

Blue LED Excitable Temperature Sensors Based on a New Europium(III) Chelate

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Abstract A new europium(III) chelate is synthesized and characterized. The wavelength of sensitization of Eu^{3+} luminescence is shifted further into visible so that efficient excitation with 425, 435 and 450-nm LEDs becomes possible. Photophysical properties and temperature dependence of luminescence are investigated in toluene solution and various polymer matrixes. The sensor materials are also characterized in terms of cross-sensitivity to oxygen and photostability. The sensor material based on the europium complex immobilized into poly(vinylidene chloride-co-acrylonitrile) shows negligible cross-sensitivity to oxygen and is particularly attractive for applications at physiological conditions. Other materials can be applied for sensing and imaging purposes at room temperatures. The new materials can also be used for compensating optical (oxygen, CO_2 etc.) sensors for temperature effects.

Keywords Optical sensor · Temperature · Luminescence · Europium

Introduction

Knowing temperature is of the highest importance in a broad variety of fields and applications and it is also essential for optical sensing of many important analytes (such as oxygen, CO_2 , etc.). Europium(III) chelates are very promising for temperature sensing and imaging since apart

from their highly temperature-dependent luminescence [1] they emit in the narrow optical window and possess long luminescence decay times in order of several hundred microseconds which are only slightly affected by oxygen [2, 3]. Most of the europium(III) probes, however, are excitable in the UV region and thus suffer from severe drawbacks such as: (a) high level of background fluorescence in many biological media; (b) low brightness and high cost of the excitation sources and (c) low transparency of the plastic fibers to the excitation light. Visible probes are more advantageous but most of them suffer from low brightnesses (defined as the product of molar absorption coefficient ϵ and luminescence quantum yield $Q.Y.$) since $Q.Y.$ rarely exceeds several percent [4, 5]. Anilinetriazine push-pull derivatives were found to be viable antenna chromophores which enable highly efficient visible sensitization of the Eu(III) luminescence in visible region [6, 7]. The brightnesses exceeded 25,000 at R.T. and 45,000 at 1 °C [7]. Although these probes were not prone to dissociation in apolar solvents, such as toluene, significant decomposition was observed in more polar solvents such as tetrahydrofuran. This results in certain difficulties when immobilizing the indicators into polymers to design optical sensor materials since luminescence from the product of dissociation, europium(III) tris- β -diketonate, can interfere. One of the possible solutions is to increase the sensitization wavelength.

Temperature sensitivity is another critical issue. For the previously reported europium(III) complexes [7] it was comparable with the sensitivity of a well-known temperature probe, ruthenium(II) tris-1,10-phenanthroline [8–10]. In fact, the luminescence decay time in toluene was reduced by ~2-fold on going from 1 to 50 °C. Higher sensitivities are desirable to provide better resolution which can be possibly achieved by using other polymer matrixes.

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Here we will report a new europium(III) temperature-sensitive probe which enables longer wavelength of sensitization and thus makes possible the excitation with blue LEDs. We will also demonstrate how the temperature sensitivity can be increased and tuned to provide maximal resolution in certain temperature ranges.

Experimental

Materials 2,4,6-trichlorotriazine, indazole, 4-bromo- *N,N*-diethylaniline, polystyrene (=PS, average MW 250,000), poly(styrene-co-acrylonitrile) (= PSAN; containing 30 wt% polyacrylonitrile, average MW 185,000), polysulfone (=PSulf, MW 26,000), anhydrous tetrahydrofuran were obtained from Aldrich (www.sigmaaldrich.com). Europium (III) tris(thenoyltrifluoroacetate) trihydrate (= Eu(tta)₃) was purchased from Fischer Scientific (www.fishersci.com). Poly(vinylidene chloride-co-acrylonitrile) (=PVlCl-PAN, MW 150,000 containing 20% wt. polyacrylonitrile) was from Polysciences (www.polysciences.com). Polymethacrylonitrile (=PMAN, MW 20,000) was purchased from Scientific Polymer Products (www.scientificpolymer.com). Ethylcellulose (=EC, ethoxy content 46%) was from Fluka (www.sigmaaldrich.com). Reversed phase silica gel (C₁₈, Ø 5 µm) was obtained from Merck (www.merck.de). Silicone primers and catalyst were purchased from ABCR. Poly(ethylene terephthalate) support (Mylar®) was from Goodfellow (www.goodfellow.com). All the solvents were obtained from Roth (www.carl-roth.de). Nitrogen and synthetic air (all of 99.999% purity) were obtained from Air Liquide (www.airliquide.at).

Phenyl Ormosil (=PhOrm) was prepared according to the literature procedure [11].

4-(4,6-dichloro-1,3,5-triazin-2-yl)-*N,N*-diethylbenzenamine was prepared according to the literature procedure [12]. 4-(4,6-di(1H-indazol-1-yl)-1,3,5-triazin-2-yl)- *N,N*-diethylbenzenamine (DEADIT) and the respective europium(III) complex (Eu(tta)₃DEADIT, Fig. 1) were prepared analogously to the published method [6]. Indazol was used instead of 3,5-dimethyl-1H-pyrazole. The europium complex with 4-(4,6-di(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazin-2-yl)- *N,N*-diethylbenzenamine (Eu(tta)₃DEADPT) was prepared according to the procedure of Yang et al. [6].

