Synthesis and Characterizations of YVO₄:Eu Colloids

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We present a new process for the synthesis of colloidal europium-doped yttrium vanadate with a particle diameter of about 10 nm. Nanocrystals are produced by precipitation of citrate complexes of rare-earth salts with sodium orthovanadate. NMR and IR studies show that the interaction between citrate ligands and lanthanide ions limits the growth of particles and ensures the stability of the colloidal solutions through electrostatic and steric repulsions. The optimized process leads to stable and highly concentrated transparent colloidal solutions in water (up to 400 g·L⁻¹).

Introduction

New technologies for display applications require the development of materials for the production of light.[1] An increasing part of research in this field is devoted to the study of potential applications of luminescent nanoparticles. A huge amount of work has already been performed on II−VI semiconductors, whose synthesis through colloidal chemistry techniques leads to a very good control of the particle size in the 2−10 nm range.[2]

Semiconductors or insulators doped with luminescent ions (transition or rare-earth ions) represent another class of highly luminescent materials.[3] In these compounds, the mechanism of the emission is different from the intrinsic recombination in pure semiconductors. Emission occurs from transitions within the electronic configuration of the doping ion, with a characteristic wavelength depending mostly on its nature.

A few studies have been reported on the synthesis of nanoparticles doped with luminescent ions. CdS and ZnS doped with either transition ions (Mn²⁺ and Cu²⁺)[4] or rare-earth ions (Eu²⁺/³⁺, Tb³⁺, and Sm³⁺)[5] have been prepared through colloidal routes. Much less work has been devoted to oxide materials such as gadolinium or yttrium oxides doped with rare-earth ions.[6,7] Indeed, the main limitation for the synthesis of these compounds comes from their high temperature of crystallization (>900 °C), which prevents any control of the grain size, dispersion, and surface state.

This limitation can be avoided when studying ternary oxide materials such as rare-earth phosphates or vanadates. These compounds can crystallize at low temperature, thus opening the way toward their synthesis as nanoparticles through colloidal chemistry. Recently, Riwotzki and Haase[8] and we[9] focused our attention on rare-earth-doped vanadates, which present a high conversion efficiency in the bulk state. Their high luminescence quantum yields (70% for the Eu³⁺ doping ion[10]) are essentially the consequence of the efficient energy transfer from the vanadate host matrix to the localized states of the doping ion, which may then occur before any nonradiative recombination. In both studies, YVO₄: Eu particles of about 10−30 nm were obtained with a red luminescence quantum yield of 15%. Nevertheless, the involved synthesis routes did not enable a good control of the size because it was found impossible to obtain particles with a lower size. Moreover, these colloids were only stabilized by electrostatic interactions between particles, whose strength was not sufficient to obtain transparent concentrated colloids.

We present here a new process for the synthesis of colloidal europium-doped yttrium vanadate using well-known citrate complexing agents both to limit the size of particles and to increase their stability. This allows one to prepare stable and highly concentrated transparent colloidal solutions in water with an average particle diameter of about 10 nm. We report on the mechanism of the formation of the particles, involving the precipitation of citrate complexes of rare-earth salts with sodium orthovanadate. Optical properties such as the red

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luminescence quantum yield and the $^5D_0$ lifetime of europium ions are investigated and discussed in relation with the doping concentration and the surface state of the nanoparticles.

Experimental Section

Synthesis of the YVO4:Eu Nanoparticles. The whole synthesis was carried out in water at 60 °C. A 0.1 mol·L^{-1} solution of (Y,Eu)(NO$_3$)$_3$ (10 mL and 1 mmol) was mixed with a 0.1 mol·L^{-1} solution of sodium citrate (7.5 mL and 0.75 mmol). This led to the formation of a white precipitate of lanthanide citrate, which was completely dissolved by the addition of a 0.1 mol·L^{-1} solution of Na$_3$VO$_4$ (7.5 mL and 0.75 mmol), whose pH was fixed at 12.5 using sodium hydroxide. The clear and colorless resulting mixture, whose pH was 8.4, was subsequently aged at 60 °C for 30 min. Finally, the solution was cooled and dialyzed against water (ionic conductivity of 6 μS·cm^{-1}) to remove the excess ions. A dialysis membrane tubing with a molecular weight cutoff of 12 000 Da (pore size of about 2.5 nm) was used, and the water was renewed each 12 h (the water/colloid volume ratio is 100).

