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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 nano-24 materials are based on octahedral metal atom clusters (M_6 , with 25 M = Mo, W, and Re) characterized by metal-metal bonds.^{1,2} 26 The M_6 cluster is surrounded by eight face-capping ligands (L^i , i =27 inner) to form a rigid $M_6Y^i_{\ 8}$ core that is coordinated to six 28 terminal ligands (L^a , a = apical) leading to an $M_6Y_8^iX_6^a$ neutral 29 or anionic unit (Y = chalocogen and/or halogen; X = halogen). 30 Solid-state materials based on such M₆Yⁱ₈X^a₆ units are easily 31 synthesized at high temperature. They have been studied for many 32 33 years for their interesting transport, catalytic, and electronic properties.³⁻⁷ Many routes now afford soluble inorganic cluster 34 precursors for soft chemistry synthesis.^{8,9} Indeed, owing to their 35 nanosized shape and their structural, redox, and photoluminescence 36

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properties, M₆Yⁱ₈X^a₆ anionic units constitute relevant building blocks for the elaboration of supramolecular assemblies, nano-materials, 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- $[\text{Re}_{6}\text{Q}_{7}^{1}\text{Br}^{1}(\text{pyz})^{a}_{3}\text{Br}^{a}_{3}] \cdot x\text{H}_{2}\text{O}$ units that self-assembly via supramolecular interactions to built an original stable cluster-based hybrid framework.¹⁶

Many experimental and theoretical works report on the luminescence properties of Mo₆, W₆, and Re₆ cluster compounds.^{22–27} It is worth noting that they emit in the red and near-infrared

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

In this framework, we recently reported the synthesis of 54 luminescent $Cs_2[Mo_6X_{14}]$ @SiO₂ nanoparticles (X = Cl, Br, or I) 55 via a water-in-oil microemulsion process wherein the cluster units 56 are embedded in monodisperse silica nanoparticles.³⁰ Micro-57 emulsions are thermodynamically stable dispersions of water 58 droplets in an oil phase, stabilized at the interface by surfactants 59 molecules. Those water droplets, also called inverted micelles, are 60 61 below 50 nm in size and constitute a suitable confined reaction medium for the synthesis of a wide variety of well-defined 62 nanoparticles with controlled size and shape.^{31,32} Using a similar 63 approach, structured bifunctional magnetic and luminescent 64 y-Fe₂O₃-Cs₂[Mo₆Br₁₄]@SiO₂ nanoparticles were obtained by 65 the introduction of maghemite nanocrystals at the core of the 66 nanoparticles.³³ Whereas nowadays the luminophores developed 67 for bioimaging and biolabeling technologies are mainly based on 68 organic dyes,^{34,35} inorganic quantum dots,³⁶ or lanthanide based nanocrystals,^{37,38} metal atom clusters such as Re₆ clusters may 69 70 offer complementary assets because they combine the important 71 properties of perfectly reproducible nanosize, photostability, and 72 NIR emission and do not show acute toxic effects.³⁹ 73

In addition to applications in biotechnology, functional silica 74 particles can also find numerous applications in a wide range of fields such as photonics,⁴⁰ catalysis,⁴¹ data storage devices,⁴² cos-75 76 metics,⁴³ and so forth. In this article, we report the preparation of 77 novel NIR-emitting nanoparticles obtained by the encapsulation 78 79 of $[\text{Re}_6\text{Q}_8\text{L}_6]^{4-}$ cluster units (Q = S or Se and L = OH or CN) in 80 silica nanoparticles by an adapted microemulsion process. Several kinds of clusters have been used to study the influence of the 81 nature of inner and apical ligands on the cluster-embedding 82 process as well as on the luminescence properties of embedded 83 clusters. The Re₆ cluster precursors involved in this work were 84

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Figure 1. Schematic representation of a $\text{Re}_6 \text{Qi}_8 \text{L}_6^a$ cluster unit. The Re_6 cluster core is represented as a gray octahedron. Inner ligands ($\text{Qi}^i = \text{S or Se}$) are in the face-capping position, and apical ligands ($\text{L}^a = \text{OH}$, CN or Br) are in terminal positions.

