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Synthesis and Characterization of $A_4[Re_6Q_8L_6]@SiO_2$ Red-Emitting Silica Nanoparticles Based on Re_6 Metal Atom Clusters ($A = Cs$ or K , $Q = S$ or Se , and $L = OH$ or CN)

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Metal atom clusters constitute very promising candidates as luminophores for applications in biotechnology because they are nanosized entities offering robust luminescence in the near-infrared field (NIR). However, they cannot be used as prepared for biological applications because of potential toxic effects and quenching of the clusters' luminescence in aqueous media, and they therefore need to be dispersed in a biocompatible matrix. We describe herein the encapsulation of octahedral rhenium clusters, denoted as $A_4[Re_6Q_8L_6]$ ($A = Cs$ or K , $Q = S$ or Se , and $L = OH$ or CN), in silica nanoparticles by a water-in-oil microemulsion process, paying particular attention to the clusters' stability. The obtained $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles are 30 nm in size with good monodispersity and a perfectly spherical shape, as shown by scanning electron microscopy (SEM). The presence of cluster units inside the silica matrix was evidenced by scanning transmission electron microscopy in annular dark-field mode (ADF-STEM). From the point of view of their optical properties, the $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles show red and NIR emission under UV excitation, even when dispersed in water. The evolution of the structural and luminescence properties of clusters before and after encapsulation was followed by Raman and photoluminescence spectroscopy.

1. Introduction

Many solid-state compounds, hybrid assemblies, and nanomaterials are based on octahedral metal atom clusters (M_6 , with $M = Mo, W,$ and Re) characterized by metal–metal bonds.^{1,2} The M_6 cluster is surrounded by eight face-capping ligands (L^i , $i =$ inner) to form a rigid $M_6Y^i_8X^a_6$ core that is coordinated to six terminal ligands (L^a , $a =$ apical) leading to an $M_6Y^i_8X^a_6$ neutral or anionic unit ($Y =$ chalcogen and/or halogen; $X =$ halogen). Solid-state materials based on such $M_6Y^i_8X^a_6$ units are easily synthesized at high temperature. They have been studied for many years for their interesting transport, catalytic, and electronic properties.^{3–7} Many routes now afford soluble inorganic cluster precursors for soft chemistry synthesis.^{8,9} Indeed, owing to their nanosized shape and their structural, redox, and photoluminescence

properties, $M_6Y^i_8X^a_6$ anionic units constitute relevant building blocks for the elaboration of supramolecular assemblies, nanomaterials, and functionalized surfaces.^{10–21} In solution or in inorganic (or organic) melts, apical ligands can be replaced by other ligands that are not stable under the synthesis conditions of the cluster. For instance, the reaction between $Cs_3[Re_6Q_7Br_7] \cdot H_2O$ ($Q = S$ or Se) and melted pyrazine (pyz) leads to the formation of *fac*- $[Re_6Q^i_7Br^i(py)_3Br^a_3] \cdot xH_2O$ units that self-assemble via supramolecular interactions to build an original stable cluster-based hybrid framework.¹⁶

Many experimental and theoretical works report on the luminescence properties of Mo_6 , W_6 , and Re_6 cluster compounds.^{22–27} It is worth noting that they emit in the red and near-infrared

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50 (NIR) regions, which constitute a very interesting emitting window
 51 for biotechnology.^{28,29} However, for such applications, it is required
 52 that no interaction occurs between clusters and tissues or biological
 53 media.

54 In this framework, we recently reported the synthesis of
 55 luminescent Cs₂[Mo₆X₁₄]@SiO₂ nanoparticles (X = Cl, Br, or I)
 56 via a water-in-oil microemulsion process wherein the cluster units
 57 are embedded in monodisperse silica nanoparticles.³⁰ Micro-
 58 emulsions are thermodynamically stable dispersions of water
 59 droplets in an oil phase, stabilized at the interface by surfactants
 60 molecules. Those water droplets, also called inverted micelles, are
 61 below 50 nm in size and constitute a suitable confined reaction
 62 medium for the synthesis of a wide variety of well-defined
 63 nanoparticles with controlled size and shape.^{31,32} Using a similar
 64 approach, structured bifunctional magnetic and luminescent
 65 γ -Fe₂O₃-Cs₂[Mo₆Br₁₄]@SiO₂ nanoparticles were obtained by
 66 the introduction of maghemite nanocrystals at the core of the
 67 nanoparticles.³³ Whereas nowadays the luminophores developed
 68 for bioimaging and biolabeling technologies are mainly based on
 69 organic dyes,^{34,35} inorganic quantum dots,³⁶ or lanthanide based
 70 nanocrystals,^{37,38} metal atom clusters such as Re₆ clusters may
 71 offer complementary assets because they combine the important
 72 properties of perfectly reproducible nanosize, photostability, and
 73 NIR emission and do not show acute toxic effects.³⁹