After 24 h of dialysis, the ionic conductivity of the transparent colloid was progressively decreased from 8 mS·cm^{-1} to 400 μS·cm^{-1}. The concentration of the transparent colloidal solutions obtained at this step was 10^{-2} M. The elimination of water at rotary evaporator under mild conditions (40 °C under vacuum) led to powders of nanocrystals or transparent colloidal solutions with a concentration of up to 400 g·L^{-1}. After 3 days of dialysis, the ionic conductivity of the colloid was 10 μS·cm^{-1}. Colloidal solutions became then slightly opalescent after aging because of a partial aggregation of nanoparticles.

Characterization. ^{51}V NMR characterizations of colloids were achieved on a Bruker MSL 360 spectrometer operating at 94.6 MHz. VOCl$_3$ was taken as the reference for the ^{51}V chemical shift. The optimum 90° pulse length and decay time were determined to be 11 μs and 1 s, respectively. A total of 1024 spectra were accumulated. ^{1}H NMR spectra were recorded on a Varian Unity Inova 500 operating at 500 MHz (pulse duration of 13.3 μs and recycle decay of 6.4 s). Chemical shifts were reported relative to tetramethylsilane (TMS). The water signal was eliminated using a presaturation sequence.

Dynamic light scattering experiments were carried out with a PCS light scattering equipment supplied by Malvern. Absorption spectra were recorded on a Shimadzu 1600 A spectrophotometer. Europium luminescence spectra as well as lifetime measurements were recorded on a Hitachi F-4500 spectrofluorometer. The quantum yields were determined by comparing the integrated emission of the colloidal solutions with the emission from a Rhodamine 6G solution in ethanol having the same optical density (OD < 0.3) and excited at the same wavelength (280 nm).

X-ray diffraction (XRD) studies were performed on the powders of nanocrystals using a Philips X-Pert diffractometer with Cu Kα radiation (λ = 1.54 Å). Transmission electron microscopy (TEM) was performed using a Philips CM 30 microscope operating at 300 kV. Samples were prepared by depositing a droplet of colloidal solution on a carbon film.

IR spectra were recorded on a Fourier transform Bomem MB 100. Samples were prepared by spreading colloids on silicon wafers.

Results and Discussion

Growth of the Nanoparticles. In all of the following experiments, the citrate/yttrium molar ratio is 0.75. This value has been fixed after preliminary experiments which have shown that both a lower (0.50) and a higher (1.0) ratio led to opaque solutions of aggregated particles. A low citrate/yttrium ratio is probably not sufficient to stabilize particles which aggregate. When the ratio is too high, the decomposition of the yttrium citrate
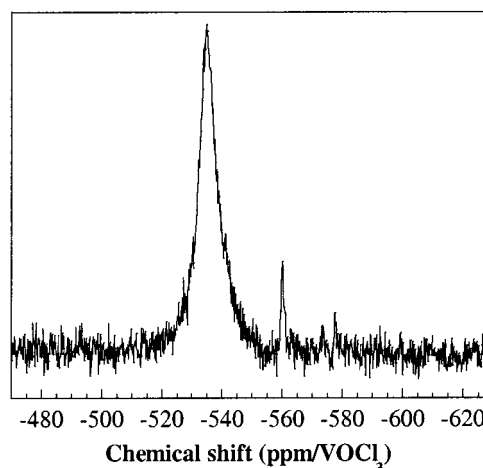

Figure 1. ^{51}V NMR spectrum after addition of 0.50 equiv of the vanadate solution in a mixture containing 1 mol equiv of (Y,Eu)(NO$_3$)$_3$ and 0.75 mol equiv of sodium citrate in water.

complex rapidly results in the aggregation of uncharacterized particles.

