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Solution, Solid State, and Film Properties of a Structurally Characterized Highly Luminescent Molecular Europium Plastic Material Excitable with Visible Light

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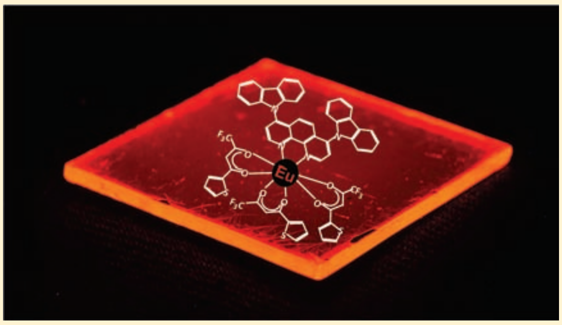
Supporting Information



ABSTRACT: The synthesis and X-ray crystal structure of the ligand L (4,7-dicarbazol-9-yl-[1,10]-phenanthroline) are reported, as well as those of the molecular complex, [Eu(tta)$_3$(L)] (**1**), (tta = 2-thenoyl trifluoroacetylacetonate). Their photophysical properties have been investigated both in solution and in the solid state. It was shown that the ligands used for designing **1** are well-suited for sensitizing the Eu^{III} ion emission, thanks to a favorable position of the triplet state as investigated in the Gd^{III} complex [Gd(tta)$_3$(L)], (**2**). The low local symmetry of the Eu^{III} ion shown by the X-ray crystal structure of **1** is also revealed by luminescence spectroscopy. Because of interesting volatility and solubility properties, **1** is shown to behave as a real molecular material that can be processed both by thermal evaporation and from solution. When doped in poly(methylmethacrylate) (PMMA), **1** forms air-stable and highly red-emitting plastic materials that can be excited in a wide range of wavelengths from the UV to the visible part of the electromagnetic spectrum (250−560 nm). Absolute quantum yields of 80% have been obtained for films comprising 1−3% of **1**. Ellipsometry measurements have been introduced to gain information on physical data of **1**. They have been performed on thin films of **1** deposited by thermal evaporation and gave access to the refractive index, *n*, and the absorption coefficient, *k*, as a function of the wavelength. A value of 1.70 has been found for *n* at 633 nm. These thin films also show interesting air-stability.

INTRODUCTION

The design of efficient and economical light emitters made of organic, inorganic, or hybrid materials is an active area of research.[1,2] These materials are of interest in a multitude of everyday life applications such as solid-state lighting[3−6] and displays.[7] In particular, organic materials are attracting a continuously growing attention as they offer chemists the possibility of molecular engineering leading to the optimization of performances and easy and cheap processing that is not feasible with inorganic materials. For the viable practical use of luminescent materials, it is of primary importance for the ratio of the number of emitted photons over the number of absorbed photons (i.e., the absolute quantum yield) to be as high as possible. This renders the design of highly efficient organic emitters still challenging.

The europium ion is receiving a continuously great deal of attention for the design of solid state emitters in the visible range, as recently highlighted by Bünzli.[8] In its trivalent state, it shows a very thin emission line around 615 nm which leads to a red color of high purity that is not affected by the environment of the ion. This makes the Eu^{III} ion very interesting for emission purposes. Molecular organic[9] and hybrid[10−14] photoemissive materials incorporating Eu^{III} occupy a place of choice in the search for new red-emissive materials as they do not need high-temperature synthesis as inorganic phosphors, and they can be processed more easily and with the cheapest techniques. Processable organic materials incorporating europium are made either of a molecular complex covalently linked to the organic matrix or of a molecular complex doped into the matrix. In this latter case, a commonly used matrix is poly(methylmethacrylate) (PMMA) as it is a cheap material that can be regarded as a transparent glass.[15] Eu^{III}-containing organic materials are investigated for various applications such as active materials suitable for displays,[16] organic light-emitting devices,[17−20] and optical fibers.[21,22] However, to date, devices made with these materials have not shown satisfying performances for industrial applications. In materials designed for photoemission, the Eu^{III} ion is generally excited through an energy transfer from organic chromophores after UV

