



HAL
open science

Europium(III) Complexes Containing Organosilyldipyridine Ligands Grafted on Silica Nanoparticles

Sandra Cousinié, Marie Gressier, Christian Reber, Jeannette Dexpert-Ghys,
Marie-Joëlle Menu

► **To cite this version:**

Sandra Cousinié, Marie Gressier, Christian Reber, Jeannette Dexpert-Ghys, Marie-Joëlle Menu. Europium(III) Complexes Containing Organosilyldipyridine Ligands Grafted on Silica Nanoparticles. *Langmuir*, 2008, 24 (12), pp.6208-6214. 10.1021/la7035983. hal-03578408

HAL Id: hal-03578408

<https://hal.science/hal-03578408>

Submitted on 17 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID :2622

To link to this article :

URL : <http://dx.doi.org/10.1021/la7035983>

To cite this version : Cousinié, Sandra and Gressier , Marie and Reber, Christian and Dexpert-Ghys, Jeannette and Menu, Marie-Joëlle (2008) [*Europium\(III\) Complexes Containing Organosilyldipyridine Ligands Grafted on Silica Nanoparticles.*](#) Langmuir, vol. 24 (n° 12). pp. 6208-6214. ISSN 0743-7463

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr

Europium(III) Complexes Containing Organosilyldipyridine Ligands Grafted on Silica Nanoparticles

Sandra Cousinié,[†] Marie Gressier,[†] Christian Reber,[‡] Jeannette Dexpert-Ghys,[§] and Marie-Joëlle Menu^{*,†}

Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux, UMR-CNRS 5085, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 9, France, Département de Chimie, Université de Montréal, Montréal QC H3C 3J7, Canada, and Centre d'Elaboration de Matériaux et d'Etudes Structurales/CNRS, 29 rue J. Marvig, BP 4347, 31055 Toulouse Cedex 9, France

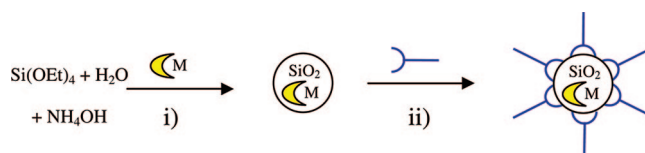
This work focuses on the grafting of transition metal complexes on silica surface nanoparticles. Nanoscale silica particles in aqueous sols are used as starting silicated materials. We have undertaken the synthesis of europium(III) complexes containing organosilyldipyridine ligands, $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{-bipy}$ (**1**) and $(\text{EtO})(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{-bipy}$ (**2**), in view of a direct grafting reaction on silica nanoparticles. Reaction of one molar equivalent of **1** and **2** with $\text{Eu}(\text{tmhd})_3$ ($\text{tmhd} = 2,2,6,6\text{-tetramethyl-3,5-heptanedionato}$), as precursor, leads to octacoordinated silylated europium(III) complexes $[\text{Eu}(\text{tmhd})_3(\mathbf{1})]$ (**3**) and $[\text{Eu}(\text{tmhd})_3(\mathbf{2})]$ (**4**) as white solids in 34–54% yields. Europium complexes were characterized by elemental analysis, mass spectrometry, FT-IR, UV, and luminescence spectroscopies. These new complexes are reacting in a 1:10 (v/v) water and ethanol mixture with silica nanoparticles colloidal sol. Elemental analysis and thermogravimetric data indicated grafting ratios of 0.41 and 0.26 mmol of europium(III) complexes per gram of silica. Functionalized silica nanoparticles were characterized by DRIFT spectroscopy and TEM microscopy. The first analysis shows that the chemical integrity of the complexes is retained on the silica surface together with the size and the monodispersity of the nanoscale particles. As expected for europium(III) complexes, luminescence is observed under UV irradiation. Emission and excitation spectra indicate that the metal coordination environment is not modified on the silica surface. Moreover, the sharpness of the luminescence bands and the strong antenna effect are maintained when complexes are covalently bonded to silica. New luminescent europium(III) complexes grafted on silica nanoparticles are therefore obtained from our approach.

1. Introduction

Besides its interest as filler, dispersant, or abrasive, silica is a versatile material because nanoscale particles are easily accessible and both their core or/and shell can be functionalized.^{1,2} Encapsulation of magnetic³ compounds and organic⁴ or inorganic⁵ dyes is possible by cocondensation with hydrolyzed tetraethoxysilane in a Stöber-type reaction,⁶ whereas the presence of reactive silanols on its surface allows surface chemical modifications. The combination of these two reactions leads to bifunctional silica nanoparticles (Scheme 1), largely used in biological applications as gene or DNA carriers,⁷ for drug delivery,⁸ as imaging tools,⁹ or separating agents.¹⁰

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ is the best known inorganic dye used in nanoprobe synthesis.^{5,11–14} Yuan and collaborators have described

Scheme 1. Metal-Incorporated (i) and Organic-Grafted (ii) Silica Nanoparticles



the encapsulation of europium¹⁵ and terbium¹⁶ complexes in 40–50 nm silica nanoparticles using a water-in-oil reverse microemulsion procedure. The choice of lanthanides as fluorophores is attractive because of their long lifetimes and sharp luminescence spectra, avoiding the overlapping spectra currently observed with most organic fluorescent probes and the natural background fluorescence of biological materials.¹⁷ Moreover, luminescence intensities of the low-energy, rare earth centered transitions are enhanced due to relaxation processes from higher energy, ligand centered absorption bands to the lanthanide in lanthanide chelate complexes.¹⁸

The silica support offers the possibility to be chemically modified through successive organic reactions. The development

* Corresponding author. Tel: (33)561558487. Fax: (33)561556163. E-mail address: menu@chimie.ups-tlse.fr.

[†] Université Paul Sabatier.

[‡] Université de Montréal.

[§] Centre d'Elaboration de Matériaux et d'Etudes Structurales/CNRS.

(1) Iler, R. K. *The Chemistry of Silica*; Wiley, New York, 1979.

(2) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*; Academic Press, San Diego, 1990.

(3) Liu, X.; Xing, J.; Guan, Y.; Shan, G.; Liu, H. *Colloids Surf. A* **2004**, *238*, 127.

(4) Van Blaaderen, A.; Vrij, A. *Langmuir* **1992**, *8*, 2921.

(5) Santra, S.; Zhang, P.; Wang, K.; Tapeck, R.; Tan, W. *Anal. Chem.* **2001**, *73*, 4988.

(6) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(7) Kneuer, C.; Sameti, M.; Haltner, E. G.; Schiestel, T.; Schirra, H.; Schmidt, H.; Lehr, C.-M. *Int. J. Pharm.* **2000**, *196*, 257.

