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Some recent developments of polysilsesquioxanes chemistry for material science

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Contents

Abstract

This review is focused on a new class of materials, the Monophasic Organic–Inorganic Hybrid Materials (MOIHM). These solids correspond to a unique phase prepared from a molecular precursor using the hydrolytic polycondensation which is used in the sol-gel preparation of oxides from alkoxides precursors. In these materials, the oxide matrix is elaborated around the organic moiety, and covalent bonds (mainly SiC bonds) link together the oxide matrix and the organic part. These solids are metastable solids of which their formation is kinetically controlled: all parameters able to modify the kinetics of the hydrolysis polycondensation process are of importance for both the physical and chemical properties of

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the solids. The organic moieties are also a main factor in both the short range organisation and the texture of the solid: weak interactions are able to control the solid formation and a substructure between the organic units can be evidenced in the case of thienyl units from polymerisation in the solid state. These materials are also a convenient way for the introduction of physical properties in the oxide matrix.

Keywords: Kinetic control of solids; Weak interactions; Short range organisation of organic units; Monophasic Organic Inorganic Hybrid Materials

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1. Introduction

The preparation of materials was based on high temperature chemistry for both monocomponent or multicomponent systems, the most thermodynamically stable products being obtained by these methods. They involve the interdiffusion of the reactants and the nucleation of crystalline intermediates which are not yet well understood [1–3]. In contrast to solid-state chemistry, synthetic molecular chemistry (organic and inorganic) is based on the kinetic control of the reaction pathway due to a good knowledge of the details of the reaction mechanism which permits an understanding of cause and effect relationships between synthetic parameters and products distribution. Thus, elaboration of solid materials is now a wide field of investigation for inorganic chemistry. The molecular chemistry succeeded in binding together most of the elements to build up very sophisticated structures and very powerful synthetic tools have been developed allowing both the preparation of very complicated natural organic architectures (vitamin B12 [4] or palytoxin [5,6] for instance) and also the elaboration of purely inorganic materials from the molecular level, like the preparation of silicon carbide fibers [7,8]. Nowadays many possibilities are open for building up solids using the tools of molecular chemistry. The organic–inorganic hybrid solids are of particular interest in this perspective. They are of two types depending on their method of elaboration: (1) the biphasic ones which are sometimes called bi-component are prepared simply by mixing organic molecules or polymers with an inorganic component. The organic units are trapped within the oxide gel network and only weak interactions, such as Van der Waals or hydrogen bonding govern the distribution of organic and inorganic components. In most cases, the organic 'dopant' can be removed by simply washing of the solid; and (2) the monophasic ones in which both organic and inorganic units are bound through strong covalent chemical bonds. This kind of material is obtained by elaboration of the inorganic matrix around an organic unit which is sometimes poorly called 'organic spacer or organic bridge'. The organic moiety and the inorganic matrix are covalently bound together and the 'organic spacer' is the most interesting part of the solid since it affords the expected physical property and since the elaboration of the material is at least in part controlled by the nature of the organic moiety. These solids correspond to an unique phase following Gibbs and could be also called 'monocomponent' by opposition to the bicomponent ones.

This short review will point out some of the aspects of the properties of these very exciting solids, the monophasic organic–inorganic hybrid materials.

2. Scope and limitations

2.1. Synthesis

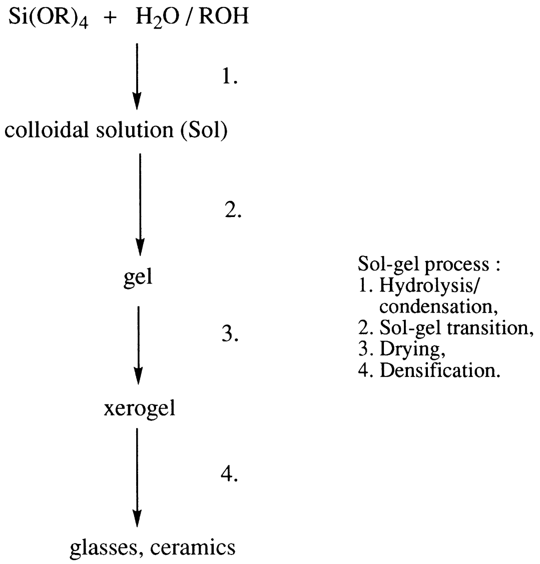
The synthesis of the monophasic organic–inorganic hybrid materials (MOIHM) is performed via the sol-gel processing techniques [9–25] which are based on the hydrolytic polycondensation of metal alkoxides. This reaction corresponds to nucleophilic attack of H_2O at the metal giving metal hydroxide groups. In succeeding steps, the metal hydroxide groups react either with alkoxide (hetero-condensation) or with hydroxide groups (homocondensation) giving rise to the M–O–M bridges.The reactions can be catalyzed by acids, bases or nucleophiles, such as F^- [26,27]. The oxide obtained is a highly crosslinked solid which is formed in a 1-pot procedure by an inorganic polymerisation reaction.

The case of SiO_2 has been extensively studied and can be taken as an example. Hydrolysis of a solution of alkoxysilane in an organic solvent, such as alcohol gives products with silanol functions, which form a sol (a colloidal dispersion of particles in a liquid) by condensation polymerisation (Scheme 1) [26–35]. The continuation of the process leads to a gel (continuous solid skeleton enclosing a continuous liquid phase). This transformation is designated the sol-gel transition. Gels may exhibit spontaneous shrinkage, called syneresis, or ageing. The network is initially supple and allows further condensations, and bond formation induces contraction of the network and expulsion of liquid from the pores. Drying of the gel by evaporation under normal conditions gives a dried gel, called a xerogel. Xerogels are interesting materials because of their porosity and high surface area, which make them useful as catalyst substrates, filters, etc. They are also useful in the preparation of dense ceramics by sintering (densification driven by interfacial energy) [26–35]. The advantage of the molecular approach to the synthesis of materials is based on the fact that the precursors can be obtained in the form of monoliths, films, fibres, and monosized powders directly from the gel state.

By extention of this general method it is possible to obtain the MOIH solids starting from precursors in which the organic unit is covalently bound to $Si(X)_3$ groups through Si–C bonds [18–25,36–57], as illustrated in Scheme 2.

2.2. Why $Si(X)_3$ groups?

The aim of the work is the preparation of monophasic materials formed by an inorganic matrix built up around a selected organic unit. The most simple way is the elaboration of an oxide matrix starting from a molecular precursor containing stable metal–carbon bonds. These bonds must be stable enough for surviving hydrolytic sol-gel conditions, oxidation in the air and the temperature of drying.

