

DC-electrochemiluminescence (ECL with a coreactant)—principle and applications in organic chemistry

Jiří Ludvík

Received: 23 August 2011 / Accepted: 25 August 2011 / Published online: 2 October 2011
© Springer-Verlag 2011

Abstract This review is focused on the so-called DC-electrochemiluminescence (or ECL with coreactant), its fundamentals and use in basic research in organic and coordination chemistry, photo(electro)chemistry and photophysics, where ECL is not still fully explored. This review is also meant to remind the fellow scientists to the substantial contribution of Prof. Fritz Pragst to this field. An appropriate attention is given to the following two types of research problems where ECL plays a crucial role: (1) selective generation of triplet states enabling investigation of their reactions and estimation of their energies; (2) Use of DC-ECL for mechanistic studies in organic electrochemistry, for interception of short-living intermediates and for visualization of electrode processes. The main aim of this paper is not to rewrite already existing reviews in another form, but to complete the whole picture of ECL research and to remind the reader to several fundamental studies, ideas, and papers hoping that they could be inspirational for organic and molecular electrochemists.

Keywords Organic compounds · Reaction mechanisms · Radical intermediates · Selective generation of triplet states · Estimation of triplet energy · ECL imaging

Introduction

In the last two decades, several reviews summarizing papers as well as monographs dealing with electrochemiluminescence (ECL) were published. However, since recently electrochemiluminescence is more and more used for analytical applications as a diagnostic tool, its contributions to organic chemistry, photo(electro)chemistry, and photophysics are underestimated and overlooked. Therefore, a lot of fundamental papers were forgotten and the broad scientific possibilities of ECL are not fully explored. In this review, the principles of ECL are briefly summarized and several examples are shown where ECL can serve as a powerful tool for answering rather complex and fundamental research questions.

From its very beginning (since the early 1970s), the development of ECL is connected with the impact of Prof. Fritz Pragst's scientific work. He contributed substantially to the field of organic mechanisms, electron- or energy-transfer reactions, and investigations of triplet states, interconnecting thus organic chemistry, electrochemistry, and photochemistry. In this review, I would like to mention more in detail these aspects of ECL, viz. the DC-type of ECL (also called as ECL with coreactant) and to give an appropriate attention to the following two types of research problems where ECL plays a crucial role:

1. Due to the inherent characteristics of the triplet ECL mechanism (according to energetic conditions), a large number of systems is able to generate selectively and exclusively only triplet states, without the simultaneous population of the first singlet state and without use of light for excitation (generation of triplet states “in dark”). Using the electron-transfer (indirect oxidations or reductions) and energy-transfer reactions (both in

The author dedicates this paper to Professor Fritz Pragst on the occasion of his 70th birthday.

J. Ludvík (✉)
J. Heyrovský Institute of Physical Chemistry,
Academy of Sciences of the Czech Republic,
Dolejškova 3,
18223 Prague 8, Czech Republic
e-mail: jiri.ludvik@jh-inst.cas.cz

homogeneous phase), it is experimentally possible to compare the energy levels and redox potentials. Then, the appearance of emission serves as a confirmation of the correctness of the theoretical considerations. In this way, it is principally possible to estimate the triplet energies and, based on known energetic criteria, also otherwise unavailable redox potentials of short-living radicalic species.

- Based on the ECL principle, that the luminescence is a consequence of a strongly exoenergetic electron-transfer reaction fulfilling fundamental energetic criteria, the observed emission serves also as an unambiguous proof of the existence of strongly oxidizing and strongly reducing species. These molecules (often radicals) are, however, in many cases, the missing links in the investigated reaction pathways. Hence, the ECL, namely the DC-type, is a very efficient alternative method for the interception and proof of unstable intermediates.

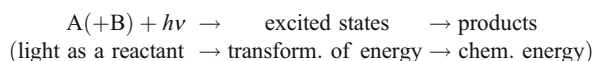
The main aim of this paper is not to rewrite already existing reviews in another form, but to complete the whole picture of ECL research and to remind the reader to several fundamental studies, ideas, and papers hoping that they could be inspirational for organic and molecular electrochemists.

Background and fundamentals of ECL

Background

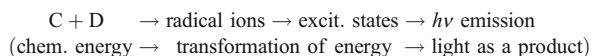
Typical photochemical reactions involve a transformation of the energy of light to chemical energy; the light hence appears on the side of reactants.

Photochemistry:



In chemiluminescence, light is generated on account of chemical energy, i.e., chemiluminescence can be considered formally as the reverse of the above given scheme of photochemistry.

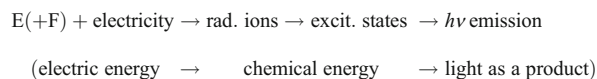
Chemiluminescence:



(In a more general sense, photochemistry can be considered as comprising both ways of energy transformation, viz. light energy into chemical energy and vice versa.)

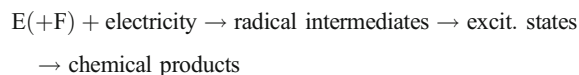
Electrochemistry, on the other hand, is a chemical discipline, where electrical energy is transformed to chemical energy (and vice versa), sometimes generating highly reactive radical ions. Electrochemically generated luminescence, i.e., ECL in fact connects photochemistry with electrochemistry, where chemical reactions of electrochemically generated radicals or radical ions result in excited states which manifest themselves by emitting light.

Electrochemiluminescence:



ECL emission in the visible part of spectrum is produced by the excited states generated during fast and highly exoenergetic electron-transfer reactions between a strong electron donor and electron acceptor [1–3].

Generally speaking, there is another possibility, the so-called electrochemically generated photochemistry or photochemistry without light. This is a combination of electrochemical generation of excited states (like in ECL), but their relaxation is accompanied by a non-radiative chemical process [4, 5] like in photochemistry.



This contribution is dealing with the ECL; nevertheless, for better understanding, the above comparison should be kept in mind.

Electrochemical generation of chemiluminescence has been described for the first time in the 1960s of the twentieth century [6, 7], and since that time, several review articles, chapters, and monographs were published (e.g., [8–16]).

Principles of ECL

Let us have a compound A (electron acceptor) which is able to be reduced reversibly by one electron to the corresponding radical anion (Eq. 1), and a compound D (electron donor) which can be oxidized reversibly in a one-electron step to the corresponding radical cation (Eq. 2). In principal, the compounds A and D may be identical ($A \equiv D$):



The electron-transfer reaction (ionic annihilation) between the two opposite electrochemically generated radical ions is always strongly exoenergetic (Eqs. 3a, 3b, 5a, 5b). If the liberated energy is sufficiently high, an excitation of one of the partners occurs.

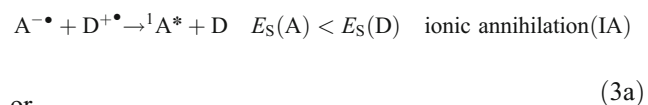
The electrochemical generation of reactive excited states has several advantages:

- a. There is a free choice of potential, which can be adjusted accurately and reproducibly.
- b. The spectrum of available potentials (E) is continuous, enabling high selectivity of the electrode process and thus high variability of the used system.
- c. Static as well as dynamic experiments are possible, with a number of variable conditions (various scan rates, various modes of change of E , etc.).
- d. The process is localized at the electrode surface and in the diffusion layer.
- e. The results can be quantified and directly correlated with electrochemical data.

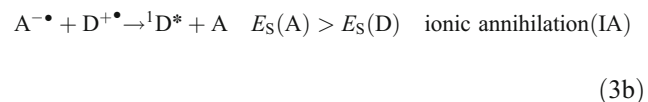
The formation of excited states in the ionic annihilation reactions (Eqs. 3a, 3b, 5a, 5b) is a manifestation of the Franck–Condon principle: the electron-transfer reaction between $D^{+\bullet}$ and $A^{-\bullet}$ is so fast and exoenergetic ($-\Delta G \sim 1.5\text{--}3.5$ eV), that the liberated energy is not re-distributed (or dissipated) into vibration or rotation modes, but is used for excitation.

In ECL, two mechanisms leading to emitting excited state are recognized:

1. Singlet mechanism (or energy sufficient, or the so-called S-route) is direct, simple, and effective, producing emission of high intensity (Eqs. 3a, 3b, 4a, 4b). On the other hand, the S-mechanism is more energetically requiring, since the liberated reaction energy must be higher than the first singlet energy E_S of the emitting species (usually $E_S > 2.8$ eV):



or

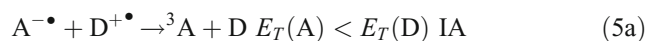


or

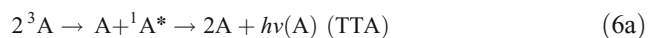
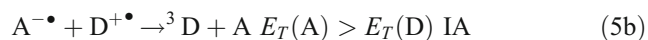


2. Triplet mechanism (or energy deficient, or the so called T-route) is an indirect process, much less effective than

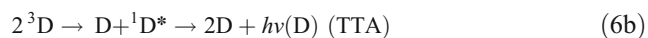
the singlet mechanism, with higher possibilities of parallel, concurrent quenching reactions, moreover, involving intersystem crossing (ISC). The formed triplet states (Eqs. 5a, 5b) undergo triplet–triplet annihilation (TTA) resulting in an excited singlet (Eqs. 6a, 6b), which emits the light (Eqs. 4a, 4b). The final emission is about two orders of magnitude weaker than in singlet case. On the other hand, the triplet mechanism has two main advantages: First, the energetic requirements are much lower, because only the triplet energy E_T should be surmounted by the liberated reaction energy (E_T reaches usually 1.5–2.4 eV). Therefore, much more systems can produce ECL which is very useful for fundamental research (see below). Second, in this way, selective and alternative generation of triplet states is possible, allowing their further study.



or



or



From the spectroscopic studies, it follows that the ECL generated in both mechanisms is of the fluorescence type; no phosphorescence from triplet states was observed.

