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Mendeleev Commun., 2024, **34**, 825–827

Mendeleev Communications

Lanthanide complexes with (4,7-dichloro-1,10-phenanthroline-2,9-diyl)-bis(pyrrolidin-1-ylmethanone): bifunctional materials for homogeneous catalysis and luminescent thermometry

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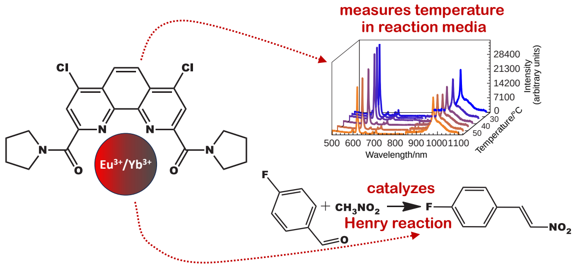
DOI: 10.1016/j.mencom.2024.10.018

The first bifunctional materials for simultaneous catalysis and temperature measurements were obtained based on europium and ytterbium complexes with (4,7-dichloro-1,10-phenanthroline-2,9-diyl)bis(pyrrolidin-1-ylmethanone). The complexes demonstrated intense visible and NIR luminescence, the ability to homogeneously catalyze the Henry reaction, and high luminescence sensitivity to temperature (S_r = 1.7% K^{-1}).



Keywords: lanthanide complexes, luminescence, homogeneous catalysis, luminescent thermometry, multifunctional materials, Henry reaction.

Homogeneous catalysis is attracting continuous attention due to its prospects such as high selectivity and low load.[1–3] For the optimization of catalyst performance, temperature is among the most important parameters to be monitored. Traditional contact thermometers (thermocouples and thermistors) are not suitable for temperature measurements at scales below 10 μm, unlike luminescent thermometers, which ensure high spatial resolution, high thermal sensitivity, and short acquisition times.[4–7] Among the thermographic phosphors, Ln^{3+}-based materials play an important role due to the narrow bands of lanthanide luminescence with constant positions, particularly suitable for calculating a luminescent intensity ratio (LIR),[8] which is the most common temperature-dependent parameter. Although early examples of luminescent thermometers used absolute intensity as a temperature-dependent parameter,[9] LIR allows for greater accuracy due to the internal standard effect. To ensure high luminescence intensity, lanthanide coordination compounds (Ln CCs) with highly absorbing antenna ligands were used.[10–14]

Lanthanides are also known as catalysts for various reactions, among which the Henry reaction is very important as it allows one to build up the carbon frame of a compound to form a new bifunctional group, namely, β-nitroalcohol.[15] For the Henry reaction, the selection of an effective catalyst is of particular importance because many secondary processes are possible in its course.[16] In addition, the condensation reaction is highly exothermic, and temperature control of the reaction mixture is important not only for obtaining the desired product but also for ensuring safety during the reaction in a large volume. The lanthanide catalysis is ensured by the strong Lewis acidity of lanthanide ions.[17,18] The combination of luminescent properties, including luminescent thermometry, and catalytic ability in one molecule can result in obtaining an ultimate bifunctional material suitable for synchronous catalysis and temperature measurements.[19–21] To design such a material, we proposed to use ligands that (a) can strongly coordinate lanthanide ions, (b) efficiently sensitize their luminescence, (c) form soluble complexes stable in solution, and (d) leave room in the lanthanide coordination sphere to ensure catalysis.

In accordance with previously published data, we selected the derivatives of 1,10-phenanthroline-2,9-dicarboxamide (Figure S1; see Online Supplementary Materials) as such ligands, some of which have already demonstrated the sensitization of europium luminescence.[22–24] These tetradentate ligands are expected to strongly coordinate lanthanide ions, even in solution, and the crystal data for their lanthanide complexes demonstrated the presence of only one ligand in the coordination sphere.[25,26] As the central metal ions, we selected both red-emitting europium and NIR-emitting ytterbium to use the luminescence intensity ratio (LIR) as the temperature-dependent signal. The ligand L was (4,7-dichloro-1,10-phenanthroline-2,9-diyl)bis(pyrrolidin-1-ylmethanone).

