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Energy Transfer Processes of Chemiluminescence Reaction Systems with Cerium(IV) Ions and Their Analytical Application: A Review

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Abstract This review is devoted to a thorough discussion of chemiluminescence of the systems containing Ce(IV) ions as oxidising agents, with particular emphasis on the energy transfer processes in such systems. The influence of sensitisers such as: rhodamines, quinine, lanthanide ions and their complexes and quantum-dots has been analysed and the practical use of reaction systems for development of new chemiluminescence methods for determination of therapeutic drugs and substances of biological importance in different matrices such as human urine or serum is indicated. The types of emitters and excited reaction products taking part in energy transfer to sensitisers and processes taking place in the chemiluminescence reaction systems containing Ce(IV) ions are presented on the basis of recent literature.

Keywords Cerium(IV) ions · Chemiluminescence detection · Energy transfer processes

Introduction

Chemiluminescence is defined as generation of light as a result of a chemical reaction. The chemical reaction produces sufficient energy to induce the transition of an electron from its ground state to an excited electronic state. These chemically excited molecules decay to the electronic ground state and emit photons from ultraviolet, visible or infra-red radiation range. Sometimes the excited product is an ineffective emitter but it can transfer the excitation energy to an efficient fluorophore added to the system. In such cases the CL emission is identical with the fluorescence of fluorophore. This process is known as indirect, sensitised, or energy-transfer CL.

Investigation of CL for analytical use began around 1970 [1] for gas-phase and around 1980 [2] for liquid-phase reactions. For over 30 years, the phenomenon of CL in the liquid phase has been the basis of spectrometric methods of analytical chemistry. In most reaction systems the redox reactions take place with the use of a variety of oxidising agents. The use of the oxygen-containing compounds such as $KMnO_4$ [3] or hydrogen peroxide [4] as oxidants has already been widely described. In contrast, no review of the use of cerium(IV) ions as the oxidant in chemiluminescent studies (especially including analytical applications of these systems) has been made yet. In this review the CL reaction systems, which contain the cerium(IV) ions as oxidiser and their analytical applications are discussed (Table 1). Selected compounds that have been detected using chemiluminescence reactions with cerium(IV) ions are presented in Fig. 1.

Reaction Conditions and Species Emitted from CL Reaction Systems Containing Ce(IV) Ions

Cerium(IV) is a strong oxidant in an acidic medium. Ce(IV) ions in aqueous H_2SO_4 media are highly stable and do not require any special precautions to prevent their photochemical decomposition [37–39]. This is why Ce(IV) in aqueous H_2SO_4 media is very often used in new analytical methods based on the phenomenon of chemiluminescence. The methods are based on the flow technique only. Development of analytical laboratory methods aims at shortening the time of analysis and maximum automation of the measuring system. These criteria are met among others by FIA – Flow Injection Analysis. It is particularly well-suited to monitoring transient light emission from

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Table 1 Examples of published analytical applications of CL systems with Ce(IV) ions

Analyte	CL reaction system	Limit of detection	Application	Ref.
The Ce(IV) - sulphite (or related species) reactions system				
Benzamides				
Sulpiride	Ce(IV) - Na_2SO_3 - H_2SO_4	1×10^{-8} g mL^{-1}	Pharmaceutical preparations,	[5]
Sultopride		1×10^{-8} g mL^{-1}	Biological fluids	
Hydrochloride				
Tiapride hydrochloride		1×10^{-8} g mL^{-1}		
Cu(II)	Ce(IV) - Na_2SO_3 - AgNCs in PMAA (AgNCs- silver nanoclusters PMAA- poly(methacrylic acid))	1.2×10^{-10} mol L^{-1}	Tap water	[6]
Norfloxacin	Ce(IV) - Na_2SO_3 - gold NPs (Gold NPs – gold nanoparticles)	8.2×10^{-8} mol L^{-1}	Human urine	[7]
Norfloxacin	Ce(IV) - $Na_2S_2O_3$ - SDS- H_2SO_4 (SDS – sodium dodecylsulphate)	2.21×10^{-9} g mL^{-1}	Pharmaceutical formulations, human urine.	[8]
Dopamine	Ce(IV) - $Na_2S_2O_3$ – C-dots- H_2SO_4 (C-dots – carbon dots)	1×10^{-9} mol L^{-1}	Human plasma	[9]
Tenoxicam	Ce(IV) - $Na_2S_2O_4$ – SDBS (SDBS – sodium dodecyl benzene sulfonate)	2.3×10^{-11} g mL^{-1}	Pharmaceutical preparations, serum, human urine	[10]
Papaverine	Ce(IV) - HSO_3^- - H_2SO_4	8.7×10^{-8} mol L^{-1}	Pharmaceutical preparations, biological fluids	[11]
Galifloxacin	Ce(IV) - $Na_2S_2O_3$ – SDBS (SDBS – sodium dodecyl benzene sulfonate)	4.87×10^{-12} g mL^{-1}	Pharmaceutical preparations, serum, human urine	[12]
Iproniazid phosphate	Ce(IV) - Na_2SO_3 - H_2SO_4	3×10^{-6} g L^{-1}		[13]
Rufloxacin	Ce(IV) - H_2SO_3 – Eu(III) - H_2SO_4	5×10^{-9} mol L^{-1}	Serum samples, urine samples	[14]
Ciprofloxacin	Ce(IV) - HSO_3^- – Tb(III) - HCl	3.1×10^{-10} mol L^{-1}	Human serum, urine samples	[15]
DNA	Ce(IV) - Na_2SO_3 – Tb(III)/CPFX (CPFX- ciprofloxacin)	7.8×10^{-9} g mL^{-1} (natural DNA) 9.5×10^{-9} g mL^{-1} (denaturated DNA)		[16]
Ofloxacin	Ce(IV) - Na_2SO_3 - H_2SO_4	1.6×10^{-8} g mL^{-1}	Pharmaceutical preparations	[17]
The Ce(IV)- analyte reactions systems				
Tryptophan	Ce(IV) - H_2SO_4	1×10^{-7} g mL^{-1} 15×10^{-9} g mL^{-1}	Tissue or protein hydrolysates	[18]
Naproxen		15×10^{-9} g mL^{-1}	Commercial formulations or in biological fluids after HPLC	[19]
Norfloxacin		1×10^{-8} g mL^{-1}	Pharmaceutical preparations	[20]
The Ce(IV)- sensitiser reaction systems				
Captopril	Ce(IV)-Rhodamine B - H_2SO_4	3.7×10^{-8} mol L^{-1}	Pharmaceutical preparations	[21]
Resorcinol		3.2×10^{-9} g mL^{-1}	Pharmaceutical preparations	[22]
L-ascorbic acid		1×10^{-13} mol L^{-1}	Fresh vegetables.	[23]
Hydrochlorothiazide	Ce(IV)-Rhodamine 6G - H_2SO_4	1.5×10^{-7} mol L^{-1}		[24]