DEADIT MS (MALDI): *m/z* calc. 483.2021 (+Na), found 483.2050. Analysis: found C 68.46%, H 5.64%, N 23.66%; calc. C 70.42%, H 5.25%, N 24.33%.

Eu(tta)₃DEADIT MS (MALDI): *m/z* calc. 1053.1091 (-1 tta), found 1053.1086; calc. 832.1207 (-2 tta), found 832.1221. Analysis: found C 48.65%, H 3.06%, N 8.74%; calc. C 48.00%, H 2.84%, N 8.78%.

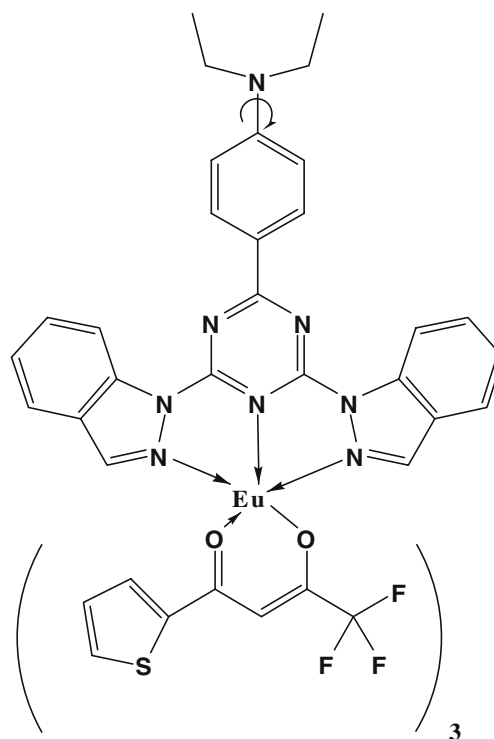


Fig. 1 Chemical structure of the temperature indicator

Preparation of the sensor films One and a half milligrams of the complex and 100 mg of a polymer were dissolved in 900 mg of a solvent. The sensor “cocktail” was knife-coated onto a 100-µm polyester support and dried at ambient air to result in ~ 8 µm-thick sensor films. Toluene was used to dissolve PS and PSAN, acetone for PMAN, chloroform for PhOrm, and THF was used for PVlCPAN.

Immobilization of the complex onto RP silica beads Five milligrams of the complex were dissolved in 2 ml of diethyl ether and the solution was added dropwise to a suspension of 500 mg of beads in 5 ml of diethyl ether. Then, 3 ml of octane were added dropwise. The solvents were evaporated under nitrogen flux. One hundred 50 milligrams of the beads were dispersed in the mixture of the silicone primers (500 mg of DMS-V21, 100 mg of HMS-301, 2 µl of SIT 7900) and 3 µl of the catalyst (SIP 6830) were added. The sensor “cocktail” was knife-coated onto a polyester support and polymerized at 60 °C for 30 min.

Spectral measurements Emission and excitation spectra were acquired on a Hitachi F-7000 fluorescence spectrometer (www.inula.at) equipped with a red-sensitive photomultiplier R 928 from Hamamatsu (www.hamamatsu.com). The emission spectra were not corrected for the sensitivity of the PMT. Absorption spectra were measured at a Cary 50 UV-Vis spectrophotometer (www.lzs-concept.com).

Relative quantum yield of luminescence was determined according Demas and Crosby [13] using 4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4H-pyrene ($\phi=0.57$) [14] as a standard ($\lambda_{\text{exc}}=420$ nm). The solutions of the dyes were thoroughly deoxygenated by bubbling nitrogen through.

Luminescence phase shifts for the dye in solution and for the sensor films were measured with a two-phase lock-in amplifier (SR830, Stanford Research Inc., www.thinksrs.com). The sensor films were excited with the LED light (λ_{max} 425 nm, www.roithner-laser.com) which was sinusoidally modulated at a frequency of 700 Hz. A bifurcated fiber bundle was used to guide the excitation light to the home-made flow-through cell and to guide back the luminescence after passing the OG 590 (Schott, www.schott.com) glass filter. The luminescence was detected with a photomultiplier tube (H5701–02, Hamamatsu, www.hamamatsu.com). Temperature was controlled by a cryostat ThermoHaake DC50 (www.thermo.com).

The photographic images were acquired using a Canon 350D digital camera (www.canon.de).

Fitting was performed using Origin[®] vs 7.5 (www.originlab.com) software.

Results and discussion

Spectral properties Absorption and emission spectra of the parent ligand DEADIT, $\text{Eu}(\text{tta})_3$ and the respective complex are shown in Fig. 2. As can be seen, a significant bathochromic shift of the intra-ligand absorption band is observed upon complexation. The molar absorption coefficient ϵ in toluene (λ_{max} 407 nm) was found to be $63,900 \text{ M}^{-1}\text{cm}^{-1}$ which is close to the value obtained previously for the pyrazole derivative ($\epsilon=71,700 \text{ M}^{-1}\text{cm}^{-1}$) [7]. Upon excitation in the CT band, the fluorescence of the ligand disappears almost completely to give the intense emission from the Eu^{3+} ion ($^5\text{D}_0 \rightarrow ^7\text{F}_1$). As can be seen from Fig. 2, the emission is substantially different from the luminescence of $\text{Eu}(\text{tta})_3$. For the $\text{Eu}(\text{tta})_3\text{DEADIT}$ complex the quantum yield of luminescence Φ in air-saturated toluene at 25 °C was estimated to be 0.4, which corresponds to the value obtained for the pyrazole derivative. The new indicator thus has excellent brightness ($\epsilon \cdot \Phi$) which exceeds 25,000 at RT. Notably, despite the fact that energy transfer efficiency is very efficient it never reaches 100%. In fact, the emission from the coordinated ligand is observed at 434 nm, compared to 408 nm for the free ligand. The quantum yield of fluorescence of the coordinated ligand, however, does not exceed 5%.

