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Exploratory Workshop Scheme

Standing Committee for Physical and Engineering Sciences (PESC)

ESF Exploratory Workshop on

Genesis and Applications of Active Metal-Organic Frameworks

Dourdan, France, 25 - 28 April 2007

Convened by:

Gérard Ferey

Institut Lavoisier (UVSQ), Département de Chimie, Université de Versailles St. Quentin en Yvelines

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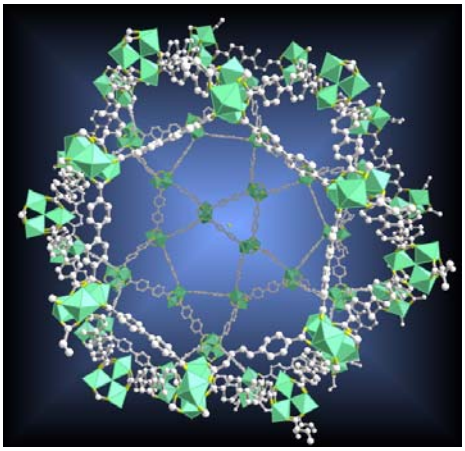

OUTLINE

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Report on the ESF Exploratory Workshop

'Genesis an applications of active Metal-Organic Frameworks'.

Dourdan (France) 25-28 April 2007

By G. FEREY, Convenor.

The meeting was organized in Dourdan, in a charming and quiet Club-House 'Villages, Vacances, Familles', located in the woods which surround the Dourdan village, located at 80 km in the west of Paris, and easily reachable by car or train. On behalf of all the participants, I can attest that the organization of the accommodation was perfect and beneficial for the informal discussions which followed the lectures. This makes the workshop a great success.

Among the invited colleagues, only one (Pr. K.-P. Lillerud, from Oslo) did not come.

As I explained in my proposal, the field of Metal-Organic Frameworks, a new class of porous solids containing in their skeleton both organic and inorganic parts exclusively linked by strong bonds) is currently exploding due to :

- their **easy synthesis** (mostly solvothermal) with quasi-infinite possibilities of association between the organic and inorganic parts ;
- their **properties**, either **enhanced** when compared to other porous solids and to their 'classical' properties (adsorption, storage, separation, delivery…), **or unprecedented** in the domain of porous solids (breathing, drugs, properties usually found in dense phases…) ;
- the **interest of industrial companies** for applications.

The workshop itself aimed at gathering the best recognized experts (mostly European, but two Asian colleagues were invited for the breakthroughs they recently published). Beside them, and for showing that MOFs correspond to a very important evolution rather than a revolution, I decided to invite a few experts not directly linked to MOFs but working on closely related fields : two coming from the 'classical' inorganic porous solids (J. Cejka (Prague) and J. Rocha (Aveiro, Portugal)) and one coming from the broad field of non porous hybrids : Dr Clément Sanchez (Paris) to give a plenary lecture. He is the most prominent scientist in this area and his broad multidisciplinary culture appeared during his talk, which was beneficial for the whole audience.

The workshop itself was divided in five half days corresponding to the following topics :

- ***Synthesis*** : new solids ; new methods ;
- ***In situ studies*** for the understanding of the reaction pathways ;
- **Structural aspects** and the informations that high resolution electron microscopy and structural simulation can afford for MOFs ;
- ***Adsorption phenomena*** (gases, liquids), their simulation and emerging applications in the fields of energy and sustainable development ;
- ***New physical properties ;***
- ***Other properties***

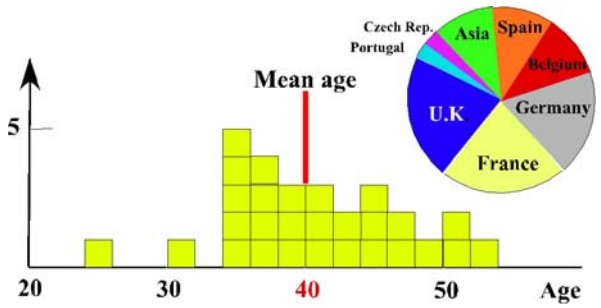
• ***Industrial aspects***.
For a better *a posteriori* information of ESF concerning the contents of the Workshop and the perspectives it opens, I decided to present the report in a non conventional way. Indeed, after a brief overview on the different presentations and the content of our conclusions, I have asked to every participant not only to write the abstract of their contribution (including addresses and telecontacts), but also to join the main paper they have recently published (or submitted) in which they show the state-of-the-art and the last developments in their own sub-field. The abstracts and related papers will be found as annexes at the end of the book. The annex will begin by the extended review I recently wrote for the plenary lecture I shall give in Beijing for the XVth International Zeolite Conference in next August.

Gérard Férey
Convenor

The MOFs V.I.P.

An overview of the contributions.

A preliminary remark. The immense majority of the 28 speakers was young (ca. forty), non conventional and brilliant, coming from seven European countries, but also from Asia (Japan, Korea), which is a strong sign for the development of the area. They also played the game of a workshop, privileging the originality rather than a polished academic presentation. It was refreshing and fruitful, with a lot of questions at every presentation…



I opened the workshop by a welcoming address followed by a presentation of ESF activities, using the documents provided for a PowerPoint presentation. It was perfectly clear and informative. No questions arose.

Instead of giving a talk which would have overlapped with many further contributions, I preferred to introduce the philosophy of this meeting, which was the first in Europe : information, confrontation of ideas, establishment of connections in view of future multidisciplinary cooperations, brain storming and finally a strategy for creating a scientific network with complementary approaches in an administrative form to define and/or select the most appropriate strategy.

This implied **a global approach** of the current problems and orientations concerning MOFs, **looking at all aspects** concerning this class of solids, including synthesis (insisting on new routes), mechanisms of formation, growth of thin films, structural aspects and their prediction, properties, either usual for porous solids (adsorption, storage, separation, catalysis…) or unprededented (conductivity, magnetism, luminescence…), and of course their potential for industrial applications.