Table 1 (continued)

Analyte	CL reaction system	Limit of detection	Application	Ref.
			Pharmaceutical preparations, in ingle form or combined with other drugs such as amiloride and lisinopril.	
L-cysteine	Ce(IV)-Rhodamine 6G- Au-Ag Alloy Nanopartcle	2.7×10^{-9} g mL^{-1}		
L-phenylalanine		8.2×10^{-9} g mL^{-1}	Biological samples	
Pyrogallic acid		1.2×10^{-9} g mL^{-1}		[25]
2,4-dihydroxybenzoic acid		6.8×10^{-10} g mL^{-1}		
Hydroquinone		2.3×10^{-9} g mL^{-1}		
Sum of flavonoid	Ce(IV)-Rhodamine 6G – H_2SO_4	38×10^{-9} mol L^{-1}	Apigenin	[26]
		840×10^{-9} mol L^{-1}	Linarin	
Tetracycline	Ce(IV)-Rhodamine B - HNO_3	1×10^{-9} g mL^{-1}	Fish samples	[27]
Cefotaxime sodium	Ce(IV)-Rhodamine 6G - HNO_3	1×10^{-8} mol L^{-1}	Flow-injection CL system with on-line microdialysis sampling can be applied to studying protein binding for cefotaxime sodium to BSA.	[28]
Tiopronin	Ce(IV)-quinine - H_2SO_4	3.4×10^{-7} mol L^{-1}	Pharmaceutical preparations	[29]
Penicillamine		15 pmol / 50 μL	Pharmaceutical preparations	[30]
Cysteine		2.5×10^{-9} mol L^{-1}	Human serum	[31]
Naproxen	Ce(IV)- Eu(III) - H_2SO_4	1.1×10^{-8} mol L^{-1}	Commercial formulations, human urine and in mixture of non-steroidal anti-inflammatory drugs (ibuprofen, naproxen, indomethacin)	[32]
Al.(III)	Ce(IV)- calcein - H_2SO_4	8×10^{-11} g mL^{-1}	Real water samples	[33]
Iodide	Ce(IV)- tween 40 - H_2SO_4	5×10^{-8} mol L^{-1}	Urine samples	[34]
Salicylic acid	Ce(IV)- tween 20 - H_2SO_4	2.5×10^{-9} g mL^{-1}	Bactericidal solution samples	[35]
Uric acid	Ce(IV)- GQDs 20 - H_2SO_4 (GQDs –graphene quantum dots)	5×10^{-7} mol L^{-1}	Human plasma Human urine	[36]

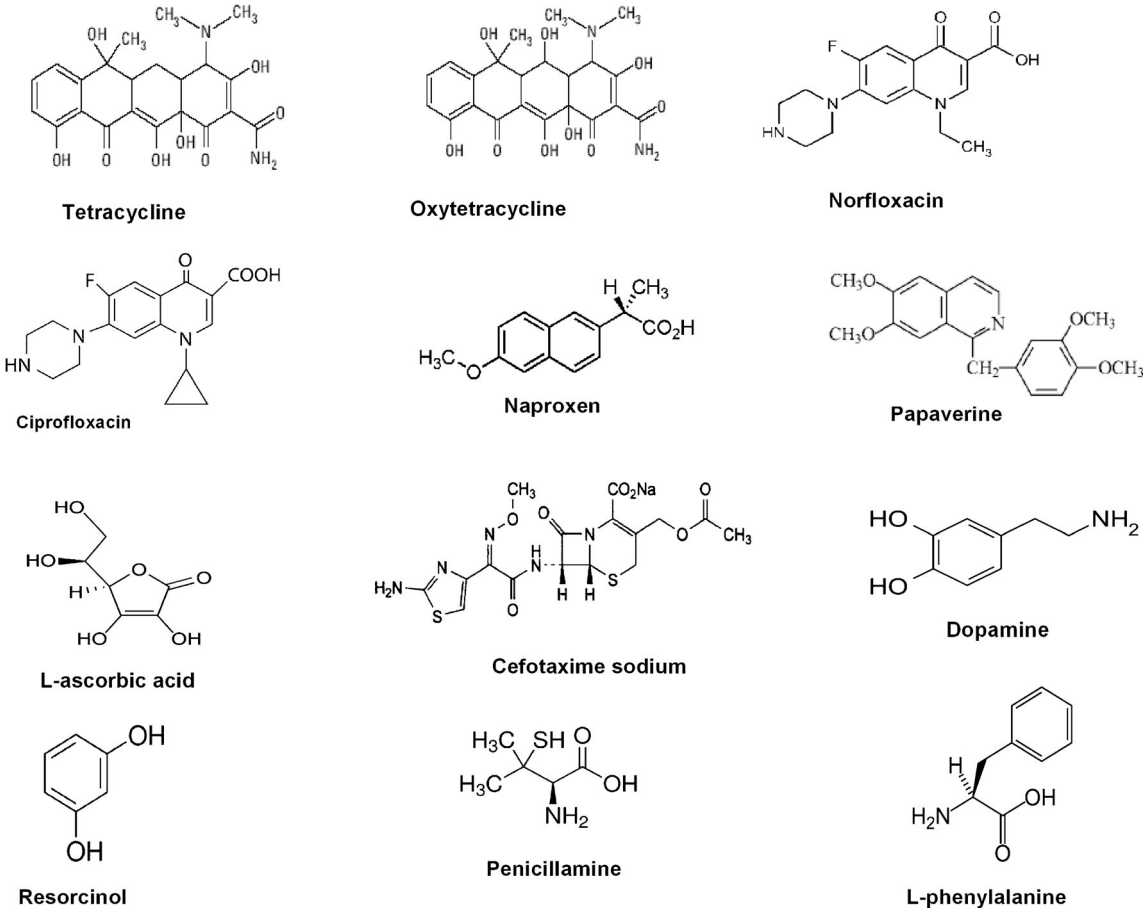


Fig. 1 Selected compounds that have been detected using chemiluminescence reactions with cerium(IV) ions

liquid phase chemiluminescence (CL) reactions as it permits rapid and reproducible mixing of sample and reagent in close proximity to the detector. A combination of CL determinations and flow injection analysis (FIA) allows combining the advantages of instrumental simplicity, rapidity and a high degree of reproducibility in signal detection [40]. Exemplary flow-injection CL analysing systems are shown in Fig. 2