Stability of the complex Previously [7] it was found that the europium(III) complex with 4-(4,6-di(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazin-2-yl)-*N,N*-diethylbenzenamine

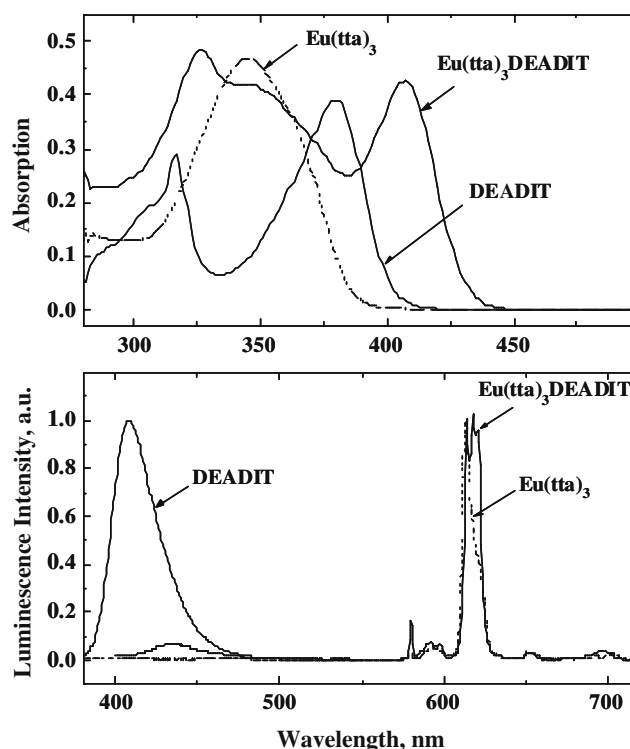


Fig. 2 Spectral properties of DEADIT, $\text{Eu}(\text{tta})_3$ and $\text{Eu}(\text{tta})_3\text{DEADIT}$ in toluene solution at 25 °C; $\lambda_{\text{exc}}=375$ nm for DEADIT and $\text{Eu}(\text{tta})_3\text{DEADIT}$, and 345 nm for $\text{Eu}(\text{tta})_3$

($\text{Eu}(\text{tta})_3\text{DEADIT}$) exhibited rather poor stability in polar solvents and in some of them (such as e.g. dimethylformamide) dissociated completely to give $\text{Eu}(\text{tta})_3$ and the respective ligand. Since the spectral properties of both dissociation products are very different from those of the complex, the degree of decomposition can be easily estimated by measuring absorption and emission spectra. Figure 3a and b shows respectively the absorption spectra of the previously reported $\text{Eu}(\text{tta})_3\text{DEADPT}$ and the new $\text{Eu}(\text{tta})_3\text{DEADIT}$ in different solvents. As can be observed, the two complexes are rather similar in their stability towards dissociation. Chloroform along with toluene was found to be the most suitable solvent since no dissociation was visible. At the concentrations of the complex of ~ 0.2 mM partial dissociation is observed in acetone and THF. The dissociation is more pronounced in diluted solutions. Both complexes are however completely destroyed in polar solvents such as ethanol (Fig. 3), methanol or DMF. Immobilization in gas blocking polyacrylonitrile (soluble in DMF) thus becomes impossible. The europium(III) complex can however be successfully immobilized in many other polymers, even if such solvents as acetone and THF are required. No visible dissociation is observed in polymethacrylonitrile (= PMAN, soluble in acetone) and poly(vinylidene chloride-co-acrylonitrile) (= PViCl-PAN, soluble in THF). The absorption spectra are indeed very similar to those obtained in other polymers (Fig. 3c). This can be explained by the fact