Energetics of ECL

For any ECL emission, certain energetic conditions must be fulfilled. From the abovementioned considerations, it is evident that the source of energy is the Gibbs energy ΔG (or enthalpy ΔH) of the ET reaction during ionic annihilation (several papers and reviews deal with the energetics of ECL [15–21]). The amount of the liberated energy is a decisive factor for an appearance of ECL and for the respective mechanism. The reaction energy can be expressed using the standard redox potentials E^0 of the electrochemical generation of primary radical ions (F is the Faraday constant)

$$\Delta G^0 = -F\Delta E^0 = -F(E_{\text{ox}}^0 - E_{\text{red}}^0) \quad (7)$$

Some authors express the reaction energy as enthalpy (Eq. 8) where the value of $-\Delta S^0$ can be determined from the temperature dependence of redox potentials (Eq. 9).

$$-\Delta H^0 = F(E_{\text{ox}}^0 - E_{\text{red}}^0 - T\Delta S^0) \quad (8)$$

$$\Delta S^0 = (d\Delta G^0/dT)_p = -(dE^0/dT)_p \quad (9)$$

Since the temperature dependence of redox potentials is not considerable (except in the media with very low dielectric constant where the formation of ionic pairs is significant), the entropic term $T\Delta S^0$ for usual laboratory conditions was calculated as 0.1 ± 0.1 eV. Therefore, in common dipolar solvents, this term can be neglected or used as a fixed value 0.1 eV (Eq. 10).

In ECL, it is very useful to express the energies in electronvolt. Then, for reversible reduction and oxidation reactions (Eqs. 1 and 2), the E^0 value can be replaced by the experimentally determined half-wave potentials ($E_{1/2}$) in volts, F is unity, the entropic term corresponds to 0.1 eV and the practically useful Eq. (10) will be in the form

$$-\Delta H^0 = E_{1/2}(\text{D}/\text{D}^{+\bullet}) - E_{1/2}(\text{A}/\text{A}^{-\bullet}) - 0.1(\text{eV}) \quad (10)$$

Based on all the abovementioned considerations, it is possible to formulate a fundamental criterion (thermodynamic condition) for ECL (Eq. 11) which can be easily estimated from electrochemical data and which can predict the possibilities of the investigated system:

$$E_{1/2}(\text{ox}) - E_{1/2}(\text{red}) - 0.1 > E_T(\text{eV}) \quad (11)$$

The situation is depicted in Fig. 1. If $-\Delta G^0$ ($-\Delta H^0$) of the ionic annihilation reaction is higher than the energy of the first singlet state, (the case of $-\Delta H_1^0$ on the Fig. 1), the strong ECL emission appears based mainly on the singlet mechanism (the triplet mechanism is naturally also operating, but its contribution to the emission is about 3%). In the case of the $-\Delta H_2^0$, the available reaction energy surmounts

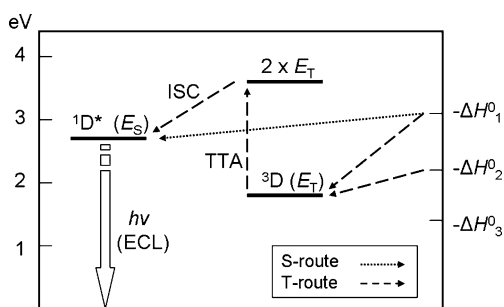


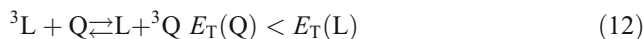
Fig. 1 The energetic diagram of possible ECL mechanisms taking into account three different reaction energies ($-\Delta H_1^0$; $-\Delta H_2^0$; $-\Delta H_3^0$) and D as a luminescent compound. (ISC intersystem crossing, TTA triplet-triplet annihilation)

only the triplet energy of the luminescent compound. Then only triplet mechanism proceeds and the observed ECL is weak. If, however, the liberated energy from ionic annihilation is even lower, its dissipation to heat occurs and no ECL emission is generated (case $-\Delta H_3^0$).

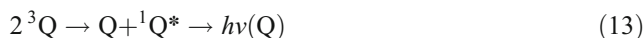
To distinguish which mechanism (singlet or triplet) is involved in the ECL generation, the influence of magnetic field on the ECL emission intensity should be studied [1, 22, 23]. Whereas the singlet mechanism is not influenced, in the case of the triplet mechanism, the emission intensity in the presence of magnetic field (0.7 T) increases by 20–30% due to stabilization of triplet states.

Sensitized ECL and quenching

The presence of triplet states can be unambiguously proved also by the so-called sensitized ECL. This approach is based on the possibility of triplet energy transfer: if the triplet energy of the compound Q is lower than that of the luminescer, the reaction 12 can proceed.

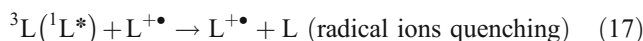
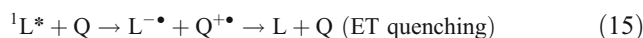
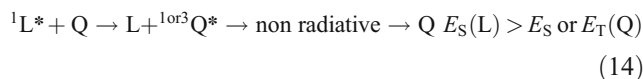


If the compound Q is better emitter than L, sensitized ECL is observed (at the wavelength typical for Q), the compound Q is then called the sensitizer, and the change of λ upon addition of Q is a proof of the triplet mechanism.



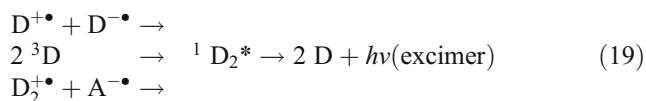
On the other hand, if the compound Q is not able to emit light, triplet quenching due to energy transfer occurs. Instead of the reaction 13, the relaxation of the triplet state proceeds in another way. The typical example of such quencher is trans-Stilben: after its excitation to triplet state, non-radiative isomerization to cis-Stilben occurs. This kind of process belongs to the abovementioned “photochemistry without light” [4, 5].

There are, however, other kinds of quenching reactions:



Excimers and exciplexes

In non-polar media or in the absence of electrolyte, where formation of ionic pairs is favorable, the ionic annihilation can result in formation of excited dimers (excimers, cf. Eq. 19) or excited complexes (exciplexes, cf. Eq. 20) [24]. Their emission is characterized by a broad band at longer wavelengths (Fig. 2) [25]. It is noteworthy that excimers and exciplexes are formed much more effectively (often exclusively) in ionic annihilation than in photoluminescence. Many examples of electrochemically generated exciplexes are mentioned in the literature (e.g., [15]), among typical exciplexes belong products of reaction between radical anion of anthracene and radical cation of 4,*N,N*-trimethylaniline or between radical anion of benzophenone and radical cation of 4-methoxythioanisole. Pragst et al. investigated intramolecular exciplexes in the ECL of 1-amino-3-anthryl-(9)-propanes [26].



Experimental techniques of ECL

The fundamental process in ECL is the electrochemical generation of radical ions. Radical anions are formed at a cathode, radical cations at an anode. Very important is their redox potential and stability of these radical ions; therefore, some prerequisites for compounds exhibiting ECL emission are necessary. First, the luminescent compounds should have large π -delocalized system of electrons enabling reversible formation of radical cations and/or anions. Such compounds should have low singlet and triplet energy. Second requirement is a large quantum yield of fluorescence.

Typical organic luminescers are polycyclic aromates, aryl-substituted heterocycles, isobenzofurans, isoindoles,

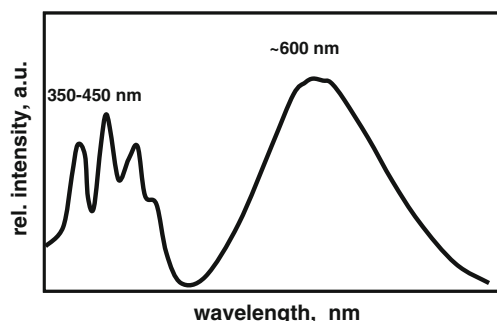


Fig. 2 Schematic picture of emission spectrum of excited monomer (350–450 nm) and of excimer (around 600 nm)

oxazoles, pyrazolines, carbazoles, pyrroles, and many others. From coordination compounds, the most used molecules are $[\text{Ru}(\text{bipy})_3]^{2+}$ and various complexes mainly of Ru, Os, Ir, Pt, Rh, Cr, Mo. Besides that, inorganic clusters like $\text{Mo}_6\text{Cl}_{14}$ or $\text{W}_6\text{X}_8\text{Y}_6$ (X, Y=Cl, Br) [27] or phthalocyanines [28] are utilized. Special systems are represented by chemiluminescent polymers [29] or micels [30]. Common aprotic solvents are generally used (acetonitrile, dimethylformamide, tetrahydrofuran, etc.), eventually mixed with toluene for better solubility of aromatic substances. On the other hand, generation of ECL in aqueous [31] or partly aqueous media [32] is also possible. (More ECL systems are presented in [15]).

The instrumentation for ECL is based on classical electrochemical equipment with potentiostat enabling two or three-electrode system. The material of the working and auxiliary electrodes is mainly platinum, but also gold, carbon, mercury, for optically transparent electrodes a fine metal gauze or indium tin oxide (ITO) on quartz. The most important is the shape of the electrochemical/ECL cell and its placing in an absolutely dark box, where there is a very sensitive photomultiplier or a camera. The simultaneous recording of the voltammetric curve (i vs. E) and the dependence of the ECL intensity on potential (I_{ECL} vs. E) is necessary. A typical arrangement for the possibility to follow and to photograph the intensity of the emitted light and to record the respective spectra was originally designed by Fritz Pragst and is described in [12, 32, 33]. The cell (for rotating disk electrode (RDE)) has a flat bottom from quartz, the cell for dropping mercury electrode (DME) or hanging mercury drop electrode (HMDE) has a side window. The black box is equipped by various openings and entrances for tight mounting of a camera or a special optical quartz fiber cable for a direct connection with a UV-vis spectrometer. This is rather universal equipment for fundamental ECL studies at various electrodes (stationary or rotating (ring)-disk, mercury drop, foil, gauze, or optical transparent ITO electrodes), for various modes of ECL generation and various solvents. More specialized types of ECL cells are presented in [15].