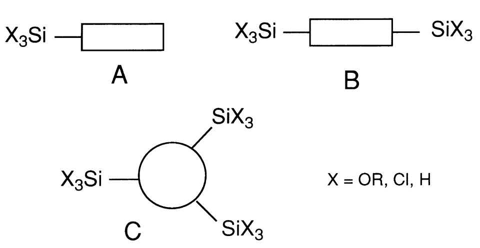


Scheme 1. Sol-gel process.

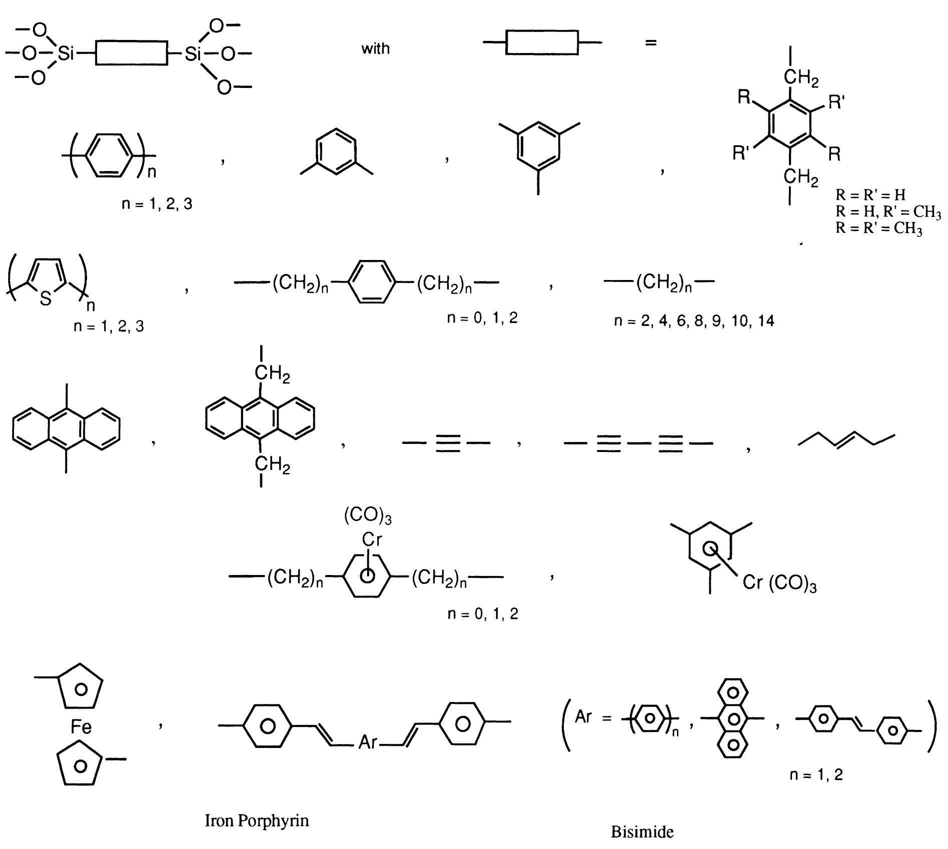
The number of metals which allow the conservation of the covalent metal–carbon bonds is limited. For instance the elements Si, P, Ge, As, Sn open possibilities, whereas transition metal and group III elements cannot be used. However, silicon is the most convenient element for many reasons: (1) silicon chemistry is well known, affording methods for the introduction of $Si(X)_3$ groups into most of the organic molecules [58]; (2) the identification of compounds is well established; and (3) the aptitude to the formation of oxide matrices is very wide permitting an easy access to materials.

Moreover many leaving groups at silicon can be used for polycondensation. In most cases, the gels were obtained by hydrolysis of $Si(OR)_3$ (R = Me, Et); SiH_3 groups [37,51] and $SiCl_3$ groups [56] have also been employed. However, $Si\text{-}NR_2$ and Si-SR could also be potentially used.

In this review, we will limit our presentation mainly to MOIH solids obtained



Scheme 2. Precursors for MOIHM.



Scheme 3. Organic spacers in MOIHM.

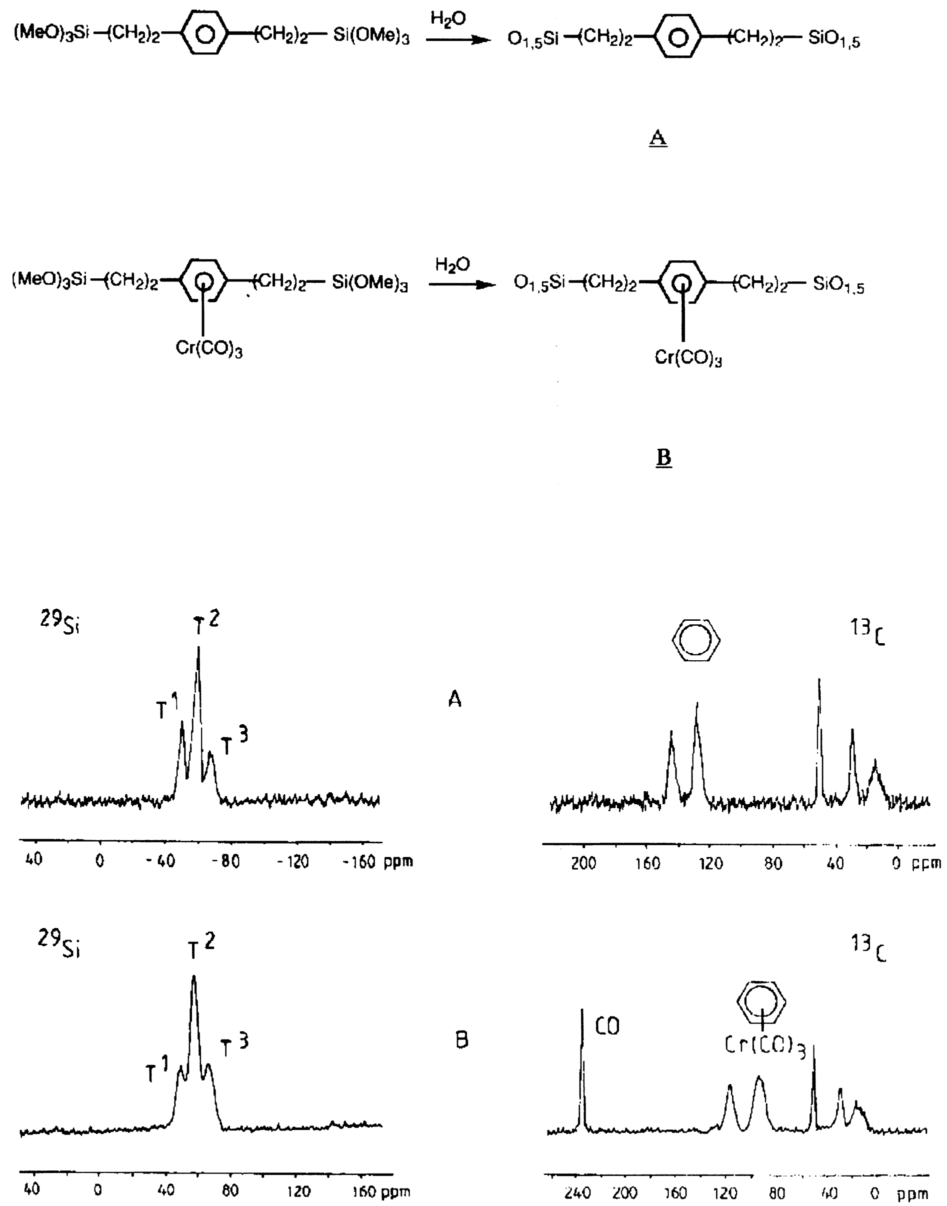
from bis-silylated precursors. In Scheme 3 most of the organic spacers studied until now are reported.