74 In addition to applications in biotechnology, functional silica
 75 particles can also find numerous applications in a wide range of
 76 fields such as photonics,⁴⁰ catalysis,⁴¹ data storage devices,⁴² cos-
 77 metics,⁴³ and so forth. In this article, we report the preparation of
 78 novel NIR-emitting nanoparticles obtained by the encapsulation
 79 of [Re₆Q₈L₆]⁴⁻ cluster units (Q = S or Se and L = OH or CN) in
 80 silica nanoparticles by an adapted microemulsion process. Several
 81 kinds of clusters have been used to study the influence of the
 82 nature of inner and apical ligands on the cluster-embedding
 83 process as well as on the luminescence properties of embedded
 84 clusters. The Re₆ cluster precursors involved in this work were

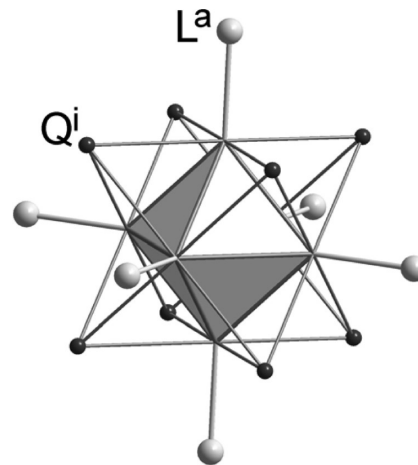


Figure 1. Schematic representation of a Re₆Q₈L₆ cluster unit. The Re₆ cluster core is represented as a gray octahedron. Inner ligands (Qⁱ = S or Se) are in the face-capping position, and apical ligands (L^a = OH, CN or Br) are in terminal positions.

85 K₄[Re₆Q₈(OH)₆] (Q = S or Se), Cs₄[Re₆S₈Br₆], and Cs_{1.68}K_{2.32}-
 86 [Re₆S₈(CN)₄(OH)₂]. These Re₆ clusters are all luminescent in the
 87 red and NIR fields, with luminescence lifetimes of a few micro-
 88 seconds depending on the ligands.^{25,44} It turns out that apical
 89 bromine in [Re₆S₈Br₆]⁴⁻ units are quite labile under preparation
 90 conditions and are replaced by hydroxo groups during the
 91 embedding process but CN groups from [Re₆S₈(CN)₄(OH)₂]⁴⁻
 92 are not exchanged. We show that the luminescence properties of
 93 clusters are preserved after they are embedded in a silica matrix.
 94 An important finding is that although the luminescence of the
 95 [Re₆Q₈L₆]⁴⁻ cluster units is originally quenched by oxygen in
 96 aqueous solutions, their luminescence properties are preserved in
 97 solution after they are embedded in silica nanoparticles.

2. Experimental Section

98
 99 **2.1. Chemicals.** Tetraethoxysilane (TEOS) 98%, polyoxyethyl-
 100 ene(4) lauryl ether (Brij30), and hydrobromic acid (HBr) 48%
 101 were purchased from Aldrich; *n*-heptane 99.0%, bromine (Br₂)
 102 79.9%, sulfur (S) 99.5%, and aqueous ammonia solution (NH₄OH)
 103 28% were purchased from Prolabo; ethanol (EtOH) 99.8% was
 104 purchased from Fluka; cesium chloride (CsCl) 99.9% and rheni-
 105 um (Re) 99.997% were purchased from Alfa Aesar; and potas-
 106 sium hydroxide (KOH) 85% was purchased from Carlo Erba. All
 107 of the chemical reagents were used as received without further
 108 purification.

109 **2.2. Synthesis of Re₆ Clusters.** Hexanuclear rhenium clus-
 110 ters consist of six metal atoms forming an octahedron linked to
 111 eight chalcogen inner ligands (here S or Se) capping the faces of
 112 the octahedron, plus six apical ligands (here OH, Br, or CN) in the
 113 terminal positions of the octahedron. For illustration, a generic
 114 Re₆Q₈L₆ cluster unit is represented in Figure 1. The whole
 115 cluster unit is roughly 1 nm in size, depending on the nature of
 116 the apical ligands, and is negatively charged; it therefore needs to
 117 be charge balanced by counter cations in the solid state (here Cs or
 118 K). Most of the clusters are prepared by gas–solid or solid–solid
 119 synthesis and generally at high temperature. The cluster precu-
 120 rors used in this study were prepared according to well-known
 121 procedures reported in the literature.^{45–47} They are briefly de-
 122 scribed in this section and summarized in Scheme 1.