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irradiation. This is the so-called antenna effect.[23] Thus, the design of such materials requires the use of ligands that are able to collect a maximum amount of energy and transfer it to the lanthanide ion. Among efficient sensitizers, β-diketonates are known for being well-suited for lanthanide luminescence, and especially for Eu^{III}.[13,24] Along these lines, we have designed the Eu^{III} complex **1** that bears three tta ligands and a new ligand derived from 1,10-phenanthroline. We report in this paper the synthesis and structural characterization of L and **1**, as well as the photophysical properties of L, **1**, and **2** both in solution and in the solid state. In addition, we report photoluminescence and ellipsometry studies on films showing that **1** can be considered as a molecular material.

■ EXPERIMENTAL SECTION

General Procedures. Reactants. The synthesis of 4,7-dicarbazol-9-yl-[1,10]-phenanthroline was performed under an inert argon atmosphere using standard techniques. Europium(III) chloride (99.99%, Aldrich), 2-thenoyl trifluoroacetylacetone (99%, Fluka), 4,7-dichlorophenanthroline (97%, Aldrich), and carbazole (95%, Aldrich) were used as received. $[Eu(tta)_3(phen)]$ (phen = 1,10-phenanthroline) and $[Eu(tta)_3(H_2O)_2]$ were synthesized as previously described.[25] Tetrahydrofuran (THF) was distilled over sodium/benzophenone immediately before use. ^1H NMR spectra were recorded in $CDCl_3$ at 23 °C on a Bruker Avance 300 spectrometer for L and on a Bruker 200 spectrometer for **1**. Elemental analyses were performed by the Service de Microanalyse, ICSN, CNRS, Gif-sur-Yvette (France) for **1**; and by Stephen Boyer (London Metropolitan University) for L and **2**, respectively.

Synthesis. *4,7-Dicarbazol-9-yl-[1,10]-phenanthroline (**L**).* A mixture of carbazole (270 mg, 1.61 mmol) and NaH (55 mg, 2.29 mmol) in THF (30 mL) was stirred at 70 °C for 30 min. 4,7-Dichloro-1,10-phenanthroline (200 mg, 0.80 mmol) was then added to the reaction mixture, which was refluxed overnight. After evaporation of the solvent under vacuum, the residue was dissolved in 20 mL of CH_2Cl_2 and filtered. The filtrate was evaporated under vacuum. The crude product was dissolved in THF and layered with pentane. Colorless crystals of L·THF were obtained (390 mg, 89%). Anal. Calcd for $C_{36}H_{22}N_4$: C, 84.68; H, 4.34; N, 10.97%; Found: C, 84.85; H, 4.28; N, 10.86%. ESI-HRMS: $m/z = 510.1845$ $[M^+]$; $C_{36}H_{22}N_4$ requires 510.1844. ^1H NMR δ 9.49 (d, 5 Hz, 2H), 8.15 (d, 6 Hz, 4H), 7.86 (d, 5 Hz, 2H), 7.33 (m, 10H); 7.07 (d, 6 Hz, 4H).

*$[Eu(tta)_3(L)]$ (**1**).* 2-Thenoyl trifluoroacetylacetone (327 mg, 1.47 mmol) and NaOH (59 mg, 1.48 mmol) were dissolved in acetonitrile (10 mL). After stirring at 65 °C for 15 min, L (250 mg, 0.49 mmol) was added, and an aqueous solution of $EuCl_3 \cdot 6H_2O$ (180 mg, 0.49 mmol) was added dropwise. The mixture was stirred at 65 °C for 2 h. After cooling at 20 °C and addition of water, the yellow precipitate was filtered off, washed with water, and dried. Slow diffusion of pentane into a chloroform solution gave yellow crystals of **1** (523 mg, 80%). Anal. Calcd for $C_{60}H_{34}F_9O_6N_4S_3Eu \cdot 1H_2O$: C, 53.61; H, 2.69; N, 4.17. Found: C, 53.70; H, 2.88; N, 4.08%. ^1H NMR δ 11.15 (br, 2H), 8.98 (d, J = 5 Hz, 4H), 8.58 (d, J = 7 Hz, 3H), 8.23 (d, J = 7 Hz, 3H), 7.69 (m, 7H), 7.01 (d, J = 5 Hz, 4H), 6.50 (t, J = 4 Hz, 4H), 6.11 (d, J = 3 Hz, 4H), 2.98 (s, 3H).

