Effects of polarity and temperature on photoluminescence of a europium(III) chelate

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The relative photoluminescence yield for (1,10-phenanthroline)europium(III) tris-thenoyltrifluoroacetonate (Eu(tta)$_3$Phen), an efficient enhancer of chemiluminescence, has been measured under the conditions (temperatures and solvents) specific for the oxidation of hydrocarbons. The yield is independent of viscosity and the presence of a heavy atom in the solvent, but the higher the polarity of the medium, the more the yield decreases as the temperature increases. The effect is interpreted as an acceleration of radiationless deactivation occurring *via* the mechanism of electron transfer from a ligand to the excited Eu^{3+} ion.

Key words: europium(III); complexes; luminescence; solvent effect; temperature effect.

Luminescent chelates of rare-earth elements (REE) are widely used in studies of energy transfer processes,[1] structures of proteins and other physiologically active compounds,[2] and mechanisms of chemiluminescence.[3,4] The luminescence of chelates is a highly sensitive and informative method for studying the structure and chemical properties of these REE complexes.[5] These studies are carried out in various media and at various temperatures; therefore, it is necessary to know the luminescent properties of chelates under these conditions.

In this work, the relative quantum yield of luminescence of (1,10-phenanthroline)europium(III) tris(thenoyltrifluoroacetonate) (Eu(tta)$_3$Phen) (**1**) was measured at 20 to 60 °C in several solvents. Complex **1** is well known to be an activator (enhancer) of chemiluminescence in the oxidation of hydrocarbons or the decomposition of peroxides.[3,6] The mechanism of the enhancement is a sequence of three efficient processes: spin-allowed energy transfer from a triplet ketone (reaction product) to the triplet ligand, intramolecular energy transfer to the Eu^{3+} ion, and finally, radiative deactivation of the ion. Complex **1** increases the luminescence 10^3—10^4 times, enhances the sensitivity of chemiluminescence methods, and makes it possible to determine the photophysical parameters of chemiluminescence and chemiexcitation yields.[3] In reactions involving charged species, REE chelates enhance chemiluminescence not only through the physical processes mentioned, but also by more complicated routes, including the formation of complexes and electron transfer reactions.[6]

Experimental

Measurements were performed in solutions of diphenylmethane (DPM) in CCl$_4$, PhH, PhBr, PhCl, Bu^{t}OH, and MeCN (*i.e.*, the solvents differed in polarity, viscosity, and the external heavy atom effect).

The photoluminescence of (1,10-phenanthroline)europium(III) tris(thenoyltrifluoroacetonate) was studied using a spectrofluorimeter designed and built in the Central Designing Bureau of the Academy of Medical Sciences of the USSR. The instrument is provided with two diffraction grating monochromators with a dispersion of 4.4 nm/mm and automatically corrects (by a quantum counter based on a solution of rhodamine B in ethylene glycol[7]) excitation spectra with an accuracy of 10 % in the range from 250 to 600 nm. The sensitivity[7] corresponds to a concentration of anthracene in ethanol of $1.0 \cdot 10^{-9}$ g/mL providing a signal at 400 nm (half-width 5 nm), which is fivefold higher than the noise at the time constant of 1 s and excitation at 250 nm with a band half-width of 10 nm.

The studied solution was placed into a 3-mL cylindrical cell of fused silica with round (23 mm in diameter) planar-parallel windows. The windows were welded to the ring-like part of a pipe (external diameter 9 mm) with flowing thermostatting water; the internal part of the cell was sealed into a larger cylinder (diameter 40, length 20 mm) also with planar-parallel windows. The space between the cylinders was evacuated. The temperature of the solutions was determined by a submergible calibrated thermal resistance.

Solvents and DPM were purified by the described procedures.[3,8] Eu(tta)$_3$Phen was synthesized by the procedure described in Ref. 9.

