CHEMCOMM
Communication
www.rsc.org/chemcomm

A simple route to organic–inorganic hybrid materials containing Eu^{3+} complexes

Robert J. P. Corriu,* Frank Embert, Yannick Guari, Ahmad Mehdi and Catherine Reyé

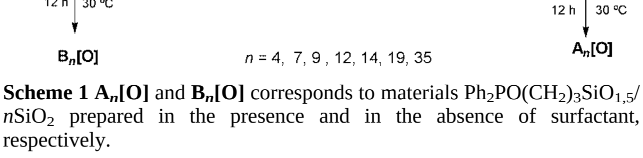
Laboratoire de Chimie Moleculaire et Organisation du Solide, UMR 5637 CNRS, Université de Montpellier II, Sciences et Techniques du Languedoc, Place E. Bataillon, F-34095 Montpellier Cedex 5, France. E-mail: reye@crit.univ-montp2.fr

Received (in Cambridge, UK) 22nd March 2001, Accepted 4th May 2001
First published as an Advance Article on the web 31st May 2001

Direct complexation of europium nitrate into HMS materials containing phosphine oxide groups covalently linked to a silica matrix is accomplished and is shown to work much better than into the corresponding materials prepared in the absence of surfactant.

The study of luminescent materials has been the subject of extensive research in the past decade.[1–3] Of particular interest are rare-earth-ion-based systems which can give rise to a variety of optical applications such as fiber amplifiers and solid-state lasers.[4,5] The sol–gel approach is an attractive means of synthesising these materials since it allows both the control of the devices and a great diversity of chemical composition.[6] Numerous studies have been carried out on nanocomposite hybrid materials prepared by incorporating Eu^{3+} or Tb^{3+} complexes into sol–gel matrices.[7–9] With a view to avoiding the inhomogeneous dispersion of rare-earth complexes within the silica matrix, we have recently studied the hydrolytic polycondensation of isolated europium complexes with phosphine oxides bearing one hydrolysable $Si(OR)_3$ group.[10] We have shown that the Eu^{3+} are well encapsulated within the resulting nanostructured hybrid materials which present highly luminescent properties. We now report a very simple and original route to Eu^{3+} containing hybrid materials. This method consists of the direct incorporation of europium salts into a hybrid organic–inorganic material containing phosphine oxide groups covalently linked to the silica matrix and able to complex Eu^{3+}.[11] This rare-earth ion was selected as a representative rare-earth ion because of its unique fluorescence properties.[12] We show that ordered HMS materials containing phosphine oxide groups prepared by using the direct synthetic approach[13] are much more convenient for the complexation of Eu^{3+} than the corresponding materials prepared in the absence of surfactant. The luminescence behaviour of the materials was considered.