2.3. *Characterisation methods*

Two kinds of techniques permit the identification of the material. The macroscopic ones describe the texture of the solid: specific surface area, porosity, granulometry, density, etc. [59–61]. Some methods derived from X-ray scattering permit the study of the solid in terms of fractality. [13,29,62].

In contrast, some spectroscopic methods, solid state NMR, IR, UV etc., provide excellent tools for the study of the organic moiety included in the material and for obtaining information about the polycondensation around silicon and about the presence of Si–C bonds in the solid [63–67].

One illustrative example can be given in the characterisation of the obtained solids A and B, respectively, before and after complexation of aromatic rings by Cr $(CO)_3$ as shown on Scheme 4 [47,48,51,52]. Thanks to ^{13}C solid state NMR it is



Scheme 4. Examples of characterisation of MOIHM by ^{13}C and ^{29}Si CP MAS NMR spectroscopy.

possible to check that the organic structure is retained in the solid without cleavage of the Si–C bond. The cleavage of Si–C bond should be easily detected by ^{29}Si NMR: in this case, the formation of Q units corresponding to silica should be observed in the range −100 to −110 ppm [63]. Futhermore ^{29}Si NMR can provide an estimation of the degree of polycondensation around the silicon atom (T units) [15,19,64–67].

In all the cases studied until now it was observed that the organic units and the Si–C bonds remain unchanged from the molecular precursor to the solid.

2.4. Dilution of organic units in the solid

It is interesting to note that it is possible to perform co-hydrolysis and co-condensation of organotrialkoxysilanes with tetraalkoxysilane according to the following reaction:

$$n[\mathrm{RSi(O\,R')_3} + x\,\mathrm{Si(O\,R')_4}] \overset{\mathrm{H_2O}}{\rightarrow} \rightarrow [\mathrm{RSiO_{1,5}};x\,\mathrm{SiO_2}]_n$$

With increasing x, the hybrid materials become ‘more inorganic’, this corresponds to a ‘dilution’ of the organic units in the solid. Such mixtures can be employed in order to adjust the physical properties of both organic and inorganic components [38,39]. However, until now there are no available data concerning the homogeneity of these solids and the distribution of the organic units in the material.

3. Texture of the solids

3.1. Kinetically controlled solids

As already observed in the sol-gel field, all parameters used for the elaboration of the solid are of great importance. A small change in the experimental conditions can lead to a completely different kind of material. The texture of the solids includes the sum of the macroscopic parameters which allow their identification, such as the density, the specific surface area, the pore volume and pore diameter, the hydrophylicity, the porosity and even the physical appearance. This texture (specific surface area and porosity for instance) is highly dependent on the experimental conditions used during the polycondensation reaction: nature of the catalyst, nature of the solvent, concentration of the reagents, temperature, etc. These observations are also valid in the case of the MOIH solids, adding the fact that the nature of both the organic unit and the leaving group Si–X are also very important parameters. In other words, the macroscopic properties of these solids cannot be predicted. *However, all the experiments are reproducible if the experimental procedure is strictly controlled leading to a solid with the same texture.*

All these facts are easily understood if we consider these solids *as kinetically controlled solids*. The polycondensation reaction is highly dependent on the kinetics of all the chemical steps involved: hydrolytic cleavage of Si–OR, condensation with formation of Si–O–Si bonds and also all the following steps which are involved in the transformation of the molecular precursor into the cross-linked solid.

Table 1 demonstrates clearly that the specific surface area of the solids obtained from the same precursor is highly sensitive to the solvent, the catalyst and the concentration of both the precursor and the catalyst [36,51,68].

This table shows also how much the nature of the organic spacer is an important parameter in the control of the formation of the solid. This point will be discussed in more detail in Section 6.

3.2. Weak interactions

The influence on the structure of the solid formed during the gelation process due to weak interactions between the organic units is illustrated by the possible inclusion of charge transfer complexes formed between bis-silylated terthiophenes and 7,7,8,8-tetracyanoquinodimethane (TCNQ) in the gels [41–44]. As shown in Scheme 5 SRC, these complexes have been included in the gel upon hydrolysis of a charge transfer complex precursor **B**. These complexes remain unchanged in the solid **C** obtained after gelation as shown by light absorption and by conductivity measurements. Interestingly, washing with ether-acetone mixture leads to the destruction of the charge transfer complex evidenced by the disappearance of both conductivity and visible absorption. This experiment shows that, although this interaction is weak, it is strong enough for controlling the structure of the amorphous solid, and also however, weak enough since simply washing permits its elimination [41–44].

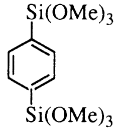
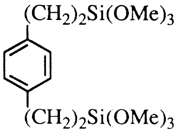
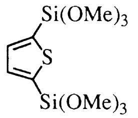
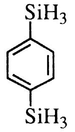
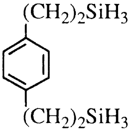
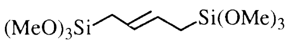
It is interesting to compare solids **D** and **D**′. The solid **D**′ is obtained by direct co-condensation of **A** with $Si(OMe)_4$ in the same experimental conditions. These two solids exhibit the same microscopic data (IR, ^{13}C and ^{29}Si NMR spectra) and very different macroscopic features. For instance the specific surface area observed for **D** is very low (9 m^2g^{-1}) whereas for **D**′ it is high (566 m^2g^{-1}). The charge transfer interactions between **A** and TCNQ modify drastically the kinetic parameters controlling the solid formation and lead to solids with two different arrangements.

