

Stabilization of Eu(II) Ions by Macrocyclic Compounds in the Oxidation Reaction with Hydrogen Peroxide

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Summary. The influence of coronands *15C5* and *18C6* and cryptands *2.2.1* and *2.2.2* on the chemiluminescence (CL) of the system Eu(II)/(III)-H₂O₂ was studied. Analysis of the chemiluminescence spectra revealed that the excited Eu(III) ions are the dominant emitter in all cases. The stabilizing effect of the macrocyclic compounds was manifested in an extension of the CL duration and was particularly strong in the systems with cryptands. The protective activity of ligands is explained by the matching of the ligand's cavity with the size of Eu(II) ions. Measurement of the Eu(II) absorption band decay ($\gamma = 248$ nm) upon oxidation by hydrogen peroxide confirmed the results of the CL studies according to which the stabilizing properties of the macrocyclic ligands towards Eu(II) ions increase in the order *15C5* < *18C6* < *2.2.1* < *2.2.2* in aqueous solution.

Keywords. Chemiluminescence; Complexes; Coronands; Cryptands; Europium(III).

Stabilisierende Wirkung von makrocyclischen Verbindungen auf Eu(II)-Ionen gegenüber Oxidation durch Wasserstoffperoxid

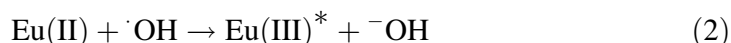
Zusammenfassung. Der Einfluß der Kronenether *15C5* und *18C6* und der Kryptanden *2.2.1* und *2.2.2* auf die Chemolumineszenz (CL) des Systems Eu(II)/Eu(III)-H₂O₂ wurde untersucht. Die Analyse der Chemolumineszenzspektren zeigt, daß in allen Fällen angeregte Eu(III)-Ionen als Emitter dominieren. Der stabilisierende Effekt der makrocyclischen Verbindungen äußerte sich in einer Verlängerung der CL-Dauer und war im Fall der Kryptanden besonders ausgeprägt. Die inhibierende Wirkung wird mit der Übereinstimmung der Größe der Hohlräume der Liganden und des Eu(II)-Ions erklärt. Messungen der Abnahme der Intensität der Absorptionsbande von Eu(II) ($\lambda = 248$ nm) während der Oxidation mit Wasserstoffperoxid bestätigten die Ergebnisse der CL-Untersuchungen, nach denen die stabilisierende Wirkung der makrocyclischen Liganden gegenüber Eu(II) in wäßriger Lösung in der Reihenfolge *15C5* < *18C6* < *2.2.1* < *2.2.2* ansteigt.

Introduction

Macrocyclic compounds, thanks to a characteristic spatial structure of their molecules (presence of cavities), exert stabilizing effect on cations of metals of

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unstable oxidation state [1]. The coordinating properties of macrocyclic compounds such as coronands and cryptands are determined by the matching between the ionic radii of the metal ions under complexation and the size of the macrocyclic compound cavity [1, 2]. Certain lanthanide ions, especially Eu(III), are particularly suitable luminescence probes due to their spectroscopic properties [3]. It has been proved that the main emitter in the chemiluminescent system of Eu(II) ions and hydrogen peroxide are Eu(III) ions excited to the emission level 5D_0 ; the excitation of europium ions is a consequence of a radical reaction (Eqs. (1), (2)) [4, 5].



Complexation of europium ions decreases or increases chemiluminescence (CL) intensity of the Eu(II)/(III)-ligand- H_2O_2 system depending on properties and structure of the ligand [4]. The studies reported in this paper were undertaken to check the usefulness of CL measurements to study the stabilizing effect of macrocyclic compounds on Eu(II) ions in the system Eu(II)/(III)- H_2O_2 .

Results and Discussion

Oxidation of Eu(II) to Eu(III) by hydrogen peroxide is accompanied by radical excitation and, as a consequence, a characteristic emission of the transitions $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$. Ligands introduced into the reaction system Eu(II)/(III)- H_2O_2 coordinate europium ions, changing the characteristics of the luminescence system. Figures 1 and 2 present the course of chemiluminescence in the fundamental system and in the system with macrocyclic ligands.

