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# Energy transfer and localization in optochemotronic emitter with electrodes modified using the Langmuir-Blodgett technique

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Problems of the excitation energy transfer and localization under biradical recombination reaction have been considered for an optochemotronic emitter containing the working electrode with a layer of electrochemiluminophore molecules deposited thereon using the Langmuir-Blodgett technique. A couple of reagents including 9,10-diphenyl anthracene and *p*-terphenyl has been proposed for efficient transformation of electric energy into light at electrochemical reaction in the system mentioned.

Рассмотрены вопросы локализации энергии возбуждения при бирадикальной рекомбинации в оптохемотронном излучателе с рабочим электродом, на поверхность которого методом Ленгмюра-Блоджетт нанесен слой молекул электрохемилюминофора. Предложена пара реагентов для эффективного преобразования электрической энергии в световую при электрохимической реакции в рассмотренной системе — 9,10-дифенилантрацен и *n*-терфенил.

Optochemotronics is a science branch that does study and use the electrochemical luminescence (ECL) phenomenon to develop novel optoelectronic devices. The essence of the electrochemical luminescence excitation is the consecutive formation of anion-radicals and cation-radicals of an organic luminophor on the electrode surfaces of an optochemotronic emitter (OCE) at electrolysis followed by the biradical recombination thereof and formation of emitting molecules in an electron-excited state [1]. The optochemotronic devices are of a great interest for analytic purposes in biology, medicine, and ecology, as well as for the development of fundamentally novel optoelectronic devices, such as coherent and incoherent high-efficiency electro-optical converters based on organic luminophors. Works are known devoted to development of a device making use of electrochemical processes to obtain coherent optical emission (optochemotronic quantum generator). In [2, 3], a novel approach to that device is considered, namely, the use of a modified working electrode (WE).

The purpose of this work is to consider the excitation energy transfer and localization processes at the solution/WE interface and to select substances suitable to provide an efficient OCE with the WE modified using the Langmuir-Blodgett (LB) technique [4]. This technique of the WE modification has some specific features and provides some advantages over the usual OCE [5].

The OCE model under consideration is a planar ECL cell with two plane-parallel electrodes (working and auxiliary ones). The electrode linear dimensions exceed considerably the interelectrode spacing, so the cell can be considered as a thin-layer one and all the mass and charge transfer therein, unidimensional ones. The interelectrode volume is filled with an active substance (activator) solution. Activator provides the charge (i.e., ions thereof) transfer across the solution from the auxiliary electrode to the working one. It is just the anode that is selected to be the WE having a modified surface where the ECL emitter formation takes place. This is connected with the fact that, at the biradical recombination of anion-radicals and cation-radicals, it is just the cation-radical transition into excited state that is most probable, judging from the general energy considerations. Thus, to obtain the excited molecules in the WE structure, the electrode must be anode of the device. A thin electrochemiluminophor (ECLP) film is deposited onto the WE surface using the LB technique. That deposition technique makes it possible to control strictly the layer thickness and the spatial molecular orientation therein. The molecular orientation control of one of the reagents at the biradical recombination is very important for the reaction rate increase, since it provides increased so-called pre-exponential orientation factor in the expression for the biradical recombination rate constant [1]. The most preferred is fixation of the reagent molecules with reactive centers directed towards the cell volume filled with the activator solution.

The OCE being considered works using DC, with the active emitting centers being formed in the ECLP layer deposited on the WE. When a voltage is supplied to the cell, the ion-radicals of the dissolved activator are formed on the auxiliary electrode. These ion-radicals diffuse towards the WE. On the latter, the ECLP ion-radicals are formed that react with those being in solution and form in the film the active centers, that is, the electron-excited molecules (ECL emitters). In that scheme of OCE operation, it is very important to provide the generation of singlet-excited molecules just in the ECLP film on the WE surface. Of critical importance in that process are physicochemical properties of ion-radicals both in the film and the solution as well as the molecular orbital energy characteristics of the particles involved in the biradical recombination reaction. It is just the energy sufficiency of a specific reaction path that defines the probability of the reaction product formation in the appropriate energy state. Besides the molecular orbital energy of the particles, the interaction of reagents and reaction products with the environment (solvent, neighboring luminophore molecules, subphase film, etc.) is of substantial importance. The energy of that interaction is different for the reagents and reaction products and depends on the environment, thus affecting considerably the energy sufficiency and realization probability of various reaction paths.

In order to provide the excitation energy localization in the film, the first singlet excited state energy of the fixed molecules should be lower than that of the dissolved activator. This is explained by the fact that at the biradical recombination of ion-radicals, a short-living transition complex is formed where the intermolecular spacing in very short (about several Å), and so a high-efficiency non-radiative energy transfer between the molecules included in the complex is realized [6].

