Development of sensors for ambient temperature measurement

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Abstract

The synthesis of novel Eu 1,3-diketone complexes as well as the evaluation of the influence of the ligand substituents R^1 and R^2 on the luminescence properties [emission intensity (I), temperature sensitivity (T), pressure sensitivity (p) and photostability] of the resulting Eu complexes are reported. Many of new temperature sensitive paints (TSPs) exhibit not only exceptional high temperature sensitivity over a wide range of temperatures but are also characterized by negligible pressure sensitivity and marked photostability. This is why they are outstandingly suitable for applications, e.g. in aerodynamics and hydrodynamics.

1 Introduction

Despite considerable progress in the development of TSPs there is still a strong demand for the development of practically applicable TSPs which combine high *T* sensitivity and negligible *p* sensitivity over a broad temperature range with high photostability. A series of Eu complexes with 1,3-diketo ligands carrying a wide variety of substituents R^1 and R^2 has been prepared (Figure 1). It has been established that the nature of R^1 and R^2 displays a significant influence on the luminescent properties of the corresponding Eu complexes. Preliminary results are presented here.

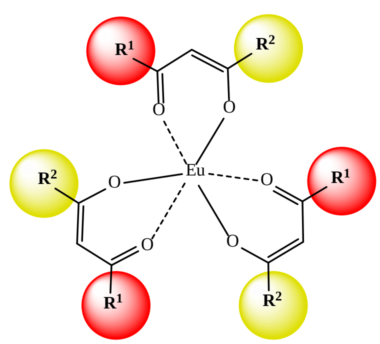
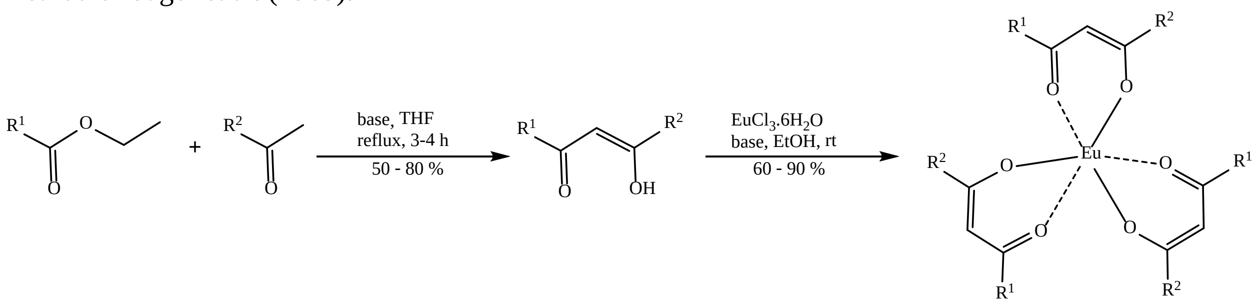


Figure 1: General structure of Eu 1,3-diketone complexes (R^1, R^2 = aryl, heteroaryl, alkyl, fluoroalkyl).

2 Comparison of the luminescent properties of synthesized Eu complexes with 1,3-diketo ligands

The 1,3-diketo ligands were obtained by Claisen condensation between the corresponding carboxylic acid esters and ketones (Scheme 1). Eu complexes were prepared in pure form and with yields up to 90% by reaction of $EuCl_3 \cdot 6\ H_2O$ with an excess of the 1,3-diketo ligands under basic conditions according to the method of Sager et al. (1965).



Scheme 1: Synthesis of Eu 1,3-diketone complexes **1-25**

The Eu complexes (c = 1 mmol·l^{-1}) were dissolved in polyurethane (PU) polymer and sprayed with a spraying gun on the Al-plates (3×3 cm) coated with PU screen layer. Samples were investigated using the calibration system at DLR Göttingen (Ondrus et al. 2015). The calibration system allows the adjustment of pressure and temperature in the range of 1 kPa < p < 150 kPa and 0 °C < T < 60 °C, respectively. The prepared samples were installed in the calibration chamber and excited by a light source with a particular spectral band width provided by the excitation monochromator of a spectrofluorometer Jasco FP-6500 (150 W continuous xenon lamp).
To determine the photostability, the samples were excited with a wave length of λ_{ex} = 405 nm. The emission light of the TSP was detected by the emission monochromator of the same spectrometer with the emission peak at λ = 615 nm every 1 s for 1 h. During this measurement the temperature and pressure in the calibration chamber were adjusted to 30 °C and 100 kPa, respectively.
All complexes were embedded in the same PU polymer (Ondrus et al. 2015) which is characterized by negligible oxygen diffusion. Thus is why the measured pressure sensitivities for all complexes presented here were below *S*p < 1%/100kPa.