 $K_4[Re_6Q_8(OH)_6]$ (Q = S or Se), $Cs_4[Re_6S_8Br_6]$, and $Cs_{1.68}K_{2.32}$ -85 $[Re_6S_8(CN)_4(OH)_2]$. These Re₆ clusters are all luminescent in the 86 red and NIR fields, with luminescence lifetimes of a few micro-seconds depending on the ligands.^{25,44} It turns out that apical 87 88 bromine in $[\text{Re}_6\text{S}^i_8\text{Br}^a_6]^{4-}$ units are quite labile under preparation 89 conditions and are replaced by hydroxo groups during the 90 embedding process but CN groups from [Re₆S₈(CN)₄(OH)₂]⁴⁻ 91 are not exchanged. We show that the luminescence properties of 92 clusters are preserved after they are embedded in a silica matrix. 93 An important finding is that although the luminescence of the 94 $[\operatorname{Re}_6 Q_8 L_6]^{4-}$ cluster units is originally quenched by oxygen in 95 aqueous solutions, their luminescence properties are preserved in 96 solution after they are embedded in silica nanoparticles. 97

2. Experimental Section

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

2.2. Synthesis of Re₆ Clusters. Hexanuclear rhenium clus-109 ters consist of six metal atoms forming an octahedron linked to 110 eight chalcogen inner ligands (here S or Se) capping the faces of 111 the octahedron, plus six apical ligands (here OH, Br, or CN) in the 112 terminal positions of the octahedron. For illustration, a generic 113 $\text{Re}_6 \text{Q}_8^{1} \text{L}_6^{1}$ cluster unit is represented in Figure 1. The whole 114 F1 cluster unit is roughly 1 nm in size, depending on the nature of 115 the apical ligands, and is negatively charged; it therefore needs to 116 be charge balanced by counter cations in the solid state (here Cs or 117 K). Most of the clusters are prepared by gas-solid or solid-solid 118 synthesis and generally at high temperature. The cluster precur-119 sors used in this study were prepared according to well-known procedures reported in the literature.^{45–47} They are briefly de-120 121 scribed in this section and summarized in Scheme 1. 122 S1

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Cs₄[Re₂Sⁱ₂Br^a₂]

^a In bold.

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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 123 S), and liquid Br₂ were mixed in stoichiometric proportions, 124 sealed under vacuum, and held at 850 °C for 2 days to obtain 125 126 binary chalcogenide compound Re₆Se₈Br₂ (or Re₆S₈Br₂, re-127 spectively). This binary compound was then mixed with KOH and held at 200 °C (or 280 °C, respectively) in ambient air to 128 obtain K₄[Re₆Se₈(OH)₆] (or K₄[Re₆S₈(OH)₆], respectively). 129 130

2.2.2. $Cs_4[Re_6S_8Br_6]$.⁴⁷ Cs₄[Re₆S₈Br₆] was prepared by the reaction of K₄[Re₆S₈(OH)₆] with CsBr in a water solution and with the pH adjusted to 2 with HBr. 132

2.2.3. $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]$.⁴⁶ ReS₂ was prepared 133 by the reaction of Re with S under vacuum at 450 °C for 2 days. 134 Cs₄[Re₆S₉(CN)₄] was then synthesized by the reaction of ReS₂ 135 with KCN in the presence of excess CsCl at 650 °C for 48 h. 45 136 Finally, $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]$ was obtained by the reac-137 tion of Cs₄[Re₆S₉(CN)₄] with KOH in water, which had been 138 139 boiled for 24 h.

2.3. Synthesis of A₄[Re₆Q₈L₆]@SiO₂ Nanoparticles. 140 141 The $A_4[Re_6Q_8L_6]$ @SiO₂ nanoparticles were prepared through a microemulsion process adapted from a previously reported synthe-142 sis for the encapsulation of nanocrystals $(CeO_2 \text{ or } ZnFe_2O_4)^{48,49}$ 143 or hexamolybdenum clusters in silica nanoparticles,³⁰ and this is 144 F2 145 illustrated in Figure 2. For all of the syntheses described here, the 146 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 147

aqueous cluster sol, 1.3 mL of ammonia, and 2 mL of TEOS. To 148 create the microemulsion, heptane (oil phase) was first mixed with 149 Brij30 (surfactant), and then an aqueous ammonia solution and 150 an aqueous cluster sol were slowly added to the mixture. The 151 aqueous cluster sol was obtained simply by solubilization of the 152 cluster precursor in water. Depending on the solubility, the cluster 153 concentration in the final aqueous phase could be adjusted. For 154 $K_4[Re_6S_8(OH)_6]$ and $K_4[Re_6Se_8(OH)_6]$, this concentration was 155 limited to 5 mM whereas it could reach 16 mM for Cs₄[Re₆S₈Br₆] 156 and 25 mM for Cs1.68K2.32[Re6(CN)4(OH)2]. Once the micro-157 emulsion became a clear, stable solution, the silica precursor 158 (TEOS) was added for the synthesis of the silica shell that 159 occurred directly inside the aqueous nanodroplets already con-160 taining the cluster units. After the addition of TEOS, the reaction 161 was stirred for 3 days and then the microemulsion was destabilized 162 with ethanol and the nanoparticles were washed twice with an 163 ethanol/heptane mixture (3:1 volume ratio) by centrifuging at 164 5000 rpm. Note that before destabilization of the microemulsion, 165 the nanoparticle surface can be easily functionalized by the addi-166 tion of a functional organosilane precursor. Finally, the nano-167 particles could be either redispersed in solution (water or ethanol) 168 or dried in ambient air. 169