Types of ECL experiments

Before starting the ECL experiments, it is necessary to perform a preliminary electrochemical study of fundamental redox behavior of the involved compounds (DC-polarography, voltammetry at an RDE or cyclic voltammetry at various electrodes) in order to estimate ΔE , the energetic possibilities of the studied system (Fig. 3).

The proper ECL experiments can be classified according to two criteria: by the mode of electrochemical generation of primary radical ions and by the mode of their mixing.

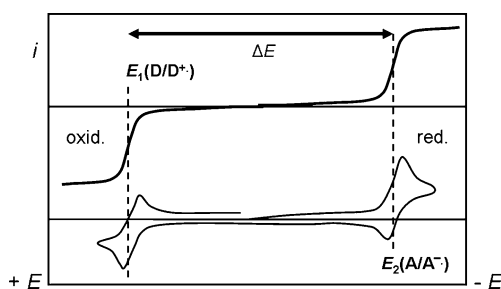


Fig. 3 Typical redox behavior of a suitable donor (*D*) and acceptor (*A*)

Heterogeneous generation at two potentials

Simultaneous at two electrodes

The radical ions are formed at two electrodes applying two different potentials (steady-state methods). Typical cases are

- an optically transparent thin-layer electrochemical cell (Fig. 4), where the distance between the anode and cathode is in tenths of millimeter and the mixing of radical ions proceeds by diffusion. The emitting zone is just between the electrodes and the light can be observed from the sides (like on a display—Fig. 4).
- a rotating RDE, where one radical ion is generated at the disk and the other at the ring and their mixing occurs by convective diffusion during rotation. The emitting zone appears at the inner edge of the ring (Fig. 5). In addition to this, variation of rotation rate enables kinetic investigations of ECL. Note, that in these two types, the ECL emission is continuous.

Sequential at the same electrode

This is probably the oldest and most broadly investigated type of ECL experiments often involving only one compound (e.g., $[\text{Ru}(\text{bipy})_3]^{2+}$). Both radical ions are generated at the same electrode by periodic switching between oxidation and reduction potential using a “double step” or “triple step” regime (Fig. 6). In this type of experiment at the electrode,

Fig. 4 Localization of ECL emission in a thin-layer cell

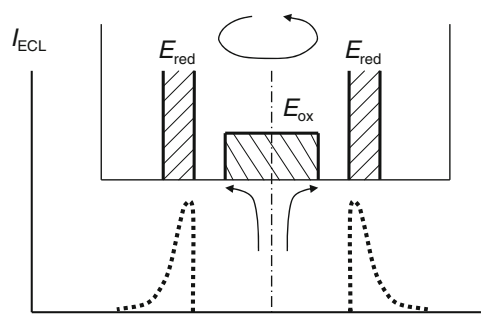
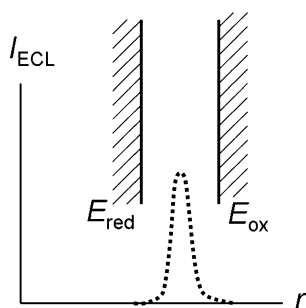
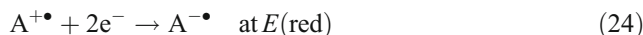
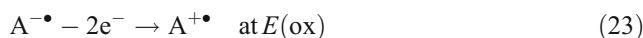
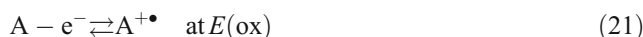


Fig. 5 Localization of ECL emission in a rotating ring-disk electrode

not only a one-electron generation of opposite radical ions proceeds (Eqs. 21, 22 – cf. Eqs. 1, 2), but also a two-electron mechanism (Eqs. 23, 24) involving the radical ions generated in the previous pulse.



The mixing of redox-reactive intermediates proceeds by diffusion and the emitting zone is localized in the diffusion layer of the electrode, where the “last” radical ions diffusing away meet the “first” opposite radical ions just generated at the electrode (Fig. 7). It is evident that in this transient method, a pulsing ECL emission is observed and for kinetic studies various frequency and length of potential steps can be applied. Note that generally, the ECL signal (I_{ECL}) should not be of the same shape and height when switching from + to – and from – to +, respectively, due to various decay kinetics and various diffusion coefficients of the respective radical ions (cf. Fig. 6).

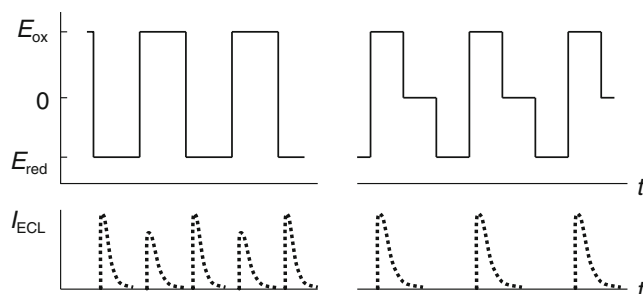
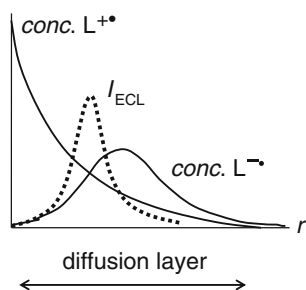


Fig. 6 A “double step” and “triple step” regime of sequential generation of ECL and corresponding luminescence response

Fig. 7 Localization of ECL emission. Concentration profiles of $L^{+\bullet}$ and $L^{-\bullet}$ after switching the potential from “-” to “+”



Examples of studied organic systems

The abovementioned ECL techniques is used namely for analytical purposes (for more information, see ref. [15]). It can be, however, used also in physical organic chemistry for mechanistic studies. An illustrative example deals with pyrazoline derivatives [34, 35].

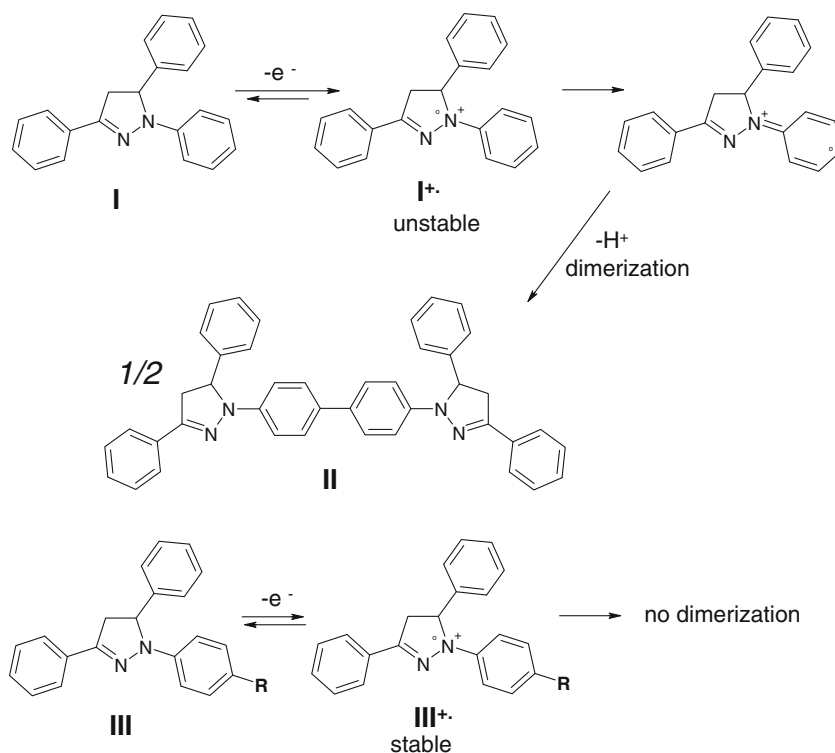
The sequential ECL (50 Hz) of 1,3,5-triphenyl- Δ^2 -pyrazoline (I) in DMF exhibited green emission, whereas the fluorescence of the above compound is blue. This phenomenon was explained by the formation of the emitting dimer (II) during the oxidation step [34]. These results were confirmed by ECL generated on the RDE using comparison of pyrazoline derivatives able to dimerize (I) with those bearing blocking substituents R (III) [35]. The expected proportionality between the ECL intensity and the square root of the rotation rate of the electrode was not confirmed because the ECL quantum yield rises with increasing rotation rate. In the case of

anodic polarization of the disk, the observed ECL at the ring is strongly affected by the formed dimer. On the other hand, during the formation of cation radicals at the ring, the influence of dimerization reaction is very small, and practically, only the monomer emission is observed (Scheme 1).

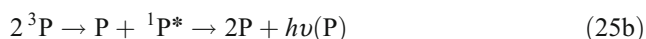
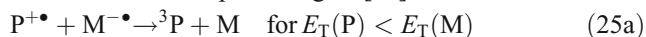
The other important contribution of ECL technique is aimed to photo(electro)chemistry, namely to studies of organic molecules in triplet states, their reactivity, and experimental measurement of their energies. It is necessary to keep in mind that during the triplet mechanism of the ECL emission, only triplet states are (in dark!) selectively generated. This fact is valuable for photophysics, since the ECL experiments represent an alternative and of photoluminescence independent way for determination of triplet energies in solvated state in condensed media. The following examples deal with the sequential mode of generation of triplet states.