Table 1**: *T* sensitivity S_T and emission intensity *I* of aryl-substituted Eu complexes 1-7**

Eu complex	**R^1**	**R^2**	**S_T [%/K, 30 °C]**	***I* [cts]**
1	4-OMe-Ph	4-OMe-Ph	3.9	4
2	4-Me-Ph	4-Me-Ph	3.5	5.1
3	Ph	2-Naph	3.4	257
4	4-CN-Ph	4-CN-Ph	3.0	177
5	2-OH-Ph	2-OH-Ph	2.9	187
6	Ph	Ph	2.9	15.4
7	Ph	Me	1.9	0.6

4-OMe-Ph = 4-methoxyphenyl; 4-Me-Ph = 4-methylphenyl; Ph = phenyl; 2-Naph = 2-naphtyl; 4-CN-Ph = 4-cyanophenyl; 2-OH-Ph = 2-hydroxyphenyl; CH_3 = methyl.

In a series of Eu complexes with 1,3-diketo ligands carrying aryl substituents R^1 and R^2 (Table 1), complexes **1** and **2** with electron donating R^1 and R^2 groups exhibit remarkably high *T* sensitivity. However, their emission intensity is three or four times lower than that of **6** (R^1, R^2 = phenyl), which is regarded as reference. Complex **4** with two electron withdrawing substituents R^1 and R^2 shows moderate *T* sensitivity, but its emission intensity is eleven times higher than that of **6**. Complex **7** with one alkyl- and one phenyl substituent is characterized by remarkably decreased *T* sensitivity as well as very low emission intensity.

Table 2**: *T* sensitivity S_T and emission intensity *I* of heteroaryl-substituted Eu complexes 8-14**

Eu complex	R[1]	R[2]	S_T [%/K, 30 °C]	*I* [cts]
8	2-Th	2-Th	5.1	220
9	2-Py	2-Py	4.5	35
10	2-Py	Ph	4.2	240
11	2-Th	2-Fu	3.8	31
12	2-Fu	2-Fu	3.7	49
13	2-Pyr	2.Pyr	3.3	2.5
14	2-NMePyr	2-NMePyr	3.1	0.6

2-Th = 2-thienyl; 2-Py = pyridyl; 2-Fu = 2-furoyl; 2-Pyr = 2-pyrrolyl; 2-NMePyr = 2-*N*-methylpyrrolyl.

For practical applications, the *T* sensitivity of sensors should not be less than 3 % K^{-1}. Especially the Eu complexes **8-12** with ligands containing two heterocyclic moieties display excellent *T* sensitivities in the range between 3.1 and 5.1 % K^{-1} (Table 2). Therefore, most of them are highly promising candidates for applications as temperature sensors. Only Eu complexes **13** and **14** are not useful as *T* sensors since their emission intensity is insufficient for intensity based temperature measurements. The 2-thienyl-substituted Eu complex **8** (R^1 = R^2 = 2-Th) not only exhibits exceptionally high *T* sensitivity over a wide range of temperatures (Table 2), but also stands out for its high emission intensity and its remarkable photostability (Ondrus et al. 2015). Therefore some other thienyl-substituted Eu complexes were synthesized und their luminescence properties were studied (Table 3).

Table 3**: *T* sensitivity S_T and emission intensity *I* of thienyl-substituted Eu complexes 8, 15-21**

Eu complex	R[1]	R[2]	S_T [%/K, 30 °C]	*I* [cts]
8	2-Th	2-Th	5.1	220
15	2-Th	2-Th-CH=CH	4.1	40
16	5-Br-2-Th	5-Br-2-Th	4.1	108
17	2-Th	3-Th	3.7	24
18	5-Br-2-Th	Me	3.7	14
19	3-Th	3-Th	3.1	149
20	2-Th	Me	2.8	0.6

2-Th-CH=CH = 2-vinylthienyl; 5-Br-2-Th = 5-bromo-2-thienyl; 3-Th = 3-thienyl; CF_3 = trifluoromethyl.