As previously discussed,[9] the pH of the aqueous vanadate solution is a crucial parameter for the synthesis. We find here that when the pH is higher than 12.8, the reaction does not take place. This may be explained by the fact that only very small particles of Y(OH)$_3$ are precipitated instead of YVO$_4$. On the contrary, when the pH is lower than 12.2, the color of the colloidal solution turns yellow, which may be attributed to the formation of polyvanadate species.[11] As a consequence, the optimum pH is found to be 12.5.

A Na$_3$VO$_4$ solution (pH = 12.5) is then added dropwise at 60 °C to a mixture of 1 equiv of (Y,Eu)(NO$_3$)$_3$ and 0.75 equiv of sodium citrate. The formation of nanoparticles is studied for a vanadate/yttrium molar ratio ranging from 0.5 to 1. In all cases, the clear solution resulting from the addition of the vanadate solution into the mixture of (yttrium, europium) and citrate is aged at 60 °C. Samples are then taken from the solution at different times, cooled to stop the reaction, and finally characterized by ^{1}H and ^{51}V NMR, luminescence spectroscopy, and dynamic light scattering.

NMR spectroscopy is used to determine the different vanadate species present during the course of the synthesis, the growth mechanism, and the advancement state of the reaction. The red luminescence of the colloidal solutions of YVO$_4$:Eu upon UV excitation is found to be a powerful tool to characterize the formation of the nanoparticles. Indeed, in a rough approximation, the intensity of the emission is directly related to the number of europium ions incorporated into the vanadate host matrix and, therefore, to the number of synthesized nanoparticles. Eventually, dynamic light scattering measurements are performed on the colloidal solutions to determine the variation of the hydrodynamic diameter of the growing nanoparticles.

After addition of 0.50 equiv of the vanadate solution, the resulting clear mixture is very slightly luminescent upon UV excitation. Its ^{51}V NMR spectrum (Figure 1) essentially exhibits a large band at −535 ppm (a weakly intense peak is also detected at −560 ppm attributed

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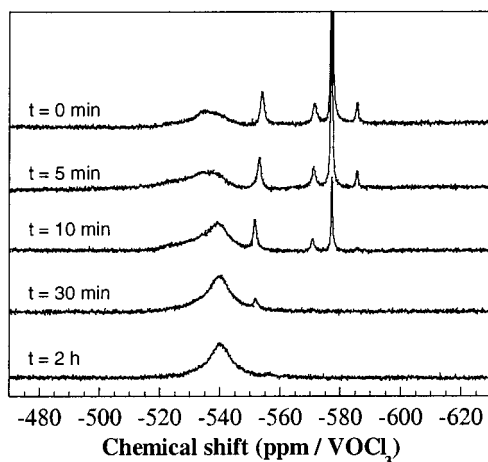
Figure 2. ^{51}V NMR spectra of the $Y_{0.95}Eu_{0.05}VO_4$ colloid taken at different reaction times. Colloid was obtained by aging at 60 °C of a clear solution obtained by adding 0.75 mol equiv of the vanadate solution in a mixture containing 1 equiv of $(Y,Eu)(NO_3)_3$ and 0.75 mol equiv of sodium citrate in water.

to the presence of a small amount of $(V_2O_7)^{4-}$ free species). A large band was also observed on the ^{1}H NMR spectrum, showing that the chemical surroundings of the citrate groups are not well defined. Besides, light scattering measurement did not allow one to measure any particle size, discrediting the presence of nanoparticles. Finally, the solid obtained after flocculation with magnesium nitrate is found to be amorphous by XRD. It can be assumed from these results that all of the vanadate species are engaged into water-soluble oligomeric species of yttrium vanadate citrate, which are responsible for the large band detected at -535 ppm on the ^{51}V NMR spectrum. The chemical shift (-535 ppm) indicates that the structure of the vanadate groups in these uncharacterized oligomeric species is close to the one of VO_4^{3-} orthovanadate groups (-540 ppm). Moreover, it should be noted that, for this particular vanadate/yttrium ratio (0.50), the solutions are perfectly stable and do not evolve toward nanoparticles after aging at 60 °C.