The question about the energy transfer influence on the ECL emitter formation is not so obvious [7], unlikely the case of multicomponent system photoexcitation [8]. The energy transfer in its pure form can be observed only in the systems where the energy acceptor is involved neither in electrochemical reactions on the electrodes nor in the homogeneous electron transfer in the solution. Such a reaction was considered in [9]. When one of reagents at biradical recombination is responsible for the ECL emission, the mechanism of excitation energy localization is not always obvious. In [10], a good correlation has been found between the ECL light emission and calculated values of the energy transfer rate constant according to long-range induction-resonance mechanism. ECL in various two-component systems was studied in [11] where it was concluded that excitation of the emitter (being also a molecule with lowest singlet excited level) is not associated with the energy transfer process but with electron transfer. One way or another, the ECL emitter in all the systems is a molecule with lower singlet excitation energy.

In this work, the excitation energy localization due to non-radiative induction-resonance singlet-singlet transfer (Foerster mechanism) [12] is considered. In conditions favoring the bidirectional energy transfer (that is, when the energy transfer between molecules forming the transition complex is possible in two directions, e.g., if the complex includes two identical molecules being in the excited and ground state, respectively, and having overlapping absorption and luminescence spectra), a multiple energy transfer occurs during the singlet state lifetime. If the singlet state energy values of the molecules included in the complex differ substantially, the excitation energy will be localized mainly on the molecule with lower excited level energy. From the standpoint of the molecular spectra, this means that the activator luminescence spectrum overlaps the ECLP absorption one while the luminescence spectrum of the ECLP and the activator absorption one are not overlapped.

In [2], 9,10-diphenyl anthracene (DPA) having the luminescence maximum near 430 nm is proposed as the ECLP to be deposited onto the WE. This luminophore is remarkable for its high luminescence quantum yield (0.9 to 1.0) in various solvents [13]. Besides, DFA is stable against excimer and dimer formation due to its non-planar molecular configuration, thus eliminating some side transformation paths of the excitation energy [14]. It has been shown [15] that DPA derivatives, when forming solid films and being deposited onto the electrode, retain the spectral characteristics and provide a high luminescence quantum yield (about 70 %). This suggests the stability of DPA electrochemiluminophore properties after deposition thereof onto the WE.

Once the ECLP is selected, the activator is to be matched thoroughly. The latter should meet various and strict enough requirements, namely:

— efficient formation of ion-radicals of the necessary sign (in our case, anion-radicals) at the auxiliary electrode;

— sufficient ion-radical stability in solution;

— high efficiency of the biradical recombination with DPA molecules fixed on the WE;

— energy sufficiency of the biradical recombination reaction for the DPA exited singlet state formation;

— the exited singlet state energy should exceed that of DPA to provide the excitation energy localization in the film;

— the oxidation potential absolute value should exceed that of DPA;

— solubility in solvents wherein DPA is insoluble.

Substances meeting all the above requirements are difficult enough to select. This is associated, first of all, with the fact that the necessary literature data are uncoordinated if not absent at all. It is just $p$-terphenyl (PTP) that satisfies completely enough all the above requirements. The Table presents some parameters for PTP in tetrahydrofurane (THF) and for DPA in N,N-dimethylformamide (DMF) [7, 13].

Table. Physicochemical properties of DPA and PTP

| Parameter | DPA | PTP |
|---|---|---|
| Oxidation potential, V | 1.26 | 1.6 |
| Reduction potential, V | −1.95 | −2.75 |
| Singlet excited level energy, eV | 3.05 | 3.97 |
| Triplet excited level energy, eV | 1.8 | 2.55 |
| Fluorescence quantum yield | 0.9 | 0.93 |
| Anion-radical stability | Stable | Stable |
| Cation-radical stability (lifetime, s) | $5\cdot10^{-3}$ | Unstable |
| Singlet excited state lifetime, ns | 8.41 | 1.43 |