*$[Gd(tta)_3(L)]$ (**2**).* Following the same procedure as described above for **1**, **2** has been obtained in 67% yield. Anal. Calcd for $C_{60}H_{34}F_9O_6N_4S_3Gd$: C, 54.13; H, 2.57; N, 4.21%; Found: C, 54.27; H, 2.23; N, 4.48%.

Crystallography. The data were collected on a Nonius Kappa-CCD area detector diffractometer[26] using graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ- and ω-scans giving complete data sets up to θ = 25.7° and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[27] Absorption effects in **1**·0.5pentane were corrected with SCALEPACK.[27] The structures were solved by direct methods (L·THF) or by Patterson map interpretation (**1**·0.5pentane) and refined by full-matrix least-squares on F^2 with SHELXTL.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters. The pentane solvent molecule in **1**·0.5pentane is disordered over two positions related by symmetry and very close to one another, and it has been refined with an occupancy parameter of 0.5 and restraints on bond lengths, angles, and displacement parameters. The hydrogen atoms were introduced at calculated positions and treated as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. The molecular plots were drawn with SHELXTL. The CCDC reference numbers are 780421 and 780422.

Crystal data for L·THF: $C_{40}H_{30}N_4O$, M = 582.68, monoclinic, space group $P2_1/n$, a = 7.0975(5), b = 15.9586(6), c = 26.1751(18) Å, β = 90.979(3)°, V = 2964.3(3) $Å^3$, Z = 4, T = 150(2) K. Refinement of 406 parameters on 5626 independent reflections out of 79461 measured reflections (R_{int} = 0.031) led to R1 = 0.057, wR2 = 0.165, S = 1.077, $\Delta\rho_{min}$ = −0.45, $\Delta\rho_{max}$ = 0.87 e $Å^{-3}$.

Crystal data for **1**·0.5pentane: $C_{62.5}H_{40}EuF_9N_4O_6S_3$, M = 1362.13, triclinic, space group $P\bar{1}$, a = 13.4910(6), b = 13.8452(6), c = 16.6331(7) Å, α = 104.790(2), β = 95.483(2), γ = 98.576(3)°, V = 2941.2(2) $Å^3$, Z = 2, T = 100(2) K. Refinement of 793 parameters on 11144 independent reflections out of 127813 measured reflections (R_{int} = 0.032) led to R1 = 0.042, wR2 = 0.119, S = 1.055, $\Delta\rho_{min}$ = −0.79, $\Delta\rho_{max}$ = 2.79 e $Å^{-3}$.

Photophysical Measurements. Absorption spectra (solution and films) were recorded on a 6800 double beam Jenway spectrophotometer, and absorption spectra of samples conditioned as powders in MgO at a concentration of 6 wt % were recorded on a Perkin-Elmer Lambda 950 instrument and PE Winlab software. Emission spectra on powders were recorded on a Horiba-Jobin-Yvon Fluorolog-3 spectrofluorimeter, equipped with a three slit double grating excitation and emission monochromator with dispersions of 2.1 nm/mm (1200 grooves/mm). The steady-state luminescence was excited by unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° for diluted solution measurements or at 22.5° for solid state measurements by a red-sensitive Hamamatsu R928 photomultiplier tube. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Measurement of the quantum yield was performed with the integrating sphere following the method of de Mello et al.[29] Briefly, to take into account the light scattering and absorption by the sphere, direct light absorption and scattered light reabsorption by the sample, three experiments were designed: with the empty sphere and the laser beam (λ_{exc} = 405 nm) (a), with the sample placed in the sphere and the laser directed on the sphere wall (b), and with the sample placed in the laser beam inside the sphere (c). For each of the experiments two measurements were done, one with the filter between the sphere and the detector, another without. The filter was chosen to absorb the excitation laser wavelength while passing the sample photoluminescence. The photodetector values were recorded, with and without filter, L_x and P_x, respectively. Afterward, the quantum yield was calculated following eq 1,