The concentration of chelate was estimated from the optical density at 345 nm ($\varepsilon \approx 5.0 \cdot 10^4$ L mol^{-1} cm^{-1}). At frontal (45°) excitation, the intensity of the luminescence ceased to increase at [A] $> 2.0 \cdot 10^{-4}$ mol L^{-1}. The reproducibility of the intensity when the cells were installed was 98.5 %; quenching by air (as compared to that by a nitrogen atmosphere) was not greater than 5 %.

[†] Deceased.

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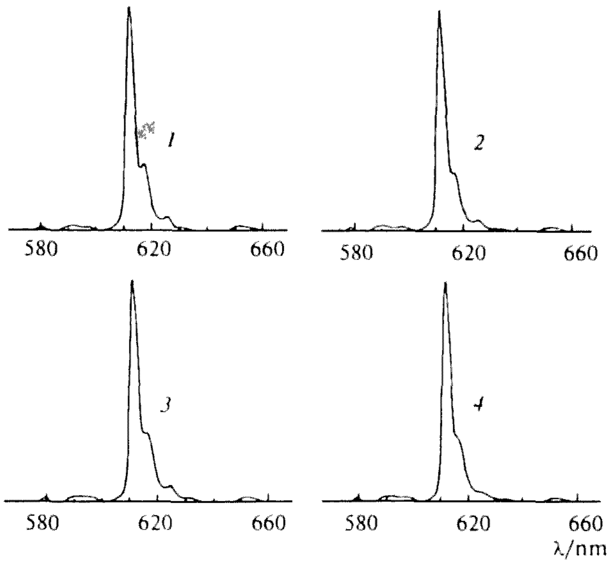

Fig. 1. Photoluminescence spectra of Eu(tta)$_3$Phen ($2.5 \cdot 10^{-4}$ mol L^{-1}) at 20 (*1*, *2*) and 60 °C (*3*, *4*) in toluene (*1*, *3*) and acetonitrile (*2*, *4*). Excitation at 345 nm.

The temperature effect on the luminescence of Eu(tta)$_3$Phen was studied at a fixed position of the cell. The results of these experiments were [$\Phi(T)/\Phi(20)$] ratios of the luminescence quantum yields (*i.e.*, photocurrents at λ_{obs} = 612 nm) measured in a given mixture at a given temperature to the yield (photocurrent) for the same mixture at 20 °C.

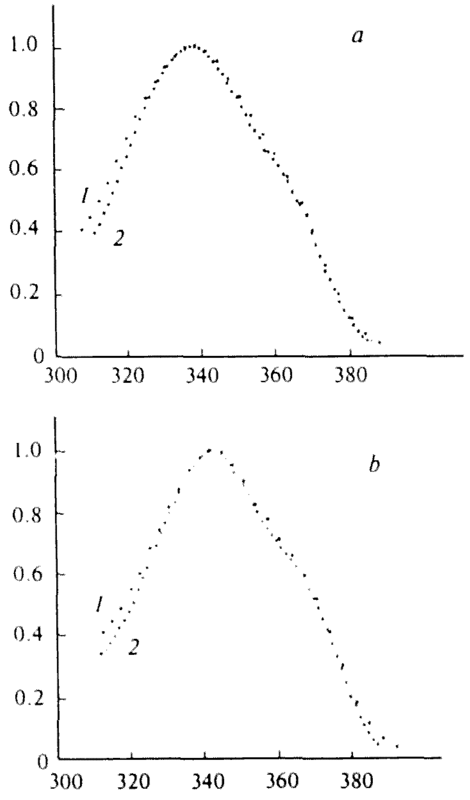

Fig. 2. Spectra of absorption (*1*) and excitation of luminescence (*2*) of Eu(tta)$_3$Phen ($2.0 \cdot 10^{-5}$ and $5.0 \cdot 10^{-7}$ mol L^{-1}, respectively) in acetonitrile (*a*) and benzene (*b*) at 20 °C.

The solvent effect was studied at 20 °C using a working cell with a solution of Eu(tta)$_3$Phen and a reference cell with a standard (a solution of chelate in acetone or toluene). In these experiments, the ratios of the yields Φ in the given and standard mixtures at 20 °C were determined.