Cs_{1.68}K_{2.32}[Re₆Sⁱ₈(CN)^a₄(OH)^a₅]

2.4. Characterization of Materials. The external morphol-170 ogy of the nanoparticles was studied by field emission scanning 171 electron microscopy (FE-SEM) with a Hitachi SU8000 working 172 at an acceleration voltage of 10 kV. For FE-SEM observations, 173 the nanoparticles were deposited on a silicon wafer and coated 174 with a 3 nm layer of platinum using a JEOL JFC-1600 auto fine 175 coater to enhance the conductivity of the sample. The micro-176 structure of the nanoparticles and the distribution of the cluster 177 units were observed using a scanning transmission electron 178 microscope (Hitachi High-Technologies, HD-2300C) equipped 179 with a spherical aberration corrector (CEOS GmbH, CESCOR) 180 and working in annular dark-field mode (ADF-STEM).^{50,51} The 181 acceleration voltage was 200 kV, the convergent semiangle was 182 27.5 mrad, and the inner angle of the annular dark-field detector 183 was 80 mrad. The spatial resolution of the instrument was about 184 0.1 nm. For ADF-STEM observation, the nanoparticles were 185 dispersed on a thin carbon film whose thickness was about 6 nm. 186 Investigations of the photoluminescence properties were performed 187 in the solid state with a Jobin Yvon Fluorolog-3 fluorescence 188 spectrometer (FL3-22, Horiba Jobin Yvon). The vibrational 189 spectra were recorded with a Raman Bruker IFS 28 spectrometer 190 equipped with a FRA 106 module. The excitation source was 191 provided by a Nd:YAG laser working at 1064 nm. The power of the 192

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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 micro-197 emulsion and its mechanism have already been widely studied and 198 described in the literature. $^{52-54}$ It is a classical sol-gel process where 199 200 an alkoxide precursor of silica (TEOS) is hydrolyzed, followed by 201 the condensation of silica monomers. In the microemulsion, TEOS is first soluble in the heptane phase but is hydrolyzed by diffusion 202 upon contact with the aqueous inverted micelles. The hydrolyzed 203 silica monomers are then soluble in the aqueous phase, where they 204 can condense via a base-catalyzed reaction. 205

The key point in the embedding of clusters in silica nano-206 particles through this microemulsion process is to obtain stable 207 cluster sols by avoiding the aggregation and precipitation of cluster 208 units. Recall that for the preparation of the previously reported 209 210 $Cs_2[Mo_6X_{14}]$ (a)SiO₂ nanoparticles, the cluster units were solubilized in a water-ethanol mixture (1:1 v/v) and the pH was adjusted to 211 2 with bromic acid^{30,31} in order to avoid the exchange of apical 212 bromine by OH groups or water molecules and the subsequent 213 precipitation of cluster units.⁵⁵ In the latter work, TEOS was added 214 prior to ammonia and its hydrolysis was acid-catalyzed, thanks to 215 the acidic aqueous cluster sol. Finally, ammonia was added to 216 allow the base-catalyzed condensation of the silica matrix. 217

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

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Figure 4. ADF-STEM pictures of $K_4[Re_6S_8(OH)_6]$ @SiO₂ nanoparticles with discrete cluster units (bright spots).

positions, Brylev et al.44 showed that, depending on the pH, 222 hexahydroxo rhenium clusters $[Re_6Q_8(OH)_6]^{4-}$ can form aqua-223 hydroxo and hexaaqua cluster complexes with the general formula $[\text{Re}_6\text{Q}_8(\text{H}_2\text{O})_n(\text{OH})_{6-n}]^{n-4}$ (Q = S or Se; n = 0-6) because of 224 225 the possible protonation of the apical -OH ligands. Such a pheno-226 menon would induce changes in the composition and structure of 227 the clusters, which might result in modifications of the lumines-228 cence characteristics or even precipitation of the clusters and 229 therefore destabilization of the microemulsion. For instance, the 230 $[\text{Re}_6\text{Se}_8(\text{OH})_6]^{4-}$ cluster units remains stable in water at pH ~14, 231 whereas they fully precipitate at neutral pH because of the forma-232 tion of [Re₆Se₈(H₂O)₄(OH)₂] clusters.⁴⁴ 233