Optimal concentrations of substances constituting the CL system were determined as those that would the highest intensity of emission. In over 90 % of the published reports on the use of acidic Ce(IV) ions chemiluminescence, the cerium(IV) concentrations were from the range 1×10^{-4} molL^{-1} and 2×10^{-3} molL^{-1}, but concentrations as high as 5×10^{-3} molL^{-1} [25] were occasionally met. Although Ce(IV) ions have been widely used in chemiluminescence systems, the processes taking place and the types of emitters in such systems have not been satisfactory established yet. In general, emitters of chemiluminescence reaction systems with cerium(IV) ions can be classified into five groups Ce(III) [8], excited sulphur dioxide (SO_2*), excited products of oxidation of determined substance [18, 19], dimols of singlet oxygen [20, 35] and fluorophores [6, 9, 14]. Cerium (III), which is formed by the reduction of cerium(IV), is a well-known fluorescent ion, with the maximum emission at λ~355 nm [41–43] and therefore, it is a possible CL emitter. Excited sulphur dioxide species (SO_2*) emit weak light at 300–450 nm [44, 45], therefore the compounds showing strong fluorescence, such as rhodamine B [28, 46], quinine [29–31] or lanthanide ions [32] are introduced to many reaction systems containing Ce(IV) ions.

The Ce(IV)-Sulphite (or Related Species) Reaction System

From among the chemiluminescence reaction systems containing Ce(IV) ions, the most abundant group are the mixtures containing inorganic sulphur oxides such as: sulphite (SO_3^{2-}) [6, 44, 45], thiosulphate ($S_2O_3^{2-}$) [8, 9] and dithionite ($S_2O_4^{2-}$) [10]. In the acidic environment, the product of HSO_3^- oxidisation by Ce(IV) should be $HSO_3^{\bullet}$ radical (Eq. 1). Two $HSO_3^{\bullet}$ radicals then combine to produce $S_2O_6^{2-}$, which gives the excited intermediate product SO_2^* (Eqs. 2 and 3).

$$Ce(IV) + HSO_3^- \rightarrow HSO_3^{\bullet} + Ce(III) \quad (1)$$

$$2HSO_3^{\bullet} \rightarrow S_2O_6^{2-} + 2H^+ \quad (2)$$

$$S_2O_6^{2-} \rightarrow SO_4^{2-} + SO_2^* \quad (3)$$

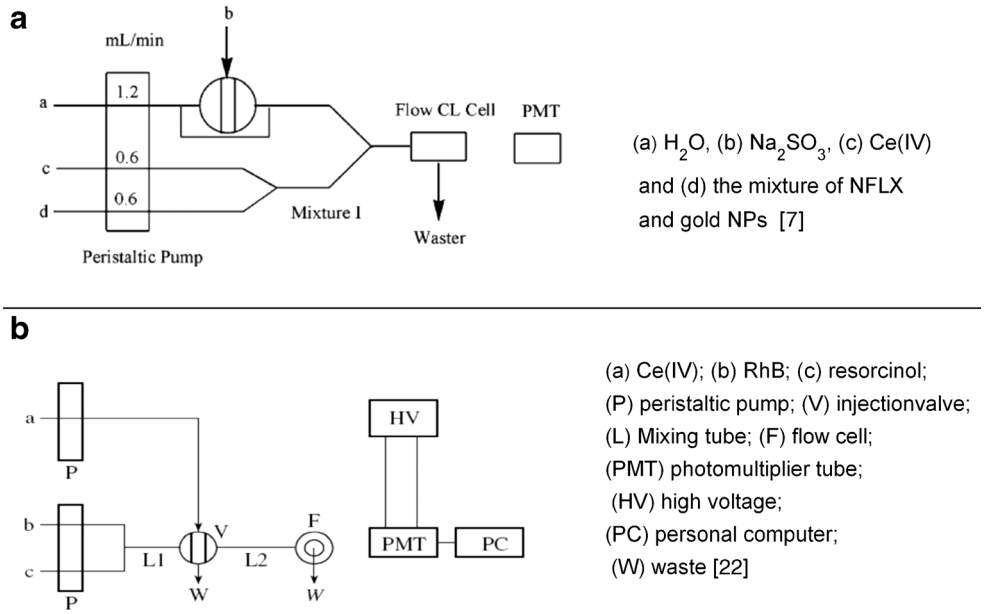


Fig. 2 Schematic diagram of CL flow system for determination of (A) norfloxacin [7] and (B) resorcinol [22]

However, the CL intensity is very weak due to the low luminescence efficiency of SO_2^*. It is reported that the energy of the excited SO_2^* could be efficiently transferred to a fluorophore [32]. Benzamides act as sensitisers [5]:

$$SO_2^* + \text{Benzamide} \rightarrow SO_2 + \text{Benzamide}^* \quad (4)$$

$$\text{Benzamide}^* \rightarrow \text{Benzamide} + \text{light} \quad (5)$$

The intensity of CL from Ce(IV)- Na_2SO_3 system increases in proportion to the concentration of three benzamide drugs: sulpiride, sultopride and tiapride. Solutions can be analysed at a rate of 190 (sulpiride), 150 (sultopride hydrochloride) and 144 samples per hour (tiapride hydrochloride). In a chemiluminescent Ce(IV)- Na_2SO_3 system the water soluble and fluorescent silver nanoclusters (Ag NCs) can be used as sensitisers [6]. Ag NCs strengthen the CL intensity of this system by accepting energy from excited SO_2^* in aqueous solution. The emission spectrum of CL from Ce(IV)- Na_2SO_3 – Ag NCs system and the fluorescent spectrum of Ag NCs solution are the same (with the emission band at 550 nm). In this system PMAA (poly(methacrylic acid) stabilised with Ag NCs shows strong fluorescence. Copper(II) ions quenched the emission by binding with the free carboxylic groups of PMAA polymers that surround the emissive Ag NCs [6, 47]. The reduction in the intensity of CL from Ce(IV)- Na_2SO_3 – Ag NCs system is proportional to the concentration of Cu(II) and this relation has been used for developing of a new sensitive method for determination of copper ions. In this method the CL inhibition is calculated as $\Delta I/I_0$ ($\Delta I = I_0 - I$), where I_0 and I are the CL intensity of Ce(IV)-Na_2SO_3- Ag NCs system without and with copper(II), respectively. The chemiluminescence of Ce(IV)–Na_2SO_3 system in the presence of gold nanoparticles (NPs) can be used to detect norfloxacin (NFLX) which is one of the synthetic antibacterial fluoroquinolone agents of the second generation [7]. The gold NPs could readily combine with various ligands containing oxygen donor atoms [48]. The possible mechanism enhancing the emission of Ce(IV)–Na_2SO_3 –NPs- NFLX system assumed the catalytic effect of gold NPs, which would facilitate the radical generations and accelerate electron-transfer processes taking place on the surface of gold NPs in aqueous solution. The excited SO_2^* and NFLX could be absorbed on the surface of gold NPs, and the energy transfer from SO_2^* to NFLX is easy (Fig. 3).

Often surfactants are applied to get the enhanced intensity of chemiluminescence as they protect emitters from reacting with other particles in solutions.. In the CL studies three types of surfactants, SDBS (sodium dodecylbenzenesulphonate), SDS (sodium dodecylsulphate) and CTAB (cetyltrimethylammonium bromide) are often used. Xie et al. have applied Ce(IV) ions to develop a new CL method for the determination of norfloxacin [8]. The method is based on the CL reaction of norfloxacin with sodium thiosulphate and Ce(IV) in sulphuric acid medium sensitised by sodium dodecylsulphate. The emitters in this system are Ce(III) ions or the complex formed between Ce(III) and norfloxacin as follows[8]:

$$S_2O_3^{2-} + 8\text{Ce(IV)} + 5H_2O \rightarrow 8\text{Ce(III)}^* + 2SO_4^{2-} + 10H^+ \quad (6)$$

$$\text{Ce(IV)} + \text{NFLX}^{\text{Red}} \xrightarrow{\text{SDS}} \text{Ce(III)}^* + \text{NFLX}^{\text{Ox}}$$
$$\text{Ce(III)}^* \rightarrow \text{Ce(III)} + hv \quad (7)$$

and/or

$$\text{Ce(III)}^* + \text{NFLX} \xrightarrow{SDS} \text{Ce}(C_{16}H_{18}FN_3O_3)_2^{3+}* \quad (8)$$

$$\text{Ce}(C_{16}H_{18}FN_3O_3)_2^{3+}* \rightarrow \text{Ce(III)} + \text{NFLX}^{\text{Ox}} + hv \quad (9)$$

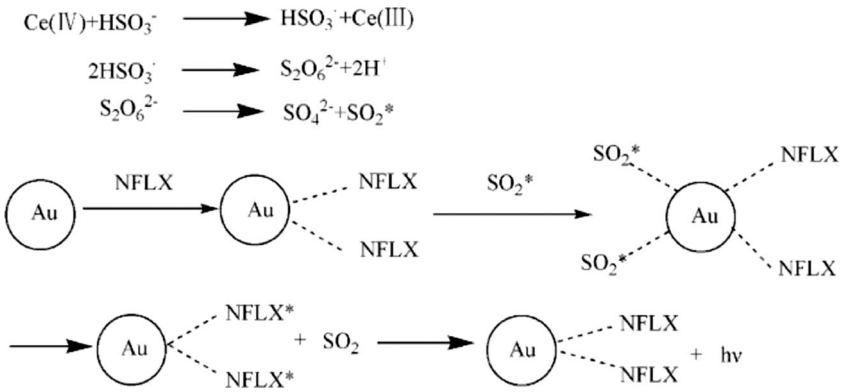


Fig. 3 Scheme of the possible mechanism of Ce(IV)–Na_2SO_3 – NPs- NFLX system [7]

A similar mechanism has been proposed for the reaction system in which Ce(IV) ions oxidise sodium hyposulphite ($Na_2S_2O_4$) sensitised by sodium dodecyl benzene sulphonate (SDBS) in the presence of gatifloxacin [12] and tenoxicam(TX) [10]. Gatifloxacin (GFLX) is the fourth generation of a new class of synthetic antibacterial fluoroquinolone agents and tenoxicam is a nonsteroidal anti-inflammatory drug belonging to the chemical class called oxicams.. The presence of GFLX or TX increases the emission from the system Ce(IV)-$Na_2S_2O_4$ – SDBS and the CL intensity is proportional to the concentration of gatifloxacin or tenoxicam, in a wide range. A comparison of the Ce(III) and GFLX or TX luminescence spectra with the spectra of the mixtures Ce(IV)- $Na_2S_2O_4$ – SDBS – GFLX(or TX) has shown that the emitters are Ce(III) ions or Ce(III)/GFLX and Ce(III)/TX complexes.

The CL system containing Ce(IV) ions, sulphurous acid and europium(III) ions is used for determination of rufloxacin (RFX), which is one of the synthetic antibacterial fluoroquinolone agents. The antibiotics of this type have a carboxyl group, which supplies a binding site with lanthanide ions, and two aromatic cycles which can absorb energy. Therefore, fluoroquinolones can transfer energy to the lanthanide ion [49–51] The new CL method for determination of RFX is based on the energy transfer from RFX to europium(III), then instead of the weak CL produced by cerium(IV)–sulphurous acid–RFX CL system, intense luminescence can be observed. Excitation of Eu(III) ions is a result of intermolecular energy transfer from SO_2* to the triplet state of the ligand, followed by intramolecular energy transfer in the $Eu(RFX)_2^{3+}$ complex to europium(III) ions that emit radiation with a maximum at λ~615 nm [14]. The unique fluorescent properties of terbium(III) ions complexed with organic ligands are applied for determination of ciprofloxacin (CPLX) [15]. The excitation of terbium(III) ions is a result of energy transfer from SO_2* to Tb(III) ions through the CPLX ligand to the Tb-CPLX complex. Tb(III) complexes with fluoroquinolones are used as a CL probe to detect and study DNA. A novel flow injection chemiluminescent system for determination of DNA, is based on the fact that DNA linearly quenches the CL intensity of Ce(IV)-/Na_2SO_3- Tb(III)/fluoquinolone antibiotic system [16]. It is shown that the quenching effect of single-stranded DNA (denatured) is greater than that of double-stranded DNA (natural) because in single-stranded DNA without helix structure, the bases and the phosphate groups get more opportunities to react with Tb(III) ions. A new class of CL emitters are carbon dots (C-dots) [36]. This class of structures has several fascinating properties including excellent photostability, simplicity of synthesis, good water solubility, low toxicity, high chemical stability and poses low environmental hazard [52, 53]. The Ce(IV)–$Na_2S_2O_3$ system in the presence of carbon dots is used for determination of dopamine [9]. Excitation of C-dots was achieved in two ways: as a result of the energy transfer process from the excited-state SO_2^* (obtained according to the Eqs. 1–3) molecules to C-dots as acceptors or as a result of C-dots oxidation by Ce(IV) ions:

$$SO_2^* + \text{C−dot} \rightarrow SO_2 + \text{C−dot*} \quad (10)$$

$$\text{C−dot*} \rightarrow \text{C−dot} + h\nu(\sim 510\text{nm}) \quad (11)$$

or

$$\text{Ce(IV)} + \text{C−dot} \rightarrow \text{Ce(III)} + \text{C−dot*} \quad (12)$$

$$\text{C−dot*} \rightarrow \text{C−dot} + h\nu(\sim 510\text{nm}) \quad (13)$$

The inhibitory effect of dopamine on the enhanced CL of Ce(IV)–$Na_2S_2O_3$ -C-dots system is used to develop a new analytical method for determination of this compound. The method has wide range of linearity, high sensitivity and good selectivity. It is indicated that

CdTe QDs (water-soluble CdTe quantum-dots (QDs)) act as a sensitiser enhancing the chemiluminescence emission from the redox reaction of SO_3^{2-} with Ce(IV) in acidic medium. In this system the energy of excited SO_2^* could be efficiently transferred to CdTe QDs used as fluorophore. Chemiluminescence of the system Ce(IV)–Na_2SO_3 – CdTe QDs is quenched by a number of organic compounds containing -OH, $-NH_2$, or -SH groups and electron-transmitting proteins (cytochrome *c*, haemoglobin and myoglobin) that react with CdTe QDs. This effect has been used for development of a new method for determination of the above compounds [54]. Cerium(IV) is known as a one-electron oxidant. It can react with organic compounds to form reactive intermediate radical [11, 55]. The Ce(IV)–HSO_3^- reaction mixture is applied for determination of papaverine. in pharmaceutical preparations and biological fluids. It is possible that papaverine is oxidised by cerium(IV) to form an intermediate radical, which reacts with sulphite to initiate a free radical reaction as follows:

$$Ce(IV) + HSO_3^- \rightarrow HSO_3^{\bullet} + Ce(III) \quad (14)$$

$$Ce(IV) + PAP \rightarrow PAP^{\bullet} + Ce(III) \quad (15)$$

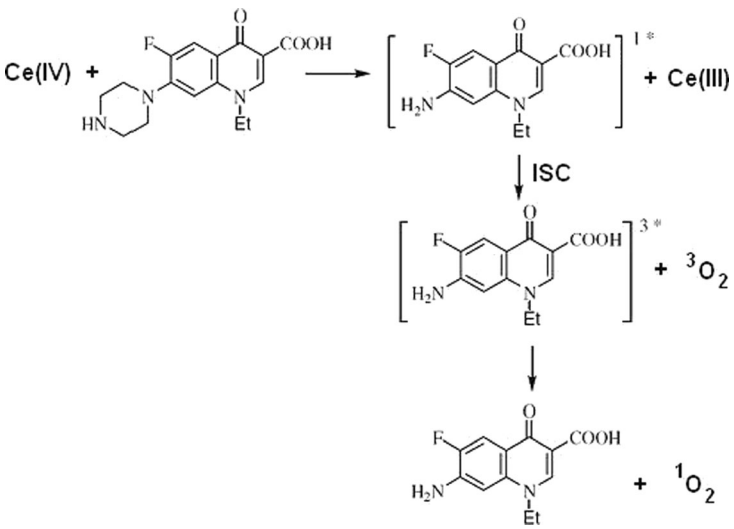
$$PAP^{\bullet} + HSO_3^- \rightarrow HSO_3^{\bullet} + PAP \quad (16)$$

The $HSO_3^{\bullet}$ radicals combine to produce $S_2O_6^{2-}$ which gives excited SO_2^* molecule (Eqs. 2 and 3). For the determination of iproniazid phosphate, a CL system based upon the oxidation of the drug by cerium(IV) in sulphuric acid medium at room temperature in the presence of sulphite has been proposed. The emitter of this system is an excited azoxy derivative, since iproniazid contains hydrazine group, which is formed by oxidation of iproniazid phosphate by Ce(IV) ions or as a result of energy transfer from excited SO_2^* [13].

The new method not only shows a high selectivity but also has another advantage – it does not require preliminary treatment of the samples studied, so it can be an alternative to chromatographic methods.

The Ce(IV)- Analyte Reactions Systems

The chemiluminescence of a few systems containing the analyte and cerium(IV) ions as an oxidant is so intense that it does not require the use of sensitisers. A new CL method for determination of tryptophan has been described, based on the reaction of tryptophan with 4cerium(IV) in 0.15 M sulphuric acid [18]. The main emitter was the excited oxidation product of tryptophan. The CL-emitting reaction between naproxen(NAP) and Ce(IV) in an acidic medium has been applied for determination of NAP in commercial formulations [19]. Intensive CL has been proved to be achievable in a system in which norfloxacin(NFLX) is oxidised with Ce(IV) in an acidic medium. The CL spectrum of Ce(IV)-NFLX contains three bands with the maxima at 475 nm, 620 nm, and 550 nm. The first two are typical of emission of singlet oxygen dimols generated in the following process of energy transfer between triplet 7-aminofluoroquinolone and dissolved oxygen [20]:



(17)

The emission with a maximum at 550 nm is assigned to the products of norfloxacine oxidation. For the system in which a redox reaction between cerium (IV) and norfloxacine takes place, a linear relation between CL intensity and NFLX concentration was found, which was applied for determination of NFLX in pharmaceutic preparations and urine. Chemiluminescence accompanies the reaction of oxidation of phosphor-organic pesticides such as omethoate, dimethoate, disulphoton-sulphoxide, methidathion, phosmet, malathion, diazinon, pirimiphos-methyl and chlorpyrifos with cerium(IV) ions. The emitters are the excited products of pesticides oxidation whose emission increases in the presence of a surfactant - hexadecylpyridinium chloride monohydrate (HPC) [56]. This fact was employed for determination of these compounds in water samples, after their preliminary separation by HPLC .