Curve A in Fig. 1 presents the CL decay for the fundamental system, Eu(II)/(III)- H_2O_2 , whereas the other two curves (B and C) hold for the systems with *15C5* and *18C6*, respectively. The polycyclic ether *15C5* slightly decreases the system's

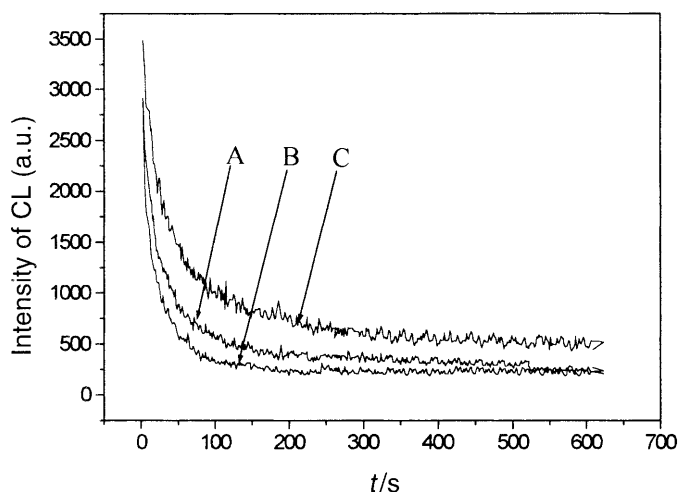


Fig. 1. Decay of chemiluminescence of the systems Eu(II)/(III)- H_2O_2 (A), Eu(II)/(III)-*15C5*- H_2O_2 (B), and Eu(II)/(III)-*18C6*- H_2O_2 (C); concentration of all reagents: $2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

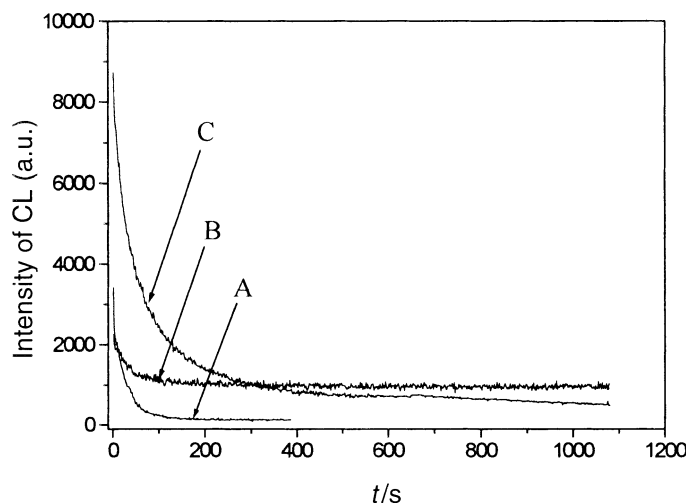


Fig. 2. Decay of chemiluminescence of the systems Eu(II)/(III)-H₂O₂ (A), Eu(II)/(III)-2.2.2-H₂O₂ (B), and Eu(II)/(III)-2.2.1-H₂O₂ (C); concentration of all reagents: $2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

emission, whereas the presence of *18C6* causes a small increase. Relatively great changes in intensity and duration of CL appeared as a consequence of addition of cryptands 2.2.1 and 2.2.2 as illustrated by curves B and C in Fig. 2.

The highest intensity and longest duration of CL among all systems is found for 2.2.1 (Fig. 2, curve C). A characteristic feature of the CL decay in the system with 2.2.2 is its long duration and a very slow decay (Fig. 2, curve B).

Emission spectra of the basic system and the systems with the macrocyclic compounds are shown in Fig. 3. The emission spectrum of the basic system (Fig. 3A) shows a band at about $\lambda = 600 \text{ nm}$ corresponding to the transitions ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ of the Eu(III) cation. The spectral distributions recorded for the systems with macrocyclic compounds are essentially similar. Besides the dominant band at $\lambda = 600 \text{ nm}$ they include a low intensity band with a maximum at about 500 nm which can be interpreted as arising from the emission of excited carbonyl groups [7, 8].

The quantum yield of the luminescence of lanthanide ions increases with decreasing number of water molecules present in the coordination sphere of the ion, which usually is a result of complexation [9]. Complexes of Eu(III) with cryptands such as 2.2.1 or 2.2.2 in aqueous solutions are much more stable than those with coronands [1, 2]. Therefore, the increase of the light sum of chemiluminescence and the quantum yield of emission of the Eu(II)/(III)-2.2.2-H₂O₂ and Eu(II)/(III)-2.2.1-H₂O₂ systems can be interpreted as a consequence of partial displacement of the coordination water from the environment of Eu(III).

