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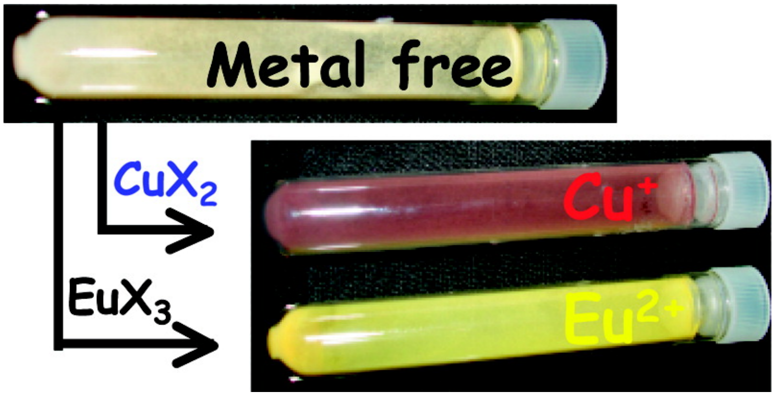

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Unexpected Coordination Chemistry of Bisphenanthroline Complexes within Hybrid Materials: A Mild Way to Eu^{2+} Containing Materials with Bright Yellow Luminescence

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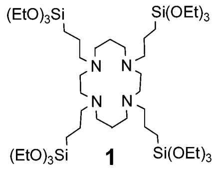
Nanostructured hybrid materials based on silica and obtained by sol−gel process have attracted considerable attention during the past decade, as they constitute a unique class of materials combining the properties of organic moieties and inorganic matrix.[1] They are obtained by hydrolysis and polycondensation of bis- or poly(trialkoxysilyl)organic precursors, leading to materials in which the organic fragments are integrated into the silica matrix by covalent bonds.[2] The interest of this class of materials resides in that their properties can be modified by changing the nature of the bridging organic groups, which renders them very attractive.[3]

We have been interested by the introduction of groups able to chelate transition-metal or lanthanide ions[4] as such materials could present various physical properties (optic, electric, or magnetic, for example) depending on the nature of the salts. They could also be promising in metal−ion separation, including actinides.

In the course of our investigations in this field, some results highly suggested that the coordination chemistry in the solid is different from that in solution. For instance, we previously observed that it is possible to incorporate Eu^{3+} ions directly inside the solid resulting from the hydrolytic polycondensation of tetrasilylated cyclam **1**, with a cyclam/Eu^{3+} ratio of 2, while complexation of Eu^{3+} by the precursor **1** was not possible in solution.[4c] That suggested that, in the solid where the mobility of chelating species is very limited, the formation of complexes originated essentially from the short-range arrangement of the chelating moieties. These results prompted us to extend our investigations in the field of the coordination chemistry in the solid. Phenanthroline (phen) has been used for many years by Sauvage and co-workers to stabilize various oxidation states of transition metals[5] as well as to create chelating electroactive films,[6] therefore, we decided to explore the chelating properties of this rigid ligand incorporated in hybrid organic−inorganic materials.



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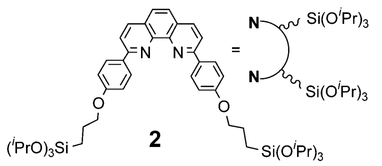

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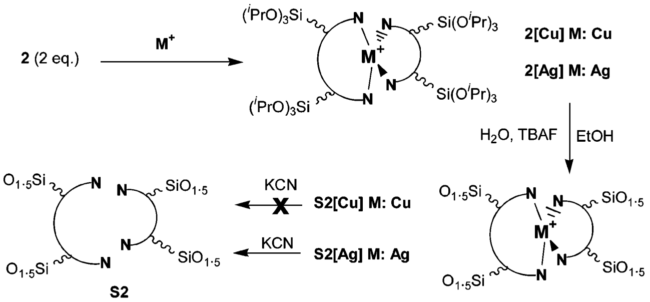
In this contribution, we describe the preparation of bisphen transition-metal complexes (Cu^+, Ag^+) with a tetrahedral geometry[7] bearing four hydrolyzable $Si(O^iPr)_3$ groups as well as their hydrolytic polycondensation which gives rise to hybrid organic−inorganic materials containing transition-metal ions. The demetalation of these materials was examined in order to study the coordination properties of the resulting materials. Indeed, we guessed that the rigid framework of 1,10-phen might force the ions incorporated after the demetalation to adopt unusual geometries, which could induce unexpected results.