The Ce(IV)- Sensitiser Reaction Systems

The Ce(IV) – Rhodamine systems

Rhodamine compounds, are a series of xanthene dyes, widely applied in analytical chemistry. Rhodamine compounds are often believed to act as sanitisers in CL systems [21, 22, 24] but Ma et al. have shown that the reaction of Ce(IV) with rhodamine B or rhodamine 6G in an acidic medium could produce significant CL. Thus, Rhodamine B and the other rhodamine compounds have been used as an illuminant, similar to luminol in basic media, not as a sensitiser [23, 57].

Rhodamine B (RhB) has been used as a sensitizer for determination of captopril [21, 58]. Two reaction systems showing CL have been chosen for this determination. The first one is based on the reaction of captopril with the luminol-hydrogen peroxide-copper(II) system. The second method is based on the reaction of captopril with acidic cerium(IV) solutions in the presence of rhodamine B (RhB) as a sensitiser. The second method proves to be 10-fold more sensitive than that with luminol-H_20_2-Cu(II) in alkaline environment. A new procedure has been proposed which allows quantitation of hydrochlorothiazide in the pharmaceutical preparations containing, amongst others, lactose, maize starch, calcium phosphate, magnesium stearate, potassium chloride and E 110 (disodium-6-hydroxy-5-(4-sulphonatophenylazo) naphthalene-2-sulphonate) as the concomitant species. The method involved the chemiluminescent reaction of hydrochlorothiazide with cerium(IV) in sulphuric acid, sensitized by the fluorescent dye rhodamine 6G, as follows:

$$\mathrm{Ce(IV)} + \mathrm{HCT^{Red}} \rightarrow \mathrm{Ce(III)^*} + \mathrm{HCT^{Ox}} \quad (18)$$

$$\mathrm{Ce(III)^*} + \mathrm{Rho\ 6G} \rightarrow \mathrm{Ce(III)} + \mathrm{Rho6G^*} \quad (19)$$

$$\mathrm{Rho\ 6G^*} \rightarrow \mathrm{Rho\ 6G} + h\nu \quad (20)$$

where, HCT, hydrochlorothiazide; Rho 6G, rhodamine 6G; Red, reduced form; Ox, oxidised form [24]. A similar mechanism has been proposed for cerium(IV)–rhodamine 6G used for determination of cefotaxime sodium (drug of the third generation cephalosporin). Rhodamine 6G played a role of typical sensitiser for these CL system, which emits its characteristic radiation at 560 nm [28]. The influence of 53 organic compounds on cerium(IV)–rhodamine 6G chemiluminescence has been checked. It has been found that 32 phenolic compounds (PCs) (mainly include phenols, polyphenols, phenolic acids, hydroxycinnamic acids and flavonoids) enhance CL [46]. The magnitude of CL was related to the type and position of substituents in the benzene ring. The maximal emission wavelength of CL spectra for all tested phenolic compounds was at about 555 nm, and luminophores were assigned to rhodamine 6G. . In these systems, excitation of rhodamine 6G is a result of energy transfer from excited Ce(III) ions (a product of reaction of oxidation of rhodamine 6G and phenolic compounds, Eq. 21 and 23) to rhodamine 6G.

$$\mathrm{Ce(IV)} + \mathrm{Rho\ 6G} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{Slow}} \mathrm{Ce(III)^*} + \mathrm{Rho\ 6G_{ox}} \quad (21)$$

$$\mathrm{Ce(III)^*} + \mathrm{Rho\ 6G} \rightarrow \mathrm{Ce(III)} + \mathrm{Rho\ 6G^*} \quad (22)$$

$$\mathrm{Ce(IV)} + \mathrm{PC} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{Fast}} \mathrm{Ce(III)^*} + \mathrm{PC_{ox}} \quad (23)$$

$$\mathrm{Ce(III)^*} + \mathrm{Rho\ 6G} \rightarrow \mathrm{Ce(III)} + \mathrm{Rho\ 6G^*} \quad (24)$$

$$\mathrm{Rho\ 6G^*} \rightarrow \mathrm{Rho\ 6G} + h\nu \quad (25)$$

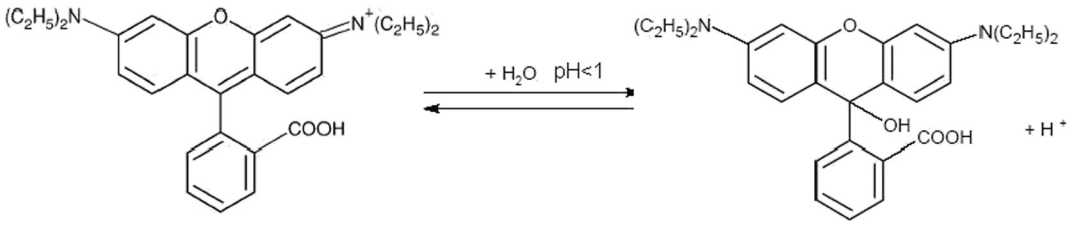
The increase in the intensity of CL of the reaction system cerium(IV)–rhodamine 6G in sulphuric acid was applied for determination of total content of flavonoids in extracts from inflorescences and leaves of Cirsium oleraceum and Cirsium rivulare species. Methanol extracts were found to show the strongest antioxidation properties and they could be used as natural preparations for human organism protection against free radicals [26].