The presence of the coronands *15C5* and *18C6* (Fig. 1) is of no significant effect upon the intensity of emission. A small increase in the presence of *18C6* may be explained as due to formation of Eu(II)-*18C6* complexes in aqueous solution. These complexes are characterized by a relatively low stability constant ($\log \beta = 2.7$) and exert some stabilizing effect on Eu(II) ions. Such an effect is not observed in the presence of *15C5*, as this coronand does not form complexes

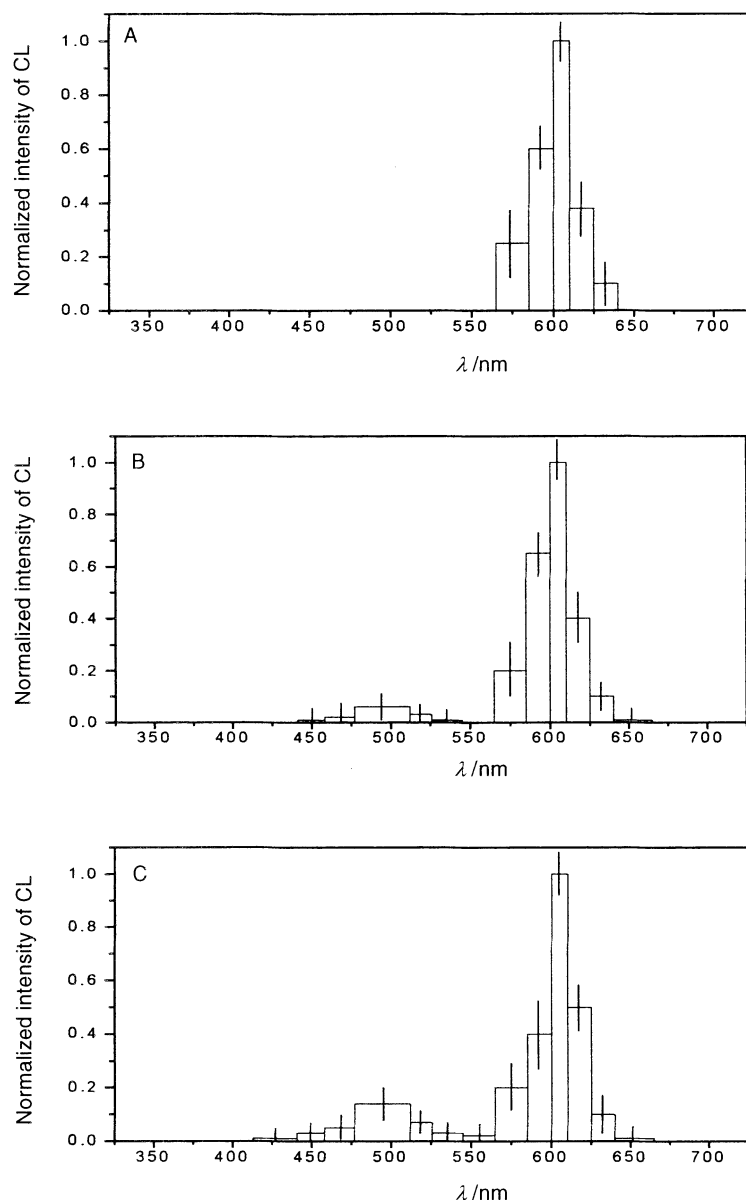


Fig. 3. Spectral distributions of CL of the systems Eu(II)/(III)-H₂O₂ (A), Eu(II)/(III)-15C5-H₂O₂ and Eu(II)/(III)-18C6-H₂O₂ (B), Eu(II)/(III)-2.2.1-H₂O₂ and Eu(II)/(III)-2.2.2-H₂O₂ (C)

with europium ions in aqueous solutions [1]. The observed CL intensity from the Eu(II)/(III)-15C5-H₂O₂ system is lower than that of the basic system as a consequence of reactive quenching of $\cdot\text{OH}$ radicals by 15C5 molecules. This reduces the yield of formation of the excited Eu(III) ions (Eq. (2)). The ligands containing hydrocarbon chains act as active quenchers and remove the hydroxyl radicals. The other applied ligands (18C6, 2.2.2, 2.2.1) most probably also act as quenchers regarding their structural similarity, but the resultant effect of competitive complexation eventually results in an increase of CL intensity.