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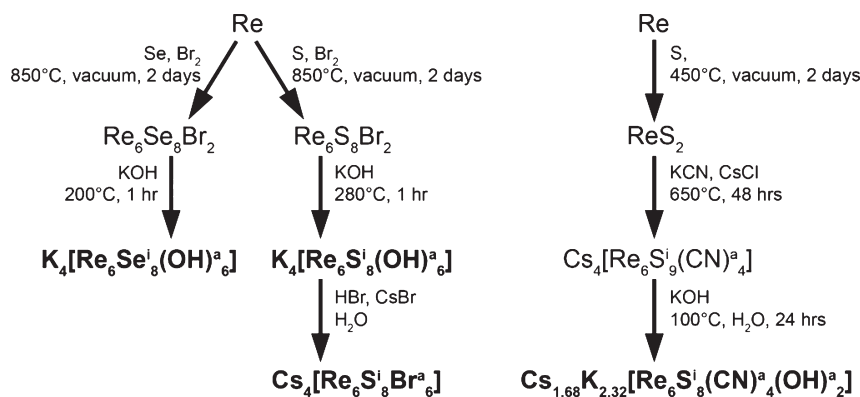
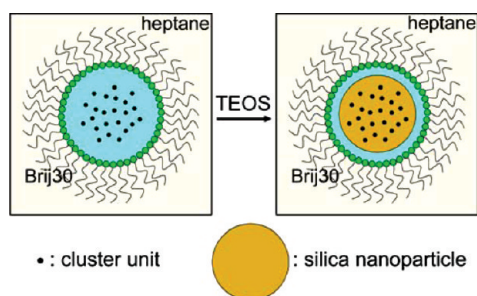
Scheme 1. Summary of the Synthesis of Re₆ Inorganic Cluster Precursors^a^a In bold.

Figure 2. Schematic representation of the microemulsion process for the encapsulation of rhenium clusters inside a silica nanoparticle.

2.2.1. $K_4[Re_6Se_8(OH)_6]$ and $K_4[Re_6S_8(OH)_6]$.⁴⁷ Re, Se (or S), and liquid Br₂ were mixed in stoichiometric proportions, sealed under vacuum, and held at 850 °C for 2 days to obtain binary chalcogenide compound Re₆Se₈Br₂ (or Re₆S₈Br₂, respectively). This binary compound was then mixed with KOH and held at 200 °C (or 280 °C, respectively) in ambient air to obtain $K_4[Re_6Se_8(OH)_6]$ (or $K_4[Re_6S_8(OH)_6]$, respectively).

2.2.2. $Cs_4[Re_6S_8Br_6]$.⁴⁷ $Cs_4[Re_6S_8Br_6]$ was prepared by the reaction of $K_4[Re_6S_8(OH)_6]$ with CsBr in a water solution and with the pH adjusted to 2 with HBr.

2.2.3. $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]$.⁴⁶ ReS₂ was prepared by the reaction of Re with S under vacuum at 450 °C for 2 days. $Cs_4[Re_6S_9(CN)_4]$ was then synthesized by the reaction of ReS₂ with KCN in the presence of excess CsCl at 650 °C for 48 h.⁴⁵ Finally, $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]$ was obtained by the reaction of $Cs_4[Re_6S_9(CN)_4]$ with KOH in water, which had been boiled for 24 h.

2.3. Synthesis of $A_4[Re_6Q_8L_6]@SiO_2$ Nanoparticles.

The $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles were prepared through a microemulsion process adapted from a previously reported synthesis for the encapsulation of nanocrystals (CeO₂ or ZnFe₂O₄)^{48,49} or hexamolybdenum clusters in silica nanoparticles,³⁰ and this is illustrated in Figure 2. For all of the syntheses described here, the quantities of precursors used to form the final mixture were the following: 47 mL of heptane, 15 mL of Brij30, 1.6 mL of an

aqueous cluster sol, 1.3 mL of ammonia, and 2 mL of TEOS. To create the microemulsion, heptane (oil phase) was first mixed with Brij30 (surfactant), and then an aqueous ammonia solution and an aqueous cluster sol were slowly added to the mixture. The aqueous cluster sol was obtained simply by solubilization of the cluster precursor in water. Depending on the solubility, the cluster concentration in the final aqueous phase could be adjusted. For $K_4[Re_6S_8(OH)_6]$ and $K_4[Re_6Se_8(OH)_6]$, this concentration was limited to 5 mM whereas it could reach 16 mM for $Cs_4[Re_6S_8Br_6]$ and 25 mM for $Cs_{1.68}K_{2.32}[Re_6(CN)_4(OH)_2]$. Once the microemulsion became a clear, stable solution, the silica precursor (TEOS) was added for the synthesis of the silica shell that occurred directly inside the aqueous nanodroplets already containing the cluster units. After the addition of TEOS, the reaction was stirred for 3 days and then the microemulsion was destabilized with ethanol and the nanoparticles were washed twice with an ethanol/heptane mixture (3:1 volume ratio) by centrifuging at 5000 rpm. Note that before destabilization of the microemulsion, the nanoparticle surface can be easily functionalized by the addition of a functional organosilane precursor. Finally, the nanoparticles could be either redispersed in solution (water or ethanol) or dried in ambient air.