(8) Csogor, Zs.; Nacken, M.; Sameti, M.; Lehr, C.-M.; Schmidt, H. *Mater. Sci. Engineer. C* **2003**, *23*, 93.

(9) Liu, Y.; Miyoshi, H.; Nakamura, M. *Int. J. Cancer* **2007**, *120*, 2527.

(10) Lian, W.; Litherland, S. A.; Badrane, H.; Tan, W.; Wu, D.; Baker, H. V.; Gulig, P. A.; Lim, D. V.; Jin, S. *Anal. Biochem.* **2004**, *334*, 135.

(11) Qhobosheane, M.; Santra, S.; Zhang, P.; Tan, W. *Analyst* **2001**, *126*, 1274.

(12) Rossi, L. M.; Shi, L.; Quina, F. H.; Rosenzweig, Z. *Langmuir* **2005**, *21*, 4277.

(13) Wang, L.; Yang, C.; Tan, W. *Nano Lett* **2005**, *5*(1), 37.

(14) Bagwe, R. P.; Yang, C.; Hilliard, L. R.; Tan, W. *Langmuir* **2004**, *20*, 8336.

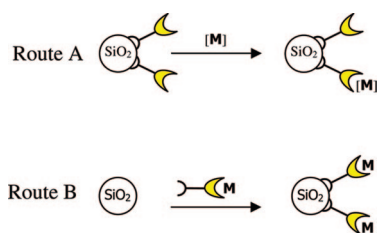
(15) Tan, M.; Ye, Z.; Wang, G.; Yuan, J. *Chem. Mater.* **2004**, *16*, 2494.

(16) Ye, Z.; Tan, M.; Wang, G.; Yuan, J. *Anal. Chem.* **2004**, *76*, 513.

(17) Bazin, H.; Trinquet, E.; Mathis, G. *Rev. Mol. Biotechnol.* **2002**, *82*(3), 233.

(18) Latva, M.; Takalo, H.; Mukkala, V. M.; Matachescu, C.; Rodríguez-Ubis, J. C.; Kankare, J. *J. Lumin.* **1997**, *75*, 149.

Scheme 2. Synthesis of Transition Metal Complexes Grafted on Silica Materials: (Route A) Complexation Reaction of Metal Ions or Chelates on Organically Modified Silica Nanoparticles and (Route B) Grafting Reaction of Organosilylated Metal Complex

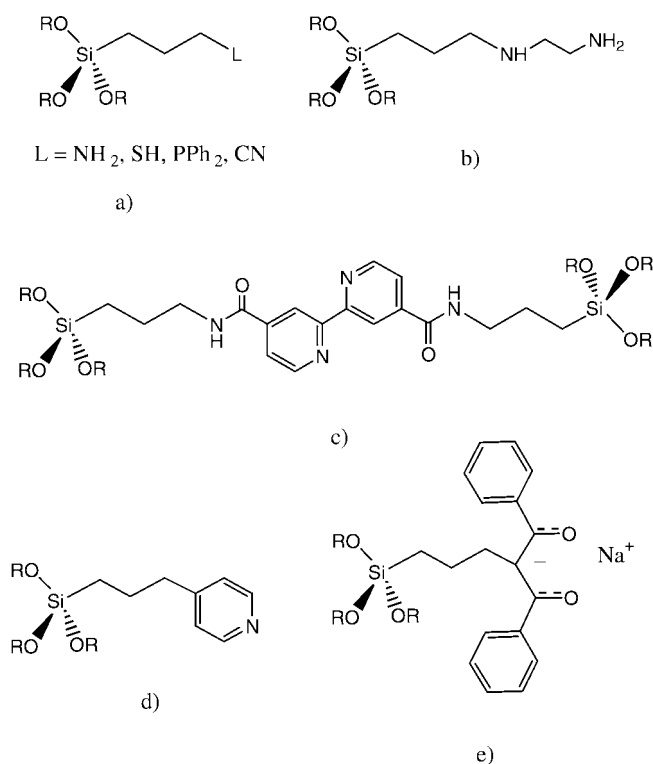


of organically modified silica nanoparticles can now be controlled and is currently leading to a boost in nanomaterials chemistry, specifically in fields such as analytical chemistry, biochemistry, and catalysis. An important challenge is the grafting of transition metal complexes on the surface of silica nanoparticles in order to combine transition metal chemistry and nanoscale silica materials chemistry. Moreover, the vastly diverse catalytic, optical, electrochemical, or coordination properties of transition metal compounds give additional importance to this new research field. Heterogeneous catalysis has also largely contributed to the development of grafted silica-based materials using microscale particles.¹⁹ The most interesting feature of nanosized particles is that each chemically modified silica nanoparticle carries thousands of active species showing enhanced properties. This synthetic chemistry is challenging, and two routes have to be considered to access to new metalated nanoparticles, as illustrated in Scheme 2.

Route A coordinates metal ions to organically modified silica surface via a coupling reaction between a metal ion or a chelate and aminated silica. In this case, organic moieties previously grafted contain coordination sites, such as amino, mercapto, nitrilo, diphenylphosphino, ethylenediamino, pyridyl, and dipyridyl groups or recently dibenzoylmethane as β -diketonate ligand²⁰ (Scheme 3).

Lin²¹ and Ziessel²² have used this approach to synthesize functionalized micronic silicated particles with the aim of catalysis or luminescent lanthanides markers with pyridyl (Scheme 3d) and aminated derivatives. Serra²⁰ and co-workers recently demonstrated the possibility to obtain metalated mesoporous submicronic particles by complexing EuCl_3 on dibenzoylmethane-modified mesoporous silica. These authors report an amount of 0.064 mmol of europium per gram of silica, corresponding to 10% of the dibenzoylmethane ligand. Route A, therefore, does not lead to homogeneous functionalized surfaces because hindrance of the complexes and/or the inaccessibility of all complexing sites result in a nonquantitative complexation reaction. This is confirmed by Li^{23,24} and co-workers, who recently reported the development of nanoparticles containing fluorescent lanthanide chelates for time-resolved fluorometric (TRF) immunoassays. The authors have obtained nanoparticles containing high concentrations of luminophores and covalently linked

Scheme 3. Alkoxysilanes with Coordinative Properties Used in Route A



lanthanide chelates onto the surface of aminated preformed silica nanoparticles according to route A (Scheme 2). However, five functionalization cycles are needed to obtain convenient nanoparticles.