4. Short range organisation in the solid

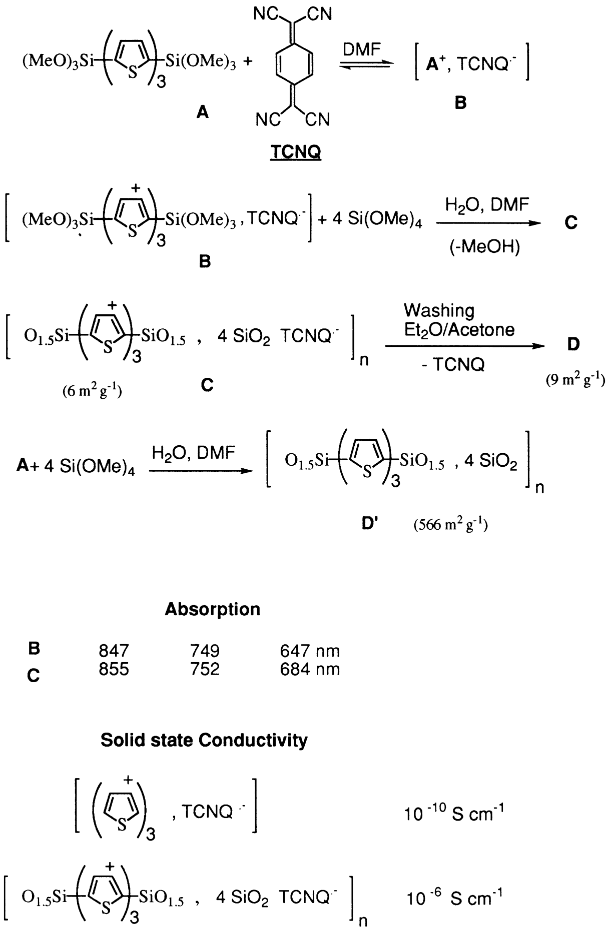
For the detection of possible short range organisation in the solid, thiophene units have been chosen because of the ability of silylated thiophenes for polymerisation by electrochemical oxidation [69,70] leading to polythiophene [71–76]. Gels containing bis-silylated mono- bis-and ter-thiophene have been prepared from the corresponding 2,5-bis (trimethoxysilyl) thiophene precursors [36,37,41–44] (Scheme 3). They were characterised by IR, ^{13}C and ^{29}Si CP MAS NMR spectroscopies which evidence that the molecular structure is maintained in the solid. The electrochemical behaviour of the gels deposited as films on a platinum electrode was studied by cyclic voltammetry. The curves obtained were characteristic of electropolymerisation reactions [41–44].

The polythiophene was identified in the film by spectroscopic techniques [41–44] and the strongest evidence for its formation within the silica matrix (Scheme 6a) came from the analysis of the Raman Resonance Spectra which exhibited diffusion

Table 1
Gelation conditions for various hybrid precursors and specific surface aresas of gels

Entry	Precursors	*c* [a]	Solv.	Catalyst [b]	*t* [c]	S [d]
1		3	MeOH	$NH_4F(10^{-3})$	10^{-1}	1030
2		1	MeOH	$NH_4F(10^{-3})$	10	516
3		1	MeOH	$Bu_4NF(10^{-2})$	4	1050
4		0.5	MeOH	$Bu_4NF(10^{-2})$	160	550
5		1	THF	$NH_4F(10^{-3})$	1	493
6		1	THF	$Bu_4NF(10^{-2})$	4	1240
7		0.5	THF	$Bu_4NF(10^{-2})$	135	370
8		0.5	THF	$NH_4OH(2.6)$	45	1260
9		0.5	THF	$NH_4OH(10^{-2})$	95	380
10		0.5	THF	$HCl(5x10^{-3})$	600	129
11		0.5	MeOH	$HCl(10^{-2})$	95	770
12		0.5	MeOH	$NH_4F(10^{-2})$	45	5
13		1	MeOH	$Bu_4NF(10^{-2})$	10 [e]	< 10
14		0.5	THF	$NH_4F(10^{-2})$	3900	< 10
15		1	THF	$Bu_4NF(10^{-2})$	2	531
16		1	MeOH	$NH_4F(10^{-3})$	15	685
17		1	THF	$NH_4F(10^{-3})$	15	19
18		0.5	THF	$Bu_4NF(10^{-3})$	300	931
19		1	THF	$Bu_4NF(10^{-3})$	0,2 [f]	1200
20		0.5	THF	$(Ph_3P)_3RhCl(10^{-3})$	5160	54
21		1	THF	$(Ph_3P)_3RhCl(10^{-3})$	1380	360
22		0.5	THF	$Bu_4NF(10^{-3})$	35	362
23		1	THF	$Bu_4NF(10^{-3})$	25	494
24		0.5	THF	$(Ph_3P)_3RhCl(10^{-3})$	30	100
25		1	THF	$(Ph_3P)_3RhCl(10^{-3})$	20	518
26		3	MeOH	$NH_4F(10^{-3})$	60	325
27		1	MeOH	$NH_4F(10^{-3})$	$2x10^{4}$	0
28		0.1	MeOH	$NH_4OH(2.6)$	30	977

[a] : concentration [mol L^{-1}]. [b] : Value in parentheses is the concentration of catalyst [mol L^{-1}].
[c] : Gel time (minutes). [d] : Specific Surface Area (m^2g^{-1}). [e] : precipitate. [f] : at -15°C.



Absorption

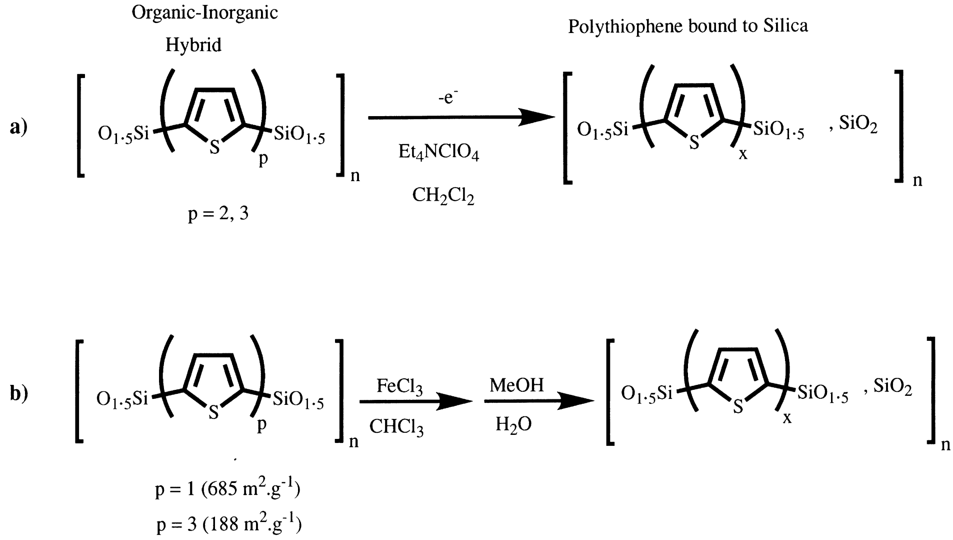
B	847	749	647 nm
C	855	752	684 nm

Scheme 5. Charge transfer complex from terthiophene and TCNQ in a polysiloxane gel.

