolved bands located at 250 nm, 377 nm and 463 nm whereas the SA sample is characterized by a large absorption background without clearly defined peaks. For the bare Ni-cyclam powders, the absorption bands are relatively narrow and well resolved at wavelength positions 278 nm, 344 nm, 514 nm and 672 nm. The assignment of the experimental absorption requires an efficient tool as it is briefly outlined below.

3.3 Assignment of the UV-VIS absorption bands

The experimental UV-VIS absorption curves are analyzed by using the support of numerical simulations. The calculations of the excitation energies and vibrational frequencies were obtained using the RESPONSE module [8] of the Amsterdam Density Functional program (ADF) [9]. Three different molecules were taken into consideration, namely pure cyclam ring, Ni-cyclam with the nickel ion bounded to one chlorine (pyramidal-like configuration) and to two chlorine ions (bi-pyramidal-like). In the first stage of computation, the geometry optimization of the structures was performed assuming C\textsubscript{1} symmetry of all molecules. At the first stage, the Generalized Gradient Approximation (GGA) was employed applying the Becke-Perdew (BP) exchange-correlation (XC) functional [10,11] using a Slater-type orbitals triple-\textit{Z} (TZ) basis set without the frozen core approximation.

In a second stage, the molecules were rotated to align their ground-state dipole moment along the Z-axis. The UV-vis absorption spectra calculations were carried out by means of the potential model based on statistical averaging of orbital potentials (SAOP) [12]. The SAOP potential was recently used in order to yield improved estimates for the second and third order optical susceptibilities \(\chi^2\) and \(\chi^3\), as well as excitation energies for prototype molecules such as \(\text{N}_2\), \(\text{C}_2\text{H}_4\), and CO in comparison with the LDA and LB94 potentials. For all considered molecules, the excitation parameters of UV–VIS spectra were calculated by using the time dependent (TD-DFT) method [13-15] implemented in the ADF-RESPONSE code and limiting all the carried out simulations to the singlet–singlet state excitations.

According to this numerical support illustrated in figure 5, it is shown that the pure cyclam molecules without nickel atom exhibit an absorption band near 250 nm while Ni-cyclam bonded to one and two chlorine absorbs respectively at 320 nm and 450 nm. From these results, it is worth noticing that, as the nickel ion is chelated by cyclam and bonded to
chlorine ions, the main absorption band is shifted to high wavelengths and exhibits a net broadening.

These facts underline the possibility to finely tune the UV-VIS absorption in the Ni-cyclam based material by a stabilization of relevant configurations defined by the number of bonded chlorine ions. As illustrated in fig. 5, a combination of the three computed spectra obtained on pure cyclam, and Ni-cyclam bonded to chlorine ions give rise to adjustable shape of the absorption spectra. The obtained curve consists in a superposition of contributions about 89.29 % from cyclam-NiCl$_2$, 1.78 % of cyclam+NiCl and 8.93 % pure cyclam without complexation by nickel ions. On the other hand, though the calculated wavelength positions are shifted with respect to the measured ones, the numerical procedure seems sound and relevant. Indeed, the calculation which consider free and isolated molecules in vacuum contrast with a real powder where molecular interactions are involved.

![Figure 5](image-url)

**Figure 5.** Calculated spectra for bare cyclam – nickel powder.

Furthermore, when the active molecules are grafted inside the mesoporous silica, constraints on the molecular configurations are induced as well as a clustering which occurs in the case of inhomogeneous media. For the SB samples it seems that three configurations of the active groups (pure cyclam, Ni-cyclam bonded to one and two chlorines) are involved. As clearly seen in the SB sample, configurations such as Ni-cyclam bonded to two chlorines dominate the features of the absorption spectrum. Finally, the comparative investigations of the two sample series (SA, SB) and the carried out experiments point out a more homogeneous distribution of active groups in SB sample series compared to SA samples.

### 4. Conclusions

Two families of mesoporous silica containing chloropropyl groups were prepared by two main approaches in to realize a homogeneous distribution of the functional groups inside the pores. Beyond checking the realization of mesoporous structures, the UV-VIS investigations give rise to characteristic bands which can be used to monitor the achievement of the synthesis process and the effective grafting of cyclam moieties within the channel pores. Computational work was performed and serves as a support for the assignment of the UV-VIS absorption bands. Tests of magneto-optical functionalities constitute challenging applications for all these synthesis work. This task is under development.

**Acknowledgment.** We are grateful to Dr.S.Kodjikian for TEM images performed on mesoporous silica matrices.
References

[1] Beck J S, Vartuli J C, Roth W J, Leonowiez M E, Kresge C T, Schimmitt K D, Chu C T –W, Olson D H, Sheppard E W, McCullen S B, Higgins J B and Schlenker J L 1992 J. Am. Chem. Soc. 114 10834.

[2] Inagaki S, Fukushima Y and Kuroda K 1993 J. Chem. Soc. Chem. Commun. 680.

[3] Moller K and Bein T 1998 Chem. Mater. 10 2950.

[4] Yang C M, Sheu H S and Chao K J 2001 Adv. Funct. Mater. 12 143.

[5] Corriu R 2003 J. Organometal. Chem. 686, Issues 1-2 32

[6] Corriu R, Mehdi A and Reyé, C 2004 J. Organometal. Chem. 689, 4437

[7] Qunli Tang; Yao Xu, Dong Wu and Yuhan Sun, 2006 Chem. Lett. 35, 474

[8] X.Ji, Hu Q, Hampsey J E, QQiu X, Gao L, He J and Lu Y, 2006 Chem. Mat. 18(9) 2265

[9] Slowing I, Trewyn B G, Giri S and Lin V S –Y 2007 Adv. Fun. Mat 17, 1225

[10] Consul J M D, Peralta C A, Benvenutti E V, Ruiz J A C, Pastore H O and Baibich I M, 2006 J. Mol. Cat. A 246 33

[11] Jal P K, Patel S and Mishra B K 2004 Talanta 62 1005

[12] Van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. 1999 J. Com. Phys. Com. 118, 119

[13] Baerends E J 1998 Theor. Chem. Acc. 99, 391

[14] Becke A D 1988 Phys. Rev. A 38, 3098;

[15] Perdew J P 1986 Phys. Rev. B (1986) 33, 8822.]

[16] Schipper P R T , Gritsenko O V, van Gisbergen S J A and Baerends E J 2000 Chem. Phys. 112, 1344

[17] Runie E and Gros E K U 1984 Phys. Rev. Lett. 52, 997.

[18] Gross E K U and Kohn W 1990 Adv. Quantum Chem. 21, 255.

[19] Van Leeuwen R 2001 Int. J. Mod. Phys. B 15, 1969.