These limitations, heterogeneous surface and low grafting ratio, urged us to develop the alternative route B illustrated in Scheme 2, for which higher grafting ratios are expected, even though it requires previous synthesis of organosilylated metal complexes. To our knowledge, no grafting reaction of organosilylated transition metal complexes on preformed silica nanoparticles in aqueous colloidal sols has been reported. Only few examples of silylated transition metal complexes grafted on silica nanoparticles have been described in organic solvents, for example, by Rocha and co-workers,²⁵ who have grafted a ruthenium(II) complex containing nitropropyltriethoxysilane, $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{CN}$, on nanoscale MCM-41 silica. These authors showed an enhanced reactivity in catalysis brought by the nanoscale mesoporous silica support.

In order to develop a general functionalization reaction of silica nanoparticles, we have chosen to react silylated transition metal complexes on aqueous silica sol. Grafting reactions requiring hydrolysis of alkoxysilane derivatives on the silanol sites of the silica surface might be carried out in any organic solvent.

This is what we have undertaken through the synthesis of organosilyldipyridine derivatives **1**, containing one trialkoxysilane function²⁶ (Scheme 4). The two sites, bidentate ligand, i.e. dipyridyl group, and a trialkoxysilane function, give an interesting silane for both complexing and grafting properties. Moreover, the intense absorption of dipyridyl groups is suitable for light-

(19) Vansant, E. F.; Van der Voort, P.; Vrancken, K. C. *Characterization and Chemical Modification of the Silica Surface*, 1st ed.; In Delmon, B.; Yates, J. T., Eds.; Studies in Surface Science and Catalysis; Elsevier: Amsterdam, 1997; Vol. 93.

(20) De Oliveira, E.; Neri, C. R.; Serra, O. A.; Prado, A. G. S. *Chem. Mater.* **2007**, *19*, 5437.

(21) Kumar, R.; Chen, H.-T.; Escoto, J. L. V.; Lin, V. S. Y.; Prusky, M. *Chem. Mater.* **2006**, *18*, 4319.

(22) Charbonnière, L. J.; Weibel, N.; Estournes, C.; Leuvrey, C.; Ziessel, R. *New. J. Chem.* **2004**, *28*, 777.

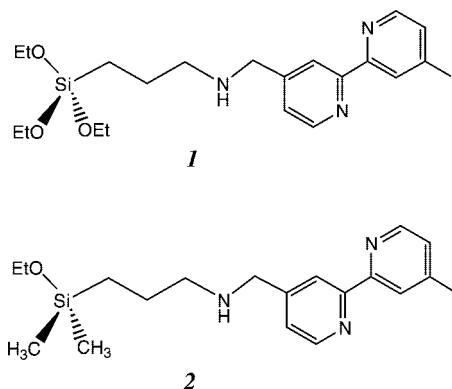
(23) Xu, Y.; Li, Q. *Clin. Mater.* **2007**, *53*(8), 1503.

(24) Zhang, H.; Xu, Y.; Yang, W.; Li, Q. *Chem. Mater.* **2007**, *19*, 5875–5881.

(25) Pillinger, M.; Gonçalves, I. S.; Lopes, A. D.; Madureira, J.; Ferreira, P.; Valente, A. A.; Santos, T. M.; Rocha, J.; Menezes, J. F. S.; Carlos, L. D. *J. Chem. Soc., Dalton Trans.* **2001**, 1628.

(26) Cousinié, S.; Gressier, M.; Alphonse, P.; Menu, M.-J. *Chem. Mater.* **2007**, *19*, 6492.

Scheme 4. Dipyridine Derivatives with Alkoxysilane Group, 1 and 2



harvesting and energy transfer in order to efficiently “feed” the metal-centered excited states. To ensure monolayer grafted nanoparticles and so an homogeneous functionalization, we have also synthesized the monoethoxydimethylsilane derivative²⁶ **2** (Scheme 4).

Our work focuses on the elaboration of new luminescent nanoparticles, based on europium complexes covalently grafted on silica nanoparticles with homogeneous functionalized surfaces. The rationale for this approach is to synthesize europium complexes containing bifunctional organosilane starting with tris(2,2,6,6,-tetramethyl-3,5-heptanedione)europium(III) to give [Eu(tmhd)₃L], **3** (L = **1**) and **4** (L = **2**). Then, neutral octacoordinated silylated europium complexes were grafted on aqueous sols of silica nanoparticles to obtained luminescent nanohybrids, the optical properties of which are studied.

2. Experimental Section

Ludox AS40 (40 wt% SiO₂, 21 ± 2 nm, pH 9) obtained from Aldrich were used as starting silica materials. Eu(tmhd)₃ was purchased from ABCR. The silylating agents 4-methyl-4'-[methylamino-3-(propyltriethoxysilyl)]-2,2'-dipyridine (**1**) and 4-methyl-4'-[methylamino-3-(propyldimethylethoxysilyl)]-2,2'-dipyridine (**2**) were synthesized as previously described by Menu and co-workers and characterization by IR, UV, MS, and ¹³C, ¹H, ²⁹Si NMR spectroscopies were given.²⁷

Pentane, diethyl ether, and dichloromethane were purified by distillation before use. All manipulations concerning the preparation of the silanes and the complexes were performed in an inert atmosphere using the Schlenk tube technique.

