Review Article

The Utility of 2,2'-Bipyrimidine in Lanthanide Chemistry: From Materials Synthesis to Structural and Physical Properties

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This paper reviews the recent investigations undertaken on the use of 2,2'-bipyrimidine (bpm) as a ligand for designing molecular complexes as well as polymeric lanthanide materials. A special emphasis is put on the ability of this polydentate neutral ligand to yield compounds of various dimensionalities, to act as a connector between these large ions, and influence their emissive and magnetic properties. This ligand can adopt a terminal or a bridging coordination mode with lanthanide ions, thus generating a wealth of frameworks of various topologies with the 4f elements. The main focus of this review is to show the originality brought by bpm in lanthanide structural chemistry and solid-state photophysics and magnetism.

1. Introduction

Lanthanide ions and their complexes with organic ligands have generated a continuously growing interest over the last decades. These elements show typical electronic properties that potentially give great advantages to the complexes they form with organic ligands. In the trivalent state, they are hard Lewis acids that have interesting applications in catalysis in the fields of polymer synthesis [1–7], organic chemistry [8–17], and bioinorganic chemistry [18–26]. Some of them possess a high number of unpaired electrons making them highly paramagnetic (the effective magnetic moment is up to $10.65 \mu_B$ for Dy^{3+}) [27] and of special interest for applications related to magnetic properties. In particular, they are widely studied for magnetic resonance imaging applications [28–32], and their paramagnetism is used for obtaining NMR shift reagents that help the elucidation of solution structures of complex molecules such as proteins [33, 34], and chiral coordination complexes are useful for the determination of enantiomers [35–38]. Also, the trivalent lanthanide ions are subject of an excited research in molecular magnetism, especially since the discovery that a ferromagnetic interaction between Cu^{2+} and Gd^{3+} could occur [39]. However, the difficulty to find efficient synthetic strategies for obtaining such mixed 3d–4f compounds has been an impediment to the progress of this research area, and most of the

studies were restricted to Cu/Gd systems [40]. Among the series, Gd^{3+} was first investigated because its ground state is orbitally nondegenerate and well separated from the excited states, giving simple single ion magnetic properties. In the last years, studies have been extended to other paramagnetic trivalent lanthanide ions, and a special interest has been devoted to their use in single molecule magnets [41–46].

Luminescence is another field of thorough investigations. Trivalent lanthanide ions show intraconfigurational transitions which result in a rearrangement of the electrons within the 4f subshell. A direct consequence is the atom-like character of their electronic spectra; that is, absorption and emission spectra show very thin lines with full-widths at half height typically of a few nanometers, giving rise to extremely pure colors of emission. A drawback of importance is the intensity of the lanthanide electronic spectra that are relatively low as the transitions are parity forbidden. In particular, the trivalent lanthanide ions show very low absorption coefficients in the 10^{-2} – $10^1 L \cdot mol^{-1} \cdot cm^{-1}$ range, and powerful sources of excitation are needed to obtain emission of the metal ion after direct excitation within the excited states of the latter. To overcome this problem that could seriously hinder the development of the 4f elements in organic and hybrid emissive materials, the antenna effect has appeared as a panacea. This is a three-step process that consists in efficient absorption of light by chromophores,

FIGURE 1: Structures and names of the commercial β -diketonates commonly used as ligands for the lanthanides.

transfer of a part of this light to the lanthanide ion which results in emission of the excited metal ion. The antenna effect has been well documented and the reader will find more precisions in some recent didactic review articles [47–49]. Another consequence to the special nature of the lanthanide luminescence is the long lifetimes of the emissive excited states that range from the μ s to the ms. Especially, Eu^{3+} and Tb^{3+} show lifetimes that frequently reach values in the ms order. This enables applications in the field of bioinorganic chemistry. In particular, lanthanide complexes have been developed in the so-called fluoroimmunoassays which consist in determining the concentration of an analyte such as antigens, hormones, or steroids for instance by using time-resolved spectroscopy [50, 51]. Sensors based on the interaction between a luminescent lanthanide ion, and an analyte have also been developed [52–57].

Among organic ligands that serve as efficient antennae, the combination of β -diketonates and aromatic polypyridines has been frequently used with luminescent lanthanides [58, 59]. β -diketonates are bidentate monoanionic ligands and some of them efficiently transfer energy to the lanthanide ions. The commercial β -diketonates that have been the most widely used with the lanthanide ions and their abbreviated names are reported on Figure 1. Lewis bases such as 2,2'-bipyridine or 1,10-phenanthroline (or their derivatives) are bidentate neutral ligands that strongly coordinate the trivalent lanthanide ions. The concomitant use of these two families of ligands leads to mononuclear neutral complexes of formulae $[\text{Ln}(\beta)_3(\text{L})]$ ($\beta = \beta$ -diketonate, $\text{L} = 2,2'$ -bipyridine (bipy) or 1,10-phenanthroline (Phen) or one of their derivatives) with increased stability and luminescent properties. In addition, these complexes (and espe-

cially those made with β -diketonates featuring fluorine atoms [60]) show good volatility, a property of paramount importance for their processing by thermal evaporation. This combination of ligands sets results in heteroleptic complexes among which the best luminescent molecular materials have been obtained. For instance, the most luminescent molecular europium complex known is $[\text{Eu}(\text{tta})_3(\text{dbso})]$ (dbso = dibenzoyl sulfoxide) with a solid-state quantum yield as high as 85% [61].