For the preparation of $A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles, the 234 cluster precursors were initially dissolved in water. Then, to 235 prevent any change in the luminescence properties and to avoid 236 precipitation of the clusters due to low pH, the microemulsions 237 were prepared by adding ammonia to the heptane/Brij30 mixture 238 prior to the aqueous cluster sol and prior to TEOS, so both the 239 hydrolysis and condensation steps in the silica synthesis were 240 base-catalyzed. The nanoparticles were then prepared according 241 to the procedure described in section 2.3. 242

3.2. Nanoparticle Morphology and Microstructure. The 243 as-prepared nanoparticles were observed by FE-SEM. The image 244 analyses of A4[Re₆Q₈L₆]@SiO₂ nanoparticles (Figure 3) showed 245 F3 that they all exhibit a perfectly spherical, monodisperse morphol-246 ogy with an average diameter of 30 nm for the synthesis condi-247 tions described in section 2.3. Supplementary experiments showed 248 that the size of the nanoparticles does not depend on the cluster 249 concentration in the aqueous phase. To study the microstructure 250 of the nanoparticles and confirm the encapsulation of the cluster 251 units, the ADF-STEM technique is the only suitable tool because 2.52 of the size of the cluster units (1 nm). Indeed, by detecting 253 electrons scattered at high angles this technique provides what 254 is known as Z-contrast images because atoms with high atomic 255 numbers will be more scattered at high angle than atoms with 256 lower atomic numbers. Thus, thanks to the large difference in 257 electron numbers between the Re cluster core and Si or O from the 258 silica matrix and the high spatial resolution of the STEM, it was 259 possible to visualize the cluster units inside the nanoparticles. For 260 example, Figure 4 shows an ADF-STEM image of K₄[Re₆S₈-261 F4 (OH)₆]@SiO₂ nanoparticles where cluster units are visible as 262 bright spots of about 1 nm in size. This image confirms that 263

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Figure 5. Normalized excitation and emission spectra (corrected signals) for both $A_4[Re_6Q_8L_6]$ cluster precursors (---) and $A_4[Re_6Q_8L_6]$ @ SiO₂ 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 $A_4[Re_6Q_8L_6]$ @SiO₂ Nanoparticles

$A_4[Re_6Q_8L_6]$ cluster precursor	$\lambda_{\rm em} (\rm nm)$	$A_4[Re_6Q_8L_6]@SiO_2$ nanoparticles	$\lambda_{\rm em} ({\rm nm})$
$K_4[Re_6S_8(OH)_6]$	680	K ₄ [Re ₆ S 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 ₆ S ₈ (CN) ₄ (OH) ₂]@SiO ₂	760
$Cs_4[Re_6S_8Br_6]$	800	$Cs_4[Re_6S_8Br_6]@SiO_2$	700

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

3.3. Luminescence Properties. The successful encapsulation 266 of the cluster units in the silica nanoparticles was also evidenced 267 by studying the luminescence properties of $A_4[Re_6Q_8L_6]@SiO_2$ 268 nanoparticles. The luminescence properties were investigated in 269 the solid state for both the $A_4[Re_6Q^i_8L^a_6]$ cluster precursors and 270 the corresponding $A_4[Re_6Q_8L_6]$ @SiO₂ nanoparticles. In Figure 5, F5 271 the excitation and emission spectra for each type of cluster are 272 plotted, and in Table 1, the wavelength values at the emission T1 273 maximum (λ_{em}) are summarized. 274

The encapsulation of the $[\operatorname{Re}_6 Q^i_8(OH)^a_6]^{4-}$ (Q = Se or S) and 275 $[\text{Re}_6\text{S}_8^i(\text{CN})^a_4(\text{OH})^a_2]^{4-}$ cluster units in the silica matrix resulted 276 in a slight shift of the emission maxima after embedding, but the 277 shape of the emission spectrum remained unchanged (Figure 5a-c). 278 The emission maxima shifts, ranging from 10 to 20 nm, to higher 279 wavelengths between solid-state precursors and the nanoparticles 280 must be due to some perturbations of the molecular orbital 281 diagram of $[\text{Re}_6\text{Q}_8^{i}\text{L}_6^{a}]^{4-1}$ units after embedding. One could suspect 282 a slight decrease in the energy gap between excited and funda-283 mental states. 284