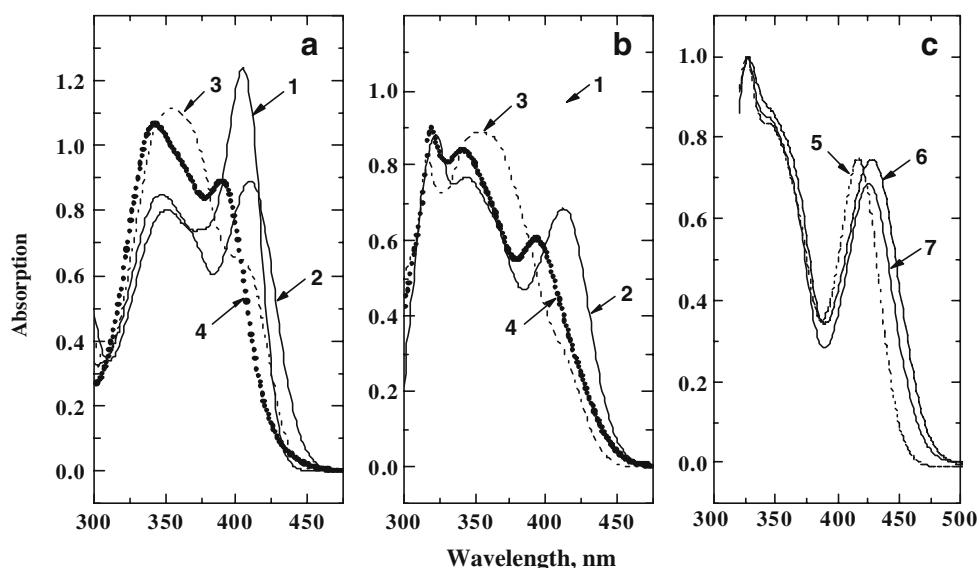


Fig. 3 Absorption spectra of $\text{Eu}(\text{tta})_3\text{DEADPT}$ (a) and $\text{Eu}(\text{tta})_3\text{DEADIT}$ (b and c) in solutions (0.17 mM, $l=1$ mm) and polymer films (1.5 wt%): 1, chloroform; 2, acetone; 3, THF; 4, ethanol; 5, phenylormosil; 6, polymethacrylonitrile; 7, poly(vinylidene chloride-co-acrylonitrile)

that rather high concentrations of the complex are required for the sensor preparation (typically ~ 1 mM), so that the complex remains stable even in acetone and THF. It should also be considered that when polymer films are prepared, the concentration of the complex is further increased due to solvent evaporation while a polymer can act as a more friendly solvent.

If immobilized into the polymer films, the absorption and excitation spectra shift bathochromically (Fig. 4, Table 1). In polystyrene, which has polarity similar to that of toluene, the shift is the lowest and the absorption peaks at 413 nm. The shift is more significant in more polar polymers such as ethylcellulose, phenylormosil, polysulfone, and poly

(styrene-co-acrylonitrile) (=PSAN) where the absorption peaks at 416, 417, 420 and 420 nm, respectively. In case of even more polar PVCl-PAN and PMAN the absorption maxima were found to be 425 and 428 nm, respectively. The excitation spectra are very similar to the absorption spectra but are typically 2–3 nm hypsochromically shifted (Fig. 5). In polystyrene, ethylcellulose, phenylormosil, polysulfone and PSAN the excitation maxima were 411, 413, 415, 417 and 419 nm, respectively. Much more significant difference between the excitation and the absorption spectra was observed in case of PVCl-PAN and PMAN. In fact, the excitation peaks at 418 and 416 nm, respectively for PVCl-PAN and PMAN, and the intensity of the intra-ligand

Fig. 4 Photophysical properties of $\text{Eu}(\text{tta})_3\text{DEADIT}$ in polymer films (1.5% w/w, ~ 10 μm thick). *Left*, absorption spectra; *right*, emission spectra compensated for the amount of the absorbed light, reflecting brightnesses of the films

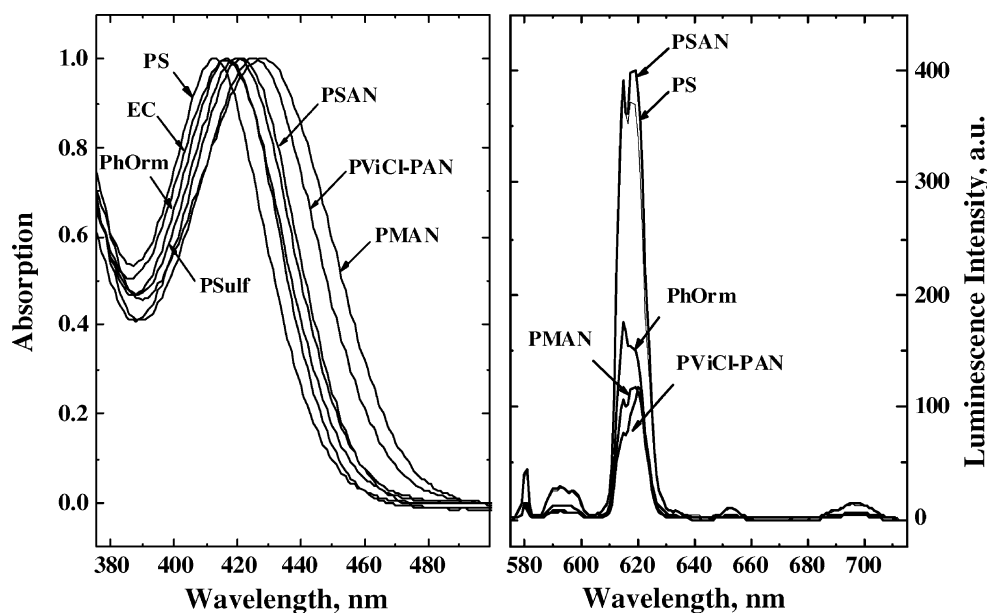


Table 1 Photophysical properties of Eu(tta)₃DEADIT in various matrixes and fit parameters (Eq. 1) for temperature dependence of the luminescence decay time