It is only recently that chemists have started to investigate the ability of 2,2'-bipyrimidine to form complexes with the lanthanide ions. Luminescence studies have been performed on mixed d-f complexes [62–66], monometallic [67–69] and homo-bi- and polymetallic complexes [67, 70–80]. In particular, bpm was shown to connect a transition metal and a lanthanide ion, allowing sensitization of the lanthanide luminescence by the transition metal [62, 81]. Also, 2,2'-bipyrimidine was shown to allow an electronic connection between two lanthanide ions as revealed by magnetism investigations. It has been reported that antiferromagnetic interactions between two 4f metal ions took place through bpm linkage [82, 83], and one report has shown that a weak ferromagnetic interaction occurred between two $\text{Eu}(\text{II})$ ions connected by bpm [84]. Most of these photophysical, and magnetism studies are closely related to the structural properties of the compounds.

This review aims at emphasizing the importance of the ligands sets used in the chemistry of lanthanides with 2,2'-bipyrimidine in the design of molecular compounds and coordination polymers of various dimensionalities. In a first section, an overview of the two coordination modes of bpm will be discussed based on the X-ray crystal structures

of the complexes reported in the literature. The second section will be devoted to the relationship between structural and physical properties of the complexes, with respect to photophysical, electroluminescent and magnetic properties.

2. Discussion

2.1. Structural Properties

2.1.1. 2,2'-Bipyrimidine as a Bridging Ligand: Bimetallic Complexes and Coordination Polymers

Heteroleptic Complexes Comprising bpm and β -diketonates. 2,2'-bipyrimidine has been shown to give rise to an interesting variety of structures when coordinated to lanthanide ions. Compounds from 0D molecular complexes to 3D hybrid organic-inorganic frameworks, through 1D bimetallic complexes and 1D coordination polymers were obtained and structurally described. In particular, when combined with β -diketonates, molecular complexes and 1D hybrid organic-inorganic frameworks were obtained and structurally described. These architectures are described hereafter.

The synthesis of lanthanide complexes with bpm and β -diketonates is relatively straightforward. Usually, the reaction is conducted by mixing the deprotonated β -diketonates, bpm and the chloride or nitrate salt of the lanthanide ion. The complex readily precipitates from the reaction mixture. In most cases, homodinuclear complexes of general formula $[\{\text{Ln}(\beta)_3(\text{X})_n(\text{solv})_m\}_2(\mu\text{-bpm})]$ ($\text{Ln} = \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Ho}, \text{Er}, \text{Yb}, \text{Lu}$; $\text{X} = \text{NO}_3^-, \text{Cl}^-$; $n = 0, 3$; $m = 0, 1$) were obtained after recrystallization [67, 70–78]. The structure of the complex $[\{\text{Nd}(\text{dbm})_3(\text{THF})\}_2(\mu\text{-bpm})]$ is shown at the top of Figure 2 as a representative example. These bimetallic compounds show that bpm can coordinate large metal ions from both sides. Polymetallic complexes of higher nuclearity were also reported with the Nd^{3+} ion (Figure 2, bottom) [67]. In these complexes, no sizeable distortion of the plan defined by the two pyrimidine rings was observed. Another coordination polymer was reported with the Nd^{3+} ion, namely, $[\{\text{Nd}(\text{hfa})_3\}_2(\mu\text{-bpm})]_\infty$ [79], and two other ones were reported with the smaller Eu^{3+} [80], and Gd^{3+} ions [79]. This structural feature is of importance in view of the use of bpm as a connecting ligand for the design of extended structures. The bond lengths between the nitrogen atoms of the bpm ligand and the metal ion are slightly higher than those reported for compounds with other Lewis bases such as 1,10-phenanthroline. For instance, the Eu-N average distance is 2.687(9) Å in $[\{\text{Eu}(\text{tta})_3\}_2(\mu\text{-bpm})]$ [72], while it is only 2.594(11) Å in $[\text{Eu}(\text{tta})_3(\text{Phen})]$ [85]. This difference is mostly related to the more pronounced basic character of the 1,10-phenanthroline compared to that of 2,2'-bipyrimidine.

By using strictly identical experimental conditions, it was shown that the β -diketonates used could induce structural changes in the final product. Indeed, the reaction conducted in absolute ethanol between the β -diketonates, an aqueous solution of sodium hydroxide as the base and neodymium chloride lead to the isolation of compounds of different

FIGURE 2: Structure of the bimetallic complex $[\{\text{Nd}(\text{dbm})_3(\text{THF})\}_2(\mu\text{-bpm})]$ (top) and of the coordination polymer $[\{\text{Nd}(\text{tta})_3\}_2(\mu\text{-bpm})]_\infty$ (bottom).