The hybrid materials $\mathbf{A}_{\boldsymbol{n}}$ (Scheme 1) were obtained by co-hydrolysis and polycondensation of a mixture of $Ph_2P(CH_2)_3Si(OMe)_3$[14] and of *n* equiv. of $Si(OEt)_4$ (n = 4, 7, 9, 12, 14, 19 and 35) in the presence of *n*-hexadecylamine as template (route A). The corresponding materials $\mathbf{B}_{\boldsymbol{n}}$ (route B) were prepared in the absence of template but in the presence of 1% TBAF as catalyst [*n* in index for materials $\mathbf{A}_{\boldsymbol{n}}$ and $\mathbf{B}_{\boldsymbol{n}}$ corresponds to the number *n* of equiv. of $Si(OEt)_4$]. The xerogels were prepared according to published procedures.[15] Treatment of the materials $\mathbf{A}_{\boldsymbol{n}}$ and $\mathbf{B}_{\boldsymbol{n}}$ with a large excess of an aqueous H_2O_2 solution for 12 h at 30 °C afforded the solids $\mathbf{A}_{\boldsymbol{n}}\mathbf{[O]}$ and $\mathbf{B}_{\boldsymbol{n}}\mathbf{[O]}$, respectively (Scheme 1).[16] After washing and drying, the solid-state ^{31}P NMR spectroscopy of the resulting white solids revealed the complete formation of P=O centres. Some relevant physical properties of these materials are given in Table 1. The BET surface areas of both materials were determined by the N_2 adsorption–desorption isotherm measurements. The materials $\mathbf{A}_{\boldsymbol{n}}\mathbf{[O]}$ (n = 4–35) exhibit type IV isotherms, characteristic for mesoporous materials while the materials $\mathbf{B}_{\boldsymbol{n}}\mathbf{[O]}$ display type II isotherms, indicative of macroporosity. The XRD patterns of the materials $\mathbf{A}_{\boldsymbol{n}}\mathbf{[O]}$ exhibit an intense diffraction peak corresponding to the d_{100} spacing (Table 1). and in some cases (for $n \geqslant 19$) a much less intense peak corresponding to d_{110} and d_{200} spacings indicating a hexagonal mesostructure. In contrast, the XRD patterns of the solids $\mathbf{B}_{\boldsymbol{n}}\mathbf{[O]}$ display no peak. Both types of solids were subsequently treated with an excess of an ethanol solution of $Eu(NO_3)_3{\cdot}6H_2O$ (2 equiv. of Eu^{3+} per P=O) heated under reflux for 14 h. The resulting solids $\mathbf{EuA}_{\boldsymbol{n}}\mathbf{[O]}$ and $\mathbf{EuB}_{\boldsymbol{n}}\mathbf{[O]}$ were copiously washed with acetonitrile to eliminate the non-complexed salt until no traces of $Eu(NO_3)_3$ were detected in the filtrate. After drying, the extent of the complexation reaction within both types of materials was first determined by solid-state ^{31}P NMR spectroscopy. For $n \leqslant 14$, the ^{31}P NMR spectra of the materials exhibit two signals (Table 2), one was attributed to the free P=O groups (33.1–37.4 ppm) and the other which was shifted upfield (−107.1 to −112.0 ppm), to P=O groups coordinated to Eu^{3+}. The percentage of complexed P=O sites was calculated by integration of the signals and the results are reported in Table 2 and in Fig. 1. When $n > 14$, the solid state ^{31}P NMR spectra of both materials display only one signal attributed to the starting phosphine oxide. Elemental analyses for Eu, P, N (and in some cases Si) were carried out, and the percentages of complexed Eu^{3+} were then calculated considering that one Eu^{3+} coordinates three P=O groups (Table 2).[17] This method of calculation afforded percentages of complexed Eu^{3+} in good agreement with the percentages calculated by ^{31}P NMR spectroscopy. This strongly suggests that the uptake of one Eu^{3+} requires three P=O groups within the materials.



Scheme 1 $\mathbf{A}_{\boldsymbol{n}}\mathbf{[O]}$ and $\mathbf{B}_{\boldsymbol{n}}\mathbf{[O]}$ corresponds to materials $Ph_2PO(CH_2)_3SiO_{1,5}/$ $n$$SiO_2$ prepared in the presence and in the absence of surfactant, respectively.

Thus, direct incorporation of $Eu(NO_3)_3{\cdot}6H_2O$ within both types of materials is possible for $7 \leqslant n \leqslant 14$. The uptake of Eu^{3+} depends highly on the type of the materials (prepared in the presence or in the absence of surfactant) and on the dilution of the organic moiety into silica (Fig. 1), the higher percentage of

Table 1 Physicochemical properties of $\mathbf{A}_{\boldsymbol{n}}\mathbf{[O]}$ materials containing phosphine oxide moieties

Sample	^{31}P NMR[a] (HPDEC MAS)	d_{100} lattice spacing/Å	D_p/Å	S_{BET}/m^2 g^{-1}	Total pore volume/ cm^3 g^{-1}
$\mathbf{A_7[O]}$	32.9	37	30	515	0.28
$\mathbf{A_9[O]}$	35.0	39.7	35	1000	0.30
$\mathbf{A_{12}[O]}$	33.9	38.1	35	680	0.35
$\mathbf{A_{14}[O]}$	33.0	40.8	37	750	0.47
$\mathbf{A_{19}[O]}$	34.3	40.5	34	1110	0.77
$\mathbf{A_{35}[O]}$	33.2	40.8	36	1025	0.92

[a] δ/ppm.