Some questions arose concerning the embedding of $[Re_6S_8^iBr_6]^{4-}$ units in silica nanoparticles. Indeed, the emission maxima for $[Re_6S_8^iBr_6]^{4-}$ units decreased from 800 nm in the $Cs_4[Re_6S_8Br_6]$ precursor to 700 nm after embedding in the silica matrix (Figure 5d). A closer look at the emission spectra shows that the shape of the emission spectrum of $Cs_4[Re_6S_8Br_6]@SiO_2$ nanoparticles (Figure 5d) and that of $K_4[Re_6S_8(OH)_6]@SiO_2$ nanoparticles (Figure 5b)



Figure 6. Aqueous solution of $[\text{Re}_6\text{S}_8(\text{OH})_6]^{4-}$ clusters (a) before and (b) after embedding in silica nanoparticles, under daylight (left picture) and under UV irradiation at 365 nm (right picture).

match perfectly. This drastic change between the luminescence 292 properties of the starting and embedded clusters can then be 293 explained by an exchange of -Br apical ligands for -OH groups 294 during the microemulsion process. In an attempt to avoid this 295 structural modification, another synthesis of $Cs_4[Re_6S_8Br_6]$ 296 SiO₂ nanoparticles was performed using acidic cluster sols (in which 297 the pH was adjusted to 2 with HBr) either in a pure water solution 298 or in a water/ethanol mixture (1:1 v/v). In both cases, the micro-299 emulsion stability was not affected but the resulting nanoparticles 300 still show a luminescence shift to lower wavelengths, probably as a 301



Figure 7. Raman spectra for both A₄[Re₆Q₈L₆] cluster precursors (---) and A₄[Re₆Q₈L₆]@SiO₂ nanoparticles (—) for (a) K₄[Re₆Se₈(OH)₆], (b) K₄[Re₆S₈(OH)₆], (c) Cs_{1.68}K_{2.32}[Re₆S₈(CN)₄(OH)₂], and (d) Cs₄[Re₆S₈Br₆].

302result of the exchange of apical bromine ligands for hydroxyl303groups. Nonetheless and as previously mentioned, $Cs_2[Mo_6Br_{14}]@$ 304SiO_2 nanoparticles prepared with a water/ethanol acidic cluster sol305(pH adjusted to 2 with HBr) did not show any luminescence shift,306meaning that no ligand exchange occurred during the encapsulation307process. This indicates that Re-Br^a bonds are much weaker than308Mo-Br^a bonds in an aqueous-alcoholic medium.

Concerning the excitation spectra, the encapsulation of the 309 clusters in a silica matrix resulted in a lowering of the efficiency of 310 311 excitation in the range of 400 to 600 nm. Once more in the case of $Cs_4[Re_6S_8Br_6]$ (a)SiO₂ the excitation spectrum radically changed 312 compared to that of the Cs₄[Re₆S₈Br₆] precursor (Figure 5d) and 313 perfectly match the excitation spectrum of $K_4[Re_6S_8(OH)_6]$ 314 SiO_2 (Figure 5b). This finding again indicates that -Br apical 315 ligands of [Re₆S₈Br₆]⁴⁻ cluster units might be substituted for 316 -OH groups during the microemulsion process.

The luminescence of clusters is usually quenched in solution 318 because of the presence of solubilized oxygen. Indeed, it has been 319 known for many years that excited octahedral clusters can be 320 relaxed through the creation of singlet oxygen.⁵⁶ This quenching 321 effect was successfully prevented by embedding the cluster units in 322 silica nanoparticles. For illustration, Figure 6 shows a compar-F6 323 ison between the luminescence properties of $[Re_6S_8(OH)_6]^{4-1}$ 324 cluster units in a water solution and after being embedded in 325 silica nanoparticles under normal light and under UV irradiation 326 at 365 nm. The $[\text{Re}_6\text{S}_8(\text{OH})_6]^{4-}$ clusters show luminescence only 327 when they are embedded in the silica matrix because they are then 328 protected from the presence of solubilized oxygen and their 329 330 luminescence is no longer quenched.