(27) (a) Data for **1**. ¹H NMR (δ ppm, CDCl₃): 0.65 (m, 2H, CH₂), 1.21 (t, 9H, CH₃, J = 7), 1.64 (m, 2H, CH₂), 2.41 (s, 3H, CH₃), 2.65 (m, 2H, CH₂), 3.79 (q, 6H, CH₂, J = 7), 3.89 (s, 2H, CH₂), 7.13 (d, 1H, CH), J = 6), 7.26 (d, 1H, CH, J = 6), 8.22 (s, 1H, CH), 8.31 (s, 1H, CH), 8.53 (d, 1H, CH, J = 6), 8.61 (d, 1H, CH, J = 6). ¹³C{¹H} NMR (δ ppm, CDCl₃): 7.9 (1C, CH₂), 18.3 (3C, CH₃), 21.2 (1C, CH₃), 23.4 (1C, CH₃), 52.3 (1C, CH₂), 53.4 (1C, CH₂), 58.2 (3C, CH₂), 120.4 (1C, CH), 122.0 (1C, CH), 124.1 (1C, CH), 125.1 (1C, CH), 148.1 (1C, C), 149.0 (1C, CH), 149.2 (1C, CH), 150.8 (1C, C), 156.0, 156.3 (2C, C). ²⁹Si NMR (δ ppm, CDCl₃): -45.3 (s). IR (pure, cm⁻¹): 3308 ν(NH), 2928 ν_{as}(CH₃,CH₂), 2884 ν_s(CH₃,CH₂), 1595, 1555 δ(dipyridine), 1456 δ(NH,CH₃), 1376 δ(CH₂), 1269 ν(SiC), 1076 ν(SiOC), 958 δ(SiO), 736 δ(CH₂,CH₃). UV (CH₂Cl₂): 243 nm (ε = 10 349 L mol⁻¹ cm⁻¹), 284 nm (ε = 11 788 L mol⁻¹ cm⁻¹). MS Cl/NH₃: m/z = 403 [M]⁺. (b) Data for **2**. ¹H NMR (δ ppm, CDCl₃): 0.01 (m, 6H, CH₃), 0.51 (m, 2H, CH₂), 1.08 (t, 3H, CH₃, J = 6), 1.44 (m, 2H, CH₂), 2.36 (s, 3H, CH₃), 2.55 (m, 2H, CH₂), 3.55 (q, 2H, CH₂, J = 6), 3.78 (s, 2H, CH₂), 7.04 (d, 1H, CH, J = 6), 7.22 (d, 1H, CH, J = 6), 8.14 (s, 1H, CH), 8.22 (s, 1H, CH), 8.45 (d, 1H, CH, J = 6), 8.52 (d, 1H, CH, J = 6). ¹³C{¹H} NMR (δ ppm, CDCl₃): 0.3 (2C, CH₃), 13.8 (1C, CH₂), 18.5 (1C, CH₃), 23.5 (1C, CH₃), 23.8 (1C, CH₂), 51.8 (1C, CH₂), 52.6 (1C, CH₂), 58.2 (1C, CH₂), 120.9 (1C, CH), 122.0 (1C, CH), 122.9 (1C, CH), 124.9 (1C, CH), 148.1 (1C, C), 148.9 (1C, CH), 149.4 (1C, CH), 150.7 (1C, C), 155.9, 156.3 (2C, C). ²⁹Si NMR (δ ppm, CDCl₃): 7.6 (s). IR (pure, cm⁻¹): 3306 ν(NH), 2960 ν_{as}(CH₃,CH₂), 2857 ν_s(CH₃,CH₂), 1597, 1556 δ(dipyridine), 1460 δ(NH,CH₃), 1377 δ(CH₂), 1252 ν(SiC), 1071 ν(SiOC), 993 δ(SiO), 735 δ(CH₃,CH₂). UV (EtOH): 240 nm (ε = 16 829 L mol⁻¹ cm⁻¹), 283 nm (ε = 19 168 L mol⁻¹ cm⁻¹). MS(DCl/NH₃): m/z = 344 [M + H]⁺.

2.2. Characterizations. We have characterized europium complexes by infrared spectroscopy in the range 4000–400 cm⁻¹ with a Bruker Vector 22 spectrophotometer and chemically modified silica nanoparticles using a diffuse reflectance technique with a Perkin-Elmer 1760 X (with DTGS detector). Mass spectra were recorded by FAB or IS techniques using a Nermag R10-10 spectrometer or a TSQ 7000 Thermo-Quest spectrometer. UV spectra were recorded using a Varian UV–visible Cary 1E spectrometer in the range 900–200 nm. Elemental analyses of C, H, and N were performed on a Carlo Erba instrument (EA 1110). Simultaneous thermogravimetric (TG) and differential thermal (DT) analyses were carried out on a SETARAM TG-DTA 92 thermobalance using 20 mg of sample; α-alumina was used as reference. The heating rate was 3.8 °C min⁻¹. The temperature range was 20–1200 °C and the analyses were done using a 1.5 L h⁻¹ air flow. The amount of grafted material, τ, in mmol per gram of silica, was determined by two methods. The first estimate is calculated from nitrogen content according the formula $\tau = \%N \times 10^3 / (14.100n_N)$, where %N and n_N represent the nitrogen content in percent and the number of nitrogen atoms in the grafted moiety, respectively. The second estimate of the grafted amount is obtained by DTA/DTG measurements with the formula $\tau = \Delta m_2 \times 10^3 / (mM)$, with Δm₂ representing the second weight loss, m the sample amount, and M the molecular mass of the organic grafted moiety.

Transmission electron microscopy (TEM) was used to determine morphology and particle size. TEM analyses were done on a JEOL 2010 (200 kV). A drop of sol was diluted in ethanol. Then a carbon-coated grid was dipped in the solution and allowed to dry at room temperature. Luminescence spectra were recorded, at room temperature, with a Renishaw RM 3000 Raman spectrometer using the 488 nm radiation as excitation laser source (spectral resolution 0.02 nm). Emission and excitation spectra along with luminescence decay measurements were also recorded using a Hitachi-F4500 spectrofluorimeter at 1 nm spectral resolution.

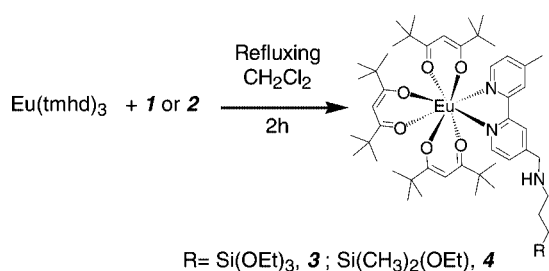
2.3. Synthesis. **2.3.1. Synthesis of Europium Complexes Containing 4-Methyl-4'-[methylamino-3-(propylalkoxysilyl)]-2,2'-dipyridine:** [Eu(tmhd)₃(**1**)], **3**, and [Eu(tmhd)₃(**2**)], **4**. Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)europium(III) (300 mg, 0.43 mmol) and appropriate organosilane (173 mg of **1** or 152 mg of **2**, 0.43 mmol) were dissolved in dichloromethane (20 mL) and stirred 2 h at reflux. The resulting solution was concentrated to 10 mL and pentane (20 mL) was added. The precipitate was collected by filtration, washed with pentane and diethyl ether, and dried. Compounds **3** and **4** were obtained in a range of 34–52% yield.

[Eu(tmhd)₃(**1**)], **3**: IR (KBr, cm⁻¹): 2964 ν_{as}(CH₃,CH₂), 2872 ν_s(CH₃,CH₂), 1654 ν(C=N), 1607, 1587 ν(CC), 1575, 1540, 1506 ν(CCO), 1490 δ(NH), 1425 δ_{as}(CH₃,CH₂), 1358 δ_s(CH₃,CH₂), 1244 ν(SiC), 1081 ν(SiOC), 959 δ(SiO), 867 δ(CSiO), 791 δ(CH_{Ar}), 467 ν(Eu-L). Elemental anal. found (calcd): C 58.70 (58.45), H 8.15 (8.00), N 3.80 (4.72). UV (CH₂Cl₂): 244 nm (ε = 27 969 L mol⁻¹ cm⁻¹), 285 nm (ε = 63 736 L mol⁻¹ cm⁻¹). MS (FAB, DMF): m/z = 922 [M - tmhd]⁺.

