

## Incorporation of $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ in molecular sieves: a “ship in a bottle synthesis” approach

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### ABSTRACT

Incorporation of  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$  (**1**) (where bipy is 2,2'-bipyridine) in the molecular sieves of the type LTA, NaY and mesoporous Al-MCM-41 by using a “ship in a bottle synthesis” approach was investigated.  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$  was successfully incorporated in the channels of mesoporous Al-MCM-41, and the product was characterized by X-ray diffraction, FTIR and BET analysis. It was found that size criteria prevented the complex to be incorporated in smaller cages of the LTA or NaY zeolites. Incorporation of the complex into the channels of Al-MCM-41, on the other hand, did not affect morphology of the host as it is evident from SEM micrographs.

**Keywords:**  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ ; Incorporation; Mesoporous; Al-MCM-41.

### 1. INTRODUCTION

Incorporation of transition metal complexes inside inorganic structures makes it possible to design catalysts which combine the advantages of homogeneous and heterogeneous catalytic systems [1]. Zeolites are attractive supports for incorporation, as they combine high thermal and chemical stability with a quite regular crystalline framework structure. The well-defined and ordered structure of zeolites provides an ideal environment to entrap active metal complexes, and the confinement leads to higher stability by reducing dimerization of active sites. These modified systems can be exploited as catalysts [2–4].

Due to the steric constraint of these hosts, however, interesting changes in

the physico chemical properties of such encapsulated complexes have been reported [5–8]. Mixed ligand complexes, on the other hand, can be a synthetic challenge to tune properties of transition metal complexes. Metal complexes containing diimine ligands such as 1,10-phenanthroline and bipyridine have attracted attention because of their versatile roles as building blocks for the synthesis of metallodendrimers and as molecular scaffolding for supramolecular assemblies, and in analytical chemistry, catalysis, electrochemistry, ringopening metathesis polymerization (ROMP) and biochemistry. However, most diimine complexes reported so far, are homoligand compounds of the general formula  $\text{M}(\text{N}-\text{N})_3$  or to a lesser extent

$M(N-N)_2X_2$ . To the best of our knowledge, little attention has been paid to the incorporation of such complexes into the molecular sieves. Our interest in the study of ion-exchanged zeolites [9, 10], prompted us to evaluate incorporation of  $[Fe(bipy)Cl_4][bipy.H]$  (**1**) in molecular sieves.

## 2. EXPERIMENTAL

### 2.1 Reagents and materials

All materials were purchased from Merck and used without further purification.  $[Fe(bipy)Cl_4][bipy.H]$  was synthesized according to Safari et al [11]. In brief, 2,2'-bipyridine (0.155g, 1 mmol) was dissolved in 0.1 M HCl (10ml).  $FeCl_3.6H_2O$  (0.135 g, 0.5 mmol) in water (10ml) was added to this solution, and the resulting red solution was stirred at 55–60 °C for 3h. The product was obtained from  $CH_3CN$  as orange prismatic crystals after 3 days. (Yield: 0.195 g, 76.3%). m.p.: 216 °C, IR (KBr,  $cm^{-1}$ ): 3060, 1615, 1599, 1583, 1443, 1311, 1270, 1248, 1229, 1174, 1158, 1021, 764, 733, 652, 630, 357, 333, 309 (Fe–Cl), 291 (Fe–Cl), 258 (Fe–N). AlMCM-41 with a Si/Al ratio of 39 was synthesized and characterized according to the literature [12]. Zeolite A with the composition  $2.3Na_2O:1.0-Al_2O_3:2SiO_2:300H_2O$ , was synthesized according to Salma et al. [13]. NaY was synthesized according to Blatter et al [14]. The  $Fe^{3+}$  ion-exchanged zeolites (FeY, FeAl-MCM-41, FeA), were obtained by overnight stirring of the corresponding zeolite with 0.05 M solution of  $FeCl_3.6H_2O$  (15 mL per g of zeolite), then filtration and washing with hot deionized water to remove any physisorbed species, as was monitored by a conductometer. The whole process repeated three times and soxhlet extraction with acetonitrile removed the ions located on the zeolite's surface. Finally, the ion-exchanged zeolites were subsequently filtered and calcined at 550 °C. In order

to encapsulate  $[Fe(bipy)Cl_4][bipy.H]$  in the zeolite hosts, 2,2'-bipyridine (0.155g, 1 mmol) was dissolved in 10 mL of a 1:1 mixture of ethanol and water and titrated by 0.1 M HCl to pH of 7.0. To this solution, 500 mg of the corresponding ion-exchanged zeolite was added and the mixture was stirred at 55–60 °C for 3h. The red precipitate was then filtrated and washed with hot deionized water three times, then soxhlet extracted with acetonitrile.