Results and Discussion

The luminescence spectrum of the substance corresponds to that known from the published data:[10] the radiation is concentrated almost entirely in a narrow band at 612 nm (Fig. 1) assigned to the $^5D_0 \rightarrow {}^7F_2$ transition in the Eu^{3+} ion. Increases in the polarity of the medium and temperature slightly worsen the resolution of bands. The luminescence excitation spectrum coincides with the absorption spectrum of the ligands (Fig. 2) and is temperature-independent (Fig. 3).

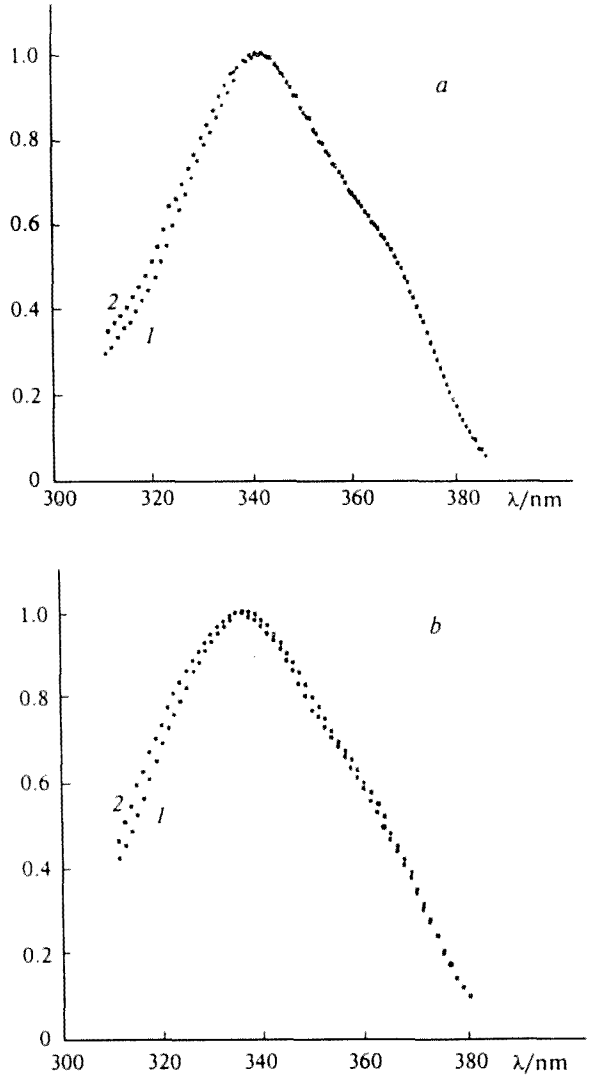

Fig. 3. Spectra of excitation of luminescence of Eu(tta)$_3$Phen ($5.0 \cdot 10^{-7}$ mol/L) in benzene (*a*) and acetonitrile (*b*) at 30 (*1*) and 60 °C (*2*).

Table 1. Ratios of quantum yields (Φ) of luminescence of Eu(tta)$_3$Phen ($2.0 \cdot 10^{-5}$ mol L^{-1}) in solvents and their mixtures with diphenylmethane to the quantum yield in acetone at 20 °C

Solvent	[DPM] (vol.%)	n (20 °C)^a	$\dfrac{\Phi}{\Phi(\mathrm{Me_2CO})}$	$\dfrac{\Phi n^2_{\mathrm{rel}}{}^b}{\Phi(\mathrm{Me_2CO})}$
Me_2CO	—	1.3589	1.00	1.00
PhMe	—	1.4969	1.13	1.37
CCl_4^{c}	10	1.4603	1.18	1.37
PhH	—	1.5011	1.12	1.37
	10		1.11	1.35
	10		1.11	1.36
PhBr	—	1.5598	1.00	1.32
	10		1.02	1.34
	50		1.01	1.33
PhCl	—	1.5258	1.10	1.38
	10		1.10	1.39
	10		1.08	1.36
	10		1.09	1.37
Me_3COH^{c}	10	1.3847	1.07	1.12
MeCN	—	1.3442	1.07	1.05
	—		1.04	1.02
	10		1.04	1.02
	50		1.03	1.00
Ph_2CH_2	—	1.5788 (17 °C)	—	—

^{a} Refractive indices n for pure solvents were taken from Ref. 11. ^{b} A correction to the quantum yield taking into account the refractive index: n_{rel} is the ratio of refractive indices of a given solvent and acetone at 20 °C.[12] ^{c} PhH (7 vol. %) was added because of the low solubility of Eu(tta)$_3$Phen.