[Eu(tmhd)₃(**2**)], **4**: IR (KBr, cm⁻¹): 2959 ν_{as}(CH₂, CH₃), 2866 ν_s(CH₂,CH₃), 1613, 1590 ν(CC), 1580, 1536, 1504 ν(CCO), 1452 δ(NH), 1426 δ_{as}(CH₃,CH₂), 1357 δ_s(CH₃,CH₂), 1249 ν(SiC), 1075 ν(SiOC), 960 δ(SiO), 867 δ(CSiO), 790 δ(CH_{Ar}), 474 ν(Eu-L). Elemental anal. found (calcd): C 59.75 (59.71), H 8.29 (8.47), N 4.02 (4.30). UV (CH₂Cl₂): 252 nm (ε = 14 853 L mol⁻¹ cm⁻¹), 285 nm (ε = 38 282 L mol⁻¹ cm⁻¹). MS (IS): m/z = 1067 [M + Na]⁺.

2.3.2. General Procedures for the Preparation of Europium-Functionalized Silica Nanoparticles: Preparation of ≡Si-3** and ≡Si-**4**.** (Modified silica are denoted ≡Si-**X** when a europium complex is grafted on the silica surface, where **X** corresponds to the number of the compound.) Ludox silica sol (350 mg, 875 mg AS40 sol), diluted with ethanol (10 mL), was reacted with 350 mg (0.33 mmol) of **3** or 350 mg (0.32 mmol) of **4**. The mixtures were left to stir for 72 h at 295 K. At the end of the reaction, the sample was centrifuged at 17 000 rpm for 5 min. The clear supernatant was decanted from the solid deposit composed of the grafted particles. The obtained solid mass was washed with ethanol, dichloromethane, and diethyl ether and then dried in vacuo for 2 h. In order to check reproductibility,

Scheme 5. Preparation of Silylated Europium Complexes 3 and 4



experiments were carried out in triplicate. Europium complexes grafted on nanoparticles are stable for more than 1 year at room temperature without any specific precautions. Solvent such as water, isopropyl alcohol, or physiological buffer were used to obtain a suspension stable enough for preliminary spectroscopic studies.

Europium complexes grafted on silica nanoparticles (355 mg, **≡Si-3**; 348 mg, **≡Si-4**) were acquired.

≡Si-3: $\tau = 0.41 \text{ mmol g}^{-1}$. Elemental anal. found (calcd): C 16.37 (23.42), H 2.25 (3.08), N 1.70 (1.70). $\tau = 0.34 \text{ mmol g}^{-1}$ by TGA. DRIFT (cm^{-1}) 2951 $\nu_{\text{as}}(\text{CH}_3, \text{CH}_2)$, 2860 $\nu_{\text{s}}(\text{CH}_3, \text{CH}_2)$, 1601, 1587 $\nu(\text{CC})$, 1574, 1535, 1506 $\nu(\text{CCO})$, 1452 $\delta(\text{NH})$, 1424 $\delta_{\text{as}}(\text{CH}_3, \text{CH}_2)$, 1358 $\delta_{\text{s}}(\text{CH}_3, \text{CH}_2)$, 1214 $\nu(\text{SiC})$, 1112 $\nu(\text{SiOSi})$, 962 $\delta(\text{SiO})$, 868 $\delta(\text{CSiO})$, 791 $\delta(\text{CH}_{\text{Ar}})$, 477 $\nu(\text{Eu-L})$.

≡Si-4: $\tau = 0.26 \text{ mmol g}^{-1}$. Elemental anal. found (calcd): C 11.72 (11.54), H 1.78 (1.61), N 1.09 (1.09). $\tau = 0.21 \text{ mmol g}^{-1}$ by TGA. DRIFT (cm^{-1}) 2957 $\nu_{\text{as}}(\text{CH}_3, \text{CH}_2)$, 2863 $\nu_{\text{s}}(\text{CH}_3, \text{CH}_2)$, 1605, 1587 $\nu(\text{CC})$, 1575, 1536, 1504 $\nu(\text{CCO})$, 1450 $\delta(\text{NH})$, 1426 $\delta_{\text{as}}(\text{CH}_3, \text{CH}_2)$, 1359 $\delta_{\text{s}}(\text{CH}_3, \text{CH}_2)$, 1233 $\nu(\text{SiC})$, 1120 $\nu(\text{SiOSi})$, 961 $\delta(\text{SiO})$, 868 $\delta(\text{CSiO})$, 801 $\delta(\text{CH}_{\text{Ar}})$, 475 $\nu(\text{Eu-L})$.

3. Results and Discussion

3.1. Synthesis of Europium Complexes 3 and 4. Eu(tmhd)₃ is used as europium precursor because of its well-known affinity toward nitrogen ligands^{28–33} to give stable octacoordinated complexes (Scheme 5). Reaction of 1 mol equiv of organosilane **1** or **2** with Eu(tmhd)₃ in refluxing dichloromethane for 2 h gives [Eu(tmhd)₃(**1**)], **3**, and [Eu(tmhd)₃(**2**)], **4**, as white solids after addition of pentane.

Both complexes are characterized by elemental analysis that is in agreement with the proposed formula. The presence of the organosilane is confirmed by IR analysis in both spectra with the ring stretching vibrations of dipyridine; the CH₃, CH₂, and NH stretching and bending vibrations of the propyl chain and secondary amino function; and the Si–O stretching and bending of the alkoxy-silyl group. The IR spectrum of **4** differs from the one of **3** by the more intense $\nu(\text{Si}-\text{C})$ stretching vibration, in agreement with the presence of two methyl groups on silicon atoms in **4**. The tmhd diketone ligands were identified by stretching vibrations at 1575, 1540, 1506 [$\nu(\text{CCO})$], and 1580, 1536, 1504 [$\nu(\text{CCO})$], respectively, for **3** and **4**. The octacoordination is ascertained by mass spectra that show major molecular peaks at $m/z = 922$ and 1067 for **3** and **4**, respectively, corresponding to $[\text{M} - \text{tmhd}]^+$ and $[\text{M} + \text{Na}]^+$. In both cases, the isotopic pattern is in agreement with the proposed formula.