The workshop itself began by a plenary lecture '*Chemistry of coordination space toward new porous materials*' given by Prof. S. Kitagawa (Kyoto University), a pionneer in the field of coordination polymers (MOFs with 0-dimensional inorganic subnetwork). He was the first to discover the exceptional qualities of MOFs for adsorption of gases as soon as 1997.
He showed the broad panel of properties that these coordination polymers (rigid or flexible) can provide, the most promising concerning the possible use of the cavities of the MOFs to induce confined polymerization, a breakthrough that he published one year ago and which opens interesting avenues for the future because polymer scientists, with their deep knowledge, will bring it to the development of MOFs in this direction.

The first topic concerned synthesis with two aspects : the results (new solids), and the alternative ways to reach them (new ways of synthesis)

The two presentations on new solids, concerned (i) new phosphonates (P.A. Wright, St-Andrews (Scotland)) of 3d and 4f transition metals using chiral ligands and tunable channels and (ii) 3d transition metal carboxylates (M. Rosseinsky, Liverpool (UK) using amino-acids as ligands which show highly selective adsorptions, specific to the functional group disposition within the sorbed molecules, with a nice computational description of host-guest interactions.

An accent was put on the new ways of synthesis for MOFs. Three contributions in this field : • the first by R.E. Morris [St-Andrews (Scotland)] described the princeps use of ionic liquids as solvents for the ionothermal preparation of new solids. This breakthrough applies not only to MOFs, but also to porous inorganic materials, as shown by the description of many structures related to both classes. This new method is probably promised to a brilliant future.

• the second [N. Stock (Kiel (Germany)] was devoted to the establishment of high-throughput methods adapted to the synthesis of MOFs. Stock nicely showed that this method is not only useful for screening and optimization, but that it reveals some aspects of the physical chemistry of reactions, necessary for a good knowledge of reaction paths, according to the influence of solvents.
• The third [S-H Jhung, Taejon (South Korea)], equally original, concerned the microwave synthesis of MOFs and, compared to classical ways of synthesis, their advantages in terms of phase selectivity, morphology control and rapid syntheses. This is also a breakthrough which must be developped by industry because it combines fast and quantitative production (60 times shorter than classical heat treatment) and enhanced purity, with sometimes the possibility of a continuous flow of synthesis.

Beside synthesis, one important feature is to know how it works, or what is the behaviour of the solid under a stimulus. It is the reason why ***in situ studies*** are necessary, but currently not developped enough.

Two lectures were dedicated to this aspect of the knowledge of MOFs. The first [R.Walton, Coventry (UK)] concerned the identification of the inorganic bricks which, preexisting in the solution, are found in the final solid. This is the keypoint for hoping tailor-made syntheses in the future. Using EXAFS spectroscopy, Walton showed, in the example of MIL-89, that the brick found in the precursor, remains invariant during all the hydrothermal reaction, even during the formation of an amorphous solid which exists before the formation of the final solid. The second one, given by M. Daturi, from Caen (France), showed the efficiency of in situ IR spectroscopy (*modulus operando system*) for determining the acid sites of the MOFs and for following the adsorption of CO_2 in MOFs. IR allows not only to evaluate the amount of adsorbed gas in real time, the sites on which adsorption occurs, but also to provide accurate informations on the effect of adsorbed species on the dynamics of the skeleton.

Related to synthesis, a possible development of MOFs is their use as oriented monolayers or ***thin films*** for possible further catalytic applications. T. Bein (Munich, Germany) explained the growth of oriented MOFs on self assembled monolayers and showed that their orientation drastically depends on the functionalization of the monolayer. A close study, performed by R. Fischer [Bochum (Germany)], using this time modified silica and alumina substrates, evidenced the special role of alumina and its influence on the oriented growth of MOFs. Fischer studied the gas adsorption properties of these thin films with the reversible loading of palladium complexes.

The ***structural aspects*** were then investigated in two ways. O. Lebedev [Antwerpen (Belgium)] nicely showed the contribution of high resolution electron microscopy to the atomic level knowledge of the structure of MOFs (and incidently the stability of these phases under the beam). C. Mellot-Draznieks [London (UK)], on her part, described the power of computer simulations for the structural *prediction* of MOFs' structures, in relation with the existence of well defined inorganic bricks during the synthesis, already evoked by Walton.

The second plenary lecture of the workshop was delivered by C. Sanchez [Paris (France)], an international expet in Hybrid materials. He developped the different chemical strategies offered by sol-gel processes together with the templated growth of inorganic or hybrid frameworks involving self-assembly with surfactant mesophases or organogels. It allows through an intelligent and tuned coding to develop innovative materials having complex architectures (thin or thick films, microparticles and fibers). Several examples were given to illustrate this concept.

As MOFs are porous solids with high performances, a huge session was devoted to ***adsorption phenomena***, in their descriptive but also thermodynamic and simulation aspects. The ability of MOFs to adsorb strategic gases like H_2, CO_2, CH_4 and others make them interesting candidates for their use in the societal domains of energy and sustainable development.

P. LLewellyn [Marseille (France)] compared the performances of several structurally different MOFs in terms of CO_2 and CH_4 uptake and showed that a combination of complementary methodologies is necessary for having a good understanding of adsorption phenomena, mainly at the atomic level. These methods include microcalorimetry, synchrotron X-ray diffraction, FTIR and computer simulation. He also showed that MIL-101, the only crystallized mesoporous MOF, exhibits the best performances for storage at room temperature and is promised to dedicated applications. G. De Weireld [Mons (Belgium)], using an original gravimetric apparatus, established a comparison of the performances of MOFs, zeolites and activated carbons during the adsorption of H_2S at room temperature. Here also, MOFs are proved to be the best materials.