DOI: 10.1039/b102681j

Table 2 Percentage of complexed P=O groups calculated from ^{31}P NMR spectroscopy and percentage of Eu^{3+} calculated from elemental analyses for materials **EuA$_n$[O]** and **EuB$_n$[O]**

Sample	^{31}P NMR chemical shifts. Complexed P=O^a (%)	Found formula^b [Eu^{3+},^{c} (%)]
EuA$_7$[O]	−107.1 (62)	$Eu_{0.18}N_{0.53}P_{1.00}$ (55)
EuA$_9$[O]	−110.3 (76)	$Eu_{0.27}N_{0.82}P_{1.00}$ (82)
EuA$_{14}$[O]	−108.5 (15)	$Eu_{0.06}N_{0.17}P_{1.00}Si_{12.30}$ (17)
EuA$_{19}$[O]	(0)	$Eu_{<0.02}N_{<0.22}P_{1.00}$ (< 8)
EuB$_7$[O]	−109.8 (18)	$Eu_{0.07}N_{0.19}P_{1.00}$ $Si_{7.96}$ (21)
EuB$_9$[O]	−112.0 (16)	$Eu_{0.06}N_{0.15}P_{1.00}$ (18)
EuB$_{12}$[O]	−110.0 (10)	$Eu_{0.04}N_{0.11}P_{1.00}$ (12)
EuB$_{19}$[O]	(0)	$Eu_{<0.03}N_{<0.22}P_{1.00}$ (< 9)

^{a} From ^{31}P NMR spectroscopy. ^{b} From elemental analyses. ^{c} Calculated by using the theoretical formula $Eu_{0.33}NP$.

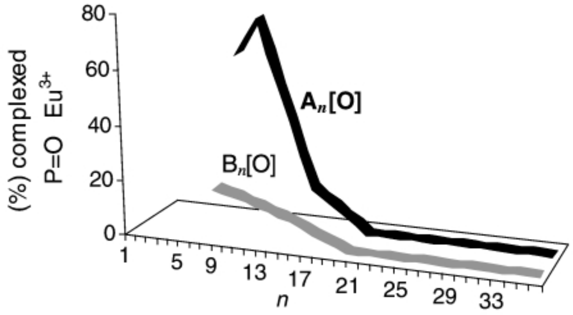


Fig. 1 Percentage of complexed P=O–Eu^{3+} groups (calculated from solid-state ^{31}P NMR spectroscopy) within **A$_n$[O]** and **B$_n$[O]** materials as a function of the 'dilution' *n*.

complexation (about 80%) being obtained for the material **A$_9$[O]**. Furthermore, it is remarkable to observe (Fig. 1) that, for a given 'dilution' of phosphine oxide moieties into silica, in particular for $n = 7$ and 9, the amount of incorporated Eu^{3+} is always low for the materials prepared in the absence of surfactant. This great difference between the properties of materials **A$_n$[O]** and **B$_n$[O]** towards the complexation of Eu^{3+}, shows that the ordered mesoporous hybrid materials **A$_9$[O]** and **A$_7$[O]** in which the P=O are located within the pores[18] are suitable for the complexation of Eu^{3+}, while the materials **B$_n$[O]** (n = 7 and 9) in which the distribution of P=O groups is uncontrolled, are not. This suggests that the complexation of Eu^{3+} requires not only three P=O groups in close proximity to each other but in a favourable geometry. It is worth noting that the complexation of Eu^{3+} is optimum but incomplete (80%) for **A$_9$[O]**. For $n < 9$, the P=O groups are certainly in close proximity to each other but nevertheless they do not allow an optimum complexation of Eu^{3+} probably for steric reasons. That illustrates how restrained is the complexation of Eu^{3+} within the materials. For the dilutions $n > 14$, there is neither complexation for the ordered materials **A$_n$[O]** nor for **B$_n$[O]**. The distances between the P=O groups are then likely much too large to allow the complexation.

The emission spectra of both types of materials were measured at 2 K under laser excitation at 325 nm. Fig. 2 displays the emission spectra of materials **EuA$_9$[O]** and **EuB$_7$[O]** as examples. The line emission of materials incorporating Eu^{3+} ions were assigned to the transition from the $^5D_0$ level to the ^7F_i levels (i = 0, 1, 2, 3, 4).[19] The strongest transition, $^5D_0 \rightarrow {}^7F_2$ occurs at 618 nm and is the characteristic 'europium red' luminescence. We observed a decrease of the red colour as the percentage of Eu^{3+} decreases. It is of note that the emission spectra are very similar for both types of materials. Of special interest is the $^5D_0 \rightarrow {}^7F_0$ emission which exhibits in both cases only one line indicating a unique chemical environment around the Eu^{3+} ions.[19] Thus, when the complexation of Eu^{3+} is possible within the materials **A$_n$[O]** or **B$_n$[O]**, the local environment around Eu^{3+} is the same whatever the route for the preparation of hybrid materials (route A or B).