Table 1. Cavities radii (R), stability constants (β), light sum of reactions (S), and half value times of light sum $T_{1/2}$; the error in the determination of S and $T_{1/2}$ is about 10%

System	$R/\text{\AA}$	$\log\beta$ Eu(II)-L	$\log\beta$ Eu(III)-L	S (a.u.)	$T_{1/2}/s$ [s]
Eu(II)/(III)-H ₂ O ₂	–	–	–	1.0	90
Eu(II)/(III)-15C5-H ₂ O ₂	1.7–2.2	not observed	not observed	0.9	70
Eu(II)/(III)-18C6-H ₂ O ₂	2.6–2.2	2.7	not observed	1.7	120
Eu(II)/(III)-2.2.1-H ₂ O ₂	1.1	10.2	6.8	32	150
Eu(II)/(III)-2.2.2-H ₂ O ₂	1.4	13.0	5.9	420	2100

An important parameter describing the kinetics of the reaction accompanied by CL is the time at which half of the total light sum of reaction is reached. As follows from Table 1, the reaction half times for the systems with cryptands are longer than those for the systems with coronands. The differences in light sums, half times of reaction, and complex formation constants between the systems Eu(II)/(III)-2.2.1-H₂O₂ and Eu(II)/(III)-2.2.2-H₂O₂ are a result of a better or worse matching between the size of Eu(II) and Eu(III) ions and the cryptand cavity.

In order to confirm the stabilizing effect of the macrocyclic compounds, all systems studied were subjected to spectrophotometric measurements. The absorption spectra were recorded before addition of H₂O₂ (Fig. 4, curve A) and 20 minutes after the oxidation reaction of europium was initiated (Fig. 4, curve B).

The absorption spectrum of Eu(II) ions includes two bands at $\lambda = 248$ and 328 nm (Fig. 4A curve A) which is attributed to the electron transitions $4f^7 \rightarrow 4f^65d$ [10]. The absorption maxima of the macrocyclic ligands and hydrogen peroxide lie below 210 nm, so they do not overlap with the absorption band of Eu(II) ions at 248 nm. Thus, the intensity of the latter is a function of Eu(II) concentration in the systems studied, and slight changes in intensity and shifts of this band are a result of the influence of the ligand's field on the energy levels of the central ion.

In the spectra of the basic system Eu(II)/(III)-H₂O₂ and in those with 15C5 and 18C6 (Fig. 4A. B. curve B) recorded 20 min after initiation of the oxidation reaction, the band at $\lambda = 248$ nm disappears, which means that there are no longer Eu(II) ions present in these systems. The situation is different for the systems with 2.2.1 and 2.2.2 (Fig. 4C, D curve B) whose spectra testify a presence of Eu(II) ions after 20 min of interaction with H₂O₂.

Figure 5 presents the dependence of the intensity of the absorption band at $\lambda = 248$ nm on the duration of the reaction for all systems studied.

The intensity decay of the band at $\lambda = 248$ nm is fastest for the basic system (Fig. 5, curve A); its decrease for the systems with the cryptands, especially 2.2.2, is much slower. Thus, absorption studies confirm that the decay of CL of the systems studied depends on the rate of Eu(II) oxidation by H₂O₂. The chemiluminescent method gives evidence of the stabilizing effect of complexing ligands on Eu(II) ions. The diameter of Eu(III) and Eu(II) ions (2.13 Å and 2.34 Å, respectively) is greater than that of the 2.2.1 cryptand cavity; therefore, Eu(II) ions are partly protruding from the cavities and are not wholly protected from oxidation. This leads to a fast decrease of CL intensity.