The hydrogen storage 'hot topic' gave rise to two communications. The first by M. Hirscher [Stuttgart (Germany)] described the hydrogen adsorption at 77K of the six most promising MOFs, whose performances roughly satisfy the DOE criteria and observed an almost linear variation of the maximum H_2 uptake (weight%) with the specific surface area of these solids. The second, presented by M. Latroche [Thiais (France)], gave an overview of the different materials for H_2 storage, their advantages and their limits, their type of adsorption (physi- or chemisorption) and some trends for the future of the topics.

From all these studies, it becomes clear that MOFs, and particularly crystallized mesoporous MOFs, are by far the best materials for adsorption of green house gases and good candidates, in some conditions, for the separation of the latter. But what about liquids ? The audience had the chance to be informed of two results (in press or submitted) which open a new window in this field. The first, by L. Alaerts, replacing D. De Vos [Leuven (Belgium)] showed for the first time that MOFs are are able to separate in a very efficient way liquid hydrocarbon mixtures (o-, m-, p- xylene and ethylbenzene), either in batch or in a column set-up, at high or at low concentration, and proposed the best known MOFs in this area. A closely related talk, presented by P. Trens [Montpellier (France)] showed similar results concerning both liquids and vapours of alkanes (C5-C9).

Finally, for finishing this session devoted to adsorption, T. Düren [Edinburgh (UK)] showed how computer simulations can help to understand adsorption phenomena in MOFs. Her talk demonstrated first their contribution for the adsorption of alkanes, CO_2 and H_2 (pure components and mixtures) but also the need to develop and combine advanced simulation techniques for a structural knowledge of the adsorption leading to an efficient and viable design strategy for MOFs.

Another classical application of porous solids concern their use in catalysis. Surprisingly, until now, only a very few studies on MOFs concern this domain. It is the reason why J. Cejka [Prague (Czech Republic)] presented an overview on the advanced hybrid catalysts based on molecular sieves. It was followed by a talk by J.-S. Chang [Daejeon (Korea)] who presented results on the crystallized mesoporous MOFs MIL-100 and -101. The first shows good catalytic activity and selectivity for Friedel-Crafts alkylation of benzene with benzyl chloride, whereas the second exhibits a huge and fast adsorption of benzene, making it a good candidate for sorptive removal of harmful organic contaminants. From these two lectures, it is clear that the possibilities of MOFs in catalysis are immense and merit to be thoroughly investigated.

All the above aspects were related to enhanced classical properties of porous solids but, at variance to all other classes of porous solids, ***MOFs present also the physical properties*** usually encountered in dense inorganic solids (magnetism, luminescence, conductivity…). According to the synthesis conditions, the dimensionnality of their inorganic subnetwork can indeed vary from 0D to 3D and for high dimensionnalities, can compete with well known dense materials. A special session was devoted to this new facet of the domain, which opens a new window and currently makes ***MOFs fascinating multifunctional materials***. Lectures concentrated on the two first aspects.

Marc Drillon [Strasbourg (France)] showed how to design MOFs with outstanding ***magnetic properties*** by playing on both the dimensionnality of the inorganic and organic parts, which can lead to antiferro-, ferri- and even ferromagnetism. The talk focused on the mechanisms responsible for the physical properties, and on the role of the organic species in these multifunctional materials. In the same way, J. Veciana [Barcelona (Spain)] gave a review of magnetic porous materials either purely organic ot hybrid framework . A particular emphasis was put on the use of organic radicals that he initiated for improving the long range magnetic interactions between the inorganic moieties. The two first lectures insisted on the role of the skeleton of the MOFs for introducing magnetic properties, but the latter can also be generated by the insertion of magnetic species (single molecular magnets, metal nanoparticles functionalized by cationic surfactants…) within the pores. This leads to observe confinement effects in the MOFs [E. Coronado, Barcelona (Spain)].

Concerning optical properties, two principal ways are currently studied : the search for MOFs with Non-Linear Optical (NLO) properties and the introduction of luminescence. If the first is just emerging, the second already gives interesting results, both from the academic and applications (sensors) point of views. Of course, the solids based on lanthanides are concerned and J. Rocha [Aveiro (Portugal)] gave an excellent lecture on 'bright new zeolites' for illustrating this new field.

All the domains described above concern chemistry, physical chemistry and physics, but what about MOFs in biosciences ? The answer was given by M. Manzano [Madrid (Spain)] in the field of controlled drug release. It is a new emerging domain, but which is promised to an interesting future. Compared to classical mesoporous solids (MCM-41 type), MOFs, particularly those with crystallized mesopores (MIL-100 and -101), present outstanding

and unprecedented properties, both in terms of adsorbed amounts, and in long release times. For example, MIL-101 takes 4 times more ibuprofen that MCM-41 with a release in six days instead of three. Such performances are obviously a breakthrough and it can be anticipated that applications in biosciences and biotechnologies will arise quickly.

Finally, the last question is : ***MOFs, for what ?...*** If this new class of solids is interesting for the improvement of academic knowledge, is it useful enough to attract the attention of companies for industrial developments owing to their potential in several domains ? The answer, given by M. Schubert [BASF, Ludwigshafen (Germany)], is clearly YES. He gave not only the reasons of the interest of companies (infinite possibilities for new architectures, world records in weight specific surface areas, ultimate porosity with absence of 'blocked' dead volumes in solid matter, ultra large and ultra small pore size, combined flexible and robust frameworks, high mobility of guest species…), but also the industrial criteria to respect for a large scale development of these solids (low costs, easy and reproducible synthesis even at the m^3 scale production, facility of shaping (extrusion, pellets…)). This was extremely useful for the audience who showed her interest by asking for many questions after the talk of M. Schubert who showed the first examples of industrial production of MOFs, with pictures of 250 kg reactors for providing the solids now known as BASOCUBE®, BASOSTOR® and BASOLITE®, useful for gas storage and gas processing applications.