Scheme 1



We show that the incorporation of Cu^{2+} and Eu^{3+} ions into hybrid materials containing free cavities is not only possible but also induces the reduction of these ions in Cu^+ and Eu^{2+}, respectively.

For this purpose, ligand **2** was prepared in a 62% yield by silylation of 2,9-diphenol-1,10-phenanthroline[8] by a Williamson-type reaction with 3-iodopropyltriisopropoxysilane.[9] The coordination of a copper(I) ion with two bidentate phen units was accomplished by treating **2** with a stoichiometric amount of $[Cu(CH_3CN)_4]BF_4$ in CH_3CN/CH_2Cl_2 at room temperature, leading quantitatively to the tetrasilylated bisphen copper(I) complex **2-[Cu]** as a deep-red colored solid (Scheme 1). The latter was fully characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopies as well as by elemental analysis. The geometry around the copper atom is essentially tetrahedral as expected for bisphen copper(I) complexes.[7a]

Sol−gel polycondensation of **2[Cu]** was performed in ethanol in the presence of a stoichiometric amount of H_2O and tetrabutylammonium fluoride (TBAF) as catalyst (Scheme 1). The gelation occurred in a few minutes. After the usual workup, the material **S2[Cu]** was obtained quantitatively as a deep-red colored powder.

Demetalation of **S2[Cu]**, that is, removal of the metal from the cavities of the material, was attempted by treating the material with a large excess of KCN in a mixture of CH_3CN and H_2O. Surprisingly, demetalation, which occurs within minutes at room temperature for bisphen copper(I) complexes in solution,[8] failed with **S2[Cu]** even when treated with a very large excess (40 equiv) of KCN for 3 days at 60 °C. This astonishing behavior underlines the difference of reactivity between solution and the solid state.

This unexpected result[10] prompted us to prepare the silver(I) complex in place of the Cu(I) one in order to allow the demetalation. **2[Ag]** was prepared by reacting $AgBF_4$ with 2 equiv of **2** in a mixture of CH_2Cl_2 and MeOH, leading to an off-white complex. The corresponding beige material **S2[Ag]** was prepared quantitatively in a similar manner to **S2[Cu]** (Scheme 1).

The Si/N as well as Si/Ag ratios in the solid **S2[Ag]** determined by elemental analysis were found to be 1.13 and 4.17, which is very close to the expected values (1 and 4, respectively) showing

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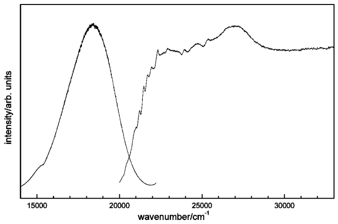
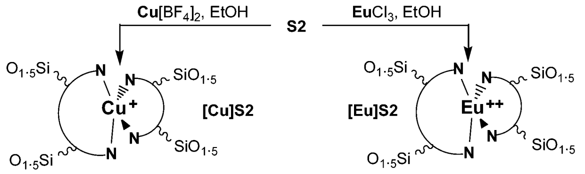


Figure 1. Emission (left) and excitation spectra (right) of **[Eu]S2**.

Scheme 2



that demetalation did not occur during the sol−gel process. Treatment of **S2[Ag]** with a large excess of KCN led quantitatively to metal-free potentially chelating material **S2** (Scheme 1) as revealed by elemental analysis.