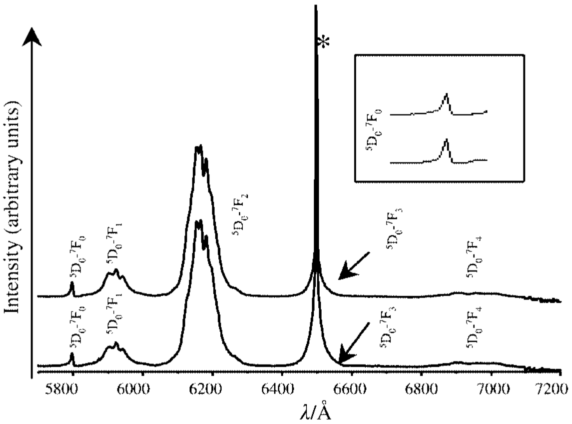


Fig. 2 Emission spectra of **EuA$_9$[O]** (upper) and **EuB$_7$[O]** (lower) recorded under laser excitation at 325 nm at 2 K. * Corresponds to 2nd order-scattered laser beam. The insert shows the $^5D_0 \rightarrow {}^7F_0$ emission.

In summary, we describe for the first time, a very simple method for the complexation of Eu^{3+} within hybrid materials. We show that the ordered HMS materials containing phosphine oxide groups within the pores are mostly convenient for the complexation of Eu^{3+} which requires three P=O centres.

Notes and references

1 J. D. Mackensie, ed., *SPIE Proc. Ser.*, 1994, 2288.
2 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31.
3 L. L. Beecroft and C. K. Ober, *Chem. Mater.*, 1997, **9**, 1302.
4 M. J. Weber, *J. Non-Cryst. Solids*, 1990, **123**, 208.
5 L. C. Klein, *Annu. Rev. Mater. Sci.*, 1993, **23**, 437.
6 C. J. Brinker and G. W. Scherer, *Sol–Gel Science*, Academic Press, Boston, MA, 1990.
7 B. Yan, H. Zhang, S. Wang and J. Ni, *Mater. Chem. Phys.*, 1997, **51**, 92.
8 B. Yan, H. Zhang, S. Wang and J. Ni, *J. Photochem. Photobiol. A: Chem.*, 1998, **112**, 231.
9 H. Li, S. Inoue, K. Machida and G. Adachi, *Chem. Mater.*, 1999, **11**, 3171.
10 R. J. P. Corriu, F. Embert, A. Mehdi and C. Reyé, *Chem. Mater.*, submitted.
11 D. R. Cousins and F. A. Hart, *J. Nucl. Chem.*, 1967, **29**, 1745.
12 J.-C. G. Bunsli and G. R. Choppin, *Lanthanide Probes in Life, Chemical, and Earth Sciences*, Elsevier, New York, 1989.
13 D. J. Macquarie, D. B. Jackson, J. E. G. Mdoe and J. H. Clark, *New J. Chem.*, 1999, **23**, 529.
14 M. Capka, *Synth. React. Inorg. Met. Org. Chem.*, 1977, **7**, 347.
15 R. J. P. Corriu, A. Mehdi and C. Reyé, *C. R. Acad. Sci. Paris, Ser. IIc*, 1999, 35.
16 J. P. Bezombes, C. Chuit, R. J. P. Corriu and C. Reyé, *J. Mater. Chem.*, 1999, **9**, 1727.
17 G. Valle, G. Casotto, P. L. Zanonato and B. Zarli, *Polyhedron*, 1986, **5**, 2093.
18 R. J. P. Corriu, C. Hoarau, A. Mehdi and C. Reyé, *Chem. Commun.*, 2000, 71.
19 F. Richardson, *Chem. Rev.*, 1982, **82**, 541.