According to another mechanism, the oxidation products of PCs such as benzoquinone or ketone quench the emissive rhodamine 6G via energy transfer, as shown below:

$$\mathrm{Rho\ 6G^*} + \mathrm{PC_{ox}} \rightarrow \mathrm{Quenching} \quad (26)$$

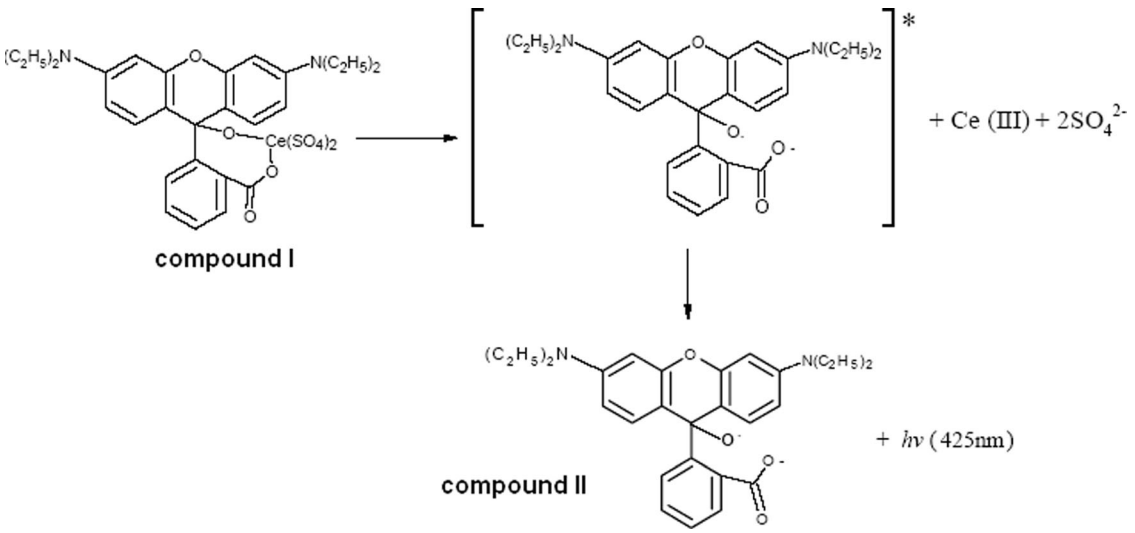
Another group of reaction systems are the mixtures in which the oxidation of rhodamine RhB could produce CL in an acidic medium (Eqs. 27–29) [57]. In the medium of sulphuric acid, Ce(IV) [59] and RhB [60] ions occur in the forms :

$$Ce(SO_4)_2 + HSO_4^- \leftrightarrow [Ce(SO_4)_3]^{2-} + H^+$$



(27)

They interact to form a transition complex (compound I) and then the redox reaction takes place with formation of excited radical transition product showing emission with a maximum at λ~425 nm:



(28)

In the presence of Ce(IV) ions and oxygen, the intermediate product (compound II) is oxidised to the final products being 1,4-benzoquinone- 2-carboxylic acid or salicylic acid.

The CL signal of Ce(IV) – rhodamine B – H_2SO_4 system is enhanced by L-ascorbic acid and a highly sensitive flow–injection (FI) method has been proposed for determination of L-ascorbic acid [23]. In this system the excited anionic radical emitters (Eq. (28)) are formed and the reaction of Ce(IV) ions with ascorbic acid (H_2A) gives $HA^{\bullet}$ radicals. The radical $HA^{\bullet}$ reacted with anionic radical of RhB to give the rhodamine B illuminant with negative oxygen ion as follows:

$$H_2A \xrightarrow[H_2SO_4]{Ce(IV)} HA^{\bullet} \tag{29}$$

$$\left[{}^{\bullet}RhB^{-}\right]_{ox} + HA^{\bullet} \xrightarrow[H_2SO_4]{Ce(IV)} \left[{}^{\bullet}R{\bullet}hB^{-}\right]^{*}_{ox} + H^{+} + A \tag{30}$$

In this way RhB was used as a CL reagent in the determination of tetracycline [27]. Introduction of UV irradiated tetracycline solutions to Ce(IV)-RhB in sulphuric acid resulted in an increase in CL intensity. The $TC^{\bullet}$ radicals, formed after UV irradiation of TCs, take part in the CL reaction with anionic radicals of rhodamine B (which are formed according to Eq. 28), so in the same way as proposed by Ma et al. for the determination of L-ascorbic acid. The CL intensity of Ce(IV)-RhB-TCs systems was proportional to the concentration of TCs and was used to develop a new HPLC-CL method for sensitive determination of tetracycline, oxytetracycline, chlorotetracycline, demeclocycline, doxycycline and meclocycline) [61].

The Au-Ag alloy nanoparticles could enhance the chemiluminescence of the rhodamine 6G-cerium(IV) system. Bimetallic nanoparticles are of special importance in the field of catalysis, since they often exhibit better catalytic properties than their monometallic counterparts. Au and Ag have very similar lattice constants and are fully miscible over the entire composition range; they can form single-phase alloys easily with any desired compositions [25, 62]. The most intensive CL signals of the rhodamine 6G-cerium(IV)-Au-Ag alloy nanoparticle system were obtained by addition of Au-Ag alloy nanoparticles at a molar ratio of 3:4. In the rhodamine 6G-cerium(IV)- Au-Ag alloy nanoparticle system, there are two emitters: rhodamine 6G (with the emission band at λ~555 nm) and the oxidised product of rhodamine 6G (with the emission band at λ~446 nm) [25]. It has been proposed that CL enhancement mechanism is based on the rhodamine 6G and Au-Ag alloy nanoparticles oxidation by cerium(IV) to form the excited-state cerium(III)*, which transfers energy to rhodamine 6G and the oxidised product of rhodamine 6G (Eqs. 31–35).

$$\mathrm{Ce(IV)} + \mathrm{Au{-}Ag} \xrightarrow[\mathrm{H_2SO_4}]{\text{Fast}} \mathrm{Ce(III)^*} + \mathrm{Ag(I)} + \mathrm{Au(III)} \quad (31)$$

$$\mathrm{Ce(III)^*} + \text{Rho 6G} \rightarrow \mathrm{Ce(III)} + \text{Rho 6G}^* \quad (32)$$

$$\text{Rho 6G}^* \rightarrow \text{Rho 6G} + h\nu\ (555\,\mathrm{nm}) \quad (33)$$

$$\mathrm{Ce(III)^*} + \text{Rho 6G}_{ox} \xrightarrow[\text{Au-Ag Fast}]{\text{Electron transfer}} \mathrm{Ce(III)} + [\text{Rho 6G}^-]^*_{ox} \quad (34)$$

$$[\text{Rho 6G}^-]^*_{ox} \rightarrow [\text{Rho 6G}^-]_{ox} + h\nu(446\mathrm{nm}) \quad (35)$$

The analytical method based on the chemiluminescence of rhodamine 6G-cerium(IV)- Au-Ag alloy nanoparticles system has been widely applied for determination of such compounds as: L-cystine, L-methionine, L-phenylalanine, L-dopamine, L-epinephrine, L-ascorbic acid, pyrogallic acid, 2,4-dihydroxybenzoic acid, *p*-aminobenzoic acid, *o*-aminobenzoic acid, phenol, *p*-aminophenol, hydroquinone, resorcinol and *p*-*t*-butylpyrocatechol.