UV spectra of organosilanes have two strong absorbances ($\epsilon = 11\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) corresponding to $\pi-\pi^*$ transitions. Complexation effects are more illustrated by the increase of intensity and by a small shift observed for all transitions, as

indicated in Table 1. Both complexes show large intense absorptions in UV range necessary for the expected powerful antenna effect for the Eu³⁺ emission.

Well-defined luminescence emission spectra, recorded on powder samples, are discussed in the following section.

3.2. Synthesis and Characterization of Luminescent Silica Nanoparticles $\equiv\text{Si-3}$ and $\equiv\text{Si-4}$. We have described²⁶ the grafting reaction of organosilanes (EtO)₃Si(CH₂)₃NHCH₂-bipy (**1**) and (EtO)(CH₃)₂Si(CH₂)₃NHCH₂-bipy (**2**) on AS40 Ludox silica in a 1:1 mixture (v/v) of water and ethanol, at 295 K during 72 h. When 2 mmol of organosilane per gram of silica are introduced, grafted amounts of 1.24 and 0.28 mmol g⁻¹ are respectively obtained for $\equiv\text{Si-1}$ and $\equiv\text{Si-2}$. This condition leads to organosilane monolayer grafted on nanoparticles with monoethoxysilane derivative **2** (Scheme 6i), whereas, with a grafting amount higher than 1 mmol of organic per gram of silica, organosilane oligomers are suspected to be grafted on nanoparticles for triethoxysilyldipyridine **1** (Scheme 6ii). This 1 mmol g⁻¹ value is the highest limit admitted for our monolayer grafted nanoparticles assuming the average surface occupied by one organic molecule (0.25 nm²) and the specific surface area of 140 m² g⁻¹ for AS40 silica nanoparticles.

For this reason and according to the lower complex solubility in water, we have introduced less than 1 mmol g⁻¹ of functionalized complexes **3** and **4** in a 1:10 (v/v) water and ethanol mixture. Purification was conducted by ultracentrifugation, giving a solid and a supernatant. The solid was washed successively with ethanol, dichloromethane, and diethyl ether; vortexed; and centrifuged. Grafting ratios, τ , of 0.41 and 0.26 mmol g⁻¹ are obtained respectively for $\equiv\text{Si-3}$ and $\equiv\text{Si-4}$. As expected in aqueous medium, grafting ratios are lower for monoethoxysilyl precursors than for triethoxysilyl ones. These values can be compared with those of the corresponding nanohybrids obtained by reaction of the free ligands. When silylated precursor contains one ethoxysilyl function, the $\equiv\text{Si-2}$ and $\equiv\text{Si-4}$ functionalized silicas present similar grafted amounts, respectively 0.28 and 0.26 mmol g⁻¹, corresponding to monolayer grafted nanoparticles, since oligomerization from hydrolyzed species is not possible. On the other hand, with triethoxysilane derivatives **1** and **3**, the grafting ratios observed for $\equiv\text{Si-1}$ and $\equiv\text{Si-3}$ are different from each other. When complex **3** reacts with silica, the grafting ratio remains clearly lower than 1 mmol g⁻¹, indicating that oligomerization from hydrolyzed species is limited, probably because of the hindrance of the complex. This result emphasizes the importance of our approach B consisting of grafting of organosilylated metal complexes.

We have studied the thermal decomposition of both silylated materials. In each case, the first weight loss of 2.81 and 2.98%, in the temperature range 70–150 °C, can be ascribed to water desorption as an endothermic process. Further heating shows, for europium complex grafted materials $\equiv\text{Si-3}$ and $\equiv\text{Si-4}$, two additional weight losses, as an exothermic process, at 240 and 380 °C. These values are higher than those observed for $\equiv\text{Si-1}$ and $\equiv\text{Si-2}$, where organic moiety decomposition begins at 200 °C. Weight losses resulting from organic moiety decomposition, corresponding to 0.34 and 0.21 mmol of complexes per gram of silica for $\equiv\text{Si-3}$ and $\equiv\text{Si-4}$, respectively, are in good agreement with the grafting ratios of 0.41 and 0.26 mmol g⁻¹ computed from elemental analysis.

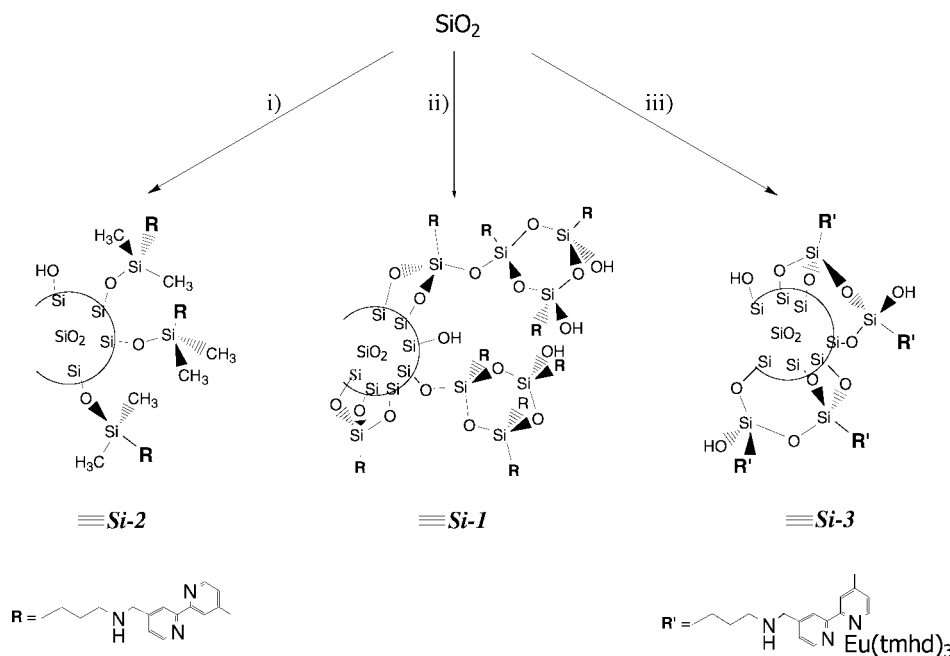
$\equiv\text{Si-3}$ and $\equiv\text{Si-4}$ are characterized by DRIFT analysis. Figure 1 presents expanded spectra of AS40 pure silica (a), complex **3** (b), and the corresponding grafted silica $\equiv\text{Si-3}$ (c) in the range 2100–400 cm⁻¹. We have unambiguous signatures of each

(28) Eisenbraun, K. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 5254.
 (29) Selbin, J.; Ahmad, N.; Bhacca, N. *Inorg. Chem.* **1971**, *10*(7), 1383.
 (30) Holz, R. C.; Thompson, L. C. *Inorg. Chem.* **1993**, *32*, 5251.
 (31) Holz, R. C.; Thompson, L. C. *Inorg. Chem.* **1988**, *27*, 4640.
 (32) Thompson, L. C.; Berry, S. J. *Alloys Compd.* **2001**, *323–324*, 177.
 (33) Yang, W.-Y.; Chen, L.; Wang, S. *Inorg. Chem.* **2001**, *40*, 507.