After addition of 1.0 equiv of vanadate, the aging of the solution leads to the growth of nanoparticles (20–30 nm in size from light scattering experiments) which exhibit the usual red luminescence after UV excitation. However, the solution becomes rapidly opaque because of the progressive aggregation of nanoparticles. This obviously suggests use of a vanadate substoichiometry (vanadate/yttrium molar ratio < 1) to improve the stability of nanoparticles through the complexation of yttrium ions by citrate groups at the surface of particles.

We then decided to focus our attention on a vanadate/yttrium molar ratio of 0.75 for which a detailed characterization of the aging process was made. ^{51}V NMR spectra of the $Y_{0.95}Eu_{0.05}VO_4$ colloidal solution at different reaction times are presented in Figure 2. At $t = 0$, one can observe sharp peaks corresponding to molecular species and a large band around -535 ppm. The attribution of the different peaks is deduced from the work of Heath and Howarth (Table 1).[12] The major free molecular group is $(V_4O_{12})^{4-}$, which is fixed by the pH
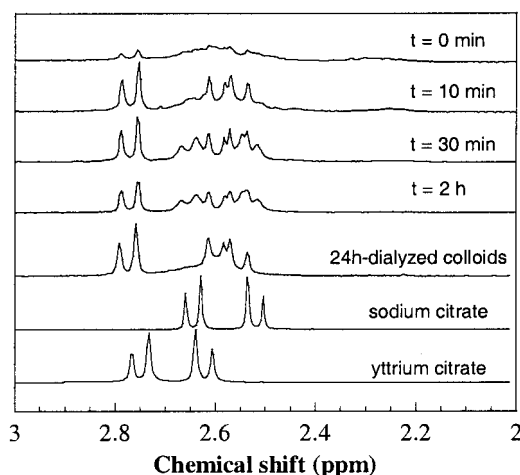
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Figure 3. ^{1}H NMR spectra of the $Y_{0.95}Eu_{0.05}VO_4$ colloid taken at different reaction times (see Figure 2 for experimental conditions). The solution was cooled after 30 min and dialyzed 24 h against water (dialyzed colloids). The spectrum of sodium citrate was recorded on an aqueous molar solution. The spectrum of yttrium citrate was performed on a clear solution prepared by adding 1.5 mol equiv of sodium citrate in an aqueous molar solution of yttrium nitrate.

Table 1. ^{51}V NMR Attribution of the Different Vanadate Species

shift (ppm)	species	shift (ppm)	species
-585	$(V_5O_{15})^{5-}/(V_6O_{18})^{6-}$	-561	$(V_2O_7)^{4-}$
-576	$(V_4O_{12})^{4-}$	-553	$(H_2VO_4)^-$
-570	$(H_2V_2O_7)^{2-}$	-535	vanadate complex

of the solution (pH = 8.4). Using the WIN-FIT program,[13] the large band can be deconvoluted into two large peaks respectively centered at -535 and -540 ppm. The first contribution at -535 ppm corresponds to the oligomeric species previously observed for the particular vanadate/yttrium stoichiometric ratio of 0.50. The second contribution at -540 ppm corresponds to the VO_4^{3-} group and is attributed to the formation of YVO_4 nanoparticles. When the aging time increases, the free molecular species are progressively consumed. Besides, we observe a change of the position and shape of the band initially centered around -535 ppm. Eventually, at $t = 30$ min, all of the free vanadate species have disappeared and the band is now centered at -540 ppm, which is the exact shift known for the VO_4^{3-} group. This indicates the complete transformation of the oligomeric precursor into YVO_4 nanoparticles.