formula, depending on the β -diketonate used. A bimetallic complex of formula $[\{\text{Nd}(\text{bta})_3(\text{MeOH})\}_2(\mu\text{-bpm})] \cdot \text{bpm}$ ($3 \cdot \text{bpm}$) was obtained after recrystallization from methanol, while the coordination polymer $[\{\text{Nd}(\text{tta})_3\}_2(\mu\text{-bpm})]_\infty$ was obtained in exactly the same experimental conditions [67]. Another similar example can be found in the literature. Two papers published by the same group have also shown that complexes of different dimensionality could be obtained depending on the β -diketonate used. Two bimetallic complexes of formula $[\{\text{Eu}(\beta)_3\}_2(\mu\text{-bpm})]$ ($\beta = \text{tta}, \text{tta}$) were obtained [73], while the one-dimensional coordination polymer $[\{\text{Eu}(\text{hfa})_3\}_2(\mu\text{-bpm})]_\infty$ has been isolated with identical experimental conditions [80]. Comparison of the products formed along the lanthanide series with the same set of ligands suffers from the scarcity of the examples that can be found in the literature. In consequence, no real influence of the metal ion can be brought out on the structure of the final compounds. Going from Nd^{3+} to Lu^{3+} , bimetallic complexes of formula $[\{\text{Ln}(\text{fod})_3\}_2(\mu\text{-bpm})]$ ($\text{Ln} = \text{Nd}, \text{Eu}, \text{Tb}, \text{Ho}$ and Lu) were obtained [77, 78]. However, the system ($\text{Ln}, \text{hfa}, \text{bpm}$) afforded one-dimensional coordination polymers of formula $[\{\text{Ln}(\text{hfa})_3\}_2(\mu\text{-bpm})]_\infty$ with the Nd^{3+} , Eu^{3+} and Gd^{3+} ions, while the monometallic complex $[\text{Tb}(\text{hfa})_3(\text{bpm})(\text{H}_2\text{O})]$ was isolated with the Tb^{3+} ion. A caveat should be put on this latter observation as this Tb complex could originate from the presence of the strongly coordinating water ligand, and, as it will be described below, a strongly coordinating solvent like water can induce structural changes in compounds formed between Ln ions and bpm. At that point, further comparison between structures of complexes reported by different authors appears to be

FIGURE 3: Structure of the 3D coordination polymer $[\text{EuCl}_2(\text{bpm})(\text{MeOH})_{0.5}]_\infty$ (see Figure 2 for legend, Cl^- : orange).

quite tricky as the experimental conditions used by each group are not identical to each other.

Some interesting investigations on the stability of the $[\{\text{Ln}(\text{fod})_3\}_2(\mu\text{-bpm})]$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Ho}$) complexes were reported [77, 78]. It was shown that these dinuclear complexes were stable at temperature as high as 200°C and melt at 215°C . In addition, their melting point is higher than that of their mononuclear analogues made with 1,10-phenanthroline and 2,2'-bipyridine. No change in these parameters seems to occur when going from one metal ion to another one, as earlier shown with the $[\{\text{Ln}(\text{nta})_3\}_2(\mu\text{-bpm})]$ ($\text{Ln} = \text{Eu}, \text{Gd}$) system [70]. These data are important in view of the use of such complexes as molecular materials processed by thermal evaporation.

The systems comprising β -diketonates described above have been the most investigated. However, a few structures of complexes comprising lanthanide ions and bpm as a bridging ligand without β -diketonates have been reported. They are described hereafter.

Complexes without β -diketonates. In addition to the 1D coordination polymers described above, some metal organic frameworks in which bpm acts as a connector between the lanthanide ions were described. The 3D coordination polymer $[\{\text{Eu}\}_2(\mu\text{-Cl})_2(\mu\text{-bpm})\cdot 0.5 \text{ MeOH}]_\infty$ was obtained by reacting EuCl_2 and bpm in anhydrous anaerobic conditions [84]. In this compound, $\{\text{EuCl}_2\}_n$ polymeric chains are formed *via* connection of the Eu^{2+} centers through the chloride ions, and the metal ions are further connected by the bridging bpm ligands so as to form a three-dimensional framework (Figure 3). This is the only 3D framework comprising bpm known with the lanthanide ions.

Only two systems comprising ligands other than β -diketonates and yielding bimetallic complexes structurally characterized were recently reported. These compounds are

$[\{\text{Nd}(\text{L})_3\}_2(\mu\text{-bpm})]$ ($\text{L} = \text{dimethyl-N-trichloroacetylphosphato}$) [69] and $[\{\text{Eu}(\text{NO}_3)_3(\text{bpm})\}_2(\mu\text{-bpm})]\cdot \text{H}_2\text{O}$ [74]. The $[\{\text{Ln}(\text{X})_3\}_2(\mu\text{-bpm})]$ complexes were synthesized from reaction in isopropanol between the sodium salt of the CAPH ligand and the nitrate salts of the lanthanide ions, and crystals suitable for X-ray diffraction of the Nd complex were grown from the reactant medium. The structure is formed of dimers made of two metal ions bridged by bpm, and each ion is coordinated by three monoanionic carbacycloamidophosphates (CAPH) that are also strongly coordinating for the lanthanides. The bimetallic complexes formed with the Eu^{3+} and Gd^{3+} ions were described and analytically characterized, and the magnetic properties of the three complexes were investigated (see Section 2).