2.4. Characterization of Materials. The external morphology of the nanoparticles was studied by field emission scanning electron microscopy (FE-SEM) with a Hitachi SU8000 working at an acceleration voltage of 10 kV. For FE-SEM observations, the nanoparticles were deposited on a silicon wafer and coated with a 3 nm layer of platinum using a JEOL JFC-1600 auto fine coater to enhance the conductivity of the sample. The microstructure of the nanoparticles and the distribution of the cluster units were observed using a scanning transmission electron microscope (Hitachi High-Technologies, HD-2300C) equipped with a spherical aberration corrector (CEOS GmbH, CESCOR) and working in annular dark-field mode (ADF-STEM).^{50,51} The acceleration voltage was 200 kV, the convergent semiangle was 27.5 mrad, and the inner angle of the annular dark-field detector was 80 mrad. The spatial resolution of the instrument was about 0.1 nm. For ADF-STEM observation, the nanoparticles were dispersed on a thin carbon film whose thickness was about 6 nm. Investigations of the photoluminescence properties were performed in the solid state with a Jobin Yvon Fluorolog-3 fluorescence spectrometer (FL3-22, Horiba Jobin Yvon). The vibrational spectra were recorded with a Raman Bruker IFS 28 spectrometer equipped with a FRA 106 module. The excitation source was provided by a Nd:YAG laser working at 1064 nm. The power of the

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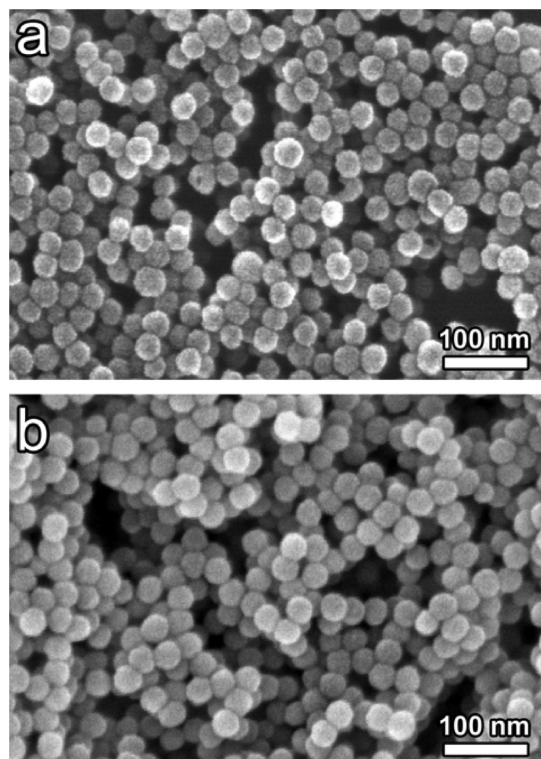


Figure 3. FE-SEM pictures of (a) $K_4[Re_6S_8(OH)_6]@SiO_2$ and (b) $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]@SiO_2$ nanoparticles.

excitation was set to 30 mW in the case of $A_4[Re_6Q_8L_6]$ precursors to avoid burning the compound and 60 mW in the case of $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles in order to get a clear signal.

3. Results and Discussion

3.1. Synthesis. The synthesis of silica nanoparticles by microemulsion and its mechanism have already been widely studied and described in the literature.^{52–54} It is a classical sol–gel process where an alkoxide precursor of silica (TEOS) is hydrolyzed, followed by the condensation of silica monomers. In the microemulsion, TEOS is first soluble in the heptane phase but is hydrolyzed by diffusion upon contact with the aqueous inverted micelles. The hydrolyzed silica monomers are then soluble in the aqueous phase, where they can condense via a base-catalyzed reaction.

The key point in the embedding of clusters in silica nanoparticles through this microemulsion process is to obtain stable cluster sols by avoiding the aggregation and precipitation of cluster units. Recall that for the preparation of the previously reported $Cs_2[Mo_6X_{14}]@SiO_2$ nanoparticles, the cluster units were solubilized in a water–ethanol mixture (1:1 v/v) and the pH was adjusted to 2 with bromic acid^{30,31} in order to avoid the exchange of apical bromine by OH groups or water molecules and the subsequent precipitation of cluster units.⁵⁵ In the latter work, TEOS was added prior to ammonia and its hydrolysis was acid-catalyzed, thanks to the acidic aqueous cluster sol. Finally, ammonia was added to allow the base-catalyzed condensation of the silica matrix.

If the optical properties of Mo_6 clusters and Re_6 clusters exhibit some similarities, then the chemistry and reactivity of Mo_6 -cluster-based units is different from that of Re_6 . In particular, for rhenium cluster units containing hydroxyl groups in apical

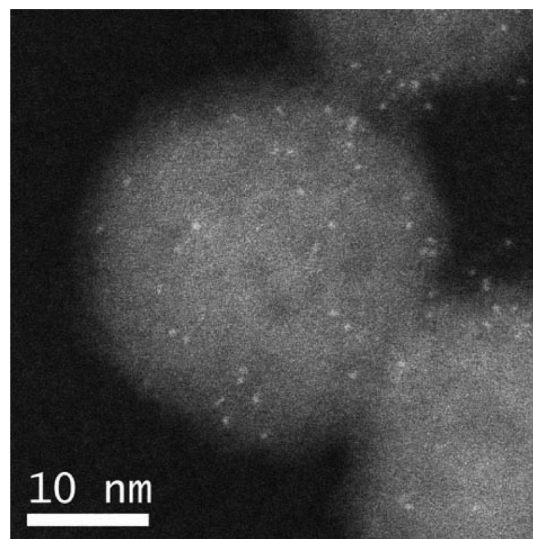


Figure 4. ADF-STEM pictures of $K_4[Re_6S_8(OH)_6]@SiO_2$ nanoparticles with discrete cluster units (bright spots).