matrix	gas	$\lambda_{\text{max}}^{\text{abs}}$, nm	$\lambda_{\text{max}}^{\text{exc}}$, nm	τ at 1 °C, μs	τ at 50 °C, μs	k_0 , s^{-1}	k_1 , s^{-1}	ΔE , $\text{kJ}\cdot\text{mol}^{-1}$
toluene	N ₂	407	406	560	240	1,700	$1.7\cdot 10^{12}$	54.6
PS	N ₂	–	–	480	270	1,960	$6.2\cdot 10^9$	40.4
	air	413	411	450	260	2,080	$2.4\cdot 10^9$	37.8
PSAN	N ₂	–	–	490	260	1,920	$4.4\cdot 10^9$	39.4
	air	420	419	460	250	2,010	$1.0\cdot 10^9$	35.3
EC	N ₂	–	–	470	190	1,890	$9.0\cdot 10^9$	39.7
	air	416	413	410	170	2,000	$5.2\cdot 10^8$	31.7
PhOrm	N ₂	–	–	510	250	1,880	$8.7\cdot 10^{11}$	53.1
	air	417	415	490	230	1,960	$1.4\cdot 10^{11}$	48.0
PSulf	N ₂	–	–	450	250	2,060	$1.4\cdot 10^9$	36.2
	air	420	417	420	240	2,190	$6.7\cdot 10^8$	34.2
PMAN	N ₂	–	–	330	170	2,240	$1.6\cdot 10^7$	22.5
	air	428	416	320	160	1,730	$1.8\cdot 10^6$	16.3
PViCl-PAN	N ₂	–	–	360	130	2,760	$7.2\cdot 10^{14}$	68.9
	air	425	418	350	130	2,780	$2.5\cdot 10^{14}$	66.3
RP silica	N ₂	–	–	350	120	2,490	$7.1\cdot 10^8$	31.5
	air	–	397	310	120	2,380	$4.4\cdot 10^9$	36.3

band is decreased (Fig. 5). This is likely to be caused by lower efficiency of energy transfer from the triplet state of the antenna ligand to the europium ion because of the very low energy gap. Nevertheless, efficient excitation by using bright LEDs is possible for all the films. Figure 6 shows the photographic images of the indicator in toluene solution and immobilized in a PMAN film when excited with the light of 405, 425, 435, 450 and 470 nm LEDs. As can be seen, the dye in solution is efficiently excitable by the light of 405, 425 and 435 nm LEDs. A 450-nm LED can also be used for excitation, however with lower efficiency. Very little luminescence is recorded if the solution is excited with the light of a 470-nm LED. In case of polymer films, the Eu³⁺ uminescence is efficiently generated by excitation with 405,

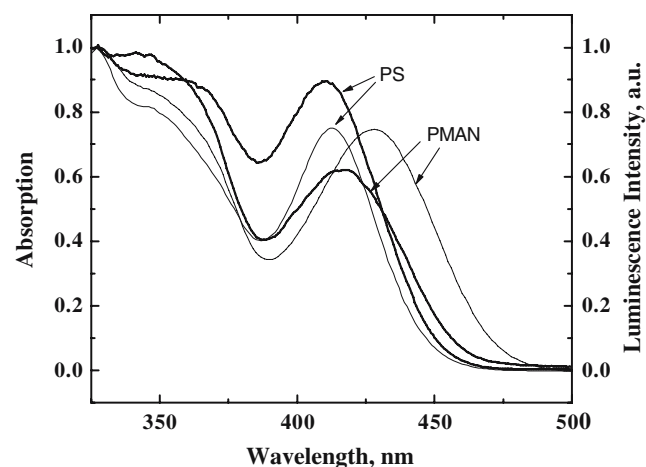


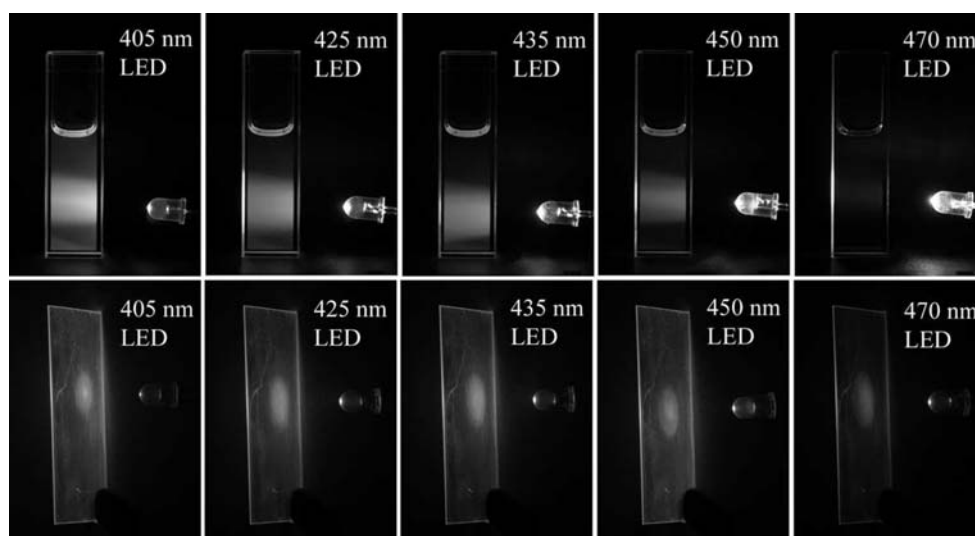
Fig. 5 Absorption (*thin lines*) and excitation (*thick lines*) spectra of Eu(tta)₃DEADIT in polystyrene and polymethacrylonitrile (1.5% w/w dye in polymer, ~10 μm thick films)

425, 435 and 450 nm LEDs. Measurements of luminescence intensity revealed similar values for these LEDs. In case of the polymer films, excitation is still possible by the light of a 470-nm LED, however the luminescence intensity was estimated to be ~5 times lower than when using other LEDs.