The existence of complex $[\{\text{Eu}(\text{NO}_3)_3(\text{bpm})\}_2(\mu\text{-bpm})]\cdot \text{H}_2\text{O}$ shows that bpm can adopt two coordination modes with the lanthanide ions, at least the Eu^{3+} ion. Indeed, in this complex, one bpm unit bridges two Eu^{3+} ions, while each metal ion also bears another bpm molecule that only coordinates through two nitrogen atoms and three bidentate nitrates. This is an example of the terminal coordination mode that can adopt bpm with lanthanide ions and which is described hereafter.

2.1.2. Monometallic Complexes: bpm as a Terminal Ligand.

One complete structural study reporting monometallic complexes along the series in which bpm acts as a terminal ligand was published by the author and colleagues [68]. It was shown that the reaction between bpm and the nitrate salts of the lanthanides in dry THF yielded a series of isomorphous complexes of formula $[\text{Ln}(\text{NO}_3)_3(\text{bpm})_2]$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}, \text{Tm}, \text{Yb}$). A view of the representative structure of the series is shown on Figure 4(a). The structure resembles that of the 2,2'-bipyridine (bipy) analogues $[\text{Ln}(\text{NO}_3)_3(\text{bipy})_2]$ [86, 87]. However, here again, the average Ln-N distances appear to be greater, by $0.03\text{--}0.05 \text{ \AA}$, than the corresponding distances in the analogues comprising the more basic bipy ligand. In this family of complexes, the usual linear relationship between the Ln-O and Ln-N distances and the radii of the Ln^{3+} ions is respected, with r^2 coefficients larger than 0.99. The structures of the products obtained from the same reaction conducted with the larger Ce^{3+} , Nd^{3+} , and Sm^{3+} ions were found to be solvent dependent. Complexes $[\text{Ln}(\text{NO}_3)_3(\text{bpm})_2]\cdot \text{THF}$ ($\text{Ln} = \text{Nd}, \text{Sm}$) and $[\text{Ln}(\text{NO}_3)_3(\text{bpm})(\text{MeOH})_2]\cdot \text{MeOH}$ ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}$) were obtained from recrystallization from THF and methanol, respectively. This feature is likely related to the fact that the bpm ligand is more tightly bound to the smaller lanthanide ions which are more Lewis acidic. A view of the structure of the complexes $[\text{Ln}(\text{NO}_3)_3(\text{bpm})(\text{MeOH})_2]\cdot \text{MeOH}$ is shown on Figure 4(b). The fact that one or two bpm molecules can coordinate to the metal ion is of interest in view of designing frameworks of different topologies. These compounds are rare examples of lanthanide complexes with bpm as a terminal ligand, and with the recently reported $[\text{Tb}(\text{hfa})_3(\text{bpm})(\text{H}_2\text{O})]$ [79] and $[\text{Nd}(\text{X})_3(\text{bpm})]$ ($\text{X} = \text{N}, \text{N}'\text{-dipyrrolidine-N''-trichloroacetylphosphortriamido}$) [69] complexes, they are the only mononuclear lanthanide

FIGURE 4: Representative structure of the (a) $[\text{Ln}(\text{NO}_3)_3(\text{bpm})_2]$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}, \text{Tm}, \text{Yb},$), (b) $[\text{Ln}(\text{NO}_3)_3(\text{bpm})(\text{MeOH})_2] \cdot \text{MeOH}$ ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}$), and (c) $[\text{EuCl}(\text{bpm})_2(\text{H}_2\text{O})_4]^+ [\text{Cl}]^- \cdot \text{H}_2\text{O}$ monometallic complexes (see Figures 2 and 3 for legend).

compounds comprising bpm to have been crystallographically characterized.

These complexes have limited stability, especially in aerated solution. The presence of a stronger coordinating solvent such as water can be responsible of partial decomposition of the compounds and can lead to the formation of complexes with unpredictable structures. A few structures of hydrated complexes have been reported: the already-mentioned terbium complex $[\text{Tb}(\text{hfa})_3(\text{bpm})(\text{H}_2\text{O})]$ [79], the cationic ytterbium complex $[\text{Yb}(\text{NO}_3)_3(\text{bpm})(\text{H}_2\text{O})_3]^+$ [68], and a more “exotic” compound that exists as a cation-anion pairs of formula $[\text{Ce}(\text{NO}_3)_2(\text{bpm})(\text{H}_2\text{O})_4]^+ [\text{Ce}(\text{NO}_3)_4(\text{bpm})(\text{H}_2\text{O})_4]^-$ [68]. It has been shown that, when dissolved in water, the 3D coordination polymer $[\{\text{Eu}\}_2(\mu\text{-Cl})_2(\mu\text{-bpm}) \cdot 0.5 \text{ MeOH}]_\infty$ was broken, and the monometallic complex $[\text{EuCl}(\text{bpm})_2(\text{H}_2\text{O})_4]^+ [\text{Cl}]^- \cdot \text{H}_2\text{O}$ (Figure 4(c)) was recrystallized from the aqueous solution.

However, lanthanide complexes with bpm were described to be relatively air stable in the solid state. Thus, investigations of their physical properties seemed to be the next step in view of their practical use.