$$\eta = (P_c - (1 - A)P_b)/L_a A \qquad (1)$$

where indices stand for the experiment type and A stands for the sample absorption coefficient, which can be found as eq 2:

$$A = (1 - L_c/L_b) \qquad (2)$$

Ellipsometry. Ellipsometry measurements were performed by using a spectroscopic ellipsometer Jobin-Yvon-Horiba UVISEL-SE.

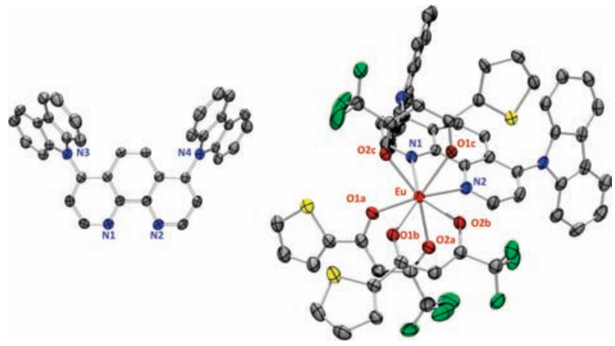

Figure 1. View of ligand L (left) and complex **1** (right, H and F atoms are omitted) with displacement ellipsoids represented at the 30 and 50% probability level, respectively.

RESULTS AND DISCUSSION

Structural Properties of L and 1. The synthesis of 4,7-dicarbazol-9-yl-[1,10]-phenanthroline (L), which is composed of a phenanthroline core and two peripheral carbazole substituents and was considered as a phosphorescent guest emitter, was reported during the course of our work.[30] We prepared molecule L in 89% yield by following the same route, that is, reaction of 4,7-dichlorophenanthroline and 2 equiv of carbazole in the presence of NaH, and obtained crystals of L·THF suitable for an X-ray diffraction characterization. A view of L is shown in Figure 1. The complex [Eu(tta)$_3$(L)] (**1**) has been designed as tta is known to efficiently transfer energy to the Eu^{III} ion[13] and 1,10-phenanthroline derivatives are used to improve the photophysical properties of the complexes and to saturate the coordination sphere of the large lanthanide ion. Thus, they avoid formation of polymeric compounds in the solid state that makes their processing by thermal evaporation difficult or even impossible. Complex **1** has been isolated in 80% yield from a one-step synthesis by reacting 3 equiv of Htta and NaOH and 1 equiv of L in dry CH_3CN under an inert atmosphere of argon. Crystals of **1**·0.5pentane suitable for X-ray diffraction were obtained by slow diffusion of pentane into a chloroform solution. A view of **1** is shown in Figure 1. The eight coordinate metal is in a distorted square antiprismatic environment, with the two square bases defined by the O(1a), O(2a), N(1), N(2) and O(1b), O(2b), O(1c), O(2c) atoms (rms deviations of 0.116 and 0.005 Å, respectively) forming a dihedral angle of 2.79(19)°. The average Eu−O and Eu−N bond lengths of 2.355(3) and 2.616(3) Å, respectively, can be compared with those measured in [Eu(tta)$_3$(phen)] [2.36(1) and 2.59(1) Å][31] and [Eu(tta)$_3$ (Me$_2$phen)] [2.37(3) and 2.58(2) Å].[32]