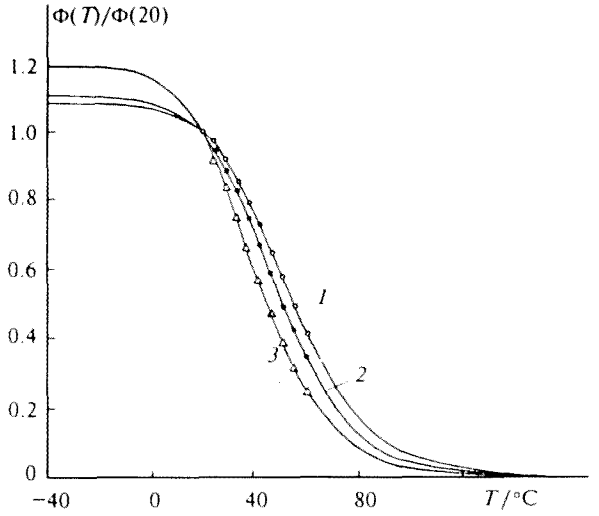

Fig. 4. Temperature dependences of the relative quantum yield of luminescence of Eu(tta)$_3$Phen ($2.0 \cdot 10^{-5}$ mol L^{-1}) in toluene (*1*), bromobenzene (*2*), and acetonitrile (*3*).

The relative luminescence quantum yields of Eu(tta)$_3$Phen are presented in Table 1. They were measured and corrected taking into account the distortion of the beam direction at the boundary of media with different refractive indices.[12] It can be seen that in polar media (*tert*-butanol, acetone, and acetonitrile) the Φ values are 20 to 30 % lower than in weakly polar media.

The yield of the luminescence of Eu(tta)$_3$Phen decreases as the temperature increases, especially in the range from 20 to 60 °C, and the effect depends on the nature of the solvent (Fig. 4).

The weakening of the luminescence by heating can be interpreted as an acceleration of nonradiative deactivation. By definition, the quantum yield of luminescence is equal to the ratio of the radiation rate constant (k_r) to the sum of the rate constants (k_{nr}) of all deactivation routes (monomolecular and pseudomonomolecular):

$$\Phi = \frac{k_r}{k_r + \sum k_{nr} + (k_{nr})_0 \exp(-E/RT)} \tag{1}$$

(the Arrhenius term is singled out in the denominator). The following expression for the experimentally measured relative quantum yield of luminescence (designated as F) is obtained from Eq. (1):

$$F(T) = \frac{\Phi(T)}{\Phi(20)} = \frac{a}{1 + b\exp(-E/RT)}, \tag{2}$$

where $a = 1 + b\exp(-E/R \cdot 293)$, $b = (k_{nr})_0/(k_r + \Sigma k_{nr})$.

Another form of Eq. (2):

$$\ln(a/F - 1) = \ln b - (E/R)/T. \tag{3}$$

Parameters b and E were determined by selecting a in such a way that the correlation coefficient of the $F(T)$ function in the coordinates of Eq. (3) was maximum. The b and E values for different media are presented in Table 2. Using these values, the relative quantum yield at any temperature can be calculated: $F(T) = \Phi(T)/\Phi(20)$. The average error of the determination of E was ±0.3 kcal mol^{-1}; however, the b parameter was determined with an accuracy below a factor of 3—4, because of its far extrapolation from the comparatively narrow range $3.0 < 1000/T < 3.4$ to the point $1000/T = 0$. The small compensation effect (lower values of b and E for some series of experiments) is caused, as has often been observed, by measurement errors, and does not affect the calculation of $F(T)$ by Eq. (2).