2.2. Photophysical, Electroluminescent, and Magnetic Properties

2.2.1. Solid State Photophysical Properties

Monometallic $[\text{Ln}(\text{NO}_3)_3(\text{bpm})_2]$ Complexes. Most of the investigations of the photophysical properties of lanthanide complexes bearing bpm ligands were performed in solution on complexes formed with β -diketonates. However, the role of bpm as a possible sensitizer of the luminescence of the lanthanide ions was not taken into consideration. Only emission spectra recorded after excitation of the β -diketonates were reported. Below is described the role that bpm plays in the sensitization process of the luminescence of the trivalent lanthanide ions, with respect to interaction with the β -diketonates in the energy migration pathway and the direct excitation of the metal ions.

Depending on the metal ion, complexes are investigated as molecular materials with potential applications as solid

FIGURE 5: Solid-state absorption spectrum of $[\text{Nd}(\text{NO}_3)_3(\text{bpm})_2]$ (5% in MgO).

state emitters in photonic or optoelectronic devices. Within these lines, it appeared desirable to study their photophysical properties in the solid state. Isolation of the monometallic complexes of general formula $[\text{Ln}(\text{NO}_3)_3(\text{bpm})_2]$ with the visible and near infrared emissive lanthanide ions allowed us to evaluate the ability of bpm to act as an antenna for these ions. Indeed, bpm was the only sensitizer present in the molecules, the nitrates ions being nonactive as far as photophysical properties are concerned. The absorption spectrum of $[\text{Nd}(\text{NO}_3)_3(\text{bpm})_2]$ is shown on Figure 5. In addition to the sharp and poorly intense absorption bands arising from the $^4\text{I}_{9/2}$ ground state of the Nd^{3+} ion, it shows a broad and intense absorption in the UV region with a maximum at 249 nm. This band was described to be a $\pi\text{-}\pi^*$ or an $n\text{-}\pi^*$ transition of the bpm. When excited within this broad band, the complexes showed the typical emission lines of the lanthanide ions. Furthermore, the excitation spectra of the complexes recorded when monitoring of the metal ion emission lines all showed a broad band attributed to $\pi\text{-}\pi^*$ and/or $n\text{-}\pi^*$ transitions within the electronic states of

FIGURE 6: Excitation (black traces) and emission spectra (of the complexes $[\text{Ln}(\text{NO}_3)_3(\text{bpm})_2]$ $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Er}, \text{Tm}, \text{Yb}$) in the solid state. Excitation spectra have been measured by monitoring the most intense band of the emission spectrum for each ion, and emission spectra have been obtained after excitation within the excited electronic states of bpm ($\lambda_{\text{exc}} = 330 \text{ nm}$).

the organic bpm ligand in addition to the typical narrow $f-f$ absorption bands of the Ln^{3+} ions (Figure 6). These spectra clearly indicate that an energy transfer occurred from the bpm to the metal ions, resulting in emission of the latter. Measurements of the overall quantum yields afforded very high values of 80.0 and 70.0% for the Tb^{3+} and Eu^{3+} complexes, respectively. An interesting value of 5.1% was measured for the Dy complex. The sensitization of the luminescence of the near-IR Yb^{3+} emitter by bpm was also found to be relatively efficient with a value of 0.8% for the overall quantum yield. As reported on Figure 6, emission of the Tm^{3+} , Nd^{3+} , and Er^{3+} ions was also observed after excitation within the excited states of the bpm, but the intensity was too low for measurements of the quantum yields. Also, a more rarely described phenomenon observed is the near-IR emission from the $\text{Sm}(\text{III})$ and $\text{Dy}(\text{III})$ ions. The three transitions $^4\text{G}_{5/2} \rightarrow ^4\text{F}_{5/2}$ (943 nm), $^4\text{G}_{5/2} \rightarrow ^4\text{F}_{7/2}$ (1024 nm), and $^4\text{G}_{5/2} \rightarrow ^4\text{F}_{9/2}$ (1169 nm) were observed for $[\text{Sm}(\text{NO}_3)_3(\text{bpm})_2]$ and emission bands with maxima at 933 ($^4\text{F}_{9/2} \rightarrow ^6\text{F}_{7/2}$), 1011 ($^4\text{F}_{9/2} \rightarrow ^6\text{F}_{5/2}$) and 1172 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{F}_{3/2}$) were observed for $[\text{Dy}(\text{NO}_3)_3(\text{bpm})_2]$. In addition to the emission of the metal ions, two broad emission lines attributed to the emission of the singlet and triplet excited states of the bpm, respectively, were observed on the emission spectra of the less luminescent Tm^{3+} , Nd^{3+} , and Er^{3+} complexes. The maximum intensity of the former was located around 230 nm, while the maximum of the emission of the triplet state was comprised between 400 and 450 nm [67, 68]. These results show that bpm can sensitize the luminescence of the lanthanide ions from the visible to the near-IR region of the electromagnetic spectrum. The

high values obtained for both the Tb and Eu complexes is an interesting result, as, usually, an efficient chromophore for the Tb^{3+} ion does not transfer efficiently energy to the Eu^{3+} ion for energy considerations.