Photophysical Properties. *Solution Studies.* The absorption spectra of L, **1**, **2**, [Eu(tta)$_3$phen], and [Eu(tta)$_3$(H$_2$O)$_2$] in acetonitrile are reported on Figure 2. The spectrum of **1** grossly shows three maxima at 230, 278, and 338 nm, with values of the corresponding molar absorption coefficients of 133080, 72310, and 57700 L·mol^{-1}·cm^{-1}, respectively. Comparison of this spectrum with those of [Eu(tta)$_3$phen] and [Eu(tta)$_3$(H$_2$O)$_2$] shows that the band with the maximum at 230 nm is due to absorption of the carbazole moieties, while the second and third bands are mostly due to absorption of the phenanthroline ring and tta ligands, respectively. Also, contrary to [Eu(tta)$_3$phen], **1** absorbs in the visible. Absorption up to 450 nm can be seen at the concentration used (1.3×10^{-5} M). This indicates that an interaction between the carbazole and the phenanthroline moieties occurs. The X-ray crystal structure of **1** described above shows that, if one carbazole ring is almost perpendicular to the phen moiety with a dihedral angle of 89.60(4)°, the other carbazole group is not perpendicular (dihedral angle of 59.90(6)°). This shows that, even though weak, an interaction can occur between the two moieties, and partial conjugation can take place, which could be responsible of the absorption of **1** at lower wavelengths with respect to [Eu(tta)$_3$phen]. To support this, it was shown that for π-conjugated systems derived from thiophene and having carbazole end-groups, the delocalization occurs over the entire π-conjugated system and the carbazole rings through the lone pair of the nitrogen atom. This electronic interaction happens even if the carbazole moieties are perpendicular to the conjugated system.[33] The absorption spectrum of **2** shows the same bands with comparable absorption coefficients than that observed for **1**.

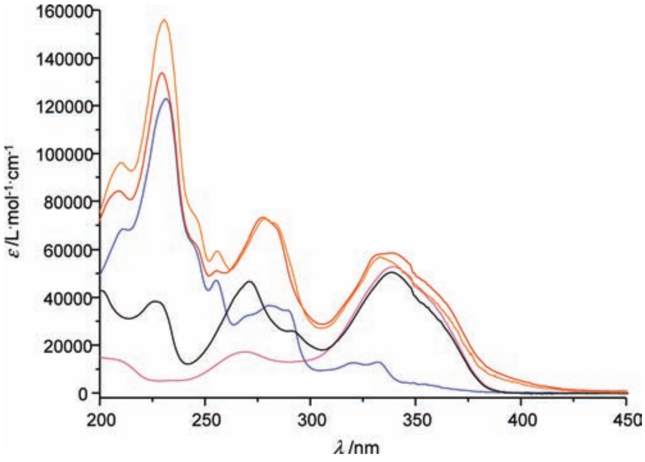

Figure 2. Absorption spectra of L (blue trace, 1.5×10^{-5} M); **1** (red trace, 1.3×10^{-5} M); **2** (orange trace, 4.5×10^{-6} M); [Eu(tta)$_3$(H$_2$O)$_2$] (pink trace, 1.4×10^{-5} M); and [Eu(tta)$_3$(phen)] (black trace, 1.3×10^{-5} M) in acetonitrile.