Lanthanide complexes $LnLCl_3(H_2O)_2 \equiv LnL$ (Ln = Eu, Yb, and Gd) were obtained by the dissolution of lanthanide chlorides and ligand (1 : 1 mol) in ethanol. The solution was stirred for 24 h and evaporated to dryness, and the obtained powder was recrystallized from water. A comparison of the IR spectra of L and EuL (Figure S2) indicated the binding of an organic ligand to a metal ion through oxygen of the amide group, as evidenced by the shift of a band at 1630 cm^{-1} to the region of lower energies. In addition, we observed a significant extinction of the C–N band of phenanthroline (1583 cm^{-1}), which indicated the ligand tetradentate binding mode of the ligand involving two nitrogen atoms of phenanthroline and two oxides of the amide group. Both IR spectroscopic and TGA data (Figure S3a) demonstrated the formation of hydrated complexes. The composition of the complexes was also confirmed by the MALDI MS data: in the spectra of YbL (Figure S3b), the signal corresponding to *m/z* = = 688 ($YbLCl_2^-$) with expected isotopic distribution was present.

Particular attention was paid to the structure of complexes in solution. The NMR data (Figure S4) demonstrated that one ligand was coordinated to the Eu ion in solution: its signals were shifted and broadened as expected due to the lanthanide-induced shift, while the addition of the second ligand resulted in the appearance of narrow and unshifted signals corresponding to the uncoordinated ligand. This ensures both intense luminescence and the ability of the complexes to catalyze the Henry reaction.

The study of luminescent properties included the determination of the energy of a ligand triplet state (T_1) from the low-temperature spectra of GdL (Figure S5), the measurement of the absorption, excitation, and luminescence spectra of EuL and YbL (Figure S6 and S7), and the measurements of quantum yields and lifetimes in powder and methanol solution. Both EuL and YbL demonstrated intense lanthanide-induced luminescence in both powders and solutions with quantum yields of up to 15% for EuL powder and 0.7% for YbL powder (Table 1).

The temperature dependence of EuL and YbL luminescence was studied in methanol solutions because the Henry reaction was further carried out in this solvent. The EuL luminescence intensity significantly decreased with temperature

$$\text{(up to } S_r = \frac{1}{I}\frac{dI}{dT} = 2.3\%\ \text{K}^{-1}\text{)},$$

while the luminescence intensity of YbL remained almost constant (Figure S7). The large difference in the temperature quenching indicated the possibility of using a mixture of EuL and YbL to obtain a luminescent thermometer. The optimal EuL and YbL ratio was obtained by dropping 2 ml of YbL solution (2 mg ml^{-1}, acetonitrile) into 10 ml of EuL solution (2 mg ml^{-1}, acetonitrile) and measuring the luminescence spectra of each mixture. Since the luminescence intensity of europium decreased significantly upon heating, we selected a composition containing 4% EuL (Figure S8).

For the mixture, we observed a decrease in the luminescence intensity of the europium band at the same rate as in the case of EuL; however, we also observed a slight decrease in the YbL luminescence intensity. As a result, the LIR for the mixture changed with a maximum sensitivity of