Table 1. UV Absorption Maxima of Organosilanes and Europium Complexes

	λ in nm (ϵ in L mol ⁻¹ cm ⁻¹)				
	Eu(tmhd) ₃	1	3	2	4
$\pi-\pi^*$ L		243 (10 349)	244 (27 969)	240 (16 829)	252 (14 853)
$\pi-\pi^*$ L	282 (39 320)	284 (11 788)	285 (63 736)	283 (19 168)	285 (38 282)

Scheme 6. Different Types of Functionalization: Organosilane Monolayer Grafted Nanoparticles (i and iii) or Organosilane Oligomer Grafted Nanoparticles (ii)^a



^a Conditions: (i) 2 mmol of **2** per gram of silica in 1:1 (v/v) water and ethanol mixture; (ii) 2 mmol of **1** per gram of silica in 1:1 (v/v) water and ethanol mixture; (iii) 1 mmol of **3** per gram of silica in 1:10 (v/v) water and ethanol mixture.

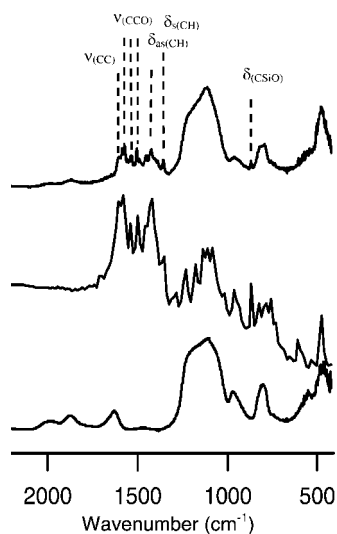


Figure 1. DRIFT spectra of pure silica (a), complex **3** (b), and metalated silica \equiv Si-3 (c).

organic fragment, i.e., bipyridine and β -diketone, indicating the chemical integrity of the complexes on the silica surface.

The morphology and size of the grafted nanoparticles were examined by TEM microscopy. Figure 2 shows TEM micrographs and particle size histograms of pure silica (a), \equiv Si-3 (b), and \equiv Si-4 (c) grafted silicas. These pictures indicate that the monodispersity of the nanosized particles was conserved. Only a slight increase in their average diameter is noticed, 27 ± 2 nm for both nanohybrids.

As expected for europium complexes, luminescence is observed when samples are irradiated by UV radiation (254 nm), as illustrated in Figure 3, parts a (**3**) and b (**4**). When complexes are immobilized on the surface of silica nanoparticles, even with a grafting ratio of 0.41–0.26 mmol g⁻¹, this property is well-preserved, as indicated by the picture in Figure 3c,d.

Solid-state emission spectra of the four samples were recorded with several excitation wavelengths. All spectra are similar, exhibiting the same spectral features. They consist of several bands related to the radiative de-excitation from the ⁵D₀ excited level of Eu³⁺. They are dominated by the hypersensitive ⁵D₀→⁷F₂ at 611.5 nm, which gives the intense red luminescence. The emission spectra recorded for the free complex **4** and for the grafted nanoparticles \equiv Si-4 exhibit very similar features (Figure 4A). All the emission lines are slightly broadened after grafting, as can be seen on the detail of ⁵D₀→⁷F₀. The ⁵D₀→⁷F₂ main component observed at 612.10 nm in **4** is split in two components at 611.54 and 612.32 nm in \equiv Si-4. A modification of relative intensities in the ⁵D₀→⁷F₃ transition at about 650 nm is also detected. The ratio of intensities of electric to magnetic dipole transition, ⁵D₀→⁷F₂/⁵D₀→⁷F₁ were measured in the spectral ranges 605–631 and 585–600 nm, respectively. It was found equal to 12 in the free complex and does not change after grafting. This value is in agreement with an Eu³⁺ in a non-centrosymmetrical environment, as observed by Reisfeld³⁴ and co-workers. So grafting results in several subtle modifications of the emission spectra, as described above, but at the same time, the ⁵D₀→⁷F₂/⁵D₀→⁷F₁ intensity ratio was not modified, because it is not

(34) Reisfeld, R.; Saraidorov, T.; Gaft, M.; Pietraszkiewicz, M. *Opt. Mater.* **2007**, *29*, 521.

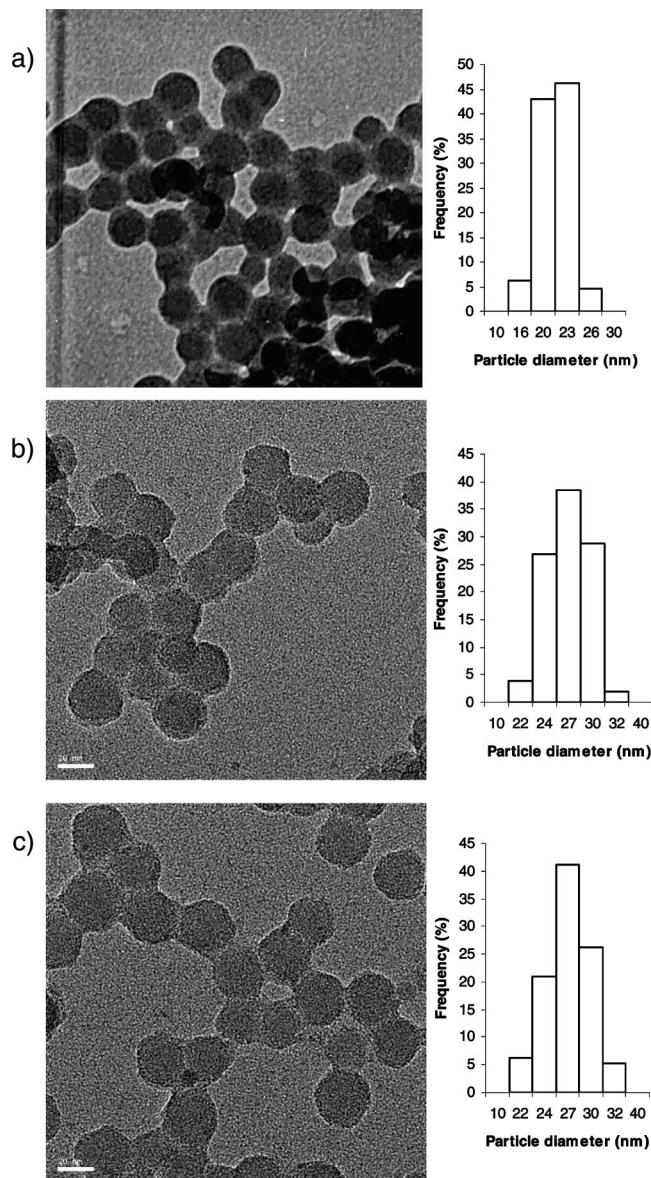


Figure 2. TEM micrographs and particle size histograms of pure silica (a), $\equiv\text{Si-3}$ (b), and $\equiv\text{Si-4}$ (c).