Figure 3 shows ^{1}H NMR spectra of the $Y_{0.95}Eu_{0.05}VO_4$ colloidal solution at different reaction times. Spectra performed on sodium and yttrium citrate solutions are used as references. The spectrum of citrate salts is well-known to be made up of two doublets due to the magnetic inequivalence of the two protons belonging to each CH_2 group of the citrate.[14] Compared with the sodium citrate, the peaks are shifted downfield for the yttrium citrate complex because of its higher cationic charge. In fact, the NMR spectrum of the yttrium citrate complex has been previously interpreted as resulting

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(14) *The Aldrich Library of ^{13}C and ^1H*, edition I; Pouchert, C. J., Behnke, J., Eds.; Aldrich Chemical Co., Inc.: Milwaukee, WI, 1993; Vol. 1, p 860.
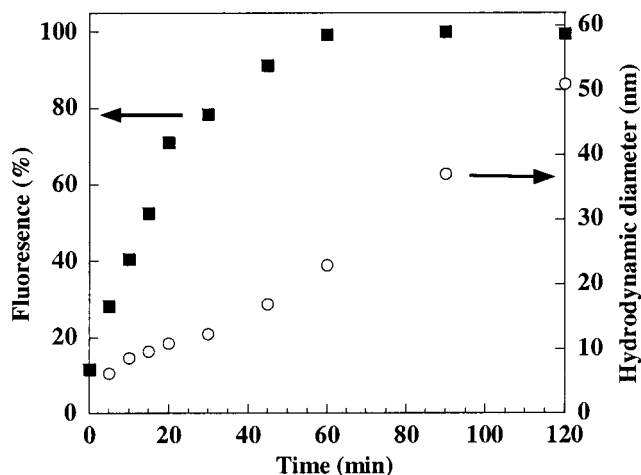
Figure 4. Luminescence intensity and size (hydrodynamic diameter) of colloids at different reaction times.

Figure 5. XRD patterns (Cu Kα) performed on a powder of $Y_{0.95}Eu_{0.05}VO_4$ nanocrystals obtained by drying of as-synthesized colloids (line 1) and on a powder of $Y_{0.95}Eu_{0.05}VO_4$ microcrystals obtained after a thermal treatment at 1000 °C (line 2).

from a rapid equilibrium between two enantiomeric tridentate compounds in which the yttrium cation is complexed by two carboxylate groups and the hydroxyl group of the citrate.[15] Concerning the evolution of the colloidal solution, a large band is observed at $t = 0$ corresponding to the oligomeric species. As the time increases, a complex structure appears which is stabilized after 30 min. An important point is the change of this spectrum in dialyzed solutions. The simplification observed after a dialysis of 24 h can be clearly attributed to the elimination of the sodium citrate which is produced during the transformation of oligomeric species into YVO₄ nanoparticles. The remaining peaks (three doublets) are then attributed to complexing yttrium citrates with a well-defined chemical environment. When the dialysis time increases, one can observe both a broadening of these NMR peaks and a decrease of their intensities. After a long dialysis step (3 days), NMR peaks disappear and a partial aggregation of particles is also observed. Consequently, the evolution of ¹H NMR spectra can be related to both a progressive decrease of the number of citrate groups and the partial aggregation of particles yielding to objects of increasing size which tumble more and more slowly in the solution. The last point accounts for the continuous fall of the signal as a consequence of NMR dipolar broadening, as was previously observed in the case of silica.[16] All of these results clearly indicate that the citrate species are localized near the surface of particles and constitute a complexing shell which contributes to the stability of colloids.

In the same period of time, between $t = 0$ and 30 min, a steep increase of the luminescence intensity of the solution is observed (Figure 4). Light scattering measurements detect the formation of nanoparticles with a hydrodynamic diameter of around 10 nm. In addition, XRD diagrams show the crystalline character of the powder of particles.

These various observations, which clearly mean that yttrium vanadate nanoparticles are synthesized, give us indications on the growth mechanism. It can then
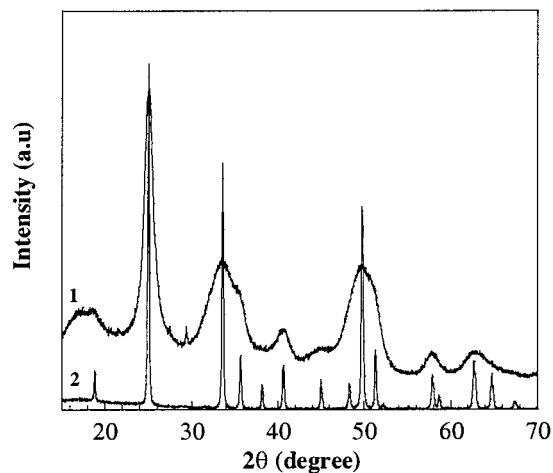
be inferred that the yttrium/vanadate/citrate oligomeric species act as a precursor for the formation of the nanoparticles. The decomposition of the oligomeric entities results in the formation of citrate ions: one part of these ions is released in the solution and the other acts as complexing agents at the surface of the particles.