positions, Brylev et al.⁴⁴ showed that, depending on the pH, hexahydroxo rhenium clusters $[Re_6Q_8(OH)_6]^{4-}$ can form aquahydroxo and hexaqua cluster complexes with the general formula $[Re_6Q_8(H_2O)_n(OH)_{6-n}]^{n-4}$ ($Q = S$ or Se ; $n = 0–6$) because of the possible protonation of the apical –OH ligands. Such a phenomenon would induce changes in the composition and structure of the clusters, which might result in modifications of the luminescence characteristics or even precipitation of the clusters and therefore destabilization of the microemulsion. For instance, the $[Re_6Se_8(OH)_6]^{4-}$ cluster units remains stable in water at pH ~14, whereas they fully precipitate at neutral pH because of the formation of $[Re_6Se_8(H_2O)_4(OH)_2]$ clusters.⁴⁴

For the preparation of $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles, the cluster precursors were initially dissolved in water. Then, to prevent any change in the luminescence properties and to avoid precipitation of the clusters due to low pH, the microemulsions were prepared by adding ammonia to the heptane/Brij30 mixture prior to the aqueous cluster sol and prior to TEOS, so both the hydrolysis and condensation steps in the silica synthesis were base-catalyzed. The nanoparticles were then prepared according to the procedure described in section 2.3.

3.2. Nanoparticle Morphology and Microstructure. The as-prepared nanoparticles were observed by FE-SEM. The image analyses of $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles (Figure 3) showed that they all exhibit a perfectly spherical, monodisperse morphology with an average diameter of 30 nm for the synthesis conditions described in section 2.3. Supplementary experiments showed that the size of the nanoparticles does not depend on the cluster concentration in the aqueous phase. To study the microstructure of the nanoparticles and confirm the encapsulation of the cluster units, the ADF-STEM technique is the only suitable tool because of the size of the cluster units (1 nm). Indeed, by detecting electrons scattered at high angles this technique provides what is known as Z-contrast images because atoms with high atomic numbers will be more scattered at high angle than atoms with lower atomic numbers. Thus, thanks to the large difference in electron numbers between the Re cluster core and Si or O from the silica matrix and the high spatial resolution of the STEM, it was possible to visualize the cluster units inside the nanoparticles. For example, Figure 4 shows an ADF-STEM image of $K_4[Re_6S_8(OH)_6]@SiO_2$ nanoparticles where cluster units are visible as bright spots of about 1 nm in size. This image confirms that

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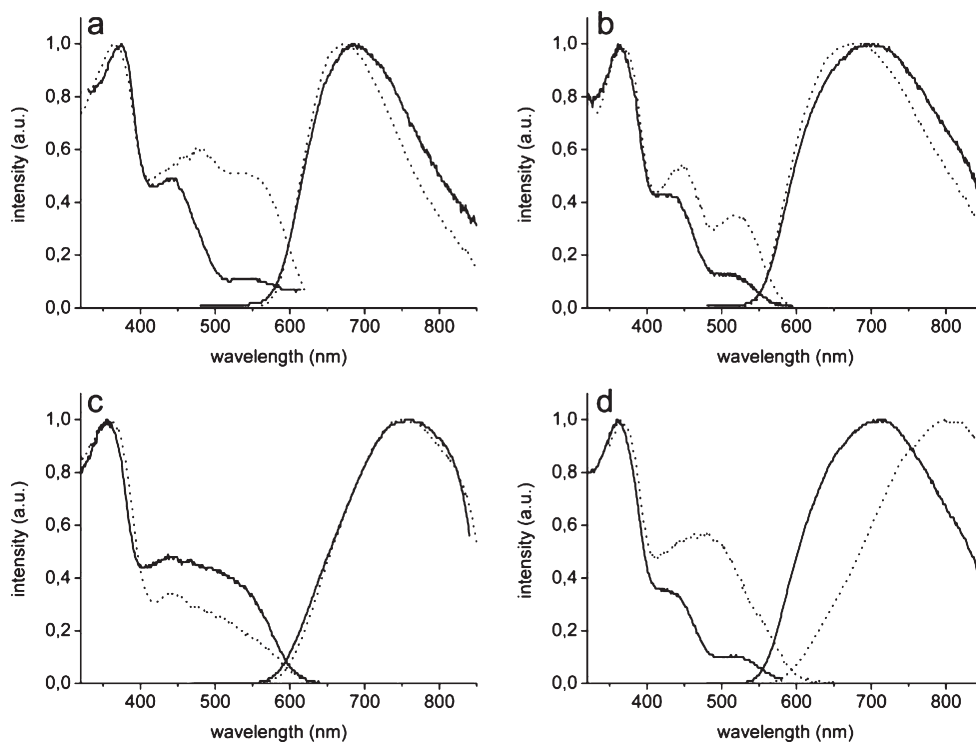


Figure 5. Normalized excitation and emission spectra (corrected signals) for both $A_4[Re_6Q_8L_6]$ cluster precursors (---) and $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles (—) for (a) $K_4[Re_6Se_8(OH)_6]$, (b) $K_4[Re_6S_8(OH)_6]$, (c) $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]$, and (d) $Cs_4[Re_6S_8Br_6]$.