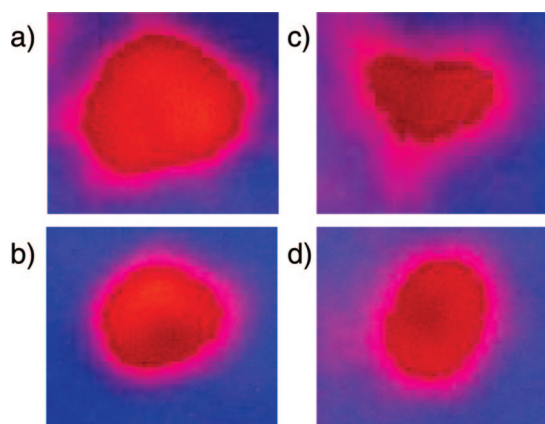


Figure 3. Pictures of solid samples irradiated by UV radiation (254 nm) of complex **3** (a), **4** (b), $\equiv\text{Si-3}$ (c), and $\equiv\text{Si-4}$ (d).

sufficiently sensitive to subtle changes in the crystal field. A ${}^5\text{D}_0$ lifetime of 0.76 ± 0.07 ms is measured at room temperature for the free complex **4** and the metalated nanohybrid $\equiv\text{Si-4}$. These

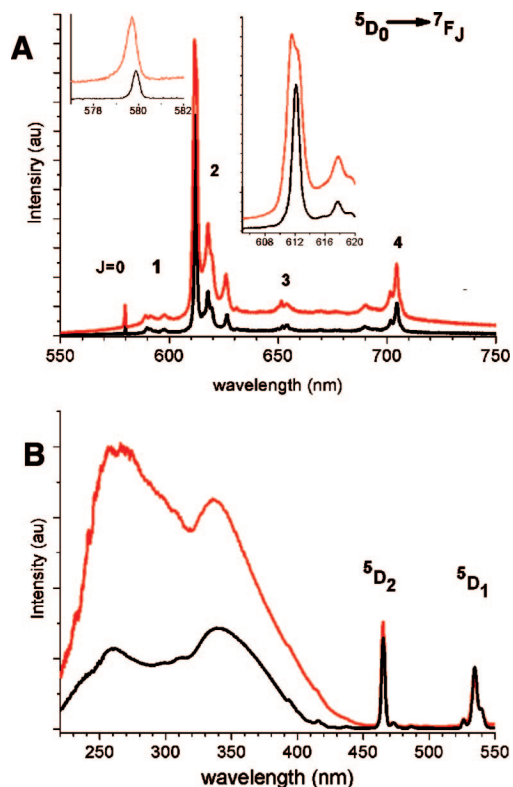


Figure 4. Solid state emission (A) and excitation (B) spectra of the free complex **4** (black line) and the corresponding grafted silica $\equiv\text{Si-4}$ (red line) at $\lambda_{\text{ex}} = 488$ nm (A) and monitoring wavelength $\lambda_{\text{em}} = 611.5$ nm (B). Excitation spectra are not corrected for system response in the UV region.

observations prove that the coordination of the europium ion in the complex remains essentially the same after grafting on the silica nanoparticles. This is also corroborated by comparing the luminescence excitation spectra displayed in Figure 4B. The narrow lines at 540 and 460 nm are due to transitions within the $\text{Eu}^{3+} 4f^6$ configuration: ${}^7\text{F}_{0,1} \rightarrow {}^5\text{D}_1$ and ${}^7\text{F}_{0,1} \rightarrow {}^5\text{D}_2$, respectively. The broad features observed at lower wavelengths are representative of the efficient antenna effect between the ligands and the Eu^{3+} ion. The broad excitation band at 260 nm may be assigned to the $\pi-\pi^*$ absorption in the dipyrindine moiety (Table 1). The other broad excitation band centered at 340 nm is ascribed to oxygen–europium charge transfer (CT). A similar assignment was done in the literature^{35,20} studying the properties of Eu^{3+} β -diketonates complexes in mesoporous silica.

Experimental investigations and theoretical considerations necessary to propose a more complete scheme of the electronic configuration in the free and the grafted complexes are beyond the scope of this paper. The important point is that both excitation bands at 340 and 260 nm are observed in a similar way for the free and the grafted complex. The UV (260 nm) and near-UV (340 nm) light harvesting is even more efficient in the grafted complex. This is evaluated by comparing the relative intensities of excitation in the ligand-related part of the excitation spectra with the intra- $4f^6$ lines. Moreover, the antenna effect in the UV range is more efficient than in the near-UV range when the complex has been grafted on the silica nanoparticles.

Using europium(III) complexes containing organosilyldipyrindine ligands in a direct grafting reaction, monolayer grafted silica nanoparticles are obtained with both mono- and trialkox-

(35) Meng, Q.; Boutinaud, P.; Zhang, H.; Mahiou, R. *J. Lumin.* **2007**, *124*, 15.

ysilane derivatives. The chemical integrity of the functionality and the morphology (spherical, 27 ± 2 nm) of the silica nanoparticles together with their solubility property are retained. With luminescent nanohybrids $\equiv\text{Si-3}$ and $\equiv\text{Si-4}$, we have shown that it is possible to combine transition metal chemistry and nanoscale silicated material chemistry. Current work is now focused on the extensive study of the luminescence properties of our nanomaterials. This grafting protocol may be now applied

to other metallic complexes with catalytic, optical, electrochemical, or coordination properties of interest.

Acknowledgment. This work was supported by the CNRS and the Ministry of Research of France. S.C. thanks MESR for a grant. The authors thank F. Baril-Robert and G. Malbec for their assistance with luminescence measurements.

LA7035983