bands at 652, 682, 700, 1047, 1171, 1220 and 1458 cm^{-1} characteristic of polythiophene. Furthermore the electronic spectra before oxidation showed a band at 420 nm whereas after oxidation a large absorption band at 490 nm was observed (520 nm for regular polythiophene).

The same reaction was possible by chemical oxidation performed on the gel (Scheme 6b). The polymer was identified in the same way. However, in both oxidation experiments it was impossible to separate the polymers obtained from the silica which formed during the polymerisation, although the ^{29}Si solid state NMR shows that most of the Si–C bonds are cleaved into Si–O bonds during the polymerisation (Scheme 7).

This difficulty of separation is easily explained taking into account the fact that the ends of the polymeric chains are always substituted by $SiO_{1,5}$ groups during the reaction and so attached to silica. The oxidative polymerisation of silylated thiophene



Scheme 6. (a) Electropolymerisation of polythiophene gels; and (b) chemical oxidation of polythiophene gels.

in solid phases implies that the thiophene units are close to each other. Thus, the observation of a fast polymerisation inside the gels suggest strongly a partial organisation in the amorphous solid. The thiophene units are more or less aggregated during the gel formation and the oxidation permits the formation of polymeric segments by coupling of proximal thiophene units.

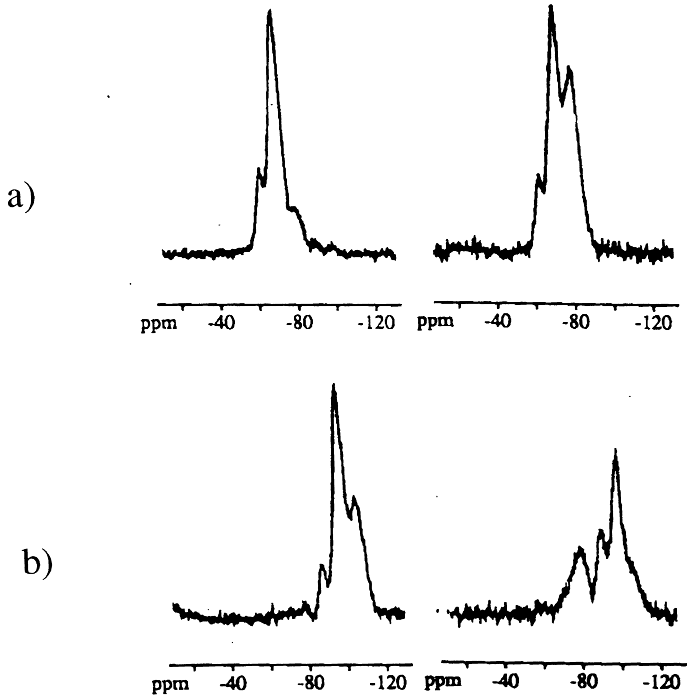
It is known that the polymerisation of thiophene units occurs by coupling two thienyl radicals which implies electronic and steric requirements between the two thienyl units (Scheme 8). Thus, taking into account the restricted mobility in the solid and the fast polymerisation experimentally observed, we can conclude that the polymerisation is possible only because of the existence of an organisation of thienyl groups in the solid.

The case of thiophene units presented here constitutes a good example of the organisation of organic moieties in the solid.

Other illustrations of the existence of a short distance organisation in the hybrid material have been evidenced in the case of acetylenic moieties [49] and in the sol-gel condensation of unsaturated monomers in the presence of Pd (intermolecular interactions due to a template effect) [50].

5. Physical properties induced by the organic moiety

The incorporation of organic units in inorganic materials leads to solids which exhibit the properties of both the organic and inorganic moieties. We can illustrate this in three cases.



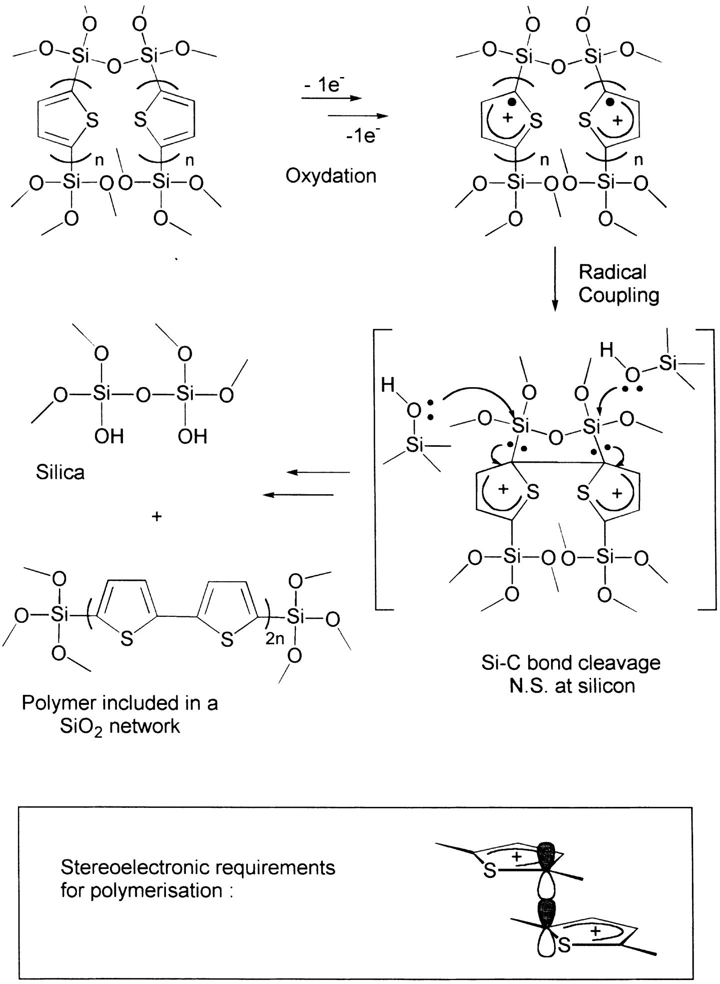
Scheme 7. ^{29}Si CP MAS NMR spectra of mono- and tertiophene gels before and after treatment with $FeCl_3$.