Temperature sensing in solution Many europium(III) chelates are known to exhibit temperature-dependent luminescence [1–3, 7] which can be explained by deactivation of the ⁵D₀ state through a low-lying ligand to metal CT state [1]. In case of Eu(tta)₃DEADIT the possible ways of deactivation are likely also to involve the antenna chromophore particularly by promoting the rotation of the diethylamino group. Figure 7 shows temperature dependence of the luminescence intensity and decay time of the toluene solution of Eu(tta)₃DEADIT. As can be observed, the luminescence intensity is much more temperature-dependent than the decay time. In fact, on going from 1 to 43 °C the decay time drops by ~1.9-fold, but the luminescence intensity is decreased by ~4.2-fold. Evidently, the decay time only reflects deactivation of the ⁵D₀ state, whilst higher temperature effect on the luminescence intensity represents the combination of two main processes including deactivation of the ⁵D₀ state of the europium ion, but also of the triplet excited state of the antenna chromophore.

Temperature sensing in polymer films For any temperature indicator be suitable for practical applications it should be immobilized into a polymer matrix. The sensors can be used in various formats including planar sensor foils, fiber-optic sensors, paints and nano- and microbeads. Generally,

Fig. 6 Photographic images of a cuvette with toluene solution of $\text{Eu}(\text{tta})_3\text{DEADIT}$ (upper row) and a sensor foil containing $\text{Eu}(\text{tta})_3\text{DEADIT}$ in polymethacrylonitrile (1.5% w/w, 10 μm -thick) upon excitation with LEDs. Concentration of the dye in solution is $6 \cdot 10^{-6}$ M



polymers can influence the properties of the obtained materials in several ways:

- by affecting the temperature sensitivity;
- by shielding the indicator from oxygen. Here, the polymers having low gas permeability will usually favor materials having lower cross-sensitivity to oxygen. Although the negligible cross-sensitivity to oxygen is very desirable, it is not easy to achieve in practice since there are few gas-blocking materials and even less are compatible with the europium complex. For example, virtually gas-impermeable poly(acrylonitrile) [8] can only be dissolved in such solvents as dimethylformamide or dimethylsulfoxide, which lead to complete dissociation of the complex to $\text{Eu}(\text{tta})_3$ and DEADIT. On the other side, the temperature-sensitive materials which possess pronounce cross-sensitivity to temperature can be reliably used only at constant oxygen

content or should be compensated for by measuring pO_2 (if it is varied).

- by promoting quenching. Some polymers can quench the luminescence of the complex e.g. by deactivating the antenna chromophore. In fact, the fluorescence of similar molecules was quenched in polar solvents by promoting rotation of the diethylamino group [15]. We have also observed the quenching of luminescence of both the antenna chromophore DEADIT and the respective complex $\text{Eu}(\text{tta})_3\text{DEADIT}$ when dissolved in acetone.

The calibration plots for the temperature-sensitive materials based on different polymers are presented in Fig. 8. All the materials were obtained in the format of planar sensor foils having an $\sim 8 \mu\text{m}$ thick sensor layer covering a transparent poly(ethylene terephthalate) support foil. Fitting (with a correlation coefficient $r^2 > 0.999$) is performed using the following Arrhenius-type equation [8]:

$$\tau = (k_0 + k_1 \exp\left(-\frac{\Delta E}{RT}\right))^{-1}, \quad (1)$$

where k_0 is the temperature-independent decay rate for the excited state deactivation, k_1 the pre-exponential factor, ΔE the energy gap between emitting level and higher excited state level, and R the gas constant. The fit parameters are compiled in Table 1.

The following trends are observed. First, significant degree of quenching is observed in PVCl-PAN and PMAN, which can be explained by high polarity of these polymers. The quenching of the excited states of the antenna chromophore in these polymers is evidently even more pronounced, since the brightness of the sensor foils (which was estimated as the luminescence intensity upon excitation at 420 nm compensated for the amount of the light

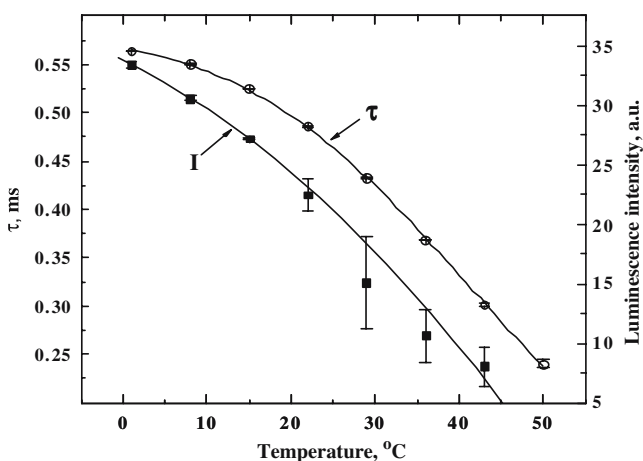


Fig. 7 Temperature dependence of the decay time and intensity of luminescence of $\text{Eu}(\text{tta})_3\text{DEADIT}$ in deoxygenated toluene ($C = 1.5 \cdot 10^{-5}$ M)