Since 1,3-diaryl- Δ^2 -pyrazolines (P) participate in the photooxidation reactions with oxygen (applicable in textile industry as a bleaching agent), their triplet energy represents a significant factor. The investigation of mixed ECL systems involving a series of non-dimerizing oxidizable pyrazolines P and several reducible hydrocarbons M with known triplet energies resulted in estimation of unknown triplet energies of the pyrazolines. The approach was based on the evaluation of (often combined) luminescence spectra, because both possible emitting species ($^1P^*$ as

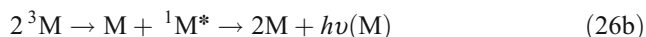
Scheme 1 Electrooxidation pathway of two types of 1,3,5-triphenyl- Δ^2 -pyrazolines (I and III) in DMF



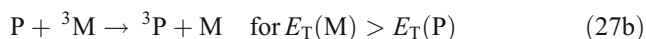
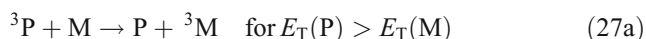
well as $^1M^*$) were observed depending on the relationship between the two triplet energies [36]:



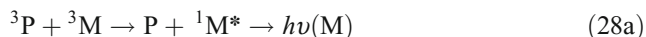
or



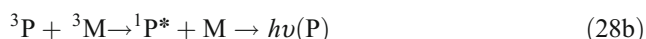
In mixed systems (e.g., the abovementioned P and M), the final triplet species — precursors of emitting excited molecules — can be generated either in ionic annihilation reactions [36], (Eqs. 25a, 25b and 26a, 26b) or by the triplet energy-transfer reactions [37].



Such an energy transfer can have both kinetic and thermodynamic nature. The interpretation of kinetically controlled energy transfer is complicated, but the evaluation of the purely thermodynamic processes depends only on the energy levels and therefore can be used for the triplet energies determination. In addition to this, a mixed triplet–triplet annihilation is also possible:



or



Similarly, using the sequentially generated ECL, the system consisting from reduced 2,4,6-triphenylpyrylium-perchlorat and oxidized rubren exhibits a strong emission, showing that not only a radical ion, but also an uncharged free radical can serve as redox partner for generation of excited state [38].

In the investigation of sequential ECL of three isobenzofuranes with or without presence of other luminescent compounds, the corresponding triplet energies of isobenzofuranes were determined using sensitized ECL. A singlet mechanism has been proved for the homogeneous ECL systems [39].

The possibilities and restrictions of the estimation of triplet energies of organic compounds using sequential electrochemiluminescence method was summarized in a review paper [40]. It was demonstrated that the accuracy of this determination based on thermodynamic relationships, sensitized ECL, or ECL quenching is ± 0.1 eV, that is

acceptable also for photophysicists. The advantage of the electrochemical approach is the possibility to investigate successfully even substances where the classical methods (phosphorescence or delayed luminescence) failed. The possible misinterpretations are there discussed.

Simultaneous heterogeneous and homogeneous generation at the same potential

This more recent and very powerful technique (from the point of view of fundamental research in molecular electrochemistry, photochemistry, and photophysics) is based on the following principle: taking a negatively polarized electrode as an example, radical anion of a luminophore is reversibly and heterogeneously generated at the surface. Simultaneously at the same electrode at the same potential, another compound is reduced, but irreversibly, following the two-electron mechanism of the electrochemical–chemical–electrochemical (ECE) type. In this mechanism, the primary radical anion is homogeneously split in the diffusion layer to a stable anion and a strongly electrophilic radical. The latter, as a strong oxidant, can react in the diffusion layer with the already present radical anion of the luminophore. This electron-transfer reaction can be (after fulfilling of necessary energetic criteria—Eq. 11) the source of energy for excitation and ECL.

The characteristic features of this type of ECL are the identical experimental conditions like in DC voltammetry (a single constant or linearly increasing working potential) resulting in a continuous, potential depending ECL emission. Hence, besides a standard current–potential (i – E) curve, the analogous dependence for ECL intensity (I_{ECL} – E) is simultaneously recorded. Due to experimental similarity, this type of ECL was called DC-electrochemiluminescence (DC-ECL).

The other characteristic feature of this method is the necessary presence of another compound, which is able to form homogeneously the second reactive intermediate. Therefore, this type of ECL is known also as “ECL with coreactant.” From the mechanistic point of view, these two terms, i.e., DC-ECL and “ECL with coreactant”, are equivalent. The difference can be seen in the aims of the respective research.

Expression “ECL with coreactant” was introduced relatively recently and is broadly used namely in analytical applications (see below the “[Analytical application — ECL in aqueous media](#)” section) where a limited number of well-studied systems are used and the ECL is generated specifically for diagnostic use, imaging, and other very modern applications (see more information, e.g., in ref. [15]), where sensitivity and reproducibility of I_{ECL} is very important. Therefore, an overwhelming majority of publications dealing with coreactant ECL is based on ruthenium(II)bipyridine complexes because of their excellent properties; on the other hand, only several compounds were used as coreactants,

namely oxalates and peroxydisulfates for aqueous media and tertiary amines (e.g., tripropylamine) for aprotic ones. Very recently, ECL of systems where tetraphenylborate anion serves as a coreactant has been described [41].

Expression “DC-ECL” was used already in the 1980s for cases, where the compound undergoing the ECE process (= coreactant) or the luminophore itself is the object of fundamental (= primary) investigation (unknown mechanisms, intermediates and their reaction or decay kinetics, unknown triplet energies and their transformations, etc.). A large number of such studied systems was and can be newly designed.

The following section is devoted to this approach, its use and challenges.

DC-ECL (ECL with a coreactant)

General reaction scheme

As mentioned generally in the “Simultaneous heterogeneous and homogeneous generation at the same potential” section, DC-ECL appears as a result of exoenergetic electron-transfer reactions of two reactive intermediates generated during electrolysis at one single electrode where a constant or continuously increasing potential is applied. One reaction partner is generated directly, heterogeneously at the electrode; the other is formed homogeneously in the diffusion layer as a one-electron intermediate of irreversible two-electron electrode reaction. The detailed reaction scheme can be described as follows.

Let us have in solution a compound CR (“coreactant”), undergoing two-electron irreversible oxidation of the ECE type. At the potential $E_{ox}(CR)$, the overall reaction proceeds (see Fig. 8):



according to the following ECE mechanism:

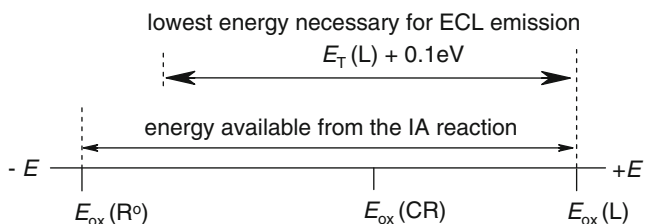
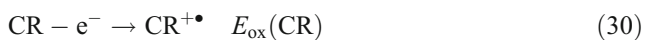


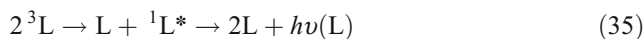
Fig. 8 Schematic view of the case, where ECL is possible, because the difference between $E_{ox}(R^\bullet)$ and $E_{ox}(L)$ is larger than $E_T(L)+0.1$ eV

In this type of reactions, the radical R^\bullet is a very strong reducing agent = electron-donating species. (Note that it is generated at positive potential!) Therefore, at the actual working potential in the cell ($E=E_{ox}(CR)$), it is very unstable and cannot be directly detected by classical methods (electron spectra, ESR,...).

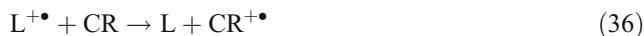
Now, let us add in the solution of CR a luminescent compound L which is reversibly oxidized at $E_{ox}(L) > E_{ox}(CR)$:



Then, at the potential $E_{ox}(L)$, the intermediates R^\bullet and $L^{+\bullet}$ are simultaneously present in the same solution and can react. If the energetic criterion (Eq. 11) is fulfilled and $E_{ox}(L) - E_{ox}(R^\bullet) > E_T(L) + 0.1$ eV, the ionic annihilation (Eq. 34) results in an ECL emission (Eq. 35):



Parallel also a homogeneous process of oxidation of CR can proceed (Eq. 36) and followed by reactions (Eqs. 31 and 34); it also results in the ECL emission.



The crucial point is always the oxidation potential of the radical R^\bullet and its potential difference from $E_{ox}(L)$ (Fig. 8).

DC-ECL investigations proceed most often at rotating solid electrodes, because in this way, a stable and continuous emission is obtained, its intensity is easy to record using a photomultiplier placed in the black box just below the quartz bottom of the cell, and simultaneously, the electrochemical behavior can be followed. Change of the photomultiplier for a camera allows to take pictures of ECL directly in the cell [42]. The use of the DME for the ECL investigations was presented for the first time by Fritz Pragst in 1981 [43] together with all experimental peculiarities including photographing [33]. The high hydrogen overvoltage at the mercury electrodes is advantageous in reductive ECL experiments due to extension of potential window.

During the DC-ECL experiment, the voltammetric (or polarographic) and simultaneously the ECL curves are recorded and evaluated. From Fig. 9, it is evident that the ECL emission appears at the potential of the oxidation of L, when both reactive intermediates are already present in the solution. Note that the oxidation wave of CR is two-electron irreversible, whereas the oxidation of L is a one-electron reversible process.

The principle of oxidative and reductive DC-ECL is identical and all considerations are analogous.