Table 1. Emission Maximum Wavelengths (λ_{em}) for $A_4[Re_6Q_8L_6]$ Cluster Precursors and $A_4[Re_6Q_8L_6]@SiO_2$ Nanoparticles

$A_4[Re_6Q_8L_6]$ cluster precursor	λ_{em} (nm)	$A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles	λ_{em} (nm)
$K_4[Re_6S_8(OH)_6]$	680	$K_4[Re_6S_8(OH)_6]@SiO_2$	700
$K_4[Re_6Se_8(OH)_6]$	675	$K_4[Re_6Se_8(OH)_6]@SiO_2$	690
$Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]$	750	$Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]@SiO_2$	760
$Cs_4[Re_6S_8Br_6]$	800	$Cs_4[Re_6S_8Br_6]@SiO_2$	700

264 clusters were successfully encapsulated and homogeneously dispersed in the silica nanoparticles.

265
266 **3.3. Luminescence Properties.** The successful encapsulation
267 of the cluster units in the silica nanoparticles was also evidenced
268 by studying the luminescence properties of $A_4[Re_6Q_8L_6]@SiO_2$
269 nanoparticles. The luminescence properties were investigated in
270 the solid state for both the $A_4[Re_6Q_8L_6]$ cluster precursors and
271 the corresponding $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles. In Figure 5,
272 the excitation and emission spectra for each type of cluster are
273 plotted, and in Table 1, the wavelength values at the emission
274 maximum (λ_{em}) are summarized.

275 The encapsulation of the $[Re_6Q_8(OH)_6]^{4-}$ ($Q = Se$ or S) and
276 $[Re_6S_8(CN)_4(OH)_2]^{4-}$ cluster units in the silica matrix resulted
277 in a slight shift of the emission maxima after embedding, but the
278 shape of the emission spectrum remained unchanged (Figure 5a–c).
279 The emission maxima shifts, ranging from 10 to 20 nm, to higher
280 wavelengths between solid-state precursors and the nanoparticles
281 must be due to some perturbations of the molecular orbital
282 diagram of $[Re_6Q_8L_6]^{4-}$ units after embedding. One could suspect
283 a slight decrease in the energy gap between excited and fundamen-
284 tal states.

285 Some questions arose concerning the embedding of $[Re_6S_8Br_6]^{4-}$
286 units in silica nanoparticles. Indeed, the emission maxima for
287 $[Re_6S_8Br_6]^{4-}$ units decreased from 800 nm in the $Cs_4[Re_6S_8Br_6]$
288 precursor to 700 nm after embedding in the silica matrix (Figure 5d).
289 A closer look at the emission spectra shows that the shape of the
290 emission spectrum of $Cs_4[Re_6S_8Br_6]@SiO_2$ nanoparticles (Figure 5d)
291 and that of $K_4[Re_6S_8(OH)_6]@SiO_2$ nanoparticles (Figure 5b)

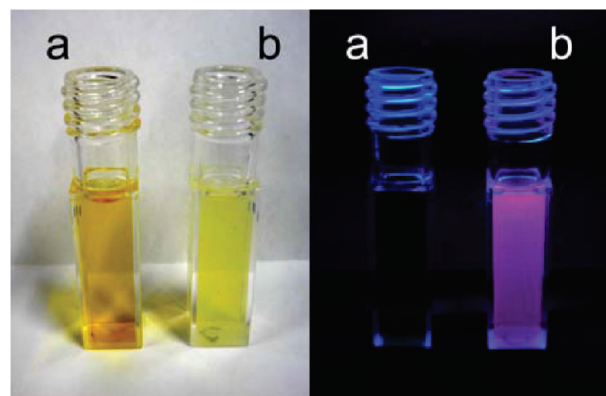


Figure 6. Aqueous solution of $[Re_6S_8(OH)_6]^{4-}$ clusters (a) before and (b) after embedding in silica nanoparticles, under daylight (left picture) and under UV irradiation at 365 nm (right picture).