5.1. Electrochemical properties

Gels formed from trimethoxysilylferrocene and 1,1′-bis(trimethoxysilyl) ferrocene copolymerized with tetramethoxysilane and deposited onto platinum allow the building of modified electrodes with interesting electrochemical properties (Scheme 9), [38,39].

The electrochemical response of the gels has been found strongly dependent on the starting molecule and its concentration. Gels B (Scheme 9) obtained from the bis-silylated ferrocene display a Cottrellian diffusion of charge transfer and exhibit classical reversible cyclic voltammograms: the peak current scales linearly with the square root of scan rate [38,39] (Scheme 10). Furthermore it is impossible to perform complete oxidation of Fe^{II} into Fe^{III} in a macroelectrolysis carried out on a suspension of the hybrid solid [77]. These observations can be accounted for by the fact that some ferrocenyl units are embedded in the core of the solid.

In the gels A (Scheme 9) issued from the monosilylated ferrocene, the charge transfer follows a law with a fractionnal exponent (Scheme 11). This unique behaviour is indicative of a particular substructure in the gels. Furthermore in this case, complete and reversible oxidation of Fe^{II} into Fe^{III} is observed in a macroelectrolysis as evidenced by Mössbauer spectroscopy [77].

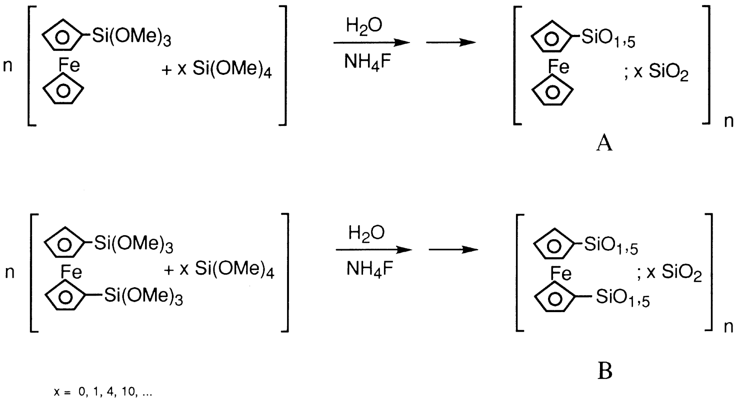


Scheme 8. Electrochemical polymerisation via coupling thienyl radicals.

Considering the high stability of these modified electrodes in aerobic conditions, their use as reference electrodes can be of interest. Such organic–inorganic hybrid gels should potentially develop a new class of modified electrodes which are very stable and with the unique feature of having a very tight bonding of the electroactive moieties to the polymer.

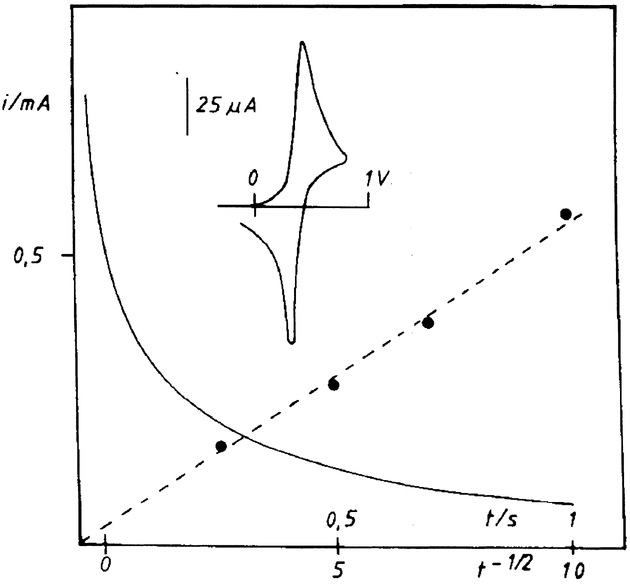
5.2. Optical properties

Gels containing oligo-1,4-phenylenevinylene segments have been easily prepared [53]. They provide a possibility for the inclusion of chromophores into silica frameworks (Scheme 12).

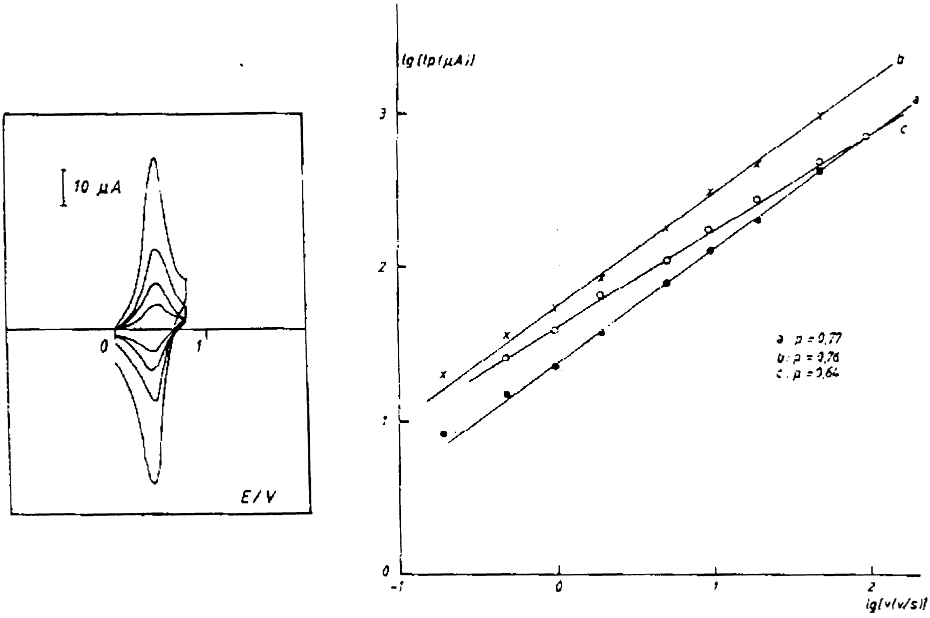


Scheme 9. Hydrolysis-polycondensation of ferrocenyl precursors.