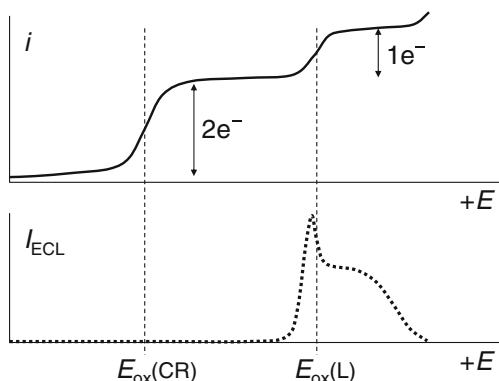


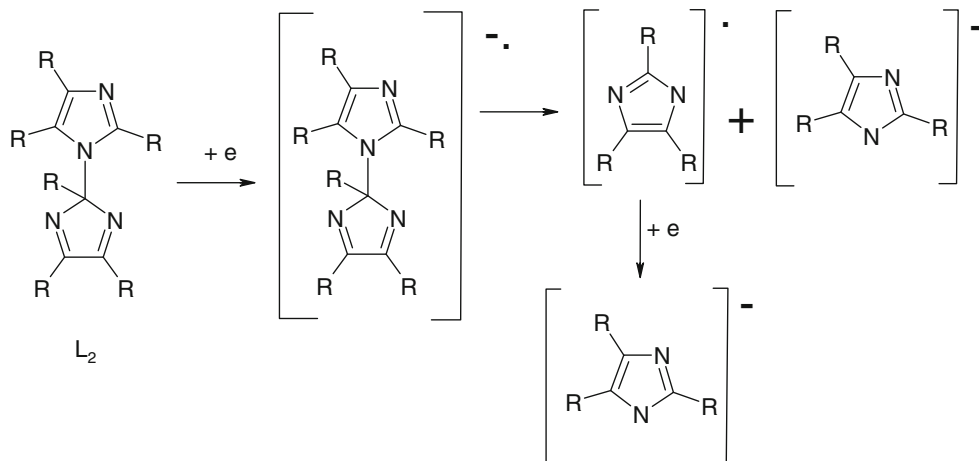
Fig. 9 Simultaneous voltammetric ($i-E$) and ECL ($I_{\text{ECL}}-E$) curves recorded in the system described in Fig. 8

Utilization 1: direct proof of short-living radical intermediates

In mechanistic investigations in organic electrochemistry, namely in the case of multielectron irreversible processes, the experiment that can decide about presence or absence of a radical intermediate is often crucial and decisive. Besides UV-vis and EPR spectrometry, the DC-ECL appeared to be a very sensitive method for detection of presence of such intermediates. The result follows directly from the fundamental principles of ECL: Observed emission during the cathodic DC-ECL represents an unambiguous proof of the participation of the strong oxidizing intermediate in the system; moreover, it is possible to estimate the range of its reduction potential. Due to the existence of the T-route for generation of ECL, the crucial electron-transfer reaction leading to the excited state is only moderately energetically demanding, and thus, the emitting ECL systems are more frequent.

As the first example of such a study, the cathodic reduction of bis-(2,4,5-triphenylimidazolyl)-1,2' (B_2) can be mentioned, reported by Pragst and Kaltofen in 1980 [44].

Scheme 2 Electroreduction pathway of bis-(2,4,5-triphenylimidazolyl)-1,2'



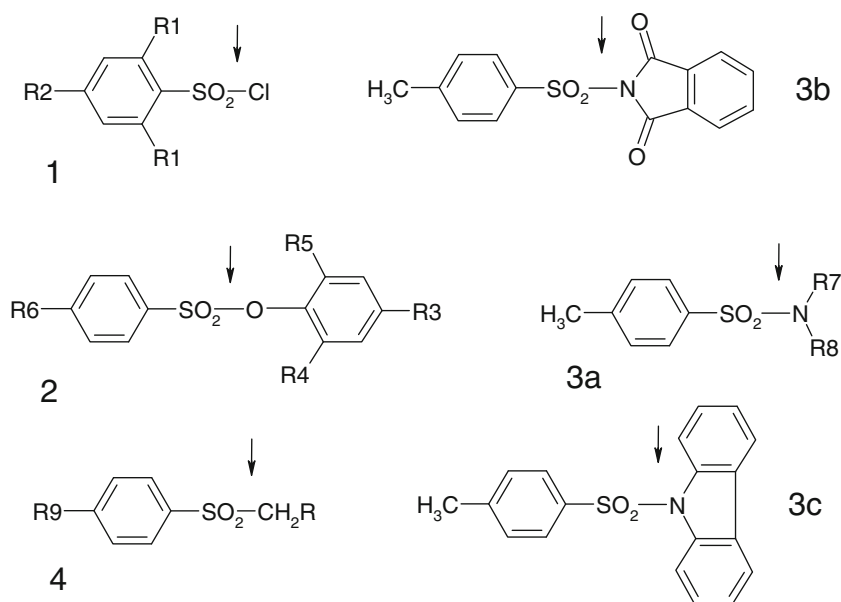
After the first electron transfer, presence of the neutral intermediate (B^{\bullet}) was proved (Scheme 2). This radical, as a strong oxidant, is responsible for the ECL emission if simultaneously radical anions of luminophore A (9,10-diphenylanthracene, 9,10-dimethylantracene, perylene, pyrene, rubrene, chrysene, fluoranthene, etc.) are present.



In 1983, Pragst and von Löwis have shown that the reduction of diphenyl disulphide in DMF [33] depends strongly on the electrode material: whereas the E_{red} at the platinum (Pt) or glassy carbon (GC) electrode is -1.6 to -1.7 V (SCE); at DME, the reduction occurs nearly by 1 V less negatively (at -0.7 to -0.8 V) and the reduction mechanism was not understood [45–47]. DC-ECL of Ph-SS-Ph and Ph-CO-SS-CO-Ph with a fluorescent aromatic hydrocarbon at DME revealed that the free radicals Ph-S $^{\bullet}$ (Ph-CO-S $^{\bullet}$) are present as intermediates in the reduction mechanism and thus a one-electron cleavage of the disulfide linkage was proved.

Another mechanistic problem studied by Pragst and Kaltofen is the reduction of aromatic sulfonyl compounds [33, 48]. During their reduction, the primary radical anion is split into a radical and an anion. Generally, a cleavage of the S-Cl, S-O, S-N and A-C bond occurs, but the question

Fig. 10 Arylsulfochlorides (1), sulfonic ethers (2), sulfonamides (3), and sulfonyls (4). The arrows point to the cleaved bond

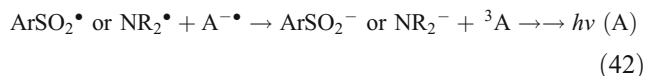


is, which part will represent the strongly oxidizing radical species because the more stable anionic leaving group is not always evident (Fig. 10).

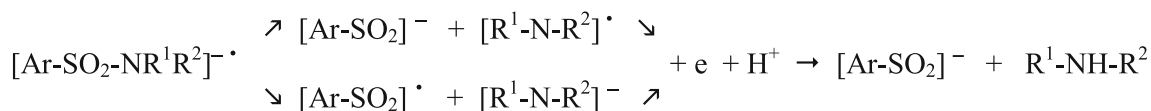
In arylsulfochlorides, the leaving group is Cl^- and a sulfinyl radical is formed. In sulfonic ethers, the cleavage leads to aryl sulfinate anion and phenolate radical. In this series of compounds, very often the ether is reduced more negatively than the luminophore and a fast homogeneous redox catalysis is observed as a pre-peak before the luminophore reduction. Just at this potential, the most intense luminescence is generated showing that the most efficient ECL proceeds through the indirect reaction pathway.

In sulfonamides, both aminyl radicals or arylsulfinyl radicals can be formed (Scheme 3).

Which of them will finally appear as the reacting radical depends on their reduction potential: the more easily reducible radical (= the stronger oxidant) will participate at the ECL process (Eq. 42). The discrimination can be made on the basis of the energetic criterion (Eq. 43) and the experimental proof can be achieved by changing A with various E_T .



$$E_{1/2}^{\text{red}}(\text{ArSO}_2^\bullet \text{ or } \text{NR}_2^\bullet) - E_{1/2}^{\text{red}}(\text{A}) - T\Delta S \geq E_T(\text{A}) \quad (43)$$



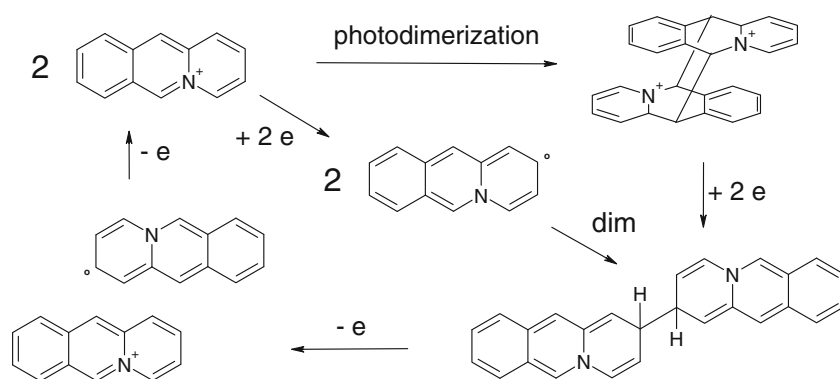
Scheme 3 Two possible reduction pathways of arylsulfonamides

The reduction of p-tolyl sulfones substituted with benzyl or acetonitrile with various luminophores did not result in any emission. This points to the fact, that the sulfinyl anion and benzyl or acetonitrile radicals are formed. These radicals, however, are not suitable for the ECL. Analysis of all data resulted in an interpretation that even when the energetic criterion is fulfilled, the structure of the radical is important: the prerequisite of a high triplet yield is a fast ionic annihilation reaction. Therefore, the large π -radicals give rise to a more intense luminescence than small π -radicals or even σ -radicals.

Besides the abovementioned examples of cathodic ECL, the anodic ECL was also investigated and due to the interception of key radical cations several mechanistic questions were solved. One of the examples is the mechanism of reduction and oxidation behavior of acridinium salt and its two different dimers, described by Pragst et al. in 1985 [49]. The radical intermediate was identified during oxidative cleavage of reduced dimer (Scheme 4).