This industrial support definitely legitimates MOFs as strategic materials for the present and the future, whose applications will touch most of the aspects of solid state science, in their physical and biologic dimensions. These solids are at the crossroad of many disciplines, far beyond the intersection of chemical sub-disciplines. This means that the interest for these solids will attract more and more scientists of other branches of science. It is impossible to predict the limits of this new field of science. It is so huge, the number of possibilities is so immense that only one thing is sure : the only limit is the imagination of scientists…

It is my honour to have initiated, thanks to the help and comprehension of ESF and the enthusiastic reply of my young colleagues, the first international Exploratory Workshop on this area. This event must not be isolated. Under the auspices of DECHEMA, I organize the 1st International Conference on MOFs (MOF 2008) next year. It will be held in Augsburg (Germany) on October 8-10th and aims at promoting this new strategic field in the international community and at initiating periodic conferences on the topics. However, it is not the most important. The most important is to create a European Network, owing to the fact that the ESF workshop revealed the need of such an organized community at the European level. To the best of my knowledge, such a network does not exist in USA or in Asia. By creating this network, Europe would be at the forefront.

Assessments and discussions for a scientific strategy

The last three hours of the workshop were devoted to the examination of the effect of the workshop, to the developments it suggests and the possibilities to extend it into a real scientific network.

Some interesting remarks :
• Many participants never met before and used the meeting for discussions on a possible way of cooperation;
• Most of the participants were not aware of *all* the possibilities provided by MOFs and discovered some aspects which would interest the development of their own domain of expertise ;
• All the participants have declared that a periodic repetition of such a meeting is absolutely essential ;
• For these reasons, all of them considered the workshop as ***a great success and the nucleation*** of a possible real scientific organization at the European level. As far as I know, such an organization does not exist in USA. Asking for the question to the Asian colleagues present at the meeting led to the same conclusion : no Asian network for the moment. Therefore, Europe is currently in advance and must concretize this advantage by ***an official support to MOFs, considered as a new category of strategic materials for energy, sustainable development and health and for which the industrial investment of a European company already exists.***

Such an organization requires first to analyse what are the European strengths compared to the expertises of other countries which make the current project a leading one at the international level. One has to bear in mind that such a project must gather a great and fast chemical creativity, an understanding of the formation of MOFs, numerous and complementary academic expertises in all the fields of characterization for facilitating the applications of the best MOFs at the industrial level. All these criteria are satisfied by the present association. **WHAT ARE THE ASSETS OF SUCH AN ASSOCIATION**, able to increase the European impact ?

A unique potential of chemical innovation.

Everything begins by innovative chemistry. In the domain of MOFs, Europe has the chance to dispose of four of the eight recognized academic leaders in original materials: in Liverpool (Rosseinsky), St-Andrews (Morris and Wright) and Versailles (Férey). The others are Yaghi (UCLA) and Long (Berkeley) in USA, and Kitagawa (Kyoto) and Fujita (Tokyo).

Moreover, among these four, at least two of them have developped unique and promising routes of syntheses : Morris (St-Andrews), with the use of ionic liquids as solvents, and Férey (Versailles), with the preliminary mastery of the active inorganic bricks in the solvothermal solution from which rational synthesis of MOFs containing these bricks become possible. Moreover, the further use of structural computer simulation to predict the possible architectures resulting from the association of these bricks with a given organic linker is unique in the world and greatly facilitates the accessibility to the structure without the need of single crystals. In terms of rational synthesis related to the knowledge of the existence of well defined inorganic bricks, in situ measurements (EXAFS, NMR..) are currently developped (Walton, Férey) to identify new ones.

For the search of new phases, a complementary approach initiated by N. Stock (Kiel) for MOFs, which uses highthroughput techniques, is currently unique and drastically increases the speed for the discovery of new interesting compounds (10 days instead of 6 months). His current cooperation with the group of Férey for the systems using aminoacids as ligand is particularly illustrative of the efficiency of the approach.

Faster screening, but also accelerated production. As soon as a MOF begins to be considered as potentially applicable, it becomes important, in a pre-industrial process, to produce it in a reproducible and short-time way. Here also, and thanks to the effective cooperation developped by the Versailles group with J.-S. Chang and S-H. Jhung [KRICT, Daejeon (Korea)], on microwave techniques for the production of MOFs, sometimes in a continuous flow, is currently unique and could be applied at the industrial scale with profit, independently from new routes of synthesis (electrochemical synthesis, discovered and currently developped by BASF.

For a historical reason , such an European potential is not used enough for the moment, despite the existence of a huge library of new interesting MOFs provided by these groups. Indeed, when scientists interested by characterization began to show interest toward MOFs, they were attracted by a famous one (MOF-5), which combined a simple structure with large porosities. They were not aware of the difficulty and the weak reproducibility of the synthesis in its original recipe and spent a lot of time to reproduce it. Moreover, its performances are not exceptional compared to those of some solids discovered in the above groups. The creation of a network would incite its members to focus on them, to bring their expertise to the possibilities of application of these MOFs.

An exceptional structural expertise and environment :

In parallel with their synthesis activity, the three sites cited above have developped an exceptional expertise for the structural determination of solids (not only MOFs).

As soon as one gets single crystals, this determination is now pure routine. However, the increasing structural complexity of MOFs makes that it becomes more and more difficult to get single crystals (It is the same problem as that encountered for proteins). Just powders are obtained, and reach the structure from X-ray (or neutrons) powder data is always a very difficult task that only a few groups in the world are able to accomplish properly. The three groups (Liverpool, St-Andrews and Versailles) belong to this group of experts. It must be clear for the project that the challenge is not only to solve the structures. It is just a step of the global approach I mentioned before. The challenge is to increase the number of known structures, sufficiently interesting by themselves to expect interesting properties and applications, and consequently to augment the palette of possible solids interesting for further developments. And what is the present status ? Due to their lack of expertise in *ab initio* structure determinations, more and more chemists who look at new chemical systems, obtain only powders (I am sure that the drawers of their desks contain an increasing number of these unusable powders) and therefore are obliged to stop their investigations. It is a pity for such a strategic field. This also means that the creation of the network would afford to other groups, which have the problems noted above, to have access to these three sites for overcoming these limits.