Heteroleptic $[\text{Nd}(\beta)_3(\text{bpm})_x(\text{sol})_n]$ Complexes. Photophysical investigations on the neodymium complexes comprising bpm and β -diketonates were also performed [67]. Emission spectra of these compounds conditioned as microcrystalline powders are reported on Figure 7. When excited at 260–270 nm (a range of wavelengths that mostly corresponds to a $\pi-\pi^*$ band of bpm) and 350 nm (within the β -diketonate $\pi-\pi^*$ bands), the complexes $[\{\text{Nd}(\text{dbm})_3(\text{THF})\}_2(\mu\text{-bpm})]$, $[\{\text{Nd}(\text{bta})_3(\text{MeOH})\}_2(\mu\text{-bpm})] \cdot \text{bpm}$ ($3 \cdot \text{bpm}$), $[\text{Nd}(\text{tta})_3(\text{bpm})]_\infty$, and $[\text{Nd}(\text{nta})_3(\text{bpm})]_x$ showed, though weak, the characteristic narrow near-IR emission bands from the $^4\text{F}_{3/2}$ excited state to the $^4\text{I}_J$ manifold. Complexes $[\{\text{Nd}(\text{bta})_3(\text{MeOH})\}_2(\mu\text{-bpm})] \cdot \text{bpm}$ ($3 \cdot \text{bpm}$), $[\{\text{Nd}(\text{tta})_3\}_2(\mu\text{-bpm})]_\infty$, and $[\text{Nd}(\text{nta})_3(\text{bpm})]_x$ exhibited bpm phosphorescence between 370 and 580 nm with a similar envelope whatever the excitation wavelength used. This emission revealed that the triplet state of the bpm was populated when the β -diketonate ligands are excited and was the consequence of an energy transfer from the singlet state of the β -diketonates to the triplet state of bpm. The energetic diagrams that show the energy pathways in these Nd complexes are shown on Figure 8. It was observed that the emission spectrum of the complex formed with dbm as the β -diketonate showed emission from both bpm and the dbm ligands. This was explained as a lower efficiency of the energy transfer between the β -diketonates and the bpm with dbm.

There are two reports in the literature dealing with the use of bimetallic complexes with the $(\text{Ln}, \beta\text{-diketonates}, \text{bpm})$ system as phosphorescent emitters in Organic Light Emitting Diodes (OLEDs). A first device with the following structure was described in 2006: ITO/PEDOT/PVK + PBD + $[\{\text{Eu}(\text{dbm})_3\}_2(\mu\text{-bpm})]$ 10 wt.-%/LiF/Al (ITO = Indium-tin oxide, PEDOT = [poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene)], PVK = poly(9-vinylcarbazole), PBD = 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) [72]. PVK and PBD were used as a hole-transporting matrix and an electron-transporting and hole-blocking material, respectively. The emitting layer was deposited from a 1,2-dichloroethane solution, and PVK was used as the matrix. Red emission was obtained from this device which showed relatively low performances, as a brightness of 25 cd/m^2 at 16 V and an external quantum efficiency of 0.021% was reported. Attempts to characterize a similar device with $[\{\text{Eu}(\text{tta})_3\}_2(\mu\text{-bpm})]$ failed as the quality of the films formed with complexes comprising ttas were described to be too bad and many pin-holes and dark spots were formed immediately when the devices were operated. The second report described the use of $[\{\text{Eu}(\text{acac})_3\}_2(\mu\text{-bpm})]$ and $[\{\text{Eu}(\text{tta})_3\}_2(\mu\text{-bpm})]$ in devices built by thermal evaporation [88]. These multilayered devices were built with the structure: ITO/CuPc/ α -NPB/CBP $[\{\text{Eu}(\beta)_3\}_2(\mu\text{-bpm})]$ /BCP/Alq₃/LiF/Al with CuPc (copper phthalocyanine)

FIGURE 7: (a) Visible emission spectra of the complexes [$\{\text{Nd}(\text{dbm})_3(\text{THF})\}_2(\mu\text{-bpm})$] (blue, $\lambda_{\text{exc}} = 270 \text{ nm}$), [$\{\text{Nd}(\text{bta})_3(\text{MeOH})\}_2(\mu\text{-bpm}) \cdot \text{bpm}$] (orange, $\lambda_{\text{exc}} = 270 \text{ nm}$), [$\{\text{Nd}(\text{tta})_3\}_2(\mu\text{-bpm})\}_\infty$] (green, $\lambda_{\text{exc}} = 270 \text{ nm}$), and [$\text{Nd}(\text{nta})_3(\text{bpm})\]_x$] (black, $\lambda_{\text{exc}} = 260 \text{ nm}$); (b) visible emission spectra of [$\{\text{Nd}(\text{dbm})_3(\text{THF})\}_2(\mu\text{-bpm})$] (blue, $\lambda_{\text{exc}} = 353 \text{ nm}$), [$\{\text{Nd}(\text{bta})_3(\text{MeOH})\}_2(\mu\text{-bpm}) \cdot \text{bpm}$] (orange, $\lambda_{\text{exc}} = 370 \text{ nm}$), [$\{\text{Nd}(\text{tta})_3\}_2(\mu\text{-bpm})\}_\infty$] (green, $\lambda_{\text{exc}} = 370 \text{ nm}$) and [$\text{Nd}(\text{nta})_3(\text{bpm})\]_x$] (black, $\lambda_{\text{exc}} = 333 \text{ nm}$); (c) near-IR emission spectra of [$\{\text{Nd}(\text{dbm})_3(\text{THF})\}_2(\mu\text{-bpm})$] (blue, $\lambda_{\text{exc}} = 370 \text{ nm}$), [$\{\text{Nd}(\text{bta})_3(\text{MeOH})\}_2(\mu\text{-bpm}) \cdot \text{bpm}$] (orange, $\lambda_{\text{exc}} = 370 \text{ nm}$), [$\{\text{Nd}(\text{tta})_3\}_2(\mu\text{-bpm})\}_\infty$] (green, $\lambda_{\text{exc}} = 343 \text{ nm}$) and [$\text{Nd}(\text{nta})_3(\text{bpm})\]_x$] (black, $\lambda_{\text{exc}} = 370 \text{ nm}$) in the solid state.