Already in the 1970s due to the high biological importance of the dihydropyridine/pyridinium redox system, detailed investigations of the oxidation mechanism of 1,4-dihydropyridines were carried out in many laboratories, where the ECE mechanism as well as the EEC and disproportionation of the primarily formed cation radical

Scheme 4 Mechanism of reduction and oxidation of acridizinium salt and its two different dimers



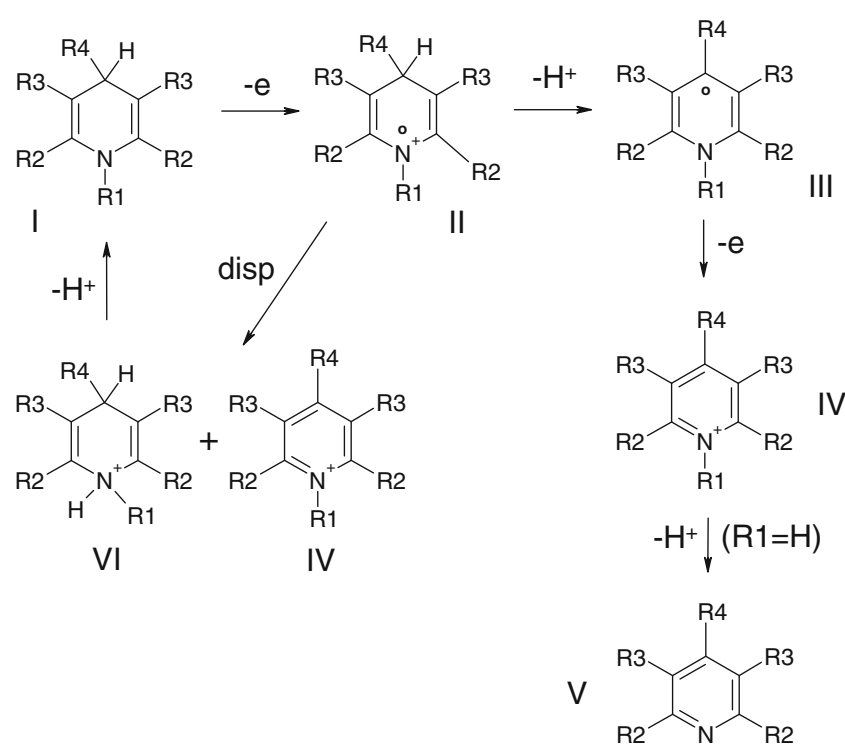
were discussed. The first direct detection of the dihydropyridine radical cation was achieved by in situ ESR-electrochemical experiment in 1977 by J. Klíma [50], but only for 1,2,3,4,4,5,6-heptasubstituted compounds. The 4-H radical cation (Scheme 5, compound II) was expected to be too short living, and no experimental evidence for the pyridinium radicals (III) was available.

Since the electrochemical oxidation of a series of 1,4-dihydropyridines with various luminophores resulted in an DC-ECL emission, the only possible explanation is based on the participation of both dihydropyridine radical cation (II) as well as the pyridinium radical (III) in the dehydrogenation process [51, 52]. In addition to this, if the oxidation potential of dihydropyridine is more positive than that of the luminophore, a practical example of the homogeneous redox catalysis is demonstrated [52].

1,4-Dihydropyridines in above experiments served as model compounds for the DC-ECL research with reduced nicotinamides and finally with authentic NADH and NADPH [32]. Although NADH and NADPH have much higher diffusion coefficient than the model nicotinamide and a tendency to the adsorption at the electrode, the ECL emission in dimethylsulfoxide was evident and well reproducible fitting perfectly to the other data. In the case of NADPH, for the solubility reasons, up to 15% of water was added. Even here, a clear luminescence was recorded proving the NAD(P)^{\bullet} radical intermediate in regeneration reaction of the coenzyme NAD(P)^+ . This type of experiment can be used also for analytical purposes.

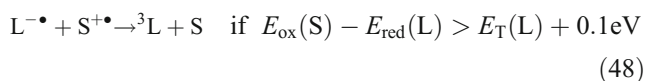
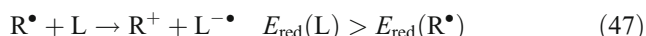
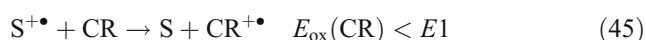
It was already mentioned that in DC-ECL homogeneous redox reactions play a significant role in generation of excited states as well as of the corresponding precursors.

Scheme 5 Electrooxidation mechanism of substituted 1,4-dihydropyridines



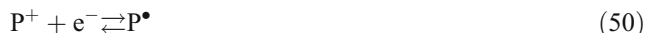
Originally, the DC-ECL represents a proof of the existence of highly reactive short-living radical intermediate generated secondarily as a product of chemical reaction in an ECE mechanism. However, Pragst and Niazymbetow have also shown that the addition of a suitable redox system to the solution can unambiguously prove also the primarily generated short-living radical ion of the substrate [53]. The idea is based on the following consideration:

For the test of the presence of radical cation of the compound S (substrate), addition of the system CR (known dimeric species serving as a coreactant) and L (luminophore) cause the following set of reactions resulting in an emission of L:



The energetic scheme is presented at Fig. 11 (an analogous scheme can be drawn for cathodic DC-ECL).

A comparison of two Pragst's papers [23, 38] is very instructive from the mechanistic point of view: The bipyranes (PP) are formed by dimerization of pyranil radicals (P[•]) which are the products of reversible reduction of pyrylium cations at negative potentials.



On the other hand, oxidation of bipyranes (PP) is irreversible two-electron process regenerating the original pyrylium cations by ECE mechanism (cf. Eqs. 29–32),

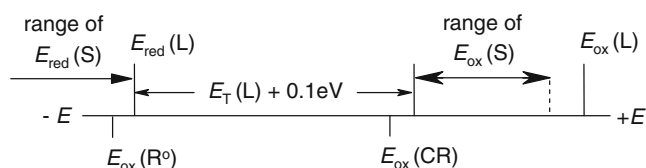


Fig. 11 Relative position of oxidation and reduction potentials of compounds involved in the experimental proof of S^{•+} using anodic DC-ECL

where the pyranil radicals (P[•]) are generated at positive potentials. Using oxidized form of rubrene (R) for ionic annihilation reaction, the same ECL can be generated either sequentially, switching potential between E_{ox}(R) and E_{red}(P^{•+}) [38], or by DC-ECL at a single positive potential, where simultaneously oxidation of R and PP occurs [23].

Utilization 2: selective generation of triplet states

The DC-ECL experiments can be taken also as a tool for selective generation of triplet states. For investigation of energetics, properties, and reactivity of molecules in triplet state, ECL represents an alternative, totally different, and “dark” method for their generation.

The appearance of triplet states was in many cases definitely proved by the abovementioned increased ECL intensity in magnetic field (e.g., [23]), by thermodynamic considerations (Eq. 11), by quenching reactions, sensitized ECL, and other triplet energy-transfer experiments.

Just the fundamental criterion (thermodynamic condition) for ECL (Eq. 11) together with systematic interception experiments offer a new way for estimation or determination of thermodynamic values like triplet energy of a luminophore L or redox potentials of unstable radical intermediates.

This approach is based on systematic change of the oxidation (or reduction) potential of one additive participant of the ECL system, continuous evaluation of corresponding ECL intensity and its correlation with the thermodynamic condition for ECL (Eq. 11).

Estimation of triplet energies

In standard methods for estimation of triplet energies (phosphorescence, absorption spectra, delayed fluorescence, ESR kinetics of quenching of triplet states, etc.) absorption of light (electromagnetic waves) is required. Generation of triplet states by ECL, however, offers an alternative possibility of excitation: exoenergetic electron-transfer reaction (annihilation) of electrochemically generated radicals or radical ions. Among the advantages, it is possible to mention different principle, high selectivity, high concentration of triplet states and low-cost instruments. On the other hand, this method is time-requiring and the compounds in the system must fulfill some energetic and chemical conditions. The accuracy of the measured E_T is acceptable: ±0.1 eV.

The principle is based on selective energy-transfer processes and on the search for the limiting situation for E_T in fulfillment of the energetic condition (Eq. 11) [40, 54].

For the measurement of triplet energy of oxidizable luminophore L (Eq. (33)), it is necessary to compose a

series of acceptors A with different reduction potentials forming the potential scale as dense as possible, and with the following properties:

- a. the reduction must be reversible; hence, the radical anion $A^{-\bullet}$ should be relatively stable



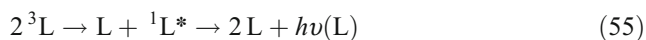
- b. triplet energy of A must be larger than that of L and the A should not exhibit a luminescence to ensure that only L will serve as luminophore

$$E_T(A) > E_T(L) \quad (52)$$

- c. the reduction potential of A must be less negative than that of R^+ (which corresponds to $E_{ox}(R^{\bullet})$ - see below)

$$|E_{red}(A)| < |E_{red}(R^+)| \quad (53)$$

As a demonstration, let us use the model system described in the “General reaction scheme” section with the coreactant CR and as the testing compound for determination of triplet energy, substituted pyrazoline L - (Eqs. 29–35). At the potential $E_{ox}(L)$ the already known reactions (Eqs. 54 and 55) will proceed:



From the apparent ECL, it follows that the energetic criterion for ECL is fulfilled; hence, the potential difference between the $E_{ox}(R^{\bullet})$ and $E_{ox}(L)$ is certainly larger than the (“unknown”) triplet energy of L ($E_T(L)+0.1$ eV); cf Fig. 12.