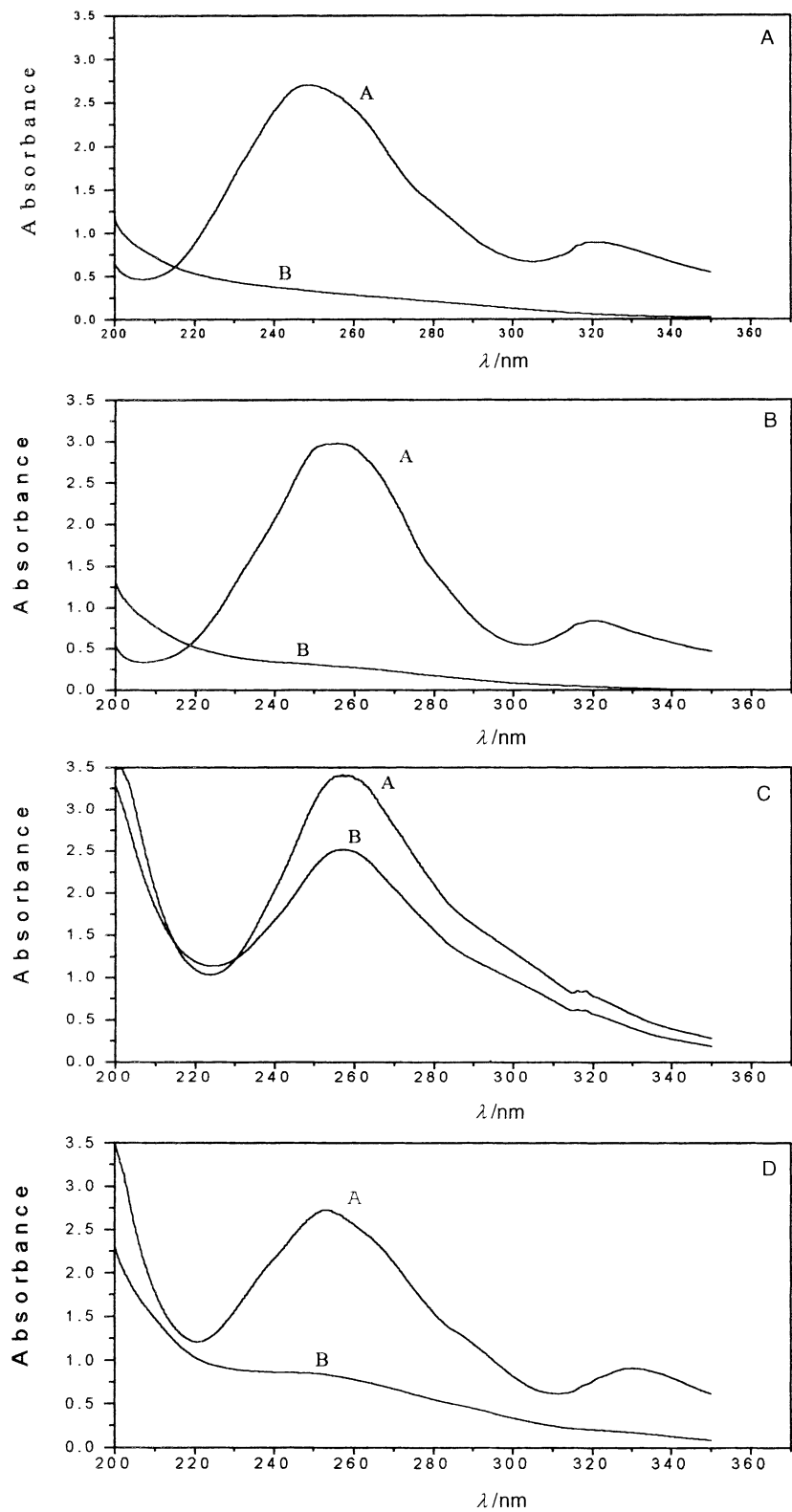


Fig. 4. Absorption spectra of the systems $\text{Eu(II)/Eu(III)-H}_2\text{O}_2$ (A), $\text{Eu(II)/(III)-15C5-H}_2\text{O}_2$ and $\text{Eu(II)/(III)-18C6-H}_2\text{O}_2$ (B), $\text{Eu(II)/(III)-2.2.1-H}_2\text{O}_2$ (C), $\text{Eu(II)/(III)-2.2.2-H}_2\text{O}_2$ (D); concentration of all reagents: $2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