$$S_r = \frac{1}{\text{LIR}}\frac{d\text{LIR}}{dT} = 1.7\%\ \text{K}^{-1}.$$

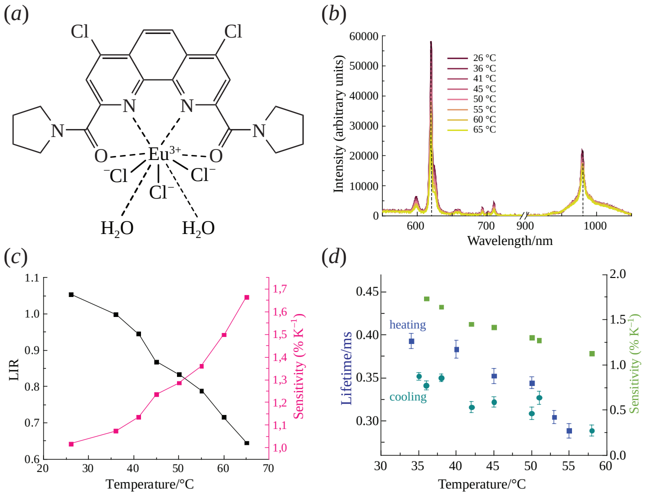


Figure 1 (*a*) Proposed structure of the EuL complex, (*b*) luminescence spectra, (*c*) LIR and sensitivity, and (*d*) Eu lifetimes and sensitivity for a mixture of EuL and YbL in MeOH.

Table 1 Photophysical properties of L and its complexes EuL, YbL.

Sample	λ_{ex}^{max}/nm	T_1/cm^{-1}	τ/μs	QY_{Eu}^{L} (%)[a]	QY_{Eu}^{Eu} (%)[b]	η_{sens} (%)[c]	QY_{Yb}^{L} (%)
powder	370	17 500	491±6	15	23	66	0.7
solution in MeOH	365	18 400	507±6	2	18	8	–

[a] QY_{Eu}^{L} – external quantum yield of Eu complex. [b] QY_{Eu}^{Eu} – internal quantum yield of Eu complex, $QY_{Eu}^{Eu} = \tau_{obs}/\tau_{rad} = \tau_{obs}\ k_{rad} = \tau_{obs}\ An^3 I_{tot}/I_{MD}$. [c] $\eta_{sens} = QY_{Eu}^{L}/QY_{Eu}^{Eu}$, effectivity of sensitization.

Thermal quenching of EuL luminescence also affected the luminescence lifetime both in the EuL solution and in the mixture. The sensitivity by the lifetime reached

$$S_r = \frac{1}{\tau}\frac{d\tau}{dT} = 1.7\%\ \text{K}^{-1}$$

for the EuL solution and for LIR measurements [Figures 1 (*b*,*d*), Figure S9].

In order to use the resulting complex as a luminescent thermometer in the reaction mixture, we carefully analyzed the effects of the reaction components on the type of luminescence spectra. In the presence of *p*-fluorobenzaldehyde vapor and the reaction product, a significant decrease in the luminescence intensity was observed, while the addition of nitromethane had almost no effect on the luminescence intensity. However, more importantly, the presence of the mixture components did not affect either the shape of the luminescence spectra or the lifetime of europium. Thus, we considered LIR and lifetime as characteristics that depend only on the temperature of the reaction mixture, and used them as parameters to determine the reaction temperature.

Finally, we studied the possibility of using the selected complexes to catalyze the Henry reaction (Figure S10). The reaction was carried out in methanol (1 ml), at a ratio of 1 : 1 between reagents in the presence of 10 mg of YbL. To check the course of the reaction, we measured ^{19}F NMR spectra (Figure S11), which clearly demonstrated the appearance of a signal due to the product in the spectrum of the reaction mixture.

Thus, we reported the synthesis of the lanthanide complexes $LnLCl_3(H_2O)_2 \equiv LnL$ with (4,7-dichloro-1,10-phenanthroline-2,9-diyl)bis(pyrrolidin-1-ylmethanone). These complexes demonstrated intense visible (EuL) and NIR emission (YbL) in powders and in methanol solution. We demonstrated that one ligand was coordinated to the central ion in solution. The complexes catalyzed the Henry reaction between *p*-fluorobenzaldehyde and $MeNO_2$. EuL, YbL, and their mixture demonstrated a temperature dependence of luminescence, and the luminescence intensity ratio of Eu and Yb did not change in the presence of the reaction components. Therefore, we considered LIR and lifetime as characteristics that depend only on the temperature of the reaction mixture and used them as parameters to determine the reaction temperature.

This work was supported by the Russian Science Foundation (grant no. 22-73-00108).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.10.018.

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Received: 3rd May 2024; Com. 24/7491