as a hole injecting layer, α -NPB (4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl) as a hole transporting layer, CBP (4,4'-N,N'-dicarbazole-biphenyl) as the matrix, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as a hole blocking layer, Alq₃ (Aluminium tris(8-hydroxyquinolate)) as an electron injecting layer, and LiF/Al as the top cathode. Devices with both tta and acac ligands afforded white light. The electroluminescence spectrum of the device made with [$\{\text{Eu}(\text{tta})_3\}_2(\mu\text{-bpm})$] is reported on Figure 9. This

surprising result was shown to be the consequence of the simultaneous yellow-green emission of an exciplex formed between the dopant and CBP and the red emission from the Eu^{3+} ion. Performances of these OLEDs were, though low, better than that of the previously described devices with [$\{\text{Eu}(\text{dbm})_3\}_2(\mu\text{-bpm})$]. The maximum brightness for the device made with [$\{\text{Eu}(\text{tta})_3\}_2(\mu\text{-bpm})$] was found to be 83 cd/m^2 at 13.9 V , and the external quantum efficiency was 0.09%.

FIGURE 8: Relative energetic positions of the lowest singlet and triplet excited states of bpm (left) and the β -diketonates dbm, bta, tta, and nta, and possible energy migration pathways and transfers occurring in the complexes $[\{Nd(dbm)_3(THF)\}_2(\mu\text{-bpm})]$, $[\{Nd(bta)_3(MeOH)\}_2(\mu\text{-bpm})] \cdot bpm$ (3·bpm), $[\{Nd(tta)_3\}_2(\mu\text{-bpm})]_\infty$, and $[Nd(NTA)_3(bpm)]_x$.

FIGURE 9: Normalized electroluminescence spectrum of the OLED made with $[\{Eu(tta)_3\}_2(\mu\text{-bpm})]$ as the dopant.

These complexes in which bpm connects two paramagnetic metal ions are also interesting candidates for the study of magnetic interactions between two adjacent ions. Investigations in the field of molecular magnetism made on lanthanides complexes comprising bpm as a bridging ligands will now be reported.

2.2.2. Magnetic Properties of Complexes with bpm Bridges. As described above, and due to its bridging coordination mode, the 2,2'-bipyrimidine can connect metal ions to afford a

great variety of structures ranging from bimetallic complexes to coordination polymers of different dimensionalities. This is of importance in view of designing magnetic systems. Indeed, bpm was shown to allow an electronic interaction between two 3d transition metal ions in polymetallic systems. For instance, bimetallic compounds made up of systems such $[Cu^{II}\text{-}Cu^{II}_2(\mu\text{-bpm})]$ [89], $[\{Fe^{II}\text{-}Cu^{II}\}_2(\mu\text{-bpm})]$ [90], $[\{Fe^{III}\text{-}Fe^{III}\}_2(\mu\text{-bpm})]$ [91], $[\{Fe^{III}\text{-}Fe^{II}\}_2(\mu\text{-bpm})]$ [92], $[\{Fe^{II}\text{-}Cu^{II}\}_2(\mu\text{-bpm})]$ [93], $[\{Co^{II}\text{-}Co^{II}\}_2(\mu\text{-bpm})]$ [94] were studied for their magnetic properties. Also, coordination polymers comprising bpm were investigated. Monodimensional $[\{Mn^{II}\text{-}Mn^{II}\}_2(\mu\text{-bpm})]_n$ [95] and $[\{Co^{II}\text{-}Co^{II}\}_2(\mu\text{-bpm})]_n$ [94, 96] systems were investigated, as well as bidimensional $[\{Cu^I\text{-}Cu^I\}_2(\mu\text{-bpm})]_n$ [97] and $[\{Ni^{II}\text{-}Ni^{II}\}_2(\mu\text{-bpm})]_n$ [98], and tridimensional $[\{Cu^{II}\text{-}Cu^{II}\}_2(\mu\text{-bpm})]$ [98] coordination polymers built up with bpm. All these compounds show antiferromagnetic couplings between two metal ions through the bpm bridge.