### 2.2 Characterization

X-ray powder diffraction (XRD) measurements were performed by using a Philips diffractometer of X'pert Company with mono chromatized  $Cu\ k_\alpha$  radiation. IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. Morphology of the synthesized samples was characterized with a scanning electron microscope (SEM) from Philips Company (XL30 ESEM).

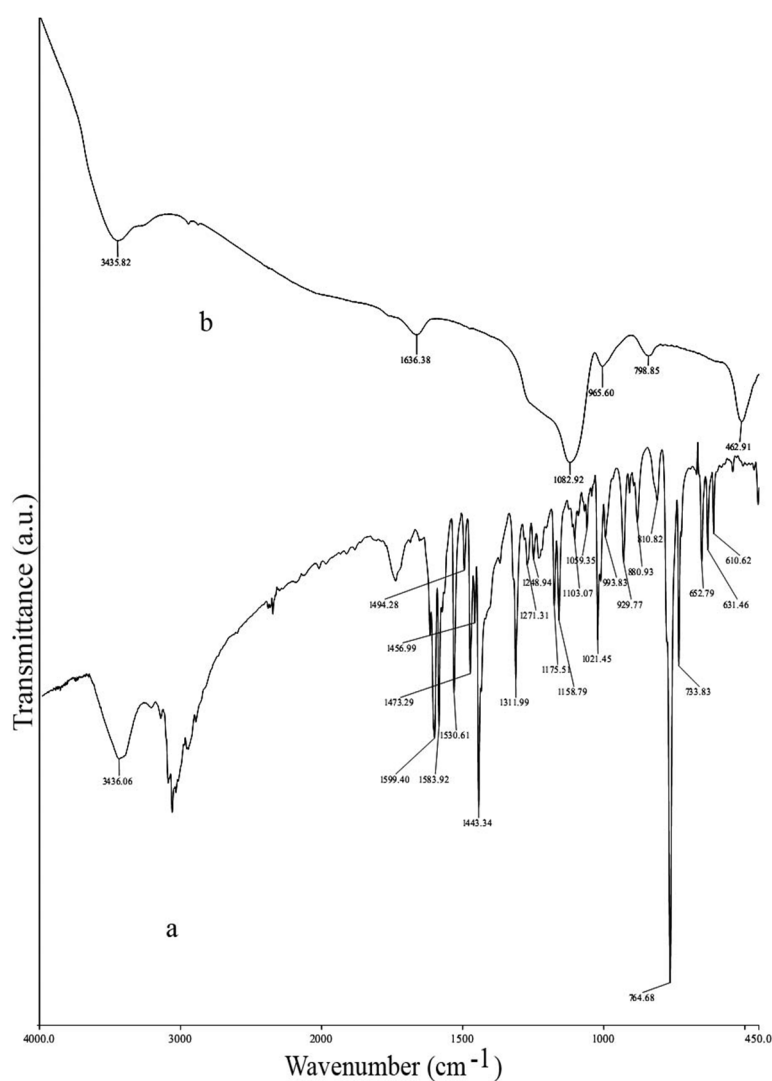
## 3. RESULTS AND DISCUSSION

### 3.1 FT-IR and XRD Analysis

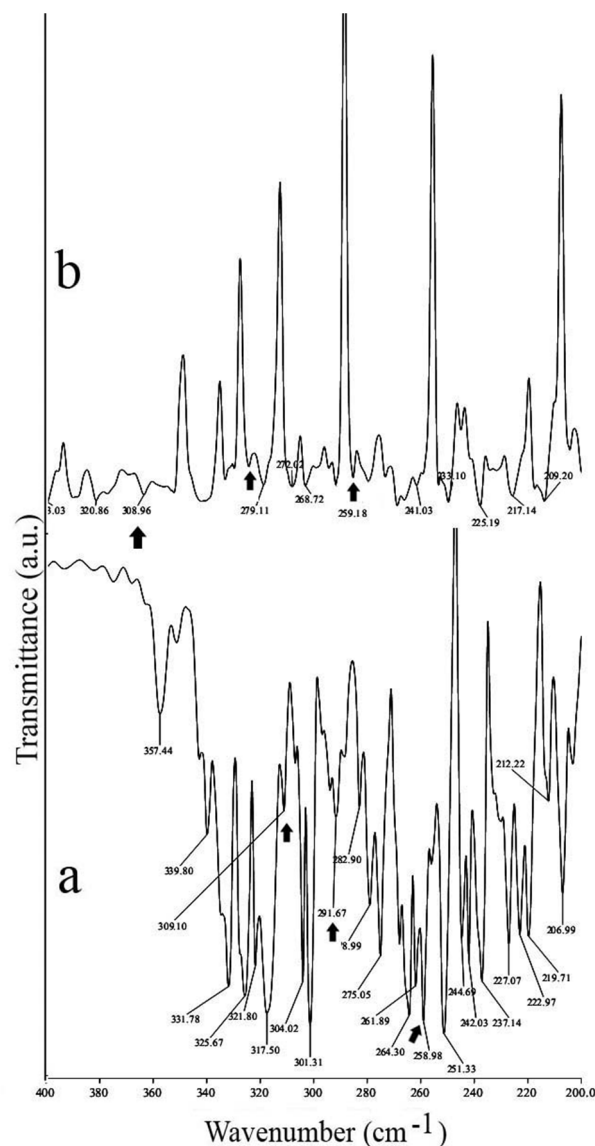
Treatment of one equivalent of  $FeCl_3.6H_2O$  with 2 equivalents of the bidentate chelating ligand, bipy, in the presence of HCl solution affords a compound with the formula  $[Fe(bipy)Cl_4][bipy.H]$ . The structure of complex **1** is unambiguously identified [15]. Considering our interest in the transition metal catalytic systems and difficulty of recovering homogeneous transition metal complexes, we decided to encapsulate complex **1** in the zeolites, as a potential heterogeneous alternative. To do so, a "ship in a bottle synthesis" approach was selected. First, Al-MCM-41 was selected as the host, since its pore diameter is large enough to admit complex **1**.  $Fe^{3+}$  loaded Al-MCM-41 (FeAl-MCM-41) is yellow in color. Upon diffusion of the 2,2'-bipyridine ligand into the channels of Al-MCM-41, however, the color changed to red, which is the first

characteristic of formation of the desired complex. Feasibility of the synthesis, however, was approved by FT-IR spectra and XRD patterns. Figure 1a shows the FT-IR spectra of **1**, and Figure 1b shows FT-IR spectra of the Al-MCM-41 loaded  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ . No peaks associated to stretching vibrations mode of Fe-O in the region of  $580\text{--}640\text{ cm}^{-1}$  were observed, which diminished the formation of iron(III) oxide during calcination. While little could be

deduced from these spectra, which is due to broad and strong absorption bands of the host, IR spectroscopy in the region of  $200\text{--}400\text{ cm}^{-1}$  provided more useful details. As it is obvious from Figure 2a, complex **1** shows three characteristic bands at  $309\text{ (Fe-Cl)}$ ,  $291\text{ (Fe-Cl)}$  and  $258\text{ (Fe-N)}\text{cm}^{-1}$ [11]. The same vibrations were observed for Al-MCM-41 loaded  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$  (Figure 2b).



**Fig. 1.** FT-IR spectrum of: (a)  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$  and (b) Al-MCM-41 loaded  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ .

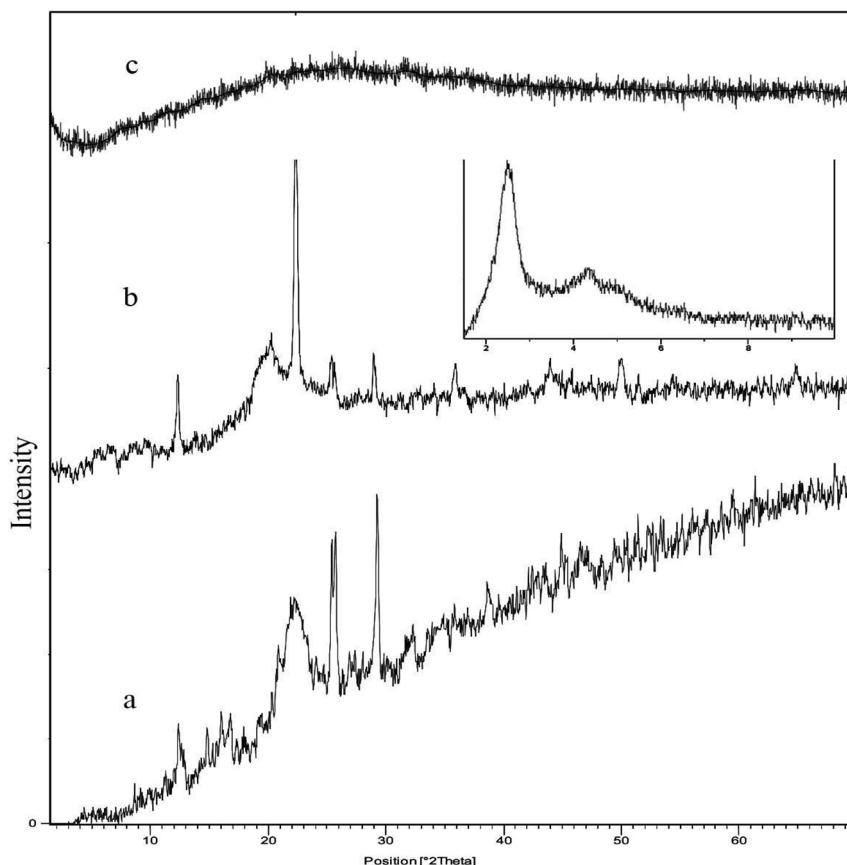


**Fig. 2.** FT-IR spectrum of complex **1** (a) and Al-MCM-41 loaded complex **1** (b) in the region of 200-500  $\text{cm}^{-1}$ .

### 3.2 XRD analysis

XRD patterns of free and Al-MCM-41-encapsulated complex **1**, also confirm feasibility of the synthesis (Figure 3). Four index peaks of the complex **1** (Figure 3a) at  $2\theta=12$ , 25.5, 26 and  $29.2^\circ$  reoccurred in the XRD pattern of

the encapsulated complex (Figure 3b). Inset of the Figure 3b, also, shows low angle pattern for the Al-MCM-41-encapsulated complex **1**, indicating that the crystal structure of Al-MCM-41 was retained after incorporation [16].