The evolution of the nanoparticle size also helps us to choose the accurate reaction time, when the conversion rate is maximum without any aggregation. As is shown in Figure 4, the hydrodynamic size of the nanoparticles (10 nm) does not increase much until a 30 min reaction time. At this stage, the conversion rate of the synthesis can be estimated as 80% from the luminescence intensity. The steady increase of the size which is observed afterward is explained by the aggregation of the nanoparticles. Indeed, the size of the crystalline domains, as deduced from XRD measurements performed on nanoparticle powders, is the same for nanoparticles heated either 30 min or 2 h (6−8 nm), discrediting a further growth of the nanoparticles. As a consequence, the accurate reaction time appears to be 30 min, which leads to a very high conversion rate without any aggregation of the nanoparticles. In other words, growth and aggregation processes of the nanoparticles can be dissociated.

Characterizations of the Nanoparticles. (i) Structure. The crystalline phase and the coherence length of the samples were checked by XRD measurements. Figure 5 displays a diagram of a $Y_{0.95}Eu_{0.05}VO_4$ nanoparticle powder. Despite the broadening caused by the small size of the particles, this pattern is found to be in agreement with the zircon-type structure of YVO₄ or EuVO₄.[17] The coherence length was determined from the full width at half-maximum of the diffraction peaks using Sherrer's law. Large deviations from one peak to another are recorded, which shows structural distortions in the nanoparticles probably resulting from surface effects related to the small size. The largest value of the coherence length which approximately corresponds to the average size of the particles, associated with the (200) peak at 25°, is 7 nm. On the contrary, the smallest

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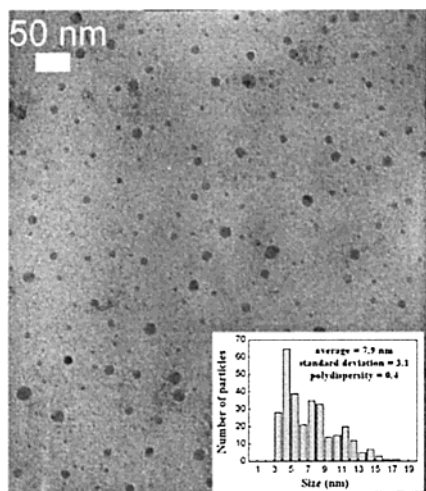(17) Schwarz, Z. *Z. Anorg. Allg. Chem.* **1963**, *322*, 143.

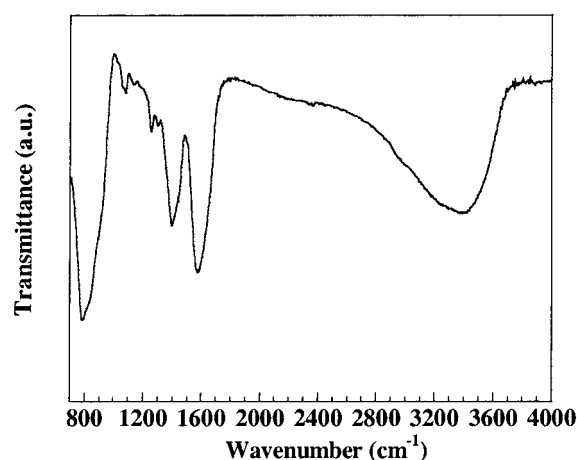**Figure 6.** TEM image of YVO$_4$ nanoparticles. Inset: size distribution curve.

Figure 7. Infrared spectrum of a colloidal solution of Y$_{0.95}$Eu$_{0.05}$VO$_4$ nanoparticles.

value, associated with the (112) peak at 33.5°, is only 3 nm. Concerning the shape of the nanoparticles, a TEM photograph (Figure 6) shows well-dispersed spherical crystallites with an average size of 8 nm and a standard deviation of 3 nm (statistics from 300 particles).