The $\Phi(T)/\Phi(\mathrm{Me_2CO})$ ratio can be determined by multiplying F by $\Phi/\Phi(\mathrm{Me_2CO})$ (Table 1), and the absolute luminescence quantum yield of the chelate in a given mixture at a given temperature can be determined if the yield in acetone at 20 °C is known (see below).

The energies of 12—14 kcal mol^{-1} are high, and the corresponding radiationless processes are slow. However, one should keep in mind that the lifetime of the

Table 2. Parameters of temperature dependences of the quantum yield of luminescence of Eu(tta)$_3$Phen ($2.0 \cdot 10^{-5}$ mol/L) in solvents and solutions of diphenylmethane

Solvent	[DPM] (vol.%)	a	$b \cdot 10^{-9}$	E /kcal mol^{-1}	ε (T/°C)[a]	η/cP (T/°C)[a]
CCl$_4$[b]	10	1.10	0.16	12.3	2.2 (50) 2.3 (20)	0.585 (60) 0.969 (20)
PhH	—	1.10	2.4	13.9	2.2 (60)	0.389 (60)
	10	1.11	1.1	13.4	2.3 (20)	0.652 (20)
	10	1.12	0.26	12.5		
PhMe	—	1.09	1.4	13.6	2.2 (60) 2.3 (20)	0.380 (60) 0.580 (20)
PhBr	—	1.11	2.7	13.9	5.0 (50)	0.720 (60)
	10	1.13	1.3	13.4	5.4 (20)	1.130 (20)
	50	1.11	0.6	13.0		
PhCl	—	1.16	0.15	12.0	5.1 (60)	0.520 (60)
	10	1.10	2.7	14.0	5.7 (20)	0.802 (20)
	10	1.14	0.42	12.7		
	10	1.13	0.58	12.9		
Me$_3$COH[b]	10	1.12	2.8	13.9	7.0 (60) 11.2 (30)	0.987 (60) 5.111 (25)
Me$_2$CO	—	1.15	4.0	14.0	18.7 (50)	0.220 (60)
—		1.22	0.20	12.0	21.4 (20)	0.320 (20)
MeCN	—	1.19	4.5	13.9	32.7 (55)	0.252 (60)
—		1.20	3.0	13.6	36.7 (25)	0.357 (20)
	10	1.22	1.3	13.1		
	50	1.13	2.6	13.8		
Ph$_2$CH$_2$	—	—	—	—	2.5 (50) 2.6 (20)	1.502 (60) 2.595 (30)

[a] The ε values for pure solvents were taken from Refs. 13—16; η for Ph$_2$CH$_2$ were measured in this work, η for Me$_3$COH was taken from Ref. 17 (p. 31), η for the other substances were taken from Ref. 13 (p. 108). [b] PhH (7 vol. %) was added because of the low solubility of Eu(tta)$_3$Phen.

excited state of a Eu^{3+} ion with an unfilled 4f-shell well protected by external electrons is very great (on the order of a millisecond[1,10,18]), and even a slow process can exert an effect during this time. Therefore, the value of Φ is sensitive to the surroundings and most of all, as can be seen from Fig. 4 and Tables 1 and 2, to the polarity of the medium.

The data in Table 2 (see also Fig. 4) can be used for the extrapolation of $F(T)$ to low values of T. It is observed that $\Phi(T)$ ceases to depend on temperature at approximately −10 °C for all studied media. In this case, $F(T < -10\ °C) = a = 1.10 - 1.22$, *i.e.*, at room temperature, Φ is 80 to 90 % of the limiting, low-temperature value.