Solution photoluminescence studies at room temperature and 77 K of **2** allowed the determination of the positions of the ligands first singlet and triplet excited states, respectively, as no energy transfer occurs from the ligands to the Gd^{III} ion. The latter has excited states in the UV at energies higher than those of the sensitizing levels of the ligands, thus avoiding a ligand-to-metal energy transfer from the organic chromophores used. The maximum of the emission band that corresponds to the ligands' fluorescence in the complex is found at 449 nm, while it is found at 488 nm for the triplet state. Analysis of the phosphorescence emission band shows that the energy of the 0-phonon transition of the triplet state (which should be used to locate the energetic position of the triplet state)[34] is comprised between 21740 and 20491 cm^{-1} (460−488 nm). Thus, the sensitizing triplet state lies above the first excited states of the Eu^{III} ion at an energy that allows an efficient ligand to metal energy transfer.[35] The excitation spectrum of **1** recorded by monitoring the $^5D_0 \leftarrow {}^7F_2$ transition at 612 nm matched the absorption spectrum, thus proving that the Eu^{III} ion is excited via an energy transfer from the ligands. Indeed, when excited within the ligands' excited states (375 nm), **1** shows the typical emission bands of the Eu^{III} ion arising from the $^5D_0$ excited state. No ligand fluorescence was detected. All the solution spectra described above are shown in Figure 3. Excitation of **1** in the ligands level yielded a monoexponential decay from which a lifetime of 0.66 ms was extracted.

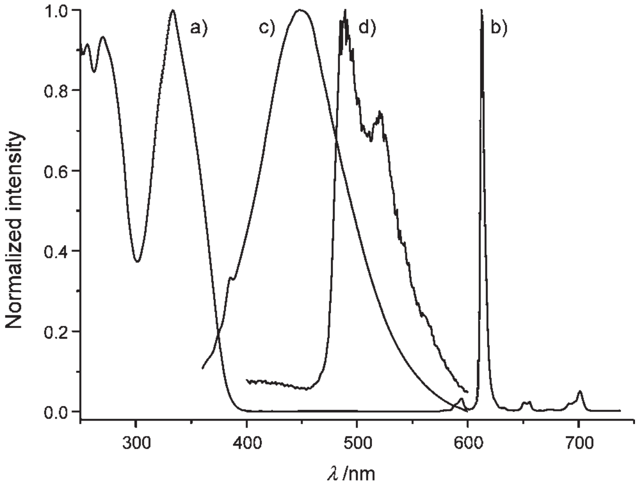

Figure 3. Normalized excitation (λ_{an} = 612 nm, a), and emission (λ_{exc} = 375 nm, b) spectra of **1** in CH_3CN at room temperature; and normalized emission spectrum of **2** at room temperature (λ_{exc} = 375 nm, c), and phosphorescence spectrum of **2** at 77 K in ^{n}BuCN (d).

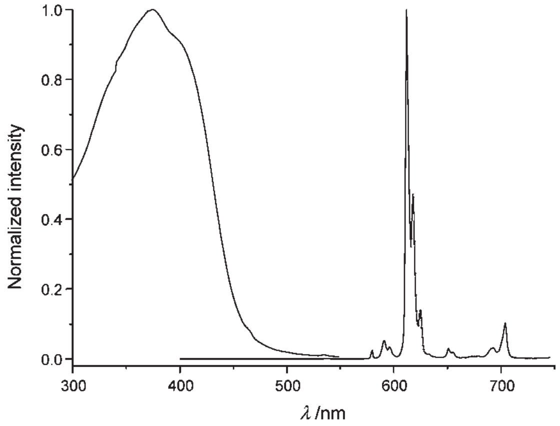

Figure 4. Normalized absorption spectrum of **1** (left, 6 wt % in MgO), and emission spectrum of pure **1** conditioned as a microcrystalline powder (right, λ_{exc} = 375 nm).

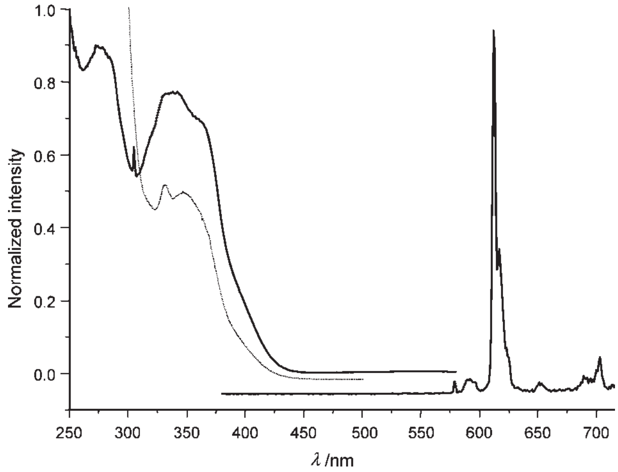

Figure 5. Normalized absorption (dotted line), excitation (λ_{an} = 612 nm) and emission (λ_{exc} = 360 nm) spectra of a film containing 1% of **1** embedded in PMMA.