The use of bpm with 4f ions in the field of molecular magnetism is also a recent field of investigations. In consequence, very few magnetostructural studies in which two lanthanide ions are directly connected and which show electronic interaction through bpm have been reported. Interactions between Yb^{3+} ions [82], two Nd^{3+} ions and two Gd^{3+} ions [69], and Ce^{3+} ions [83] were described. In all cases, variable-temperature magnetic susceptibility measurements have revealed that the interaction was weakly antiferromagnetic with values of $-0.0195(4)$ and -1.1 cm^{-1} for the $J_{Gd\text{-}Gd}$ and $J_{Ce\text{-}Ce}$ coupling constants in $[\{Gd(X)_3\}_2(\mu\text{-bpm})]$ ($X = \text{dimethyl-N-trichloroacetylamidophosphato}$) [69], and $[\{Ce(dmf)_3(H_2O)_4\}_2(\mu\text{-bpm})]^{3+}[W(CN)_8]_2^{3-} \cdot 3H_2O$, and $[\{Ce(dmsO)_4(H_2O)_2\}_2(\mu\text{-bpm})]^{3+}[W(CN)_8]_2^{3-} \cdot 4H_2O$, respectively [83].

The Gd^{3+} ion has been the most investigated trivalent lanthanide ion for magnetic purpose as it is a highly paramagnetic ion that possesses seven unpaired electrons. The divalent europium ion is isoelectronic to Gd^{3+} . However, because of the easy oxidation to Eu^{3+} and the resulting instability of the Eu^{2+} complexes, it has not been paid a real attention to the latter in the field of molecular magnetism. We have reported the sole example to date of a magnetic interaction between two Eu^{2+} ions in compounds formed with organic ligands [84]. These compounds were the two 1D coordination polymers of formulae $([\{\text{Eu}(\text{H}_2\text{O})_3\}_2(\mu\text{-bpm})]^{2+}[\text{I}]_2^{2-} \cdot 0.5 \text{ bpm})_\infty$ and $([\{\text{EuI}(\text{MeOH})\}_2(\mu\text{-bpm})]^{+}[\text{I}]^{-})_\infty$, respectively, and the 3D framework $[\{\text{Eu}\}_2(\mu\text{-Cl})_2(\mu\text{-bpm}) \cdot 0.5 \text{ MeOH}]_\infty$. Weak ferromagnetic interactions occurring between two Eu^{2+} ions separated by about 7 Å by the bridging bpm ligand were described. The coupling constant was found to be positive and values of +0.02 and +0.01 cm^{-1} were determined for $([\{\text{Eu}(\text{H}_2\text{O})_3\}_2(\mu\text{-bpm})]^{2+}[\text{I}]_2^{2-} \cdot 0.5 \text{ bpm})_\infty$ and $([\{\text{EuI}(\text{MeOH})\}_2(\mu\text{-bpm})]^{+}[\text{I}]^{-})_\infty$, respectively. The values of the effective moments deduced from experimental data were found to be 7.8, 7.7, and 7.7 μ_B for $[\{\text{Eu}\}_2(\mu\text{-Cl})_2(\mu\text{-bpm}) \cdot 0.5 \text{ MeOH}]_\infty$, $([\{\text{Eu}(\text{H}_2\text{O})_3\}_2(\mu\text{-bpm})]^{2+}[\text{I}]_2^{2-} \cdot 0.5 \text{ bpm})_\infty$, and $([\{\text{EuI}(\text{MeOH})\}_2(\mu\text{-bpm})]^{+}[\text{I}]^{-})_\infty$, respectively. As the theoretical value for the free Eu^{II} ion amounts to 7.9 μ_B , these experimental values definitely confirmed the presence of the europium ions in the divalent state in the three compounds.

3. Conclusion

This review intended to emphasize the recent interest devoted to the use of 2,2'-bipyrimidine in designing molecular lanthanide complexes as well as lanthanide-containing hybrid organic-inorganic materials of various dimensionalities and for the role it plays on the solid-state physical properties of these materials. All the studies reported to date show the great potential that bpm can bring to lanthanide chemistry and physics. The wealth of structures that can generate this neutral Lewis base is due to the two coordination modes this ligand can adopt with the lanthanide ions. Indeed, compounds with terminal and bridging bpm ligands were isolated and structurally characterized. It is anticipated that some of these compounds could serve as molecular building blocks for more sophisticated architectures with improved physical properties. In particular, the simultaneous use of bpm with other bridging ligands such as CN^- [65, 99–102], Cl^- [84], or other bridging ligands allowing an electronic interaction between two metal ions can lead to heteropolymetallic metal-organic frameworks with interesting magnetic properties.

It is to be hoped that the use of 2,2'-bipyrimidine in lanthanide chemistry will be more investigated for designing original lanthanide-containing frameworks and molecular materials in a close future. Much remains to be made, as, for instance, no investigation on the magnetic properties of mixed *d-f* complexes structurally characterized in which transition metals and lanthanide ions are directly connected by bpm have been reported to date. Also, the very efficient

sensitization of the luminescence of both the Tb^{3+} and Eu^{3+} ions by bpm is worth to be exploited for designing new highly emissive solid state hybrid materials.

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