3.4. Raman Study. The vibrational properties of the A₄- **3.4. Raman Study.** The vibrational properties of the A₄- **3.5.** [Re₆Q₈L₆] cluster precursors and those of A₄[Re₆Q₈L₆]@SiO₂ **3.6.** nanoparticles were investigated by Raman spectroscopy. The **3.7.** characterization of M₆Qⁱ₈L^a₆ units by Raman spectroscopy is **3.7.** not usual. The few published results show typical vibrations in the **3.7.** by the symmetry of the M₆Qⁱ₈L^a₆ units deviates from O_h symmetry. On the basis of the experimental and theoretical 338 Raman investigations performed on $\text{Re}_6\text{Q}_8^{i}\text{L}_6^{a}$ -cluster-unitbased compounds by Gray et al.,⁵⁷ it turns out that the Raman 340 bands correspond to different kinds of L_6^{a} , Q_8^{i} , and Re_6 breathing 341 modes. 342

The Raman spectra of the cluster precursors and of the 343 corresponding cluster-based silica nanoparticles are represented 344 in Figure 7. For all of the sulfide derivates (Figure 7b-d), the 345 F7 strong peaks at 280 and 430 cm⁻¹ are easily identifiable in spectra 346 of corresponding A₄[Re₆Q₈L₆]@SiO₂ nanoparticles and are 347 respectively attributed to the T_{2g} vibrational mode and the A_{1g} -348 symmetric S_8 breathing mode of the clusters. For $Cs_{1.68}K_{2.32}$ -349 $[Re_6S_8(CN)_4(OH)_2]$ @SiO₂, another strong peak is easily identifi-350 able at 2120 cm⁻¹ (data not shown here), which is due to the A_{1g} 351 vibrational mode of the CN groups. Concerning K₄[Re₆Se₈-352 $(OH)_6]$ @SiO₂ nanoparticles (Figure 7a), the two intense peaks 353 at 200 and 260 cm⁻¹ can be observed and attributed to the T_{2g} and 354 Se₈-A_{1g} vibrational modes, respectively, although they are slightly 355 shifted (about 10 cm^{-1}) compared to the corresponding peaks in 356 the starting cluster precursor. The spectra of $K_4Re_6Se_8(OH)_6(a)$ 357 SiO_2 , $K_4Re_6S_8(OH)_6@SiO_2$, and $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2]@$ 358 SiO₂ nanoparticles exhibit all of the typical Raman signatures of 359 the corresponding cluster precursor. This consequently confirms 360 the successful encapsulation of the cluster units without signifi-361 cant structural modification. In contrast, the spectrum of Cs₄-362 $[Re_6S_8Br_6]$ @SiO₂ nanoparticles does not fully agree with the 363 Raman signature of the Cs₄[Re₆S₈Br₆] cluster precursor. Actu-364 ally, the shape of the Raman spectrum for $Cs_4[Re_6S_8Br_6]@SiO_2$ 365 nanoparticles (Figure 7d) is similar to the spectrum of the 366 $K_4[Re_6S_8(OH)_6]$ @SiO₂ nanoparticles (Figure 7b). Moreover, in 367 Figure 7d the two intense peaks at 140 and 160 cm^{-1} , which were 368 attributed to Re-Br^a vibrational modes by Gray et al., are clearly 369

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identifiable in the $Cs_4[Re_6S_8Br_6]$ compound but absent in the $Cs_4[Re_6S_8Br_6]@SiO_2$ nanoparticles. This observation shows that apical -Br ligands of $[Re_6S_8Br_6]^{4-}$ clusters are removed during the encapsulation process.

4. Conclusions

NIR-emitting nanoparticles were achieved by embedding 375 376 hexarhenium clusters in silica nanoparticles using an adapted 377 microemulsion process. K₄[Re₆S₈(OH)₆], K₄[Re₆Se₈(OH)₆], and Cs1.68K2.32[Re6S8(CN)4(OH)2] were successfully encapsulated 378 without any drastic changes in their luminescence properties. 379 Attempts to embed Cs₄[Re₆S₈Br₆] quaternary precursor in silica 380 nanoparticles led to an exchange of apical -Br ligands during the 381 microemulsion process, resulting in nanoparticles with physico-382 structural properties close to those obtained using the K₄[Re₆S₈-383 (OH)₆] precursor. 384

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 embedded in silica the luminescence of the clusters is not quenched by oxygen in solution.

Toxicological studies are currently performed to evaluate the391toxicological potential of such nanoparticles. If the silica shell392efficiently proves to prevent any toxic effect from the metal atom393clusters, then such material will have numerous potential applica-394tions in the field of biotechnology.395

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