In a series of Eu complexes with 1,3-diketo ligands carrying a) two 2-thienyl substituents (**8**), b) two 3-thienyl substituents (**19**) and c) one 2-thienyl- and one 3-thienyl substituent (**17**) the *T* sensitivity increased in the order **19** < **17** < **8**. Complex **15**, with one conjugated 2-thienyl group, displays high *T* sensitivity, but the emission intensity is six times lower than that of **8**. Complex **20** with one 2-thienyl and one methyl group as substituents displays decreased *T* sensitivity and emission intensity. Surprisingly, europium (III) thenoyltrifluoroacetonate $Eu(TTA)_3$, one of the most frequently used *T* sensors (Kolodner and Tyson 1983), shows the lowest *T* sensitivity of S_T = 0.6%/K when embedded in the PU polymer, but high emission intensity at peak excitation wave length λ_{ex} = 370 nm.
In comparison to **8** (R^1 = R^2 = 2-thienyl), the values of *T* sensitivity and emission intensity of brominated Eu complex **16** (R^1 = R^2 = 5-Br-2-thienyl) are high, but lower than that of **8**. The brominated Eu complex **18** exhibits remarkably higher *T* sensitivity (more than 30 %) and its emission sensitivity is more than twenty times higher than that of non-brominated Eu complex **20**.
In the series of Eu complexes **21-25** with 1,3-diketo ligands carrying nonaromatic substituents (Table 4), only compounds **21** and **22** display interesting *T* sensitivities. In addition, the emission intensity of Eu complexes **21-24** is not sufficient for intensity based temperature measurements. Therefore, the use of nonaromatic substituted Eu complexes for intensity based temperature measurements is not promising.

Table 4**: *T* sensitivity S_T and emission intensity *I* of nonaromatic-substituted Eu complexes 21-25**

Eu complex	R[1]	R[2]	S_T [%/K, 30 °C]	*I* [cts]
21	$C(CH_3)_3$	$C(CH_3)_3$	3.7	2.7
22	$C(CF_3)_3$	$C(CF_3)_3$	3.1	2.1
23	CH_3	CH_3	2.8	0.2
24	CH_3	$-OCH_2CH_3$	1.9	0.2
25	CH_3	C_3F_7	1.7	27

$C(CH_3)_3$ = *tert*-butyl; $C(CF_3)_3$ = *tert*-perfluorobutyl; $-OCH_2CH_3$ = *O*-ethyl; C_3F_7 = heptafluoropropyl.

In Figure 2 the excitation and emission spectra of samples **1-7** are plotted with the emission measured at same excitation wave length for all samples around λ_{ex} = 405 nm and excitation measured at λ_{em} = 615 nm. The emission peaks of all complexes appear around 615 nm. This is in contrast to the excitation peaks, whose maxima appear to shift between 390 nm and 420 nm.

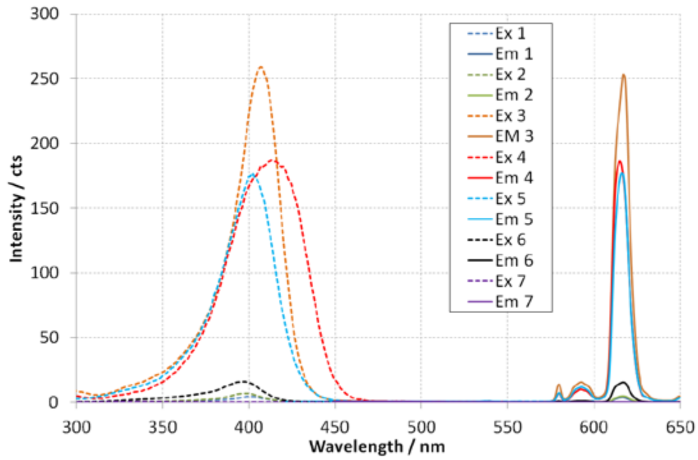


Figure 2: Emission and excitation spectra for samples **1-7** (30 °C, 100 kPa).

This effect is even stronger in samples **8** and **15-19**, where the excitation peak appears to shift between 385 nm and 423 nm as shown in Figure 3. Sample **20** was not considered due to its low emission intensity. These results suggest that the selection of an appropriate complex should be considered in cases where a specific light source is at hand and has to be used.