Now, let us add the first (the most negatively reduced) compound A (A_1) to the existing ECL system exhibiting ECL. Then the additional process (Eq. 56) occurs and if the reduction potential of A_1 is more negative than the

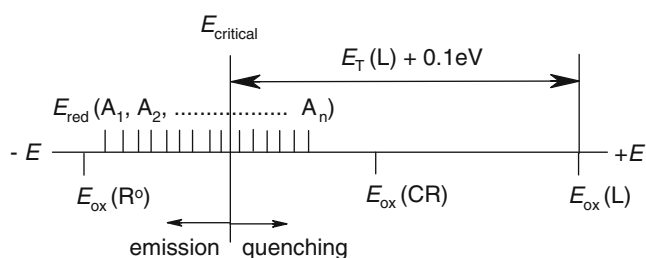
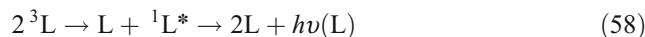


Fig. 12 Schematic view of the case, where the triplet energy of oxidizable L is estimated using the search for $E_{critical}$ by means of a series of acceptors A with different reduction potential

critical potential $E_{critical}$, the emission is observed (Eqs. 57 and 58):



If, however, the reduction potential of the acceptor A_n will be less negative than the critical potential $E_{critical}$, the reaction (Eq. 57) will not produce the triplet states and no emission will be observed.

When plotting the ECL intensities corresponding to the presence of individual compounds A against their reduction potentials, a sharp drop of I_{ECL} to zero is observed (Table 1) at the critical potential. Then, the triplet energy is given just by the difference between the $E_{critical}$ and $E_{ox}(L)$ increased by the entropic term 0.1 eV.

From the Table 1 follows that in this illustrative case, the $E_{critical}$ is between -1.29 and -1.37 V. Oxidation potential of L (1-*p*-anisyl-3,5-diphenyl-2-pyrazoline) is $+0.67$ V. Using the energetic criterion (Eq. 11) in the limit form

$$E_{ox}(L) - E_{critical} - 0.1 = E_T(\text{eV}) \quad (59)$$

the $E_T(L)$ should reach the value between 1.86 and 1.94 eV. (In reality, the tabulated value is 1.88 eV; hence, the accuracy is in the frame of 0.1 eV).

The same coreactant can be used also for estimation of triplet energy of reducible luminophore



In that case, the $E_{red}(L)$ should be less negative than $E_{ox}(R^{\bullet}) \equiv E_{red}(R^+)$ and, in fact, L is replacing the compounds

Table 1 Typical series of electron acceptors A used for estimation of triplet energy of L (1-*p*-anisyl-3,5-diphenyl-2-pyrazoline) and the appearance of ECL (data taken from [54])

A-carbonyl substance	$E_{red}(A)$ (V)	ECL
Anthraquinone	-0.86	-
4,4'-Diphenylbenzil	-1.06	-
Benzil	-1.14	-
1,4-Dicinnamoylbenzene	-1.18	-
1,4-Bis-[β -benzoylvinyl]-benzene	-1.20	-
<i>p</i> -Methoxybenzil	-1.22	-
Fluorenone	-1.28	-
Dibenzalacetone	-1.29	-
<i>p</i> -Cyanobenzophenone	-1.37	+
<i>N-p</i> -tolylphthalimide	-1.40	+
4,4'-Diacetylbiophenyl	-1.58	+
Benzophenone	-1.76	+
<i>p</i> -Methylbenzophenone	-1.82	+
4,4'-Bis-dimethylamino-benzophenone	-2.00	+

A in the previous system. Then, for estimation of $E_T(L)$, a series of donors D exhibiting reversible one-electron oxidation at increasing oxidation potentials should be composed and the critical oxidation potential of D should be found (cf. Fig. 13).

Both presented examples were based on electrochemical oxidation reactions where the ECL is observed at the oxidation potential of L or D (anodic DC-ECL), but the same considerations and analogous redox reaction schemes are valid for the cathodic DC-ECL utilizing the reducible coreactant and the same series of A and D.

It is necessary to mention that the triplet energies may be estimated in analogous way also using the sequential ECL (the possibilities and restrictions were summarized by Pragst et al. in the ref. [40]). Nevertheless, the DC-ECL offers a simplified procedure which was successfully applied [54].

The possibilities of estimation of triplet energies by ECL can be extended using a transfer of triplet energy from L to a further component Q [40]. Sensitized ECL is observed if Q can serve as a luminophore (cf. “Sensitized ECL and quenching” section, Eqs. 12–13), ECL quenching occurs if 3Q has a very short lifetime, if the TTA is ineffective or if Q has a very small fluorescence yield. Both ways were experimentally tested and their applicability was proved [54].

Estimation of unavailable redox potentials of radical intermediates

The systematic measurements of ECL intensity in DC-ECL systems with addition of abovementioned various acceptors A or donors D (or luminiscers L, eventually), can be used also for the determination of otherwise unavailable redox potentials of radical intermediates and for the evidence of participating or absence of certain radical intermediates in the investigated mechanism.

This is well illustrated in the case of cathodic ECL of 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl₂) in DMF. Siegel and Mark [55, 56] and later Boto and Bard [57] investigated this mechanism where three reaction pathways appeared to be possible. To solve this problem, the mentioned approach to ECL investigations

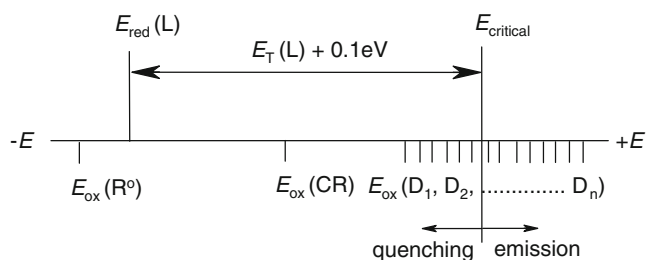


Fig. 13 Schematic view of the case, where the triplet energy of reducible L is estimated using the search for $E_{critical}$ by means of a series of donors D with different oxidation potential

was used by Pragst et al. [58] and the participation of $DPA^{+•}$ in the luminescence process has been proved.

Two DC-ECL mechanisms

Up to now, for simplicity, the ECL intensity (I_{ECL}) was taken as a single, more or less qualitative entry. A more detailed shape analysis of the potential dependence of I_{ECL} reveals, however, that this curve always starts with a sharp peak followed by a broad plateau. Since the ECL appears always simultaneously with the most positive oxidation process (anodic DC-ECL), or most negative reduction process (cathodic DC-ECL), the I_{ECL} vs. E curve can be directly correlated with the voltammogram (cf. Fig. 9). The peak is situated always at the bottom of the voltammetric wave, before its half-wave potential ($E_{1/2}$), the plateau then approximately follows the last part of the wave and the limiting current. The proportion of heights between the peak and plateau is influenced by several factors, including the kinetic ones. Generally, it is possible to state, however, that it depends mainly on the difference between the oxidation potential of coreactant - $E_{ox}(CR)$ - and that of the luminescent compound - $E_{ox}(L)$ (in the case of anodic DC-ECL, cf. Fig. 9): When the $E_{ox}(CR)$ occurs far before the $E_{ox}(L)$, the peak is suppressed and the plateau represents the main ECL signal. On the other hand, when both potentials are closer, the sharp peak is dominating [42]. In the extreme case, when $E_{ox}(CR)$ is more positive than $E_{ox}(L)$, peak and plateau cannot be distinguished [59]. Due to the fact that the peak and the plateau were observed at mercury, platinum as well as at the glassy carbon electrodes [42, 44], adsorption does not play here an important role.

The possible explanation of this phenomenon based on different mechanism was suggested by Pragst et al. [43, 44]. At the potential of the peak (bottom of the oxidation wave of L), the concentration of L at the electrode surface is low, whereas the oxidation of CR (and thus the generation of the radical $R^•$) proceeds heterogeneously at the limiting current conditions (cf. the model case in the “General reaction scheme” section). The ionic annihilation (Eq. 34) proceeds very effectively in the close vicinity of the electrode and the ECL intensity sharply increases with raising potential forming the peak.

Around the half-wave potential of L, the number of $L^{+•}$ at the electrode surface exceeds the number of available short-living radicals $R^•$ and the more stable radical cations $L^{+•}$ diffuse away from the electrode, reacting with the bulk CR molecules and generating thus radicals $R^•$ homogeneously (Eqs. 36 and 31). The ionic annihilation reaction (Eq. 34) proceeds now more distant from the electrode and the ECL intensity decreases.

The further raising potential, however, generates more and more radical cations $L^{+•}$; therefore, the effectivity of the mentioned homogeneous oxidation of CR increases and

the ECL intensity follows the shape of voltammetric wave up to the limiting current and the ECL plateau is observed. The $L^{+\bullet}$ acts thus also as a one-electron “shuttle” mediating the homogeneous oxidation of CR.

The decrease of the plateau at even more positive potentials is coincident with the next oxidation step (for example, with the oxidation of $L^{+\bullet}$ to a dication).

Visualization of electrode processes

Due to the fact that during DC-ECL, a steady light emission is produced, the photographing or video recording of ECL can offer information about displacement of the luminescence at the electrode surface or changes of ECL with time. The DC-ECL thus represents authentic visualization of electrode processes.

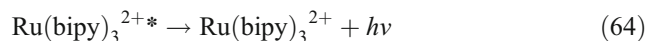
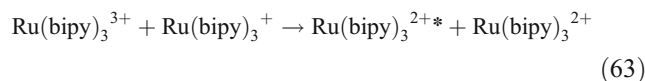
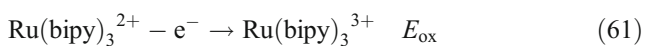
In this way, luminescence oscillations at the falling mercury drop were revealed and explained [33]. They arise from an interplay of hydrodynamically caused concentration differences between the front and back sides of the falling drop, leading to a corresponding difference in the potential. All this manifests itself in surface tension and surface movement of mercury as the retroactive effect.

Another example is photographing of DC-ECL at platinum rotating disk (or ring) electrodes (RDE or RRE) at different potentials [42]. Although the theory of RDE is based on equal accessibility of any place of electrode surface [60], non-uniform current density was observed both at the potential of the ECL peak as well as at the potential of the plateau. This phenomenon depending also on the rotation rate has evidently kinetic reasons connected with the change of ECL mechanism from the heterogeneous to the homogeneous one.