Solid State Studies (Bulk). The room temperature solid state emission spectrum of **1** conditioned as a microcrystalline powder is shown on Figure 4. Only emission from the $^5D_0$ level of the Eu^{III} ion was detected. A value of 0.80 ms was measured for the $^5D_0$ excited state after excitation within the ligands excited states. The absorption spectrum (6 wt % in MgO) is also reported on Figure 4. It clearly shows that **1** absorbs in the visible, at least up to 550 nm. This is an interesting feature in view of practical applications (see below).

Solid State Studies (Films). Quantitative photophysical data on films made of luminescent complexes embedded in PMMA are crucial information for the realization of practical optical applications. Indeed, such composites lead to final materials that possess the emission properties of the lanthanide ions associated with the properties of plastics such as good mechanical properties, low-weight, and good impact resistance. In particular, PMMA shows transparency in the visible range. The good solubility of complex **1** in organic solvents is favorable for its deposition from solution. Films (~ 6.5 μm thick) of **1** doped (1−3 wt %) in PMMA were deposited on glass substrates from a solution of PMMA in 1,1,2-trichloroethane (300 g/L), and their photophysical properties were investigated. Excitation and emission spectra of the film doped with 1% of **1** are shown in Figure 5. When the $^5D_0 \leftarrow {}^7F_2$ (612 nm) transition of the Eu^{III} ion is monitored, the resulting excitation spectrum consists of two main bands centered in the UV region with maxima at 270 and 340 nm (shoulder at 355 nm). Note that this spectrum matches very well the absorption spectrum of this film reported on Figure 5, demonstrating that the Eu^{III} ion is excited through an energy transfer from the ligands. After excitation within the ligands' excited states (360 nm), emission from the $^5D_0$ level of the Eu^{III} ion is observed. The characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 0−4) transitions are observed with maxima at 579, 591, 612, 652, and 703 nm, respectively, the $^5D_0 \rightarrow {}^7F_2$ transition being the most intense and responsible of the bright red light emitted by **1**. Only emission from the Eu^{III} ion was observed. This shows that an efficient energy transfer from the organic chromophores occurs. Emission from the Eu^{III} ion is observed after excitation within the 250−560 nm range (Supporting Information, Figure S1). This indicates that the Eu^{III} ion can be excited with visible light and is consistent with the absorption in the visible shown in Figure 4. Overall photoluminescence quantum yields were determined with excitation at 405 nm by using an integrating sphere as previously described.[29] The same high value of 80% (within experimental error ±10%) was measured for the three films. Identical results were obtained after two months, thus showing the stability in air of these films and the absence of phase separation within this period of time. The value of the quantum yield is identical (within experimental errors) to that recently reported for two other molecular europium complexes embedded in PMMA.[36,37] A value of 78% was also earlier reported for an heteroleptic Eu^{III} complex bearing a phosphine oxide ligand and three deuterated hexafluoro-acetylacetonate ligands,[38] and values comprised between 20 and 40% for some other europium molecular complexes bearing β-diketonates and doped in a pure PMMA matrix were found in the literature.[39] In particular, one of the most studied complex of the family, [Eu(dbm)$_3$(phen)] (dbm = dibenzoylmethano), showed a value of 29.4%.