The Other Ce(IV) – Sensitiser Systems

A quinine is a sensitizer of the reaction of thiol-containing drugs with cerium(IV) in sulphuric acid medium [29–31]. Quinine is a good fluorescent substance ($\varphi = 0.577$), having an emission maximum at about 450 nm [63]. The process taking place in thiol-containing compound-Ce(IV) reaction systems may be described with the following equations:

$$\mathrm{Ce(IV)} + \mathrm{analyte^{Red}} \rightarrow \mathrm{Ce(III)^*} + \mathrm{analyte^{Ox}} \quad (36)$$

$$\mathrm{Ce(III)^*} \rightarrow \mathrm{Ce(III)} + h\nu(\text{weak CL})$$
$$\text{and/or} \mathrm{Ce(III){-}analyte\ complex^*} \rightarrow \mathrm{Ce(III){-}analyte\ complex} + h\nu \quad (37)$$

$$\mathit{Ce(III)^*} + \mathit{quinine} \rightarrow \mathit{Ce(III)} + \mathit{quinine^*}$$
$$\text{and/or} \mathrm{Ce(III) - analyte\ complex^*} + \text{quinine} \rightarrow \mathrm{Ce(III) - analyte\ complex} + \text{quinine}^* \quad (38)$$

It is found that apart from potassium ferricyanide [64], another oxidant Ce(IV) could oxidise calcein to generate CL. In addition it is observed that Al(III) ions, enhanced the CL of Ce(IV)-calcein system and the CL intensity was strongly dependent on Al(III) concentration [33]. The mechanism of the processes taking place in this system involves formation of Ce(IV)/calcein complex, which is the only CL emitter (with a maximum at about 515 nm). This complex is an acceptor of the reaction (39) energy, as a result of which it undergoes excitation.

$$\mathrm{Ce(IV)} + \text{calcein} \rightarrow \text{Energy} + \text{product} \quad (39)$$

It has been demonstrated that europium(III) ions acted as sensitiser in the Ce(IV)-naproxen CL system. A characteristic feature of luminescence spectra of europium ions is the presence of bands of a small full width at half maximum [65–69]. It permits the use of a proper cut-off filter of a steep short-wavelength pass limit. The use of such filters reduces the emission of the analytical matrix. With applying the cut-off filters method, the reaction mixture of NP-Ce(IV)-Eu(III) has been used for the determination of naproxen in commercial formulations, in human urine and in mixture of non-steroidal anti-inflammatory drugs (ibuprofen, naproxen, indomethacin) [32]. The cerium(IV) ions reacted with a surfactant Tween 20 in an acidic medium to generate chemiluminescence. The maximum emission wavelength was about 478 nm, so it was a typical emission band of singlet oxygen molecular pairs $O_2(^1\Delta_g)O_2(^1\Sigma_g^-)$ [35,

70]. The mechanism of singlet oxygen generation in the system Ce(IV)-Tween 20 has not been conclusively resolved yet. Three pathways of its generation have been proposed [35]:

a) $$\mathrm{Ce(IV)} + \mathrm{Tween20} \rightarrow \mathrm{Ce(III)} + \mathrm{X} \quad (40)$$

$$\mathrm{X} \rightarrow {}^1\mathrm{O}_2^* + \mathrm{X}' \quad (41)$$

$${}^1\mathrm{O}_2^* \rightarrow {}^3\mathrm{O}_2 + \mathrm{hv} \quad (42)$$

b) $$\begin{array}{l} \mathrm{X} + \mathrm{O}_{2\mathrm{dis}} \rightarrow (\mathrm{O}_2\text{–}\mathrm{X}) \rightarrow {}^1\mathrm{O}_2^* + \mathrm{X} \\ {}^1\mathrm{O}_2^* \rightarrow {}^3\mathrm{O}_2 + \mathrm{h}\ \mathrm{v} \end{array} \quad (43)$$

c) $$\mathrm{X} + \mathrm{O}_{2\ \mathrm{dis}} \rightarrow \left({}^1\mathrm{O}_2 \text{---} \mathrm{X}\right)^* \rightarrow {}^3\mathrm{O}_2 \rightarrow \mathrm{X} + \mathrm{hv} \quad (44)$$

where: X, X′ and O_{2dis} represent oxidative intermediates of Tween 20, a degradation product of X, and dissolved oxygen in the solution, respectively. O_2–X and $^1O_2$–X are the complexes of X with O_2 and $^1O_2$, respectively. It has been shown that salicylic acid (one of the main active ingredients in bactericidal solution) strongly increased the intensity of CL but did not influence the CL spectra, which revealed that the emitter was the same in the presence and in the absence of salicylic acid. This finding has been used in a new method proposed for determination of salicylic acid in bactericidal solutions. The other surfactant Tween 40 acted as enhancer of the oxidation reaction of cerium (IV) with iodide which regulates a wide variety of physiological processes in living organisms. In this system the emitter was singlet oxygen and the mechanisms of this reaction can be described by Eqs. 40–44. Moreover, it has been proved that the sensitised CL of the reaction mixture Ce(IV)-Tween85- citrate could be used for determination of polyphenol compounds, including 17 aminoacids [71]. The presence of surfactants in these CL generating systems additionally stabilises the singlet oxygen state [34].

Conclusions

The method of flow-through analysis with CL detection based on the reaction systems with Ce(IV) ions, in which energy transfer processes take place, has been widely applied for analysis of therapeutic drugs and other biomolecules. The interest in CL systems follows from the fact that low limit of detection and limit of quantitation of the analyte are achieved with the use of a relatively simple equipment. Moreover, the analysis does not take much time and is inexpensive. The area for improvement in CL method is related to the synthesis of new more efficient CL-active molecules and the proper choice of a sensitiser. Improvement in this area will result in getting a stronger signal, reduction of background and increase in the sensitivity of the CL based methods. Another important area of research is finding materials that will act as catalysts in the reaction mixtures. The acceleration of redox processes results in higher concentrations of the excited product per unit of time and thus contributes to higher intensities of CL.

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