Beyond the structures themselves, the groups developped expertise in thermodiffractometry, an *in situ* technique which allows in addition to know not only the thermal behaviour and the phase transitions of the solids (up to their collapse), but also their behaviour under the action of external stimulii.

It is worthy to note that these three groups are familiar with the use of Very Large Facilities since a long time, and have regular accesses to them in several places [Daresbury and the future 'Diamond' equipment in UK, ESRF, Soleil (X-ray synchrotron radiation) and ILL (Institut Laüe-Langevin for neutrons) in France]. If one adds the increasing contribution of computer simulation for the prediction of structures (initially developped in Versailles), this means that the whole network could benefit of this sometimes unique knowledge.

An old habit of demand in the characterization of the porosities.

This aspect was well developped since a long time by the teams dedicating their research to zeolites and porous inorganic solids. For MOFs, it is of course rather new, but the main teams which had expertise in the measurements on these 'old' solids have understood the interest of MOFs in this area and now, participate more and more to this aspect. This a nice example of what cooperation already provides in this field.

At variance to other groups in the world which are satisfied by just providing adsorption isotherms, the colleagues involved in the project are thermodynamicians, as interested by the isotherms as by the thermodynamics of adsorption including measurements of the heats of adsorption, entropy effects… in relation with the knowledge of the host-guets interactions. In connection with the above structuralists, they begin to complement their approach with the identification of the adsorption sites (X-rays, IR), an essential structural information which, in conjunction with the binding energies, provides useful informations for possible chemical substitutions more convenient for the searched application (increased storage or separation and/or easier delivery). Computer simulation, described later, also helps them.

The participants of the workshop are already numerous and active and devote their activity according to three topics :

• H_2 storage : M. Latroche [Thiais(France)] and M. Hirscher [Stuttgart (Germany)] are among the recognized leaders in this strategic field. They already develop bilateral cooperation with basic (Versailles) or applied research (BASF, Renault, Peugeot…) ;

• greenhouse gases, with a particular emphasis on CH_4, carbon oxides, NO_x, H_2S. On this point, both in France and UK, an efficient subnetwork already exists, working on all the aspects evoked above. In France, for instance, it gathers the groups of Versailles, Marseille and Mons (Belgium) with a lot of joint publications in the very good journals (Angew. Chem, JACS…) ;

• liquids and vapors. There, two groups [Montpellier (alkanes) and Leuven (branched aromatics)] which are among the pionneers when MOFs are concerned.

Pionneers in computer modelling in MOFs

Computer modelling is a young science. Its initiators were J.M. Thomas and R. Catlow [Royal Institution, UK] who paved the way and showed the extraordinary power of this approach for the knowledge, the description and the prediction of properties and structural characteristics of solids. The main applications of this tool mainly concerned catalysis in zeolites and MCM and the knowledge of nucleation and growth processes in solids.

The community begins to understand the importance of the contribution of this tool and the (young) experts in this field (beside Snurr in USA and Zhong in China) were invited to the workshop. They belong to four centers : Edinburgh (T. Düren), London (R. Bell and C. Mellot (on leave of Versailles)), Montpellier (G. Maurin) and Versailles (C. Mellot) (alphabetic order). Only G. Maurin did not participate to the meeting, only because of the limited number of French hosts imposed by ESF.

All of them already cooperate in an informal way with the 'chemists' of the future network (St-Andrews, Versailles) with joint publications on MOFs. They are mainly interested by the simulation of gases (H_2, CH_4, carbon oxides, NO_x, H_2S) adsorption phenomena and their principal current work is already to establish valuable force fields for the bonds (framework and host –guest interactions). The first results are already available and give excellent agreements with experience.

The other aspect of modelling concerns the prediction of structures, already evoked above. In order to increase the tunability of the MOFs, a special effort is being made on the evolution of given structures with the functionalization of the organic linkers by reactive or attractive groups (halides, amino- or nitro groups…) which can have a drastic influence on the geometry and on the reactivity of the pores, and therefore, on the related properties of catalysis and adsorption. This aspect is increasingly important for the development of MOFs.

Pionneers in the new properties of MOFs

<u>*Physical properties*</u>. Beside the 'classical' properties of porous solids described above, recent breakthroughs occurred, due to the discovery in Versailles (as soon as 1997) of the possibility, playing on temperature to modulate the dimensionnality of the inorganic subnetwork in MOFs. As a consequence, MOFs with inorganic dimensionalities $\geq$ 1D can exhibit the same types of physical properties as those encountered in dense solids (magnetism, conduction, optical properties…). It was proved last year by the Versailles group for all of them. Compared to many other porous solids, this represents a specificity of MOFs which must be strengthened and amplified by other groups of the future network.

The first domain to develop is magnetism which explains the presence of three international experts (E. Coronado, M. Drillon, J. Veciana) ready to invest in magnetic MOFs, playing either on the framework (Drillon), on the magnetic ligand (J. Veciana) and even on magnetic species inserted within the pores (Coronado). This interest has another advantage compared to the classical chemistry $\wedge$properties approach. The expertise of these scientists in the field of magnetism can lead them to propose to chemists, with their deep knowledge of magnetic phenomena and their applications, suggestions for new systems, new choices of cations, new ligands… for improvements in the magnetic properties. This top-down approach will be beneficial to the domain of MOFs.

The two other fields are more emerging. They have been validated by some of the participants but need to be developped by introducing new partners from physical sciences in the future network, including electrochemists familiar with the problems of energy (fuel cells, batteries…) and colleagues from optical properties, in particular in the domains of luminescence, NLO, and antenna effects (energy transfer from the ligand to the inorganic, useful for UV sensors and associated devices).