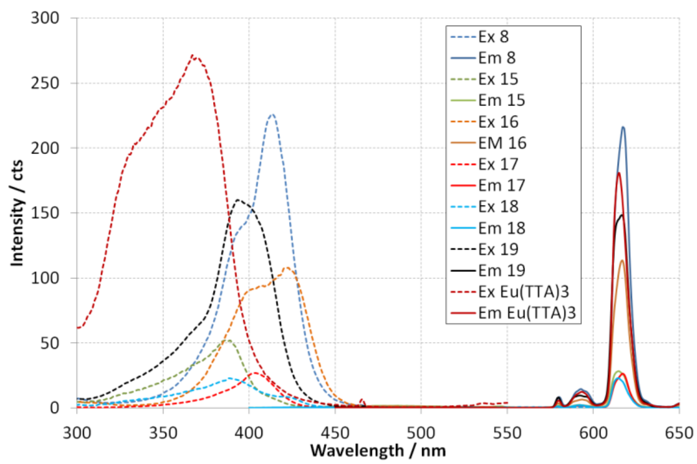


Figure 3: Emission and excitation spectra for samples **8**, **15-19** and **$Eu(TTA)_3$** (30 °C, 100 kPa).

3 Applications of synthesized Eu complexes with 1,3-diketo ligands

A typical result obtained in aerodynamic applications by means of a temperature sensitive paint based on a Eu 1,3-diketone complex is shown in Figure 4. The TSP was applied in a pocket manufactured on the upper side of a two-dimensional wind tunnel model, which had a chord of 1 m, a span of 1 m, and a supercritical airfoil as cross section. The experiments were performed in the Transonic Wind-Tunnel Göttingen (DNW-TWG) at Mach number M = 0.72, Reynolds number $Re = 9.2 \cdot 10^6$ and angle of attack AoA = 1.2°. In the TSP result, laminar and turbulent flow regions correspond to areas of high and low surface temperatures, respectively. At the examined transonic conditions, laminar-to-turbulent transition was induced by a shock at approximately 28 % of the model chord length. The strips of lower temperature visible in the turbulent region were due to the smaller model thickness in those areas, which led to a rate of inwards heat conduction larger than on the rest of the model surface. The distribution of the surface temperature T_w shown in Figure 4 was obtained via calibration of the used TSP.

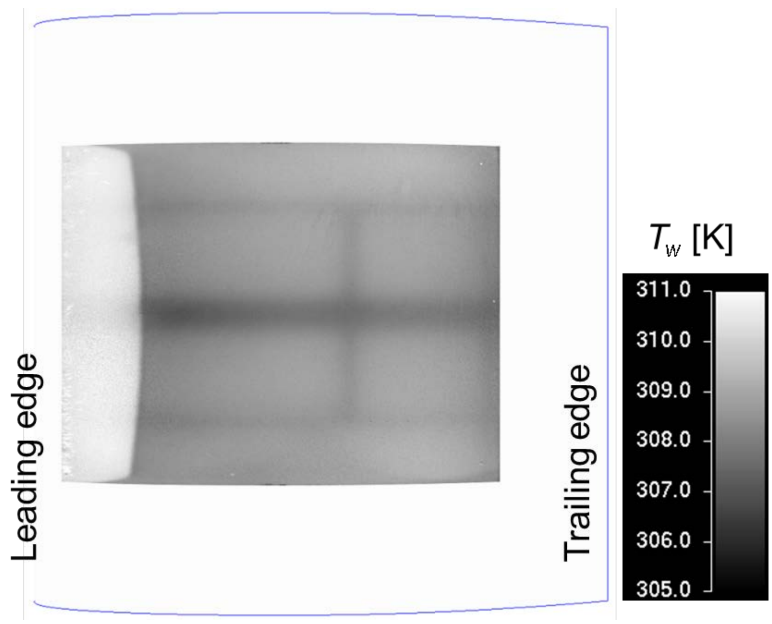


Figure 4: Result obtained by application of a Eu 1,3-diketone complex based TSP on a two-dimensional model at transonic flow conditions. Experiment performed in the DNW-TWG wind tunnel at AoA = 1.2°, M = 0.72 and $Re = 9.2 \cdot 10^6$

4 Conclusion

A series of Eu complexes with 1,3-diketo ligands carrying a wide variety of substituents R^1 and R^2 has been prepared and studied. It has been established that the structure of R^1 and R^2 has a significant influence on the luminescent properties of the corresponding Eu complexes. Eu complexes with 1,3-diketo ligands carrying aryl- or heteroaryl groups display higher *T* sensitivities as well as higher emission intensities than the Eu complexes with nonaromatic groups. The compound with the highest *T* sensitivity and emission intensity, i.e. **8** ($R^1 = R^2$ = 2-Th), has already been applied for intensity based temperature measurements in aerodynamics and hydrodynamics. Further studies will focus on the use of Eu complexes as *T* sensors in chemistry, biology and medicine.

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