Local Symmetry As Probed by Luminescence Spectroscopy. The induced electric dipole $^5D_0 \rightarrow {}^7F_2$ transition can be regarded

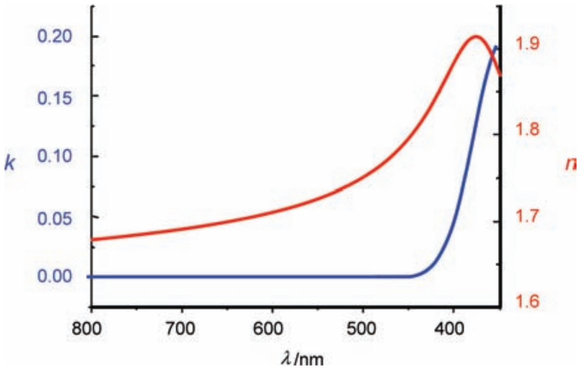

Figure 6. Absorption coefficient (*k*, blue line) and refractive index (*n*, red line) of **1** deposited as a thin film as a function of the wavelength.

as a probe of the local environment of the Eu^{III} ion.[40] Indeed, the relative intensity of this transition is very sensitive to the symmetry of the complex. The emission spectra of **1** described above are typical of species with low metal-ion site symmetry, and are dominated by the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. This is consistent with the C_1 point group of symmetry determined by X-ray diffraction. The ratio between the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition over the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition amounts to 33, 20, and 22 for **1** being conditioned in solution, as a powder and as a dopant in a film of PMMA, respectively. This shows that the local symmetry of the Eu^{III} ion in the molecular complex **1** is retained whatever the chemical conditions used. In particular, the emission spectra of **1** conditioned as a microcrystalline powder (Figure 4) and doped in a PMMA matrix (Figure 5) are very similar.

In view of its remarkable luminescence properties, **1** could be considered for optical applications, and further characterization of **1** as an optical material seemed desirable.

Ellipsometry. Ellipsometry was used to determine the optical properties of **1** when deposited as a thin film. Films with various thicknesses (10−63 nm) were obtained by vapor deposition on silicon and glass substrates. No in-plane or out-of-plane anisotropy was revealed by rotating the samples in the plane or by varying angles of incidence during spectroscopic ellipsometry measurements.[41] The multisample approach has been applied to obtain the optical refractive index, *n*, and the absorption coefficient, *k*, of these films (Figure 6).[42] The films are transparent in the spectral range above 455 nm (below 2.7 eV), and the refractive index *n* is equal to 1.70 at 633 nm. Finally, these films are air-stable for at least two weeks as we did not observe any change in these data after leaving the samples in air for this period of time.

CONCLUSION

In summary, we have reported a new Eu^{III} molecular complex that behaves as a real molecular material. It can form thin films by thermal evaporation that are air-stable for at least a few weeks. The good solubility of **1** makes possible the formation of PMMA films doped with **1**. The resulting plastic materials are highly luminescent and stable in air for months. The absolute quantum yield of these organic polymeric materials amounts to 80%. This value places these materials at the top rank of the most emissive europium materials made of a molecular complex doped in a PMMA matrix. We have introduced ellipsometry to determine the absorption coefficient and the refractive index of **1** as a function of the wavelength (Figure 6). These parameters are of importance in view of using **1** as an emitter in devices where light extraction occurs. Another interesting behavior of these red-emitting plastics is the wide range of wavelengths from the UV to the visible that can be used to obtain the Eu^{III} emission. A few studies describing Eu^{III} luminescence sensitized by visible light in molecular complexes bearing β-diketonates or other organic ligands or transition metal sensitizers have been reported.[43−50] As β-diketonates are known to be sensitive to photobleaching,[51] the high luminescence efficiency of **1** under visible light excitation is of importance and makes this material an interesting candidate for practical applications such as polymer optical fibers,[52] as silicon solar cells luminescent concentrator,[53] or as dopant in organic light-emitting devices.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic data of ligand L·THF and complex **1** in CIF format. Intensity of the Eu(III) $^5D_0 \rightarrow {}^7F_2$ transition of a film made of 1% of **1** in PMMA as a function of the excitation wavelength. This material is available free of charge via the Internet at http://pubs.acs.org.

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