(ii) Stability of the Colloidal Solutions. Figure 7 shows the IR spectrum of dialyzed Y$_{0.95}$Eu$_{0.05}$VO$_4$ nanoparticles. The large band peaking at 792 cm^{-1} is due to the valence vibrations of the V$-$O bond.[18] The two bands at 1396 and 1570 cm^{-1} are respectively ascribed to the symmetrical and asymmetrical valence vibrations of the carboxylate groups. The two small peaks at 1076 and 1256 cm^{-1} correspond to C$-$O stretching bands of the citrate.[19] This clearly attests the presence of the citrate ligands on the surface of the nanoparticles. Taking into account the initial stoichiometry, the citrate/yttrium ratio can be determined using the integration of the IR carboxylate signals. The values are 0.45 and 0.2 after 1 and 3 days of dialysis, respectively.

If we consider again the ^{1}H NMR spectrum of 24 h dialyzed nanoparticles (Figure 3), the existence of three doublets obviously implies at least two types of com-

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(19) Lin-Vien, D.; et al. *The handbook of IR and Raman characteristic frequencies of organic molecules*; Academic Press: New York, 1991; p 137.

Chart 1: Newman Representations for Tridentate (I) and Bidentate (II) Complexations of Yttrium Ions by Citrate Groups in the Complexing Shell of Particles
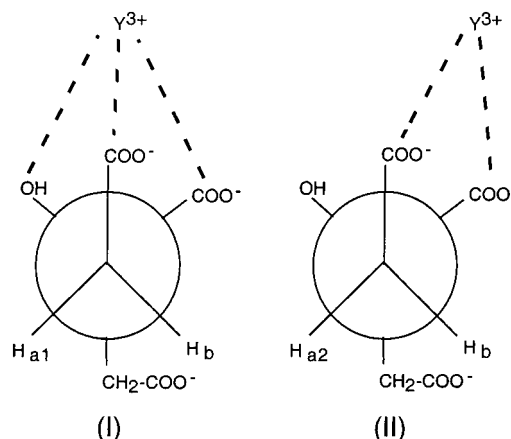
plexation for the citrate ions. One possibility is the superposition of a tridentate complexation as shown in the yttrium citrate complex (two doublets) and a bidentate complexation of yttrium ions by two adjacent carboxylate groups (two doublets). As shown by Newman representations (Chart 1), only the surroundings of one proton of each CH$_2$ group (noted H$_a$) are affected by the change of the complexation mode. The two doublets corresponding to the unaffected proton (noted H$_b$) in each complex are superposed, leading to the presence of three doublets on the NMR spectrum. In agreement with this interpretation, it has to be noted that the intensity of the downfield-shifted doublet is about equal to the sum of the intensities of the two other doublets.

Therefore, the role of citrate is twofold in this synthesis. First, it limits the growth of the nanoparticles through interactions with lanthanide ions. Second, it also ensures the stability of the colloidal solutions through electrostatic (via the COO$^-$ groups) and steric repulsions. The more ligands in the complexing shell of the nanoparticles there are, the better is the stabilization. Therefore, to optimize the covering rate, it appears relevant to have a surface enriched with lanthanide ions rather than vanadate groups. That is why the synthesis is carried out with an excess of lanthanide ions versus vanadate. We found that when the ratio Y/V is equal to 1, the stabilization of the colloidal solutions is more uncertain. In this case, the growth and aggregation steps cannot be clearly separated, certainly because of a shortage of citrate groups on the surface of the nanoparticles.

The fact that the nanoparticles can be easily dispersed into water at very high concentrations (up to 400 g·L^{-1}) also attests to the excellent stability of the colloidal solutions when the dialysis step is controlled. The distribution size (10 ± 3 nm), as measured by light scattering, is exactly the same after dispersion in water of the nanocrystal powder. No aggregation at all occurs through this concentration step, which can be explained by the presence of enough citrate groups in the complexing shell of the nanoparticles.