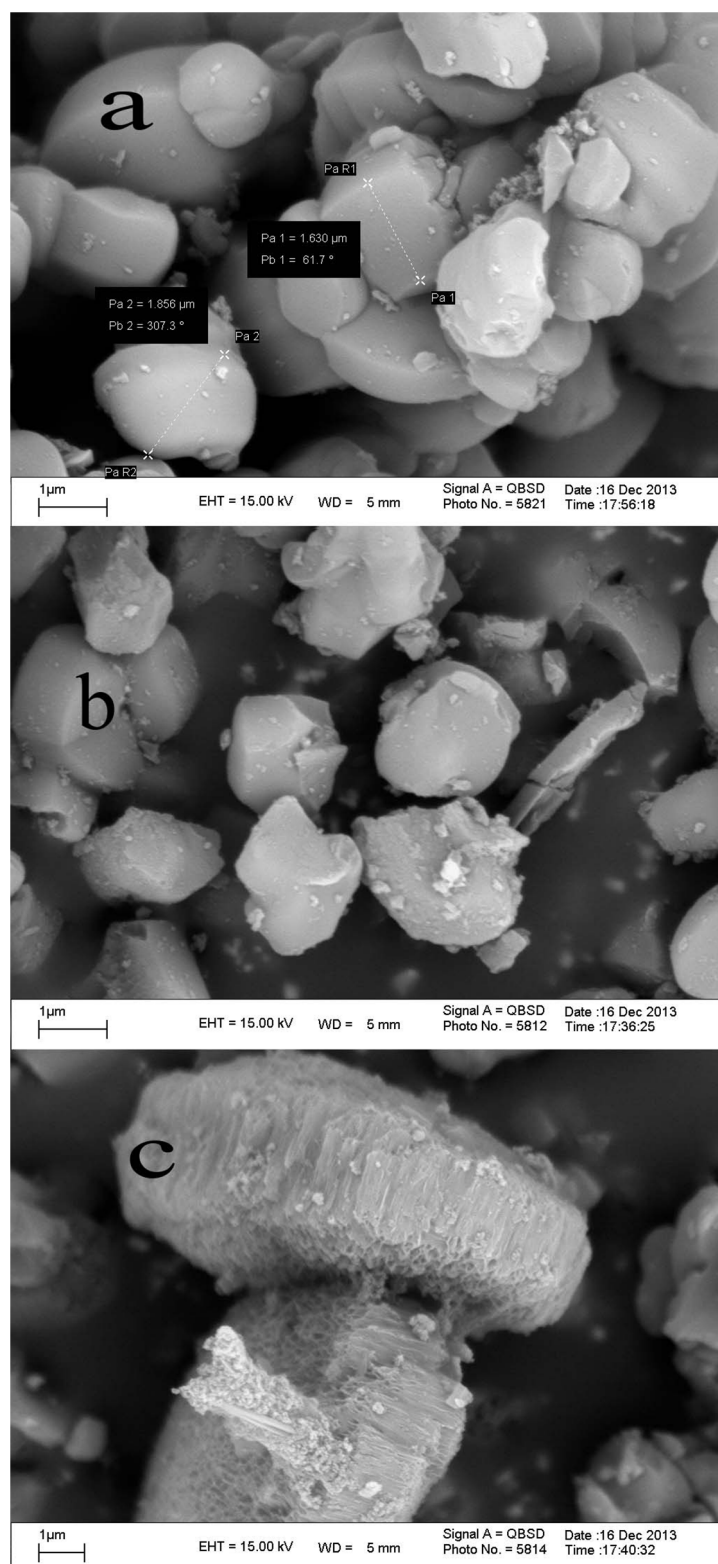


**Fig. 3.** XRD patterns of: (a)  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ , (b) Al-MCM-41-encapsulated  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$  and (c) zeolite Y encapsulated  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ . Inset shows low angle pattern for the Al-MCM-41-encapsulated complex  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ .

### 3.3 SEM Analysis

Incorporation of the complex **1** into the channels of Al-MCM-41 did not affect morphology of the host as it is evident from SEM micrographs. As shown in Figure 4, the Al-MCM-41 crystallites of about 1  $\mu\text{m}$ , preserved their size and shape after hosting the complex, and a close-up image also showed that the structure of channels were also, preserved. Meanwhile, BET surface area of Al-MCM-41 drops from 630.0  $\text{m}^2/\text{g}$  to 403.9  $\text{m}^2/\text{g}$  for impregnated host. Drop in pore volume was from 0.58  $\text{mL/g}$  to 0.19  $\text{mL/g}$ . Encouraged by these results, we decided to incorporate complex **1** into the microporous structure of zeolite Y. The supercage diameter of 12  $\text{\AA}$  of zeolite Y which is surrounded by 10 sodalite cages, is proportional to the dimension

of inner coordination sphere of complex **1**. However, the synthesis was un-successful as it is evident from the XRD pattern of the product (Figure 3c). This may be due to the negative charge of the complex and necessity of presence of its cationic counterpart ( $[\text{bipy.H}]^+$ ) which destroys the crystal structure of the zeolite. In fact, the structure of complex **1** consist of alternating stacks of  $[\text{Fe}(\text{bipy})\text{Cl}_4]^-$  anions and  $(\text{bipy.H})^+$  cations, linked together by hydrogen bonds. Each anion binds to organic donors through  $\text{N-H}\cdots\text{Cl}$  hydrogen bonds [11]. Similar result was obtained when zeolite A was used, which further confirmed this assumption.



**Fig. 4.** SEM images of: (a) Al-MCM-41 and (b, c) Al-MCM-41 loaded [Fe(bipy)Cl<sub>4</sub>][bipy.H].

#### 4. CONCLUSION

In conclusion, we have successfully incorporated the complex [Fe(bipy)-Cl<sub>4</sub>][bipy.H] into the channels of mesoporous Al-MCM-41 with no considerable change in the size and shapes of the host. Size criteria, however, prevented the complex to be hosted in the smaller cages of zeolite Y or zeolite A. Further investigation in this context, along with catalytic studies of the product is currently under way in our laboratory.

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## تشکیل کمپلکس $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$ در قفس‌های مولکولی: رهیافت "سنتز کشتی در بطری"

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### چکیده:

تشکیل کمپلکس  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$  (۱) (که در آن لیگاند  $\text{bipy}$  ۲ و ۲-بی پیریدین است) در قفس‌های مولکولی  $\text{LTA}$ ،  $\text{NaY}$  و مزوپور  $\text{AlMCM-41}$  با استفاده از رهیافت "سنتز کشتی در بطری" مورد بررسی قرار گرفت.  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy.H}]$  بطور موثر در درون کانال‌های  $\text{Al-MCM-41}$  تشکیل شد و محصول با کمک پراش پرتو  $\text{X}$ ،  $\text{FTIR}$  و آنالیز  $\text{BET}$  مشخصه یابی شد. مشخص شد که عامل اندازه مانع از تشکیل کمپلکس درون قفس‌های کوچکتر زئولیت‌های  $\text{LTA}$  و  $\text{Y}$  می‌شود. از سوی دیگر تشکیل کمپلکس در درون کانال‌های  $\text{Al-MCM-41}$  همانطور که از تصاویر  $\text{SEM}$  بر می‌آید تاثیری بر ریخت شناسی میزبان ندارد.

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