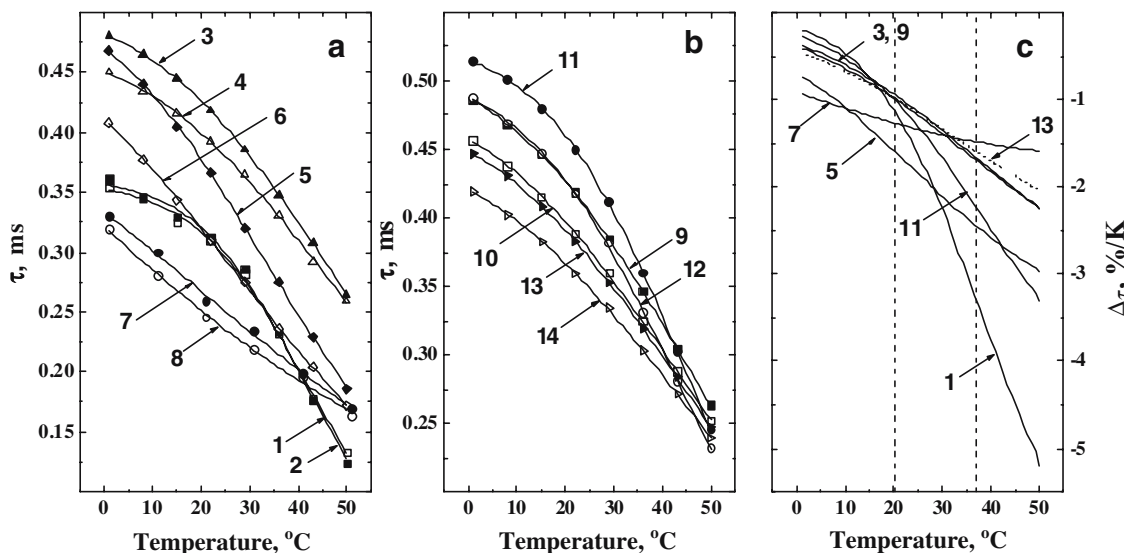


Fig. 8 Temperature dependence of the luminescence decay time of $\text{Eu}(\text{tta})_3\text{DEADIT}$ immobilized into polymer films under N_2/air (a and b) and calculated relative temperature sensitivities (c): 1/2, PVCl-PAN; 3/4, PS; 5/6, EC; 7/8, PMAN; 9/10, PSAN; 11/12, PhOrm; 13/14, PSulf

absorbed) drops more significantly than the decay time (Fig. 4, right). In fact, the brightnesses in case of PVCl-PAN and PMAN are only $\sim 30\%$ of the values obtained for PS and PSAN.

Second, cross-sensitivity to oxygen is varied substantially ($\text{EC} \gg \text{PS} \approx \text{PSAN} \approx \text{PhOrm} \approx \text{PSulf} \gg \text{PMAN} \gg \text{PVCl-PAN}$) which roughly correlates with gas permeabilities of the polymers. Cross-sensitivity to oxygen is virtually negligible in gas-blocking PVCl-PAN.

Third, the temperature dependence of the luminescence decay time is substantially influenced by the polymer matrix. The curves are quite similar in case of PS, PSAN and PSulf and the relative signal change varies from $\sim 0.5\%/K$ at lower temperatures to $\sim 2\%/K$ at higher temperatures (Fig. 8c). On the other side, $\text{Eu}(\text{tta})_3\text{DEADIT}$ in PVCl-PAN, EC and

PhOrm is highly temperature-dependent at temperatures exceeding 20 $^{\circ}\text{C}$. Several potential ranges of interest can be distinguished. For measurements at RT, the EC-based sensors are the most sensitive ($1.6\%/K$); this material, however, suffers from high cross-sensitivity to oxygen. Therefore, the PMAN-based material can be preferred ($1.26\%/K$). Other materials are slightly less sensitive ($0.94\text{--}1.1\%/K$). For measurements at physiological conditions (37 $^{\circ}\text{C}$) the PVCl-PAN-based material is clearly the most advantageous since the sensitivity is as high $3.3\%/K$ and virtually no cross-sensitivity to oxygen is observed. Finally, some more exotic applications can include mea-

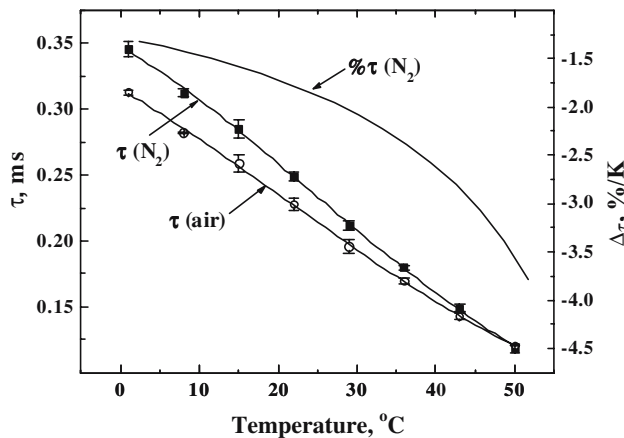


Fig. 9 Temperature dependence of the luminescence decay time of $\text{Eu}(\text{tta})_3\text{DEADIT}$ immobilized onto 5 μm reversed phase silica beads (1% w/w). The beads are dispersed in an 80 μm -thick silicone layer (20% w/w of beads in silicone)