The efficiency of the excitation energy induction-resonance transfer was evaluated using the Forester theory that makes it possible to determine the rate constant for the induction-resonance energy transfer between a donor molecule and an acceptor one [12]. The main condition of the energy transfer is the resonance between the donor and acceptor excitation energy that is characterized by the overlapping integral of the fluorescence and absorption spectra thereof, respectively. The transfer rate constant is expressed [12] as

$$k_F = \frac{9000\ln(10)k^2\varphi_D}{128\pi^5 N_a n^4 \tau_D R^6}\int_0^\infty \frac{f_D(\nu)\varepsilon_A(\nu)}{\nu^4}d\nu \approx \tag{1}$$

$$\approx 8.71\times10^{23}\frac{k^2\varphi_D}{n^4\tau_D R^6}J,$$

$$J = \int_0^\infty \frac{f_D(\nu)\varepsilon_A(\nu)}{\nu^4}d\nu,$$

where $k^2$ is the relative orientation factor of transition dipole moments for the donor and acceptor; $\varphi_D$, the donor fluorescence quantum yield when the acceptor is absent; $N_a$, the Avogadro number; $n$, the medium refractive index; $\tau_D$, the excited donor state lifetime when the acceptor is absent; $J$, overlapping integral of the donor fluorescence spectrum and the acceptor absorption one; $f_D(\nu)$, the donor fluorescence spectrum normalized to unity; $\varepsilon_A(\nu)$, the acceptor absorption spectrum normalized to unity.

The expression (1) includes the orientation factor $k^2$ taking the values 0 through 4. The maximum value 4 corresponds to collinear geometry; $k^2 = 1$ at parallel but not collinear geometry; $k^2 = 0$ at orthogonal geometry; at random chaotic orientation of the donor-acceptor pairs, where all the possible orientations are present, $k^2 = 2/3$. This case answers to the energy transfer in solution and is referred to as "dynamically averaged limit". The latter case is not to be confused with the random orientation in a solid medium where all the possible orientations may be present but any motion is impossible (in this case, $k^2 = 0.475$). In our case, the energy transfer occurs between an ordered fixed monolayer and chaotically oriented molecules in the solution volume; that is why the estimation $k^2 = 2/3$ (as in solution) has been selected as the lower estimate.

Figure presents the normalized luminescence spectrum of PTP and the absorption one of DPA [13]. A considerable overlap of those spectra allow to expect an efficient energy transfer and thus an efficient localization of the excitation energy in the fixed ECLP layer at the biradical recombination. The calculated energy transfer rate constant at distances typical for the transition complex (3 to 5 Å) amounts $1.064\cdot10^{15}$ to $4.966\cdot10^{13}$ s$^{-1}$, that corresponds to the mean transfer time of $9.396\cdot10^{-16}$ to $2.014\cdot10^{-14}$ s. Those transfer time values are substantially shorter than the lifetime of the donor excited state (see Table), therefore, a very efficient localization of the excitation energy on the fixed ECLP molecules at the biradical recombination is to be expected in that system. The calculation of the energy transfer "critical distance" $R_0$ (the donor-acceptor distance at which the energy transfer probability is 50 %, that is, the transfer is equiprobable to all other donor deactivation paths) using the Eq.(2) below gives the value 31.9 Å for the system under consideration.

$$R_0^6 = \frac{9000\ln(10)k^2\varphi_D}{128\pi^5 N_a n^4}\cdot J \approx \qquad (2)$$

$$\approx 8.71\times10^{23}\frac{k^2\varphi_D}{n^4}\cdot J.$$

The proposed OCE structure with modified working electrode makes it possible to use different substances as sources of anion-radicals and cation-radicals, providing the localization of emitting centers and a substantial improvement of the biradical recombination efficiency with the emitting center formation by selection of optimum reagents. The further studies are aimed at search for the optimum activators among substances which are not electrochemiluminophors.

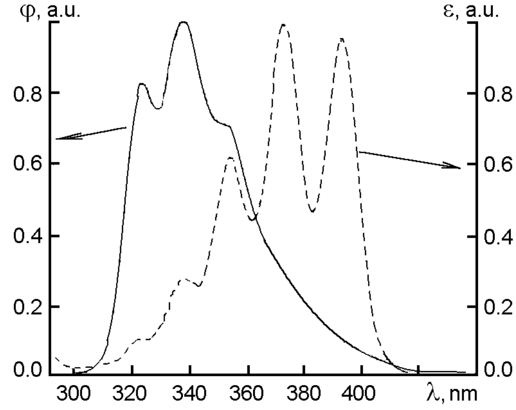

Fig. Normalized spectra of PTP luminescence (φ) and DPA absorption (ε).

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# Перенос та локалізація енергії збудження в оптохемотронному випромінювачі з електродами, модифікованими за технологією Ленгмюра-Блоджетт

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Розглянуто питання локалізації енергії збудження при бірадикальній рекомбінації в оптохемотронному випромінювачі з робочим електродом, на поверхню якого методом Ленгмюра-Блоджетт нанесений шар молекул електрохемілюмінофора. Запропоновано пару реагентів для ефективного перетворення електричної енергії у світлову при електрохімічній реакції у розглянутій системі — 9,10-дифенілантрацен та *n*-терфеніл.