292 match perfectly. This drastic change between the luminescence
293 properties of the starting and embedded clusters can then be
294 explained by an exchange of $-Br$ apical ligands for $-OH$ groups
295 during the microemulsion process. In an attempt to avoid this
296 structural modification, another synthesis of $Cs_4[Re_6S_8Br_6]@$
297 SiO_2 nanoparticles was performed using acidic cluster sols (in which
298 the pH was adjusted to 2 with HBr) either in a pure water solution
299 or in a water/ethanol mixture (1:1 v/v). In both cases, the micro-
300 emulsion stability was not affected but the resulting nanoparticles
301 still show a luminescence shift to lower wavelengths, probably as a

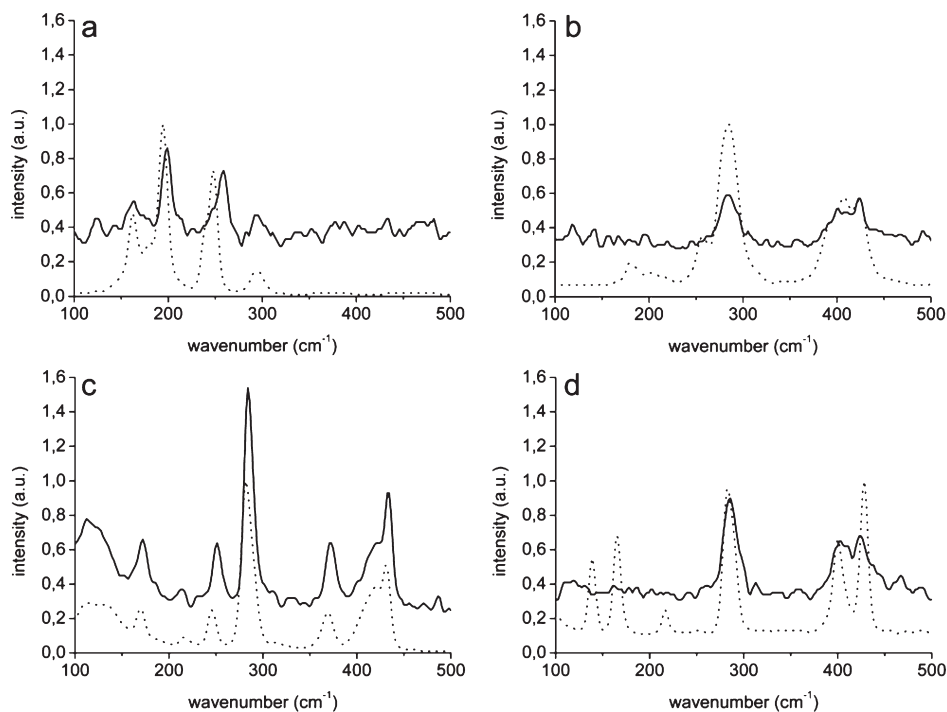


Figure 7. Raman spectra for both $A_4[Re_6Q_8L_6]$ cluster precursors (---) and $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles (—) for (a) $K_4[Re_6Se_8(OH)_6]$, (b) $K_4[Re_6S_8(OH)_6]$, (c) $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]$, and (d) $Cs_4[Re_6S_8Br_6]$.

302 result of the exchange of apical bromine ligands for hydroxyl
 303 groups. Nonetheless and as previously mentioned, $Cs_2[Mo_6Br_{14}]@$
 304 SiO_2 nanoparticles prepared with a water/ethanol acidic cluster sol
 305 (pH adjusted to 2 with HBr) did not show any luminescence shift,
 306 meaning that no ligand exchange occurred during the encapsulation
 307 process. This indicates that $Re-Br^a$ bonds are much weaker than
 308 $Mo-Br^a$ bonds in an aqueous–alcoholic medium.

309 Concerning the excitation spectra, the encapsulation of the
 310 clusters in a silica matrix resulted in a lowering of the efficiency of
 311 excitation in the range of 400 to 600 nm. Once more in the case of
 312 $Cs_4[Re_6S_8Br_6]@SiO_2$ the excitation spectrum radically changed
 313 compared to that of the $Cs_4[Re_6S_8Br_6]$ precursor (Figure 5d) and
 314 perfectly match the excitation spectrum of $K_4[Re_6S_8(OH)_6]@$
 315 SiO_2 (Figure 5b). This finding again indicates that $-Br$ apical
 316 ligands of $[Re_6S_8Br_6]^{4-}$ cluster units might be substituted for
 $-OH$ groups during the microemulsion process.

318 The luminescence of clusters is usually quenched in solution
 319 because of the presence of solubilized oxygen. Indeed, it has been
 320 known for many years that excited octahedral clusters can be
 321 relaxed through the creation of singlet oxygen.⁵⁶ This quenching
 322 effect was successfully prevented by embedding the cluster units in
 323 silica nanoparticles. For illustration, Figure 6 shows a compar-
 324 ison between the luminescence properties of $[Re_6S_8(OH)_6]^{4-}$
 325 cluster units in a water solution and after being embedded in
 326 silica nanoparticles under normal light and under UV irradiation
 327 at 365 nm. The $[Re_6S_8(OH)_6]^{4-}$ clusters show luminescence only
 328 when they are embedded in the silica matrix because they are then
 329 protected from the presence of solubilized oxygen and their
 330 luminescence is no longer quenched.