Drug storage and delivery. This was also evidenced last year in Versailles and the exceptional properties of crystallized mesoporous MOFs for both storage and delivery make this aspect very important for the future because it implies biologists and the associated companies, not yet implied in the present project of network, but who have already declared their interest for deep cooperations and future actions.

Last but not least : the effective industrial implication of BASF.

With such an attitude, the strategic character of MOFs has not to be proved anymore…

DEFINITION OF A STRATEGY FOR THE DEVELOPMENT OF MOFs.

The first point consists to say that all the participants are convinced that an official support of Europe is needed in this domain first ***for economic reasons***. The leadership of Europe is clear, alimented by both a deep academic knowledge with identified European experts and by the strategic decision of an European company to be at the forefront of a field which already has clear consequences on the current societal problems which concern energy, sustainable development and health. Being the first opens new markets…

Scientific contribution.

The developped assets prove that there is a potential of European scientists at the forefront of the domain, covering the majority of the aspects and a real desire to drastically improve the cooperations within the participants of the workshop. This is the positive point but a strategy requires to define not only the forces but also the current weaknesses, which can transform, if well identified, into an increased power. Here, weakness means that some points of economical importance have not been exposed here (the limited number of participants is one of the explanations of this current weakness).

Beside the items already evoked (conductive and optical MOFs, bioMOFs) whose weakness is inherent to their youth, but for which strengthening is potentially available with identified partners, the main weak point concerns **catalysis**, which is a gold mine for inorganic porous solids. Paradoxically, whereas the potential of MOFs seems to be immense for this domain of applications, only a few recent studies refer to this property, but every time, prove the superiority of MOFs, at least when low temperatures (< 350°C) are concerned. It is probably this limitation which makes that the experts in catalysis, used to work at high temperatures, are for the moment reluctant for a deep investment in MOFs. Therefore, one of the main problems will be to convince outstanding leaders of catalytic phenomena (and they exist in Europe, and some are friends !) to invest a part of their activity with MOFs. As the most interesting MOFs can be provided to the colleagues on request or on recommandation, this would facilitate their involvement in the field, and therefore better cover the facets of development of MOFs.

Such a network will imply changes in the mentality of the participants, even if it is on the way for those who already have practice of networks. At variance to the old days when a laboratory tried to do most things by itself for a recognition of its competitivity, networks imply more ecumenism and less ego, but the result is accelerated and more complete science. At a period when competition between continents is more and more effective, competitivity passes through high quality works provided by association of experts, and not experts alone. For the domain of MOFs, such a new mentality is already present, with effective cooperations giving rise to joint papers and exchange of students, as proved by the map of the currently known collaborations within the participants to the workshop.

The nucleation of the network, provided by this ESF exploratory workshop, has also been considered by all the participants, as essential. They all ask for a continuation of such limited meetings, where the main leaders of the different aspects discuss during a few days, which could be considered as the '*think tank*' of the domain, with a variable geometry in order to fit with actuality and even propose new breakthroughs. The periodicity could be 18 months. Our Asian colleagues were very fond of this idea, and even proposed to organize it the next time.

Improved scientific information.

As the domain of MOFs becomes increasingly important, it is vital to attract more and more scientists on this topics. This implies mediatization toward the relevant ministeries and national agencies, the creation of international scientific meetings for experts, but also the organization of summer schools for young students and PhD.

Since the end of the workshop, some of us have worked in this way and the first results are the following :
• organization under the auspices of DECHEMA of MOF 2008, the first International Meeting on Metal-Organic Frameworks and other open frameworks. (Augsburg (Germany) October 8-10th 2008)
• organization of a summer school for young researchers, favourably considered by CERC3, under the auspices of CNRS and possibly DFG.
• creation of a 'Priority Program' concerning MOFs by DFG. A similar action is asked to CNRS, but these actions remain national whereas there is an urgent need of European cooperation.

What structure ?

This is the crucial point and, as most of the participants are not familiar with the European possibilities, there is not a clear tendency in the replies, except on the point of administration. The best structure would be that which requires the minimum of time devoted to administrative tasks and reports, a time-consuming work which penalizes the scientific activity and decreases the time devoted to scientific actions. Some suggest several limited actions (7-8 laboratories involved). Other would incline toward an organization including all the participants, but the lack of pertinent information made that no decision was extracted, and it is suggested that, after the drafting of this report and its communication to ESF, I meet the director of the ESF organization in Strasbourg for a discussion with her and look at the most efficient possibilities.

GENERAL CONCLUSION

It is clear that this ESF Exploratory Workshop, which gathered the best European experts in the field of MOFs, was a great success. It revealed first that the European experts (academic and industrial as well) are currently the leaders of the field and that their potential covers the majority of the domains implied by the originality of MOFs. Owing to these multiple expertises, there is an an urgent need for the structuration of this activity at the European level and the ***creation of an European Network***.

The different contributions given during the workshop gave first an overview of all the potentialities of MOFs, potentialities which were not known by all the participants. This was the first positive consequence of the workshop. From these contributions, it became possible to extract what are ***the assets*** on which the participants can play for asking the creation of an European Network. The capital interest and investment of an European industry is a major reason of this requirement.

Beside the assets, ***new developments*** for the future were examined, looking at the forces and at the current weaknesses (with their analysis) of the project, at the ways of ***promotion of the domain*** at different levels and at the ***current actions*** for doing this. Finally, the choice of the appropriate network structure for the best results will be discussed with ESF.

Versailles, June 16th 2007.