(iii) Optical Properties. As was previously shown,[8,9] the luminescence spectrum upon UV excitation of Y$_{1-x}$Eu$_x$VO$_4$ colloids is in a large part in agreement with
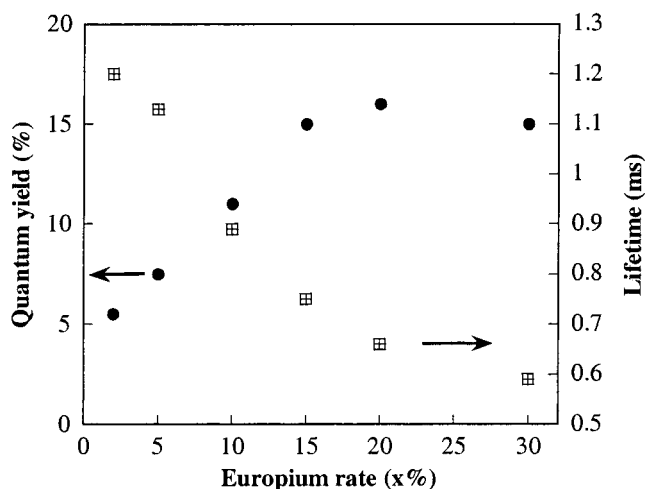
Figure 8. Quantum yields and $^5D_0$ lifetime of a set of $Y_{1-x}Eu_xVO_4$ colloids ($0 < x < 0.5$).

what is reported for the bulk material:[20] the most intense emission is related to the europium $^5D_0-^7F_2$ transition at 617 nm, and the emission mechanism is an energy transfer between the vanadate group, which absorbs the UV light, and the europium ions.

The quantum yields as well as the europium $^5D_0$ lifetimes of a set of $Y_{1-x}Eu_xVO_4$ colloids ($0 < x < 0.3$) are shown in Figure 8. The curve representing the quantum yield as a function of the europium content exhibits a slightly marked maximum of 16% for $x = 0.20$. Meanwhile, the europium $^5D_0$ lifetime steadily decreases with an increasing doping rate (from 1.2 ms for $x = 0.05$ to 0.6 ms for $x = 0.3$). These results obviously contrast with the behavior of the bulk material where the maximum quantum yield is 70% and the $^5D_0$ lifetime for $x = 0.05$ is 0.525 ms. More surprising is the contrast with colloids prepared by Riwotzki and Haase[8] for which the maximum quantum yield of 15% is observed for $x = 0.05$, i.e., as is generally observed in the bulk material.[21] This indicates that the europium ion interactions are less efficient in our colloids, which

could be either due to a better chemical homogeneity as shown by Van Uitert and Johnson[22] in bulk materials or a more important structural disorder which prevents the energy transfers.

Nanoparticles of 7 nm in size are then transferred into deuterated water. This leads to a maximum quantum yield of 37% for the $x = 0.15$ composition and a $^5D_0$ lifetime of 1.5 ms for the $x = 0.05$ composition (15% and 1.1 ms, respectively, in H₂O). The increase of the quantum yield as well as the lifetime is mainly associated with the decrease of the number of OH groups at the surface (isotopic D/H ratio of 98%) which are well-known to be very efficient quenchers of the luminescence of lanthanide elements through multiphonon relaxation.[23] The high value of the $^5D_0$ lifetime in colloids indicates a lower oscillator strength than that in the bulk material, which is probably related to the structural disorder induced by the large surface area of the nanoparticles, making the luminescence quantum yield intrinsically lower than the one in the bulk material.

Conclusion

The key points of the new process to prepare highly luminescent transparent colloids of yttrium vanadate can be summarized as follows: (1) the use of citrate ligands interacting with lanthanide ions, which enables to one limit the growth of the particles and form a complexing shell around the particles which prevent their aggregation; (2) the ability to prepare a homogeneous clear solution containing yttrium/vanadate/citrate oligomer species which can be used as precursors; (3) the progressive decomposition of these precursors by adding sodium vanadate, leading to the growth of nanoparticles stabilized by citrate groups.

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