The UV-VIS and fluorescence spectra of the gels exhibit maxima at 495–496 nm, similar to the values of the precursor in the solid state. However, the high energy emission of the precursor at 466 nm is absent (Scheme 13). The optical properties of the chromophores are retained in the solid and afford information about the conformational structure and environment of the silica core. They are suitable materials for optical and electroptical applications.



Scheme 10. Typical chronoamperometric curve and lineary Cottrell curve of a gel prepared from disilylated ferrocene precursor.



Scheme 11. Cyclic voltammogram of a modified electrode coated with a film of cogel issued from trimethoxysilylferrocene and the corresponding Log/Log variation of the peak currents with the scan rate for different concentrations.

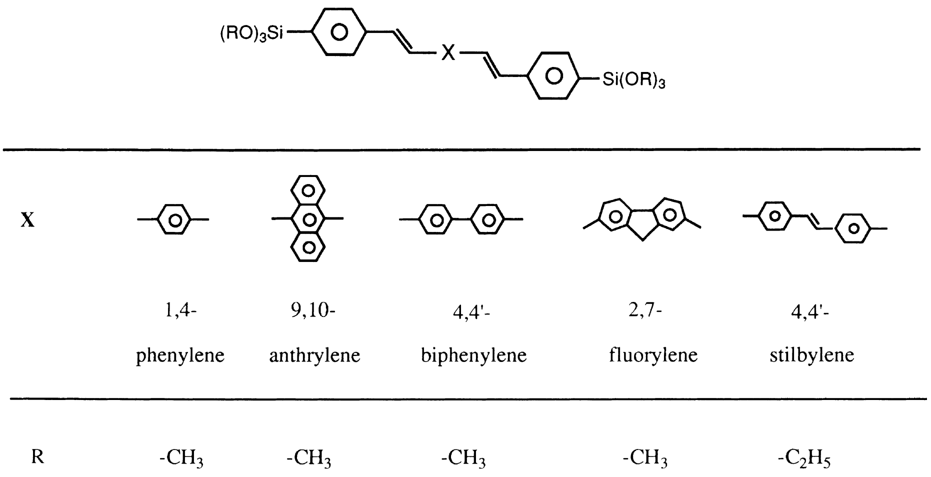
5.3. *Second-order non-linear optic (NLO) properties*

The incorporation of organic molecules in oxide matrices offers new attractive possibilities in the domain of optical information storage and non-linear optics. For example, organic–inorganic films prepared from a functionalised alkoxide in which the optically non-linear disperse Red 1 molecule (DR1) (Scheme 14a) was covalently bound to the inorganic silica network exhibit a large resonant second order susceptibility and an excellent room temperature stability [78].

Another example which illustrates these properties concerns the hybrid organic–inorganic nanocomposites synthesised through hydrolysis and co-condensation between ICTES-Red 17 (Scheme 15b) and tetramethoxysilane. Coatings of these hybrid systems exhibit the highest non-resonant SHG response reported up to now for sol-gel derived NLO materials [79].

6. Location of the organic units

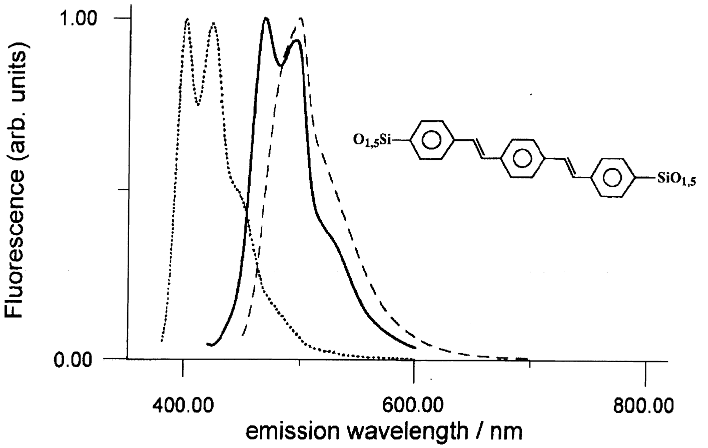
The spectroscopic techniques described in Section 2.3, clearly shows evidence that the Si–C bond is completely maintained during the solid formation. However, it is important to determine the location of the organic moieties. These units can be located at the surface or in the bulk of the solid. The electrochemical behaviour



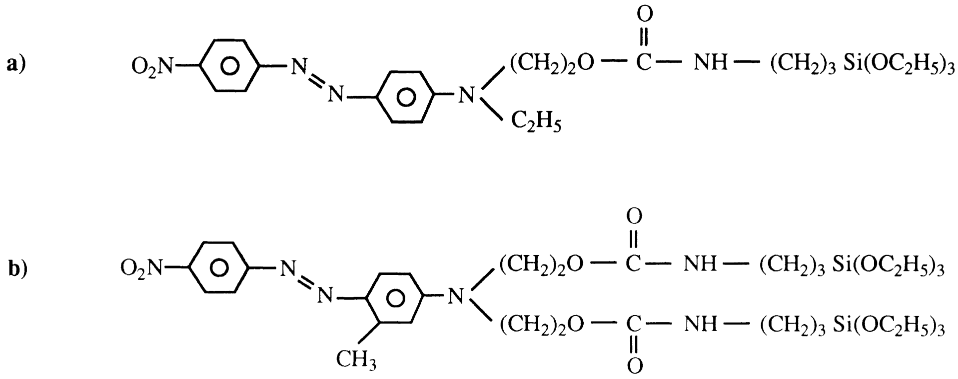
Scheme 12. Oligo-1,4-phenylenevinylene precursors.

[38,39] in the case of ferrocenyl hybrids (Section 5.1), appears to be a reliable tool for determining the location of the organic entities. In the same way the chemical reactivity can also be used. For example in the case of hybrid solids elaborated from paraphenylene organic units (Scheme 15), the rigid precursor ($n=0$) and the flexible one ($n=2$) lead to the same experimental conditions for different solids. When $n=0$, a highly hydrophilic solid is obtained and the aromatic groups are not chemically accessible, the reactivity towards $Cr(CO)_6$ is very poor, whereas when $n=2$, a hydrophobic solid is obtained which reacts with $Cr(CO)_6$ [47].