Remetalation of the material by ions, which do not usually adopt a tetrahedral geometry, was attempted in order to investigate the consequences of such a coordination. Treatment of **S2** with an ethanolic solution containing 1 equiv of Cu(BF$_4$)$_2$ gave rise to the brown-red material **[Cu]S2** after a 12 h reflux (Scheme 2). Titration revealed that 60% of the metal-free sites were remetalated. As the brown-red color of the material suggested the reduction of Cu(II) into Cu(I), ESR measurements were carried out. The amount of Cu(II) within **[Cu]S2** determined by this method was found to be very low (<1%) as indicated by the weak absorption at 3009 G ($g = 2.248$) (spectrum available as Supporting Information). In addition, the UV/vis absorption spectrum of **[Cu]S2** was obtained. The absence of the band at 680 nm corresponding to the Cu(II) complex[5] as well as the similarity between this spectrum and that of **S2[Cu]** led us to suggest that reduction of Cu(II) to Cu(I) occurred during the remetalation process (both spectra and the one of **S2** are available as Supporting Information).

Incorporation of Eu(III) into **S2** was also attempted (Scheme 2). **S2** was treated with an ethanolic solution of anhydrous EuCl$_3$ (1.4 equiv) heated at reflux for 3 h. After washing copiously with ethanol, the content in Eu within the material was determined. Titration revealed that 30% of metal-free sites were occupied.

The emitting properties of the material were investigated. Samples of **[Eu]S2** show a very bright yellow emission when irradiated with a UV lamp. The respective emission and excitation spectra are presented in Figure 1. They clearly prove that Eu^{2+} ions are incorporated in the material. Indeed, no peak of Eu^{3+} which should be located with the largest intensity at about 610 nm (16 400 cm^{-1}) was detected. The emission spectrum of **[Eu]S2** consists of two bands, the one with a maximum at 18 400 cm^{-1} (543.5 nm) having a much higher intensity than the one at about 15 800 cm^{-1} (633 nm). The bands can be assigned to the typical $4f^7 \leftrightarrow 4f^65d^1$ transitions of this ion. That suggests at least two very different positions for Eu^{2+} ions. While the position of the latter is in the same range as those of typical inorganic ionic nitrides, the former is at surprisingly high energy.[11] This can be explained by the small crystal field splitting for this site probably due to the rigidity of the ligands. It is worth noting that the emission spectrum of the ligand **2** displays two bands at higher energies (23 000 and 24 400 cm^{-1}).

To the best of our knowledge, there are very few examples of hybrid organic−inorganic materials containing Eu^{2+} obtained under mild conditions.[12] In contrast to our work, the emission maxima for these compounds are located in the blue range because of the probable different Eu^{2+} coordination. Additionally, Eu^{3+} transitions are observed in all cases leading to a rather bad color quality. It is worth noting that Zhang and co-workers[13] prepared a hybrid material containing Eu^{3+} phen complexes covalently bonded to a silica matrix. This material was obtained by hydrolytic polycondensation of tetraethoxysilane and phen bearing two Si(OEt)$_3$ groups, in the presence of Eu^{3+} ions. Interestingly, the emission spectrum of this material was characteristic of Eu^{3+} ions. This result points out the role of the tetrahedral cavities in our case.

The observed reduction of Eu(III) to Eu(II) results from the unusual geometry, which was imposed by the procedure. Reduction of Cu^{2+} to Cu$^+$ was previously observed within hybrid materials. Guilard and co-workers demonstrated that the reduction occurred through electronic transfer between ions and ethanol.[14] As ethanol was also the reaction solvent in the present study, we propose a similar process to explain the electron transfer.

In conclusion, we described the preparation of hybrid materials containing bisphen transition-metal complexes (Cu$^+$, Ag$^+$) with a tetrahedral geometry. The demetalation−remetalation of the Ag$^+$ containing material was possible. We showed that the incorporation of Cu^{2+} and Eu^{3+} ions within hybrid material containing free tetrahedral cavities induced their reduction into Cu$^+$ and Eu^{2+}. The luminescence of Eu^{2+} containing material revealed an extremely bright emission in the yellow range. That renders this air-stable material of particular interest. Indeed, it could be a promising candidate for luminescence applications such as energy saving LEDs.

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Supporting Information Available: EPR spectra of **[Cu]S2**, UV−vis spectra of **S2**, **S2[Cu]**, and **[Cu]S2**, and details of the luminescence measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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