Prof. Gérard FEREY, *Convenor*

PROGRAMME

Wednesday 25 April 2007

16.00-20.00 *Registration / Welcome party*

20.00 *Dinner*

Thursday 26 April 2007

09.00-09.45 **Introduction**

09.00-09.30 **G. Férey** - *Hybrid solids*

09.30-09.45 **Presentation of the European Science Foundation (ESF)**
G. Férey

09.45-10.30 **Plenary Lecture**

S. Kitagawa - *Chemistry of coordination space towards new porous materials*

10.30-11.00 *Break*

11.00-12.00 **Synthesis: New Solids**

P. Wright- *Metal phosphonate MOFs: microporosity and functionality*

M. Rosseinsky - *Selective chiral sorption and reactivity within metal-organic frameworks*

12.30-13.00 **Other properties**

T. Bein - *Growth of oriented metalorganic frameworks on self-assembled monolayers*

13.00-15.00 *Lunch*

15.00-16.30 **Synthesis: New Methods**

R. Morris - *The ionothermal synthesis of zeolites and metal organic frameworks*

N. Stock - *High-troughput methods in the synthesis of inorganic-organic hybrid compounds*

S. H. Jhung - *Microwave syntheses of nanoporous materials: phase selectivity, morphology control and rapid syntheses*

16.30-17.00 *Break*

17.00-18.00 **Synthesis: in-situ studies**

R. Walton - *Understanding the hydrothermal crystallisation of nanoporous materials*

M. Daturi - *Infrared spectroscopy: a powerful methodology for porous materials investigation*

18.00-19.00 **Structural aspects**

O. Lebedev - *Crystallized frameworks with giant pores: what kind of information can we expect from advanced TEM?*

C. Mellot-Draznieks - *Statistical thermodynamical methods and their applications*

20.00 *Dinner*

Friday 27 April 2007

09.15-10.00 **Plenary Lecture**

C. Sanchez - *Functional nano-structured inorganic hybrid materials*

10.00-10.30 *Break*

10.30-12.30 **Adsorption of gases**

P. Llewellyn - *Understanding adsorption phenomena in metal organic framework type materials: example of greenhouse gases*

M. Hirscher - *Hydrogen storage in metal-organic frameworks*

M. Latroche - *Combining ad- and absorption in highly porous composite materials, a solution for hydrogen storage*

G. De Weireld - *High pressure and high temperature adsorption isotherms of CO_2, CH_4 and H_2S on activated carbon, zeolite and metal organic frameworks*

15.00-16.30 **Adsorption of liquids / Dynamics / Simulation**

D. Devos - *Separation of liquid hydrocarbon mixtures on MOF materials*

P. Trens- *Adsorption of liquids by metal organic frameworks*

T. Düren - *Towards the rational design of metal-organic frameworks: Using molecular simulations to understand adsorption phenomena in MOFs*

16.30-17.00 *Break*

17.00-19.00 **Physical Properties**

M. Drillon - *How to design organic-inorganic assembling with outstanding magnetic properties?*

J. Veciana - *Magnetic porous materials with purely organic and metal-organic frameworks*

E. Coronado - *Insertion and organization of magnetic molecules and nanomagnets into host materials*

J. Rocha - *Bright new zeolites: photoluminescent lanthanide silicates*

20.00 *Conference Dinner*

Saturday 28 April 2007

09.00-11.30 **Other properties**

J. Cejka - *Advanced hybrid catalysts based on molecular sieves*

J.-S. Chang - *Sorption and catalytic properties of porous hybrid solids*

R. Fischer - *Selective and oriented growth of MOFs at surfaces*

M. Manzano - *Porous materials as drug controlled release systems*

11.00-11.15 *Break*

11.15-11.45 **Industrial aspects**

M. Schubert - *Industrial strategies for the use of MOFs*

11.45-12.45 **Final discussions on possible follow-up activities and / or collaborative actions**

12.45 *Lunch and departure*

PARTICIPANTS

Statistical information on participants

- number of attendees:
29 (including the convenor), plus 4 persons from IL Versailles (organizing committee)
- repartition:
2 women and 27 men; average age 43 year old

age (years)	number of participants
25-30	1
31-35	1
36-40	9
41-45	7
46-50	3
51-55	5
56-60	2

- country of origin:

country	number of participants
Germany	6
Czech republic	1
Korea	2
Japan	1
Spain	3
France	7
Belgium	3
United Kingdom	5
Portugal	1

- scientific speciality:

speciality	number of participants
synthesis and structural characterization	6
adsorption	6
other physical properties	4
computer simulation	2
catalysis	2
thin films	3
spectroscopies	3
bio applications	1
industry	1

List of participants

Gérard Férey (convenor)
Institut Lavoisier, UMR CNRS 8180
Université de Versailles St. Quentin en Yvelines
45, avenue des Etats-Unis
78035 Versailles Cedex, France
Tel: +33 139 254 359
Fax: +33 139 254 379
E-mail: ferey@chimie.uvsq.fr

Thomas Bein
Department of Chemistry and Biochemistry
University of Munich
Butenandtstr. 5-13 (E)
81377 Munich
Germany
Tel:+49-89-2180-77623 or -77621
Fax: +49-89-2180-77622
E-mail: bein@lmu.de

Jiří Čejka
J. Heyrovský Institute of Physical Chemistry
Academy of Sciences of the Czech Republic
Dolejškova 3
CZ-182 23 Prague 8
Czech Republic
Tel : +420-26605-3795
E-mail : jiri.cejka@jh-inst.cas.cz

Jong-San Chang
Catalysis Center for Molecular Engineering
Korea Research Institute of Chemical Technology (KRICT)
P.O. Box 107, Yusung
Daejeon 305-600,
Korea
Tel : +82 42 860 7673
Fax : +82 42 860 7676
E-mail : jschang@krict.re.kr

Eugenio Coronado Miralles
Instituto de Ciencia Molecular
Universidad de Valencia
Polígono de la Coma, s/n
46980 Paterna
Spain
Tel.: +34 96 354 44 15
E-mail :eugenio.coronado@uv.es

Marco Daturi
Laboratoire Catalyse et Spectrochimie
ENSICaen
6, Boulevard Maréchal Juin
14050 CAEN Cedex, France
Tel. +33-2.31.45.27.30
Fax +33-2.31.45.28.22
Marco.Daturi@ensicaen.fr