Recently we have reported that Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is an efficient method for analysing the surface of MOIH materials



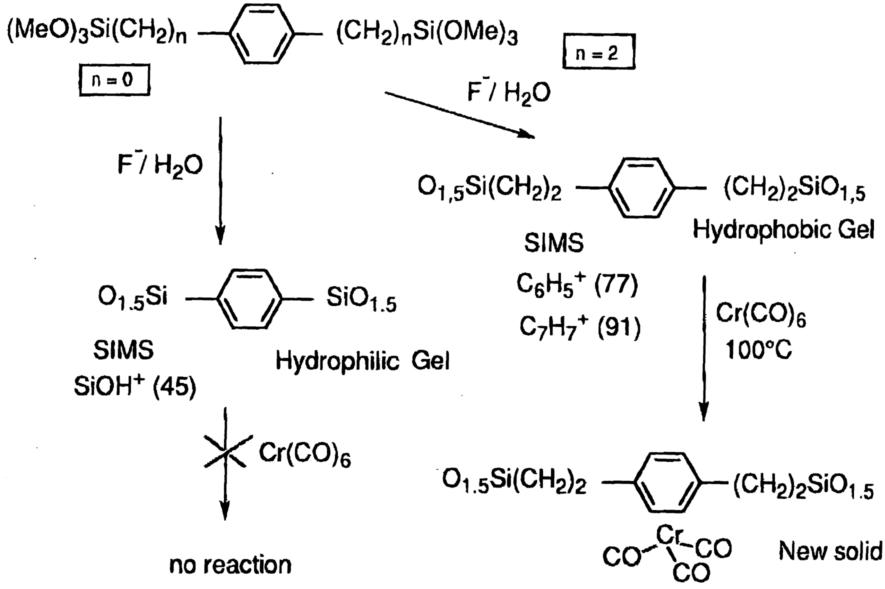
Scheme 13. Photoluminescence spectra of an oligo-1,4-phenylenevinylene precursor in THF (· · ·) and in KBr (———) and the corresponding gel (- - -).



Scheme 14. (a) DR1 molecule covalently grafted on a sol-gel precursor; and (b) semideveloped formula of the ICTES-Red 17 precursor.

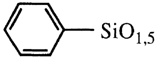
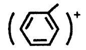
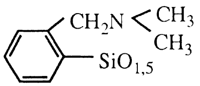
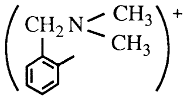
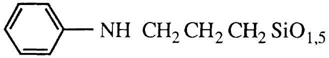
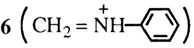
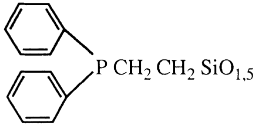
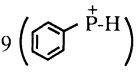
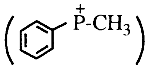
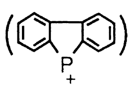
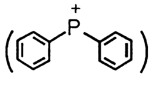
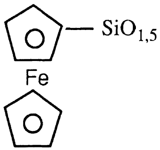
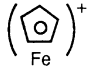
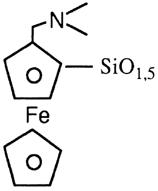
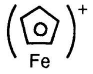
[80]. When the organic precursor contains only one Si–C bond (Scheme 2A) the hydrolysis of the $Si(OR)_3$ groups leads to a cross-linked solid in which most of the organic groups are located at the surface [80] since the main ions detected by SIMS are the fragments which are characteristic of the organic groups in all the cases studied. Table 2 illustrates very well this assumption.

In contrast, when the organic molecule contains at least two Si–C bonds (Scheme 2B and C), the situation is completely different. In this case, the incorporation of the organic spacer inside of the inorganic network is now highly dependent



Scheme 15. Reactions of gels containing bis-silylated paraphenylene groups.

Table 2
Main ions observed in the time of flight-secondary mass spectra of various gels (major fragments are in bold characters

Entry	Hybrid Gel	Ions
1	$CH_3SiO_{1,5}$	**15** $(CH_3)^+$; **43** $(SiCH_3)^+$
2	$ICH_2CH_2CH_2SiO_{1,5}$	**127** $(I)^+$; 141 $(ICH_2)^+$; 155 $(ICH_2CH_2)^+$ (Negative ions : **127** I^- ; **254** I^{2-})
3	$H_2NCH_2CH_2CH_2SiO_{1,5}$	**30** $(CH_2=\overset{+}{N}H_2)$; 44 $(H_2NCH_2CH_2)^+$
4		77 
5		**58** $\left(CH_2=\overset{+}{N}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$; 134 
6		**106** 
7		109  ; 123  ; **183**  ; 185 
8		**56** $(Fe)^+$; 121  [Negative ions : 65 ]
9		56 $(Fe)^+$; **58** $\left(CH_2=\overset{+}{N}\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$; **121** 

on the nature of the spacer (rigid or flexible) [81]. This can be illustrated by two examples: the first one is the case of rigid solids containing paraphenylene organic units reported in Scheme 15. The main ions detected by SIMS are completely different when $n=0$ or $n=2$: only a peak at $m/z=45$ ($SiOH^+$) is detected in the case of the rigid group ($n=0$). This is in agreement with OH groups at the surface (hydrophilicity) and a poor chemical reactivity. In contrast when $n=2$, ions at $m/z=77$ (phenyl) and $m/z=91$ (tropylium) are observed, in agreement with an hydrophobic solid with a high chemical reactivity. That means that with two similar organic spacers, the interactions between the aromatic groups are completely different during the hydrolysis polycondensation process, leading to totally different arrangements of the organic moieties: in the core ($n=0$) and mainly at the surface ($n=2$) (Scheme 15) in good agreement with the chemical reactivity of $Cr(CO)_6$ with paraphenylene derived hybrid gels.

Another noteworthy illustration is the case of ferrocene. The SIMS analysis of hybrid solid formed from 1,1′-bis(trimethoxysilyl) ferrocene reveals no characteristic ions: the ferrocene units are located in the core of the solid whereas for the corresponding monosilylated ferrocene derivatives (Table 2 entries 8 and 9), ions due to ferrocene unit are detected, indicating that the organic groups are mainly located at the surface. These SIMS analysis are in agreement with the electrochemical behaviour of ferrocene hybrid solids (Section 5.1): the cyclic voltammetry of the gels derived from bis-silylated ferrocene shows a classical reversible apparently-diffusive limited pattern, the anodic peak currents scale linearly with the square root of the scan rate [38,39].

7. Conclusion

The results presented here are a short illustration of the wide possibilities opened by this class of solids for the inorganic chemistry. The monophasic organic–inorganic hybrid materials (MOIHM) prepared by the sol-gel route, based on the hydrolytic polycondensation of metal alkoxides, are metastable and kinetically controlled solids. All the parameters able to modify the kinetics of reactions during the polycondensation process control the solid formation and are of importance on the nature and the texture of the hybrid material. The materials obtained exhibit a short range organisation evidenced by the chemical reactivity. Moreover weak interactions between the organic units are able to induce drastic modifications in both the texture and the structure of the solid. The properties of the ‘organic spacer’ are maintained in the solids.

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