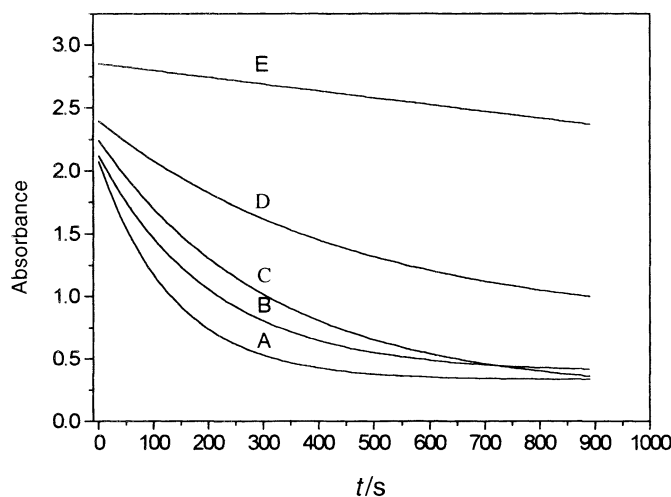


Fig. 5. Changes in absorbance of the band for $\lambda = 248$ nm with the time elapsed from initiation of the oxidation reaction for the systems Eu(II)/Eu(III)-H₂O₂ (A), Eu(II)/(III)-15C5-H₂O₂ (B), Eu(II)/(III)-18C6-H₂O₂ (C), Eu(II)/(III)-2.2.1-H₂O₂ (D), Eu(II)/(III)-2.2.2-H₂O₂ (E); concentration of all reagents: $2 \cdot 10^{-3}$ mol · dm⁻³

In aqueous solutions, the coronands in which oxygen atoms act as donors are weaker ligands than cryptands containing additional nitrogen atoms [1]. The small diameter of their cavity combined with poor complexing properties are responsible for the fact that in the Eu(II)/(III)-15C5-H₂O₂ system this coronand acts only as a radical quencher. 18C6 forms a weak complex with Eu(II) ions, and thus CL is a little increased in this case. The values of the half CL decay times (Table 1) confirm the stabilizing effect of the macrocyclic ligands. The lowest value of $T_{1/2}$ is obtained for the basic system; in systems with coronands and cryptands, in particular 2.2.2 extended $T_{1/2}$ values are observed.

On the basis of the results presented above we conclude that the specific spatial structure of the macrocyclic ligands, enabling complexation of Eu(II) ions inside their cavities, effectively protect the ions against aggressive reagents as hydrogen peroxide and hydroxyl radicals.

Experimental

Solutions of EuCl₂ were obtained by reduction of EuCl₃ according to the *McCoy* method [6]. The macrocyclic compounds 1,4,7,10,13-Pentaoxacyclododecane (15C5), 1,4,7,10,13,16-Hexaoxacyclooctadecane (18C6), 4,7,13,16,21-Pentaoxa-1,10-diazabicyclo[8.8.8]tricosane (*Kryptofix 2.2.1*), and 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (*Kryptofix 2.2.2*) (98%, Merck) were used without further purification (Fig. 6).

Solutions were prepared with redistilled water. The degree of europium ion reduction was determined by iodometric titration directly prior to measurement. All measurements were made in $2 \cdot 10^{-3}$ M HCl prepared from 35% HCl (pure for analysis, Merck). The CL intensity and emission spectra were measured as presented elsewhere [5]. Spectrophotometric measurements were performed using a UV/Vis spectrophotometer Shimadzu 2401 PC.

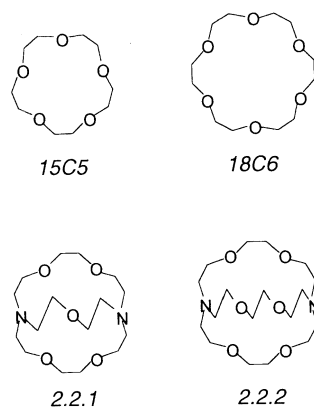


Fig. 6. Structural formulae of the coronands and cryptands used

Sample preparation

To a solution containing Eu(II) ions, $2 \cdot 10^{-2} M$ hydrochloric acid and a solution of a given macrocyclic compound at an appropriate concentration were added. Then, H_2O_2 was injected in an equimolar ratio relative to Eu(II). The reaction mixture was mixed by passing argon (99.99%) through the system before each measurement.

Spectral distributions were obtained using the cut-off filter method. The light sum of chemiluminescence was defined as the area under the kinetic curve and calculated from the moment of the reaction initiation to the time of reaching the background level.

Acknowledgements

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