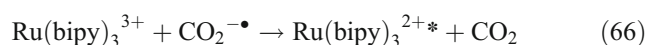
Besides that, recording of ECL can be used also for detailed studies of the electrode surface, for searching of non-homogeneities [61, 62] or for observation of the so-called edge effect [63, 64].

Analytical application—ECL in aqueous media

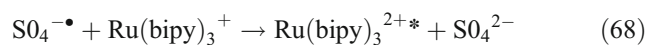
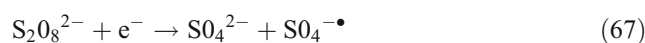
Majority of luminescent compounds are organic molecules, mostly based on aromatic hydrocarbons or heterocycles, which are not soluble in water. In attempts of the generation of ECL even in aqueous solutions, the utilization of $\text{Ru}(\text{bipy})_3^{2+}$ (and other charged metal chelates) was a good choice due to their solubility. A problem has arisen, however, with a narrow potential window in water (compared to non-aqueous media). The ECL reaction scheme (Eqs. 61 to 64) working in aprotic media by sequential potential switching between E_{ox} and E_{red} could not proceed in water due to potential unavailability of the E_{red} .



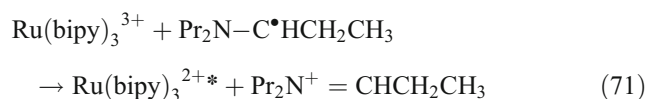
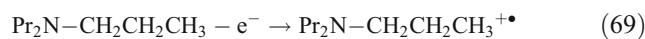
Using oxalate as a coreactant for anodic (oxidative) ECL (Eqs. 65 and 66), the DC-ECL mechanism yields an ECL emission at a single positive potential [65].



For cathodic ECL, a suitable coreactant is peroxodisulphate $\text{S}_2\text{O}_8^{2-}$, which being reduced, gives a strong oxidation agent $\text{SO}_4^{-\bullet}$ [66].



Later a more efficient coreactant tri-*n*-propylamine was found [67, 68] which is the most utilized coreactant up to now [69].



These approved DC-ECL systems (with a coreactant) have many applications in chemical analysis [70]. Note, however, that reaction schemes of all coreactants are analogous to Eqs. 29–35 and the most used luminescent redox system remains that of $\text{Ru}(\text{bpy})_3^{2+}$.

Conclusions

Electrochemically generated chemiluminescence, namely its DC-type (with a coreactant) during the last 20 years became a very sensitive, powerful, and promising method

for various applications: in medical analysis and diagnostics, in biosensors, in trace analysis, liquid chromatography, capillary electrophoresis, as ECL markers, etc. It is useful not only in biology and biochemistry, but also in polymer sciences or in membranes research. In addition to this, other related topics are developing like ECL imaging, ECL in semiconductors, ECL in scanning microscopy at ultramicroelectrodes, ECL in material chemistry for light-emitting devices, and others. (This is summarized, e.g., by Dini [71]).

Nevertheless, all these achievements are based on ideas and experimental work, where the contribution of Professor Fritz Pragst is remarkable and significant. In this context, the present review should inspire, provoke, and encourage the scientists to fundamental research in the field of ECL and to the use of ECL for obtaining thermodynamic and mechanistic information in organic and coordination chemistry, photochemistry, and photophysics.

Acknowledgments The support of the grant IAA 400 400 813 (GAAVCR) is gratefully appreciated.

References

- Pragst F (1978) *Z Chem* 18:41
- Park SM, Tryk DA (1981) *Rev Chem Intermed* (Verlag Chemie) 4:43
- Faulkner LR, Glass RS (1982) Chemical and biological generation of excited states. Academic, New York, p 191
- Freed DJ, Faulkner LR (1971) *J Am Chem Soc* 93:3565
- Kunkely H, Merz A, Vogler A (1983) *J Am Chem Soc* 105:7241
- Hercules DM (1964) *Science* 145:808
- Visco RE, Chandross EA (1964) *J Am Chem Soc* 86:5350
- Zweig A (1968) *Adv Photochem* 6:425
- Chandross EA (1969) *Trans NY Acad Sci Ser II* 31:571
- Bard AJ, Santhanam KSV, Cruser SA, Faulkner LR (1967) In: Guilbault GG (ed) *Fluorescence*. Marcel Dekker, NY, p 627
- Hercules DM (1971) In: Weissberger A, Rossiter B (eds) *Physical methods of chemistry*. Wiley, NY, p 257, vol 1, part II B
- Rozhitskii NN (1992) *J Anal Chem USSR* 47:1288
- Ludvik J (1994) *Chem List* 88:696
- Rozhitskii NN, Bykh AI, Krasnogolovetz MA (2000) *Electrochemical luminescence*. KNURE, Kharkiv
- Bard AJ (2004) *Electrogenerated chemiluminescence*. Marcel Dekker, New York
- Faulkner LR, Bard AJ (1977) In: Bard AJ (ed) *Electroanalytical chemistry*. Marcel Dekker, New York, p 1, vol 10
- Weller A, Zachariasse K (1967) *J Chem Phys* 46:4984
- Hoytink GJ (1968) *Disc Faraday Soc* 45:14
- Van Duyne RP, Reilley CN (1972) *Anal Chem* 44:142
- Visco RE, Chandross EA (1968) *Electrochim Acta* 13:1187
- Pighin A (1973) *Can J Chem* 51:3467
- Faulkner LR, Bard AJ (1969) *J Am Chem Soc* 91:6497
- Pragst F, Ziebig R (1978) *Electrochim Acta* 23:735
- Weller A, Zachariasse K (1971) *Chem Phys Lett* 10:590
- Park S-M, Caldwell RA (1977) *J Electrochem Soc* 124:1859
- Ziebig R, Hamann HJ, Jugelt W, Pragst F (1980) *J Lumin* 21:353
- Mussell RD, Nocera DG (1990) *Inorg Chem* 29:3711, and references therein
- Wheeler BL, Nagasubramanian G, Bard AJ, Schechtman LA, Dinny DR, Kenney ME (1984) *J Am Chem Soc* 106:7404
- Fan FF, Mau A, Bard AJ (1985) *Chem Phys Lett* 116:400
- Ouyang J, Bard AJ (1988) *Bull Chem Soc Jpn* 61:17
- Chang M, Saji T, Bard AJ (1977) *J Am Chem Soc* 99:5399
- Ludvik J, Volke J (1988) *Anal Chim Acta* 209:69
- Pragst F, von Loewis M (1982) *J Electroanal Chem* 133:173
- Pragst F (1973) *J Prakt Chem* 315:549
- Ziebig R, Pragst F, Jugelt W (1978) *Z Phys Chem (Leipzig)* 259:1009
- Pragst F, Ziebig R, Kunze J, Jugelt W, Krause M (1976) *Z Phys Chem (Leipzig)* 257:465
- Ziebig R, Pragst F (1979) *Z Phys Chem (Leipzig)* 260:748
- Pragst F (1976) *Electrochim Acta* 21:497
- Ziebig R, Pragst F (1979) *Z Phys Chem (Leipzig)* 260:795
- Pragst F, Ziebig R, Boche E (1979) *J Lumin* 21:21
- Zholudov Y, Bilash O, Kukoba A, Rozhitskii M (2011) *Analyst* 136:598
- Ludvik J, Volke J (1990) *Electrochim Acta* 35:1983
- Pragst F (1981) *J Electroanal Chem* 119:315
- Pragst F, Kaltofen B (1980) *J Electroanal Chem* 112:339
- Magno F, Bontempelli G, Pilloni G (1971) *J Electroanal Chem* 30:375
- Persson B, Nygaard B (1974) *J Electroanal Chem* 56:373
- Persson BJ (1978) *J Electroanal Chem* 86:313
- Pragst F, Kaltofen B (1982) *Electrochim Acta* 27:1181
- Mitzner R, Bendig J, Ziebig R, Graichen F, Kreysig D, Pragst F (1985) *J Prakt Chem* 327:241
- Klíma J, Kurfuerst A, Kuthan J, Volke J (1977) *Tetrahedron Lett* 31:2725
- Pragst F, Kaltofen B, Volke J, Kuthan J (1981) *J Electroanal Chem* 119:301
- Ludvik J, Volke J, Pragst F (1986) *J Electroanal Chem* 215:179
- Pragst F, Niazymbetov M (1986) *J Electroanal Chem* 197:245
- Ludvik J, Pragst F, Volke J (1984) *J Electroanal Chem* 180:141
- Siegel TM, Mark HB (1971) *J Am Chem Soc* 93:6281
- Siegel TM, Mark HB (1972) *J Am Chem Soc* 94:9020
- Boto KG, Bard AJ (1975) *J Electroanal Chem* 65:945
- Pragst F, Brandt B (1979) *J Electroanal Chem* 99:357
- Ludvik J – unpublished results
- Bard AJ, Faulkner L (1980) *Electrochemical methods*, p 283. Academic Press/Wiley, New York
- Engstrom RC, Johnson KW, Desjarlais S (1987) *Anal Chem* 59:670
- Kukoba AV, Rozhitskii NN (1993) *Electrochim Acta* 29:261
- Newman J (1966) *J Electrochem Soc* 113:501–502
- Engstrom RC, Pharr CM, Koppang MD (1987) *J Electroanal Chem* 221:251
- Rubinstein I, Bard AJ (1981) *J Am Chem Soc* 103:512
- White HS, Bard AJ (1982) *J Am Chem Soc* 104:6891
- Noffsinger JB, Danielson ND (1987) *Anal Chem* 59:865
- Leland JK, Powel MJ (1990) *J Electrochem Soc* 137:3127
- Miao W, Choi J-P, Bard AJ (2002) *J Am Chem Soc* 124:14478
- Fahnrich KA, Pravda M, Guilbault GG (2001) *Talanta* 54:531
- Dini D (2005) *Chem Mater* 17:1933