Luc Alaerts
Centre for Surface Chemistry and Catalysis
Katholieke Universiteit Leuven
Kasteelpark Arenberg 23
3001 Leuven, Belgium
Tel (32) 16 32 1639
Fax (32) 16 32 1998
E-mail : dirk.devos@biw.kuleuven.be

Guy De Weireld
Laboratoire de Thermodynamique,
Faculté Polytechnique de Mons,
7000 Mons, Belgium
E-mail : guy.deweireld@fpms.ac.be

Marc Drillon
Institut de Physique et Chimie
des Matériaux de Strasbourg
23 rue du Loess
67034 Strasbourg, France
Tel : 33 388107131
Marc.Drillon@ipcms.u-strasbg.fr

Tina Düren
Institute for Materials and Processes
School of Engineering and Electronics
University of Edinburgh
King's Buildings
Edinburgh, EH12 3JL
United Kingdom
Tel : +44 131 6504856
E-mail : tina.duren@ed.ac.uk

Roland A. Fischer
Chair of Inorganic Chemistry II,
Organometallics and Materials Chemistry,
Ruhr-University Bochum,
D-44870 Bochum,
Germany
E-mail : roland.fischer@rub.de

Michael Hirscher
Max-Planck-Institut für Metallforschung
Heisenbergstr. 3
70569 Stuttgart
Germany
Tel : +49 711 689 1808
Fax : +49 711 689 1952
E-mail : hirscher@mf.mpg.de

Sung Hwa Jhung
Catalysis Center for Molecular Engineering
Korea Research Institute of Chemical Technology (KRICT)
P.O. Box 107, Yusung
Daejeon 305-600,
Korea
Tel : +82 42 860 7674
Fax : +82 42 860 7676
E-mail : sung@krict.re.kr

Susumu Kitagawa
Department of Synthetic Chemistry and Biological Chemistry
Graduate School of Engineering
Kyoto University
Katsura, Nisikyo-ku, Kyoto 615-8510
Japan
Phone +81-75-383-2733
Fax +81-75-383-2732
E-mail: kitagawa@sbchem.kyoto-u.ac.jp

Michel Latroche
Laboratoire de Chimie Métallurgique des Terres Rares – UPR CNRS 209
2, rue Henri Dunant
94320 Thiais, France
Tel : +33 1 49 78 12 10
Fax : +33 1 49 78 12 03
E-mail : michel.latroche@glvt-cnrs.fr

Oleg Lebedev
EMAT research group,
University of Antwerp,
Groenenborgerlaan 171,
B-2020 Antwerp, Belgium
Email : oleg.lebedev@ua.ac.be,

Philip Llewellyn
MADIREL , UMR6121 CNRS-Université de Provence
Centre de Saint-Jérôme
13397 Marseille Cedex 20
Tel. +33 (0) 491 63 71 16
Fax +33 (0) 491 63 71 11
E-mail : pllew@up.univ-mrs.fr

Miguel Manzano
Departamento de Química Inorgánica y Bioinorgánica,
Facultad de Farmacia de la UCM
Plaza Ramón y Cajal s/n.
28040 Madrid
Spain
Tel: 91 3941861
Fax: 91 3941786
E-mail: manzano@farm.ucm.es

Caroline Mellot
The Royal Institution of Great Britain,
Davy Faraday Research Laboratory,
21 Albermarle street, London,
United Kingdom,
Tel: 00 44 (0) 207 679 0050
E-mail : caroline@ri.ac.uk,

Russell Morris
EaStCHEM School of Chemistry
University of St Andrews
Purdie Building
St Andrews KY16 9ST
UK
Tel : +44 1334 463804
Fax : +44 1334 463808
E-mail : rem1@st-and.ac.uk

João Rocha
Department of Chemistry, CICECO
University of Aveiro
3810-193 Aveiro, Portugal
Tel : +351 234 370 730
Fax : +351 234 370 084
E-mail : rocha@dq.ua.pt

Matthew J. Rosseinsky
Department of Chemistry
University of Liverpool
Liverpool, L69 7ZD
United Kingdom
Tel : +44 151 794 3499
E-mail : m.j.rosseinsky@liv.ac.uk

Clément Sanchez
Laboratoire de Chimie de la Matière Condensée (CNRS/UPMC UMR 7574)
4, place Jussieu 75252 Paris cedex 05
tél. (33) 01.44.27.55.34
E-mail : clems@ccr.jussieu.fr

Markus M. Schubert
Catalysis Research - Zeolite Catalysis
BASF Aktiengesellschaft, GCC/PZ, M301
67056 Ludwigshafen
Germany
Tel : +49 621 60 56190
E-mail : markus.schubert@basf.com

Norbert Stock
Christian-Albrechts-Universität zu Kiel
Institut für Anorganische Chemie
Otto-Hahn-Platz 6/7
24118 Kiel
Germany
Tel : +49 431 880 1675
Fax : +49 431 880 1675
E-mail : stock@ac.uni-kiel.de

Philippe Trens
Laboratoire des Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618
8, rue de l'Ecole Normale
34296 Montpellier cedex 5, France
Tel: +33 4 67 16 34 84
E-mail : ptrens@enscm.fr

Jaume Veciana
Institut de Ciencia de Materials de Barcelona (CSIC)
Campus de la UAB, Bellaterra
E-08193 Cerdanyola
Spain
Tel : +34 93 580 1853
E-mail : vecianaj@icmab.es

Richard Walton
Department of Chemistry
university of Warwick
Gibbet Hill Road
Coventry
CV4 7AL
tel: +44 24 76 52 32 41
fax: +44 24 76 52 41 12
r.i.walton@warwick.ac.uk,

Paul Wright
School of Chemistry, University of St. Andrews
St. Andrews, Fife, KY16 9ST, UK
Tel : +44 1 33 44 46 37 93
Fax : +44 1 33 44 46 38 08
E-mail : paw2@st-andrews.ac.