It can be seen from Table 1 that at 20 °C the quantum yields in weakly polar media differ slightly, and the difference is somewhat higher in polar media, especially taking into account the refractive index. The measurements of the absolute intensities of chemiluminescence are not highly accurate; therefore, for the determination of the absolute yield of the excitation of chemiluminescence, one may use the published values of Φ of the chelate *at room temperature* for any of the solvents used in this work. It seems likely that the absolute yield of the photoluminescence of chelate Eu(tta)$_3$Phen was most reliably measured in acetone: 0.56±0.08 (25 °C);[19] for Eu(tta)$_3$(tta), which has similar luminescent properties, the value of 0.46 at 27 °C was obtained.[18]

Deactivation of the luminescent state of lanthanide ions, in particular, Eu^{3+}, can occur *via* several mechanisms:[1,20,21]

(1) electronic-to-vibrational energy transfer to overtones of the high-frequency modes of C—H bonds of the surroundings;

(2) transition to higher states of the ion ($^5D_1$,$^5D_2$) or ligand (vibronic T_1) followed by energy loss in some side process that does not result in the formation of the $^5D_0$ state;

(3) electron transfer.

The first process is highly improbable in our case, because there are no C—H bonds in the nearest surroundings of the ion: they are replaced by C—F bonds to decrease the role of this quenching mechanism and to increase Φ.

The possibility of partial energy loss in the ligand is evidenced by the somewhat different effects of temperature on the relative quantum yields and lifetimes of Eu(tta)$_3$Phen luminescence.[21] The obtained activation energies (12—14 kcal mol^{-1}) are higher than the gap between the $^5D_0$ level and the zero-phonon $T_1(\nu = 0)$ level of the ligand (~9 kcal mol^{-1}). Formally, this could indicate the necessity of the vibrational activation of a radiationless process at T_1 of *the acceptor rather than the donor* of energy. However, it is difficult to impart a physical meaning to this explanation.

The last of the mentioned mechanisms seems to be the most probable. It has been well studied for many processes of physical and chemical quenching in organic photochemistry. The energy, kinetics, and mechanisms of electron transfer between two solvated particles have been studied in detail by many authors (see, *e.g.*, the generalizing works[22—25]), including transfer between groups separated by a $(CH_2)_n$ bridge, which is the closest to our case.[26]

For the electron transfer process, the change in the free energy (ΔG^0) is equal to the difference in the potentials of the half-waves of oxidation of the donor and reduction of the acceptor minus the excitation energy of the acceptor, and the free energy of activation ($\Delta G^{\neq}$), which determines the reaction rate, also depends on E_r, the "reorganization energy" of the solvent: $\Delta G^{\neq} = 0.25 \cdot E_r(1 + \Delta G^0/E_r)^2$. Slow reorganization of the medium (heat fluctuations of the solvate shell) prepares the electron transfer step: it changes the energies both of the donor and of the acceptor levels so that fast isoenergetic (Franck—Condon) electron transfer occurs when they become equal.

We believe that a similar approach, taking into account the peculiarities of the structure of Eu(tta)$_3$Phen can also be used in this case. In fact, the excitation of the central ion results in the formation of an unoccupied site (hole) in its ground state, and the Eu^{3+} ion gains the properties of an electron acceptor. The nonexcited ligand plays the role of a donor. The specific feature of this case is that the solvent exerts no effect on the energy of the Eu^{3+} ion (only insignificant broadening of the emission bands is observed, see Fig. 1). Moreover, it is not affected even by ligands tightly bound to the ion: the emission spectrum of the free ion is the same as that of an ion bound in the complex.[27] However, the solvent unambiguously affects the energy of the ligand, which is indirectly evidenced by the small (~2 kcal mol^{-1}) shift of the absorption spectrum in polar acetonitrile (Fig. 2).

Thus, due to thermal fluctuations of the solvent, the energy of the ground state of the ligand increases, and electron transfer occurs when it becomes equal to the energy of the accepting level of the ion. This is followed by a slower irreversible relaxation to the nonexcited state by the redistribution of energy among vibrations and by reverse transfer of the electron. In order to analyze in detail this mechanism, special studies must be performed. Now it should be noted that the reorganization energy E_r is proportional to the $(n^{-2} - \varepsilon^{-2})$ value. In fact, the data in Tables 1 and 2 show a tendency for the activation energy to increase in media with lower refractive indices.

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