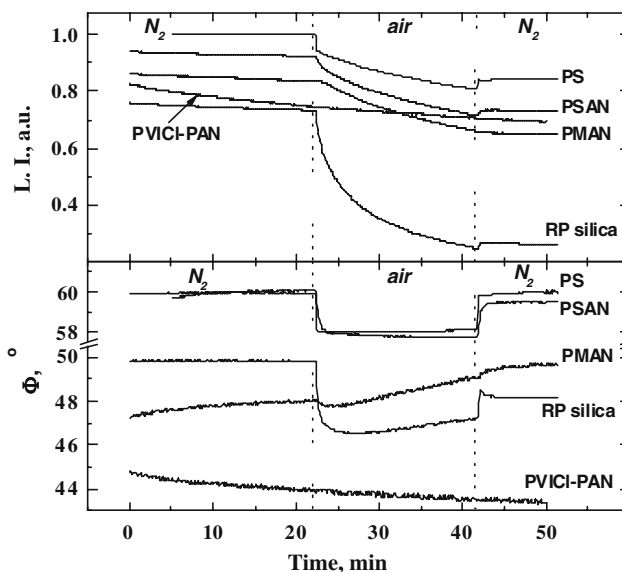


Fig. 10 Photodegradation of $\text{Eu}(\text{tta})_3\text{DEADIT}$ in polymer films ($\lambda_{\text{exc}}=425 \text{ nm}$, 25 $^{\circ}\text{C}$)

surement at temperatures close to 0 °C. In this temperature range, the substantial sensitivity is preserved for the PMAN-based material (~1%/K).

We also have investigated the possibility of increasing the temperature sensitivity by immobilizing the europium (III) complex onto a reversed-phase (C₁₈) silica particles. The lipophilic moieties are likely to provide high flexibility for the indicator and thus enhance probability of rotation of the diethylamino group which can result in thermal quenching. High degree of thermal quenching is indeed observed for the immobilized indicator (Fig. 9). Notably, a linear fit nicely describes the experimental data ($r^2=0.9996$). The linearity is preserved even at lower temperatures where high sensitivities of 1.5%/K are achieved. The material also is rather sensitive at RT (1.7%/K) and at physiological conditions (2.4%/K). It should be noted, that the microbeads can only be dispersed in a polymer by using a solvent-free procedure (e.g. by using silicone primers which are subsequently polymerized). They however are not applicable in any other polymers requiring solvents for preparation of the “cocktails” since the complex is eventually extracted into the polymer.

Photostability Photostability of the temperature-sensing materials was investigated by continuously irradiating a sensor foil with the light of a 425-nm LED and monitoring of luminescence intensity and phase shift. The results are presented in Fig. 10. The europium(III) complex in gas blocking PViCl-PAN exhibits virtually identical photodegradation rates (20% degradation of intensity and 1.6° drift in the phase shift per every hour of irradiation) both in the absence of oxygen and at air saturation. In case of the other materials, the photobleaching is much faster in the presence of oxygen. In fact, PS and PSAN films are very photostable in nitrogen atmosphere, however ~50% of the dye is bleached out after 1 h irradiation at air saturation. The phase shift of luminescence is evidently much less affected by the photobleaching and drifts by <1°/h. in case of PS and PSAN. The photobleaching is faster in case of the PMAN-based material. Finally, the europium(III) complex immobilized onto RP-silica in the absence of oxygen shows photobleaching rates similar to the other materials. At air saturation, however, the photodecomposition is increased dramatically and is as high as 5% degradation of intensity per every minute of irradiation. This renders the material practically unsuitable for real-world applications.

It should be mentioned that photostability of the complex in polymer films (except for RP silica) is adequate for the most applications where continuous irradiation is not required. In this case lifetime of the sensors can be extended significantly.

Conclusion

The new europium(III) chelate enables sensitization of the Eu³⁺ luminescence upon excitation with visible LEDs and can be successfully immobilized in polymer films. Efficient excitation with the light of 425, 435 and 450 nm LEDs becomes possible. The polymer type has pronounced effect on the form of calibration curves and cross-sensitivity to oxygen. The highest sensitivities are obtained for the europium(III) complex contained in poly(vinylidene chloride-co-acrylonitrile) and for the indicator immobilized onto reversed phase silica beads. The former material is particularly suitable for measurements at physiological conditions due to its high temperature coefficient. The most materials possess good photostability in the absence of oxygen. Although the photostability is substantially lower at air saturation it is still adequate for most applications if phase shift of luminescence is monitored. The material based on the reversed phase silica beads shows extremely high photodegradation rates in presence of oxygen and is therefore not suitable for any long-term applications. Other materials can be used for optical sensing of temperature and for compensating optical sensors for temperature effects.

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