331 **3.4. Raman Study.** The vibrational properties of the A_4-
 332 $[Re_6Q_8L_6]$ cluster precursors and those of $A_4[Re_6Q_8L_6]@SiO_2$
 333 nanoparticles were investigated by Raman spectroscopy. The
 334 characterization of $M_6Q^iL^a_6$ units by Raman spectroscopy is
 335 not usual. The few published results show typical vibrations in the
 336 50 to 400 cm^{-1} region. Their assignment is particularly tricky
 337 when the symmetry of the $M_6Q^iL^a_6$ units deviates from O_h

338 symmetry. On the basis of the experimental and theoretical
 339 Raman investigations performed on $Re_6Q^iL^a_6$ -cluster-unit-
 340 based compounds by Gray et al.,⁵⁷ it turns out that the Raman
 341 bands correspond to different kinds of L^a_6 , Q^i_8 , and Re_6 breathing
 342 modes.

343 The Raman spectra of the cluster precursors and of the
 344 corresponding cluster-based silica nanoparticles are represented
 345 in Figure 7. For all of the sulfide derivatives (Figure 7b–d), the
 346 strong peaks at 280 and 430 cm^{-1} are easily identifiable in spectra
 347 of corresponding $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles and are
 348 respectively attributed to the T_{2g} vibrational mode and the A_{1g} -
 349 symmetric S_8 breathing mode of the clusters. For $Cs_{1.68}K_{2.32}$ -
 350 $[Re_6S_8(CN)_4(OH)_2]@SiO_2$, another strong peak is easily identi-
 351 fiable at 2120 cm^{-1} (data not shown here), which is due to the A_{1g}
 352 vibrational mode of the CN groups. Concerning $K_4[Re_6S_8-$
 353 $(OH)_6]@SiO_2$ nanoparticles (Figure 7a), the two intense peaks
 354 at 200 and 260 cm^{-1} can be observed and attributed to the T_{2g} and
 355 Se_8-A_{1g} vibrational modes, respectively, although they are slightly
 356 shifted (about 10 cm^{-1}) compared to the corresponding peaks in
 357 the starting cluster precursor. The spectra of $K_4Re_6S_8(OH)_6@$
 358 SiO_2 , $K_4Re_6S_8(OH)_6@SiO_2$, and $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]@$
 359 SiO_2 nanoparticles exhibit all of the typical Raman signatures of
 360 the corresponding cluster precursor. This consequently confirms
 361 the successful encapsulation of the cluster units without signifi-
 362 cant structural modification. In contrast, the spectrum of Cs_4-
 363 $[Re_6S_8Br_6]@SiO_2$ nanoparticles does not fully agree with the
 364 Raman signature of the $Cs_4[Re_6S_8Br_6]$ cluster precursor. Actu-
 365 ally, the shape of the Raman spectrum for $Cs_4[Re_6S_8Br_6]@SiO_2$
 366 nanoparticles (Figure 7d) is similar to the spectrum of the
 367 $K_4[Re_6S_8(OH)_6]@SiO_2$ nanoparticles (Figure 7b). Moreover, in
 368 Figure 7d the two intense peaks at 140 and 160 cm^{-1} , which were
 369 attributed to $Re-Br^a$ vibrational modes by Gray et al., are clearly

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370 identifiable in the $\text{Cs}_4[\text{Re}_6\text{S}_8\text{Br}_6]$ compound but absent in the
371 $\text{Cs}_4[\text{Re}_6\text{S}_8\text{Br}_6]@\text{SiO}_2$ nanoparticles. This observation shows that
372 apical $-\text{Br}$ ligands of $[\text{Re}_6\text{S}_8\text{Br}_6]^{4-}$ clusters are removed during
373 the encapsulation process.

374 4. Conclusions

375 NIR-emitting nanoparticles were achieved by embedding
376 hexarhenium clusters in silica nanoparticles using an adapted
377 microemulsion process. $\text{K}_4[\text{Re}_6\text{S}_8(\text{OH})_6]$, $\text{K}_4[\text{Re}_6\text{Se}_8(\text{OH})_6]$, and
378 $\text{Cs}_{1.68}\text{K}_{2.32}[\text{Re}_6\text{S}_8(\text{CN})_4(\text{OH})_2]$ were successfully encapsulated
379 without any drastic changes in their luminescence properties.
380 Attempts to embed $\text{Cs}_4[\text{Re}_6\text{S}_8\text{Br}_6]$ quaternary precursor in silica
381 nanoparticles led to an exchange of apical $-\text{Br}$ ligands during the
382 microemulsion process, resulting in nanoparticles with physico-
383 structural properties close to those obtained using the $\text{K}_4[\text{Re}_6\text{S}_8-$
384 $(\text{OH})_6]$ precursor.

385 All of the cluster-based nanoparticles studied in this work are
386 30 nm in size with good monodispersity and exhibit a perfectly
387 spherical shape. The cluster units are homogeneously dispersed

inside the nanoparticles. A very important feature is that when 388
embedded in silica the luminescence of the clusters is not quenched 389
by oxygen in solution. 390

Toxicological studies are currently performed to evaluate the 391
toxicological potential of such nanoparticles. If the silica shell 392
efficiently proves to prevent any toxic effect from the metal atom 393
clusters, then such material will have numerous potential applica- 394
tions in the field of biotechnology. 395

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